BNL-98466-2012-CP

High-temperature treatment of In-doped CZT crystals grown by the high-pressure Bridgman method

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Presented at the 2012-SPIE Optics and Photonics Conference
San Diego, CA
August 12-16, 2012

August 2012

Nonproliferation and National Security Department

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High-temperature treatment of In-doped CZT crystals grown by the high-pressure Bridgman method

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ABSTRACT

We evaluated the effect of high-temperature treatment of $Cd_{0.9}Zn_{0.1}Te$:In single crystals using Hall-effect measurements, medium- and high-temperature annealing under various deviations from stoichiometry, and infra-red (IR) transmission microscopy Annealing at ~730 K sharply increased the electrical conductivity (by ~1-2 orders-of-magnitude). Plots of the temperature- and cadmium-pressure dependences of the electrical conductivity, carrier concentration, and mobility were obtained. Treating previously annealed Cd-samples under a Te overpressure at 1070 K allowed us to restore their resistance to its initial high values. The main difference in comparing this material with CdTe was its lowered electron density. We explained our results within the framework of Kröger's theory of quasi-chemical reactions between point defects in solids.

Keywords: Single crystals, $Cd_{0.9}Zn_{0.1}Te$:In, point defects, inclusions, annealing, Hall effect, high-pressure Bridgman growth method.

1. INTRODUCTION

$Cd_{1-x}Zn_xTe$ (CZT) is an important semiconductor material whose use increasingly is becoming widespread. It is a leading material for fabricating room temperature X- and γ-radiation detectors [1, 2]. Presently, CZT detector technology is limited due to the insufficient quality of the available crystals. Its potential applications demand nearly perfect single crystals with high resistivity and high carrier mobility. One method suitable for growing such crystals is the high-pressure Bridgman method (HPBM) [3, 4]. Ingots, grown by HPBM, are of p-type conductivity, have a resistivity of 2×10^9 - 5×10^{11} Ohm×cm, and display good transport properties for detectors [3]. Indeed, Komar et al. [5] improved these required properties by employing multi-zone furnaces to grow the crystals.

Recently, the results were published of an I-DLTS investigation of point defects (PDs) in CZT crystals grown by different methods (HPBM, BM, THM and floating zone) [6]; the authors identified 12 different energy-levels from 7 meV to 1.1 eV. Energy-level diagrams of different crystals look similar, implying that the spectrum of PDs in them is similar. Nevertheless, crystals grown by HPBM do not have an energy level at 780 meV (probably, Te_{Cd}); rather, they have an energy level at 1.1 eV.

Despite the thorough research into the properties of CZT, the nature and the concentration of intrinsic- and introduced PDs are scantily understood, and methods for managing them remain elusive [7]. Previously we attempted to describe the behavior of PDs in CZT:In grown by the Bridgman method [8, 9]. It is well known that the properties of the material grown by different techniques can strongly differ. So, the goal of our work, described herein, was to explore the nature of PDs in HPBM-grown samples, cut at different positions from one ingot. We studied the carrier concentration and mobility and electrical conductivity in the samples during high-temperature PD equilibrium, and compared the findings

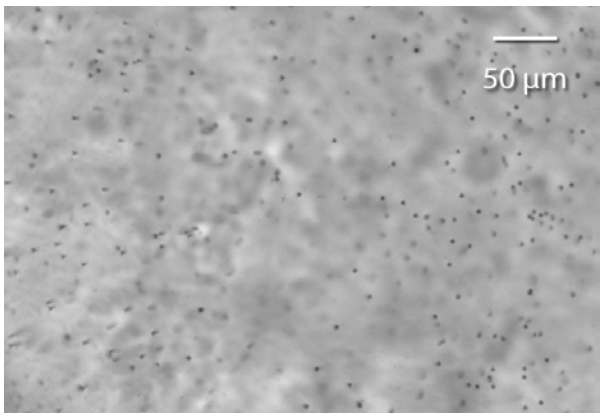
to those previously calculated for CdTe [10], assuming that the enthalpies of defect formation did not differ greatly for the low content of Zn (~10%) in the $Cd_{1-x}Zn_xTe$ samples under investigation.

2. EXPERIMENTAL PROCEDURES

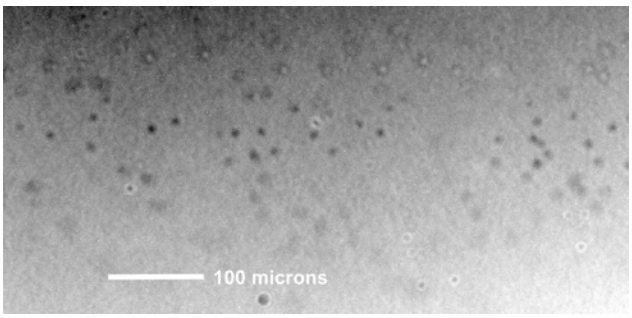
Three samples were taken from a $Cd_{0.9}Zn_{0.1}Te$:In ingot, grown by the HPBM method, that had been doped with indium in the melt at a concentration of ~50 ppm. The sample we designated CZT1 was cut from the bottom of the ingot, CZT2 from its middle, and CZT3 from the end (23, 48 and 68 mm from the growth beginning, accordingly; the total ingot length was 72 mm). The samples were cut out with a wire saw, and then polished successively with Al_2O_3 abrasive powders down to 0.1–μm grit, and finally etched in either a Br_2-methanol. Electrical measurements were acquired in an automated facility [11]; a DC voltage of 1-5 V and a constant magnetic field of 0.5 T were used for taking the Hall-effect measurements. An evacuated ampoule containing the sample was placed in a two-zone furnace inside the magnet. The first zone was responsible for controlling the sample's temperature, while the second zone maintained the Cd component pressure, so allowing us to modulate the Cd vapor pressure. The samples were exposed to temperatures of between 400 and 1200 K for a large range of Cd over-pressures (0.0001 - 3 atm).
The polished and etched CZT samples prepared for the annealing experiments were ~8x6x3 mm^3 in size. The infrared transmission images were obtained by a Nikon IR microscope. For electrical measurements, we used a Keithley 6517A electrometer both as a voltage supply and current meter. Gold contacts were used in all of the I-V experiments.

3. RESULTS AND DISCUSSION

Annealing the inclusions:
The middle part of the ingot contained small inclusions (~2-5 microns in diameter), located separately or along lines (Fig 1). In the last solidified crystal fractions, we noted different distributions of the inclusions (Figs. 2a-b). After the annealing under Cd- or Cd-Zn-alloy overpressure at 1000 K for 10 hours, almost all visible inclusions had disappeared (Fig. 2c); only the surface remained covered with a straight-lined network (Fig. 3), similar to that described in [11]. Figure 4 shows the overall distribution of inclusions in CZT2, which was taken from the middle of the ingot.

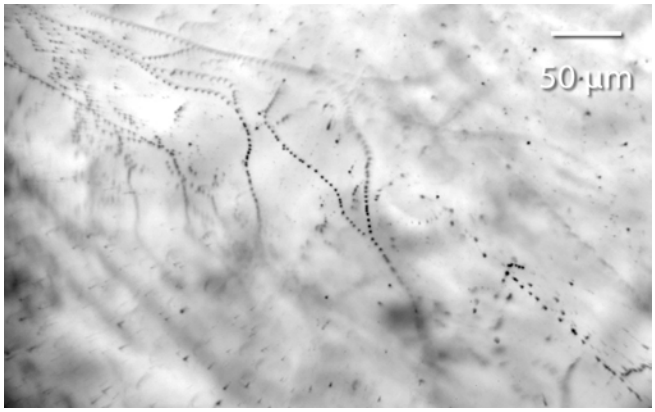


a)



b)

Fig. 1. IR images from the middle of an as-grown CZT ingot (a) and (b). Inclusions are distributed uniformly. Their sizes don't exceed 10-12 μm.



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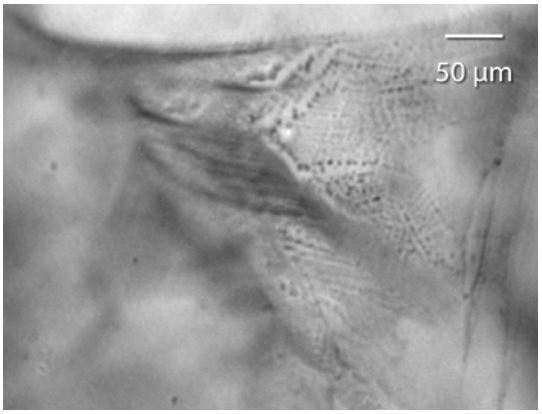

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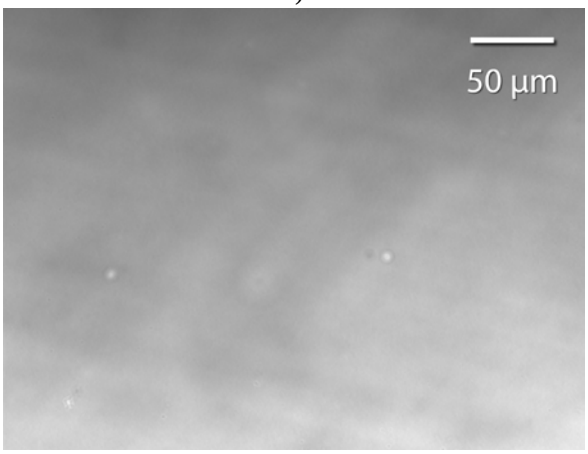


c)

Fig. 2. IR transmission images from the end of an as-grown CZT ingot (a, b) and after annealing (c).
Inclusion density is higher than in the middle of the ingot. Mainly they form lines (a), however in some cases they occupy almost fully the observed areas. After the annealing all inclusions disappeared (c).

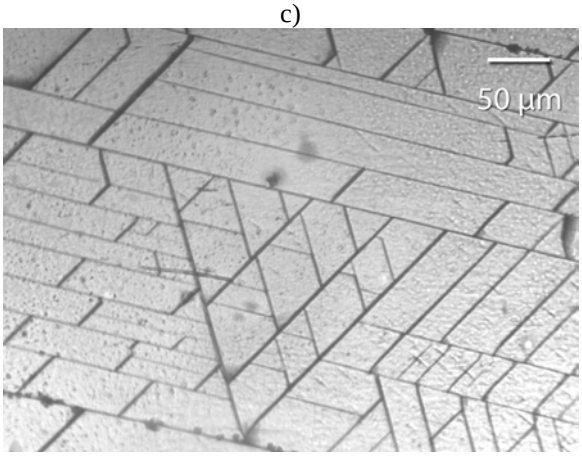


Fig. 3. IR image of the annealed CZT sample's surface.
Annealing conditions: temperature - 1000 K;
Cd-Zn-alloy overpressure; duration - 10 hours;
Cooling rate – 2 K/min.
The surface layer contains the higher Zn content than the matrix therefore the mismatch of lattice parameter is enough large. The incipient stresses form straight lines

I-V measurements:

The initial resistances of investigated as-grown samples were above 10^9-10^{10} Ohm (Fig. 5); after annealing under Cd overpressure (800ºC, 4 hours, cooling rate ~5K/min, P_{Cd}=1 atm.) they declined to ~10^5 Ohm (Fig. 6) due to the incorporation of interstitial Cd atoms into the lattice. We performed a series of two-step treatments to raise the samples' resistance to their initial values. In the first step, we annealed them in Cd-saturated vapor pressure at 1100 K for 4 hours to reduce the size and density of the inclusions. In the second step, annealing was conducted under Te overpressure at different conditions (CZT sample temperature, duration, and cooling rate) to increase the resistivity. The highest resistance was obtained after treating at 1070 K for 4 hours with a cooling rate of ~2 K/min (figs. 5, 6, and 7).

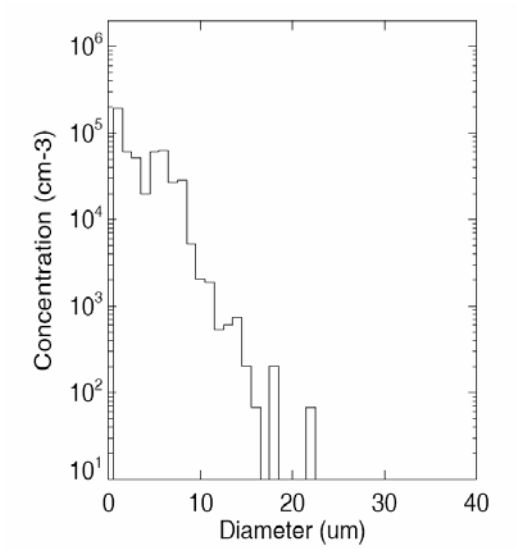


Fig. 4. Distributions of Te inclusions near the middle of the ingot.

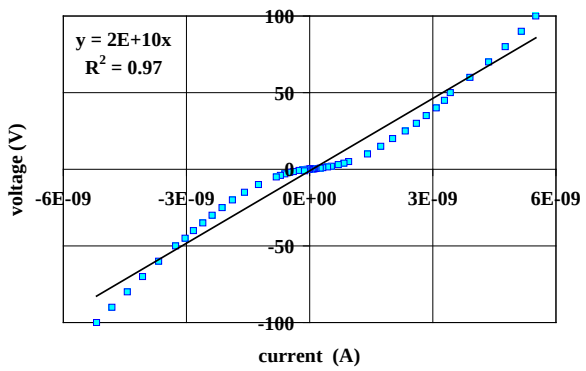


Fig. 5. I-V curve of as-grown CZT sample.

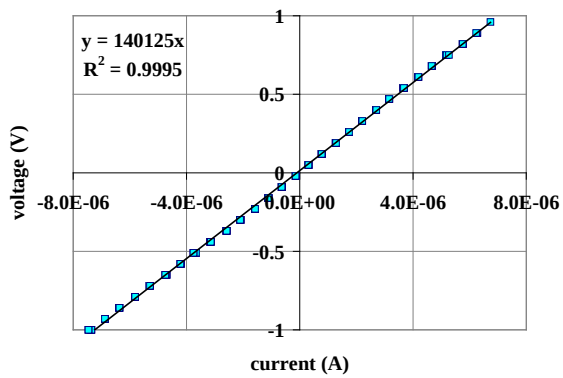


Fig. 6. I-V curve of CZT sample after 1st step annealing under Cd overpressure.

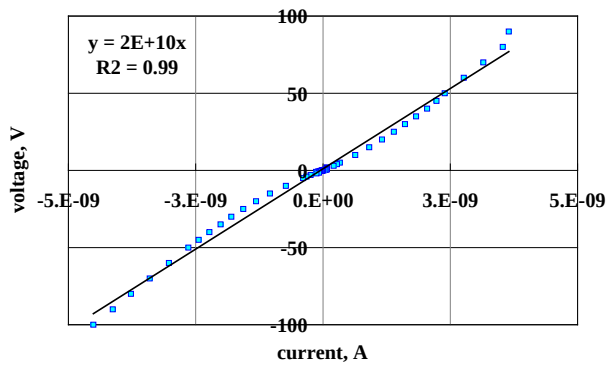
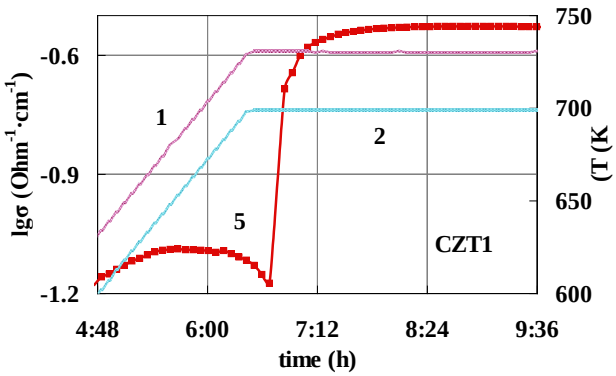


Fig. 7. I-V curve of CZT sample after 2nd step annealing under Te overpressure.

<u>High-temperature Hall-effect measurements</u>:

During annealing of sample CZT1 at ~730 K, we observed a sharp increase of the electrical conductivity (Fig. 8a) and the carrier concentration (Fig. 8b), followed by oscillations of the values of the carrier mobility (Fig. 8c). Similar phenomena were evident for sample CZT2. However, here, the oscillations in the charge-carrier density before the "jump" in electrical conductivity were much higher (Fig. 9). After the effect, the reproducibility of measurements improved; we conjectured that the electrical homogeneity of the crystal also improved. For sample CZT3, no such electrical conductivity "jump" was observed. We associated the "jump" in samples' electrical properties with melting of

the tellurium inclusions. Uncontrolled impurity atoms that are concentrated inside the inclusions begin to diffuse into the crystal's volume, ionizing and generating additional charge carriers.



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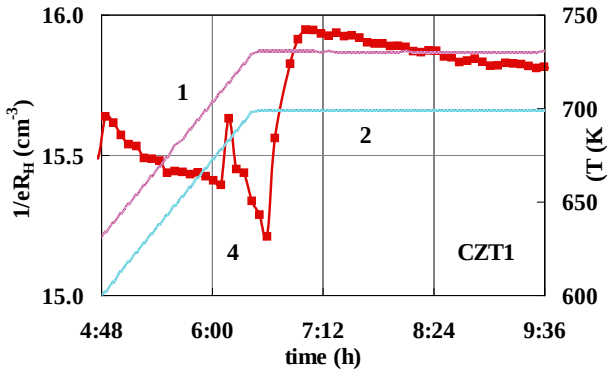

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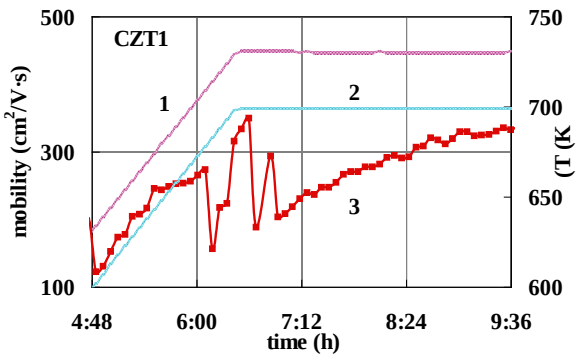

c)

Fig. 8. Time-dependence of electrical conductivity (a), carrier concentration (b), and mobility (c) in the CZT1 versus sample (1) and the component (Cd) (2) zone temperature.
1 - sample temperature;
2 - Cd temperature;
3 – charge carrier mobility;
4 – 1/eR$_H$, where e – electron charge, R$_H$ – Hall constant; in the majority of cases this variable corresponds to charge carrier density;
5 – sample's conductivity.

Fig. 10 shows the carrier mobility dependence on temperature in CZT3 sample. At the beginning of the measurements, this sample showed a typical hole conductivity type (μ is ~40-50 cm^2/V·s). After heating to ~740 K in the Cd vapor, it was converted to n-type because of the introduction of additional intrinsic donors (Cd_i^{2+} and V_{Te}^{2+}); it did not change in latter measurements. CZT1 and CZT2 samples showed similar behavior; the initial hole-conductivity was, in the same way, converted into electron conductivity (n-type). In these samples, the inversion of the conductivity type happened at different temperatures because of the different In dopant content. Therefore, depending on the compensation process, a different annealing treatment time and Cd vapor pressure may be required.

The observed changes can be discussed in the framework of point-defect theory in CdTe crystals using the Kröger quasi-chemical defect approach [12]. We assume that the pattern is quite close to that of the CZT crystals we are investigating. The transition of the semi-insulating crystal from p-type conductivity into low-resistivity n-type during the heating in Cd vapor is explicable by the sample becoming saturated by Cd atoms (Fig. 10). Intrinsic Cd interstitials Cd_i^{2+} and Te vacancies V_{Te}^{2+} are formed following Eqs. 1-2, which introduces additional quantities of electrons. Also, the Cd vacancies responsible for p-type conductivity in the as-grown samples are annihilated, leading to the generation of electrons (Eq. 3). At the same time, associations formed between indium and cadmium vacancies ($In_{Cd}^{+}\ V_{Cd}^{2-}$) play an important role in the samples' high resistivity (Eq. 4).

$$Cd(g) \leftrightarrow Cd_i^{2+} + 2e^- \quad (1)$$

$$Cd(g) \leftrightarrow Cd_{Cd}^{o} + V_{Te}^{2+} + 2e^- \quad (2)$$

$$Cd(g) + V_{Cd}^{2-} \leftrightarrow Cd_{Cd}^{o} + 2e^- \quad (3)$$

$$Cd(g) + (In_{Cd}^{+}\ V_{Cd}^{2-})^- \leftrightarrow In_{Cd}^{+} + Cd_{Cd}^{o} + 2e^- \quad (4)$$

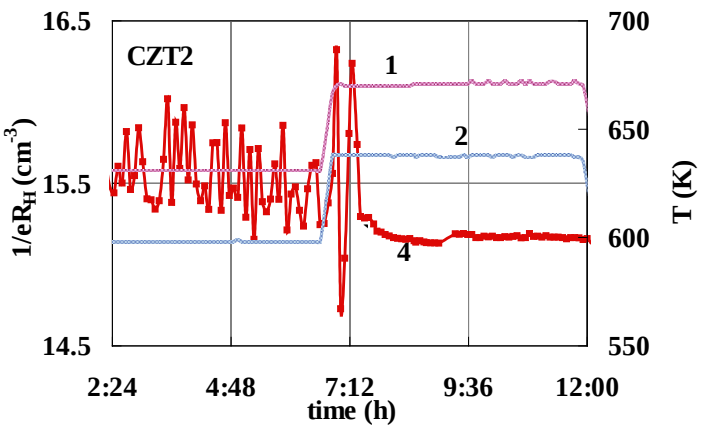

Fig. 9. Time dependence of carrier concentration (4) in the CZT2 sample (1) and the component (Cd) (2) zone temperature

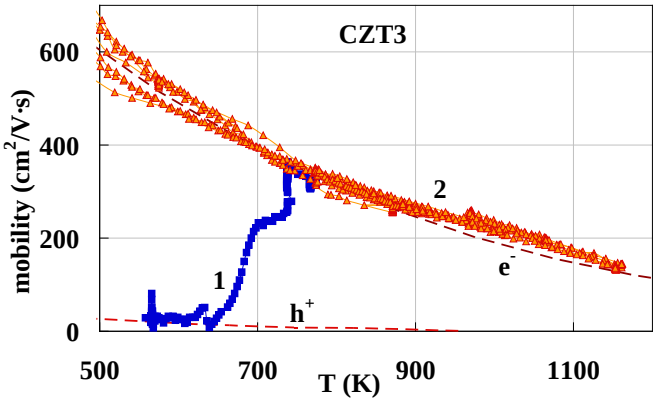

Fig. 10. Temperature-dependence of charge-carrier mobility in the CZT3 sample. The initial hole mobility (squares) changed to electron conductivity (2, triangles) during heating to ~740 K.

Dashed lines – modeling for hole mobility (lower line) and electron mobility (upper line) in undoped CdTe.

It is well-known that in heavily doped semiconductors the free-carrier density frequently does not depend on the temperature or stoichiometry ratio (in the case of compound semiconductors). This phenomenon is called 'controlled' conductivity and is a technique widely used in semiconductor technology for assuring a desired resistivity. The simplest approximated electro-neutrality equation for donor-doped crystals (provided that the donor does not create any complicated defects can be written as Eq. 5. Here, the electron density depends only on the concentration of shallow donors that are fully ionized at room temperature, RT.

$$[e^-] \approx [D^+] \qquad (5)$$

In our case, the electron density is determined not only by the dopant but also by intrinsic defects. At the same time it is very important that indium-related defects may not only be positively charged (In_{Cd}^{+}), but also negatively, as associates such as $(In_{Cd}^{+}\ V_{Cd}^{2-})^{-}$. Hence, the following equation can be used to calculate the electron density (Eq. 6).

$$[e^-] = [In_{Cd}^{+}] + 2[V_{Te}^{2+}] + 2[Cd_{i}^{2+}] + [h^+] - 2[V_{Cd}^{2-}] - [(In_{Cd}^{+}\ V_{Cd}^{2-})^{-}] \qquad (6)$$

The measured electron density depends upon the donor part of the uncompensated indium concentration, and also upon the intrinsic content of PDs whose concentration is defined by the crystal's stoichiometric ratio, and by the temperature. In the region of low temperature (line 1 and 2 in Fig. 10) the dependence upon electron density changes, because of the redistribution of intrinsic- and extrinsic-PD content that entails not only new intrinsic PD concentrations, but also an automatic change of the ratio of dopant donors and acceptors. This relationship may be one of the main reasons for the stability of the electron density in the temperature range of 500-750 K.

In regions with minor changes in the electron density (Fig. 11), other factors might play a role in addition to those included in equation 5. Equations 1-4 demonstrate that the process of intrinsic PD generation also covers the interaction with the external phase (Cd or Te vapor). The involvement of all these factors is confirmed by the PDs equilibrium at

high temperatures of over ~750 K. But at lower temperatures the defect-formation reactions gradually decline. Furthermore, the mass exchange with the external phase ceases. Provided that the flat range depicted in figure 11 is observed at T≤ 700 K, we can assume that such stabilization of electrical properties of the CZT1, CZT2 and CZT3 crystals is caused by the factors detailed above. Heating to temperatures over 800 K activates other mechanisms of PD formation and establishes solid-vapor equilibrium.

We also must take into account the low concentration of dopants in the bottom of the ingot. The concentration of doping with In donors and intrinsic acceptors, such as Cd vacancies, introduced during growth process is approximately equal; the indium concentration can be estimated using Pfann's equation [13]. The concentration of In dopant in the bottom part of the ingot equals the initial concentration multiplied by the dopant's segregation coefficient ($1.7\cdot10^{18}\times0.04 \approx 2\cdot10^{16}$ at/cm^3).

At RT, the carrier density in all three samples was very low (Fig. 5), but after heating above 870 K the electron density value increased to ~10^{16} cm^{-3} and slightly increased during further heating (Fig. 10, lines 1 and 2). However, the thermal cycling at temperatures no higher than 700 K facilitates the establishment of a partial PD equilibrium, including extrinsic self-compensation. Thermal cycling at 800-1100 K renews the solid-liquid equilibrium and establishes full PD equilibrium. Lowering the temperature to 500 K or more freezes the solid-vapor equilibrium again.

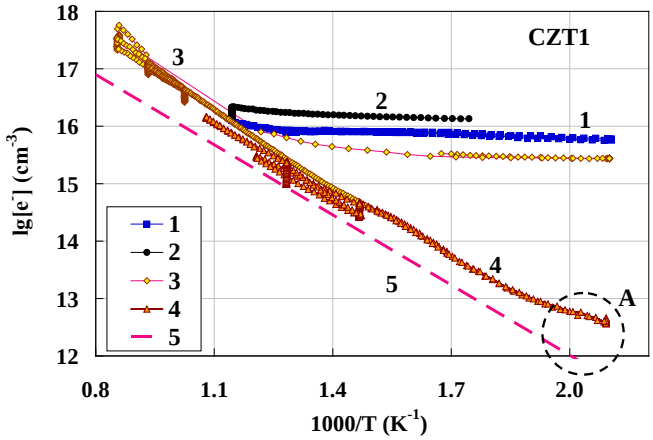

Fig. 11. Carrier concentration dependence versus temperature for CZT1 sample at $P_{Cd,\,max}$. Numbers 1-4 indicate order of measurements. Dashed line 5 – intrinsic carrier concentration in undoped CdTe. Region A is described in text.

After several heating-cooling cycles, the electron density in CZT1 sample dropped three orders-of-magnitude from ~10^{16} cm^{-3} (Fig. 11, region A). This information can be used in the post-growth annealing of CZT:In samples, when electrical properties, close to intrinsic ones, should be obtained.

We note than only the CZT1 sample became semi-insulating after thermal cycling. The other two samples have a higher dopant content (it increases from the beginning to the end of the ingot because k<1 for indium in CZT). The excess of In in CZT2 and CZT3 samples cannot ensure automatic self-compensation in the crystal, so the free-carrier concentration increases in the "plateau" region. After thermal cycling, the excess of In prevents the sample from attaining high resistivity at RT.

During the high-temperature (1100-1200 K) measurements at saturated Cd vapor overpressure, the concentration of cadmium vacancies fell to very low values because of the reactions shown in Eqs. 3-4. At the same time, when the electron density appreciably exceeds the values for undoped CdTe, it is determined by the content of donor dopants and the concentration of complexes of donor – Cd vacancies. Such an explanation corresponds to the fact that the value of In segregation coefficient is much lower than unity [14] and, plausibly, is close to the same in CZT for a ZnTe content less than 10-12 %. Consequently, the In concentration is slightly lower from the beginning to the end of the ingot.

In Fig. 12, the isobaric electron-density temperature dependences for CZT2 sample are shown. (Figure 11 is for CZT1) For each curve, we calculated the carrier generation enthalpy. It is significant that the overall aspect of the dependences looked similar for all samples. We explain this by the fact that, at high temperatures (above 1000 K), the electron density in the samples with low dopant content is determined by the concentration of intrinsic donors. Different values for the activation energy of the process (the slope of curves in Fig. 12) are determined by the effect of In doping and by the ratio of the different major donors, and V_{Te}^{2+}, at different temperatures [15]. Above 1000 K the electron density in CZT crystals is lower than in CdTe. This phenomenon is due to the presence in CdTe matrix ~10% of ZnTe. The possible

influence of Zn atoms is caused by 2 reasons: the increasing content of native acceptors (Zn vacancies) that is typical for ZnTe and augmentation of the formation energy of Cd_i^{2+} [9].

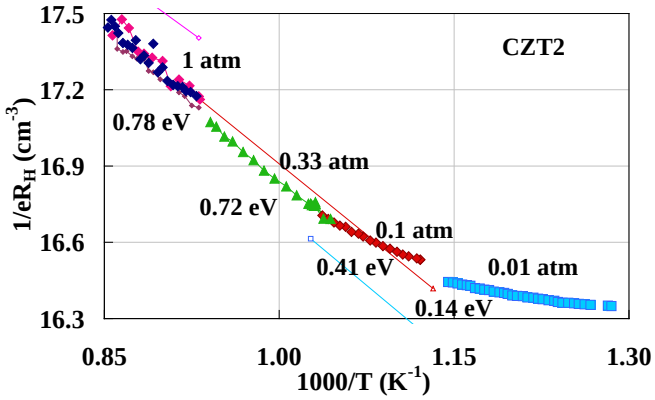

Fig. 12. Electron-density dependences on temperature in the CZT2 sample at constant Cd overpressure (0.01÷1 atm.). Dashed lines are for same isobars for undoped CdTe. Line slopes (in eV) were calculated using the Arrhenius equation.

SUMMARY AND CONCLUSIONS

1. We successfully removed Te-rich secondary phases (i.e., inclusions) from CZT samples, prepared from an HPBM-grown ingot, by annealing at 1070 K under Cd or Cd-Zn saturated vapor pressure for several hours.
2. The following treatment allowed us to restore the initial high resistance of previously Cd-annealed samples to their initial values via the following conditions: Vapor atmosphere - Te overpressure, temperature – 1070 K, duration - 4 hrs., cooling rate - ~2 K/min.
3. High-temperature Hall-effect measurements of the HPBM-grown $Cd_{0.9}Zn_{0.1}Te$:In samples in the Cd vapor displayed some differences in comparison with CdTe. The main difference is a lowered free-carrier concentration, plausibly caused by Zn atoms in the lattice.
4. Our analysis of the stability of the free-carrier concentrations at 500-700 K was explained in the framework of self-compensation and partial "freezing" of quasi-chemical defect-creating reactions inside the crystal.
5. The electrical characteristics of the crystals, cut from three different positions in the $Cd_{0.9}Zn_{0.1}Te$:In ingot show a slight increase in the In concentration along the ingot; we estimate the segregation value as quite close to the one in CdTe.
6. We determined that at a low In content in the CZT crystal (~10^{16} at/cm^3), thermal cycling of the sample at 470-1170 K engenders electrical properties close to intrinsic $Cd_{0.9}Zn_{0.1}Te$.

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