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Conductivity Compensation in CdZnTe:Cl Crystals with Variable Zinc Content

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Received September 22, 2006

Abstract—The effect of cadmium vapor pressure during postgrowth annealing on the compensation of conductivity has been studied in semi-insulating $\text{Cd}_{1-x}\text{Zn}_x\text{Te:Cl}$ crystals with variable zinc content ($x = 0.005$, 0.01 , and 0.05), which are used in nuclear radiation detectors. At a small zinc content ($x = 0.005$ and 0.01), the main role in the in $\text{Cd}_{1-x}\text{Zn}_x\text{Te:Cl}$ crystals is played by the cadmium point defects. In crystals with a higher zinc content ($x = 0.05$), the compensation of charged defects is incompletely controlled by changing the cadmium vapor pressure, which is evidence of a significant influence of the zinc point defects.

PACS numbers: 07.85.Fv, 61.72.-y, 72.40.-w

DOI: 10.1134/S1063785007040268

In recent years, much attention has been devoted to crystals of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te:Cl}$ system, which are used in nuclear radiation detectors [1–5]. However, the applications of detectors based on such crystals are restricted because of low values of the product of charge carrier (hole) mobility and lifetime ($\mu_h\tau_h \leq 10^{-5} \text{ V}^{-1} \text{ cm}^2$) [2, 6]. Both conductivity and the transport characteristics (including $\mu\tau$) of doped semiconductor crystals are determined by processes of (i) the mutual compensation of charged point defects and (ii) their complexation, which take place during the postgrowth cooling of crystals [7–11] and depend on the temperature and the cadmium vapor pressure [7, 9, 11].

In order to study the process of conductivity compensation in CdTe:Cl crystals, we have developed a method of their annealing under controlled cadmium vapor pressure [12]. The first results of the annealing of $\text{Cd}_{1-x}\text{Zn}_x\text{Te:Cl}$ crystals with $x = 0.05$ showed evidence of a change in the character of inversion of the conductivity type in this system as compared to that in zinc-free CdTe:Cl crystals [13].

This Letter presents the results of investigation of the compensation of conductivity in $\text{Cd}_{1-x}\text{Zn}_x\text{Te:Cl}$ crystals with variable zinc content ($x = 0.005$, 0.01 , and 0.05) in the course of their annealing at various cadmium vapor pressures.

The samples of $\text{Cd}_{1-x}\text{Zn}_x\text{Te:Cl}$ crystals were grown by the horizontal directional solidification (HDS) method under controlled cadmium vapor pressure (P_{Cd}) [14]. The concentration of dopant (Cl) in the crystal is determined by the amount of CdCl_2 charged in the growth ampule. According to mass-spectrometric data,

this concentration ($\sim 10^{17} \text{ cm}^{-3}$) was the same in all ingots. The initial (as-grown) samples had a hole conductivity with $p = 10^8\text{--}10^9 \text{ cm}^{-3}$. The postgrowth annealing of crystals was performed in a sealed quartz ampule evacuated to a residual pressure of $\sim 10^{-4} \text{ Pa}$, which had three zones—sample, charge, and P_{Cd} control. The temperatures of the sample and charge zones (900 and 905°C , respectively) and the interval of cadmium vapor pressures P_{Cd} were selected based on the results of our preliminary investigations of $\text{Cd}_{1-x}\text{Zn}_x\text{Te:Cl}$ crystals [13]. In each test, the sample was kept for $\sim 5 \text{ h}$ at a preset annealing temperature and then slowly (over about two days) cooled to room temperature.

The charge carrier density in annealed crystals was determined using the results of Hall emf measurements. Figure 1 shows plots of the free charge carrier density versus cadmium vapor pressure. As can be seen, the $n(P_{\text{Cd}})$ curves for the samples with various zinc contents are similar to each other. Note three characteristic regions on each curve: (1) conductivity type inversion; (2) electron density buildup; and (3) saturation.

Let us consider the region of P_{Cd}^* (Fig. 1, region I shown only for $x = 0$), in which the annealed samples of CdTe:Cl crystals exhibit p – n inversion of the conductivity type. For the samples of $\text{Cd}_{1-x}\text{Zn}_x\text{Te:Cl}$ crystals, the values of P_{Cd}^* were determined by extrapolating P_{Cd} to a minimum electron density obtained on the zinc-free (CdTe:Cl) samples ($n = 10^7 \text{ cm}^{-3}$), since the explicit form of the curve of hole density versus P_{Cd} was not established.

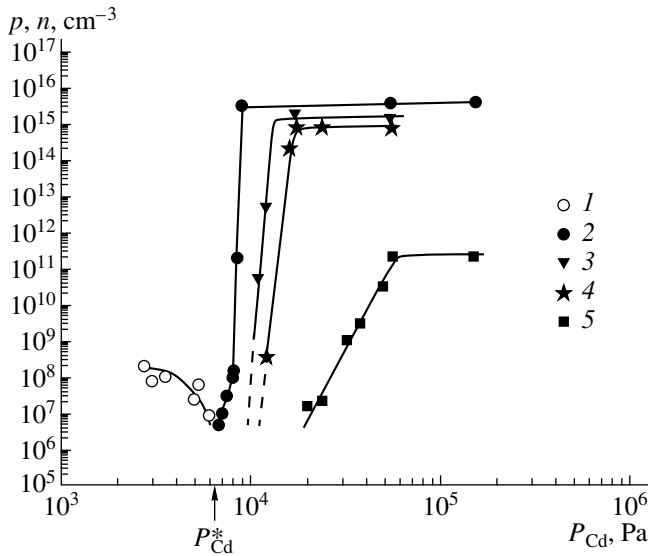


Fig. 1. Plots of (1) hole density and (2-5) electron density in annealed samples of CdTe and Cd_{1-x}Zn_xTe:Cl crystals versus cadmium vapor pressure P_{Cd} during the annealing: (1, 2) $x = 0$; (3) $x = 0.005$; (4) $x = 0.01$; (5) $x = 0.05$.

As can be seen, a minimum in the electron density (i.e., the inversion from n to p type) shifts toward higher P_{Cd} upon the annealing of Cd_{1-x}Zn_xTe:Cl crystals with higher Zn contents. The minimum density of free carriers (left branch of the $n(P_{Cd})$ curves in Fig. 1) is observed at a certain cadmium vapor pressure corresponding to the equality of concentrations of the main donor and acceptor point defects [15, 16]:

$$[V_{Cd}^{-2}] + [V_{Zn}^{-2}] \approx \frac{1}{2}[Cl_{Te}^{+}]. \quad (1)$$

Evidently, the samples with higher Zn concentration also contain a greater number of zinc vacancies (V_{Zn}). Therefore, the above relation between the donor and acceptor centers implies that a higher P_{Cd} (i.e., a decrease in $[V_{Cd}^{-2}]$) is required for the inversion from acceptor to donor state.

Figure 2 shows a plot of P_{Cd}^* (corresponding to the inversion of the conductivity type) versus the content of Zn in Cd_{1-x}Zn_xTe:Cl crystals. The observed linear dependence can be explained proceeding from the condition of equality (1) of the concentrations of donor and acceptor point defects. Taking into account the relation for the Frenkel defects, $[V_{Cd}][Cd_i] = K_F$, and the dependence of their concentration on the cadmium vapor pressure over the crystal, $n[Cd_i] = K_r P_{Cd}$, and using relation (1), we obtain

$$P_{Cd} = \frac{nK_F}{K_r \left(\frac{1}{2}[Cl_{Te}^{+}] - [V_{Zn}] \right)},$$

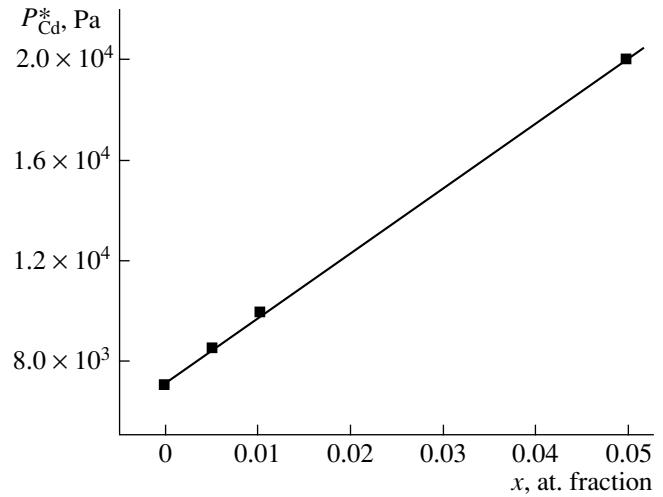


Fig. 2. A plot of P_{Cd}^* (corresponding to the inversion of the conductivity type upon annealing) versus the content of Zn in Cd_{1-x}Zn_xTe:Cl crystals.

where K_F and K_r are constant quantities [9]. It should be recalled that the concentration of chlorine in all samples is the same. For small $[V_{Zn}^{-2}]$ values (compared to $[Cl_{Te}^{+}]$), the dependence of P_{Cd}^* on x is close to linear, since a change in the concentration of zinc vacancies in the crystal is proportional to the zinc content x .

Let us proceed to the region of electron density buildup (Fig. 1, region 2). The slopes of all curves are approximately the same for the solid solutions with small zinc content ($x = 0.005$ and 0.01) and significantly increases for $x = 0.05$. This result indicates that the rate of compensation with increasing cadmium vapor pressure decreases for the crystals with higher zinc content. Note that the crystals with $x = 0.005$ and 0.01 exhibited relatively high values of the products $\mu_e \tau_e = (4-6) \times 10^{-4} \text{ V}^{-1} \text{ cm}^2$ and $\mu_h \tau_h = (5-10) \times 10^{-5} \text{ V}^{-1} \text{ cm}^2$, while the crystal with $x = 0.05$ has a ten times lower value of the latter product: $\mu_h \tau_h = (5-10) \times 10^{-6} \text{ V}^{-1} \text{ cm}^2$. This fact is indicative of a high concentration of deep centers ($V_{Cd}^{-2} + V_{Zn}^{-2}$) in the crystal with $x = 0.05$, which can be explained either by a small degree of association of V_{Zn}^{-2} into a neutral complex $(2ClV_{Zn})^0$ or by the formation of a different deep center (e.g., Te_{Cd}^{-2} [17, 18]).

In the region of saturation with increasing P_{Cd} (Fig. 1, region 3), the electron density has different values for the Cd_{1-x}Zn_xTe:Cl crystals with various Zn concentrations and exhibits a decrease with increasing x . This behavior cannot be explained by a limited solubility of donor point defects $Cl_{Te}^{+} + Cd_i^{+}$ in

$\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$ solid solutions, since it is known [13, 19] that the concentration of Cd_i^+ in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$ with $x = 0.05$ is higher than the obtained saturation values. According to the mass-spectrometric data, the concentration of chlorine in all crystals was $\sim 1 \times 10^{17} \text{ cm}^{-3}$.

The limitation can be related to the mutual compensation of elementary donor and acceptor point defects. Indeed, the electron density in the compensated $\text{CdZnTe}:\text{Cl}$ can be expressed as

$$n = [\text{Cl}_{\text{Te}}^+] + [\text{Cd}_i^+] - 2[V_{\text{Cd}}^{-2}] - 2[V_{\text{Zn}}^{-2}] - [(V_{\text{Cd}}\text{Cl}_{\text{Te}})^-] - [(V_{\text{Zn}}\text{Cl}_{\text{Te}})^-]. \quad (2)$$

In $\text{CdTe}:\text{Cl}$ samples annealed at a high P_{Cd} , the acceptor point defects of cadmium V_{Cd}^{-2} and $(V_{\text{Cd}}\text{Cl}_{\text{Te}})^-$ annihilate and only the donor point defects Cl_{Te}^+ and Cd_i^+ are retained to determine the electron density. The samples of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$ annealed at a high P_{Cd} retain, in addition to the same donor point defects (Cd_{Te}^+ and Cd_i^+), the acceptor point defects of zinc V_{Zn}^{-2} and $(V_{\text{Zn}}\text{Cl}_{\text{Te}})^-$. The latter defects determine, depending on the concentration of zinc in the crystal, the saturation electron density.

Thus, an analysis of the dependence of the free electron density n in annealed $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$ crystals on the P_{Cd} value leads to a conclusion about the presence of charged point defects of zinc, which influence the conductivity compensation in these crystals. At a small zinc content ($x = 0.005$ and 0.01), the main role in the conductivity compensation in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$ is played by the point defects of cadmium. In the crystals with $x = 0.05$, the dependences of n on P_{Cd} is less pronounced. Here, the compensation of charged defects is incompletely controlled by changing the cadmium vapor pressure, which is evidence of a significant influence of the zinc point defects. Therefore, in order to grow $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{Cl}$ crystals with $x \geq 0.05$ for nuclear radiation detectors, it is necessary to control both cadmium and zinc vapor pressures in the course of growth and annealing.

Acknowledgments. This study was supported by the Presidential Program of Support for Leading Scien-

tific Schools in Russia (project no. NSh2006.59202) and the Federal Agency for Science and Innovations (project no. 02.445.11.7270).

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Translated by P. Pozdeev