ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 20, № 2 (2019) С. 144-148
DOI: 10.15330/pcss.20.2.144-148

PHYSICS AND CHEMISTRY OF SOLID STATE
V. 20, № 2 (2019) P.144-148

UDK 539.2

SSN 1729-4428

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Electro-Physical Properties of Ge-doped $Cd_{1-x}Mn_xTe$ (x < 0.1) Crystals

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Ge-doped $Cd_{1-x}Mn_xTe$ (x = 0.02, 0.04, 0.08) crystals were grown by the Bridgman method. Carried out electrical measurements in the temperature range 280 – 420 K have found that the crystals' hole conductivity is controlled by the deep compensated acceptors, whose ionization energy (ε_A) was increased with the content Mn (x) according to the relation $\varepsilon_A = 0.6\,(1 + 2x)$ eV. At 300 K: $\rho = (10^8\text{-}10^9)$ (Ohm×cm), $R_H = (5\times10^9\text{-}5\times10^{10})$ cm^3/C; mobility of current carriers ~ 50 $cm^2/(V\times s)$.

Key words: $Cd_{1-x}Mn_xTe$, solid solutions, electrical properties, Hall effect, Germanium.

Work arrived to the editor 06.06.2019.; accepted for printing15.06.2019.

Introduction

Active studies of cadmium-manganese telluride ($Cd_{1-x}Mn_xTe$) solid solutions' crystals are associated with prospects for use in opto- and photo-electronics: from them it is possible to make optical filters, X- and gamma-ray detectors, photorefractive elements, etc. [1-5]. The required semi-insulating state in these single crystals is usually achieved by doping with impurities having the occurrence depth of the energy levels in the band gap, which corresponds to the working area of application.

Studies [6-10] indicate that Ge-doped CdTe crystals are relatively high-resistance with a resistivity of $\rho = (10^8 – 10^9)$ (Ohm×cm) and p-type conductivity at room temperature controlled by a deep acceptor level near the middle of the band gap E_V + (0.65 - 0.68) eV. The existence of the level E_V + (0.65 - 0.69) eV was confirmed both by electric [11, 12] and magneto-optical studies [13, 14]. In the paper [15], the $Ge^{2+/3+}$ level was found to be ~ 0.6 eV above the valence band top. By comparing the structural and electrical properties, two deep donor levels were identified, located near E_C-0.31 eV and in the middle of the band gap. An activation energy of the last level, which was associated with the appearance of the Ge-clustering effect in CdTe:Ge crystals, was 0.82 eV [16]. Characteristics of CdTe:Ge crystals (22 % resolution - full width at half maximum (FWHM) for Cs-137 and 7 % for Ag-110, respectively) indicate that they can be used as detectors [17]. Electrical measurements have shown [18] that in the case Ge concentration exceeding more than 5.7×10^{17} atm/cm^3, the conductivity type of CdTe:Ge crystals varies from hole to electron ones.

According to Kröger's assumption [19], the high-resistance state of CdTe:Ge crystals is achieved by self-compensation between different forms of Ge-impurity. This view was also confirmed by other authors [20]. The authors assumed that the compensating level corresponds to the associative defect $(Ge_{Cd}^{+}V_{Cd}^{2-})^{-}$, which acts as an acceptor. By the researches of electric, optical and magnetic properties of CdTe:Ge crystals after high-temperature annealing in the cadmium vapor atmosphere it has been established the low values of the electron capture cross-section at r-centers and the corresponding for holes, indicating the presence of acceptor centers $(Ge_{Cd}^{+}V_{Cd}^{2-})^{-}$ [21]. Theoretical calculations [22] indicate the possibility of the Ge atoms' location in Te sites acting as an acceptor (Ge_{Te}) under the conditions of cadmium vapor saturation.

It was found [23] that $Cd_{1-x}Mn_xTe$ crystals' doping by Sn-impurity leads to an increase of the crystals' resistivity; at x = 0.2, deep donors are introduced, and at x = 0.4 - deep acceptors. It is to be expected that such features of CdTe:Ge crystals as high resistivity, significant photosensitivity will be maintained in the crystals of Ge-doped $Cd_{1-x}Mn_xTe$ solid solutions. However, up to now, such crystals have not been studied at all, therefore, the study of electrical characteristics of Ge-doped $Cd_{1-x}Mn_xTe$ crystals are relevant.

I. Experimental procedure

Ge-doped $Cd_{1-x}Mn_xTe$ (x=0.02-0.08) crystals (impurity concentration in the melt - 8×10^{18} cm^{-3}), were obtained from the initial components of the purity class not less than 5N. Ge impurity was loaded into a quartz

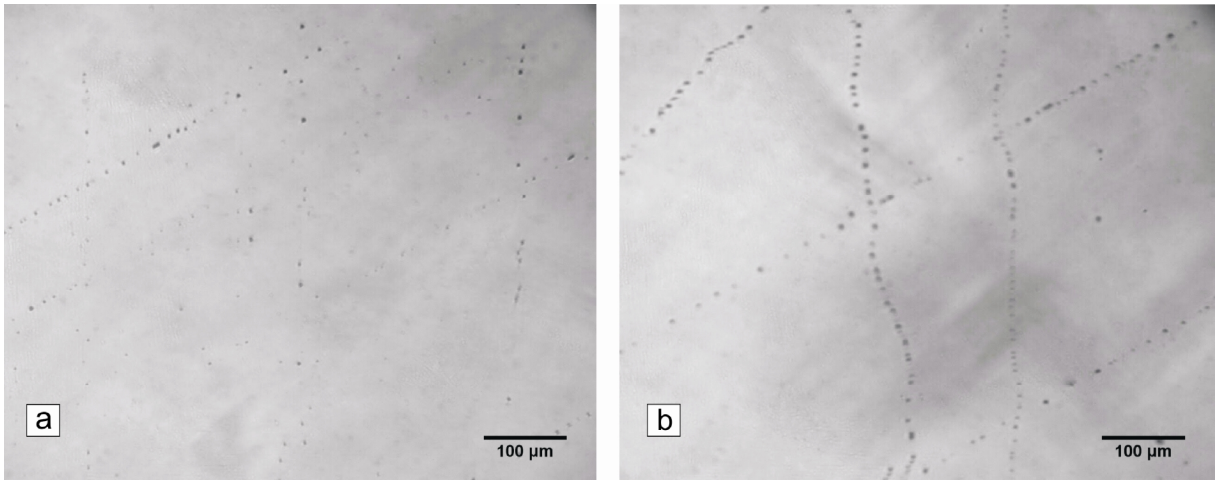

Fig. 1. IR-images of Ge-doped $Cd_{1-x}Mn_xTe$ (x = 0.08) crystal samples (a - the beginning of the ingot, b - the end f the ingot).

ampoule together with the initial components Cd, Te and Mn. Long-term synthesis (70 – 72 hours) provided an uniform distribution of components in the melt, after which the growth of single crystals was carried out by the Bridgman method in a modified setup with a massive traveling heater. The pre-growth melt maximum temperature was about 1400 K, that was enough to melt the high-temperature solid phases in it. The temperature gradient at the crystallization interface was 10 ÷ 15 K/cm, the growth rate was 2 mm/h. For growth, a quartz container of 40 mm in diameter with a flat bottom and a heat transfer in the lower center was used to provide the large monocrystalline grains [24]. After the crystallization, the ingot was annealed at 1173 K for 48 hours, and then was cooled down to room temperatures with a rate of 20 K/h.

Samples of grown crystals were examined with IR microscope Leitz, equipped with an IR camera Pixelink PL-A741 for a presence of second phase inclusions. Since the $Cd_{1-x}Mn_xTe$ crystal matrix is transparent for IR-wavelengths, and the Te inclusions are opaque, that makes it possible to observe their localization, structure and size.

Electro-physical measurements were made on the rectangular monocrystalline samples (12×2×1.5 mm^3) with two pairs of potential contacts. The current and probe contacts to the samples were made by copper deposition from a drop of $CuSO_4$ saturated solution on the freshly-etched sample [25]. The electrical signals were recorded by an electrometer with an input resistance of 10^{12} Ohm, which ensured no shunting by the surface or by the setup elements. The temperature (280 – 420 K) dependences (TD) of the resistivity ρ and the Hall coefficient R_H, as well as the Hall mobilities of current carriers $\mu = R_H/\rho$, were investigated in the mode of direct current and at the magnetic field induction of 0.5T. The charge carriers concentration p(n) was calculated by the formula $p(n) = (e \times R_H)^{-1}$. Hall-factor was taken equal to one.

II. Results and discussion

Fig. 1 shows the IR-images of two samples cut from the beginning (a) and the end (b) of the $Cd_{1-x}Mn_xTe$ (x = 0.08) ingot, respectively. One can see the presence of both single inclusions and inclusions, accumulated on the dislocation networks, especially in the crystal from the end of the ingot.

Fig. 2 shows the samples' resistivity dependences (300 K) of undoped (1) [26] and Ge-doped (2) $Cd_{1-x}Mn_xTe$ crystals on ingot composition (x). Measurements were made on samples from different parts of each ingot, as evidenced by the error interval ρ indicated in Fig. 2. It is evident that the macroscopic homogeneity of the doped crystals is even better than undoped ones, which may be due to less influence of uncontrolled impurities. Increase in resistivity of the doped crystals in all compositions reached 6 orders of magnitude.

Fig. 3 shows the Hall coefficient TD of three typical samples of the doped crystals with different composition. By sign of the Hall coefficient, all samples (and not

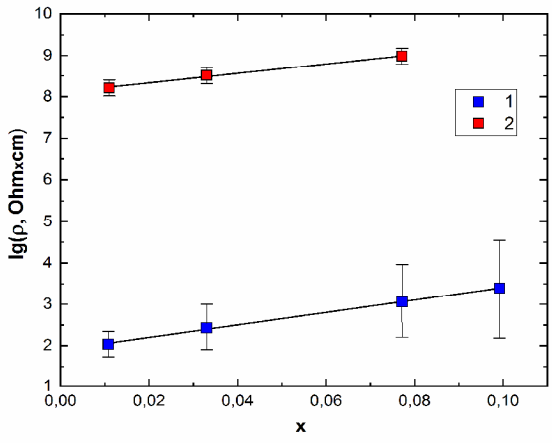

Fig. 2. Resistivity dependence of Cd(Mn)Te (1) and Cd(Mn)Te-Ge samples (2) on the composition (x). T= 300 K.

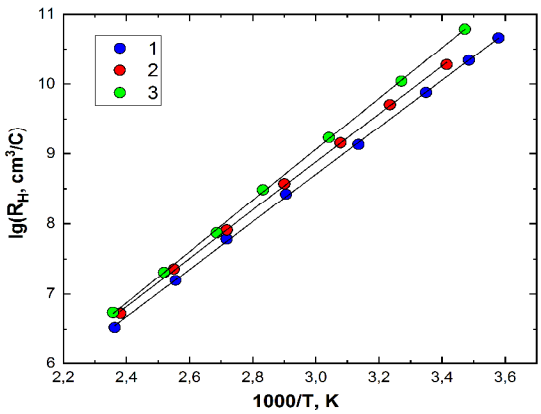

Fig. 3. Hall coefficient temperature dependence of Cd(Mn)Te-Ge samples of different composition: 1 - x = 0.02; 2 - x = 0.04; 3 - x = 0.08.

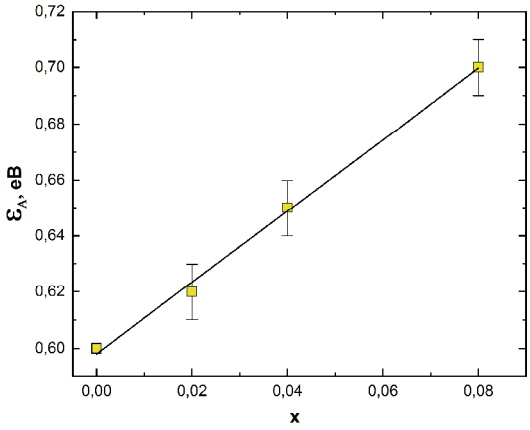

Fig. 4. Dependence of an ionization energy of acceptors *A* on the composition (x) of $Cd_{1-x}Mn_xTe$-Ge crystals.

shown in this figure) had a hole conductivity. Hall mobility of holes of all experimental samples over 300 K lied within (45 - 60) $cm^2/(V \cdot s)$ and practically did not depend on the crystal composition (x). In the "heating-cooling" cycles, the results of R_H and ρ were reproducible, and there were no isothermal relaxations characteristic for undoped Cd(Mn)Te crystals [27]. In this respect, these crystals were not different from the p-CdTe-Ge crystals [6, 7].

To determine the ionization energy (ε_A) of acceptor *A*, which controls p-conductivity in Cd(Mn)Te-Ge crystals, the results of Fig. 3 were analyzed using a compensated semiconductor model that determines the position of the donor or acceptor levels relative to the edges of the corresponding bands at 0 K. For calculations, the values of the effective masses of states' densities $m_n^* = 0.11m_0$, $m_p^* = 0.63m_0$ for pure cadmium telluride [28] and the values of the band gap width for Cd(Mn)Te at 0 K and at 300 K, were used in the works [29, 30]. A linear dependence of ε_A on the content Mn (Fig. 4) was found, which is described by the equation $\varepsilon_A = 0.60\ (1 + 2.0x)$ eV. It was interesting to compare

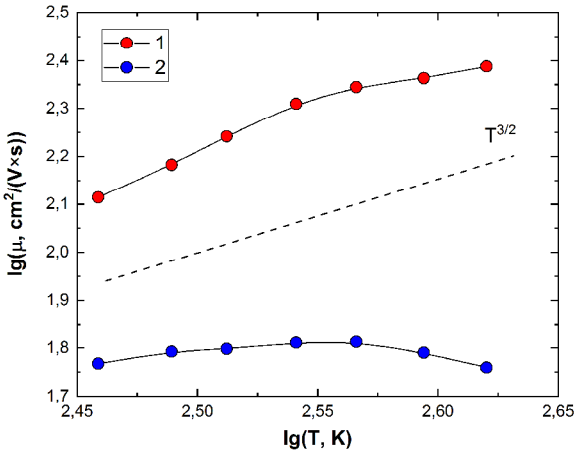

Fig. 5. Temperature dependence of the Hall mobility of current carriers in samples: 1 - n-$Cd_{1-x}Mn_xTe$-In (x = 0.05); 2 - p-$Cd_{1-x}Mn_xTe$-Ge (x = 0.04).

this dependence with the same for the bandgap width {$E_g = 1.49\ (1 + 0.92)$ eB} and for the main acceptors A_2 in undoped Cd(Mn)Te crystals {$\varepsilon_{A2} = 0{,}12\ (1 + 5{,}5x)$ eB}[31]. It is seen that the distancing rate from the V-band peak of the acceptor level in the Cd(Mn)Te-Ge is significantly less than of acceptor A_2 level in un-doped crystals. But it is quite close to the distancing rate of the C-band bottom from the V-band top. Therefore, it can be argued that the acceptor *A* (or its constituents) is localized in the cationic sublattice.

Based on R_H TD it was not possible to determine the concentration of electrically active centers (N_I), since full ionization region of *A*-centers was absent. In this respect, the TD of the mobility of current carriers was more informative (Fig. 5, curve 2). TD of μ_p in p-$Cd_{1-x}Mn_xTe$-Ge sample can be described using classical scattering mechanisms (on fluctuations of the crystal lattice and ionized centers), taking into account the presence of regions, including areas of Weissberg space charge [32], opaque to current carriers. The maximum μ_p TD at T > 300 K indicated that N_I cannot be less than 5×10^{17} cm^{-3}.

For comparison Fig. 5 shows the TD of the Hall electron mobility (curve 1) in the semi-insulating In-doped n-$Cd_{1-x}Mn_xTe$ sample. It is seen that at low temperatures, μ_n TD is much stronger than $T^{3/2}$. Therefore, in this case we should consider the scattering not on isolated ionized centers, but on collective drift barriers caused by micro-inhomogeneities of the point defects' system. It should be noted that such barriers exist in other semi-insulater crystals with electron conduction type (CdTe, CdTe-Cl, Cd(Zn)Te-In), in which overcompensation is provided by shallow donors.

Conclusions

The values of the resistivity ρ and the Hall coefficient R_H in the samples with the same amount of Ge impurity increase with Mn content increase; at 300 K:

$\rho = (10^8 - 10^9)$ Ohm×cm, $R_H = (5\times10^9\text{-}5\times10^{10})$ cm^3/C, the charge carrier concentration is equal to $1{,}2\times10^9$ - 1.2×10^{10} cm^{-3}, the mobility of current carriers ~ 50 $cm^2/(V\times s)$.

The hole conductivity is controlled by deep compensated acceptors with ionization energy ε_A whose magnitude lies in the range of 0.61 - 0.71 eV, while the dependence of ε_A on the content Mn(x) is described by the relation $\varepsilon_A = 0.60\ (1 + 2.0x)$ eV.

No micro-inhomogeneities were found that cause the existence of drift barriers for current carriers, which is usually observed in high-resistance CdTe crystals and related solid solutions.

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Електрофізичні властивості кристалів $Cd_{1-x}Mn_xTe$ (x < 0,1), легованих германієм

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Методом Бріджмена вирощено кристали $Cd_{1-x}Mn_xTe$ (x = 0,02; 0,04; 0,08), леговані домішкою Ge. Електричними вимірюваннями в інтервалі температур 280 – 420 К встановлено, що діркова провідність кристалів контролюється глибокими компенсованими акцепторами, енергія іонізації яких (ε_A) збільшується з вмістом Mn(x) згідно зі співвідношенням $\varepsilon_A = 0,6\ (1 + 2x)$ еВ. При 300 К: $\rho = (10^8\text{-}10^9)$ (Ом·см), $R_X = (5\times10^9 - 5\times10^{10})$ см^3/Кл; рухливість носіїв струму ~50 см^2/(В·с).

Ключові слова: $Cd_{1-x}Mn_xTe$, тверді розчини, електричні властивості, ефект Холла, Германій.