COMPENSATED IMPURITY CONDUCTIVITY OF SINGLE CRYSTALS $Cd_{1-x}Zn_xTe$

L.A. KOSYACHENKO, Z.I. ZAKHARUK, A.V. MARKOV, O.L. MASLYANCHUK, I.M. RARENKO, V.M. SKLYARCHUK

Fed'kovych Chernivtsi National University
(2, Kotsyubyns'kyi, Chernivtsi 58012, Ukraine; e-mail: lakos@chv.ukrpack.net)

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We have studied the mechanism of conductivity of single crystals $Cd_{1-x}Zn_xTe$ ($x = 0.05$) with regard for deep acceptor impurities (defects) of several types and their compensation by donors and determined the ionization energy and the compensation level for acceptors responsible for the material conductivity. The optimum conditions for increasing the resistivity depending on the impurity ionization level are formulated.

Introduction

Cadmium telluride and a solid solution $Cd_{1-x}Zn_xTe$ ($x = 0.05 \div 0.1$) on its base are main materials for semiconductor detectors of ionizing electromagnetic radiation which do not require cryogenic cooling [1—3]. One of the key parameters defining the characteristics of such detectors is the conductivity of a semiconductor used. It is important that the material conductivity should be close to the intrinsic one, otherwise the sensitivity and energy resolution of a detector are considerably deteriorated. The modern technology of growing the semiinsulating single crystals $Cd_{1-x}Zn_xTe$, as well as CdTe, is not controlled to the full extent. Therefore, the crystals for detectors (mostly $3\times3\times2$ mm in size) are selected among many manufactured ones. To decrease conductivity, compensating impurities (Ti, V, or Cl) are introduced or thermoelectric cooling is used [4, 5]. Eventually, this leads to an extremely high cost of devices. The further success in overcoming the above-mentioned difficulties is hampered to a considerable extent by the fact that the peculiarities of conductivity of $Cd_{1-x}Zn_xTe$ related to deep levels of impurities (defects) of a few types, the processes of compensation of acceptors by donors, etc. are not investigated in detail [4, 6]. The clarification of these questions is the goal of the present work.

1. Experimental Results

The optical measurements showed that the bandgap width for Bridgman-grown single crystals $Cd_{1-x}Zn_xTe$ ($x = 0.05$) was 1.51 eV (1.47 eV for CdTe by the same procedure) at room temperature [7]. The single crystals possess p-type conduction, and their resistivity ρ does not exceed $10^2 - 10^3\,\Omega\cdot$cm, as usual, at room temperature. To enhance ρ, we annealed plates of 1.5—2 mm in thickness, that were cut from an ingot, in a Cd vapor under excessive pressure. As a result, the value of ρ increased up to $10^8 - 10^9\Omega\cdot$cm (sometimes almost to $\sim10^{10}\,\Omega\cdot$cm), but only for the plates cut from the central part of an ingot. Different specimens were different not only in their resistivity, but also in their dependence on temperature (we consider this characteristic to be important because the working temperature interval of a detector must cover at least 220—350 K).

In Fig. 1, we present the typical temperature dependences $\rho(T)$ of specimens made of $Cd_{1-x}Zn_xTe$: two high-resistivity (semiinsulating) ones and, for the sake of comparison, one low-resistivity specimen.

We chose the coordinate system in view of the expected temperature dependence of resistivity $(en\mu_n + ep\mu_p)^{-1}$, where e is the electron charge, n and p are, respectively, the concentrations of electrons and holes, and μ_n and μ_p are their mobilities.

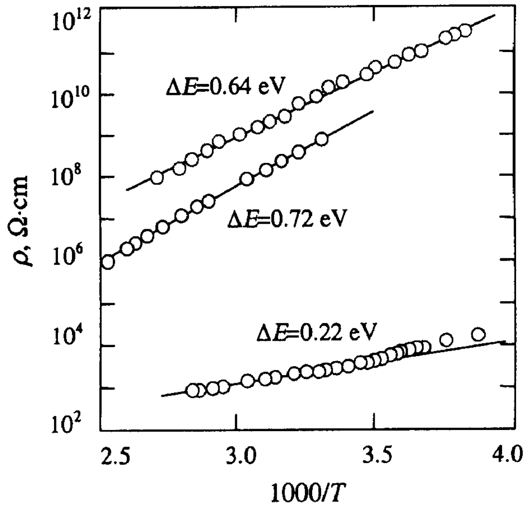

Fig. 1. Resistivity versus temperature $\rho(T)$ for three specimens made of $Cd_{1-x}Zn_xTe$ with different ρ at 300 K: $2 \cdot 10^{10}\,\Omega$·cm (ΔE = 0.64 eV), $1 \cdot 10^9\,\Omega$·cm (ΔE = 0.72 eV), and $3 \cdot 10^3\,\Omega$·cm (ΔE = 0.22 eV). Solid lines is a linear approximation of experimental data. ΔE is the conduction activation energy

By $\Delta\mu$, we denote the energy distance of the Fermi level from the valence band (or "Fermi level energy"). Then we can write

$$n = N_c \exp\left(-\frac{E_g - \Delta\mu}{kT}\right), \tag{1}$$

$$p = N_v \exp\left(-\frac{\Delta\mu}{kT}\right), \tag{2}$$

where $N_c = 2(m_n^* kT/2\pi\hbar^2)^{3/2}$ and $N_v = 2(m_p^* kT/2\pi\hbar^2)^{3/2}$ are, respectively, the effective state densities in the conduction and valence bands, m_n^*=$0.11m_0$ and $m_p^* = 0.35m_0$ are the effective masses of an electron and a hole (m_0 is the electron mass in vacuum), and the rest of notations are standard.

At temperatures higher than ~200 K, the mobilities of electrons and holes in CdTe and $Cd_{1-x}Zn_xTe$ at small x are defined by scattering by deformation potential (rather than by impurities or defects) and well described with the formulas [8,9]

$$\mu_n = 5.5 \cdot 10^6 T^{-3/2} \mathrm{cm}^2/(\mathrm{V \cdot s}), \tag{3}$$

$$\mu_p = 4 \cdot 10^5 T^{-3/2} \mathrm{cm}^2/(\mathrm{V \cdot s}). \tag{4}$$

Since the effective state densities in the bands and the mobilities of carriers are proportional to $T^{3/2}$ and $T^{-3/2}$, respectively, the temperature dependence of resistivity is defined only by the exponent, i.e., the plot of lgρ vs $1000/T$ should be a straight line. As seen from Fig. 1, this holds well except for the reliably reproduced deviation on the lower curve in the region of the lowest temperatures. The conduction activation energies ΔE found by the slope angles of lines for three specimens are 0.22, 0.64 and 0.72 eV.

The experimental data given in Fig. 1 cannot be explained in the frame of a model of semiconductor with a sole type of impurity levels with different depths (acceptors, in the given case). In this case, the observed experimental dependences $\rho(T)$ would testify to the weak ionization of impurities, and the determined activation energies ΔE would define the impurity ionization energy E_a equal to $2\Delta E$, i.e., to 0.44, 1.28, and 1.44 eV, respectively. This assumption does not stand up. Indeed, the most pure and structurally perfect single crystals CdTe and $Cd_{1-x}Zn_xTe$ always contain impurities and defects which create levels with various depths in the bandgap [4, 10, 11]. For example, the impurities of Ag, As, and P in the initial, even superpure Cd, Zn, and Te create shallow acceptor levels of 0.06—0.15 eV in depth; Cd vacancies always present in a specimen — a deep level of 0.40—0.45 eV; Cd vacancies in complexes with impurity atoms (the so-called A-centers) — a deeper acceptor level ~ 0.76 eV; and the acceptors related to Zn have an ionization energy of 0.25 eV. The concentration of all these impurities and defects determined by the method of electron paramagnetic resonance (EPR) is in the range 10^{15}—10^{16} cm^{-3} [10]. In view of the discussed problem, it is important that, without the compensating action of donors, the presence of shallow acceptors decreases the influence of deeper acceptors on the conductivity of a semiconductor. A simple calculation shows that, in the presence of acceptors with an ionization energy, for example, of 0.1 eV and a concentration of 10^{15} cm^{-3}, deep acceptors with an ionization energy of 0.3—0.7 eV and a concentration of 10^{16} cm^{-3} have really no effect on the position of the Fermi level (a shallow acceptor completely defines the position of the Fermi level and, hence, the low resistivity of a crystal).

Thus, the presence of the levels of shallow acceptors makes it impossible to reach the experimentally observed semiinsulating state of a semiconductor with resistivity $\rho = 10^9 \div 10^{10}\,\Omega$·cm at 300 K. On the other hand, conductivity of $Cd_{1-x}Zn_xTe$ (as well as that of CdTe) should be significantly affected by noncontrolled or specially introduced impurities and defects of the donor type. In particular, such are donors that are created in the process of growth of a crystal and upon the annealing in a Cd vapor. All donor impurities and defects, whose

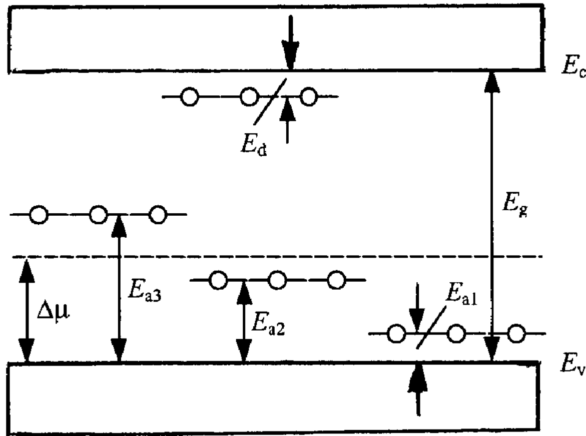

Fig. 2. Scheme of energy levels of a semiconductor

levels are positioned in the upper part of the bandgap (regardless of a specific value of the ionization energy), compensate the available acceptors, by decreasing the conduction of a single crystal.

2. Account of the Compensation of Acceptors of Several Types by Donors

Consider a semiconductor, whose energy scheme includes a donor level (ionization energy $E_d = 0.1$ eV) and three acceptor levels: a shallow level ($E_{a1} = 0.1$ eV), a deep one $E_{a2} = 0.44$ eV), and that located near the middle of the bandgap $E_{a3} = 0.72$ eV) (Fig. 2). By N_d, N_{a1}, N_{a2}, and N_{a3}, we denote, respectively, the concentrations of donors and acceptors. The Fermi level energy $\Delta\mu$ and the ionization energy of acceptors and donors are counted off, respectively, the edge of the valence band and the bottom of the conduction band.

We found the Fermi level energy from the electroneutrality condition

$$n + N_{a1}^- + N_{a2}^- + N_{a3}^- = p + N_d^+, \quad (5)$$

where N_d^+, N_{a1}^-, N_{a2}^-, and N_{a3}^- are the concentrations of charged donors and acceptors. The concentrations of free electrons n and holes p are defined by formulas (1) and (2), that of charged donors is

$$N_d^+ = \frac{N_d}{g_d \exp\left(-\frac{E_g - E_d - \Delta\mu}{kT}\right) + 1}, \quad (6)$$

and the concentration of charged acceptors is

$$N_a^- = \frac{N_a}{g_a \exp\left(\frac{E_a - \Delta\mu}{kT}\right) + 1} \quad (7)$$

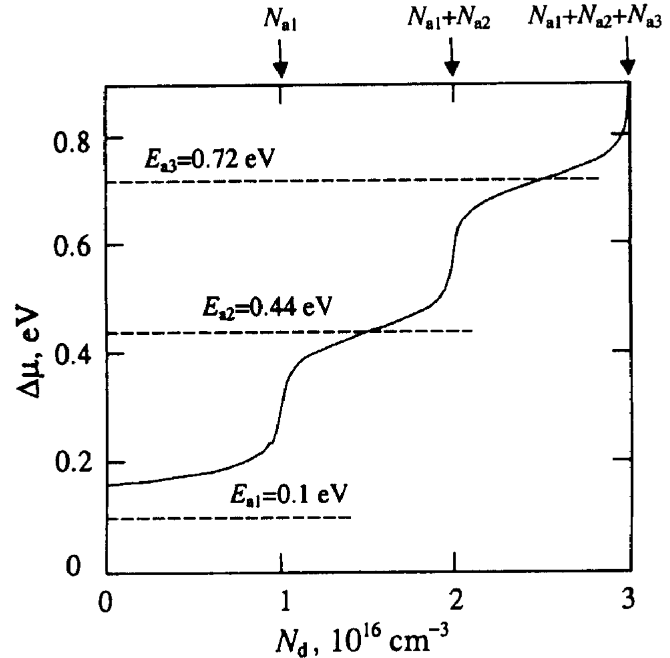

Fig. 3. The Fermi level energy $\Delta\mu$ versus the concentration of a compensating donor impurity N_d for three acceptor levels E_{a1}, E_{a2}, and E_{a3}, whose concentration is 10^{16} cm^{-3}. Temperature is 300 K

with corresponding indices "1", "2", and "3" for N_a, E_a, and N_a^-. Within the simplest model of spin degeneration of donors and acceptors, we have, respectively, $g_d = 1/2$ and $g_a = 2$ [12, 13]. In what follows, we take $g = g_d = g_a = 1$, which introduces an error of at most $kT \ln g = \pm 0.01$ eV at 300 K to the ionization energy.

The results of computer calculations of the Fermi level energy $\Delta\mu$ as a function of the concentration of donors N_d are given in Fig. 3. The concentrations of the three acceptors N_{a1}, N_{a2}, and N_{a3} are taken equal to 10^{16} cm^{-3}.

As seen, the position of the Fermi level in compensated semiconductors is defined no longer by an impurity or a defect with the least ionization energy. At a low concentration of donors (that is insufficient for the compensation of the most shallow acceptor), the Fermi level moves gradually away from the valence band ($\Delta\mu \approx E_{a1}/2$ for $N_d = 0$ and $T \to 0$) with increase in N_d. As N_d approaches N_{a1}, this withdrawal becomes faster. At $N_d = N_{a1}$, the Fermi level moves rapidly to the region of energies $\Delta\mu \approx E_{a2}$. Upon the further increase in N_d, the Fermi level begins again to gradually withdraw from the valence band as long as N_d approaches $N_{a1} + N_{a2}$. When N_d becomes equal to $N_{a1} + N_{a2}$, the Fermi level makes a new "jump" to the energy region $\Delta\mu \approx E_{a3}$.

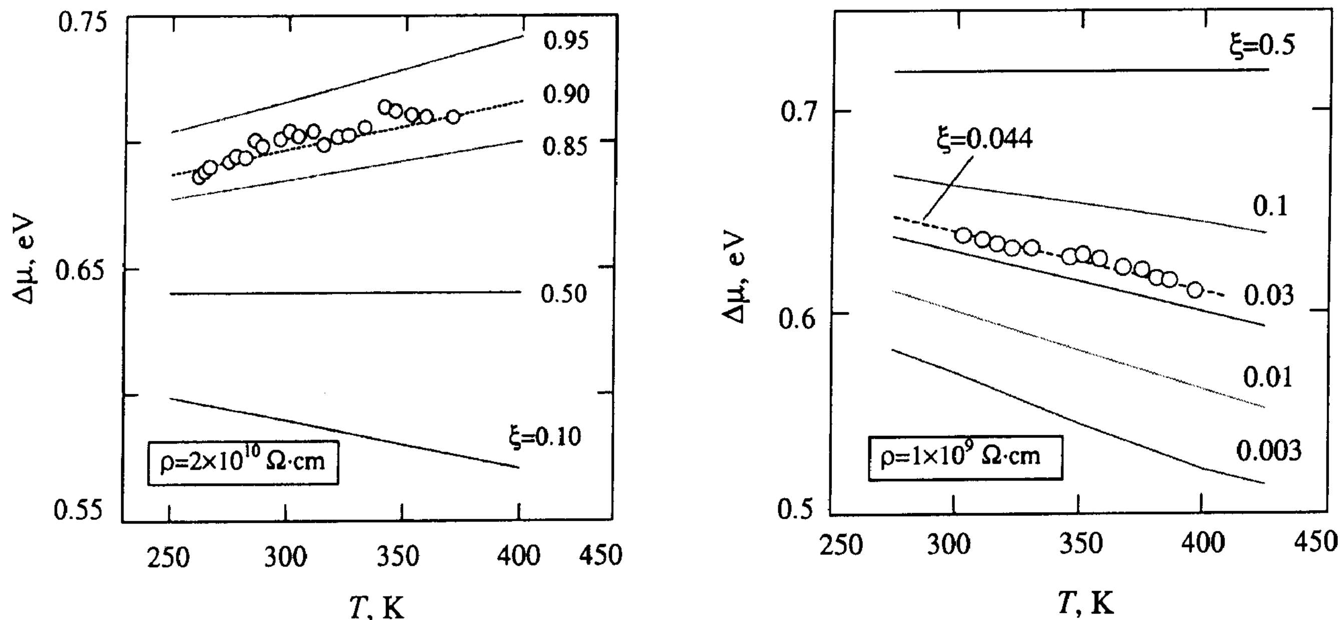

Fig. 4. Comparison of the temperature dependence of the Fermi energy determined by the experimental curve $\rho(T)$ (circles) with curves $\Delta\mu(T)$ calculated at various degrees of compensation $\xi = N_d/N_a$ (solid lines) for single crystals with $\rho = 2 \cdot 10^{10}$ and $1 \cdot 10^9$ Ω·cm (300 K)

If, at last, the value of N_d exceeds the total concentration of all acceptors $N_{a1} + N_{a2} + N_{a3}$, the Fermi level moves into the upper half of the bandgap, and the conduction of a semiconductor becomes the electron one. It is worth noting that the presence of already completely compensated levels does not influence the process of compensation (the dependence of $\Delta\mu$ on N_d) of a deeper level. The role of compensated levels is reduced only to the fact that their compensation consumed the necessary amount of donors.

As known from the statistics of electrons and holes, the concentration of holes in a compensated semiconductor with conduction of the p-type is described with one of the following characteristic analytic formulas. For a considerable compensation and at sufficiently low temperatures [12, 13],

$$p \approx \frac{N_a - N_d}{N_d} N_v \exp\left(-\frac{E_a}{kT}\right), \tag{8}$$

whereas, for a slight compensation and at high temperatures,

$$p \approx \sqrt{N_a N_v} \exp\left(-\frac{E_a}{2kT}\right). \tag{9}$$

It is clear from the above that E_a, N_a, and N_d in these formulas should mean, respectively, the ionization energy of the deepest level that is not else completely compensated, its concentration, and the concentration of all the already compensated, more shallow acceptors.

In view of the considerable concentration of impurities and defects in the materials under study, it is natural to assume that the high resistivity of two crystals from those presented in Fig.1 is caused by a high degree of compensation. Then, according to (8), the activation energy ΔE found with the use of the slope of the experimental curve $\rho(T)$ is equal to the ionization energy of an impurity E_a. Given E_a, we can determine now the degree of compensation by comparing the calculated dependences $\Delta\mu$(T) with the experimental curves.

For this purpose, we can find the concentration of holes for a p-semiconductor at any temperature as $p = (e\rho\mu_p)^{-1}$ by using formula (2) for the mobility of holes. In this case, the Fermi level energy is

$$\Delta\mu = kT \ln\left(\frac{N_v}{p}\right). \tag{10}$$

Because the conduction of one of the specimens is quite close to the intrinsic one, we must substitute (10) by a formula that takes both the electron and hole components of conduction into account. By solving the equation $\rho=(en\mu_n+ep\mu_p)^{-1}$ for $\Delta\mu$, we get

$$\Delta\mu = kT \ln\left(\frac{1 - \sqrt{1 - 4e^2\rho^2\mu_n\mu_p n_i^2}}{2e\rho\mu_n n_i^2/N_v}\right) \tag{11}$$

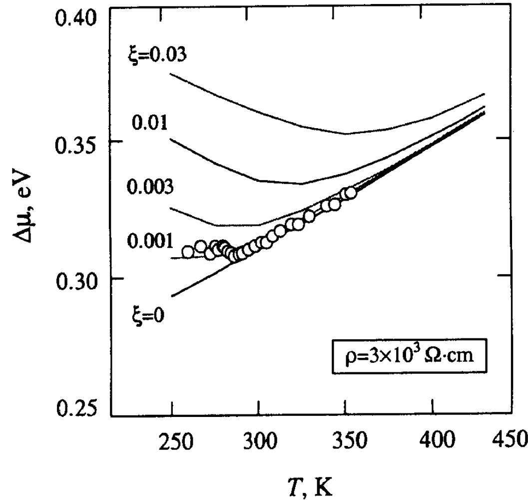

Fig. 5. The same as in Fig. 4, but for a single crystal with $3 \cdot 10^3$ Ω·cm (300 K)

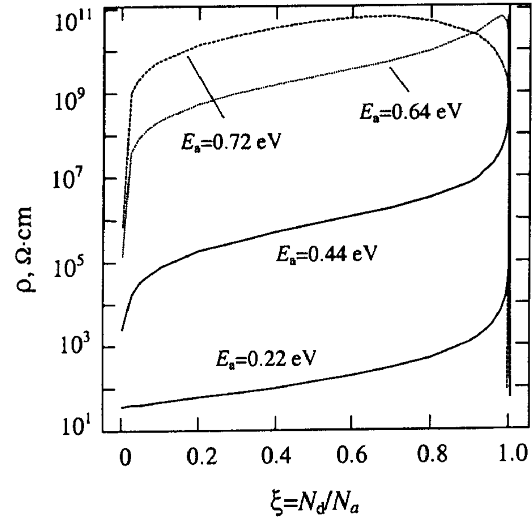

Fig. 6. Resistivity ρ versus the degree of compensation of acceptors by donors ξ at various ionization energies of acceptors E_a (E_d = 0.1 eV, $N_d = 10^{16}$ cm^{-3}, T = 300 K)

where $n_i = (N_c N_v)^{1/2} \exp(-E_g/2kT)$ is the intrinsic carrier concentration.

Circles in Fig. 4 represent the dependences $\Delta\mu(T)$ found from experimental data on $\rho(T)$ by formula (11) for single crystals with $\rho = 2 \cdot 10^{10}$ Ω·cm (E_a = 0.64 eV) and $1 \cdot 10^9$ Ω·cm (E_a = 0.72 eV), and solid lines show the dependences $\Delta\mu(T)$ calculated from the electroneutrality equation (5) with regard for (1), (2), (6), and (7) at various degrees of compensation $\xi = N_d/N_\text{a}$.

As seen, the results of calculations for single crystals with $\rho = 2 \cdot 10^{10}$ and $1 \cdot 10^9$ Ω·cm well agree with experiment, respectively, for $\xi \approx 0.92$ and ≈ 0.044 (the calculations were carried out for $N_a = 10^{16}$ cm^{-3}). In this case, we note that the position of the Fermi level in compensated semiconductors is independent of the concentration of an acceptor impurity in a certain temperature interval according to (8). The calculations indicate that, in this case, such an independence is observed in the whole temperature interval under study for N_a varying in the limits $10^{14} - 10^{16}$ cm^{-3}.

Contrary to the results given in Fig. 3, a low-resistivity single crystal ($\rho = 3 \cdot 10^3$ Ω·cm) reveals the difference between the experimental data on $\Delta\mu(T)$ and the theoretical curves calculated in the same way both in $\Delta\mu$ and the temperature dependence form. We note that this should be expected because the weak compensation of a single crystal yields its low resistivity. But, in this case, formula (9) is valid, rather than (8), i.e. the impurity ionization energy E_a is equal now to the doubled activation energy ΔE (Fig. 1). In Fig. 5, we show the results of calculations of $\Delta\mu(T)$ at E_a = 0.44 eV (rather than at 0.22 eV) and for various levels of compensation. As seen, the experimental data on $\Delta\mu(T)$ for the low-resistivity crystal coincide with the results of calculations at $\xi \approx 0.001$, i.e. for the degree of compensation which is considerably less than that of high-resistivity crystals. We note that the bend on the experimental curve corresponds at low temperatures to the deviation from a straight line seen in Fig. 1 (the lower curve).

Resistivity of $3 \cdot 10^3$ Ω·cm corresponds to the concentration of holes $p = 3 \cdot 10^{13}$ cm^{-3}. Given p, we can find the concentration of acceptors N_a by using (9). For E_a = 0.44 eV, it turns out to equal $4 \cdot 10^{15}$ cm^{-3}, which well agrees with the literature data [10]. Thus, a number of facts confirms both the correctness of the proposed scheme of levels in the bandgap and the interpretation of the experimental data derived. As was expected, a high resistivity is inherent only in the crystals with a high degree of compensation due to a considerable concentration of uncontrolled impurities and defects. However, the result of compensation depends also on the position of a compensated acceptor level in the bandgap.

In Fig 6, we show the dependences of the material resistivity on the compensation degree $\xi = N_d/N_a$ that are calculated for several values of the acceptor ionization energy E_a (for simplicity, we assume that there exists only one of these acceptors).

As seen, for all acceptor levels, a resistivity close to the intrinsic one is attained as a result of the compensation. However, this occurs at a practically complete compensation for E_a = 0.22 and 0.44 eV and at a considerably less compensation for E_a = 0.64 and

0.72 eV. It is important that, for $E_a = 0.72$ eV, the resistivity changes only by two times if the degree of compensation varies in the interval $\xi = 0.3$—0.9. For the same change in ρ and for $E_a = 0.64$ eV, the range of variation in ξ is narrowed up to 0.92—0.99. In this case, the least increment in ξ above 0.99 leads to the catastrophic decrease in the material resistivity. For $E_a = 0.44$ eV, especially for 0.22 eV, a conduction close to the intrinsic one is possible under the full compensation, being held with a high accuracy (we say about a deviation of at most ~0.01%). These results clearly confirm the following conclusion important from the practical viewpoint: a semiinsulating state can be reached in the simplest way by compensating the impurities (defects), whose levels are located as close as possible to the middle of the bandgap. It is more difficult or practically impossible to reach this required result by the compensation of shallow impurities.

It is clear that a conduction close to the intrinsic one can be established by the compensation of deep donors by acceptors [4]. For this purpose, it is necessary that donor levels be located near the middle of the bandgap and the total concentration of donors be more than the total concentration of acceptors. Both conditions are satisfied, in particular, if single crystals CdTe are doped with vanadium or titanium to enhance the photorefractive effect. But it should be noted that "undercompensation" of available acceptors by donors (by annealing in a Cd vapor or by doping in the process of growing a crystal) has advantage as compared with "overcompensation" by donors, because an increase in the concentration of the donor levels located near the middle of the bandgap yields an additional decrease in the lifetime of charge carriers, i.e. it destructively influences this key parameter of detectors of ionizing radiation.

Conclusions

The comparison of the temperature dependences of resistivity $\rho(T)$ and the Fermi level energy $\Delta\mu(T)$ with the results of computer simulation allowed us to clarify the mechanism of the compensation of acceptors by donors in single crystals $Cd_{1-x}Zn_xTe$. In the studied single crystals with high resistivity, a position of the Fermi level is defined by the deepest partly compensated level, and the temperature activation energy $\Delta\mu(T)$ coincides with the ionization energy of this level. The reason for the low resistivity of the material is a slight compensation of acceptors. In this case, the position of the Fermi level is defined by a relatively shallow level. Moreover, the conduction activation energy equals a half ionization energy of this level. The performed calculations testify to that the material conduction close to the intrinsic one can be most easily realized by compensating the impurities (defects of the crystal lattice), whose levels are located near to the middle of the bandgap. It is practically impossible to create a semiinsulating material with reproduced parameters by the compensation of shallow acceptors.

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КОМПЕНСОВАНА ДОМІШКОВА ПРОВІДНІСТЬ МОНОКРИСТАЛІВ $Cd_{1-x}Zn_xTe$

Л.А. Косяченко, З.І. Захарук, А.В. Марков, О.Л. Маслянчук, І.М. Раренко, В.М. Склярчук

Р е з ю м е

Досліджено механізм електропровідності монокристалів $Cd_{1-x}Zn_xTe$ ($x = 0,05$) з урахуванням глибоких акцепторних домішок (дефектів) декількох типів та їх компенсації донорами. Визначено енергію іонізації та ступінь компенсації акцепторів, відповідальних за електропровідність матеріалу. Сформульовано оптимальні умови збільшення питомого опору в залежності від глибини акцепторного рівня.