UDK 546.47'24

ISSN 1729-4428

Ye.S. Nykoniuk¹, Z.I. Zakharuk², S.V. Solodin², P.M. Fochuk², S.G. Dremluyzhenko², I.M. Yuriychuk², B.P. Rudyk¹

Peculiarities of Electrical Characteristics of Semi-Insulating CdTe-Cl crystals

¹National University of Water Management and Nature Resources Use, 11, Soborna Str., Rivne, 33000, Ukraine, e-mail: <u>b.p.rudyk@nuwm.edu.ua</u>

²Yuriy Fedkovych Chernivtsi National University, 2, Kotziubynskoho Str., Chernivtsi, 58012, Ukraine, e-mail: <u>serhii.solodin@gmail.com</u>

Electrical properties of semi-insulating CdTe-Cl crystals, grown by the vertical Bridgman and the travelling heater method, have been studied. It is found that the travelling heater method provides electron conductivity of the crystals, and the vertical Bridgman method – hole conductivity. Specific resistance of the samples is of (10^8-10^9) Ohm-cm at 300 K, and Hall mobility of the holes and electrons is of $(45 - 55) \text{ cm}^2/\text{V} \cdot \text{s}$ and $(10 - 20) \text{ cm}^2/\text{V} \cdot \text{s}$ respectively. Very low values of electron mobility and an exponential temperature dependence of μ_n are due to drift barriers with a height of $\epsilon_b \approx 0.20 \text{ eV}$. Formation of the barriers is caused by the fluctuations of the potential relief resulting from the microheterogeneity of the defect-impurity system. Quasi-photochemical reactions that reduce electron mobility after photo-excitation have been observed in n-CdTe-Cl samples. In p-CdTe-Cl samples, neither drift barriers, nor quasi-photochemical reactions were detected.

Key words: transport phenomena, scattering of charge carriers, cadmium telluride.

Article acted received 25.07.2017; accepted for publication 05.09.2017.

Introduction

Wideband CdTe semiconductor compound [1, 2] is of considerable interest due to production of efficient incoherent light sources, lasers, solar cells, X-ray and gamma detectors etc. on its base [1-7]. However, the difficulties in controlling electron spectrum and, as a consequence, the properties of CdTe (especially doped) restrict wide practical use of cadmium telluride. Therefore, the study of growth and doping mechanisms in this compound is very important.

For most of the devices, a material with a high specific resistance and maximum values of drift mobility and lifetime of nonequilibrium carriers is required. Typically, high resistivity CdTe crystals are obtained by controlled doping with shallow donors (In, Cl) which compensate intrinsic acceptors (V_{Cd}) [1-3, 6, 7]. At optimal doping, semi-insulating CdTe-In crystals are mostly of n-type, while CdTe-Cl crystals show both electron and hole conductivity. Peculiarities of the electrical properties of the latter are the subject of our study.

I. Growing and experimental methods

Pre-synthesized from elemental Cd and Te components (6N purity) specimens were used for growing CdTe-Cl crystals. In the case of growing by the travelling heater method, the ligature in the form of CdCl₂ was introduced into the telluride melts. The temperature of the hot zone was of 1020 K, and the growth rate was of 0.58 cm/day. In the case of growing by the Bridgman method, the ligature was placed in the growth ampule with the synthesized specimen at 1380 K, the temperature gradient at the crystallization front was of (10÷15) K/cm, and the growth rate was of 2 mm/h. The concentration of Chlorine in the melt was of ~1×10¹⁸ at/cm³ in both processes.

The samples for the studies were prepared with a string cutting of the grown crystals. The surface of the samples was polished with the diamond powders and slicked with the diamond pastes. Finishing surface treatment was carried out by chemical etching [8].

Electrical measurements were carried out within $(290 \div 420)$ K and $(673 \div 1173)$ K temperature intervals

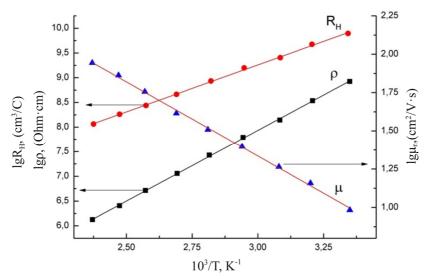


Fig. 1. Temperature dependence of specific resistance ρ , Hall coefficient $R_{\rm H}$ and electron mobility μ in n-CdTe-Cl sample.

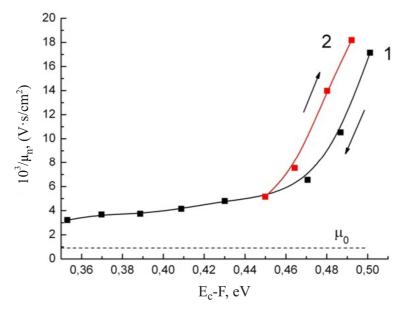


Fig. 2. Inverse Hall mobility of photoelectrons versus position of Fermi quasi-level: 1- increase of light intensity *I*; 2 - decrease of *I* (the dotted line denotes the maximum possible value of the electron mobility).

using rectangular samples $(12 \times 2 \times 1.5 \text{ mm}^3)$ with two pairs of potential contacts in the direct current mode. The temperature dependences (TD) of the specific resistance (ρ) and Hall coefficient (R_{H}), as well as Hall mobility of the carriers $\mu = R_{\text{H}}/\rho$, were studied.

II. Results and discussion

Specific resistance (at 300 K) of the experimental samples of both types of conductivity produced from the ingots with different doping level is in a wide range from 1 to 10^9 (Ohm·cm). In the case of semi-insulating crystals ($\rho \ge 10^8$ Ohm·cm) the method of the travelling heater gives n-type crystals, while the Bridgman method – p-type crystals.

Temperature dependencies of electric characteristics (ρ , $R_{\rm H}$, μ) of typical n-CdTe-Cl sample (Fig. 1) show

difference between TD activation energies of specific resistance and Hall coefficient. Such feature come out in strong (exponential) temperature dependencies of Hall electron mobility. This is due to the presence of microinhomogeneities in the spatial distribution of point defects (deep donors and compensating acceptors), which lead to the fluctuations of the potential relief and an emergence of the drift barriers for current carriers [9, 10].

For the sample presented in Fig. 1 one can conclude that a height of the drift barriers is $\varepsilon_b = 0.20 \text{ eV}$. Activation energy of $R_{\rm H}$ temperature dependency is not a characteristic of the ionization energy of the deep donors which control n-type conductivity in the region of barrier mobility. Ionization energy can be expressed through the activation energy of the specific resistance temperature dependency: $\varepsilon_D^0 = 0.53 \text{ eV}$. At the same time, $R_{\rm H}$ temperature dependency gives the value $\varepsilon_1 = 0.35 \text{ eV}$. The difference between these energies (0.18 eV) is

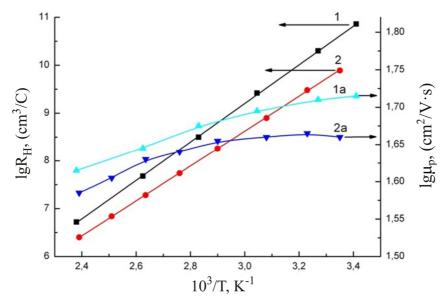


Fig. 3. Temperature dependence of Hall coefficient and hole mobility in p-CdTe-Cl samples.

somewhat less than the height of the drift barriers ε_{b} = 0.20 eV. This means that a degree of donor compensation is greater than 0.5 [9], that is, equilibrium Fermi level should be below the level of donors. Indeed, Fermi level is placed at E_c -0.54 eV at 300 K, and the level of donors at E_c -0.50 eV.

It was considered in the calculations that the effective mass of electrons is $m_n^* = 0.1 m_o$, and temperature dependency of donor ionization energy of is given as $\varepsilon_D = \varepsilon_D^0 - \alpha_g T \varepsilon_D^0 / E_g^0$, where $E_g^0 = 1.6$ eV is CdTe band gap at 0 K, $\alpha_g = 4 \cdot 10^4$ eV/K – band gap temperature coefficient.

The presence of the drift barriers, "killers" of carrier mobility, is confirmed by a strong shift of the inverse Hall mobility of the photoelectrons (Fig. 2). In this case, Fermi quasi-level (in the process of increasing of light intensity in the region of the self-absorption edge) crosses the energy level of the donors at $(E_{\rm c} - 0.50)$ eV. Such shift is related to the concentration $N_{\rm t}$, the cross section of the scattering centers S and the thermal electron velocity by the ratio v $\Delta(1000/\mu) = 10^{3} v \ (m_{n}^{*}/e) \ (N_{t}S) = 2.2.10^{-6} (N_{t}S) \ (V \cdot s/cm^{2})$ (at 300 K). Then, for $\Delta(1000/\mu) = 100$ one can obtain $N_{\rm t}S \approx 4.10^7 \,{\rm cm}^{-1}$. If we assume that isolated Coulomb centers are recharged ($S \approx 4.10^{-13}$ см² при 300 K), then $N_{\rm t} \approx 10^{20} \,{\rm cm}^{-3}$. Of course, such value of defect concentration is unacceptable not only in this case, but also for cadmium telluride crystals in general. Therefore, the model of collective drift barriers should be considered. The shift at $(E_c - 0.42)$ eV is obviously also due to the "elimination" of the drift barriers caused by micro-heterogeneity of the spatial distribution of fully compensated donor centers with the ionization energy of ~ 0.42 eV.

It should be noted that quasi-photochemical reactions take place in these samples. These reactions are followed by a decrease of photo-mobility at illumination of the samples, which results in Fig. 2 by a non-matching of the curves taken at different directions of the change of light intensity I: an increase of I (curve 1), and then its

decrease (curve 2). So, the height of the drift barriers increases, which can be explained by an expansion of space charge regions which is caused by microheterogeneity of point defects system. It is known [11] that in CdTe-Cl crystals the main defects are Cl_{Te} shallow donors and V_{Cd} acceptors, but these defects also form associates of different configurations. Under a sufficiently strong photo-excitation, when quasi-Fermi level is approaching corresponding bands, a recharging of the centers which are the component of the associates takes place. Radiation-accelerated diffusion can affect the configuration the associates and thus the screening of space-charge region.

The anomalies of the electric characteristics in n-CdTe-Cl crystals have not been detected in p-CdTe-Cl crystals. Fig. 3 shows the temperature dependencies of Hall coefficient and hole mobility in two p-CdTe-Cl samples (from different ingots). Since the changes of carrier mobility are negligible (not exceeding 20%), activation energies of $R_{\rm H}$ and ρ temperature dependencies almost coincide and are of 0.76 and 0.68 eV for samples 1 and 2 respectively. Although, there are no drift barriers for the carriers in p-type samples, complete microhomogeneity of the defect-impurity system can not be ensured. In particular, two scattering mechanisms (on the lattice vibrations and ionized centers) are not enough for the explanation of μ_p temperature dependencies. It is necessary to take into account a third weak temperature dependence mechanism. It can be scattering on nonoverlapping space-charge regions ($\mu_s \sim T^{5/6}$) [12]. This condition is possible with a sufficiently high screening charge at low concentration of the carriers. It is clear, that a weak compensation (not exceeding 30%) of working acceptors is a favorable factor for this matter.

Conclusions

Electrical properties of semi-insulating CdTe-Cl crystals, grown by the vertical Bridgman and the travelling heater method, have been studied. It is found

that the travelling heater method provides electron conductivity of the crystals, and the vertical Bridgman method – hole conductivity. Specific resistance of the samples is of (10^8-10^9) Ohm cm at 300 K, and Hall mobility of the holes and electrons is of (45 - 55) cm²/V·s and (10-20) cm²/V·s respectively. Very low values of electron mobility and an exponential temperature dependence of μ_n are due to drift barriers with a height of $\epsilon_b \approx 0.20$ eV. Formation of the barriers is caused by the fluctuations of the potential relief resulting from the microheterogeneity of the defect-impurity system. Quasi-photochemical reactions that reduce electron mobility after photo-excitation have been observed in n-CdTe-Cl samples. In p-CdTe-Cl samples, neither drift barriers, nor quasi-photochemical reactions were detected.

Nikoniuk E.S. - Ph.D., Associate Professor, Department of Chemistry and Physics;

Zakharuk Z.I. - Senior Researcher at the Educational Scientific Center "Functional Materials and Technology"; Solodin S.V. - post-graduate student of the department of inorganic chemistry of solids and nanodispersed materials: Dremlyuzhenko S.G. - Ph.D., senior researcher of the educational-scientific center Technology of functional materials: Fochuk P.M. - Professor, Doctor of Chemical Sciences, Vice-Rector for Science and International Relations; Ph.D., Associate Professor, Yuriychuk I.M. Department of Semiconductor Physics and Nanostructures;

Rudyk B.P. - Head of the Laboratory of the Department of Chemistry and Physics.

- [1] D.V. Korbutyak, S.V. Melnychuk, Ye.V. Korbut, M.M. Borisyuk, Cadmium Telluride: impurity-defect states and detector properties (Ivan Fedorov, Kyiv, 2000).
- [2] K. Zanio, Cadmium Telluride 13, 235 (1978).
- [3] L. Zou, Z. Gu, N. Zhang, Y. Zhang, Z. Fang, W. Zhu and Xinhua Zhong, J. of Material Chemistry 18, 2807 (2008).
- [4] K. Shcherbin, S. Odoulov, Z. Zakharuk, I. Rarenko, Optical Materials 18, 159 (2001).
- [5] K.L. Chopra, P.D. Paulson, V. Dutta, Progress in Photovoltaics: Research and Applications 12, 69 (2004).
- [6] M.Fiederle, V.Babentsov, J.Franc, A.Fauler, J.-P.Konrath, Cryst. Res. Technol. 38, 588 (2003).
- [7] A. Zaiour, M. Ayoub, A. Hamié. A. Fawaz, M. Hage-ali, Physics Procedia 55, 476 (2014).
- [8] S.G. Dremluzhenko, Z.I. Zakharuk, I.M. Rarenko, V.M. Srtebegev, A.G. Voloshchuk, I.M. Yurijchuk Semiconductor Physics, Quantum Electronics & Optoelectronics 7(1), 52, (2004).
- [9] A.Ya. Shik, ZhETF 71, 1159 (1976).
- [10] P.M. Fochuk, E.S. Nikonyuk, Z.I. Zakharuk, G.I. Rarenko, S.G. Dremlyuzhenko, Scientific Journal of Chernivtsi University, 771:Chemistry 56 (2016).
- [11] Cadmium Telluride and related Compounds, Physics, Defects, Hetero- and Nanostructures, Crystal Growth, Surfaces and Applications (Elsevier, Amsterdam-Oxford, 2010).
- [12] L.R. Weisberg, J. Appl. Phys. 33, 1817 (1962).

Є.С. Никонюк¹, З.І. Захарук², С.В. Солодін², П.М. Фочук², С.Г. Дремлюженко², І.М. Юрійчук², Б.П. Рудик¹

Особливості електричних характеристик напівізолюючих кристалів CdTe-Cl

¹Національний університет водного господарства та природокористування, м. Рівне, вул. Соборна, 11, 33000, Україна, <u>b.p.rudyk@nuwm.edu.ua</u>

²Чернівецький національний університет імені Юрія Федьковича, м. Чернівці, вул. Коцюбинського, 2, 58012, Україна, <u>serhii.solodin@gmail.com</u>

Досліджено електричні властивості напівізолюючих кристалів CdTe-Cl, вирощених вертикальним методом Бріджмена та методом рухомого нагрівника. Встановлено, що метод рухомого нагрівника забезпечує електронну провідність, а вертикальний метод Бріджмена – діркову. При 300 К питомий опір зразків становить $\rho = (10^8 - 10^9)$ Ом·см, холлівська рухливість: дірок $\mu_p = (45 - 55)$ см²/B·с, електронів $\mu_n \approx (10 - 20)$ см²/B·с. Дуже низькі значення і експоненційна температурна залежність μ_n зумовлені дрейфовими бар'єрами з висотою $\varepsilon_b \approx 0,20$ еВ. Формування останніх пов'язане з флуктуаціями потенціального рельєфу за рахунок мікронеоднорідностей дефектно-домішкової системи. Крім того, в зразках n-CdTe-Cl мають місце квазіфотохімічні реакції, що полягають у зменшенні рухливості електронів після фотозбудження. В зразках p-CdTe-Cl не виявлено ні дрейфових бар'єрів, ні квазіфотохімічних реакцій.