EFFECT OF PRE-GROWTH ANNEALING ON THE PROPERTIES OF NONPURIFIED CADMIUM TELLURIDE SINGLE CRYSTALS OBTAINED BY SUBLIMATION METHOD

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The effect of high-temperature annealing of a nominally undoped CdTe charge under dynamic vacuum conditions on the electrical and optical properties of single crystals grown from this charge with the use of a modified physical vapor transport method has been examined. It is shown that the annealing results in the disappearance or an extinction of chlorine-related lines in the low-temperature photoluminescence spectra and the absorption bands in the long-wavelength absorption-edge spectra of the crystals concerned, as well as in a drastic fall of their resistivity. The observed alterations are explained by a removal of the Cl impurity during the annealing owing to a high volatility of chlorine compounds.

1. Introduction

Bulk single crystals of cadmium telluride are applied to the manufacture of electro-optical modulators, photorefractive sensors, recording media in optical computers, detectors of high-energy radiation, and substrates for the epitaxy of thin-film matrices for passive detectors of infra-red radiation [1]. For today, their industrial growing is carried out from the liquid phase by means of various modifications of the Bridgman, gradient crystallization, and travelling heater techniques. However, a high temperature of the growing from a melt and instabilities at the liquid phase–crystal interface induce the formation of a considerable number of micro- and macrodefects. The contact between the liquid and the container walls gives rise to an additional contamination, and the growing from a nonstoichiometric solution promotes the precipitation of the excess component. Those shortcomings lead to a reduction in the yield of a material with required parameters and to its high cost. Therefore, promising are the development, improvement, and introduction into the production of alternative methods for the growth of CdTe crystals from the gas phase. A technique that is the simplest in implementation is the physical vapor transport method. Namely, owing to the temperature difference, the preliminarily synthesized polycrystalline charge is sublimated in the hot zone of an ampoule, which can be evacuated or filled with an inert gas, and deposited in its cold section [2, 3].

However, the region of existence for solid cadmium telluride is narrow, which makes it difficult to produce a charge for the following growing of crystals in a closed system with the use of the sublimation technique. Moreover, even if the charge composition is varied within this region, this results in a change of the partial pressures of components at the crystal growth temperature and, as a consequence, the rates of material transfer by orders of magnitude [3–5]. Attention should also be paid to the fact that rather small deviations from a composition of congruent sublimation can stimulate the condensation of the liquid phase on the crystal surface and the transition from the two- (solid–vapor) crystallization mechanism to the three-phase (solid–liquid–vapor) one, by worsening the structural quality of a grown material [6]. It is almost impossible to provide a required accuracy during the weighting of components and to avoid uncontrollable losses, when the charge is load into an ampoule for the synthesis, and when the ampoule is sealed off. Even the existing errors in the molar mass values adopted for Cd and Te can be a probable reason for such a deviation from the stoichiometric content, which does not allow the process of growing to be carried out successfully [7]. Therefore, for a potentially available excess component to be removed and for the necessary degree of stoichiometry to be achieved, an additional thermal treatment of the initial charge is often applied [8, 9]. In this work, we studied the influence of the pre-growth stoichiometrizing annealing of a charge on the electrical and optical properties of final single crystals of nominally undoped CdTe produced with the use of the sublimation technique.

2. Experimental Results and Their Discussion

Crystals to study were fabricated by a technique specially developed by us. It consists in that the charge was synthesized under conditions that ensure a deviation from the stoichiometric content as small as possible. Moreover, the following growing of crystals in a purposely designed and constructed arrangement [10] was carried out by applying a modified method of physical transport through the gas phase. The technique allowed us to obtain reproducibly large enough CdTe ingots, either undoped or doped with chlorine, which usually consist of a single crystalline block.

The stoichiometrization of an undoped synthesized material was performed according to the technique described in work [8]. Namely, the charge was put into an ampoule and annealed under dynamic vacuum conditions, i.e. together with a simultaneous evacuation. This routine gave rise to the sublimation of the excess component in the cold zone of the system, i.e. in the ampoule neck, which was sealed off after the annealing process had been terminated. The annealing temperature fell with the limits 860–870 °C, the duration of the procedure was 10 min, and the residual pressure in the ampoule was about 10^{-5} Torr. Material losses did not exceed 5% of the charged amount. The treatment was carried out immediately in the growth container, so that the material was not contaminated. Therefore, the differences revealed between the properties of crystals grown from annealed and unannealed charges under identical conditions can be associated just with the stoichiometrization.

The Hall effect was measured, by using the six-probe method. The results of measurements showed that both types of crystals had hole conductivity. However, the magnitudes of their specific resistances differed substantially. For the material obtained by sublimating a charge preliminarily subjected to the thermal treatment, the corresponding value was only 3–10 $\Omega\times$cm. Specimens of nominally undoped cadmium telluride, which were grown from the unannealed charge, were characterized by a much lower conductivity; their specific resistance reached 10^5 $\Omega\times$cm. It should be noted that approximately the same value was typical of crystals weakly doped with chlorine, with the content of this element in the initial batch being $N_{\rm Cl} = 10^{17}$ cm^{-3}.

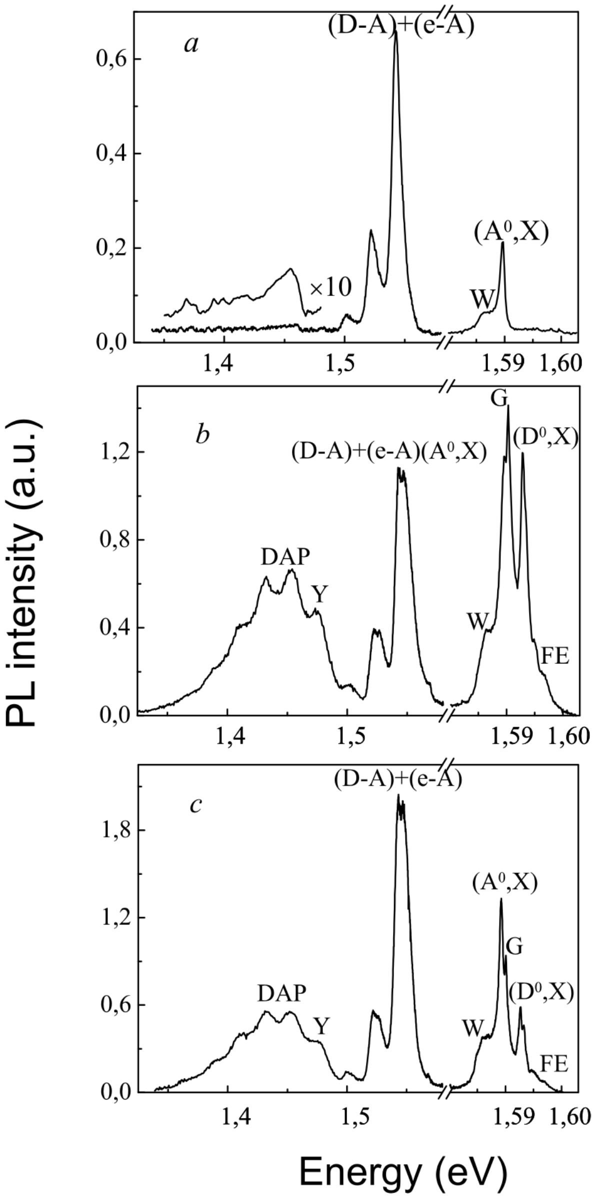

Fig. 1. Typical PL spectra measured at T = 4.5 K for various CdTe specimens grown up by the modified physical vapor transport method: (*a*) an undoped specimen grown up from the annealed charge, (*b*) a nominally undoped specimen, and (c) a CdTe:Cl specimen ($N_{\rm Cl} = 10^{17}$ cm^{-3}). The spectra in panels (*b*) and (*c*) are taken from work [11]

In Fig. 1,*a*, a typical spectrum of low-temperature (at 4.5 K) photoluminescence (PL) obtained for a specimen fabricated from the charge subjected to the annealing before the crystal growing is exhibited. The researches were carried out on the fresh (110) cleavage surface of single crystals. For the excitation, we used a continuous-wave Ar^+-laser LGN-404 with the radiation wavelength $\lambda = 488$ nm. Radiation emission by specimens was analyzed with the help of an SDL-1 spectrometer and a cooled FEU-62 photomultiplier. The energy resolution was not worse than 0.12 meV. In Fig. 1,*b*, the spectrum of a crystal grown from the thermally untreated charge is shown for comparison; the figure is taken from the previous work [11]. It is evident that those spectra differ strongly. In the excitonic spectral region of CdTe grown from the annealed charge, the most intense is the line (A^0, X) with the energy maximum at 1.5896 eV. According to literature data, it is associated with the radiative recombination of excitons localized at neutral copper atoms, the latter being a usual and incontrollable impurity for the given compound [12, 13]. On the long-wave side of the (A^0, X) line, at about 1.586 eV, a less pronounced band W with a weaker intensity is observed. The excitonic PL spectrum of CdTe grown from the thermally untreated charge contains, besides (A^0, X) and W, the strongly pronounced lines (D^0, X) and G with the maxima at about 1.5928 and 1.590 eV, respectively. The line (D^0, X) corresponds to the emission of excitons bound to shallow neutral donors. The appearance of such donors can be associated with the presence of impurity centers connected with elements of group III located at Cd sites or with elements of group VII located at Te sites [14, 15]. The bands W (at about 1.586 eV) and G (at about 1.591 eV) were identified as a result of the radiative recombination of excitons bound to complexes (V_{Cd}–Cl) and (V_{Cd}–2Cl), respectively [16, 17]. In addition, the PL spectrum in Fig. 1,*b* reveals free exciton (FE) lines from the upper and lower polariton branches, which are practically absent for the material grown from the annealed charge.

The PL spectra for undoped CdTe of both kinds contain a series of lines in the range of 1.50–1.57 eV, which is induced by the transitions of two types: the high-energy component, e–A, corresponds to electron transitions from the conduction band onto shallow acceptor centers, and the low-energy one, D–A, to donor-acceptor transitions [17, 18]. In Fig. 1,*a*, those transitions are not separated, whereas the zero-phonon line and the first phonon replication of edge luminescence bands compose a doublet in the spectrum of the crystal grown with the use of the stoichiometrized charge. It is conventionally accepted that the donors that manifest themselves in the edge PL are shallow hydrogen-like centers responsible for the (D^0, X) line in the excitonic spectral range. The nature of acceptors is less clear: it can be connected with the presence of cadmium vacancies or uncontrollable impurity centers related with copper, sodium, or lithium atoms [12, 19].

In the PL spectrum of cadmium telluride grown from the unannealed charge, the intense band emerges in the energy range of 1.3–1.5 eV. This band contains a number of components, and its structure is determined by the radiative recombination engaging longitudinal optical phonons. A component with the zero-phonon line at an energy of about 1.455 eV is associated with the transitions from shallow donors–e.g., isolated chlorine atoms–onto an A-center composed of a cadmium vacancy and the nearest substitutional atom, e.g., $\mathrm{Cl_{Te}}$ [20, 21]. The band Y with a zero-phonon transition at an energy of 1.477 eV is usually associated with the radiative recombination of excitons captured by the field of extended defects (dislocations) [22, 23]. The PL intensity in this spectral range is very weak for a specimen grown from the thermally treated material; the zero-phonon transition in the DAP band can be distinguished only if the plot is scaled up substantially.

In the previous work [11], the presence of the intense lines (D^0, X), W, G, and DAP in the PL spectra of CdTe crystals grown from the stoichiometrized charge by the sublimation technique, as well as their similarity with the spectra of CdTe:Cl with $N_{\mathrm{Cl}} = 10^{17}$ cm^{-3} (see Fig. 1,*c*), was explained by a high content of uncontrollable substitutional shallow donors – mainly, chlorine – in this material. As was marked earlier [11], this circumstance is connected not only with an insufficient purity of initial species, where the chlorine content can reach 10^{17} cm^{-3} [24], but also with technological features of the CdTe crystal fabrication from the gas phase. The assumption put forward is completely confirmed by a comparative analysis of spectra in Figs. 1,*a* and *b*. Really, it was shown in work [25] that the resublimation under dynamic vacuum conditions considerably reduces the content of impurities, the volatility of which is higher than that of the compound. $\mathrm{CdCl_2}$ is characterized by the highest partial vapor pressure for solid CdTe:Cl at $T > 800$ °C [26]; therefore, the chlorine content in the annealed charge considerably decreases, because chlorine gets removed into the ampoule neck. This scenario explains the absence of the (D^0, X) and G lines in the PL spectra depicted in Fig. 1,*a* and the very weak intensity of the emission band by donor-acceptor pairs. On the contrary, if the crystals are grown in sealed ampoules, a high volatility of chlorine compounds results in that this element becomes transferred almost completely from the charge into the crystal.

An additional proof of the CdTe crystal purification owing to the pre-growth high-temperature annealing of a synthesized charge under dynamic vacuum conditions was obtained, when studying the corresponding absorption spectra in the range near the long-wave intrinsic absorption edge. Such spectra were obtained with the help of a UNICAM UV 300 two-beam spectrometer. The spectral resolution was 0.5 nm, and the maximal transmission error did not exceed 1%. For researches, we used chemically-mechanically polished specimens in the form of parallelepipeds, with light falling onto their wide faces. As is seen from Fig. 2, the thermal treatment gives rise to a reduction of the photon absorption at energies $h\nu < 1.455$ eV. It is evidently associated with a reduction in the number of associates of the $(V_{\rm Cd} - 2D)$ and $(V_{\rm Cd} - 2{\rm Cl})$ types with the energy levels of E_V+(0.047–0.050) eV [14, 17, 27], correspondingly. It is worth to note that the high-temperature annealing of CdTe crystals grown in vacuum, on the contrary, enhances the absorption owing to the growth in the number of singly ionized cadmium vacancies $V_{\rm Cd}$ with the energy level of E_V+(0.065–0.069) eV [28, 29].

In our opinion, the low resistance of crystals grown from the thermally treated charge is also a consequence of its purification from chlorine and other shallow substitutional donors in the course of annealing. This reduces the compensation degree for intrinsic defects of the acceptor type; in particular, those connected with the presence of cadmium vacancies, which are the main type of acceptors in undoped CdTe [30, 31]. At the same time, the background content of those elements in a non-stoichiometrized material turns out obviously sufficient for the specific resistance to achieve the value close to that in slightly doped CdTe:Cl, i.e. it is of the order of 10^{17} cm^{-3}.

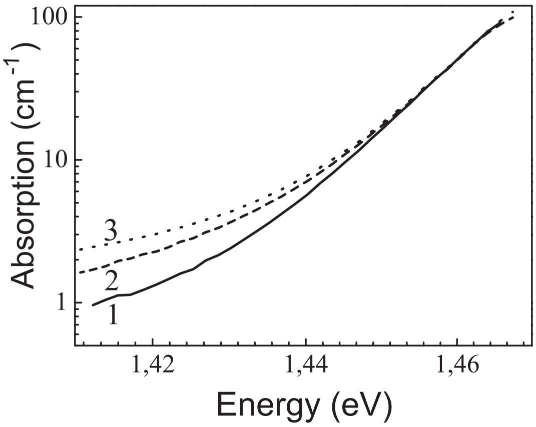

Fig. 2. Spectral dependences of the absorption coefficient measured at $T = 300$ K for CdTe single crystals in the range of the long-wave intrinsic absorption edge: (*1*) an undoped specimen grown up from the annealed charge, (*2*) a nominally undoped specimen grown up from the unannealed charge, and (*c*) a CdTe:Cl specimen ($N_{\rm Cl} = 10^{17}$ cm^{-3})

3. Conclusions

Our researches of the spectra of low-temperature photoluminescence and optical absorption and variations in the electric conductivity testify that the short-term pre-growth high-temperature (860–870 °C) annealing of a charge of nominally undoped CdTe under dynamic vacuum conditions carried out according to the technique described in work [8] not only approaches its composition to the stoichiometric one, but also reduces the concentration of Cl and, probably, other noncontrollable shallow donor substitutional impurities in it. Therefore, in our opinion, it is reasonable to carry out such annealing in order to additionally purify the undoped material. However, this technique is inexpedient to be used in the case of CdTe:Cl, because it leads to an uncontrollable reduction in the concentration of the doping impurity in both the synthesized charge and the crystals grown from it.

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ВПЛИВ ПЕРЕДРОСТОВОГО ВІДПАЛУ ВИХІДНОГО МАТЕРІАЛУ НА ВЛАСТИВОСТІ НЕОЧИЩЕНИХ МОНОКРИСТАЛІВ ТЕЛУРИДУ КАДМІЮ, ОТРИМАНИХ МЕТОДОМ СУБЛІМАЦІЇ

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Резюме

Розглянуто вплив високотемпературного відпалу шихти номінально нелегованого CdTe у динамічному вакуумі на електричні та оптичні властивості монокристалів, вирощених з неї модифікованим методом фізичного транспорту через газову фазу. Показано, що відпал приводить до зникнення чи послаблення пов’язаних з хлором ліній випромінювання у спектрах низькотемпературної фотолюмінесценції і смуг поглинання у спектрах крайового довгохвильового поглинання кристалів, а також до різкого зменшення їх питомого опору. Ці зміни пояснено очисткою шихти від неконтрольованої домішки хлору у процесі відпалу, що зумовлено високою летючістю хлорних сполук.