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SPECTROSCOPY, INTERACTION  
WITH RADIATION

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## Spectra of Low-Temperature Photoluminescence in Thin Polycrystalline CdTe Films

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**Abstract**—The band of intrinsic ( $e-h$ ) radiation emission by the subsurface potential barriers of crystal grains and the edge doublet band arising as LO-phonon replicas of the  $e-h$  band are observed in the spectra of the low-temperature (4.2 K) photoluminescence of fine-grained (with a grain size of  $d_{cr} \leq 1 \mu\text{m}$ ) CdTe films. Film doping with the In impurity results in quenching of the doublet band, while heat treatment leads to activation of the intrinsic band, a short-wavelength shift of the red boundary ( $\Delta E_r = 16-29 \text{ meV}$ ) and the half-width modulation ( $\Delta_A = 6-17 \text{ meV}$ ) of which correlate with the height of micropotential barriers and the temperature of recombining hot photocarriers.

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### 1. INTRODUCTION

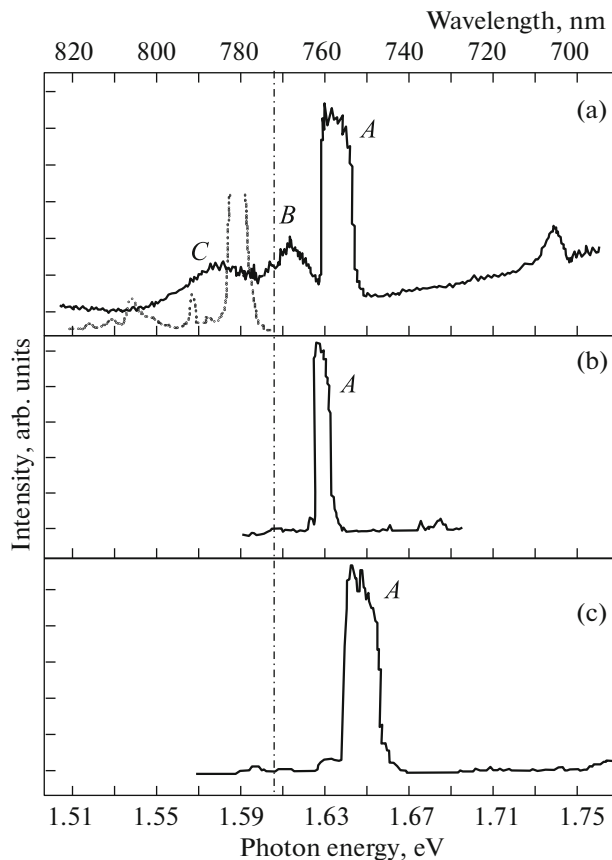
At present, the spectra of the low-temperature photoluminescence (LTPL) of CdTe crystals are being investigated in detail, and methods for the prediction and controlled modification of the physical properties of semiconductor structures on their basis are being proposed. For example, by means of studying the dynamics of a variation in the photoluminescence (PL) spectra, the authors of [1, 2] proposed a method of deep sample purification and obtained polycrystalline CdTe with stoichiometric structure, in the photoluminescence spectrum of which there is no impurity radiation at all and only the exciton part remains. Via analysis of the edge-radiation shape under laser excitation, the electron spectra of CdTe:In [3] and CdTe:Fe [4] solid solutions were investigated. In [5, 6], the role of intergrain boundaries in the formation of the PL spectrum of coarse-grained cadmium telluride was investigated by methods of microphotoluminescence probing and it was shown that the impurity-defect composition of the edge and internal regions of single-crystal grains 1–2 mm in size are rather markedly different. However, to date, practically no PL-spectrum formation for thin fine-grained (the grain size  $d_{cr} \leq 1 \mu\text{m}$ ) semiconductor samples, the intergrain boundaries in which significantly affect their properties, were considered depending on the density of structural and point defects.

The purpose of this study lies in investigating the formation mechanisms of the spectra of the intrinsic and edge LTPL of CdTe and CdTe:In films depending on structural imperfections. Previously in [7, 8], it was reported that doping with an In impurity and subse-

quent heat treatment (HT) substantially affect the photovoltaic parameters of the CdTe films. Here we analyze the spectra of the intrinsic and edge PL of these films at  $T = 4.2 \text{ K}$ . It is found that no channels of radiation of excitons and the donor-acceptor pairs (DAPs) manifest themselves in the LTPL spectra of fine-grained polycrystalline CdTe and CdTe:In films, in contrast to single crystals and coarse-block polycrystals; the cause is the process of the generation of photovoltage in the edge regions of the crystal grains resulting in the stimulation of intrinsic ( $e-h$ ) luminescence and to the appearance of its longitudinal optical (LO) phonon replicas in the spectra of undoped samples. We reveal a substantial short-wavelength shift ( $\Delta E_r \approx 20 \text{ meV}$ ) of the red edge of the  $e-h$  band and modulation of its half-width (the width at half-height)  $\Delta_A \approx 10 \text{ meV}$  as a function of point and structural defects of crystal grains. The method for analyzing the LTPL spectra proposed here together with the photoelectric properties of fine-grained CdTe polycrystals can be used with success for also studying the properties of other semiconductor film structures.

### 2. RESULTS OF EXPERIMENTS

To measure the LTPL spectra, Cd and CdTe:In film samples with sizes of  $5 \times 20 \text{ mm}$  and a thickness of  $\sim 1 \mu\text{m}$  fabricated by the method of thermal vacuum evaporation onto a glass substrate and with a fine-grained structure with sizes of  $d_{cr} \leq 1 \mu\text{m}$  of crystal grains with the cubic modification [7, 8] were directly immersed in pumped liquid helium at a temperature of 4.2 K. The spectra were detected using an installation



**Fig. 1.** Experimental PL spectra of (a) the CdTe nominally undoped film and the CdTe film doped with an In impurity (b) before and (c) after heat treatment. The dashed line is the PL spectrum of a nominally undoped CdTe single crystal [6], and the dashed–dotted vertical line shows the band-gap energy at  $T = 4.2$  K.

assembled on the basis of a DFS-24 spectrometer operating in the photon-counting mode at the smallest gap width of 0.04 meV. Intrinsic excitation of the semiconductor was carried out at a wavelength of  $\lambda = 476.6$  nm by the radiation of a CW gas-discharge Ar<sup>+</sup> laser, focused on the CdTe surface layer into a spot of  $0.4 \times 4$  mm in size at a light-flux power of  $\sim 7$  mW. The experiment was carried out in the normal-illumination configuration and almost normal radiation.

The LTPL spectrum of an undoped CdTe film in the vicinity of the fundamental absorption band is shown in Fig. 1a. For comparison, we here also show the PL spectrum of a nominally-undoped single-crystal sample from [6], which extends only into the region of photon energies lower than the band gap,  $\hbar\omega < E_g$ , and consists of the exciton ( $E_{\text{ex}} \approx 1.59$  eV), the donor–acceptor emission line ( $E_{DA} \approx 1.54$  eV), and their LO-phonon replicas. As can be seen from the figure, the LTPL spectra of the polycrystalline film and of the CdTe single crystal are radically different. The main contribution to the film LTPL is produced by the radiative recombination of  $e$ – $h$  free carriers (the  $A$  line

with a half-width of  $(14.2 \pm 0.1)$  meV) and edge luminescence with a relatively wide doublet structure { $B$ - and  $C$ -lines of emission with half-widths of  $(18.5 \pm 0.1)$  and  $(32.2 \pm 0.1)$  meV}, while the exciton one, the DAP channels of emission, and their phonon replicas are imperceptible or lacking against the background of spectral lines  $A$ ,  $B$ , and  $C$ . In the region of frequencies  $\hbar\omega > 1.65$  eV, “hot” photoluminescence caused by the radiative recombination of energy-relaxing hot electron–hole pairs (the frequency of excitation laser radiation  $\hbar\omega = 2.60$  eV) is observed. The sharp long-wavelength edge  $\hbar\omega = 1.627$  eV of the intrinsic emission band is evidence that individual grains have a perfect crystal structure. No tails of density of states induced by pronounced violations of the crystal lattice are found in the LTPL spectra. It should be noted that the red edge of the  $A$  line is shifted towards shorter wavelengths by an energy of 0.021 eV in comparison with the lower boundary of the conduction band of CdTe single crystals (the vertical dashed–dotted line in Fig. 1a) at  $T = 4.2$  K ( $E_g = 1.606$  eV [9]). It is difficult to attribute, for example, stresses in a thin CdTe film to the presence of internal mechanical tension due to a difference in the thermal coefficients of expansion or in the interatomic distances in the film and the substrate leading to an increase in the band-gap width  $E_g$ .<sup>1</sup>

From Fig. 1a, it also can be seen that the position of the peaks of emission lines  $A$ ,  $B$ , and  $C$  with the errors of measurement taken into account, differs by the energy of the longitudinal optical phonon  $\hbar\omega_{\text{LO}} = 0.021$  eV in CdTe [9]. It enables us to assert that the symmetric line  $B$  is the LO-replica, and the line  $C$  is the 2LO-replica of the intrinsic  $A$ -band of emission, which were also lacking in the spectrum of the single crystal and the coarse-block polycrystal at a set intensity of laser excitation of  $\sim 0.44$  W/cm<sup>2</sup> the same as the fundamental band. The flatter peak of the line of  $C$  emission is behind the  $A$  line by an energy slightly exceeding  $2\hbar\omega_{\text{LO}}$  and has a long-wavelength tail. It means that this spectral line is obviously formed as a result of  $e$ – $h$  recombination with the subsequent emission of 2LO +  $n$ LA phonons ( $n = 1, 2, 3, \dots$ ); i.e., longitudinal acoustic (LA) phonons also participate in the formation of the  $C$  line in addition to the LO-phonons.

In Fig. 1b, we show the LTPL spectrum of the CdTe:In film without HT. It can be seen that the process of doping of the film with an indium impurity, the bulk concentration of which proved to be no less than  $10^{17}$ – $10^{18}$  cm<sup>−3</sup> [7, 8], appreciably deforms the LTPL spectrum. First, the half-width of the  $A$  line (decreases to 6 meV) for a freshly prepared CdTe:In film is significantly narrowed in comparison with an undoped

<sup>1</sup> For the CdTe single crystal, the linear baric coefficient of the variation in  $E_g$  under single-axis deformation  $dE_g/dP = 1.46 \times 10^{-1}$  eV/Pa [10]. Then to obtain a change in the band gap  $\Delta E_g(P) = 0.021$  eV, it is necessary to assume that there is an internal mechanical stress  $P \approx 1.4 \times 10^9$  Pa in the film, which causes doubt.

CdTe film; second, the edge-luminescence band (lines *B* and *C*), the same as the hot-PL channel, disappears; third, the sharp red edge of the intrinsic emission is shifted to longer wavelengths by an energy of  $\sim(3-5)$  meV and is behind the upper band-gap boundary of the single crystal by an energy of 16–18 meV. It is also difficult to attribute the last fact to a decrease in  $E_g$  as a result of weakening of the internal mechanical stress in the doped sample. Obviously, donor centers of replacement  $\text{In}_{\text{Cd}}$  or interstitial  $\text{In}_i$  in CdTe:In form a powerful channel of nonradiative recombination, thus, strongly decrease the role of LO- and LA-phonons. In this case, the red edge of the *A* line of emission is shifted to longer wavelengths, its half-width decreases, and also the electrical conductivity of the film increases [7, 8].

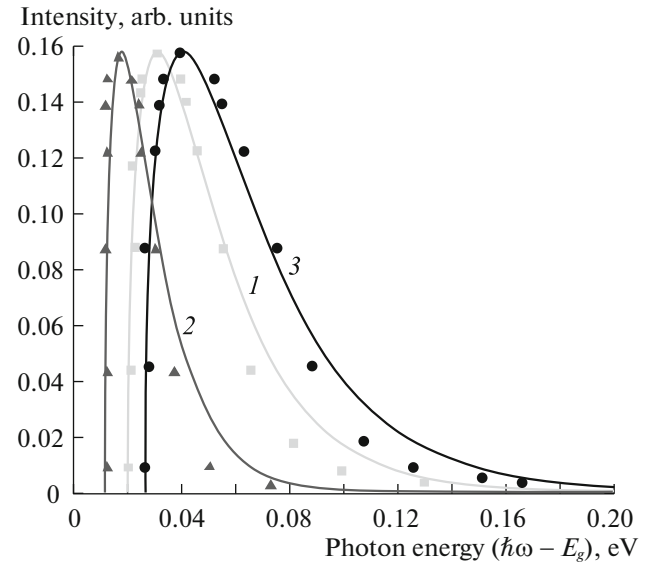
As can be seen from Fig. 1c, the LTPL spectrum qualitatively undergoes no noticeable modification after optimum HT of the CdTe:In film. However, we note straightaway that the HT results in broadening of the *A* line almost three times (the half-width attains a value of  $\sim 17$  meV) and in the shift of its red edge by  $\sim 11$  meV to shorter wavelengths in comparison with the unannealed CdTe:In film, which are also difficultly to explain at first glance. Apparently, the HT process as a result of the self-compensation of donor and acceptor pairs [11] both in the bulk and on the surface of grains stimulates the intrinsic LTPL band of the doped film.

### 3. DISCUSSION OF RESULTS

We now try to qualitatively analyze the formation mechanism of the spectral *A* line and to interpret its basic parameters as a function of technology factors. Strictly speaking, the PL of a polycrystalline film is formed at different depths and microregions on the basis of various mechanisms of radiative transitions. Exact analytical calculation of the PL spectrum for the fine-grained films under consideration presents significant difficulties. However, preliminary quantitative spectral analysis of the *A* line of emission shows that, as a first approximation, the emission intensity can be described by the following formula:

$$L(\omega) = A_0 \sqrt{\hbar\omega - (E_g + \Delta E_r)} \times \exp\left(-\frac{\hbar\omega - (E_g + \Delta E_r)}{kT_{eh}}\right), \quad (1)$$

where  $A_0$  is a constant depending on the type of film and the conditions of its photoexcitation;  $E_g$  is the band gap in a CdTe single crystal;  $k$  is the Boltzmann constant;  $T_{eh}$  is the average characteristic temperature of photocarriers, which significantly differs from the lattice temperature  $T$ ; and  $\Delta E_r = \hbar\omega_r - E_g$  is the difference between the red edge of the *A* line and  $E_g$ . Naturally, the second and third coefficients on the right-hand side of formula (1) are caused by the densities of states in the simple bands and the quasi-equilibrium functions of the distributions of photocarriers.



**Fig. 2.** Comparison of the theoretical (solid curves) and experimental (dots) spectra of the LTPL fundamental band for fine-grained films: (1) CdTe, (2) CdTe:In before HT, and (3) CdTe:In after HT.  $T = 4.2$  K.

In Fig. 2, we show a comparison of the theoretical and experimental spectra of the LTPL fundamental band for the fine-grained CdTe and CdTe:In films. The values of parameters  $\Delta E_r \approx kT_{eh}$  are chosen from the short-wavelength shift of the red edge of the *A* line from the experimental spectra in Figs. 1a, 1b, and 1c:  $\Delta E_r = 21$  meV (curve 1, CdTe undoped film), 17 meV (curve 2, CdTe:In without HT), 29 meV (curve 3, CdTe:In after HT). It can be seen that roughly calculated spectral curves 1–3 well agree with the results of the experiment. However, there are substantial divergences in the short-wavelength edge of the spectra. The experiment shows the more pronounced thermalization of hot photocarriers with the characteristic temperature  $T_{eh} < \Delta E_r/k$ , which is evidence of additional channels of the scattering of high-energy non-equilibrium free carriers.

The physical meaning of the value of  $\Delta E_r$  can be explained as follows. Because the laser excitation of the semiconductor is implemented at a reasonably high frequency,  $\hbar\omega = 2.60$  eV, in comparison with  $E_g = 1.606$  eV at  $T = 4.2$  K, high-energy photoelectrons and photoholes, relaxing in energy, approach the corresponding boundaries of bands with a certain residual temperature  $T_e$  and  $T_h$ , not cooling completely to the crystal-lattice temperature. This is facilitated also by internal electrostatic fields of the space-charge region (SCR) near the boundary of crystal grains spatially separating the generated electron–hole pairs and accelerating photocarriers. In the latter case, electrons and holes are heated additionally acquiring an energy equal in order of magnitude to the height of the sub-

surface potential barrier  $\varphi_i$ .<sup>2</sup> Then, considering that the hot-electron energy is  $\Delta E_e \approx \varphi_i + kT_e$  with respect to the conduction-band bottom, while it is  $\Delta E_h \approx \varphi_i + kT_h$  for the holes, we obtain

$$\Delta E_r = \Delta E_e + \Delta E_h \approx 2\varphi_i + kT_{eh}, \quad (2)$$

where  $T_{eh} = T_e + T_h$ . It means that the value of  $\Delta E_r$  is determined according to expression (2) by the kinetic energy of hot photocarriers and the modulated height of the subsurface potential barrier  $\varphi_i$  under the action of light. Here, we deal with the effect of a shift of the edge of the intrinsic LTPL under the intense laser excitation of hot carriers in fine-grained polycrystals of direct-gap semiconductors depending on structural defects determining the parameters of the boundary-potential barriers of single-crystal grains.

From formula (1), it is possible to formally determine the spectral half-width of the A line. We introduce the dimensionless value of  $x = \{\hbar\omega - (E_g + \Delta E_r)\}/kT_{eh}$ . Then Eq. (1) accepts the following functional form:

$$L(x) = A'\sqrt{x} \exp(-x)$$

with the peak  $L_{\max} = A'/\sqrt{2e}$  at  $x = 1/2$ , where  $e = 2.718$  is the natural-logarithm base. We determine the half-width of the A line as the difference between two solutions of the transcendental equation  $x \exp(-2x) = (8e)^{-1}$ , i.e., as

$$\Delta_A = kT_{eh}(x_2 - x_1) \approx 0.67kT_{eh}. \quad (3)$$

From here, we draw the conclusion that the spectral half-width  $\Delta_A$  of the A line is directly proportional to the photocarrier temperature inducing the short-wavelength shift of its red edge  $\Delta E_r$ . It qualitatively corresponds to modifications of the spectral characteristics of the A line in Figs. 1a–1c. In fact, doping of the CdTe film with an In impurity results in a decrease in  $\varphi_i$  and  $kT_{eh}$ ; from here, we see a decrease in  $\Delta E_r$  by 3–5 meV in Fig. 1b, while  $\Delta_A$  decreases almost three times (to 6 meV). In this case, the film passes to a lower-resistance state. Subsequent optimal HT converts the film to a high-resistance state as a result of processes of self-compensation [11] because of an increase in  $\varphi_i$  and expansion of the space-charge region. From Fig. 1c, we obtain correspondingly that  $\Delta_A$  increases to 17 meV, while  $\Delta E_r$  increases to 29 meV; i.e., estimate formula (1) is carried out with a relative error of 8% if condition  $\Delta E_r \approx kT_{eh}$  is considered valid.

#### 4. CONCLUSIONS

On the basis of analysis of the LTPL spectra of fine-grained polycrystalline CdTe and CdTe:In films, it is possible to make the following conclusions.

<sup>2</sup> It is natural that the PL and the photoelectric phenomena accompany each other in polycrystalline semiconductor samples with grain sizes of  $d_{gr} \leq L_D$ , where  $L_D$  is the Debye screening length.

(i) In the LTPL spectrum of the undoped CdTe film, the fundamental band of emission with a spectral half-width of  $\Delta A \approx 10$  meV, which is associated with the e–h recombination of hot photocarriers separated by the electric field of the boundary space-charge region of crystal grains, and also its LO- and 2LO-phonon replicas are observed.

(ii) The effect of a short-wavelength shift of the red edge of the A line ( $\Delta E_r = 16$ –29 meV) and modulations of its half-width  $\Delta_A = 6$ –17 meV are found depending on structural defects in the film. Correlated values of  $\Delta E_r$  and  $\Delta_A$  depend on the height of micropotential barriers and are determined by the characteristic temperature  $kT_{eh}$  of recombining hot photocarriers.

(iii) In the LTPL spectra of the CdTe and CdTe:In films, in contrast to the CdTe single crystals and coarse-block polycrystals, no exciton nor donor–acceptor channels of emission manifest themselves; the cause of this is the fine-grained structure of the film and the process of photovoltage generation in the edge regions of the crystal grains resulting in the stimulation of intrinsic luminescence and the appearance of its LO-phonon replicas in nominally undoped samples.

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#### REFERENCES

1. A. V. Kvit, Yu. V. Klevkov, S. A. Medvedev, V. S. Bagaev, A. Perestoronin, and A. F. Plotnikov, *Semiconductors* **34**, 17 (2000).
2. V. S. Bagaev, Yu. V. Klevkov, S. A. Kolosov, V. S. Krivobok, and A. A. Shepel', *Phys. Solid State* **52**, 37 (2010).
3. V. V. Ushakov and Yu. V. Klevkov, *Semiconductors* **37**, 1042 (2003).
4. V. V. Ushakov and Yu. V. Klevkov, *Semiconductors* **37**, 1259 (2003).
5. V. P. Vneshchuk, A. Baidullaeva, A. I. Vlasenko, V. A. Gnatyuk, B. K. Daultemuratov, S. N. Levitskii, O. V. Lyashenko, and T. Aoki, *Phys. Solid State* **52**, 469 (2010).
6. S. A. Permogorov, T. P. Surkova, and A. N. Tennishev, *Phys. Solid State* **40**, 826 (1998).
7. M. A. Karimov and N. Kh. Yuldashev, *Bull. Russ. Acad. Sci.: Phys.* **71**, 1151 (2007).
8. M. A. Karimov and N. Kh. Yuldashev, *Fiz. Inzh. Pov-erkhn.* **2** (5), 42 (2006).
9. V. I. Gavrilenko, A. M. Grekhov, D. V. Korbutyak, and V. G. Litovchenko, *Optical Properties of Semiconductors: A Handbook*, (Kiev, Nauk. dumka, 1987), Chap. 3, pp. 410, 414 [in Russian].
10. A. N. Georgobiani and M. K. Sheinkman, in *Physics of II–VI Compounds* (Nauka, Moscow, 1986), Supplement, p. 292 [in Russian].
11. O. A. Matveev and A. I. Terent'ev, *Semiconductors* **32**, 144 (1998).

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