

PACS: 78.55.-m ; 78.55. Et

On the origin of 300 K near-band-edge luminescence in CdTe

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Abstract. A careful analysis of 300 K near-band-edge luminescence from bulk CdTe and cadmium telluride films is made. It is shown that: (i) the observed difference in 300 K peak positions of the near-band-edge luminescence $h\nu_m$ in CdTe crystals and films, and (ii) the $h\nu_m$ shift to lower energies as the excitation intensity is increased, could not be satisfactorily explained by an assumption that free excitons dominate in the formation of the above luminescence. So, the origin of 300 K near-band-edge luminescence in CdTe is not mainly the free exciton one as was proposed earlier, and needs further examination.

Keywords: 300 K near-band-edge luminescence, CdTe crystals and films, free excitons, emission intensities, exciton-phonon coupling.

Paper received 02.10.03; accepted for publication 11.12.03.

1. General remarks

The near-band-edge emission (its peak position $h\nu_m = 1.491\text{--}1.510$ eV) is observed in 300 K luminescence spectra of non-degenerated CdTe crystals and cadmium telluride films (see, for example [1–4]). Some earlier [4], an attempt was made to determine the origin of this emission. The authors of the cited paper [4] considered that 300 K near-band-edge emission from CdTe crystals and films occurs mainly due to annihilation of free excitons in the $n = 1$ ground state (further X_1 excitons) and the $n = 2$ excited state (further X_2 excitons) with only limited contribution (up to 30%) of band-to-band transitions, as the luminescence peak energy is less than 300 K CdTe bandgap $E_g = 1.513$ eV. Then, to explain the observed emission regularities (see Figs 1 and 2): (i) the difference in $h\nu_m$ values for CdTe films and crystals, and (ii) the shift of $h\nu_m$ values to lower energies with the growing excitation intensity L (power density P), they assumed the following. (a) A strong free exciton-phonon coupling exists in CdTe crystals, but not in CdTe films (this obviously shifts the discussed spectrum to lower energies), and (b) the excitation-induced change in the contribution (i.e. in a relative strength) of free excitons in $n = 1$ and $n = 2$ states to the formation of the near-band-edge emission. But practically no careful analysis confirming the adopted suppositions was made. In this paper, a de-

tailed analysis of assumptions made in [4] will be given. On its basis, we will show that the dominant free exciton contribution in the formation of the 300 K near-band-edge CdTe emission cannot explain the regularities observed when the cadmium telluride type (crystal or film) and the excitation intensity are varied. So, the nature of recombination transitions leading to a formation of 300 K cadmium telluride near-band-edge emission needs reexamination.

2. On the free exciton-phonon coupling in CdTe

The free exciton-phonon coupling (phonon-assisted radiative transitions, i.e. phonon replicas of emission lines) could really be observed in 4.2 K luminescence spectra of both CdTe films and crystals (see, for example, [5–9]). Obviously, it is difficult to observe directly the exciton-phonon coupling at the room temperature due to a considerable thermal broadening of the free exciton induced emission lines. But there is no obvious reason to suppose that the free exciton-phonon coupling could differ in bulk CdTe and cadmium telluride films (in any case, this conclusion should be made from the direct observation of 4.2 K free exciton-induced luminescence spectra of CdTe films and crystals; but unfortunately, no free exciton recombination lines were resolved in 4.2 K luminescence spectra of CdTe films and crystals investi-

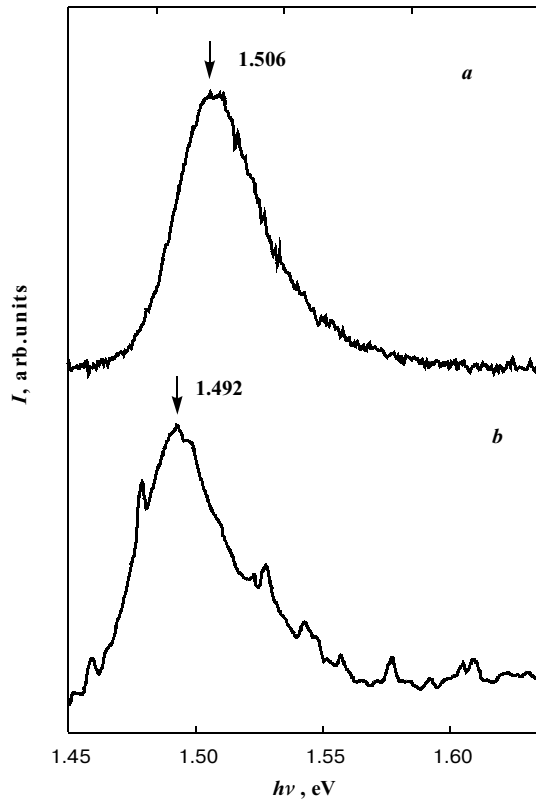


Fig. 1. Representative 300K photoluminescence from CdTe film (a) and bulk CdTe (b) in a region of $h\nu_m$ independent on the =excitation intensity [4].

gated in the discussed paper [4]). Moreover, nearly the same free exciton-phonon coupling is observed in experiment in 4.2 K luminescence spectra of cadmium telluride films [7] and crystals [5,6,8,9]. So, it seems to us that the proposed in [4] explanation of different peak positions in 300 K near-band-edge emission for bulk CdTe and cadmium telluride films as arising due to a different free exciton-phonon coupling in them could not be taken as a correct one, i.e. as well grounded.

3. Intensities of free exciton-induced emission bands in the near-band-edge luminescence spectra of non-degenerate semiconductors

Let us consider non-degenerate semiconductors (where concentrations of equilibrium free electrons and holes are n_0 and p_0 and of non-equilibrium δn and δp). Let the excitonic luminescence spectrum be formed by annihilation of thermalized free excitons (their distribution is given by the Maxwell-Boltzmann function) in the ground state $n = 1$ (their excess concentration n_{X1} , binding energy ϵ_{X1} , a probability of radiative annihilation α_{X1}), and the excited state $n = 2$ [their excess concentration n_{X2} , binding energy ϵ_{X2} , a probability of radiative annihilation α_{X2} [naturally, $\alpha_{X2} < \alpha_{X1}$ ($\alpha_{Xn} \sim 1/n^3$ for allowed direct

transitions as follows from the well-known correlation between the free exciton absorption coefficient and the luminescence intensity [10]]. Obviously, for the discussed case, emission intensities induced by annihilation of free excitons in the ground (I_{X1}) and excited (I_{X2}) states are:

$$I_{X1} = \alpha_{X1}n_{X1}, \tag{1}$$

$$I_{X2} = \alpha_{X2}n_{X2}. \tag{2}$$

To find the I_{X1} and I_{X2} dependence on L , one should obtain n_{X1} and n_{X2} values (obviously, they are determined by the rates of free exciton generation, their radiative annihilation and thermal dissociation). They could be found from the following kinetic equations (see also [11-13]):

$$\frac{dn_{X1}}{dt} = b_{X1}(n_0\delta p + p_0\delta n + \delta p\delta n) - (\alpha_{X1} + q_{X1})n_{X1} = 0, \tag{3}$$

$$\frac{dn_{X2}}{dt} = b_{X2}(n_0\delta p + p_0\delta n + \delta p\delta n) - (\alpha_{X2} + q_{X2})n_{X2} = 0, \tag{4}$$

where b_{X1} and b_{X2} are the probabilities of binding of free electrons and holes into free excitons in the ground and excited states (obviously, $b_{X1} > b_{X2}$), q_{X1} and q_{X2} are the probabilities of thermal dissociation of X_1 and X_2 excitons on free electrons and holes (obviously, $q_{X1} < q_{X2}$) {a definite correlation between q_{X1} and b_{X1} [$q_{X1} = n_{X1}^*b_{X1}$, where $n_{X1}^* = N_X^* \exp(-\epsilon_{X1}/kT)$], q_{X2} and b_{X2} [$q_{X2} = n_{X2}^*b_{X2}$, where $n_{X2}^* = N_X^* \exp(-\epsilon_{X2}/kT)$]($N_X^* = (m_r kT / 2\pi\hbar^2)^{3/2} = 2.4 \cdot 10^{15} (m_r/m_0)^{3/2} T^{3/2} \text{ cm}^{-3}$, where $m_r = m_e m_h / (m_e + m_h)$ is the reduced exciton mass) exists [11-13]}. When writing Eqs (3) and (4), we assumed that direct annihila-

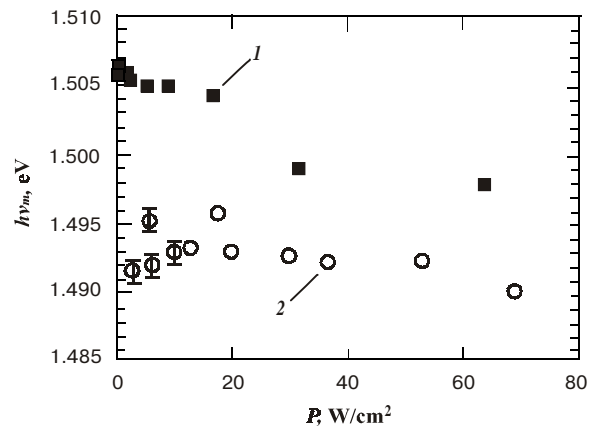


Fig.2. Excitation power dependence of 300 K emission peak energy for CdTe film (1) and bulk CdTe (2) [4].

tion of free excitons proceeds mainly with the photon emission and took into account that quasi-equilibrium exists between thermalized free excitons in $n=1$ and $n=2$ states.

Solving Eqs (3) and (4) one finds the n_{X1} and n_{X2} values. They are:

$$\begin{aligned} n_{X1} &= \frac{b_{X1}}{\alpha_{X1} + q_{X1}} (n_0 \delta p + p_0 \delta n + \delta p \delta n) = \\ &= \frac{b_{X1}}{\alpha_{X1} + n_{X1}^* b_{X1}} (n_0 \delta p + p_0 \delta n + \delta p \delta n), \end{aligned} \quad (5)$$

$$\begin{aligned} n_{X2} &= \frac{b_{X2}}{\alpha_{X2} + q_{X2}} (n_0 \delta p + p_0 \delta n + \delta p \delta n) = \\ &= \frac{b_{X2}}{\alpha_{X2} + n_{X2}^* b_{X2}} (n_0 \delta p + p_0 \delta n + \delta p \delta n), \end{aligned} \quad (6)$$

So, as one can see from Eqs (1), (2), (5) and (6), a relation between intensities I_{X1} and I_{X2} does not depend on the excitation intensity L , i.e.

$$\begin{aligned} I_{X1} : I_{X2} &= \alpha_{X1} \frac{b_{X1}}{\alpha_{X1} + q_{X1}} : \alpha_{X2} \frac{b_{X2}}{\alpha_{X2} + q_{X2}} = \\ &= \alpha_{X1} \frac{b_{X1}}{\alpha_{X1} + n_{X1}^* b_{X1}} : \alpha_{X2} \frac{b_{X2}}{\alpha_{X2} + n_{X2}^* b_{X2}} \neq \varphi(L) \end{aligned} \quad (7)$$

{the validity of the obtained correlation $I_{X1} : I_{X2} \neq \varphi(L)$ follows also from the direct calculation of I_{X1} and I_{X2} values from the well-known relation between the absorption coefficient and the recombination rate using detailed balance arguments [10,12,14]}.

Therefore, the free exciton-induced luminescence spectrum in semiconductors, in particular, in CdTe, does not change its shape with excitation, i.e. the relative weight of recombination flows via $n=1$ (I_{X1}) and $n=2$ (I_{X2}) excitonic states {obviously, $I_{X1} > I_{X2}$ at any L [see Eq. (7)] contrary to the accepted in [4]}, is not influenced by the excitation intensity. So, the proposed in [4] explanation of 300 K $h\nu_m$ shift with L in CdTe as connected with the excitation-induced redistribution of recombination flows via $n=1$ and $n=2$ free exciton states, is not well founded. So, free excitons could bring a definite, but not the dominating contribution into the formation of 300 K near-band-edge luminescence of cadmium telluride.

4. Conclusion

300 K near-band-gap luminescence in cadmium telluride crystals and films does not originate as a result of dominating free exciton transitions (they bring some but not the dominating contribution). Further investigations are needed to arrive at the exact origin of 300 K near-band-edge luminescence from cadmium telluride. One of them concerns the detailed measurement of temperature-induced (in the range of 4.2 to 300 K) variations in the intensity and the line shape of the free exciton (as well as bound exciton) emissions and band-to-band transitions from cadmium telluride crystals and films. It will permit to find the exact contribution to 300 K near-band-edge luminescence from CdTe of free and bound excitons, band-to-band and band-to-band tail states.

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