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# LUMINESCENCE AND ENERGY RELAXATION OF LOCALIZED EXCITONS IN CdS QUANTUM DOTS GROWN IN A LOW-PERMITTIVITY MATRIX

N.V. BONDAR, M.S. BRODYN

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Institute of Physics, Nat. Acad. of Sci. of Ukraine  
(46, Nauky Ave., Kyiv 03680, Ukraine; e-mail: jbond@iop.kiev.ua)

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The results of our researches of borosilicate glasses with CdS quantum dots (QDs), the dimensions of which are smaller than the exciton Bohr radius, are reported. The mean size of quantum dots for a given CdS concentration has been calculated in the effective mass approximation, the result obtained being in good agreement with X-ray data. In the same approximation, the exciton binding energy has also been calculated, with and without the dielectric mismatch between the semiconductor and the matrix being taken into account. Two channels of radiative recombination associated with the annihilation of excitons in quantum-mechanical and surface (localized) states have been shown to exist in such QDs, and the efficiency of exciton relaxation between those channels has been demonstrated to depend on the QD size. For the first time, a photoluminescence (PL) band has been found for specimens excited in the long-wave range of their absorption spectrum; the band is due to the recombination of excitons in localized states, and its characteristic properties are typical of other disordered structures. A conclusion has been drawn about a universal character of both the energy relaxation process and the PL band shape for excitons localized at QDs and quantum wells (superlattices) with a disorder that are located at heterointerfaces, as well as in amorphous semiconductors and solid solutions.

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## 1. Introduction

Optical properties of QDs made of II–VI semiconductors have been studied intensively recently, because one may hope those objects to become an element base of opto- and quantum electronic devices. Among various factors that can worsen the quality of the latter, one of the most serious factors that substantially affects the optical characteristics of QDs is a disorder created by surface atoms at the QD–matrix interface. This allows QDs to be referred to a wide class of structures with disorder, such as amorphous semiconductors, solid solutions, quantum wells, and superlattices. A common feature of those structures is the availability of a dominating band in their PL spectra; this band is associated with a recombination of excitons in disorder-induced localized states (LSs) and is red-shifted with respect to the maximum in the exciton absorption spectrum (the so-called Stokes shift) [1–4].

Despite that a great progress was achieved in understanding the dimensional quantization of the charge carrier energy in QDs, the LS nature and the features of electron-hole pair energy relaxation in LSs still remain a matter of discussion [5–16]. Nowadays, the disorder in QDs is adopted to result from their disordered interfaces. It was found that a disorder is created by surface atoms with dangling bonds or by an oxidized surface, as it occurs in Si QDs grown up in a SiO<sub>2</sub> matrix [5]. According to theoretical concepts, the surface states with a fixed energy  $E_s$  that is located in the QD energy gap can emerge only in QDs with small radii. In other words, there is a critical radius  $R_c$  for QDs, at which the surface state can be split off from the extremum of the valence or conduction band. Making use of a method that was based on the time evolution of the electron wave function, the authors of work [17] showed that the domination of Cd atoms over the surface of CdS QDs with small radii gives rise to the formation of surface states; the energy of the lowest of these surface states,  $E_s \approx 2.7$  eV, falls within the QD energy gap. Similar surface states, but with different energies, are formed if sulfur atoms dominate over the surface.

Using InP QDs as an example, the authors of work [18] demonstrated that the surface state splits off from the extremum of the valence or conduction band at a definite  $R_c$ , with the corresponding values being different for those bands. For instance, in InP QDs, the lowest surface state splits off from the bottom of the conduction band at  $R_c \approx 29$  Å, and its energy remains almost constant if the QD radius decreases. If the excess of surplus atoms at the QD surface increases, a quasi-continuous tail in the LS density rather than a new surface state arises, and this tail decays toward the depth of the QD energy gap [5, 19]. Surface LSs almost do not reveal themselves in the QD absorption spectrum. Therefore, one of the evidences for the formation of the density tail is the PL intensity decay curve which possesses two sections: the fast one ( $< 10$  ps) is associated with intraband relaxation of charge carriers

in quantum states, and the slow one ( $> 1000$  ns) with recombination of electron-hole pairs, where either or both carriers are localized on the surface [8].

This work aims at studying, first, the features of charge carrier (exciton) relaxation between quantum and surface states in CdS QDs with radii smaller than the Bohr one and, second, their recombinations in LSs formed by external atoms with nonsaturated bonds. It can be interesting from both physical and practical viewpoints, because a considerable lifetime of electron-hole pairs reduces the optical response of structures with QDs, which is a serious obstacle to their usage in elements of quantum and optoelectronics. The results obtained also make it possible to explain, at a qualitative level, why the decay time of the PL signal in CdS and other (Si, CdSe, CdTe) QDs [5, 8–16] is so large.

## 2. Experimental Part

In our researches, we used specimens of borosilicate glass, CdS-doped to the concentration  $x = 0.03\%$ . The procedure of their synthesis was described earlier [7, 15]. The analysis of X-ray data showed that the mean size of emerged QDs was  $R_0 = (20 \pm 5)$  Å, which is less than the Bohr radius of excitons in a bulk CdS ( $a_x = 28$  Å). To excite PL spectra, we used two He–Cd lasers: (i) with the wavelength  $\lambda_1 = 325$  nm ( $E_1 = 3.84$  eV) and the mean power  $P_0 = 10$  mW (the  $E_1$ -laser), and (ii) with the wavelength  $\lambda_2 = 441.6$  nm ( $E_2 = 2.807$  eV) and the mean power  $P_0 = 20$  mW (the  $E_2$ -laser). The QD sizes in studied specimens have dispersion around  $R_0$ . Therefore, the  $E_1$ -laser could excite QDs with all dimensions, whereas the  $E_2$ -laser only QDs with  $R > R_0$  which belonged to the tail of the distribution function. The radiation emission flux of the  $E_1$ -laser was  $j_p \approx 10^{20}$  photon/cm<sup>2</sup>, and the transverse absorption cross-section of a QD with the radius  $R_0$  was  $\sigma_\alpha \approx 10^{-17} \div 10^{-18}$  cm<sup>2</sup>. Therefore, we used attenuator filters to reduce the number of electron-hole pairs in a QD to  $N_{eh} = j_p \sigma_\alpha < 1$ . All PL spectra obtained in such a way were reproducible, and no photoinduced darkening of specimens was observed, even if they were subjected to a long irradiation.

Before the experiment, the specimens were placed into a helium cryostat that provided the temperature,  $T$ , variation within the interval 4.5 – 300 K. To record the PL signal, we used a DFS-12 monochromator with a resolution not worse than 5 Å/mm. Registration of spectra was carried out following the usual scheme of photon counting.

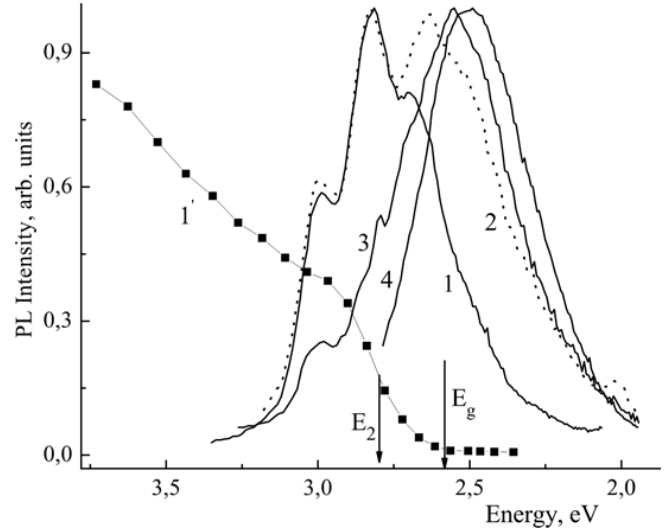


Fig. 1. Absorption and photoluminescence spectra of borosilicate glass specimens with CdS QDs: 1' – absorption spectrum at  $T = 300$  K; 1 – PL spectrum at the excitation by the  $E_1$ -laser (PL1); 2 – PL spectrum at the excitation by the  $E_1$ - and  $E_2$ -lasers simultaneously (PL2); 3 – PL spectrum, the intensity of the  $E_1$ -laser is two orders of magnitude lower (PL3); 4 – PL spectrum at the excitation by the  $E_2$ -laser (PL4). Arrows denote the position of  $E_2$  and the energy gap  $E_g$  in a massive CdS

In Fig. 1, the absorption and PL spectra obtained in this work are depicted. The absorption spectrum demonstrates a peculiarity around 2.998 eV. Its shift toward short waves with respect to the forbidden gap energy in a bulk CdS ( $E_g = 2.583$  eV, denoted by an arrow at the figure bottom) testifies to the formation of QDs and the strong dimensional energy quantization of charge carriers in them. It should be noted that the absorption and PL spectra of pure borosilicate glass (not shown in the figure) did not demonstrate any noticeable structure in the interval 2 – 3.3 eV. Wide band PL1 was recorded at  $T = 4.5$  K, the  $E_1$ -laser being used for specimen excitation. The band has a three-peak structure. The position of the first, short-wave, peak coincides with that of the mentioned peculiarity in the absorption spectrum. The other peaks are red-shifted, but fall within the range  $E > E_g$ . When the specimens were excited by the  $E_2$ -laser (the arrow under the figure), band PL4 was obtained. Its shape differs drastically from that of band PL1. Below, it will be shown that such a shape is typical of amorphous semiconductors, solid solutions, and quantum wells with disorder at interfaces (ZnS–ZnSe [4]).

To elucidate the mechanisms of such sharp variations of the shape and the spectral position of the PL band,

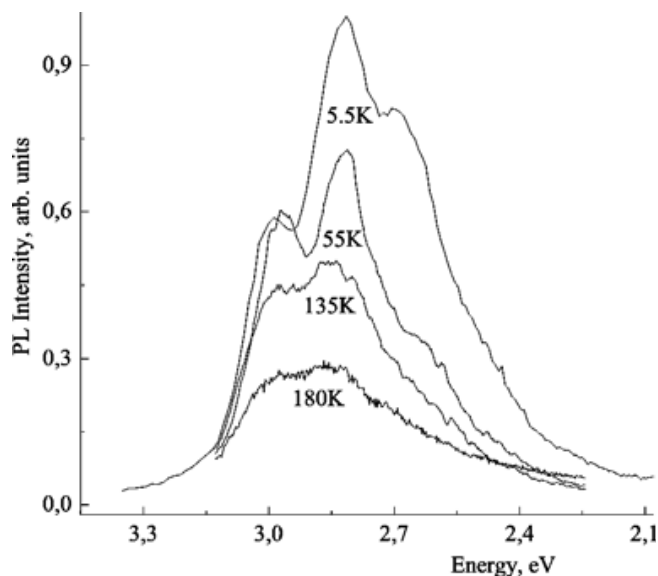


Fig. 2. Dependences of the shape and the intensity of band PL1 in an untreated specimen on the temperature

the specimens were excited simultaneously by two He–Cd lasers described above (their excitation spots were brought together on the specimen surface). As was pointed out, it allowed CdS QDs of every dimension in the bulk to be excited, as well as the group of QDs with  $R > R_0$ , so that band PL2 (Fig. 1) was obtained. Despite that the excitation was executed by means of two lasers, the intensity of this band remained the same as that of band PL1; however, its third peak got broadened and shifted toward long waves by about 70 meV. A reduction of the  $E_1$ -laser intensity was accompanied by a modification of the band PL2 shape. Namely, the intensities of the first and the second peaks of the emission band decreased, but their spectral positions remained invariable; at the same time, a further shift of the third peak by about 130 meV toward long-wave range was observed. Band PL3 was recorded when the intensity of the  $E_1$ -laser was 0.01 of the maximal one, and the intensity of the second laser remained invariable.

Figure 2 illustrates the dependences of the shape and intensity of band PL1 on the temperature  $T$ . The first two peaks in the band turned out highly robust to increasing  $T$  (up to about 250 K). This stability may probably be explained by the fact that those peaks are formed by internal (quantum-mechanical) states of QD. At the same time, the third peak in the band almost totally disappeared already at  $T > 50$  K. Therefore, the states that are responsible for it are most likely not internal for QDs.

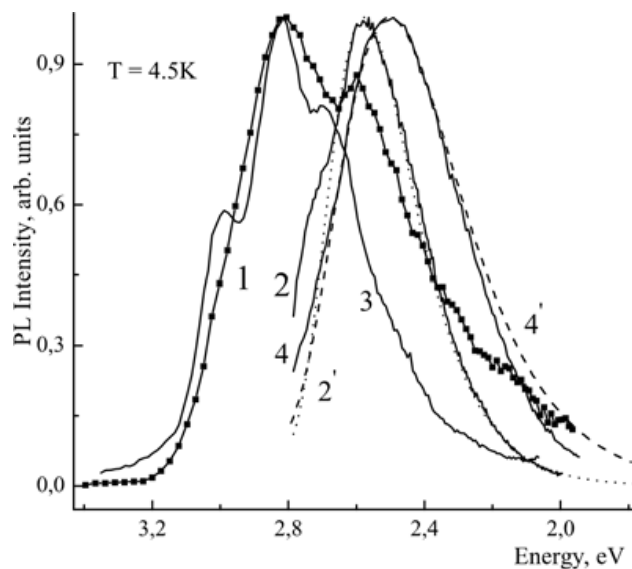


Fig. 3. Photoluminescence spectra of a specimen warmed at  $T = 500$  °C for 5 h. 1 and 2 – bands  $PL_{t1}$  and  $PL_{t2}$  in a warmed specimen at the excitation by the  $E_1$ - and  $E_2$ -lasers, respectively; 3 and 4 – bands PL1 and PL4 from Fig. 1; curves 2' (points) and 4' (dashed) –  $n(\varepsilon)$ -dependences

The increase of the average radius of QDs enables the changes in the spectral position of PL band peaks to be traced. It can be done by the thermotreatment of specimens thermally, so that the QD dimensions grow up due to the so-called Ostwald ripening [7]. Figure 3 demonstrates bands  $PL_{t1}$  and  $PL_{t2}$  for a specimen warmed for 5 h at  $T \approx 500$  °C. The bands were excited by the  $E_1$ - and  $E_2$ -lasers, respectively, and recorded at  $T = 4.5$  K. For the sake of comparison, Fig. 3 also exhibits bands PL1 and PL4 observed in an unwarmed specimen (these are the same, as in Fig. 1). According to our estimations, the heat treatment of specimens gave rise to an increase of  $R_0$  to about 25 Å, which stimulated a red shift of the free-exciton peak and its merging with the central peak (so that those peaks became unresolvable). On the long-wave wing of band  $PL_{t1}$ , there appeared a new peak at an energy of about 2.6 eV, the position of which coincided with the maximum of band  $PL_{t2}$ . Figure 3 also demonstrates that band  $PL_{t2}$  became more asymmetric in comparison with band PL4, and the shift of its maximum toward the red side is much smaller than that of band PL4. In addition, the band got much narrower, which is evidently a direct consequence of the specimen heat treatment.

### 3. Discussion of Results

**3.1.** To analyze the results obtained, let us proceed from estimating the energy of excitons in the ground quantum state ( $1S_e - 1S_{3/2}$ ) in a QD with  $R \approx R_0$ . We use the effective mass approximation and the infinite barrier model, where the wave functions of electrons and holes are zero at the QD boundary. Taking the discontinuity of the dielectric constant into account, the Hamiltonian of an electron-hole pair in a sphere with radius  $R$  can be written down as  $H = H_0 + H_p$ , where the term  $H_0$  includes the kinetic energy of charge carriers and the Coulomb interaction between them, and the term  $H_p$  describes the contribution of the surface polarization energy. If the dielectric constants of the QD,  $\varepsilon_1$ , and the matrix (glass),  $\varepsilon_2$ , are equal,  $\varepsilon_1 = \varepsilon_2$ , there is a well-known solution obtained in the framework of the single-band model [21]:

$$E_{1s}(R) = E_g + (\pi^2 \hbar^2) / 2\mu R^2 - 1.786e^2 / \varepsilon_1 R - 0.248\varepsilon_x,$$

where  $\mu$  is the reduced mass of excitons, and  $\varepsilon_x$  their binding energy in a bulk semiconductor. If  $\varepsilon_1 \neq \varepsilon_2$ , the solution reads [20, 22]

$$E_{1s}(R) = E_g + \frac{\hbar^2}{2R^2} \left[ \frac{\pi^2}{m_e^*} + \frac{\varphi_1^2}{m_h^*} \right] + \frac{e^2}{\varepsilon_1 R} g(\varepsilon) - E_x, \quad (1)$$

where  $g(\varepsilon) < 1$ ,  $\varepsilon = \varepsilon_1 / \varepsilon_2$ ,  $\varphi_1 \approx 4.49$  is a root of the Bessel function,  $E_x = (e^2 / \varepsilon_1 R) [(\varepsilon_1 + \varepsilon_2) / \varepsilon_2 - \text{Si}(2\pi) / \pi - \text{Si}(4\pi) / 2\pi]$ , and  $\text{Si}(x)$  is the integral sine ( $\text{Si}(2\pi) = 1.42$  and  $\text{Si}(4\pi) = 1.492$ ). If  $\varepsilon_1 = \varepsilon_2$ , we have  $E_x = 1.786e^2 / (\varepsilon_1 R)$ . Using the absorption spectrum shift magnitude (of about 415 meV) with respect to  $E_g$  and the equalities  $m_e^* = 0.2m_0$ ,  $m_h^* = 0.9m_0$ ,  $\varepsilon_1 = 8.42$ ,  $\varepsilon_2 = 2.25$ , and  $g(\varepsilon_1 / \varepsilon_2 = 3.74) \approx 0.573$ , we obtain  $R_0 \approx 19 \text{ \AA}$  for the average size of QDs in the specimens under investigation. This magnitude agrees well with the data of X-ray measurements and confirms that both the peculiarity in the absorption spectrum and the short-wave peak in band PL1 are generated by the recombination of free excitons in their ground quantum state. In addition, we find that, in a QD,  $E_x = 386 \text{ meV}$ , if the dielectric mismatch is made allowance for, and  $E_x = 152 \text{ meV}$  otherwise (in a bulk CdS,  $E_x = 28 \text{ meV}$ ).

The central peak in band PL1 is shifted by approximately 160 meV with respect to the absorption spectrum. It may be induced by the recombination of electrons in the ground state and holes captured onto an acceptor level located above the ground quantum hole state. However, this hypothesis requires the further verification (see the scheme in work [10]). Hence, the

results obtained testify that the origins of the first two peaks and the third one in band PL1 are different. Appropriate confirmations can also be obtained by analyzing the initial peak quenching temperature, i.e. the temperature at which the peak intensity becomes substantially reduced. Figure 2 demonstrates that the quenching temperature is considerably higher for the first two peaks in the band, owing to a larger binding energy of excitons in quantum and impurity states. This circumstance allows one to observe these peaks at temperatures up to room one. However, the third peak in band PL1 disappears completely already at  $T \approx 50 \text{ K}$ , which testifies that it was generated by states that are not internal for QDs.

**3.2.** On the basis of the results obtained, we may suppose that there are two channels of radiative recombination in the studied CdS QDs. One of them is due to the annihilation of excitons in quantum and impurity states. It is responsible for the first two peaks in band PL1. The other is caused by excitons captured at the LSs that were formed by surface atoms with dangling bonds. This channel is responsible for the appearance of the third peak in this band. The efficiency of the charge carrier relaxation between those channels depends on the QD radius or, in other words, on the energy gap between the ground quantum state and the surface one. This gap changes mainly at the expense of charge carriers in quantum states (the dimensional effect), because the energy of charge carriers in surface states practically does not depend on the QD size; this fact was pointed at in works [6, 8–13]. However, despite that, none of those authors have analyzed states that formed the second channel and the behavior of charge carriers (excitons) in them.

A significant time of the PL intensity damping in structures with QDs (more than 1000 ns) testifies that these states are not isolated. On the contrary, they form a quasi-continuous tail of LSs, the situation being similar to that in solid solutions and amorphous semiconductors. Therefore, the energy distribution of the LS density, as in the latter case, can be approximated by an exponential distribution  $g(\varepsilon) = [N_0 / \varepsilon_0] \exp[-(\varepsilon / \varepsilon_0)]$ , where  $\varepsilon > 0$  is the charge carrier binding energy in the LS reckoned from the mobility threshold,  $N_0$  is the LS concentration, and  $\varepsilon_0$  is the energy scale of the density tail. The formation of LSs in QDs is responsible for the existence of the mobility threshold which divides localized and quantum (internal) exciton states. In our case, we suppose this threshold to coincide with the energy of the lowest surface state ( $E_s \approx 2.7 \text{ eV}$ ), i.e., that it is located near the maximum of the third peak in

band PL1. In our work [15], we showed that the position of this peak was almost independent of the size of CdS QD in the range  $R_0 < 40 \text{ \AA}$ . Our result agrees with the conclusion of works [17, 18] that there exists a critical radius  $R_c$  of QD, at which a surface state splits off from the bottom of the conduction band. If the QD radius grows above  $28 \text{ \AA}$ , the ground quantum level of excitons falls down below  $E_s$  and, in what follows, plays the role of mobility threshold.

Thus, after the specimens have been excited by the  $E_1$ -laser, electrons and holes relax into their ground states, and the efficiency of their capture from the first channel into the second one depends on the difference  $E_{1s}^{\text{ex}} - E_s$ , where  $E_{1s}^{\text{ex}}$  is the ground quantum level of excitons at given  $R_0$ . In the studied QDs, this difference exceeded  $300 \text{ meV}$ . Therefore, the phonon mechanisms (LO, LA+LO, TA) could not provide the complete relaxation of electrons in LSs. As a result, the emission from both channels was observed. In this case, the relaxation of electrons in LSs could occur by means of the  $e - h$  interaction of the Auger type or through a similar mechanism [10].

Ultimately, electrons first find themselves in shallow states with  $\varepsilon \approx 0$  (i.e.  $E_s$ ), then relax into the depth of the density tail. Therefore, the  $E_s$ -state is always filled, and it has a significant intensity. If the pump intensity decreases, a red shift of the maximum of the band that corresponds to the emission from LSs is observed—as it happens, e.g., in amorphous semiconductors and solid solutions—and this shift results from the redistribution of charge carriers over the density tail [2]. It was not observed in our case, and the position of the maximum of the third peak in band PL1 did not change, even if the intensity of the  $E_1$ -laser became 2–3 orders of magnitude lower, which confirms the relaxation scheme given above.

The formation of a quasi-continuous tail in the LS density proves also to be true by exciting the specimens simultaneously by two ( $E_1$  and  $E_2$ ) lasers (band PL2 in Fig. 1). In QDs with  $R > R_0$ , the difference  $E_{1s}^{\text{ex}} - E_s$  is smaller because  $E_{1s}^{\text{ex}}$  is smaller. Therefore, the phonon mechanisms are already important in these QDs, and electrons relax not only into the  $E_s$ -state but also into deeper LSs, which gives rise to a broadening of the third peak and its shift by about  $70 \text{ meV}$ . A smooth reduction of the intensity of the  $E_1$ -laser and, accordingly, a smooth decrease of the number of charge carriers in states with  $\varepsilon \approx 0$  are accompanied by a shift of the maximum of the third peak by about  $130 \text{ meV}$  with respect to  $E_s$  (band PL3), which is a characteristic attribute of the formation of a quasi-continuous tail in

the LS density [2, 4]. If the specimens are excited by the  $E_2$ -laser only, charge carriers are totally captured into the second channel, and they relax over the LSs, which brings about the specific shape and the spectral position of band PL4 (Fig. 1).

Another evidence for the enhancement of the charge carrier relaxation process between channels are the PL spectra of thermally treated specimens (Fig. 3). In this case, since the parameter  $R_0$  of QDs increases, the difference  $E_{1s}^{\text{ex}} - E_s$  decreases. Therefore, even if such specimens are excited by the  $E_1$ -laser, the efficiency of the charge carrier relaxation grows considerably, which stimulates the occurrence of a peak in the interval of about  $2.6 \text{ eV}$  (band PL<sub>t</sub>1). The capture is almost complete, if the specimens are excited by the  $E_2$ -laser, and, as a result, the intensity of band PL<sub>t</sub>2 becomes more than 2 times larger in comparison with that of band PL4.

Now, let us consider factors that affect the positions of maxima of bands PL<sub>t</sub>2 and PL4, and govern their shapes. Significant shifts of those maxima with respect to  $E_s$  testify to the effective relaxation of excitons into deep states in the density tail that occurs during their life. If this is not the case, the maxima of those bands would coincide with  $E_s$ . But, in contrast to the case of solid solutions and amorphous semiconductors, where the energy relaxation of excitons is accompanied by their spatial jumps between LSs, excitons can move in our case only within the limits of QDs, because the concentration of the latter is low.

Let us recall briefly the key ideas that explain the shape of the emission band and its spectral position with respect to the mobility threshold [2, 3]. In solid solutions, a localized exciton is an electron–hole pair, in which holes (electrons) are localized due to composition fluctuations, and electrons (holes) are connected with them by means of the Coulomb potential. The PL band shape under stationary conditions of excitation is governed by the energy distribution of one of the charge carriers over the LS tail. This distribution is a result of the competition between the radiative recombination of localized excitons characterized by the lifetime  $\tau_0$  and the tunnel jump of an electron or a hole characterized by the time interval  $\tau_h(r_m) = \nu_0^{-1} \exp(2r/\alpha_0)$ , where  $r$  is the distance between the nearest LSs,  $\nu_0 \approx 10^{13} \text{ s}^{-1}$ , and  $\alpha_0$  is the radius of state localization [2]. While relaxing, charge carriers are accumulated in deep states of the density tail, which manifests itself as a shift of the PL band maximum with respect to the LS mobility threshold toward long waves. The maximal shift  $\varepsilon_m$  corresponds to the energy of state, in which the relation  $\tau_h(r_m) \approx \tau_0$ , where  $r_m$  is the maximal distance passed

by an exciton before the recombination, is fulfilled [2]. This scenario is quite acceptable for the explanation of the shift magnitudes of the maxima of bands PL4 (about 200 meV) and PL<sub>t</sub>2 (about 125 meV) relative to  $E_s$ . However, it is impossible to determine the QD dimension, which would satisfy this relation, because there are no calculations dealing with the dependence of the LS energy on the QD size.

Under stationary conditions of excitation, a short-wave shift of the maximum of the emission band induced by localized excitons can be observed. It occurs when the pump source power is high enough for the processes of LS population by excitons to play a substantial role [1–3]. In our case, the dependences of the maxima of bands PL4 and PL<sub>t</sub>2 on the  $E_2$ -laser intensity or the temperature  $T$  were not observed. This circumstance testifies that the LS population by excitons can be neglected, i.e. there is no exciton redistribution over the LSs in the density tail either at a reduction of their number or at a temperature  $T$  growth [2, 4]. Therefore, the shapes of the long-wave sections of bands PL4 and PL<sub>t</sub>2 reflect the  $g(\varepsilon)$ -dependence with  $\varepsilon_0 \approx 180$  and 125 meV, respectively (Fig. 3). Concerning the short-wave sections of these bands, the situation is much more difficult and interesting than that in solid solutions and amorphous semiconductors, where those sections are generated by the so-called localized hopping states. For the latter, the relation  $\tau_h(r) < \tau_0$  is valid, which enables excitons to relax during their lifetime and to gather in the deep states of the density tail [2]. In the QD case, the formation of LSs with different energies of exciton localization  $\varepsilon$  is proportional to the QD surface area  $S = 4\pi R^2$ : almost every QD possesses shallow LSs, because the probability of their formation is maximal; at the same time, deep LSs are possible only on QDs with large dimensions, because a considerable surface is needed for them. Since the concentration of QDs in the bulk is low, excitons are not able to tunnel between them and reach deep states in the density tail. The emission from shallow LSs should seemingly dominate, even if specimens are excited by the  $E_2$ -laser. But not every LS takes part in the formation of short-wave sections of bands PL4 and PL<sub>t</sub>2. The  $E_2$ -laser can excite only QDs with  $R > 23 \text{ \AA}$ , in which the level  $E_{1s}^{\text{ex}}$  is located above  $E_s$ . However, in QDs with  $R \geq 28 \text{ \AA}$ , this level drops below  $E_s$ , so that shallow LSs in such QDs become excluded from the process of section formation. Therefore, LSs with  $\varepsilon \approx 0$  can participate in the formation of short-wave sections of bands PL4 and PL<sub>t</sub>2 only in the range of QD sizes  $R = 23 \div 28 \text{ \AA}$ . If only those QDs with large dimensions, where the level  $E_{1s}^{\text{ex}}$  is located considerably

lower than  $E_s$ , would be excited, one could observe an enhancement of the asymmetry of bands PL4 and PL<sub>t</sub>2 due to the drastically decaying short-wave sections. This phenomenon can be partially observed making use of band PL<sub>t</sub>2 as an example (Fig. 3).

**3.3.** Now, let us determine the energy distribution of localized excitons  $n(\varepsilon)$  in both specimens and compare it with the shapes of bands PL4 and PL<sub>t</sub>2 (Fig. 3). Since the QD concentration is low, the relaxation of localized excitons occurs within QDs rather than between them, as it does in solid solutions and amorphous semiconductors. Every jump of an exciton from one point on the QD surface to another one is accompanied by the tunneling through a potential barrier, the height of which is  $\gamma(\varepsilon) = (E_{1s}^{\text{ex}} - E_s + \varepsilon)$ . The time of a jump depends on both the distance between LSs and the radius of state localization. Let a localized state be a rectangular potential well, which contains an electron with the localization energy  $\varepsilon_m$ . The radius of such a state can be evaluated as  $\alpha_0 = \hbar / (2m_e^* \varepsilon_m)^{1/2}$ ; so that choosing  $m_e^* = 0.2m_0$ , we obtain  $\alpha_0 = 9.7 \text{ \AA}$  for an untreated specimen and  $\alpha_0 = 12.3 \text{ \AA}$  for a thermally treated one.

Figure 3 exhibits the  $n(\varepsilon)$ -dependences (curves 2' (points) and 4' (dashed)) calculated in the framework of the theory expounded in works [1–4]. The satisfactory agreement between  $n(\varepsilon)$  and band PL4 was achieved with the parameters  $N_0 \approx 4.5 \times 10^{17} \text{ cm}^{-3}$ ,  $\varepsilon_0 = 180 \text{ meV}$ , and  $N_0 \alpha_0^3 = 4.2 \times 10^{-4}$ , and between  $n(\varepsilon)$  and band PL<sub>t</sub>2 with  $N_0 \approx 3.2 \times 10^{17} \text{ cm}^{-3}$ ,  $\varepsilon_0 = 125 \text{ meV}$ , and  $N_0 \alpha_0^3 = 5 \times 10^{-4}$ . In both cases, the time of radiative recombination of excitons  $\tau_0$  was selected to be of about 100 ns [5, 6, 8], whence  $\nu_0 \tau_0 = 10^6$ . The magnitudes of  $\varepsilon_0$  and  $\alpha_0$  agree well with literature data, though they were obtained for the first time for such structures. The parameters obtained can be used to estimate the maximal distance passed by an electron within the QD limits before the recombination:  $r_m \approx 67 \text{ \AA}$  for an unwarmed specimen and  $r_m \approx 85 \text{ \AA}$  for a thermally treated one. However, as was already pointed out, it is impossible to determine the radius of QD, in which this relation holds true.

To summarize, we have analyzed the low-temperature spectra of the emission from CdS QDs. The spectra are considered to be caused by the recombination of free excitons in quantum states and excitons localized at external atoms of QDs with nonsaturated bonds. The change of the mechanism of charge carrier (exciton) relaxation between quantum and surface states is found; the change occurs if either the QD size increases or the specimen is excited in the long-wave part of its

absorption spectrum. It is also established that, in contrast to the cases of solid solutions, amorphous semiconductors, and quantum wells and owing to a low concentration of QDs, the exciton relaxation over the states in the density tail runs within the QD limits rather than between QDs. This circumstance brings about a considerable time of PL intensity damping in such structures. However, in spite of that, the process of energy relaxation of charge carriers over the LS density tail has much in common with that in solid solutions, amorphous semiconductors, and quantum wells. So, it can be described in the framework of a common approach.

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ЛЮМІНЕСЦЕНЦІЯ ТА ЕНЕРГЕТИЧНА  
РЕЛАКСАЦІЯ ЛОКАЛІЗОВАНИХ ЕКСИТОНІВ  
У КВАНТОВИХ ТОЧКАХ CdS, ВИРОЩЕНИХ  
В НИЗЬКОДІЕЛЕКТРИЧНІЙ МАТРИЦІ

*М.В. Бондар, М.С. Бродин*

Резюме

В роботі наведено результати досліджень зразків боросилікатного скла з квантовими точками CdS, розміри яких менші за борівський радіус екситонів. В наближенні методу ефективної маси розраховано середній розмір квантових точок для даної концентрації CdS, який добре узгоджується з рентгенографічними даними, а також енергією зв'язку екситонів з і без врахування діелектричного непогодження напівпровідника та матриці. Показано, що в таких квантових точках існують два канали випромінювальної рекомбінації, пов'язані з анігіляцією екситонів в квантових та поверхневих (локалізованих) станах і ефективність релаксації екситонів між каналами залежить від розміру квантових точок. Під час збудження в довгохвильову ділянку спектра поглинання зразків вперше виявлено смугу фотолюмінесценції, сформовану рекомбінацією екситонів виключно в локалізованих станах, характерні властивості якої притаманні іншим структурам з непорядком. Зроблено висновок про універсальний характер процесу енергетичної релаксації і форми смуги фотолюмінесценції локалізованих екситонів в квантових точках та ямах з непорядком на гетеромежах, аморфних напівпровідниках і твердих розчинах.