

## TEMPERATURE DEPENDENCE OF PHOTOLUMINESCENCE OF CdTe QUANTUM DOTS IN A POLYMER MATRIX

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Temperature dependences of photoluminescence (PL) spectra of CdTe quantum dots (QDs) in a polymer matrix have been studied. The CdTe QDs in a polymer matrix were prepared by transferring them from an aqueous colloid solution. A long storage of specimens was found to result in a bimodal distribution of CdTe QDs by their size in the polymer matrix. The activation energies of the temperature quenching of photoluminescence bands of CdTe QDs in the polymer matrix that correspond to PL bands produced by QDs with different sizes have been determined. The photoluminescence of investigated specimens was found to have the exciton mechanism, which is confirmed by the temperature dependence of the PL peak position and the dependence of the integral PL intensity on the optical excitation intensity.

### 1. Introduction

In the last years, a large attention has been paid to the development of new technologies for the fabrication of high-quality stable quantum dots (QDs) on the basis of semiconductor substances in solid matrices of various types and to the research of their luminescence characteristics [1–6]. The interest in such researches is associated with the opportunity of practical applications of QDs, in particular, the creation of highly efficient light-emitting devices on their basis. The radiation wavelength in such devices can be controlled by varying QD dimensions only, not changing their chemical composition. By introducing QDs of different sizes into a solid matrix, one can obtain white light sources, light-emitting diodes, and low-threshold lasers that are characterized by low power consumption and high durability [7–10]. The most applied technique for manufacturing A<sub>2</sub>B<sub>6</sub> QDs is their synthesis in aqueous colloid solutions and their subsequent transfer into solid polymer matrices. The radiation efficiency of such QDs at room temperature reaches 80%, which is much higher

than that for light-emitting diodes fabricated on the basis of *p-n*-junctions.

For the high light-emitting characteristics of A<sub>2</sub>B<sub>6</sub> QDs to be practically implemented into the manufacture of new-generation optoelectronic devices, a detailed profound study of their luminescence properties, which substantially depend on the QD manufacture technique, is required. Researches of PL spectra emitted by QDs (made up of A<sub>2</sub>B<sub>6</sub> and other semiconductor materials), which were fabricated under different technological conditions, in wide ranges of temperature and QD excitation intensity, allow, first, the regimes for synthesizing stable QDs to be optimized and, second, important information concerning the fundamental characteristics of QDs (the energy parameters of charge carriers; their dependences on the state of the QD surface and the properties of a matrix, in which they are located; the mechanisms of radiation recombination; the exciton parameters; the features of electron-phonon and exciton-phonon interaction, *etc.*) to be obtained. We have also analyzed the temperature dependences of the photoluminescence produced by CdTe QDs in a polymer matrix.

### 2. Specimen Fabrication and Experimental Technique

CdTe QDs stabilized by thioglycolic acid were synthesized in an aqueous solution at room temperature following the standard technique [11, 12]. The following reactants were used to synthesize CdTe QDs: “chemically pure” CdCl<sub>2</sub>, thioglycolic acid (Aldrich, purity higher than 98%), “pure” 0.1 M solution of NaOH, “pure” 0.1 M solution of HCl, tellurium of TV-4 grade, and deionized water (a specific resistance of 18 MΩ).

Polymer films with CdTe QDs were fabricated following the technology of level-by-layer (LBL) deposition of

oppositely charged components on the substrate surface [13, 14]. As a polycation component of composite films, the polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA) (Aldrich) was used. Films were deposited onto glass substrates which had been preliminary washed out and kept in the “piranha” mixture (“chemically pure” concentrated  $\text{H}_2\text{SO}_4$  and a 30% solution of “analytically pure”  $\text{H}_2\text{O}_2$  taken in the ratio 3:1). Owing to this washing out, the surface was hydroxylized, and a substantial negative surface charge was created, which promoted the polycation adsorption from the aqueous solution.

The films were deposited automatically, using the cyclic repetition of operations to deposit 30 layers: the adsorption deposition of a monomolecular layer of PDDA polycation onto the prepared wafer surface by means of immersing the substrate into the polycation solution, washing out a wafer from the excess of polymer molecules in deionized water, and the adsorption deposition of a CdTe QD monolayer onto the previously deposited polymer monolayer by immersing the substrate into the CdTe QD solution.

PL spectra were measured in the temperature range from 5 to 300 K in an optical helium cryostat of the UTREKS system supplied with a K.41 electronic block to control and to stabilize the temperature to an accuracy of about 0.1 K. PL was excited by a He-Cd laser with a wavelength of 325.0 nm and a radiation power of 10 mW. The PL signal was registered using an installation on the basis of an MDR-23 spectrometer equipped with a FEU-100 photomultiplier with the computer-assisted control over the spectrum scanning.

### 3. Experimental Results and Their Discussions

In Fig. 1, the PL spectra of CdTe QDs in a colloid solution (curve 1), after their transfer from the colloid solution into PDDA (curve 2), and after holding this specimen at room temperature for about 2.5 years (curve 3) are depicted. In all cases, the measurement temperature was  $T = 300$  K. One can see that the PL band of CdTe QDs in the colloid solution with  $E_{\text{max}} = 2.37$  eV became shifted toward the high-energy region to  $E_{\text{max}} = 2.41$  eV after CdTe QDs had been transferred into PDDA, and its halfwidth decreased a little (from 230 to 180 meV). This shift testifies that QDs of smaller dimensions are presumably incorporated into the PDDA polymer at the selected way of their transfer from the colloid solution. In other words, the insertion process is size-selective (the average size of CdTe QDs evaluated on the basis of literature data and by calculations in the framework of effective mass approximation for CdTe QDs [15] taking

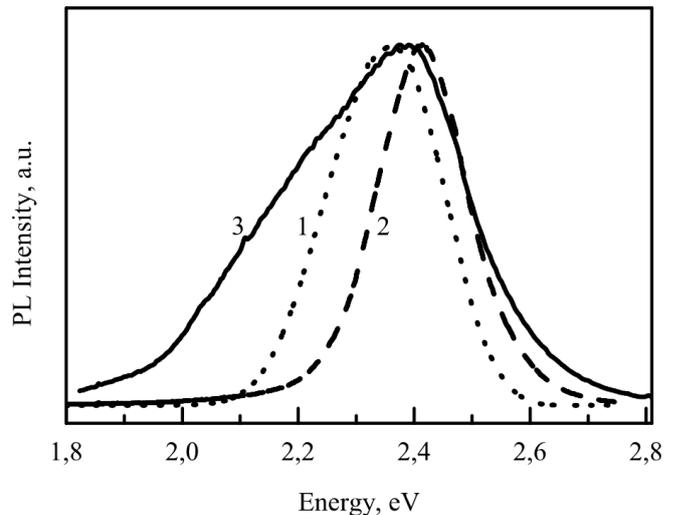


Fig. 1. Normalized PL spectra of CdTe QDs synthesized in a colloid solution (1), after transferring CdTe QDs from the colloid solution into a PDDA polymer matrix (2), and after holding the PDDA specimen with CdTe QDs for 2.5 years at room temperature (3). The spectra were measured at  $T = 300$  K

the maximum position of the first absorption band into account [16] amounts to 3.8 nm for the colloid solution and to 3.7 nm for the PDDA one).

It is worth to note that the long holding of PDDA specimens with incorporated CdTe QDs gave rise, first, to an about twofold reduction of the integral PL intensity and, second, to a QD enlargement which manifested itself in a shift of the PL band toward the low-energy range with a considerable “stretching” of its low-energy side. The changes observed can originate from the polymer dehydration and the absorption of atmospheric gases, which results in a compensation of positively charged molecules of PDDA polymer, a corresponding reduction of the intermolecular distance in the film and between QDs, and their possible coagulation. This process is very slow (in our case, it took two and a half year), but the increase of QD dimensions clearly manifests itself in the PL spectra. Another explanation of the described phenomenon can be the solid-state diffusion of CdTe QDs in the polymer, which results in their aggregation.

Let us analyze the shape of the PL band produced by CdTe QDs inserted into the polymer matrix and held for 2.5 years (Fig. 2). The pronounced bend in the low-energy wing of PL band points to the possibility to resolve this band (in the first approximation, by assuming that the QD dimension distribution is Gaussian-like) into two ones: band 1 at  $E_{\text{max}} = 2.17$  eV and band 2 at  $E_{\text{max}} = 2.41$  eV (Fig. 2). Hence, the long holding of QDs in the PDDA polymer brought about, in our case,

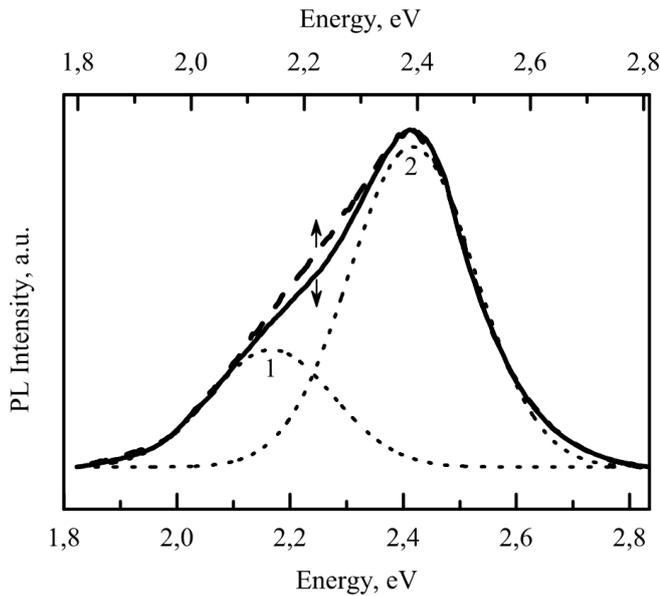


Fig. 2. Solid curve is the PL spectrum of CdTe QDs in PDDA at  $T = 7$  K. Curves 1 and 2 are PL bands determined by decomposing the major spectrum assuming the Gaussian-like distributions of QDs over their dimensions. Dashed curve is the PL spectrum of CdTe QDs in PDDA at  $T = 280$  K normalized by the intensity to the corresponding PL spectrum at  $T = 7$  K

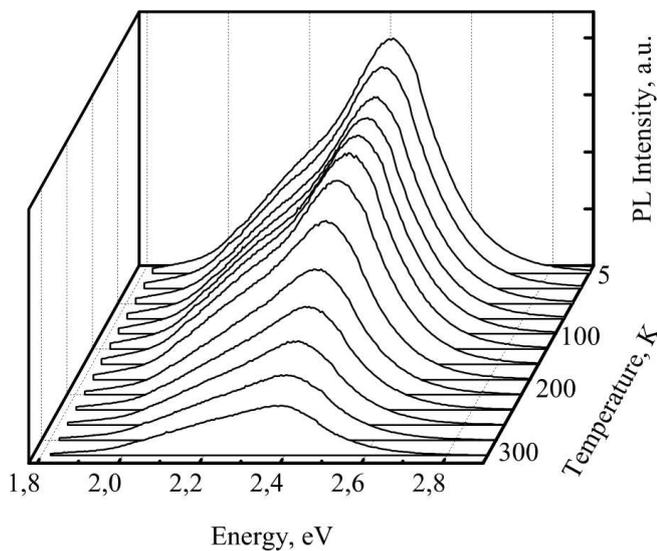


Fig. 3. PL spectra of CdTe QDs in PDDA at various temperatures in the interval  $T = 5 \div 300$  K

a bimodal distribution of CdTe QDs over their dimensions.

The shape of the PL band produced by CdTe QDs in PDDA, when the measurement temperature grew from 7 to 280 K, turned out, at first glance, a little unexpected

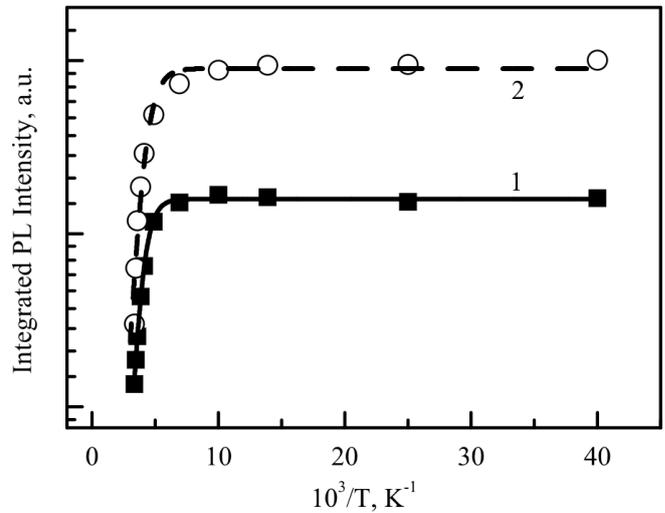


Fig. 4. Temperature dependences of the integral intensities of PL bands 1 ( $E_{\max} = 2.17$  eV) and 2 ( $E_{\max} = 2.41$  eV). Points correspond to the experimental results, curves depict the results of theoretical calculations

(Fig. 2, dashed curve). To make the matter more clear, the maximum of the PL band measured at  $T = 280$  K was normalized to the maximum of the PL band measured at  $T = 7$  K. One can see that the low-energy wing became smoother, and the bend observed at  $T = 7$  K practically did not manifest itself.

The detailed researches concerning the temperature dependence of the shape of the PL spectrum produced by CdTe QDs in the range 5–300 K showed that the bend becomes gradually “smoothed out” on its low-energy side at  $T > 100$  K (Fig. 3). The described behavior of the PL band shape became clear after studying the temperature dependences of the integral intensities of PL band 1 ( $E_{\max} = 2.17$  eV) and 2 ( $E_{\max} = 2.41$  eV).

In Fig. 4, the corresponding experimental dependences of the integral intensities of bands 1 and 2 on  $10^3/T$  are depicted and confronted with the dependences theoretically calculated by the formula

$$I = \frac{I_0}{1 + C \exp\left(-\frac{E_a}{k_B T}\right)},$$

where  $E_a$ , the activation energy of temperature quenching of the PL integral intensity, is a fitting parameter. The calculated values of  $E_a$  are 150 meV for the first band ( $E_{\max} = 2.17$  eV) and 128 meV for the second one ( $E_{\max} = 2.41$  eV). Hence, the activation energy is lower for the second (located at higher energies) band. That is why the second band is quenched much more than the first one, when the measurement temperature grows

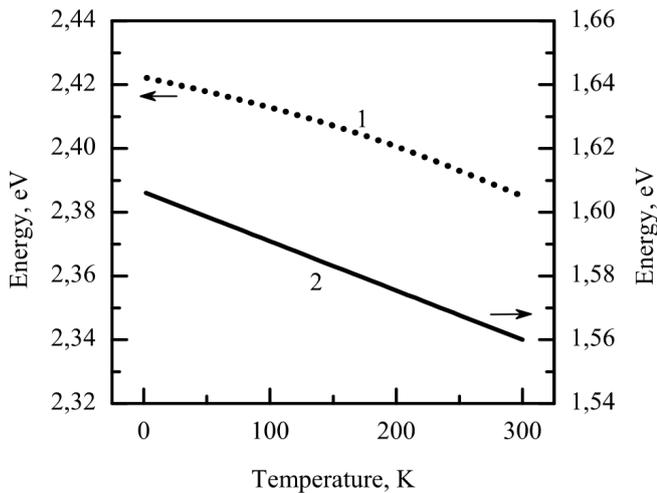


Fig. 5. Temperature dependences of the energy positions of the PL maximum of CdTe QDs incorporated into the PDDA polymer matrix (1) and the energy gap width in a bulk CdTe (2)

from 7 to 280 K. In so doing, the intensity ratio  $I_1/I_2$  changes in favor of  $I_1$ , as the temperature grows, which, in its turn, “smoothes out” the bend in the low-energy wing of the PL band produced by CdTe QDs in PDDA. Concerning the lower activation energy of the temperature quenching of the second PL band (located at higher energies, which corresponds to smaller average dimensions of QDs) in comparison with that for the first band, it is evident that such a character of the temperature PL quenching is governed by peculiarities in the behavior of charge carriers in quantum-dimensional structures. The thermal emission of charge carriers into the barrier or onto the defect states at the quantum structure surface is known to be the major mechanism of temperature PL quenching in quantum-dimensional structures. Earlier, we demonstrated that the imperfection degree of CdTe QDs grows at a reduction of their size. Therefore, the integral PL intensity decreases faster for the second band, which corresponds to smaller QD dimensions – maybe, owing to a larger imperfection of the QD surface and as a result of the corresponding charge carrier caption at surface traps [17].

To elucidate the mechanism of radiation recombination in CdTe QDs that were incorporated in the PDDA polymeric matrix, we analyzed the temperature dependence of the energy position of the PL maximum (Fig. 5). The same figure exhibits the temperature dependence of the energy gap width in bulk CdTe. According to Fig. 5, the PL maximum shift ( $E_{\max}$ ) toward the low-energy region, as the temperature increases from 5 to 300 K, is about 40 meV, with the dependence

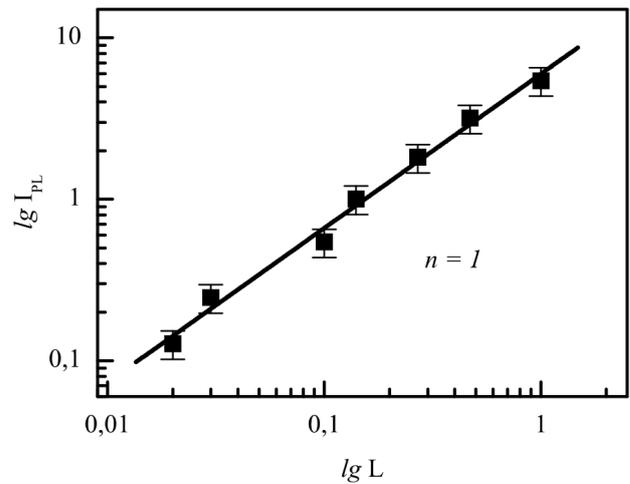


Fig. 6. Dependence of the PL intensity of CdTe QDs in PDDA on the optical pumping intensity on the log-log scale

$E_{\max}(T)$  as a whole completely reproducing the temperature modification of the energy gap width  $E_g(T)$ . Such a character of the dependence  $E_{\max}(T)$  testifies to the exciton mechanism of PL in CdTe QDs under consideration. Note that a similar correlation between  $E_g(T)$  and  $E_{\max}(T)$  in CdSe/ZnS nanocrystals allowed the authors of work [18] to interpret the observed PL line by the exciton mechanism of radiation recombination.

In our case, an additional support in favor of the exciton mechanism of PL in CdTe QDs in PDDA is a linear dependence of the PL intensity logarithm on the optical excitation intensity logarithm (Fig. 6). Such a dependence is characteristic of PL produced by coupled excitons, including excitons localized in quantum-dimensional structures.

#### 4. Conclusions

Techniques for the synthesis of CdTe quantum dots in an aqueous colloid solution and their transfer into a PDDA polymer matrix have been developed. A bimodal distribution over the dimensions of CdTe QDs in PDDA after their long storage (for 2.5 years) at room temperature was established; this distribution manifests itself in the PL spectra in the form of two bands (at 2.17 and 2.41 eV). The activation energies  $E_a = 150$  and 128 meV of temperature quenching of two PL bands produced by CdTe QDs in a PDDA polymer matrix are determined. The exciton mechanism of photoluminescence produced by CdTe QDs incorporated into a PDDA polymer matrix is established.

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#### ТЕМПЕРАТУРНА ЗАЛЕЖНІСТЬ ФОТОЛЮМІНЕСЦЕНЦІЇ КВАНТОВИХ ТОЧОК CdTe У ПОЛІМЕРНІЙ МАТРИЦІ

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#### Резюме

Досліджено температурні залежності спектрів фотолюмінесценції (ФЛ) квантових точок (КТ) CdTe у полімерній матриці, виготовлених шляхом перенесення їх з водного колоїдного розчину. Встановлено бімодальний розподіл за розмірами КТ CdTe у полімерній матриці в результаті їх тривалої витримки. Визначено енергії активації температурного гасіння смуг фотолюмінесценції КТ CdTe, інкорпорованих у полімерну матрицю, що відповідають смугам ФЛ квантових точок різних розмірів. Встановлено екситонний механізм фотолюмінесценції досліджуваних зразків, який підтверджується температурною залежністю положення максимуму ФЛ та залежністю інтегральної інтенсивності ФЛ від інтенсивності оптичного збудження.