EFFECT OF ANNEALING ON THE LUMINESCENT CHARACTERISTICS OF CdSe QUANTUM DOTS IN A POLYMER

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We study the influence of the low-temperature annealing in a range of 350-480 K in air on the luminescent properties of CdSe quantum dots embedded in a gelatine or polyvinyl alcohol matrix. The photoluminescence (PL) spectra of films of both types are the same and consist of two bands originating from the recombination of carriers through the surface defect states. It is found that the thermal annealing at 350-480 K during 10 min results in both the enhancement of the PL intensity and a shift of the PL bands to the low-energy spectral region. At a long annealing time (more than 1 h), a decrease of the PL intensity is observed. All the effects relax during the storage (ageing) of samples at room temperature in air and appear after the repeated annealing. A shift of the PL bands to the low-energy region is explained by an increase of the density of surface defects which act as the centers of radiative recombination and tentatively arise due to the break of the bonds of cadmium surface atoms with functional groups of gelatine molecules. The enhancement of the PL intensity is supposed to result from an increase of the potential barrier height for the carrier transition from quantum dots to the centers of nonradiative recombination. Another possible reason of the PL enhancement can be a decrease in the nonradiative defect density. The mechanism of a reduction of the PL intensity at a long annealing time is not yet clear.

1. Introduction

The investigation and application of semiconductor quantum dots (QDs) produced by chemical methods are the important tasks of modern nanophysics and nanoelectronics. High-quality QDs 1–6 nm in diameter and a 5-% dispersion in size can be conveniently synthesized using "wet" colloidal chemistry techniques which are characterized by relative simplicity and low prime cost [1]. Such QDs based on II–VI compounds exhibit the size-dependent tunable photoluminescence (PL) with a

narrow emission bandwidth of 30-45 nm that spans over the visible spectrum [2,3]. This, as well as the opportunity to embed QDs in different polymeric matrices, opens wide prospects of their numerous applications. The embedding of QDs in polymeric matrices not only improves the passivation of surface defects and increases the QD excitonic emission in such a way, but also allows one to create hybrid materials with new properties. It is expected that a combination of a polymer and QDs used in the technology of light-emitting diodes and solar cells will give a possibility to create devices with good optical and electrical properties [4]. In particular, it is reported that the embedding of QDs in a conductive polymer can improve its transport properties [5–7] and increase the efficiency of solar cells and light-emitting diodes based on polymers [8,9].

On the other hand, the simultaneous embedding of QDs of different sizes in a transparent polymer gives a possibility to create structures which can emit light in a wide spectral range due to the dependence of the emission energy on the QD size. Such composites can be the basis for the production of white light-emitting devices. In particular, it is possible, for this purpose, to use a combination of a QD-polymer composite emitting light in the green and red spectral regions with a blue light-emitting diode as an excitation source [10]. The structures composed of QDs of a particular size embedded in a transparent polymer can also be used as flexible colored optical filters [10].

One of the important characteristics of composite materials is the dependence of their properties on the temperature and, in particular, their thermal stability. However, this subject is studied insufficiently. In fact, the

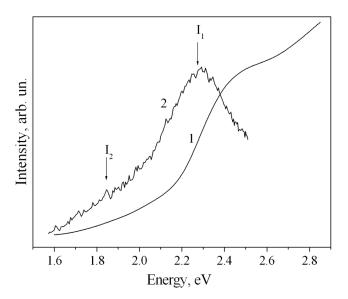


Fig. 1. Normalized absorption (curve 1) and PL (curve 2) spectra of CdSe QDs in the PVA matrix, $T{=}300~{\rm K}$

investigations of the temperature dependence of luminescent properties of QDs in solid matrices are scarce and have been carried out mainly at below-room temperatures (see, e.g., [11,12]). A decrease of the PL intensity of QDs observed as the temperature increased was explained by its thermal quenching due to the presence of surface centers of nonradiative recombination. Above room temperature, the characteristics of QDs were mainly studied in colloidal solutions [13–15].

Here, we present the results of our investigations of the influence of annealing at 350–480 K on the luminescent properties of structures composed of CdSe QDs embedded in polymer films of gelatine or polyvinyl alcohol (PVA). These polymers are optically transparent and have remarkable photochemical and mechanical stability. In the systems under study, they stabilize initial colloid solutions of cadmium selenide and serve as hosting polymer matrices for CdSe QDs. These features, as well as a low cost, "green" synthesis procedure, and "friendliness" of the above-mentioned polymers toward the environment and biological objects, stimulate their investigation as the basis for novel nanostructured materials.

2. Samples under Study and Experimental Methods

The studied structures were the films containing CdSe QDs in gelatine or in PVA deposited on a glass.

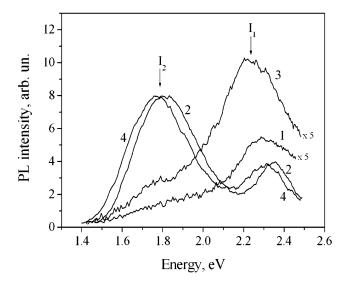
Reagents purchased from Aldrich were used without additional purification. For CdSe nanocrystal synthesis, a water solution containing gelatine of 3 mass %, CdSO₄of 0.05 M, Na₂SeSO₃ of 0.05 M, and Na₂SO₃ of 0.15 M was cooled down up to the gelation. The gel was stored at 279 K during 24 h until nanocrystals were formed. Aged gel was reduced to fragments and washed out in a large (0.5–1 l) volume of distilled water to remove salts which did not reacted or were formed during the synthesis. Dialysis was performed during 48 h at 279 K, water being changed periodically. The concentration of CdSe formed was estimated to be 1.33×10^{-2} M using the procedure described in [16]. A detailed description of the procedure of sodium selenosulfate solution preparation, as well as the synthesis of colloidal CdSe nanocrystals in gelatine solutions, can be found elsewhere [16, 17].

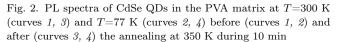
To produce polymer films on glass, the purified gel was transformed into a solution by heating up to 310 K and by mixing with a PVA solution of 20 mass.% or a gelatine solution of 10 mass.%. A thin film of the mixture obtained was deposited onto a glass substrate (4 mL per a 2×8 cm² fragment of a microscope slide) cleaned before in a mixture of concentrated sulfuric acid and hydrogen peroxide and dried in a black-out drying box at 293 K and a natural ventilation. A thickness of polymeric films on glass was measured to be 0.18–0.20 mm to within ±0.01 mm. The samples studied were annealed during 10-205 min at 350-480 K in a temperature-stabilized furnace in air. Before annealing, the films were separated from glass.

PL was excited with a halogen lamp light passed through a grating monochromator. The wavelength of light used for the excitation of PL spectra was 460 nm. The PL and PL excitation (PLE) spectra were recorded using a prism monochromator equipped with a photomultiplier and an amplifier with a synchronous detector. The PL and PLE spectra were measured both at 300 K and 77 K.

3. Experimental Results

In Fig. 1, the absorption (curve 1) and PL (curve 2) spectra of a sample with CdSe QDs in a PVA matrix measured at room temperature before annealing are presented. In the absorption spectrum, a maximum at 2.49 eV is observed. This maximum is shifted significantly to higher energies as compared to the absorption edge of bulk CdSe, whose band gap is equal to 1.74 eV at 300 K [18]. This indicates the formation of CdSe particles with a pronounced quantum size effect – CdSe QDs. From





the position of the absorption maximum, the average diameter of QDs was estimated to be 2.6 nm, by using the procedure developed in [19]. The formation of CdSe QDs was confirmed earlier [20] by the resonance Raman scattering spectroscopy. The Raman spectra revealed a peak caused by longitudinal optical phonon (LO) at 206.6 cm⁻¹, as well as by its overtone (2 LO) at 411 cm⁻¹. The LO phonon peak position was shifted to the low-frequency region compared to the position of a bulk CdSe peak at 210 cm⁻¹ [21]. The fact originates from the spatial phonon confinement in QDs and testifies to the presence of nanocrystals with diameters smaller than 10 nm.

The PL spectrum at 300 K contains an emission band I_1 near the absorption edge of QDs and a weak wide band I_2 in the region of 1.6–2.0 eV shifted significantly to lower energies from both the I_1 band and the absorption edge of QDs. The I_2 band is usually attributed to the radiative recombination of carriers via deep levels of surface defects [22]. It should be noted that the type of a matrix (gelatine or PVA) does not influence essentially the shape of both absorption and PL spectra. At the same time, the I_1 band spectral position varies in the range 2.28–2.31 eV for different samples irrespective of the matrix type.

The value of Stokes shift ΔS of the I_1 peak position from the absorption maximum was found to be rather large amounting to 200 meV for all the samples studied. Typical ΔS values are within 100 meV, but very large

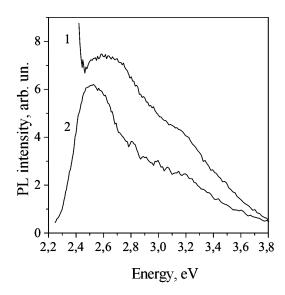


Fig. 3. PLE spectra of the I_1 (curve 1) and I_2 bands (curve 2) of CdSe QDs in a PVA matrix, $T{=}77~{\rm K}$

shifts (up to 300 meV) were also observed in some cases [23,24]. The origin of the Stokes shift in CdSe QDs is explained mainly by the "dark excitons" model [25,26]. However, the model involving the recombination through surface traps was also extensively used, especially to explain large ΔS values [27,28]. We believe that this model can be applied to the samples under study.

As the temperature is decreased down to 77 K, the I_1 band position shifts toward higher energies according to the CdSe band gap change. At the same time, the integrated PL intensity increases (Fig. 2, curves 1, 2) with the major contribution from the I_2 band peaked at 1.8–1.82 eV in different samples (Fig. 2, curve 2).

Figure 3 shows the excitation spectra of I_1 and I_2 bands (curve 1 and 2, respectively). These spectra are detected in the PL band maximum at T=77 K in a sample with the PL spectrum shown in Fig. 1. The PLE spectra presented in Fig. 3 are similar and contain a distinct maximum. As the detection energy is decreased within the I_1 band, the spectral position of this PLE maximum shifts to the low-energy region. However, as the detection energy is decreased within the I_2 band, the spectral position of the PLE maximum remains unchanged. As the temperature is increased from 77 to 300 K, the spectral position of the PLE maximum shifts to the low-energy region in accordance with the CdSe band gap change, approaching the QD absorption maximum at T=300 K. The facts indicate that both the I_1 and I_2 bands are excited by means of the light absorption in QDs. This implies that these bands are caused by

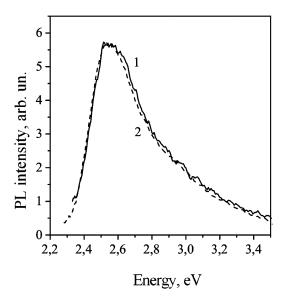


Fig. 4. PLE spectra of the I_2 band measured before (solid curve 1) and after the annealing at 350 K during 10 min (dashed curve 2) of the sample in a PVA matrix, T=77 K

the radiative recombination of carriers through defects located either in the bulk or on the surface of CdSe QDs.

Under the annealing at 350–480 K, the intensity of I_1 and I_2 bands measured at 300 K in the samples of both types increases (Fig. 2, curve 3). At the same time, the intensity of PL bands measured at 77 K does not change appreciably (Fig. 2, curve 4). The annealing at temperatures mentioned above results also in a shift of I_1 and I_2 bands to the low-energy region. The shift is observed at 300 and 77 K (Fig. 2, curves 1-4) and has the same value for both PL bands.

It should be noted that the position of the PLE maximum does not change under the annealing. More clearly, this can be observed for the I_2 band excitation spectrum which does not overlap with the PL spectrum. The PLE spectra of this band measured at 77 K before and after the annealing at 350 K are shown in Fig. 4.

The dependences of the I_1 band intensity and the spectral position on the annealing temperature and the annealing duration are presented in Fig. 5, a and Fig. 5, b, respectively. The experimental data shown in Fig. 5, a were obtained under the annealing of different pieces of the same film during 10 min at every temperature. The dependences presented in Fig. 5, b were obtained under the annealing of the same piece of the film at 350 K. As the annealing temperature rises from 350 to 480 K, the intensity of the PL band increases, and the spectral position of its maximum shifts to the low-energy region (Fig. 5,a). At the same time, the dependence of the

PL intensity on the annealing duration is nonmonotonic (Fig. 5,b). As the annealing time increases from 10 to 205 min, the PL intensity grows at first and then falls, but the PL peak position keeps shifting to lower energies.

An important feature of the effects revealed is their reversibility. It is found that, a week storage of annealed samples at room temperature results in the recovery of both the initial PL band intensity and the peak position, the latter being faster. After the repeated annealing, the described changes of the PL spectra appear again.

4. Discussion

The presented data demonstrate that the annealing of polymeric films containing CdSe QDs at 350–480 K during 10 min gives rise to two effects: (i) enhancement of the PL intensity and (ii) spectral shift of the PL band position to lower energies.

The enhancement of the PL intensity is observed when PL is measured at 300 K and becomes insignificant at 77 K. Figure 2 shows that the thermal quenching of the PL intensity occurs, as the temperature is elevated from 77 K to room temperature. Thus, the enhancement of the PL intensity stimulated by the annealing is observed at temperatures from the thermal quenching range and is absent at low temperatures, when the effect of the PL intensity thermal quenching can be neglected. This means that the most probable reason for the PL intensity enhancement at the annealing is a reduction of the effect of thermal quenching. This effect is known to be caused by the thermally activated escape of photogenerated carriers from QDs over a potential barrier and their further nonradiative recombination. Therefore, one of the reasons of a reduction of the thermal quenching effect can be an increase of the potential barrier height. A similar effect was found for CdSe/ZnS QDs under the irradiation by ultraviolet light [29] and was explained by an increase of the barrier height for the carrier escape from QDs as a result of the recharging of surface defects. Another reason can be a decrease of the density of nonradiative centers.

Since the recoveries of the PL intensity and the peak position upon the storage of samples in air occur with different rates, both effects can be associated with different processes.

We now discuss probable reasons for a spectral shift of the PL peak position due to the annealing. As Figs. 2, 4, and 5 show, the shift of I_1 and I_2 bands is not accompanied by the shift of the maximum in their PLE spectra. Invariability of the peak position in the PLE spectra indicates that the shift of the PL bands is not caused by a

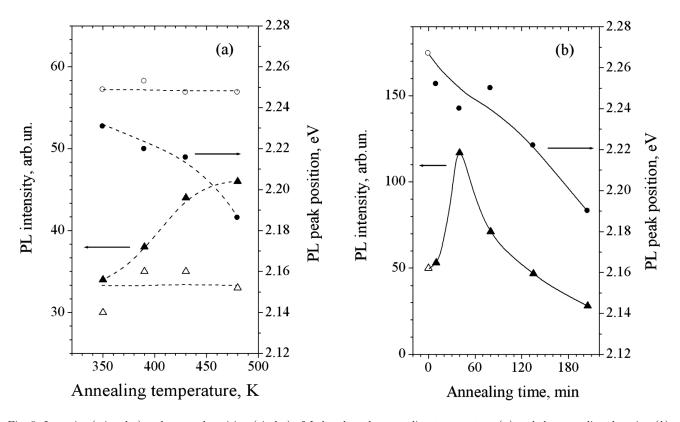


Fig. 5. Intensity (triangles) and spectral position (circles) of I_1 band vs the annealing temperature (a) and the annealing duration (b). The annealing duration is 10 min (a) and annealing temperature is 350 K (b). Intensity and spectral position of I_1 band in as-prepared samples are shown by open triangles and open circles, respectively. T=300 K, the sample in a PVA matrix

change of the QD energy level position. This means that, after the annealing, the Stokes shift increases. Therefore, it could be deduced that a shift of the I_1 peak position to lower energies can be accounted for by the appearance of an additional recombination channel associated with shallow defect levels. Simultaneous and equal shifts of the I_1 and I_2 band positions can be explained by the participation of these levels in the recombination processes responsible for both PL bands.

As was mentioned above, the effects examined here were found to be nearly the same in the cases of both polymer matrices studied. Most likely, this is caused by the presence of a small amount of gelatine used as a stabilizer during the synthesis of initial colloidal CdSe QDs in the PVA matrix. Therefore, it can be supposed that the effects observed are associated with the presence of gelatine on the surface of QDs.

The defects produced by the annealing can be Cd atoms. In fact, it is known that there are many uncoordinated cadmium atoms in the surface layer of CdSe QDs. These surface atoms act as defect states, if they are not passivated by organic ligands or by wider-band-

gap semiconductor materials. It is known that organic ligands, as a rule, are not capable to passivate simultaneously cationic and anionic defects. Specifically, gelatine can passivate surface Cd atoms with amino groups and carboxyls, as well as with peptide -NH-CO- fragments of the polymer chains. Thermal annealing can cause a dissociation of these relatively unstable coordination bonds, by increasing a contribution of Cd surface atoms to recombination processes. Therefore, the defects which arise under annealing and cause the appearance of an additional recombination channel can be Cd atoms. The recovery of a PL maximum position after the sample storage at room temperature during one week can be explained by the recovery of the bonds of Cd surface atoms with functional groups of the polymer that results in the re-passivation of defects.

As was mentioned above, somewhat different effect occurs if the annealing lasts more than 1 h. The effect consists in the reversible degradation of the PL intensity and is observed even at the lowest annealing temperature of 350 K. This effect was not found when the dependence of the PL intensity on the annealing temperature was

studied due to, apparently, a short duration of the annealing used in that experiment. The effect of the PL intensity degradation is also observed for both types of matrices and is obviously associated with the presence of gelatine. It is possible that it can be caused by a decrease of the passivation of nonradiative recombination centers. But the nature of these centers and the passivation mechanism are not clear now.

5. Conclusions

The effect of the annealing on the luminescence of CdSe QDs embedded in polymer matrices of two types - gelatine and polyvinyl alcohol with an admixture of gelatine has been reported. The luminescence spectra of both types of the films are similar and consist of two bands. One of them is located near the edge of the QD absorption band and is caused, probably, by the recombination of carriers through shallow defect states, while the other one is due to the recombination of carriers through deep levels of surface defects.

It is revealed that the thermal annealing of the films of both types at 350–480 K during 10 min in air results in two effects: the enhancement of the PL intensity and the shift of the PL band maxima to the low-energy spectral region. At a long annealing time (more than 1 h), a decrease of the PL intensity is observed. All these effects relax during the storage of samples at room temperature in air and appear after the repeated annealing.

From the comparison of the PL and PLE spectra, it is concluded that the reason for the spectral shift of both PL bands is an increase of the density of surface defects contributing to the radiative recombination. It is supposed that these levels are related to surface atoms of cadmium and are formed owing to the break of the bonds of these atoms with functional groups of gelatine. The PL intensity enhancement can be caused by an increase of the potential barrier height for the escape of carriers from QDs and their transition to the centers of nonradiative recombination or by a decrease of the density of these centers. The reduction of the PL intensity observed at a long time of the annealing is supposed to be due to a decrease of the passivation of centers of nonradiative recombination, but the nature of these centers and the nature of a passivator are not clear now.

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ВПЛИВ ВІДПАЛІВ НА ЛЮМІНЕСЦЕНТНІ ХАРАКТЕРИСТИКИ КВАНТОВИХ ТОЧОК CdSe В ПОЛІМЕРІ

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Резюме

Досліджено вплив низькотемпературних відпалів в інтервалі 350-480 К на повітрі на люмінесцентні характеристики квантових точок CdSe, вміщених в матрицю з желатину або полівінілового спирту. Показано, що спектри фотолюмінесценції (ФЛ) обох типів плівок подібні і складаються з двох смуг, пов'язаних з рекомбінацією носіїв через рівні поверхневих дефектів. Виявлено, що термічний відпал протягом 10 хвилин в інтервалі 350-480 К приводить до зростання інтенсивності люмінесценції та зсуву максимумів смуг ФЛ в низькоенергетичний бік спектра. При довготривалому (більше 1 години) відпалі спостерігається зменшення інтенсивності ФЛ. Всі ефекти релаксують з часом при витримуванні зразків за кімнатної температури на повітрі і відновлюються після повторного відпалу. Запропоновано, що причиною низькоенергетичного зсуву максимумів смуг ФЛ є збільшення густини поверхневих дефектів, які діють як центри випромінювальної рекомбінації і утворюються внаслідок розриву зв'язків поверхневих атомів кадмію з функціональними групами молекул желатину. В той же час причиною зростання інтенсивності ФЛ може бути збільшення висоти потенціального бар'єра для звільнення носіїв з рівнів квантових точок та переходу їх на центри безвипромінювальної рекомбінації. Іншою причиною зростання інтенсивності ФЛ може бути зменшення концентрації центрів безвипромінювальної рекомбінації. Причина зменшення інтенсивності $\Phi \Pi$ при довготривалому відпалі поки що не з'ясована.