PHOTOLUMINESCENCE OF CdSe NANOPARTICLES IN ELECTRIC FIELD

YU.YU. BACHERIKOV, M.O. DAVYDENKO[1], S.V. OPTASYUK, I.M. DMITRUK[1]

V.E. Lashkarev Institute of Semiconductor Physics, Nat. Acad. Sci. of Ukraine
(41, Nauky Prosp., Kyiv 03680, Ukraine; e-mail: yuyu@isp.kiev.ua),

[1]**Taras Shevchenko Kyiv National University, Faculty of Physics**
(2, Academician Glushkov Ave., Kyiv 03680, Ukraine; e-mail: davydenko@univ.kiev.ua)

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We investigate the influence of an electric field on photoluminescence (PL) spectra of CdSe nanoparticles of 1.6 and 2.8 nm in size. The electric field was varied in the range 0–4×10^6 V/m. In PL spectra, bands corresponding to the exciton, defect, impurity, or surface transitions are observed. Under the action of the electric field, the intensity of the exciton PL bands of CdSe nanoparticles of various sizes decreases. In the electric field lower than 1.8×10^6 V/m, there occur a decrease of the intensity of the exciton band for nanoparticles 2.8 nm in size and the intensification of the defect-impurity one, which can be explained by the transfer of charge carriers between various radiation centers. In the electric field higher than 1.8×10^6 V/m, one observes an abrupt decrease of the intensity of luminescence, which probably represents a result of the extraction of carriers beyond the limits of the region of radiative recombination under the action of the electric field.

1. Introduction

Large progress in the field of low-dimension structures opens possibilities for both the miniaturization and development of devices with basically new functional possibilities for nanoelectronics, optoelectronics, communication facilities, new information technologies, measuring technique, etc. [1, 2]. The application of nanotechnologies is believed to solve the main problems of current semiconductor electronics, among them the increase of the effectiveness of computation systems, rise of information capacity, quality of information display systems with simultaneous decrease of power consumption, enhancement of sensor devices, etc. The further development of the technologies of information reading and recording stimulates a great interest in the investigation of the uncontrolled turning on and off of radiative transitions in semiconductor nanoparticles [3], especially from the standpoint of recent papers [2, 4, 5] concerning the development of single-electron transistors.

In order to create new-generation devices, it's especially important to find the ways to control the transitions of carriers both from one center to another and to centers located on the surface. That's why it's necessary to develop the possibilities allowing one to control the processes with participation of charge carriers by means of various external influences such as the optical or other excitation and, first of all, the excitation by an electric field. The problem of the controlled transfer of carriers between several competitive transitions represents one of the most urgent problems in optoelectronics, because the redistribution of charge carriers between states will allow one to enhance the potentialities of the devices created on the base of these elements or to structurally simplify them.

2. Experimental Technique

CdSe nanocrystals were grown using the chemical method in a two-phase water/toluene system [6, 7]. As the sources of Se^{2-} and Cd^{2+} ions, we used, respectively, sodium selenosulfate Na_2SeSO_3 and a water solution of cadmium nitrilotriacetate. The reaction ran in the presence of a complexing component, methanol, and a surfactant. The formation of nanoparticles in the water phase was followed by their transition to toluene. After the completion of synthesis, the colloid solution was dried under pumping-out for the purpose of obtaining a powder of nanoparticles. In the process of synthesis, the average size of nanoparticles in the ensemble was roughly determined by the colour of the solution. A more exact control of the size and dispersion (Δd/d) of nanoparticles was performed by the absorption spectra [7]. In the present paper, we investigate CdSe nanoparticles of red (sample 1) and yellow (sample 2) colors.

The transmission and PL spectra were obtained with a KSVU-23 setup ($T = 300$ K). Absorption spectra were obtained from the ratio of the transmission spectra of the colloid solution of CdSe nanoparticles and pure toluene.

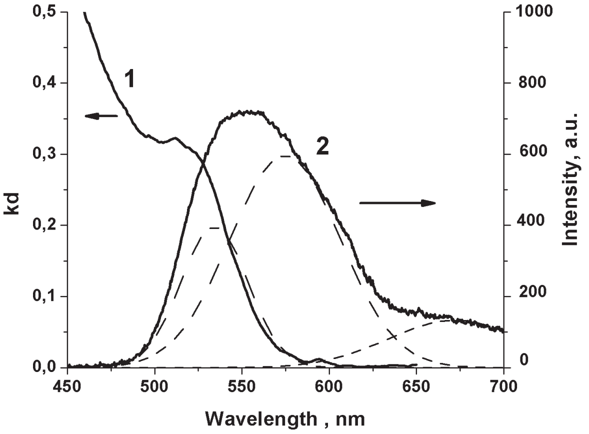

Fig. 1. Spectra of optical absorption (*1*) and photoluminescence (*2*) of sample 1. Dotted line – individual bands obtained by the decomposition of the PL spectrum into components

The excitation of PL was performed with the help of the radiation of an LGI-21 nitrogen laser ($\lambda_{\text{exc}} = 337.1$ nm).

Luminescent investigations in the case of the simultaneous action of the electric field and the optical excitation were performed for samples produced in the form of an optically transparent capacitor (OTC) [8]. The active layer of OTC consisted of a mixture of CdSe nanoparticles and a dielectric binder ($\varepsilon = 4$, $\eta = 0.985$ Pa·s) in the volume ratio 1:7. The thickness of the OTC active layer (D) ~100 μm. The amplitude of the sinusoidal electric field (a frequency of 50 Hz) was varied in the range 0–550 V.

The electric field in a particle E_1 was estimated by the formula [9]

$$E_1 = \frac{U}{D}\frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2 - C(\varepsilon_2 - \varepsilon_1)}, \tag{1}$$

where U is the voltage applied to OTC; D is the thickness of the suspension layer; ε_1 and ε_2 represent relative permittivities of the dielectric binder and CdSe nanoparticles; C is the volume concentration of the luminophor in the dielectric (the part of volume occupied by nanoparticles). The electric field in a nanoparticle amounted to $0 - 4\times10^6$ V/m ($U = 0 \div 550$ V, $D = 100$ μm, $\varepsilon_1 = 4$, $\varepsilon_2 = 9.4$, $C = 0.125$).

We note that the lifetime of an electron in a conduction band amounts to 10^{-12}–10^{-10} s, the lifetime at an impurity level is equal to 10^{-9}–10^{-8} s [10,11], and, according to our estimates for the investigated sizes, an electron passes the distance from the center of a nanoparticle to its surface during ~10^{-14} s. Therefore, we consider the electric field (a frequency of 50 Hz) in the course of analysis of the processes running in the material to be constant.

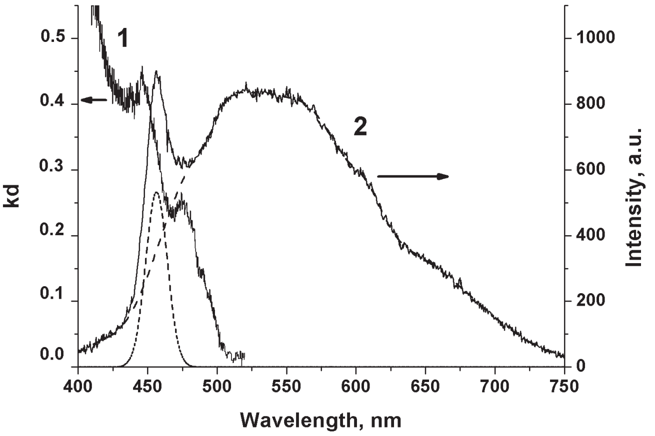

Fig. 2. Spectra of optical absorption (*1*) and photoluminescence (*2*) of sample 2. Dotted line – the individual band and the summary resultant of individual bands in the region of the PL spectrum 475 – 750 nm obtained by the decomposition into components

3. Experimental Results and Discussion

Absorption spectra of colloid solutions of CdSe nanoparticles in toluene are presented in Figs. 1 and 2 (curves *1*). As seen, there exists one peak with the maximum at 523 nm in the spectrum of sample 1 (Fig. 1, curve *1*). The given peak corresponds to the transition between the dimensionally quantized energy levels of the valence and conduction bands. As a rule, this transition is called the exciton one [12], as the electron-hole pair formed after the absorption of a quantum of light is similar to a Wannier–Mott exciton in a bulk crystal by the spatial distribution of charge carriers. As is well known, the bandgap (the distance between the levels of an electron and a hole) changes depending on the size of a nanoparticle due to the quantum size effect [13]. Thus, the position of the absorption maximum allows one to determine the average size of nanoparticles in the ensemble d, while the halfwidth determines the dispersion $\Delta d/d$ [7, 14]. In the present paper, we use the empirical dependence of the wavelength of the absorption maximum on the size of nanoparticles [7], which allowed us to estimate $d = 2.8$ nm and $\Delta d/d = 20\%$. In the absorption spectrum of the colloid solution of sample 2 (Fig. 2, curve *1*), one can see two absorption bands with the maxima at 449 and 479 nm, which testifies to the presence of two types of CdSe nanoparticles with average sizes 1.6 and 2.0 nm, respectively, in the given solution.

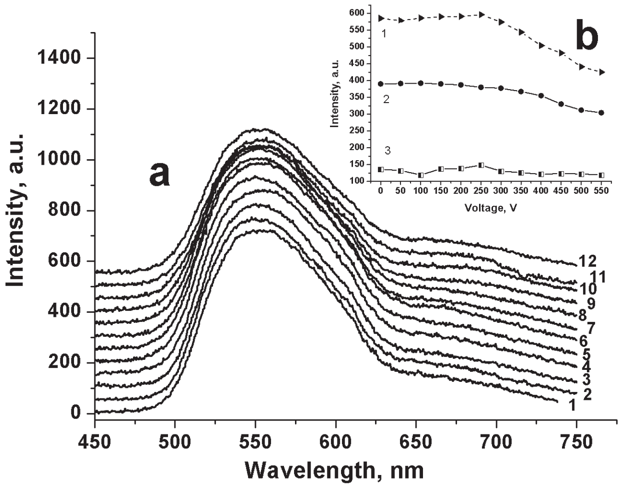

Fig. 3. PL spectra of OTC (sample 1) for various voltages applied to OTC (*a*) (*1* – 0, *2* – 50, *3* – 100, *4* – 150, *5* – 200, *6* – 250, *7* – 300, *8* – 350, *9* – 400, *10* – 450, *11* – 500, *12* – 550 V). Spectra *1–12* are distributed vertically for better visualization. Dependences of the intensities of PL bands at various voltages applied to OTC (*b*) (*1* – $\lambda_{\max} = 570$ nm, *2* – $\lambda_{\max} = 534$ nm, *3* – $\lambda_{\max} = 665$ nm)

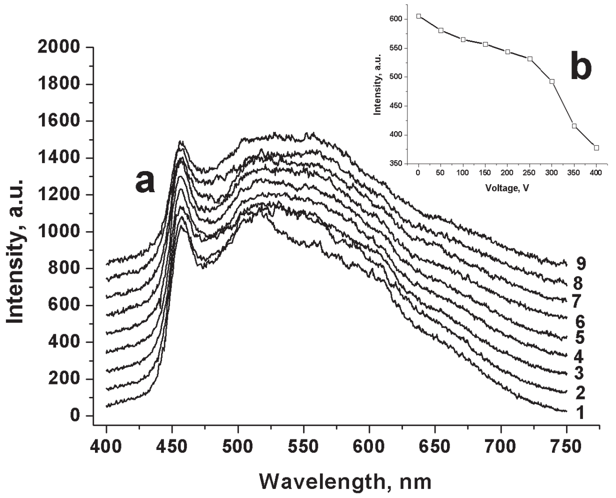

Fig. 4. PL spectra of OTC (sample 2) for various voltages applied to OTC (*a*) (*1* – 0, *2* – 50, *3* – 100, *4* – 150, *5* – 200, *6* – 250, *7* – 300, *8* – 350, *9* – 400 B). Spectra *1–9* are distributed vertically for better visualization. Dependence of the intensity of the PL band with the maximum at 457 nm at various voltages applied to OTC (*b*)

The PL spectrum of OTC produced from sample 1 has a form of a wide asymmetric band with the maximum close to 550 nm (Fig. 1, curve *2*). In the spectrum, one observes a bend in the region of 640 nm and a shoulder with the maximum at 665 nm, which indicates its nonelementary character. In this connection, in the course of analysis, we used a procedure of decomposition of the given spectrum into individual bands proposed by Fock [15, 16]. The fact underlying the Alentsev–Fock method [15] is that, in the case of variation of excitation conditions, a luminescence spectrum is deformed due to the change of the relative intensity of bands corresponding to different luminescence centers. Using several different luminescence spectra measured under different conditions, one can extract each individual band by means of calculations. In the present paper, PL spectra were obtained for different values of the electric field applied to OTC (PL spectra of sample 1 are given in Fig. 3,*a*, those of sample 2 – in Fig. 4,*a*). According to the performed analysis, the PL spectrum of sample 1 represents a result of the superposition of three bands with $\lambda_{max} \sim 534$, 570, and 665 nm indicated by a dotted line in Fig. 1.

The PL spectrum of OTC produced from sample 2 is given in Fig. 2, curve *2*. As one can see from the figure, the spectrum has two maxima. The first one ($\lambda_{\max} \sim 457$ nm) corresponds to a narrow band with the halfwidth $\Delta\lambda = 8$ nm. As the halfwidth of the given peak is close to that of the corresponding absorption peak (Fig. 2, curve *1*), it can be considered as individual. The other one ($\lambda_{\max} \sim 540$ nm) corresponds to a wide band ($\Delta\lambda = 67$ nm) that probably represents the superposition of at least five bands. In the given case, the application of the Alentsev–Fock method doesn't allow us to unambiguously decompose the spectrum into individual bands, but it gives a possibility to extract the contribution of the band with $\lambda_{\max} \sim 457$ nm to the total contour.

According to the literature data [12, 14], the bands with $\lambda_{\max} \sim 534$ nm (sample 1) and $\lambda_{\max} \sim 457$ nm (sample 2, $d = 1.6$ nm) correspond to edge luminescence which is also called as the "band to band" or exciton transition. An exact interpretation of the long-wave PL bands of sample 1 ($\lambda_{\max} \sim 570$ nm and $\lambda_{\max} \sim 665$ nm) isn't presented in the literature, but a number of authors [17,18] predicts the defect or impurity nature of centers responsible for the radiation in the given region or the participation of states localized at the surface in the radiation process. The interpretation of the wide PL band of sample 2 with $\lambda_{\max} \sim 540$ nm is more complicated. According to the absorption spectrum (Fig. 2, curve *1*), the given sample contains particles with two different sizes, which allows one to assume two sets of exciton and impurity bands, whose strong overlapping results in the impossibility of both the unambiguous decomposition of the given spectral region and the analysis of individual bands. Thus, the wide band in the PL spectrum of sample 2 represents a result of the superposition of the exciton PL band of nanoparticles with the average size $d = 2.0$ nm as well as bands corresponding to transitions with the participation of defect, impurity, and surface states in nanoparticles of both sizes.

Figure 3,*b* presents the dependences of the intensities of PL bands with the maxima at 534, 570, and 665 nm (sample 1), whereas Fig. 4,*b* – those of the band with the maximum at 457 nm (sample 2) on the magnitude of the applied voltage in the range 0–550 V. The intensities of the PL bands were obtained by means of the decomposition of each individual PL spectrum into component bands. It's worth noting that, in spite of large electric field applied to the samples, we didn't observe the appearance of electroluminescence that could be registered.

As one can see from Fig. 3,*b* and Fig. 4,*b*, all the curves are well described with two linear regions: 0–250 and 250–550 V. In the range 0–250 V, the intensity of the bands with $\lambda_{\max} \sim 534$ and 457 nm corresponding to exciton transitions decreases, whereas the intensity of the defect bands with $\lambda_{\max} \sim 570$ and 665 nm rises. In Fig. 5, one can see the intensities of each band normalized to the corresponding value in the absence of the electric field (as the band with $\lambda_{\max} \sim 665$ nm (sample 1) has a much less intensity, its quantitative analysis isn't presented). The tangent of the slope angle for the PL band with $\lambda_{\max} \sim 534$ nm amounts to $(-9 \pm 4) \times 10^{-5}$ 1/V, while, for the band with $\lambda_{\max} \sim 570$ nm, the tangent in the given region is equal to $(10 \pm 3) \times 10^{-5}$ 1/V. Thus, the rate of attenuation of the band with $\lambda_{\max} \sim 534$ nm is close to the rate of intensification of the band with $\lambda_{\max} \sim 570$ nm in the corresponding region. Such a behavior of attenuation corresponds to the mechanism of external luminescence decay [19] conditioned by the transition of localized carriers between radiation centers, which results in a decrease of the radiation intensity at former centers and increase at latter ones. Thus, the attenuation of the exciton PL band and the intensification of the defect one are probably conditioned by transitions of carriers from the quantum well to the region of the recombination of defect, impurity, and surface transitions. Or, in other words, there occurs the transfer of carriers between states under the action of the electric field. The tangent of the slope angle of the exciton PL band with $\lambda_{\max} \sim 457$ nm (sample 2) amounts to $(-46 \pm 4) \times 10^{-5}$ 1/V which is lower than the corresponding value of the tangent of the slope angle $(-9 \pm 4) \times 10^{-5}$ 1/V of the exciton band with $\lambda_{\max} \sim 534$ nm (sample 1). This fact is caused by a less time of extraction of a carrier from the region of radiative recombination.

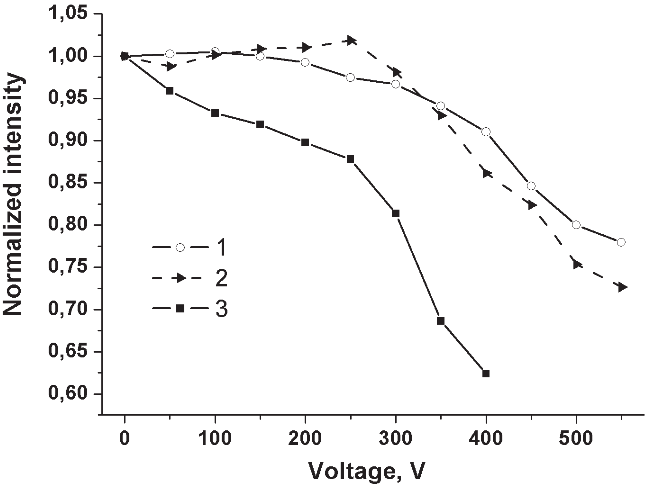

Fig. 5. Dependences of the intensities of PL bands (*1* – $\lambda_{\max} = 534$ nm, *2* – $\lambda_{\max} = 570$ nm, *3* – $\lambda_{\max} = 457$ nm) at various voltages applied to OTC normalized to the intensity of the corresponding band in the absence of the field

In the case where the applied voltage is higher than 250 V ($E = 1.8 \times 10^6$ V/m), one observes an abrupt decrease of the intensity of all the considered PL bands in samples 1 and 2, which probably represents a result of the extraction of carriers beyond the limits of the region of recombination under the action of the electric field.

Thus, the results presented in this paper testify to the redistribution of carriers between the recombination channels that correspond to the exciton and defect-surface PL bands under the action of electric fields that don't exceed 1.8×10^6 V/m. This fact is probably caused by the transfer of charge carriers from the quantum well to defect-surface states. In addition, the behavior of the dependence of the intensity of the exciton band on the magnitude of the electric field is also determined by the size of particles. The strength of the electric field higher than 1.8×10^6 V/m results in an abrupt decay of luminescence, which is probably caused by the extraction of carriers beyond the limits of the recombination region under the action of the field.

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ФОТОЛЮМІНЕСЦЕНЦІЯ НАНОЧАСТИНОК CdSe В ЕЛЕКТРИЧНОМУ ПОЛІ

Ю.Ю. Бачеріков, М.О. Давиденко, С.В. Оптасюк, І.М. Дмитрук

Резюме

В роботі досліджено вплив електричного поля на спектри фотолюмінесценції (ФЛ) наночастинок CdSe розміром 1,6 та 2,8 нм. Напруженість електричного поля змінювалась в межах 0–$4{\cdot}10^6$ В/м. В спектрах ФЛ спостерігали смуги, які відповідають екситонному переходу та дефектним, домішковим чи поверхневим переходам. Під впливом електричного поля спостерігається загасання екситонних смуг ФЛ наночастинок CdSe різного розміру. Для напруженостей електричного поля, що не перевищують $1,8 \cdot 10^6$ В/м, для наночастинок розміром 2,8 нм відбувається загасання екситонної смуги і розгоряння дефектно-домішкової, що може бути пояснено перекачуванням носіїв заряду з одних центрів випромінювання на інші. Для напруженостей більших за $1,8 \cdot 10^6$ В/м спостерігається різке зменшення інтенсивності люмінесценції, що ймовірно є наслідком виходу носіїв за межі області випромінювальної рекомбінації під дією електричного поля.