

## EFFECT OF STATIC ELECTRIC FIELD ON LUMINESCENCE SPECTRA OF QUANTUM-SIZE CdS, PbI<sub>2</sub> PARTICLES AND CdS MONOCRYSTALS

G.P. Yablonski<sup>1</sup>, Yu.P. Rakovich<sup>1</sup> and M.V. Artemyev<sup>2</sup>

<sup>1</sup> Inst. of Physics, Belarussian Acad. of Sciences, F. Skoryna Ave 68, Minsk 220072, Belarus

<sup>2</sup> Physico-Chemical Problems Research Institute of Belarussian State University,  
Leningradskaya Str. 14, Minsk 220080, Belarus

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The influence of static electric field on the luminescence spectra of quantum confined CdS and PbI<sub>2</sub> particles as well as bulk CdS monocrystals has been studied in this work. The applied electric field causes the increase in the excitonic luminescence intensity of quantum-size CdS and PbI<sub>2</sub> particles accompanied with the spectral shift of their luminescence bands. Application of high electric field can follow to the field-induced desorption of surface impurities, such as oxygen and reorganization of surface emitting states.

### INTRODUCTION

The nanocrystals of various semiconductors are studied now extensively. The spatial confinement of the carriers motion in the semiconductor nanocrystals results in dramatic transformation of their band structure due to quantum confinement effect [1-3], as well as the dynamics of excited states. There are a number of works on the influence of external electric field on the linear and non-linear absorption spectra of the direct-gap semiconductors nanocrystals in various matrices [4-6]. The development of Quantum-Confined Stark Effect (QCSE) was observed in the many experiments [1, 4-6].

In this work we present the results of investigation of the external electric field influence on the excitonic photoluminescence (PL) spectra of quantum-sized CdS and PbI<sub>2</sub> particles as well as bulk CdS monocrystal. The excitonic states relate to fundamental phenomena in semiconductors. Such a study can give the information about the relaxation dynamics of the excitonic states, including the influence of surface states, exciton-free layers and defect formation.

The application of high electric field normally results in the homogenous quenching of PL intensity in II-VI semiconductors [7]. However, in this work we present some unusual behavior of excitonic luminescence of QS CdS and PbI<sub>2</sub> nanocrystals, when the external electric field causes the substantial growth in the luminescence intensity. For bulk CdS hexagonal monocrystals we observed the field-induced dip formation in the resonant PL band at the polar surface.

### EXPERIMENT

We prepared the CdS nanocrystals by the reaction between cadmium acetate, dissolved in methanol with the polyvinylpyrrolidone PVP as the polymer-stabilizer and the gaseous H<sub>2</sub>S,

bubbled through that solution. The mean diameter of CdS particles was 3 nm, estimated from the transmitted electron microscopy. The prepared CdS colloidal solution was placed onto the quartz glass with thin conducting SnO<sub>2</sub> layer as a one electrode and dried until the transparent PVP film with CdS particles had formed. The thin copper foil served as a second electrode was placed above PVP film with the 2 mm teflon spacer.

The PbI<sub>2</sub> nanocrystals were prepared by the fast cooling of hot saturated PbI<sub>2</sub> solution in water containing 1–2 percents of poly(vinyl alcohol) PVA as the polymer-stabilizer. The average size of PbI<sub>2</sub> nanocrystals was determined by X-ray diffraction analysis. The thin hexagonal PbI<sub>2</sub> particles prepared in PVA solution have the thickness of less than 1nm and the diameter of 3 nm. The sample with PbI<sub>2</sub> particles was prepared in the same way, as described above CdS ones.

For the experiment we used the commercial computer-controlled photoluminescence spectrophotometer with the He–Cd cw laser as a pump source, operating at  $\lambda=325$  nm with the 3 mW output. The dc electric field of up to 18 kV was applied from the power block. The samples with polymeric films containing CdS or PbI<sub>2</sub> particles as well as CdS monocrystals were illuminated through the quartz/SnO<sub>2</sub> layer and the luminescence recorded in the backward.

## RESULTS AND DISCUSSION

Fig. 1 represents the PL spectra and relative PL spectra of CdS particles in PVP film before and during the application of electric field. The relative PL spectra were determined as  $I/I_0$ , where  $I_0$  and  $I$  are the PL intensity before and during application of electric field, respectively. Note, that the pure PVP, as well as PVA films have a negligible luminescence at the same conditions. The maximum of PL spectra in Fig.1 (curve 1) lies around 2.6 eV, so the shift of 0.15 eV to the high energy region of the excitonic luminescence band of QS CdS nanocrystals takes place comparable with the bulk CdS. We interpreted this shift as the effect of quantum confinement in CdS nanocrystals. The application of the electric field results in clear changes in the low energy side of PL spectra (Fig. 1, curves 2a–4a). The PL intensity grows up with the increase of the electric field strength.

Figure 1. PL spectra and relative PL spectra of QS CdS nanocrystals in PVP film at the applied dc electric field of different strength, kV cm<sup>-1</sup>: 1 – 0; 2 and 2a – 14; 3 and 3a – 17; 4 and 4a – 20.

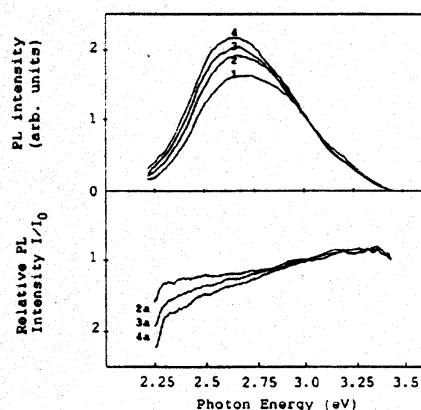
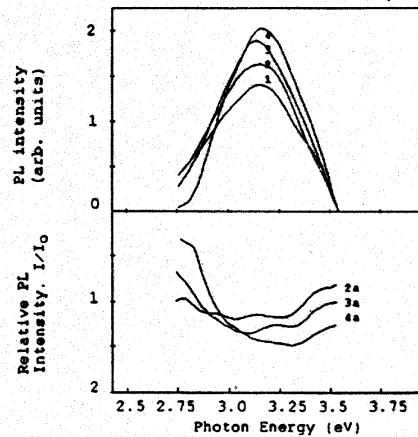


Fig. 2 shows the influence of a high electric field on the PL spectra of QS PbI<sub>2</sub>

nanocrystals in PVA film. In this case we observed the growth of a high energy side of PL spectra at the increasing electric field. Simultaneously, the partial decrease in the low energy side of PL spectra develops so, that the total narrowing of PL band appears under the electric field action. It can be seen, also the presence of at least two local maximum in the relative PL spectra, which shift to the high energy region with the increasing of the field strength.

Figure 2. PL spectra and relative PL spectra of QS  $\text{PbI}_2$  particles in PVA film at the applied dc electric field of different strength,  $\text{kV cm}^{-1}$ : 1 - 0; 2 and 2a - 10; 3 and 3a - 14; 4 and 4a - 16.



The results obtained we interpreted based on the three-level model of the excitation and relaxation of excitonic states in QS semiconductor nanocrystals [9]. Since, the electron/hole wave functions of excited states in QS particles extend to their surface [1], the electrons or holes can be captured easily at the surface states, caused by the adsorption of the atmospheric oxygen. Such excitons bound with the surface state relax partially through the non-radiative way, decreasing the total PL intensity from QS nanocrystals. Moreover, the mixing of the pure excitonic states with the surface ones causes the substantial inhomogeneous broadening of the PL bands. It is well-known the oxygen molecules or atoms being the good acceptors for the photoelectrons cause the photoluminescence inhibition. Oxygen easily adsorbs both at the covalent and ionic semiconductor surface [10]. Applied electric field results in the field-induced desorption of the oxygen from the surface of QS nanocrystals. Therefore, the narrowing of the QS  $\text{PbI}_2$  PL band at the high electric field accompanying the increase in band intensity reflects the withdrawal of surface states contribution in the excitonic luminescence.

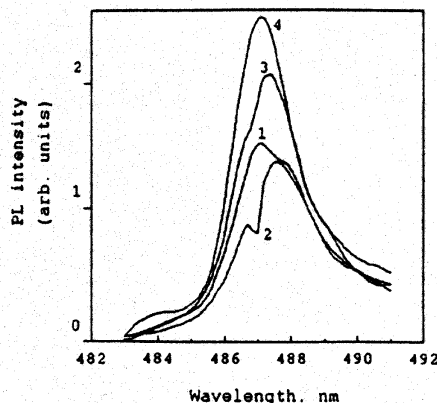
Fig.3 shows the influence of electric field on the free-excitonic emission band of CdS monocrystal. The application of the negative bias at the front  $\text{SnO}_2$  electrode causes the dip formation in the PL band (Fig.3, curve 2). The change of bias sign and the increase of the field strength reduces the dip depth (Fig.3, curve 3) and it vanishes completely when the field strength reaches  $18 \text{ kV cm}^{-1}$  (Fig.3, curve 4). We did not observe the same effect on the high-resistance CdS monocrystals.

The analogous effect of the spectral dip formation occurs after the cycling heating to 396 K and cooling to 77 K of the same CdS monocrystal.

The dip formation in the free-excitonic PL band is similar to the self-reversal of spectra lines in atomic spectroscopy, when the emission passes through the gas with the gradient of concentration of excited atoms [11]. We believe the application of electric field causes the

development of near-surface layer with the low concentration of excitons and the effect of self-absorption of the free-exciton emission can take place.

Figure 3. The influence of the sign and strength of the static electric field on the free-exciton PL band of low-resistant CdS monocrystals. The value of field strength,  $\text{kV cm}^{-1}$ ; 1 = 0; 2 = -19; 3 = +10; 4 = +18



We explain the appearance of depletion layer during the CdS crystal heating resulting from the thermostimulated oxygen adsorption at the crystal surface. The fast cooling of crystal causes the "freezing" of adsorbed oxygen [12], which is a good acceptor of electrons from the conduction band in low-resistant CdS samples, or photoelectrons in high-resistant ones. As the consequence, the strongly increasing surface electric field changes the excitons and carriers distributions in the space charge layer.

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