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Formation of Intrinsic Defects in the Growth of CdS Nanocrystals

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Cadmium sulfide nanocrystals (NCs CdS) are synthesized by sol-gel method. It's have sufficiently intense photoluminescence in the visible region of the spectrum and have a size of 3.2-4.1 nm. It is shown that in the early stages of growth of nanocrystals own lattice defects and the corresponding luminescence centers are not formed at the same time. Defects occur first - cadmium vacancies having luminescence band at long wavelengths with $h\nu_{max} = 1.9$ eV. Further, defects are begin to form by with the growth of NCs, and are represented – cadmium vacancy and oxygen in place of sulfur. Complex-cadmium vacancy and sulfur vacancy is formed after. Interstitial cadmium is appears last. With further growth of NCs, all luminescence bands of already formed defects are shifted to longer wavelengths synchronously with further decrease in the effective bandgap.

Keywords: Photoluminescence, Nanocystals of CdS, The sol-gel method, Defects.

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1. INTRODUCTION

Formation of nanocrystals in polymer matrices based on sol-gel technology is widespread. We used a gelatin as a matrix. It allows to synthesizing nanocrystals by size from 1.5 nm and more. The resulting nanocrystals of cadmium sulfide have sufficiently high quantum yield of luminescence at room temperature. It's making possible to apply the fluorescent method for study the formation of intrinsic defects and properties of nanocrystals during their growth. The aim of this work is to study of the intrinsic defects formation in the time of growth nanocrystals CdS.

2. EXPERIMENTAL PROCEDURE

Synthesis of CdS NCs conducted according to a proven method [1] based on sol-gel technology [2]. In this paper the synthesis was carried out based on the chemical reaction of substitution of cadmium salt and of sodium sulphide salt dissolved in water:

$$CdBr_2 \cdot 4H_2O + Na_2S \rightarrow CdS + 2NaBr + 4H_2O.$$

Neutral gelatin was used as the polymer matrix for the spatial separation of the growing nanocrystals, it was melted in water at 40 °C.

During synthesis 23 of the sample was selected. The first sample was selected at 0.5 minutes after the start of reagents feeding, the second – after a minute. Further samples were taken at intervals of 2 minutes. Samples were watered on glass plates of the same size and shape for measurement the absorption and luminescence spectra.

Effective bandgaps was determined by absorption spectra. From these values, the diameters NCs were calculated: $d_1 = 3.2$ nm – $d_{23} = 4.1$ nm [3]. Photoluminescence spectra of received CdS NCs were filmed on automatic spectral device in range 400-800 nm. Light-emitting diode HPL-H77V1BA-V2 with the wavelength $\lambda = 380$ nm was used for photoluminescence excitation. Measurement of the intensity of the stationary photoluminescence was conducted at ambient temperature of 25 °C.

3. DISCUSSION

Luminescence spectra are represented in the form of wide bands in the visible region of the spectrum from 420 nm to 800 nm. Half-width of band for all samples varies in the range from 100 nm to 150 nm. This suggests that the bands are not elementary and consist of several narrower bands which are responsible for the different centers of luminescence. It is known that in single crystals and powders of cadmium sulfide luminescence band are formed by four kinds of defects [4]. In [5] it is shown that in the CdS NCs the same types of defects are responsible for the luminescence. Therefore experimental luminescence spectra were decomposed into four elementary bands. Result of the decomposition of the sample number 4 (nanocrystals have a size of 3.28 nm) is shown in Fig. 1.

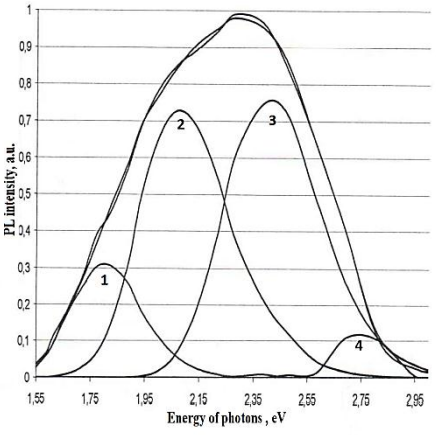

Fig. 1 – Decomposition of the luminescence spectrum of the sample number 4 NCs CdS on four elementary band

Upon decomposition, the half-width of elementary components was equal 60 nm to take into account the variation of the nanocrystals size due to not monodispersity.

According to [5] the intrinsic luminescence determined by defects, which are single vacancies cadmium

(curve 1 in Fig. 1), cadmium vacancies in combination with sulfur vacancies (curve 2 in Fig. 1), cadmium vacancies in combination with oxygen in place of sulfur (curve 3 in Fig. 1) and interstitial atoms of cadmium (curve 4 in Fig. 1). In this paper we assume that and for nanocrystals their luminescence defined the same lattice defects formed during the initial stages of the formation and growth of nanocrystals. Fig. 2 shows a generalized band diagram for series of obtained CdS nanocrystals.

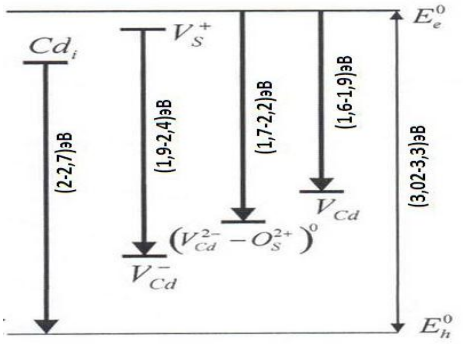

Fig. 2 – Energy-level diagram of defects for NCs CdS ($3{,}2 \le d \le 3{,}85$ nm)

Figure 3 shows the dependence of the maxima for the four basic components of the luminescence spectrum from the diameter of the nanocrystals. Exploring the curves in this figure can draw two conclusions. First, defects and related luminescence bands appear successively at the initial stages of CdS NCs growth. Secondly, highs of all the bands are shifted to longer wavelengths in accordance with the quantum size effect by increasing the size of CdS NCs.

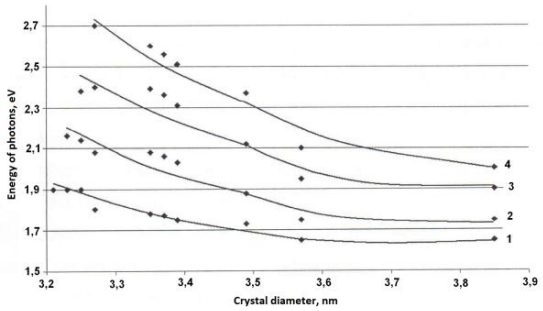

Fig. 3 – Dependence of the maxima of elementary constituents bands the luminescence from NCs CdS diameter

4. SUMMARY

Exploring the decompositions of the luminescence spectra into elementary bands and comparing obtained data with the values of the energy levels of defects we can make the following conclusions. In the early stages of growth of nanocrystals own lattice defects and the corresponding luminescence centers are not formed at the same time. Defects occur first – cadmium vacancies having luminescence band at long wavelengths with $h\nu_{max} = 1.9$ eV. Further, defects are begin to form by with the growth of NCs, and are represented – cadmium vacancy and oxygen in place of sulfur. Complex - cadmium vacancy and sulfur vacancy is formed after. Interstitial cadmium is appears last. With further growth of NCs, all luminescence bands of already formed defects are shifted to longer wavelengths synchronously with further decrease in the effective bandgap.

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