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INFLUENCE OF NANOCRYSTALLITE SIZES ON THE ABSORPTION SPECTRUM OF CDS NANOCRYSTALS

Recently, special attention is paid to the magnetic and semiconducting nanomaterials, and the interest in them is increasing. This is due to the enormous practical importance of these classes of materials for the development of information, medical, chemical, and electronic technology. Nanomaterials based on semiconductors (eg, $A_{II}B_{VI}$ and $A_{IV}B_{VI}$) have unique optical properties and are promising materials for the active elements of nonlinear optics and nanoelectronics devices.

In this paper, the synthesis of nanocrystals was performed by two different methods: the first is with the introduction dopped aqueous solution of sodium sulfide in an aqueous solution of cadmium nitrate, the second is by blowing hydrogen sulfide in a container with an aqueous solution of cadmium nitrate. The technology of obtaining nanocrystalline structures with colloidal solutions by both methods were worked, we've found conditions and reagent concentrations necessary to produce nanocrystals of a given size. The characteristic size of the nanocrystals on the optical absorption spectra. With the help of the data was calculated energy level spectrum, characteristic of these objects. The good agreement between the values obtained with the theoretical data podtverdaet possibility of approximation of the form of a spherical semiconductor nanocrystal quantum dots.

We investigated the cadmium sulfide nanocrystals obtained by two independent methods: the first method nanocrystals formed by a chemical reaction of colloidal solutions of cadmium nitrate (Cd $(NO_3)_2$) and sodium sulfide (Na_2S) in aqueous solution photo jelly (14 g gelatin in 100 ml of water, 14%). Gelatin has the properties of isolated nanoparticles in the volume and acts as a dielectric matrix. Chemical reactions was performed on formula:

$$Cd(NO_3)_2 + Na_2S \rightarrow CdS + 2NaNO_3 \qquad (1)$$
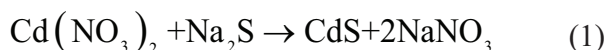
In the course of chemical reactions in aqueous solution Cd $(NO_3)_2$ (0.007 g, 0.06 g and 0.05 g per 50 ml of distilled water) mixed with an aqueous solution of gelatin in 1:1, with continuous stirring,

drip (droplet diameter 3 mm), with a period of dropping τ = 3-4 sec. (for uniform response components), an aqueous solution of Na_2S (300 drops). Throughout the time of preparation of the samples, the temperature of the solution was kept constant of 60 ± 5 °C (was fixed by thermometer).

The second method as an alternative method for making nanocrystals used technology in which cadmium sulfide nanocrystals prepared by blowing hydrogen sulfide in a container with a solution of cadmium nitrate. The chemical reaction of the synthesis:

$$Cd(NO_3)_2 + H_2S \rightarrow CdS\downarrow + 2HNO_3 \qquad (2)$$
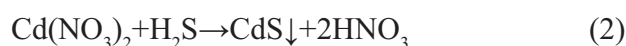
Cadmium is a source of hydrated Cd $(NO_3)_2 \cdot 4H_2O$ c concentration of 0.007 grams per 50 ml of water. As a stabilizer used 9% of photographic gelatin.

Hydrogen sulfide is obtained by decomposition of concentrated aqueous sodium sulphide by the 30% solution of the orthophosphoric acid. We slowly dripped acid (100, 200 and 300 drops) to a solution of sodium sulfide.

Was synthesized two series of samples, one for each method, each with three samples with different concentrations of reagents: the first one was 0.007, 0.06 and 0.05 g of Na$_2$S per 50 ml of water in 14% aqueous solution of gelatin in the first method, the second one was with 0.007 g Cd (NO3) 2 in 50 ml of water with a 9% aqueous content photo gelatin for the second method.

Usually, we obtain reducing the size of the nanocrystals shifts the fundamental absorption edge to shorter wavelengths [1, 2]. The shape of the absorption band depends on the conditions of synthesis of nanocrystals and the number of initial reagents. The absorption spectra obtained by the first method, are shown in Fig. 1:
The absorption spectra for the second alternative method of obtaining CdS nanocrystals are shown in Fig. 2:

The absorption spectra of the second series in Fig. 2, obtained by the second method has more complex structure than the absorption spectrum on Fig. 1. This indicates the presence of different types of optical transitions.
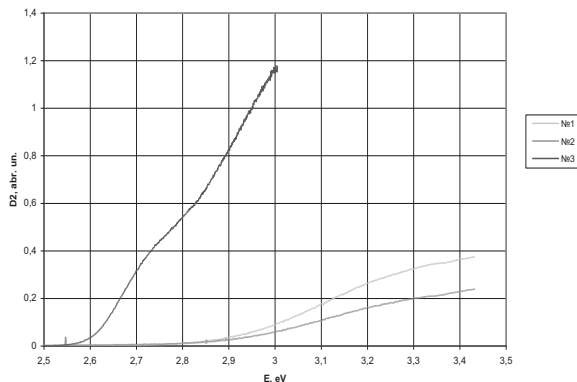

Fig. 1. *Spectra of absorption of nanocrystals CdS (№ 1 - 0.06 g of Cd(NO$_3$)$_2$ in 50 ml of water, 300 drops of Na$_2$S with concentration 0.1 g of Na$_2$S per 50 ml water, 14% aqueous solution of gelatin; № 2 - 0.06 g of Cd(NO$_3$)$_2$ in 50 ml of water, 300 drops of Na$_2$S with concentration of 0.05 g of Na$_2$S per 50 ml water, 14% aqueous solution of gelatin; № 3 -0.007 g Cd(NO$_3$)$_2$, 300 drops of Na$_2$S with concentration of 0,05 g of Na$_2$S per 50 ml water, 14% aqueous solution of gelatin)*
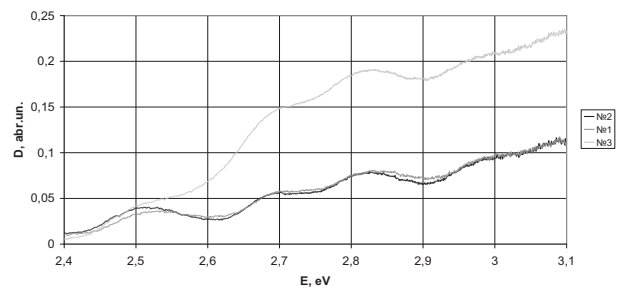

Fig. 2. *The absorption spectra of the samples with 9% concentration of gelatin (№ 1 - 0.007 g Cd (NO3) 2, 50 ml of water, 100 drops of H 2 S, 9% gelatin, № 2 - 0.007 g Cd (NO3) 2 in 50 ml of water, 200 drops of H2S, 9% gelatin № 3 - 0.007 g Cd (NO3) 2) in 50 ml of water, 300 drops of H 2 S, 9% gelatin)*

To better define the edge of the fundamental absorption bands were calculated first derivative of the absorption spectra of Fig. 2. They are shown in Fig. 3. The fundamental absorption edge is defined as the highest peak:
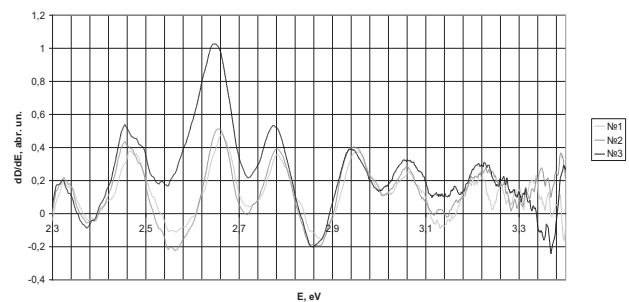

Fig. 3. *The first derivatives of the absorption spectra of 9% concentration of gelatin (№ 1 - 0.007 g of Cd (NO$_3$)$_2$, 50 ml of water, 100 drops of H$_2$S, 9% of gelatin, № 2 - 0.007 g of (NO$_3$)$_2$ in 50 ml of water, 200 drops of H$_2$S, 9% of gelatin № 3 - 0.007 g of Cd (NO$_3$)$_2$) in 50 ml of water, 300 drops of H$_2$S, 9% of gelatin)*

Values of the effective band gap, determined by the maximum extremum in Fig. 3 (№ 1-2.64 eV, № 2-2.66 eV, № 3-2.67 eV) were obtained by extrapolation of the absorption edge to the energy axis, into the eq. (3) [1] to find the effective size of the nanocrystals:

$$R = \sqrt{\frac{\hbar^2 \varphi_{1n}^2}{2\mu(E_{eff} - E_g)}} \tag{3}$$

where R- the radius of the nanocrystal, m

To determine allowed optical transitions of different types are necessary to build second derivative of the absorption spectra of Fig. 2, which are shown in Fig. 4:
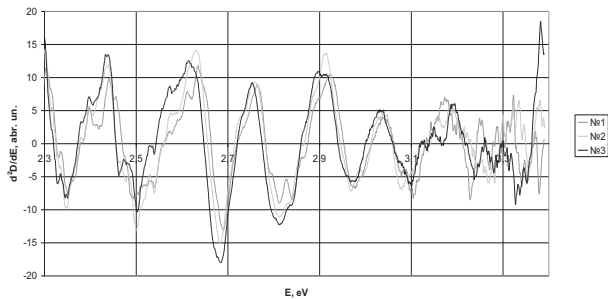

Fig. 4. The second derivatives of the series with a 9% of gelatin content gelatin (№ 1 - 0.007 g of Cd (NO₃)₂, 50 ml of water, 100 drops of H₂S, 9% of gelatin, № 2 - 0.007 g of (NO₃)₂ in 50 ml of water, 200 drops of H₂S, 9% of gelatin № 3 - 0.007 g of Cd (NO₃)₂) in 50 ml of water, 300 drops of H₂S, 9% of gelatin)

Table 1						
Number of transition →	1s	1p	1d	1f	1g	2s
$E_{trans,theor}$, eV	2.68	2.82	3.06	3.25	3.68	3.16
$E_{trans,e \div p}$, eV	2.68	2.8	2.97	3.24	--	3.16
Number of nuclons	2	6	10	14	18	2

Thus, in this paper, the necessary conditions for the formation and concentration of reagents to prepare nanocrystals of a specific size were obtained. Displacement measurement edge of the main absorption band in the short wavelength region with decreasing the size of the nanocrystals [5] allowed us to calculate the effective size of the objects. A comparison of the radii, calculated theoretically and experimentally obtained from the optical absorption spectra confirms the theoretical assumption about the shape of the spherical nanocrystals as quantum dots [6, 7].

Conclusion. Based on these data the energy-level diagram (Fig. 5), which can be interpreted as single-particle states of infinite square well for several values of l <6 and n. This shows that with the increase of the well depth levels are dropping. Also the decreasing of the energy level occurs with increasing width of the well, i. e., the parameter *R*. Table 1. shows that the course of the levels in a square well reproduces the first two magic numbers 2 and 8. Number 2 corresponds filled 1s-state, the number of 8 corresponds filled 1s-and 1p-states. We can assume that also played a third magic number of 20, because the levels of 1d and 2s Rural location close to each other. In this case, the number 20 corresponds to the filling of 1s-, 1p-, 1d-and 2s-states. The numbers 28, 50, 82 and 126 can not be obtained by filling a rectangular well nucleons levels without spin-orbit interaction.

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Abstract

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Keywords: nanocrystals, absorption, energy bands.

Кисс А. В., Смынтына В. А., Зубрицкий С. В.

ВЛИЯНИЕ РАЗМЕРОВ КРИСТАЛЛИТОВ НА СПЕКТРЫ ПОГЛОЩЕНИЯ НАНОКРИСТАЛЛОВ CDS

Резюме

В последнее время особое внимание уделяется магнитным и полупроводниковым наноматериалам, причем интерес к ним постоянно возрастает. Это связано с огромной практической значимостью этих классов материалов для развития информационных, медицинских, химических, электронных технологий. Наноматериалы на основе полупроводников (например, $A_{II}B_{VI}$ и $A_{IV}B_{VI}$) обладают уникальными оптическими свойствами и являются перспективными материалами для активных элементов нелинейной оптики и устройств наноэлектроники.

В данной работе синтез нанокристаллов проведен двумя различными методами: первый — с помощью покапельного введения водного раствора сульфида натрия в водный раствор нитрата кадмия, второй — путем продувки сероводорода в емкости с водным раствором нитрата кадмия. Отработана технология получения нанокристаллических образований с коллоидных растворов по двум методам, найдены условия и необходимые концентрации реагентов для получения нанокристаллов заданного размера. Определены характерные размеры нанокристаллов по спектрам оптического поглощения. С помощью полученных данных был рассчитан энергетический спектр уровней, характерных для данных объектов. Хорошее совпадение полученных значений с теоретическими данными подтвердает возможность использования приближения о форме нанокристаллов как сферических полупроводниковых квантовых точках.

Ключевые слова: нанокристаллы, поглощение, энергетические зоны.

УДК 621. 315. 592

Кисс А. В., Смінтина В. А., Зубрицький С. В.

ВПЛИВ РОЗМІРІВ КРИСТАЛІТІВ НА СПЕКТРИ ПОГЛИНАННЯ НАНОКРИСТАЛІВ CDS

Резюме

Останнім часом особлива увага приділяється магнітним і напівпровідниковим наноматеріалам, причому інтерес до них постійно зростає. Це пов'язано з величезною практичною значущістю цих класів матеріалів для розвитку інформаційних, медичних, хімічних, електронних технологій. Наноматеріали на основі напівпровідників (наприклад, $A_{II}B_{VI}$ та $A_{IV}B_{VI}$) володіють унікальними оптичними властивостями і є перспективними матеріалами для активних елементів нелінійної оптики і пристроїв наноелектроніки.

У даній роботі синтез нанокристалів проведений двома різними методами: перший - за допомогою покапельного введення водного розчину сульфіду натрію в водний розчин нітрату кадмію, другий - шляхом продувки сірководню в ємность з водним розчином нітрату кадмію. Відпрацьована технологія отримання нанокристалічних утворень з колоїдних розчинів за двома методами, знайдені умови і необхідні концентрації реагентів для отримання нанокристалів заданого розміру. Визначено характерні розміри нанокристалів за спектрами оптичного поглинання. За допомогою отриманих даних був розрахований енергетичний спектр рівнів, характерних для даних об'єктів. Гарний збіг отриманих значень з теоретичними даними подтвердає можливість використання наближення про форму нанокристалів як сферичних напівпровідникових квантових точках.

Ключові слова: нанокристали, поглинання, енергетичні зони.