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Effective mass and peculiarity of optical properties of Cadmium Sulfide nanoparticles

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X-ray diffraction data, electron microscope and optical properties of cadmium sulfide nanoparticles were analyzed. It is shown that the value of the reduced effective mass of charge carriers in nanoparticles differs from bulk crystals. Changes of effective mass and "red shift" in values of band gap are explained by the occurrence of additional electronic potential in nanoparticles.

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1. Introduction

Nanoparticles based on cadmium sulfide are one of the prospective materials for solar cell elements [1], high-speed devices [2-4, 8] and radiating elements [5] thanks to good luminescence properties. There are many methods for formation of cadmium sulfide nanoparticles: successive ionic layer adsorption and reaction (SILAR) [6-10], sonochemistry method [11,12], microwave radiation [13], deposition from solutions of electrolytes [1,8,10,14-16], sol-gel [17,18], processing of polymer films containing cadmium atoms or ions with a vapor of hydrogen sulfide [19], MBE (molecular beam epitaxy) [20], photochemical synthesis [20] and others.

Depending on the method used, the conditions of formation of the nanoparticles change. This promotes change of packing, defective crystal structures, and change of the geometry of the nanoparticles. Changes of these parameters should influence the character of the electronic potential of the nanoparticles that in turn, should be reflected in the physical and chemical properties of the nanosystem.

Depending on the sizes of the particles, the interatomic distance from the center to the surface of the particles varies. In certain cases, this difference can reach 17% [21]. Clearly, the translation symmetry and application of the Bloch function for these systems are incorrect. On the surface of the nanoparticles, there are broken chemical bonds. With reduction in the sizes of the particles, the ratio of surface to volume of particles increases and the share of the broken chemical bonds by unit area increases. The broken bonds give an additional contribution to electronic potential in the nanosystem. With reduction in the sizes of the particles, the influence of this factor on changes in electronic potential will increase.

During formation of the nanoparticles, different mechanisms of stabilization are used. In the case of formation by ultrasound, such stabilizers are polyvinyl-pyrrolidone [22], ethylenediamine [23], trioure [24], and tiophenol [25]. In the case of formation in polymer [26], the polymeric matrix is the stabilizing factor. In all of these cases, there should be an interaction between the stabilizing substance and the nanoparticles. This may lead to changes in electronic potential and physical parameters (effective mass, band gap, etc.). Knowledge of the true values of the physical parameters is important from an engineering point of view. These parameters are widely used in calculation of the characteristics of the devices produced on the basis of the nanomaterials used.

The purpose of this work is the analysis of the experimental data on the change of band gap and effective mass depending on the sizes of the cadmium sulfide nanoparticles used. Analyses are conducted on the basis of our own experiments and literature data.

2. Experimental

Cadmium sulfide nanoparticles have been formed in a polymer matrix through SILAR [8]. As a source of cations and anions, aqueous solutions of $Cd(NO_3)_2\bullet 4H_2O$ and $Na_2S\bullet 9H_2O$ salts were used with a concentration of 0.2 M. The size of the particles increased with increasing number of cycles of formation. Transmittance spectra of the samples were measured with a Perkin-Elmer Lambda-40 spectrophotometer in the range 300–800 nm.

3. Results and discussion

For direct optical transitions, the coefficient of absorption depends on the frequency as follows [27]:

$$\alpha \sim (h\nu - E_g)^{\frac{1}{2}} \cdot \frac{1}{h\nu} \tag{1}$$

On the basis of measurement spectra of transmitting structures, CdS/gelatin dependences $(\alpha\ h\ \nu)^2$ versus $(h\nu)$

(Fig.1) have been constructed. From these dependences, the band gaps of nanoparticles with various sizes have been defined.

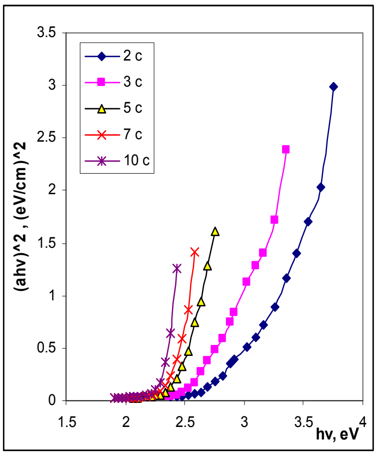

Fig. 1. Dependence $(\alpha h\nu)^2$ *from the energy of photons for samples with various cycles of formation (2, 3, 5, 7, 10 cycles).*

Table 1.

Number of cycles	2	3	5	7	10
Band gap (eV)	2.90	2.58	2.40	2.32	2.28

The values of the band gaps, depending on the number of cycles of formation of CdS nanoparticles are shown in Table 1. Apparently from Table 1, at lower numbers of cycles and small particle sizes, the band gap is greater than the values for bulk crystals – 2.42 eV. This is connected to quantum-dimensional effects in nanoparticles [26]. With increased number of cycles, the band gap decreases and becomes less than the values for bulk crystals.

Analysis of the literature data showed that, in certain cases in nanoparticles, red displacement of the cadmium sulfide band gap is observed. In Ref. [28], CdS nanoparticles have been generated in volume layered nanocomposites. The band gap in these structures depended on the matrix formation and varied from 2.11 eV to 2.40 eV, i.e., in all of the samples, the band gap is less than in the bulk crystals. Such red displacement of the band gap is also observed in cadmium sulfide nanoparticles produced by magnetron sputtering [29], a chemical method [30], and SILAR [8]. Analysis of the optical properties of cadmium sulfide and cadmium selenide nanoparticles, produced by the ultrasonic method [11,22-25,] showed that the band gap varies in the range 2.60–4.69 eV. In this case, red displacement is not observed.

Table 2.

№	Method of formation	Method of analysis of particle size	Particle size (nm)	Band gap (eV)	Effective mass approximation [44]	Hyperbolic Band model [45,46]	Reference
1	Ultras	XRD SEM	3–5 5	3.10	0.06143 0.02212	0.10778 0.03879	[22]
2	Ultras	HRTEM	5	3.80	0.01089	0.01697	[23]
3	Ultras	XRD	9.1	2.60	0.02522	0.04866	[25]
4	Ultras	XRD	5	2,94	0,02892	0.05225	[11]
5	Ultras	XRD	5.8	4.69	0.00492	0.00671	[24]
6	Microwave	XRD	12	2,84	0,00621	0.01144	[11]
7	Microwave	XRD TEM	5.6 7	2.63	0,05711 0,03654	0,10948 0,07007	[31]
8	Chem.	XRD TEM	10 8	2.82	0.00940 0.01469	0.01737 0.02714	[34]
9	Chem.	XRD TEM	7 6	2.78	0.02131 0.02901	0.03969 0.05403	[34]
10	Chem.	XRD TEM	5.1 5.5	2.59	0.08503 0.07312	0.16436 0.14132	[35]
11	Chem.	XRD TEM	2.1 4	2.66	0.35525 0.09792	0.67718 0.18665	[36]
12	Chem.	XRD	1.3	3.39	0.22937	0.38228	[37]
13	Chem.	XRD TEM	10 5-10	3.25	0.00453 0.01812	0.00774 0.03095	[38]
14	Chem.	HRTEM DLS	4.2 3.8	3.30	0.02422 0.02969	0.04101 0.05009	[39]
15	Chem.	DLS	3.6	4.13	0.01697	0.02508	[40]
16	Chem.	XRD AFM	4.2 10	2,67	0,08536 0,01504	0.16221 0.02861	[12]
17	Chem.	TEM	5.8	2.70	0.03992	0.07549	[41]
18	Chem.	TEM	10	2.57	0.02507	0.04864	[42]
19	Chem.	XRD	4 27	3.16 3.87	0.03176 0.00035	0.05511 0.00121	[43]

Apparently from the analysis of the literature data, in certain cases (basically depending on the method of formation), red displacement is observed in nanoparticles, i.e., the band gap of the nanoparticles of cadmium sulfide produced is less than in bulk crystals. This is mainly because the electronic potential of the nanoparticles strongly differs from the bulk crystals. The potential energy of electrons and holes in the nanosystem basically influences the following factors: infringement of transmitting symmetry in nanoparticles; presence of broken chemical bonds on a surface; defects, displacements, etc.; the shape of nanoparticles, etc. Change in electronic potential should lead to a change in the electronic spectrum of the charge carriers and should influence the values of effective mass of electrons and holes.

We have calculated the effective mass of charge carriers on the basis of the published experimental data for cadmium sulfide on the basis of band gap, Eg, and the sizes of the particles, d. Table 2 lists the data on band gap and the size of the cadmium sulfide nanoparticles (defined by electron microscopy and X-ray diffraction) produced by various methods. On the basis of these data, in the approach of effective mass [44] and the approach of Hyperbolic Band Model [45-46], values of the effective mass of the charge carriers in the nanoparticles have been calculated. Apparently from Table 2, values of effective mass vary in a wide range. These values differ from the value of effective mass electrons in a bulk crystal $m_e^* = 0.19\ m_e$ [44] and reduced effective mass $\mu^* = 0.1398$ [45,46]. It should be noted that when the sizes of the particles are less than the value of the Bohr radius ($a_b = 5.6$ nm), then it is necessary to compare them to the effective mass of electrons, and at greater particle sizes, it is necessary to compare them to the reduced effective mass of charge carriers.

The observable red displacement of CdS and the difference in effective mass of nanoparticles from bulk crystals are connected with the change in electronic potential of charge carriers in small particles. The equation for the wavefunction of charge carriers in crystals is [47]:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{i\hbar^2}{m}k\nabla + V(r)\right]U_k(r) = \left(E_k - \frac{\hbar^2 k^2}{2m}\right)U_k(r) \qquad (2)$$

Here $\frac{i\hbar^2}{m}k\nabla$ describes system disturbance. As has been noted in the Introduction, the broken bonds, defects, displacements, translation symmetry breakdown, and interaction with the shape of the nanoparticles can influence the electronic potential of charge carriers in nanoparticles. All of these factors can affect the disturbance factor. Depending on the insertion contribution to disturbance, the character of interaction between the charge of the carriers and the crystal lattice will vary. A change in character of interaction will lead to a change in the type and curvature of an energetic zone. A change in curvature of an energetic zone will lead to a change in effective mass and band gap of the nanomaterial.

4. Conclusions

Analysis of experimental data on the optical properties and the results of X-ray diffraction and electron microscopy studies have shown that the band gaps of cadmium sulfide and cadmium selenide nanoparticles vary in a wide range. Depending on the method of formation of the samples, in some cases, red displacement on band gap of CdS is observed. The reduced effective mass of charge carriers differs from the value for bulk crystals. These phenomena are connected to the change in electronic potential as a result of interaction with defects, the cover, broken bonds, shape, etc. As a result of formation of additional electronic potential, the character of interaction of charge carriers with the crystal lattice changes. This in turn leads to a change in the effective mass of the charge carriers and the band gap of CdS nanoparticles.

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