

## Influence of sulfurization on optical properties of CdS nanocrystals

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**Abstract.** Optical properties of 1D nanocrystals of cadmium sulfide synthesized by vapor–liquid–solid growing were investigated as the function from such technological parameter as overpressure of sulfur vapor at the synthesis process or post-processing by the additional annealing in the sulfur atmosphere (sulfurization). The analyses of UV-vis absorption and photoluminescence spectra indicate considerable dependences of CdS nanocrystals optical parameters from sulfur compensation degree at the synthesis process. The photoluminescence spectra are characterized by changing the ratio of intensities of the defect level and near band edge emissions at overpressure sulfur vapor treatment. A significant decrease in the intensity of defect level emission after the growth or post-growth treatment in sulfur vapor has been observed. Optical absorption edge calculated using the Tauc relation demonstrates improvement of the crystal structure, which is reflected by the rising optical band gap value that approaches to the value for the bulk material at curing of sulfur vacancies by different technological ways. Optical properties obtained by absorption and luminescent measurements demonstrate total correlation, which corresponds to applied technology.

**Keywords:** CdS, nanocrystals, sulfurization, absorbance, photoluminescence, crystal morphology.

<https://doi.org/10.15407/spqeo26.04.442>

PACS 68.70.+w, 71.55.Gs, 78.55.-m

Manuscript received 13.07.23; revised version received 04.09.23; accepted for publication 22.11.23; published online 05.12.23.

### 1. Introduction

Nowadays, great variety of semiconductor nanostructured materials has been synthesized and widely employed for creating active components of modern photonic and electronic devices. Next generation of nanoscale devices based on nanostructured materials have some potential benefits over traditional wafer-based or thin-film devices related to optical, electrical, thermal, and strain relaxation effects, as well as the cost [1].

II-VI compound semiconductors are of great interest as functional materials for application in optoelectronic, photovoltaics, photodetection, biological and chemical sensors [2–7], owing to a wide band-gap, high quantum efficiency and high photosensitivity. Among these materials, cadmium sulfide (CdS) is the most interesting direct bandgap (2.42 eV at 300 K) *n*-type material with excellent thermal and chemical stability, superior optical properties, excellent photochemical properties, and photocatalytic performance under visible and UV light irradiation. Unique physical properties of nanostructured CdS are widely exploited for development of such optoelectronic devices as solar

cells, photosensors, light emitting diodes, lasers, non-linear integrated optical devices, and in various fields of photocatalysis [8–11]. It is now ascertained that one-dimensional nanostructures can exhibit high optical absorbance exceeding that of thin film of an equivalent thickness [12]. Today one-dimensional nanostructures CdS are used for improving the spectral transmission of the buffer layer in window-absorber type thin film solar cells with such absorber layers as CdS–CdTe, CdS–CIGS, CdS–CZTSSe, *etc.* [13]. As a result, enhanced absorption and carrier generation in absorber layer are observed, thus enhancing the quantum efficiency of solar cells and other optoelectronic devices.

Various techniques can be used to obtain one-dimensional CdS nanostructures, *e.g.*, thermal evaporation, electrodeposition, chemical vapor deposition, vapor – liquid – solid growth (VLS) and others. Synthesis of CdS nanostructures by using the VLS technique is more promising as the bottom-up method, which gives the opportunities for predictable growth of nanocrystals on arbitrary substrates with high crystallinity, monodispersity and enables to control all key parameters of nanostructures.

In order to boost the performance and to optimize characteristics of nanosized devices, deeper understanding of physical properties of nanomaterials defined by their growth mechanisms and the nature of defects are needed for controlled fabrication of high quality nanostructures.

In 1D nanostructures, where the surface-to-volume ratio is rather high, such parameters as chemical composition, size, shape, morphology, stoichiometry, and surface effects provide the great influence on size-dependent properties [14]. Particularly, the nature and concentration of the structural defects (vacancies and interstitial atoms, stacking fault defects, impurities) define main optical properties of CdS nanostructures [15–18]. Among native defects, the Cd and S vacancies have the strongest effect on the electronic structure of nanostructured CdS. Variation of Cd to S ratio during synthesis gives the opportunity to control the stoichiometry of 1D nanostructures CdS, and so governs their electrical and optical characteristics [19–23].

During the device preparation process, the defect densities of CdS nanostructures can be changed because of the crystal phase transformations occur. As known, CdS can crystallize in different phases (cubic zinc blend, hexagonal wurtzite, rock-salt phase), and their formation depends on technological growth conditions, namely: applied preparation temperature, crystallite size, and/or pressure. The phase transformation is reflected in the change of optical properties, such as variation of the band gap, crystal lattice disorder, modification of the refractive index, transparency, and luminescence emission [24, 25].

For example, alteration of the molar ratio Cd/S can govern both morphology and the phase composition of CdS nanostructures, and hence the photocatalytic activities. The opportunity to manage the photocatalytic activity of samples grown using the solvothermal method by controlling the molar ratio of Cd and S sources were demonstrated [26]. It was noted that the samples with 1:2 Cd/S molar ratio exhibited higher photocatalytic activities in comparison with those prepared at other Cd/S molar ratios attributed to the improved charge separation at the zinc blende/wurtzite junction interface.

Today, defect engineering has been explored as perspective idea to improve the photocatalytic activity and efficiency of optoelectronic applications. Such intrinsic semiconductor defects as vacancies, functioning not only as adsorption centers but also as traps for electron-hole recombination capturing a free electron and a hole. For example, it was reported [27], that the sulfur vacancies rich CdS composite photocatalyst CdS@g-C<sub>3</sub>N<sub>4</sub> exhibits superior photocatalytic activity for volatile organic compounds (VOCs) degradation. This fact makes it a promising material for H<sub>2</sub> energy development as well as an ideal tool to remove VOCs contaminants from air. Detailed analysis of photoconductivity in thin CdS films showed that large and persistent photoconductivity happens due to the trapping of photo-generated minority carriers at crystal defects

correlated with sulfur deficiency [22]. Investigation of the role of structural defects in the optical properties of hexagonal CdS demonstrated that the presence of cadmium vacancies on the surface alters the electronic structure of cadmium sulfide by forming acceptor levels in the forbidden band of the semiconductor [21]. Therefore, the control and manage of structural defects offers a viable opportunity for the design of modern nanodevices with desired characteristics.

In our previous papers [14, 15], we investigated the influence of technological growth parameters on the morphology and optical properties of CdS nanowires. We demonstrated a correlation of the ratio of intensities of near-band-gap and defect band emission with the quality of grown CdS nanocrystals. This work is devoted to investigation of the optical properties of one-dimensional CdS nanocrystals grown using the chemical vapor condensation synthesis in dependence on technological parameters determining the concentration of sulfur vacancies. We compare the properties of two types of CdS nanocrystals: as-grown and after the sulfurization made either during the growth process or by post-processing annealing.

## 2. Experimental section

### 2.1. Sample preparation

CdS nanocrystals have been synthesized using chemical vapor condensation by the technique of quasi-closed volume with hot walls. As a source of vapor, we used the decompositive sublimation of CdS powder in a high-temperature reactor situated inside a vacuum chamber together with an additional sulfur evaporator. This technique allows growing single crystals of cadmium sulfide with a diameter of tens to hundreds of nanometers and a length of up to millimeters. Evacuation stages of a silica reactor with graphite stage for samples were performed by a cryogenic sorption vacuum pump with the residual pressure in the chamber of  $\sim 10^{-5}$  Torr. The CdS decompositive sublimator temperature was 750 °C. The temperature of additional sulfur source during annealing in the quasi-closed volume was tuned to the temperature of grown crystals substrate. The CdS powder was of semiconductor purity. A more detailed description of the features of the technology was published earlier [28, 29].

Thermodynamic equilibrium of A<sup>2</sup>B<sup>6</sup> crystal with sulfur vapor is known to be shifted to the creation of nonstoichiometric defects resulting in the growth from stoichiometric vapor composition crystals with sulfur vacancies [14]. Two sulfurization approaches are used to compensate this problem: either the growth from nonstoichiometric composition with oversaturated pressure of sulfur produced by the second evaporator or the post-annealing of grown crystals in atmosphere of sulfur vapor to compensate surface and bulk interstitial cadmium atoms. It was shown in our previous works [30] that both approaches decrease defectiveness of CdS nanocrystals noticeably.

Nanocrystals used in the present investigation were grown on molybdenum glass slides as the substrate with gold seeds as nucleation centers. The gold nucleation seeds were prepared by deposition of a thin Au film of about 2 nm mass thickness on the substrate by thermal evaporation followed by annealing in vacuum. The film thickness during deposition was controlled by quartz microbalance and calculated through the mass uptake value.

Both approaches were used in this work to clarify the influence of the technological parameters on the optical properties of grown nanocrystals.

## 2.2. Characterization

The growth and optical properties of CdS nanocrystals were investigated using UV-visible absorption and photoluminescence (PL) spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction.

The optical properties of these materials were investigated measuring ultraviolet-visible (UV-vis) absorption and photoluminescence excited with a semiconductor laser with the wavelength 407 nm at room temperature with an automatic optical system based on MDR-23 spectrometer and PMP-100 photomultiplier as a detector.

SEM studies were performed using JEOL JSM35, JXA-8200. The phase composition of the films was controlled by *ex-situ* X-ray diffraction carried out with a Philips X'Pert PRO X-ray diffractometer with  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.154$  nm). The qualitative phase analysis of the diffractogram was carried out using the ICDD database, PDF-2 Release 2012. As before [14, 15], XRD confirmed the good crystallinity of our samples.

## 3. Results and discussion

Fig. 1 shows typical scanning electron microscopy (SEM) images of the as-grown CdS nanocrystals on a glass substrate. As it is seen, the large amount of 1D CdS nanocrystals is distributed randomly on the substrate. The typical length of nanocrystals is in micrometer scale and an average diameter is in the scale of hundreds of nanometers. The phase structure has been investigated by

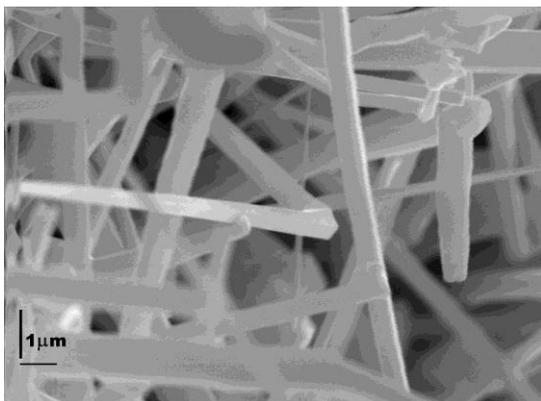


Fig. 1. SEM images of as-prepared CdS nanocrystals.

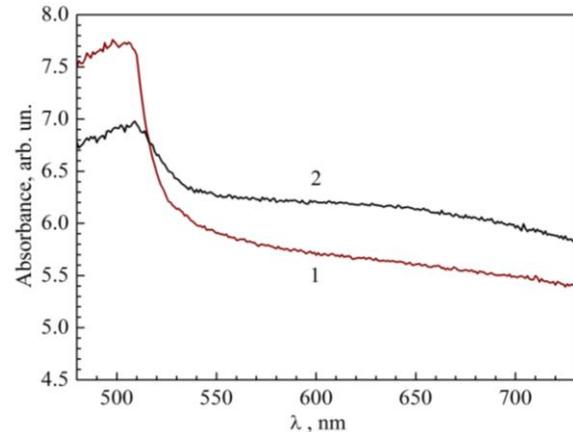


Fig. 2. Absorption spectra of CdS nanocrystals, grown with the sulfur compensation (1) and with the deficiency of sulfur (2) at synthesis process.

conventional X-ray diffraction demonstrating that grown CdS nanocrystals has high crystalline wurtzite crystal structure [14].

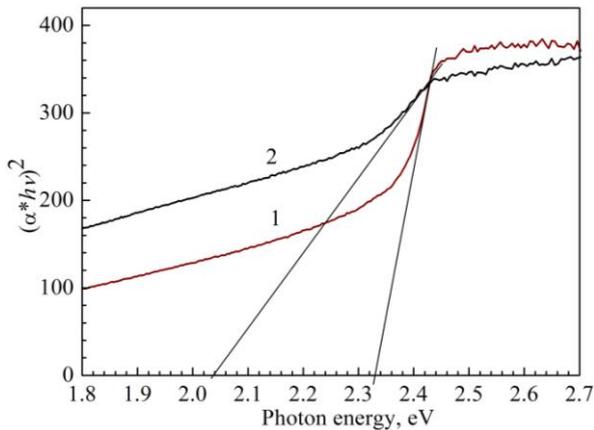
UV-visible absorption spectroscopy has been used to monitor the optical properties of investigated CdS nanocrystals. Optical absorption provides information concerning the band structure and energy gap of nanomaterials. This information is one of the most important parameters in different optoelectronic applications, particular for the development of modern solar cells.

Typical absorption spectra of our CdS nanocrystals are shown in Fig. 2. These spectra correspond to crystals grown with additional sulfur compensation at the synthesis (1) and grown from stoichiometric CdS vapor, which results in a higher number of sulfur vacancies (2). It is possible to separate some distinct regions near the optical absorption edge of semiconductors. Two distinct absorption behavior above and below the band-edge are clearly visible. If the absorption at shorter wavelengths than visible sharp change is defined by the band-band transitions, the absorption at longer wavelengths is exhibited as a long “tail” defined by defect and impurity levels in the band gap. It is worth to note that this tail for the sample grown without additional sulfur vapor (2) is noticeably higher than for the sample grown with additional sulfur compensation (1).

To determine the optical band gap of nanocrystals and to define the nature of involved optical transitions, the well-known Tauc method was applied [31]. This method set the relationship between absorption coefficient (near and above the absorption edge) and optical band gap as

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g), \quad (1)$$

where  $h$  is Planck's constant,  $\nu$  is the photon frequency,  $\alpha$  is the absorption coefficient,  $E_g$  is the band gap,  $A$  is a proportionality constant related to the effective masses of carriers in the valence and conduction bands. The value of the exponent denotes the nature of the direct ( $n = 1/2$ ) or indirect ( $n = 2$ ) electronic transition.



**Fig. 3.** Tauc plots of CdS nanocrystals grown with the sulfur compensation (1) and with the deficiency of sulfur (2) at synthesis process.

Fig. 3 gives the plot  $(\alpha hv)^2$  versus the photon energy ( $hv$ ) using the data obtained from the experimental optical absorption spectra shown in Fig. 2. The second degree –  $(\alpha hv)^2$  – was used because CdS have a direct allowed transition. As well as absorption, the Tauc plots can be separated into two main regions: the weak absorption tail at energies lower than band gap and the high absorption region where the absorption value gets stronger and demonstrates a region of saturation.

The optical band gap is obtained using linear extrapolation of the sharpest spectral part to the energy axis according to the Tauc expression (1).

Within the range of lower photon energies in accord with the fundamental absorption edge, the optical absorption coefficient deviates from linearity and do not go to zero. This deviation is identified as the “Urbach Tail” [32] due to some “smoothing” of a sharp band edge by defect levels. The equation for the approximation of the absorption in the Urbach tail by defect levels has an exponential form into the gap.

$$\alpha = \alpha_0 \exp(hv/E_U), \quad (2)$$

where  $\alpha$  and  $hv$  are the absorption coefficient and photon energy, respectively,  $\alpha_0$  is a constant, and  $E_U$  denotes the Urbach energy.

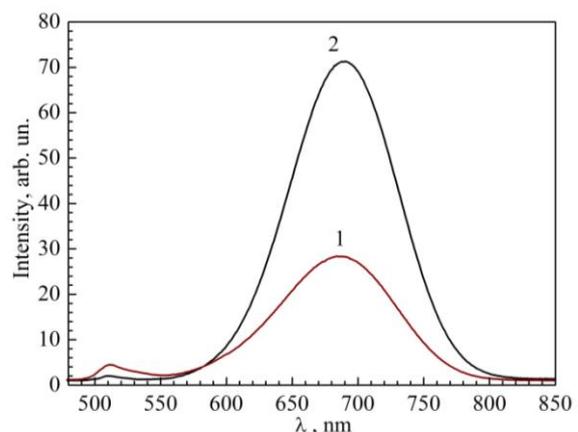
Urbach tail describes both the degree of disorder of semiconductor structure and the presence of defects and impurities in the band gap, which leads to the exponential distribution of the density of localized states near the edge of conduction and valence bands [33].

Considering that X-ray investigation of our nanocrystals demonstrated high degree of crystallinity, the main reason of Urbach tail in our case is the existence of defect levels in the forbidden gap. So, higher value of Urbach tail in our nanocrystals corresponds to the bigger number of additional energy levels in the forbidden gap of the sample with bigger number of defect levels.

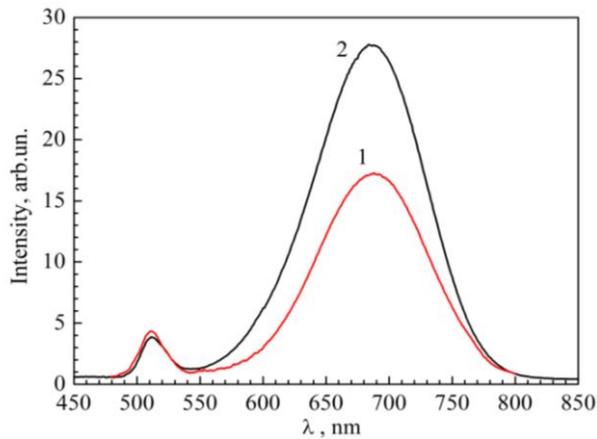
Despite application of Tauc extrapolation for low-dimensional structures with strong Urbach tail is disputed, the theoretical analysis allowed application of this technique safely to semiconductor nanocrystals [34]. We use this approach for qualitative analysis of the influence of technological sulfurization approaches on the effective position of the band edge. As it is seen from Fig. 3, the linearity of the Tauc plot is as good as in bulk materials, therefore the Tauc extrapolation can be safely applied to our CdS nanocrystals.

Based on the obtained experimental data of absorption and in accord with evolution of  $(\alpha hv)^2$  versus  $hv$  shown in Fig. 3, the width of the optical band gap of the samples grown under different technological conditions was determined. The optical band gap of CdS nanocrystals grown with the deficiency of sulfur at synthesis process is found to be 2.04 eV, while for the sample grown with sulfur compensation this energy raises to 2.33 eV, what is much closer to the band gap of bulk CdS 2.42 eV. We unambiguously prescribe the decrease of the optical band gap value in CdS nanocrystals grown with the deficiency of sulfur to the bigger number of defect levels in the forbidden gap [35] due to noticeably larger number of sulfur vacancies. Independently of all possible reservations about precise values of the band gap determined for our nanocrystals, qualitative changes after decreasing the number of sulfur vacancies are clearly visible.

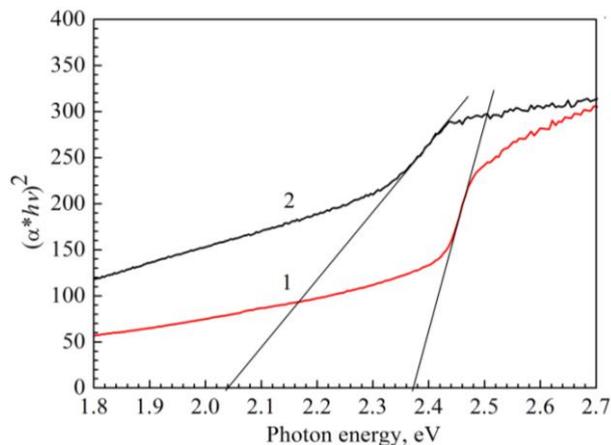
Our conclusions are confirmed by the photoluminescence spectra of these CdS nanocrystals grown under various technological conditions (Fig. 4). PL spectra of CdS nanocrystals consist of typical two emission peaks, which origin from different excited states. The high-energy emission band is assigned to the near-band edge (NBE) emission, whereas the low-energy emission peak is attributed to the radiative recombination of carriers on deep states in the forbidden gap (defect level emission, DLE). The PL spectroscopy allows identifying the structural changes in nanocrystals during growth,



**Fig. 4.** Photoluminescence spectra of CdS nanocrystals with sulfur compensation at synthesis (1) grown with Au as nucleus and the deficiency of sulfur (2).



**Fig. 5.** Room temperature photoluminescence spectra of CdS nanocrystals: 1 – CdS nanocrystal annealed in sulfur vapor, 2 – as-grown CdS nanocrystal with the deficiency of sulfur.



**Fig. 6.** Optical absorption edge calculated using Tauc method for CdS nanocrystals. 1 – CdS nanocrystals annealed in sulfur vapor, 2 – as-grown CdS nanocrystal with the deficiency of sulfur.

because these changes are reflected in the peak position, intensity, and width of spectral bands. As known, the ratio of the intensities of the DLE and NBE emissions may serve as an indicator of the quality of grown CdS nanocrystals [14]. PL spectra demonstrate that the sample with deficiency of sulfur (2) and CdS nanocrystals with the additional sulfur compensation at the synthesis (1) exhibit two emission peaks: strong and wide low-energy emission peak DLE, ranging from 550 nm to 800 nm, and weak high-energy emission NBE band around 510 nm. The use of the additional sulfur compensation at the synthesis results in noticeable reduction of the intensity of DLE emission  $I_{DLE}$  and growing of the NBE intensity  $I_{NBE}$ .

Similar behavior is observed at post-annealing of the grown crystals in sulfur vapor. For the investigation of the influence of this technological approach, the samples grown with the deficiency of sulfur at the synthesis process has been annealed in a sulfur-rich ambient environment at 450 °C for two hours.

As it is shown in Fig. 5, the DLE emission in PL spectra undergoes the notable decrease after the treatment, while NBE emission exhibits minor changes. It again clearly indicates the decrease in the number of defect levels in the band gap due to curing of the crystal structure by the sulfur compensation.

Essential accompanying changes were observed in UV-vis absorption spectra, too. It can be seen from the Tauc plot for the samples grown without additional sulfur vapor and the same sample post-annealed in sulfur vapor that the absorption edge of the nanocrystals CdS after its treatment in sulfur vapor shifts towards the higher energy, indicating the increase in the optical band values (Fig. 6). In this case, after the annealing in sulfur vapor, the energy value of the band gap reached 2.37 eV, which is much higher than that before treatment (2.042 eV).

Changes in the optical parameters are associated with modification of crystal structure of CdS nanocrystals at different technological processes, which results in significant variation of the optical band gap. Additional annealing of CdS nanocrystals in sulfur vapor affects the number of defect levels and so the quality of structures. Analogous influence of the sulfurization was noticed in other works, too [36, 37].

As well as in consideration of the influence of the oversaturation of sulfur vapor during the crystals' growth on the crystal quality, PL and absorption measurements demonstrate complete correlation. The noticeable decrease in the DLE emission after sulfurization clearly indicates the decrease in the number of defect levels in the band gap as compared to as-grown crystals. In turn, it results in the decrease of defect absorption and the increase of the optical band gap due to improvement of the crystal quality after filling the vacancies or compensation of the interstitial Cd atoms. The shift of maximum NBE emission is not observed. This fact is the evidence of the absence of changing of lattice parameter, which would take place as a result of transformation of crystal structure from cubic to the hexagonal one, when introducing sulfur into interstitial sites [37].

Unfortunately, the direct comparison of the results for two approaches is impossible, because of different mechanisms responsible for the defects curing at excessive sulfur vapor during the growth technological process and post-annealing in the sulfur vapor of grown crystals with sulfur vacancies.

#### 4. Conclusions

Investigations of CdS nanocrystals synthesized from gas phase demonstrated strong dependences of its properties on sulfurization both during the growth and by after-treatment of the grown crystals. On the base of obtained data, we can conclude that the main contribution to the optical properties of these CdS nanocrystals stems from the presence of sulfur vacancies. The deficiency of sulfur at technological growth process causes formation of a large number of defect levels in the forbidden gap, which results in creation of the broad DLE emission band in

photoluminescence spectra due to relaxation through defect levels [15] and decrease in the value of the optical band gap in absorption spectra of CdS nanocrystals. Both sulfurization approaches to improve the structure of the grown CdS nanocrystals, either by oversaturation of the sulfur vapor at the growth or by the addition of sulfur at the post-annealed process demonstrate improvement of optical properties and, respectively, structural properties of these nanocrystals. Namely, yellow emission in PL spectra, which represents an electron/hole recombination occurring through defect levels in the band gap [15], noticeably decreases along with the decrease of the intensity of the Urbach tail as well as approaching the band gap value to that of bulk CdS. As the optical properties of nanostructures are highly sensitive to surface quality, the control of nanostructural defects is important for the development of nanosize devices of perfect quality.

The obtained results unambiguously demonstrate the change of optical properties of CdS nanocrystals as the result of improvement of their stoichiometry by curing of sulfur vacancies due to addition of sulfur into the crystal structure during the growth process or by the post-treatment of the grown nanocrystals. In spite of this clear illustration of the improvement of the lattice quality of CdS nanocrystals, the question of the origin of defects is still ambiguous to some extent and needs the further detailed study.

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## Вплив сульфування на оптичні властивості нанокристалів CdS

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**Анотація.** Досліджено оптичні властивості одновимірних нанокристалів сульфїду кадмію, синтезованих методом вирощування “пара–рідина–кристал”, як функцію від такого технологічного параметра, як надлишковий тиск пари сірки у процесі синтезу або додатковий відпал в атмосфері сірки вирощених кристалів (сульфування). Аналіз спектрів УФ-поглинання та фотолюмінесценції вказує на значну залежність оптичних параметрів нанокристалів CdS від ступеня компенсації сірки у процесі синтезу. Спектри фотолюмінесценції характеризуються зміною співвідношення інтенсивностей дефектної та крайової смуг при відпалі у парі сірки. Спостерігається зниження інтенсивності фотолюмінесценції дефектної смуги як у зразках, вирощуваних з додатковою компенсацією парою сірки, так і при використанні післяростової обробки у парі сірки. Край оптичного поглинання, розрахований за допомогою співвідношення Тауца, демонструє покращення кристалічної структури, що відображається збільшенням величини оптичної забороненої зони, наближаючись до величини для об’ємного матеріалу при затвердінні вакансій сірки різними технологічними підходами. Оптичні властивості, отримані за допомогою абсорбційних і люмінесцентних вимірювань, демонструють повну кореляцію, що відповідає технології.

**Ключові слова:** CdS, нанокристали, сульфування, поглинання, фотолюмінесценція, морфологія кристалів.