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**ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
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Effect of deposition time on the optical properties of CdSe nanostructured films

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Cadmium selenide nanostructured films were prepared using high-frequency magnetron sputtering method. All samples were deposited on quartz substrates in disk form with a radius of 16 mm. The temperature of the substrate was similar for all samples and kept at 180 °C. The deposition times were 3, 6, 9, 12 and 20 min. The effect of deposition time on the optical properties of CdSe nanostructured films were investigated by X-ray diffraction (XRD), optical absorption spectra (OAS), scanning electron microscope (SEM) and energy-dispersive X-ray analyzer (EDX). XRD analysis of the obtained samples exhibited a cubic structure with a preferred (200) orientation. The average crystallite size of the CdSe nanostructured films was determined using the Scherrer equation. The EDX shows that the CdSe nanostructured films are formed from the desired elements, and their distribution is uniform. SEM analysis shows that the surface morphologies of the CdSe nanostructured films were dependent on the deposition time. OAS was analyzed by the Tauc model. The absorption spectrum fitting (ASF) method was applied to estimate the optical band gap and Urbach energy of the CdSe nanostructured films. The optical band gap and Urbach energy was found to decrease with increasing deposition time.

Keywords: cadmium selenide, $A^{II}B^{VI}$, band gap, Urbach energy, absorption spectra.

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Introduction

CdSe is widely studied because of its industrial and biomedical applications. Cadmium selenide is a semiconductor with a direct band gap. The band gap energy for the bulk crystal of E_g= 1.74 eV at room temperature [1] is very close to the near-IR region. CdSe nanostructures have potential importance as nonlinear optical materials [1]. Nanocrystalline semiconducting materials of II–VI group (CdSe in particular) offer unique electronic and optical properties attributed to the so-called quantum confinement effects [2]. The optical properties of such compounds can be adjusted by altering the dimensions of the nanoparticles.

The influence of deposition time on the optical properties of $A^{II}B^{VI}$ films has also been investigated for other compounds, specifically for CdS [3], CdSe [4, 5], ZnTe [6], ZnS [7] and ZnSe [8]. In particular, Ref. [3] examined CdS thin films deposited by the chemical bath deposition (CBD) method. It demonstrated changes in crystallite size, optical band gap (Eg change from 2.4 to 2.22 eV), and optical absorption with deposition time. Regarding the CdSe compound, the effect of dip time on the optical and structural properties of CdSe films was investigated, in particular, the changes in optical band gap, specific conductivity, and morphology with increasing deposition time [4]. In contrast, Ref. [5] established the influence of synthesis time on the optical properties of colloidal CdSe nanoparticles, which is directly related to the variation of spectral characteristics over time. Depending on the type of synthesis, CdSe can result in three structure forms (wurtzite, sphalerite, and rock-salt). They have hexagonal and cubic structures, respectively [1]. It should be noted that no information was found regarding the effect of deposition time on the optical properties of CdSe nanostructured films deposited by high-frequency (HF) magnetron sputtering method and crystallized in the cubic structure. This constitutes the novelty of the present study.

The principal aim of the present work is to study the effect of deposition time on the optical properties of cadmium selenide nanostructured films. Therefore, to achieve the stated goal, the following experimental research methods were used: X-ray diffraction (XRD), optical absorption spectra (OAS), scanning electron microscope (SEM) and energy-dispersive X-ray analyzer (EDX). The chosen research methods are sufficient to determine the effect of deposition time on the optical properties of CdSe nanostructured films.

In this work, we use the absorption spectrum fitting (ASF) method to analyses the OAS, as in Ref. [9]. We note that this method requires only the measurement of the absorbance spectrum, and no additional information, such as the film thickness or reflectance spectra, is needed [9].

I. Details of experimental

CdSe nanostructured films were deposited on quartz substrates by a HF magnetron sputtering (~13.6 MHz) method using a VUP-5M vacuum station (Selmi, Ukraine). A single CdSe crystal disc of 99.99 % purity with a thickness of 2 mm and a diameter of 40 mm was used as a target. The target – substrate distance was 70 mm. The deposition time was 3, 6, 9, 12 and 20 min. Before the sputtering process, the chamber was evacuated. The gas pressure inside the chamber was 4×10^{-4} Pa. The sputtering was carried out at a pressure of argon between 1.0–1.3 Pa. The power of the HF magnetron was maintained at the level of 50 W and the temperature of the substrate at 180 °C.

The phase analysis and crystal structure refinement was examined with XRD obtained on DRON-2.0M diffractometer at room temperature with the Kα radiation (λ= 1.936087 Å) of Fe.

The surface morphology and elemental composition of the CdSe nanostructured films were studied using a Tescan VEGA 3 LMU SEM and equipped with an energy-dispersive X-ray analyzer (Oxford Instruments Aztec ONE with X-MaxN20). Before these measurements, Cu thin film with a thickness of 10 nm was deposited onto CdSe nanostructural films/quartz.

The spectral dependence of the OAS of the obtained samples in the visible regions is studied at room temperature (AvaSpec-ULS2048-UA-50 (Avantes)).

Deposited CdSe nanostructured films are composed of nanoparticles. Based on the Brus model [9, 10] with the Coulomb attraction (see equation (1)), the diameter (D= $2R$) of the quantum dot was determined.

$$E_g^{NP} = E_g^{bulk} + \frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e}+\frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon\varepsilon_0 R} \qquad (1)$$

where E_g^{NP} is band gap of the CdSe nanostructured film, E_g^{bulk} is the bulk band gap, and R is the radius of the quantum dot, m_e, m_h, and ε are electron mass, hole mass, and dielectric constant, respectively. The following fundamental parameters were used in this model for analysis of the CdSe nanostructured films: E_g^{bulk}= 1.74 eV [1], m_e= $0.13m_0$ [11], m_h= $0.3m_0$ [11], ε= 9.56 [11].

To determine the width of the synthesized CdSe nanostructured films, equation (2) was used [12].

$$E_g^{NP}=E_g^{bulk}\left(1+\frac{2d}{3h}\right) \qquad (2)$$

In equations (2), d is the diameter of an atom (d = 0.268 nm [12]), h is width of the film.

II. Results and Discussion

The surface morphology of the obtained CdSe nanostructured films with time depositions 3 and 12 min is shown in Fig. 1. Based on the analysis of these results, average grain size (diameter) was determined, as presented in Table 1. As a result, we can see an increasing average grain size with increasing deposition time ($|t|$).

Table 1.

Results of the EDX analysis of the CdSe nanostructured films

t, min	Cd, at.%	Se, at.%	Range of the grain size, nm
3	42.01	57.99	60–190
6	45.46	54.54	110–300
9	42.07	57.93	130–340
12	45.30	54.70	80–570

EDX analysis gives the chemical composition of CdSe nanostructured films (see Fig. 2). The spectra show that the sample is formed from the desired elements (Cd–Se). The identified Si and O based on the results of EDX analysis are attributed to the contribution of the substrate. Also, the chemical composition obtained from EDX spectroscopy is listed in Table 1.

As reported above (see Introduction section), CdSe can crystallize in hexagonal or cubic structures. Crystal structure of CdSe nanostructured films has been determined from XRD (see Fig. 3). All synthesized CdSe nanostructured films are crystallized in a cubic structure. This is confirmed by the presence of a single intense peak in the 2θ ~ 32° region for all samples. This peak is characteristic of the cubic structure rather than the hexagonal one.

It was observed from the XRD pattern that the largest intensity of the reflex corresponds to the (200) plane for all samples. All other observed peaks are suppressed compared to (200). The observed insignificant noise can be explained by reflexes from the substrate.

The crystallite size (D_{XRD}) was estimated from the peaks broadening using Scherrer's equation [13]:

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (3)$$

where λ is the wavelength of X-rays, β is full width at half maximum (FWHM) and θ is the Bragg's angle.

The crystallite sizes obtained from XRD are listed in Table 2. The D_{XRD} was found to increase with increasing deposition time. This behavior is typical and expected, as an increase in deposition time leads to the formation of a continuous, thick polycrystalline film with physical parameters close to those of the CdSe bulk sample.

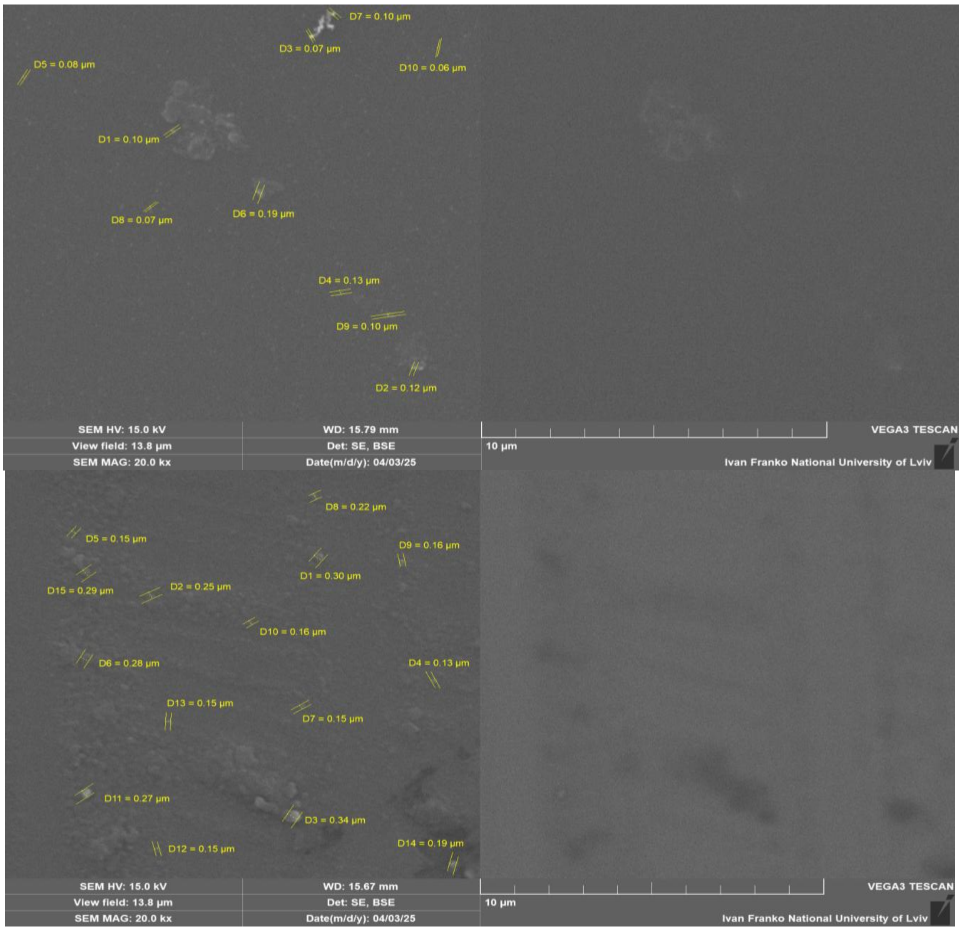

Fig. 1. Surface morphology of the CdSe nanostructured films (time deposition: top – 3 min, bot – 12 min).

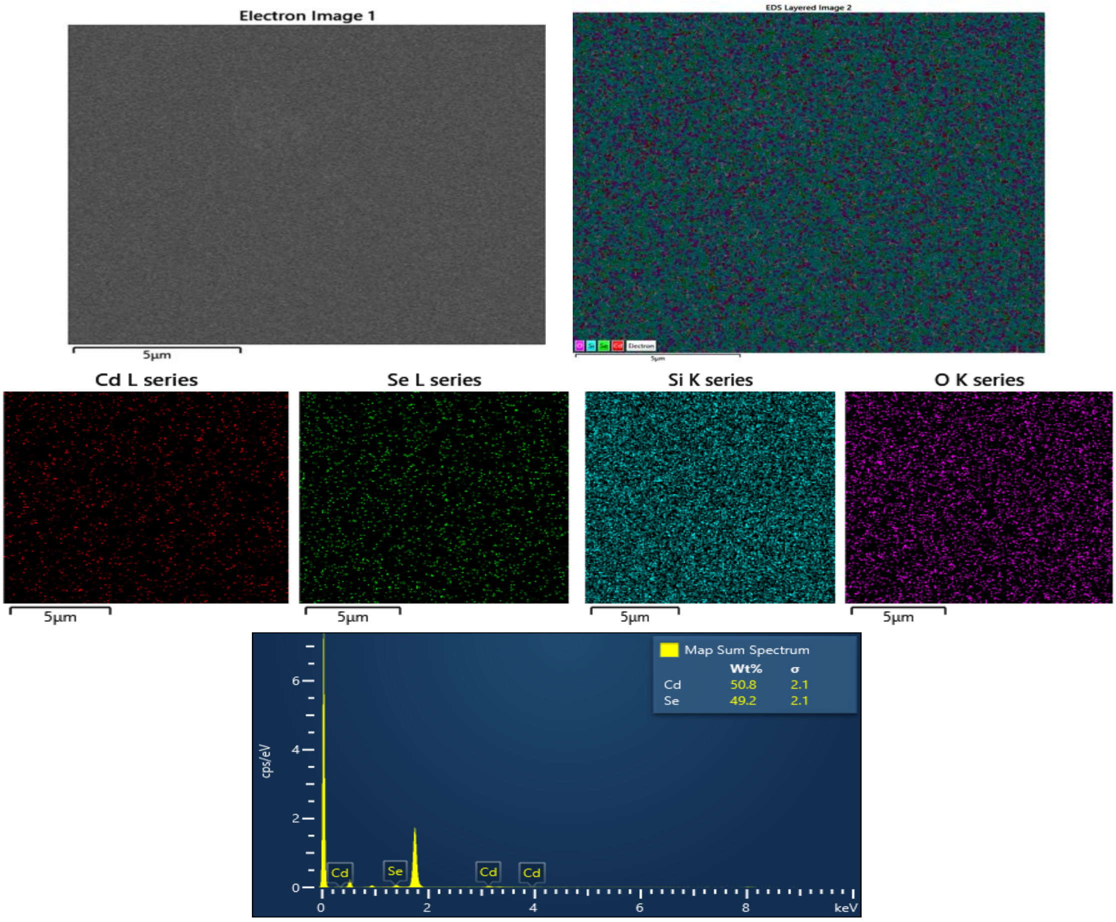

Fig. 2. Surface morphology of the Cu(10 nm)/CdSe nanostructured films/quartz (time deposition – 3 min).

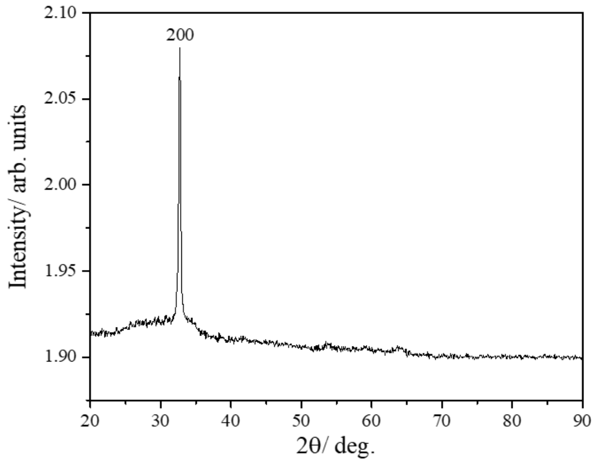

Fig. 3. XRD pattern of CdSe nanostructured films (time deposition – 6 min).

Table 2.

Results of the XRD analysis of the CdSe nanostructured films

t, min	*hkl*	2Θ, deg.	β	D_{XRD}, nm
6	200	32.69566	0.42011	0.49±0.01
9	200	32.90262	0.3771	0.55±0.01
12	200	32.62435	0.36682	0.57±0.01
20	200	32.82274	0.23803	0.87±0.01

Fig. 4 shows the optical absorption spectra of the CdSe nanostructured films. From Fig. 4, we can see a decrease in the absorption with the increase in wavelength and a change in slope or reverse behavior near 700–850 nm. In semiconductors, the relation between absorption coefficient and photon energy [14] is used:

$$\alpha(v)hv = B\left(hv - E_g\right)^m. \qquad (4)$$

α, E_g, *B*, and h*v* are the absorption coefficient, optical gap, constant, and incident photon energy, respectively. But to analyze absorption spectra using equation (4) we need to know the thicknesses of the sample (according to Beer-Lambert's law: $\alpha(v) = [2.303\mathrm{Abs}(\lambda)]/d_{\mathrm{film}}$, where d_{film} – thickness of the films). CdSe nanostructured films are studied, and determining their thickness using a mechanical method (by profilometer) or other method is a problem. Considering this, we have chosen the absorption spectrum fitting (ASF) [9] method (see Fig. 5).

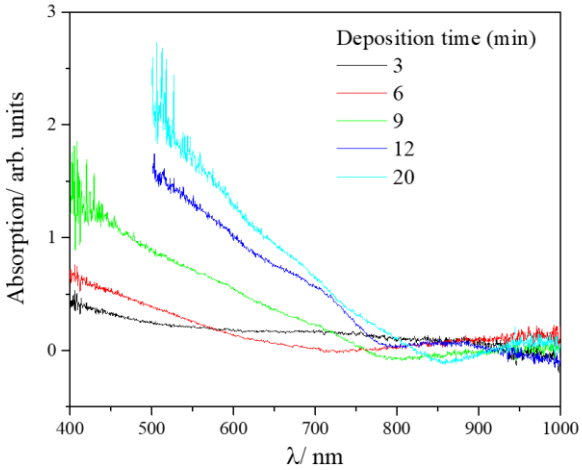

Fig. 4. Optical absorption spectra of the CdSe nanostructured films with different deposition times.

The optical band gap can be obtained by the linear extrapolation of the plot $(\mathrm{Abs}(\lambda)/\lambda)^{1/m} = f(\lambda^{-1})$ at $(\mathrm{Abs}(\lambda)/\lambda)^{1/m} = 0$ (see Fig. 5). By using the least squares technique (R^2), it was observed that the best fitting occurs for $m = 1/2$.

The optical band gaps (E_g) obtained for the CdSe nanostructured films are listed on Fig. 6 and in Table 3. The least squares method ($R^2 = 0.981 - 0.994$) was employed to calculate the E_g values.

We can see that the optical band gap is decreased by increasing the deposition time. This is connected with increasing particle size with increasing deposition time. This is confirmed with results of the XRD and morphological analysis of the CdSe nanostructured films.

The values of Urbach energy (E_U) were obtained from the slope of the linear region of the *ln*(Abs(λ))= $f(\lambda^{-1})$ curves (see Fig. 7) using the equation $E_U = 1239.83/\mathrm{slope}$. Urbach energy obtained for the CdSe nanostructured films are listed in Table 3. Also, as for optical band gap, Urbach energy is decreased by increasing the deposition time. This means that with increasing deposition time of CdSe nanostructured films was decreases the energetic disorder and the increasing sharpness of the absorption edge.

Based on the energy properties (E_g), the size parameters (*D* diameter of the quantum dot and *h* width of the film) of the CdSe nanostructured films was obtained with using equations (1) and (2).

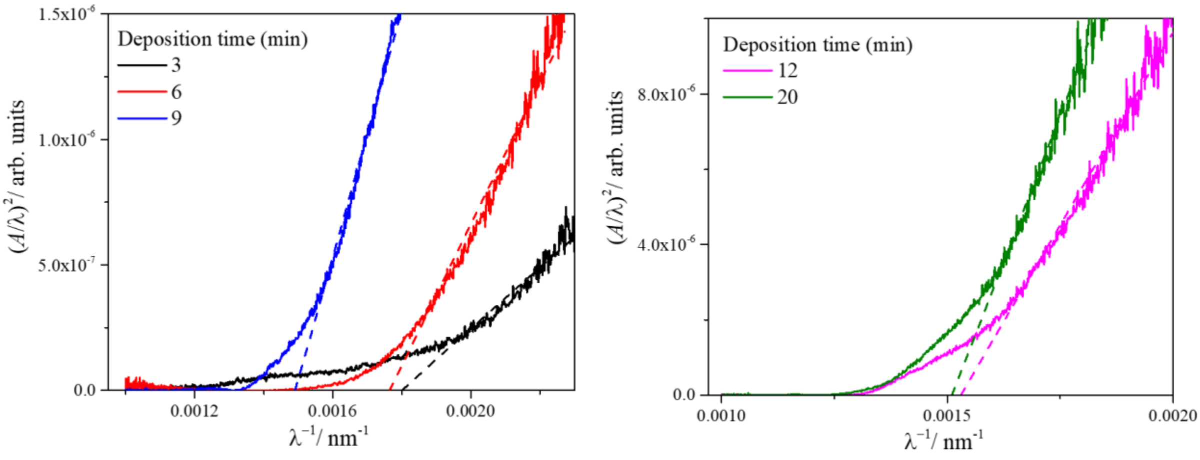

Fig. 5. ASF plots for CdSe samples with different deposition times.

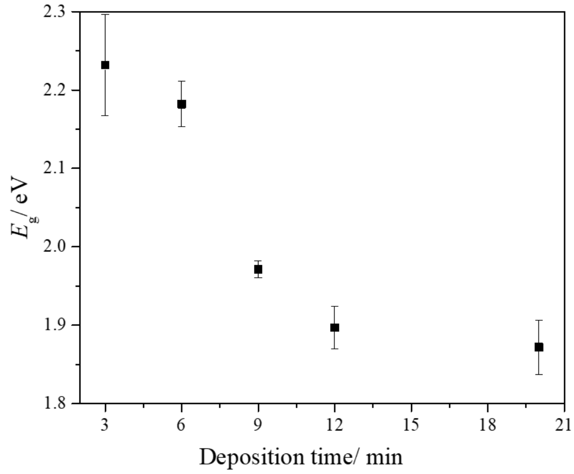

Fig. 6. Dependence of the optical band gap vs. deposition time for CdSe nanostructured films.

Table 3.

Optical band gap and Urbach energy for CdSe nanostructured films

t, min	E_g, eV	E_U, eV
3	2.23±0.07	1.32±0.04
6	2.18±0.03	1.22±0.02
9	1.97±0.01	1.20±0.01
12	1.90±0.03	1.20±0.02
20	1.87±0.04	0.60±0.02

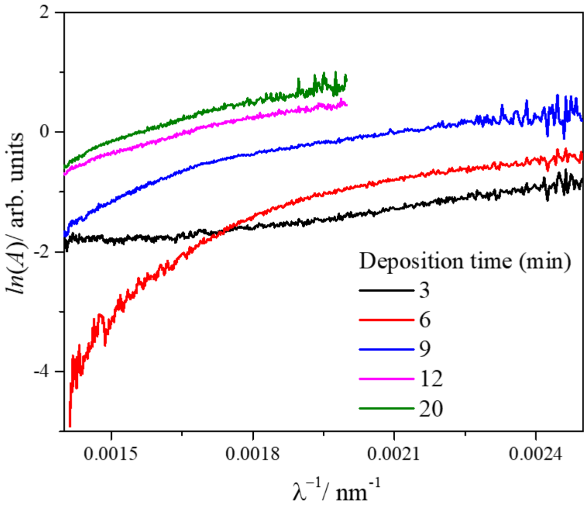

Fig. 7. Plots of $ln(\mathrm{Abs}(\lambda))$ vs. (λ^{-1}) for CdSe samples with different deposition times.

Fig. 8 shows the correlation of the optical band gap energy (E_g) and size parameters of the CdSe nanostructured films. It is important that the decreasing value of the optical band gap is observed with the increases of the size parameters (D and h). These dependencies are not linear, being rather described by a quadratic function (see the legend of Fig. 8). Also, we note that the experimental value of the optical band gap and its dependence on the width of the film (h) show a good relation with the theoretical results [12].

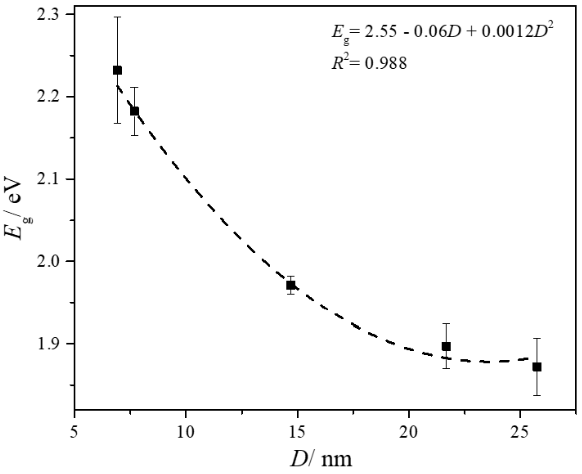

Fig. 8. Dependence of the optical band gap vs. D diameter of the quantum dot (top) and h width of the film (bot) for the CdSe.

Finally, the summary of the experimental results of the size parameters obtained from XRD and OAS analysis is in Table 4.

The analysis of the results above reveals that the observed decrease in optical band gap energy with increasing crystallite size (film thickness, deposition time) is consistent with trends reported for other compounds within the $A^{II}B^{VI}$ group [3, 15–18]. Specifically, the study by [15] demonstrated the impact of deposition time on the optical properties of ZnSe thin films deposited via the chemical bath deposition method. It was shown that the optical band gap of ZnSe decreases as deposition time increases, concomitant with an increase in crystallite size [15]. Comparable behavior of these parameters was observed in the present study for the CdSe deposited by the HF method. The similarity in the influence of deposition time on fundamental energy parameters corroborates the validity and robustness of the employed ASF method for analysis of the optical absorption spectra.

Conclusion

In the present investigation, CdSe nanostructured thin films were deposited onto quartz substrates using the HF method, with controlled variation of the deposition duration. The influence of deposition time on the optical, structural, and morphological properties of CdSe nanostructured films has been systematically investigated using a range of advanced characterization techniques. Analysis of the SEM morphology and EDX analysis confirms that the thin film is composed of the intended elements, exhibiting a homogeneous spatial distribution. XRD analysis revealed that the deposited films exhibit a nanocrystalline structure. XRD analysis indicates that all samples possess a cubic phase, with a dominant crystallographic orientation along the (200) plane. Furthermore, an increase in deposition time was found to result in a corresponding increase in crystallite size (D_{XRD}). Estimation of the optical band gap and Urbach energy was carried out using the ASF method, based on the theoretical framework provided by the Tauc model. With increasing deposition time, a reduction in the optical band gap and

Urbach energy was observed, indicating modifications in the electronic structure and disorder of the films. This behavior is ascribed to the growth in particle size. Ultimately, it can be inferred that CdSe nanostructured films possess characteristics favorable for utilization in optical device technologies.

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Вплив часу осадження на оптичні властивості наноструктурованих плівок CdSe

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Наноструктуровані плівки селеніду кадмію були отримані методом високочастотного магнетронного розпилення. Зразки були нанесені на кварцові підкладки у формі диска з радіусом 16 мм. Температура підкладки була однаковою для всіх зразків і підтримувалася на рівні 180 °C. Час осадження становив 3, 6, 9, 12 та 20 хвилин. Вплив часу осадження на оптичні властивості наноструктурованих плівок CdSe досліджували за допомогою X- променевої дифракції (XRD), оптичних спектрів поглинання (OAS), сканyючого електронного мікроскопа (SEM) та енергодисперсійного рентгенівського аналізатора (EDX). За результатами аналізу X- променевих дифрактограм синтезованих зразків було встановлено, що вони володіють кубічною структурою з переважною орієнтацією (200). Середній розмір кристалітів наноструктурованих плівок CdSe визначали за допомогою рівняння Шеррера. EDX показує, що наноструктуровані плівки CdSe утворюються з бажаних елементів, а їх розподіл є рівномірним. SEM-аналіз показує, що морфологія поверхні наноструктурованих плівок CdSe залежала від часу осадження. OAS було проаналізовано за моделлю Тауца. Для оцінки ширини оптичної забороненої зони та енергії Урбаха наноструктурованих плівок CdSe було застосовано метод апроксимації спектра поглинання (ASF). Було виявлено, що ширина оптичної забороненої зони та енергія Урбаха зменшуються зі збільшенням часу осадження.

Ключові слова: селенід кадмію, $A^{II}B^{VI}$, заборонена зона, енергія Урбаха, спектри поглинання.