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Effect of deposition time on the optical properties of CdSe nanostructured films

Andrii Kashuba[1], Hryhorii Ilchuk[1], Vasyl Kordan[2], Ihor Semkiv[1], Myron Rudysh[2], Mykola Solovyov[1]

[1]Lviv Polytechnic National University, Bandera Str. 12, 79013 Lviv, Ukraine

[2]Ivan Franko National University of Lviv, Kyrylo & Mephodiy Str. 8, 79000 Lviv, Ukraine

INTRODUCTION & AIM

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].

METHOD

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)).

RESULTS & DISCUSSION

The surface morphology of the obtained CdSe nanostructured film with time depositions 3 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	D_{XRD}, nm
3	42.01	57.99	60–190	-
6	45.46	54.54	110–300	0.49±0.02
9	42.07	57.93	130–340	0.55±0.01
12	45.30	54.70	80–570	0.57±0.01

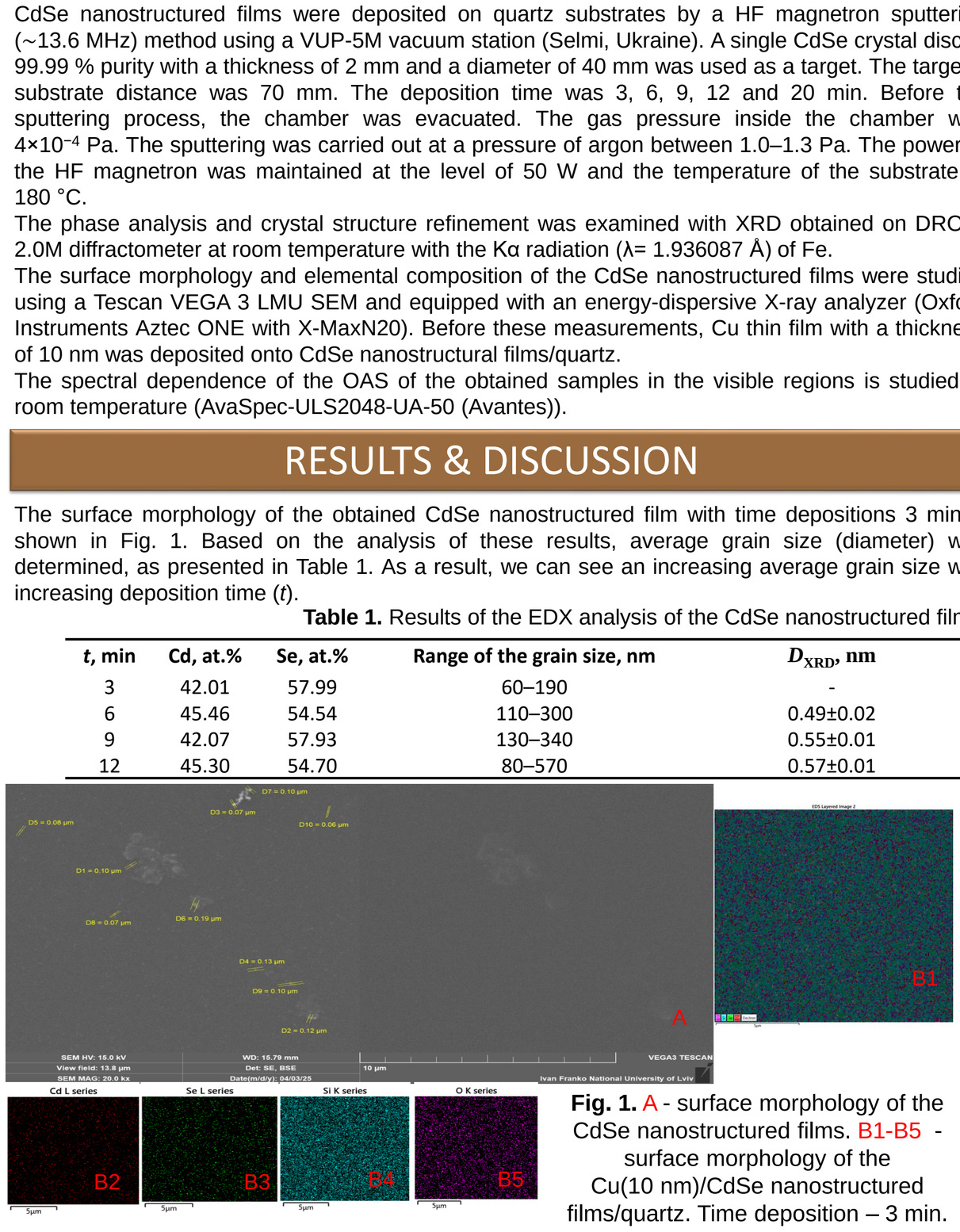

Fig. 1. A - surface morphology of the CdSe nanostructured films. B1-B5 - surface morphology of the Cu(10 nm)/CdSe nanostructured films/quartz. Time deposition – 3 min.

Fig. 2(A) shows the optical absorption spectra of the CdSe nanostructured films. From Fig. 2(A), 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. The optical band gap can be obtained by the linear extrapolation of the plot $(Abs(\lambda)/\lambda)^{1/m}= f(\lambda^{-1})$ at $(Abs(\lambda)/\lambda)^{1/m}= 0$ (see Fig. 2(B1 and B2)). 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. 2(C). The least squares method (R^2= 0.981−0.994) was employed to calculate the E_g values. The values of Urbach energy (E_U) were obtained from the slope of the linear region of the $ln(Abs(\lambda))= f(\lambda^{-1})$ curves (see Fig. 2(D)) using the equation E_U= 1239.83/slope.

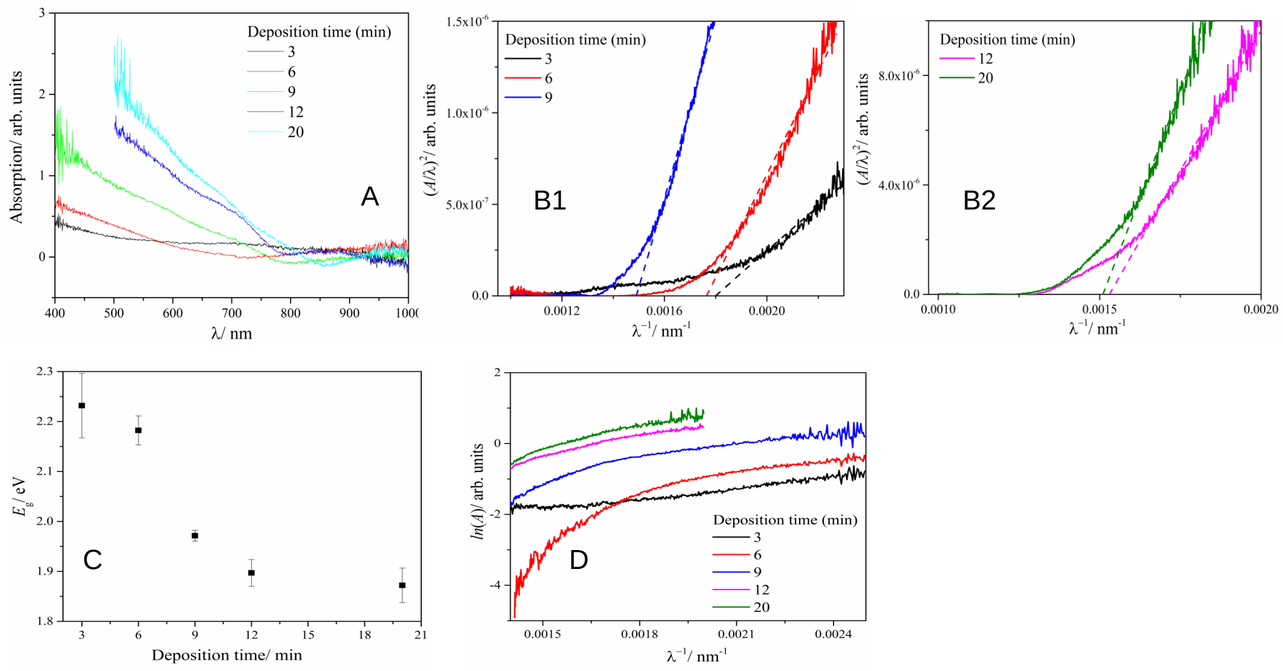

Fig. 2. A - Optical absorption spectra of the CdSe nanostructured films with different deposition times. B1 and B2 - ASF plots for CdSe samples with different deposition times. C - Dependence of the optical band gap vs. deposition time for CdSe nanostructured films. D - Plots of $ln(Abs(\lambda))$ vs. (λ^{-1}) for CdSe samples with different deposition times.

Urbach energy and optical band gap obtained for the CdSe nanostructured films are listed in Table 2. 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.

Table 2. 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

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. All samples were deposited on quartz substrates in disk form with a radius of 16 mm. The temperature of the substrate was maintained at 180 °C for all samples. The deposition times were 3, 6, 9, 12 and 20 min. The effect of deposition time on the optical properties of CdSe nanostructured films was investigated by X-ray diffraction (XRD), optical absorption spectra (OAS), scanning electron microscope (SEM) and energy-dispersive X-ray analyser (EDX). 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. 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 [10].

FUTURE WORK / REFERENCES

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