

## Chemical surface deposition of Cd(S,Se) films: influence of the starting cadmium-containing salt on microstructure and optical properties

Ruslana GUMINILOVYCH<sup>1\*</sup>, Pavlo SHAPOVAL<sup>1</sup>, Iosyp YATCHYSHYN<sup>1</sup>, Victor KUSNEZH<sup>2</sup>, Hryhorii IL'CHUK<sup>2</sup>, Martyn SOZANSKIY<sup>3</sup>

<sup>1</sup> Department of Analytical Chemistry, Lviv Polytechnic National University, S. Bandera St. 12, 79013 Lviv, Ukraine

<sup>2</sup> Department of Physics, Lviv Polytechnic National University, S. Bandera St. 12, 79013 Lviv, Ukraine

<sup>3</sup> Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

\* Corresponding author. e-mail: guminilovych@gmail.com

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**The influence of the nature of the initial cadmium-containing salt on the structure, microstructure, morphology and optical properties of semiconductor CdS and CdSe films, obtained by chemical surface deposition (CSD), was studied. Transmission and absorption optical spectra and the surface morphology of the films were investigated. The obtained films are characterized by the availability of a fundamental absorption edge, which is formed by direct interband optical transitions. The results of the study of the surface morphology by atomic force and scanning electron microscopy showed that the conglomerates on the surface coatings are CdS and CdSe particles with different stoichiometry than the film. The content of cadmium ions in the obtained coatings was determined by inversion voltammetry. The thickness of the semiconductor films was calculated from the mass of cadmium. The possibility of producing stable CdS and CdSe films, suitable for solar cells based on heterojunctions, was demonstrated.**

**Semiconductor films / Chemical surface deposition / Structure and morphology of thin films / Atomic force and scanning electron microscopy**

### Introduction

At the present stage of development of photosensitive thin film heterostructures based on cadmium chalcogenides Cd(S,Se,Te), the demands for specific surface properties of the semiconductors, e.g. surface roughness, purity, homogeneous distribution of surface macrodefects over large areas, have sharply increased. This is due to the fact that the surface morphology of the films determines the electrophysical properties of the interface.

The structure of a film differs from the structure of the bulk material of similar composition and can vary depending on the preparation conditions. The processes of obtaining epitaxial films are related with the interaction of the atoms of the deposited compound with the substrate surface. Complex processes occur at the boundary, which affect the mechanism of the film deposition, the adhesion to the substrate, the character of nucleation and the film growth. All of these can be the cause of changes in the

geometry, optical and electrical properties of the interface at the local and global levels.

The interconnections between the compositional, morphological, optical, and electrical properties, structure and microstructure of semiconductor films, determine the dependence of the properties on the method of preparation and the parameters of the deposition process. The establishment of such regularities creates the preconditions for the tailored synthesis of semiconductor epitaxial films with predetermined properties. Therefore it is important to carry out studies of the surface properties of semiconductor films under different conditions and at different stages of their preparation.

A powerful method, both for the investigation and for the rapid analysis of the surface of semiconductor films of cadmium chalcogenides Cd(S,Se) is atomic force microscopy (AFM). This technique is characterized by a high resolution that is inherent to electronic and scanning tunneling microscopes, but simultaneously does not require the same complex

preparation of samples and the mandatory electrical conductivity. Compared with the electron microscopy, AFM allows reconstructing the three-dimensional topography of the selected area with nanometer resolution, making it possible to investigate, together with the morphology, the electrophysical characteristics of the surface.

## Experimental

CdS and CdSe semiconductor films can be obtained by many methods. A technologically convenient way to obtain them is the method of chemical surface deposition (CSD) [1]. Compared with other methods, it allows carrying out the deposition at temperatures below 100°C on large-sized substrates of different nature, using different combinations of starting substances.

CdS and CdSe films were obtained from the following cadmium-containing salts: cadmium chloride (CdCl<sub>2</sub>), cadmium iodide (CdI<sub>2</sub>), cadmium acetate (Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O), cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O), cadmium sulfate (CdSO<sub>4</sub>·8/3H<sub>2</sub>O). In addition to the selected cadmium-containing salt, the following compounds were included in the composition of the working solution: for the deposition of cadmium sulfide (CdS) films – thiourea CS(NH<sub>2</sub>)<sub>2</sub> and ammonium hydroxide NH<sub>4</sub>OH, and for the deposition of cadmium selenide (CdSe) films – sodium selenosulphate Na<sub>2</sub>SeSO<sub>3</sub>. Sodium selenosulphate was prepared by dissolving powdered selenium in an aqueous solution of sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) at 60°C and maintaining constant stirring for 3 h. After the ending of the reaction and cooling, the solution was filtered. The concentration of the cadmium-containing salt was equal to 0.02 M, that of thiourea 1.0 M, sodium selenosulphate 0.1 M. The deposition time was 3 minutes. The temperature for CSD was 70°C.

The deposition was carried out on a pre-prepared and thermostated glass substrate with an area of 3.96 cm<sup>2</sup>, by the method described in [2,3]. The dosed causing of the working solution ensured uniform heating of the surface substrate and, therefore, uniform deposition of the films. The substrate was eliminated after heating; the surface was washed with a jet of distilled water and dried in air.

The investigation of the surface morphology of the films was carried out using a scanning electron microscope EVO-40XVP (Carl Zeiss, Germany) with a system of microanalysis INCA Energy 350 (Oxford Instruments, England) and an atomic force scanning probe microscope Solver P47 PRO (NT-MDT, Russia). AFM investigations were carried out by the semicontact and by the contact methods with a scan frequency of 1 Hz, using a silicon probe of type 10 NSG A with a radius of curvature of the tip of 10 nm. All the investigations were carried out in air. The processing of the experimental data and the

calculation of the parameters of the surface morphology were carried out using the software package Image Analysis 2 (NT-MDT, Russia).

Absorption-transmittance optical spectra of CdSe and CdS films were obtained with a spectrophotometer AvaSpec-ULS2048 (Avantes, Netherlands). A comparative signal was passed through a substrate identical to the substrates used for the investigated films.

The quantity of CdS and CdSe in the obtained films was determined by the method of stripping voltammetry (analyzer AKV-07 MK, Akvilon, Russia). The experiment was designed based on [4-7].

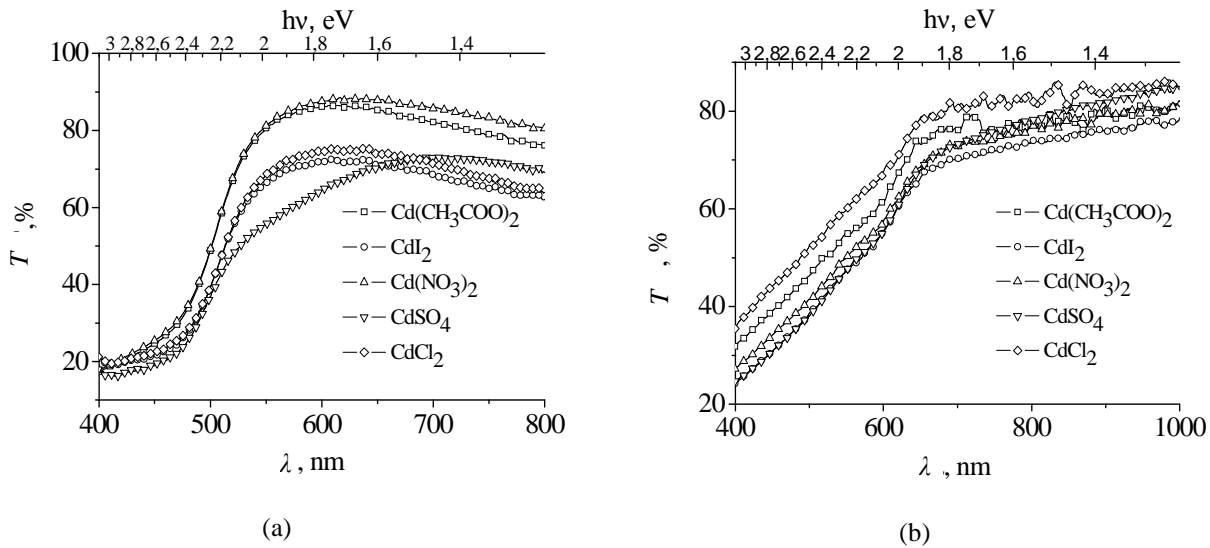
From to the values obtained for the mass concentration of cadmium, the area of the substrate and tabulated data for the density of CdS and CdSe, the thickness of the films was calculated, without taking into account roughness, by the method of [8].

## Results and discussion

CdS and CdSe films in photosensitive batteries perform the function of a layer that transmits the incident radiation into the region of generation of charge carriers. Therefore, the optical properties of these films have a direct effect on the efficiency of the photoconversion. After completion of the CSD process, the working surface of the substrates was covered by continuous films with a characteristic yellow-green color for CdS and red-orange color for CdSe. The spectral dependences of the optical transmittance in the visible and near-infrared region confirmed the existence of the compounds CdS and CdSe in all of the films (Fig. 1).

For all the samples an increase of the transmittance (*T*) was observed in the transition from the short-wave to the long-wave region. The maximum values of transmission were achieved in the neighborhood of 550-600 nm and were within 72-88% for the deposition of CdS films (Fig. 1a), depending on the nature of the starting cadmium-containing salt. The transmission *T*(λ) reached the maximum values for films deposited from cadmium acetate (86%) and cadmium nitrate (88%), whereas for the other films it was at the level of 75%. The smallest value of transmittance was observed for the films obtained from cadmium sulfate.

For the deposition of CdSe (Fig. 1b), the maximums of transmission were shifted to the long-wavelength region. Their absolute values were close to the values of transmission of CdS and varied in the range from 69 to 86%. There is an obvious predominant absorption in the vicinity of 650 nm, close to the band gap of CdSe (1.8-2.0 eV). The coefficient *T*(λ) in the region of fundamental transmission takes maximum values for the films deposited from cadmium chloride and cadmium acetate. The smallest values of transmittance, as in the



**Fig. 1** Optical transmittance spectra of CdS (a) and CdSe (b) films for different starting materials.

case of CdS, were obtained for the films prepared from cadmium sulfate.

For the CdSe films the nature of the change in the transmission is not the same as for the CdS films. In the case of CdS the sharp increase of the transmittance near the transition from the short- to the long-wavelength region, ends with a pronounced maximum at the beginning of the long-wave region, then the transmittance begins to decrease linearly. For the CdSe films the increase of transmittance is not so sharp, has no maximum, and increases in the long-wave region.

The spectral dependences of the absorption of the CdS and CdSe films in the coordinates  $(\alpha \times hv)^2 - hv$  demonstrate the availability of the fundamental absorption edge. The extrapolation of the linear parts of the curves  $(\alpha \times hv)^2$  to the intersection with the energy axis was used to define the optical band gap of the films (Table 1) [9].

The linear character of the dependence  $(\alpha \times hv)^2 = f(hv)$  in the range 2.35-2.41 eV for the CdS films (Fig. 2a) and 1.85-1.90 eV for CdSe (Fig. 2b), points to the formation of an absorption edge by direct interband optical transitions and is consistent with literature data [10,11]. The long-wavelength edge of the curves of absorption (Fig. 2b) indicates the possible existence of impurity and defect energy levels in the band gap semiconductor of the CdSe films. This behavior may be caused by the availability of defects, both in the volume and on the surface of the film, which arise from the contamination of the films by impurities. The quantity of impurities depends on the nature of the starting substances and on the mechanism of deposition.

Straight-line behavior of the graphs  $(\alpha \times hv)^{2/3} - hv$  (direct forbidden transitions),  $(\alpha \times hv)^{1/2} - hv$  (indirect allowed transitions),  $(\alpha \times hv)^{1/3} - hv$  (indirect forbidden transitions) was not observed. These graphs (not presented here) confirm the formation of an absorption

edge of direct allowed interband transitions. In addition, the band gap was determined by the location of the maximum in the curve dependence of the first derivative of the transmission  $dT(\lambda)/d\lambda$  of  $\lambda$ .

When using CSD, the film deposition proceeds *via* heterogeneous nucleation of the compound on the substrate surface during heat transfer to the working solution. The deposition of CdS thin films from aqueous solutions pass through the formation of a complex ion of tetraamine cadmium  $[Cd(NH_3)_4]^{2+}$  [12], and, for CdSe films, of a complex anion of selenosulfate  $[Cd(SeSO_3)_2]^{2-}$  in an alkaline medium by a heterogeneous mechanism [13,14].

A solution of ammonium hydroxide was used as complexing agent for CSD of CdS films. Attempts to obtain CdSe films according to the technique used to obtain CdS, were not successful. Addition of ammonium hydroxide to the working solution increased the minimum deposition time and a small amount of working solution leads to its drying. Reducing the CSD temperature and, accordingly, increasing the deposition time led to the formation of not continuous surfaces and a large amount of CdSe in the working solution. So, we abandoned the use of ammonia as a complexing agent and used, for the deposition of CdSe films, a working solution consisting of a solution of the selected cadmium-containing salt and  $Na_2SeSO_3$ .

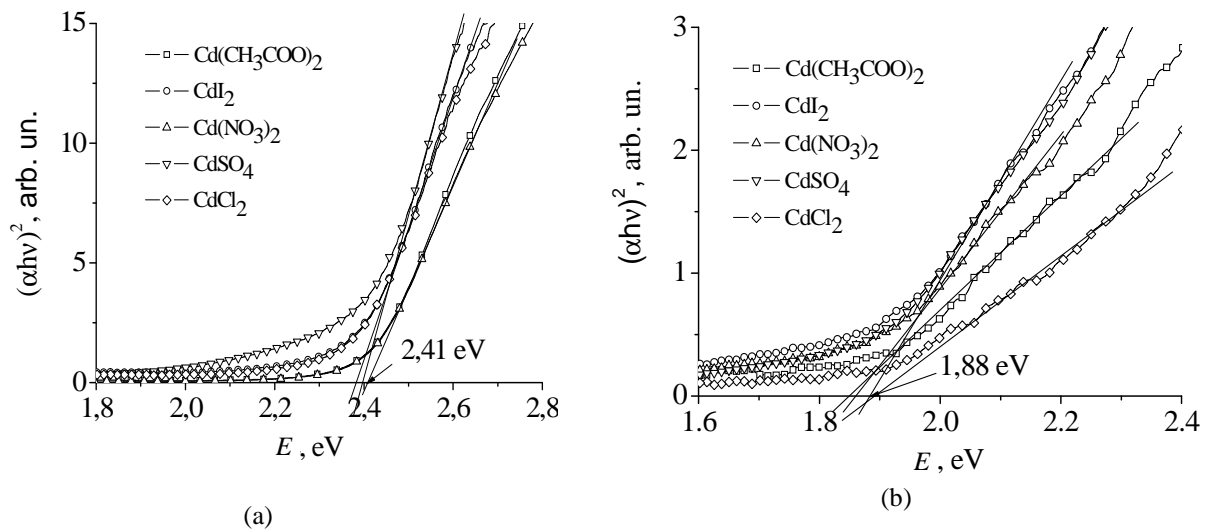
The mechanisms of the reactions given in [12-14] show that the deposition of sulfide and selenide films, passing through a stage with formation of coordination compounds, presents certain features. The inner sphere of the complexes may contain different anions depending on the composition of the working solution. In our case, the immediate environment of the cadmium atoms can be atoms of sulfur, halogens and oxygen. The presence of defects affects both the film structure and the surface morphology.

**Table 1** Optical parameters of CdS and CdSe films.

Starting material	CdS					CdSe				
	T, %		E <sub>g</sub> , eV			T, %		E <sub>g</sub> , eV		
	λ = 450 nm	λ = 700 nm	(α×hv) <sup>2</sup> →0	dT/dλ	Average	λ = 450 nm	λ = 700 nm	(α×hv) <sup>2</sup> →0	dT/dλ	Average
Cd(CH <sub>3</sub> COO) <sub>2</sub>	25	86	2.41	2.47	2.42	39	76	1.85	–	1.85
CdI <sub>2</sub>	22	72	2.37	2.47	2.42	31	70	1.88	–	1.88
Cd(NO <sub>3</sub> ) <sub>2</sub>	26	88	2.41	2.46	2.42	34	73	1.86	–	1.86
CdSO <sub>4</sub>	19	64	2.38	2.43	2.41	31	73	1.88	–	1.88
CdCl <sub>2</sub>	22	75	2.40	2.46	2.42	44	80	1.89	–	1.89

**Table 2** Results of the analysis of AFM-images of CdS and CdSe film surfaces and thicknesses.

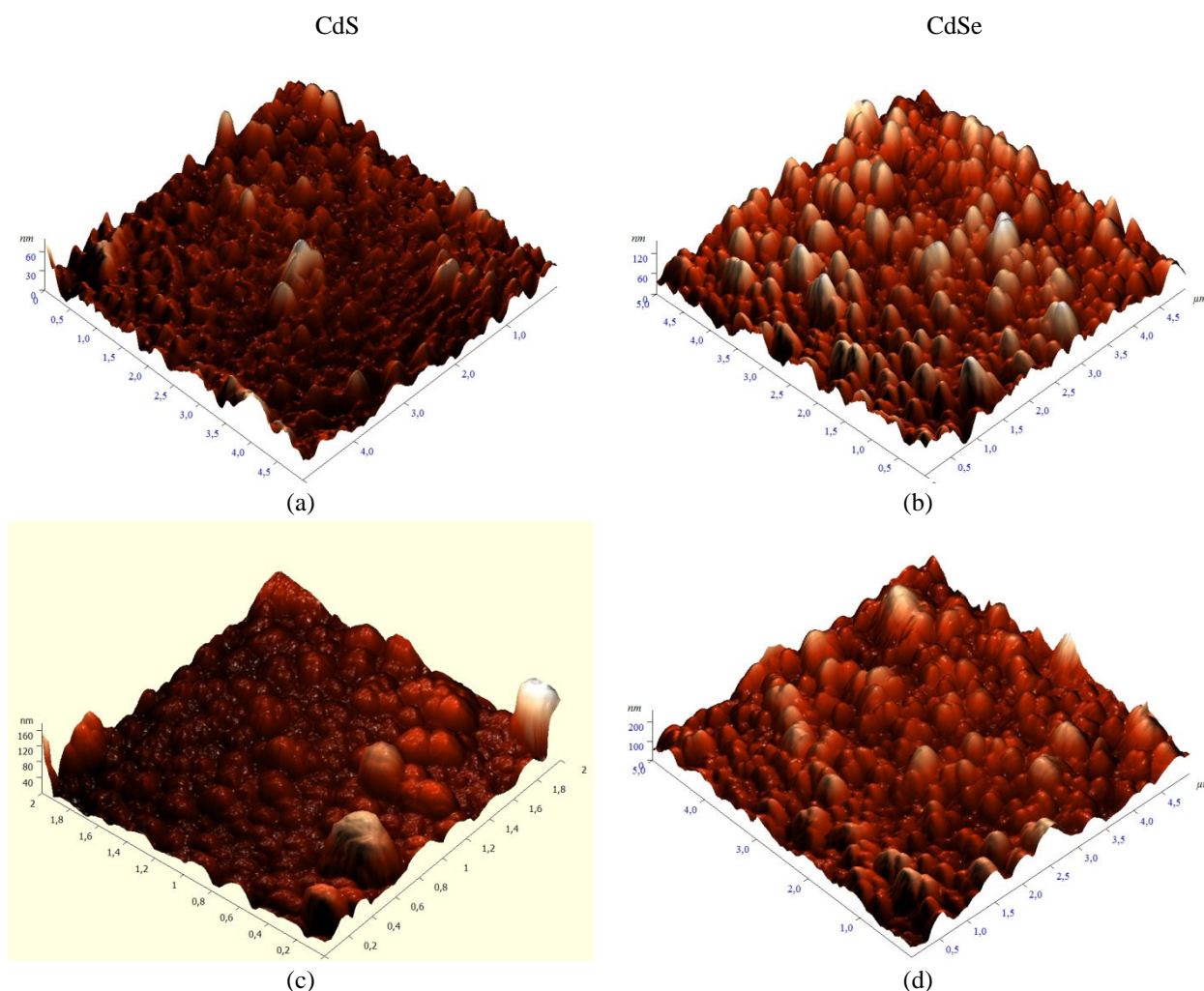
Starting material	CdS				CdSe			
	Average height, nm	Average roughness, nm	Mean diameter, nm	Thickness, nm	Average height, nm	Average roughness, nm	Mean diameter, nm	Thickness, nm
Glass	2.1	0.4	–	0	2.1	0.4	–	0
Cd(CH <sub>3</sub> COO) <sub>2</sub>	45.8	11.6	176	91.9	73.2	19.0	216	58.6
CdI <sub>2</sub>	80.8	18.6	196	86.8	107.5	29.0	255	67.6
Cd(NO <sub>3</sub> ) <sub>2</sub>	26.6	7.3	157	92.4	102.7	25.2	234	63.3
CdSO <sub>4</sub>	57.6	11.9	118	105.5	77.2	24.3	275	56.5
CdCl <sub>2</sub>	40.8	9.8	55	108.8	134.2	31.6	294	72.7

**Fig. 2** Absorbance spectra of CdS (a) and CdSe (b) films in  $(\alpha \times hv)^2 - hv$  coordinates.

In order to establish the effect of the conditions of the CSD on the structure and surface morphology of the films, the content of cadmium ions in the coatings was determined by the method of stripping voltammetry. Based on the obtained values, the average thickness of the CdS and CdSe films was calculated. Images of the deposited films were obtained by the AFM method, and the parameters of

the surface morphology were calculated from their analysis. The results are shown in **Table 2**.

Analysis of the surface morphology of the CdS and CdSe films (**Fig. 3**) and the calculated histograms of the height of the crystal grains over the total surface of the CSD films (**Fig. 4**) confirmed that the method of deposition and the nature of the starting cadmium-containing salt affect the structure of the films.



**Fig. 3** Three-dimensional AFM-micrographs of CdS and CdSe films, obtained from cadmium chloride (a, b) and cadmium nitrate (c, d).

In the case of deposition of CdS, the largest thickness of the deposited films at the lowest average values of grain size and of surface roughness was achieved when the salt  $\text{CdCl}_2$  was used for CSD. The lowest values of surface roughness were reached when using cadmium nitrate, but the average diameter of the grains on the surface was three times larger than for deposition from cadmium chloride. This difference is explained by the formation of conglomerates of large size on the surface of the films (Fig. 3) at the final stages of deposition.

For the deposition of CdSe, the dispersion of the average values of film thickness, surface roughness and grain size are much smaller than for the deposition of CdS. For all the samples, after deposition the thickness of the CdS films was 1.5-2 times larger than the thickness of the CdSe films obtained from the same starting salts. On the other hand, for almost all the samples of cadmium selenide, larger values of roughness and average diameter of the particles were observed. These results can be explained by adhesion of aggregates of colloidal particles in the solution to the surface of the CdSe films.

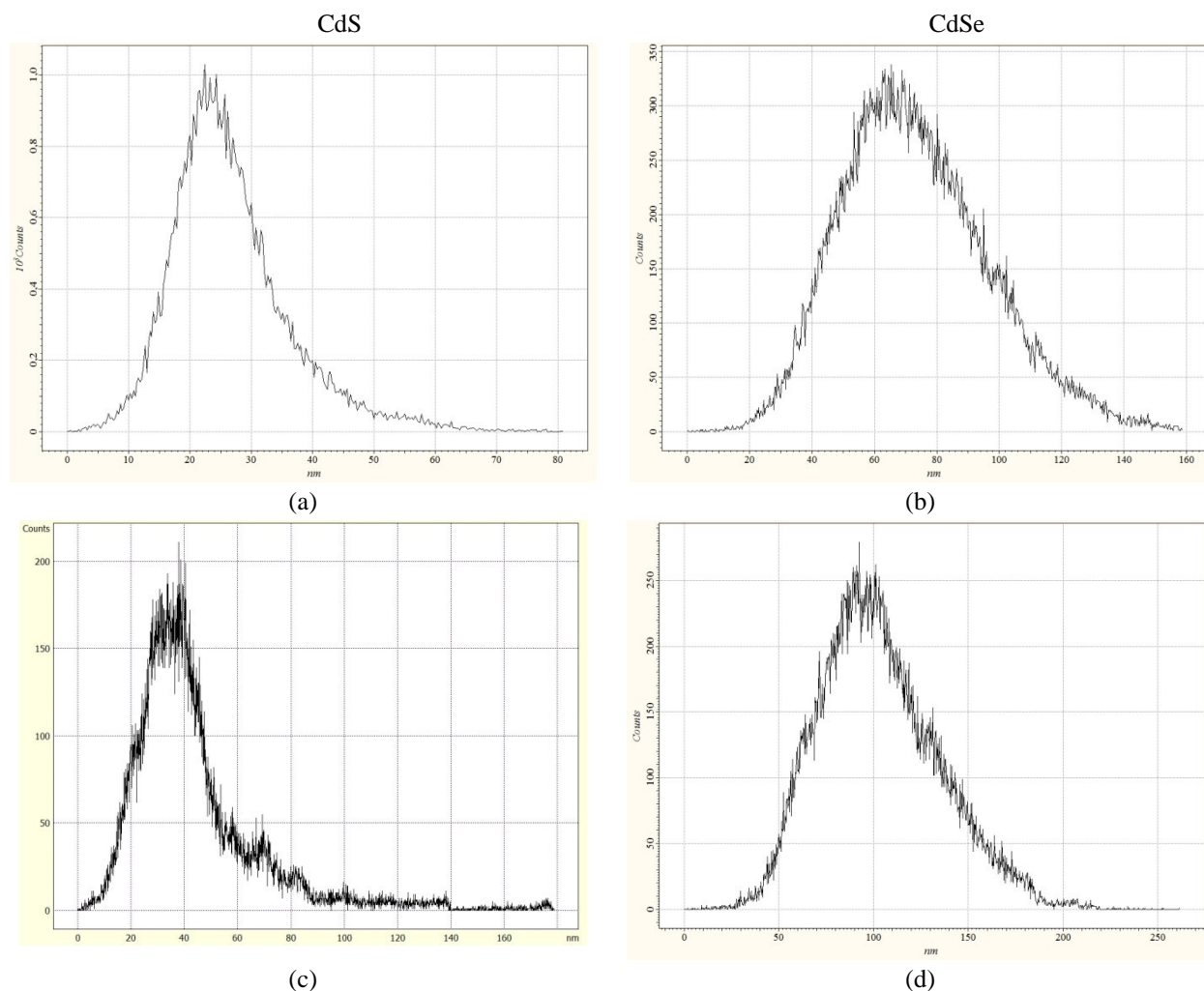
The investigation of the surface morphology of the films by scanning electron microscopy with a system of microanalysis confirmed the presence of impurities and two types of macrodefect: in the form of particle conglomerates and massive dendrites (Fig. 5). The CdS and CdSe films completely covered the substrate and were homogeneous and continuous over the whole area. The juxtaposition of images in the modes of reflected and secondary electrons (not shown here) confirmed that the excrescences of heavier phase were on the surface of the film.

The amount of particles on the surface was lower for deposited CdS than for CdSe. The results of the morphology and X-ray microanalysis showed that the formations on the surface were particles of CdS and CdSe with a different stoichiometry than in the films. The difference in stoichiometry between the particles and the film was conditioned by the presence of sulfur (Table 3).

Aggregates of colloidal particles are formed at the final stage of deposition when the film formation is terminated, as a result of the depletion of the boundary layer, and spontaneous formation of a deposit, which

**Table 3** Results of the microanalysis of the surface morphology of CdS and CdSe films.

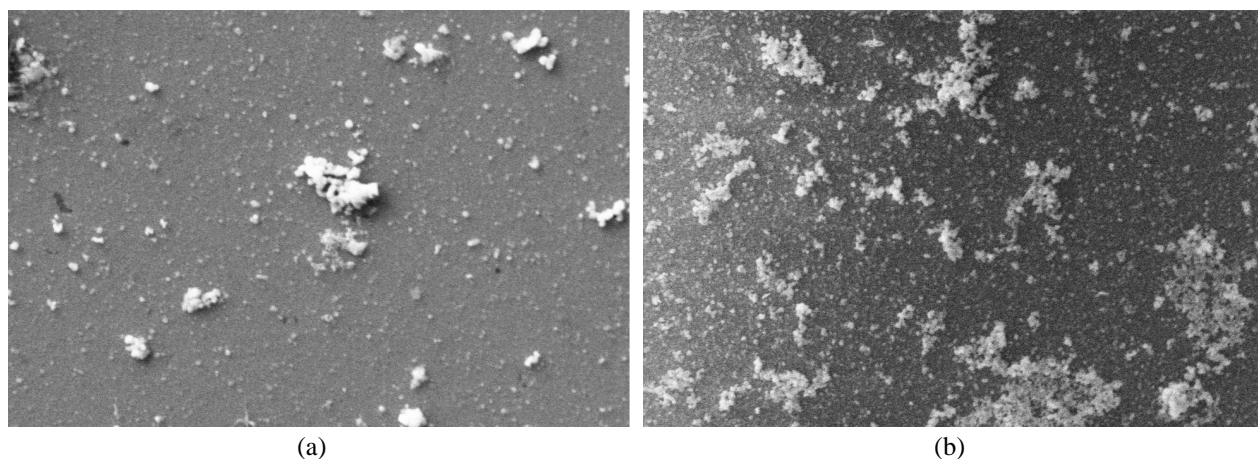
Compound	Component	Atomic %		Weight %	
		Surface	Grain	Surface	Grain
CdS	S	49.51	51.39	21.86	23.17
	Cd	50.49	48.61	78.14	76.83
CdSe	S	8.71	6.52	3.07	2.26
	Se	42.86	43.99	37.16	37.57
	Cd	48.43	49.48	59.77	60.16

**Fig. 4** Distribution of the height of the crystal grains (nm) in CdS and CdSe films, obtained from cadmium chloride (a, b) and cadmium nitrate (c, d), above the total zero level.

adsorbs onto the surface, becomes dominant. The larger amount of particles on the surface of the selenide films can be explained by the absence of a complexing agent that promotes the spontaneous formation of the deposit, because of the by several orders of magnitude lower value of the solubility product of CdSe compared to CdS. The problem concerning the choice of a complexing agent with which one can regulate the amount of free metal ions in the working solution during CSD of chalcogenides films, requires further investigations.

## Conclusion

The influence of the nature of the starting cadmium-containing salt on the structure, microstructure, morphological and optical properties of semiconductor CdS and CdSe films obtained by CSD, was investigated. The results of the study of the surface morphology by atomic force and scanning electronic microscopy revealed the formation of CdS and CdSe particles, having a different stoichiometry than the film, on the coating surface. The difference in



**Fig. 5** Surface morphology of CdS (a) and CdSe (b) films obtained from CdCl<sub>2</sub>.

stoichiometry between the particles and the film was conditioned by the presence of sulfur. The obtained continuous, stable films are suitable for making photosensitive semiconductor structures.

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