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SURFACE MORPHOLOGY AND OPTICAL PROPERTIES OF CdSe FILMS OBTAINED BY THE CLOSE-SPACED VACUUM SUBLIMATION TECHNIQUE

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Investigation of the surface morphology, growth mechanisms and optical properties of CdSe films obtained by the close-spaced vacuum sublimation (CSVs) technique, which are promising for use as the absorption layers of tandem solar cells and photodetectors, was carried out in the present paper. Measurements of the optical characteristics of the layers were performed by the spectrophotometric analysis method near the “red boundary” of semiconductor photoactivity. Performed investigations allowed to obtain the spectral distributions of the transmission $T(\lambda)$, reflection $R(\lambda)$, absorption $\alpha(\lambda)$, and refraction $n(\lambda)$ coefficients, and the real $\varepsilon_1(\lambda)$ and imaginary $\varepsilon_2(\lambda)$ parts of the optical dielectric constant of the samples and to define their dependence on the film deposition temperature.

Keywords: CADMIUM SELENIDE FILMS, SURFACE MORPHOLOGY, TRANSMISSION COEFFICIENT, REFLECTION COEFFICIENT, BAND GAP.

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1. INTRODUCTION

Cadmium selenide films are intensively studied due to their availability as the base layers of tandem solar cells, photo- and gas detectors, high-efficiency thin-film transistors, vidicons, green light-emitting diodes, lasers with electron-beam pumping, electroluminescent devices et al. [1-2].

Optimization of the structure, optical and electrophysical characteristics of CdSe films is necessary for the practical use of these films in micro- and optoelectronics. It is well known that these characteristics are determined by the method and physical and technological regimes of the condensate deposition [3-4].

Nowadays a lot of methods are used to obtain CdSe films, such as, aqueous solution pyrolysis [5], submersion in a chemical solution [6], electron-beam [7] and thermal [2, 8-11] evaporation, hot wall deposition [1] and CSVs technique [12]. Due to the structural features of evaporator the last method allows to obtain the stoichiometric films of multi-component semiconductors in the controlled technological process. And therefore the CSVs technique

found a wide application under deposition of A_2B_6 films [3, 13]. At the same time CdSe polycrystalline films, except of [12], were not obtained by this technique.

In the present work some structure and optical characteristics of CdSe films deposited by the thermal evaporation method in QCV, which is promising for condensation of the two-component semiconductor layers with controlled properties, are investigated. Study of these films has a practical interest in addition to the scientific one.

2. FILM PRODUCTION AND INVESTIGATION

Thin CdSe films were obtained on the cleaned glass substrates in the vacuum plant VUP-5M at the residual gas pressure in the chamber not more than $5 \cdot 10^{-3}$ Pa. The furnace-charge evaporation of semiconductor purity was performed there. The evaporator temperature was $T_e = 973$ K, the substrate temperature varied in the range $T_s = 373-873$ K, the time of layer condensation was $t = 8-10$ min.

The film surface morphology was investigated using the scanning microscopy (REMMA-102). The average grain size (D) in the condensates was found by the Jeffries method with the formula $D = k\sqrt{S/M^{-2n}}$, where k is the coefficient of grain shape; S is the area of the micrograph region; M is the amplification; n is the number of grains on the chosen region. We used films of the thickness of $d = 0,4-1,1$ μm to measure the optical properties and thicker layers with $d = 4-6$ μm to study the structural characteristics. Thickness of the thick CdSe films and their growth mechanism were determined by the fractography method (by the photographing of the cleavage surface of the condensates). Thickness of the thinner films was measured by the interferometric method using the microscope MII-1.

The optical characteristics of the condensates were measured using the spectrophotometer SF-26 in the wavelength range $\lambda = 300-900$ nm. We obtained the spectral dependences of the reflection $R(\lambda)$ and the transmission $T(\lambda)$ coefficients. To measure the $R(\lambda)$ spectrums we used the add-on device PZO-2, which provided the double reflection of light from the surface of experimental samples taking into account the reflection from the check pattern. Calculation of the reflection coefficient (in percents) was carried out using formula $R = 10\sqrt{B}$, where B is the ammeter scale reading. Calculation of the optical constants of the material was performed with the Maple 7 environment.

3. RESULTS AND DISCUSSION

As a result of investigations it is established that CdSe film growth occurred in the same way as the growth of the condensates of other chalcogenides [14, 15]. At low substrate temperatures ($T_s < 673$ K) films were found to be the fine-crystalline with the grain size, which did not exceed $D = 0,1-0,3$ μm (Fig. 1a,b). Their growth occurred layer-by-layer, and the condensates themselves consisted of the grains placed one above the other (Fig. 1b). Increase in the grain size with the film thickness in the low-temperature region of their condensation did not take place, but D increased with the substrate temperature. The columnar structure was typical for the high-temperature condensates ($T_s > 673$ K). The grain size in the films was determined by the

layer thickness and the substrate and evaporator temperatures increasing with the growth of d and T_s and with the decrease of the temperature difference $\Delta T = T_e - T_s$. In this case, in the condensates obtained at $T_s = 873$ K the grain size reached the value of $D = 3-4 \mu\text{m}$ at the CdSe layer thickness of $d = 5-6 \mu\text{m}$. All films had the single-phase hexagonal structure.

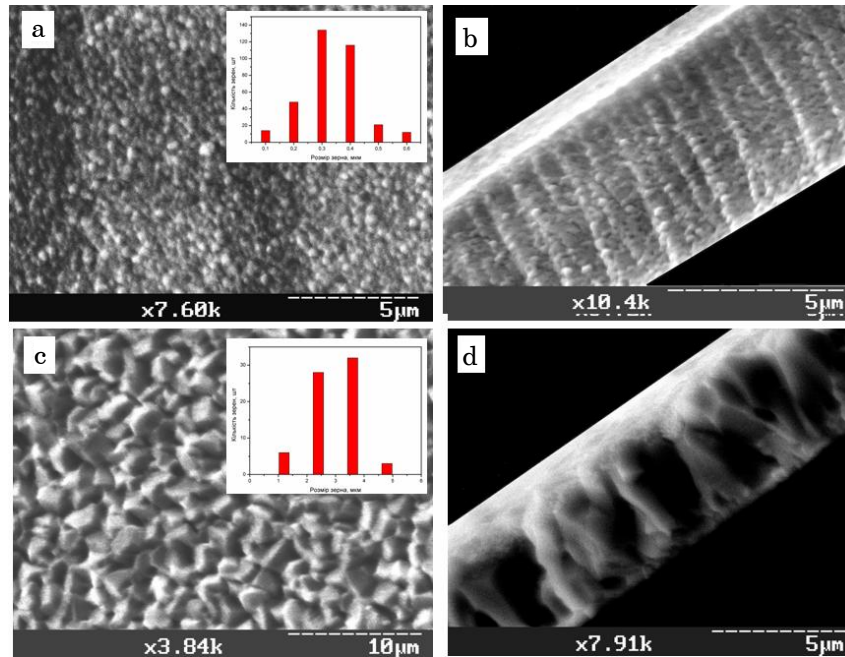


Fig. 1 – Surface microstructure of CdSe films (a, c) and their fracture patterns (b, d). The substrate temperature T_s , K: 373 (a, b), 873 (c, d). The film thickness is $d = 5 \mu\text{m}$, 4,6 μm

Spectral dependences of the reflection $R(\lambda)$ and the transmission $T(\lambda)$ coefficients for CdSe films obtained at different condensation temperatures are presented in Fig. 2. As seen from this figure the studied two-layer structures glass-CdSe film, where semiconductor layers are deposited at the temperatures $T_s < 673$ K, are characterized by the sufficiently high reflection coefficient, which is equal to 10-30% and increases with λ .

This is conditioned by the weakly pronounced relief of the low-temperature condensates and the reflectivity of their surface (see Fig. 1a). For the condensates obtained at higher substrate temperatures the reflection coefficient is substantially less, and in some wavelength range ($\lambda < 600$ nm) it is equal to zero. To our opinion this is connected with the pronounced relief of such layers (Fig. 1c). The pyramidal relief (illumination of the two-layer structures was performed from the chalcogenide film side) promotes the light absorption by the films, and in a number of cases it is formed artificially [13].

Transmission spectrums of CdSe films obtained at different condensation regimes have the same behavior (Fig. 2b). At the radiation wavelengths more than $\lambda \sim 640-650$ nm (at energies less than E_g of the material) the substantial

increase of the transmission coefficient of CdSe condensates takes place. In this wavelength range the transmission coefficient of the films is equal to 60-75% in most cases. Both on $R(\lambda)$ and $T(\lambda)$ dependences the maximums and minimums of intensity connected with the radiation interference in thin layers of chalcogenide (their thickness is $d \leq 1,1 \mu\text{m}$) are observed. The interference peaks on these spectrums imply about the uniformity of investigated films in area.

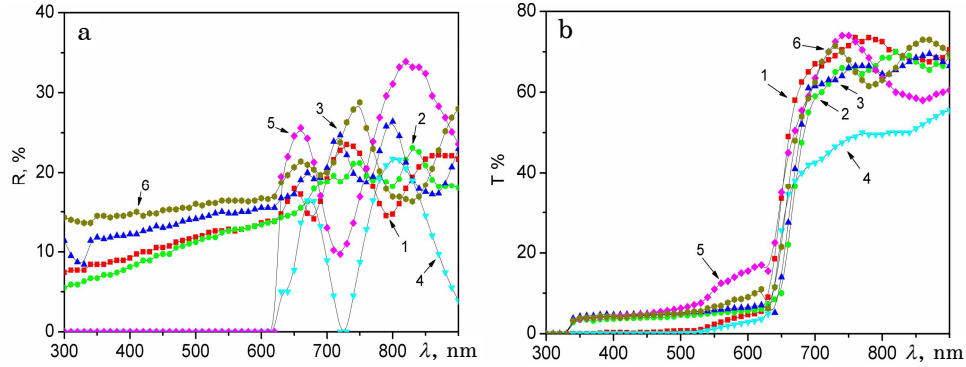


Fig. 2 – The reflection (a) and the transmission (b) spectrums of CdSe films obtained at different T_s , K: 373 (1); 473 (2); 573 (3); 673 (4); 773 (5); 873 (6)

Analysis shows that with the increase of the substrate temperature from $T_s = 373 \text{ K}$ to $T_s = 873 \text{ K}$, the transmission coefficient of CdSe films at first decreases and then increases again. Layers obtained at $T_s = 673 \text{ K}$ have the minimum transmission coefficient. This cannot be explained by the increase in the film thickness obtained at these substrate temperatures (for them $d = 0,55 \text{ nm}$, which is the mean thickness) and, most likely, this is connected with the structural peculiarities of such condensates.

To determine the optical band gap E_g for CdSe we used the following general correlation, which takes place for both direct band gap and indirect band gap semiconductors:

$$\alpha h\nu = A(h\nu - E_g)^m, \quad (1)$$

where A is some constant depending on the effective mass of the charge carriers in the material; $h\nu$ is the energy of an optical quantum; α is the absorption coefficient of the material; m is the exponent defined by the mechanism of photon absorption in the semiconductor.

For direct band gap semiconductors, which CdSe is, $m = 1/2$. This means that the extrapolation of the linear part of the curve $(\alpha h\nu)^2 - h\nu$ on the energy axis allows to determine the band gap of the semiconductor (Fig. 3). The absorption spectrums of chalcogenide films necessary for the calculation of E_g were obtained using the spectrums of light transmission and reflection and also with relation $\alpha = \ln[T/(1 - R)^2]/d$. This expression was obtained by the calculation of energy flows in the system with multiple light reflections from the film surface [16, 17]. The absorption coefficient of the films in the radiation energy region more than the band gap of the material was usually equal to $\alpha = (10^5\text{-}10^6) \text{ m}^{-1}$.

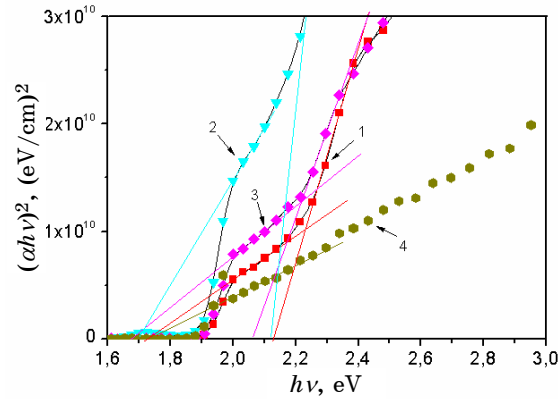


Fig. 3 – $(\alpha h\nu)^2 - h\nu$ dependences of CdSe films obtained at different T_s , K: 373 (1); 673 (2); 773 (3); 873 (4)

As seen from this figure, two linear sections, extrapolation of which allows to obtain two different values of the energy, are observed on $(\alpha h\nu)^2 - h\nu$ dependences in most cases. Smaller values $E_{g1} = 1,67-1,74$ eV (see Table 1) correspond to the band gap of the material. These values correlate well with the band gap of the bulk CdSe monocrystals.

Table 1 – Some optical characteristics of CdSe films obtained at different T_s ($\lambda = 850$ nm)

T_s , K	d , nm	E_{g1} , eV	E_{g2} , eV	n	k	ε_1	ε_2
373	0,70	1,73	2,13	2,74	10^{-2}	7,53	0,05
473	1,10	1,67	–	2,68	$4,6 \cdot 10^{-3}$	7,21	0,03
573	1,10	1,74	–	2,44	$3,9 \cdot 10^{-3}$	6,00	0,002
673	0,55	1,70	2,13	2,23	$4,4 \cdot 10^{-2}$	7,50	0,19
773	0,40	1,68	2,06	2,64	$4,2 \cdot 10^{-2}$	7,12	0,30
873	0,60	1,73	–	2,50	$8,8 \cdot 10^{-3}$	7,04	0,04

In accordance with [18] at room temperature $E_{g1} = 1,71$ eV when $E \perp c$ and $E_{g1} = 1,73$ eV when $E \parallel c$. Obtained values of the band gap of film condensates ($E_{g1} = 1,73-1,74$ eV) imply about the presence in such layers of the pronounced texture, at which the c -axis of the grating is perpendicular to the substrate. This is confirmed by the X-ray diffractometer investigations of the films, which exhibit the growth texture [002]. Smaller values of the band gap of film condensates ($E_{g1} = 1,68-1,71$ eV) deposited by the vacuum evaporation were obtained in [11].

The authors of Ref. [1] have studied the change of the band gap of CdSe films prepared by the hot wall deposition technique at the substrate temperature $T_s = 400$ K subject to their thickness. With the increase in d from 350 nm to 1800 nm E_{g1} decreased from 1,69 eV to 1,61 eV. These values of the energy are also less than those we have obtained.

To our opinion, larger energy values obtained from the graphs $(\alpha h\nu)^2 - h\nu$ ($E_{g1} = 2,06-2,13$ eV, see Table 1) correspond to the charge carrier transitions

induced by the light between the conduction band and the lower valence band of the material segregated due to the spin-orbit interaction. Really, if take into account that in the compound $\Delta_0 = 0,40$ eV [18] it is easy to obtain that the energy gap for the bulk crystals with a hexagonal structure and its different orientations relative to the direction of the light incidence is equal to $E_{g2} = 2,11-2,13$ eV. These values correlate well with those obtained experimentally. We have to note, that such transitions were observed in [11] where for the film samples deposited by the thermal evaporation the following energies were found: $E_{g2} = 1,87-2,25$ eV. Here the lower value is typical for the freshly deposited CdSe films, and the upper one – for the films annealed in air at 673 K.

Using the spectral distributions of the reflection $R(\lambda)$ and the absorption $\alpha(\lambda)$ coefficients we calculated the refraction $n(\lambda)$ and the extinction $k(\lambda)$ spectrums of CdSe films. It is well known that the corresponding coefficients are connected by the Fresnel formula

$$R = [(n - 1)^2 + k^2] / [(n + 1)^2 + k^2], \quad (2)$$

where $k = \alpha\lambda/4\pi$.

Calculating k we can find the refraction coefficient of the material

$$n = \left(\frac{1 + R}{1 - R} \right) + \sqrt{\frac{4R}{(1 - R)^2} - k^2}. \quad (3)$$

Taking into account the foregoing expressions we determined the values of k and n for chalcogenide films at different radiation wavelengths. Knowing them we can find the real ε_1 and imaginary ε_2 parts of the optical dielectric constant of CdSe films using the following relations:

$$\varepsilon_1 = n^2 - k^2, \quad (4)$$

$$\varepsilon_2 = 2nk, \quad (5)$$

where expressions (4) and (5) satisfy the condition $\varepsilon = \varepsilon_1 + \varepsilon_2 = (n + ik)^2$.

$k(\lambda)$ and $\varepsilon_2(\lambda)$ dependences obtained in such a way are presented in Fig. 4.

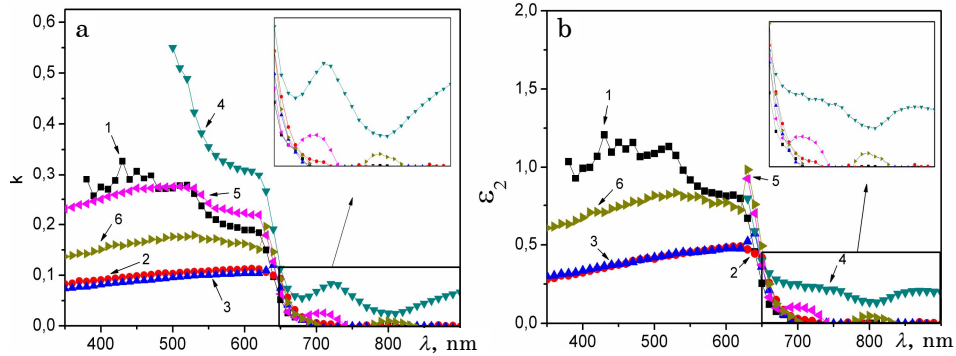


Fig. 4 – Spectral dependences of the extinction coefficient $k(\lambda)$ (a) and the imaginary part of the optical dielectric constant $\varepsilon_2(\lambda)$ (b) of CdSe films deposited at different T_s , K: 373 (1); 473 (2); 573 (3); 673 (4); 773 (5); 873 (6)

As seen from Fig. 4, k and ε_2 decrease with the radiation wavelength increase that, in turn, is connected with the reduction of the incident photon energy ($h\nu$). Difference in behavior between the obtained dependences and the values given by the classical Cauchy correlation $n = A + B/\lambda^2$, where A and B are some constants is conditioned by the interference effects in the films.

Values of the refraction n and the extinction k coefficients and the real ε_1 and imaginary ε_2 parts of the optical dielectric constant of CdSe films calculated at the wavelength $\lambda = 850$ nm ($E = 1,46$ eV) are presented in Table 1. To determine these parameters we used approximation of the corresponding curves by the roll-off functions. Established, that values of the refraction coefficient of the investigated material vary in the range $n = 2,23-2,74$ that correlates well with the values presented in [19] for the bulk semiconductor $n = 2,50-2,65$ ($\lambda = 700-1000$ nm). The authors of [1] obtained values of the refraction coefficient of film material, which were in the range $n = 2,0-2,6$, for CdSe layers of the thickness of $d = 0,3-1,8$ μm prepared by the hot wall deposition technique in vacuum.

The extinction coefficient k of the investigated films was substantially less than n and varied from $4,6 \cdot 10^{-3}$ to $4,4 \cdot 10^{-2}$. The authors of [1] obtained larger values of k ($k = 1,0-2,5$), but they did not point the wavelength, the calculations were performed for.

Values of ε_1 and ε_2 calculated for $\lambda = 850$ nm are also presented in Table 1. Real part of the optical dielectric constant of the material turned out to be equal to $\varepsilon_1 = 6,0-7,5$. These values also correlate well with those for the monocrystal bulk CdSe, $\varepsilon_1 = 6,0-7,9$ [4, 19]. Imaginary part of the optical dielectric constant is less than the real part by one-three orders of magnitude and is equal to $\varepsilon_2 = 0,002-0,3$.

As the performed investigations of the structure and optical constants of CdSe films prepared by the CSVS technique imply, such layers can be used in tandem solar cells for the effective absorption of light with the length λ more than 700 nm ($E > 1,77$ eV). In this case the condensates deposited at the substrate temperatures $T_s > 623-673$ K have the optimal characteristics for application in photo-converters as the absorption layers. Such films have the single-phase columnar coarse-grain structure with pronounced pyramidal relief.

4. CONCLUSIONS

In this work we have studied the surface morphology, growth mechanisms and optical characteristics of thin CdSe films deposited by the CSVS technique at different physical and technological condensation regimes. Performed investigations allowed to obtain the spectral distributions of the transmission $T(\lambda)$, reflection $R(\lambda)$, absorption $\alpha(\lambda)$ and refraction $n(\lambda)$ coefficients, and the real $\varepsilon_1(\lambda)$ and imaginary $\varepsilon_2(\lambda)$ parts of the optical dielectric constant of the samples and to define their dependence on the film deposition temperature. It is shown that on $(\alpha h\nu)^2 - h\nu$ dependences of CdSe films two linear sections, the extrapolation of which allows to obtain different values of the energy, are observed. Smaller values $E_{g1} = 1,67-1,74$ eV correspond to the band gap of the material, and the larger values $E_{g2} = 1,87-2,25$ eV – to the charge carrier transitions induced by the light between the conduction band

and the lower valence band of the material segregated due to the spin-orbit interaction. The physical and technological regimes of the CdSe film deposition are established. These regimes are characterized by the optimal parameters, which allow to apply such films as absorption layers in tandem heterojunction solar converters.

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