OPTICAL PROPERTIES OF CdS FILMS OBTAINED BY HOT-WALL TECHNIQUE

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The structure of CdS films deposited with the use of the hot-wall technique has been studied. The growth of a film thickness was found to result in a reduction of mechanical stresses in the films, with compressive and tensile macrostresses being observed in thin and thick films, respectively. The increase of a CdS film thickness was found to be accompanied by an increase in the energy gap width E_g, which is associated with an extension of the coherent scattering region. It is established that CdS films about 0.3 μm in thickness annealed in air are expedient to be used as wide-gap “windows”, while fabricating the efficient solar cells based on CdS/CdTe heterosystems.

1. Introduction

While designing thin-film solar cells on the basis of CdTe, the effect of wide-gap window [1] is used to intensify photo-electric processes, which allows the negative influence of the surface recombination of nonequilibrium charge carriers to be reduced by moving the region of their active generation away from the illuminated surface. Cadmium sulfide film with the energy-gap width $E_g = 2.4$ eV is actively used as a wide-gap “window” for the solar radiation. In this work, to optimize the parameters of a wide-gap “window” in polycrystalline film heterosystems ITO/CdS/CdTe, which are promising from the viewpoint of the creation of effective and economic solar cells for the terrestrial usage, the influence of the crystalline structure of CdS layers fabricated using the hot-wall technique on their optical properties has been studied.

2. Experimental Part

The crystalline structure of CdS films fabricated using the hot-wall technique in vacuum ($p = 3.2 \times 10^{-5}$ mm Hg) was studied for various times of deposition (35, 45, and 60 min) onto glass substrates. The evaporator temperature during the CdS film deposition was 650 °C, and the temperature of the glass substrate was 400 °C. The X-ray diffractometric analysis of cadmium sulfide films with various thicknesses subjected to radiation of the cobalt anode tube was carried out, and the spectra of their optical transmittance in the spectral interval of 300–1100 nm were examined. Several specimens obtained at different deposition times were annealed in air at a temperature of 450 °C for 30 min.

3. Results and Discussion

Experimental diffraction patterns obtained for cadmium sulfide layers are depicted in Figs. 1 to 3. For the cadmium sulfide film deposited for 35 min, the diffraction patterns demonstrate a strongly pronounced halo (Fig. 1) which is formed by a fine-crystalline X-ray-amorphous phase. This halo serves as a background for the reflection given by a family of (002) planes in the hexagonal modification of cadmium sulfide. It should be noted that the probability for the both phases – hexagonal and metastable cubic ones; the latter being, in effect, a hexagonal phase with a high concentration of periodically arranged packing defects – to coexist in thin films of cadmium sulfide is rather high. Therefore, both phases may exist in the examined CdS films with a small thickness. The studies of the mechanism of cadmium sulfide growth at its condensation in vacuum testify to the formation of nuclei characterized by various crystal orientations on the substrate surface [2]. The highest growth rate is characteristic of the most densely populated (002) planes in the hexagonal phase. Therefore, it is natural that an increase of the CdS layer thickness results in an enhancement of the peak (002) intensity in X-ray

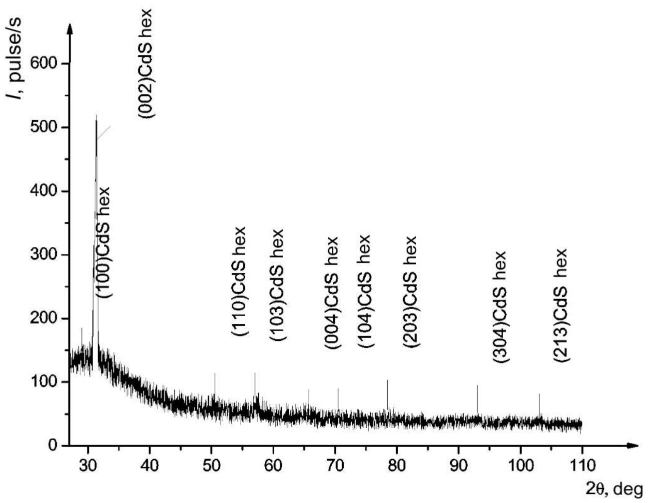

Fig. 1. X-ray diffraction pattern of a CdS film fabricated by the hot-wall technique with a deposition time of 35 min

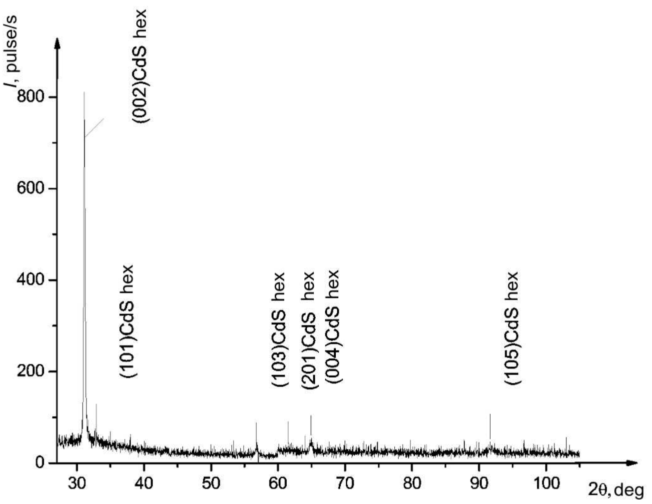

Fig. 2. The same as in Fig. 1, but for a deposition time of 45 min

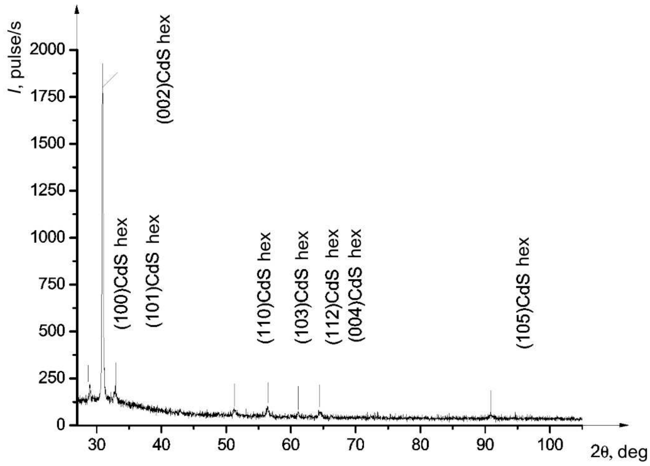

Fig. 3. The same as in Fig. 1, but for a deposition time of 60 min

diffraction patterns, which is clearly observed for CdS films deposited for 45 and 60 min. In this case, other reflections appear as well. In particular, for the family of (004) planes in the hexagonal modification, the intensity of peak (002) increases, as the thickness of CdS films grows.

On the basis of experimental diffraction patterns obtained for a cadmium sulfide film deposited for 35 min, we cannot determine the dimensions of the coherent scattering region (CSR) and the microdeformation magnitudes. It is so, because no multiple diffraction peaks were observed in the X-ray diffraction pattern. Therefore, to trace how the integrated peak width changes with the variation of the film thickness, we treated peak (002) without taking the halo area into account. The variation of the integrated width of this peak testifies to the variation of CSR dimensions, because these reflections are observed at small angles, and it is the CSR size that gives the major contribution to the broadening of diffraction maxima at such angles.

It is worth noting that, for all analyzed X-ray diffraction patterns, we decomposed the K_α-doublet [3], i.e. we extracted the $K_{\alpha 1}$-component and subjected it to a further analytical treatment in order to determine the structural parameters of cadmium sulfide films.

Having analyzed the X-ray diffraction patterns of cadmium sulfide specimens deposited for 45 and 60 min (Figs. 2 and 3, respectively), we analytically examined multiple diffraction peaks (002) and (004) to determine microdeformations and CSR dimensions. First, we calculated the actual broadening of the diffraction peak. To extract the instrument-induced broadening, we used an X-ray diffraction pattern given by a structurally perfect CdTe film as a reference one. The corresponding experimental diffraction pattern was used to plot the calibration curve for the dependence of the instrument-induced broadening on the diffraction angle. On the basis of this curve, the peak broadening was determined, the plots of the dependence $\beta\cos\theta$ versus $\sin\theta$ were constructed (see Fig. 4), and the CSR dimensions and microdeformation magnitudes were found. The data obtained are quoted in Table 1.

The data in Table 1 demonstrate that the integrated width $B_{(002)}$ of peak (002) decreases from 0.440 to 0.260, as the film thickness increases, whereas peak (004) gets wider at that (its integrated width $B_{(004)}$ increases from 0.420 to 0.580). The growth of the CdS film thickness is accompanied by a reduction of microdeformations –

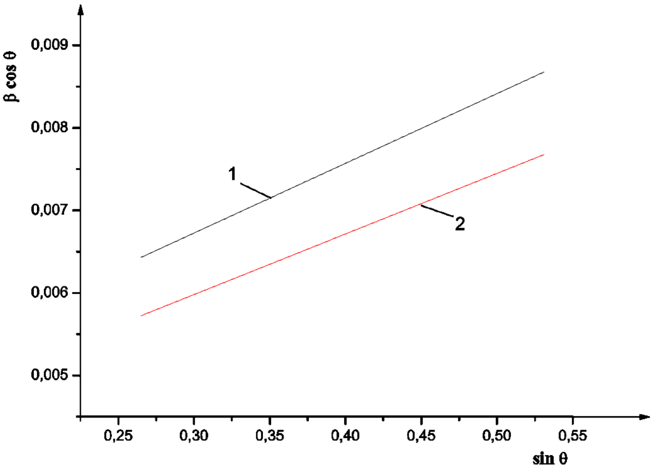

Fig. 4. Williamson-Hall plots at the approximation by the Cauchy function for specimens with a deposition time of 45 (*1*) and 60 min (*2*)

from 21 to 16.7 – and an increase of the CSR size L – from 27.9 to 31.4 nm. This can take place, provided that the film and the substrate have different coefficients of thermal expansion. Hence, adhesion improves as the film thickness grows.

Using the Wolf–Bragg equation, we calculated the plane-to-plane distances for the family of (002) planes. The diffraction angle was determined by the position of the maximum, which was found using the method of medians. The results of calculations are presented in Table 2.

As the film thickness grows, the plane-to-plane distance for the family of (002) planes increases from 3.32 Å (at a layer thickness of 0.14 μm) to 3.36 Å (at a layer thickness of 0.28 μm). According to the tabular data, the theoretical value of interplane distance for this family of planes amounts to 3.357 Å. A comparison between experimental and theoretical values demonstrates that there arise the compressive macrostresses, if the film thickness is small (t = 0.14 μm), and tensile ones, if the thickness is large (t = 0.28 μm). As the film thickness increases, the compressive macrostresses grow. At a film thickness of 0.21 μm (the deposition time is 45 min), macrostresses vanish. Afterward, if the film thickness

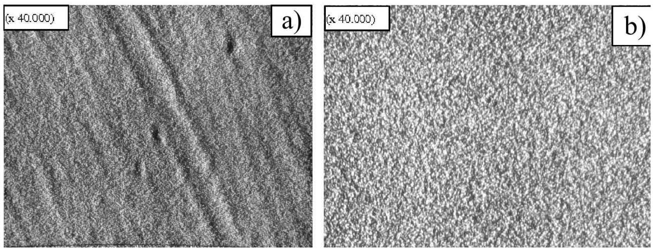

Fig. 5. Micrographs of the surfaces of cadmium sulfide films 0.14 (*a*) and 0.21 μm (*b*) in thickness

grows further, the macrostresses change their sign, i.e. they become tensile and start to increase. Hence, tensile macrostresses bring about the formation of a film that contains a stable hexagonal modification, and they are responsible for the formation of single-phase films of cadmium sulfide.

While fabricating CdS films, it is necessary to provide the absence of through pores. The appearance of the latter is connected with the shadowing effect arising when films are deposited using the hot-wall technique. Namely, the grains oriented in those crystalline planes, which have the highest growth rates, screen the growth surface. The availability of through pores in thin cadmium sulfide films leads to the shunting of the separating barrier, through which the front ITO electrode contacts with the base CdTe layer. Therefore, we carried out raster electron microscopy researches of film surfaces making use of an REM-1M device for the determination of the CdS film thickness, which would be optimal from the viewpoint of the absence of pores in the CdS layer. At a thickness of 0.14 μm of the initial CdS layer, large through pores of 40 nm in diameter were observed experimentally (Fig. 5,*a*). A further increase of the CdS film thickness was accompanied by a reduction of both the number and the size of through pores (Fig. 5,*b*).

The optical properties of CdS films fabricated by the hot-wall technique were studied by analytically treating the transmission spectra (Fig. 6) of three specimens with different deposition times. After the deposition, the specimens were annealed in air for 30 min at a temperature of 450 °C. The corresponding transmission spectra are depicted in Fig. 7.

T a b l e 1. Dependences of structural properties of CdS films on the film deposition time

Depos. time CdS, min	t, μm	B_{002}, deg	B_{004}, deg	$\varepsilon \times 10^{-4}$, rel. units	L, nm
35	0.14	0.44	–	–	–
45	0.21	0.28	0.42	21.0	27.9
60	0.28	0.26	0.58	16.7	31.4

T a b l e 2. Calculation data for interplane distances for specimens with different thicknesses

Deposition time CdS, min	Specimen thickness t, μm	Interplane distances d_{002}, Å
35	0.14	3.32
45	0.21	3.35
60	0.28	3.36

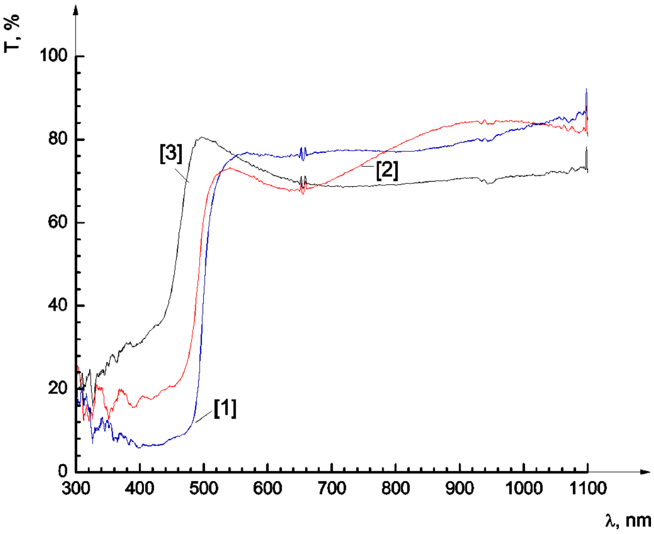

Fig. 6. Dependences of the transmittance coefficient on the wavelength for glass/CdS specimens fabricated by the hot-wall technique with various deposition times of 35 (*1*), 45 (*2*), and 60 min (*3*)

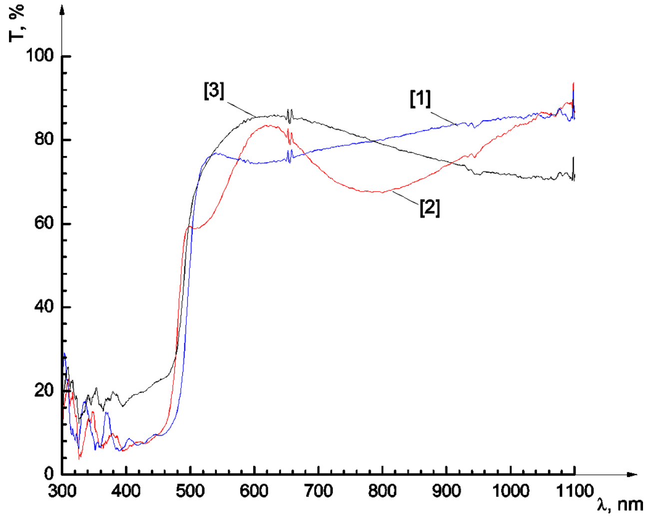

Fig. 7. The same as in Fig. 6, but after the annealing of a specimen

In the wavelength range of 550–850 nm, we calculated the average transmittance coefficients for three specimens of cadmium sulfide films before and after their annealing in air. The obtained data are quoted in Table 3.

Let us analyze the transmittance of CdS films in the range of the solar cell photosensitivity (550–850 nm). In particular, with increase in the deposition time, the average transmittance in the indicated wavelength range decreased from 76.8 to 70.2%. This effect is mainly associated with the increase of the film thickness. The analysis of the transmittance coefficients for annealed specimens testifies that the effect of annealing depends on the layer thickness.

After the annealing, the average coefficient of transmittance in the range of the solar cell photosensitivity, $T_{\mathrm{aver}(550-850)}$, became higher for every examined specimen (Table 4). For instance, $T_{\mathrm{aver}(550-850)}$ increased from 76.8 to 77.6% for the glass/CdS specimen with $t_{\mathrm{depos}} = 35$ min, from 72.8 to 73.7% for the glass/CdS specimen with $t_{\mathrm{depos}} = 45$ min, and from 70.2 to 72.4% for the glass/CdS specimen with $t_{\mathrm{depos}} = 60$ min. Hence, for films 0.14 and 0.21 μm in thickness, the growth of the integrated transmittance amounted to 0.8 and 0.9%, respectively. At the same time, the increase in the transmittance of a thick film (0.28 μm) reaches 2.2%.

Using the transmission spectra and the known values of film thicknesses, we determined the optical width of the energy gap (E_g) in the films. The data obtained are presented in Table 4. One can see, that, as the film thickness grows, the energy gap width increases from 2.51 to 2.56 eV. This increase is associated with a reduction of light scattering and absorption at grain boundaries. As a result, the energy gap width in cadmium sulfide films approaches the corresponding value for the cadmium sulfide single crystal, $E_g = 2.55$ eV. After the annealing, the energy gap width also grows from 2.5 to 2.55 eV with increase in the cadmium sulfide film thickness. This effect can be connected with increase in the CSR size L.

To provide the maximal flux density of photons that arrive at the CdTe base layer, the most expedient in the solar cell design is the usage of CdS films 0.14 μm in thickness, for which $T = 77.6\%$ after the annealing. However, electron microscopy researches of CdS films with $t < 0.2$ μm evidence the presence of through

T a b l e 3. Calculation data for the average transmittance coefficients for specimens with different thicknesses before and after their annealing

No.	Specimen	t, μm	T_{aver}(550–850 nm), % before (after) annealing
1	glass/CdS(35 min)	0.14	76.8 (77.6)
2	glass/CdS(45 min)	0.21	72.8 (73.7)
3	glass/CdS(60 min)	0.28	70.2 (72.4)

T a b l e 4. Calculation data for the energy gap width for specimens with different thicknesses before and after their annealing

Film thickness, μm	Energy gap width E_g, eV	
	Before annealing	After annealing
0.14 (35 min)	2.51	2.50
0.21 (45 min)	2.53	2.51
0.28 (60 min)	2.56	2.55

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pores (Fig. 5). This makes the application of such layers as wide-gap windows in solar cells on the basis of CdS/CdTe heterosystem impossible, because, in this case, the instrument structure becomes shunted owing to a contact between the base layer and the electrode.

4. Conclusions

Our researches dealing with the structure of cadmium sulfide films fabricated using the hot-wall technique testify that, as the layer thickness grows, a reduction of microdeformations is accompanied by an increase in the CSR dimensions. This effect can follow from a reduction of the mechanical stresses that arise in CdS layers owing to the difference between the coefficients of linear expansion in the film and the glass substrate. A comparison between the experimental and theoretical values of interplane distances also demonstrates that the macrostresses that emerge in the films are compressive, if the film thickness is small, and tensile, if it is large.

The evolution of optical properties of CdS layers corresponds to a modification of the film crystalline structure. For instance, the increase of the energy gap width E_g with the growth of the CdS film thickness is connected with increase in the CSR size. It was found that CdS films about 0.3 μm in thickness annealed in air, which are characterized by optimal relationships between the optical properties and the crystalline structure, are expedient to be used as wide-gap "windows" for the creation of effective solar cells on the basis of CdS/CdTe heterosystem.

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ОПТИЧНІ ВЛАСТИВОСТІ ПЛІВОК СУЛЬФІДУ КАДМІЮ, ОТРИМАНИХ МЕТОДОМ ГАРЯЧОЇ СТІНКИ

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Р е з ю м е

Досліджено структуру плівок сульфіду кадмію, отриманих методом гарячої стінки. Встановлено, що зі збільшенням товщини шарів зменшуються механічні напруження, при цьому при малих товщинах плівки спостерігаються стискаючі макронапруження, а при більших товщинах – розтягуючі. При збільшенні товщини плівки CdS збільшується ширина забороненої зони (E_g), що зумовлено збільшенням розміру областей когерентного розсіювання. Встановлено, що у ролі широкозонних "вікон" для створення ефективних сонячних елементів на основі гетеросистеми CdS/CdTe доцільно використовувати відпалені на повітрі плівки CdS товщиною близько 0,3 мкм.