J. Nano- Electron. Phys.
1 (2009) No2, P. 36-42

PACS numbers: 81.15.Lm, 78.66. – w, 61.05.cp, 68.37.Hk

CHEMICAL SURFACE DEPOSITION OF CdS THIN FILMS FROM CdI_2 AQUEOUS SOLUTION

G. Il'chuk, V. Kusnezh, P. Shapowal, F. Tsupko, R. Petrus, S. Tokarev, O. Horbova

Lviv Polytechnic National University,
12, S. Bandera Str., 79013, Lviv, Ukraine
E-mail: gilchuk@polynet.lviv.ua

For the first time using CdI_2 solution CdS films on glass and ITO coated glass substrates were produced by the method of layerwise chemical surface deposition (ChSD). CdS thin films with the widths from 40 nm to 100 nm were obtained for windows in solar cells based on CdS/CdTe heterojunctions. Changes of the structural and optical properties of CdS films due to air annealing are shown.

***Keywords**: CdS FILMS, CHEMICAL SURFACE DEPOSITION, STRUCTURE AND MORPHOLOGY OF THIN FILMS.*

(Received 7 July 2009, in final form 30 July 2009)

1. INTRODUCTION

High prices of the classical solar cell production stimulate the search of low cost methods and materials, appropriate for the solar energy photoconversion. Improvement of the photoconversion effectiveness in solar cells of CdS/CdTe type, where CdS film is used as a window, require loss reduction for optical absorption of photons with the energies $h\nu < 2{,}5$ eV. This can be achieved using CdS thin films. In spite of that there are a lot of deposition methods of CdS thin films nowadays, only some of them allow to deposit continuous films on large areas at the temperatures less than 100°C. The process of chemical bath deposition (ChBD) is among them, where CdS films are deposited in a bath on certain substrates from a solution containing the cadmium salt and the sulfur compounds [1, 2]. But a lot of cadmium-containing wastes and defects on a film surface is the disadvantage of ChBD.

We used the method of chemical surface deposition (ChSD) to obtain CdS thin films. Its fundamental difference from the ChBD method consists in the using of a sample surface as a heat source, that allows to localize the area of CdS film deposition on a substrate surface. In this case the surface tension of a solution provides minimization of the volume of reacting mixture and its holding on a substrate.

In the present work we used CdI_2 aqueous solution for the ChSD of CdS thin films, CdS films are obtained, and the annealing influence on the film properties is investigated.

2. EXPERIMENTAL TECHNIQUE

Freshly prepared 0,015 M solution of the cadmium iodide CdI_2, 1,5 M solution of the thiourea $CS(NH_2)_2$, 14,28 M solution of the ammonium hydroxide NH_4OH, and the distilled water were used for ChSD. The initial

molar concentrations of the solution components were the following: $C(CdI_2)$ = 0,001 mole/l; $C(CS(NH_2)_2)$ = 0,1 mole/l; $C(NH_4OH)$ = 1,8 mole/l, and the value pH = 12. The corresponding preparation of the substrates (glass and ITO/glass, 16 mm × 20 mm) preceded the deposition process. The deposition process and the prior preparation were carried out by the proven technique [3]. Air annealing of the films was realized in enclosed volume at the temperature 400°C during 30 min [4, 5].

Widths of CdS films and rates of their growth were determined using the ellipsometer LEF-3M via the experimental data processing by the changes of polarization characteristics of radiation after its reflection from the interface air/CdS film. Morphology of the film surface and the elemental composition were investigated using the scanning electron microscopes REMMA-102-02 and JSM-6490LV. Crystallinity of the CdS film structure was investigated using the automated X-ray diffractometer HZG-4A. Optical absorption spectrums of CdS films were obtained using the computerized monochromator MDR-23.

3. ChSD PROPERTIES OF CdS FILMS

Sets of samples with different number of CdS layers deposited in equal technological conditions are produced (see Table 1). Process of elementary deposition was ceased in three minutes not reaching saturation of the film thickness. Typical data of ellipsometric measurements of the film thickness and the averaged rates of their deposition are represented in Fig. 1.

Table 1 *– ChSD conditions of CdS thin films from CdI_2 aqueous solution at* 70°*C*

Sample's number	Number of depositions	Duration of one deposition, min	Total duration of film deposition, min
11, 21, 33	4	3	12
22	1	3	3
23	2	3	6
24	3	3	9

Fig. 1 illustrates the interesting dependence of the film thickness versus the deposition duration; it is linear for the three first depositions. After the fourth deposition the film thickness starts to decrease, that implies about the priority of the film dissolution process over the process of its deposition. Rate of the first film deposition on a glass substrate is the maximal one and equals 15 nm/min. On the second and the third steps of a layerwise deposition this rate decreases to ~ 12 nm/min, since the preformed CdS film is a substrate there. Because of this the growth rates of the following deposited layers are equal, and thickness of the total film increases uniformly. This allows to control their thickness with high accuracy. Accuracy of the ellipsometric measurements increased with the growth of the total film width in such a way that the absolute error varied in the range from ± 12 nm to ± 5 nm (Fig. 1). Among all cadmium salts ($CdSO_4$, $CdCl_2$) used for ChSD at the temperature 70°C the largest deposition rate of CdS films was observed for CdI_2 salt. High deposition rates can condition the considerable film imperfection.

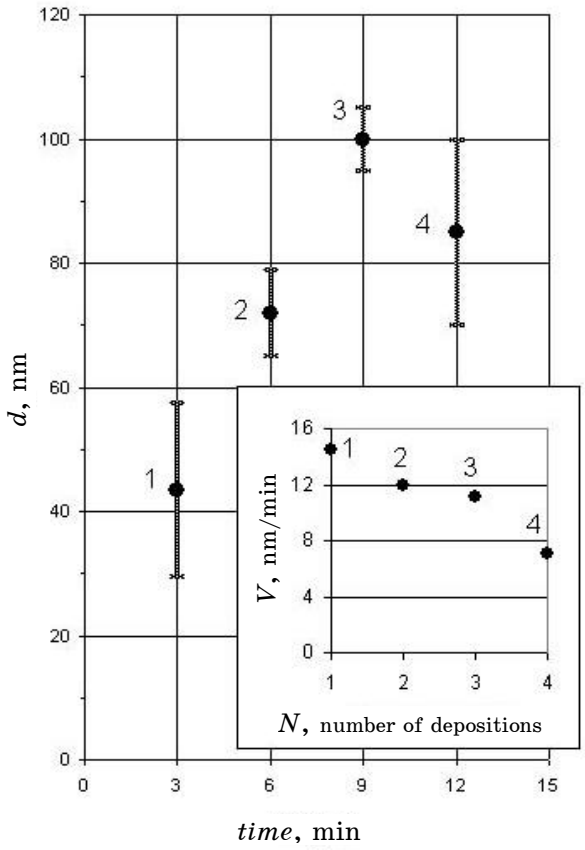

Fig. 1 *– Generalized dependence of the width d of CdS films deposited from CdI_2 aqueous solution by the ChSD method versus the time and the number of elementary depositions, samples 11 (dot 4), 22 (dot 1), 23 (dot 2), 24 (dot 3). On the inset: generalized rates of CdS film deposition for these samples, duration of one deposition is 3 min*

Investigation results of the surface morphology of CdS films are shown in figures: in the secondary-electron mode (Fig. 2a represents the surface topography) and the reflected-electron mode (Fig. 2b qualitatively represents the surface composition: the lighter a dot, the heavier an element). As seen from Fig. 2, 3, CdS film ($d \sim 100$ nm) completely coats a substrate, and through holes and surface particles are observed all over the sample area. Comparison of figures of CdS films obtained in the reflected and secondary-electron modes (Fig. 2) verifies that the heavier phase inclusions are on a film surface. Thus, these inclusions (particles on a surface) are probably formed on the final stage of film deposition. The particle concentration on a surface in investigated CdS films is 10^6-10^7 cm^{-2} (sample 11). For the comparison, the best results for particle concentration on a surface during deposition from a solution in a volume are 10^8 cm^{-2} [6]. Generalized results of the surface morphology and the X-ray microanalysis of CdS films deposited from different cadmium salts are represented in Table 2.

Established, that particles on a film surface are the CdS particles with another stoichiometry than a film has. Stoichiometry deviations towards the sulfur are unusual enough. As a rule, the lack of sulfur is the problem for most of methods of CdS thin film deposition. Composition of the films deposited from CdI_2 solution is more similar to the stoichiometric one in comparison with the films deposited from two other salts (see Table 2). Surplus of sulfur in CdS ChSD films allows to annealing in usual air medium, but not in a sulfur-containing one, since it is not necessary to additionally inject sulfur into film for providing the stoichiometry of a compound.

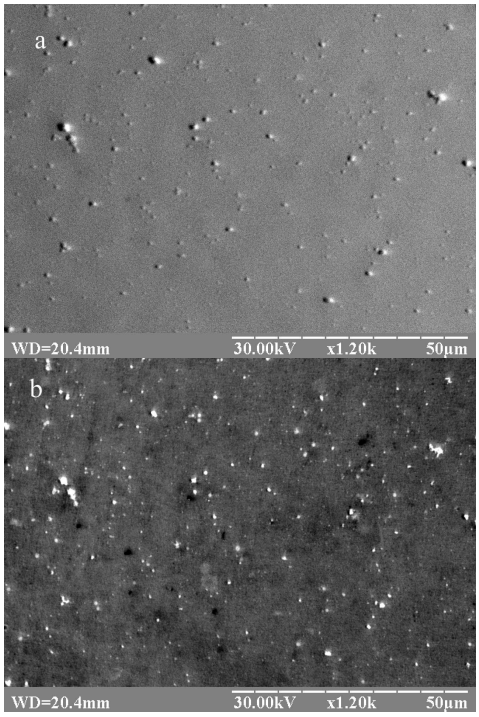

Fig. 2 *– Surface morphology of CdS film, sample 11, REMMA-102-02. Images of a film surface in the secondary-electron mode (a) and reflected-electron mode (b). Accelerating voltage is* 30 *kV, scale is* 1:1200

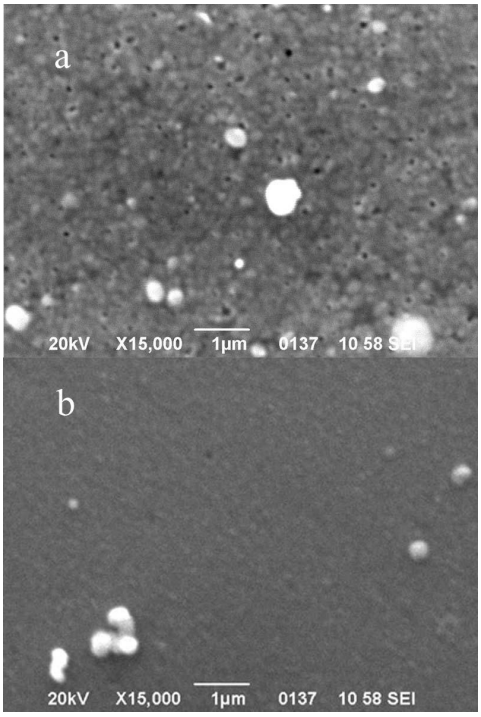

Fig. 3 *– Surface morphology of CdS film before (a) and after (b) annealing, sample 11, JSM-6490LV. Accelerating voltage is* 20 *kV, scale is* 1:15000

Experimental diffractograms obtained from CdS films on a glass before and after annealing are shown in Fig. 4. Amorphism of CdS films with appreciable presence of a cubic phase is pronounced for investigated samples before annealing (curve 3). The first peak 26,45° for a cubic phase (curve 3) is weakly pronounced and shifted with respect to the corresponding peak (which is shown for comparison) of the diffractogram from CdS monocrystal (curve 1). This displacement can be explained by small grain sizes in CdS films and mechanical stresses in films caused by the relatively high deposition rates (15-12 nm/min). In addition to the peak 26,45° one more

weakly pronounced peak 52,00° is observed, which corresponds to a cubic phase. Thermal treatment of CdS film in a closed volume leads to essential increase of peak intensity (peaks 26,45° and 52,00°) and appearance of the third peak 43,90° (curve 2). This implies about reduction of content of the amorphous phase, which is transformed into the crystalline phase, and about considerable reconstruction of ChSD films.

Table 2 *– Generalized results of investigations of the surface morphology and the X-ray microanalysis of CdS films deposited from different cadmium salts*

Salt	Number of particles on a surface, cm^{-2}	Cd/S ratio in a film	Cd/S ratio (in particles) on a film surface
$CdSO_4$	10^6-10^7	0,880	0,800
$CdCl_2$	10^7	0,898	0,908
CdI_2	10^6-10^7 *	0,911	1,061
* holes are observed in a film; for films deposited from two other salts such holes are almost absent			

Evidently, that investigated CdS film cannot be completely crystalline because of the absence of orienting action of a glass substrate it is deposited on. Carried out annealing leaded to essential film reconstruction (Fig. 4, curves 2 and 3, peak 26,45°), and a substrate has the greatest influence on its structure at investigated widths.

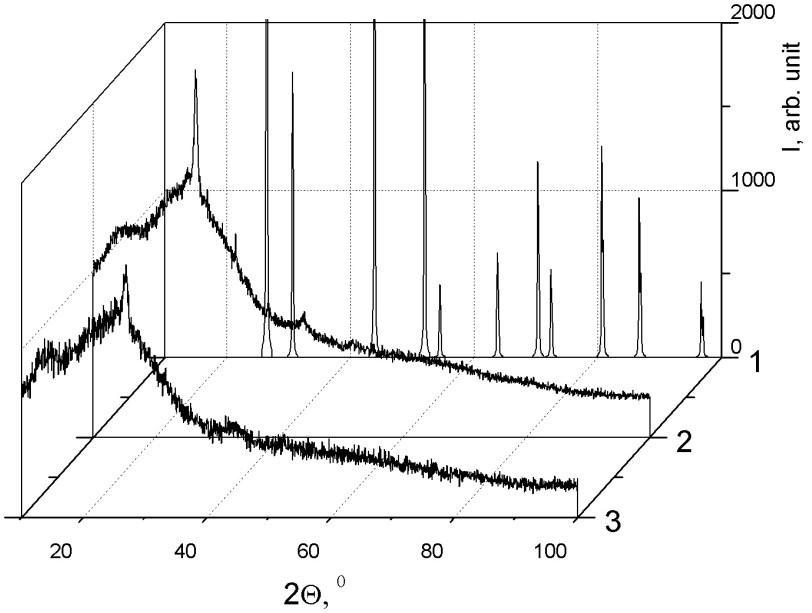

Fig. 4 *– Diffractograms of CdS films deposited layerwise on the glass substrates. Diffraction peaks of the cubic modification of CdS monocrystal (curve 1) are shown for comparison. Curves 3 and 2 correspond to the sample 11 before and after annealing, respectively*

Spectrums of optical transmission in a visible region of CdS ChSD films before and after annealing are presented in Fig. 5. The main feature of the spectrums is negligible (0,033 eV) displacement of the edge of fundamental absorption of CdS films into long-wave region and decrease of optical transmission by 20% due to annealing. Transmission reducing is caused by not absorption only but essential changes of a film structure after its annealing. Images of a film surface show that holes, which are numerous in the freshly prepared films (Fig. 3a), completely disappear after annealing (Fig. 3b). X-ray diffractograms (Fig. 4, curves 3 and 2) also confirm sufficient increase of film structure crystallinity due to annealing in spite of indifference of a glass substrate. Spectrums of absorption of CdS films in $(\alpha^* h\nu)^2/(h\nu)$ coordinates are represented in Fig. 5b. They show the presence of the edge of fundamental absorption, which is localized in the region 2,5 eV that in accordance with other publications (2,4-2,5 eV) for CdS monocrystals of a cubic modification [7]. Linear character of the dependence $(\alpha^* h\nu)^2 = f(h\nu)$ in a region of the edge of absorption for all investigated CdS samples implies that this edge is formed by the direct optical interband transitions as well as it occurs in CdS monocrystal. CdS ChSD films both before and after annealing have very abrupt edge of fundamental absorption that points on negligible amount of defects in these films.

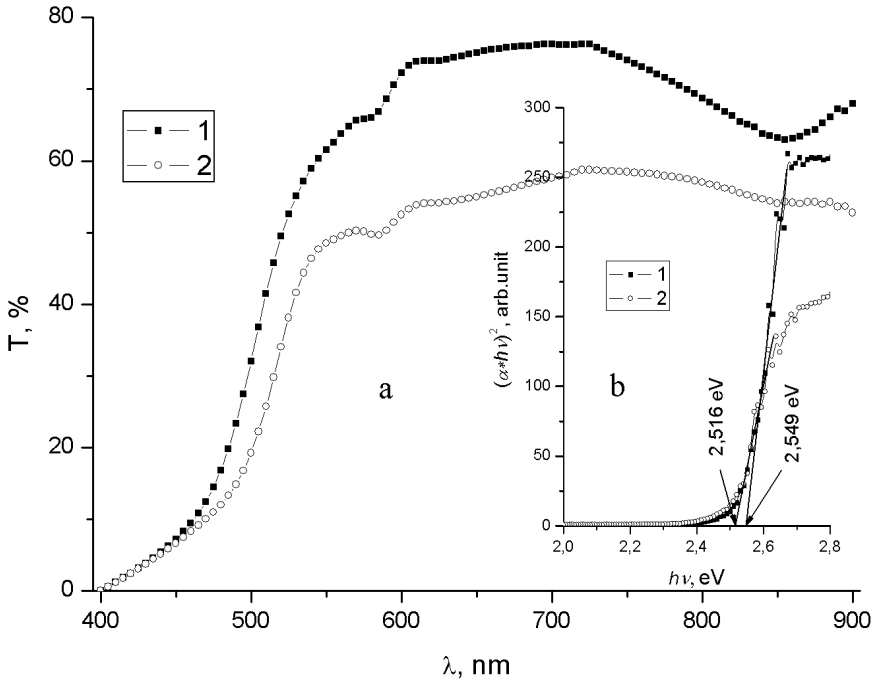

Fig. 5 *– Transmission spectrums of CdS films. Curves 1 and 2 correspond to the films 11(33) and 21 before and after annealing, respectively. On the inset b: dependences of CdS film transmission in the region of fundamental absorption in $(\alpha^* h\nu)^2$, $(h\nu)$ coordinates*

Increase of the long-wave tail of the absorption curve of annealed film (Fig. 5, curve 2), which is conditioned by the absorption growth near the surface of CdS film due to formation of oxides on its surface, is almost inconspicuous. The value of absorption coefficient in the region of fundamental absorption for all investigated CdS samples was not more than 10^5 cm^{-1}. The feature of localization of the edge of fundamental absorption in CdS films in comparison with monocrystal CdS consists in that in films it is displaced into region of higher energies 2,549 eV, and after annealing its value tends to the monocrystal one.

4. CONCLUSIONS

For the first time using CdI_2 solution by the ChSD method CdS films are produced on glass and ITO coated glass substrates. Shown, that under layerwise deposition the width of CdS film increases almost linearly with the number of depositions up to saturation during the fourth deposition. Composition of CdS thin films (40-100 nm) deposited from CdI_2 solution is more similar to the stoichiometric one. For using CdS ChSD films made from CdI_2 at 70°C in heterostructures of CdS/CdTe type the annealing is necessary for hole removal on their surface. Carried out annealing leaded to the total hole disappearance, essential reconstruction of the film crystallinity, and a substrate has the greatest influence on the film structure at investigated widths.

REFERENCES

1. M. Estela Calixto, M. Tufino-Velazquez, G. Contreras-Puente, O. Vigil-Galan, M. Jimenez-Escamilla, R. Mendoza-Perez, J. Sastre-Hernandez, A. Morales-Acevedo, *Thin Solid Films* **516**, 7004 (2008).
2. P.H. Mugdur, Y.-J. Chang, S.-Y. Han, Y.W. Su, A.A. Morrone, S.O. Ryu, T.-J. Lee, C.-H. Chang, *J. Electrochem. Soc.* **154(9)**, D482 (2007).
3. G.A. Il'chuk, V.V. Kusnezh, P.Yo. Shapowal, F.I. Tsupko, V.O. Ukrainets, A.M. Kostruba, R.Yu Petrus, *FKhTT* **9** No4, 757 (2008).
4. M.D. Archbold, D.P. Halliday, K. Durose, T.P.A. Hase, D. Smyth-Boyle, K. Govender, *31-st IEEE Photovoltaic Specialists Conference*, 476 (2005).
5. N. Romeo, A. Bosio, R. Tedeschi, V. Canevari, *Thin Solid Films* **361-362**, 327 (2000).
6. B.E. McCandless, W.N. Shafarman, *3rd World Conference on Photovoltaic Energy Conversion*, 562 (2003).
7. *The Landolt-Bornstein database. Numerical data and functional relationship in science and technology. Group III* **17b** (Springer-Verlag: Berlin,·Heidelberg,·New York: 1982).