

CdS films growth by chemical bath deposition technique with substrate vibrating agitation

N.P.Klochko, G.S.Khrypunov, N.D.Volkova , V.R.Kopach,
V.M.Lyubov, D.A.Kudiy, M.M.Kharchenko, V.O.Nikitin*

National Technical University "Kharkiv Polytechnical Institute",
21 Frunze St., 61002 Kharkiv, Ukraine

*N.Zhukovsky National Aerospace University "Kharkiv Aviation Institute",
17 Chkalov St., 61070 Kharkiv, Ukraine

Received November 2, 2010

Composition, surface morphology, optical and structural properties of cadmium sulfide (CdS) films prepared by chemical bath deposition have been investigated. CdS films obtained by ion-by-ion mechanism in sulfate solution (thiourea to cadmium salt ratio S/Cd = 2.7) safe from the viewpoint of degradation CdS/CdTe based solar cell with substrate vibrating agitation were perfectly adherent and smooth. In chloride solution (S/Cd = 1.3) CdS layers were deposited by cluster mechanism and therefore had rough surfaces and poor adhesion. The films had optical properties inherent in cadmium sulfide and consisted mainly of CdS wurtzite modification, average crystallite size was approximately 50 nm.

Исследованы состав, морфология поверхности, оптические и структурные свойства слоев сульфида кадмия (CdS), изготовленных методом жидкофазного химического осаждения. Благодаря механизму ионного осаждения пленки, полученные в режиме вибрации подложки в безопасном с точки зрения деградации солнечного элемента на основе CdS/CdTe сульфатном растворе (соотношение в растворе тиомочевины и соли кадмия S/Cd = 2,7), были гладкими и хорошо сцепленными с подложками. В хлоридном растворе (S/Cd = 1,3) слои CdS осаждались по кластерному механизму и потому обладали развитым микрорельефом и плохой адгезией. Пленки имели свойственные сульфиду кадмия оптические свойства, состояли преимущественно из CdS модификации вюрцит, средний размер кристаллитов составлял около 50 нм.

1. Introduction

Cadmium sulfide (CdS) films obtained by chemical bath deposition (CBD) are widely used as buffer layers in Cu(In,Ga)Se₂ and CdTe based solar cells [1–5]. Although the CBD–CdS films have the least perfect structure compared to those deposited by laser ablation, close space vapor transport and vacuum sputtering, they can give excellent results for photovoltaic application due to better morphological properties (roughness and pinhole density) than CdS films grown by other techniques. At the same time, the main task, namely the obtaining of films perfectly adherent to substrate, free of sul-

fur surplus on grain boundaries and of hillocks on the film surface have not completely understood and attained. The cause is occurring of two possible mechanisms of CdS CBD. The first one is ion-by-ion deposition process producing compact highly reflecting films with excellent adherence to the substrate [5, 6]. According to the second mechanism, CdS or Cd(OH)₂/CdS particles (clusters) formed in the solution are deposited on the substrate or on the surface of the underlying compact CdS film and produce low quality porous layer. So the growth of a CdS film occurs through cluster-by-cluster process, which results in a light scattering layer inhomogeneous in

Table 1. Parameters of films deposition CdS

Sample No.	Solution	S/Cd ratio	Substrate	Agitation regime
15	0.011 M CdCl ₂ 1.0 M NH ₄ OH 0.014 M (NH ₂) ₂ CS	1.3	glass	magnetic
16			ITO/glass	
23	0.011 M CdCl ₂ 1.0 M NH ₄ OH 0.014 M (NH ₂) ₂ CS	1.3	glass	oscillating
24			ITO/glass	
31	0.0015 M CdSO ₄ 1.5 M NH ₄ OH 0.004 M (NH ₂) ₂ CS	2.7	ITO/glass	oscillating
32			glass	

physicochemical properties. The last explains interest to the detailed research of CBD mechanisms from the viewpoint of working solution compositions and agitation techniques. In our work, we went after authors [4] and used vibrating agitation of substrate during CdS thin film growth by CBD technique. The depositions were fulfilled in sulfate and chloride solutions that differ not only in anionic composition but also by ratio of sulfide and cadmium ions (S/Cd relation) in the solutions (Table 1). Search for the bath formula other than described in [4] is explained by degradation processes inherent in the solutions with $S/Cd \geq 5$ in CdS/CdTe solar cells [1, 2, 7] because of sulfur surplus on grain boundaries. As a result of the degradation processes, efficiency of photovoltaic devices diminishes by 50–80 % after 3 years storage. Note that authors [4] used for CBD CdS solution with $S/Cd = 10$ favoring the solar cell degradation. The purpose of this work is the investigation of CBD–CdS films composition, surface morphology, optical and structural properties vs. chemical bath formulas and agitation techniques and revealing the abilities of the bath composition together with vibrating agitation to influence the substitution of cluster-by-cluster film growth mechanism by ion-by-ion film deposition.

2. Experimental

The CdS depositions were accomplished in aqueous solutions containing cadmium chloride or sulfate, thiourea and ammonia (Table 1). As substrates, used were either clean glass sheets or those coated with magnetron sputtered transparent conductive tin oxide (TO) or indium tin oxide (ITO) layers. The solution was heated up to 75°C and continuously agitated by magnetic stirrer or by substrate holder vibrating at 37 Hz. The deposition took place during 15 min and

then films were rinsed in distilled water and dried by flowing hot air.

The film phase composition and structure were estimated by XRD using a DRON-4M X-ray diffractometer with CoK_{α} radiation according to $\theta-2\theta$ scheme. The scanning step was 0.01–0.02 degree; the exposure time was 3 s. The obtained compounds were identified by comparison of experimental results with JCPDS data for crystal lattice parameters of cubic CdS_c (sphalerite (JCPDS No.10–454)) and hexagonal (CdS_h, wurtzite (JCPDS No.6-0314)) cadmium sulfide modifications, of TO and ITO substrates, possible impurities Cd(OH)₂, S, CdCN₂, CdOHCl, CdCO₃, CdO, (NH₄)₂CO₃ and some other most probable compounds of cadmium and sulfur. The crystallite size for CdS film was estimated by approximation method for isotropic crystallite properties using the Scherer formula [6, 8, 9]. The morphology of CBD–CdS film surfaces was studied using a REM-100U scanning electron microscope at following parameters: accelerating voltage 200 V, collector voltage 200 V. The transmittance spectra of the films were measured by an SF-46 double beam spectrophotometer in the spectral range 0.4–0.9 μm. The optical transition type and band gap values of CdS films were obtained graphically by plotting $(\alpha h\nu)^n$ vs. $h\nu$ in accordance with [6, 8]. The film thickness was determined by gravimetric method as the difference of substrate weight prior to deposition and substrate plus CdS film weight after CBD using the known data on the film area and cadmium sulfide density.

3. Results and discussion

Our experiments concerning CdS chemical bath deposition in chloride solutions containing ratio $S/Cd = 1.3$ and agitated by magnetic stirring or by vibrating have revealed that in both cases the cluster-by-clus-

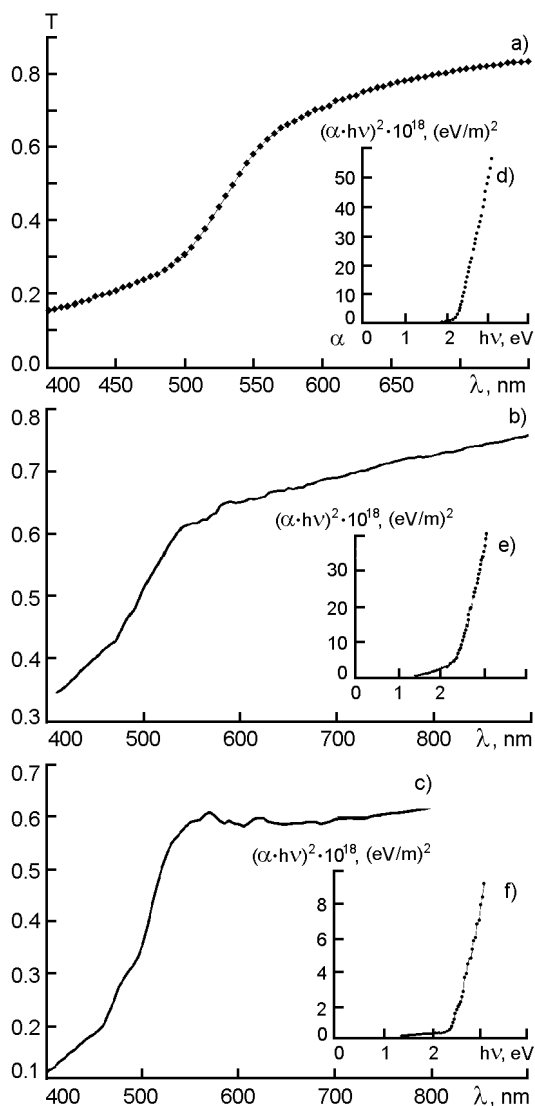


Fig. 1. Optical properties of CBD-CdS films on glass substrates: a, d — sample 15; b, e — sample 23; c, f — sample 32.

ter deposition is not avoided. During the CdS film deposition, colloidal particles were formed in the solution firstly and then they converted initially to white and later on to yellow flakes. The upper layer of the films was poor adherent and readily removed from the surface as a dust. The films were rough, so they dispersed light. Analysis of their optical properties have revealed that optical band gap for allowed transitions E_g equals 2.2 eV for Sample 15 deposited at agitation by magnetic stirrer and 2.3 eV for samples 23 and 24 obtained at substrate vibration (Fig. 1a, b, d, e; Fig. 2, curve 1). According to [8], narrower optical band gap compared to that typical of single CdS crystal ($E_g = 2.4$ eV) [9] is characteristic for

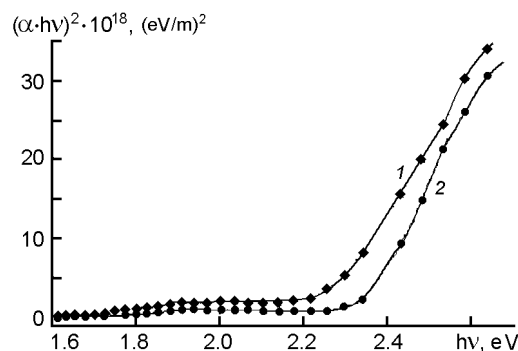


Fig. 2. $(\alpha \cdot hv)^2$ vs. hv for CBD-CdS film on glass/TO (sample No.16): 1) as grown film, 2) after air annealing at 400°C for 30 min.

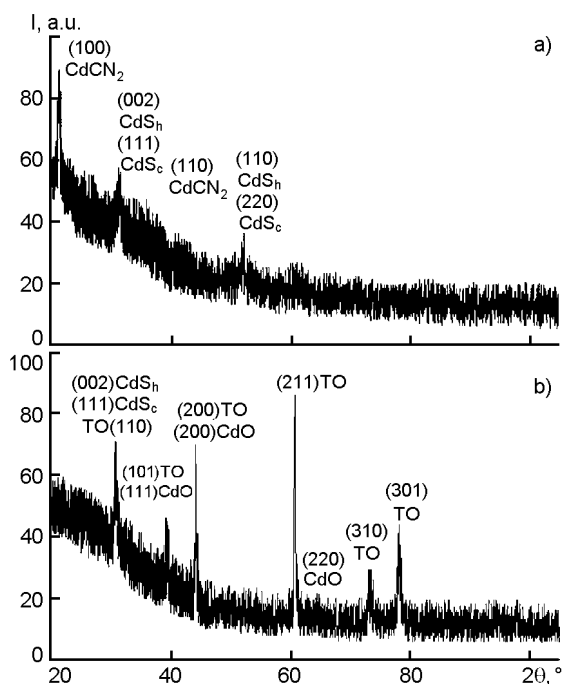


Fig. 3. X-ray diffractions of CBD-CdS films deposited by applying of magnetic agitation in chloride solution with ratio S/Cd = 1.3: a) – on the glass substrate (sample No.15) and b) – on substrate glass/ITO (sample No.16 after air annealing at 400°C for 30 min).

CBD-CdS films and correlates with structure imperfection. Moreover, as it is seen in $(\alpha hv)^2$ vs. hv plots (Fig. 1d, e; Fig. 2), they contain marked Urbach tails at sub-bandgap photon energies and so they are characterized by comparatively wide Urbach energies, that associated with disorder in the film material and with the reduction of the E_g from their standard value in the crystalline material [8]. As is seen in Fig. 2, Urbach energy reduces and band gap grows

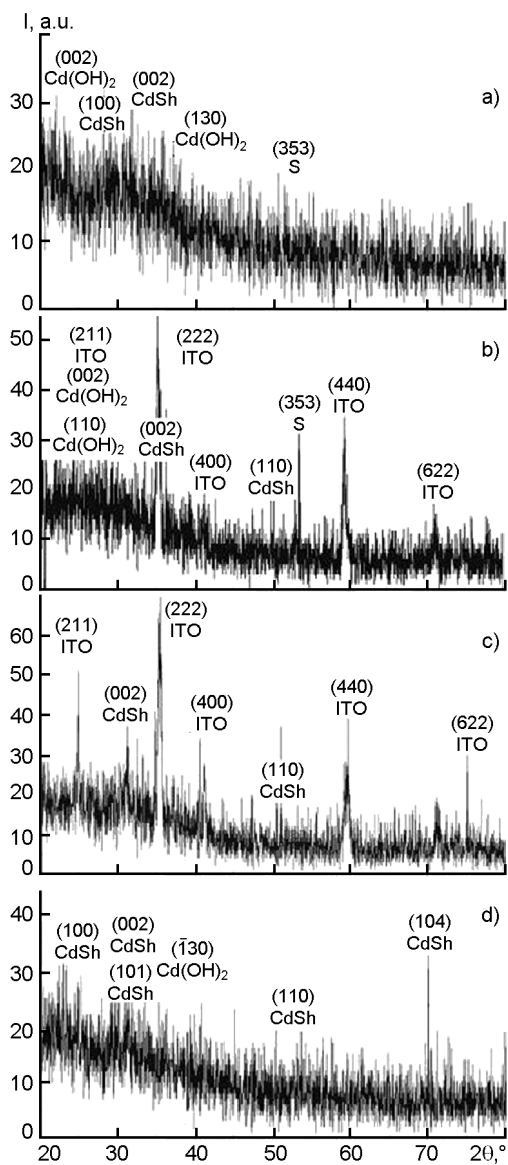


Fig. 4. X-ray diffractions of CBD-CdS films deposited by applying of substrate oscillation in chloride solution with ratio S/Cd = 1.3 (samples No.23 (a) and No.24(b)) and in sulfate solution with ratio S/Cd = 2.7 (samples No.31(c) and No.32 (d)).

from 2.25 eV up to 2.35 eV after air annealing of the films.

X-ray analysis of cadmium sulfide film deposited from chemical bath on glass substrate at magnetic stirring have revealed (Fig. 3, a) that this film contains besides of cadmium sulfide commensurable amounts of impurity cadmium cyanamide phase CdCN₂ (JCPDS No.36-0657), that is typical of CBD-CdS layers [10]. X-ray diffraction pattern of CBD-CdS layer air annealed at 400°C for 1 h (Fig. 3, b) differs substantially from as-

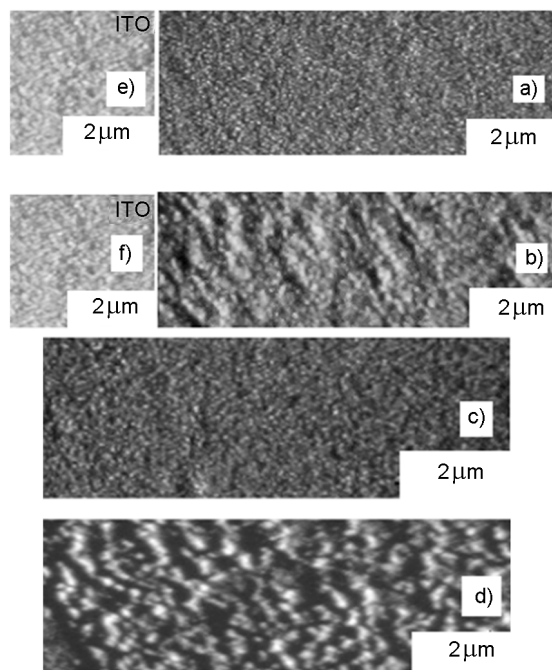


Fig. 5. Scanning electron microscopy images of CdS films deposited by applying substrate oscillation: a) sample 31; b) sample 23; c) sample 32; d) sample 24; f) and e) substrate ITO.

deposited one — it has no cadmium cyanamide peaks. Instead, after the annealing, a weak CdO (220) diffraction peak (JCPDS No.5-0640) at $2\theta = 64^\circ$ was revealed side by side with TO (JCPDS No.41-1445) peaks because, according to [10], at elevated temperatures in oxygen containing atmosphere CdCN₂ must turn into cadmium oxide. Note that other main CdO peaks are impossible to distinguish against the background of TO substrate. The X-ray diffraction patterns of CdS films grown with substrate vibrating agitation in chloride solution at the ratio S/Cd = 1.3 are shown in Fig. 4 (a and b). In spite of the low peak intensity, we have identified the CdS_h phase using the "New profile" program based on approximation method for isotropic crystallite properties developed at X-ray laboratory of Metals and Semiconductors Physics Department of National Technical University "Kharkiv Polytechnical Institute" [9]. Besides of cadmium sulfide, these films contained impurities Cd(OH)₂ (JCPDS 20-0179; 18-0258 and/or No.40-0760) and sulfur (JCPDS 23-0562), which particularly shape together with glass substrate a rather intense halo at 2θ from 20° up to 40° . The grain sizes estimated using the Scherrer formula were about 50 nm. This agrees well with the absence of the "blue shift", which could sig-

nificantly broaden E_g if crystallite diameter would be less than 40 nm [9].

By increasing the S/Cd ratio up to 2.7, we have realized the ion-by-ion chemical bath deposition in the case of substrate vibrating agitation in sulfate solution. During the growth, no flakes arise in the solution volume; the CdS films were perfectly adherent and had mirror-smooth surface. Fig. 5 demonstrates the surface morphology of these films (Fig. 5a, c) in comparison with the layers obtained in chloride solution with ratio S/Cd = 1.3 (Fig. 5b, d) and with glass/ITO substrate surfaces (Fig. 5e, f). X-ray spectra in Fig. 4, c and d evidence that these films consist predominately of CdS_h, but contain some Cd(OH)₂ impurity, which first of all forms together with glass substrate the halo at 2θ from 20° up to 40°. Analysis of shape of CdS_h peaks using the "New profile" program and estimation using the Scherer formula has revealed that CdS_h average grain size was 50 nm. Optical analysis of these improved CdS films has shown (Fig. 1c, f) that they have optical band gap 2.4 eV typical of cadmium sulfide for allowed straight transitions. The Urbach tails for these films are small, that confirms the better crystallinity of cadmium sulfide films grown in sulfate solution with ratio S/Cd = 2.7 by applying substrate vibration. Absence of "blue shift" for such films confirms in accordance with [10] the correctness of the estimations by using the Scherer formula. Thus, chemical bath deposition technique with substrate vibrating agitation provides the avoiding of cluster-by-cluster chemical bath deposition and the preparation of perfectly adherent mirror-smooth impurity sulfur free CdS films in the solution contained thiourea and cadmium sulfate in ratio S/CdS < 5, which does not cause the degradation of CdS/CdTe base solar cell.

4. Conclusion

Thus, the results of the above studies make it possible to conclude what follows. By means of change of S/Cd ratio in solu-

tions for chemical bath deposition causing not the degradation of CdS/CdTe base solar cell agitated by magnetic stirring or by vibration, we have determined the conditions for transition from cluster-to-cluster to ion-by-ion deposition, which provides the preparation of perfectly adherent mirror-smooth impurity sulfur free CdS films. X-ray analysis of CBD-CdS films has shown that all layers consist predominately of CdS_h, average grain size value is 50 nm, that is confirmed by optical investigation of these films. Depending on solution composition, agitation mode and annealing, the CBD-CdS films contain some impurities of CdCN₂, Cd(OH)₂, CdO or S.

Acknowledgment. The work was supported by Science and Technology Center in Ukraine, Grant STCU 4301.

References

1. O.Vigil-Galan, A.Arias-Carbajal, R.Mendoza-Parez et al., *Semicond. Sci. Technol.*, **20**, 819 (2005).
2. O.Vigil-Galan, A.Arias-Carbajal, R.Mendoza-Parez et al., *Solar Energy Mater. & Solar Cells*, **90**, 2221 (2006).
3. Chemical Bath Deposition Growth of Cadmium Sulphide, <http://www.cranfield.ac.uk/cds/cfi/solar/deposition.jspid=redirect>
4. Y.A.Salazar, R.Potino, J.I.Pena et al., *Brazilian J. Phys.*, **36**, 1058 (2006); M.G.Sandoval-Paz, R.Ramirez-Bon, *Thin Solid Films*, **517**, 6747 (2009).
5. G.Hodes, *Chemical Solution Deposition of Semiconductor Films*, New York-Basel, Marcel Dekker, Inc. (2002).
6. R.Mendoza-Perez, J.Sastre-Hernandes, G.Contereras-Puente et al., *Solar Energy Mater. & Solar Cells*, **93**, 79 (2009).
7. H.Moualkia, S.Hariech, M.S.Aida, *Thin Solid Films*, **518**, 1259 (2009).
8. O.G.Alaverdova, O.V.Arinkin, O.F.Bogdanova et al., *Structure and Physical Properties of Solids*, ed. by L.S.Palatnik, Vyscha Shkola, Kyiv (1992) [in Russian].
9. B.Malinowska, M.Rakib, G.Durand, *Solar Energy Mater. & Solar Cells*, **86**, 399 (2002).
10. N.I.Ivanova, D.S.Rudelev, B.D.Sum, *Vestnik Moskov. Univ., Ser. 2. Khimia*, **42**, 405 (2001).

Вирощування плівок CdS рідиннофазним хімічним осадженням у режимі вібрації підкладки

***Н.П.Клочко, Г.С.Хрипунов, Н.Д.Волкова, В.Р.Копач,
В.М.Любов, Д.А.Кудій, М.М.Харченко, В.О.Нікітін***

Досліджено склад, морфологію поверхні, оптичні та структурні властивості шарів кадмій сульфід (CdS), виготовлених методом рідиннофазного хімічного осадження. Завдяки механізму осадження іон-за-іоном плівки, одержані у режимі вібрації підкладки в безпечному для деградації сонячного елемента на основі CdS/CdTe сульфатному розчині (співвідношення у розчині тіосечовини і солі кадмію S/Cd = 2,7) були рівними і добре зчепленими з підкладками. У хлоридному розчині (S/Cd = 1,3) шари CdS осаджувалися за кластерним механізмом і тому відзначалися розвиненим мікрорельєфом і поганою адгезією до підкладки. Плівки мали притаманні кадмій-сульфіду оптичні властивості, склалися переважно з CdS модифікації вюрцит, середній розмір кристалітів становив близько 50 нм.