

Investigation on chemical bath deposited CdS thin films

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Received: 23 May 2011, accepted: 30 September 2011

Abstract

This paper presents the effect of solution temperature on optical, electrical and photoconducting properties of CdS films prepared by chemical deposition method. The solution temperatures used varied between 55 and 75 °C. X-ray diffraction analysis showed that the prepared films have a hexagonal structure with (002) reflection. The transmittance data analysis showed a high transmission coefficient in visible range (85%) and an optical band gap lying between 2 and 2.4 eV. Scanning electron microscopy (SEM) and electrical measurements showed a pronounced effect of the solution temperature on thickness, dark conductivity and photoconductivity to dark conductivity ratio ($\sigma_{\text{photo}}/\sigma_{\text{dark}}$) parameters. The evolution of such parameters as a function of temperature are presented and discussed. It was found that the ($\sigma_{\text{photo}}/\sigma_{\text{dark}}$) ratio reaches high values of the order of 10^4 and 10^5 at 55 and 65 °C, respectively. These results indicate that CdS thin films prepared at these temperatures are convenient for optoelectronic and photovoltaic applications.

Keywords: CdS thin films, Chemical bath deposition (CBD), Physical properties, Solar cell.

1. Introduction

Nowadays, the fabrication of high efficiency solar cells based on CdS/CdTe, CdS/CuInSe₂ and CdS/CuIn(Ga)Se₂ thin films heterostructure [1-4] has increased the studies on this technologically relevant semiconductor material. The chemical bath deposition (CBD) of thin films is the most widely employed method [5] for fabricating n-type window layers on CuIn(Ga)Se₂, CuInSe₂ and CdTe solar cells [6-9]. Several studies reported in the literature showed the role of the chemically deposited CdS films window layer on solar cells efficiency [2, 3, 10]. For this purpose several properties are required for the CdS thin films such as: (i) relatively high transparency and wide band gap (ii) relatively large conductivity to reduce the electrical solar cells losses and higher photoconductivity to not alter the solar cell spectral response. However, the production of CdS films still requires further investigation. In the present work, CdS thin films were grown by chemical bath deposition method. Optical, electrical and photoconducting properties have been investigated as a function of bath temperature in order to study their growth mechanism and achieve highly transparent, conductive and photoconductive layers.

2. Experimental

The CdS thin films were deposited on glass substrates from a chemical bath containing deionised water, cadmium acetate Cd(CH₃COO)₂·2H₂O (5 10⁻³ M), Thiourea SC(NH₂)₂ (2 10⁻² M) and ammonia NH₄OH (2M). Cadmium acetate and thiourea were employed as cadmium and sulphur sources, respectively. The substrates were cleaned ultrasonically in acetone and methanol, rinsed in distilled water and dried in hot air. After drying, the samples were inserted vertically into the chemical bath. The solution temperatures were varied from 55 to 75°C. The deposition time was 60 min for each film.

After elaboration, films thicknesses were determined from profilometry measurements. The surface morphology of the films was analysed by scanning electron microscopy (SEM). The structural characterization was carried out by the X-ray diffraction (XRD) technique using an X-ray diffractometer (Philips X'Pert) with CuK α radiation. The transmittance of the films was studied using a Shimadzu 3101 PC UV-visible spectrophotometer. The electrical conductivity and the photoconductivity of the films were measured in a coplanar structure obtained by evaporation of two golden strips on the film surface. For the photoconductivity measurements, the samples were illuminated by unfiltered white light from a halogen lamp; the light intensity was 3000 Lx.

3. Results and discussion

3.1 Structure and morphology

The SEM images of CdS films deposited at the solution temperatures: (a) T_s = 60°C and (b) T_s = 65°C are shown in Figure 1. The images display homogeneous and continuous thin layers with small crystallites. These thin layers are originated from heterogeneous reaction via the ion by ion mechanism as has been reported in previous works [11, 12]. Figure 2 shows XRD pattern of CdS thin film deposited at T_s = 60°C. It shows only one line that corresponds to the (002) reflection of the hexagonal structure in accordance with earlier findings where several authors have observed that the preferential orientation of the CdS thin films is along the (002) direction [13-15]. It is also interesting to note that CdS thin film with hexagonal structure is highly favourable for solar cell applications as a window layer due to its stability [16].

The variation of the thickness of CdS thin films as a function of the solution temperature is presented in Figure 3. It is clear from the figure that the thickness increases with increasing temperature up to 65 °C, then decreases at higher

solution temperature ($T_s > 65^\circ\text{C}$). This latter behaviour can be interpreted as follows:

(i) In the temperature range ($T_s \leq 65^\circ\text{C}$), the thickness increase is attributed to the increase of the releasing rate of the Cd^{2+} and S^{2-} ions which nucleate on the substrate to form CdS particles. Moreover, in accordance with SEM analysis, the CdS thin film grow with an ion by ion mechanism and it is known that the ion by ion mechanism yields films with larger thickness [17].

(ii) At higher temperature ($T_s > 65^\circ\text{C}$) the releasing rate of Cd^{2+} and S^{2-} ions become too high because of the thermal effect. Hence, the deposition mechanism changes into cluster by cluster which needs higher temperatures to occur as shown in our previous work [18].

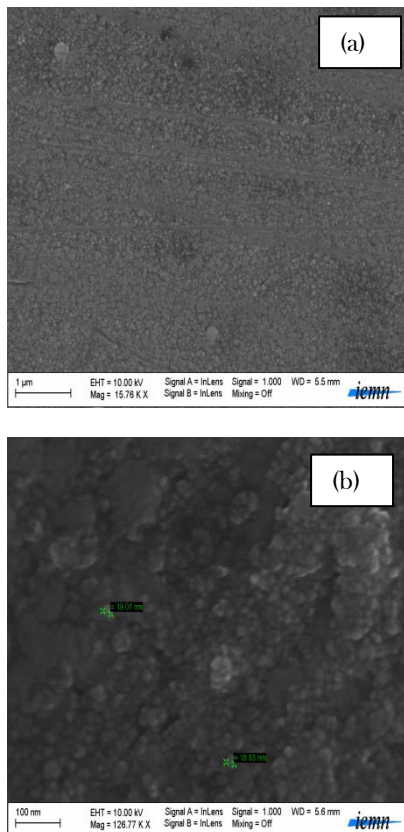


Figure 1: SEM micrograph of CdS sample deposited at the solution temperatures (a) $T_s = 60^\circ\text{C}$, (b) $T_s = 65^\circ\text{C}$

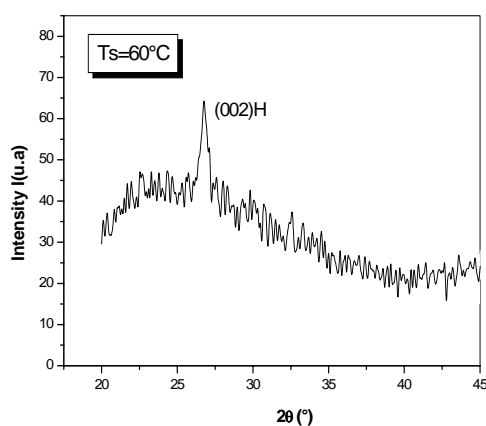


Figure 2: X-Ray spectrum of a typical CBD-CdS sample deposited at the solution temperature $T_s = 60^\circ\text{C}$

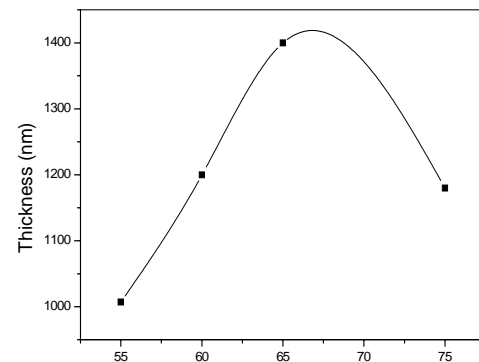


Figure 3: Evolution of CdS thickness with the solution temperature

In this deposition process conditions, CdS can take place by both heterogeneous and homogeneous reactions leading to the formation of continuous CdS film at the surface of the substrate and to the formation of large CdS particle (Clusters) in the bulk of the solution, respectively. The heterogeneous reaction competes with the homogeneous one, which depletes the reactants to form CdS particles in the bulk solution resulting in a decrease of the thickness.

3.2. Optical properties

Figure 4 shows the optical transmittance of CdS thin films deposited at various solution temperatures. All films exhibit optical transmittance more than 60 % for wavelengths larger than 500 nm, which is one of the prerequisites for solar cells window layer [19]. We note a sharp absorption edge in the range of 400 - 440 nm [20, 21]. The transmittance in the low wavelength region extends to 300 nm. This means that there are disorder effects or presence of amorphous components in the film [21].

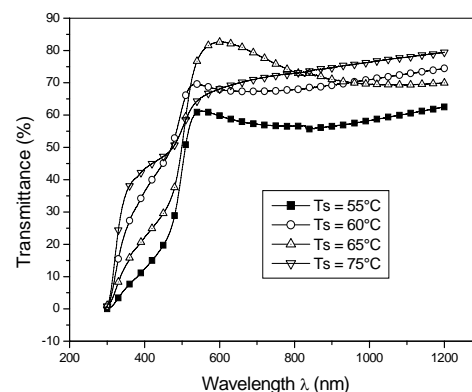


Figure 4: Influence of solution temperature on the optical transmittance of CdS films

The absorption coefficient α of CdS thin films was calculated from the transmittance spectra using the Beer-Lambert approximation. The absorption coefficient α can be expressed by Urbach relation:

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (1)$$

Where A is a constant, E_g is the energy band gap, ν is the frequency of the incident radiation and h is Planck's constant. The exponent n is 0.5 for direct allowed transitions. CdS is a direct band gap material; several workers reported this type of transition [22-24]. The energy band gap of the films at various temperatures have been determined by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ versus $h\nu$ to the energy axis. The band tail width E_t (the so-called Urbach energy) was deduced from the slope of the graph $\ln(\alpha) = f(h\nu)$. The band gap and the band tail width E_t for different solution temperatures are given in table 1. The same band gap values ($E_g = 2-2,4$ eV) were reported by A. Ates et al. [25].

Table 1: Optical parameters of CdS thin films for different solution temperatures

Samples	Solution temperatures (°C)	Band gap (eV)	Urbach's energy E_t (meV)
1	55	2,3	257
2	60	2,2	380
3	65	2,4	209
4	75	2	590

3.3. Electrical properties

The variation of the dark conductivity as a function of reverse temperatures is illustrated in Figure 5.

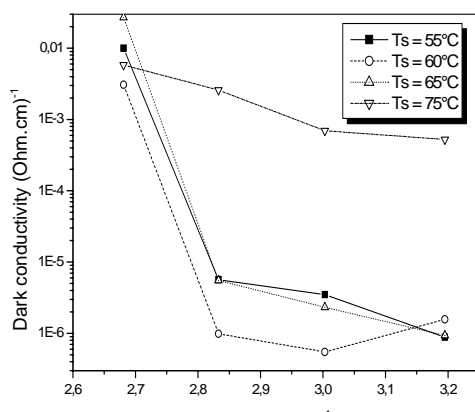


Figure 5: Variation of the dark conductivity as a function of reverse temperatures for different samples

The dark conductivity increases with increasing measurement temperature indicating the semiconducting nature of the films. From the variation of the dark conductivity versus $(1000/T)$ we have deduced the electrical activation energy E_t (see table 2).

To determine the Fermi level position in the forbidden band, one calculates the ratio $\left(\frac{2E_t}{E_g}\right)$. The results are presented in table 2.

Table 2: $\left(\frac{2E_t}{E_g}\right)$ ratio of CBD-CdS films.

Samples	Solution temperatures (°C)	E_t	$\left(\frac{2E_t}{E_g}\right)$
1	55	0,24	0,208
2	60	0,32	0,290
3	65	0,40	0,333
4	75	0,13	0,13

As can be seen from the table 2, the $\left(\frac{2E_t}{E_g}\right)$ values are less

than the unity for all solution temperatures indicating that the deposited films are of n-type. This is in agreements with earlier findings [26, 27].

The variation of the dark conductivity as a function of the solution temperature, T_s , is presented in Figure 6. For T_s lower than 65 °C, where the growth mechanism is achieved via the ion by ion mechanism, the dark conductivity varies from 10^{-6} to 10^{-7} ($\Omega \text{ cm}$) $^{-1}$. These values are too low due probably to the presence of structural disorders and dislocations as interpreted by D. Padiyan and al [28]. However, in the high temperature region ($T_s > 65^\circ\text{C}$), where the deposition is achieved via cluster by cluster process, the conductivity reaches 10^{-4} ($\Omega \text{ cm}$) $^{-1}$. This behaviour is probably due to the presence of the hydroxide cadmium $\text{Cd}(\text{OH})_2$ or to the sulphur deficiency in the deposited films. Indeed, Lincot et al. [29] concluded that the coexistence of the oxide and hydroxide cadmium forms is the possible reason for the sulphur deficiency.

Consequently, we suggest that CdS thin films deposited at high temperatures contain a high concentration of sulphur vacancies and cadmium interstices which act as donors defects in CdS thin films. We conclude that by varying the growth temperature it is possible to promote the deposition mechanism in order to obtain a high conductivity.

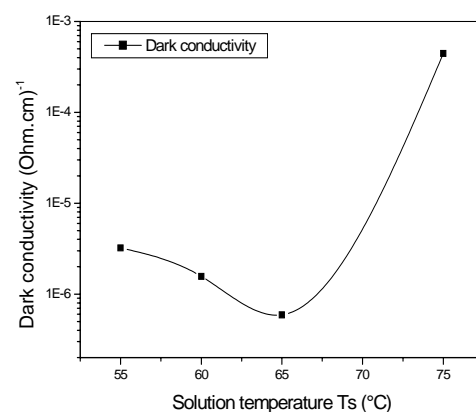


Figure 6: Dependence of dark conductivity on the solution temperature

The variation of the photoconductivity to the dark conductivity ratio $\frac{\sigma_{phot}}{\sigma_{dark}}$ as a function of the solution temperature is shown in figure 7. The photoconductivity of

the deposited films is two to five orders of decade larger than the dark conductivity. The $\frac{\sigma_{phot}}{\sigma_{dark}}$ ratio is higher in the case of films deposited at 55 and 65°C. Its value is of the order of 10^5 and 10^6 at 55 and 65°C, respectively. Whereas, films deposited at temperatures 60 and 75°C exhibit low $\frac{\sigma_{phot}}{\sigma_{dark}}$ ratio. As discussed above the films deposited at these temperatures contain more structural defects (see table 1). These defects act as traps for photogenerated carriers, and hence the reduction in their photoconductivity as suggested by Rakhshani et al [30].

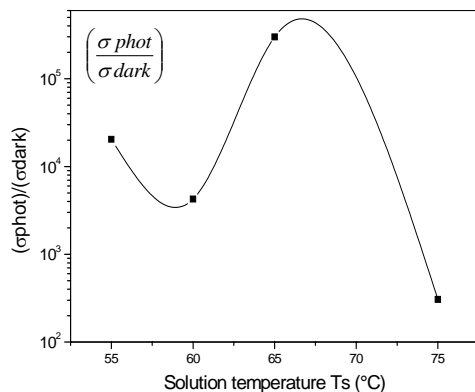


Figure 7: Variation of the photoconductivity on the dark conductivity ratio $\frac{\sigma_{phot}}{\sigma_{dark}}$ as a function of the solution temperature.

4. Conclusion

In this paper, we have successfully deposited CdS thin films by the chemical bath deposition method with varied solution temperature and using a Cd(CH₃COO)₂·2H₂O as a cadmium source. The films present hexagonal crystalline structure as confirmed by X-ray diffraction measurements. From the variation of the thickness and SEM images as a function of solution temperature we concluded that the CdS films are grown by the ion by ion mechanism at low temperatures (Ts < 65 °C), then changes towards cluster by cluster mechanism at higher deposition temperatures (Ts > 65 °C). Films grown show good optical transmission in visible light range and band gap values vary between 2 and 2.4 eV. The solution temperature shows a pronounced effect on the electrical property where the dark conductivity values increase from 10^7 to 10^8 (Ω.cm)⁻¹ at higher temperature (Ts > 65°C). The photoconductivity of the deposited films is two to five decade larger than the dark conductivity. According to our experimental data the deposited films possess good properties which are the prerequisites for opto-electronic devices, especially for solar cell window layers.

References

- [1] A. Romeo, D.L. Batzner, H. Zogg, C. Vignali, A.N. Tiwari, Sol. Energy Mater. Sol. Cells 67 (2001) 311.
- [2] M.A. Contreras, M.J. Romeo, B. To, F. Hasoon, R. Noufi, S. Ward, K. Ramanathan, Thin Solid Films 403 -404 (2002) 204-211.

- [3] R. Mendoza-Pérez, J. Aguilar-Hernandez, J. Sastre-Hernandez, N. Ximello-Quebras, G. Contreras-Puente, G. Santana-Rodriguez, O. Vigil-Galan, E. Moreno-Garcia, A. Morales-Acevedo, Sol. Energy 80 (2006) 682.
- [4] H. Bayhan, A. S. Kavasoglu, Sol. Energy 80 (2006) 1160.
- [5] K.L. Chopra, R.C. Kainla, D.K. Pandya, A.P. Thakoor, Phys. Thin Films 12 (1982) 167.
- [6] T.L. Chu, S.S. Chu, C. Ferekides, C.Q. Wu, J. Britt, C. Wang, J. Appl. Phys. 70 (1991) 7608.
- [7] L. Stolt, J. Hedström, J. Kessler, M. Ruckh, K.O. Velthaus, H.W. Schock, Appl. Phys. Lett. 62 (1993) 597.
- [8] A. Catalano, Solar Energy Mater. Solar Cells 41-42 (1996) 205.
- [9] B. Dimmler, E. Gross, R. Menner, M. Powalla, D. Hariskos, M. Ruckh, U. Rühle, H.W. Schock, Proc. 25th IEEE Photovoltaic Specialists Conf., Washington, DC, (1996)757.
- [10] X. Wu, J. Keane, R. Dhere, C. de Hart, A. Duda, T. Gessert, S. Asher, D. Levi, P. Sheldon, in: Proceedings of the 17th European Photovoltaic Solar Conference, Munich, Germany, 22 -26, October 2001, p. 995.
- [11] M.L. Breen, J.T. Woodward, D.K. Schwartz, A.W. Applett, Chem. Mater. 10 (1998) 710.
- [12] M. Kostoglou, N. Andritsos, A.J. Karabelas, Ind. Eng. Chem. Res. 39 (2000) 3272.
- [13] L. Wenyi, C. Xun, C. Qiulong, Z. Zhibin, Mater. Lett. 59 (2005) 1.
- [14] S.N. Sharama, R.k. Sharma, K.N. Sood, S. Singh, Mater. Chem. Phys. 93 (2005) 368.
- [15] J.H. Lee, Thin Solid Films 515 (2007) 6089.
- [16] I. Kaur, D.K. Pandya, K.L. Chopra, J. Electrochem. Soc. 127 (1980) 943.
- [17] G. Hodes, Chemical Solution Deposition of Semiconductor Film, Marcel Dekker, Inc 2002.
- [18] H. Moualkia, S. Hariech, M.S. Aida, N.Attaf, E.L. Laifa, J. Phys. D: Appl. 42 (2009) 135404 (7pp)
- [19] J. Hiie, T. Dedova, V. Valdna, K. Muska, Thin Solid Films 511-512 (2006) 443.
- [20] F. Chen, W. Jie, X. Cai, Thin Solid Films 516 (2008) 2827-28.
- [21] J.N. Ximello-Quebras, G. Contreras-Puente, J. Aguilar-Hernandez, G. Santana-Rodriguez, A. Arias-Carbajal Readigos, Sol. Energy Mater. & Sol. Cells 82 (2004) 265.
- [22] S. G. Munde, M. P. Mahabole, R. S. Khainar, J. Instrum. Soc. India 30 (1) (2000) 25.
- [23] S. S. Kale, U. S. Jadhav, C. D. Lakhande, Indian J. Pure, Appl. Phys. 34 (1996) 324.
- [24] G. C. Morris, R. Vanderveen, Sol. Energy Mater. Sol. Cells 27 (1992) 305.
- [25] A. Ates, M.A. Yildirim, M. Kundakci, M. Yildirim, Chin. J. Phys. 45 (2-I) (2007) 135.
- [26] L. Wenyi, G. Xun, C. Qiulong, Z. Zhibin, Mater. Lett. 59 (2005) 5.
- [27] O. A. Ilperuma, C. Vithana, K. Premaratne, S.N. Akuranthilaka, S.M. Megregor, I.M. Dharmadasa, J. Mater. Sci. 9 (1998)367.
- [28] D. P. Padiyan, A. Marikani, K. R. Murali, Mater. Chem. Phys. 78 (2002)51. [29] D. Lincot, R. Ortega-Borgees, M. Froment, Philos. Mag. B 68 (1993)185.
- [30] A. E. Rakhshani, A. S. Al-Azab, J. Phys: Condens. Matter 12 (2000)8745-8755.