CdS films deposited by Chemical Bath Deposition for solar cells application

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The CdS thin films were deposited on glass substrate by chemical bath deposition (CBD). The influence of the preparation technique on the structural, optical and electrical properties of the polycrystalline CdS films was investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) optical transmission. The materials have been prepared using simple aqueous solutions containing Cadmium acetate, as source of Cadmium, and thiourea as source of sulfur and ammonium hydroxide as the complexing agent. The temperature of the bath was maintained at low temperature of 90 ° C. The nanoparticles of CdS was obtained with an energy band gap of 3.8 eV. This study confirms that the energy band gap depends of the grain particle size.

(Received April 17, 2013; accepted June 12, 2013)

*Keywords:*CdS, Chemical Bath Deposition, Energy band gap, Grain size, Nanoparticles

1. Introduction

CdS has been used as a window material in high efficiency thin film solar cells base on CdTe and Cu(In,Ga)Se 2 (CIGS) [1, 2]. It has been used in the deposition of CdS semiconductor thin films since the 1960s [3,4] and many techniques including electro-deposition, spray pyrolysis [5], vacuum evaporation [6], sputtering, electroless deposition, dip growth and Chemical Bath Deposition (CDB) [7,8].

CBD is known to be a simple method, with low temperature and inexpensive large area deposition technique, it use an aqueous solution and then we can control the chemical parameters of solution like (temperature, molar concentration, PH, time of deposition, stirring rate., etc.). Therefore we can control the thickness of the film and grain size of the particle then the energy band gap. In this study we use Chemical Bath Deposition method for elaborate CdS nanoparticles thin film and we focus on the consequences of nanoparticles on the energy band gap of the semiconductor compared with literature and bulk sample.

The CdS deposition by CBD is based on the controlled precipitation of metallic ions in a solution containing sulfide ions of controllable concentrations. This can be achieved mainly through two mechanisms:

a) Ion by ion (heterogeneous reaction) or
b) Cluster by cluster (homogeneous reaction).

The formation process of CdS nanoparticles are proposed as follows [9]:

The cationic precursor solution releases Cd^{2+} ions from $[Cd\ (tartaric\ acid)]^{2+}$ as:

$$[Cd(tartaric\ acid)]^{2+} \rightarrow Cd^{2+} + tartaric\ acid \quad (1)$$

In the anionic precursor solution, thiourea hydrolysis occurs and gives S^{2-} ions according to:

$$(CS\ (NH_2)_2) + OH^- \rightarrow OC\ (NH_2)_2 + SH^- \quad (2)$$

$$SH^- + OH^- \rightarrow S^{2-} + H_2O \quad (3)$$

Finally the CdS are formed by combinaison of Cd^{2+} with S^{2-} ions as:

$$Cd^{2+} + S^{2-} \rightarrow CdS \quad (4)$$

2. Experimental details

2.1 Sample preparation

Our purpose studies thin films of CdS have been deposited by chemical deposition, using the stock solution of 1 M Thiourea (CS $(NH_2)_2$) in the presence of 1 M Cadmium acetate ($Cd(OOCCH_3)_2$, $2H_2O$) in a basic solution with 30-33% ammonium hydroxide (NH_4OH) as the complexing agent and distilled water. The stock solution was first homogenized by stirring with a small magnetic bar at room temperature, and the pH value was kept at 11.

Films were deposited on glass substrates (Micro slides Glass) thickness (1.35 mm) and size (75x25 mm), these substrates were emerged in ultrasonic bath (in different solution such as ethanol, acetone) for 30 minutes and finally washed by distilled water, in order to clean them. The bath was covered and continuously stirred during the deposition to ensure homogeneous distribution of the chemicals. All the films used in the present investigation were deposited simultaneously from the same bath

deposited using the same chemical solution at different time of deposition and annealed with a fix temperature.

Fig. 1 shows the schematic diagram of the experimental method.

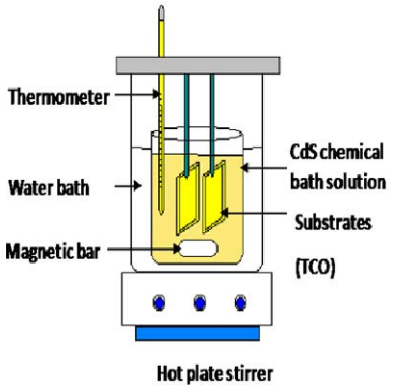


Fig. 1. Schematic diagram of Chemical Bath Deposition.

2.2 Characterization

The surface morphology of the nanostructure films was investigated with scanning electron microscope (SEM). The phase structure of the deposited films was studied using X-ray diffractometer model EQUINOX 3000 with a high-intensity Cu-Kα1 radiation and (λ =1.54060 Å) optimized operating conditions of 30 mA and 30 kV at a scanning rate of 0.5° in 2-theta range of (10-90°). The size D of the crystallites was calculated from the Scherer's formula [10]:

$$L=K\lambda/(\beta \cos \Theta) \quad (5)$$

In this case of small spherical scrystallites, the relation between L and D, the diameter of crystallite, is given by L= (3/4) D. The average particle size of CdS was found to be 1.5 nm.

3. Results and discussion

3.1 Scanning electron microscopy (SEM)

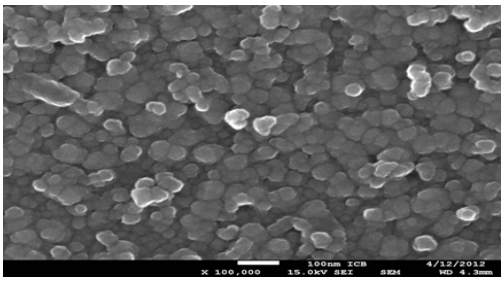
Fig. 2 shows the scanning electron microscope (SEM) images for thin films of CdS deposited at T =90°C, and different time of deposition and annealing which are cited respectively in Table 1.

Table 1. CdS thin films deposited with different parameters.

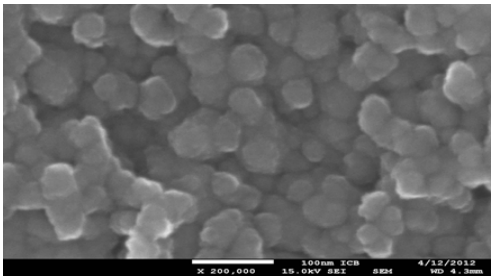
Samples	Time deposition (min)	Time annealing (min)	Temp of deposition (° C)	Temp of annealing (° C)
1	60	30	90	300
2	60	60	90	300
3	90	30	90	300
4	90	60	90	300

The surface of the thin films displays an inhomogeneous appearance in all scanned areas of the sample as shown in Fig. 2.

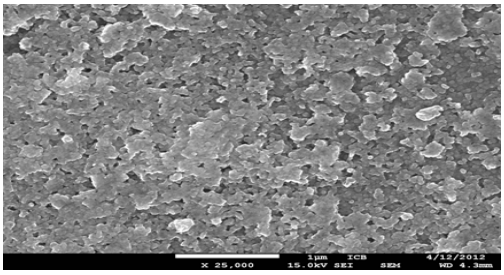
The films also showed the crystallite size but in this case it was difficult to calculate exactly the size directly in the SEM images and they approximately calculated around 2-5 nm but they were calculated values from the XRD patterns widths at half maximum of the peaks by Scherer's formula and confirmed by Brus equation [11] .



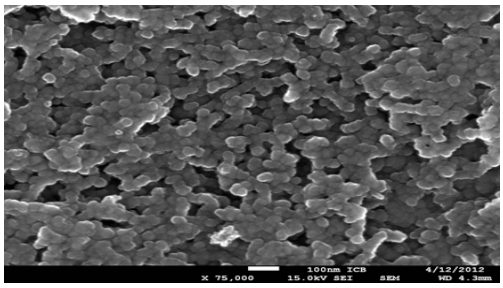
Sample 1



Sample 2



Sample 3



Sample 4

Fig. 2. SEM images of CdS thin films.

3.2 X-ray diffraction

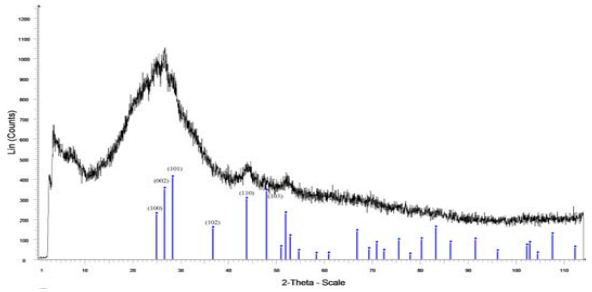


Fig. 3. X-Ray diffraction out of plane pattern of the CdS (Sample 4).

Fig. 3 shows the XRD patterns of the thin films of CdS deposited at T =90°C, all the samples exhibit a hexagonal wurtzites structures with four diffraction peaks (100) 24.83°, (002) 26.52°, (101) 28.21° and (110) 43.73° [12], indicating the multi- orientation character of CdS films, the intensity of the four peaks gradually increases. The CdS crystallites calculated by the Scherer formula are 1.5 nm. The reflection peaks can be well index hexagonal phase CdS with lattice constants a =4.136 Å and c =6.716 Å which are in good agreement with the literature values.

The composition of the product was studied by energy dispersive X-ray analysis and is depicted in Fig. 3. The curve exhibits the presence of Cd and S peaks with an average atomic percentage ratio of 29:11, which is rich in cadmium.

3.3 Optical properties of produced CdS thin films

Fig. 4 presents the optical transmittance in the wavelength range (300-1200 nm) for the CdS thin films deposited at T =90°C. The average transmittance in the visible part of the spectre (400-1200 nm) was over 90%.

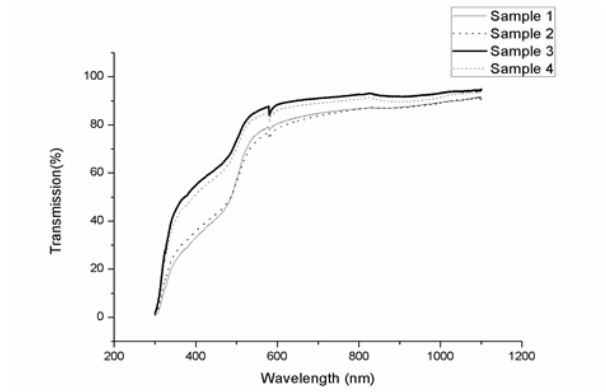


Fig 4.Transmittance spectra of produce CdS thins films

The changes of transmittances are associated to the increase measured over the visible range. The optical absorption coefficient α was evaluated from the transmittance (T) using the relation:

$$\alpha - (\ln(1/T)/t) \qquad (6)$$

were t is the thickness of the films. To determinate gap energy of direct transition (E_g) of the CdS thin films optical method was used. In this method, the plots of $(\alpha h\nu)^2$ versus ($h\nu$) for CdS thin films are shown in Fig. 4. The linear intercept at the ($h\nu$) axis gives the value of the direct band gap.

The optical energy band gap of the film increase from 3.78 eV to 3.80 eV [12].

To get more confirmation, the size of nanoparticles is calculated in the frame of the effective mass approximation. According to this approximation, the band gap of semiconductor Nano crystal considered as a sphere with radius R is given by:

$$Eg\,(\mathrm{R}) = Eg\,(\mathrm{bulk}) + [h^2/8\,\mu\,R^2] - 1.78e^2/(\varepsilon R) \qquad (7)$$

where Eg (R) is the band gap value of the nanoparticles, Eg (bulk) is the band gap value of the bulk material, h is Plank's constant, e is electron charge, R and ε are the radius and the dielectric constant of the CdS and $\mu = m_e^* m_h^* / (m_e^* + m_h^*)$, where m_e^* and m_h^* are effective masses of electrons and holes, respectively [13,14]. Thus, the calculated particles size is shown in Table 2 which value is in good agreement with the results obtained from XRD and with admissible resolving power limit observed from SEM images.

Table 2. Optical parameters of CdS nanocrystals calculated by Brus equation.

Samples	E_g (bulk)(eV)	E_g (nano)(eV)	Size grain(nm)
1	2.42	3.80	1.28
2	2.42	3.78	1.29
3	2.42	3.87	1.25
4	2.42	3.82	1.27

Fig. 5 shows the variation $(\alpha h\nu)^2$ with ($h\nu$). From graph the band gap of particles is determined. Particles size obtained for four different samples were presented in Table 2 and the reduction in particle size gives a shift in the optical band gap. The absorption is onset is about 340 nm corresponding to a band gap of 3.80 eV which is higher than the band gap of bulk CdS (2.42 eV).

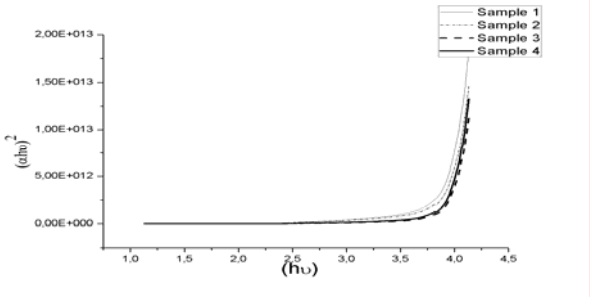


Fig. 5. Graph of $(\alpha h\nu)^2$ versus $(h\nu)$ in different samples.

The graph in Fig. 6 shows when the size decreases the band gap increases.

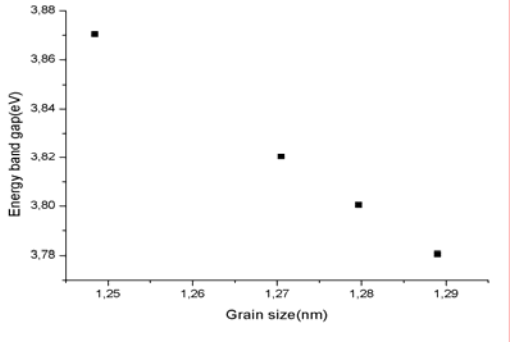


Fig. 6. Variation of CdS nanoparticles size controlled the energy band gap.

Optical band gap depends on the grain size of a thin film. We observe a blue shift with decreased grain size, i.e. band gap is increased with smaller grain sizes.

4. Conclusion

In this paper, we used a simple and easily-controllable method to elaborate CdS nanoparticles thus a good quality, adherent, uniform and pinhole-free CdS films were obtained by CBD method. The films have hexagonal phase and a preferred orientation in the (0 0 2) plane. The variation of the band gap was attributed to the strain of the films. This study compared with bulk CdS and confirmed that the band gap is depended by the particle size.

Acknowledgements

This work was supported by the all member of Laboratory of Electronic Microscopy and Materials Science in University of Science and Technology of Oran and NanoForm of ICB university of Bourgogne Dijon France. We would like to thank Mr Nicolas GEOFFROY for XRD and F.HERBST for SEM.

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