

## CHARACTERIZATION OF NANOSTRUCTURED CdS FILM DEPOSITED AT LOW GROWTH RATE USING CBD TECHNIQUE

ZAHID RIZWAN\*, AZMI ZAKARIA, M. NORIZAM,  
M. G. M. SABRI, REZA ZAMIRI, MONIR NOROOZI  
*Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400  
Serdang, Selangor Darul Ehsan Malaysia*

Cds film was deposited by chemical bath deposition (CBD) on commercial glass substrate at the constant bath temperature 72 °C. The deposition time was varied from 1 to 4 hours. The film growth rate varies from 0.89 nm to 0.26 nm. It was found that the adhesion was very good for all film deposition times. Film thickness was measured by ellipsometer and ranges from 52.7 to 56 nm for all deposition times. XRD analyses show that the film was cubic with crystallite size from 38 to 45 nm. The optical energy band gap ( $E_g$ ), Urbach energy ( $E_{oo}$ ) and absorption coefficient ( $\alpha$ ) was calculated from the transmission spectral data.

(Received June 1, 2010; accepted June 26, 2010)

*Keywords:* CBD, CdS, Optical properties

### 1. Introduction

The application of thin films is widely used in the modern technology. A variety of techniques like thermal evaporation, radio frequency sputtering, pulsed laser evaporation, spray pyrolysis, metal organic vapor deposition etc and chemical bath deposition have been used for thin film growth. However Chemical bath deposition (CBD) is known to be simple, low temperature, inexpensive large area deposition technique. Easy coating of large surface deposition makes it appropriate for large area industrial application. This technique also offers excellent control when depositing thinner films. CBD is also known as solution growth or chemical deposition technique. This technique has been used for the deposition of Cadmium Sulfide (CdS) film since 1960s [1, 2]. CBD is known to greatly enhance the performance of CdS window layer as compared to the other film deposition techniques. The highest efficiency were obtained when CBD technique was used to grow the thin polycrystalline CdS window layer or buffer layer for CdTe and CIGS solar cells [3, 4]. It is used as a window layer material in the fabrication of high efficiency thin film solar cell. It is also used in other electronic and optoelectronic devices. [5, 6]. CdS is known to be an excellent heterojunction partner for P-type CdTe, CuInSe<sub>2</sub> Cu(In,Ga)Se<sub>2</sub> (CIGS) due to its wide band gap (2.42 eV), photoconductivity, high index of refraction (2.5) and its high electron affinity [7, 8]. The properties like uniformity, transparency, crystallinity and good electrical characteristics are required for the use of CdS film in solar cell and other sophisticated device fabrication. The immersion of substrate is required to grow CdS film in alkaline aqueous solution containing Cd<sup>2+</sup> and S<sup>2-</sup> resulting from the chemical reaction in the solution [9, 10]. Several conditions like temperature, deposition time, relative concentrations of the reactive, providing the Cd<sup>2+</sup> and S<sup>2-</sup> ions for chemical reaction and PH of aqueous solution are required for the deposition of the CdS film on substrate in CBD technique. In this study, CBD technique has been used to deposit the nanostructured CdS film on microscopic glass substrate at very low growth rate for different deposition times at constant bath temperature 72 °C. Optical and structural properties of the film are discussed in this paper.

---

\*Corresponding author: zahidrizwan64@gmail.com

## 2. Experimental

CdS solution was prepared using Cadmium Chloride [ $\text{CdCl}_2$ , 99.99 % purity Alfa Aesar] and Thiourea [ $((\text{NH}_2)_2\text{CS}$ , 99 % purity Alfa Aesar] on commercial microscope glass slides  $5\text{cm} \times 3\text{cm}$  used as a substrate. Substrates were washed with detergent using distilled water. Substrates were cleaned ultrasonically in acetone and methanol for 20 minutes and dried.  $\text{NH}_3$  in aqueous solution was used as a complexing agent. An aqueous solution of 60 ml was prepared in beaker using doubly deionized water from  $\text{CdCl}_2$  (0.02M) for the source of  $\text{Cd}^{2+}$  ion at room temperature under continuous stirring. Also 60 ml aqueous solution was prepared using doubly deionized water in beaker from  $(\text{NH}_2)_2\text{CS}$  (0.04M) for the source of  $\text{S}^{2-}$  at room temperature under continuous stirring.  $\text{CdCl}_2$  solution was placed in temperature bath and its temperature was raised to  $65^\circ\text{C}$  while stirring. Digital hot plate was used for this purpose. Aqueous  $\text{NH}_3$  was added drop by drop in the  $\text{CdCl}_2$  solution to dissolve the white precipitate of cadmium hydroxide under constant stirring conditions. PH was stabilized at 11. The temperature of 60 ml solution of  $((\text{NH}_2)_2\text{CS}$  was maintained at  $65^\circ\text{C}$  in a separate temperature bath. The solution of  $((\text{NH}_2)_2\text{CS}$  was added in the  $\text{CdCl}_2$  solution in 1 minutes under vigorous stirring. The temperature was raised to  $72^\circ\text{C}$  and then cleaned substrates were immersed vertically using special holders in the solution and then the container was covered to avoid the evaporation of ammonia. The 2 inch magnetic bar was used for constant stirring throughout the deposition time 1-4 hours to ensure the homogeneous distribution of the chemicals in the solution at constant bath temperature  $72^\circ\text{C} \pm 1^\circ\text{C}$ . Mercury thermometer was also used to monitor the temperature variations. Samples were taken out from the bath after 1, 1.5, 2.5, 3, 3.5 and 4 hours deposition time. Substrates were washed in deionised water ultrasonically to remove the loosely adhered CdS particles and dried in air. Thickness of the film was measured by ellipsometer.  $\text{Cu K}_\alpha$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ) with PANalytical (Philips) X'Pert Pro PW1830 was used for XRD analysis. The XRD data were analyzed by X'Pert High Score software for the identification of the crystalline phases in the films. Crystallite size was calculated from the Scherrer equation,

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where  $\beta$  is the full width at half maximum (FWHM) of the peak corrected for instrumental broadening and  $\theta$  is Bragg angle.  $\lambda$  is the wavelength of X-ray and K is Scherrer constant taken 0.94 for the calculations [11]. Spectral transmission (T) data was recorded using double beam photospectrometer (Shimadzu) in the wavelength range 350 to 1100 nm. The absorption coefficient ( $\alpha$ ) was calculated using the equation,

$$\alpha = -\frac{\ln T}{d}$$

Absorption coefficient ( $\alpha$ ) can be used to calculate the optical energy band gap ( $E_g$ )

$$\alpha = \frac{A([\hbar\nu - E_g])^n}{\hbar\nu}$$

Where A is constant  $\hbar\nu$ , is photon energy,  $n$  is  $\frac{1}{2}$  for direct allowed transition as CdS is a direct band gap material. [12]. Hence  $(\alpha\hbar\nu)^2$  is related to  $\hbar\nu$  linearly.  $E_g$  is obtained by extrapolating the linear fitted region from the plot of  $(\alpha\hbar\nu)^2$  versus  $\hbar\nu$ .

Absorption coefficient ( $\alpha$ ) of thin films shows a tail for sub-band gap energy. The Urbach energy ( $E_{00}$ ) associated with the width of the tail can be measured from the equation [13]:

$$\alpha = \alpha_0 e^{\frac{\hbar\nu - E_{00}}{E_0}}$$

Where  $\alpha_0$  is the constant. The reciprocal of the slop from the plot of  $\ln\alpha$  versus photon energy ( $E_g$ ) gives the value of Urbach energy ( $E_{00}$ ) eV.

### 3. Results and discussion

XRD pattern of CdS film deposited for the different deposition time that varies from 1 - 4 hours exhibits polycrystalline in nature, Fig. 1. It is clear from the pattern that the peak at  $2\theta = 26.7242^\circ$  (ref: 01-075-0581) belongs to (111) plane of cubic CdS. Other prominent peaks at the angle  $2\theta = 44.0932^\circ$ ,  $52.3741^\circ$  (ref: 01-075-0581) are also assigned to the reflections (220) (311) of the cubic CdS structure [14, 15]. The most attractive feature of CdS film grown by CBD technique is its polymorphism nature (cubic phase and Hexagonal phase) as a structural point of view as observed by many authors. [16]. Only cubic phase was observed in our present experiment. It is also noted that the relative percentage error in observed and standard d value (3.3544, ref: 01-075-0581) is below 0.5% for all samples deposited for different deposition times. It is also observed that the crystallinity slightly increases with the increase of the deposition rate and the preferred orientation is (111). This indicates that the preferred orientation (111) is due to the controlled nucleation process which is associated with the slow growth rate of the film. [17].

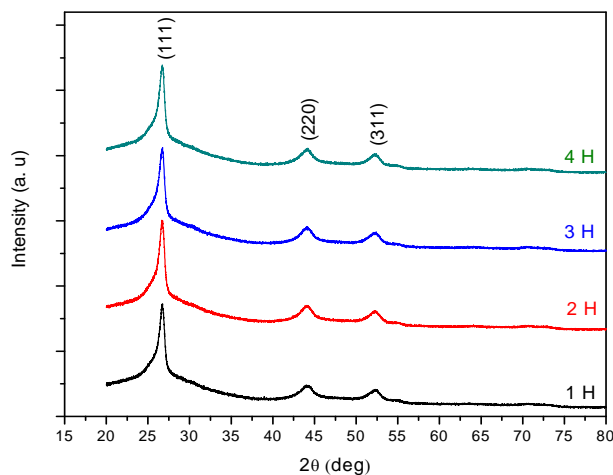


Fig. 1 XRD pattern of CdS film for 1 to 4 hours deposition time

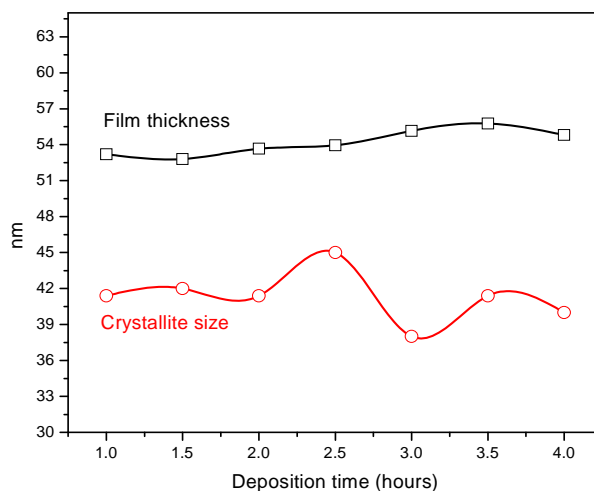
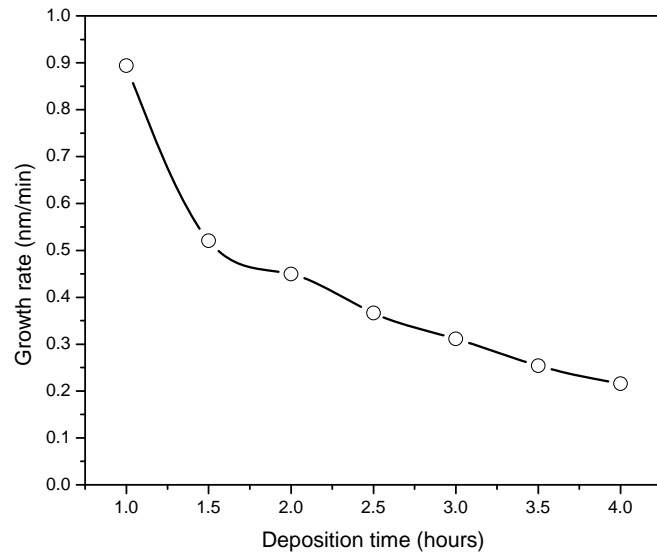
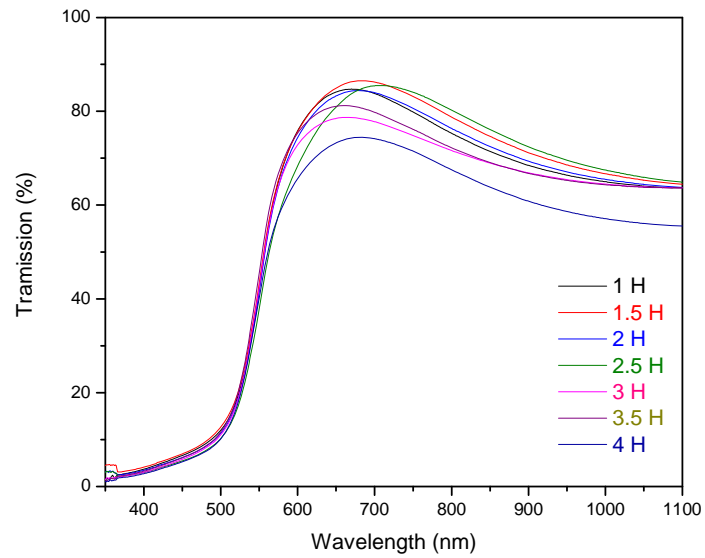


Fig. 2 Film thickness and crystallite size vs deposition time.



*Fig. 3 Film growth rate dependence at film deposition time*



*Fig. 4 Transmittance spectra for the different deposition time.*

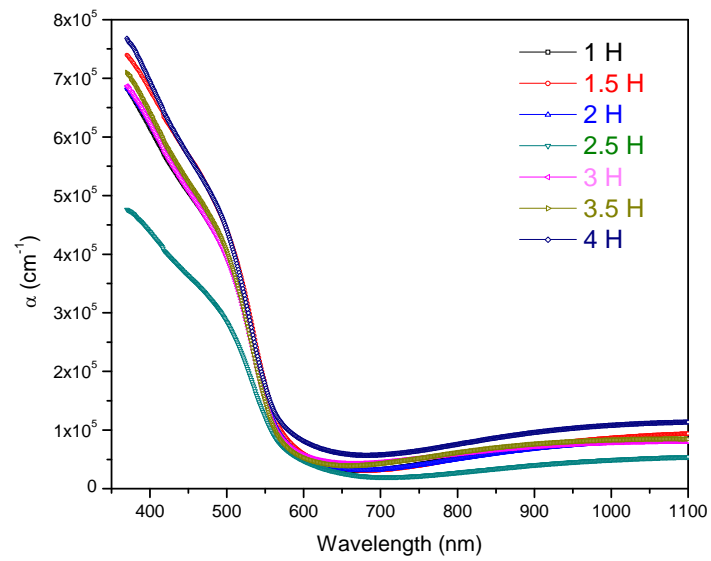


Fig. 5. Absorption coefficient ( $\alpha$ ) at different deposition time

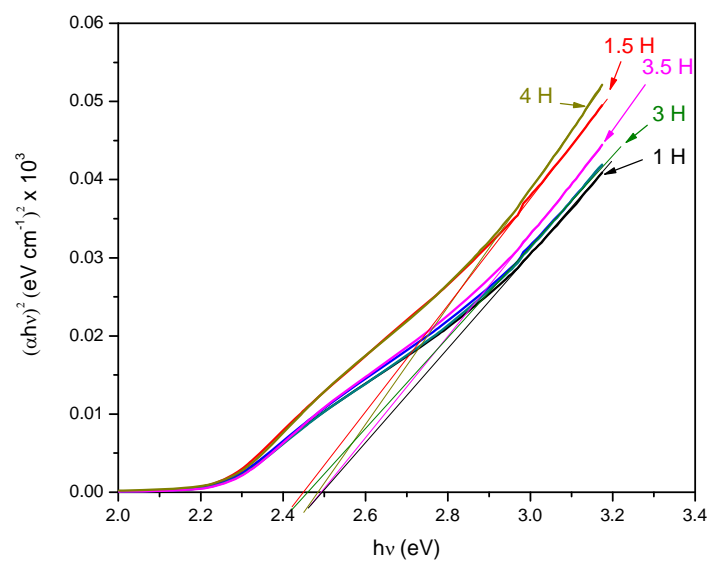


Fig. 6. Variation of  $E_g$  at different film deposition time

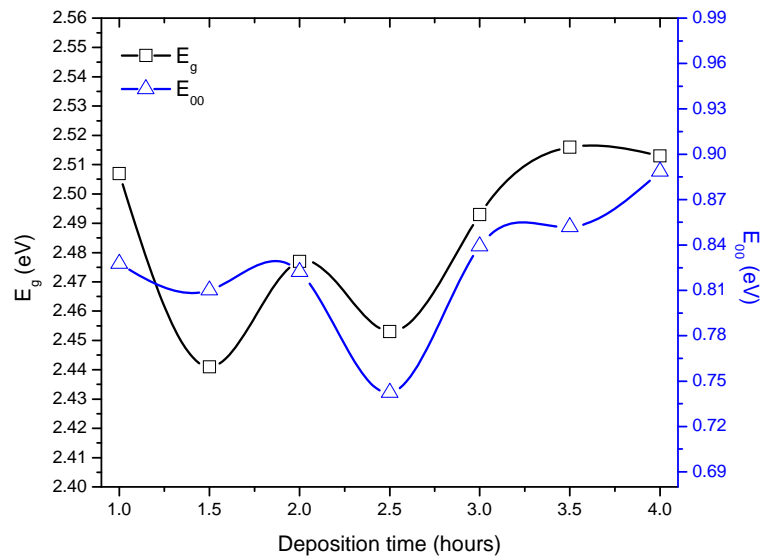


Fig. 7 Variation of optical energy band gap ( $E_g$ ) and Urbach energy ( $E_{oo}$ ) with deposition time

Film thickness is 53.21 nm for the 1 hour deposition time and increases to 55.77 nm for the 3.5 hours deposition time, Fig. 2. Its thickness decreased to 54.81 nm for 4 hours deposition time. Film growth rate is shown in the Fig. 3. The average crystallite size was 41.4 nm for 1 hour deposition time and reached to 45 nm for the 2.5 hours deposition time estimated from the intense peak related to (111) reflection by Scherrer formula. The average crystallite size again reduced to 40 nm for 4 hours film deposition time. The increase in the average crystallite size is due to the complete deposition processing occurring. It is observed that the crystallite size slightly reduces with the increase of film thickness and with the increase of deposition time.

The specular transmittance spectra of the CdS film ranged from 350 to 1100 nm is shown in Fig. 4. The spectra show transmittance dependence of the film deposition time that is from 1 to 4 hours. Transmission is about 10 % at the wavelength of 500 nm for all deposition times. It increases linearly from 10 to 56 % at the 565 nm wavelength range. It indicates that the growth of all films is same in this wavelength range for all deposition times. It is found that the transmittance has the maximum value upto 88% for the deposition time of 1.5 hours before the absorption edge. It reduces to 74 % with the deposition time of 4 hours. So the best transmittance is obtained at the deposition time of 1.5 hours. The transmittance is reducing from about 88 % to 65 % with the increase of the wavelength upto 100 nm but its value is about 56 % for the deposition time of 4 hours. Transmission spectra shifts, Fig. 4, towards lower wavelength rang with the increase of the film deposition time indicating the increase in the optical band gap energy, Fig. 7 [18]. The optical absorption coefficient ( $\alpha$ ) is shown in Fig. 5 for the different deposition times. Its value is lower for the 2.5 hours deposition time as the crystallite size is higher for this deposition time Fig. 2.

The graph  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) is shown in Fig. 6 Optical energy band gap ( $E_g$ ) is 2.50 eV for 1 hour deposition time. Fig. 7. The value of  $E_g$  decreased to about 2.44 eV for the deposition time of 1.5 to 2.5 hours of deposition time. This is possibly due to the increase of the crystallinity in the film structure. It is also observed that the  $E_g$  increased to 2.52 eV and is constant at about 2.51 eV for 3.5 and 4 hours deposition time. It is noted that the film thickness slightly increases with deposition time 2 to 3 hours of deposition time also  $E_g$  slightly increases for this deposition time. This is possibly due to the slight increase in the film thickness.  $E_{oo}$  is called Urbach energy and is shown in the Fig. 6. It is also called the band tail width. It is due to the disorder in the film material. The deviation of bond length and bond angle from their standard

value in the crystalline material is called disorder. It is clear that the optical band gap is about opposite to the disorder. This behavior indicates that the optical band gap obtained is governed with the disorder variation.

#### 4. Conclusions

In this experiment, the CdS films were grown by CBD technique for the different deposition times at the constant bath temperature. XRD analysis show that the film is in cubic structure and no hexagonal or other phase was observed. The maximum and minimum crystallite size 45 nm, 38 nm for 2.5 and 3 hours deposition time was obtained, respectively. Crystallite size is about 41 nm at all other deposition times. The maximum film growth rate, 0.89 nm/min., was obtained for 1 hour film deposition time. The optical band gap is governed with the disordering phenomena. The optical absorption is slightly varies with the film deposition time.

#### Acknowledgement

Ministry of Higher Education, Malaysia through FRGS Project # 01-01-07-139FR

#### References

- [1] S. Mokrushin, Y. Tkachev, *Kolloidn.Z.* **23**, 438 (1961)
- [2] G. Kitaev, A. Urtskaya, S. Mokrushin, *Russ. J. Phys.Chem.* **39**, 1101 (1965)
- [3] Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, R. Noufi, *Prog. Photovolt, Res. Appl.* **7**, 311 (1999)
- [4] S. Wu, J. Keane, R. Dhere, D. Dehart, D. Albin, A. Duda, T. Gessert, S. Asher, D. Levi, P. Sheldon, *Proceedings of the 17<sup>th</sup> European Photovoltaic Solar Energy Conference Munich Germany October 22-26, 2001* p995
- [5] I. Oladeji, L. Chow, C. Ferekides, V. Viswanathan, Z. Zhao, *Sol. Energy Mater. Sol. Cells* **61**, 203 (2000)
- [6] M. Contreras, M. Romero, B. To, F. Hasoon, R. Noufi, S. Ward, K. Ramanathan, *Thin Solid Films* 403/404, 204 (2002)
- [7] T. L. Chu, S. S. Chu, C. Ferekides, C. Q. Wu, J. Britt, C. Wang, *J. Cryst. Growth* 117 (1-4), 1073 (1992)
- [8] C. Ferekides, J. Britt, *Sol. Energy Mat. Sol. Cells* **35**, 255 (1994)
- [9] I. Kaur, D. K. Pandya, L. Chopra, *J. Electrochem. Soc.* **127**, 943 (1980)
- [10] M. Froment, D. Lincot, *Electrochim. Acta* **40**, 1293 (1995)
- [11] M. Caglar, Y. Caglar, S. Ilıcak, *Journal of Optoelectronics and Advanced Materials*, vol. **8**, No. 4, 1410 (2006)
- [12] V. B. Sanap, B. H. Pawar *Chalcogenide Letters* vol. **7**, No. 3, . 227-223 (2010)
- [13] M. V. Kurik, *Phys. Status Solidi. A* **8**, 9 (1971)
- [14] K. R. Murali Mary Mathelina Rita Johnb *Chalcogenide Letters* Vol. **6**, No.9, 483 (2009)
- [15] S. Soundswarm, O. SenthilKumar, R. Dhanasekaran, *Mater.Lett.* **58**, 2381 (2004)
- [16] G. C. Morris, R. Vanderveen, *Sol. Energy Mater. Sol. Cells* **27**, 305 (1992)
- [17] G. Sasikala, P. Thilakan, C. Subramanian, *Sol. Energ. Mat. & Sol. C.*, **62**, 275 (2000)
- [18] Fangyang Liu, Yanqing Lai JunLiu, Bo Wang, Sanshuang Kuang, Zhian Zhang, Jie Li Yexiang Liu *Journal of Alloys and Compounds* **493**, 305 (2010)