Chalcogenide Letters Vol. 6, No. 9, September 2009, p. 433 – 436

VARIATION OF OPTICAL BAND GAP WITH POST DEPOSITION ANNEALING IN CdS/PVA THIN FILMS

J. C. OSUWA*, C. I. ORIAKU, I. A. KALU
Department of Physics, Michael Okpara University of Agriculture Umudike. P.M.B 7267, Abia State, Nigeria.

Thin films of CdS were prepared in the matrix of polyvinyl alcohol (PVA) via chemical bath deposition technique. The resulting films were thermally annealed at temperatures 373 K, 473 K, 573 K and 673 K in an electric furnace. The band gap of the thin films determined from absorption and transmission spectra in the UV-VIS-NIR region of the electromagnetic spectrum were 2.80 eV-2.30 eV. The annealed films exhibited blue shift in the direct allowed transition energy band gaps when compared with bulk CdS. The blue shift of the absorption edge towards lower wavelength can be attributed to the crystallite size effect exhibited by the films on thermal annealing.

(Received August 4, 2009; accepted September 29, 2009)

Keywords: CdS/PVA thin film, chemical bath, annealing, band gap shift

1. Introduction

In the resent years, group II-VI compound semiconducting chalcogenide thin film materials have attracted much attention due to their potential applications in optoelectronics [1], heterojunction photovoltaic devices [2,3], and infrared detectors. They are also known to exhibit non linear optical, luminescent properties and quantum size effect [4]. Several techniques that have been used to synthesize these materials include electrodeposition, screen printing [1], close space sublimation method , brush plaiting [5], pulsed laser deposition [6], Chemical bath deposition (CBD) [7], hot wall epitaxy [8], and vacuum evaporation [9]. Among other deposition techniques, CBD method is found to be a cheap and simple way to deposit large surface area metal chalcogenide thin films.

The band gap energy is the most important parameter in semiconducting thin film material. It is reasonably affected by deposition conditions (e.g. pH, deposition time, bath temperature etc), and post deposition substrate annealing.

Cadmium sulphide thin film is the most widely studied chalcogenide material. It is a wide band gap semiconductor with energy band gap $E_g \approx 2.42$ eV [4]. In this communication, we report the post deposition annealing temperature dependence behaviour of CdS/PVA polymer thin films.

2. Experimental method

Cadmium sulphides thin films were deposited on polyvinyl alcohol (PVA) matrix on glass substrates using the CBD method. The reagents used were aqueous $CdCl_2.21/2H_2O$, thiourea $[CS(NH_2)_2]$, ammonia and PVA $[CH_2CH(OH)^-]_n$. In the reaction bath, 5ml of 1M ammonia solution was added to a 50ml beaker containing 3ml of 1M $CdCl_2.21/2H_2O$. The resulting mixture was added 5ml of 1M thiourea and solution of 3% PVA to make up the bath solution. The solution

*Corresponding author: jordan4cj@yahoo.com

bath was stirred continuously for 5minutes and a previously cleaned glass substrate, which was degreased in HCl for 48hours, rinsed in deionised water and dried in air was vertically inserted into the reaction bath. The bath was allowed to stay for 1hour at an elevated temperature of 338K in an incubator. The substrates coated with CdS/PVA thin films were withdrawn and rinsed in deionised water and dried in air. The films were uniform, thoroughly adherent to substrates, and yellowish in colour. Resulting samples were air- annealed in a hot plate at 373K, 473K, 573K and 673K at 1hour.

3. Results and discussions

The energy band gap of both as- deposited and annealed thin films were studied by optical transmission and absorption measurements using Unico UV-2102 PC spectrophotometer. During scanning process, a blank glass slide was placed in one of the beam direction and another glass with film deposit was in the other beam's direction. Thus, the absorption and transmission spectra displayed by the spectrophotometer were as a result of the films deposited on the glass slides. The transmission and absorption spectra (Figs. 1&2) were recorded at wavelengths between 200nm and 998nm. The details of the mathematical determination of absorption coefficient from absorption and transmission data have been reported [10, 11].

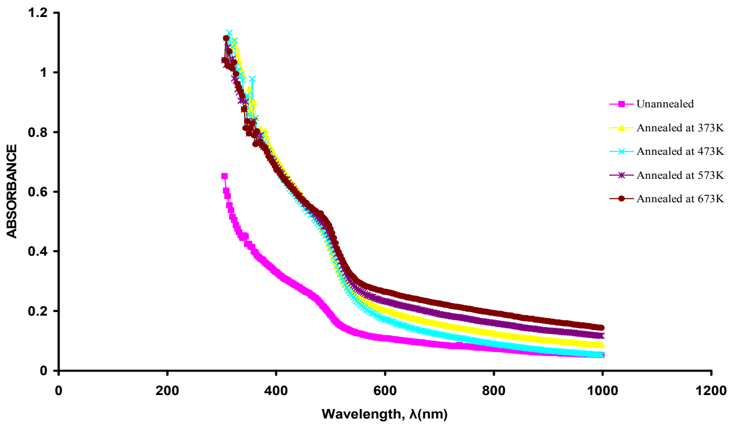


Fig. 1. Absorption spectra

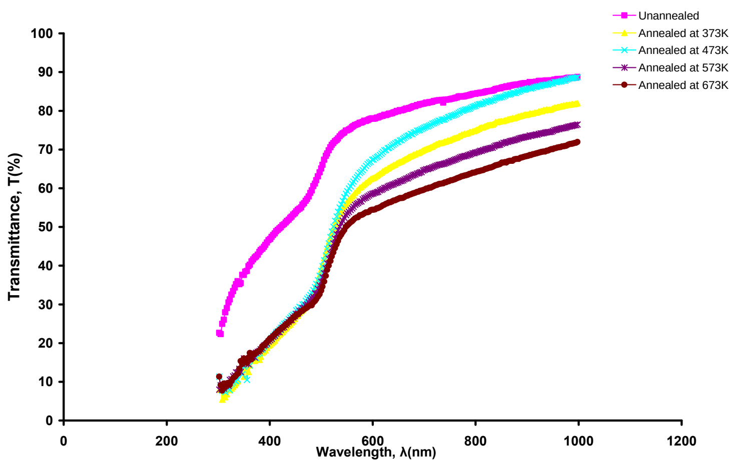


Fig. 1. Transmittance spectra

The thin film samples tend to show slight drop in transmission of photon energy as the annealing temperature decreases (Fig 2) and increase in absorption of photon energy as the annealing temperature decreases (Fig 1).

The fundamental absorption edge in most semiconductors follows the exponential law. Above the exponential tail, the absorption coefficient of semiconductors has been observed to obey the relation [10].

$$\alpha h\upsilon = A\,(h\upsilon - E_g)^n \qquad (1)$$

where A is a constant, E_g is the optical band gap energy, and the index can be any value between ½ and 3 depending on the nature of the inter-band electronic transition. It has been established that for direct allowed band gap semiconductors, the measured absorption data fits well to equation (1) for n = ½ [12]. Hence, the graph of $(\alpha h\upsilon)^2$ vs $h\upsilon$ was plotted to calculate the energy band gap of the thin films. We can readily observe for both the unannealed films of CdS/PVA, a linear relationship between $(\alpha h\upsilon)^2$ and $h\upsilon$ except at low photon energies where there is band tailing (Fig.3).

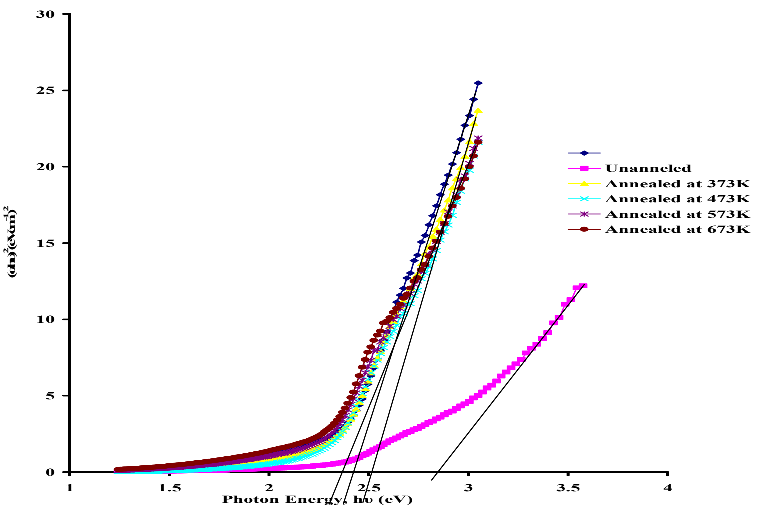


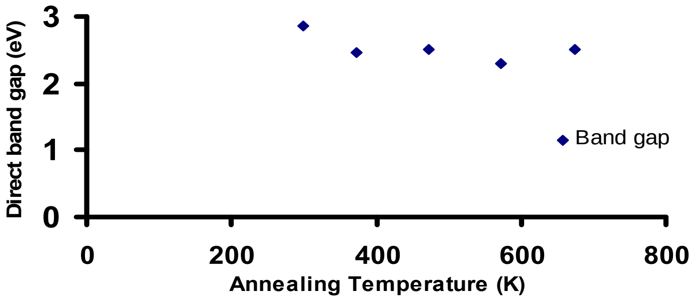
Fig. 4. Plot of $(\alpha h\nu)$ versus photon energy (eV)

The values of optical band gap energies E_g were obtained by extrapolating the straight portion to the $h\upsilon$ axis at $(\alpha h\upsilon) = 0$. Table.1 shows the measured energy band gap, band gap shifts, and annealing temperatures. The measured band gap of the unannealed thin films of CdS/PVA is 2.85eV.

Table1: Band gap dependence of annealing temperature of CdS/PVA films.

Annealing temperature (K)	Direct band gap (eV)	Band gap shift (eV)
Unannealed	2.85	0.43
373	2.45	0.02
473	2.50	0.08
573	2.30	0.12
673	2.51	0.09

This is in agreement with $E_g \approx 2.48 - 2.80$ eV reported [13] at varying concentration of Cd ions between 0.1M and 1M. Also it agrees fairly with $E_g \sim 2.51$ eV – 3.06 eV at deposited at different pH of 1.6 – 2.2 [14]. Energy band gap for bulk CdS semiconductors is 2.42 eV. It can be clearly observed from fig 4, that the direct band gap measured for the as- deposited (i.e. 300K) sample of CdS/PVA showed higher values than the annealed films.



The increase in the band gap energy (Blue shift) measured by thin film samples annealed at 373K, 473K and 673K when compared with the band gap of bulk CdS, can be attributed to the crystallite size effect. This effect has been observed to be more pronounced when the thin film particle size drops to smaller values. This blue shift of the absorption edge indicates decrease of the crystallite sizes of the samples [13].

4. Conclusion

CdS thin films were deposited in polyvinyl alcohol matrix using chemical bath deposition method. The resulting CdS/PVA thin films showed band gap between 2.32 eV- 2.80 eV. Films annealed at 373 K, 473 K, and 673 K exhibited blue shifts in optical direct allowed band gap. This can be attributed to crystallite size dependence band gap energy, which was induced by thermal annealing.

References

[1] M. G. Mahesha, V. B. Kasturi and G. K. Shivakumar Turk. J. Phys. **32**, 151, (2008).
[2] V. Kumar, J. K. Gaur, M. K. Sharma, T. P. Sharma, Chalcogenide Lett. **5**, 171, (2008).
[3] K. R. Murali, K. Sivaramamoorthya, S. Asath Bahadurb, M. Kottaisamy, Chalcogenide Lett. **5**, 249, (2008).
[4] P. Raji and K. Ramachandran, International Journ. Nanosci. **6**, 51, (2007).
[5] K.R. Murali and B. Jayasutha , Mat. Sci. in Semiconductor processes, **10**, 36, (2007).
[6] S.K. Pandey , U. Tiwari, R. Raman, C. Prakash, V. Krishna, V. Dutta, K. Zimik. Thin Solid Films, **473**, 54, (2005).
[7] C.I. Oriaku, F.I. Ezema, and J.C. Osuwa, Pacific Journ. Sci..Tech, **10**, 413, (2009).
[8] Y. Bilovych, A. Soshnikov, L. Darchuk, M. Apatskaya, Z. Tsybril, M. Vuychik, A. Boka, F. Sizov, O. Boelling J. Crystal. Growth, **275**; 1177. (2005).
[9] E.I Ugwu, and D.U. Onah. Pacific Journ. Sci..Tech.. **8**, 160, (2007).
[10] C.I Oriaku and J.C Osuwa., Pacific Journ. Sci. Tech. **9**, 2, (2008).
[11] M. Altaf, M. Ashraf Chaudhry, M. Shakeel Bilal, and M. Ashfaq Ahmad, Journ. Research (Science),**13**, 10, (2002)
[12] F. I. Ezema, R.U. Osuji, Chalcogenide Lett., **4**, 73, (2007).
[13] R. Devi, P. Purkayastha, P. K Kalita and B K Sarma, Bull. Mater. Sci., **30**, 127, (2007).
[14] J. Barman, J. P. Borah, K. C. Sarma, Chalcogenide Letters, 511, p. 265, (2008).