



## Chalcogenide thin films for development of Nanoscale photovoltaic applications

S. S. Kawar<sup>1,\*</sup> and B. H. Pawar<sup>2</sup><sup>1</sup>Dr. R. G. Rathod Arts & Science College, Murtizapur, Dist. Akola.<sup>2</sup>Department of Physics, Amravati University, Amravati.

### ARTICLE INFO

#### Article history:

Received: 1 August 2012;

Received in revised form:

31 August 2012;

Accepted: 19 September 2012;

#### Keywords

Chalcogenides,

Deposition Parameters,

Thin Films.

### ABSTRACT

We deposited CdS and ZnS chalcogenides thin films on different substrates by Chemical Bath Deposition Technique. Structural, Surface Morphology and Optical properties of as deposited CdS and ZnS films were investigated by XRD, SEM, FTIR and UV-VIS Spectrophotometer. It is found that, the average grain size of CdS and ZnS in the films is 08 to 130nm and 08 to 113nm. The band gap is also calculated from the equation relating absorption co-efficient to wavelength. The band gap indicates the film is transmitting within the visible range and the band gaps changes because of the grain size of the CdS and ZnS in the films. We also observed that, the change in preparative parameters affects the deposition rate of thin films. From the observation, it is clear that the growth rate increases as the deposition temperature, deposition time, molarities of the solution increases. It is also clear that the growth rate increases as the film thickness and grain sizes increases while band gap decreases.

© 2012 Elixir All rights reserved.

### Introduction

Cadmium Sulfide and Zinc Sulfide is compound semiconductors with a wide range of potential applications. This material has existed in cubic or hexagonal forms and is wide-direct-band gap semiconductors. The CdS and ZnS is an excellent material used with the semiconductor cadmium telluride to fabricate solar cells given its optimal band gap energy (2.42eV) for optical windows, while great importance in the optoelectronic applications and a diverse range of applications for thin films of this semiconductor including as waveguides, hetero junction devices and in thin-film electroluminescent displays in which it is the most commonly used host material [1]. Applications in optoelectronic methods or photovoltaic devices is another area receiving attention, In CdS based solar cells, the use of wider band gap materials such as ZnS or CdZnS could lead to decreases in window absorption losses and improvements in the short circuit current of the cells [1,5].

In this work we report the preparation of the CdS and ZnS n-type semiconductor thin films having a nanometer grain size by using Chemical Bath Deposition (CBD) Technique and study the effect of deposition rate on the properties of thin films. The CBD is one of the most convenient, reliable, simplest, inexpensive method and useful for large area industrial applications as well as preparation of thin film at close to room temperatures. The technique of CBD involves the controlled precipitation from solution of a compound on a suitable substrate. The technique offers many advantages over the more established vapor phase synthetic routes to semiconductor materials, such as CVD, MBE and spray pyrolysis. Factors such as control of film thickness and deposition rate by varying the solution pH, temperature and reagent concentration are allied with the ability of CBD to coat large areas, in a reproducible and low cost process. Another advantage of CBD method with

respect to other methods is that the films can be deposited on different kinds, shapes and sizes of substrates. [1, 5]

### Materials And Methods

Thin films of CdS were deposited from a solution of analytical grade CdSO<sub>4</sub> (Cadmium Sulphate) a Cd<sup>++</sup> ion source and Thiourea as a S<sup>-</sup> ion source in an alkaline solution of Ammonia. Commercial glass slides, used as substrates, were cleaned in acetone and methanol ultrasonically, and finally, again washed with methanol ultrasonically before use. After cleaning the glass slides were kept vertically in a closed beaker with the help of a special holder which is attached to AC Motor having a constant speed of 60 r. p. m. We have double distilled water in a beaker and then added CdSO<sub>4</sub> of particular molarity as a Cd<sup>++</sup> ion source slowly under Magnetic stirring. Add liquid Ammonia slowly to the solution for adjusting the pH of solution which is measured on pH meter, providing the temperature to the solution by means of heating coil. Add Thiourea (SC (NH<sub>2</sub>)<sub>2</sub>) of particular molarity as a S<sup>-</sup> ion source was slowly poured into the solution only when the appropriate temperature i.e. 60°C was reached. Finally the temperature was kept constant with the help of a temperature controller in the range 70°C to 72°C. The time for the deposition was varied from 10 to 60 Min. after achieving constant temperature. After the deposition, the CdS films were washed with methanol ultrasonically to remove the loosely adhered CdS particles on the film and finally dried in air. The same procedure is repeated for different time durations [6].

The crystallographic structure of films was analyzed with a diffractometer (XPERT-PRO) by using Cu-K $\alpha$  lines ( $\lambda = 1.54 \text{ \AA}$ ). The average grain size in the deposited films was obtained from a Debye-Scherrer's formula. Surface morphology was examined by JEOL model JSM - 6400 Scanning Electron Microscope. IR spectra of representative sample 0.1M was recorded with the FTIR-8400S (SHIMADZU, Japan).

Tele:

E-mail addresses: [shashankawar@yahoo.com](mailto:shashankawar@yahoo.com)

© 2012 Elixir All rights reserved

The absorbance vs the wavelength was recorded with the UV-VIS spectrometer (Perkin Elmer: Lambda 35) in the wavelength range 200–600 nm for a different molarities [6]. Also we were changing the different parameters such as Time, Molarities, pH and Temperature and note the effects of deposition rate on the properties of thin films.

## Result And Discussion

### Effect of deposition temperature on film thickness

Figure 1 shows the variation of film thickness as a function of deposition time at different temperatures. Various temperatures from 313<sup>o</sup>K to 345<sup>o</sup>K in steps of 10<sup>o</sup>K were used in the depositing CdS to obtain the optimal temperature. Figure 3.9 shows an increase in film thickness as the temperature increases from 313<sup>o</sup>K to 345<sup>o</sup>K. The rise in the film thickness may be due to the dissociation of the Cadmium-complexes (with ammonia and with thiourea) and increase in the hydrolysis of SC(NH<sub>2</sub>)<sub>2</sub> as the temperature increases [32]. At higher temperatures, the decomposition of thiourea will be faster setting more S<sup>2-</sup> ions free, according to reactions (3.1) and (3.2). Additionally, the Cadmium-complex dissociation is greater and gives higher concentrations of free Cd<sup>2+</sup> in the solution, which in turn results in higher deposition rates or in other words for a constant buffer layer thickness, in shorter deposition times. Also the kinetic energy of the ions in solution is higher at higher temperature, which brings about increased interaction between them and subsequent deposition at volume nucleation centers of the substrate [33]. It can be seen from figure, the average growth rate is high at 345<sup>o</sup>K (9.478nm/min) and it is slow at 313<sup>o</sup>K (7.622nm/min).

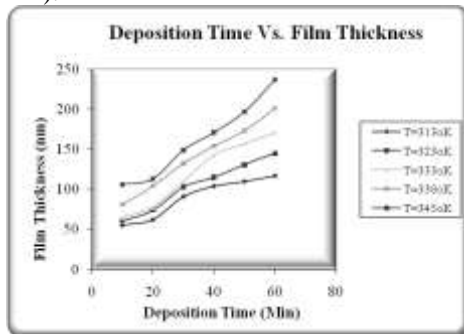


Figure 1: Variation Of Film Thickness As a Function Of Deposition Time At Different Temperatures.

### Effect of deposition temperature on grain size

Figure 2 shows the variation of Grain Size as a function of film thickness at different deposition Temperature. Figure shows an increase in Grain Size as the film thickness increases at the temperature increases from 323<sup>o</sup>K to 345<sup>o</sup>K. Grain size variation with thickness of CdS films determined from the full width at half maximum of most intense X-ray diffraction peak using Scherrer formula.

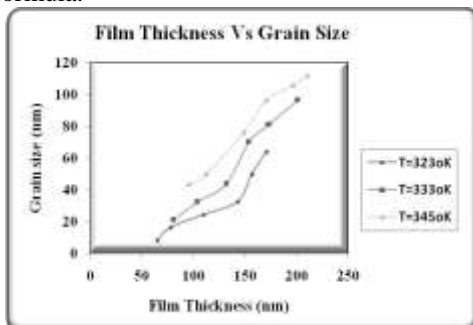


Figure 2: variation of grain size as a function of film thickness at different deposition temperature.

The chemical deposition of CdS at low temperature is based on the slow release of free Cd<sup>2+</sup>. The CdS formed homogeneously throughout the solution grows into clusters where they aggregate into layers. At higher temperatures, the thermal dissociation of the complex and anion is increased and the rate of release of S<sup>2-</sup> from thiourea is more and growth of cluster occurs. Thus, at higher temperature the CdS film thickness increases and corresponding the large grains are obtained [33]. At low temperature, degree of super saturation is higher and therefore the CdS film thickness and grain size tend to decrease. It can be seen from the figure the grain size increases from 8.11 to 112nm. The maximum film thickness 211nm and the grain size 112nm obtained at the highest temperature 345<sup>o</sup>K.

### Effect of deposition temperature on energy band gap

Energy Gap variation with thickness of CdS films determined from the UV-VIS Spectroscopy study. To study the influence of deposition temperature on the energy band gap of CdS films, the deposition temperature was maintained at 323, 333 and 353<sup>o</sup>K.

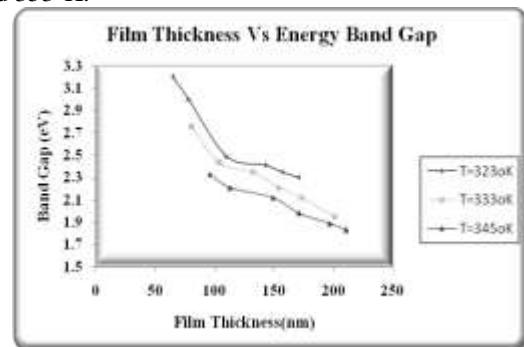


Figure 3: variation of energy gap as a function of film thickness at different deposition temperature.

Figure 3 shows the variation of band Gap as a function of film thickness at different deposition Temperature. Figure shows a decrease in Band Gap as the temperature increases from 323<sup>o</sup>K to 345<sup>o</sup>K. As the deposition temperature is increased, the crystallite size of CdS films is increased resulting in to decrease in band gap [33]. The energy band gap decreases from 3.2 to 1.83eV when the temperature increases from 323 to 345<sup>o</sup>K. The average Energy gap of CdS 2.42eV is obtained from the UV-VIS study.

### Effect of deposition time on film thickness

To study the influence of deposition time on film thickness of CdS films, the deposition time is taken as 10, 20, 30, 40, 50 and 60 Minute. Figure 4 shows the variation of film thickness as a function of deposition time.

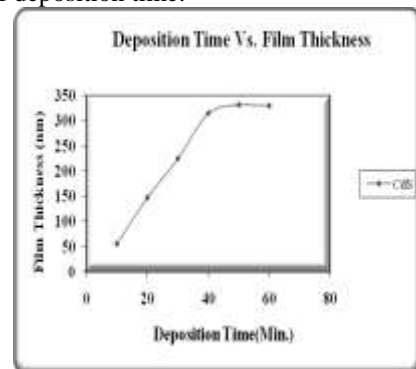


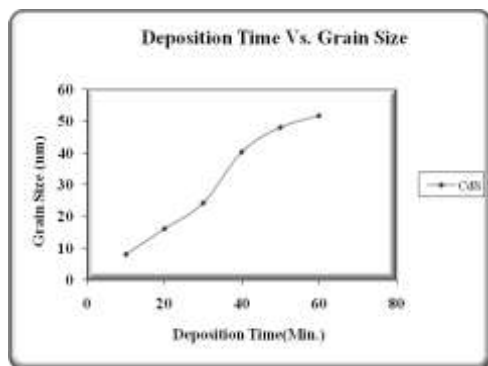
Figure 4: variation of film thickness as a function of deposition time.

The Figure 4 shows an increase in film thickness as the deposition time increases. The deposition process clearly shows two different growth phases: quasi linear phase and saturation phase. Many researchers have observed similar growth rate dependence on temperature for CdS and  $\text{Sb}_2\text{S}_3$  film by CBD (Lincot and Vedel 1991; Dona and Herrero 1992; Savadogo and Mandal 1992). It can be seen from this figure that the rate of deposition is high in the initial process of growth due to high concentrations of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$ . As more and more CdS is formed, solution becomes deficient in ions giving lower rate of deposition and film attains terminal thickness [34].

Deposition time is optimized by taking a substrate out of bath at regular interval of 10 Minute and film thickness is monitored after each 10 Minute. It is observed in the experiment that the film thickness increases up to 40 Minute deposition time and then remains nearly constant. The average rate of deposition is 6.72 nm/Minute. The maximum film thickness obtained by this method is about 330 nm. The maximum rate of deposition is 7.87 nm/Minute. Table1 shows variation of film thickness with deposition time.

#### Effect of deposition time on grain size

To study the influence of deposition time on Particle size of CdS films, the deposition time is taken as 10, 20, 30, 40, 50 and 60 Minute. Figure 5 shows the variation of Grain Size as a function of deposition time at constant deposition temperature ( $72^\circ\text{C}$ ).



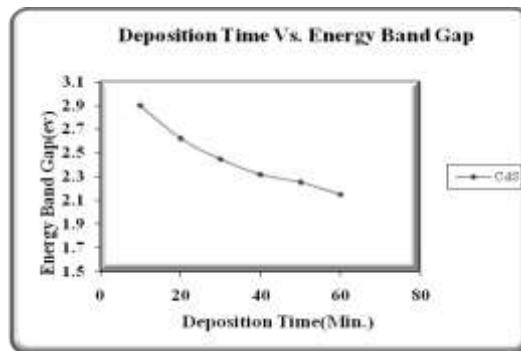
**Figure 5: Variation Of Grain Size As A Function Of Deposition Time**

Grain size variation with thickness of CdS films determined from the full width at half maximum of most intense X-ray diffraction peak using Scherrer formula. It is clear from the figure that the grain size increases continuously with Deposition time up to 40 Minute. The rate of deposition is high in the initial process of growth due to high concentrations of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  and growth of cluster occurs. The rate of increase of film thickness with deposition time was initially higher and linear, as more and more CdS is formed; solution becomes deficient in ions giving lower rate of deposition and film attains terminal thickness [35]. Thus the grain size increases linearly up to 40 minute and then approximately saturates. The average gain size of 31.53nm was obtained after 30 minute of deposition time. With longer deposition times the increment in the grain size was less marked leading to average grain size. This indicates that for longer deposition time (60 minute), a recrystallization process takes place and not properly a grain growth.

#### Effect of deposition time on energy band gap

To study the influence of deposition time on Energy gap of CdS films, the deposition time is taken as 10, 20, 30, 40, 50 and 60 Min. Figure 6 shows the variation of Energy Band Gap as a

function of deposition time at constant deposition temperature ( $72^\circ\text{C}$ ).

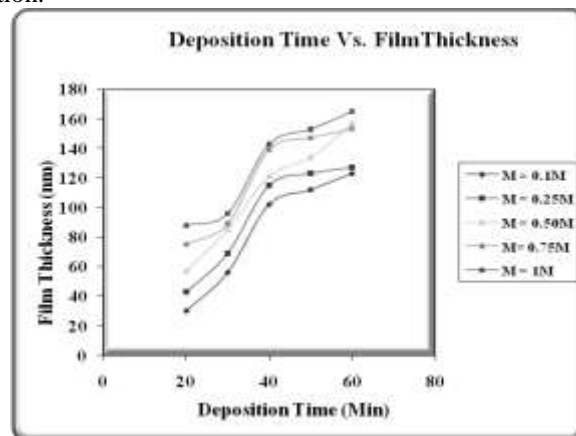


**Figure 6: Variation Of Energy Gap As A Function Of Deposition Time**

The energy band gap of CdS films is determined from UV-VIS absorption studies. It is clear from the figure that the Band Gap decreases continuously with deposition time. The rate of increase of film thickness with deposition time was initially higher and linear up to 40 Minute therefore the grain size increases up to this time linearly, as the grain size increases the band gap decreases from 2.9eV to 2.32eV, sharply up to 40 Minute. The average Energy gap of 2.44eV was obtained after 30 Minute.

#### Effect of molarities on film thickness

To study the influence of reagent concentration on the film thickness of CdS films, the reagent  $\text{CdSO}_4$  and  $(\text{NH}_2)_2\text{CS}$  concentrations were taken as 0.1, 0.25, 0.5, 0.75 and 1M. Figure 7 shows the variation of Film Thickness as a function of deposition time at different reagent concentrations of the solution.



**Figure 7: variation of film thickness as a function of deposition time at different molar concentration.**

It is clear from the figure that the film thickness increases linearly up to 40 Minute and slighter decreases for further deposition time. This has been due to porous outer layer. Since deposition of CdS thin films occurs when ionic product of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  ions exceeds the solubility product of CdS [ $K_{sp} = 7.1 \times 10^{-28}$ ]. The supply of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  ions in the solution controls the rate of CdS formation. It can be seen from the figure that when we increase the reagent concentration more number of ions are produced and ionic product exceeds the solubility product and the thickness increases [36]. So it is clear that the rate of deposition increases with the increase in reagent concentration [37]. As more and more CdS is formed, solution becomes deficient in ions giving lower rate of deposition and the film thickness decreases after 40 Minute.

### Effect of molarities on grain size

To study the influence of reagent concentration on the grain size of CdS films, the reagent concentrations CdSO<sub>4</sub> and (NH<sub>2</sub>)<sub>2</sub>CS were taken as 0.1, 0.25, 0.5, 0.75 and 1M. Figure 8 shows the variation of Grain Size as a function of film thickness at different reagent concentrations of the solution.

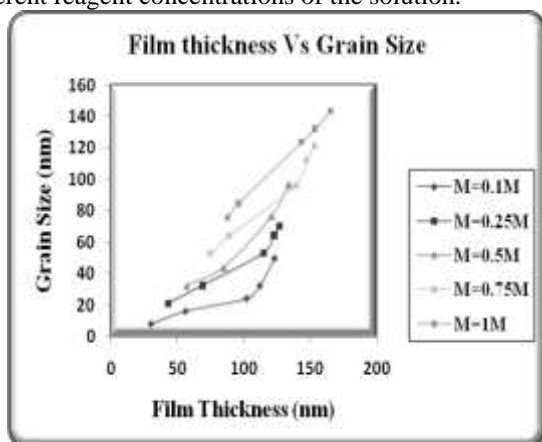


Figure 8: variation of grain size as a function of film thickness at different reagent concentrations.

It is clear from the figure that the grain size increases linearly with reagent concentration. The deposition time of the all the set of experiment was varying from 10 to 60 minutes keeping all other parameters are constant.

At higher Concentration [1M], the rate of release of free Cd<sup>2+</sup> ions from CdSO<sub>4</sub> and free S<sup>2-</sup> from thiourea is more and growth of cluster occurs. Thus, higher growth rate occurs and CdS film thickness increases and relatively larger grains are obtained [38].

### Effect of molarities on energy band gap

To study the influence of reagent concentration on the Energy Gap of CdS films, the reagent concentrations CdSO<sub>4</sub> and (NH<sub>2</sub>)<sub>2</sub>CS were chosen as 0.1, 0.25, 0.5, 0.75 and 1M. Figure 9 shows the variation of Energy Band Gap as a function of film thickness at different reagent concentrations of the solution.

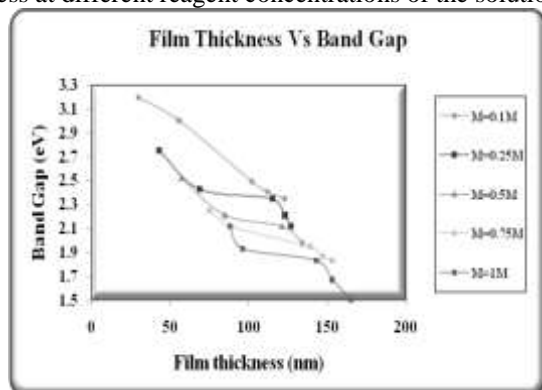


Figure 9: variation of energy band gap as a function of film thickness at different reagent concentrations.

The Energy Band gap of CdS films determined from UV absorption studies. It is clear from the figure that the Energy Gap decreases linearly with reagent concentration. The deposition time of all the set of experiments was varying from 10 to 60 minutes and keeping all other parameters constant. The

deposition rate increases due to increase in reagent concentration therefore thickness increases and correspondingly the grain size also increases. As the grain size increases the energy band gap decreases from 3.2eV to 1.5eV [36-38]. The average energy gap 2.42eV was obtained.

### Conclusion

The influence of the growth parameters on the properties of thin films includes the deposition temperature, deposition time and reagent concentration of the solution dependence of the film thickness, grain size and energy band gap. From the present study, it is observed that, the film thickness changes with deposition temperature. As the deposition temperature increases, the film thickness and grain size increases while the band gap decreases. Therefore it may be conclude that the growth rate depends on the deposition temperature. It is found that, the film thickness changes with deposition time, from the analysis of the study it is clear that, as the deposition time increases, the film thickness and grain size increases while the band gap decreases. After the study of effect of precursor concentration in the solution on the properties of samples like film thickness, grain size, optical band gap and deposition rate, it is observed that as the molarities of the solution increases the film thickness and grain size increases while band gap decreases. It is observed that the deposition rate also changes with molarity of the solution.

### References

1. R.B. Kale, C.D. Lokhande, *Appl. Surf. Sci.*, 252, 929 (2005).
2. H.Tang, Mi Yan, Hui Zhang, M.Xia, DerenYang, *Materials letter* 59, 1024 (2005).
3. Pankaj Tyagi and A. G. Wedeshwar, *Bull. Mater. Sci.* 24, (3), 297 (2001).
4. S. Shrivastava and B. Verma; *Cryst. Res. Technol.* 42(5), 466 (2007).
5. J. Barman, J. P. Borah, K. C. Sarma; *Chalcogenide Letters* 5, (11), 265 (2008).
6. S. S. KAWAR, B. H. PAWAR, *Chalcogenide Letters* Vol. 6, No. 5, May 2009, p. 219 - 225
7. S. Herrera, C. M. Ramos, R. Patino, J. L. Pena, W. Cauich, A. I. Oliva; *Brazilian Journal of Physics*, 36, 3B, September, 2006.
8. P.Raji, C. Sanjeeviraja and K Ramachandran; *Bull. Mater. Sci.*, 28(3), 233 (2005).
9. Mahanty, S, Basak, D, Rueda, F, Leon, *M Journal of Electronic Materials*, May 1999
10. F.I. Ezema and C. E. Okeke; *Academic Open Internet Journal*; Volume 9, 2003.
11. H. M. Pathan and C. D. Lokhande, *Bull. Mater. Sci.* 27(2), 85 (2004)
12. J.M. Dona and J. Herrero, *Thin Solid Films*, 268, 5-12 (1995).
13. Hani Khallaf a, Isaiah O.Oladeji b, Guangyu Chai c, Lee Chowa,,*Thin Solid Films* 516, 7306 (2008).
14. Martin T P et al. *Spectrochim. Acta* A38, 655 (1982).
15. Periasamy A et al 1997 *Proceedings of the national conference on spectrophysics* (ed.) S Gunasekaran, p. 95
16. He R et al *Mater. Lett.* 57, 1351 (2003).
17. Williams D H and Fleming I 2004 *Spectroscopic methods in organic chemistry* (New Delhi: Tata McGraw-Hill) 5th ed., p. 57.

**Table 1: Variation of Deposition time with growth parameters**

Deposition Time (Min.)	Thickness (nm)	Grain Size (nm)	Band Gap (eV)	Dep. Rate (nm/Min.)	Dep. Rate (nm/Sec.)
10	55	8.11	2.9	5.5	0.0916
20	147	16.22	2.62	7.35	0.1225
30	225	24.33	2.45	7.5	0.125
40	315	40.45	2.32	7.87	0.1311
50	332	48.21	2.25	6.64	0.1106
60	330	51.9	2.15	5.5	0.0916