Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **1(8),** 31-35, Nov. **(2011)** *Res.J.Chem.Sci.*

Chalcogenide Thin Films Having Nanometer Grain Size for Photovoltaic Applications

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Available online at: www.isca.in
(Received 20th August 2011, revised 01st September 2011, accepted 17th September 2011)

Abstract

Cadmium chalcogenides with appropriate band gap energy have been attracting a great deal of attention because of their potential applications in optoelectronic devices. CdS in the form of thin films is prepared at different substrate by a simple and inexpensive chemical bath deposition technique. The as deposited thin films have been characterized by XRD, SEM and Optical techniques. The XRD patterns shows that the films are polycrystalline with crystallite size 11 to 121 nm for the film deposited at optimized preparative parameters. SEM studies reveal that the grains are uniform with uneven spherically shaped, distributed over the entire surface of the substrates. FTIR spectrum shows that the percentage transmittance of the films has high transmittance in the range between 65 and 70% in the UV-VIS-NIR regions. The optical band gap energy was found to be 2.42 eV with direct allowed band-to-band transition.

Key words: Chalcogenides, chemical bath technique, X-ray diffraction, morphological and optical properties.

Introduction

CdS is one of the most interesting II–VI semiconductors owing to its interesting optical, electrical and optoelectronic properties. Possessing a wide fundamental band gap, they have been used in a large variety of applications such as electronic and optoelectronic devices[1]. Thin films of CdS hold promise in photovoltaic applications as window coatings in many types of solar cells with absorber materials such as Cu(In,Ga)Se_2[2], CdTe[3] or $CuInSe_2$[4] and for thin film transistors[5]. Furthermore CdS nanocrystals are applied for lasers[6], as biological labels[7] and they are investigated as photo conducting cells in sensors for ultraviolet radiation[8]. In recent years, considerable interest has been shown in the synthesis and photo electrochemical test of semiconductor thin films. CdS belongs to the II-VI group[9] and it is typically sulphur deficient, possessing the sulphur vacancies with a high electron affinity. This causes CdS to acquire electrons easily, resulting in CdS material n type in nature. Electron hole pairs generated in CdS are well separated with electrons being highly localized[10]. So it is the most studied nanocrystalline semiconductor as a photo anode in photo electrochemical (PEC) solar cells because of its suitable band gap, long lifetimes, important optical properties, excellent stability, easy fabrication and numerous device applications. CdS thin films have been prepared by diverse techniques: sputtering[11], vacuum evaporation[12], spray pyrolysis[13], electro deposition[14] and chemical bath deposition (CBD)[15]. Among these various techniques, chemical bath deposition is a rather simple and inexpensive technique which enables the production of large area uniform and transparent films with good adherence and reproducibility at close to room temperatures. The technique of CBD involves the controlled precipitation from solution of a compound on a suitable substrate. 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[15]

The main objective of the present work is to developed, the cadmium based binary and ternary II–VI compounds n-type of semiconductors CdS thin films by using chemical bath deposition (CBD) Technique. Structural, Surface Morphology and optical properties of as deposited CdS films were investigated by XRD, SEM, FTIR and UV-VIS Spectrophotometer. The results obtained are discussed and compared whenever possible.

Material and Methods

The aqueous solutions of Cadmium Sulphate ($CdSO_4$) and thiourea ($(NH_2)_2CS$) were prepared by dissolving appropriate amounts of these salts (A.R. Grade) in double distilled water. The equimolar solutions were mixed together in appropriate volumes to obtain the Cd S ratio as 1:1 and then deposited on glass substrates. These substrates were washed with water, then 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 attached with AC Motor having a constant speed of 60 r. p.m. Add liquid

Ammonia in the bath for adjusting the pH of solution which is measured by pH meter and providing the temperature to the solution by heating coil was kept constant with the help of a temperature controller in the range 70°C to 72°C, by keeping all other parameters constant. 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 [16, 17, 18].

The as deposited thin films of CdS were characterized for structural, morphological and optical properties. The CdS film thickness was measured using gravimetric weight difference method by assuming bulk density of corresponding materials. X-ray diffraction (XRD) patterns of the film were recorded on X-ray diffractometer (XPERT-PRO) by using Cu-Kα lines (λ= 1.54 Å) for Cu Kα radiation for the diffraction angle range $0–60^0$. The surface morphology and composition was studied by scanning electron microscopy. To study the optical characteristics of the film, absorbance spectra were recorded in the range 200–800 nm by means of UV-VIS-NIR spectrophotometer (Perkin Elmer: Lambda 35).

Results and Discussion

Film Structure Studies: It has been reported that CdS may have either cubic or hexagonal crystal structure depending on the synthesis condition such as deposition temperature and precursor concentration. The as-grown CdS thin films were characterized by the XRD technique scanned in the 2θ range of $0–60^0$. The diffractograms were obtained for the films grown on the amorphous glass substrates.

The diffractograms depict that the deposits are polycrystalline in nature. It is seen that the plane (1 1 1) of CdS appears with higher peak intensity in all the diffractograms. A well matching of the observed and the standard d-values from JCPDS data card [19, 20] confirms the formation of compound CdS with mixed cubic and hexagonal crystal structure. The calculated values of lattice constant with cubic crystal structure are found to be a = b = c = 5.8200 Å agreeing well with the standard values CdS[20]. The grain size was calculated for all cases for the reflections from the C (111) plane by using the well known Debye-Scherrer formula,

$$D = 0.9\lambda/\beta\cos\theta \text{---------- (1)}$$

where D is the particle size, β is the full width broadening of the diffraction line measured at half of its maximum intensity in radians (FWHM), λ is the X-ray wavelength(1.5406 Å) and θ is Bragg diffracting angle. From particle size analysis it is clear that the films are nanocrystalline in nature. The grain sizes were found to be within the range of 11 to 121nm[21-24].

Surface Morphology Studies: The surface morphology of deposited CdS thin films was investigated by SEM at different magnifications as shown in figure 2.

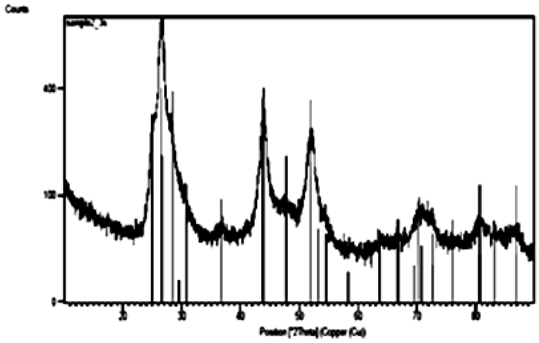

Figure-1
X-ray diffraction pattern of as deposited CdS thin films on glass substrate

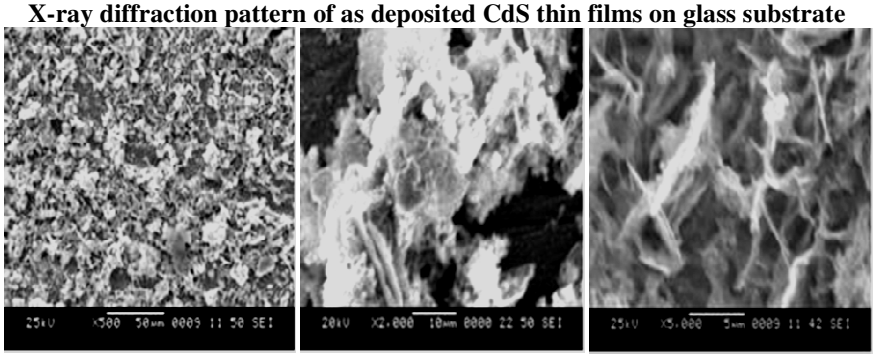

Figure-2
Scanning Electron Micrograph of as deposited CdS thin film at 500, 2000 and 5000 resolutions magnification

The deposits are compact, pinhole free with spherical grains from few nanometers up to clusters of 157 nm and the films are well covered on the substrate. From the figure, it is observe that the small nanosized grains engaged in a fibrous-like structure, which clearly indicates the nanocrystalline nature along with some amorphous phase of CdS thin films. The average grain size of the CdS nanoparticles is about 130 nm. This result is in consistent with results obtained from X ray diffraction studies [25-27].

Optical Absorption Studies: The optical absorption spectrum of the deposited CdS thin films on glass substrate was studied in wavelength range 200 to 800 nm. The nature of the transition involved (direct or indirect) during the absorption process was determined by studying the dependence of the absorption coefficient α, on photon energy hυ as[28]

$$\alpha h\upsilon = A\,(h\upsilon - Eg)^n \text{ ----------(2)}$$

Where A is the constant, Eg is the band gap energy, hυ is the photon energy, n= ½ or 2 for direct or indirect transition. The value of absorption coefficient is found to be of the order of 10^4 cm^{-1}. The optical data was further analyzed to determine the nature of transition that takes place in CdS thin film. The plots of $(\alpha h\upsilon)^2$ versus hυ as shown in the figure 3.

The straight line nature of the graphs supports the direct band gap nature of the semiconductor. The straight-line portion was extrapolated to the energy axis at α = 0, to obtain the band gap of CdS thin films. The direct optical band gap of the CdS film estimated to be 2.42 eV agrees well with the reported value for CdS material[28].

IR Studies: IR spectra of CdS nanoparticles, is presented in figure 4.

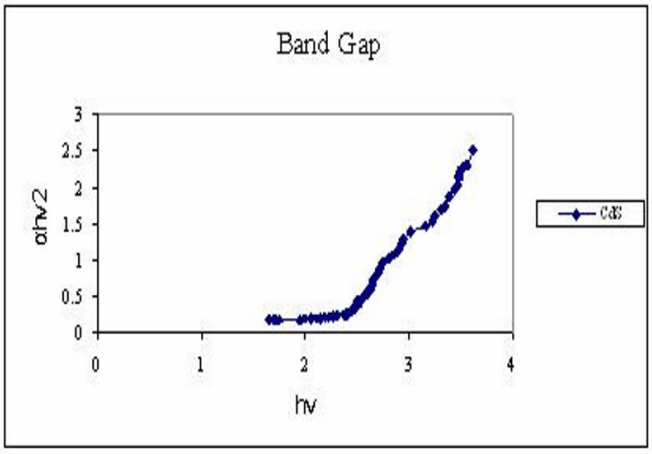

Figure-3
Plots of $(\alpha h\nu)^2$ versus hν of as deposited CdS thin films on glass substrates

Figure-4
IR spectra of CdS thin film deposited on glass substrate

The IR frequencies along with the vibrational assignments for CdS nanoparticles are given in table 1. The band at 3584.82 cm^{-1} is due to O-H stretching vibrations of water molecules. The band at 2746.73 cm^{-1} are due to C-H stretching vibrations. The bending vibrations of C=N appeared at 1574·93 cm^{-1}. CdS particles showed two stretching bands of C-O at 1182.4 and 1282.71cm-1. Trace amount of SO_4^- as impurity is seen as there are small absorptions around 1018.4 cm^{-1}. At 668·36 cm^{-1} and 703·8 cm^{-1}, there are medium to strong bands which have been assigned to Cd–S stretching. The vibration absorption peak of the Cd–S band is at 262.33 cm^{-1}.

Table-1
IR frequencies with vibrational assignments of CdS nanoparticles

Positions (cm^{-1})	***Intensities***	***Assignments***
3584.82	Strong	O-H stretching
2746.73	Strong	C-H Stretching
1574·93	Strong	C=N stretching
1182·4 1282.71	Doublet Medium	C–O stretching
1018.4	Weak (trace)	SO_4^-
668·36 703.8	Doublet Medium	Cd–S stretching
262.33	Medium	Cd-S Stretching

Conclusions

The n-type semiconductor thin films of CdS have been successfully deposited by simple and inexpensive chemical bath deposition technique. Polycrystalline nature of as deposited thin films was predicted from X-ray diffraction studies. Scanning electron microscopy studies revealed uniform deposition with the average grain size of 130 nm. The UV absorption studies on films clearly show an increase in band gap with reduction in particle size as compared to bulk materials, which supports the formation of nanocrystallites in these films. The optical band gap was found to be 2.42eV with direct allowed transition. FTIR spectroscopy showed that the bonding peaks and the percentage transmittance of the films were found to have high transmittance in the range between 65 and 70% in the UV-VIS-NIR regions; hence they could be effective as thermal control window coatings for cold climates and antireflection coatings.

Acknowledgement

The authors would like to acknowledge Head, DME, VNIT, Nagpur for providing XRD and SEM facilities. We would also like to acknowledge Head, Instrumentation cell, SGBAMU for FTIR and UV-VIS facilities.

References

1. Chu T.L. and Chu S.S., 13.4% Efficient Thin Film CdS/CdTe Solar Cells, *Prog. Photovolt*, **1**, 31 **(1993)**

2. Hashimoto Y., Kohara N., Negami T., Nishitani N. and Wada T., Chemical bath deposition of Cds buffer layer for GIGS solar cells, *Sol. Energy Mater. Sol. Cells,* **50**, 71 **(1998)**

3. Maruyama T. and Kitamura R., Transformations of the wavelength of the light incident upon CdS/CdTe solar cells, *Sol. Energy Mater. Sol. Cells,* **69**, 61, **(2001)**

4. Bär M., Weinhardt L., Heske C., Muffler H.-J., Umbach E., Lux-Steiner M.Ch., Niesen Th.P., Karg F. and Fischer Ch.-H., Cd^{2+}/NH_3 treatment of $Cu(In,Ga)(S,Se)_2$ thin-film solar cell absorbers: a model for the performance-enhancing processes in the partial electrolyte, *Prog. Photovolt,* **13,** 571-577**(2005)**

5. Duan X., Niu C., Sahi V., Chen J., Parce J.W., Empedocles S. and Goldman J.L.,High-performance thin-film transistors using ... semiconductor nanowires and nanoribbons, *Nature,* **425**, 274 **(2003)**

6. Klimov V.I., Mikhailovsky A.A., Xu S., Malko A., Hollingsworth J.A., Leatherdale C.A., Eisler H.-J. and Bawendi M.G., Optical gain and stimulated emission in nanocrystal quantum dots, *Science*, **290**, 314-317 **(2000)**

7. M. Bruchez Jr., Moronne M., Gin P., Weiss S., Alivisatos A.P., Semiconductor Nanocrystals as Fluorescent Biological Labels, *Science,* **281**, 2013 **(1998)**

8. Howie J.A.B., Rowles G.K. and Hawkins P., An inexpensive sensor for ultraviolet-A and ultraviolet- B radiation, *Meas. Sci. Technol.,* **2**, 1070 **(1991)**

9. Bilgin V., Kose S., Atay F. and Akkyaz I., Optical and structural properties of thermally evaporated cadmium sulphide thin films on silicon (1 0 0) wafers, *Mater. Chem. Phys.* **94**, 103 **(2005)**

10. Brien P.O. and Pickett N.L., Nanocrystalline Semiconductors: Synthesis, Properties, and Perspectives, *Chem. Mater.,* **13**, 3845 **(2001)**

11. Akkad F. El- and Abdel Naby M., Photoinduced current transient spectroscopy technique applied to the study of point defects in polycrystalline CdS thin films, *Journal of Applied Physics,* **105,** 093113 – 093113 **(2009)**

12. Chamseddine A. and Fearkeily M.L, Improved CdS buffer/window layers for thin film solar cells, *Thin Solid Films*, 3, **247 (1994)**

13. Martinuzzi S., Trends and problems in CdS/Cu_xS thin film solar cells: A review, *Sol. Cells,* **5**, 243 **(1982)**

14. Baranski A.S., Bennet M.S. and Fawcett W.R., The physical properties of CdS thin films electrodeposited from aqueous diethylene glycol solutions, *J. Appl. Phys*. **54**, 6390 **(1983)**

15. Zelaya-Angel O. and Lozada-Morales R., Sphalerite-wurtzite phase transformation in CdS*, Phys. Rev. B*, **62**, 13064 **(2000)**

16. Hankare P.P., Chate P.A. and Sathe D.J, CdS thin film: Synthesis and characterization, *Solid State Sciences,* **11**, 1226 **(2009)**

17. Abdel Hady D., El-Shazly A.A., Soliman H.S. and El-shazly E.A., The thermoelectric power, the dark electrical resistivity and the grain boundary potential barrier in $CdIn_2Se_4$ thin films, *J. Phys. A.,* **226**, 324 **(1996)**

18. Brien P.O. and Saeed T., Deposition and characterization of cadmium sulfide thin films by chemical bath deposition, *Journal of Crystal Growth*, **158**,497-594 **(1996)**

19. JCPDS Data Card No.: 80-0006

20. JCPDS Data Card No.: 80-0019

21. Zhong H., Li Y. and Zhou Y. and Yang C., Controlled synthesis of 3D nanostructured $Cd_4Cl_3(OH)_5$ templates and their transformation into $Cd(OH)_2$ and CdS nanomaterials, *Nanotechnology*, **17**, 772–777 **(2006)**

22. Sasikala G., Dhanasekaran R. and Subramanian C. Electrodeposition and optical characterisation of CdS thin films on ITO-coated glass, *Thin Solid Films,* **302**, 71-76 **(1997)**

23. Boyle D.S., Novel approach to the chemical bath deposition of chalcogenide semiconductors, *Thin Solid Films*, **361**, 150-154 **(2000)**

24. Pankove J.I., Optical Processes in Semiconductors, first ed., Prentice-Hall, USA **(1971)**

25. Williamson G.K. and Hall W.H., Acta Metall., 1, 22–31 **(1953)**

26. Kelly J.J., Vanmaekelbergh D. and Hodes G., Electrochemistry of Nanomaterials, Wiley-VCH, Weinheim, 103–136 **(2001)**

27. Cao G., Nanostructure and Nanomaterials, first ed., Imperial College Press, London **(2004)**

28. Tong X.L., Jiang D.S., Hu W.B., Liu Z.M. and Luo M.Z., The comparison between CdS thin films grown on Si (111) substrate and quartz substrate by femtosecond pulsed laser deposition *Appl. Phys. A* **84**, 143 **(2006)**