Growth and characterization of cadmium sulphide films synthesized by low cost technique for photovoltaic device applications

Bhatu. Y. Bagul

Vasantrao Naik Arts, Commerce and Science College, Shahada, 425409, M.S., India

Email-bybagul@gmail.com

Abstract

Cadmium chalcogenides with appropriate band gap energy have been attracting a great deal of attention because of their potential applications in optoelectronic devices. This paper describes structural, morphological and optical properties of CdS thick films prepared by using screen printing method. For the preparation of CdS thick film, powder of CdS nanoparticles was prepared by using chemical precipitation method using cadmium acetate and sodium sulphide flakes nonhydrate as a source of Cd^{2+} and S^{2-} respectively. The as-deposited film has been characterized by XRD, FESEM, EDAX and UV-VIS measurement techniques. The XRD patterns show that the films are polycrystalline with pure hexagonal crystal structure of CdS with crystallite size of the order of 26.27 nm with Cd/S = 0.71. FESEM studies reveal that the films covered with formation of identical nearly spherically shaped grains of submicron size. Compositional analysis reveals that the material formed is non-stoichiometric and the presence of Cd and S elements in the prepared film. The absorption spectra of as prepared CdS thick film were recorded by using JASCO V-630 spectrophotometer in the wavelength range of 504-722 nm from which optical band gap energy has been determined and is found to be 2.37 eV for as-prepared CdS thick film.

***Keywords*:** Chalcogenides, Co-precipitation, Thick film, X-ray diffraction, FESEM, Optical properties.

1. INTRODUCTION

In recent past much importance has been given in the field of II-VI class of semiconducting compounds because of their optoelectronic properties and applications [1, 2]. 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 [3]. 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 [4], CdTe [5] or Cu$InSe_2$ [6] and for thin film transistors [7]. Furthermore CdS nanocrystals are applied for lasers [8], as biological labels [9], and they are investigated as photo conducting cells in sensors for ultraviolet radiation [10]. In recent years, considerable interest has been shown in the synthesis and photo electrochemical properties of semiconductor thin films. CdS belongs to the II-VI group and n-type in nature [11]. Electron hole pairs generated in CdS are well separated with electrons being highly localized [12]. 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 films have been prepared by various deposition techniques such as sputtering [13], vacuum evaporation [14], spray pyrolysis [15], electro deposition [16], chemical bath deposition [17] and screen printing [18].

Among these various techniques, screen printing is a rather simple and inexpensive technique which enables the production of large uniform area and transparent films with good adherence and reproducibility.

In the present work, synthesized chemically precipitated powder of CdS nanoparticles was used for the deposition of CdS films on borosilicate glass substrates using screen printing technique and the structural, morphological and optical properties of as-deposited thick film are studied. The results obtained are discussed and compared.

2. EXPERIMENTAL DETAILS

2.1 PREPARATION OF PRECURSOR SOLUTION

In the present work, raw materials used for synthesis of CdS nanocrystalline materials were cadmium acetate dehydrate 99% AR grade $Cd(CH_3COO)_2.2H_2O$ and sodium sulphide flakes nonhydrate ($Na_2S.9H_2O$) as a starting compounds were used as source for Cd^{2+} and S^{2-} ions, respectively for synthesis of CdS powders, as a starting compounds purchased from Loba chemical Pvt. Ltd. All chemicals are used in this work without further purification. All the solutions were prepared in fresh distilled water (Merck) and acetone is used for glassware cleaning purpose. For preparation of precursor solutions of desired concentrations, we have used the formula **Eq. (1)**,

$$W=\frac{M \times C \times Q}{1000} \quad (1)$$

where, W is the weight of solute in gm, M is the molecular weight of the solute/salt, C is the concentration (molarity) and Q is quantity of solvent in ml. Different powders can be prepared for each composition by precipitation method.

2.2 SYNTHESIS OF CDS NANOPOWDER

In the present work, powder of CdS nanoparticles was prepared by the chemical precipitation method using AR grade cadmium acetate $Cd(CH_3COO)_2.2H_2O$ and sodium sulphide flakes nonhydrate ($Na_2S.9H_2O$) as a starting compounds. Chemical reaction was carried out at room temperature, 50 ml solution of 1M $Cd(CH_3COO)_2.2H_2O$ and 50 ml solution of 1M $Na_2S.9H_2O$ were prepared separately using distilled water. Then dissolved solutions of sodium sulphide were added drop wise into cadmium acetate solution and the mixture continuously and vigorously stirred for 3 hours at constant stirring at 800 rpm and consequently a yellow CdS precipitate formed which was filtered out and washed several times with distilled water and methanol. Finally, the product was dried for 24 hours in dry air. After drying the precipitate was crushed to fine powder by grinding process using a mortar and pestel.

2.3 DEPOSITION OF CDS THICK FILM

A paste for the preparation of CdS thick film was prepared by mixing synthesized powder with ethyl cellulose (Ethocel) (BDH limited Poole England), a temporary binder in a mixture of organic solvents such as butyl cellosolve (2-Butoxyethanol, butyl glycol) $C_6H_{14}O_2$ (SDS), 1 Acetoxy-2 butoxy ethane (Fluka nika), and terpinol anhydrous $C_{10}H_{18}O$ borrowed from Loba chemical Pvt. Ltd. The ratio of inorganic part to organic part was kept as 75:25 in formulating the paste. The prepared paste was screen printed on glass substrates which have been pre-cleaned. The obtained film was dried under the IR lamp and then fired at 120°C for 1 h to remove organic binder and to avoid the cracks in the film [19, 20].

2.4 CHARACTERIZATION OF THE PREPARED FILM

The CdS thick film prepared by using screen printing technique was further characterized by using XRD, FESEM and UV-VIS spectroscopy. X-ray diffraction (XRD) analysis is carried out for the determination of structure and crystallite size. The surface morphology and chemical composition of the films were analyzed by field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDAX). The optical properties of the films were determined by JASCO V-630 UV-VIS spectrophotometer.

3. RESULT AND DISCUSSIONS

3.1 STRUCTURAL PROPERTIES

The crystallite size and crystal structure of the CdS thick films was determined by using XRD pattern. **Fig. (1)** Shows XRD pattern of as-prepared CdS thick film deposited by using screen printing method.

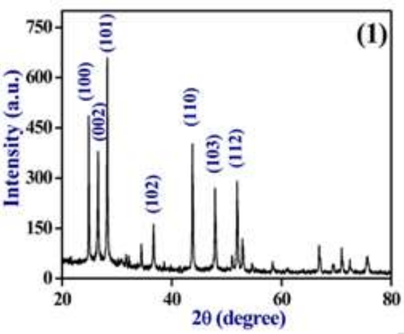

Fig. (1): The X-ray diffraction patterns of the as-synthesized CdS films elaborated with [Cd]/[S] ratios = 0.71

The sharp intense peaks of CdS thick films confirm the good polycrystalline nature and besides no other impurity peaks are seen, suggesting the formation of single phase CdS. The diffraction peak in the XRD pattern for film sample are observed at position 2θ ≈ 24.87°, 26.55°, 28.234°, 36.68°, 43.79°, 47.92° and 51.92° corresponding to reflections (100), (002), (101), (102), (110), (103) and (112) respectively. These peaks are well indexed as single hexagonal phase of CdS of JCPDS data card 80-0006 having preferred orientation (100), (002) and (101) [21]. The crystallographic parameters like lattice constant (a), inter-planar spacing (d), crystalline size (D), internal strain (ε), dislocation density (δ) and number of crystallites per unit area (N) were calculated and tabulated in **Table 1**. [22]

3.2 MORPHOLOGICAL STUDIES

Fig. (2) shows FESEM image of as prepared CdS thick film sample. The image reveals a systematic evaluation of morphology of the prepared sample. It is observed that the preparation technique plays the important role for the formation of nanocrystals. FESEM has been proved to be a unique, convenient and versatile method to analyse surface morphology of thick films and to determine the grain size.

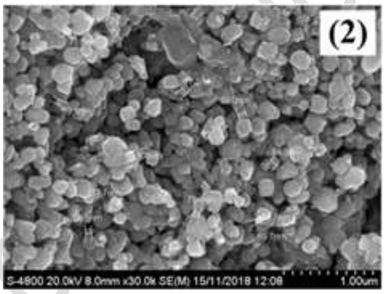

Fig (2): The FESEM micrographs of CdS film deposited with [Cd]/[S] ratio = 0.71

The high resolution FESEM micrograph shows that the as-prepared films are found to be homogeneous and uniform.

These micrographs show that the obtained films have good adherence on the substrates without pinholes or cracks and have identical nearly spherically shaped grains of submicron size. The average grain size of these films varies between 37.7 nm to 300 nm.

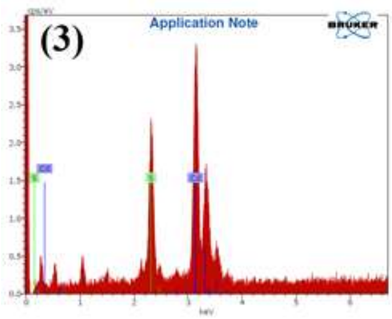

Fig (3): The EDAX patterns of CdS thick film with [Cd]/[S] ratios 0.71.

Fig. (3) the EDAX patterns were recorded for elemental analysis of the as-prepared CdS thick films of with [Cd]/[S] ratio = 0.71 qualitatively. The spectrum peaks revealed to the presence of cadmium and sulphide. The EDAX analysis revealed to the formation of nonstoichiometric films with average atomic percentage of Cd:S is found to be 41.73:58.27. The variation in elemental composition also reveals to the corresponding lattice constants as well as angular positions of the prominent peaks in the X-ray diffraction pattern.

3.3 OPTICAL PROPERTIES

The optical properties of CdS film were measured in the wavelength range 504-722 nm and the absorbance along

Table 1: The crystallographic parameters of as-grown CdS thick film.

samples	2θ °	(hkl)	d (Å)		a = b (Å)		D (nm)	ε x 10^{-2}	δ x10^{11} cm^{-2}	N x10^{12} cm^{-2}
			Obs.	Std.	Obs.	Std.				
As-grown	28.234	(101)	3.1580	3.1480	3.6465	4.121	26.27	1.96	1.44	13.78

Table 2: Refractive index, band gap (Eg) and average absorption coefficient values of the as-prepared CdS film.

[Cd]/[S]	Band gap Eg (eV)	Average Absorbance	Average transmittance	Refractive index n	Absorption coefficient α x10^4
0.71	2.37	1.09	9.55	2.56	1.00

with transmittance spectra are shown in **Fig. (4)**. The film shows good absorbance in the visible region and observed to be Decreased with increase in wavelength which might be ascribed to the charge carrier absorption.

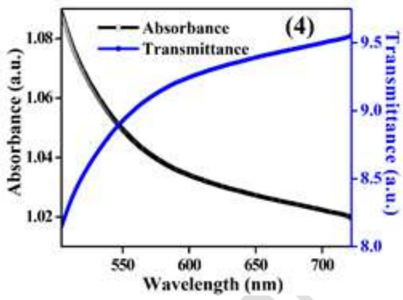

Fig. (4): Optical absorbance and transmittance spectra of CdS films prepared with [Cd]/[S] ratios = 0.71.

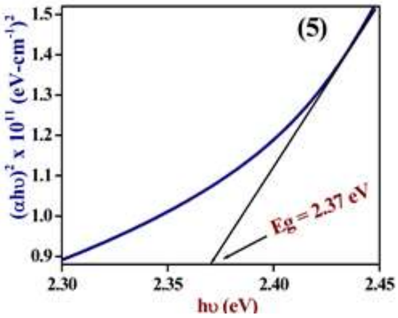

Fig. (5): Variation of $(\alpha h\upsilon)^2$ v/s (hυ) for CdS films elaborated with [Cd]/[S] ratios = 0.71

The transmittance is found to be increased at higher wavelength range that revealed to the homogeneous nature of deposited thin films [23]. The results are agreed with the reported work of Samantilleke et. al.[24]. Optical absorption measurements were carried out in order to evaluate the band gap. The band gap energy Eg was determined

by plotting the Tauc plot $(\alpha h\upsilon)^2$ v/s hυ of film are shown in **Fig. (5).**

The refractive index, band gap (Eg) and average absorption coefficient values were calculated and also depicted in **table 2**.

4. CONCLUSION

In this work , the CdS nanocrystals prapared by coprecipitation method and films are deposited by screen printing method. The structural, morphological and optical analysis of CdS thick film has been done. The film prepared with the optimized deposition parameters shows sample having wrutzite hexagonal structure with preferred orientation along (100), (002) and (101) plane with polycrystalline nature. From diffraction data, crystalline size was evaluated from Scherer's formula which was 26.27 nm. From FESEM image show that the films have identical nearly spherically shaped grains of submicron size. The average grain size of these films varies between 37.7 nm to 300 nm. The compositional analysis shows that the presence of Cd and S elements with average atomic percentage of Cd:S is found to be 41.73:58.27 shows nonstoichiometric nature. The optical energy band gap was found to be 2.37 eV.

ACKNOWLEDGMENTS

The authors are thankful to the UGC-DAE Consortium for Scientific Research Indore for providing characterization facilities. Authers like to thanks to the Principal, Pratap College, Amalner for providing laboratory facility. The author B.Y.Bagul gratefully acknowledges Dr.S.R.Gosavi of C.H.C. Arts, S.G.P. Commerce, and B.B.J.P. Science College, Taloda (M.S.) India for providing laboratory facilities required to carry out the research work and for providing UV-VIS facility and also gratefully acknowledges to Mr. Prasad Mogare, UICT, KBCNMU, Jalgaon for providing FESEM facility.

REFERENCES

[1] Yadav A.A., Barote M.A., Masumdar E.U., Studies on nanocrystalline cadmium sulphide (CdS) thin films deposited by spray pyrolysis, Mater. Chem. Phys. 12.7 (2010): 1173-1177.

[2] Yadav A.A., Barote M.A., Dongre P.M., Masumdar E.U., Studies on growth and characterization of $CdS_{1-x}Se_x$ ($0.0 \leq x \leq 1.0$) alloy thin films by spray pyrolysis, J. Alloys Compd. 493.1.2 (2010): 179-185.

[3] Chu T.L., Chu S.S., Thin film II-VI photovoltaics., Solid State electron, 38 (1995): 533-549.

[4] Hashimoto Y., Kohara N., Negami T., Nishitani N., Wada T., Chemical bath deposition of CdS buffer layer for GIGS solar cells, Sol. Energ. Mater. Sol. Cells 50.1.4 (1998): 71-77.

[5] Maruyama T., Kitamura R., Optimization of Nanocrystalline Cadmium Sulphide (CdS) Thin Films for Solar Cells, Sol. Energ. Mater. Sol. Cells 69 (2001): 61-66.

[6] Bar M., Weinhardt L., Heske C., Muffler H.-J., Umbach E., Lux-Steiner M.Ch., Niesen Th. P., Karg F., Fischer Ch.-H., Multi-Layer Deposition and Characteristics of Nanocrystal CdS Thin Films by an In situ Chemical Reaction Process, Sol. Energ. Mater. Sol. Cells 90.18.19 (2006): 3151-5157.

[7] Duan X., Niu C., Sahi V., Chen J., Parce J.W., Empedocles S., Goldman J.L., High-performance thin-film transistors using semiconductor nanowires and nanoribbons, Nature 425(2003): 274-278.

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

[9] Bruchez Jr. M., Moronne M., Gin P., Weiss S., Alivisatos A.P., Semiconductor nanocrystals as fluorescent biological labels, Science 281(1998): 2013-2016.

[10] Howie J.A.B., Rowles G.K., Hawkins P., An inexpensive sensor for ultraviolet-A and ultraviolet-B radiation, Meas. Sci. Technol. 2(1991): 1070 -1073.

[11] Bilgin V., Kose S., Atay F., Akkyaz I., Optical and structural properties of thermally evaporated cadmium sulphide thin films on silicon (100) wafers, Mater. Chem. Phys. 94 (2005): 103-107.

[12] Brien P.O., Pickett N.L., Nanocrystalline Semiconductors: Synthesis, Properties, and Perspectives, Chem. Mater. 13 (2001): 3843-3845.

[13] 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 (2009): 093113-093117.

[14] Enríquez J.P., Mathew X., CdTe/CdS Solar cells on flexible molybdenum substrates, Solar Energy Materials and Solar Cells 76 (2003): 313-322.

[15] Martinuzzi S., Trends and problems in CdSCuS thin film solar cells: A review, Sol. Cells 5 (1982): 243-247.

Vol 11, Issue 5,May/2020
ISSN NO:0377-9254

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

[17] Zelaya-Angel O., Lozada-Morales R., Sphalerite-wurtzite phase transformation in CdS, Phys. Rev. B 62 (2000): 13064-13069.

[18] Sharma M., Kumar S., Sharma S., Sharma L.M., Sharma T.P., Hussain M., CdS sintered films: growth and characteristics, Physica B, 348 (2004): 5-20.

[19] Zargar R.A., Chackrabarti S., Joseph S., Mohd. S. Khan, Husain R., Hafiz A.K., Optik, 126 (2015):4171-4178.

[20] Kumar V., Sharma D.K., Sharma K., Dwivedi D.K., Investigation on physical properties of polycrystalline nickel sulphide films grown by simple & economical screen-printing method, Optik, 156 (2018): 43-48.

[21] JCPDS, International Center for Differaction Data, USA Card No. 80-0006 (CdS, hexagonal structure).

[22] Spalatu N., Hiie J., Mikli V., Krunks M., Valdna V., Maticiuc N., Raadik T., Caraman M., Effect of $CdCl_2$ annealing treatment on structural and optoelectronic properties of close spaced sublimation CdTe/CdS thin film solar cells v/s deposition conditions, Thin Solid Films 582 (2015): 128-133.

[23] Chander S., Dhaka M. S., Optical and structural constants of CdS thin films grown by electron beam vacuum evaporation for solar cells, Thin Solid Films. 638 (2017): 179-188.

[24] Samantilleke A.P., Cerqueira M.F., Heavens S., Warren P., Dharmadasa I.M., Muftah G.E.A., Silva C.J.R., Mari B., Characterisation of chemical bath deposited CdS thin films on different substrates using electrolyte contacts, Thin Solid Films 519 (2011): 7583-7586.