

Investigation of the structural, optical and photoluminescence properties of electrosynthesized hexagonal nanocrystalline $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film

H.D. DHAYGUDE, V.J. FULARI*

Holography and Material Research Laboratory, Department of Physics, Shivaji University, Kolhapur-416004, India

In this paper, $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film has been electrodeposited from aqueous bath containing CdSO_4 , ZnSO_4 , $\text{Na}_2\text{S}_2\text{O}_3$ and EDTA, having pH ~ 14 . The structural, optical, morphological, surface wettability and photoluminescence properties of the film were investigated. The XRD pattern showed that the film consisted of mixed phases of CdS and ZnS with polycrystalline structure. The bandgap of the film was evaluated as 2.69 eV. The AFM study revealed that the $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film contained spherical grains with root mean square roughness of 6.09 nm. The water contact angle measurement showed that the thin film was hydrophilic in nature. Moreover, the PL study revealed that the excitation wavelength was 460 nm.

Keywords: *electrodeposition; $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film; XRD; photoluminescence*

1. Introduction

Electrodeposition is an attractive method for preparation of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin films. The main advantage of this method is an easy control of growth rate through appropriate choice of deposition parameters. The method has been successfully employed for fabrication of thin films of elemental, binary and ternary semiconductors [1–6]. It also offers many attractive features for thin film heterojunction solar cells, such as an isothermal process, low operating temperature, and easy formation of the junction [7]. Cadmium sulfide together with Cu_2S forms the well-known CdS/ Cu_2S solar cells. The low efficiency of CdS/ Cu_2S solar cells results mainly from mismatching of lattice constants and differences in electron affinities. To overcome the problems, $\text{Cd}_x\text{Zn}_{1-x}\text{S}/\text{Cu}_2\text{S}$ solar cells have been fabricated by introduction of zinc into CdS. Increase in open circuit voltage (V_{oc}) without affecting fill factor (FF) and short circuit current (I_{sc}) has been reported for $\text{Cd}_x\text{Zn}_{1-x}\text{S}/\text{Cu}_2\text{S}$ solar cells having optimal value of x in the range of 0.2 to 0.3 [8]. In the present study, we have studied

electrodeposition of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ films from aqueous solutions to optimize the preparation parameters.

2. Experimental

In present investigation, $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film was fabricated by using an electrolytic bath containing 0.07 M CdSO_4 , 0.07 M ZnSO_4 , 0.7 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.1 M EDTA in the volumetric ratio of 1:4:3. The pH of the solution was maintained at ~ 14 . A three electrode system was used for the deposition. The system was composed of a saturated calomel electrode (SCE) used as a reference electrode, a graphite electrode used as a counter electrode, and indium tin oxide (ITO) coated glass and steel substrates used as the working electrodes with dimensions 5 cm \times 1 cm \times 0.1 cm. Prior to the deposition, the indium tin oxide (ITO) and steel substrates were ultrasonically cleaned in acetone and ethanol for 20 min. In order to obtain high quality films, the deposition potential was maintained at -0.85 V/SCE during the deposition process. The optimized deposition time was 15 minutes.

*E-mail: vijayfulari@gmail.com

3. Results and discussion

3.1. X-ray diffraction study

XRD pattern of the $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film was recorded using an X-ray diffractometer. The nature of the XRD pattern indicates that the film is polycrystalline with hexagonal crystal structure. The XRD pattern of the $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film is shown in Fig. 1.

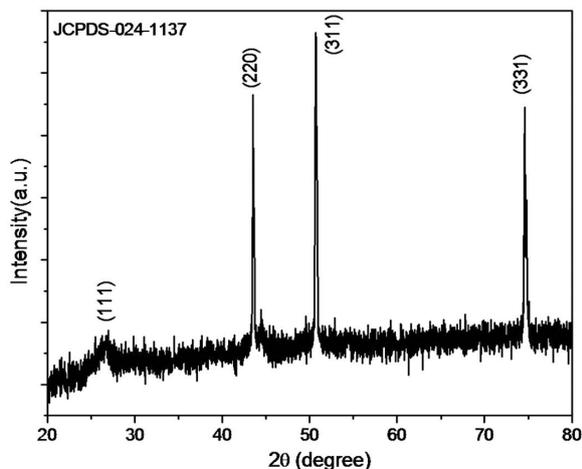


Fig. 1. X-ray diffraction pattern of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film.

It is seen that a degradation of crystallinity appeared as zinc content has increased [9, 10]. The experimental d-values and standard d-values (JCPDS Card No. 0024-1137) are in good agreement. The thin film shows preferred orientation along (3 1 1) plane. Average crystallite size in the film is 75 nm.

3.2. Fourier transform infrared (FT-IR) study

Fig. 2 shows the FT-IR spectrum of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film electrodeposited in galvanostatic (GS) mode. From Fig. 2, absorption at 2959 cm^{-1} and 2869 cm^{-1} is observed which indicates the presence of hydroxide. The peak at 2364 cm^{-1} in the spectrum is assigned to both symmetric and asymmetric stretching vibrations of $\text{C}=\text{O}$ [11]. The absorption bands at 1620 cm^{-1} , 1134 cm^{-1} and 1000 cm^{-1} correspond to stretching vibrations of $\text{C}-\text{O}$ group [12, 13]. The band at 667 cm^{-1} is due

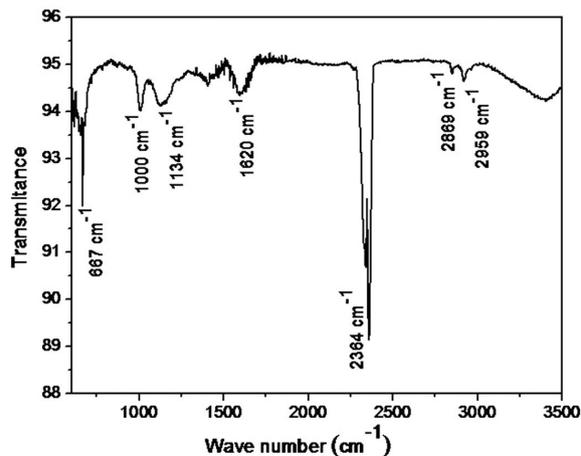


Fig. 2. FT-IR spectrum of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film.

stretching vibration of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ bond. Thus, the FT-IR result suggests the presence of bonding between Cd, Zn, S and some constitutional water incorporated in the $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ structure. Thus, the formation of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ compound has been confirmed from FT-IR study.

3.3. Atomic force microscopic (AFM) study

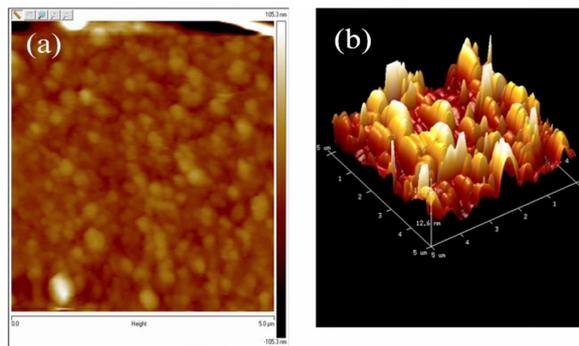


Fig. 3. (a) 2D and (b) 3D images of AFM of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film.

Atomic force microscopy (AFM) is a technique to suitable study the morphology of thin films. Fig. 3 presents the AFM image of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film. It can be observed that the film is uniform, well-defined, and consists of spherical grains that cover the ITO substrate uniformly. The spherical grains have also been obtained for

$\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film by solution growth technique and chemical bath deposition method reported in the literature [14, 15].

From the AFM measurement, we have obtained the root mean square (RMS) roughness of 6.09 nm, particle size of 244 nm, surface area of $14.1 \mu\text{m}^2$ and surface roughness of 4.93 nm. Thus, AFM images indicate that regular, homogeneous surface and large grain size were obtained under these conditions.

The larger grain size of the films may provide larger surface area for liquid electrolyte/electrode junction in photoelectrochemical (PEC) cell applications [16].

3.4. Surface wettability study

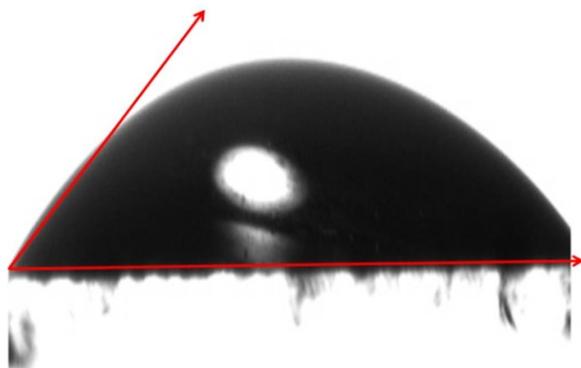


Fig. 4. Contact angle measurement of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film.

Surface wettability involves the interaction between a liquid and a solid. This behavior is characterized by the value of contact angle, a macroscopic parameter. The surface wettability has a sound influence on the performance of solar cells [17]. Fig. 4 shows the digital photograph of water contact angle of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film which was found to be 40° meaning that the surface of the film is hydrophilic in nature.

3.5. Optical absorption study

The variation of optical absorption (αt) with wavelength (λ) is shown in the inset of Fig. 5. The band gap of the film is determined by using $(\alpha h\nu)^2$ versus $(h\nu)$ plot as shown in Fig. 5. The band gap of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film is observed

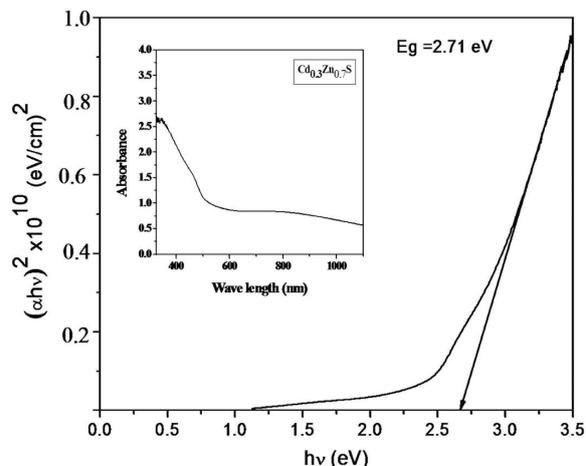


Fig. 5. Plot of $(\alpha h\nu)^2$ versus $(h\nu)$ (Inset shows the variation of absorption (αt) with wavelength (λ) of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film on ITO coated glass substrate.

to be 2.69 eV. The dependence of bandgap on Zn content was nonlinear. A similar type of nonlinear dependence has been reported for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films prepared by spray, chemical bath and vacuum evaporation method [18–20].

3.6. Photoluminescence (PL) study

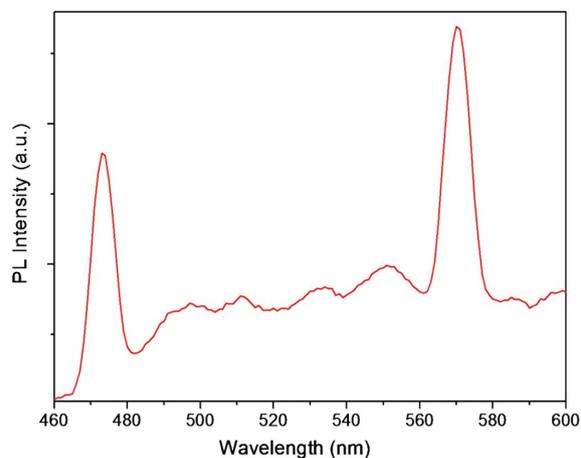


Fig. 6. Photoluminescence spectrum of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film.

The PL study of semiconductor materials can yield important information about the quality of the materials. Fig. 6 shows the PL spectrum

of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film. From the figure, it is seen that the broad emission bands centered at 570 nm and 473 nm respectively have occurred. The excitation wavelength was 460 nm. As the peak energies are less than the energy band gap (E_g), these bands can be definitely identical with transitions involving donors, acceptors, free electrons and holes [21]. The blue shift of PL spectrum is probably due to the structural effect [22].

4. Conclusions

In present work, the $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film has been successfully deposited by electrodeposition technique. XRD studies revealed that the sample is polycrystalline with hexagonal structure and the average crystallite size of 75 nm. The band gap energy value of the $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film was found to be 2.69 eV, which is suitable as a window material for solar cells. The particle size of the $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ thin film observed by AFM was found to be 244 nm and surface roughness was 4.93 nm. The contact angle for the film was 40° , which is less than 90° meaning that the surface is hydrophilic. The FT-IR study, confirmed the formation of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ compound. The excitation wavelength obtained from PL study was found to be 460 nm. Thus, the crystalline nature and optical band gap are suitable for various optoelectronic applications.

Acknowledgements

Author is very much thankful to the U.G.C. for providing leave under the F.D.P. and also thankful to the Physics Department, the Shivaji University, Kolhapur, for providing all characterization facilities (PIFC).

References

- [1] ELWELL D., *J. Crystal Growth*, 52 (1981), 741.
- [2] ROSAMILLA J.M., MILLER B., *J. Electroanal. Chem.*, 215 (1986), 249.

- [3] HODES G., MANASSEN J., NEAGU S., CAHEN D., MIROVSKY Y., *Thin Solid Films*, 90 (1982), 433.
- [4] BHATTACHARYA R.N., RAJESHWAR K., *J. Electrochem. Soc.*, 131 (1984), 2032.
- [5] CHANDRA S., SAHU S.N., *J. Phys. D: Appl. Phys.*, 10 (1984), 2115.
- [6] LOKHANDE C.D., *J. Phys. D Appl. Phys.*, 20 (1987), 1213.
- [7] LIABREM J., DELMOS V., *6th EEC Photovoltaic Solar Energy Conference*, London, 15 – 19 April, 1985.
- [8] BONNET D., *J. Phys. Stat. Solidi. A*, 11 (1972), 135.
- [9] AGNIHOTRI O.P., GUPTA B.K., *J. Appl. Phys.*, 18 (1979), 317.
- [10] DUCHEMIN S., BOUGNOT J., KAKA M., CADENE M., *Thin Solid Films*, 136 (1986), 289.
- [11] TAUC J., *Plenum*, New York, 1974, p. 159.
- [12] SINGH R.S., GUPTA A., SINGH A.K., DEO S.R., DESHMUKH L., PANDEY G.P., *Res. Chem. Intermed.*, 41 (2013), 535.
- [13] CHAVHAN S.D., SENTHILARASU S., LEE J., LEE S.H., *J. Phys. D Appl. Phys.*, 41 (2008), 165502.
- [14] SADEKAR H.K., DESHPANDE N.G., GUDAGE Y.G., GHOSH A., CHAVHAN S.D., GOSAVI S.R., SHARMA R., *J. Alloy. Compd.*, 453 (2008), 519.
- [15] NASR T.B., KAMOUN N., GUASCH C., *J. Mater. Chem. Phys.*, 96 (2006), 84.
- [16] MAHALINGAM T., CHITRA J.S.P., CHU J.P., MOON H., KWON H.J., KIM Y.D., *J. Mater. Sci. Mater. El.*, 17 (2006), 519.
- [17] LOKHANDE C.D., BARKSCHAT A., TRIBUTSCH H., *J. Sol. Energ. Mater. Sol. C.*, 79 (2003), 293.
- [18] DAVIS E.A., LIND E.L., *J. Phys. Chem. Solids*, 29 (1968), 79.
- [19] UPLANE M.D., PAWAR S.H., *Solar Cells*, 10 (1983), 177.
- [20] LOKHANDE C.D., YERMUNE V.S., PAWAR S.H., *J. Mater. Chem. Phys.*, 20 (1988), 283.
- [21] GAEDWANG N., GAEDWANG T., *J. Mater. Lett.*, 59 (2005), 3577.
- [22] LI G.R., BU Q., ZHENG F.L., SU C.Y., TONG Y.X., *J. Cryst. Growth Des.*, 9 (2009), 1538.

Received 2016-04-02

Accepted 2019-04-23