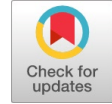


Silar Deposited Ternary CuCdS_2 Thin Film for Solar Cell Application



A. Murugan, V. Siva, A. Shameem, S. Asath Bahadur

Abstract: The CuCdS_2 thin film have been deposited on over the glass substrate by successive ionic layer adsorption and reaction method. The film was characterized by Structural, Functional group, Morphology and Optical properties. The powder X-ray diffraction pattern result showed that the deposited film has confirmed CuCdS_2 phase with hexagonal structure. Fourier-transform infrared spectroscopy confirmed the functional group metal vibration of deposited film. The deposited film surface morphology was analysis by scanning electron microscope and no visible cracks. The deposited film has a good absorbance in the visible range and calculated energy band gap is 1.77 eV. This film as a good applicant for economical thin film solar cells.

Keywords: CuCdS_2 , SILAR, Hexagonal structure, Bandgap.

I. INTRODUCTION

The last few years, there is an excessive deal of importance in research of chalcopyrite semiconductors due to their suitable optical energy bandgap and extraordinary optical absorption coefficient for potential application in thin film solar cells [1]. The copper based semiconducting materials were used as absorber layers in photovoltaic technology. Current year, significance is agreed to non-hazardous semiconductors from both the fundamental and technological points of view for thin film solar cell materials. The CuCdS_2 film presented hexagonal structure with an optical energy direct band gap is 1.42 eV, it is a p-type semiconductor and suitable candidate for photovoltaic cells. They increased crystallinity of CuCdS_2 film and discovered that the environment of electrical conductivity

can be tuned between p-type and n-type [2]. Decreasing the optical energy band gap of $\text{Cu}_{(1-x)}\text{Cd}_x\text{S}_2$ film from 2.45 eV to 2.2 eV due to increasing copper concentration of the deposited films. The synthesized zinc blend CuCdS_2 nanocrystals prepared by single step synthesis has the application in tunable color Light emitting diode application [3]. The copper concentration powerfully effects on the optical energy band gap, electrical properties of CuS , subsequently decide the application to be used [4]

The CuCdS_2 thin film has been synthesized by non-vacuum chemical technique of successive ionic layer adsorption and reaction (SILAR)[5]. SILAR technique associated with other non-vacuum chemicals methods is a simple, less expensive, luxury to handle and low temperature, thus the method are deposited in large area and any shape of the substrate. The SILAR method, both conducting and non-conducting substrate are successively immersed into the precursor solution bath during the deposition process and has easy control of film thickness by varying number of deposition cycles which is the beauty of this method. Thus the method, dipping time and number of deposition cycles are main parameters for preparation of nano-size CuCdS_2 thin film. The reaction time favors to the thorough chemical reaction and hence produces pure phase compounds without any secondary phases. In the present work reports the synthesis of CuCdS_2 thin film deposited on over the glass substrate by SILAR method and its characterization for structural, morphological, elemental composition, functional group and optical properties.

II. EXPERIMENTAL

A. Material and methods

All raw materials were used by AR grade and without any further purification. Cupper Chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), Cadmium Chloride hydrate ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$) and Thiourea($\text{CH}_4\text{N}_2\text{S}$) were used as precursors, double distilled(DD) water, acetone, Ammonia solution and micro glass slide as a substrate. Before the film deposition, the substrates (2.5mm X7mm) were cleaned in soap oil solution, rinsed double distilled water, and sequentially substrate boiled in chromic acid for 30 minutes, after that substrate rinsed in double distilled water. The rinsed glass substrate were vertically immersed in dilute HF for 1 minute to etch the depositing substrates and finally the substrates were cleaned using ultrasonic water bath for 30 minutes, in order to eliminate surface dust particles and organic impurities present if any. Deposit nano-scale CuCdS_2 thin film by a simple SILAR method, the following baths were prepared.

Manuscript published on 30 December 2019.

* Correspondence Author (s)

S. Asath Bahadur*, Department of Physics, Kalasalingam Academy of Research and Education, Krishnankoil-626 126, India, and Condensed Matter Physics Laboratory, International Research Centre, Kalasalingam Academy of Research and Education, Krishnankoil-626 126, India.

Email: s_a_bahadur@yahoo.co.in

A. Murugan, Department of Physics, Kalasalingam Academy of Research and Education, Krishnankoil-626 126, India, and Condensed Matter Physics Laboratory, International Research Centre, Kalasalingam Academy of Research and Education, Krishnankoil-626 126, India.

Email: murugan027@gmail.com

V. Siva, Department of Physics, Kalasalingam Academy of Research and Education, Krishnankoil-626 126, India, and Condensed Matter Physics Laboratory, International Research Centre, Kalasalingam Academy of Research and Education, Krishnankoil-626 126, India.

Email: vsiva33.physics@gmail.com

A. Shameem, Department of Physics, Kalasalingam Academy of Research and Education, Krishnankoil-626 126, India, and Condensed Matter Physics Laboratory, International Research Centre, Kalasalingam Academy of Research and Education, Krishnankoil-626 126, India.

Email: shameemirfu@gmail.com

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an [open access](https://creativecommons.org/licenses/by-nc-nd/4.0/) article under the CC-BY-NC-ND license <http://creativecommons.org/licenses/by-nc-nd/4.0/>



Silar Deposited Ternary CuCdS_2 Thin Film for Solar Cell Application

The cationic and anionic precursor solutions were taken from 0.1 M CuCl_2 , 0.05M CdCl_2 and 0.15 M $\text{CH}_4\text{N}_2\text{S}$ dissolved in 50ml of double distilled water respectively. The one cycle of deposition of CuCdS_2 film by SILAR method involves the following four steps. The etched substrate is Immersion in cationic(Cu^{2+} , Cd^{2+}) solution for 30 seconds. Where cations are adsorbed on the surface of the substrate. Thus the substrate was rinsed for 20 seconds in DD water to remove the lightly bound cations on the surface of the substrate. Sequentially the substrate was plunged in the anionic(S^{2-}) solution for 30 seconds. The sulfide ions reacted with adsorbed cations on the substrate surface. Thus the substrate finally was rinsed for 20 seconds in double distilled to remove loosely bound unreacted ions present on the substrate surface, both water baths were placed on magnetic stirrer and maintained at 75°C end of the deposition process. The thin films taken for the present work is prepared with 40 cycles. Further the prepared film was dried at 60°C under the oven for 1h. In SILAR method concentration, temperature of precursor solutions, dipping time and number of cycles are important parameters to get a good film. Film was annealed at 400°C for 2h in muffle furnace in air atmosphere.

B. Characterization

The structural properties of CuCdS_2 film were studied using powder XRD pattern of the thin film ($\text{CuK}\alpha$ wavelength (λ) = 1.54056 Å) (Bruker - D8 advance ECO XRD systems). The functional group analysis by Fourier transform infrared spectra of the thin film were recorded the range of 4000–400 cm^{-1} (Shimadzu-IR Tracer-100). The surface morphology taken by scanning electron microscopy (SEM), (JEOL, JSM-6360, Japan) and elemental compositional of deposited film were carried out by energy dispersive X-ray (EDX) analyzer. Deposited film analyzed optical absorption property's using UV-vis spectrophotometer the wavelength range of 400–1100 nm (Shimadzu-1800, Japan).

III. RESULTS AND DISCUSSION

A. Structure analysis

The nano-crystalline structure of CuCdS_2 were studied by powder X-ray diffraction pattern. From figure 1 show in the XRD pattern of the CuCdS_2 thin film. The indexed X-ray diffraction peaks are appeared at $2\theta = 23.4, 27.67, 29.3, 35.8, 42.7, 47.9$ and 52.2 were indexed planes as (100), (002), (101), (102), (110) and (103) respectively of CuCdS_2 planes corresponds to wurtzite phase with a hexagonal structure[6] (JCPDS No. 80-0006). A peak corresponding to the glass substrate is observed as a broad hump with 2θ ranging from 15° to 35° . The grain size of the film can be estimated according to the scherrer's equation as follows [7].

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where k is a structural constant, λ is X-ray wavelength by the source of $\text{CuK}\alpha$, β - full width at half maximum and θ the bragg's diffraction angle. Grain size of the deposited CuCdS_2 thin film calculated using the high intensity peak corresponding to the plane of (101) is about 37 nm.

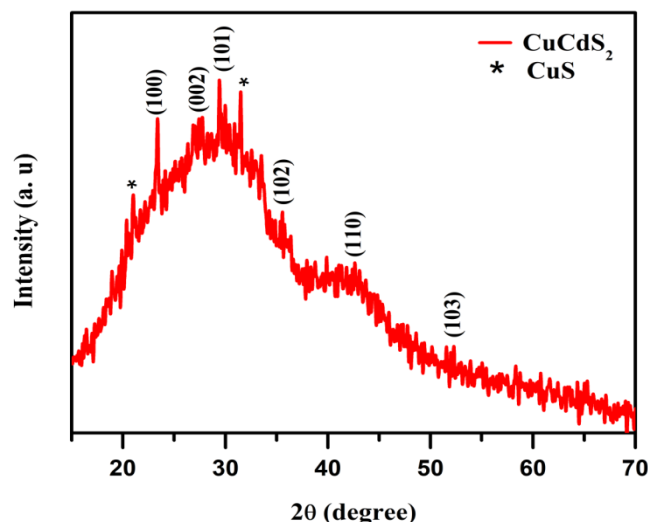


Fig. 1. Powder XRD pattern of CuCdS_2 thin film

B. Fourier Transform Infrared

Figure 2 shows in FTIR spectrum of CuCdS_2 thin film and spectrum recorded in the range 4000–400 cm^{-1} . The functional groups of substrate surface bound molecules are identified by FTIR. Expected functional groups were present and metal sulphide vibration at 912, 768 and 616 cm^{-1} is attribute to substrate peak (figure 2 shows inside glass substrate FTIR spectrum) and Cd-S vibration. These vibrations are also in good agreement with previous literature (8).

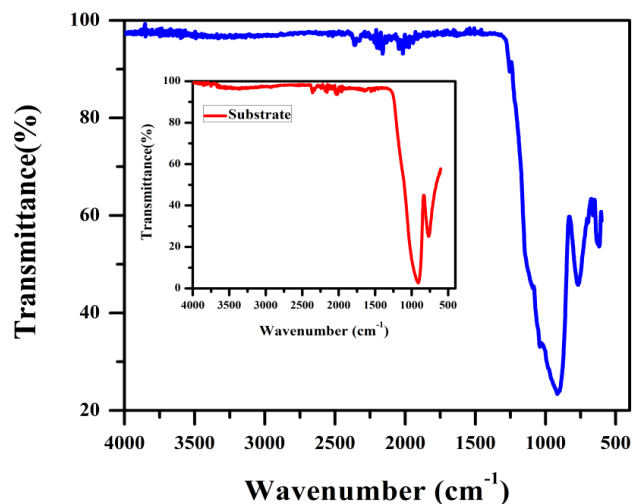


Fig. 2. FTIR spectra of CuCdS_2 thin film and inset glass substrate

C. SEM with EDX

Figure 3 displays the SEM images of CuCdS_2 thin film, and its corresponding EDX spectrum. SEM images shows in different magnification, according to this micrograph, film surface has well deposited and without any visible cracks. Film surface images show that nanoplates like structures with rough surface.

Copper, cadmium and sulfur ions are presented, which shows that purity of the materials. Hence, the EDX analysis is the confirmation of presented elements of Cu, Cd, and S, in figure 3 shows in EDX spectrum of the deposited film and observed high intensity peak(Si and O) due to using of glass substrate, it also confirmation of the deposited film and does not contain any other elemental impurities.

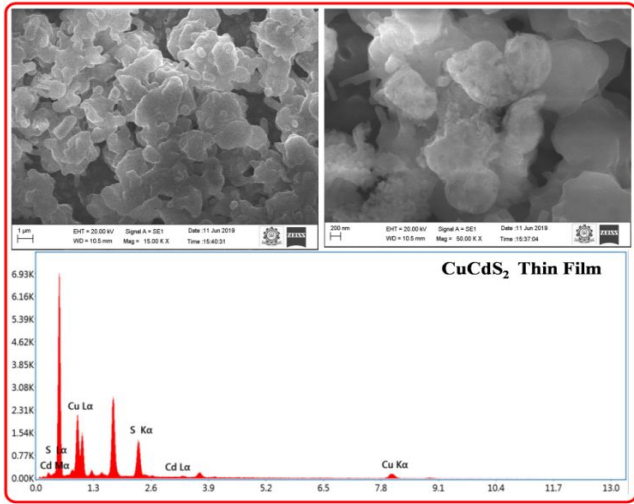


Fig. 3. Morphology and elemental computation images of the CuCdS₂ thin film

D. Optical properties

Figure 4 shows the UV-Vis absorbance spectra of CuCdS₂ film. Thus the film shows good absorbance in the visible spectrum rang 400 to 800 nm confirm that this is a good applicant for economical and environment friendly solar cell absorber layer and has suitable band gap for thin film solar cell. The optical energy band gap of the film is calculated using the Tauc's plots [9].

$$\alpha = \frac{A(E - E_g)^n}{E}$$

From equation α is the absorption coefficient, E is the photon energy(eV), E_g is the band gap energy (eV). The superscript n is a constant which is allotted values 1/2, 3 and 3/2 for direct allowed, indirect and indirect forbidden allowed respectively. Figure 5 shows the Tauc's plots for the annealed CuCdS₂ film. The optical energy band gap of the CuCdS₂ film is calculated is 1.77 eV.

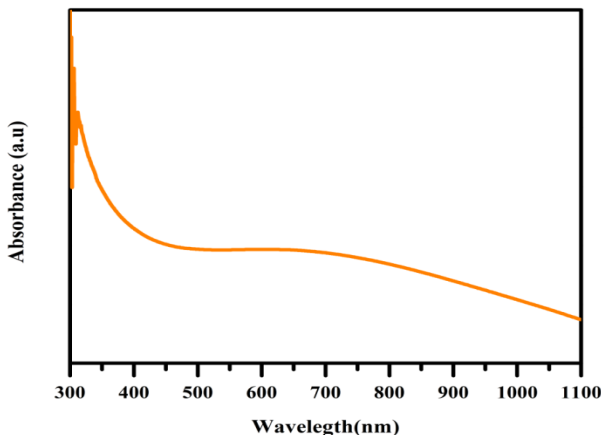


Fig. 4. UV-Vis. absorbance spectrum of CuCdS₂

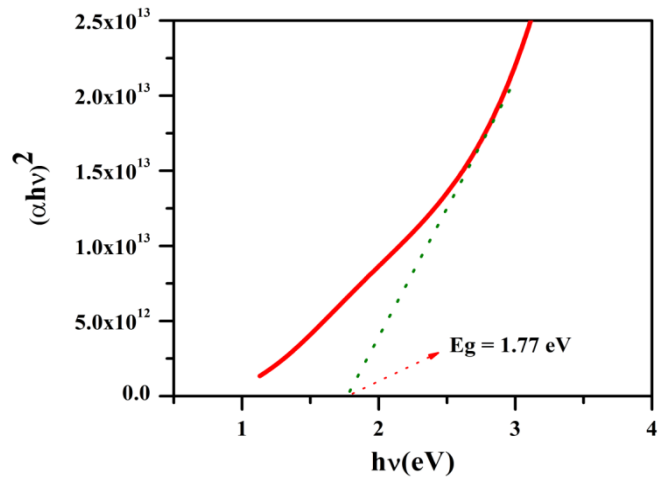


Fig. 5. Tauc's plot of CuCdS₂ thin film

IV. CONCLUSION

The CuCdS₂ thin films were deposited on micro glass slide by successive ionic layer adsorption and reaction method. Powder XRD shows good crystalline nature and grain size of the CuCdS₂ thin film evaluate by scherrer's equation as 37 nm. The morphology of annealed film shows nanoplates like structures with rough surface and well uniformly deposited without any crack. Optical property of the film shows good absorbance in visible wavelength it is suitable for solar cell absorber material because, the optical energy band gap is 1.77 eV.

ACKNOWLEDGMENT

The author A. Murugan and S. Asath Bahadur are thankful to Department of Science and Technology-Science and Engineering Research Board (DST-SERB) - New Delhi, for the financial support (No : EMR/2016/006874).

REFERENCES

1. J. Tang, S. Hinds, S.O. Kelley, and E.H. Sargent, "Synthesis of Colloidal CuGaSe₂, CuInSe₂, and Cu(InGa)Se₂ Nanoparticles," Chemistry of Materials, vol. 20(22), Oct. 2008, pp.6906-6910
2. V.N. Kumar, R. Suryakarthick, S. Karuppusamy, M. Gupta, Y. Hayakawa, and R. Gopalakrishnan, "Effect of precursor concentration on the properties and tuning of conductivity between p-type and n-type Cu_{1-x}Cd_xS₂ thin films deposited by a single step solution process as a novel material for photovoltaic applications," RSC Advances, vol. 5(29), Feb.2015 pp.23015-23021
3. A.H. Khan, A. Dalui, S. Mukherjee, C.U. Segre, D.D Sarma, and S. Acharya, "Efficient Solid-State Light-Emitting CuCdS Nanocrystals Synthesized in Air," Angewandte Chemie International Edition, vol. 54(9), Feb. 2015, pp.2643-2648
4. Z. Fang, C. Wang, F. Fan, S. Hao, L. Long, Y. Song, and T. Qiang, "Phase Evolution of Cu-S System in Ethylene Glycol Solution: The Effect of Anion and PVP on the Transformation of Thiourea," Chinese Journal of Chemistry, vol. 31(8), Feb. 2013, pp.1015-1021
5. A. Shameem, P. Devendran, V. Siva, M. Raja, S.A. Bahadur, and A. Manikandan, "Preparation and characterization studies of nanostructured CdO thin films by SILAR method for photocatalytic applications," Journal of Inorganic and Organometallic Polymers and Materials, vol. 27(3), May. 2017, pp.692-699
6. A. Singh, C. Coughlan, M.J. Delia, and K.M. Ryan, "Solution Synthesis and Assembly of Wurtzite-Derived Cu-In-Zn-S Nanorods with Tunable Composition and Band Gap," Chemistry of Materials, vol. 27(5), Feb. 2015, pp.1517-1523



Silar Deposited Ternary CuCdS_2 Thin Film for Solar Cell Application

7. S. Das, K Sa, P C Mahakul, J Raiguru, I Alam, BVRS Subramanyam, and P Mahanandia, "March. Synthesis of quaternary chalcogenide CZTS nanoparticles by a hydrothermal route," In IOP Conference Series: Materials Science and Engineering., vol. 338, 2018, pp. 012062
8. S.S. Kavar., and B. H. Pawar. "Synthesis and characterization of cds n-type of semiconductor thin films having nanometer grain size," Chalcogenide Letters., vol. 6(5), 2009,
9. R. Sani, R. Manivannan, and S.N. Victoria, "one step electrochemical deposition of czts for solar cell applications," ChalcogenideLett., vol. 14, May. 2017, pp. 165 - 170

AUTHORS PROFILE



A. Murugan is a Senior Research Fellow in the Department of Physics at Kalasalingam Academy of Research and Education. He has joined as Junior Research Fellow in the Department of Physics under DST-SERB funded project, Govt. of India in the year of 2017. He has received his Master's Degree in Physics from Government Arts College (Autonomous), Coimbatore, which is affiliated to Bharathiar University in the year

2013. His research focus is thin film for solar cell applications and the design of materials enhanced for energy applications.



Dr. V. Siva obtained Ph.D in Physics from Kalasalingam Academy of Research and Education in 2018. He has received his Bachelor's Degree and Master's Degree in Physics from Government Arts College (Autonomous), Coimbatore, which is affiliated to Bharathiar University in the years 2010 and 2012, respectively. He has expertise in the areas of Crystallography, Crystal growth and

Computational Physics. To his credit, he has published more than 20 articles in journals of international repute besides ten more as proceedings. Further, he has presented papers in various conferences and seminars. His current research interest is development of Metal-Organic Frameworks (MOFs) for sensor and energy storage application.



A. Shameem is a Research scholar in the Department of Physics, School of Advanced Sciences at Kalasalingam Academy of Research and Education, India. He received his B.Sc. degree in Physics from Jamal Mohamed College, Tiruchirappalli, in 2010, and his M.Sc. degree in Physics from Government Arts College (Autonomous), Coimbatore, in 2012. His research interest is in the field of nanomaterials for energy

and environmental applications.



Dr. S. Asath Bahadur is a Senior Professor in the Department of Physics, School of Advanced Sciences at Kalasalingam Academy of Research and Education, India. He has obtained Ph.D in the area of X-ray crystallography from Madurai Kamaraj University in 1994 and also received his M.Phil and M.Sc. Degree in physics from Madurai Kamaraj University, He has expertise in the areas of Crystallography and Material science.

He has published more than eighty five peer review research articles in journals of international repute besides seventy more as proceedings.