Structural, Morphological, Compositional, Electrical, and Optical Characterizations of CuZnS Thin Films Prepared using Chemical Bath Deposition Method

Preetha K C[1,2,a] and Bini S[1,b]

[1] *Department of Physics, Sree Narayana College, Nattika, University of Calicut, Kerala, India.*
[2] *Research Department of Physics, Sree Kerala Varma College, Thrissur, University of Calicut, Kerala, India.*

[a] preethasajitht@gmail.com
[b] binis@keralavarma.ac.in

Abstract

The universality, affordability and abundance of solar energy combined with its free and high energy output make it an exceptional renewable energy source. Solar cells play a vital role in converting sunlight into electrical energy. CuZnS has gained significant attention as a potential absorber material for solar cells. In the present work, we report the preliminary results of the preparation of CuZnS thin films using a relatively low-cost Chemical Bath Deposition technique, from a precursor solution containing 0.1M concentrations of copper chloride, zinc chloride, and thiourea. Triethanolamine (TEA) is used as the complexing agent, and ammonia is used to control the pH of the solution. The samples were prepared by keeping the pH at 11.6, maintaining the temperature at 80°C, and a deposition time of 1 hour. Structural, morphological, compositional, electrical, and optical analyses of the prepared samples were done. From the SEM analysis grain size calculated is 177 nm. The observed bandgap value was 2.61 eV at a Cu/(Cu+Zn) ratio of 83%. The prepared sample is a p-type semiconductor with a conductivity 1.646X10$^{-3}\Omega^{-1}$cm^{-1}. XRD [Bruker Kappa Apex II], SEM-EDAX [Jeol 6390LA/OXFORD XMX N], Hall effect measurement system [Ecopia HMS 3000s], and UV-Vis Spectrophotometry [JASCO V-670 UV-Vis NIR Spectrophotometer] were used for the characterization of the samples.

Keywords: CuZnS, Chemical bath deposition, Preparation of thin film, Characterization of thin film.
Received 28 January 2025; First Review 22 March 2025; Accepted 24 April 2025.

*** Address of correspondence**
Preetha K C
Department of Physics, Sree Narayana College, Nattika, University of Calicut, Kerala, India.

Email: preethasajitht@gmail.com

How to cite this article
Preetha K C and Bini S, Structural, Morphological, Compositional, Electrical, and Optical Characterizations of CuZnS Thin Films Prepared using Chemical Bath Deposition Method, J. Cond. Matt. 2025; 03 (02): 128-132.

Available from:
https://doi.org/10.61343/jcm.v3i02.77

Introduction

CuZnS is a semiconductor with highly desirable photovoltaic properties, including a high absorption coefficient and a direct bandgap. The direct bandgap energy varies from 1.8 to 3.5 eV as the Cu/(Cu+Zn) ratio increases from 0 to 67%. CuZnS film prepared using spray pyrolysis with Cu/(Cu+Zn) ratio of 50% exhibited a bandgap of 2 eV [1]). Reported bandgap for the CuZnS films prepared using the SILAR method is 2.4 to 2.6 eV for copper-rich CuZnS samples [2]. In our present study the observed bandgap value was 2.61 eV at a Cu/(Cu+Zn) ratio of 83%. These thin films are used as an absorber or window layer, and their electrical and optical characteristics can be adjusted by changing the atomic ratios of copper and zinc [3-5]. Furthermore, CuZnS cells employ affordable, nontoxic, and plentiful (rare-earth-free) metals [2]. It is a favorable material for numerous applications in photovoltaic cells and photoconductor devices [6-8]. Ternary materials are appropriate for use in window-layer solar cells and optoelectronic devices [9]. The various techniques used to develop thin films include thermal evaporation [10], chemical spray pyrolysis [1], successive ionic layer adsorption and reaction [2], electrochemical deposition [11], photochemical deposition [12], pulsed laser deposition [13] and chemical bath deposition [14]. The chemical bath deposition method has drawn much attention due to its low cost, non-toxicity, ease of use, and compatibility for large-area deposition and film homogeneity [15,16]. In this study, we used the chemical bath deposition method to prepare CuZnS thin films and electrical, optical, morphological, structural, and compositional characterizations of these films were done.

Experimental Details

1. Materials

CuZnS thin film was prepared using a low-cost chemical bath deposition technique. The precursor solution contains copper chloride, zinc chloride, triethanolamine (TEA), ammonia, and thiourea. TEA acts as a complexing agent, and ammonia regulates the pH of the solution. Samples were prepared to optimize the molarity of the reactants, amount of TEA, pH of the solution, deposition time, and temperature. Magnetic stirrer was used to mix the solution during the deposition process. Thoroughly cleaned and dried glass substrates were placed in the precursor solution. The glass plates were kept in the solution for one hour at a temperature of 80 °C. The best sample was obtained from a solution containing 5 ml of 0.1M copper chloride, 5 ml of 0.1M zinc chloride, 10 ml of 0.1M thiourea, 4 ml of TEA, and 3 ml of ammonia. This film was analysed using different characterization techniques.

2. Method

To prepare the thin film, 2 ml of Triethanolamine (TEA) was mixed with 5ml of 0.1M copper chloride solution to form a complex. Then, 2 ml of TEA and 3ml of ammonia were mixed into 5 ml of 0.1 M zinc chloride solution to make another complex. The individually made complexes were combined and thoroughly stirred for 5 minutes until homogeneous. 10 ml of 0.1 M thiourea and 5 ml of distilled water were added dropwise from the burette to the solution while stirring. Then the solution was heated to 80°C using a water bath, and well-cleaned glass substrates were dipped in it for one hour, maintaining a constant temperature. The solution gradually changes its colour from blue to brown, and glass substrates are uniformly coated with CuZnS. These films were washed, dried, and used for various analyses. Figure 1 shows the experimental setup and the CuZnS samples prepared using CBD.

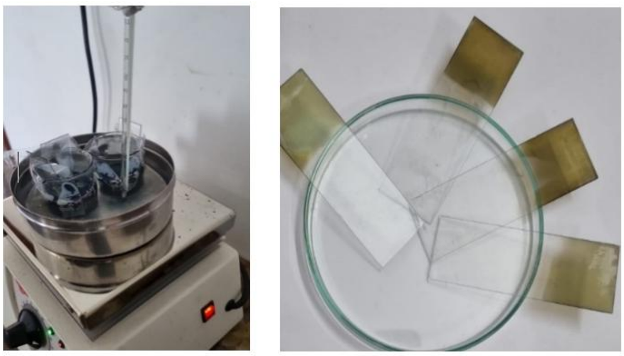

Figure 1: Experimental setup and the CuZnS samples prepared using CBD.

Results and Discussion

X-ray Diffraction Spectroscopy (XRD)

XRD can provide information on the material structure, phase composition, and crystal characteristics of prepared thin films [17]. Additionally, we can identify whether the thin film is crystalline or amorphous. For XRD analysis is, Bruker Kappa Apex II with CuKα wavelength 1.5406 Å was used. The XRD spectrum spans the 2θ range from 10° to 90°. Figure 2 depicts the XRD pattern of the CuZnS thin film, with the broadening of peaks reflecting the formation of nanoparticles.

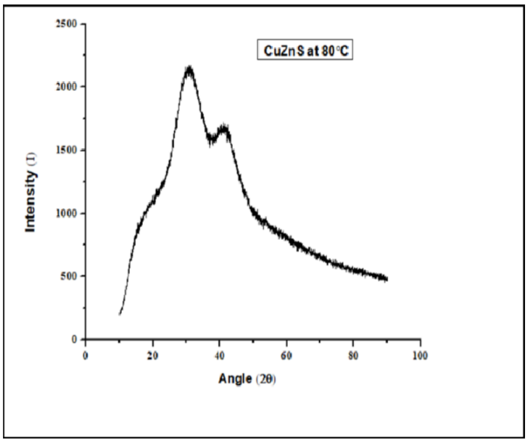

Figure 2: XRD pattern of CuZnS thin films prepared by CBD method.

The structural study of CuZnS thin film samples obtained by XRD shows two peaks, one at 30.881° and the other at 41.066°.

Table 1: Comparison of observed values with ICSD standard reference code.

Chemical formula	Standard 2θ Values	Intensity (in percentage)	Observed 2θ Values	Observed Intensity (in percentage)	hkl	D[Å]
ICSD Reference code: 98-062-8980						
Cu(0.12)Zn(3.88)S2(4)	30.018	100	30.881	100	0 0 2	2.9745
	42.967	50.3	41.066	79	0 2 2	2.1033
ICSD Reference code: 98-062-8979						
Cu(3.2)Zn(0.8) S2(4)	30.683	100	30.881	100	0 0 2	2.9115
	43.945	48.7	41.066	79	0 2 2	2.0587

These peak values are compared with the standard ICSD reference values (ICSD Ref codes 98-062-8979 and 98-062-8980), which are listed in Table 1. The two peak values correlate to the ICSD values for planes (002) and (022), indicating a cubic structure based on these ICSD values. The hundred percentage peak matched well with ICSD Ref code 98-062-8979, while the second peak has a 1º discrepancy in 2θ value compared to ICSD Ref codes of Cu((0.12)Zn(3.88)S2(4)). The change in results could be attributed to the existence of distinct phases of CuZnS in the sample or to variations in the Cu to Zn ratio. The crystallite size of the material can be calculated using the Debye–Scherrer formula from X-ray diffraction (XRD) data.

$$D = \frac{K\lambda}{\beta \, Cos\theta}$$

Where:
D = average crystallite size
K = Scherrer constant ~ 0.94 (depends on shape factor)
λ = X-ray wavelength in nm or Å, 1.5406 Å for Cu Kα lines
β = Full width at half maximum of the peak in radians
θ = Bragg angle

The crystallite size calculated using Debye-Scherrer formula is 1.35nm.

Energy Dispersive X-ray Spectroscopy (EDAX)

Energy Dispersive X-ray spectroscopy analysis was used to determine the elemental composition of the CuZnS sample [18]. The EDAX spectrum of the sample is displayed in Figure 3.

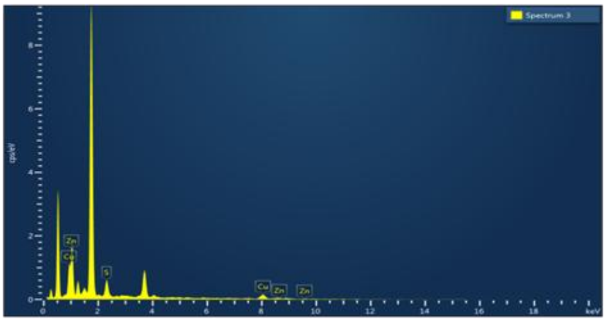

Figure 3. EDAX spectrum of CuZnS thin film prepared by CBD method.

Table 2: Elemental composition of CuZnS.

Element	Line Type	Wt %	Atomic%
Cu	K series	55.43	41.72
Zn	K series	10.77	7.88
S	K series	33.79	50.40
Total	K series	100	100

The atomic and weight percentages of the given sample are shown in Table 2. The CuZnS sample has an atomic percentage ratio of 41.72**:**7.88**:**50.40, and weight percentages of 55.43**:**10.77**:**33.79. Elemental analysis reveals that the prepared samples are enriched in copper with a low percentage of zinc. Zn deficiency has been reported in CuZnS thin films generated via the Silar technique [2]. Attempts are being made to improve the Zn content in the samples.

Scanning Electron Microscopy (SEM)

SEM examined the surface topography, microstructure and grain size of the CuZnS thin film samples [18,19]. This study exposes characteristics including conductivity and optical behaviour. There are no obvious cracks on the surface of the thin film. The particles are spherical in shape, nanostructured, uniform, and densely packed, making them suitable for photovoltaic applications. The thickness of the thin film was measured using a Dektak stylus profilometer and found to be 131 nm. Figure 4 (a), (b), (c), and (d) displays SEM images of CuZnS at varying resolutions (50 µm, 10 µm, 2 µm, 1 µm). The average particle size calculated from SEM analysis is 177nm. This is different from the value obtained from XRD (less than 5nm). It may be due to the grains themselves must be formed by the merging of closely packed nanocrystallites. This has been reported earlier [18].

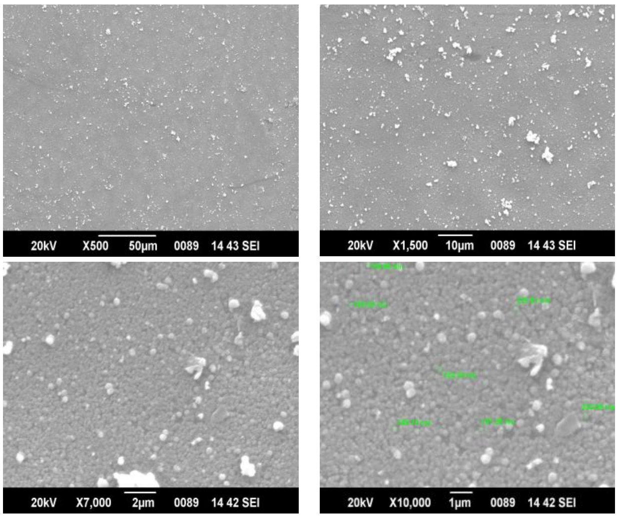

Figure 4: (a), (b), (c), (d) SEM images of CuZnS thin film prepared by CBD method.

UV Visible spectroscopy

The analytical method (UV-Vis) is used to determine the optical properties, electrical structure, and material composition of the sample. JASCO V-670 UV-Vis NIR Spectrophotometer was used for optical analysis. The optical absorption spectra of CuZnS thin films were studied within 350 and 900 nm. Figure 5 shows the absorption spectra of CuZns. The direct bandgap of CuZnS was determined using a Tauc's plot ((αhυ)2 vs. hv plot) [20]. Figure 6 shows the Tauc's plot of CuZnS, with a bandgap value of 2.61eV. This value falls within the standard range 1.8 - 3.5 eV reported in spray pyrolysis [1]) and 2.4 to 2.6 eV reported in SILAR method is for copper-rich CuZnS samples [2].

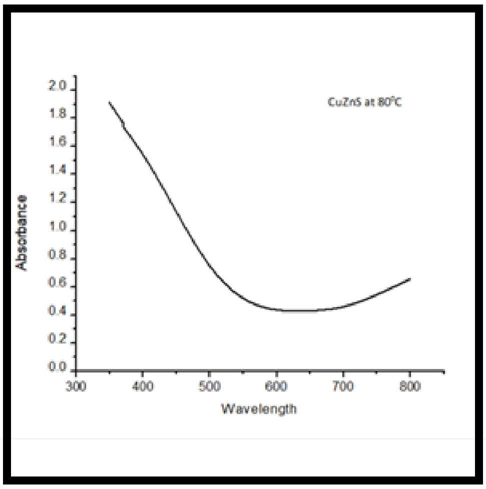

Figure 5: Absorption spectra of CuZnS thin film.

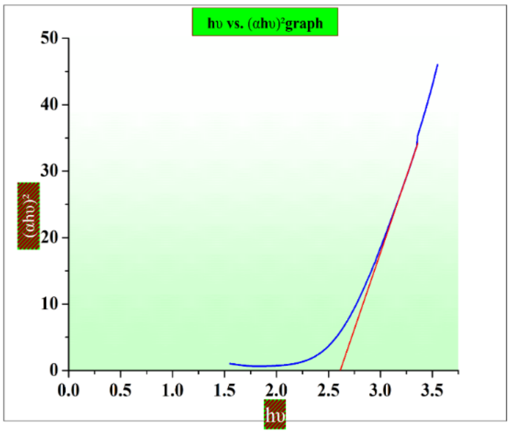

Figure 6: Tauc's plot (Direct bandgap of CuZnS thin film)

Hall Effect measurement

The Hall Effect measurement technique is extremely accurate for electrical analysis. The Hall coefficient value can detect whether the material is p-type or n-type. Thin film samples are analyzed to determine the sample's bulk concentration, mobility, sheet resistance, resistivity, conductivity, and average Hall coefficient. Optimizing semiconductor electrical properties can improve their applications in solar cells as well as sensors. Based on the Hall coefficient measurement of the CuZnS samples, the average Hall coefficient value obtained is $4.701 \times 10^4 cm^3/C$. This clearly indicates that the prepared samples are of p-type conductivity.

The conductivity of the sample is $1.646 \times 10^{-3}\ \Omega^{-1}cm^{-1}$. The conductivity value reported earlier for thermal evaporated film is $63.3\ \Omega^{-1}cm^{-1}$ [10] and for MOCVD (Metal oxide chemical vapour deposition method) is 5.48×10^{-1} to $8.0 \times 10^{-1}\ \Omega^{-1}cm^{-1}$ [15]. Table 3 shows the Hall parameters of CuZnS thin films.

Table 3. Hall parameters of CuZnS thin film

Hall Parameters	
Bulk concentration in cm^3	1.328×10^{14}
Mobility in cm^2/vs	7.738×10^1
Sheet resistance in Ω/sq	4.637×10^7
Resistivity in Ωcm	6.075×10^2
Conductivity in $\Omega^{-1}cm^{-1}$	1.646×10^{-3}
Average Hall coefficient in cm^3/C	4.701×10^4

Conclusion

The CuZnS samples are relatively homogeneous. The XRD study confirms that the hundred percentage peak corresponds to ICSD Ref code 98-062-8980. However, the second peak differs by 1° in 2θ value from the same ICSD Ref code. The EDAX analysis reveals that the prepared samples are enriched in copper with a low percentage of zinc. SEM analysis revealed that the particles exhibited a spherical shape and the average particle size is 177nm. The samples are more or less uniform. Based on the optical characterization, the prepared sample has a bandgap energy of 2.61 eV. The average Hall coefficient value of $4.701 \times 10^4 cm^3/C$ indicates that the prepared sample is a p-type semiconductor. The samples resistivity is 6.075×10^2 and conductivity is $1.646 \times 10^{-3}\ \Omega^{-1}cm^{-1}$, these values fall within the benchmark value for semiconductors.

Future plans

As the samples exhibit Zn deficiency, further research is needed to increase the Zn content. Attempts are being made to improve the Zn content and to make the film more stoichiometric.

Acknowledgments

The authors truly acknowledge the funding support from DST-FIST & KSCSTE Thiruvananthapuram. We are thankful to DST SAIF COCHIN and SAIF IIT Bombay for providing support and thankful to the Department of Physics, Sree Narayana College, Nattika, the Research Department of Physics, Sree Kerala Varma College, Thrissur and the Directorate of Research, university of Calicut for extending facilities for the research work.

References

1. Kitagawa, N, Ito S, Nguyen D and Nishino H, "*Copper zinc sulfur compound solar cells fabrication by spray pyrolysis deposition for solar cells*", Natural Resources, DOI: 10.4236/nr.2013.41A018, 2013
2. Edwin Jose, M C Santhosh Kumar, *"Room temperature deposition of highly crystalline Cu-Zn-*

S thin films for solar cell applications using SILAR method", Alloys and Compounds, DOI:10.1016/j.jallcom.2017.04.097, 2017.

3. M S Sreejith, D R Deepu, C Sudha Kartha, K P Vijayakumar, *"Tuning Of Properties of Sprayed CuZnS Films"*, AIP Conference Proceedings, DOI: 10.1063/1.4873096, 2014.
4. P A, M C S, *"Deposition and characterization of earth abundant CuZnS ternary thin films by vacuum spray pyrolysis and fabrication of p-CZS/n-AZO heterojunction solar cells"*, Int J Energy Res., DOI:10.1002/er.5515, 2020.
5. J. Jubimol, M. S. Sreejith, C. Sudha Kartha, K. P. Vijayakumar, and Godfrey Louis, *"Photoluminescence studies on copper zinc sulfide thin films synthesized through chemical bath deposition"*, AIP Conference Proceedings, DOI:10.1063/1.5093865, 2019.
6. Jubimol J, Sreejith M S, Kartha C S, Vijayakumar K P, Louis G., *"Analysis of spray pyrolysed copper zinc sulfide thin films using photoluminescence"*, Luminescence, DOI: 10.1016/J.JLUMIN.2018.06..079, 2018.
7. Uhuegbu C C and Babatunde E B, *"Spectral analysis of copper zinc sulphide ternary thin film grown by solution growth technique"*, American journal of scientific and industrial research, DOI:10.5251/ajsir.2010.1.3.397.400 2010.
8. W.T.R.S. Fernando, K M D C Jayathilekea, R P Wijesundera and W. Siripala, *"Growth of CuZnS thin films for PV applications"*, Conference: Proceedings of the 33rd Technical Sessions, 33 (2017) 12-18, Institute of Physics at University of Kelaniya, Sri Lanka,2017
9. Uhuegbu C. C. and Babatunde E.B., *"The Study of Copper Zinc Sulphide ($CuZnS_2$), Thin Films"*, Turkish Journal of Physics, Vol. 32, No.1, Article 6 (39 – 47), 2008.
10. Sundaram, Saravanan Krishna, Subramanian, Selladurai, Panneerselvam, Vengatesh, Salammal, Shyju Thankaraj, "*Temperature-dependent phase transition of CuZnS thin films and its effects on morphological"*, optical and electrical properties, Thin Solid Films, DOI:10.1016/j.tsf.2021.138810, 2021.
11. K. Yang, Y. Nakashima and M. Ichimura, *"Electrochemical Deposition of CuxS and CuxZnyS Thin Films with p-Type Conduction and Photosensitivity"*, J. Electrochem. Soc. 159 (2012) H250, DOI:10.1149/2.042203jes, 2012
12. M. Dula, K. Yang and M. Ichimura, *"Photochemical deposition of a p-type transparent alloy semiconductor CuxZnyS"*, Semicond. Sci. Technol., 27 (2012) 125007, DOI:10.1088/0268-1242/27/12/125007, 2012
13. A. M. Diamond, L. Corbellini, K. R. Balasubramaniam, S. Chen, S. Wang, T. S. Matthews, L. Wang, R. Ramesh and J. W. Ager, *"Copper-alloyed ZnS as a p-type transparent conducting material"*, Physica Status Solidi (a), 209 (11) (2012) 2101-2107, DOI:10.1002/pssa.201228181, 2012
14. C. C. Uhuegbu, and E. B. Babatunde, *"Spectral analysis of copper zinc sulphide ternary thin film grown by solution growth technique"*, Am. J. Sci. Ind. Res., 1 (3) (2010) 397-400, DOI:10.5251/ajsir.2010.1.3.397.400, 2010
15. Joseph Onyeka Emegha, Bolutife Olofinjana, Ukhurebor, Joseph Adegbite, *"Electrical Properties of Semiconducting Copper Zinc Sulphide Thin Films"*, Current Applied Science and Technology, DOI:10.55003/cast.2022.01.22.003, 2021.
16. Kavita Sahebrav Jadhav, Nanasaheb Huse, *"Investigation of Optical and Electrical Properties of CuZnS Thin Film Deposited by Chemical Bath Deposition Method"*, Innovative Research in Science, Engineering and Technology (IJIRSET), Volume 10, Issue 8, 2347-6710, 2021.
17. Gardew Dubale, Derejaw, Abza Abshiro, Tizazu, and Gashaw Hone, Fekadu, *"Synthesis and Characterization of Copper Zinc Sulfide ($Cu_xZn_{(1-x)}S$) Ternary Thin Film by Using Acidic Chemical Bath Deposition Method"*, Thin Films Science and Technology, 2021, digitalcommons.aaru.edu.jo/ijtfst/vol10/iss1/4.
18. Fatemeh Aghaei, Reza Sahraei , Ehsan Soheyli, Ali Daneshfar, *"Dopant-Concentration Dependent Optical and Structural Properties of Cu-Doped ZnS Thin Films"*, J Nanostruct 12(2): 330-342, Spring 2022, DOI: 10.22052/JNS.2022.02.010, 2022.
19. Adel H. Omran Alkhayatt, Azher Abdul Wahab Habieb, Abbas Hadi Abbas Al-Noaman and Ali Abdulhussein Hameed, *"Structure, surface morphology and optical properties of $Cu_xZn_{1-x}S$/Au NPs layer for photodetector application"*. IOP Conf. Series: Journal of Physics: Conf. Series, DOI 10.1088/1742-6596/1234/1/012012, 2012
20. Ifeyinwa Amaka Ezenwa and Okoli Nonso L. *"Characterization of chemically synthesized Copper Zinc Sulphide ($CuZnS_2$) thin film"*, European open applied physics journal, Vol.1, No.1, 1-9, 2015.