

# Effect of Complexing Agent on the Optical Properties of Zinc Sulphide (ZnS) thin films using Chemical Bath Deposition.

Isi, P. O.<sup>1,\*</sup>, Jeroh, D. M.<sup>2</sup>, Isah, J.<sup>3</sup>, Obiajulu, O.<sup>4</sup>, Ndukwe, F.O.<sup>5</sup>

Department of Physics and Industrial Physics, Nnamdi Azikiwe University Awka, NIGERIA.<sup>1,2,4,5</sup>

Department of Physics, University of Abuja, Nigeria.<sup>3</sup>

\*Correspondence e-mail address: po.isi@unizik.edu.ng

**Abstract:** Zinc sulphide thin films were deposited at room temperature by chemical bath deposition technique. The films deposited are highly uniform but poor in adherence. The optical properties were determined using the absorbance data measurement from M501 Single Beam Scanning UV/Visible Spectrophotometer at normal incidence of light, in the wavelength range of 380nm-700nm. From the results, the transmittance and reflectance were calculated. The band gap energy obtained is in the range of 3.0-3.3eV for different variations of TEA, Time and NH<sub>3</sub>. The transmittance and reflectance increase at higher concentration of complexing agent-TEA whereas the absorbance decreases. The transmittance also increases with time of deposition. Their high transmittance makes them suitable for use as an aesthetic window glass and good material for selective coatings for solar cells. The thickness of the thin films was also found to increase with time of deposition and the concentration of complexing agent-TEA. Also increase in the NH<sub>3</sub> concentration decreases absorbance. This study explores the impact of complexing agents on the optical properties of ZnS thin films fabricated via chemical bath deposition, with the goal of enhancing their performance for optoelectronic applications.

**Keywords:** Chemical bath, Complexing agent, thin films, Transmittance, ZnS.

## I. INTRODUCTION

Zinc Sulphide is a milky-yellowish crystalline fluorescent compound that occurs naturally as Sphalerite or wurtzite and is nontoxic unlike CdS that is not environmental friendly [1, 6]. It is an inorganic compound with the chemical formula of ZnS. Zinc Sulphide belongs to the II-VI compound of semiconducting material [2, 5].

Zinc sulfide (ZnS), a member of the II-VI family of semiconducting materials [3], has garnered significant attention due to its wide range of applications in optoelectronics and photonics, with a bulk band gap between (3.5–3.9eV) [4]. ZnS is capable of emitting [5] visible light without absorption and efficiently transporting high-energy electrons, making it a promising material for various technological applications [7].

This property also allows ZnS to offer enhanced transparency in the short-wavelength region between 350 and 550 nm [1]. ZnS is widely used in the fabrication of optoelectronic devices such as blue light-emitting diodes [8], electroluminescent devices [9, 10], electro-optic modulators, optical coatings, n-window layers for thin-film heterojunction solar cells, photoconductors, and photovoltaic devices.

Various deposition techniques are employed to fabricate ZnS thin films, including molecular beam epitaxy [11, 12], chemical vapor deposition [23], sputtering [13], thermal evaporation [14, 20], chemical bath deposition [16] pulsed laser deposition [17, 18], electrochemical deposition [19] and spray pyrolysis [15, 21, 22]. Among these, chemical bath deposition (CBD) has emerged as the most suitable method for depositing ZnS thin films for photovoltaic applications, due to its efficiency, cost-effectiveness, and scalability [16].

Due to its poor ability to absorb solar radiation at large concentration of TEA, this study is therefore aimed at utilizing less or low concentration of TEA for proper absorption of solar radiation.

## II. MATERIALS & METHOD

The solvents and reagents used for the deposition of ZnS thin films include zinc chloride ( $\text{ZnCl}_2$ ), triethanolamine (TEA), thiourea ( $\text{CH}_4\text{N}_2$ ), ammonia solution ( $\text{NH}_3$ ), and distilled water ( $\text{H}_2\text{O}$ ). The equipment and materials employed in the process consisted of a beaker, stirrer, digital Mettler balance, thermometer, pH meter, syringes, substrates, substrate holder, masking tape, detergent, pen and paper, gloves, a mouth and nose mask, spatula, and chemical deposition technique.

### 2.1 Experimental Details

Prior to deposition, the glass substrates were degreased in ethanol for ten (10) minutes, followed by ultrasonically cleaned with distilled water and finally dried in clean air. The reagents were added according to the order in table below. The glass substrates were dipped vertically into all of the five reaction baths. The baths were left to stand for 12hours, 24hours, 36hours, 48hours and 60hours at room temperature, after which the substrate were removed, rinsed with distilled water and dried in clean air.

0.1 Mole solutions were measured in the order as indicated in the table 1 above, to the five chemical baths. Distilled water was added equally to the chemical baths by volume to bring the solution in each chemical bath up to 50ml of volume.

Finally, the glass substrates were suspended into the chemical bath using slide holder to hold the substrates firmly with the tip not touching the bottom of the beaker. Keeping other parameters constant, time of deposition of the chemical baths were varied for 12hrs, 24hrs, 36hrs, 48hrs and 60hrs from the chemical bath 1 to chemical bath 5 respectively. Dip times were maintained at different hours for each chemical bath.

## III. OBSERVATION (PHYSICAL)

The longer the time of deposition, the higher the thickness of the thin films deposited on the substrate.

Table 1: Variation of Triethanolamine (TEA) at constant time (24hrs)

| SOLUTION                          | VOLUME (ml)     |                 |                 |                 |                 |
|-----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                   | Chemical Bath 1 | Chemical Bath 2 | Chemical Bath 3 | Chemical Bath 4 | Chemical Bath 5 |
| Zinc Chloride                     | 5               | 5               | 5               | 5               | 5               |
| Triethanolamine (TEA)             | 2               | 4               | 6               | 8               | 10              |
| Ammonia solution( $\text{NH}_3$ ) | 5               | 5               | 5               | 5               | 5               |
| Thiourea                          | 5               | 5               | 5               | 5               | 5               |
| Distilled water                   | 33              | 31              | 29              | 27              | 25              |
| PH                                | 11.77           | 11.90           | 12.04           | 12.08           | 12.19           |

0.1 Mole solutions were measured in the order as indicated in the table 1 above to the five chemical baths, the volume of TEA was varied thus; 2ml, 4ml, 6ml, 8ml and 10ml in the chemical bath 1 to chemical bath 5 respectively. Distilled water was added to the chemical baths by volume to bring the solution in each bath up to 50ml of volume.

Finally, the glass substrates were suspended into the chemical bath using rack holder to hold the substrate firmly with the tip not touching the bottom of the beaker. Dip times was maintained at exactly 24hours before withdrawal of the substrates from the chemical baths.

### 3.2 Observation

On addition of TEA solution to the chemical baths, the solution turned light or pale yellow, which was sparingly soluble on the addition of ammonia solution.

### 3.3 Precautions

i. We ensured that substrates were properly washed with detergent and water to remove dirt or dust particles, and then rinsed with distilled water.

- ii. We avoided double approximation during mathematical calculations.
- iii. Measurement from the cylinder and beaker were taken from the lower meniscus so as to avoid error due to parallax.
- iv. The digital mettler balance was zero out before measurements were taken.
- v. The precipitations were done under normal room temperature.

#### IV. RESULTS AND DISCUSION

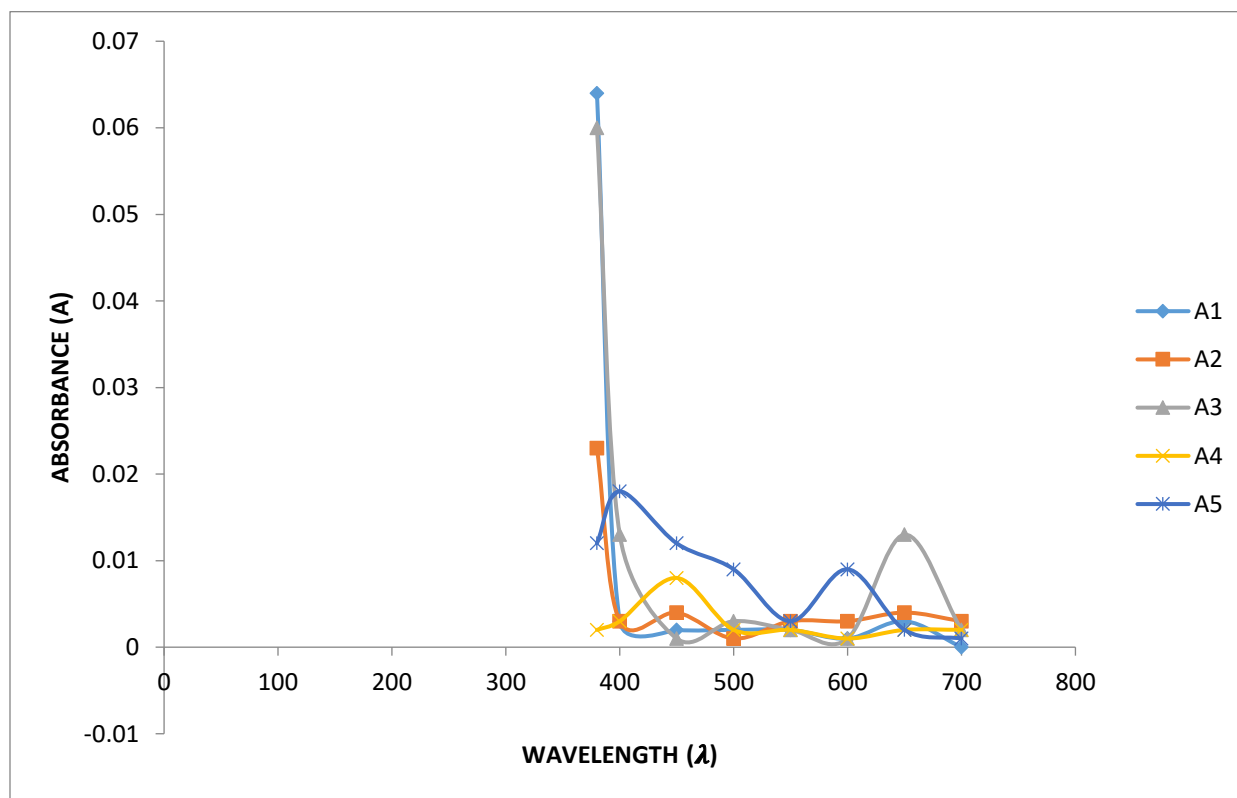


Figure 1: Plots of Absorbance against Wavelength ( $\lambda$ )

From the above graph (Fig.1), it can be observed that the thin film, generally, have a very low absorbance but the slide number one (5) with 10ml concentration of TEA has the highest absorbance than others. This implies that increases in the concentration of the complexing agent decreases absorbance.

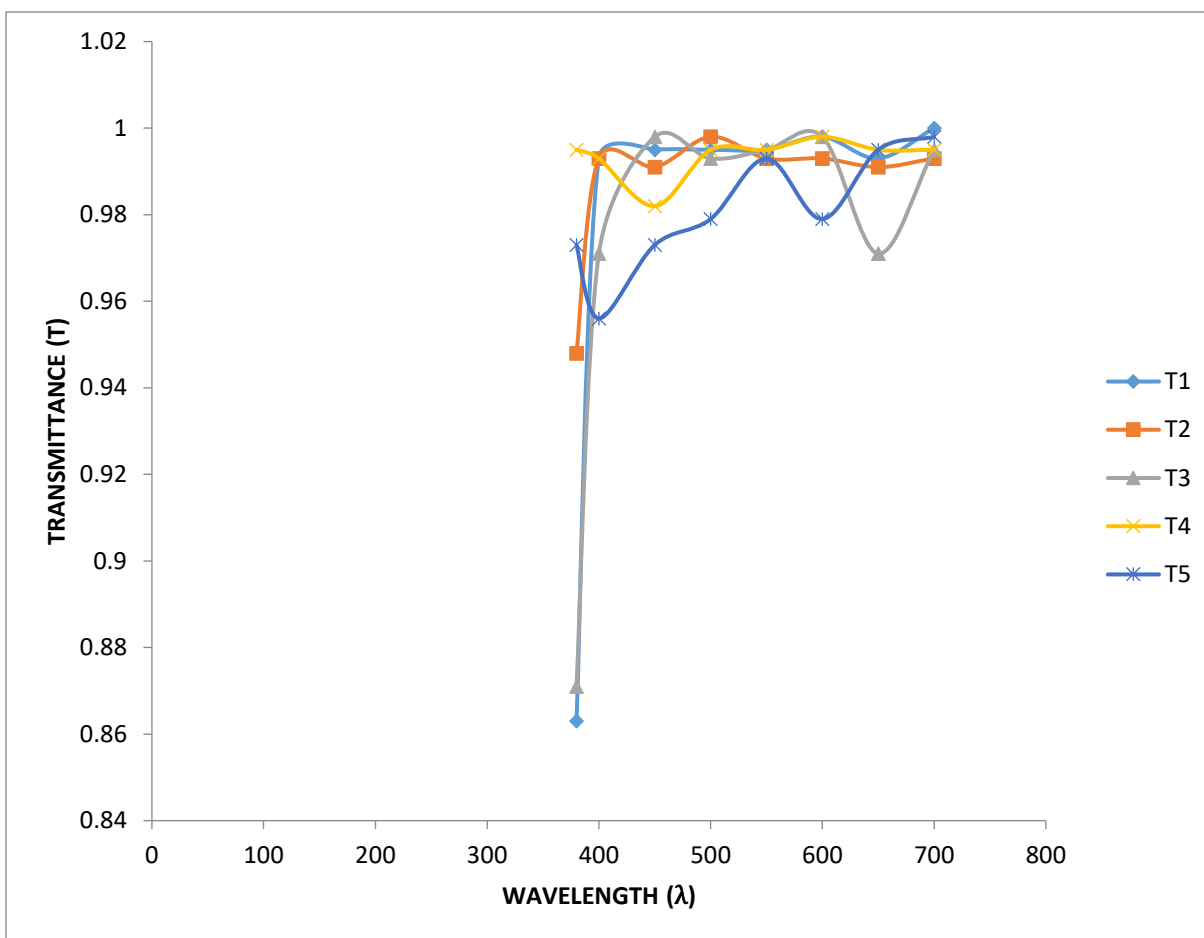


Figure 2 Plots of Transmittance against Wavelength ( $\lambda$ )

From the above graph (Fig. 2), it can be observed that the thin films, generally, have a higher transmittance but the slide number (5) with 10ml concentration of TEA has the highest transmittance. Increase in the complexing agent increases transmittance.

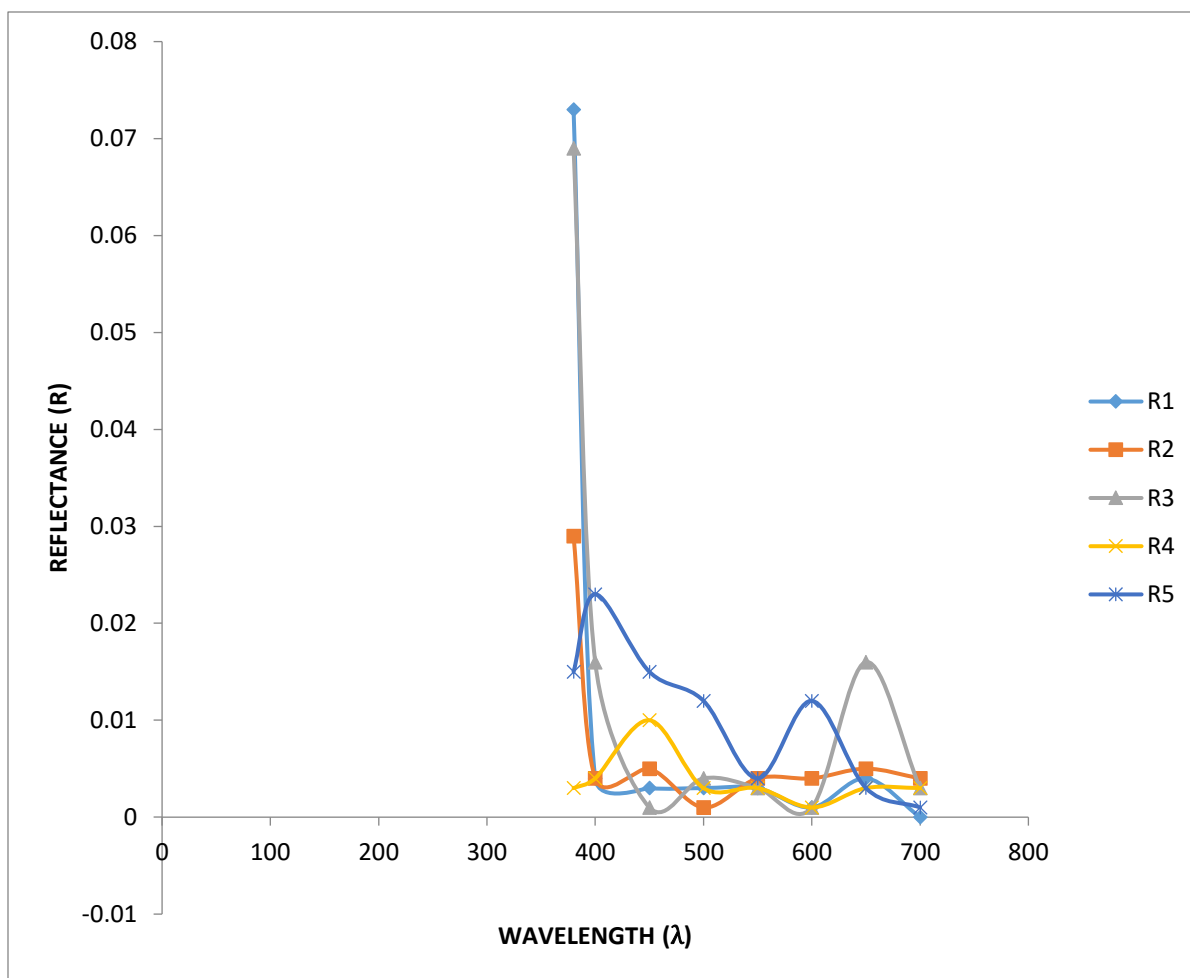


Figure 3 Plots of Reflectance against Wavelength ( $\lambda$ )

From the above graph (Fig. 3), it can be observed that the thin films have a very low reflectance but slide number one (5) with 10ml concentration of TEA has the highest reflectance than others, this indicates that less concentration of TEA increases reflectance.

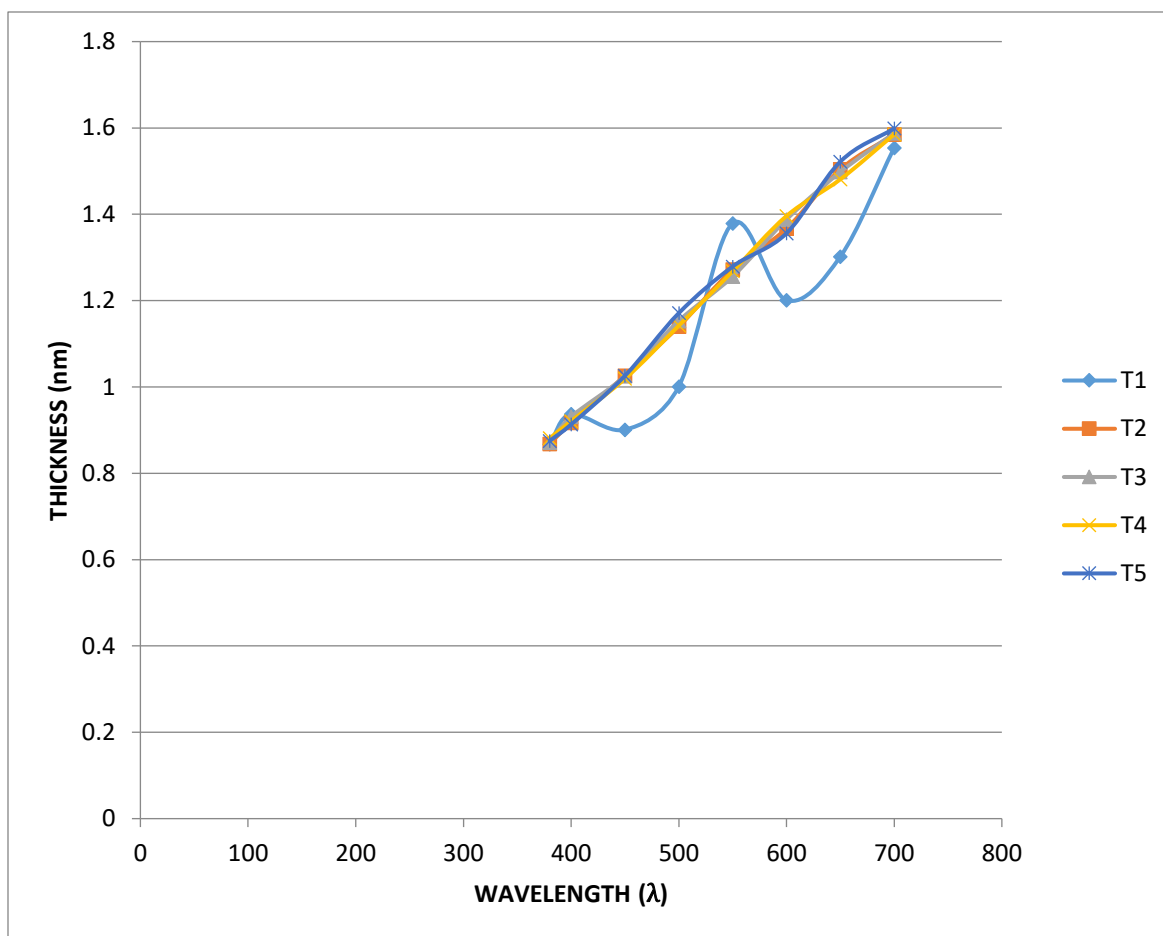


Figure 4 Plots of Thickness against Wavelength ( $\lambda$ )

From the above graph (Fig. 4) for the variation of TEA concentration, it can be observed that the thickness decreases with the wavelength, while increase in the concentration of the complexing agent increases the thickness of the thin films. Hence, the thin films can be applied to the photovoltaic devices.

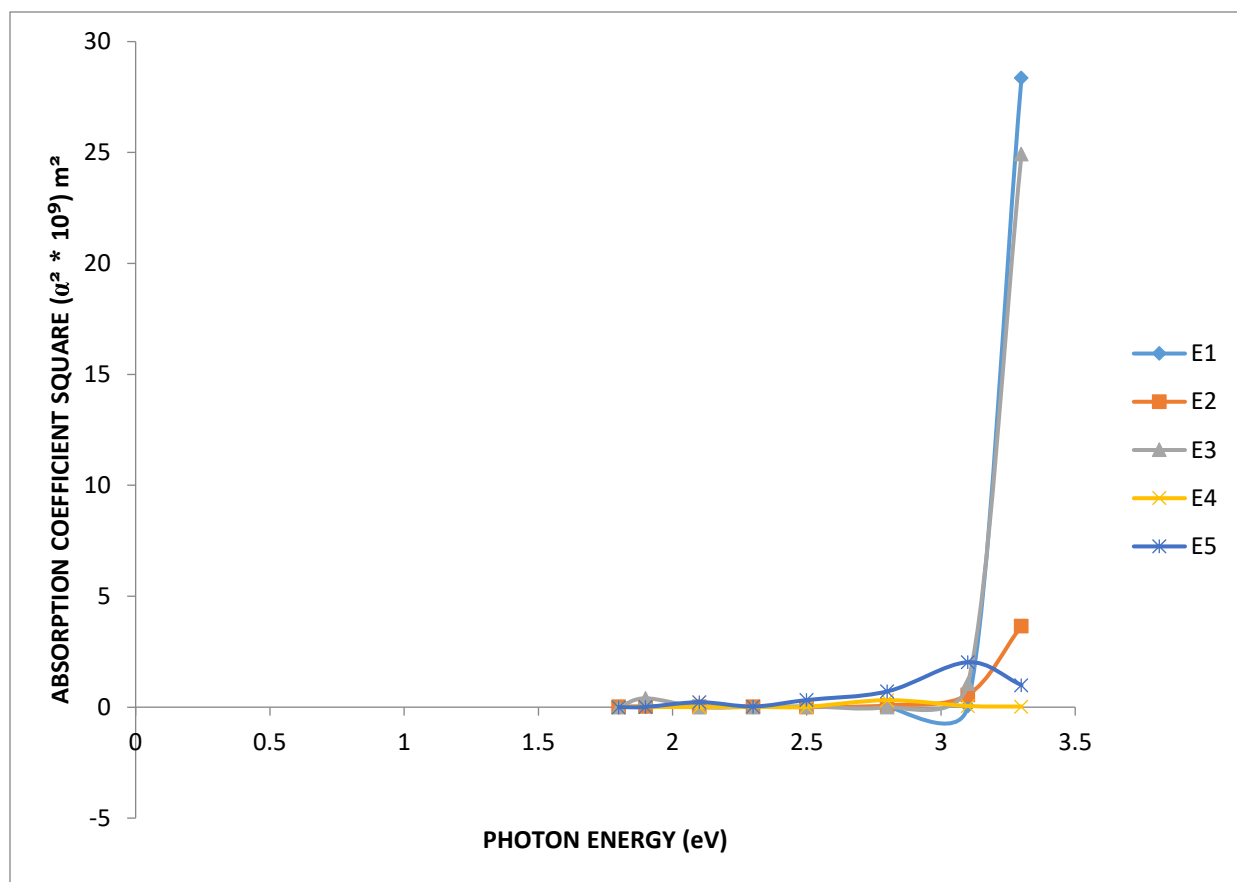


Figure 5: Plots of Square of Absorption Coefficient against Photon Energy (Ev)

From Figure. 5 above, it can be observed that the values of band gap energy for Zinc sulphide thin films are in the range 3.1 - 3.3eV. These results are in good agreement with the reported values for ZnS thin films prepared the same method [16]. The graph also reveals, increase in the concentration of the complexing agent decreases the absorption coefficient square. Thus, it can be applied in the photovoltaics devices.

## V. CONCLUSION

The thin films of ZnS has been successfully deposited on substrates using Chemical bath technique at room temperature. The thin films had poor adherence to the substrate. The optical characterization of the deposited films was done with M501 single beam scanning Spectrophotometer and it was observed that increase in the concentration of the complexing agent decreases the absorption and as well increases transmittance. It was also observed that increase in time of deposition increases the thickness of the deposited thin films. Values of band gap energy for the deposited ZnS thin films were determined at the ranges 3.1 - 3.3eV.

## REFERENCES

- [1]. Mukherjee A., Chattopadhyay S., Mitra, P., (2015), "Characterization of ZnS Thin Film Synthesized by CBD using Zinc Acetate Precursor" Journal of Physical Sciences, Vol. 20,195-203 ISSN: 2350-0352 (print), [www.vidyasagar.ac.in/journal](http://www.vidyasagar.ac.in/journal)
- [2]. Busarian, N., Chinvetkitvanich, P., Sripichai, I., Chityuttakan, C (2008), "The influence of growth conditions on the chemical bath deposited ZnS thin films", Journal of Metals, Materials and Minerals, Vol.18 No.2 Pp.49-52.
- [3]. Hu. C. (2010), "Moder Semiconductor Device for Integrated Circuits". 1<sup>st</sup> edition, Berkeley:Pearson, USA.

- [4]. Ahmed, Z. Rahman T., Hussain K.M.A, Khatun, M.T., Chowdhury M.S.S., Faruque, T., Toma, F.T.Z., Ahmed, Y., Khan, M.N., and Alam, M.M., (2022), Characterization and optimization of ZnS thin film properties synthesis via chemical bath deposition method for solar cell buffer layer. *Sega journals*. Volume 22, issue1
- [5]. Roy, P.; Ota, J.R.; Srivastava, S.K. (2006) "Crystalline ZnS thin films by chemical bath deposition method and its characterization". *Thin Solid Films*, Elsevier, 515, 1912–1917.
- [6]. B. Liu, R. Luo, Q. Liang, Y. Zheng, B. Li, J. Zhang, W. Li, L. Wu, L. Feng, Preparation of novel CdS/ZnS composite window layer for CdTe thin film solar cell. *J. Mater. Sci.-Mater. Electron.* 26(12), 9985–9990 (2015). <https://doi.org/10.1007/s10854-015-3677-9>
- [7]. Abdessamad N., Bouchaib H., Hicham L., Salah F., Mehmet E. and Philippe T., (2022) Synthesis of ZnS thin films using the spray pyrolysis technique. *Journals of Material Science: Material Electron.* <https://doi.org/10.1007/s10854-022-08428-x>
- [8]. Nadeem, M.Y., Ahmed, W, (2000) Optical Properties of ZnS Thin Films. *Turk Journal of Physics*, 24, 651 - 659.
- [9]. Hasse, M.A. Qiu, J. DePuydt, J.M. Cheng, H. (1991), *Appl. Phys. Lett.*, 59 pp1272.
- [10]. Hirabayashi, K. Kozawaguchi, H., (1986) *Jpn. J. Appl. Phys.*, 25 711.
- [11]. Jeffery, P. Bosco, Faisal Tajdar, and Harry A. Atwater. (2012) "Molecular beam epitaxy of n-type ZnS: A wide band gap emitter for heterojunction PV devices" Conference Paper in Conference Record of the IEEE Photovoltaic Specialists Conference. <https://doi.org/10.1109/PVSC.2012.6318105>
- [12]. Nguyen H. Tran, Andreas J. Hartmann, Robert N. Lamb. (2020) "Epitaxial ZnS thin films grown by single source chemical vapor deposition" *J. Phys. Chem. B* vol. 104, issue 6, 1150–1152. <https://doi.org/10.1021/jp993758h>
- [13]. Hwang, D.H., Ahn, J.H., Hui, K.N. and Guk Y. S. Structural and optical properties of ZnS thin films deposited by RF magnetron sputtering. *Nanoscale Res Lett* 7, 26. <https://doi.org/10.1186/1556-276X-7-26>
- [14]. Benyahia K., Benhaya A., and Aida M.S. (2015) "ZnS thin films deposition by thermal evaporation for photovoltaic applications" *J. Semiconductor*. Vol. 36, number 10, 103001. <https://doi.org/10.1088/1674-4926/36/10/103001>.
- [15]. Najim, A. Hartiti, B., Labrim H. Thevenin, P., Ertuğrul M and Thevenin, P. (2022) "Synthesis of ZnS thin films using the spray pyrolysis technique" *Journal of Materials Science: Materials in Electronics* 33(16). <https://doi.org/10.1007/s10854-022-08428-x>
- [16]. Arsad, A.Z., Bahrudin, M.S., Arzaee, N.A., Rahman, Mohd Nazri Abd , Chau, C.F., Abdullah, S.F. Mahmood Zuhdi A.W., (2024), "Zinc sulfide thin films deposited by chemical bath: Tuning consideration of structural, optical band gap, and electrical properties for CIGS solar cells application" *Ceramics International*, Volume 50, Issue 7, Part B, Pages 11776-11786
- [17]. Eid, A.H., Salim, S.M., Sedik, M.B., Omar, H., Dahy, T., Abou \_elkhair, H.M. (2010) preparation and characterization of ZnS thin films. *Journal of Applied Sciences Research*, 6(6): 777-784, INSInet publication.
- [18]. Yang, K.; Li, B.; Zeng, G. (2019) "Effects of temperature on properties of ZnS thin films deposited by pulsed laser deposition". *Superlattices Microstruct.* , 130, 409–415.
- [19]. Zakerian, F.; Kafashan, H. (2018) "Investigation the effect of annealing parameters on the physical properties of electrodeposited ZnS thin films". *Superlattices Microstruct.* , 124, 92–106.
- [20]. Vishwakarma, R. (2015) "Effect of substrate temperature on ZnS films prepared by thermal evaporation technique". *J. Theory. Appl. Phys.* 9, 185–192.
- [21]. Elidrissi, B.; Addou, M.; Regragui, M.; Bougrine, A.; Kachouane, A.; Bernède, J.C. (2001) "Structure, composition and optical properties of ZnS thin films prepared by spray pyrolysis". *Mater. Chem. Phys.* 68, 175–179.
- [22]. 6. Djelloul, A.; Adnane, M.; Larbah, Y.; Sharaoui, T.; Zegadi, T.; Maha, C.; Rahal, B. (2015) "Properties Study of ZnS Thin Films Prepared by Spray Pyrolysis Method". *J. Nano Electron. Phys.* 7, 4–8. [Google Scholar]
- [23]. PanelJan-Otto C., Peter M. M., (2010), *Handbook of Deposition Technologies for Films and Coatings*. Chapter 7 - Chemical Vapor Deposition. Science, Applications and Technology, Pages 314-363 <https://doi.org/10.1016/B978-0-8155-2031-3.00007-7>