**Effect of Dye Extract Volume Variation on the Optical Properties of Spray-Deposited ZnS Thin Films**

**Abstract**

ZnS doped with various volumes of *H. Sabdariffa* (Zoborodo) dye extracts were deposited onto ultrasonically cleaned soda-lime glass substrate at the substrate temperatures of 200oC using the low-cost and scalable chemical spray pyrolysis technique. The final spray solution for the deposition of the films contained aqueous solutions of ZnSO4.7H2O, SC(NH2)2, and *H.Sabdariffa* (Zoborodo) dye extracts. ZnSO4.7H2O and SC(NH2)2 served as precursors for Zn2+ and S2- respectively while *H.Sabdariffa* (Zoborodo) was used as dye. The absorbance measurements were carried out in the wavelength range (400-1100) nm using (HINOTEK 756S UV-VIS) Spectrophotometer. The optical analysis for ZnS-dye doped with various volumes of *H. Sabdariffa* (Zoborodo) extracts indicated that A ≤ 4.3, T ≤ 63.7%, R ≤ 20%, α ≤ 0.15 x 109m-1, Eg ranged from 2.33 to 2.81eV, $ρ$ ≤ 9.6. Based on the high absorbance of the films in the ultra-violet regions, the films are suitable materials for solar thermal applications. Based on the high transmittance of the films across the entire electromagnetic spectrum, the films are materials for solar control coatings inside buildings. Based the on relatively low reflectance of the films in all the regions of electromagnetic spectrum, they are suitable materials for anti-reflection coatings such as in the coating of windscreens and driving mirrows to minimize effect of dazzling light from vehicles following behind at night. Based on the high band gap indicated by the films, they are suitable for photovoltaic applications.

Keywords: Transmittance, dye extracts, *Hibiscus Sabdariffa* (Zoborodo), solutions, band gap.

**Introduction**

Over the years zinc sulphide compound has been under investigation for use in various device designs. The applications in optoelectronic devices, medicinal use, luminescence materials, and in various industrial uses have been widely reported. For instance, in solar cell applications, ZnS has been used as window layers to partner the p-type absorber layers in heterojunction solar devices. It has been established that ZnS can be grown by several techniques including Spray Pyrolysis (SP) (Offor *et al*. 2018; Offor *et al*. 2020), Chemical Bath Deposition (CBD) (Nwofe, 2017;Igweoko, 2018; Onochie *et al*. 2021; Ukpai, 2021), Dip Technique (DT) (Balachander *et al*. 2015), Pulsed-Laser Deposition (PLD), Successive Layer Adsorption and Reaction (Ashith and Gowrish, 2018), Electrodeposition method (Patil *et al*. 2015)

Among these various deposition methods, spray pyrolysis technique is more commonly used technique because of its simplicity and low cost, ease of introducing different doping materials, reproducibility, speed growth rate and mass production capability for uniform large area coatings (Cachet, *et al.* 2014). In the present investigation, the aim of this study is to grow thin films of ZnS doped with varying volume of *H.Sabdariffa* (Zoborodo) dye extracts, and to characterize the films using optical spectroscopy to investigate the optical paramters. The obtained results are discussed and compared with other research results reported. This work is a fundamental step toward exploring new pathways for utilization of ZnS-based thin films in different device designs.

**2. Materials and Method**

**2.1 Substrate cleaning and reagents**

Substrate cleaning plays a vital role in thin film deposition. The soda-lime substrates (glass slides) of area 75mm by 25mm, thickness 1.0mm were procured from local suppliers. Before the spray, the soda-lime substrates were dipped in concentrated hydrochloric acid for 60minutes, removed and washed with sponge in a kiln detergent solution and rinsed with sachet water. Thereafter, the glass slides were rinsed in distilled water. Lastly, they were properly dried inside a sterilizing oven.

**2.2 Extraction of the *Hibiscus Sabdariffa* (Zoborodo) dye extracts**

The dried leaves of *Hibiscus Sabdariffa* locally called Zoborodo were purchased in Ogige Market, Nsukka. 100g of dry leaves of Zoborodo were boiled in 200ml distilled water at 70oC for 4hrs. The leaves were carefully removed from the extraction solvent. The dye extracts were filtered into an already clean and dry container, sealed with cap and stored at room temperature.

**2.3 Deposition of ZnS thin films doped with different volumes of *H. Sabdariffa*(Zobo) extracts**

 20ml of 0.02M ZnSO4.7H2O, 20ml of 0.02M SC(NH2)2 and 5ml of*H. Sabdariffa* were measured into 50ml glass beaker. The mixture was stirred forcefully under high speed for about 15minutes using magnetic stirrer to obtain a homogeneous solution. Following the stirring, 10ml of the solution was measured out using pump syringe into spray pyrolysis sample bottle which was fastened on the nozzle valve rod of the air brush. The precursor was then sprayed for 30seconds on the heated substrates (glass slides) at the substrate temperature of 200oC using electrical hot plate. The other three samples were synthesized with the same procedure but with variation in the volume of dye extracts to 10 ml, 15 ml and 20 ml and keeping the volumes of thiourea solutions and volumes of zinc sulphate solutions constant. The idea was to study the influence of volumes of *H.Sabdariffa* (Zoborodo) dye extracts on growth of ZnS thin films. The volumes of the *H.Sabdariffa* (Zoborodo) dye extracts were measured with a beaker and recorded as shown in Table 1. Table 1 shows the spray constituents for the growth of ZnS thin films doped with varying volumes of *H.Sabdariffa* (Zoborodo) dye extracts.

Table 1 Variation of Volume of *H.Sabdariffa* (Zoborodo) dye extracts on the spray deposited ZnS Thin Films.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample |  ZnSO4.7H2O (ml) |  SC(NH2)2 (ml) |  *H.Sabdariffa* dye  (ml) |
| ZnS:5ml Dye Extracts |   20.00 |  20.00 |  5.00 |
| ZnS:10ml Dye Extracts |  20.00 |  20.00 |  10.00 |
| ZnS:15ml Dye Extracts |  20.00 |  20.00 |  15.00 |
| ZnS:20ml Dye Extracts |  20.00 |   20.00 |  20.00 |

**2.4. Characterization and Computation of Optical Properties**

Optical characterization of the films was carried out using HINOTEK 756S UV-VIS spectrophotometer at wavelength interval of 400 nm to 1100 nm. Absorbance values of the films were obtained using the spectrophotometer and other optical properties such as transmittance, reflectance, absorption coefficient, energy band gap and optical density were calculated using the following equations as obtained from literatures. Transmittance of the films were calculated using equation (1) given by (Emegha *et al*. 2019, Offor *et al*. 2020)

 T = 10-A (1)

Reflectance of the films were obtained using the expression in Equation (2) as given by (Offor *et al*. 2020)

 R = 1- (A+T) (2)

The absorption coefficient (α) of the films were calculated from the transmittance values using the Equation (3) as given by (Igweoko, 2018; Ukpai, 2021)

 $α$ = 2.303A/t (3)

Were (t) is the thickness of the deposited thin films.

The energy band gaps were calculated using Tauc’s model given in Equation (4) as (Meshram and Thombre, 2019; Meshram and Thombre, 2021).

 (𝛼ℎ𝑣) n = (ℎ𝑣 − 𝐸𝑔) (4)

Where β is a constant, n = 2 for direct band gap. The energy band gaps of the films were obtained by extrapolating the straight portion of the plot of (αhv)2 against the photon energy (hv) at (αhv)2 = 0.

Optical densities were estimated using Equation (5) (Nwofe, 2017)

 $ρ$ = αt (5)

Where t is the film thickness.

**3 Results and Discussion**

**3.1 Absorbance spectra**

Fig.1 depicts the plots of absorbance against wavelength for ZnS thin films doped with varying volumes of *H.Sabdariffa* (Zoborodo) dye extracts. The absorbance generally decreased with increase in wavelength. It was also noticed that all the films exhibited maximum absorbance at the wavelength of 400nm, and from there the absorbance decreased as the wavelength increased towards the NIR region. Similar observation of decrease in absorbance with increase in wavelength have been reported by Offor *et al.* (2020) for ZnS deposited by spray-pyrolysis method, Meshram and Thombre (2019) for CdZnS deposited by spray-pyrolysis method and Ozutok *et al.*(2012) for ZnS:Mn deposited by spray-pyrolysis method. For ZnS thin films doped with 20ml volume of *H.Sabdariffa* (Zoborodo) dye extracts, absorbance decreased from 3.7 at 400nm to 0.6 at 1100nm. For ZnS thin films doped with 15ml volume of *H.Sabdariffa* (Zoborodo) dye extracts, absorbance decreased from 4.3 at 400nm to 0.5 at 1100nm. For ZnS thin films doped with 10ml volume of *H.Sabdariffa* (Zoborodo) dye extracts, absorbance decreased from 1.7 at 400nm to 0.3 at 1100nm. For ZnS thin films doped with 5ml volume of *H.Sabdariffa* (Zoborodo) dye extracts, absorbance decreased from 1.3 at 400nm to 0.2 at 1100nm. In addition, the overall absorbance of 4.25 observed is above the limit of 2.0 stipulated by Lambert-Beer’s law. The excess absorbance may be attributed to the concentration of the reagents used in the deposition of the films. Strong absorptions were observed at wavelength of 400nm. Thus, the films have potential application in fabrication of solar cells.

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**Fig.1:** Plots of absorbance against wavelength for ZnS thin films doped with varying volumes of *H.Sabdariffa* (Zoborodo) dye extracts

**3.2 Transmittance spectra**

 Fig.2 shows the plot of transmittance against wavelength for ZnS thin films doped with varying volumes of *H.Sabdariffa* (Zoborodo) dye extracts. All the films samples showed that transmittance increased exponentially from UV region towards the NIR region. The properties of moderately high transmittance in the VIS-NIR exhibited by the film samples make the films good materials for coating of poultry roofs and walls. Again, the moderately high transmittance in VIS-NIR indicated by the films make them good materials for thermal control coatings inside buildings. It was also observed that the results indicated a downward trend in the transmittance of the films as the volume of *H.Sabdariffa* (Zoborodo) dye extracts increased. Decrease in transmittace implies increase in film thickness in accordance with Lambert-Beer’s law. That is to say, the film thickness varied with dye volume and decreased the transmittance. Moreso, the transmittance of all the films increased as their wavelengths increased. For ZnS dye doped with 20ml volume, transmittance increased from 0.2% at 400nm to 25.42% at 1100nm. For ZnS dye-doped with 15ml volume, transmittance increased from 0.2% at 400nm to 35.72% at 1100nm. For ZnS dye-doped with 10ml volume, transmittance increased from 2.1% at 400nm to 51.60% at 1100nm. For ZnS dye-doped with 5ml volume, transmittance increased from 5.6% at 400nm to 63.7% at 1100nm. Similar behavior of downward trends in transmittance have been reported for spray-deposited manganese-doped ZnS thin films by Ghazai *et al.* (2020), for spray-deposited cadmium-doped ZnS thin films by Meshram and Thombre (2019), for spray-deposited lead-doped ZnS thin films by Suhail and Ahmed (2014), and Ozutok *et al*. (2012) for ZnS doped with manganese thin film deposited by spray-pyrolysis technique. This decrease in transmittance with increase in volume of the dye extracts may be caused by the crystallite size (Rahman, 2013). However, different behaviors of upward trends in transmittance have been reported for copper-doped ZnS thin films deposited by Suhail and Ahmed (2014). Furthermore, ZnS thin films doped with 5ml volumeof *H.Sabdariffa* (Zoborodo) dye extracts showed the highest transmission, followed by ZnS thin films doped with 10ml volumeof *H.Sabdariffa* (Zoborodo) dye extracts while ZnS thin films doped with 20ml volumeof *H.Sabdariffa* (Zoborodo) dye extracts showed the lowest transmission. The properties of moderately high transmittance in the VIS-NIR exhibited by film samples make the films good material for coating of poultry roofs and walls. This will ensure that young chicks which have not developed protective thick feather are protected from UV radiation while the heating of the poultry house is maintained by the heating portion of the electromagnetic spectrum, and as well allow for admittance of VIS light in the house.



**Fig.2:** Plots of transmittance against wavelength for ZnS thin films doped with varying volumes of *H.Sabdariffa* (Zoborodo) dye extracts

**3.3 Reflectance spectra**

As observed in the reflectance spectra (Fig.3), the peak reflectance is about 20% for all the films. All the film samples exhibited low reflection, suggesting that most of light were either absorbed or transmitted. Similar observations have been reported in the literature (Ukpai, 2021). Material with overall reflectance ≤ 20% is good for anti-reflection applications such as in the coating of our spectacles and photographic lenses to reduce unwanted reflection from surfaces. Again, this low reflectance property is important since, for the window layer part of solar cell, reflectivity is supposed to be as low as possible (Wanjala *et al.* 2016). Thus, reflectance properties exhibited by all the films in this research work make them suitable materials for window layer parts of solar cells in the solar industry.



**Fig.3:** Plots of reflectance against wavelength for ZnS thin films doped with varying volumes of *H.Sabdariffa* (Zoborodo) dye extracts

**3.4 Absorption cofficient**

The graphs (Fig.4) show that absorption coefficient ($α$) generally increased with increase in photon energy. For ZnS thin films doped with 20ml volumeof *H.Sabdariffa* dye extracts, absorption coefficient increased from 0.02 at 1.1eV to 0.11 at 3.1eV. For ZnS thin films doped with 15ml volumeof *H.Sabdariffa* (Zoborodo) dye extracts, absorption coefficient increased from 0.02 at 1.1eV to 0.15 at 3.1eV. For ZnS thin films doped with 10ml volumeof *H.Sabdariffa* (Zoborodo) dye extracts, absorption coefficient increased from 0.01 at 1.1eV to 0.08 at 3.1eV. For ZnS thin films doped with 5ml volumeof *H.Sabdariffa* (Zoborodo) dye extracts, absorption coefficient increased from 0.001at 1.1eV to 0.06 at 3.1eV. This variation in absorption coefficient with photon energy concurs with the report of other authors (Offor *et al*. 2020; Meshram and Thombre, 2021; Ali *et al*. 2023; Saeed and Suhail, 2012, Igweoko, 2018, Onochie *et al*. 2021). The absorption coefficient values indicated by the films suggest that they could be used in photovoltic applications.



**Fig.4:** Plots of α as a function of hv for ZnS thin films doped with varying volumes of *H.Sabdariffa* (Zoborodo) dye extracts

**3.5 Band gap**

As observed in Fig.5, the energy band gap, Eg, of the films were determined from extrapolation of the straight portion to the energy axis at (αhv)2 = 0. They were found to be 2.81eV, 2.70eV, 2.33eV and 2.55eV for 5ml, 10ml, 15ml and 20ml volumes of *H.Sabdariffa* (Zoborodo) dye extract thin films respectively. As can be seen, there was no clear trend in the variation of energy band gap with the volumes of *H.Sabdariffa* (Zoborodo) dye extracts. Similar observations of no clear trend in variation of energy band gap have been reported by other authors (Derbali *et al*. 2017). The energy band gaps obtained in this work are in consonant with the ranges 2.42-2.89eV and 2.14-2.17eV obtained from other studies (Meshram and Thombre, 2019; Meshram and Thombre, 2021). In view of the needed band gap energy for the different layers of heterojunction solar cells, the *H.Sabdariffa* (Zoborodo) dye-doped ZnS thin films grown here under different volumes can be said to demonstrate large values of energy band gap. The wide band gap values suggest that the films could be used for high temperature and frequency applications (Shen, 2014)



**Fig. 5:** Plots of (αhv)2 as a function of hv for ZnS thin films doped with varying volumes of *H.Sabdariffa* (Zoborodo) dye extracts

**3.6 Optical density**

The graph of optical density as a function of photon energy for ZnS doped with varying volumes of *H.Sabdariffa* (Zoborodo) dye extracts are shown in Fig.5. It was observed that the optical density increases as photon energy increases for all the films under investigation. For ZnS thin films doped with 20ml volumeof *H.Sabdariffa* (Zoborodo) dye extracts, optical density increased from 1.4 at 1.1eV to 8.4 at 3.1eV. For ZnS thin films doped with 15ml volumeof *H.Sabdariffa* (Zoborodo) dye extracts, optical density increased from 1.1 at 1.1eV to 9.6 at 3.1eV. For ZnS thin films doped with 10ml volumeof *H.Sabdariffa* (Zoborodo) dye extracts, optical density increased from 0.7 at 1.1eV to 4.0 at 3.1eV. For ZnS thin films doped with 5ml volumeof *H.Sabdariffa* (Zoborodo) dye extracts, optical density increased from 0.4 at 1.1eV to 2.9 at 3.1eV. The optical density exhibited similar curves with the (αhv)2 vs hv graphs. The optical density was typically in the range 0.4-9.6. Similar variations in optical density with photon energy have also been reported elsewhere (Nwofe, 2017; Nwofe, 2017; Nwofe, 2017). Furthermore, the obtained range of values are higher in magnitude than the values reported by Nwofe (2017) for ZnS dye-doped with *Naulcea latifolia*(Uvuru-ilu) deposited by chemical bath method. The difference in the range of values could be attributed to the chemical constituents of the dye, deposition conditions and method used in the film growth. The optical densities indicated by films suggest that the films are good materials for anti-reflection coatings in optics.



**Fig.6:** Plots of $ρ$ as a function of hv for ZnS thin films doped with varying volumes of *H.Sabdariffa* (Zoborodo) dye extracts

**4. Conclusion**

The influence of *H. Sabdariffa*(Zoborodo) dye extracts volume variation on the optical properties of ZnS thin films is reported. The results show that the volume variation of dye extracts modified the optical properties significantly. In particular, the transmittance of the films indicated a downward trend as the dye volume was increased. The direct energy band gap of the films ranged from 2.33eV to 2.81eV. The above results demonstrated that the grown films produced by a simple, low cost spray pyrolysis technique could be useful for designing optical devices such as solar cells, optical window layers of photovoltaic cells, photodetectors, photoresistors, etc.

**References**

Ali, R. S., Rasheed, H. S., Abdulameer, N. D., Habubi, N. F., & Chiad, S. S. (2023). Physical properties of Mg doped ZnS thin films via spray pyrolysis. *Chalcogenide Letters*, *20*(3)

Ashith, V.K. & Gowrish, K. (2018).Structural and Optical Properties of ZnS thin films by SILAR technique obtained acetate precursor. *IOP Conf. Ser. Mater. Sci.Eng 360, 012058*

Balachander, M., Saroja, M., Venkatalachalam, M. & Shankar, S. (2015). Preparation and characterization of zinc sulphide thin film deposited by dip coating method. *International Journal of Innovative Science, Engineering and Technology, 2 (10), 381-383.*

Cachet H, Bruneaux,J, Folcher, G, C. Leı´ vy-Cleıment, C, ´, Vard, C , Neumann Spallart, M (2014). n-Si/SnO2 junctions based on macroporous silicon for photoconversion. *Sol. Energy Mater. Sol. Cells* 46, 101–114.

Derbali, A., Attaf, A., Saidi, H., Benamra,H., Nouadji, M.,Aida, M.S.,Attaf, N., & Ezzaouia, H. (2017) Investigaation of Structural, Optical and Electrical Properties of ZnS Thin Films Prepared by Ultrasonic Spray Technique for Photovoltaic Applications*. Optik-International Journal for Light and Electron Optics, PP. 1-8*

Emegha, J. O., Elete, E. D., Efe, F. O. O., & Adebisi, A. C. (2019). Optical and electrical properties of semiconducting ZnS thin film prepared by chemical bath deposition technique. *catalysis*, *4*, 1-8.

Ghazai, A. J., Abdulmunem, O. M., Qader, K. Y., Chiad, S. S., & Habubi, N. F. (2020). Investigation of some physical properties of Mn doped ZnS nano thin films. *AIP Conference Proceedings 2213, 020101 (2020)*

Igweoko, A.E. (2018). M.Eng. Department of Metallurgical and Materials Engineering, Enugu state University of Science and Technology, Enugu, Nigeria.

Meshram, R.S. & Thombre, R.M. (2019). The Effect of Zn Composition on Optical and Structural Properties of CdZnS Thin Films Prepared by Spray Pyrolysis Technique. *International Journal of Current Engineering and Scientific Research, Volume: 6, issue: 1 Pp. 829 – 833.*

Meshram, R.S. & Thombre, R.M. (2021). Optical Properties of CuS Thin Films Prepared by Spray Pyrolysis Technique at 3000oC Temperature. *International Journal of Recent Scientific Research Research Vol. 12, Issue, 09 (C), pp. 43127-43129*.

Nwofe, P.A. (2017). Influence of Film Thickness on the Optical Properties of Antimony Sulphide Thin Films Grown by the Solution Growth Technique. *European Journal of Applied Engineering and Scientific Research, 4(1): 1-6*.

Nwofe, P.A. (2017). Influence of Annealing Temperatures on the Optical Properties of Chemically Deposited Antimony Trisulphide Thin Films. *Journal of Nanotechnology and Advanced Materials, No. 2. 115-121.*

Nwofe, P.A. (2017) Effect of Dye Extracts on the Optical Properties of Chemically Deposited ZnS Thin Films. *Journal of New Technology and Materials, Vol. 07, No. 2, Pp. 93-99.*

Offor ,P.O., Ude1,S.N., Whyte,G.M., Obayi,C.S., Nnamchi, P.S., Omah,A .D., F. U. Whyte,F.U., S. Madu,S., Ogbuefi,U.C., Daniel-Mkpume,C.C., B.O. Anyaka, B.O, Okorie, B.A. & Ezema, F.I (2020). The Influence of Substrate Temperature on Properties of Zinc Sulphide Thin Films Synthesized by Chemical Spray Pyrolysis*, Asian Journal of Basic Science & Research (AJBSR) Volume 2, Issue 1, Pages 01-15*

Offor, P. O., Okorie, B. A., Lokhande, C. D., Patil, P. S., Ezema, F. I., Omah, A. D., ... & Ezema, I. C. (2018). The Properties of Spray-Deposited Zinc Sulfide Thin Films Using Trisodium Citrate Complexant. *The International Journal of Advanced Manufacturing Technology*, *95*, 1849-1857

Onochie, U.P., Ikpeseni, S, C., Igweoko, A.E, Owamah, H. I., Aluma, C.C., & Augustine, C (2021) Optical Properties of Zns Thin Films Coated with Aqueous Organic Dye Extracts for Solar and Optoelectronic Device Applications. *Journal of Electronic materials.*

Ozutok, F., Erturk, K., & Bilgin, V. (2012). Growth, Electrical, and Optical Study of ZnS: Mn Thin Films. *Acta Physica Polonica A*, *121*(1), 221-223.

 Patil, J. S, Dhasade S.S, Thombare, & V. J. Fulari, V.J (2015) Structural, Morphological and Optical Studies of ZnS Thin Films Produced by Electrodeposition Method, Journal of Shivaji University (Science & Technology), Volume No. 41 (2)

Rahman, F., Podder, J., & Ichimura, J. (2013) Structural and Optical Characterization of In-Zn-S Ternary Thin Films Prepared by Spray Pyrolysis Technique, *International Journal of Optics and Photonics (IJOP), Vol. 5, No. 2, Pp. 79-84*

Saeed, N. M., & Suhail, A. M. (2012). Enhancement the Optical Properties of Zinc Sulfide Thin Films for Solar Cell Applications. *Iraqi journal of science*, *53*(1), 88-95.

Shen, S.C. (2014). Wide-bandgap device research and development, Georgia Institute of Technology Semiconductors Research Laboratory, USA.

Suhail, M.H. & Ahmed, R.A. (2014). Structural, Optical and Electrical Properties of Doped Copper ZnS Thin Films Prepared by Chemical Spray Pyrolysis Technique. *Advances in Applied Science Research,5(5):139-147*

Suhail, M.H. & Ahmed, R.A. (2014). Structural, Optical and Electrical Properties of Lead Doped Zinc Sulphide Thin Films Prepared by Chemical Spray Pyrolysis Technique. *International Journal of Information Technology, Volume 2, issue 9*

Ukpai, P.A. (2021). Ph.D Thesis, Department of Industrial Physics, Ebonyi State University.

Wanjala, K. S., Njoroge, W. K., & Ngaruiya, J. M. (2016). Optical and Electrical Characterization of ZnS: Sn Thin Films for Solar cell Application, *Int. J. Energy Engineering*, *6*(1).