

**To Cite:**

Udejah VN, Onah DU. The effect of iron dopants concentration on the optical properties of SILAR deposited ZnSFe thin films for solar thermal applications. *Indian Journal of Engineering*, 2023, 20, e21ije1649  
doi: <https://doi.org/10.54905/diss/v20i53/e21ije1649>

**Author Affiliation:**

<sup>1</sup>Department of Industrial Physics, Ebonyi State University, Abakaliki, Nigeria

Email: vakadujah45@gmail.com

<sup>2</sup>Department of Industrial Physics, Ebonyi State University, Abakaliki, Nigeria

Email: d\_onah@yahoo.co.uk

**Peer-Review History**

Received: 03 May 2023

Reviewed & Revised: 07/May/2023 to 03/June/2023

Accepted: 06 June 2023

Published: 09 June 2023

**Peer-Review Model**

External peer-review was done through double-blind method.

Indian Journal of Engineering  
pISSN 2319-7757; eISSN 2319-7765



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# The effect of iron dopants concentration on the optical properties of SILAR deposited ZnSFe thin films for solar thermal applications

Udejah VN<sup>1</sup>, Onah DU<sup>2</sup>

**ABSTRACT**

This article studied the influence of iron dopants concentration on Zinc Sulphide (ZnS) thin films deposited on glass substrates via successive ionic layer adsorption (SILAR) Technique using Zinc acetate, Zn (CH<sub>3</sub>COO)<sub>2</sub>, thioacetamide (S<sub>2</sub> H<sub>5</sub> NS), Iron (II) Chloride dehydrate (Fe Cl<sub>2</sub>. 2H<sub>2</sub> O), ethanol and ammonia in alkaline medium annealed between 283K and 500K were investigated. This article studies the effects of iron dopant concentration (x = 0.05, 0.03 and 0.02) on the optical and solid-state properties of Zinc Sulphide (ZnS) thin films. The percentage elemental composition studies were performed by Electron Dispersive Spectroscopy (EDS) Analysis. The UV-visible studies were done using spectrometer in the Technical University, Ibadan. The direct band gap varied from 4.81eV for 0.01M, 4.50eV for 0.02M and 4.00eV for 0.05M. The indirect band gap varied from 3.80eV for 0.01M, 3.67eV for 0.02M and 3.40eV for 0.05M. The values of the optical properties and solid-state values were concentration dependent. The large band gap possessed by ZnSFe thin films suggests that the films can be used for applications where high voltage, frequencies and temperature are required.

**Keywords:** Iron dopant, optical properties, Zinc Sulphide iron thin films

**1. INTRODUCTION**

The growth of thin films using advanced and expensive method has become an industry in developed countries. Actually, the continuous increase in population and industrialisation in almost every country in the world has been very responsible for the ever growing or increasing energy demand. It is the energy crisis in the world that gave rise to the thin film growth research as a way to cushion problems associated with it. In Nigeria, less than 40% of the country is connected to the national electric grid and less than 60% of the energy demand by this group is generated and distributed (Bala et al., 2008; Nwoke et al., 2008; Whitefield, 2000).

The advantage of energy is facilitation of the provision of those things

which are necessary for the welfare of human existence: Health, heat, food, light, clothing, shelter and transport, etc. Energy availability improves the standard of living (Chetan, 2014). Solar energy, an energy obtained from the sun, is the world's most abundant and cheapest source of energy available from Nature (Agbo and Nnabuchi, 2011). It is free and automatically renewable every day. In the world over, emphasis has shifted from the use of hydro and fossil-powered electricity generation to renewable energy (thin film growth).

Successive ionic layer adsorption and reaction (SILAR) technique growth cycle for  $\text{ZnS}_x\text{Fe}_{(1-x)}$  thin films has six steps. In this research, the optical properties were investigated from spectroscopy measurements of absorbance, etc.

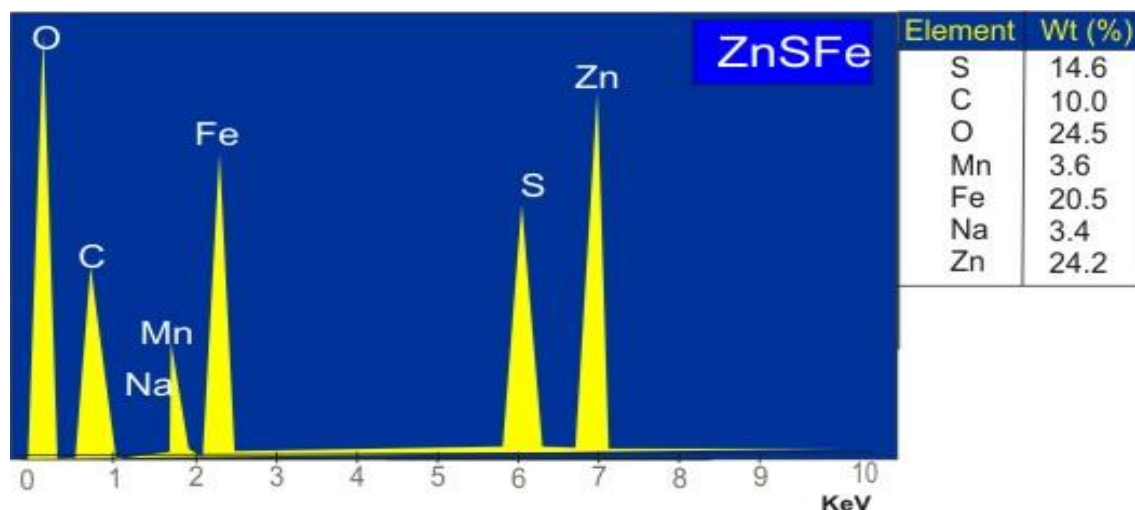
## 2. EXPERIMENTAL PROCEDURE

The synthesis and deposition of zinc sulphide thin films was done with zinc acetate. The number of deposition cycles for ZnS and Fe was adjusted to obtain various compositions of  $(\text{Fe})_{1-x}(\text{ZnS})_x$ . Fe (2%, 3% and 5%) doped ZnS nanoparticles were prepared by using SILAR method at room temperature. Zinc acetate dihydrate  $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ , ferric nitrate nonahydrate  $[\text{Fe}_2(\text{NO}_3)_9 \cdot 9\text{H}_2\text{O}]$  were dissolved in deionised water to prepare solutions (cationic precursor). Aqueous solution of sodium sulphide  $[(\text{Na}_2\text{S})]$  was the anionic precursor. 2 grams of ferric nitrate was mixed with ethanol and used after 3 hours. These formed the source of iron ions. The deposition temperature was about  $40^\circ\text{C}$ . Actually, one of the most important II–VI semiconductors is ZnS nanoparticles with the band gap energy of 3.68 eV. In this case, for the deposited ZnS nanoparticles, several potential and actual applications have been deduced and they agreed with other researchers findings, i.e. in optoelectronic devices, light emitting displays, photo catalysis, solar cells and luminescent materials (Allah et al., 2007; Ansari et al., 2012; Ashcroft and Mermin, 1976; Denisyuk and Fokina, 2010; Igweoke et al., 2018; Jayanthi et al., 2007; JCPDS, 2003; Jiang et al., 2012; Jiban et al., 2005; Kumar et al., 2008; Inwudiwe and Ajibade, 2011; Manzoor et al., 2004; Rand, 2011; Rotello, 2004; Sangamesha et al., 2013; Seoudi et al., 2010).

## 3. RESULTS

### Energy Dispersive spectroscopy Analysis (EDS) of $(\text{ZnS})_x(\text{Fe})_{(1-x)}$ composite thin films

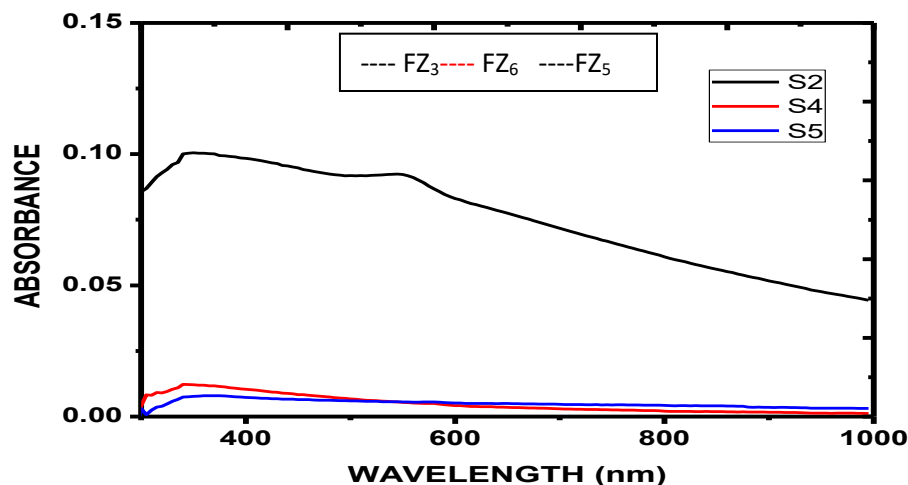
The Energy Dispersive Spectroscopy Analysis (EDX) showing the percentage elemental composition (Figure 1). The percentage composition of iron was 20.5wt%



**Figure 1** EDS of  $(\text{ZnS})_x(\text{Fe})_{(1-x)}$  composite thin films

### Optical and solid Properties of $(\text{ZnS})_x(\text{Fe})_{(1-x)}$ composite thin films

The absorbance property of the  $(\text{ZnS})_x(\text{Fe})_{(1-x)}$  composite thin films is emphasised (Figure 2). The absorbance is generally higher in the UV region compared to other regions. From Figure 2, it is observed that the absorbance of the three samples decreased with increasing wavelength.



**Figure 2** Plot of absorbance against wavelength for ZnSFe thin films

The reflectance of the film samples was calculated using the relation:

$$R = 1 - [T \exp(A)]^{1/2} \quad (1)$$

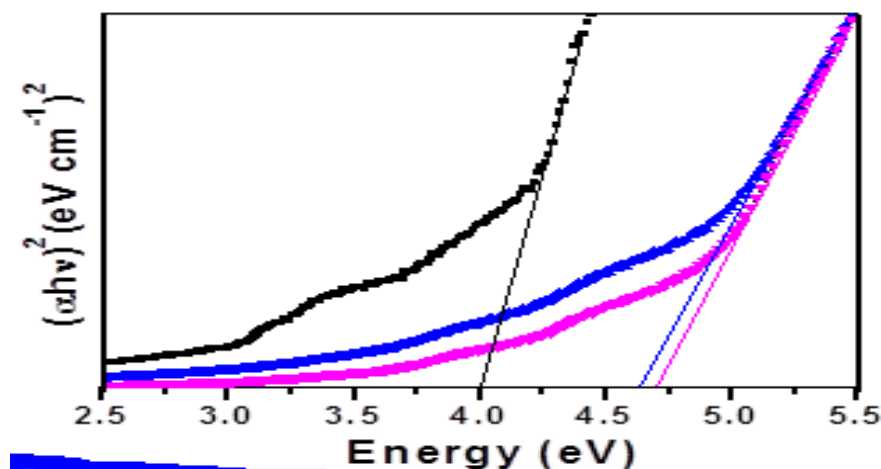
Where R is the reflectance, T is transmittance and A is the absorbance. The following equation for a direct inter-band transition was applied (Serrano et al., 2009).

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

Where  $\alpha$  is the optical absorption coefficient, A is an energy independent constant but depend on the refractive index and the effective masses of the hole and electron respectively (Table 1). The band gap was calculated from transmittance values (Figure 3). The solid-state property considered here is the band gap (Figure 3).

**Table 1** Thickness and Grain sizes of  $(\text{ZnS})_x(\text{Fe})_{(1-x)}$  thin films (From Transmittance)

S/No	Film composition	Grain Size(nm)	Band gap
A	$(\text{ZnS})\text{Fe}_{(0.1)}$	9	4.81
B	$(\text{ZnS})\text{Fe}_{(0.2)}$	8	4.50
C	$(\text{ZnS})\text{Fe}_{(0.5)}$	4	4.0



**Figure 3** Plots of  $(\alpha h\nu)^2$  as a function of  $h\nu$  of Zinc Sulphide Thin Films

## 4. DISCUSSION

### Optical and Solid Properties of ZnSFe- Absorbance

The graph of absorbance against wavelength for ZnSFe thin films (Figures 2). The absorbance of ZnSFe thin films is maximum with a value of about 2.40 (a.u.) in the visible region in the wavelength range 475-575nm and minimum value of about 1.15 (a.u) in the infrared red region corresponding to 1000nm. The maximum absorbance is above the value of 2.0 (a.u) stipulated by Lambert-Beer's

law (<http://www.wikilectures.eu/index-php>). This may be attributed to the concentration of reagents used in the deposition of ZnSFe thin films. At high concentration, the assumptions of Lambert-Beer law no longer hold (<http://www.wikilectures.eu/index-php>). Particle attractive forces come into play at high concentration; the particles may not act independently of one another so far as absorbing light. Thus, most of the light is absorbed by the particles thereby reducing the transmission of light as it passes through the sample.

The range of absorbance of ZnSFe thin films is in agreement with that of Manzoor et al., (2004) and Inwudiwe and Ajibade, (2011) for ZnS thin films. The high absorbance displayed by ZnSFe films may be used as spectrally selective coating for solar thermal applications. Solar collectors for heating fluids require increasing the reception area of the solar radiation and/or to increase the absorbance of the surface coating in order to improve thermal efficiency (Rand, 2011; Rotello, 2004; Sangamesha et al., 2013; Seoudi et al., 2010).

## 5. CONCLUSIONS

A simple, cheap and convenient SILAR method was employed to deposit good quality ZnSFe composite thin films. The deposited films were uniform and adherent to the substrate. Their structural and morphological properties of those composite thin films were studied. The compositional analysis was done using energy dispersive spectroscopy (EDS). EDS studies showed that in  $(\text{ZnS})_{1-x}(\text{Fe})_x$  thin film, the iron content was 20.5wt%. The XRD and morphological studies revealed that ZnSFe thin films were Nano crystalline in nature depending on film composition. The average crystallite size was found to vary for ZnSFe thin films between 14 and 22 and depending on film composition. The variation in thickness, strain and dislocation densities was also composition dependent. The samples annealed at different temperatures (383K-500K) never showed any prominent peaks structurally and morphologically. From literature, considerable changes can be seen for temperatures up to 700 °K (Serrano et al., 2009; Shinde et al., 2011; Stern, 1963; Uhuegbu, 2007; Virpal et al., 2017; Wei et al., 2013). The high absorbance displayed by ZnSFe films may be used as spectrally selective coating for solar thermal applications. Solar collectors for heating fluids require increasing the reception area of the solar radiation and/or to increase the absorbance of the surface coating in order to improve thermal efficiency. These properties can be well used in solar energy conversion devices and optoelectronics.

### Acknowledgment

The authors are grateful to Nano science Research Group, University of Nigeria Nsukka

### Ethical issues

Not applicable.

### Informed consent

Not applicable.

### Funding

This study has not received any external funding.

### Conflict of Interest

The author declares that there are no conflicts of interests.

### Data and materials availability

All data associated with this study are present in the paper.

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