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Synthesis and Characterization of Zinc Iron Sulphide (ZnFeS) of Varying Zinc Ion Concentration

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ABSTRACT

The nano-crystalline thin films of Zn-doped FeS were deposited onto glass substrates by chemical bath deposition (CBD) method at room temperature (300K). The incorporation of varying concentration of zinc ion (0.02 M, 0.04 M and 0.06M) in FeS changed the energy band gaps for both direct and indirect transitions decreasing with increase in Zn ion concentration ranging from 2.17 to 2.31 eV and 1.77 to 1.82 eV respectively. The optical properties as a function of wavelength, photon energy and doping concentration were studied in detail. The properties studied include the absorbance, reflectance, absorption coefficient, thickness, refractive index, extinction coefficient, optical conductivity and dielectric constant. The electrical conductivity was found to be of the order of 0.5 x 10^{-4} $\Omega^{-1}m^{-1}$ and it increases as Zn ion concentration decreases. The SEM study shows that the surface morphology of the film is highly influenced by the concentration of doping ion.

Keywords: *Ternary Thin Films, Surface Morphology, Chemical Bath Deposition, Electrical Properties, Optical Properties*

1. INTRODUCTION

In the contemporary time, attention on the deposition and study of physical properties of ternary thin film compound has increased. This is mainly because they allow tuning of the semiconductor properties most commonly, the band gap and therefore spectral sensitivity [3]. Ternary compounds are found to be promising materials for screening off UV portion of the electromagnetic radiation by absorbance and the admittance of the visible and near infrared radiation by transmission. These properties confirm the films good materials for coating poultry buildings, eyeglasses coating, solar thermal conversion, solar control, anti-reflection coating and solar cells fabrication [4] and [10]. Most materials are applied in the form of thin films due to their specific electrical, magnetic and optical properties or wear resistance [9]. The properties of thin films are extremely sensitive to the preparation methods, several techniques have been developed for the deposition of the thin films of metals, alloys, polymer and superconductors on a variety of substrate materials [6]. So far, many ternary semiconductor thin films deposited by chemical bath deposition (CBD) method have been reported including $CuSbS_2$ [8], Cu:CdS [5], Ag doped ZnS [7], Pb_{15},$Cd_{45}S_{40}$ [6], $AgAlS_2$ [2], ZnFeS [1], etc. In this paper, we present the synthesis of ZnFeS thin films using chemical bath deposition method. The effect of varying Zn ion concentration on structural, morphological, optical and electrical properties of CBD-deposited ZnFeS thin films has been discussed.

2. MATERIALS and METHOD

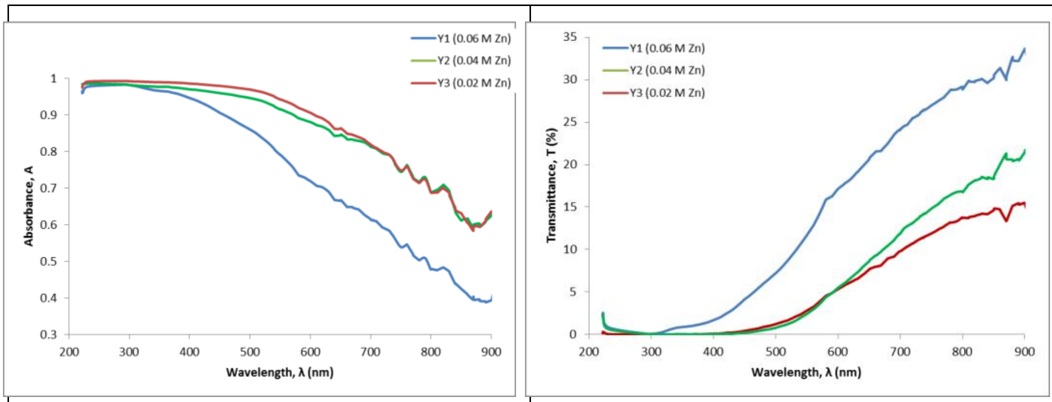
Chemical bath deposition technique was used to deposit zinc iron sulphide thin films on glass substrate. Prior to the deposition, the substrates were degreased by dipping them in concentrated HCl and HNO_3 in the ratio 3:1 respectively, washed with detergent, rinsed with distilled water and died in air. The degreased and cleaned substrate surfaces have the benefit of providing nucleation centers for the growth of the films, hence yielding highly adhesive and uniform deposited films. The deposition of ZnFeS thin films by chemical bath method was based on the reaction between aqueous solutions of ferrous nitrate and zinc nitrate as precursors and thiourea as precursors of iron, zinc and sulphur ions using ethylenediaminetetraacetate (EDTA) and triethanolamine (TEA) as the complexing agent and sodium hydroxide as a pH stabilizer.

The reaction baths constitute a mixture of 5 ml of 1 M ferrous nitrate solution, 5 ml of 0.06 M zinc nitrate, 10 ml of 1 M thiourea, 3 ml of ammonia, 3 ml of 7.4 M TEA, 5 ml of 0.1 M EDTA, 20 ml of distilled water. The mixture was stirred with stirrer until it became a homogeneous mixture. The cleaned substrates were immersed vertically into the reaction baths and were allowed to stay for 5 hours at constant room temperature (300 K). Varying concentrations (0.02 M and 0.04 M) of zinc nitrate (the source of zinc ions) were prior mixed with iron nitrate and stirred. Other bath reagents were orderly added as in 0.06 M of ZnFeS deposition and the resulting mixture was stirred thoroughly. The bath was left undisturbed for the same time interval of 5 hours and temperature (300 K), after which the substrates were removed, rinsed with distilled water and finally allowed to dry in air.

3. RESULTS AND DISCUSSIONS

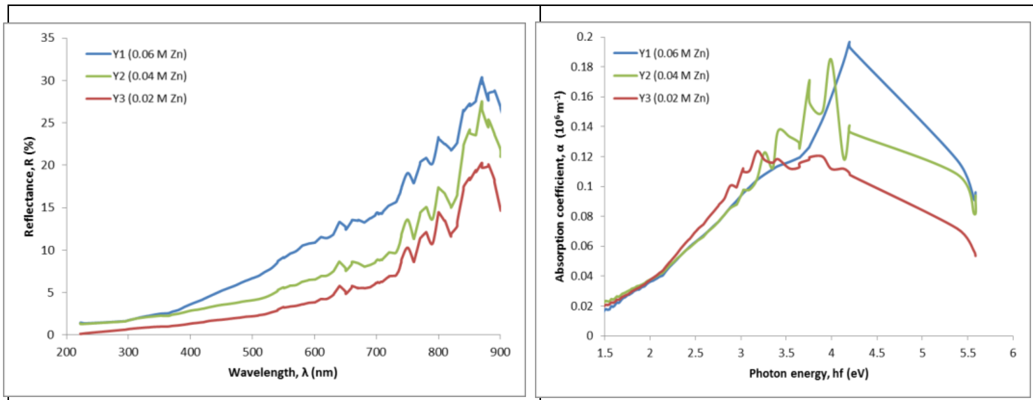
Fig. 1(a) and Fig. 1(b) show the plot of absorbance and transmittance against wavelength. Observations were that the absorbance was high in UV-VIS and low in NIR regions, while the transmittance was low in UV-VIS region and high in NIR regions. Transmittance increases with increasing Zn ion concentration and the reflectance of the samples appeared to be reducing NIR-region. Fig. 2 shows that the reflectance's of ZnFeS thin films were low in UV-VIS region and high in the NIR regions. The films show noticeable change in the optical properties for varying zinc ion concentration. The absorption coefficient ranged from 0.02 x 10^6 m^{-1} to 0.2 x 10^6 m^{-1}, 0.02 x 10^6

m^{-1} to 0.18 x 10^6 m^{-1} and 0.02 x 10^6 m^{-1} to 0.13 x10^6 m^{-1} for 0.06 to 0.02 M of Zn ions respectively. Increasing concentration of Zn varied the absorption coefficient noticeably for photon energies greater than 3.5 eV.



a) (b)

Fig. 1 (a) Plot of absorbance versus wavelength (b) plot of transmittance versus wavelength for varying Zn ion concentration on FeS thin films.



(a) (b)

Fig. 2(a) Plot of reflectance versus wavelength (b) plot of absorption coefficient versus photon energy for varying Zn ion concentration on FeS thin films.

The refractive index Fig 3(a) ranged from 1.3 to 2.9, 1.3 to 2.4 and 1.1 to 2.2 respectively. The values of the extinction coefficient Fig. 3(b), ranged from 0.001 to 0.003, 0.0015 to 0.033, 0.0013 to 0.0038 respectively. The effects of increasing Zn ion concentration on refractive index were noticeable between photon energies of 1.5 eV and 3.4 eV. The direct band gap and indirect band gap depicted in Fig. 4(a) and 4(b) ranged from 2.17 to 2.31 eV and 1.77 to 1.82 eV respectively. The real part of the dielectric constant ranged from 1.5 to 8.5 as shown in Fig. 5(a). Increasing real dielectric constant, ε_r with increasing concentration of Zn ions was more prominent at low photon energies. The XRD result depicted peak broadening for higher concentrations of Zn ions while Table 1 shows the crystallite sizes obtained.

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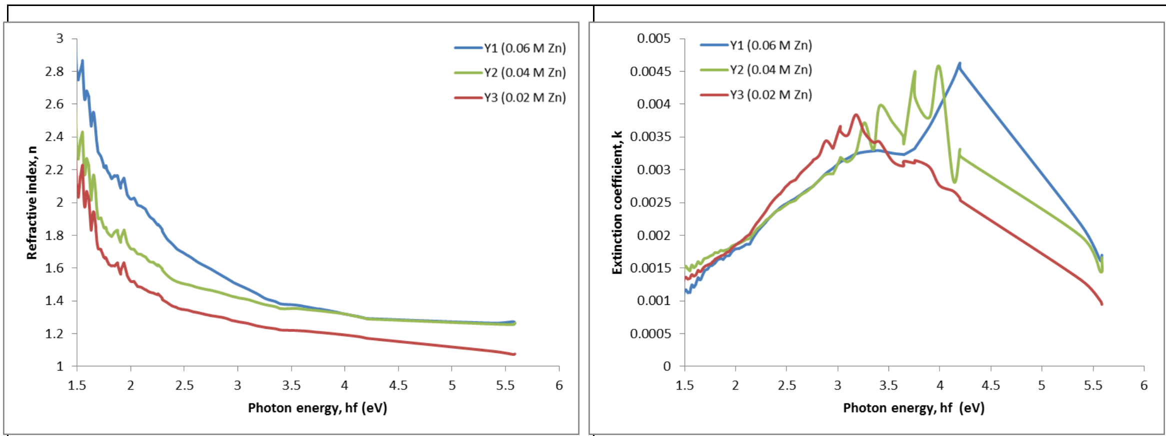
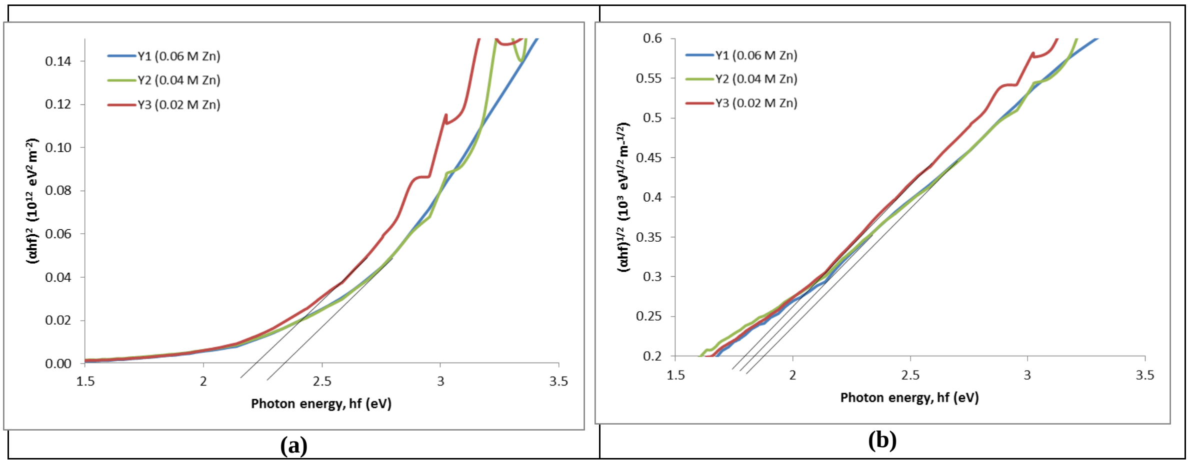
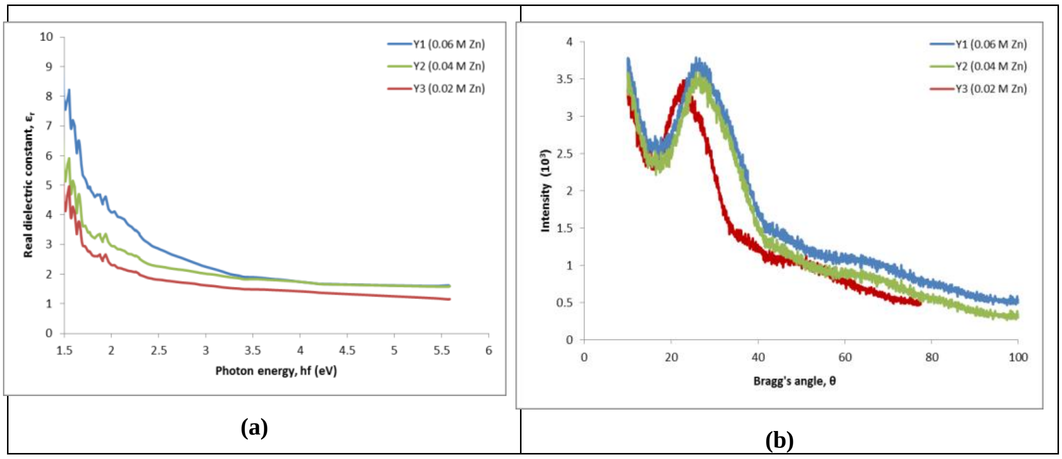


(a) (b)

2 **Fig. 3 (a) Plot of refractive index versus photon energy (b) plot of extinction coefficient versus photon energy**



3 **Fig. 4 (a) plot of $(\alpha hf)^2$ versus photon energy (b) plot of $(\alpha hf)^{1/2}$ versus photon energy for varying Zn ion concentration**



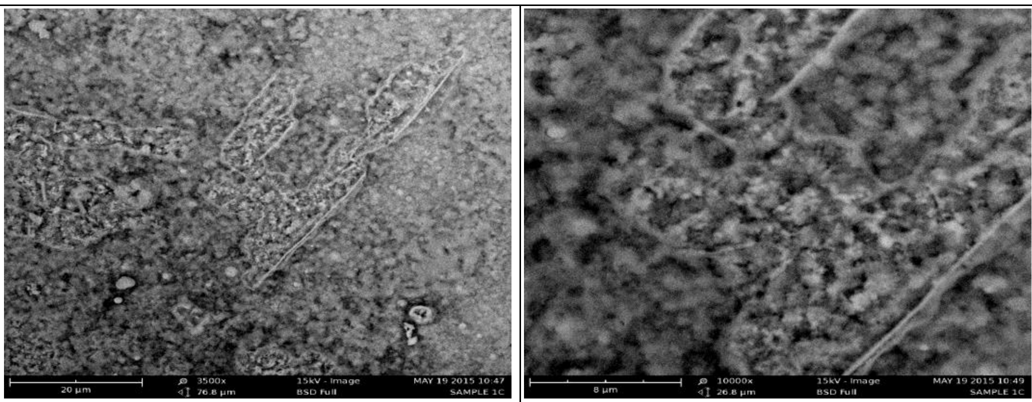
4 **Fig. 5 (a) Real dielectric constant versus photon energy (b) XRD pattern of ZnFeS thin films for varying Zn concentration.**

5

Table 1 The FWHM of XRD and calculated grain sizes of varying concentrations of Zn ions on FeS.

Sample label	Diffraction angle (°)	FWHM	Lattice strain	Calculated crystallite sizes (nm)
Y1	25.75	0.058	0.0011	141.92
Y2	25.71	0.061	0.0011	141.80
Y3	23.23	0.068	0.0014	131.06

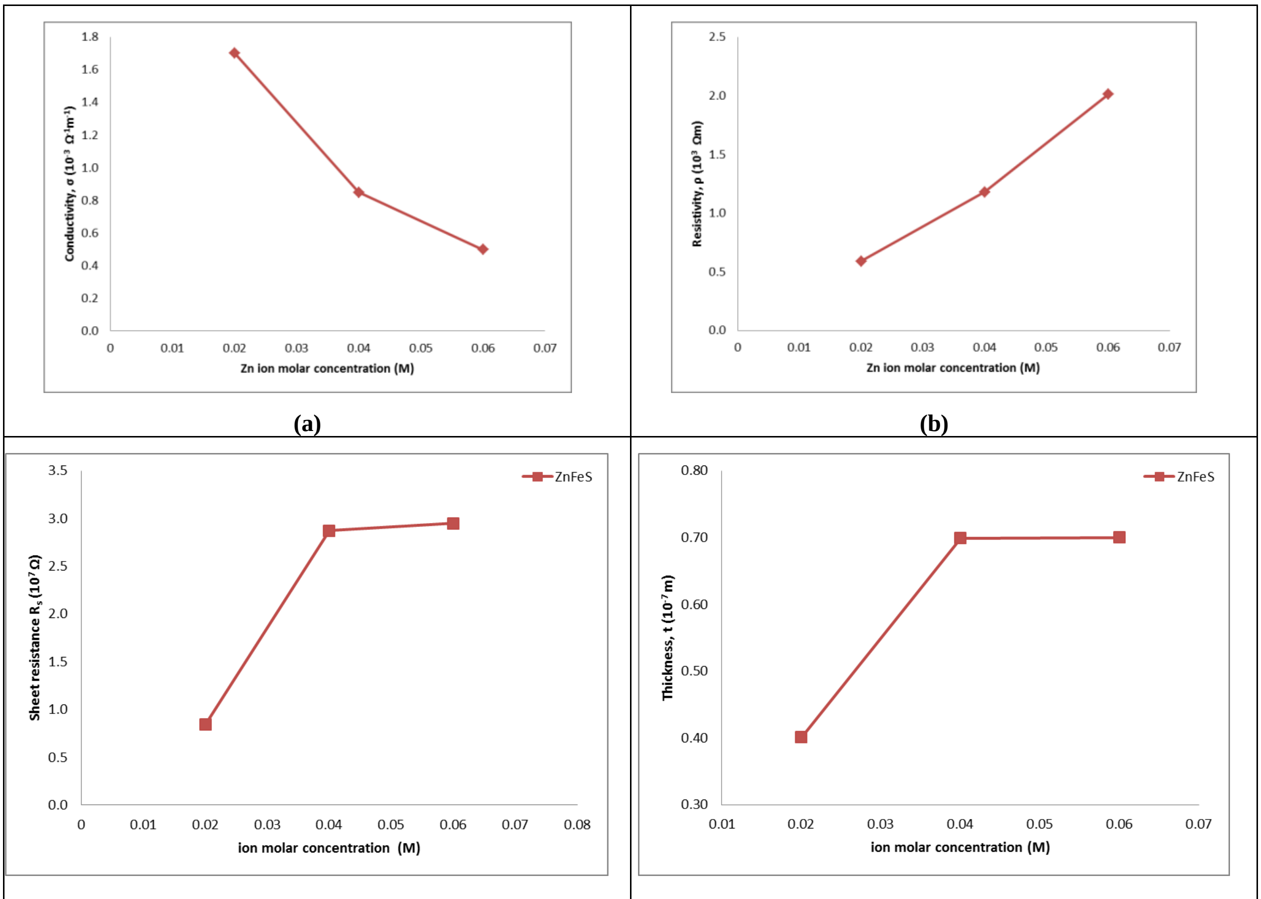
Fig. 5(b) shows the XRD result depicting peak broadening for higher concentrations of zinc ions while Table 1 shows the crystallite sizes obtained. Note that the FWHM for the samples got smaller with increasing concentrations meaning the sizes of crystal increased with increasing molar concentration. The diffraction peak for ZnFeS thin films appear at 2θ = 25.75°, 2θ = 25.71° and 2θ = 23.23° for (0.06 M, 0.04 M and 0.02 M) of Zn ion respectively.In Fig. 6, the results of the SEM for two magnifications of 0.04M of zinc ion concentration are shown, depicting the morphology of the crystal structure. The observed small Nano sized grains engaged in a fibrous like structures, clearly indicates the glassy nature of the compound.



(a) SEM of ZnFeS (Y1) at 3500x | (b) SEM of ZnFeS (Y1) at 10000x

Fig. 6 SEM micrograph of ZnFeS thin film with 0.06 M Zn concentration (a) at 3500X and (b) at 1000X magnification

The electrical property reported in this paper includes conductivity, resistivity, sheet resistance and thickness. In Fig. 7 (a-d) the plots of conductivity, resistivity, sheet resistance and thickness of ZnFeS thin films versus zinc ion concentrations are also shown.



(a) (b) (c) (d)

Fig. 7 (a) Plot of electrical conductivity versus concentration (b) plot of resistivity versus concentration (c) plot of sheet resistance versus concentration (d) plot of thickness versus concentration for varying Zn ion concentration on FeS thin film

The range of the resistivity and conductivity for ZnFeS thin films are 1.42 x 10^3 Ωm and 1.2 x 10^{-3} $\Omega^{-1}m^{-1}$ respectively. ZnFeS thin films resistivity increases with an increase in thickness for thickness values less than 0.7 x 10^{-7}m. There were no significant changes in the thickness and sheet resistance for Zn ion concentrations between 0.04 M and 0.06 M for the ZnFeS samples as seen in Fig 6(c and d).

4. CONCLUSION

Zinc Iron Sulphide (ZnFeS) ternary thin films were successfully deposited on glass substrates using chemical bath deposition technique. ZnFeS shows average absorbance of 0.66, 0.82 and 0.82 in the electromagnetic spectrum range of 200 nm to 900 nm wavelength, which decreases further as Zn ion concentration increases. The films show average transmittance of 19.78 %, 10.56 % and 7.82 % respectively. The reflectance is generally low in the NIR-VIS region of electromagnetic spectrum. The refractive indexes ranged from 1.1 to 2.9 while the extinction coefficient ranged from 0.001 to 0.0038. The band gap energy also ranged from 2.17 to 2.31 eV.

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