INFLUENCE OF ZN CONCENTRATION ON OPTICAL AND MORPHOLOGICAL PROPERTIES OF ZNS THIN FILM DEPOSITED BY CHEMICAL BATH DEPOSITION METHOD FOR PHOTOVOLTAIC APPLICATION.

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ABSTRACT

The effect of Zn concentration was investigated on optical and morphological properties of synthesized Zinc Sulphide thin film (ZnS). . ZnS thin films were prepared at different concentrationsof $ZnSO_4$(zincsulphate) onto the glass substrates by chemical bath deposition technique at a constant deposition temperature and time of 50^0C and 1 hour respectively. .The precursor was prepared using mixed aqueous solution of zinc sulphate as a source of zinc and thiourea as a source of sulphur while ammonia serves as a complexing agent. After the deposition, thickness of the samples were determined using double weighing method. Morphological and optical properties of the films were determined using scanning electron microscope (SEM PHENON WORD) andUV-visible double beam spectrophotometer (ATICO) respectively. The result shows that transmittance spectral increases in the visible region of wavelength 400nm to 800nm and decreases in the infrared region at above 800nm wavelength.. The extrapolated optical band gap energy for the film deposited is between 3.6 -3.8 eV. The microstructural images of all the samples were rough and the grains were dense.

Keywords- ZnS, CBD,SEM, Spectrophotometer, Band gap , Transmittance

INTRODUCTION

ZnS is a compound semiconductor that forms from II-VI element (Djelloul et al., 2015).It is an N-type conducting materials and has a wide optical band gap energy . These properties make it a promising electronic material for an optoelectronic device such as solar cell, electroluminescent device, data transfer and UV –sensitized coating(Erken, Gunes, Ozaslan, & Gumus, 2017). This new class of materials has not only provided many unique opportunities but also exhibited novel optical and transport properties, which are potentially useful for technological application(Jafarov, Nasirov, Jahangirova, & Jafarli, 2015). ZnS thin films are promising replacements for toxic CdS buffer layers in thin-film solar cells. Though CdS layers are suitable and available in application level for efficient photovoltaic cells a requirement for replacement of CdS buffer layers is due to its toxic nature and less transparency(Silvena, John, Rajesh, & Joseph, 2017). ZnS thin films are non-toxic to the human body, very cheap and abundant(Ashraf, Akhtar, Ali, & Qayyum, 2011). The interest in ZnS semiconductor thin film becomes increasingly popular because it has advantages of economical and capability of large area deposition(Patil, Dhasade, Thombare, & Fulari, 2015).This film exists in two main crystal forms, the more stable cubic form is known as zinc blende or sphalerite and the hexagonal form is known as the mineral wurtzite. Both sphalerite and wurtzite are intrinsic, wide-bandgap semiconductors. The cubic form has a bandgap of 3.54 eV at 300 K whereas the hexagonal form has a bandgap of 3.91 eV. It can be doped as both N and P-type semiconductor(Harish & Mahesh, 2017). ZnS is used as a window layer in heterojunction solar cells such as CdTe and CIGS solar cells due to its wide bandgap which decreases the window absorption loses and improves the short circuit current of the cell. The film transmits more high-energy photons to the P-N junction of thin-film solar cells and enhances the blue region, it provides better lattice matching with absorbers having energy band gaps in the range of 1.3 - 1.5 eV (Manjulavalli & Kannan, 2015). Several methods have been used to prepare ZnS thin film. These include metal oxide chemical vapour deposition method(Fang, Holloway, & Yu, 1993), electrodeposition method(Kulkarni, 2017), chemical spray pyrolysis method(Kulkarni, 2017), thermal deposition method(Bioki & Zarandi, 2011). Chemical bath deposition method has been employed by many researchers due to its inexpensive equipment requirement, low cost of required chemicals and easy to deposit even at low temperature. This method was used to deposit ZnS thin film and investigate structural and optical properties of nanocrystalline ZnS by(Mohammad & Al-jumaili, 2014), Effect of precursor on the efficient formation of ZnS thin films for buffer layer was investigated using chemical bath

deposition method(Silvena et al., 2017), effect of pH on the properties of ZnS thin film grown by chemical bath deposition method was investigated by(Silvena et al., 2017). Also, the effect of doping ZnS with Sn was investigated by(Silvena et al., 2017) using a chemical bath deposition method. In this study, ZnS thin film was deposited onto glass substrates and effect of concentration of zinc sulphate as asource of zinc was investigated on optical and morphological properties of ZnS thin film.

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MATERIALS AND METHOD

Materials

The reagents used for this study were Zincsulphate pentahydrates ($ZnSO_4.5H_2O$), Ammonia solution NH_3 and Thiourea $SC(NH_2)_2$. They were analytically pure and used as purchased without further purification. The solutions were prepared using distilled water as solvent

Preparation of glass substrates

The glass substrates were labeled as T1, T2and T3 using diamond glass cutter and then soaked in HCl acid for 24 hours, thereafter, washed with detergent soap, rinsed with distilled water and then dried in oven for 15minutes at 30^0 C. They were then kept in beaker and covered with aluminium foil to avoid being contacted with dust.

Deposition of ZnS thin film

The chemical bath is prepared by mixing 30ml of 0.20 M , 0.40 M and 0.60Zinc sulphate ($ZnSO_4$) as asource of zinc were poured into three different beakers labelled as T1, T2 and T3 respectively and stirred for 120seconds ,20ml of 3M (NH_4OH) solution as a complexing agent was added to each of the beaker and 30 ml of 1.20 M Thiourea ($SC(NH_2)_2$) as the source of Sulphur was added to each of the beaker slowly under continuous stirring for several minutes until the solutions turned milky after which became colourless. Finally, the mixtures were poured into three different 100ml in chromatography tanks labelled T1, T2 and T3 respectively .The cleaned three samples T1, T2 and T3 were immersed vertically in the chromatography tank T1 , T2 and T3respectively . The tankswere then placed inside the preheated water bath. The deposition was allowed to stay for 1 hour, the temperature of the bath (Tb) was maintained at 50^oC. Thereafter, the glass substrates were removed and found coated with ZnS observed to have been coated with milky white deposits which the thickness varies according to the concentration of Zinc sulphate, then one side of the substrate was cleaned using cotton wool with HCl and annealed at constant temperatures of 100^oC for 15minutes in an oven. The mass of chemical reagent for the various molar solution was calculated from the relation 1 .

$$m=\frac{Dc*Dv*W}{1000} \quad (1)$$

Where m is the mass of salt required, Dc is the required concentration; Dv is the volume of distilled water required and W is the molar mass of the chemical salt.

Measuring the films thickness

The thickness of the films was determined gravimetrically by measuring the weight of the substrate before and after deposition. The thickness of the films was calculated using the equation 2.

$$t=\frac{w2-w1}{A\,\rho}*10^4\mu m \quad (2)$$

W1 and *W2* are the weights of the substrate before and after film deposition in gm respectively ., *A* is the area of film deposition in cm^2 and ρ is the theoretical density of ZnS.

Characterization of the films

The surface morphology of all synthesized ZnS thin films was observed by Scanning Electron microscopy (SEM)-SEM PRO (PHENONWORD) accelerating at 10 KV .The absorbance of the thin films were measured using DOUBLE BEAM UV/V is spectrophotometer (ATICO). The film coated glass substrate was placed across the sample radiation pathway while the uncoated glass substrate was used as a reference frame. The absorbance data

were obtained directly from the spectrophotometer and other parameters such as photon energy, transmittance, reflectance, and optical band gap energy were calculated using equations 3-10 respectively.

$$E = hf \quad (3)$$

Where h is Planks constant with numerical value of 6.63×10^{-34}Js

$$f = \frac{c}{\lambda} \quad (4)$$

where is frequency of radiation , c is the speed of light with numerical value 3×10^{8} ms^{-1} while λ is the measured wave length

$$E = \frac{hc}{\lambda} \quad (5)$$

By substituting the entire constant and convert the energy to eV .The energy then becomes

$$E = \frac{1243}{\lambda} \quad (6)$$

The transmittance of the films was obtained from the relation below

$$T = 10^{-A} \quad (7)$$

Where A is the measured absorbance, the reflectance were calculated using the relation below.

$$R = 1 - (A + T) \quad (8)$$

The absorption coefficient (α) was calculated using

$$\alpha = A\, x\, 10^{\lambda} \quad (9)$$

The band gap energy of the film is extrapolated from the plot of $(\alpha hv)^2$ against the photon energy in eV according to equation below

$$(\alpha hv)^2 = A(hv - Eg)^2 \quad (10)$$

RESULTS AND DISCUSSION

Thickness of the film

The result of thickness of ZnS thin film grown at different concentration of zinc sulphate is shown in table 1. The table shows that the thickness of film deposited on glass substrates increases as concentration of zinc increases. This is in good agreement with (Akinyemi, Ojo, Kolebaje, & Abiodun, 2016).

Table 1: Thickness of deposited ZnS thin film at different concentration of Zn

Sample code	Length of substrate (cm)	Breath of substrate (cm)	Area $(cm)^2$	Mass of substrate before deposition (g)	Mass of substrate after deposition (g)	Change in mass(g)	Film thickness t (μm)
T1	19.35	4.1	79.335	5.111	5.113	0.002	2.52
T2	19.35	4.1	79.335	5.116	5.119	0.003	3.78
T3	19.35	4.1	79.335	5.113	5.121	0.008	5.05

Optical properties

The transmittance and reflectance spectra of synthesized ZnS thin film at various concentration of zinc sulpahate are shown in figures 1 and 2 respectively. These spectral (Transmittanand Reflectance spectral) read from 190 nm to 1100nm. The transmittance spectrum increases in the visible region of wavelength from 400nm to 800nm and decreases in the infrared region above 800nm wavelength. The transmittance values are 68 %, 60 %, and 52 % for 0.2 M, 0.4 M and 0.6 M of zinc sulphate respectively. This shows that the increase in concentration reduces the transmittance of the films. This agrees with(Mammah, Opara, & Sigalo, 2012). Also, the reflectance spectra reveal that the film has the same percentage of 0.3 % for various concentration of zinc sulphate . The optical band gap energies of the film extrapolated and shown in figures 3a, 3b and 3c are 3.80 eV, 3,70 eV and 3.6 eV for the film deposited from 0.2 M, 0.4 M and 0.6 M of zinc sulphate respectively.It shows that the increase in Zn concentration decreases the band gap energies of the film, this is in good agreement with the report of(Alami, Salem& Gaidi, 2015). This similar higher band gap energies of 3.84 eV-3.96 eV have reported by(Manjulavalli & Kannan, 2015)Also,(Djelloul et al., 2015)reported 3.89 eV-3.96 eV for ZnS bang gap energy. This wider bandgap energy makes these films good material for potential applications in optoelectronic devices such as multilayer dielectric filters, and solar cell due to decreases the window absorption loses and that will improve the short circuit current of the cell (Djelloul et al., 2015)

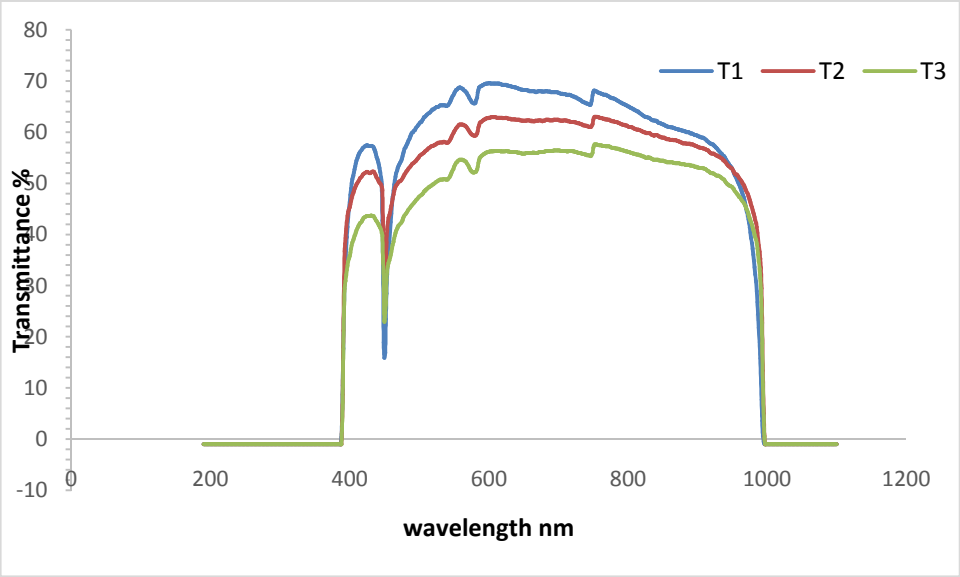

Figure 1:The transmittance spectra of ZnS at various concentration of zinc sulphate

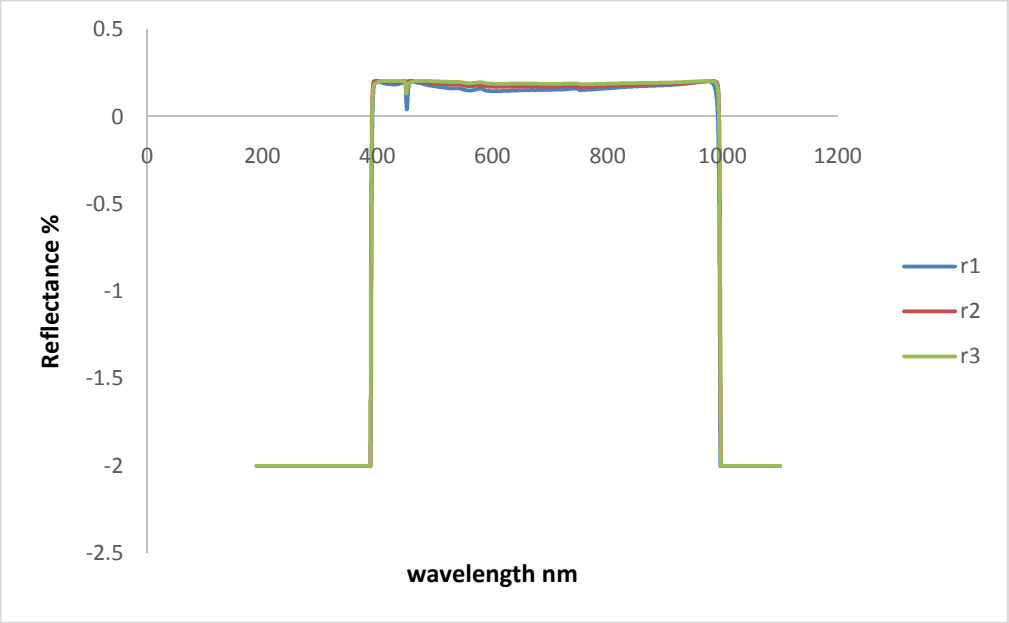

Figure 2: The reflectance spectra of Zns at various concentration of zinc sulphate

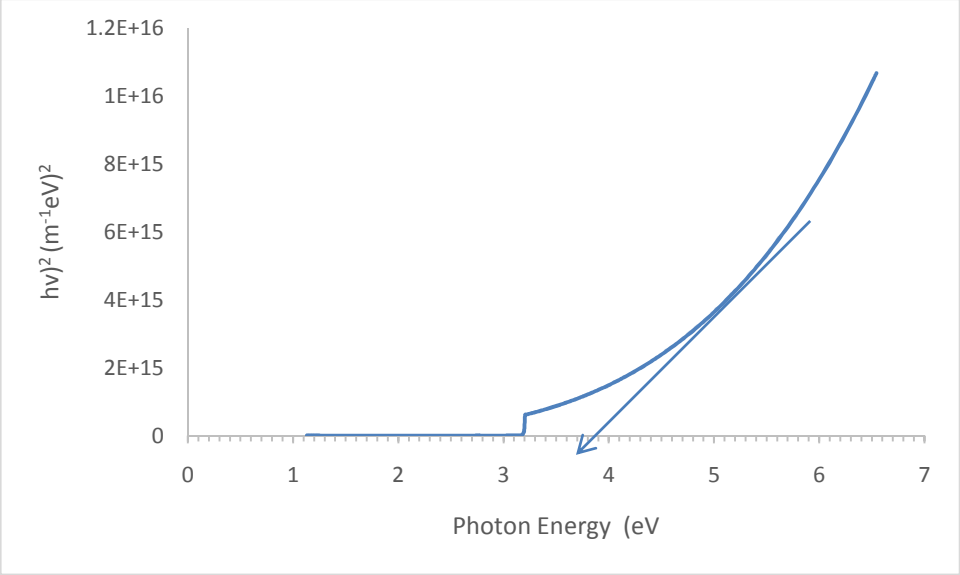

Figure 3a: The graph of $(\alpha h\nu)^2$ against photon energy of the film at 0.2 M of zinc sulphate

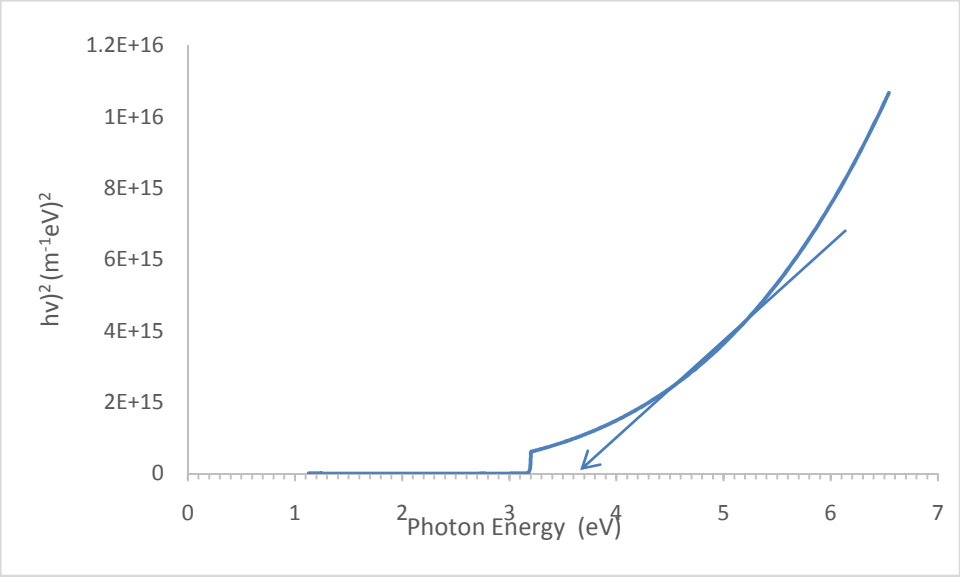

Figure 3b: The graph of $(\alpha hv)^2$ against photon energy of the film at 0.4 M of zinc sulphate

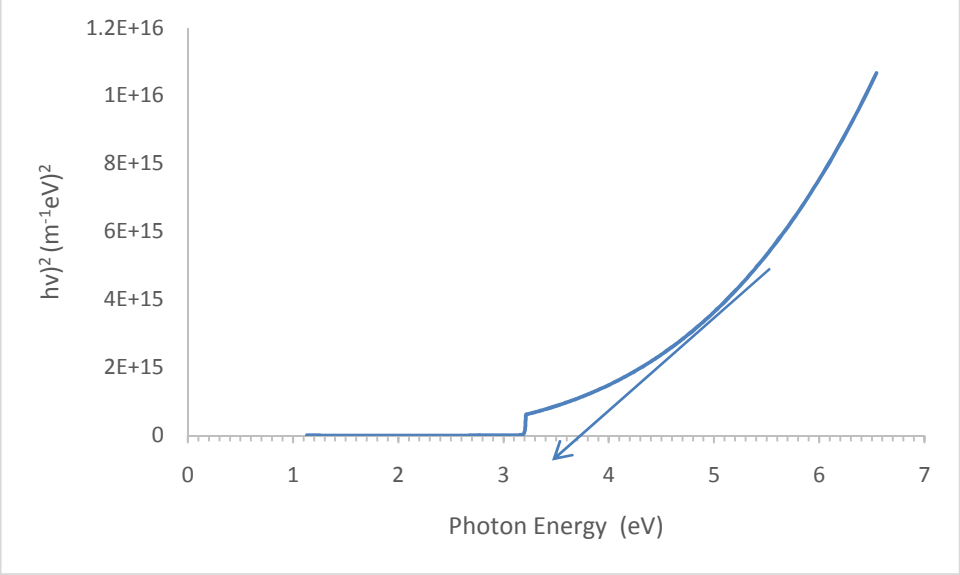

Figure 3c: The graph of $(\alpha hv)^2$ against photon energy of the film at 0.6 M of zinc sulphate

Morphological property

The microstructural images of the ZnS thin film deposited at three different concentration of zinc sulphate when viewed with a scanning electron microscope (SEM) are as shown in the figures 4a,4b and 4c. SEM images of the ZnS thin film obtained from the deposition shows a rougher surface which is in good agreement with(Kulkarni, 2017). The micrograph images show that the density of microcrystals are densely packed as concentration of Zn increases.

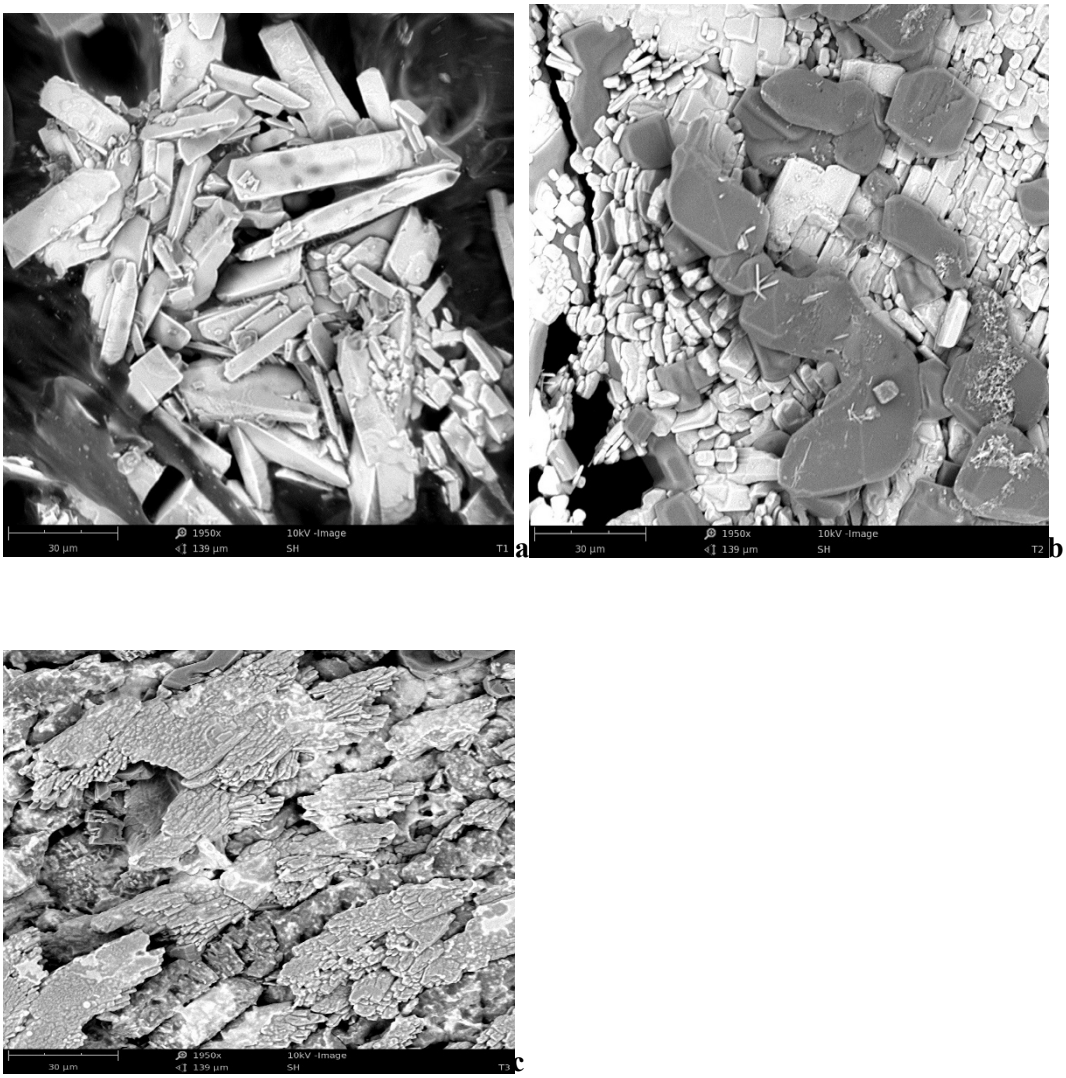

Figure 4:SEM images of ZnS thin films at different concentration of $ZnSO_4$ (a=0.2 M, b=0.4 M and c=0.6 M)

CONCLUSION

ZnS thin films were successfully deposited on the glass substrate using a chemical bath deposition method. The effect of Zn Concentration on optical and morphological characteristics of the films was investigated. The optical result shows the films have high transmittance, low reflectance in the visible region and also high optical band gap energy decreased from 3.8eV to 3.6 eV as the concentration of Zn increases. The morphological properties of all the film are rough and dense. But the clustering of the film increases as the concentration of Zn increases dep. All these results indicate that the films can be used as a window to replace toxic CdS in the fabrication of thin film CdTe, CIGS hetero-junction solar cell.

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