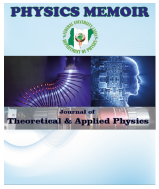

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Original Research

Effects of Deposition Time of ZnS Thin Film on Optical and Morphological Properties of ZnS Deposited by Chemical Bath Deposition Method for Photovoltaic Application

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Abstract

The effect of deposition time was investigated on optical and morphological properties of synthesized ZnS thin film. ZnS thin films were prepared at different temperatures and different deposition period of 1 hour, 2 hours and 3 hours onto the glass substrates by chemical bath deposition technique at a deposition temperature of 50°C. The precursor was prepared using mixed aqueous solution of zinc sulphate as source of zinc and thiourea as source of sulphur while ammonia serves as complexing agent. After the deposition, thickness of the samples were determined using double weighing method, the morphological and optical properties of the films were determined using Scanning Electron Microscope (PHENON WORD), UV-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 transmittance spectral of the film deposited for 2 hours shows highest value of 70% while the films deposited for 1 hour and 3 hours have transmittance of 55% and 37% respectively. 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. The samples deposited for 3 hour and 2 hours are more clustered and smoother compared to the sample deposited for 1 hour.

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

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1. Introduction

Zinc sulphide is a compound semiconductor that forms from II-VI element [1]. It has a wide direct band gap energy and n-type conducting materials. These properties make it a promising electronic material for an optoelectronic

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device such as solar cell, electroluminescent device. 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 [2]. 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, inefficient photovoltaic cells is a requirement for replacement in CdS buffer layers due to its toxic nature and less transparency [3]. ZnS thin films are nontoxic to the human body, very cheap and abundant. The interest in ZnS semiconductor thin film becomes increasingly popular because it has advantages of economical and capability of large area deposition [4]. This film exists in two main crystal forms, the more stable cubic form is known as zinc blende or sphalerite, the hexagonal form is known as the mineral wurtzite. Both sphalerite and wurtzite are intrinsic, wide-bandgap semiconductors. The cubic form has a band gap of 3.54 eV at 300 K whereas the hexagonal form has a band gap of 3.91 eV. It can be doped as both N and P-type semiconductor [5]. ZnS is used as a window layer in heterojunction solar cells such as CdTe and CIGS solar cells due to its wide band gap 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 and provides better lattice matching with absorbers having energy band gaps in the range of 1.3 - 1.5 eV [6].

Different methods have been used to prepare a ZnS thin film. These include MOCVD method [7], electrodeposition method [8], chemical spray pyrolysis method [9], thermal deposition method [10]. Chemical bath deposition method has been employed by many researchers due to no expensive equipment is required, low cost of required chemicals, easy to deposit even at low temperature. The method was used to deposit ZnS thin film and investigate Structural and optical properties of nanocrystalline ZnS by [11]. Effect of precursor on the efficient formation of ZnS thin films for buffer layer was investigated using chemical bath deposition method [3], effect of pH on the properties of ZnS thin film grown by chemical bath deposition method was investigated by [12]. Also, the effect of doping ZnS with Sn was investigated by [13] using a chemical bath deposition method.

In this work, ZnS thin film was deposited onto glass substrates and effect of time of deposition was investigated on optical and morphological properties of ZnS thin film.

2. Materials and Method

2.1. Materials

The reagents used for this experiment were Zinc sulphate 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 the solvent preparation of glass substrates.

The glass substrates were labeled with 1H, 2H and 3H using diamond glass cutter and then soaked in HCl acid for 24 hours, after they were washed with detergent soap and rinsed with distilled water and then dried in oven for 15 minutes at 30°C. They were then kept in beaker and covered with aluminum foil to avoid being contacted with dust.

2.2. Deposition of ZnS thin film

The chemical bath is prepared by mixing 30ml of 0.10 M Zinc sulphate ($ZnSO_4$) as source of zinc, 30ml of 1.20M Thiourea ($SC(NH_2)_2$) solution as a source of sulphur and 20ml of 3M (NH_4OH) solution as complexing agent. While preparing the solution, firstly 30ml of 0.10M $ZnSO_4$ was poured into beaker and stirred for 30sec, then 30ml of 1.20M Thiourea ($SC(NH_2)_2$) was added, while ammonia solution 20ml was added slowly and stirred vigorously for several minutes with a magnetic stirrer until the solution becomes a milky after the solution later become colourless. Finally, the mixture was poured into 100ml in chromatography tank and the cleaned three samples were immersed vertically in the chromatography tank, the tank was then placed inside the preheated water bath. The deposition was allowed to carry out for 1 hour, 2 hours and 3 hours. The temperature of the bath (Tb) was maintained at 50°C. 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 their time of deposition, then one side of the substrate was cleaned using cotton wool with HCL and later with distilled water and placed in Petri dish to annealed at constant temperatures of 100°C for 15minutes in an oven. The mass of chemical reagent for the various molar solutions was calculated from the relation below.

$$m = \frac{D_c \times D_v \times W}{1000} \tag{1}$$

Table 1. Constituents Precursors

Reagent/Concentration	Bath Temperature (°C)	Deposition Period	Samples Code
$ZnSO_4.5H_2O$ = 0.10M $SC(NH_2)_2$ = 1.20M NH_3 = 3M	50.0	60minutes	1H
$ZnSO_4.5H_2O$ = 0.10M $SC(NH_2)_2$ = 1.20M NH_3 = 3M	50.0	120minutes	2H
$ZnSO_4.5H_2O$ = 0.10M $SC(NH_2)_2$ = 1.20M NH_3 = 3M	50.0	180minutes	3H

Where m is the mass of salt required, D_c is the required concentration; D_v is the volume of distilled water required and W is the molar mass of the chemical salt. Table 1 shows the constituents of precursor.

2.3. 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:

$$t = \frac{w_2 - w_1}{A\rho} \times 10^4 \mu m \tag{2}$$

w_1 and w_2 are the weights of the substrate before and after film deposition in gm., A is the area of film deposition in cm^2 and ρ is the theoretical density of ZnS.

2.4. 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 was done for each sample. The absorbance of the thin films were measured using DOUBLE BEAM UV/V in 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 (6), (7), (8) and (10), respectively.

$$E = hf \tag{3}$$

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

$$f = \frac{c}{\lambda} \tag{4}$$

Where f is frequency of radiation, c is the speed of light with numerical value $3 \times 10^8 ms^{-1}$ while λ is the measured wave length

$$E = \frac{hc}{\lambda} \tag{5}$$

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

$$E = \frac{1243}{40\lambda} \tag{6}$$

Table 2. Table 2: Thickness Measurement of Deposited ZnS Thin Film at Different Deposition Time [**D** = Deposition, **Substr** = Substrate, **MSbeforeD** = Mass of Substrate Before Deposition, **MSafterD** = Mass of Substrate After Deposition]

Time of **D.**	Length of **Substr.** (cm)	Breath of **Substr.** (cm)	Area $(cm)^2$	**MSbeforeD** (g)	**MSafterD** (g)	Change in Mass (g)	Film Thickness t (m)
1 h	19.35	4.1	79.335	5.123	5.159	0.360	4.12
3 h	19.35	4.1	79.335	5.135	5.183	0.480	4.15
3 h	19.35	4.1	79.335	5.175	5.327	0.152	4.23

The transmittance of the films were obtained from the relation below

$$T = 10^{-A} \tag{7}$$

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

$$R = 1 - (A + T) \tag{8}$$

The absorption coefficient α was calculated using

$$\alpha = A \times 10^{\lambda} \tag{9}$$

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

$$(\alpha h\nu)^2 = A(h\nu - Eg)^2 \tag{10}$$

3. Results and Discussion

3.1. Thickness of the film

The result of thickness of ZnS thin film grown at different deposition time is shown in table 2. The table shows that the thickness of film deposited on glass substrates increases as deposition period increases. This is in good agreement with [14].

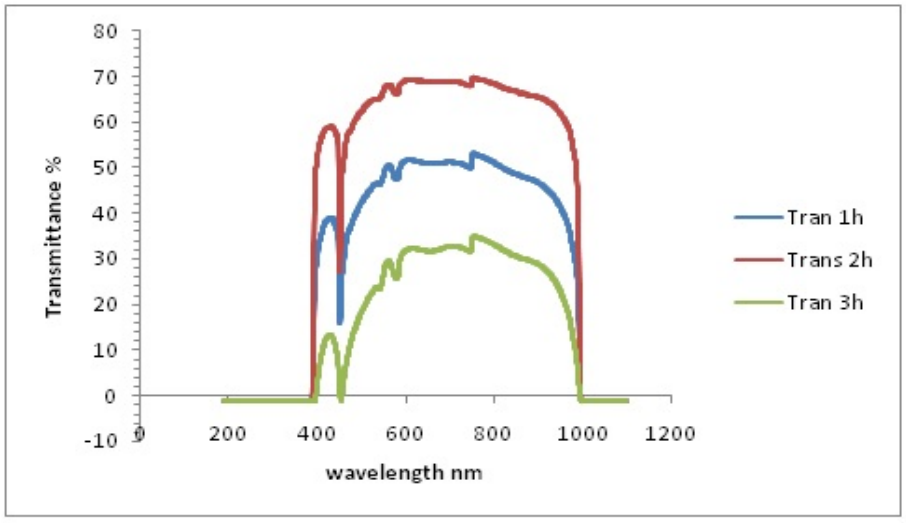

Figure 1. The transmittance spectral of ZnS at different deposition time

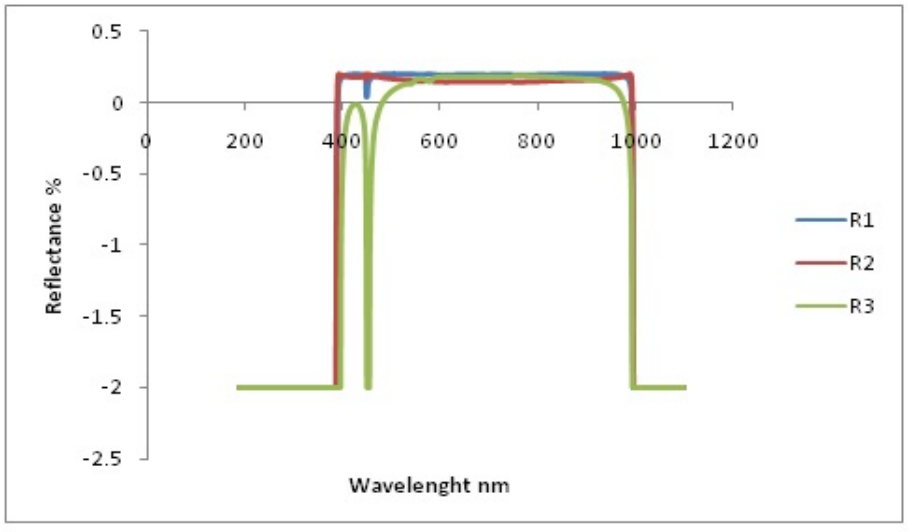

Figure 2. The reflectance spectral of ZnS at different deposition time

3.2. *Optical properties*

The transmittance and reflectance spectra of synthesized ZnS thin film at different hours are shown in figures 1 and 2 below. These spectral (Transmittance spectral and Reflectance spectral) read from 190nm 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 film deposited for 2 hours shows the highest transmittance of 72°C while the one deposited for 3 hours show the lowest transmittance of 37°C and a film deposited for 1 hour has a transmittance of 55°C. Also, the reflectance spectra reveal that the film has the same percentage of 0.3°C for all depositions time. The optical band gap energies of the film were extrapolated and show in figure 3, 4 and 5 for the film deposited for 1 hour, 2 hours and 3 hours respectively. The values of band energies are 3.60eV, 3.70eV and 3.80eV for the film deposited for 1 hour, 2 hours and 3 hours respectively. The result of the band gap for the film deposited for 1 hour is in agreement with the reported bang gap of 3.6eV of bulk ZnS, while the film deposited for 2 hours and 3 hours have an energy gap of 3.7eV and 3.8eV respectively. This similar higher band gap energies of

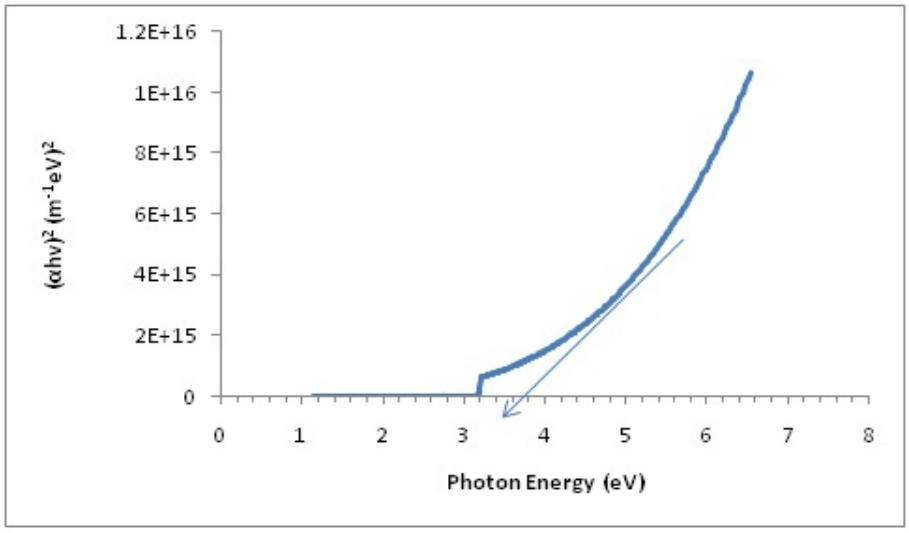

Figure 3. Graph of hv (eV) against $(\alpha hv)^2$ for ZnS thin film deposited for 1 hour

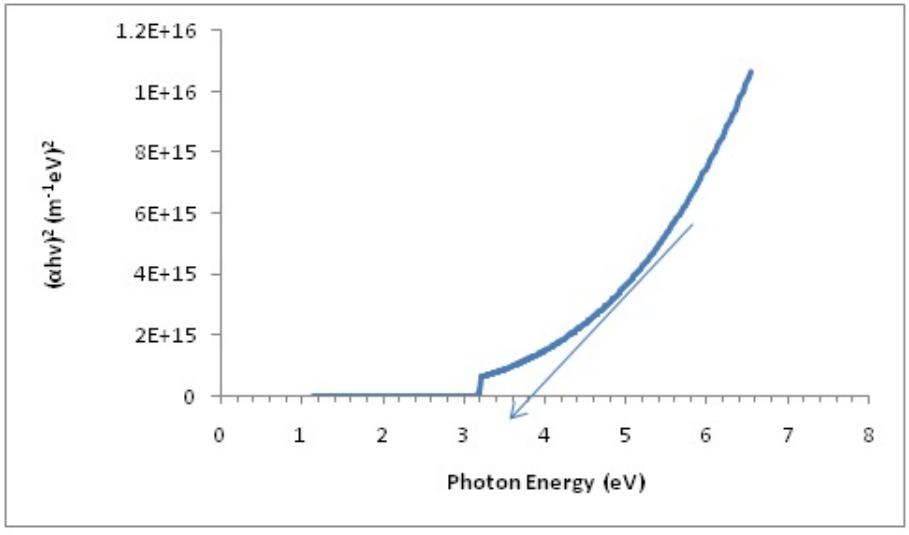

Figure 4. The graph of hv(eV) against $(\alpha hv)^2$ for ZnS thin film deposited for 2 hours

3.84eV-3.96eV were reported by [6]. Also, [1] reported 3.89eV-3.96eV for ZnS band gap energy. It is seen that the band gap energy increases as the time of deposition increases. This agrees with the results of [15]. This wider band gap 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.

4. Conclusion

ZnS thin films were successfully deposited on the glass substrate using a chemical bath deposition method. The effect of deposition time 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 from 3.6 eV to 3.8 eV as the time of deposition increases. The morphological properties of all the film are rough and

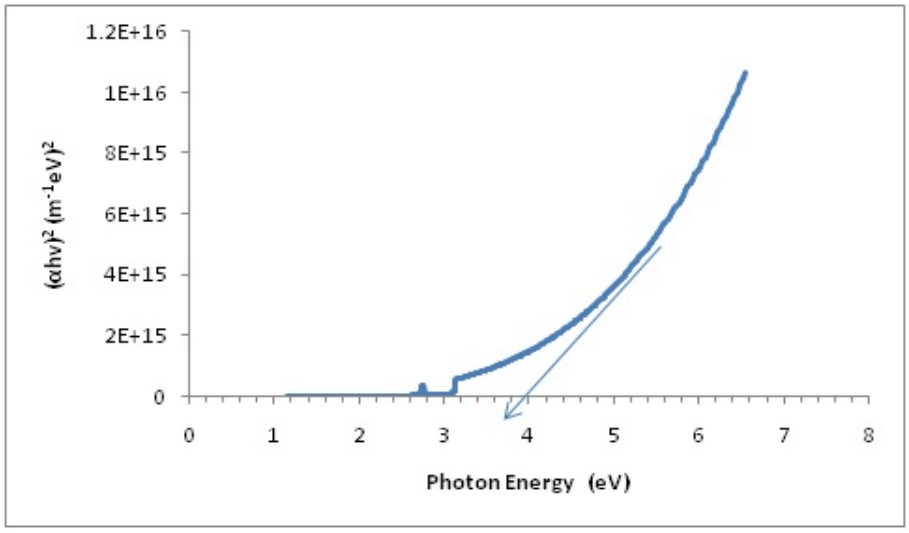

Figure 5. The graph of hv(eV) against $(\alpha hv)^2$ for ZnS thin film deposited for 3 hours

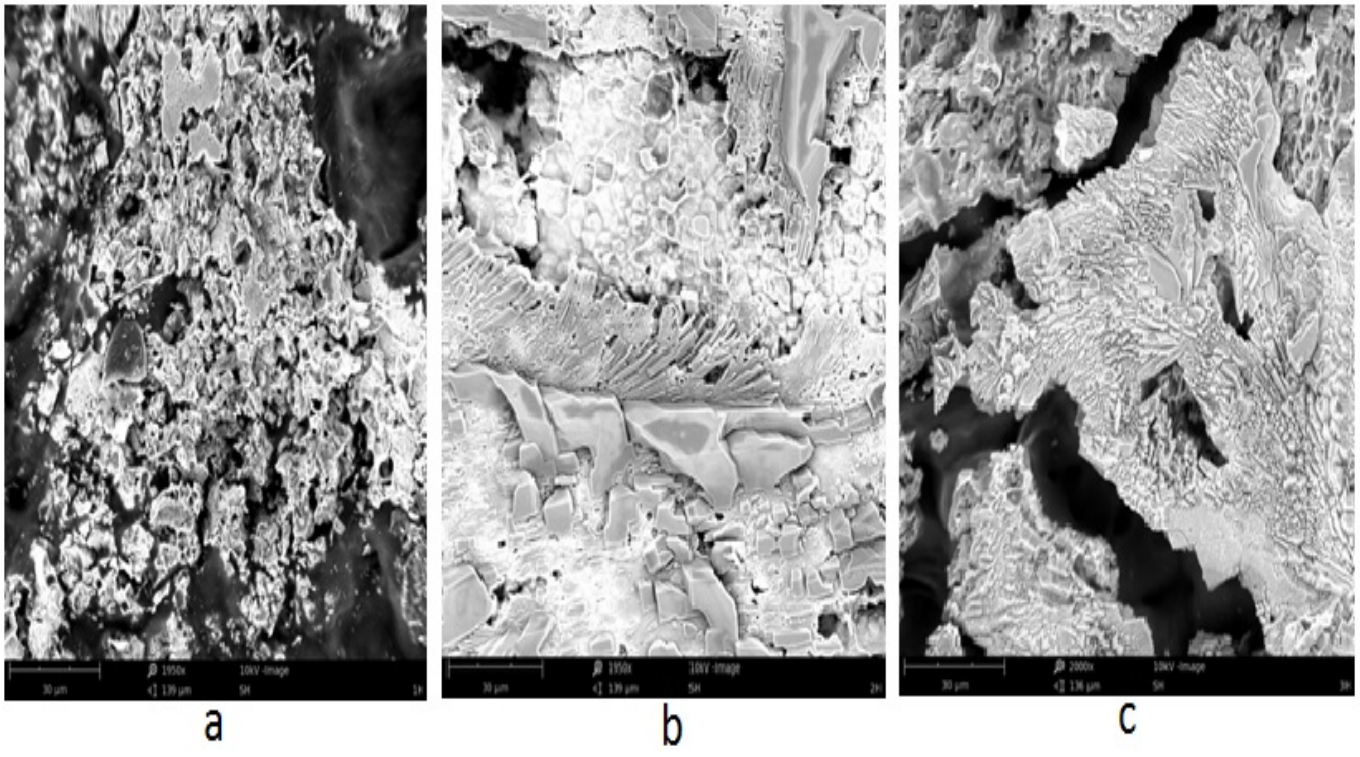

Figure 6. SEM images of ZnS thin films (a=1H, b=2H and c=3H)

dense. But the film deposited for 3 hours shows that the grains are more connected. All these results indicate that the films can be used as a window layer in the fabrication of thin film hetero-junction solar cell.

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