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Preparation and Characterization of Zns Thin Film for Solar Radiation Control Coating

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ABSTRACT
The aim of solar radiation control is to decrease the amount of radiation penetrating into the interior of a building. The optical characterization and growth rate of thin film prepared using chemical bath deposition (CBD) method have been examined. Results shows that the film thickness increases as the thiourea concentration increases in the bath. An increase in the chemical bath temperature also leads to increase in deposition of the film. The transmittance of the ZnS films in the visible region decreases from about 81% about 18% while reflectance for the films produced was found to be between 10% and 20%. Energy band gap of 3.64eV was obtained from the extrapolated graph of photon energy against absorbance coefficient. The results have shown that ZnS can provide necessary illumination into the interior building and prevent over-heating.

I. SECTION I: INTRODUCTION

Zinc Sulfide (ZnS) semiconductor material is an important thin film receiving ever increasing attention. It is a low-cost, environmentally friendly compound, with convenient mechanical properties, such as good fracture strength and hardness (Pino et al., 2017).Its applications includes electroluminescent panels (Karl et al., 2002), field-effect transistors (FET), photoluminescence, light-emitting diodes (LEDs), field emission (FE), sensors, dye-sensitized solar cells, and photocatalysisbased on ZnS nanostructures (Xianfu et al., 2013), opto-electronics devices such as light emitting diode in blue to ultravioletspectralregionduetoitswidebandgapofE$_g$= 3.5-3.84eV(Elidrissietal.,2001)andn-typeconductivity(Poulomietal.,2006), ZnS is applicable in optics for use as a reflectors (Ruffner et al., 1989) and it also been used as a dielectric filters (Ledger, 1979), this is because it has a high transmittance in visible range as well as high refractive index (2.35).The ZnSThinfilmissuitablefor use as awindowlayerinheterojunctionphotovoltaicsolarcells, this is because itsewidebandgapdecreasesthewindowabsorptionlosesandalso improveson theshortcircuitcurrent ofthecell(Poulomietal.,2006).Therearevarioustechniquesusedtodeposit ZnSthinfilms,includingspraypyrolysis(Elidrissietal.,2001),ChemicalBathDeposition(CBD)(Lietal.,2010),RFmagnetronsputtering(Dongetal.,2012),sol-geldeposition(Anilaetal.,2015),cathodicelectrodeposition(Anuaretal,.2010)anddipcoating(Anilaetal.,2015).However,chemical bath techniqueforpreparingt hinfilms(Balachanderetal.,2015)iscosteffective.It is an interesting techniquebecauseitiscapableofdepositionofuniform, homogeneouslayers and opticallysmooth films, inexpensive andsimple to use. AlsoincomparisonwithCdS,theadvantagesofZnSincludeitsnon-toxic(Anilaetal.,2015)andenvironmentallysafeto handleaswellasitsabilitytoprovidebetterlatticematching(Dongetal.,2012).ZincSulphidethinfilmwasdeposited bychemical bath depositionmethodonaglasssubstrate.The nature of the substrate is a very important factor in determining the characteristics of the film. Often substrates can have a substantial effect on the film structure, tending to make the film more

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crystalline. Films deposited on amorphous substrates such as glass is usually composed of a large number of small polycrystalline grains. Use of single crystal substrates together with the proper deposition parameters; can result in the formation of single crystal films. In order that the film can be of this quality, the deposition rate must be slow enough and the substrate temperature high enough, so that the impinging atoms can arrange themselves to a sufficient degree. The effect of Ammonia(NH_3) on the deposition of ZnS film using chemical bath deposition method was report by (Vidal et al., 1999) and Mokili et al., (1995) reported the effect of inclusion of ammine in the chemical composition. It was observed that the addition of the compounds leads to increase in growth rate and deposition of films.The growth rate of the coatedthinfilmwasstudied by varying the composition of reagents at a fixed time and also by varying the time of deposition at a fixed molarity. The remaining parts of this work are structured as follows: In section II we discuss the materials and methods, section III is on results and discussion. and in sectionIV we conclusion on the suitability of ZnS for solar control system.

II. SECTION II:MATERIALS AND METHOD

Materials

Bath Constituents

The Zinc sulfide film was deposited from chemical bath with the constituents in Table 1. The reagents were prepared by dissolving an appropriate amount of the solid in distilled water.

Table 1: Reagent constituents for ZnS thin film deposition at different molar concentration

Composition in parameter (X/mol)	**Concentration of ZnCl/mol (g)**	**Concentration of $(NH_2)_2CS$/mol (g)**
0.2	6.8145	3.806
0.4	13.629	7.612
0.6	20.444	11.418
0.8	27.258	15.224
1.0	34.073	19.030

Ammonia (NH_3) solution (25%) was added to give a pH of between 10 and 12for the bath. Other materials used includes glass slides, beakers, Bunsen burner, weighing machine, Tallysurf, infrared spectrophotometer, (Pu 9700 series), Absorption spectrophotometer (PVC UNICAM SPE-400 UN/VIS), conducting paste, Halogen lamp distilled water and oven. The zinc chloride was the source of cation (Zn^{2+}) and thiourea was the source of anions (S^{2-}). By varying the relative ration of zinc chloride and thiourea ions using the equation below, ZnS thin films with composition parameters X = 0.2m, 0.4m, 0.6m, 0.8m and 1.0m were deposited on the glass substrates.

$$X = \frac{\text{concetration in grams}/dm^3}{\text{molar mass}} \quad (1)$$

Methods

Chemical bath deposition method has advantage over other forms of thin film deposition methods due to its great flexibility of substrate selection. In other to select the substrate for this work, the possibility of film attachment and substrate not dissolving in the bath were considered.We used pre-cleaned commercially available glass slides (3.0cm x 2.5cm x 1.0mm). The films were deposited on the glass slides in an enclosed room under the following conditions:

- Temperature of the chemical bath use are 27^oC and 70^oC
- The duration for deposition was varied from 30 – 120 minutes
- The Zn:S ratio was varied as 1:1 and 1:2.

The bath constituents were mixed in a glass trough and then poured in 250ml beaker where the glass slides were immersed in the bath. The chemical bath was then stirred gently as long as the deposition lasted considering the deposition conditions listed above. The substrates were removed from the bath and were allowed to dry in an oven, the deposited samples obtained by this method were noted to be smooth, uniform, adherent and pinhole free. The effect of the above variation was studied on the growth rate, optical properties and electrical properties.We characterizedthethinfilmsbymeasuringthegrowthrat e by observing the mass loss of the CdS on substrate and the plane substrate andopticalproperties using infrared spectrophotometer (Pu 9700 series) and (PVE UNICAM SPE- 400 UV/VIS).

III. SECTION III – RESULTS AND DISCUSSIONS

Growth Rate

The Thinfilms thickness (t) was observed by measuring the mass of the glass slides before and after deposition has taken place. The mass of ZnS was used to determine the thickness of the film by using the density formula. Table 2 shows the relationship between the film thickness and deposition time, this was measured by varying the chemical bath temperature and Zn:S ratio. Figures 1 and 2 is the plot of deposition time against film thickness at different ratios of Cd:S for bath temperatures 27^{o}C and 70^{o}C respectively. It wasobserved that deposition can be speeded up by using higher thiourea concentration in the bath. Also an increase in the bath temperature lead to an increase in film deposition this phenomenon is due to the increase in kinetic energy of the ions.

Table 2: Effect of deposition time, bath temperature, $T_B$and Zn:S ratioon ZnS film thicknesst.

Samples	Deposition Time (mins)	Film Thickness t (nm)			
		$T_B = 27^oC$ Cd:Tu =1:1	$T_B = 70^oC$ Cd:Tu =1:1	$T_B = 27^oC$ Cd:Tu =1:2	$T_B = 70^oC$ Cd:Tu =1:2
A	30	104	215	235	425
B	40	126	317	292	481
C	50	167	431	311	579
D	60	213	562	367	716
E	70	352	592	423	886
F	80	455	648	535	990
G	90	660	772	750	1001
H	100	832	869	930	1120
I	110	972	1210	1367	1695
J	120	1003	1443	1577	1809

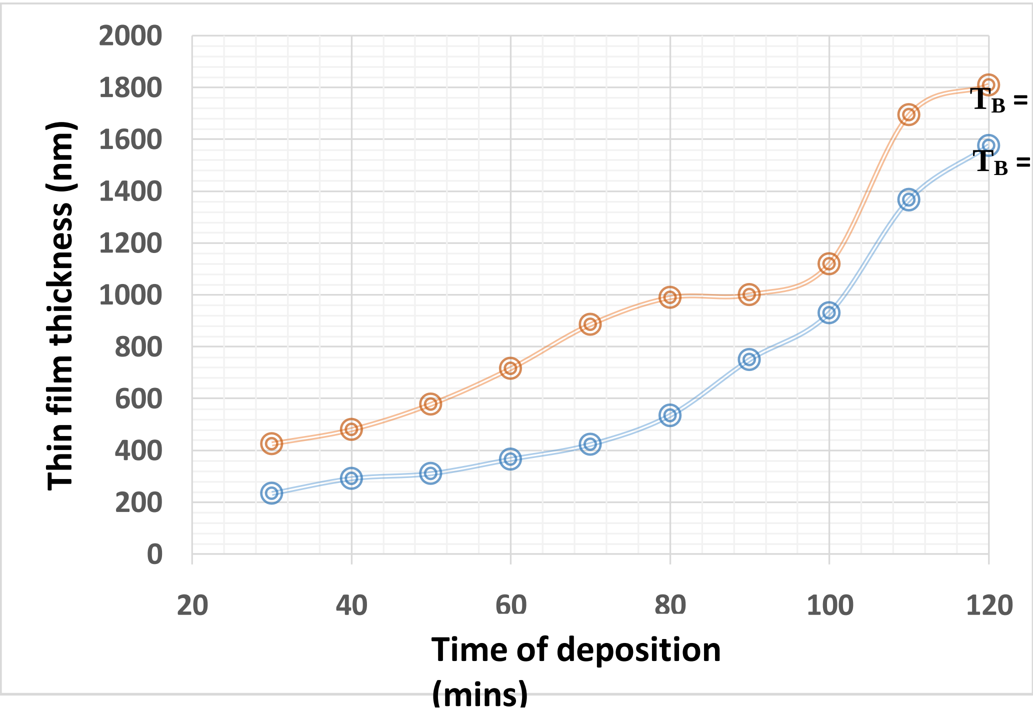

Figure 1: Graph of deposition time against thin film thickness t(nm) for different chemical bath temperatures**T_B**. Zn:S deposition ratio is 1:1.

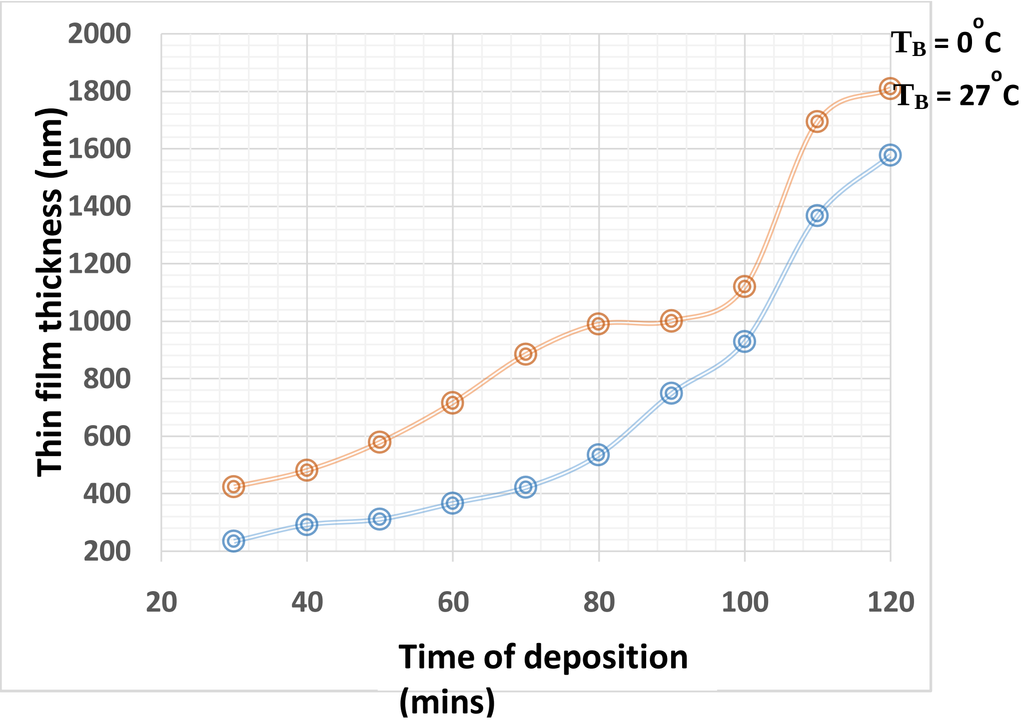

Figure 2: Graph of deposition time against thin film thickness t(nm) for different chemical bath temperatures$\mathbf{T_B}$. Zn:S deposition ratio is 1:2.

OpticalCharacterization

Study of opticalpropertiesformsaconsiderablepartwhenevaluatingathinfilm.We obtained the IR-UV transmittance spectra of the film at room temperature in the spectral range of 2.5 – 100 µm by UV-IR spectroscopy.For this study we made use of samplesA –E deposited using ratio 1:2 for Zn:S at 70^{o}C bath temperature.After deposition the films were rinsed in distilled water and kept to dry after which a side of the substrates were etched with HCl. Mathematically, we obtained both absorbance (A) and reflectance (R) spectra from transmittance spectra (T) using equations 2 and 3. The absorbance coefficient (σ) was calculated using equation 4.

$$T = 10^{-A} \quad (2)$$

$$R = 1 - (T + A) \quad (3)$$

$$\sigma = \frac{1}{t}\left(\ln\frac{1}{T}\right) \quad (4)$$

The relationship between absorbance coefficient (σ) and photon energy (eV) is;

$$(\sigma h\vartheta)^2 = A\left(h\vartheta - E_g\right) \quad (5)$$

Tables 3 and 4present the results obtained from the optical parameters in the UV-IR spectrum. Figures 3 shows the graphs of transmittance against wavelength using UV/VIS spectrophotometer. We observed from the plot that transmittance decreases from sample A to E as the ZnS film thickness increases. The transmittance of the ZnS films in the visible region decreases from about 78% to 18% while reflectance was found to be between 20% and 7%. In the infrared region transmittance decreased from 81% to 44% while reflectance was found to be between 20% and 10%.The results obtained confirmed that ZnS thin film is applicable for solar radiation control, this is in agreement with a similar work reported by – Fei-Peng (2014). Using the transmission results obtained for sample A and the square of the calculated absorption coefficient σin (Table 5), we obtained the semiconductor energy band gap by plotting the graph of photon energy (hυ) against $(\alpha h\upsilon)^2$as shown in figure 4, by linear extrapolation of the graph the direct band gap of 3.64eV was obtained which is in agreement with reported band gap range of ZnS.

Table 3: Optical parameters of ZnS films for visible spectrum (**T_B = 70 ^oC**).

Sample Label	t (nm)	T (%)	A (%)	R (%)
A	425	78	11	11
B	481	62	21	17
C	579	41	39	20
D	716	27	57	16
E	886	18	75	7

Table 4: Optical parameters of ZnS films for infrared spectrum (**T_B = 70 ^oC**).

Sample Label	t (nm)	T (%)	A (%)	R (%)
A	425	81	09	10
B	481	70	16	14
C	579	57	24	19
D	716	52	28	20
E	886	44	36	20

Table 5: UV-IR spectrum data of ZnS film (sample A) to calculate energy band gap

$\sigma^2 x10^{12} (m^{-2})$	λ (μm)	$\vartheta = \frac{v}{\lambda}$	$h\vartheta x10^{-19}$	$(h\vartheta)^2 x10^{-38}$	$(\sigma h\vartheta)^2 x10^{-16}$
0.111	0.79	3.820	2.533	6.414	0.712
0.043	0.55	5.413	3.589	12.888	0.558
0.038	0.60	5.000	3.319	11.022	0.424
0.031	0.65	4.621	3.064	9.388	0.291
0.025	0.64	4.698	3.115	9.702	0.242
0.022	0.63	4.709	3.122	9.749	0.217
0.019	0.64	4.683	3.105	9.644	0.182
0.016	0.64	4.686	3.107	9.653	0.153
0.012	0.63	4.719	3.129	9.794	0.122
0.009	0.61	4.918	3.261	10.634	0.104
0.007	0.69	4.734	3.139	9.851	0.072
0.006	0.74	4.056	2.689	7.232	0.041
0.005	0.99	3.038	2.014	4.057	0.023
0.005	1.79	1.679	1.113	1.240	0.007

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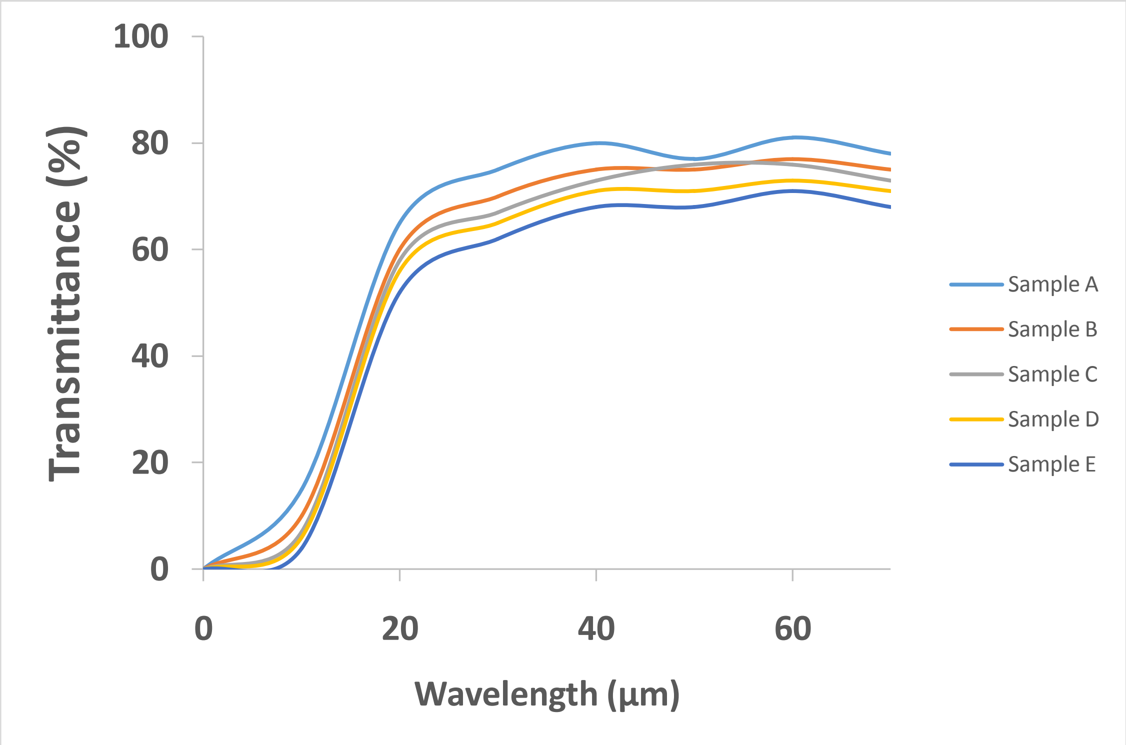

Figure 3: Graph of Wavelength Vs Transmittance for ZnS thin film. The graph was obtained from the UV/IR absorbance spectra.

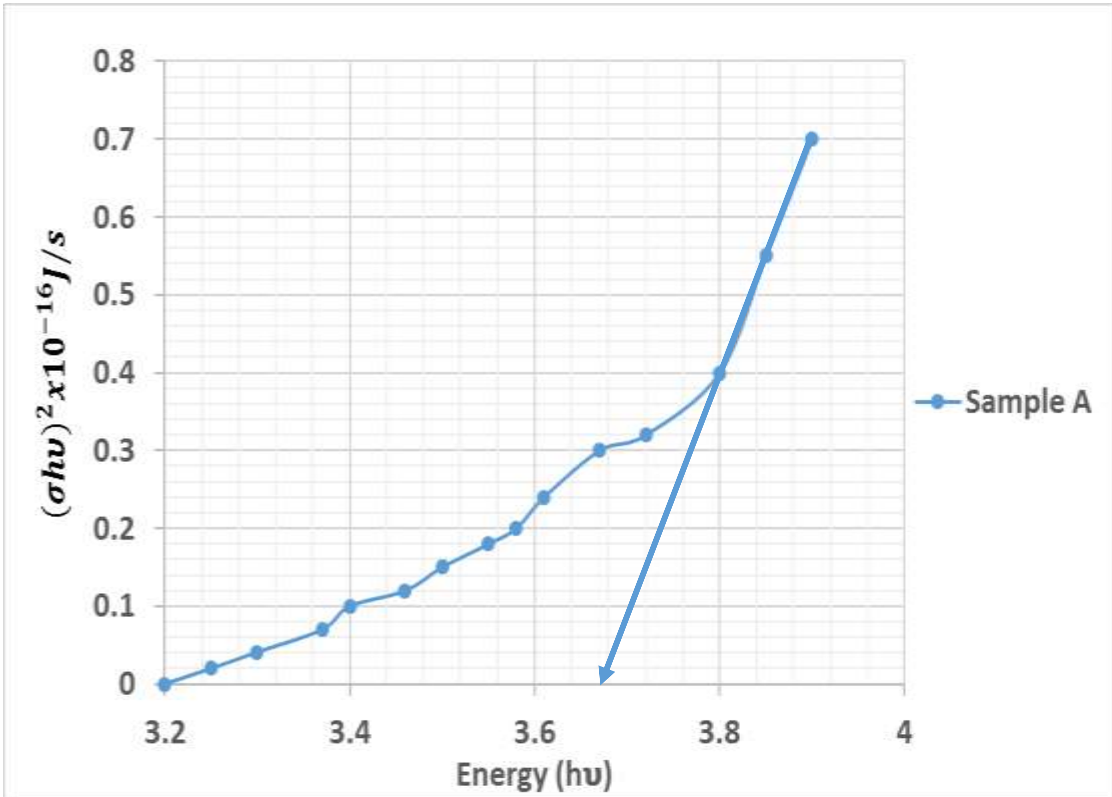

Figure 4: Graph of $(\alpha h\upsilon)^2$ vs photon energy showing the energy gap of ZnS thin film.

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IV. SECTION IV

CONCLUSION

ZnS thin films have been prepared by the chemical bath deposition method using $ZnCl_2$ as the source of zinc and $(NH_2)_2CS$ as the source of sulfide. The chemical bath temperature, duration for deposition and Zn:S ratio were varied to study the growth rate and application of the film for solar radiation control coating.The growth rate measurements reveal that deposition can be speeded up and increased by using higher thiourea concentration and increasing thebath temperatureof the reagents due to an increase in kinetic energy of the ions. A range of transmittance values suitable for solar control application were recorded. Transmittance through the material was observed to decrease as the film thickness increases, these transmittance values provides necessary illumination for most indoor activities. The films with 425 nm thickness deposited at 70°C gave a direct band gap estimated to be 3.64 eV. Band gaps provide information on the density of the electrons which is applicable in to show our appreciation to the study of conductivity of semiconductors.

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