Optical Properties of ZnS Thin Films Annealed at Constant Temperature 250^{o}C and Varying Times Prepared by Chemical Bath Deposition.

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Abstract

*ZnS thin films were successfully deposited using chemical bath deposition technique, from zinc chloride $ZnCl_{2(aq)}$ and thiourea $CS(NH_2)_{2(aq)}$. Liquid ammonia was used as the complexing agent to moderate the mobility of cations in the solution in other to obtain, uniform depositions. The compositions and thicknesses of two representative samples annealed for one hour and three hours, were determined by Rutherford Back Scattering and EDXRF. ZnS thin films were confirmed on the samples, with thicknesses of 40nm and 60nm annealed for three hours and one hour respectively. The percentage ratio of zinc to sulphur for the two samples are 50.1:49.9 and 51.0:49.0 for one hour and two hours annealed at 250^{o}C respectively. Optical properties of the films – Transmittance **T**, Reflectance **R**, Absorbance **A**, Absorption coefficient **α**, Refractive index n, Extinction coefficient **k**, Optical conductivity **σ**, Real and Imaginary parts of dielectric constant ε_1 and ε_2 and Energy band gap E_g, were determined. The energy band gap of the two samples are **3.38eV ± 0.05eV** and **3.33eV ± 0.05eV** with average value of **3.36ev ± 0.05eV.***

Keywords: optical properties, annealing temperature, transmittance, reflectance, extinction coefficient, band gap, refractive index

Introduction

ZnS semiconductor thin films were prepared on glass substrates using cheap chemical bath deposition. ZnS is II-IV group compound material l with wide band gap between 3.40eV-3.70eV depending on the method of deposition. It has useful applications as an antireflection coating for heterojunction solar cells (Bloss, 1988), light emitting diode (Katamaya,1975) electro-luminescence devices and photovoltaic cells in flat panel displays (Beard, 2002), sensors and lasers (Klimov, 2002). Several methods have been adopted in the deposition of ZnS thin films such as Thermal evaporation (Durrani,2000), Spray pyrolysis (Afifi, 1995), Molecular beam epitaxy (Shaoi, 2003), RF reactive sputtering (Shaoi, 2003), Chemical bath deposition (Cheng, 2003). In this work, ZnS thin film have been deposited using Chemical bath deposition method. The effects of time of annealing at constant temperature were studied.

Experiment

The formation of ZnS films on glass substrate by means of Chemical Bath Deposition Technique was based on the reaction between $ZnCl_{2(aq)}$ and thiorea $CS(NH_2)_{2(aq)}$ according to the equation;

$$\mathbf{ZnCl_{2(aq)} + 4NH_{3(aq)} \quad [Zn(NH_3)_4]^{2+} + 2Cl^- \rightarrow}$$

$$\mathbf{[ZnNH_3]_4^{2+} + CS(NH_2)_{2(aq)} \quad ZnS_{(s)} + 4NH_3 + CN_2H_{4(aq)}}$$

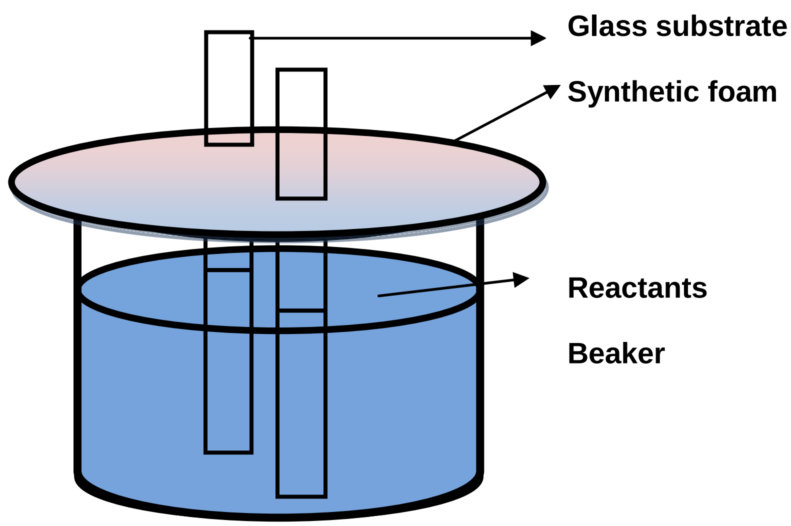

Fig. 1 The Experimental Set-up

An excess aqueous ammonium was added to 20ml of 0.4M solution of $ZnCl_2$ to form a white (**$Zn[NH_3]_4^{2+}$**) which dissolved completely on stirring to form a clear solution. 13ml of 0.6M solution of

$CS(NH_2)_2$ was added to the resulting solution and stirred. 10ml of 0.15M solution of NaOH was finally added to form an alkaline medium for the deposition process to take place. The PH of the final solution was measured to be 9.1 and was done at room temperature. Glass substrates were then immersed vertically into the final solution as shown above and optimum deposition was obtained after four hours

Results and Discussion

Many samples were deposited under different set of conditions of reactant concentration , temperature and PH of solution, as shown in the table in the previous chapter. Four slides were immersed in each beaker representing a given set of conditions. Optimum depositions were observed on the slides immersed in one of the beakers under the conditions;

Concentration and volume of reactants; 20ml of 0.4M $ZnCl_{2(aq)}$ + 7ml of 3M $NH_{3(aq)}$ + 13ml of 0.6M $CS(NH_2)_{2(aq)}$ + 10ml of 0.15M $NaOH_{(aq)}$

Deposition temperature; at 23^{o}C

PH of final solution; 9.1

Deposition time; 4 hours

Annealing temperature; 250^{o}C for two representative samples

Annealing time; one hour and three hours for, each of the two representative samples.

Volume ratio; 20:7:13 which gave the desired deposition.

Composition and thickness measurements

Two representative samples were selected out of the four samples deposited under the same conditions at room temperature of 23^{o}C.**Energy Dispersive X-ray florescence** (**EDXRF**) test confirmed the presence of Zn^{2+}. But to confirm the presence ZnS on the films, the two samples were subjected to **Rutherford Back Scattering** test. The presence of Zn^{2+} and S^{2-} ions were confirmed in the ratio of 0.51:0.49 by number of atoms. This implies that 51% of Zn^{2+} and 49% of S^{2-} are present in the samples deposited. The thicknesses of the films were also determined to be 60nm and 40nm for the samples annealed for one hour and three hours respectively from the **RBS** test as shown in Figs. 3 and 4. The tables 1 and 2 are the **EDXRF** results of one of the two samples and blank glass slide.

Since RBS can determine both composition and thickness, only one sample was scanned for XRF while both of the samples were scanned for RBS.

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EDXRF quantitative analysis

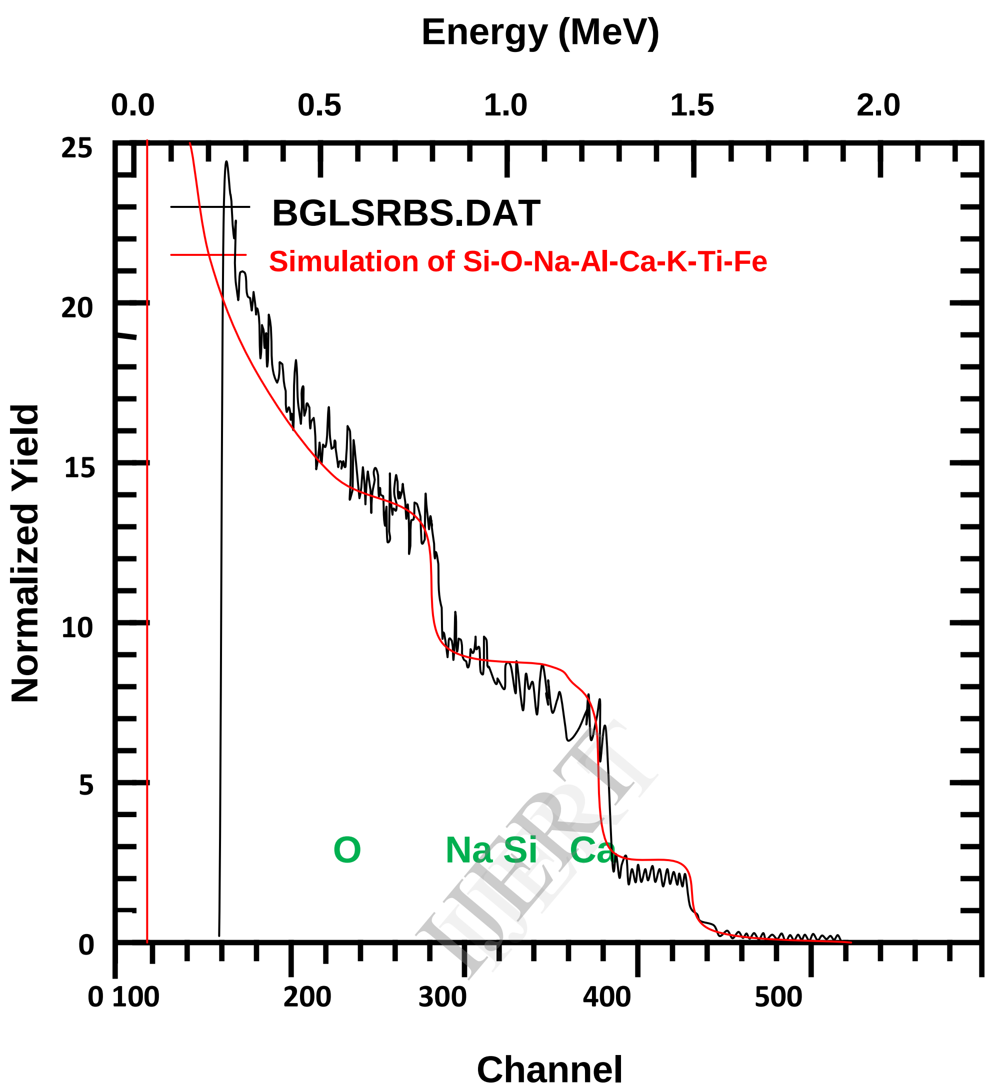
Report created on 10-04-2012
Calibration file: C:\AXIL\SPECT\JMU2012A\IMU 01.CAL
Created on: 10-03-2012
Tube excitation: Ag Anode Operating at: 25.0kV
Measurement date: 10-03-2012
Live time: 1000 sec
Tube current: 0.050mA
Method used: DIRECT COMPARISON OF COUNT RATES

Table 1 EDXRF result for plane glass

Sample:	Blank GLASS
ELEMENT	CONCENTRATION
K	3.066 ± 0.338 %w
Ca	9.278 ± 0.217 %w
Ti]	548.087 ± 34.683 ppm
Mn< 12.127	
Fe	167.755 ± 4.675 ppm
Ni	10.985 ± 3.092 ppm
Cu	35.629 ± 5.418 ppm
Zn	164.429 ± 15.984 ppm

Table 2 EDXRF result for three hours annealed sample

ELEMENTS	CONCENTRATION	
K	2.033 ± 0.362	%w
Ca	9.141 ± 0.228	%w
Ti	255.946 ± 23.031	pm
Mn	25.473 ± 2.361	pm
Fe	290.616 ± 8.285	pm
Cu	39.820 ± 5.330	pm



Identifier: BGLSRBS.DAT

Beam: 2.20 MeV 4He+ 10.00 uCoul @ 0.58 nA

Geometry: IBM Theta: 0.0 Phi: 15.00 Psi: 0.00

MCA: Econv: 4.403 -22.670 Firstchan: 0.0 NPT: 1022

Detector: FWHM: 12.0 keV Tau 0.5 Omega: 0.833

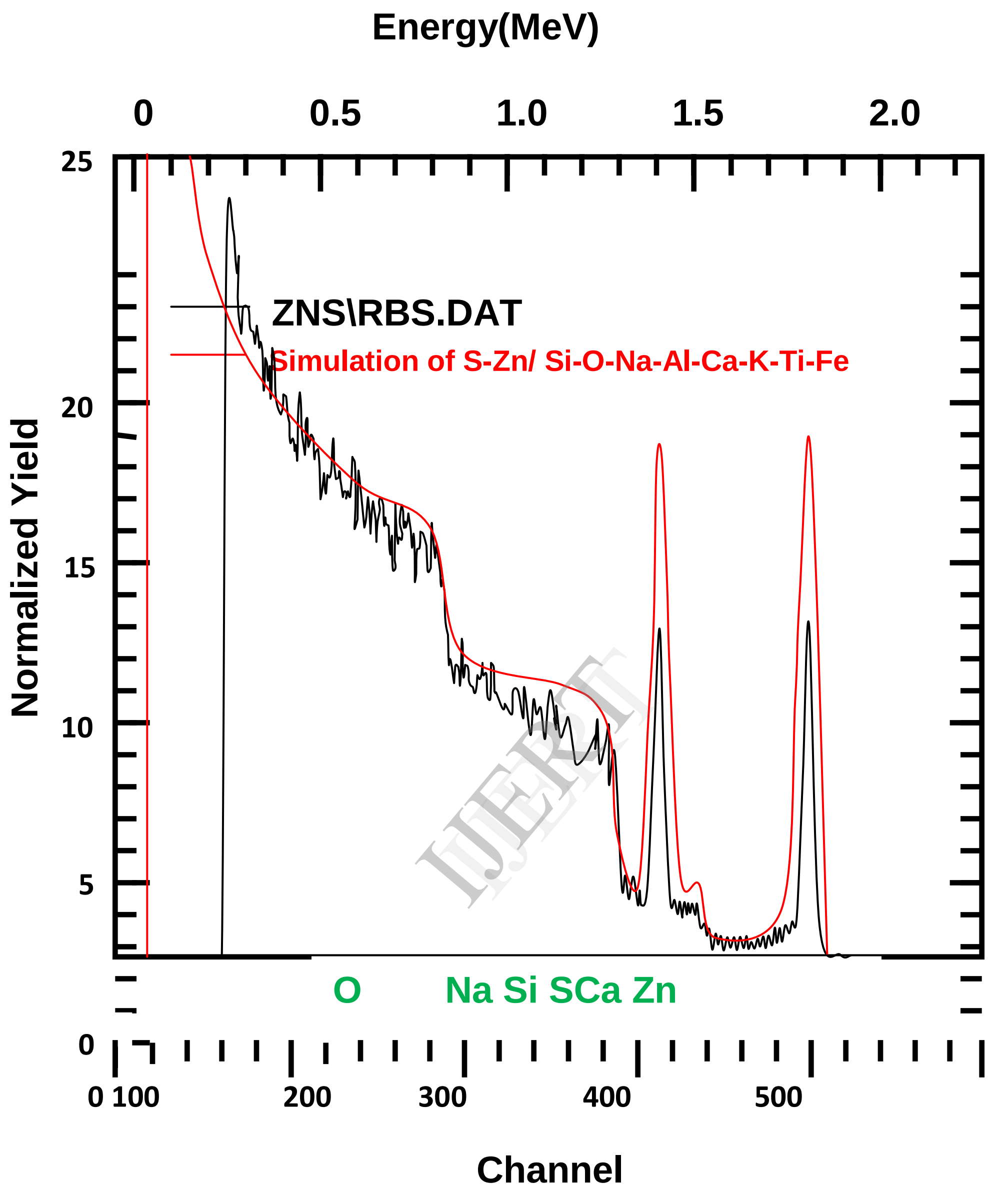
Correction: 1.0000

 # Thickness Sublayers Composition …

1 9000.00 nm auto Si 0.186 O 0.551 Na 0.126 Al 0.096

Ca0.031 K 0.005 Ti 0.002 Fe 0.003

Fig. 2 RBS result for blank glass substrate



LAYER	Thickness	Sublayers	Composition …
1	40.00 nm	auto	Zn 0.51 S 0.49
2	9000.00 nm	auto	Si 0.186 O 0.551 Na 0.126 Al 0.096 Ca 0.031 K 0.005 Ti 0.002 Fe 0.003

Fig. 3 RBS result for three hours annealed sample.

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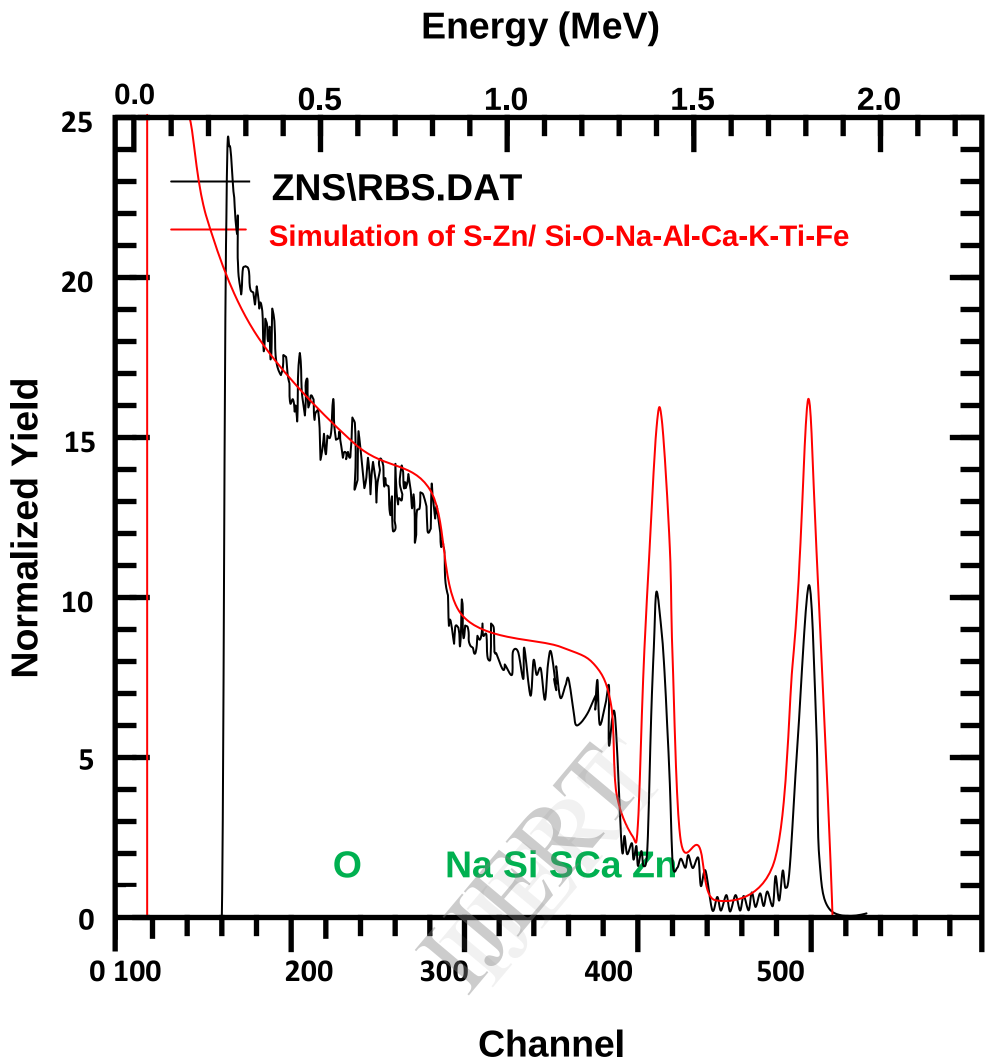

LAYER Thickness Sublayers Composition …

1 60.00 nm auto Zn 0.501 S 0.499

2 9000.00 nm auto Si 0.186 O 0.551 Na 0.126 Al 0.096

Ca 0.031 K 0.005 Ti 0.002 Fe 0.003

Fig. 4 RBS result for one hour annealed sample.

Optical properties

Transmittance

The transmittance, which is the ratio of the incident intensity to the transmitted intensity of the radiation was measured **using UVI double beam Spectrophotometer with serial number 061514.**

Absorbance, reflectance and other optical properties were calculated from the values obtained from the transmittance values using appropriate equations.

For the sample annealed for three hours, T increased from 0.45 to 0.735 as the wavelength increased from 338nm to 978nm. For the sample annealed for one hour, it increased from 0.62 to 0.872 within the same range of wavelength. This means that ZnS can be used as window in infrared optics, since it has high transmittance in the near infrared region. Also it can be used as UV shield, since it has low transmittance in the UV region. The graphs for the two samples are shown in **Fig. 5** .

Absorbance

The absorbance is calculated using Eqn. (1)

$A = \log_{10}\{1/T\}$ …………………….1

There was a sharp fall from about 0.4 to 0.27 in the absorbance from 320nm to 338nm (which is a UV portion), for the three hours annealed sample. It slowly falls to about 0.13 and 0.05 for the three hours and one hour annealed samples respectively, in the infrared region. This show that suitably long time annealed ZnS will be a good UV absorber and can be used as UV sensors in UV spectroscopy. The graph of absorbance for the two samples are shown **Fig.6**

Reflectance

This is the ratio of the reflected intensity to the incident intensity. It was calculated using Eqn.(2)

$R = 1 – (T+A)$…………………2

ZnS showed a small almost linearly decreasing reflectance with increasing wavelength. For the one hour annealed sample, the reflectance decreased from 0.19 to 0.06 from UV (320nm) down to infrared (996nm). For the three hours annealed sample, it dropped from 0.2 to 0.13 within the same region. In general, the reflectance is relatively low. It can therefore be used in multi-film technology to form antireflection coatings of almost zero reflectance in the visible region, for solar energy collectors. The graph R for the two samples is shown in **Fig. 7**

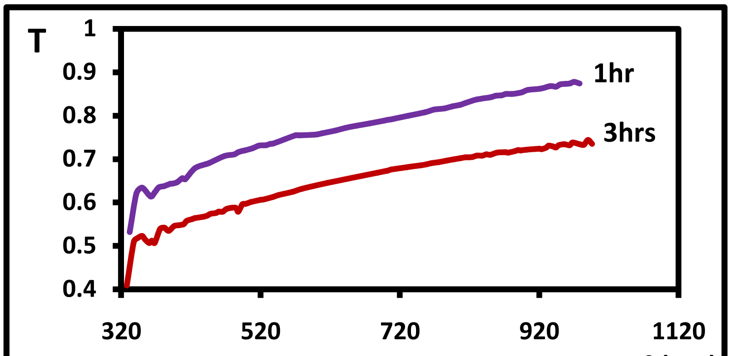

Fig. 5 Transmittance against wavelenght

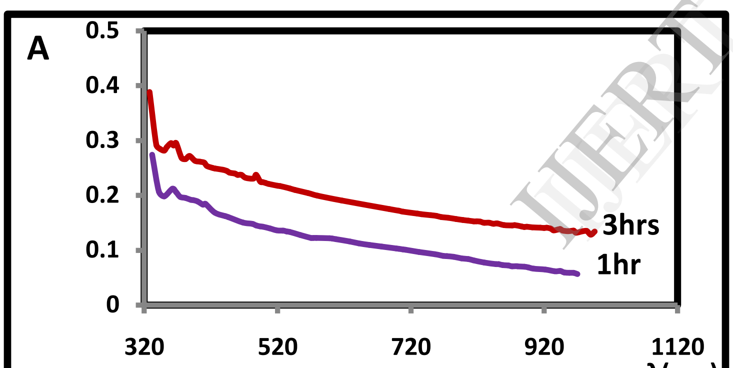

Fig. 6 Absorbance against wavelenght

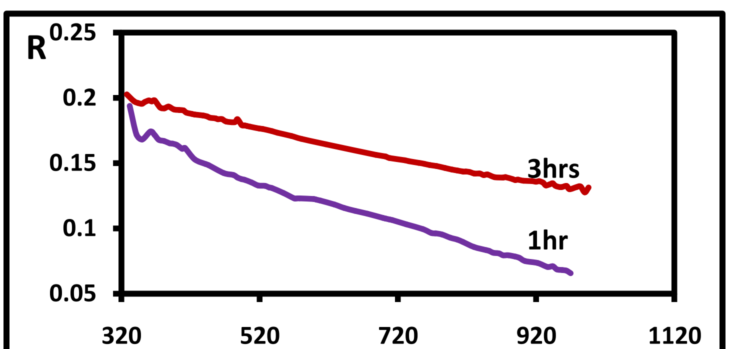

Fig.7 Reflectance against wavelenght

Absorption coefficient α

This is the attenuation per unit thickness of the film. It varies with wavelength of the impinging electromagnetic radiation. It is related to the transmittance by;

α = {ln[1/T]}/x ……………………………(3)

Where x is the thickness of the films (40nm and 60nm). **Fig. 8** shows the effect of annealing time on the absorption coefficient of ZnS thin film. It decreased from 16833616/m to 7731156/m as the wavelength increased from 338nm to 978nm, for the three hours annealed sample. Within the same range of wavelength, it decreased from 7940403/m to 2263662/m, for the one hour annealed sample

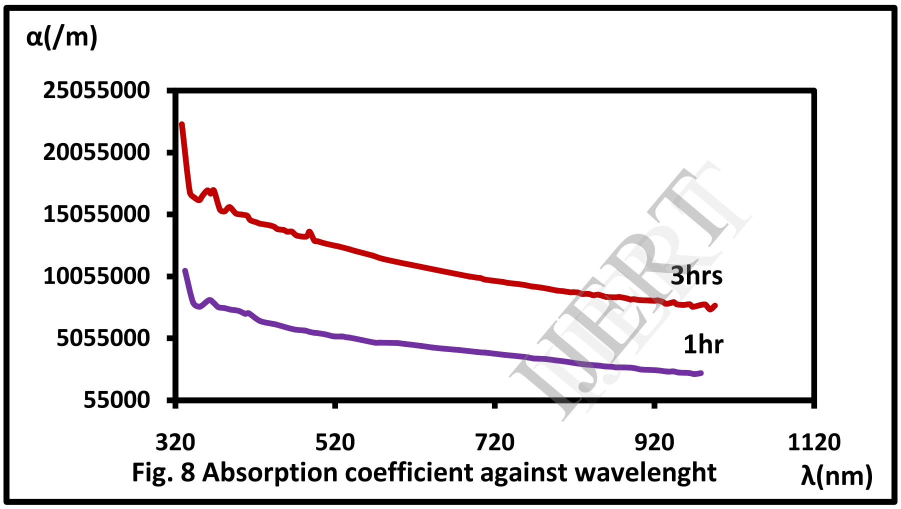

Fig. 8 Absorption coefficient against wavelenght

Refractive index, n

The refractive index is given be equation (7)

$$n = \{1+(R)^{1/2}\}/\{1-(R)^{1/2}\} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

For the sample annealed for three hours, the refractive index was decreasing from 2.638 at 320nm (near UV) to 2.136 at 996nm (near infrared). For the other sample, it was from 2.57 to 1.70 within the same wavelength range. In each case, the refractive index was decreasing with increasing wavelength. Compared to glasses which have constant refractive index throughout the entire visible spectrum, ZnS can separate or disperse visible wavelengths as each will be deviated by different angles due to the varying refractive index in the spectrum. So the different wavelengths that made up a beam of light can be known by placing ZnS films close to each other in front of the beam so that the be beam will be obliquely incident on the films. On emerging from the last film, the colours would fully be separated.

The graphs of n of the two samples are shown in **Fig. 9**. In the figure, longer time annealing has the effect of reducing the slope of n. n decreases faster with increasing wavelength for the one hour annealed sample.

Extinction Coefficient, k

This is a measure of absorption when the radiation travels a distance in the sample equal to its wavelength in free space. It is related to the absorption coefficient α by;

$$K = \alpha\lambda/4\pi \quad \text{……………………(5)}$$

K increased linearly from 0.45 to 0.6 from 338nm to 978nm, for the three hours annealed sample. For the sample annealed for one hour , it is almost constant within the same spectrum with average value of about 2.0 as shown in **Fig. 10 .**

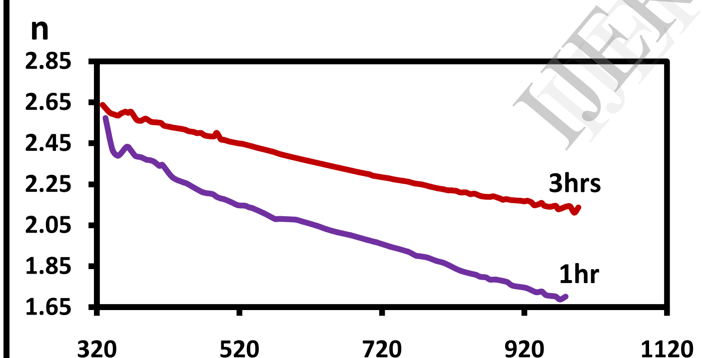

Fig.9 Refractive index against wavelenght

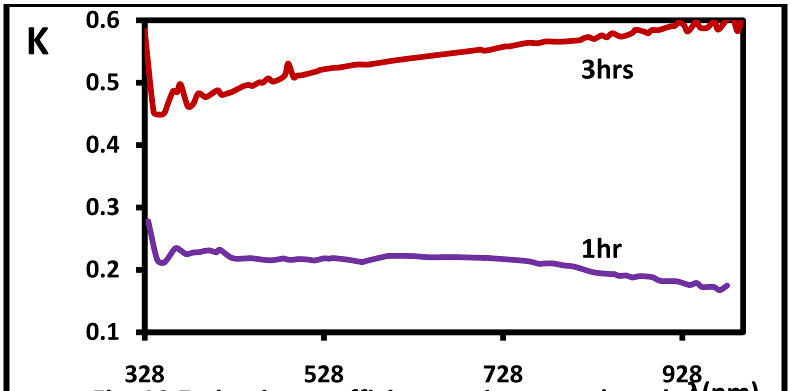

Fig. 10 Extinction coefficient against wavelength

Real dielectric constan

This is given by the equa

$$\varepsilon_1 = n^2 - k^2 \text{ ....(6)}$$

For the three hours annealed sample, ε_1 decreased from 6.55 to 4.18, from 338nm to 978nm or and for one hour annealed sample, decreases from 6.55 to 2.88, within the same wavelength range as shown in **Fig.11** .

Imaginary dielectric constant, ε_2

It is given by the equation

$$\varepsilon_2 = 2nk \text{ ....(7)}$$

It is approximately constant with the value of about 2.4 throughout the entire range of wavelengths (338nm to 978nm), for the three hours annealed sample. But it decreased from 1.43 to 0.589 as the wavelength increased from 338nm to 978nm, for the one hour annealed sample as shown in **Fig. 12**.

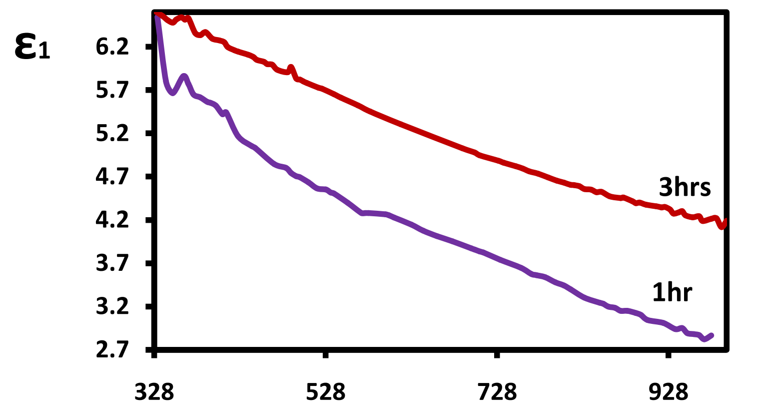

Fig.11 Real part against wavelength

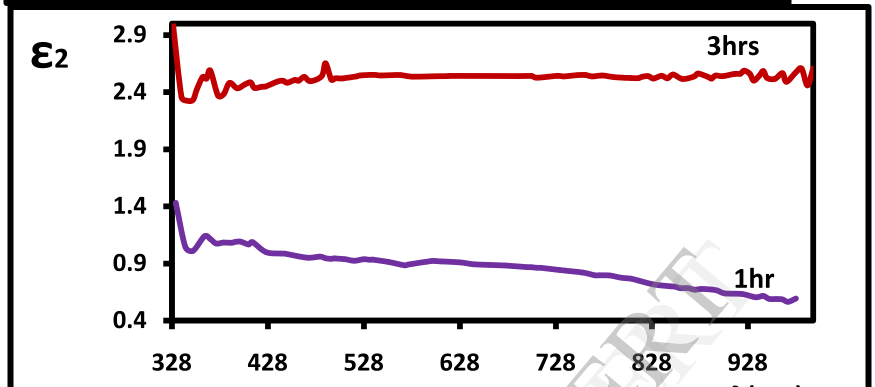

Fig.12 Imaginary part against wavelenght

NB : Real and imaginary parts of complex dielectric constant of two ZnS films of thicknesses 40nm and 60nm annealed for different times of 3hrs and 1hr respectively at 250°C.

Optical conductivity, σ

This is the number of photons absorbed per second by the film. This is an important parameter in designing solar cells. It is related to absorption coefficient by;

σ = (αnc)/(4π)………………………..(8)

The graphs of σ for the two samples are shown in figure 4.9 below. The values of σ decreased from 1.4×10^{15}/s to 3.9×10^{14}/s, as the wavelength increased from 338nm to 978nm, for the sample annealed for three hours. For the one hour annealed sample, it decreased from 6.5×10^{14}/s to 9.2×10^{13}/s within the same wavelength range. This is shown in **Fig. 13.**

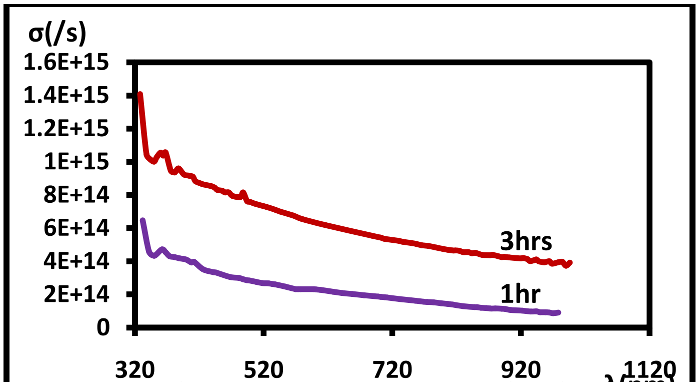

Fig. 1 Optical conductivity against wavelenght

Energy band gap E_g

The band gap is determined from the graph of $(\alpha hv)^2$ against *hv*, by extrapolating the straight portion of the curve where α*hv*=0. The band gap of the two samples were found to be ***3.38eV ± 0.05eV*** and***3.33eV ± 0.05eV*** for the samples annealed for 1hour and 3hours respectively. The band gap is ***3.36eV ± 0.05eV*** in average which is in agreement with the literature value and (Shubbaiah, 2006). This is shown in **Fig. 14.**

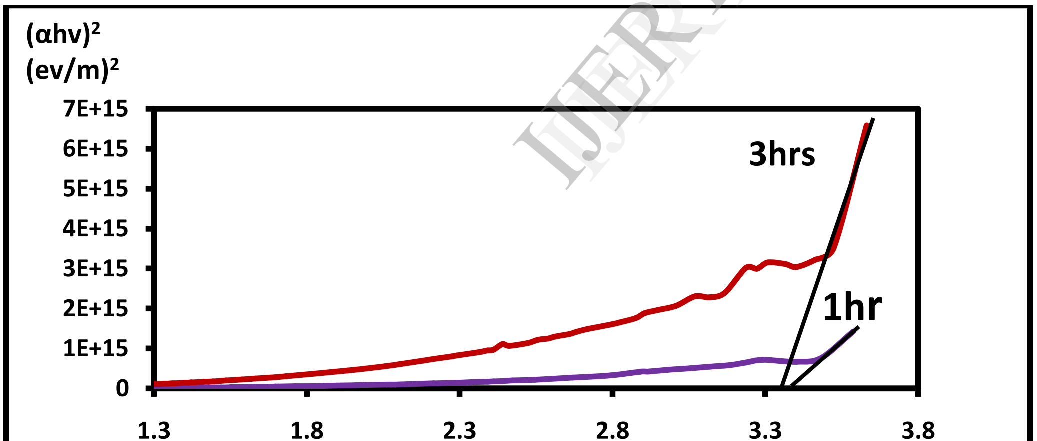

Fig. 14 $(\alpha hv)^2$against *hv*

5.Conclusions and summary

Almost pure ZnS thin films have been successfully deposited using the **Chemical Birth deposition,** from thiourea (**$CS(NH_2)_{2(aq)}$**) and zinc (II) chloride (**$ZnCl_{2(aq)}$**), using ammonia (**NH_3**) as complexing agent. 7ml of 3M $NH_{2(aq)}$ was added to 20ml of 0.4M $ZnCl_{2(aq)}$ and stirred. 13ml of 0.6M $CS(NH_2)_{2(aq)}$ was added to the mixture and stirred. 10ml of 0.15M $NaOH_{(aq)}$ was added to the mixture and stirred. The mixture was at room temperature of 23^{o}C. The PH was measured to be 9.1. Four glass substrates were then inserted vertically into the beaker containing the reactants for four hours. RBS test carried out on two representative samples annealed for one hour and three hours, confirmed the presence of ZnS on the glass substrates with film thicknesses of 60nm and 40nm respectively.Optical measurement carried out on the samples showed the following values of optical constants from UV to near infrared.

Table 5.1Summary of values of optical constants for two ZnS films of thicknesses 40nm and 60nm annealed for three and one hour respectively.

Optical constants	One hour annealed sample	Three hours annealed sample
T increased	from 0.62 to 0.872	from 0.51 to 0.735
R decreased	from 0.19 to 0.06	from 0.2 to 0.13
A decreased	from 0.13 to 0.05	from 0.4 to 0.27
α decreased	from 7940403/m to 2262662/m	from 16833616/m to 7731156/m
K	Decreased m 0.27 to 0.17	Increased from 0.45 to 0.6
n decreased	from 2.57 to 1.70	From2.638 to 2.136 to
ε_1 decreased	from 6.55 to 2.88	From 6.55 to 4.18
ε_2	Decreased from 1.43 to 0.589	≈ 2.4 within the spectrum
σ decreased	From 6.5×10^{14}/s to 9.2×10^{13}/s	From 1.4×10^{15}/s to 3.9×10^{14}/s
Energy band gap	3.38eV ±0.05eV	3.33eV ± 0.05eV
thickness	60.00nm	40.00nm

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