EFFECTS OF DEPOSITION TEMPERATURE OF ZnS THIN FILM on OPTICAL AND MORPHOLOGICAL PROPERTIES of ZnS DEPOSITED BY CHEMICAL BATH DEPOSITION METHOD FOR PHOTOVOLTAIC APPLICATION

By

Rasaq Ayinla Babatunde*& Opeyemi Olayinka Adegboyo

Department of Science Laboratory Technology, Federal Polytechnic, Ilaro. OgunState

*corresponding author: rasaq.babatunde@federalpolyilaro.edu.ng

Phone: +23408053238648

Abstract

The effect of deposition temperature was investigated on optical and morphological properties of synthesized ZnS thin film. ZnS thin films were prepared at different temperature and constant deposition period of 60 minutes onto the glass substrates by chemical bath deposition technique at a deposition temperature of 50^0C, 70^0C and 90^0C . The precursor was prepared using a mixed aqueous solution of zinc sulphate as a source of Zinc and thiourea as a source of sulphur while ammonia serves as the complexing agent. After the deposition, the thickness of the samples was determined using a 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 at 70^0C shows the highest value of 96% while the films deposited at 50^0C and 90^0C have the same value of 66%. The extrapolated optical band gaps of energies for the film deposited at 500C, 700C and 90 are 4.0 eV. 3.7 eV and 3.9 eV respectively. The microstructural images of all the samples were rough and the grains were dense. But the images show that the density of the film is inversely proportional to deposition temperature while the size of the particle becomes larger and clearer as deposition temperature increases. All the results indicated that the films were good material for a window layer in the fabrication of thin-film heterojunction solar cell. It is therefore recommended to replace toxic CdS for window layer in CdTe and CIGS heterojunction solar cells and

other optoelectronic devices because of its environmentally friendly, exhibits high bandgap energies and shows high transmittance

INTRODUCTION

The demand of energy has increased all over the world and the condition poses a threat on the sources of energy like fossil fuel, natural gas, coal etc. by the year 2030-2050, if any alternative source does not substitute or supplement them (Gahlawat et al,2009). The world's fossil fuel resources are unable to sustain global current energy requirement beyond the next few decades and so the need for inexpensive alternative is now urgent. Since these are non-renewable sources of energy there has been a step decline in energy reserves. Moreover, burning of fossil fuels is conceded to the largest contributing factors to atmospheric pollution. In order to deal with the imminent global energy scarcity, alternative and renewable energy source are being developed. Renewable energy is energy which is generated from natural source i.e. sun, wind, rain, tides and can be generated again and again when the needs are required. They are available in plenty and by far most clean source of energy available on this planet(Ayeshamariam et al.,2014). These energy sources have huge potential of reducing environmental pollution, develop domestic employment and indigenous technology and also reduce dependency on fossil fuel, and other conventional energy sources (Garba&Mangset, 2006). Solar energy is the conversion of sunlight into electricity, either directly using photovoltaic (PV) or indirect using concentrated solar power (CSP). The CSP systems use lenses or mirrors and tracking system to focus a large area of sunlight into a small beam. PV converts light into electric current using the photoelectric effect. (Lewis et al, 2010). The basic unit of solar energy is called solar cell which is an electronic device that converts the energy of light directly into electricity by the photovoltaic effect.(Wanjala,Njoroge, & Ngaruiya, 2016) Solar cell are typically made from semiconducting material and they are classified as first, second and third generation cells. The first generation also called conventional, made up of crystalline silicon (Askari,Mirzae &Mirhabibi,2015). In the laboratory the crystalline silicon solar cell has the highest conversion efficiency of 24.7% while the large scale of production efficiency was 15%. It has various applications for both domestic and industrial purposes because of its long durability. However, the silicon

solar cell is unaffordable by average income earners because of the cost price of silicon. The thin film solar cell is brought to overcome the challenge which is the second generation of solar cell. The advantages of thin film devices over the bulk materials are low material consumption, easy processing and possible use of flexible substrates (Poortmans&Arkhipoy, 2006). Among the thin film solar cells are: Amorphous silicon (a-Silicon), Cadmium Telluride (CdTe) and Copper-Indium-Gallium-Diselenide (CIGS) solar cells are semiconductors with direct band gap, these are called hetero-junction solar cell which are made up of two layers (absorber and window layers). The main function of this layer in hetero-junction is to form a junction with the absorber layer while transmitting a maximum amount of light to the junction region and absorber layer. Also this layer should have small absorption loses and electrical resistance in photo-generated charge carriers driving out (McCandless&Hegedus, 1991).

ZnS belong to group II-VI semiconductor compound, with direct wide band gap ranging from3.4 to 3.7eV at room temperature which has hexagonal crystal structure or both at the same time (Thriumavalavan,Mani &Sagadevan ,2015). It is a potentially useful material to be used as an antireflection coating for hetero-junction solar cells. Also it can use for fabrication of optoelectronic devices such as blue light-emitting diodes, electroluminescent devices and window layer for thin film hetero-junction solar cells (Hariharan. Shenbaga, Moorthi,. & Dharani 2016).. The deposition of high quality ZnS thin film over a large area is required if it is to be effectively used in electroluminescent device and solar cells (Oladeji& Chow, 1999).

Several works has been carried out to deposit thin films using chemical deposition methods. ZnS thin film was deposited on glass by Shaban, Zayed, Ahmed and Hamdy (2015) growing different zinc sulphide (ZnS) nanostructured thin films on glass substrates at low temperatures by combining successive ionic layer adsorption and reaction (SILAR) method and chemical bath deposition (CBD). Morphologies and structures of the samples were investigated by X-ray diffraction (XRD), energy-dispersive x-ray spectroscopy (EDX) and scanning electron microscopy (SEM). Patil, Dhasade, Thombare and Fulari (2015) using electrodeposition method to investigate the Structural, Morphological and Optical Studies the film and found that the Zinc sulfide thin films are polycrystalline in nature with cubic structure. Optical band energy of zinc sulfide thin film is 3.94eV .This film suggests their possible application for window buffer layer material for solar cell.

MATERIALS AND METHOD

Materials

The under listed reagents were used to synthesis ZnS thin film on glass substrates. The reagents were analytically pure and used as purchased without further purification. The solutions were prepared using distilled water as solvent

1. Zincsulphatepentalhydrate ($ZnSO_4.5H_2O$)
2. Ammonia solution NH_3
3. Thiourea ($SC(NH_2)_2$
4. Water Bath
5. Oven

Preparation of glass substrates

The glass substrates were labeled as T1, T2 and T3 using diamond glass cutter and then soaked in HCl acid for 24hours, after they were washed with detergent soap and rinsed with distilled water and then dried in oven for 15minutes at 30^0 C. They then kept in beaker and covered with aluminum foil to avoid being contacted with dust.

Preparation of precursor and growing of ZnS thin film

The chemical bath is prepared by mixing 30ml of 0.10 M Zinc sulphate ($ZnSO_4$) as source of zinc, 30 ml of 1.20 M Thiourea ($SC(NH_2)2$) solution as source of sulphur and 20ml of 3M (NH_4OH) solution as complexing agent. While preparing the solution, firstly 30ml of 0.10M $ZnSO_4$ were poured into beaker and stirred for 30sec, then 30 ml of 1.20 M 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 baths at temperature of 50^0 C, 70^0 C and 90^0 C . The deposition was allowed to carry out for 1hour. 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 temperature 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^oC for 15minutes in an oven.

The mass of chemical reagent for the various molar solution was calculated from the relation below.

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

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. The table below shows the constituents of precursor

Table 1: Constituents of Precursors

Reagent/ concentration	**Bath Temperature ^{0}C**	**Deposition Period**	**Samples Code**
$ZnSO_4.5H_2O$ = 0.10M **$SC(NH_2)_{2=}$ 1.20M** **$NH_{3=}$ 3M**	50.0	60 minutes	T1
$ZnSO_4.5H_2O$ = 0.10M **$SC(NH_2)_{2=}$ 1.20M** **$NH_{3=}$ 3M**	70.0	60 minutes	T2
$ZnSO_4.5H_2O$ = 0.10M **$SC(NH_2)_{2=}$ 1.20M** **$NH_{3=}$ 3M**	90.0	60 minutes	T3

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:

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

W1 and *W2* 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.

Characterization of the films

The surface morphology of the all synthesized ZnS thin films were observed by Scanning Electron microscopy (SEM)-SEM PRO (PHENONWORD)accelerating at 10 KV were done for each sample. The absorbance's of the thin films were measured using DOUBLE BEAM UV/V isspectrophotometer (ATICO).The film coated glass substrate was placed across the sample radiation path way while the uncoated glass substrate was used as reference frame. The absorbance data was obtained directly from the spectrophotometer and other parameters such as transmittance, reflectance, photon energy and optical band gap energy were calculated using the relevant known equations.

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

Where h is Planks constant with numerical value of $6.63x10^{-34}$Js

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

where is frequency of radiation , c is the speed of light with numerical value $3\ x10^8\ ms^{-1}$ while λ is the measured wave length

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

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

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

The transmittance of the films were obtained from the relation below

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

Where A is the measured absorbance, the reflectances 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 deposition temperature is shown in table 2. The table shows that the thickness of film deposited on glass substrates decreases as deposition temperature increases increases.

Table 2: Thickness measurement of deposited ZnS thin film at different deposition temperature

Temperature of deposition/ C^0	**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)**
50.0	19.35	4.1	79.335	5.136	5.167	0.310	5.04
70.0	19.35	4.1	79.335	5.154	5.170	0.160	3.78
90.0	19.35	4.1	79.335	5.132	5.372	0.240	2.39

Optical properties

The transmittance and reflectance spectral of synthesized ZnS thin film at differentdeposition temperature are shown in figures 1,2 and 3 for film deposited at 50^0 C , 70^0 C and 90^0 C respectively. These spectra read from 190 nm to 1100nm. The transmittance spectral increase in the visible region of wavelength from 400nm to 800nm and decreases in the infrared region above 800nm wavelength. The film deposited at 70^0 C shows the highest transmittance of 92.0% while the films deposited at 50^0 C and 90^0 C have the same transmittanve of 66 % . The optical band gap energies of the film were extrapolated and shown in figure 4, 5 and 6 for the film deposited at at 50^0 C , 70^0 C and 90^0 C respectively. The value of band energies are 4.00 eV, 3.70 eV and 3.90 eV for the film deposited for the film deposited at 50^0C, 70^0 C and 90^o C respectively. These results are not in agreement with the reported bang gap of 3.6 eV of bulk ZnS. But similar higher band gap energies of 3.84 eV-3.96 eV has reported by Manjulavill and Kannan (2015). Also, Djellou, et al (2015) reported 3.89 eV-3.96 eV for ZnS bang gap energy. The band gap energy of 4.08eV was reported by Patra, Mondal and Mitra (2009). 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 improves the short circuit current of the cell (Djellou et al., 2015).

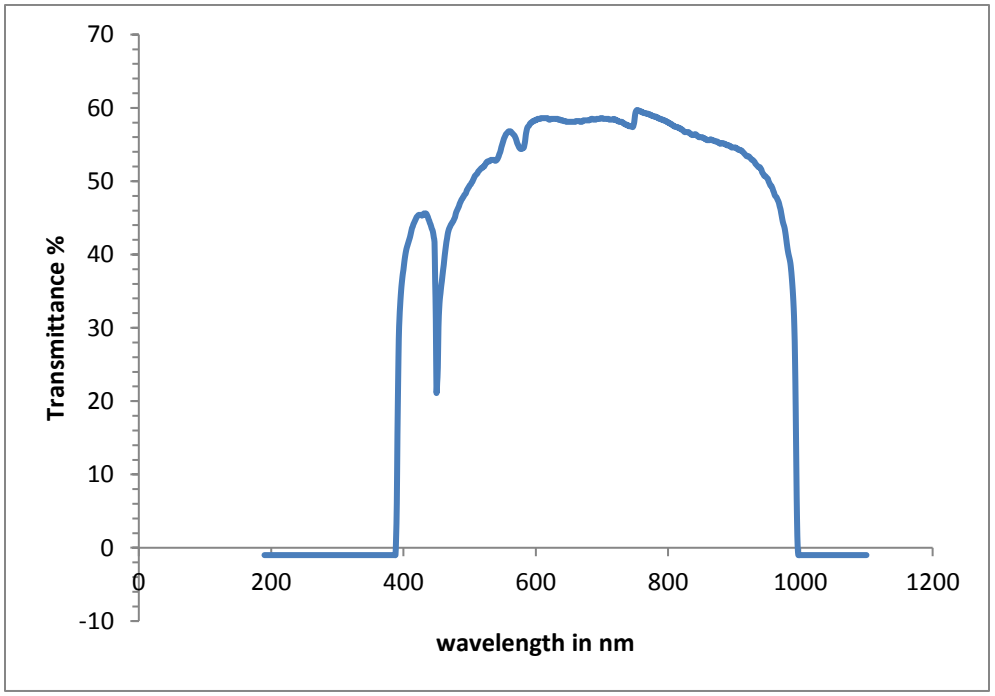
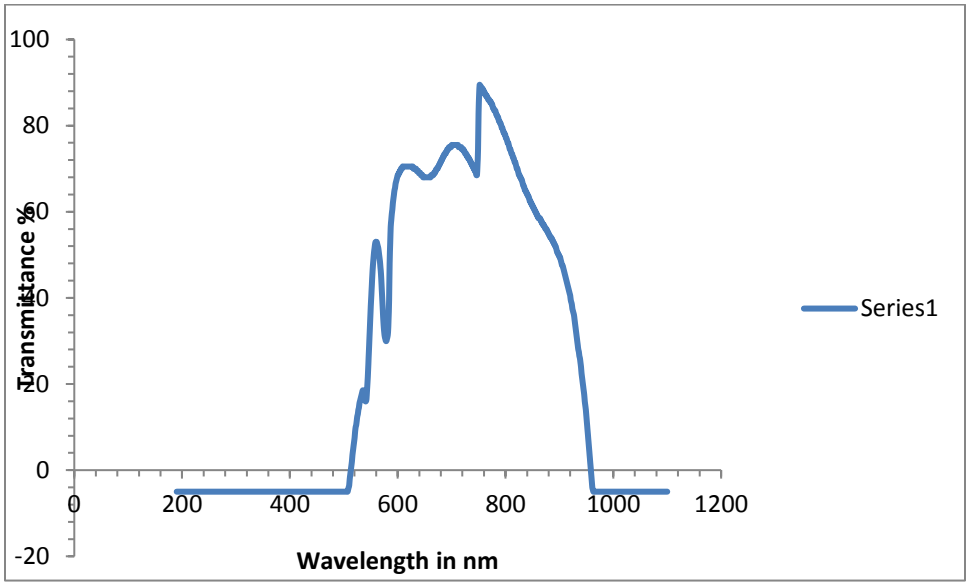
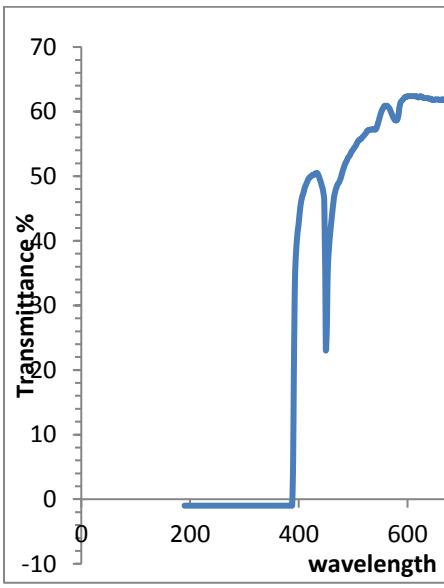


Figure 1: Transmittance spectral of film deposited at 50^0 C



` Figure 2: Transmittance spectral of film deposited at 70^0 C



` Figure 3: Transmittance spectral of film deposited at 90^0 C

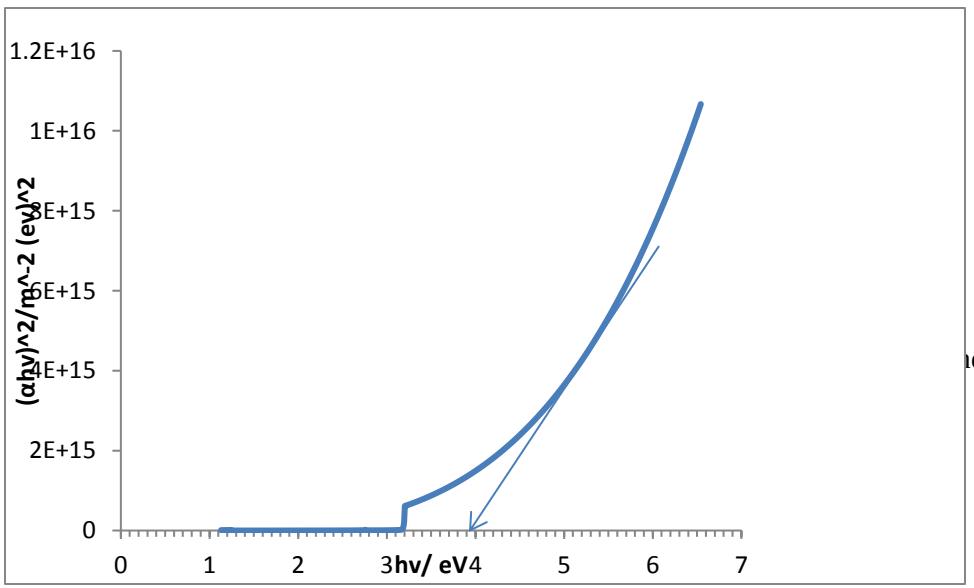


Figure 4: Graph of hv (eV) against $(\alpha hv)^2$ for ZnS thin film deposited at 50^0 C

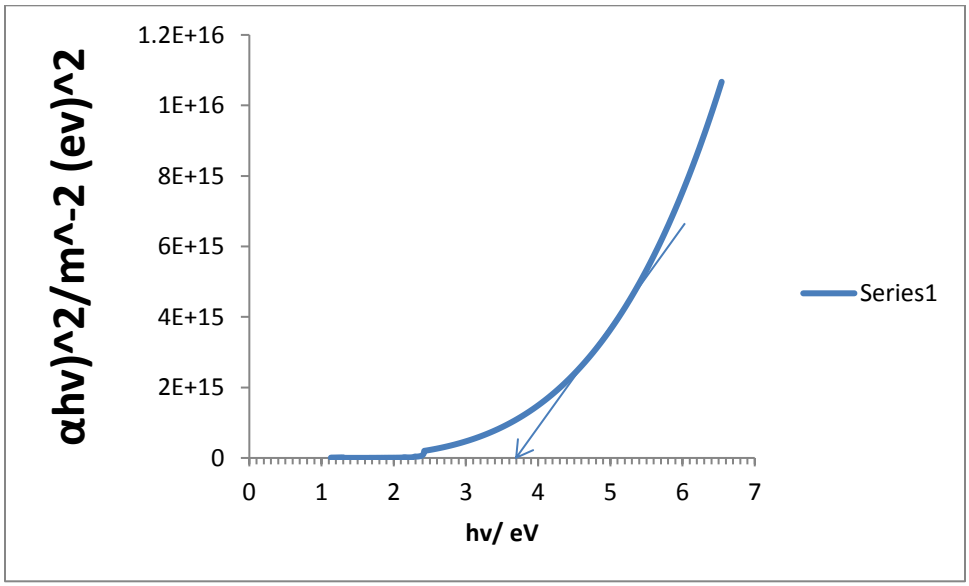


Figure 5: Graph of hv (eV) against $(\alpha hv)^2$ for ZnS thin film deposited at 70^0 C

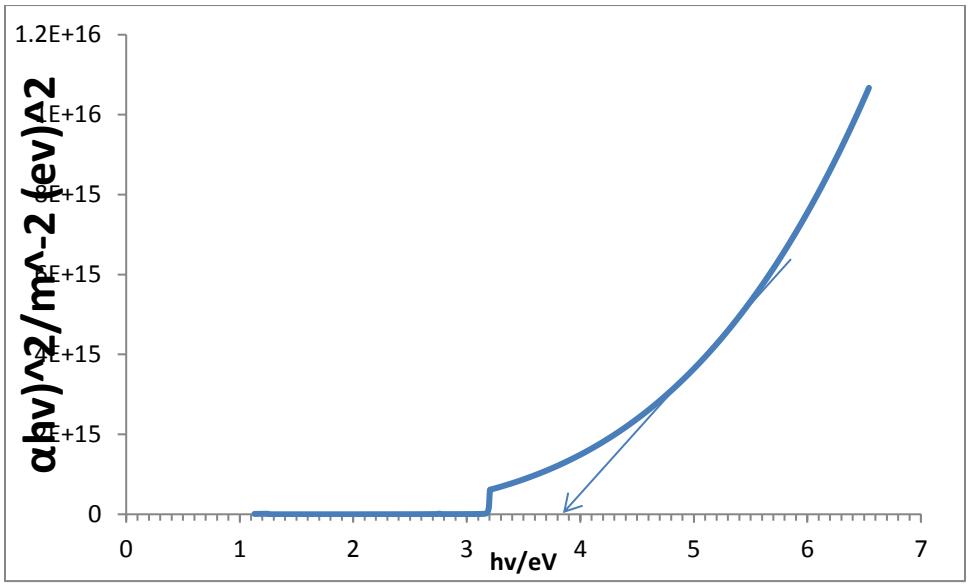
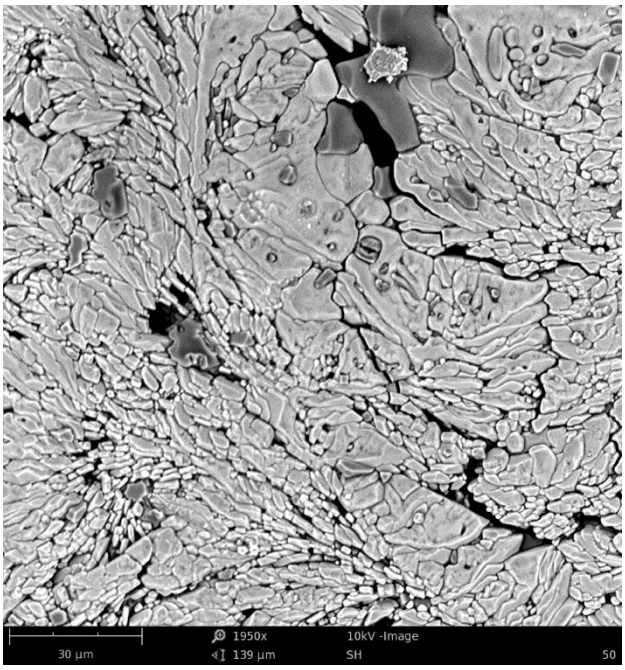


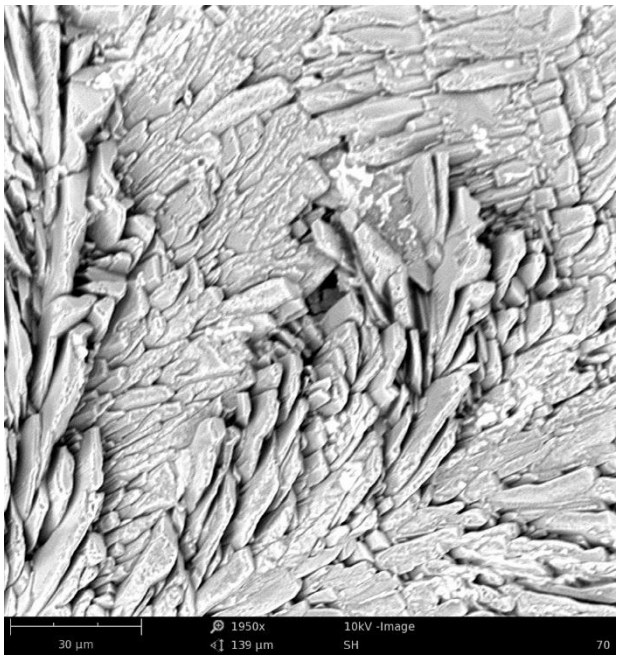
Figure 6: Graph of hv (eV) against $(\alpha hv)^2$ for ZnS thin film deposited at 90^0 C

Morphological Analysis

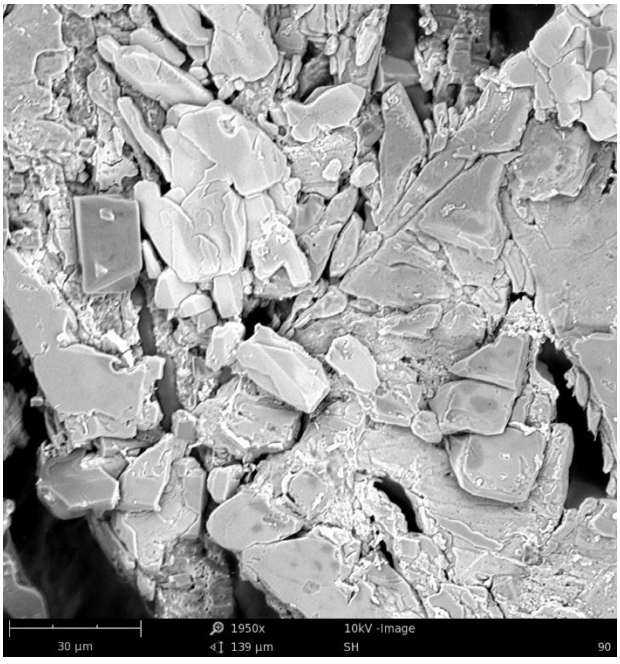
The micro-structural images of the ZnS thin film deposited at three different temperature of 50^0 C , 70^0 C and 90^0 C respectively when viewed with scanning electron microscope (SEM) under the same magnification of 1950 are as shown in the figures below. SEM images of the ZnS thin film obtained from the deposition shows a rougher surface which is in good agreement with Lopez, Espinos, Martin, Leinen and Ramos (2005).But the images show that the density of the film is inversely proportional to deposition temperature while the size of the particle becomes larger and clearer as deposition temperature increases


1950x
10kV -Image
30 µm
139 µm
SH
50

T2


1950x
10kV -Image
30 µm
139 µm
SH
70

T1


1950x
10kV -Image
30 µm
139 µm
SH
90

T3

Plate 1: Images of ZnS thin film at different deposition temperature T (T1=50^0 C, T2= 70^0 C and T3= 90^0 C)

Conclusion

ZnS thin films were successfully deposited on glass substrate using chemical bath deposition method. The effect of deposition temperature on optical and morphological characteristics of the films was investigated. The optical result shows the films have high transmittancebetween 66-92%and also high optical band gap energies between 3.70 eV to 4.00 eV were extrapolated. The morphological properties of all the film are rough and dense.The images show that the particle size increases and more clear as deposition temperature increases. All these results indicate that the films can be used as a window layer in the fabrication of thin film hetero-junction solar cell.

REFERENCES

Askari, M. B., Nurzeal, M.A., & Mirhabibi, M., (2015). Types of solar cell and application. American journals of optics and phonics'. 5 (3), 94-113.

Ayeshamariam, A., Kashif, M., Muthu, S., Jagadeswari, S., Saravananankumar, D., Alhaji, N. M. I., & Uduman, A. (2014). Optical Characterisation of ZnSe Thin Films by Using Electro Deposition Technique. *International Journal of Emerging Technology and Advanced Engineering, 4*(5).

Djelloul, A., Adnane, M., Larbah, Y.,Sahraoui, T., Zegad, C., Maha,A., & Rahal,B.(2015). Properties Study of ZnS Thin Films Prepared by Spray Pyrolysis Method. Journal of Nano and Electronic Physics,7(4),40-45

Gahlawat, N., Harper, L., Hendricks, P., Okoye, C. Pankow, J. & Serpico, B. (2009).Renewable Energy and Developing Countries: The Cases of India and Nigeria.Energy & Energy Policy BPRO 29000 , 3-12

Garba, M. L., & Mangset, S.E. (2006). The need for renewable energy source. International journal science and technology research, 2 (3).11-13

Hariharan,G., Shenbaga,V., Moorthi, N.K. & Dharani, A.P (2016). Synthesis and structural characterization of nano structurd zinc sulphide thin films grows on glass substrates by chemical bath deposition. International journal of advanced engineering technology, 2 (7) 1191-1194.

Lopez, M.C., Espinox, J. P., Martin, F, Leinan. D.,& Ramasa-Barrado, J. R. (2005). Growth of ZnS thin films obtained by chemical spray pyrolysis: The influence of precursors. Journal of crystal growth, 285, 66-75.

Manjulavalli, J.E, & Kannan,A.G.(2015). Structural and optical properties of ZnS thin films prepared by chemical bath deposition method. International Journal of ChemTech Research.
11 (8), 396-402.

McCandless, B.& Hegedus, S. (1991). Influence of CdS window layers on thin film CdS/ CdTe solar cell performance. In Photovoltaic Specialists Conference, Conference Record ofthe Twenty Second IEEE.(4), 967–972.

Oladeji,I.O & Chow, L. (1999). A study of the effects of ammonium salts on chemical deposited ZnS thin films. Thin Solid Films, 339,148-153

Patra, S., Mondal, S., &Mitra, P. (2009). Preparation of ZnS and SnS Nanopowders by Modified SILAR Technique. Journal of Physical Sciences, 13, 229-234

Poortmans, J.& Arkhipov, V. (2006). Thin film solar cells: fabrication; characterization and applications, 5, West Sussex, England: John Wiley & Sons.

Patil, J.S., Dhasade, S.S., Thombare, J.V., & Fulari,V.J., (2015). Structural, morphological and optical studies on zinc sulphide thin film produced by electrodeposition method. Journal of shivaji university science technology 41(2), 1-3.

Shaban, M., Zayed, M., Ahmed, A.M. & Hamdy, H. (2015).Influence of growth time on the morphology of ZnO nanostructures prepared by low-temperature chemical bath deposition. Journal of Applied Physics.7 (4), 35-40.

Thirumavalavan, S., Mani, K., & Sagadevan, S (2015). Studies on structural, surface morphology and optical properties of ZnS thin film prepared by chemical bah deposition. International Journal of Physical Science, 10(6), 204-209

Wanjala, K.S., Njoroge,W.K., & Ngaruiya, J.M. (2016). Optical and Electrical Characterization of ZnS:Sn Thin Films for Solar Cell Application. International Journal of Energy Engineering. 6 1(1), 1