Scientia Africana, Vol. 16 (No. 2), December 2017. Pp 106-115
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

CHEMICAL BATH DEPOSITION AND CHARACTERIZATION OF ZINC SULPHIDE THIN FILM FOR POSSIBLE DEVICE APPLICATION

R. E. Oloko and E. O. Chukwuocha

University of Port Harcourt, Department of Physics P.M.B 5323, Choba , Port Harcourt, Rivers State, Nigeria.
E-mail: rolioloko@yahoo.com, roli.oloko@uniport.edu.ng
Phone number: 08067900027

Received: 29-09-16
Accepted: 08-02-17

ABSTRACT

This work involved the chemical bath deposition (CBD), and study of the optical and solid state properties of zinc sulphide films for possible device application. The zinc sulphide film was prepared from different host solutions comprising zinc sulphate and zinc chloride as precursors used, in order to ascertain the precursor type that is better for the deposition of zinc sulphide films. Ammonia solution was used as a complexing agent along with hydrazine hydrate as complementary complexing agent which facilitated the deposition time. The zinc sulphide film was deposited as optical coating on glass slide and the spectral transmittance data of the zinc sulphide films from both host solutions were estimated from UV-VIS spectrophotometer at normal incidence of light in the wave length range of 200-1100nm. The analysis of the optical properties show that the transmittance spectral of zinc sulphide film deposited from zinc sulphate has a maximum value of 75% in the visible/NIR of the spectrum which is higher than that of the other host solution. The absorbance spectral and absorption coefficient decreases as the photon wavelength increases for the zinc sulphide film deposited from zinc sulphate solution, but for the film from zinc chloride, it is different. The optical energy bandgap shows a higher value of 3.99eV for the sample deposited from the zinc sulphate solution. The analysis of the optical and solid state properties of the samples reveals that the zinc sulphide film deposited using zinc sulphate solution gives better qualities needed for application in devices such as solar cells, diodes and similar applications.

Key words: CBD, ZnS, NIR, UV-VIS, Solar cells, Thin film

INTRODUCTION

The role energy plays in nation building cannot be over emphasized. In fact the standard of living of a nation currently depends on the energy consumption because a reduction in its supply can lead to abrupt changes in the life style of the people and affect national security. As a result energy which occurs in a low grade form such as sun, wind, tides etc. must be converted to a high one through some conversion mechanisms in order to make it presentable in a consumable form [Allouche et. al. (2010), Anthony et. al.(2005), Okujagu and Okeke (1999)]. Researchers of solar energy focus on finding a conversion system that have the simultaneous promise of efficiency, durability and low cost as well as solar devices whose absorption of solar radiation are wavelength dependent [Wagner et. al.(1975), James and James (2005)]. To achieve this goal, photovoltaic cells made of polycrystalline thin films are used. Thin films are a few atomic layers thick, very fragile and may be formed from a liquid or a paste in which case they are called "thick films". It is not the thickness that is important in defining a film, but rather the way it is created which has consequential effects on its microstructure and properties [Allouche et. al. (2010)]. There are different techniques for the preparation of thin films. One common feature associated with these methods is that each deposition technique requires a substrate to initiate the heterogenous nucleation and growth process for thin film formation. The vapour atoms impinging on the substrate lose their kinetic energy and are absorbed on the surface as ad-atoms. The movement of these ad-atoms depends on many conditions, in particular, the energy of the vapour atoms, the rate of impingement, the absorption topography, chemical nature of the substrate and lastly the substrate temperature [Allouche et. al. (2010), Okujagu (1992)]. The interaction of the absorbed atoms through collision on the surface leads to the formation of critical nuclei is the beginning of the thin film formation. A particle approaching the substrate enters close to its surface, a field of attraction short range London forces with exchange energy proportional to $1/r^6$. At a shorter distance, r, repulsive forces proportional to e^{-r}/constant resist the penetration of the electro clouds of surface atom [Thun (1985)]. The size of the nuclei is governed by the material being condensed and it depends to a reasonable extent on the energy of formation. The polycrystalline thin film considered in this research is ZnS that is relatively inexpensive and consist of readily available materials [Okujagu (1992),Yu et. al. (2006)] . This is the reason for the aim and objectives of this research, which deposited ZnS thin films using chemical bath deposition (CBD) technique and then characterized the asdeposited ZnS thin films for the optical and solid state properties suitable for device application. The CBD process used a controlled chemical reaction to initiate the deposition of a thin film by precipitation. The process relies on the release of S^{2-} ions into a solution in which the free metal ion is buffered at a low concentration [Paul et. al.(2000), Limei et. al.(2011), Anthony et. at. (2005), Zang et. al.(2010)]. The free metal ion concentration, is most often controlled by the formation of complex species e.g.$[Zn(NH_3)_4]^{2+}$. the supply of sulphide ions is achieved by decomposition of an organic sulphur containing compound, usually thiourea [Ran et. al. (2005), Paul et. al. (2000)].

MATERIALS AND METHODS

The experimental procedures adopted in this work for the deposition of ZnS thin film involves the setting up of two separate CBD system, named A and B containing different precursors, Solution A contains $ZnCl_2$ precursor while solution B contains $ZnSO_4$ precursor. The salts Zinc tetraoxosulphateVI and Zinc chloride are chosen to release the metal ion (Zn^{2+}) while thiourea is a source material for the non-metallic ion (S^{2-}) when its aqueous solution is made. Ammonia solution acts as the complexing agent while hydrazine hydrate is the complementary complexing agent, this is necessary because previous work has shown that a complementary complexing agent is required for the deposition of Zinc compounds [Johnston et. al. (2002), Akira et. al. (2006), Zhou et. al. (2009)]. Without such an agent, deposition is minimal or does not occur at all.

Each of the analytical grade (AG) laboratory reagents was weighed in the electronic spring balance, dissolved in water to form the required concentration and placed inside a reagent bottle. In this work, the use of the two CBD systems (A and B) was considered with the view to study and compare their efficiencies in the deposition of Zinc sulphide thin films. Zinc sulphide film was grown using the chemical bath deposition method and the film were characterized to study their optical and solid state properties which makes it suitable in device application. The substrates also called slides were first cleaned because such cleaned surfaces have the advantage of providing high adhesiveness and uniformity of the deposited film.

In the experimental set-up, the slides are mounted in pairs because mounting the slides together in pairs prevented deposition on the surfaces in contact with each other, resulting in deposition on one surface.

CBD of Zinc sulphide in Zinc salt-Ammonia-Thiourea system consist of the complexation of the zinc cations by the ammonia and the consecutive reaction with the sulphide ions provided in the hydrolysis of thiourea.

The films are prepared by CBD separately from two sources of Zinc ion i.e. Zinc sulphate and Zinc chloride, for both of the growth solution, films are deposited at a temperature of 90^0C. After each deposition run, the substrate was rinsed in distilled water and dried in air. Two CBD systems (Bath1 and 2)

Bath 1

The chemical bath was prepared as follows: 0.08M solution of Zinc chloride, $ZnCl_2$ (20ml) was placed in a 50ml beaker to which 1.39M of Ammonia, NH_3 (5ml) and 2.29M solution of hydrazine hydrate, $N_2H_4.2H_2O$ (5ml) was added and stirred very well. Also, 0.07M of thiourea, CH_4N_2S ($SC(NH_2)_2$) (10ml) was added and stirred thoroughly for a few seconds with a glass stirrer.

Bath 2

The chemical bath was prepared as follows: 0.25M solution of Zinc chloride, $ZnCl_2$ (20ml) was placed in a 50ml beaker to which 1.39M of ammonia, NH_3 (5ml) and 2.29M solution of hydrazine hydrate, $N_2H_4.2H_2O$ (5ml) was added and stirred very well. Also, 0.24M of thiourea, ($SC(NH_2)_2$) (10ml) was added. Then the solution was stirred thoroughly for a few seconds with a glass stirrer.

The cleaned substrate was then placed in pair vertically with a cork to prevent impurities into the reaction bath. The time white deposits starts covering the slide is noted, and then the slide was left to stand for about 10 hours, after which the samples were removed. The substrate was again weighed to get the mass of the film by taking the mass differential, before and after deposition. The depth of the immersion of the substrates in the solution bath was also recorded in order to calculate the area the film covered on the glass substrate.

Also, the spectral transmittance and absorbance of the samples were measured using a UNICAM UV1061408 double Beam spectrophotometer. The thickness of the Zinc sulphide films was computed using the gravimetric method. This method uses the equation.

$$t = \frac{M}{PA} \quad (1)$$

Where M = Mass of deposited film
P = Density of Zinc film
A = Area of deposited film
t = Thickness

RESULTS

The precursor type ($ZnCl_2$ or $ZnSO_4$) is considered in the determination of thickness of film and deposition time, the results obtained is presented in Table 1.

Table 1: The film thickness, t, and deposition time (hours) from two different ZnS precursors using gravimetric method.

Precursor Type	**Area of Film A (m^2)**	**Thickness of Film(nm) (t=M/*P*A)**	**Deposition Time (hours)**
$ZnCl_2$	$7.5x10^{-4}$	489	8
$ZnSO_4$	$7.5X10^{-4}$	685	6

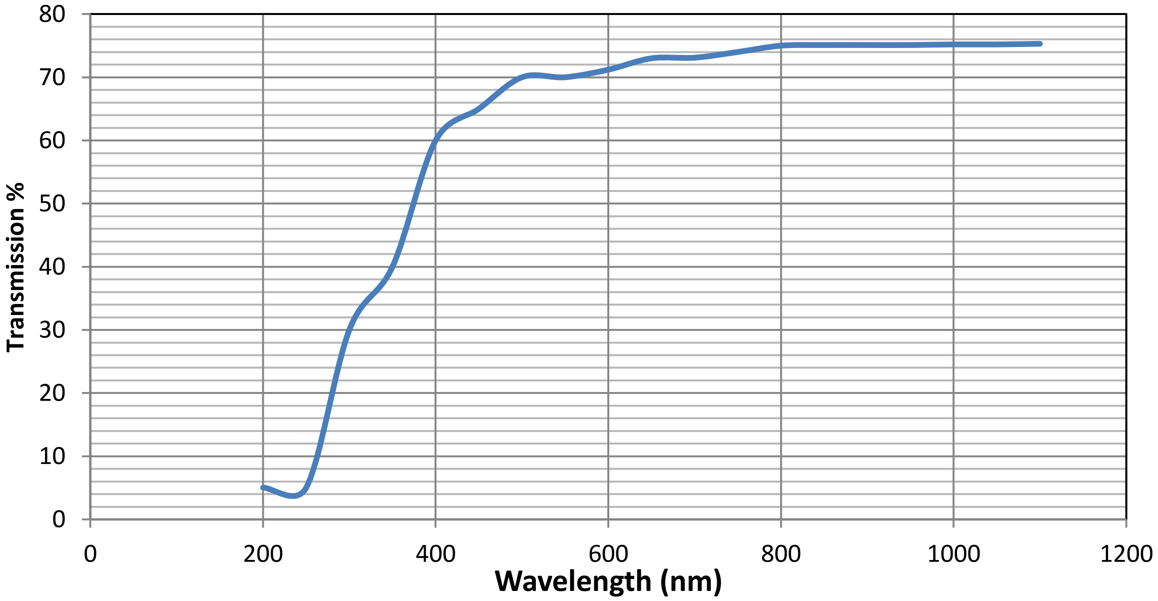

Figure 1. Spectra transmittance for ZnS prepared from growth solution of $ZnSO_4$.

Scientia Africana, Vol. 16 (No. 2), December 2017. Pp 106-115
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

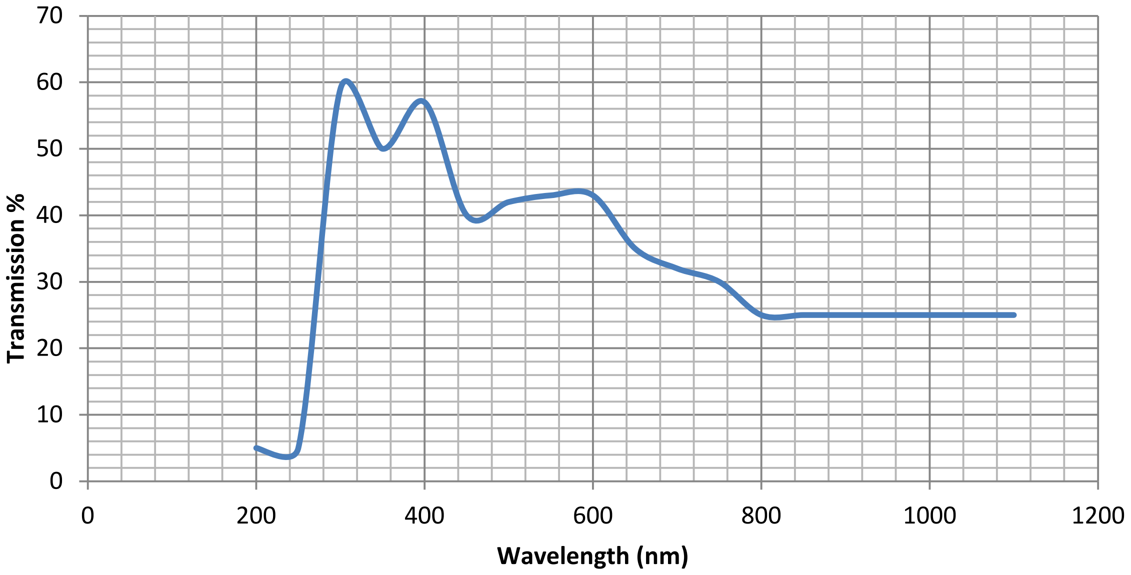

Figure 2. spectral transmittance for ZnS films prepared from growth solution of $ZnCl_2$.

The absorbance A of the ZnS film was computed using the equation.

$A = \mathrm{Log}_{10} {}^{1}/_{T}$ (2)

Where T is the transmittance

The values of absorbance A, computed using equation (2) were plotted against the incident photon wavelength to obtain the absorption spectra of the ZnS film.

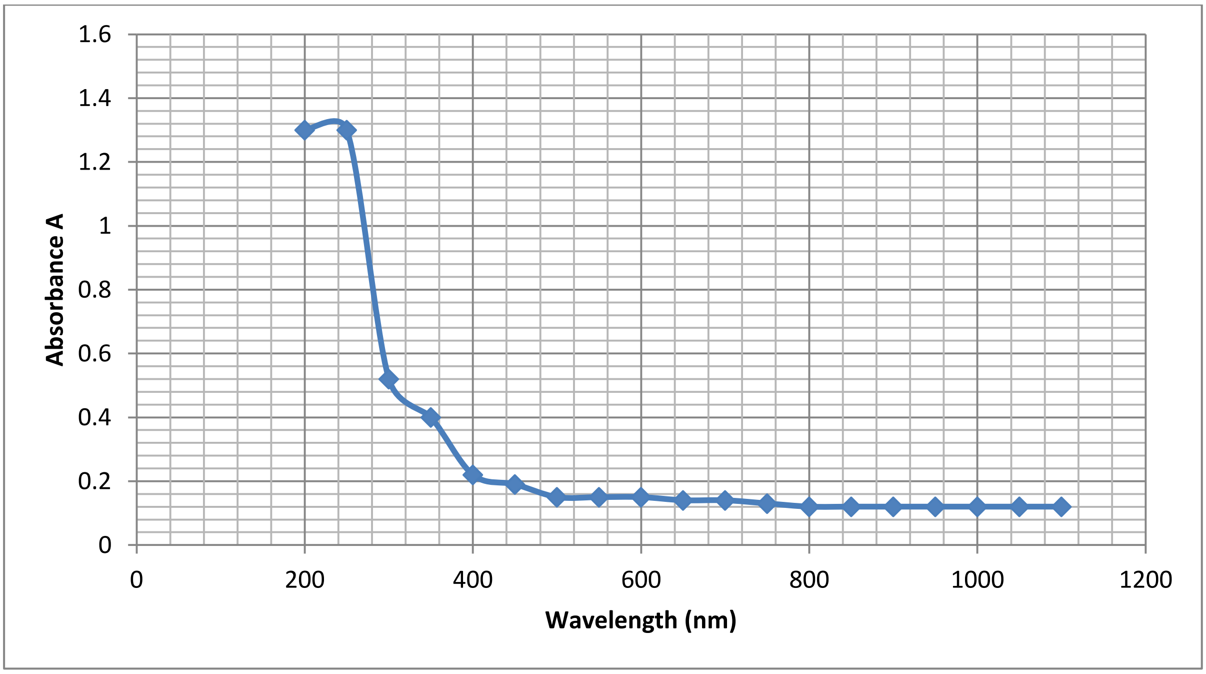

Figure 3 Spectra absorption for ZnS films prepared from growth solution of $ZnSO_4$.

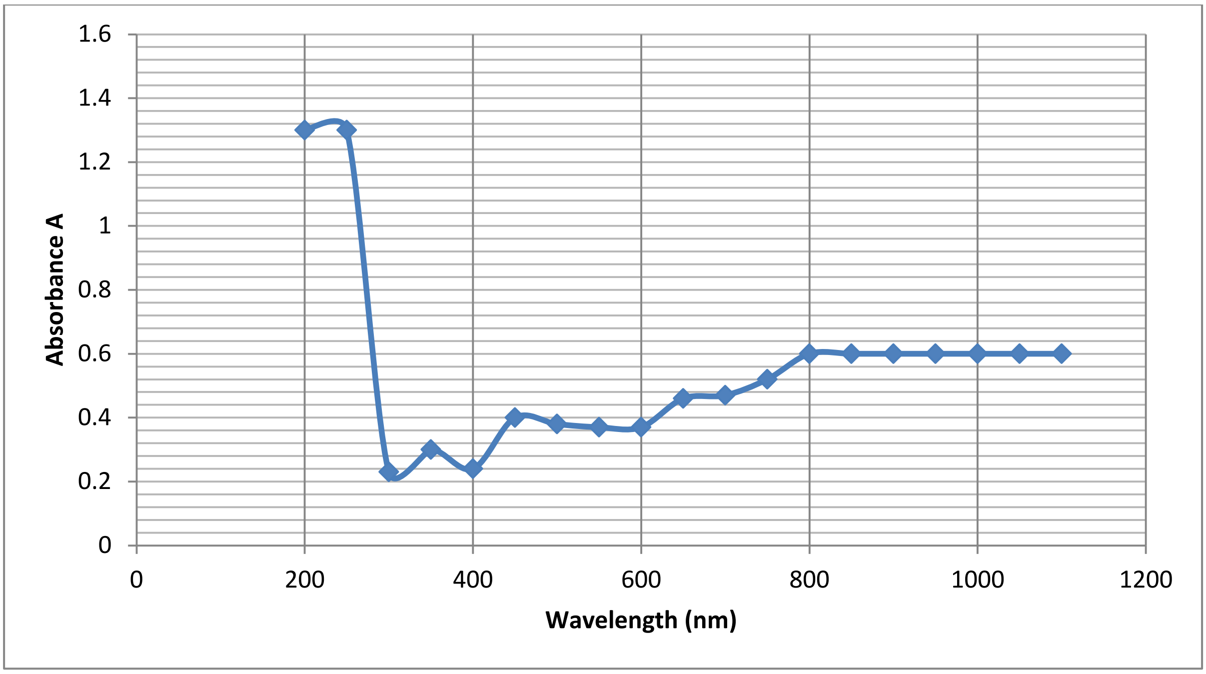

Figure 4 Spectra absorption for ZnS films prepared from growth solution of $ZnCl_2$ solution.

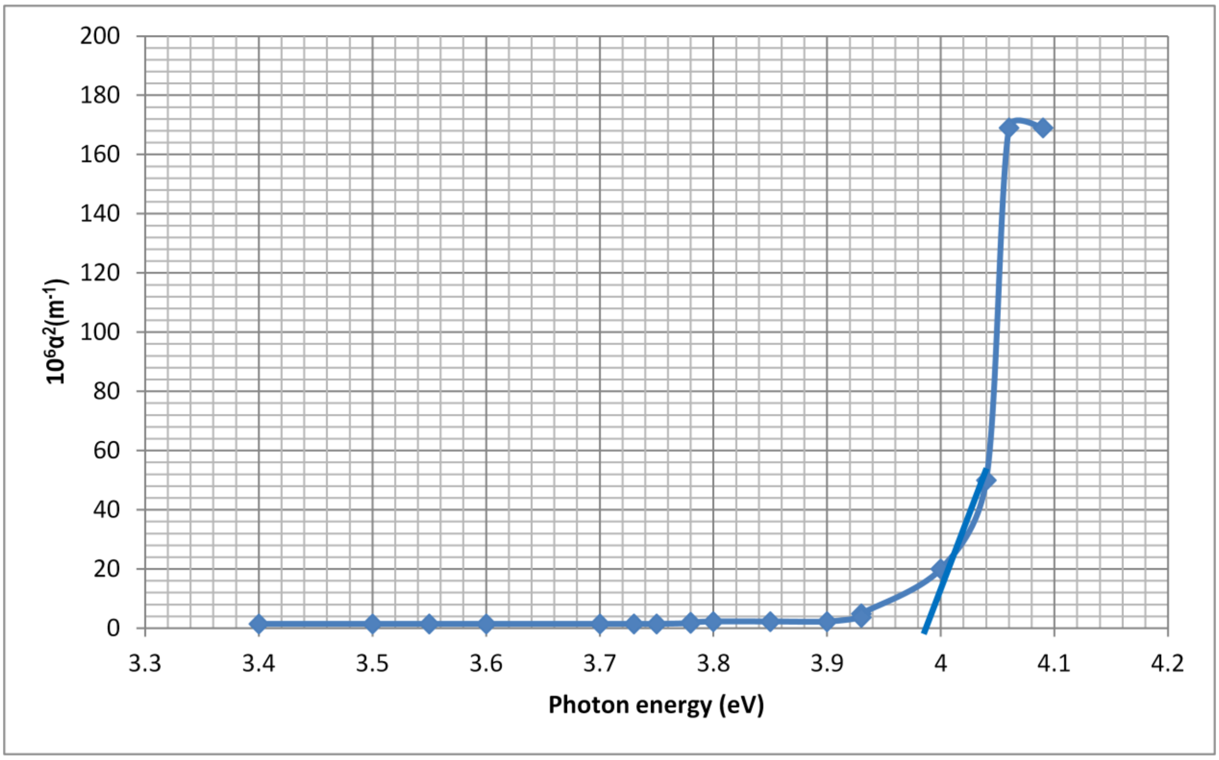

Figure 5 Square absorbance spectra of ZnS film deposited from bath containing $ZnSO_4$.

Scientia Africana, Vol. 16 (No. 2), December 2017. Pp 106-115
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

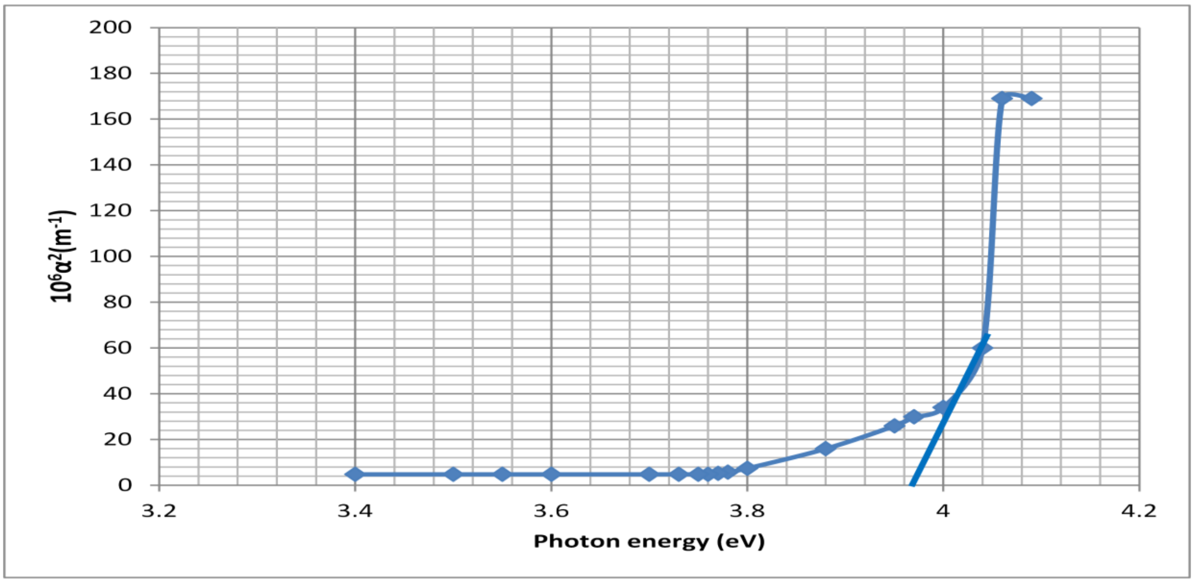

Figure 6. Square absorbance spectra of ZnS film deposited from bath containing $ZnCl_2$.

Table 2: The Energy Band gap (eV) of ZnS thin film using different precursor types

PrecursorType	**Energy Band Gap (eV) of ZnS**
$ZnCl_2$	3.97
$ZnSO_4$	3.94

DISCUSSION

Figure 1 shows the UV-Vis transmittance spectra of ZnS in the range of 200-1100nm film deposited from $ZnSO_4$ solution. From Table 1, the film thickness is 685nm as computed using gravimetric method. This value is comparable to that obtained (700nm) by Allouche et. al. (2010). The transmittance spectra shows a sharp increase from 5%-30% in the wavelength region 200nm-300nm. Also there is an increase of 30%-65% within the wavelength region 0f 300nm-450nm. The transmittance increase continues to 75.3% between 850nm and 1100nm which is the maximum transmittance value taking place at the near infrared region. The increase is as a result of the thickness of the ZnS film and the wavelength of the electromagnetic radiation.The maximum transmission value collaborates with literature, Sartale et. al. (2005),Sultan and Sultan, 2015.

Figure 2 Shows the transmission spectra of ZnS prepared from $ZnCl_2$ solution. The film thickness is 489nm as computed using gravimetric method of thin film thickness computation. In the wavelength region of 200-300nm a sharp increase in transmittance is observed but drops from 59% to 40% within the wavelength range of 300nm to 450nm. The maximum transmission of about 60% is observed in the visible range (450nm-850nm) but decreases to about 25% for the ZnS film prepared from $ZnCl_2$ precursor [Allouche et. al. (2010)].

Figure 3 and Figure 4 show the absorbance of ZnS for $ZnSO_4$ and $ZnCl_2$ precursors respectively having wavelength of complete absorption between 200nm-250nm at which the absorbance is greater than 1 for the ZnS film deposited from both precursors.

Figure 3 Shows the absorption spectra of ZnS film deposited from $ZnSO_4$ solution. The wavelength of onset of absorption (λ_o) is 200nm and the wavelength of maximum absorption (λ_m) occurs between 200nm-280nm having an absorption coefficient of $13.0 \times 10^6 m^{-1}$ as computed.

Figure 4 shows the absorption spectra of ZnS film deposited using $ZnCl_2$ precursor. The wavelength of onset of absorption (λ_o) is 200nm and the wavelength of maximum absorption (λ_m) occurs between 200nm-280nm having an absorption coefficient of $13.0 \times 10^6 m^{-1}$. The values of the absorbance obtained for both host solutions have some discrepancies from earlier reports in literature[Kelvin et. al. (2007)]. This may be due to the process of experimentation and characterization.

Again the plot of the square of the absorption coefficient versus the photon energy is shown in Figure 5 and Figure 6 for the ZnS film prepared from $ZnSO_4$ and $ZnCl_2$ solution bath respectively.

In Figure 5 an energy band gap of 3.94eV for the ZnS film prepared from $ZnSO_4$ was obtained which collaborates with earlier reports from literature [Allouche et. al. 2010].

Figure 6 Shows energy band gap of 3.97eV for the ZnS film prepared from $ZnCl_2$ solution.

Table 1 shows the dependence of the film thickness and deposition time on the precursor type used. In this study, the growth period required a moderate period of incubation of about 6hours ($ZnSO_4$) and 8hours ($ZnCl_2$). The visual analysis shows that ZnS films from both $ZnCl_2$ and $ZnSO_4$ solution are whitish in colour as stated in literature [Allouche et. al. 2010, Anthony et. al. (2005)].

The ZnS film deposited from $ZnSO_4$ solution bath has a higher thickness (685nm) than ZnS film (489nm) deposited from $ZnCl_2$ solution bath. This result might be due to the fact that the ZnS film deposited from $ZnSO_4$ precursor exhibit higher aggregation on glass substrates, hence they are easily deposited on the glass substrate [Allouche et. al. 2010].

Figures 2 and 3 are the relationship between the wavelength and transimissivity of the samples. As could be seen, transmissvity for the ZnS samples was more than 75% ($ZnSO_4$ host solution). The trend of the transmissivity was upward within the range of 200nm-1100nm wavelength of incident light. In the ZnS film deposited from $ZnCl_2$, the maximum transmittance which is about 60% rapidly drops to 25%[Anthony et. al. (2005)]. The absorption coefficient decreases gradually as the photon wavelength increases for the film deposited from $ZnSO_4$, but the absorption coefficient varies between moderate values as the photon wavelength increases [Anthony et. al. (2005)]. Table 2 shows the energy band gap of the ZnS film from the different precursor types as shown in Figs. 5 and 6. The ZnS film has a direct energy band gap of 3.99eV ($ZnSO_4$ precursor) and 3.97eV ($ZnCl_2$ precursor) as stated in earlier reports [Allouche et. al. 2010, Anthony et. al. (2005)]. Hence the energy band gap of ZnS films obtained in this study could be taken as standard values.

This study shows that the optical and solid state properties (film thickness) of ZnS films were found to vary with the precursor

Scientia Africana, Vol. 16 (No. 2), December 2017. Pp 106-115
© Faculty of Science, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

type. Thin films prepared from chemical bath containing Zinc Sulphate solution exhibit optical transmission above 75% in the visible region and beyond. The zinc sulphide film deposited from zinc sulphate has higher thickness which improves its crystallinity. The films produced from the zinc sulphate precursor look transparent and smooth compared to the ones grown from the zinc chloride precursor. Direct bandgap of 3.94eV was obtained for the zinc sulphide films deposited from $ZnS0_4$ which is higher than the other film. Properties such as large bandgap has advantages associated with it. These include higher breakdown voltage, ability to sustain large electric field, low electronic noise, stable at higher temperature and high power operation[Kernzinger and De-Andrade (2007)].As a result of its high transmittance, low absorbance and low reflectance, which is the general properties peculiar to the Zns films from both $ZnS0_4$ and $ZnCl_2$ precursors, the film could be used as solar filters (solar cell fabrication) and solar control coating on windows [Chopa and Das (1983)].It is a good material for the fabrication of laser diodes and light emitting diodes (LEDs) [Chopa and Das (1983)].

REFERENCES

Akira, I., Masashi, H., Takuya, A., Tsukasa, D., Tokio, N., 2006. Ultrasonic chemical bath deposition of ZnS (O, OH) buffer layers and its application to CIGS thin film solar cell. Solar energy materials and solar cells (90) 3130 – 3135.

Allouche, N. K., Nasr, T. B., Kamoun, N. T., Guash, C., 2010. Synthesis and properties of chemical bath deposited ZnS multilayer films. Materials Chemistry and Physics (123) 620-624

Anthony, A., Murali, K. V., Manoj, R., Jarayaj, M. K.,2005. The effect of pH value on the growth and properties of chemical- bath-deposited ZnS thin films. Material chemistry and physics (90) 106-110.

Chopra, K.I., Das, S.K., 1983. Thin film solar cells. Plenum press, New York.5, 6, 7, 204, 205.

Heavens, O.S, 1991. Optical properties of thin solid films. Dover publication Inc, New York.

James, K., James, D., 2005. Planning and installing solar thermal systems. The German solar energy society, Ecolys, Germany vol 7(2) 98

Johnston, D.A, Carlettoa, M.H., Reddy, K.T.R., Forbes, I, Miles, R.W.,2002. chemical bath deposition of zinc sulfide based buffer layers using low toxicity materials. Thin solid films 403-404 (2002) 102-106.

Kelvin, J. H., Poorna, R., Chekesha, M. L., 2007.Chemical bath deposition synthesis of sub-micron ZnS- coated polysterene. Journal of colloid and interference. (308)112-120.

Kernzinger, A., De-Andrade, A.C., 2007 Accurate outdoor glass thermographic thermometry applied to solar energy device solar energy 81(8) 136-140.

Limei, Z., Nan, T., Sumei, W., Xiaofei, H., Yuzhi, X., 2011. Influence of deposition time on ZnS Thin films performance with chemical bath deposition. Physics procedia 22,354 – 359.

Okujagu, C.U., 1992. Growth and characterization of thin selective surfaces and their possible application, Ph.D thesis, University of Nigeria, Nsukka.

Okujagu, C.U., Okeke C.E., 1999. Thin film technology for energy supply and regulation in Nigeria Journal of applied science and environment management. (3)5-9.

Paul, O. B., David, J. O., David, S. B., 2000. Importance of tenerary complexes in defining basic conditions for the deposition of ZnS by aqueous chemical bath deposition. Thin Solid Films 361 – 362, 17 – 21.

Ran, Z., Shubo, W., Haiyan, X., Hao, W., Hui, Y., 2005. Rapid formation of CdS, ZnS thin films by microwave assisted chemical bath deposition. Materials letters (59) 1497 – 1501.

Sartale, S. D., Sankapal, B. R., Lux-Steiner, M., Ennaoui*, A.,2005. Preparation of nanocrystalline ZnS by a new chemical bath deposition route. Thin Solid Films 480-48 (2005) 168-172

Sultan, Z., and Sultan, N.,2015. Analysis of Reflectance and Transmittance Characteristics of optical thin film for various film materials, thickness and substrates. J. of electrical and electronic systems.104172/2332-0796.

Thun, R.E., 1985. Thin films, the encyclopedia of physics (3rd edition) van No strand Reinhold, New York. 1239

Wagner, S., Shay, J.L., Bachmann, K.J., Beubler, L; 1975. Solar energy conversion prentice Hall, New York.

YU, V., Gonzalez-hernandez, J., Vorobiev, P., Bulat L., 2006. Thermal-photovoltaic solar hybrid system or efficient solar energy conversion solar energy, 80 (1)170-176.

Zhang, Y., Dang, J. J., Yu, T., Li, B. Z., He, Q., Li, F. Y., Sun, Y., 2010. ZnS thin film deposited with chemical bath process directed by different stirring speeds. Applied surface science (256) 6871 – 6875.

Zhou, L., Xue, Y. Z., Jianfeng L. I., 2009. Study on ZnS thin films prepared by chemical bath deposition. Journal of environmental sciences supplement S76 –S79.