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Investigating the Optical and Electricalproperties of ZnSe Thin Films Prepared by Chemical Bath Deposition Technique.

O. O. Olusola[1], O. I. Olusola[2], K. A. Aduloju[3], G. E. Adesakin[4], E. A. Odo[5]
[1]*Department of Physics, School of Science, College of Education, IkereEkiti, Ekiti State, P.M.B. 250, Nigeria.*
[2]*Condensed Matter and Statistical Physics Research Unit,Department of Physics, School of Science, The Federal University of Technology, Akure, P.M.B. 704, Nigeria.*
[3, 4]*Department of Physics, Faculty of Science, Ekiti State University , Ado Ekiti, P.M.B. 5363, Nigeria.*
[5]*Department of Physics, Federal University Oye-Ekiti, P.M.B. 373, Nigeria.*
Corresponding author:O. O. Olusola[1]

***Abstract*:** *The optical and electrical properties of chemical bath deposited ZnSe thin films of thickness ~500 nm have been investigated using UV-Visible spectrophotometer and four-point probe measurement techniques respectively. Optical parameters such as energy bandgap and optical constants were determined using the data obtained from UV-Visible spectrophotometer. The energy bandgap of as-deposited ZnSe films was estimated to be 2.70±0.02 eV and this corresponds to the energy bandgap of bulk ZnSe semiconductors. The optical constants which are mainly refractive index and extinction coefficients were estimated to be ~2.28 and 0.298 respectively. The electrical properties such as resistivity and activation energy were estimated at different measurement temperatures. It was observed that the resistivity of the chemical bath deposited ZnSe layers decreasedwith increase in the measured temperatures. The activation energy of the deposited ZnSe thin films was estimated to be 0.75 eV from the Arrhenius plot.*

Keywords: *Semiconductor, Chemical Bath Deposition, Energy Bandgap, activation energy, Resistivity, temperature*

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I. Introduction

Over the years, research on semiconductors has become very significant due to its application and usefulness to humanity. Group II-VI compound semiconductors like Zinc Telluride(ZnTe), Cadmium Selenide (CdSe) and Zinc Selenide (ZnSe) have received great attention due to their low cost and high absorption coefficient in their application to electronic devices, photovoltaic and photoelectrochemical cells[1].Among these II-VI binary compound semiconductors, Zinc Selenide (ZnSe) has been chosen as a potential material for device applications due to its unique features which make it suitable for applications in optoelectronic devices [2].For the deposition of II-VI binary compound semiconductors, various methods have been used. Some of which include molecular beam epitaxy[3], spray pyrolysis [4], metal-organic chemical vapour deposition [5], electrodeposition[6], vacuum evaporation [7] and chemical bath deposition [8]. Chemical bath deposition (CBD) has been used because it is easy to handle, more rapid, reproducible , less expensive and suitable for deposition on large substrates at room temperature.

II. Experimental

2.1 Substrate preparation

The glass substrates were first cleaned by mild soap solution, de-greased with organic solvents (acetone) and etched with hydrogen chloride (HCl) for 30 minutes to remove any surface impurities. The cleaned glass substrates were finally rinsed in de-ionized water and dried in air.

2.2 Preparation of Na_2SeSO_3 electrolyte as Se precursor

All solutions were prepared using double distilled water. The sodium selenide-sulphite (Na_2SeSO_3) solution was prepared by mixing 12.5 grams of selenium (Se) metal powder with 39.5grams of Sodium Sulphite (Na_2SO_3) in a glass beaker containing 500ml of distilled water. The beaker containing the mixture of electrolyte was subjected to heating as reported elsewhere [9]. The heating process was controlled and stopped at temperature 85^{o}C. The prepared solution was allowed to cool down and then filtered so as to obtain a clear solution of the Na_2SeSO_3 electrolyte. The filtered solution was then used in conjunction with the Zinc acetate ($Zn(CH_3CO_2)_2$) to carry out the ZnSe thin film deposition [10].

2.3Deposition of ZnSe thin films using Zn and Se precursors.

Before the deposition of ZnSe thin films, the electrolyte for Zn deposition was prepared by adding zinc acetate ($Zn(CH_3CO_2)_2$) and Hydrazine Hydrate (H_6N_3O) with uniform stirring. Liquor ammonia was gradually added to the above prepared solution to improve its clarity. NaOH was also added to vary the pH of the electrolyte. The prepared solution was then heated to a temperature of 90^oC before adding the Se precursor (Na_2SeSO_3). The heating was maintained under constant stirring condition so as to obtain layer uniformity. The cleaned glass substrates were positioned vertically inside the electrolyte beaker with the aid of a retort stand.

The deposition of ZnSe thin films then took place on the substrates for48 hours at room temperature, after which each substrate was removed from the beaker. The ZnSe thin film obtained was washed with double-distilled water and then dried in air. The deposited film was then kept in an airtight plastic container for proper preservation [10].

2.4 Measurement of thickness.

The equipment or machine used to determine the surface roughness and thickness of thin films deposited on solid substrates is called profilometer. In carrying out this measurement, sample was mounted on the stage of the profilometer and stylus (probe) was brought in contact with the sample.

The desired scan parameter (scan length, depth, speed, duration etc) were then specified after which the probe was made to scan across the simple single scratch made on the sample. The thickness obtained was ~***500 nm***.

III. Optical Characterisation

UV-visible spectrophotometer is a simple machine used for the characterisation of the optical property (for example, transmittance, reflectance and absorbance) of a material. The equipment consists of light source that generates a light at a particular frequency, sample stage that holds the sample in position for scanning, spectrophotometer that is used in scanning the sample through the whole range of UV-Vis frequency, a complete computer system that runs the software (Avasoft 7.0) for UV-Vis and optical fiber cable that transmits and carries the light ray through the sample.

Some of the incident light was transmitted, reflected or absorbed. The UV-Vis spectrophotometer took the reading at different wavelengths.

IV. Results And Discussion

4.1 Optical measurements of chemical bath deposited ZnSe layers

UV-Vis spectrophotometer was used in obtaining the optical absorption measurements of chemical bath deposited ZnSe thin films within the wavelength range of 300-800 nm. The optical absorption measurement versus wavelength for ZnSe layer is shown in ‘‘ Fig 1’’ . Extrapolation of the absorption curve to the wavelength axis of ZnSe film with thickness 500 nm gives a wavelength of 460 nm.The estimated wavelength of 460 nm for ZnSe film of ~500 nm thickness is equivalent to the wavelength which corresponds to the energy bandgap (E_g) of bulk ZnSe. The CBD ZnSe layer has the highest and lowest absorption in the UV and infrared region. A decrease in the absorption of photons was observed from the visible to the infrared region. This experimental result agrees with the work published by Agool*et al.*,[11] that thermal evaporated ZnSe thin films have high absorbance in the UV region.

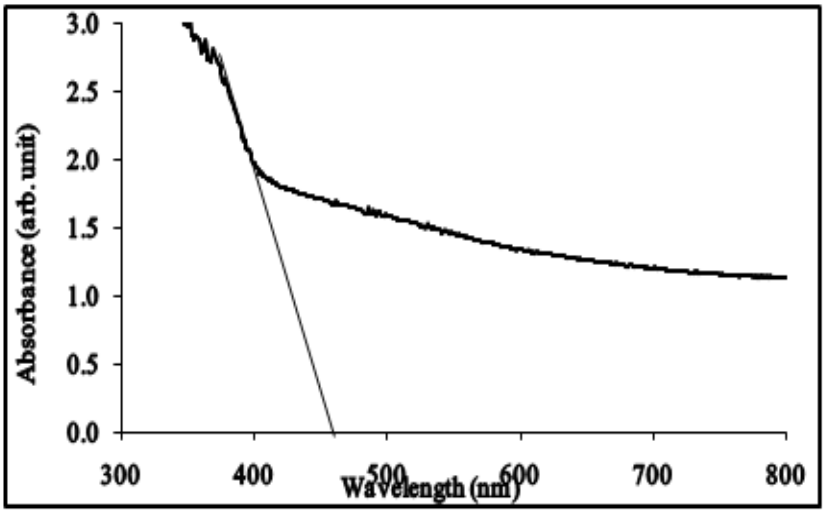

Figure 1. Plot of absorbance versus wavelength (λ) for ZnSe thin film

The energy bandgap of CBD ZnSe layers was determined by plotting the square of (α) as a function of photon energy as shown in ''Fig. 2 ''. The bandgap was estimated by extrapolating the line of best tangent of the curve to the horizontal axis (or photon energy axis) when $(\alpha)^2$plotted on the vertical axis equals to zero. The estimated energy bandgap value for ZnSe layers was estimated to be 2.70 eV. The energy bandgap of 2.70eV obtained bandgapfor ZnSe film corresponds to the bandgap reported for bulk ZnSe layers reported elsewhere[12]. The linearity of the extrapolated portion of the $(\alpha)^2$ versus photon energy of the ZnSe films described in ''Fig. 2'' explains the direct bandgap nature of the semiconductor.

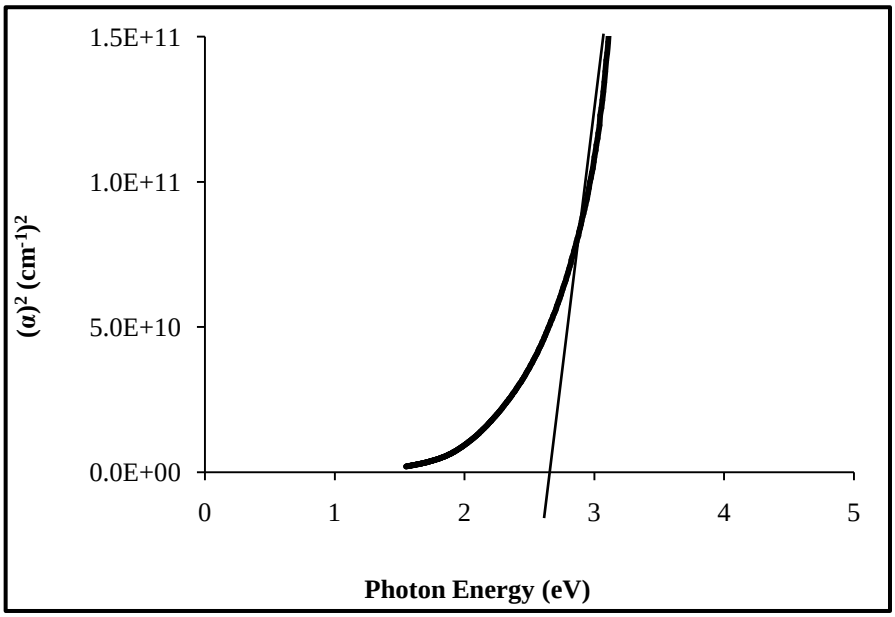

Figure 2. Graph of $(\alpha)^2$ versus photon energy (hν) for ZnSe thin films

The data used in plotting the transmittance *(T)* spectrum shown in Figure 3 was obtained from absorbance *(A)* by using Equation (1);

$$A = log_{10} \frac{1}{T} = log_{10} T^{-1} = -log_{10} T \quad (1)$$

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

Converting (2) in log_{10} to *ln* gives (3) ;

$$-2.303\ A = ln\ T \quad (3)$$

The transmittance, *T* can be obtained from (3) by finding the exponential of both sides of the equation;

$$T = e^{-2.303\ A} \quad (4)$$

''Fig.3'' illustrates the optical transmittance spectrum for chemical bath deposited ZnSe thin films within the wavelength range of 300 – 800 nm. As shown in ''Fig. 3'', the amount of photons transmitted within the ultraviolet region ($\lambda < 400$ nm) is very small when compared to the percentage of photons transmitted in the visible ($400\ nm \leq \lambda \leq 700\ nm$) and infrared region ($\lambda > 700$ nm).From the visible to infrared region, a progressive increase was observed in the amount of photons transmitted in the ZnSe layers.

The high transmission of photons in the infrared region of ZnSe thin films may therefore be one of the main reasons why ZnSe semiconductor materials are preferred as suitable candidate to use with high power infrared laser [13].

The low transmittance of incident photons in the UV region can be explained in terms of the high energy bandgap of ZnSe thin films. Mostly in electronic devices, high energy photons are usually absorbed in the UV region of the solar spectrum while low energy photons are absorbed in the infrared region.

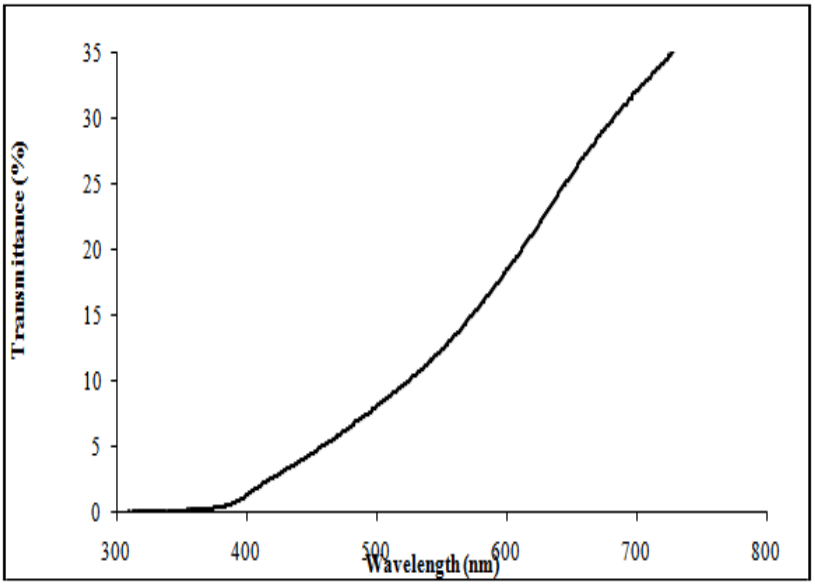

Figure 3.Optical curves of ZnSe thin films showing theplot of transmittance in percentage versus wavelength in nanometre.

‘‘Fig.4 ’’ illustrates the optical reflectance spectrum of ZnSe films within the wavelength range of 300 to 800 nm. As depicted in ‘‘Fig.4 ’’, there was no reflectance of the incoming photons in the UV region. The reflectance effect started originating in the visible region when the wavelength is ~560 nm. It was observed that the percentage of reflected photons increase from the visible to the infrared region. In the far end of the infrared region, the reflectance value tends to attain a maximum position.
The small values of absorbance and reflectance in the visible region enable the ZnSe semiconducting materials to be useful as light emitting diodes (LED) and visible laser diodes (VLD) [11].

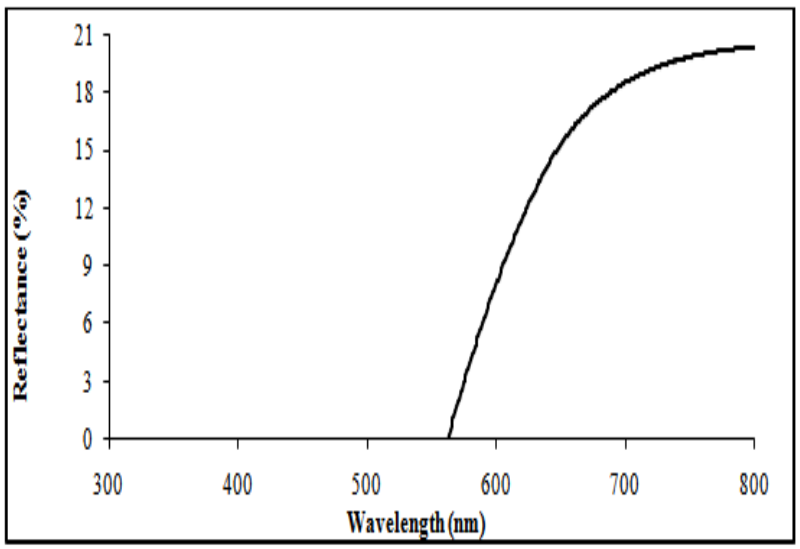

Figure 4. Optical curve of ZnSe thin films showing the plot of reflectance in percentage versus wavelength in nanometer**.**

The optical parameters summarised in ‘‘Table 1’’ are the energy bandgaps and corresponding wavelengths, average absorption coefficient ($\alpha_{average}$), average extinction coefficient, ($k_{average}$) and average refractive index ($n_{average}$).

Table 1. Optical parameters obtained from chemical bath deposited ZnSe thin film.

Thickness (nm)	Energy Bandgap, E_g±0.02 (eV)	Corresponding Wavelength, λ (nm)	Average Absorption Coefficient, α (cm^{-1})	Average Extinction Coefficient, *k*	Average Refractive Index,*n*
500	2.70	~460	7.94×10^4	0.298	~2.28

4.2 Electrical characterization of chemical bath deposited ZnSe layers

The current-voltage characteristics of ZnSe thin films obtained at measurement temperatures of 303-333 K at an interval range of 10 K are shown in ‘‘Fig.5’’. The I-V curves exhibit ohmicbehaviour with their straight lines passing through the origin. As illustrated in ‘‘Fig.5’’, measured temperatures influence the electrical properties of the chemical bath deposited ZnSe layers. Annealingtemperature is one of the external parameters that can be varied to modify the electrical conductivity of semiconductor materials[14].

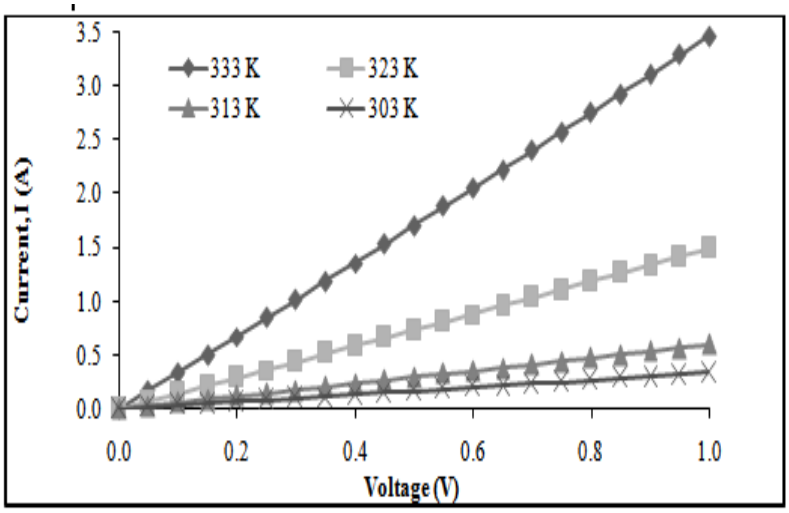

Figure 5. Current-voltage characteristics of ZnSe layers taken at different measurement temperatures ranging between 303 and 333 K

The electrical resistivity decreases from the order of 10^4 Ω.cm at 303 K to the order of 10^3 Ω.cm as the measurement temperature increases to 333 K as shown in ‘‘Table 2’’. This result thus shows that the electrical resistivity of the semiconducting film decreases with increase in temperature; this type of feature exhibited by the ZnSe film is a typical behaviour of semiconductor materials.

For most semiconductor materials, the resistivity decreases with temperature increase [14].Ashraf *et al*[15] explained that reduction of resistivity with temperature increase may be as a result of thermal excitation of carriers from the boundary of the grains to the grain regions. The experimental results obtained in this work agreed with the work reported byKale and Lokhande[16] andHankare *et al*[12]; the authors demonstrated how increase in temperature brought about increase in the thin film electrical conductivity or decrease in the thin film electrical resistivity.

Table 2. Resistivityof ZnSe layers at different measurement temperatures.

Temperature, T (K)	303	313	323	333
Resistivity,ρ(Ω.cm)	6.00×10^4	3.36×10^4	1.34×10^4	$5.8x10^3$

From the Arrhenius equation stated in (5), a plot of *ln* (conductivity) was obtained as a function of reciprocal of temperature;

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \qquad (5)$$

$$\ln \sigma = \left(-\frac{E_a}{k}\right)\left(\frac{1}{T}\right) + \ln \sigma_o \qquad (6)$$

Equation (6) represents the linear equation of the form $y = mx + c$. From (6), a graph of $ln\ \sigma$ plotted against 1/T gives a slope, *m* of $\left(-\frac{E_a}{k}\right)$ and intercept, *c*of $ln\ \sigma_o$. E_a is the activation energy for conduction, σ is the specific conductivity measured in $(\Omega.cm)^{-1}$ and k is the Boltzmann's constant, 1.38×10^{-23} JK^{-1}.

The plot of $ln\ \sigma_o$ against T^{-1} illustrated in ''Fig.6 '' showed a negative slope of -8750. The slope was obtained from the linear portion of ''Fig.6 ''. The activation energy, E_a is estimated from the slope as given in Equation (7);

$E_a = slope \times -k$ (7)

The value of E_a as estimated from (7)on the 500 nm thickness is~0.75 eV

Different researchers who worked on ZnSe semiconductors got various values for the activation energy of ZnSe thin films. Ashraf *et al*., 2011 worked on ZnSe thin films and obtained E_a of ~0.45 eV for as-deposited materials. The E_a obtained byHankare *et al* [17] from the electrical characterization of ZnSe thin films at higher temperature is ~0.61 eV.

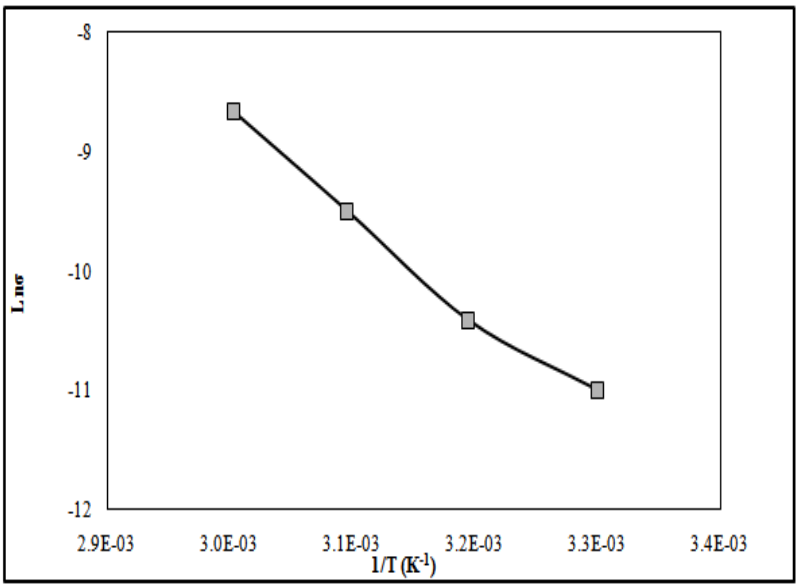

Figure 6. Theplot of lnσ versus 1/Tfor ZnSe thin films. (Note: the graph shows the dependence of electrical conductivity on temperature**)**

V. Conclusion

ZnSe thin films was successfully deposited on glass substrates by using chemical bath deposition technique.The energy bandgap exhibited by the film investigated in this work falls within the energy range required for a semiconductor to effectively function as either buffer or window layers for photo-voltaic applications.The *I-V* characteristics at different measurement temperatures of the ZnSethin films obeyed Ohms law and they showed linear response within the operating range of applied voltage. The experimental results revealed that as the measurement temperature increases, the resistivity of the ZnSe semiconductor reduces.

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