

Electrical and Structural Properties of ZnSe Thin Films by Electrodeposition Technique

I.L. Ikhioya and A.J. Ekpunobi

*Department of physics and Industrial Physics, Nnamdi Azikiwe University,
Awka, Anambra State, Nigeria.*

Abstract

Zinc selenide (ZnSe) thin films semiconductor were studied at room temperature by electrode position technique. XRD pattern of ZnSe showed cubic structure with a preferred orientation along (111) plane. The optical properties of the films were investigated in the wavelength range of 300-900nm. The optical band gap energy was 2.3-2.1eV.

Keywords: Thin Film, ITO, ZnSe, SeO_2 , characterization, application

1.0 Introduction

Zinc selenide is an n-type semiconducting material with wide band gap (2.7 eV). It is a suitable material for red, blue and green light emitting diodes, photovoltaic, laser screens, thin film transistors, photoelectron chemical cells [1- 4]. The buffer layer determines properties of thin film solar cells such as intensity of the electric field in the absorber interfacial states and electronic bands alignment. It is also involved in the long-term stability of the cells and light soaking effect [5]. ZnSe thin film has been used as n-type window layer for thin film hetero junction solar cells [6]. Thin films of ZnSe have been deposited using molecular beam epitaxy, electron beam evaporation, chemical deposition, electrodeposition, vacuum evaporation, successive ionic layer adsorption and reaction (SILAR) technique [7 – 11]. Electrodeposition technique seems to be an inexpensive, low temperature method that could produce good quality films for device applications. The attractive features of this method are the convenience for producing large area devices and possibility to control the film thickness, morphology and stoichiometry of the films by adjusting the deposition parameters and concentration of precursors in electrolyte.

In this paper, we report the electrodeposition of ZnSe thin films from an aqueous solution bath containing $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and SeO_2 . The influence of growth conditions such as deposition potential, temperature on crystallinity and composition of the film was studied. XRD and optical transmission techniques were employed for characterizing the deposited films.

2.0 Materials and Methods

ZnSe thin films were deposited by electrodeposition technique using 20cm³ of 0.063M of selenium IV oxide (SeO_2) mixed 20cm³ of 0.069M of Zinc tetraoxosulphate VI Heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and 5cm³ of potassium tetraoxosulphate VI (K_2SO_4) solution then, 5cm³ of 0.4M of tetraoxosulphate VI acid (H_2SO_4). Which used to acidify the solution, it was added into the mixture and stirred well. The indium doped tin oxide (ITO) glass was used as substrate. The ultrasonically cleaned glass substrate was immersed vertically into the solution for electrodeposition process. The films growth was carried out at 300K. During deposition process, the deposited films were tested for adhesion by subjecting it to a steady stream of distilled water. X-Ray diffractometer (XRD) analysis was carried out using DM-10 diffractometer for the 2θ ranging from (15- 53°) with $\text{CuK}\alpha$ ($\lambda = 1.540598$ Å) radiation. Optical absorbance study was carried out using M501 UV-Visible spectrophotometer. The films coated indium thin oxide glass was placed across the sample radiation pathway while the uncoated the reference path. The absorption data were manipulated for the determination of band gap energy.

3.0 Electrical Analysis of ZnSe Films

The electrical properties of the films were investigated using a standard four point probe technique. The arrangement was made in such a way that the voltage across the transverse distance of the films and the corresponding values of the current were measured using silver paste to ensure good ohmic contact to the film. Table 1 shows the result obtained.

Corresponding author: I.L. Ikhioya, E-mail: ikhioyalucky@gmail.com, Tel.: +2348038684908

The results clearly show that ZnSe films have high resistivity. The high resistivity makes ZnSe suitable as buffer layer in thin film technology. It is a semiconductor that has large potential applications in thin films like photo luminescence and electroluminescent devices. The results are comparable with the value reported in [12], whose value of resistivity is of the order of 10^{-4} - 10^{-5} (Ωm)⁻¹ [13-14]

Table 1: Electrical Property of ZnSe Films

SLIDES	THICKNESS, t (nm)	RESISTIVITY, (Ωm) ⁻¹	CONDUCTIVITY, (Ωm) ⁻¹
X	164	1.500×10^9	7.892×10^{-5}
Y	201	4.861×10^9	2.057×10^{-5}
Z	220	4.339×10^9	2.304×10^{-5}

4.0 Structural Properties of Zinc Selenide Films

X-ray diffractometer using CuK α radiation ($\lambda = 1.540598$ Å). The X-ray diffraction patterns of ZnSe thin films are presented in Figure.1-3. The X-ray diffraction patterns show a cubic structure which correspond to (111-222) planes. The diffraction angle 2θ value is 16.31° , 16.61° and 16.17° with $d = 5.432$ Å, $d = 5.336$ Å and $d = 5.480$ Å. The preferred orientation lies along the (111) plane. The lattice constant was given in the X-ray diffraction analysis is found to be $a = 5.6667$ Å. The crystallite size was determined by means of the X-ray line broadening method using Scherer equation [15]

$$D = \frac{0.9 \lambda}{\beta} \quad (1)$$

Where λ is the wavelength of CuK α radiation ($\lambda = 1.540598$ Å), β is the full width of half maximum FWHM of the (hkl) peak of the diffracting angle hkl 2θ . The average grain size D , the dislocation density ρ is calculated using the following relation [16]

$$\rho = \frac{1}{L^2} \text{ lines/m}^2 (2)$$



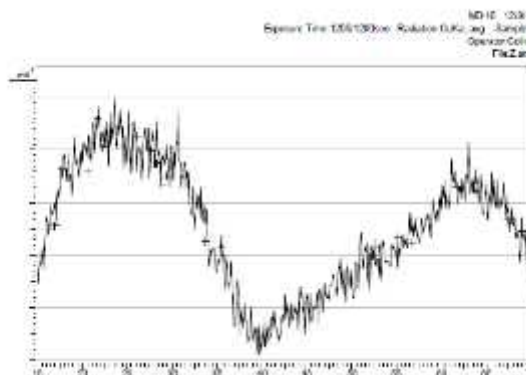
Figure 1: X-ray diffraction pattern of ZnSe film (slide X)

Table 2: The structural parameters of ZnSe film (X)

Slide	h k l	2θ		d(Å)	d(Å)	Lattice constant (Å)	FWHM (rad.)	Grain size, (D) (nm)	Dislocation density, (ρ) (lines/m ²)	Micro strain
		Deg.	Rad.							
X	111	16.31	0.284	5.431	5.432	5.67	0.76246	1.836	1.330	0.565
	200	16.99	0.296	5.218	5.219		0.76246	1.837	1.276	0.613
	220	17.31	0.302	5.122	5.123		0.76246	1.838	1.252	0.637
	311	17.78	0.310	4.987	4.988		0.76246	1.839	1.218	0.673
	222	18.10	0.315	4.900	4.901		0.76246	1.840	1.196	0.698

**Figure 2:** X-ray diffraction pattern of ZnSe film (slide Y)**Table 3:** Structural parameters of ZnSe film (Y)

Slide	H k l	2		d(d(Lattice constant (FWHM (rad.)	Grain size, (D)(Dislocation density,	Micro strain
		Deg.	Rad.							
Y	111	16.61	0.289	5.335	5.336	5.67	0.61122	2.291	1.046	0.912
	200	20.43	0.356	4.345	4.346		0.14643	9.617	2.617	0.242
	220	20.65	0.360	4.299	4.300		0.16597	8.488	0.227	1.927
	311	20.98	0.366	4.233	4.234		0.65342	0.882	0.882	1.284
	222	21.37	0.372	4.157	4.158		0.4173	0.552	0.552	3.270

**Figure 3:** X-ray diffraction pattern of ZnSe film (slide Z)**Table 4:** Structural parameters of ZnSe film (Z)

Slide	H k l	2		d(d(Lattice constant (FWHM (rad.)	Grain size, (D)(Dislocation density,	Micro strain
		Deg.	Rad.							
Z	111	16.17	0.282	5.479	5.480	5.67	1.1452	1.222	2.015	0.246
	200	17.72	0.309	5.004	5.005		0.45208	3.102	0.725	1.902
	220	20.60	0.359	4.309	4.310		0.6999	2.012	0.962	1.078
	311	21.25	0.370	4.179	4.180		0.49187	1.410	0.655	2.327
	222	21.61	0.377	4.111	4.112		0.37872	3.725	0.496	4.063

5.0 Optical properties of zinc Selenide films

The optical properties of Zinc selenide films were studied using a M501 UV-Visible spectrophotometer in a wavelength range of 300-900nm. The transmission spectra of the Zinc selenide thin films deposited shows in Figure 5. The transmittance spectra show very high transmittance in the VIS-NIR regions of the electromagnetic spectrum. In Figure 4 the absorbance of Zinc selenide film show high in the UV region and IR regions. The high absorbance in UV region makes the material useful in formation of p-n junction solar cells with other suitable thin film materials for photovoltaic application. These results agree well with the report in [12]. These optical properties make Zinc selenide thin films nice glazing material for maintaining cool interior in buildings in warm climate regions while still keeping the rooms well illuminated. To ensure that the thermal radiation from the warm glazing to the interior is inhibited and the thermal energy dissipated in the glazing due to absorption is predominantly transferred to the exterior by enhanced convective heat transfer of the glazing to the exterior.

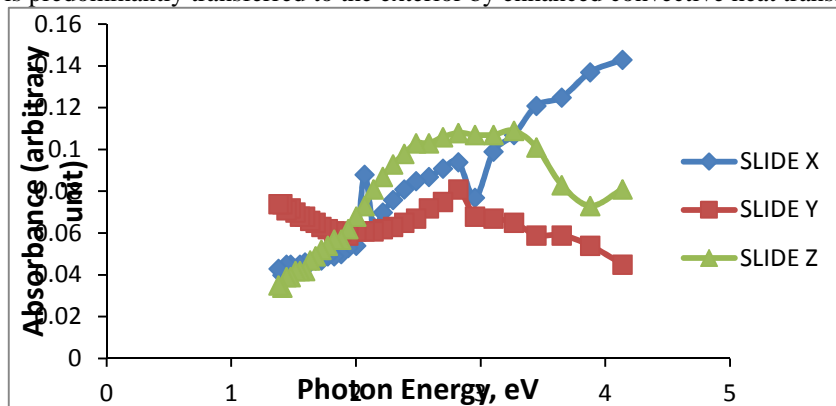


Figure 4: Plot of absorbance against photon energy for ZnSe Film (slide XYZ)

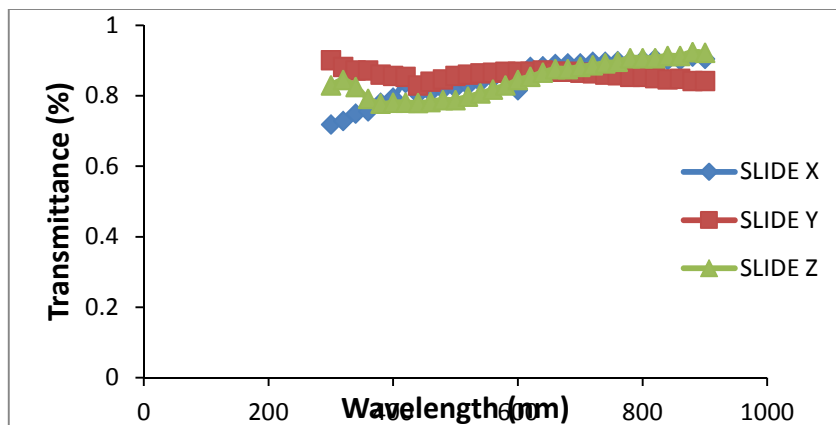


Figure 5: Plot of transmittance against wavelength for ZnSe film (slide XYZ)

6.0 The Band Gap Energy

The band gap energy and transition types were derived from mathematical processing of the data obtained from the optical absorbance versus photon energy with the following relationships for near edge absorption [17].

$$= (h\nu - E_g) n/2$$

Where ν is the frequency, h is the Planck's constant, while n carries the value of either 1 or 4. The band gap E_g could be obtained from a straight line plot of ν^2 as a function of $h\nu$; an extrapolation of the value of ν^2 to zero will give band gap. If a straight line graph is obtained from $n=1$, it indicates a direct transition between the states of the semiconductor, whereas the transition is indirect if a straight line graph is obtained from $n = 4$ as shown in Figure 6. The band gap energy of 2.3eV band gap energy has been obtained which correspond to the band gap energy obtain in [14]. Band gap energy of 2.1eV and 2.2eV was obtained in Figures 7-8 due to slight increase in pH

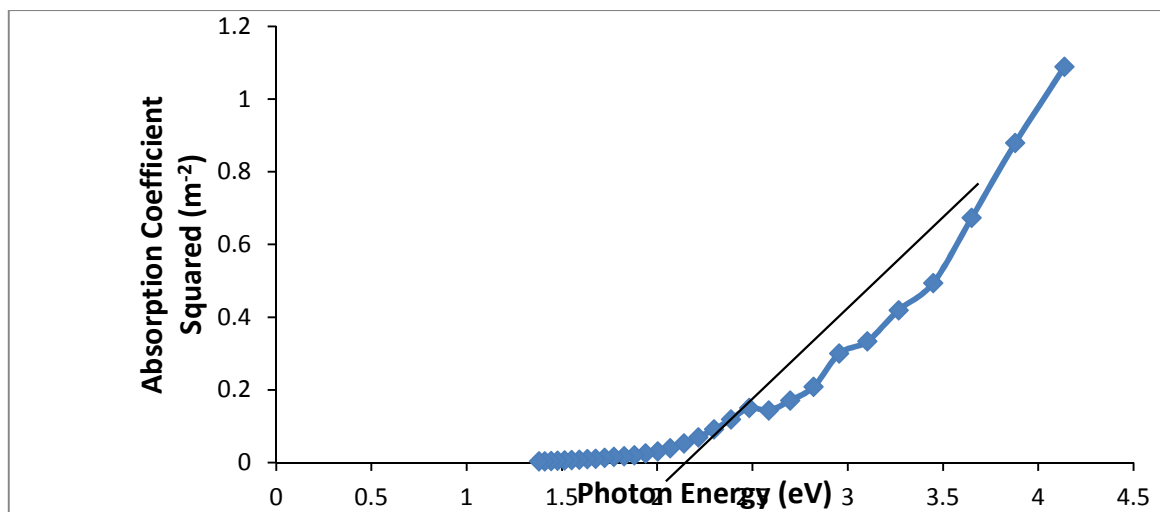


Figure 6: Plot of absorption coefficient squared (α^2) against photon energy For ZnSe thin film (slide X)

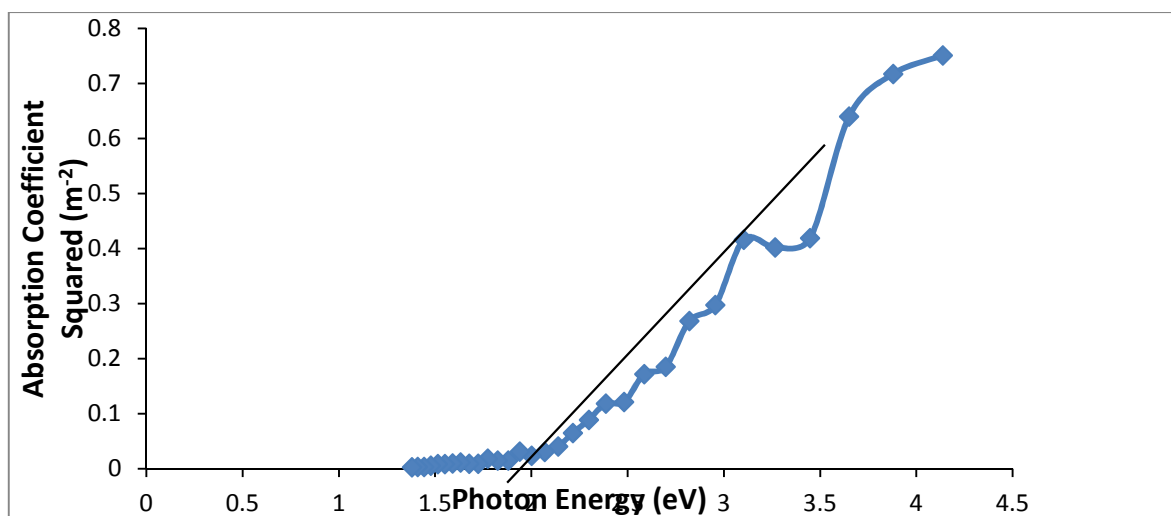


Figure 7: Plot of absorption coefficient squared (α^2) against photon energy For ZnSe thin film (slide Y)

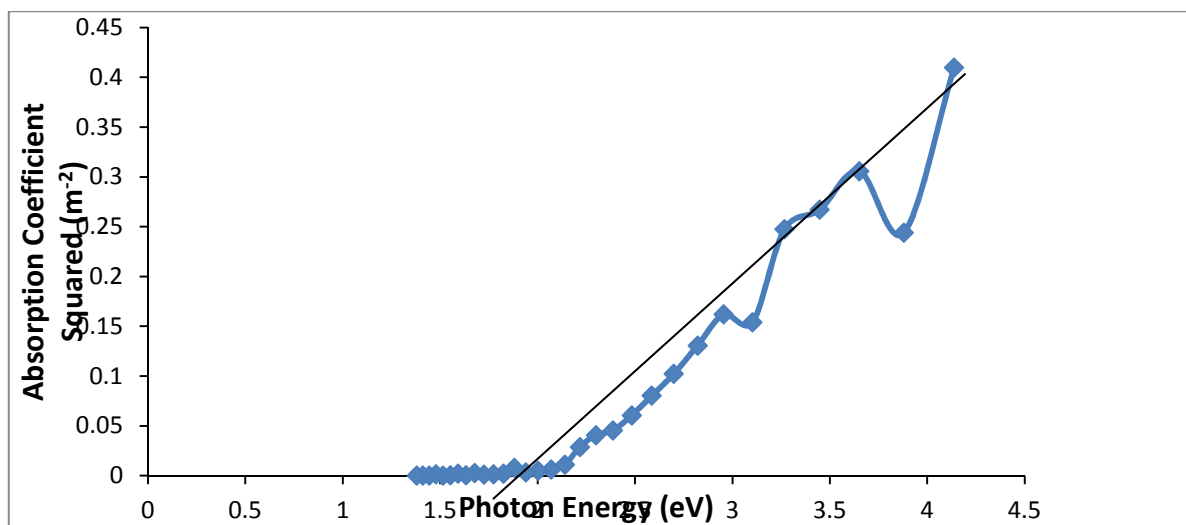


Figure 8: Plot of absorption coefficient squared (α^2) against photon energy For ZnSe thin film (slide Z)

7.0 Conclusion

Zinc selenide thin films have been prepared by electrodeposition technique. The films have peak transmittance in infrared region of the electromagnetic spectrum and high rate of absorption in the UV and NIR regions. These make Zinc selenide thin films excellent glazing material for solar control in warm climatic regions. The obtained value of the optical band gap energy was 2.7eV, and the relation indicates indirect transition. XRD analysis showed that the ZnSe thin films, so deposited, exhibit cubic structure with a preferred orientation along (111) plane.

8.0 References

- [1] O. Akira, S. Noriyoshi, S. Zembutsu, J. Appl. Phys. 64, 654 (1988).
- [2] A. Ennaoui, S. Siebtritt, M.Ch. Lux-Steiner, W. Riedl, F. Karg, Solar Energy Mater. Solar Cells 67, 31 (2001).
- [3] M. P. Kulapov, G. A. Murovick, V. N. Ulasyuk et al., Izv Akad Nauk SSSR Neorg. Mater. 19, 1807 (1983).
- [4] R. R. Alfano, O. Z. Wang, J. Jumbo, B. Bhargava, J. Phys. Rev. A 35, 459 (1987).
- [5] A. M. Chaparro, M. T. Gutierrez, J. Herrero, J. Klaer, Mater. Res. Soc. Symp. Proc. 668, (2001).
- [6] N. Katsumura, K. Maemura, T. Mori, J. Saraie, J. Crystal Growth, 159, 85 (1996).
- [7] R. Islam, D.R. Rao, J. Mater. Sci. Lett., 13, 1637 (1994).
- [8] A. M. Chaparro, M. T. Gutierrez, J. Herero, Electrochim. Acta, 47, 977 (2001).
- [9] A. Chandramohan, T. Mahalingam, J.P. Chu, P.J. Sebastian, Sol. Energy Mater. Sol. Cells, 81, 371 (2004).
- [10] P. K. R. Kalita, B. K. Sarma, H. L. Das, Bull. Mater. Sci, 23, 313 (2000).
- [11] R. B. Kale, C.D. Lokhande, Mater. Res. Bull, 39, 1829 (2004).
- [12] Zulfiqar Ali, Akram K.S. Aqili, M. Shafique, Asghari Maqsood (2006). Physical properties of ZnSe films prepared by two-source evaporation and a study of post doping effect, Journal of Non-crystalline solids 352. Pp.409-414.
- [13] K.R. Murali, K. Thilakvathy, S. Vasantha, Rachel Oomen. (2008). Properties of ZnSe Films Pulse Plated on High Temperature Substrates, Chalcogenide Letter Vol. 5, No.6, pp.111-116.
- [14] N.A. Okereke, A.J. Ekpunobi (2011). ZnSe buffer layer deposition for solar cell application. Journal of Non-Oxide Glasses, vol. 3 No.1, No. 3, pp.31-36
- [15] Abeles, F. (Ed). Optical Properties Of Solid, North-Holland Pub.Co. Amsterdam.
- [16] G. Harbeke (1972). Optical Properties Of Semiconductors, North-Holland Pub.Co. Amsterdam
- [17] Nair P.C. Nair M.T.S., Fernandez, A, Ocampo M, J. Phys. D: Appl. Phys. 22, 829. (1989)