



## Synthesis and characterization of ZnSe thin films deposited by thermal vacuum evaporation method for photovoltaic application

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### Abstract

ZnSe bilayer thin films of thickness 343 Å were deposited onto soda-lime glass substrates by thermal vacuum evaporation technique using NANO 36 thermal evaporator, under vacuum pressure of  $2.91 \times 10^{-5}$  torr. The optical characteristics of the film were done by using AVANTEX UV spectrophotometer in the wavelength range from 239.534 nm to 999.495 nm. The surface morphology studies were also observed by ASPEX 2030 Scanning Electron Microscopy (SEM) operated at accelerating 16 KV potential. Also the electrical characteristics of the thin films were investigated using a KEITHLEY four-point probe technique. The investigation of the optical properties of the thin films as deposited and annealed at different temperatures showed high transmission in the NIR region with good absorption in the visible and UV region. The extrapolated band gap energies were high between 3.60 eV and 4.15 eV and electrical resistivities were low between 0.475 Ωm and 9.070 Ωm.

**Keywords:** Hetero-junction, Evaporator, Morphological, ZnSe, Bandgaps

### 1. Introduction

Non renewable energy source such as fossil fuel cannot meet the global energy needs due to its nature of inability to renew itself after being used [1,2]. Aside, the problem of finite in supply of renewable energy, it also constitute large amount to the global warming [3]. In order to ensure availability of energy it is necessary to consider the energy that will not be depicted and has low negative impact in our environment such as a solar energy.[4] Solar energy is the most popular among renewable energy sources due to the unlimited supply of energy by the sun at no cost [5,6] However, to convert solar

radiation into electricity a device is needed called solar cell or photovoltaic [7]. A solar cell is a p-n junction which operates on the principle of photovoltaic

effect where when a photon of energy which is equal or greater than the energy gap, is absorbed by the semiconductor material the electron from the valence band excited to the conduction band and the excess energy, if any, gets dissipated by interaction with matter [8]. However solar cell made from silicon is called first generation solar cell. This cell is more efficient and longer lasting than non silicon based cells. However, silicon cell is more at risk to lose some of their efficiency at higher temperatures [9]. The price of silicon solar cell is expensive which makes the cell unaffordable by large populace [10]. The second-generation cell is called thin-film solar cell which has some advantages over first-generation solar cell. These advantages include having a very thin thickness and minimum material usage which reduce the cost of the cell, easy to design and lightweight [11]. The thin-film solar cell is considered as the hope of humanity in the solar market because of its relatively inexpensive [12]. Thin-film solar cell is formed by sandwiching two electronically dissimilar materials i.e a p-type absorber layer (narrow band gap) and a n-type window layer (wider band gap) together [10]. Among the p-type absorber layer are cadmium telluride (CdTe) [13], CIGS [14], CIS [15] and CZTS [16]. CdS is the mostly used as an n type window layer but the toxicity of cadmium led researchers to study other material such as ZnS [17,18], ZnO [19–21] and ZnSe e.t.c. (ZnSe) is a family of group II-VI compound semiconductor [22]. The compound semiconductor [23] of group II-VI plays important role in the fabrication of photovoltaic and other optoelectronic devices such as light-emitting diode [24,25]. ZnSe Zinc is an n-type semiconducting material with wide band gap (2.7eV). It is a suitable material for red, blue and green light emitting diodes, photovoltaic, laser screens, thin film transistors, photoelectron chemical cells [26]. It has cubic and/or hexagonal crystal structure, it has Optical band gap in the range 2.6-3.1eV [27]. Different methods of deposition has been employed by different researchers to synthesis ZnSe thin film.: chemical bath deposition (CBD)[27], electrodeposition[6], thermal [28]. Due to peculiarity of thermal evaporation technique of capable to form multiple layers on a single substrate, easy to monitor the deposition rate and thickness of the film by a quartz crystal thickness monitor equipped with a vacuum coating unit. No wastage of materials and time saver of the technique necessitated the method for this study.

## 2. Materials and method

ZnSe films were deposited onto soda-lime glass. before the deposition the glass substrates cleaned thoroughly with liquid detergent; then washed with distilled water, and finally purified ultrasonically in acetone. The cleaned substrates were dried in hot air for 20 minutes. Zn-Se bilayers were grown by vacuum thermal evaporation with pressure  $2.91 \times 10^{-5}$  torr in NANO 36 thermal evaporation chamber supplied by Kurt J. Lesker company. The high purity Zn (99.99%, shots-1-2 mm size from Sigma Aldrich, UK) and Se (99.99+%, pellets < 4mm, Sigma Aldrich, UK) were placed in two different boats in the vacuum system. The glass substrates were placed in the substrate holder above the boats carrying the materials. The Zn layer was first deposited and later Te layer deposited to get bilayers of Zn-Te thin films. The deposition rate of  $10 \text{ \AA} / \text{s}$  was maintained to deposit  $250 \text{ \AA}$  and  $93 \text{ \AA}$  of Zn and Te respectively. After

the deposition, one of the substrates was annealed at 100 °C, the second was annealed at 120 °C for 15 minutes in UNISCOPE SM9053 laboratory oven while the third one was not annealed and used as a control.

## 2.1. Characterization of the film

### 2.1.1. Optical Characteristics

Transmittances and reflectance of both annealed and control layers were measured using AVANTEX UV spectrophotometer in the wavelength range from 239.534 nm to 999.495nm. The absorbance coefficients were determined from Lambert's law

$$I = I_0 e^{(-\alpha t)} \quad (1)$$

Where  $I/I_0$  = Transmittance (T),  $t$  is the thickness of the film deposited and  $\alpha$  = absorbance coefficient

$$\alpha = -\ln \frac{T}{I_0} \quad (2)$$

The reflectance and transmittance were plotted against incident wavelength to determine the percentages transmitted and reflected. The band gap of the film is determined by plotting  $(\alpha h\nu)^2$  against  $(h\nu)$  in eV, where  $h$  is Planck's constant of value  $6.62 \times 10^{-34}$  Js and  $\nu = \frac{c}{\lambda}$  where  $c$  is the speed of light =  $3 \times 10^8$  ms<sup>-1</sup> and  $\lambda$  is an incident wavelength.

### 2.1.2. Morphological Characteristics

The surface morphology of the as-deposited as well as annealed ZnSe thin films were observed by ASPEX 2030 Scanning Electron Microscope (SEM), operated at accelerating 16 KV potential under 50, 100, 250 and 500 magnifications were done for each sample.

### 2.1.3. The Electrical Characteristics

The electrical characteristics of the as-deposited as well as annealed ZnSe thin films were investigated using a KEITHLEY 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. The sheet resistivities  $\rho$  of the films at room temperature were calculated using the expression:

$$\rho = (\pi t \ln 2) \frac{V}{I} = 4.53 R t \quad (3)$$

where  $V$  is the potential difference (voltage) across the transverse distance of the film.  $I$  is the corresponding values of the current and  $t$  is the thickness of the film deposited

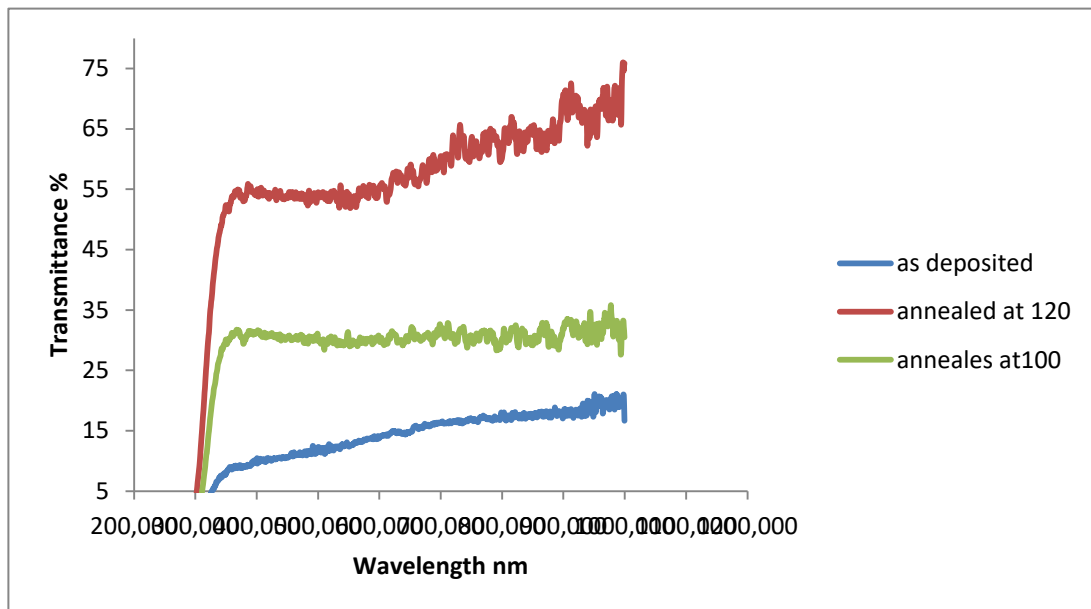
The conductivities were calculated using:

$$\sigma = \frac{1}{\rho} \quad (\Omega m)^{-1} \quad (4)$$

### 3. Results and discussion

#### 3.1. Optical Properties

The optical transmittance spectral showed in Fig.1 for ZnSe thin films reveals that transmittance increases smoothly from 300 nm to a maximum value of 800 nm in the visible region of wavelength and becomes almost consistent in the infrared region. This agrees with the report of [22] The spectral shows that as deposited has 20% transmittance, annealed at 100°C has a maximum of 30% while annealed at 120°C has a maximum of 75% transmittance. The transmittance increases as annealing temperature increases this agrees with the report of [29] . The optical band gaps energy were extrapolated from Figures. 2, 3 and 4 for the ZnSe films annealed as deposited , annealed at 100°C and 120°C respectively were found to be 4.15 eV, 4.00 eV and 3.60 eV respectively. The band gap decreases as annealing temperature increases this conforms with the report of [30] But these deviate from the theoretically value of band gap energy of the film 2.7 eV at room temperature and the values are also higher than stacked bilayer of ZnSe reported by[31] The deviation could be because of the difference between the ratio of the thickness of the elemental layers or because of the low annealing temperature. This kind of deviation was reported by [32] where CdTe film was grown and band gap energy of 2.8 eV was obtained instead of 1.5eV and they concluded that the increasing band gap energy makes CdTe a good candidate for an electroluminescent display device and window layer in n-CdTe/p-CdTe homojunction device. Some researchers also obtained 2.98 eV for CdS thin film instead of 2.4 eV and it was concluded that this makes the film a better window material in an n-CdS/p-CdTe heterojunction solar cell [32]



**Figure 1:** Transmittance Spectral for ZnSe thin film

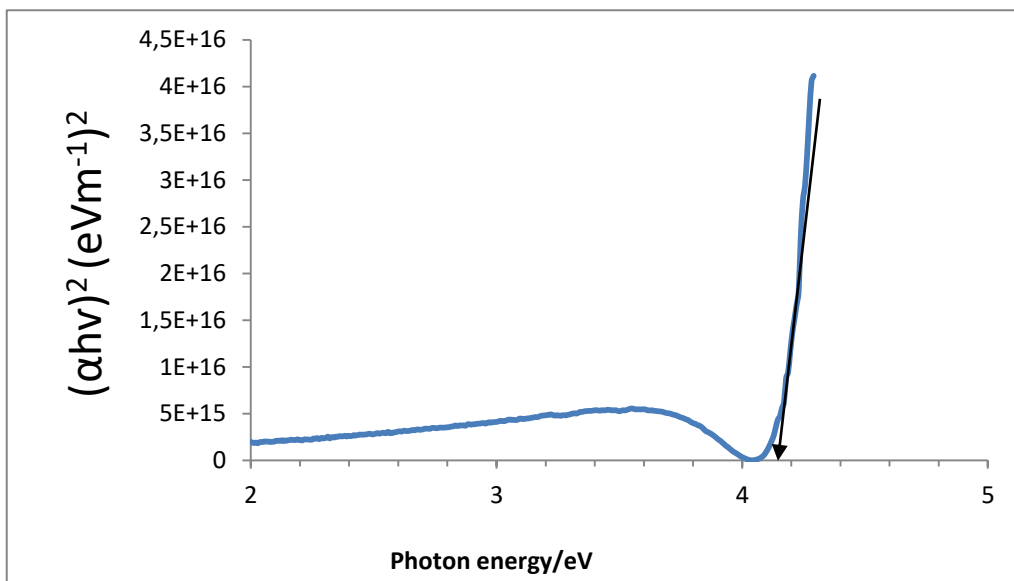


Figure .2 : Graph of  $(\alpha h\nu)^2$  against photon energy in eV for ZnSe as deposited

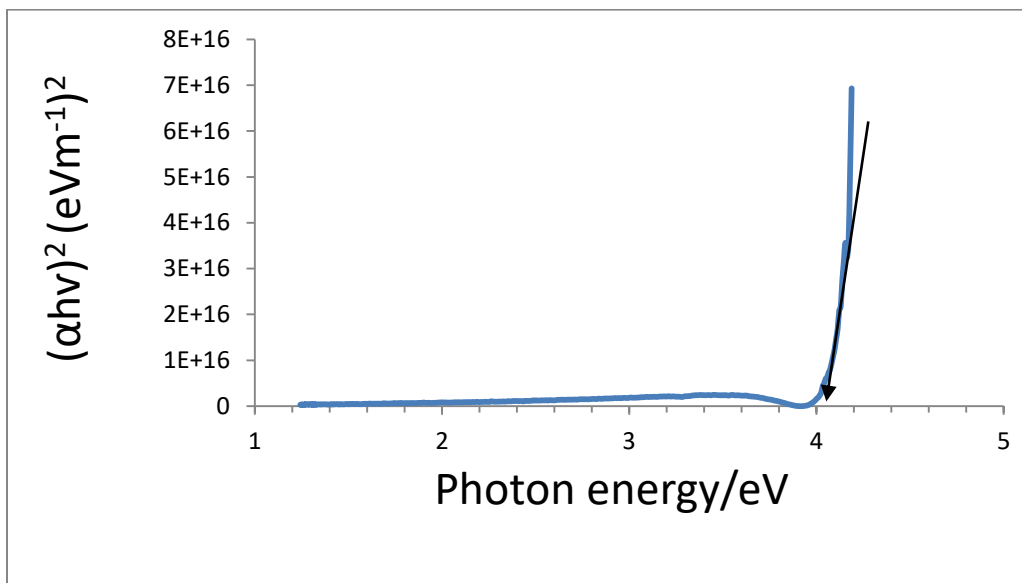
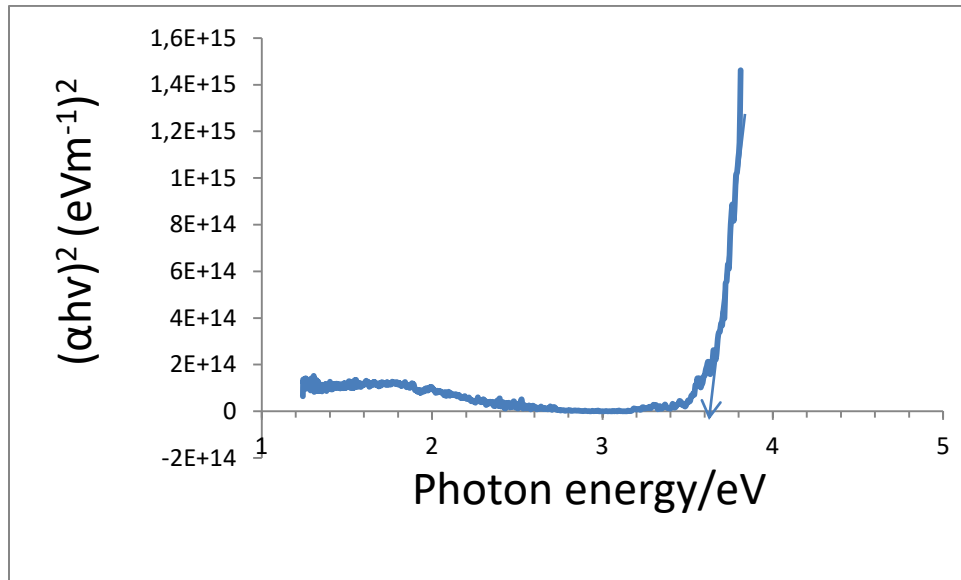


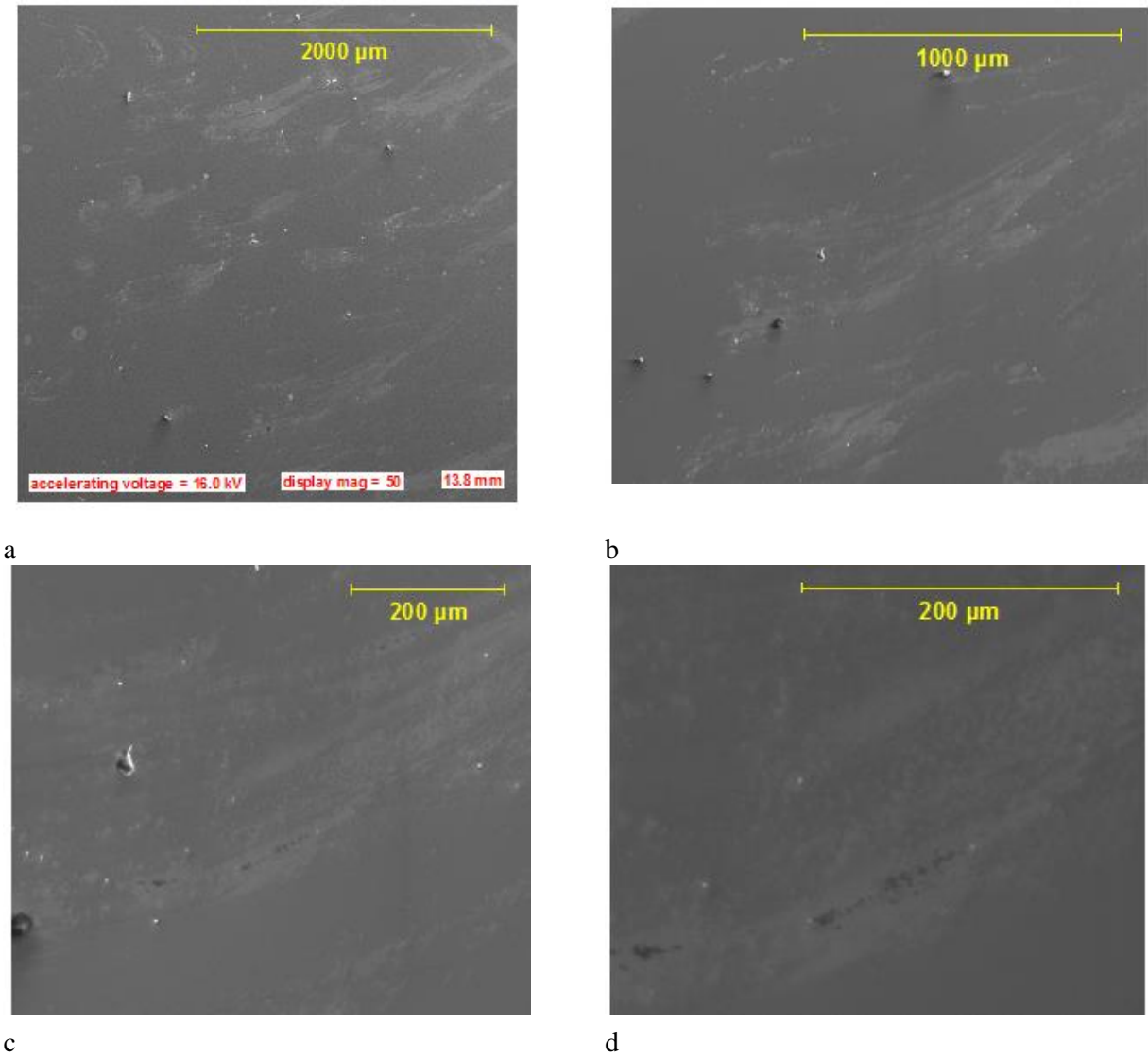
Figure 3 : Graph of  $(\alpha h\nu)^2$  against photon energy in eV for ZnSe annealed at  $100^\circ\text{C}$



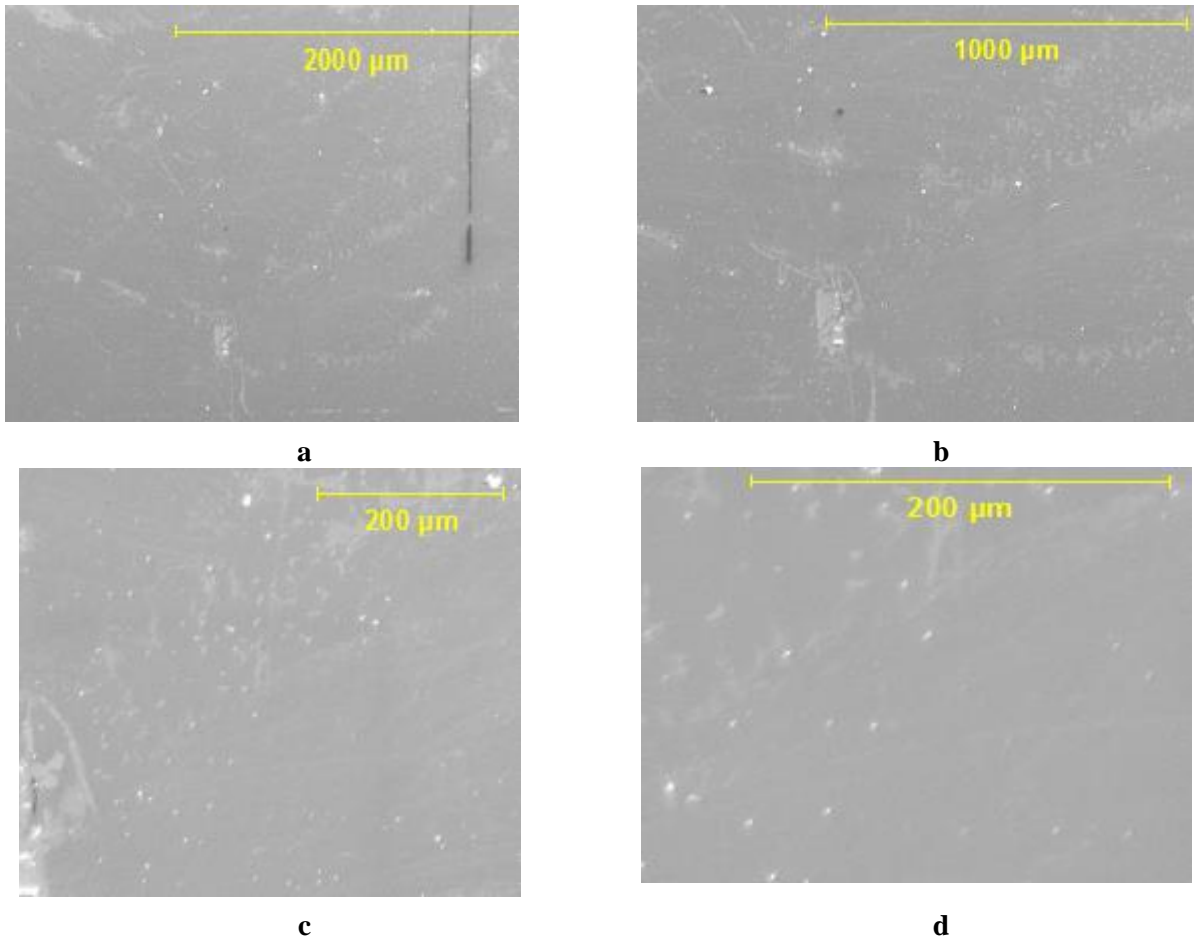
**Figure 4** : Graph of  $(\alpha h\nu)^2$  against photon energy in eV for ZnSe annealed at  $120^\circ\text{C}$

### 3.2 Morphological Studies

The images of as deposited, annealed at  $100^\circ\text{C}$  and  $120^\circ\text{C}$  are shown in plates 1, 2 and 3 respectively. The micrographs reveal that the ZnSe thin films deposited are smooth and high compactness of these films which are continuous and homogeneous. This is similar to the report of [33]. Both ZnSe films for as deposited and annealed consist of network of grains which are scanty over the surface area. However, the consistency in morphologies suggests uniformity in growth with large grains of about  $200\mu\text{m}$  in breadth with magnification of 500. This agrees with the report of [34]. Where CdS was fabricated as window layer the images of as deposited as annealed films were scanty over the surface area and large grain of about  $10\mu\text{m}$  in breath with magnification of 10000. The results were also similar to the report of [35] where the grains have similar shapes and sizes for as deposited at  $600^\circ\text{C}$  and thermally annealed at  $250^\circ\text{C}$  ZnSe films. The morphological images of ZnSe bilayers formed is in agreement with images of ZnSe thin films by electrodeposition method [6]. The closely packed grains provide a pinhole free morphology, which could lead to better spatial contact between the grains, which is desirable for use in photoelectrochemical cells [23].

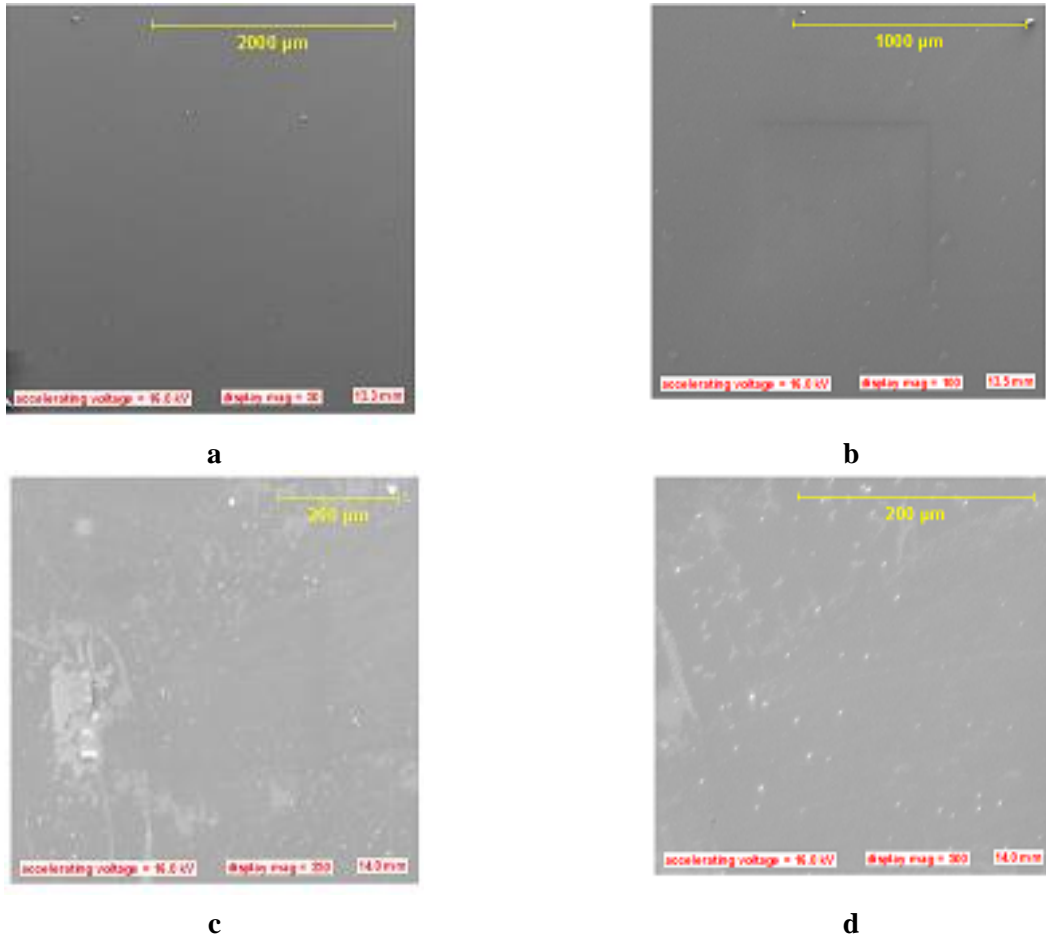


**Plate 1;** Images of ZnSe as deposited (a =50X,b=100X,c=250X,d=500X)



**Plate 2;** Image of ZnSe annealed at 100°C (a =50X,b=100X,c=250X,d=500X)





**Plate 3;** Image of ZnSe annealed at 120<sup>0</sup>C (a =50X,b=100X,c=250X,d=500X)

### 3.3 The Electrical parameters

The resistivities and conductivities of the films as deposited and annealed are shown in the Table 1. The resistivity of the ZnSe thin film for as deposited and annealed at 100<sup>0</sup>C and 120<sup>0</sup>C are 0.475Ωm, 1.244Ωm and 2.020Ωm respectively. This showed that the resistivity was increasing as the temperature increased. This agrees with report by [30]. But the result does not agree with the reported value by [36] whose value of resistivity of ZnSe of thickness 1.502µm is of the order of 10<sup>4</sup> to 10<sup>12</sup> Ωm. This could be caused by excess layer of Zn deposited than Se deposited.

**Table 1:** Electrical results

Sample	Voltage/V	current/A	Resistivity (Ωm)	Conductivities (Ωm) <sup>-1</sup>
ZnSe (as deposited)	110.00E-3	36.00E-9	0.475	2.105
ZnSe (100 <sup>0</sup> C)	240.00E-3	30.00E-9	1.244	0.804
ZnSe (120 <sup>0</sup> C)	260.00E-3	20.00E-9	2.020	0.495

#### 4. Conclusion

ZnSe thin films were successfully deposited on glass substrates by stacked elemental layer method using NANO 36 thermal evaporator in high vacuum at about  $10^{-5}$  torr. The investigation of the optical properties of the thin films as deposited and annealed at different temperatures showed high transmission in the NIR region with good absorption in the visible and UV region. The extrapolated band gap energies were high between 3.60 eV and 4.15 eV and the images of films when viewed with scanning electron microscope showed that the surface is very smooth and covered over the substrate surface. These properties indicate that the films can be used as a window layer in the fabrication of thin film heterojunction solar cell and other optoelectronic devices

#### References

1. V.C. Netravati, U. M. & Patil, Technology 3 Int. J. Adv. Res. Comput. Sci. Technol. 3 (1), (2015) 2014–2015. [www.ijarcst.com](http://www.ijarcst.com).
2. R.J. Mustafa, M.R. Gomaa, M. Al-Dhaifallah, H. Rezk, Sustainability. 12 (2020) 1–17. <https://doi.org/10.3390/su12020608>.
3. C.N. Ezugwu, J. Clean Energy Technol. 3 (2015) 68–71. <https://doi.org/10.7763/JOCET.2015.V3.171>.
4. J. Vourdoubas, J. Agric. Life Sci. 2 (2015) 111–118.
5. S. Sharma, K.K. Jain, A. Sharma, Solar Cells: In Research and Applications—A Review, Mater. Sci. Appl. 06 (2015) 1145–1155. <https://doi.org/10.4236/msa.2015.612113>.
6. A. Ayeshamariam, M. Kashif, S. Muthu, S. Jagadeswari, D. Saravanankumar, N.M.I. Alhaji, A. Uduman, Int. J. Emerg. Technol. Adv. Eng. 4 (2014) 584–590.
7. A. Mohammad Bagher, Am. J. Opt. Photonics. 3 (2015) 94. <https://doi.org/10.11648/j.ajop.20150305.17>.
8. A.H. Chander, M. Krishna, Y. Srikanth, IOSR J. Electr. Electron. Eng. Ver. I. 10 (2015) 151–154. <https://doi.org/10.9790/1676-1061151154>.
9. M. Imamzai, M. Aghaei, Y.H. Thayoob, Proc. Natl. Grad. Conf., 2012: pp. 8–10. <https://doi.org/10.3873/j.issn.1000-1328.2009.00.039>.
10. K.L. Chopra, P.D. Paulson, V. Dutta, Prog. Photovoltaics Res. Appl. 12 (2004) 69–92. <https://doi.org/10.1002/pip.541>.
11. S. Siebentritt, Curr. Opin. Green Sustain. Chem. 4 (2017) 1–7. <https://doi.org/10.1016/j.cogsc.2017.02.001>.
12. A. Acevedo-Luna, R. Bernal-Correa, J. Montes-Monsalve, A. Morales-Acevedo, J. Appl. Res. Technol. 15 (2017) 599–608. <https://doi.org/10.1016/j.jart.2017.08.002>.
13. J.A. Luceño-Sánchez, A.M. Díez-Pascual, R.P. Capilla, Int. J. Mol. Sci. 20 (2019). <https://doi.org/10.3390/ijms20040976>.
14. H. Firoozi, M. Imanieh, J. Electr. Comput. Eng. Innov. 6 (2018) 7–14. <https://doi.org/10.22061/JECEI.2018.798>.
15. D.C. Nguyen, K. Takehara, T. Ryo, S. Ito, Energy Procedia. 10 (2011) 49–54. <https://doi.org/10.1016/j.egypro.2011.10.151>.
16. M.Q. Hamzah, A.H. Jabbar, S.O. Mesan, Int. J. Sci. Eng. Res. 5 (2017) 2015–2017.

17. F.Z. Boutebakh, M.L. Zeggar, N. Attaf, M.S. Aida, Opt. - Int. J. Light Electron Opt. 144 (2017) 180–190. <https://doi.org/10.1016/j.ijleo.2017.06.080>.
18. M.Y. Nadeem, W. Ahmed, Turkish J. Phys. 24 (2000) 651–659.
19. T.O. Berestok, D.I. Kurbatov, N.M. Opanasyuk, A.D. Pogrebnjak, O.P. Manzhos, S.M. Danilchenko, J. Nano- Electron. Phys. 5 (2013) 4–7.
20. H. Khallaf, G. Chai, O. Lupan, H. Heinrich, S. Park, A. Schulte, L. Chow, J. Phys. D. Appl. Phys. 42 (2009). <https://doi.org/10.1088/0022-3727/42/13/135304>.
21. S. Cisse, Am. J. Mater. Synth. Process. 4 (2019) 1. <https://doi.org/10.11648/j.ajmsp.20190401.11>.
22. M.T. Chowdhury, M.A. Zubair, H. Takeda, K.M.A. Hussain, M.F. Islam, AIMS Mater. Sci. 4 (2017) 1095–1121. <https://doi.org/10.3934/matserci.2017.5.1095>.
23. M. Kavitha, M. Saroja, V.R. Kumar, G. Jenifer, Int. J. Thin Film. Sci. Technol. 141 (2016) 137–141.
24. C.H. Hsu, C.F. Tseng, Y.T. Yu, P.C. Yang, C.H. Lai, J. Sen Lin, H.W. Yang, Adv. Mater. Res. 608–609 (2013) 1314–1317. <https://doi.org/10.4028/www.scientific.net/AMR.608-609.1314>.
25. T. Potlog, N. Maticiu, A. Mirzac, P. Dumitriu, D. Scortescu, Proc. Int. Semicond. Conf. CAS. 2 (2012) 321–324. <https://doi.org/10.1109/SMICND.2012.6400772>.
26. Nnamdi Azi, Journal of the Nigerian Association of Mathematical Physics 29 (2015) 325–330.
27. A. Buba, Br. J. Appl. Sci. Technol. 14 (2016) 1–7. <https://doi.org/10.9734/BJAST/2016/23622>.
28. S. Shanmugan, D. Mutharasu, Medziagotyra. 18 (2012) 107–111. <https://doi.org/10.5755/j01.ms.18.2.1908>.
29. J. Sharma, D. Shikha, S.K. Tripathi, Rom. Reports Phys. 66 (2014) 1002–1011.
30. J. Sharma, D. Shikha, S.K. Tripathi, Rom. Reports Phys. 66 (2014) 1002–1011.
31. K.C. Bhahada, B. Tripathi, N.K. Acharya, P.K. Kulriya, Y.K. Vijay, Chalcogenide Lett. 5 (2008) 137–142.
32. R.S. Singh, V.K. Rangari, S. Sanagapalli, V. Jayaraman, S. Mahendra, V.P. Singh, Sol. Energy Mater. Sol. Cells. 82 (2004) 315–330. <https://doi.org/10.1016/j.solmat.2004.02.006>.
33. S.R. D. Saravanakkumar, M. Kashif, V. Rethinasami, B. Ravikumar, S. Pandiarajan, A. Ayeshamariam, S. Sivaranjani, M. Bououdina, J. Ovonic Res. 10 (2014) 175–184.
34. F.I. Ezema, Y. Kayama, I.C. Amaechi, T. Hiramatsu, A.C. Nwanya, R.U. Osuji, M. Malik, M. Sugiyama, S. West, W.C. Province, S. Africa, P. Africa, Chalcogenide Lett. 11 (2014) 629–638.
35. O.T. S. Antohe, L. Ion, Mihaela, G, Rom. Reports Physics, 2013 (2013) 805–811.
36. N.A. Okereke, A.J. Ekpunobi, J. Non-Oxide Glas. 3 (2011) 31–36.