Chalcogenide Letters Vol. 9, No. 8, August 2012, p. 337 - 344

GROWTH CHARACTERISTICS AND EFFECT OF THERMAL ANNEALING ON THE OPTICAL AND SOLID STATE PROPERTIES OF ZnSe THIN FILMS

M.N. NNABUCHI[a], R.A. CHIKWENZE[b*]
[a]*Department of Industrial Physics, Ebonyi State University, Abakikili*
[b]*Nwafor Orizu College of Education, Nsugbe*

Zinc selenide (ZnSe) thin films were deposited on glass substrates using the chemical bath deposition technique at room temperature from aqueous solutions of zinc sulphate and sodium selenosulphate in which ammonium solution was employed as the complexing agent. Three of the as-grown ZnSe thin films were annealed in the oven at different temperatures for 1 hour, which affected the optical properties. Optical properties such as absorption coefficient and refractive index were calculated using the absorbance measurement from Unico UV-2102 PC Spectrophotometer at normal incidence of light in the wavelength range of 400-700nm. The highest transmittance of the as-grown film in the entire wavelength of interest was recorded as 52.48%. The band gap energy determined for the as-grown film is 2.90eV, which decreased progressively with the annealing temperature. The band gap energy of the films is in the desire range for their application in solar cell fabrication.

(Received February 27, 2012: Accepted August 10, 2012)

1. Introduction

The spectrum of solar light energy spreads from the ultraviolet region (300nm) to the infrared region (3000nm). When the photon energy is less than band gap of the semiconductor, the light is transmitted through the material, that is, the semiconductor is transparent to the light. When the photon energy is larger than band gap, the electrons in the valence band are excited to the conduction band. It means that a photon is absorbed to create an electron-hole pair. This process is called intrinsic transition or band-to-band transition. The cutoff wavelength λo is very important in choosing the solar cell material because the light with wavelength longer than cutoff wavelength cannot be used for solar energy conversion (Soga, 2006; Ezema et al, 2010).

Zinc selenide belong to the II – VI family of semiconducting material and is receiving ever-increasing attention due to its wide range of applications. Owing to its wide band gap (ZnSe, bulk crystal Eg = 2.7 eV at 300K), it can be used for fabrication of optoelectronic device such as blue light emitting diodes, electroluminescent devices, window layers for thin film heterojunction solar cells, photoconductors etc (Kumar et al, 2007; Suyver, 2000). Generally, Cadmium sulphide (CdS) is one of the most extensively used materials as 'buffer layer' in solar cells based on CdTe and $CuInS_2$ absorber layer (Ferekids et al, 1996). However, due to the toxic hazards with respect to the production and use of CdS layers, much attention has been focused on developing Cd-free buffer layers. One such possible replacement for CdS is ZnSe.

Subsequently, several techniques have been used to produce ZnSe thin film such as hydrothermal synthesis (Jiang et al, 2005), metal-organic chemical vapour deposition (Shan et al, 2006), vacuum evaporation method (Venkatachalan et al, 2006), aqueous colloidal precipitation (Kumar et al, 2007) and chemical bath deposition (CBD) (Estrada et al, 1994). Among these, CBD method is most commonly used because it is very simple, cost effective and economically reproducible technique that can be applied in large area deposition at low temperature. This

*Corresponding author: racy_c@yahoo.com

technique is based on the controlled release of metal ion (M^{2+}) and sulphide (S^{2-}) or selenide (Se^{2-}) ions in an aqueous bath in which the substrates are immersed. In this process, release of metal ion (M^{2+}) is controlled by using a suitable complexing agent. The deposition begins with nucleation phase followed by growth phase in which the thickness of film increases with duration up to the terminal phase where film depletion into constituent ions occurs after a certain time. Therefore, to achieve well-adhered films, optimisation of the deposition conditions is of paramount importance in chemical bath deposition.

In this article, we report chemical bath deposition of well-adhered ZnSe thin films and the characterization and analysis of the optical and solid-state properties for possible integration into solar cell architecture.

2. Materials and method

The reaction baths for the deposition of ZnSe thin films contain 10ml of NH_3, 20ml, 1M of Na_2SeSO_3 and 20ml, 1M of $ZnSO_4$ put in that order into 50ml beaker. A clean microslide was then inserted vertically through synthetic foam into the mixture. Four films were deposited using four different baths but with the same constituents. In each case the deposition lasted for 8 hrs, after which the coated substrate was removed from the bath, washed well with distilled water and allowed to dry. Three of the as-grown samples were annealed in the oven for 1 hr. at 100^{o}C (labeled X), 200^{o}C (labeled Y) and 300^{o}C (labeled Z). The as-grown film is labeled U.

The structure of the films was studied with optical microscope and Philips PW 1500 XRD. The band gap of the films was determined by using the absorbance and transmittance measurement from Unico – UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 400-700nm.

3. Results and discussion

3.1 X-ray diffraction study

Typical XRD diffractograms of CBD ZnSe are presented in Fig.1. The pattern for the thin film of ZnSe displayed diffraction peaks at 2θ values of approximately 25.90^o, 31.50^o, 54.05^o, 55.17^o, 56.19^o and 60.85^o, corresponding to (100), (200), (112), (201), (222) and (202) planes respectively. A close observation of the diffractograms show that the as-grown film and the film annealed at 100^{o}C has poor crystallinity. However, the film annealed at 200^{o}C for 1 hour showed an improvement in the crystalline structure, having increased intensity in the diffraction peaks. This means that the crystallinity of ZnSe thin films could be improved by annealing the as-grown film at higher temperature.

The grain sizes is estimated using Scherrer relation, $D = k\lambda/\beta\cos\theta$, where k is a constant taken to be 0.94, λ the wavelength of X-ray used (λ = 1.54Å). The mean crystallite size calculated from the Scherrer relation is 31.96nm.

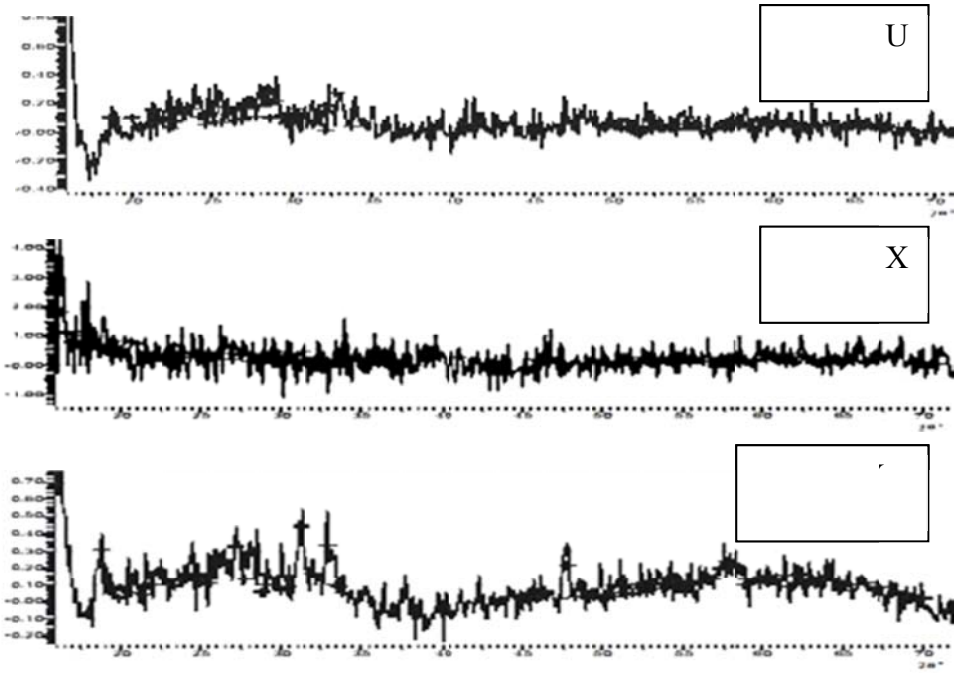

Fig.1: XRD of ZnSe thin films

Photomicrography Study

The surface microstructure of the films were obtained by taking the photomicrographs of the films coated on the transparent glass slides with wide KPL-W10x/ 18 Zeiss Standard 14 photomicroscope with M_{35} 4760+2-9901 camera at a magnification of X200. The photomicrographs of the films are displayed in fig. 2. A close observation of the optical micrographs of PbSe films shows that homogeneity and crystallinity of the films increased with post deposition annealing. Similar observation has been reported in other work (Asogwa et al, 2009).

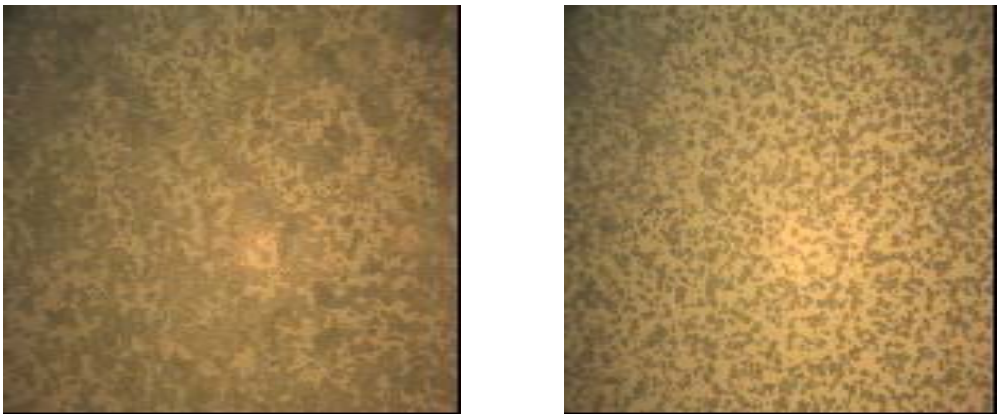

Fig.2: Photomicrograph of ZnSe thin films annealed at (a) 100^{o}C and (b) 300^{o}C

3.3 Optical and Solid-State Studies

Fig 3 & 4 are plots of absorbance vs. wavelength and transmittance vs. wavelength for ZnSe thin films grown in this work.

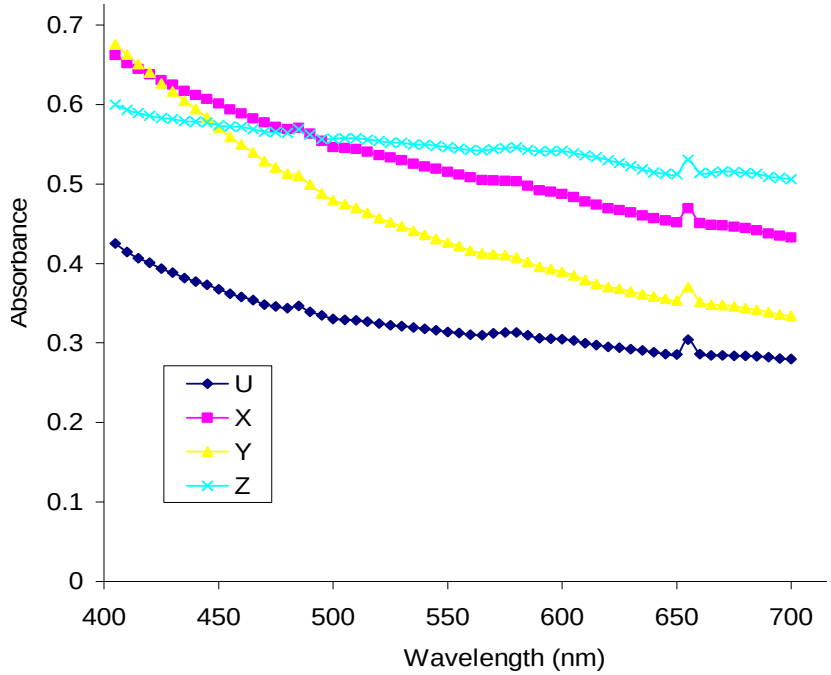

Fig. 3: Plots of absorbance vs. wavelength for ZnSe thin films

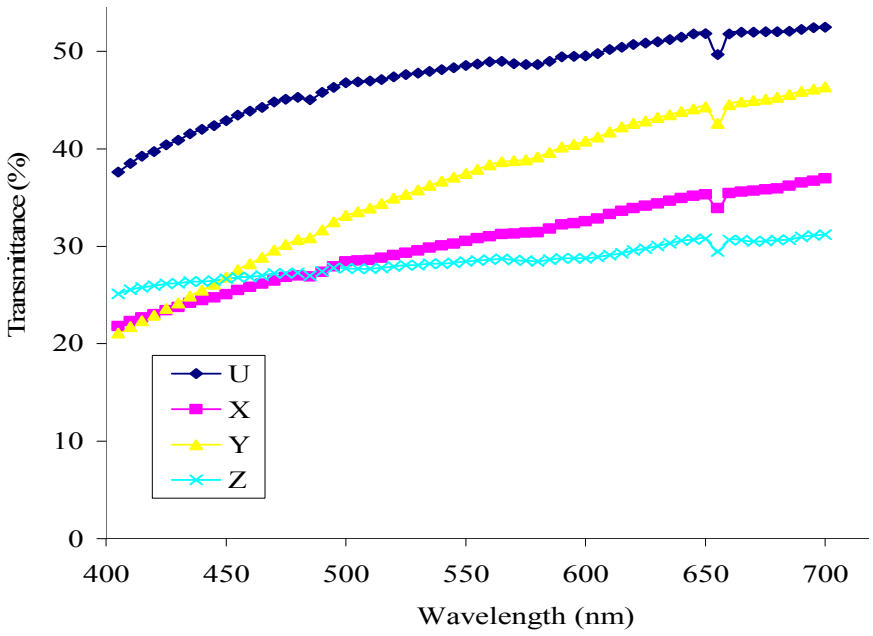

Fig.4: Plots of transmittance vs. wavelength for ZnSe thin films

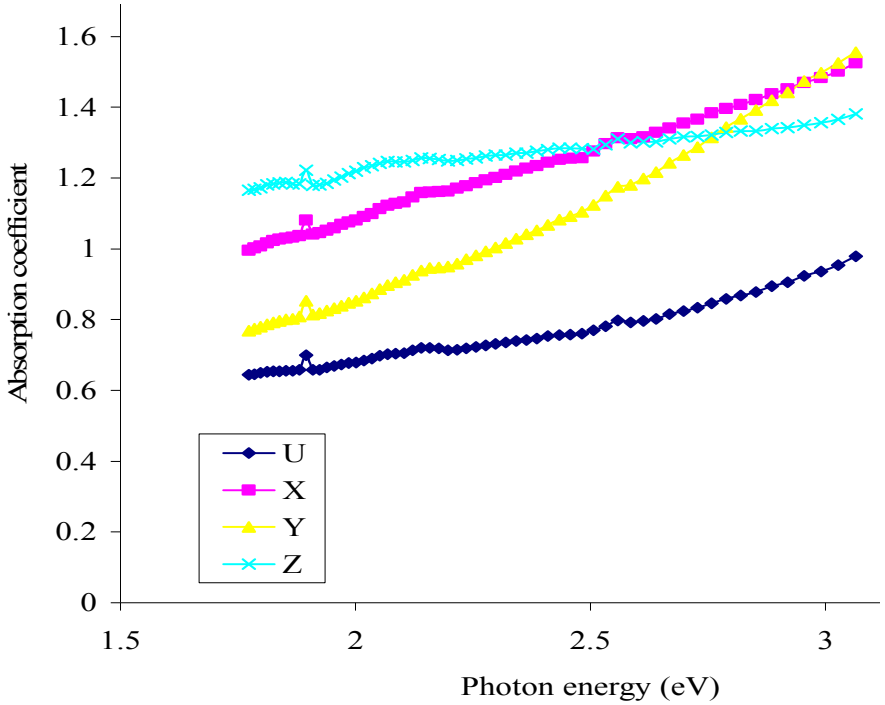

Fig. 5: Plots of absorption coefficient vs. photon energy for ZnSe thin film.

The optical absorption spectra of ZnSe thin films deposited on a glass substrate were studies at room temperature in the range of wavelengths 400 – 700nm. The variation of absorbance and transmittance with wavelength are shown in figs. 3 and 4 respectively. The details of the mathematical determination of the absorption coefficient could be found in literature (Ndukwe, 1996; [b]Ezema, 2005; Estrella et al, 2003), while the plots of absorption coefficient against photon energy is shown in fig.5. These absorption spectra, which are the most direct and perhaps simplest method for probing the band structure of semiconductors, are employed in the determination of the energy gap E_g. The films show a decrease in absorbance and an increase in transmission after annealing in the oven.

The band gap energy was determined using the following relation ([a]Ezema, 2005; Estrella et al, 2003):

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

where A is a constant, E_g is the band gap of the material and the exponent n is equal to ½ for direct band gap semiconductors. The estimated band gaps from the plots of $(\alpha h\upsilon)^2$ versus hυ are shown in fig.6. The linear nature of the plot indicates the direct nature of the transition.

The band gap was determined by extrapolating the straight portion of the energy axis at α = 0. It was found to lie in the range of 2.4 – 2.9 eV for ZnSe thin films. This is close to the reported value 2.60 – 2.72 eV (Venkatachalan et al, 2006) but higher than 1.70 – 1.75 eV reported elsewhere (Ezema, 2006). We notice a decrease in the band gap of the deposited films with annealing temperature. The decrease from 2.9 to 2.4 eV shows that annealing the films causes a strong 'redshift' of 0.5 eV in the optical spectra. These changes have been attributed to the crystallite size-dependent properties of the energy band gap. Similar 'redshift' in band gap energy values for the films have been reported for chemically deposited ZnSe thin films (Venkatachalan et al, 2006).

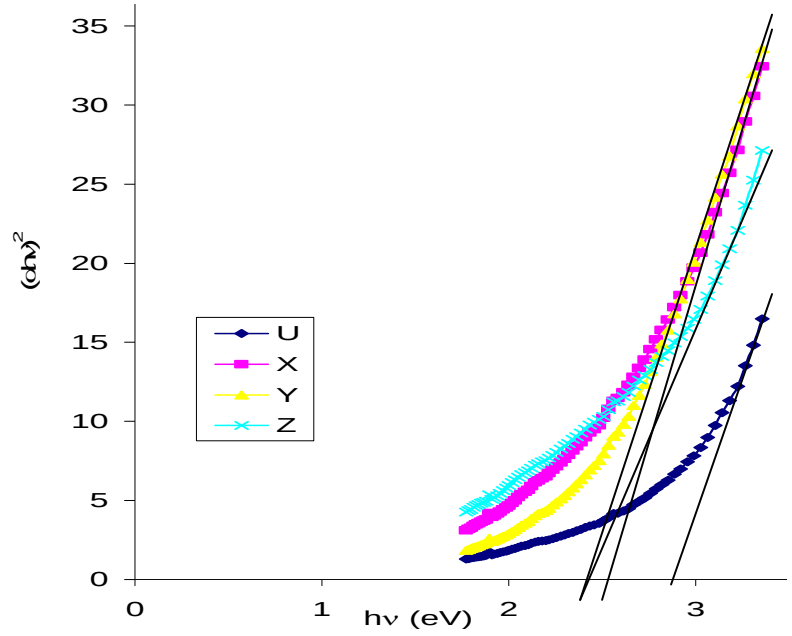

Fig .6: Plot of $(\alpha h\upsilon)^2$ vs. hυ for ZnSe thin films

There is a relationship between k and α given by (Ezema et al, 2007):

$$k = \alpha\lambda/4\pi$$

where α is the absorption coefficient of the film and λ is the wavelength of the electromagnetic wave. The equation above was used to determine the extinction coefficient. The plots of k, the extinction coefficient and n, the refractive index against photon energy are given in figs. 7 and 8 respectively.

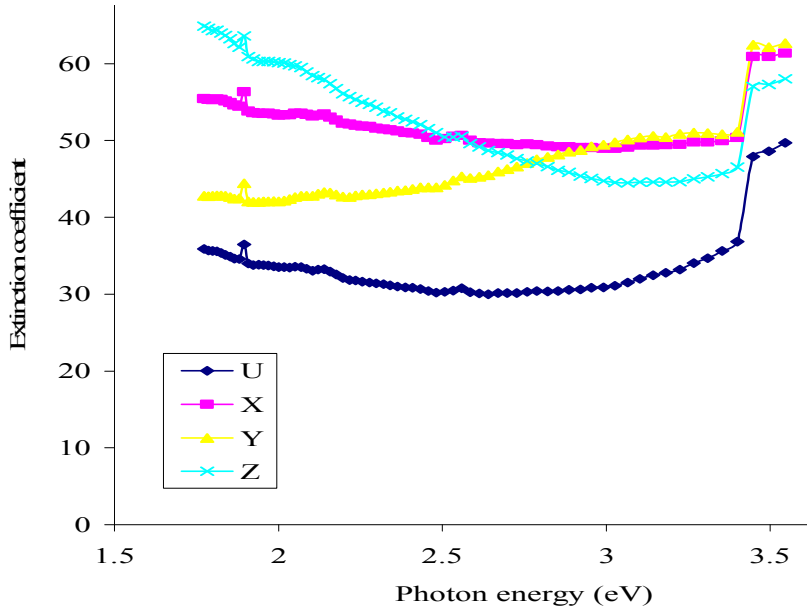

Fig.7: Plots of extinction coefficient vs. photon energy for ZnSe thin films

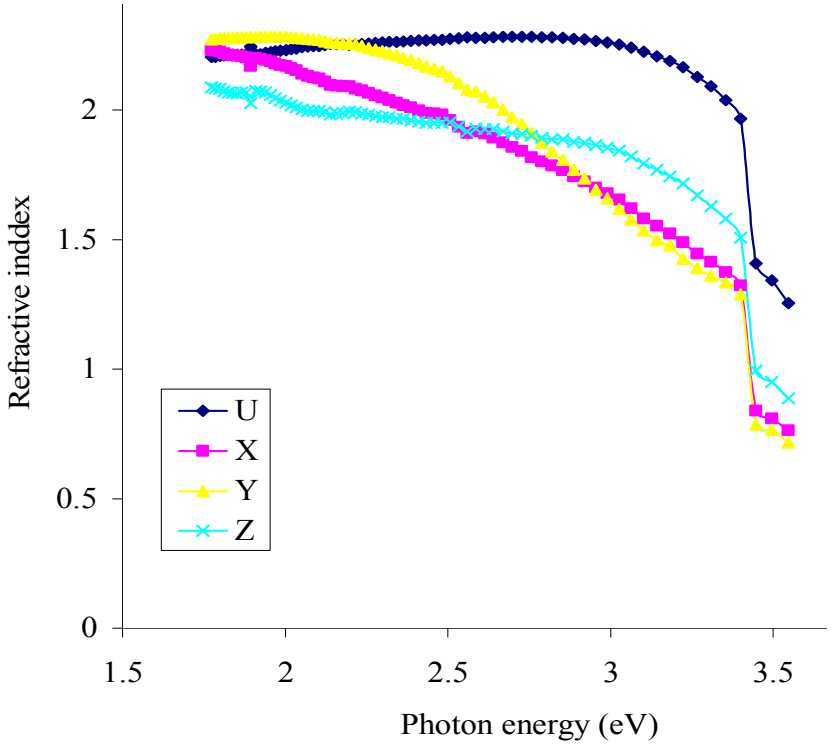

Fig. 8: Plots of refractive index against photon energy for ZnSe thin films

We observe an increase in the extinction coefficient of the films with annealing temperature. Fig. 8 shows the graph of refractive index vs photon energy (eV). The highest value as shown corresponds to the unannealed film. It could also be established that this property decreases with increase in annealing temperature.

4. Conclusion

In conclusion, we observed that the synthesis of ZnSe thin films carried out exhibited optical and solid state properties that are easily predictable. There is well defined trend in each of the properties studies. In any case, all the films showed high values of absorbance, direct band gap energy and absorption coefficients. From literature, thin films with direct transition band gap greater than 1.9eV and moderate transmittance can be applied as window layer in solar cell architecture, which normally facilities larger energy spectrum to be accommodated and trapped for absorption by absorption layer. In the ongoing research by scientist all over the globe for efficient thin film solar cell material, CdS has, at various times been used as window layer in such structures as SnO_2:F/CdSCdTe and ZnO/CdS/$CuInSe_2$ (Ferekids et al, 1996) in which the systems SnO2:F/CdS and ZnO/CdS act as optical windows and CdTe and CuInS2 as the absorbent layers. However, environmental impact assessment reveals that CdS thin film is both toxic and environmentally unfriendly. Besides, poor conductivity as low as 10^{-8} $(\Omega m)^{-1}$ has also been reported (Soga, 2006). For high performance of solar cell devices, it is necessary to use an appropriate window as well as absorber materials.

In our view, the as-grown ZnSe thin film deposited in this work could serve as possible replacement for the CdS film for commercialization of above system of thin film solar cells, since at present, there is no know toxicity associated with the use of ZnSe film.

Reference

[1] Asogwa P.U, Ezugwu S.C. Ezema F.I. Ekwealor A.B.C. Ezekoye B.A. and Osuji R.U., J. Optoelectron. Adv. Mater. **11**, 7 (2009) 940

[2] Ezema F.I., Pacific J. Sci Technol. **6**(1) 6 (2005)

[3] Ezema F.I., Turk J. Phys. **29**, 105 (2005)
[4] Ezema F.I. Asogwa P.U. Ekwealor A.B.C. Ugwuoke P.E. and Osuji R.U., J. of the University of Chem Techno. and Metallurgy **42**(2), 217 (2007)
[5] Ezema F.I. Ekwealor A.B.C. and Osuji R.U., Turk J. Phys. **30**, 157 (2006)
[6] Ezema F.I. Ezugwu S.C. Osuji R.U. Asogwa P.U. Ezekoye B.A. Ekwealor A.B.C. and Ogbu M.P., J. Non-Oxide Glasses **1**(1), 45 (2010)
[7] Estrada C.A. Nair P.K. Nair M.T.S. Zingaro R.A. and Meyers E.A., J. Electrochem Soc. **141**, 3 802 (1994)
[8] Estrella V. Nair M.T.S. and Nair P.K., Semicond. Sci. Technol. **18**, 190 (2003)
[9] Ferekids C.S. Mariskiy D. Tesali T. Oman D. and Morel D.L., 25th IEEE PVSC (Washington 1996) p. 751
[10] Jiang C. Zhang W. Zou G. and Yu W., Nanotech **16**, 551 (2005)
[11] Kumar S. Sharma N. Verma N.K. and Chakarvarti S.K., Optoelectron. Adv. Mater. – Rapid. Comm. **1**, 12 (2007) 677
[12] Ndukwe I.C., Sol Ener. Mater. Sol. Cells **40**, 123 (1996)
[13] Shan C.X. Liu Z. Zhang X.T. Wong C.C. and Hark S.K. Nanotech, **17**, 5561 (2006)
[14] Soga T. Nanostructured Materials for Solar Energy Conversion, Elsevier, Radarweg Amsterdam, The Netherlands, 12 (2006)
[15] Suyver J.F. Wuister S.F. Kelly J.J and Meijerink A., Phys. Chem. Chem. Phys. **2**, 5445 (2000)
[16] Venkatachalam S. Mangalaraj D. and Narayandass K., J. Phys. D: Appl. Phys. **39**, 5561 (2006)