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The effect of Pb^{2+} precursor concentration on the optical and solid state properties of annealed PbSe thin films grown by solution growth method

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

Lead Selenide (PbSe) thin films were deposited on glass substrates by Chemical Bath Deposition (CBD) method at 60°C. The baths for the films deposition were composed of lead nitrate, the source of the anion, sodium citrate, the enhancing agent, sodium hydroxide, the complexing agent, sodium selenosulphate, the source of the cation and distilled water. All the deposited films were subjected to the same post-deposition annealing of 150°C, in the oven, for 2hours. The structures were investigated using X-ray diffraction and the crystallinity of the films were observed to decrease with increasing Pb^{2+} precursor concentration. The composition and optical properties were studied using RBS machine 1.7W TANDEM PELLETRON-model 5SDH and optical spectrophotometer respectively. The films deposited at lower Pb^{2+} precursor concentration have higher absorption coefficient and lower band gap. The range of the band gap of the films was 1.70 – 2.20 ± 0.05 eV. From this band gap and the result of the absorption coefficient of the films, it could be used for absorber layer in the fabrication of solar cell.

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Keywords: CBD, PbSe thin films, Optical properties

1. Introduction

Over the last decades, interest in the binary and ternary Chalcogenide thin films has lead to increased research in this area. These films have a number of applications in various fields, including coatings, interference filters, solar cells, photoconductors, IR detectors, magnetic and superconducting films and microelectronic devices (Mane and Lokhande, 2000; Janickis et al, 2004). Many metal selenide compounds have excellent optical properties in the visible and IR region of solar spectrum (Ezema and Osuji, 2007; Ezema et al, 2006; Estrada et al, 1994; Pathan et al, 2003). These properties can easily be investigated by making use of spectrophotometer to record directly the absorbance and transmittance of thin films. Deduction from mathematical relations in which absorbance and transmittance values are used as inputs can lead to evaluation of other optical and solid state properties, such as refractive index, extinction coefficient, absorption coefficient, band gap energy, etc (Ezema et al, 2009).

Many researches have been carried out on Chalcogenide thin films to investigate the variation of optical and solid-state properties of thin films with annealing temperature (Ezema et al 2010; [a]Chikwenze and Nnabuchi, 2010), the deposition time (Ezugwu et al, 2009; Asogwa et al, 2009), deposition medium and pH ([b]Chikwenze and Nnabuchi, 2010; Rakesh, 2006), deposition temperature (Valenzuela-Jauregui et al, 2003) as well as the nature of substrate used (Gaiduk, 2008). However, few reports are available on the effect of precursor concentration on the properties of PbSe thin films.

In this article, we report on the effect of Pb^{2+} precursor concentration on the optical and solid-state properties of PbSe thin films. Analyses of these properties are carried out to determine the suitability of the films for solar cell application.

2. Materials and methods

Glass microscope slides were cleaned by degreasing them in dilute hydrochloric acid for 2 hours, washed in detergent solution, rinsed in distilled water and dried in oven at 30°C above room temperature. In a typical deposition set up, the bath was composed of 5 ml of 1M $PbNO_3$, 8ml of 1M $(C_3H_4(OH)COONa)_3.2H_2O$, 5ml of 2M NaOH, 5ml of 1M Na_2SeSO_3 and 40ml of distilled water put in that order. The clean glass substrate was inserted vertically into the solution with the use of synthetic foam. The deposition lasted for 7 hours in the oven set at 60°C. After the expiration of 7 hours, the coated substrate was removed, washed well with distilled water and allowed to dry. A total of three experimental set-ups were prepared with different concentration of Pb^{2+} precursor, and labelled 1A (1.00M $PbNO_3$), 1B (0.75M $PbNO_3$) and 1C (0.25M $PbNO_3$). The films were annealed at 150°C for 2 hours.

The chemical reaction for the deposition of PbSe by CBD is given by

$Pb(NO_3)_2 + 4NaOH \leftrightarrow Na_2[Pb(OH)_4] + 2NaNO_3$
$Na_2[Pb(OH)_4] \leftrightarrow Pb^{2+} + 2NaOH + 2OH^-$
$Na_2SeSO_3 + OH^- \leftrightarrow HSe^- + Na_2SO_4$
$Hse^- + OH^- \leftrightarrow Se^{2-} + H_2O$
$Pb^{2+} + Se^{2-} \leftrightarrow PbSe$

The structures of the films were studied with Philips PW 1500 XRD. The composition of the films was determined by using Rutherford back scattering. The absorption coefficient (α) and the band gap of the films were calculated, using the absorbance and transmittance measurement from Unico – UV-2102PC spectrophotometer at normal incidence of light in the wavelength range of 200-1100nm.

3. Results and analysis

3.1. X-ray Diffraction Study

Typical XRD diffractograms of CBD PbSe thin film are presented in fig. 1. The samples were loaded into a 2.5cm diameter circular cavity holder and ran on an MD 10 mini diffractometer. CuKα was selected by a diffracted beam monochromator. The thin films were scanned continuously between 0 to 75 at a step size of 0.03 and at a time per step of 0.15sec. Phase identification was then made from an analysis of intensity of peak versus 2θ.

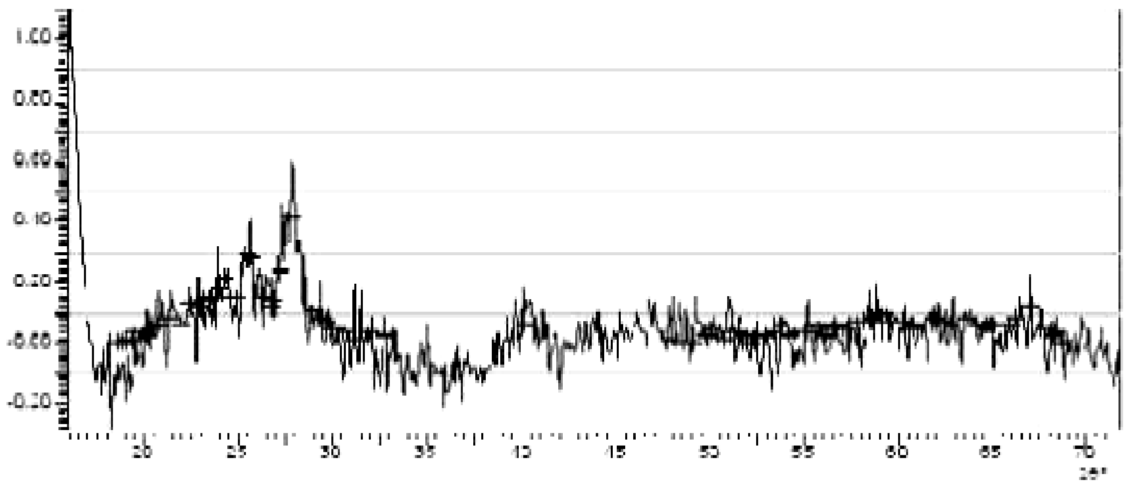

Fig. 1a. The XRD pattern of PbSe thin film from 1.0 molar concentration

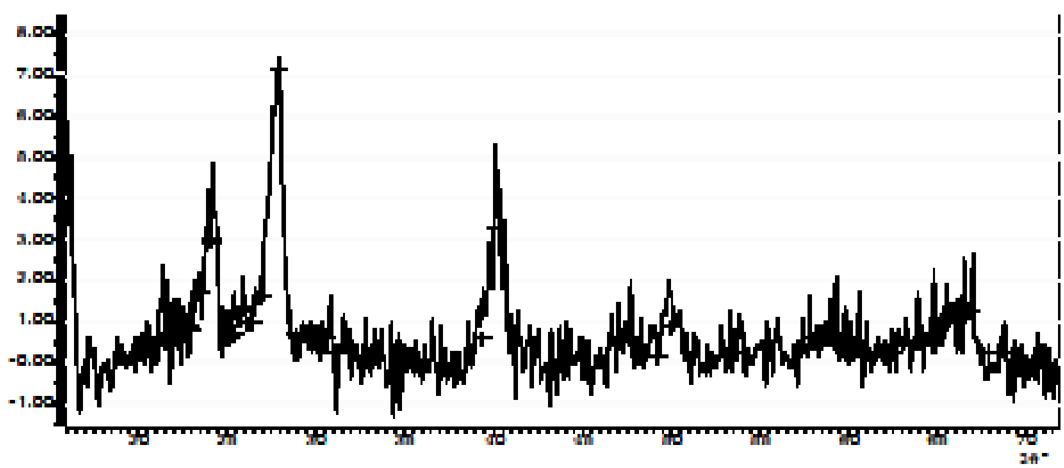

Fig. 1b. The XRD pattern of PbSe thin film from 0.25 molar concentration.

The XRD pattern displayed several diffraction peaks at 2θ values of around 23.50^0, 27.82^0, 29.12^0, 39.36^0 and 62.72^0. Intensity of the peaks increased with decrease in Pb^{2+} precursor concentration. That is, the film deposited at lower concentration showed better crystal structure. The most prominent peak in fig.1a is a reflection at 2θ angle of 29.12^0, corresponding to (200) plane. In fig. 1b, the reflection at 2θ values of 23.50^0, 27.82^0, and 39.36^0 correspond to (111), (200) and (212) planes respectively.

The grain size is estimated using Scherrer relation, D = kλ/ βcosθ, 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 18.9nm.

3.2. Optical and solid-state properties

Fig. 2 gives the plot of absorbance against the wavelength for PbSe thin films deposited in this work. The plot of absorbance against wavelength shown in fig. 2 indicates that the absorbance of the films decreased with both the wavelength of solar radiation and the concentration of Pb^{2+} precursor. The films generally showed good absorption of the visible portion of solar radiation.

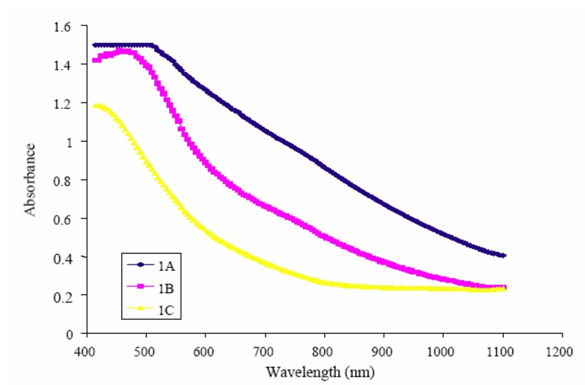

Fig. 2. Absorbance vs. wavelength for PbSe thin films deposited at different concentrations of Pb^{2+} precursor.

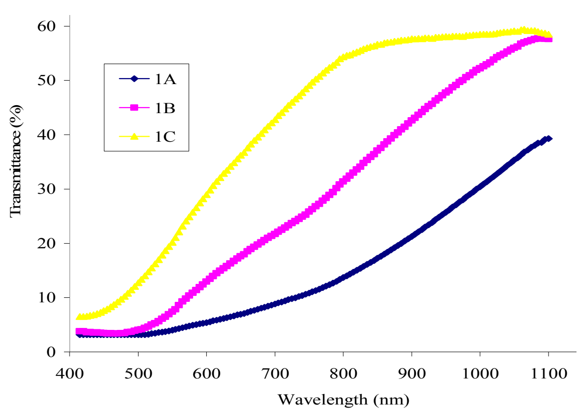

Fig. 3. Transmittance vs. wavelength for PbSe thin films deposited at different concentrations of Pb^{2+} precursor.

The spectral transmittance and reflectance of the films deposited in this work are shown in figs. 3 and 4 respectively. A close observation of fig. 3 shows that the transmittance of PbSe thin films increased with wavelength throughout the VIS and NIR spectra. The film deposited from the lowest concentration of Pb^{2+} precursor has the highest transmittance of 59.42% at 1065nm. However, the transmittance of PbSe thin film is in general below 50% in the visible region of solar spectrum. Human eye is sensitive only to the range 400 – 700nm and is peaked at 500nm (Ezema et al, 2007). This is an important factor in window coatings but is not met in these films. The films however are opaque in the visible region, making it unsuitable for this purpose.

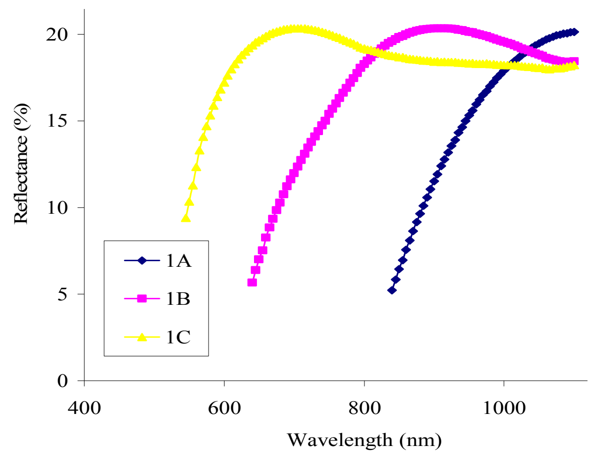

Fig. 4. Reflectance vs. wavelength for PbSe thin films deposited at different concentrations of Pb^{2+} precursor.

Plots of refractive index and extinction coefficient against photon energy are displayed in figs. 5 and 6. The refractive index of the films decreased with photon energy irrespective of the concentration of the precursor. However, the plot in fig.5 shows that film deposited at higher concentration has the lowest refractive index. It has been shown that thin films refractive index lower than 1.9 could be employed as anti-reflecting material and could improve the transmittance of glass from 0.91 to 0.96 (Brinker and Harringston, 1981; Petit and Brinker, 1986). This condition is realised in the film deposited at higher precursor concentration.

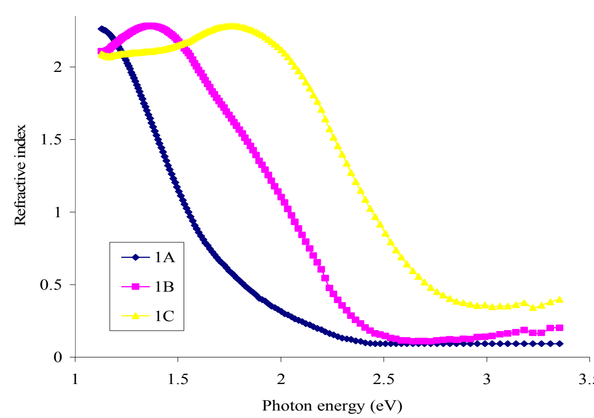

Fig.5. Refractive index as a function of photon energy for PbSe thin films.

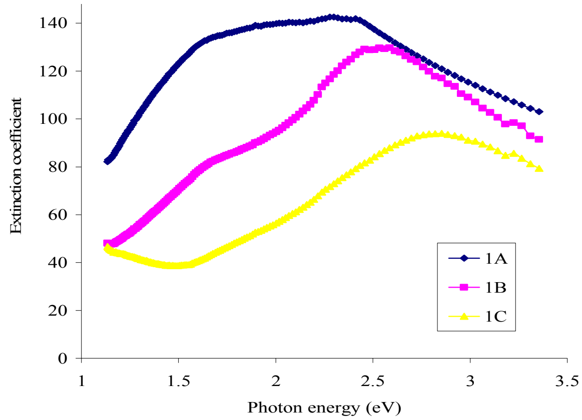

Fig.6: Extinction coefficient as a function of photon energy for PbSe thin films.

The variation of the extinction coefficient with photon energy displayed in Fig. 6 shows that films with high absorbance, low reflectance and low refractive index have high extinction coefficient. Such films are highly absorbing and could be employed as absorption layer in solar cell architecture. This implies that the film deposited at 1.0M concentration could be used for this purpose.

The details of the mathematical determination of the absorption coefficient (α) can be found in literature (Estrella et al, 2003; Ndukwe, 1996) while the plots of absorption coefficient against photon energy is shown in fig. 7

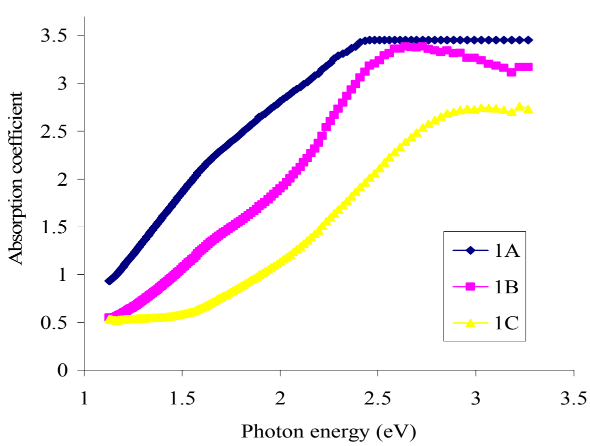

Fig.7. Absorption coefficient vs. photon energy for PbSe thin films.

The absorption spectra, which is the most direct and perhaps the simplest method for probing the band structure of semiconductors, is employed in the determination of the energy gap, E_g. The E_g was calculated using the following relation; $\alpha = A(h\nu - E_g)^n / h\nu$, (Ndukwe, 1996; Tauc, 1974):

Where A is a constant, hν is the photon energy, α is the absorption coefficient, n depends on the nature of the transition. For direct transitions n = ½ or ⅔, while for indirect transitions n = 2 or 3, depending on whether they are allowed or forbidden, respectively.

The intercept on the hυ axis of the extrapolation of a plot of $(\alpha h\upsilon)^2$ against hυ determines the band gap.

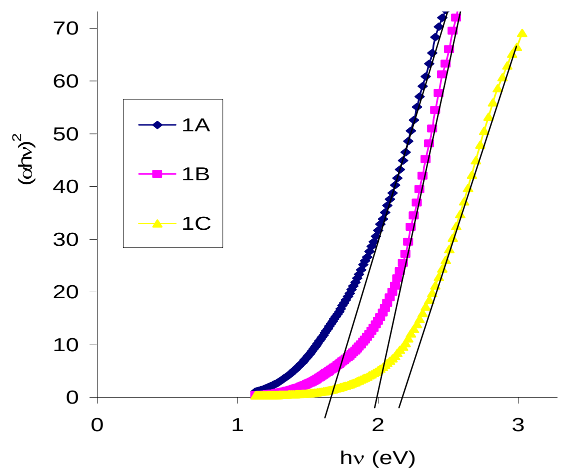

Fig. 8. Direct band gap plot for PbSe thin films.

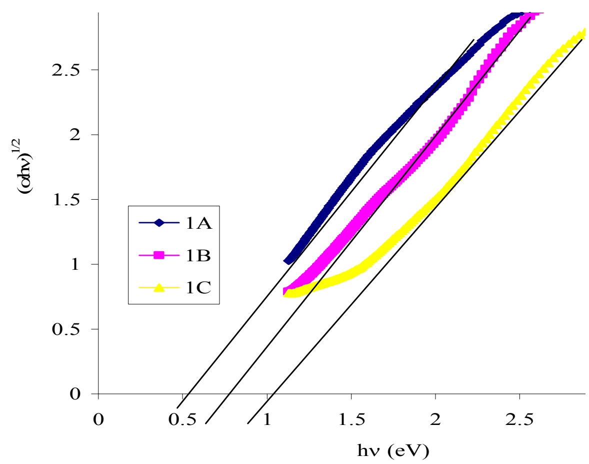

Fig. 9. Indirect band gap plot for PbSe thin films

The calculated values of the direct energy band gap, from figure 8 lie in the range of 1.6 – 2.2eV. The values obtained for the indirect energy band gap lie within 0.5 – 1.0eV. Increasing the precursor concentration lowers the values of both the direct and the indirect band gap energies of PbSe thin films under study. These may be a consequence of the increase in crystallite size (Erat and Metin, 2007). Literature survey shows that processes that increase the particle size decreases the band gap of most thin films (Jana et al, 2008, Djelloul, et al, 2008). This suggests that the films deposited at lower concentration had small grain size/crystallite size. This is a desired property for application requiring large band gap energy. Such thin films could be used as window layer in solar cell architecture.

3.3 Composition Study

The elemental composition and chemical state of the films were analysed by Rutherford Backscattering (RBS). The results are presented in fig. 10. From the film composition presented in table 1, we can deduce that PbSe thin film deposited in this work has no impurity content.

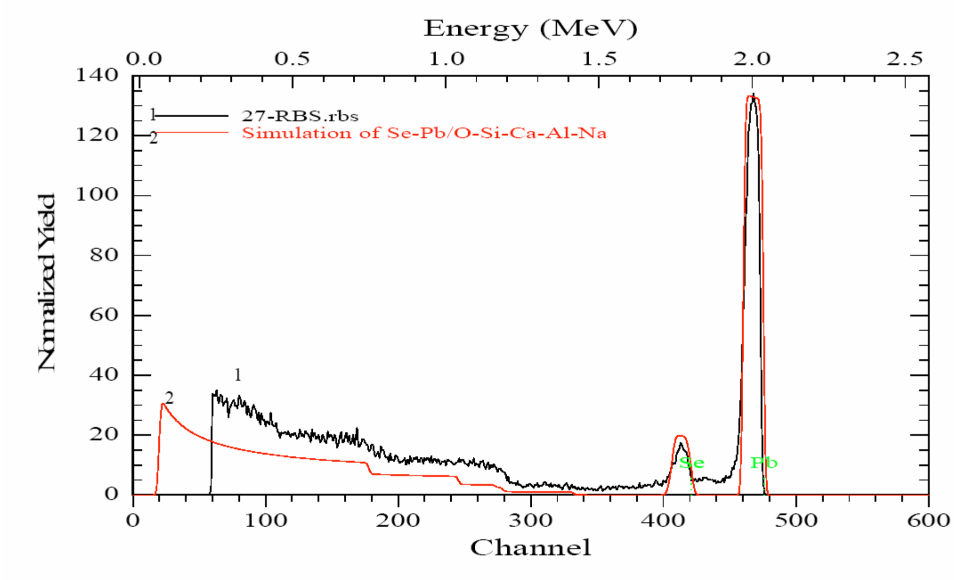

Fig. 10. RBS result for PbSe thin film annealed at 150°C

Table 1 The composition of substrate and PbSe film from RBS analysis.

	Lead	Selenide	Silicon	Calcium	Aluminium	Sodium	Oxygen
PbSe thin film	0.370	0.309	-	-	-	-	-
Glass substrate	-	-	0.080	0.025	0.050	0.230	0.615

4. Conclusion

This study focuses on the synthesis, structural and optical characterization of thin films of PbSe deposited with different concentrations of Pb^{2+} precursor. The films were deposited using chemical bath deposition technique. XRD study reveals that highly crystalline PbSe thin films could be obtained at a relatively lower precursor concentration. However, result from optical and solid-state analysis showed that the film deposited at 1.0M concentration has suitable properties for the application as absorber layer in solar cell fabrication.

References

[1] P. U. Asogwa S. C. Ezugwu F. I. Ezema, R.U. Osuji, Chalc. Letters **6**(7), 287 (2009).
[2] C. J. Brinker, M. S. Harringston, Sol. Energy Mater. **52**, 159 (1981).
[3] R. A. Chikwenze, M. N. Nnabuchi, Chalc. Letters **7**(5), 283 (2010).
[4] R. A. Chikwenze, M. N. Nnabuchi, Chalc. Letters **7**(6), 389 (2010).
[5] A. Djelloul, K. Bouzid, F. Guerrab, Turk J. Phys. **32**, 1 (2008).
[6] S. Erat, H. Metin CP899, Sixth International Conference of the Balkan Physical Union, edited by Cetin S.A. and Hikmet I., 249 (2007).
[7] C. A. Estrada, P. K. Nair, M. T. S. Nair, R. A. Zingaro, P. K. Meyers, J. Electrochem. Sos. **141**(3), 802 (1994).
[8] V. Estrella, M. T. S. Nair, P. K. Nair, Semicond. Sci Technol. **18**, 190 (2003).
[9] F.I. Ezema, P. U. Asogwa, A.B.C. Ekwealor, P.E. Ugwuoke, R. U. Osuji, J. University of Chemical Technol. and Metall. **42**(2) 217 (2007).
[10] F. I. Ezema, A. B. C. Ekwealor, R.U. Osuji, Turk J. Phys. **30**, 157 (2006) .
[11] F. I. Ezema, S. C. Ezugwu, P. U. Asogwa, A. B. C. Ekwealor, J. Ovonic Research **5**(5) 149 (2009).
[12] F. I. Ezema, S. C. Ezugwu, R. U. Osuji, P. U. Asogwa, B. A. Ezekoye, A. B. C. Ekwealor, M. P. Ogbu, J. Non-Oxide Glasses **1**(1), 45 (2010).
[13] F. I. Ezema, R. U. Osuji, Chalc. Letters **4**(6), 69 (2007).
[14] S. C. Ezugwu, F. I. Ezema, R. U. Osuji, P. U. Asogwa, A. B. C. Ekwealor, B. A. Ezekoye, Optoelectron. Adv. Mater. – Rapid Comm. **3**(2), 141 (2009).

[15] A. P. Gaiduk, P. I. Gaiduk, A. N. Larsen, Thin Solid Films **516**, 3791 (2008).
[16] S. Jana, R. Thapa, R. Maity, K. K. Chattopadhyay, Physica E (2008) doi;10.1016/j.physe.2008.04.015.
[17] V. Janickis, I. Ancutiene, Bruzaite and Jasulaitiene V. Mat. Sci. **10**, 231 (2004).
[18] R. S. Mane, C. D. Lokhande, Mater. Chem. Phys. **65**, 1 (2000).
[19] I. C. Ndukwe, Sol Ener. Mater. Sol. Cells **40,** 123 (1996).
[20] H. M. Pathan, C. D. Lokhande, D. P. Amalnerkar, T. Seth, Applied Surf. Sci. **211**, 48 (2003).
[21] R.B. Petit, C. J. Brinker, Solar Energy Materials **14**, 269 (1986).
[22] K. J. Rakesh, Solid State Communications **139**, 201 (2006).
[23] J. Tauc, Amorphous and Liquid Semiconductors (New York, Plenum) p. 159 (1974).
[24] J. J. Valenzuela-Jauregui, R. Ramirez-Bon, A. Mendoza-Galvan, M. Sotelo-Lerma, Thin Solid Films **441,** 104 (2003).

*Corresponding author: racy_c@yahoo.com