Influence of the Annealing Temperature on the Optical and Solid Stateproperties of Lead Selenide (PBSE) Thin Films Grown by Chemical Bath Deposition (CBD) Technique.

Igwe, Hilary U,Ugwu, Emmanuel I, Onah Daniel.U and Oshionwu, Lucky C
Depatrment of Industrial Physics, Ebonyi State University, Abakaliki, Nigeria
ugwuei@yahoo.com

Abstract

The study of the influence of annealing temperature on Lead Selenide (PbSe) thin films deposited on glass substrates using chemical bath deposition technique were carried out. The growth of the first group of the films (Set 1: $P_{(9)}$ &$P_{(14)}$) was based on the decomposition of lead citrate and sodium selenosulphite in the presence of sodium citrate and sodium hydroxide with Ammonia and Triethalamine(TEA) acting as complexing agents and P.H stabilizers; while in the second group (Set 2: $P_{(15)}$), the reaction bath was made up of solutions of lead nitrate $Pb(NO_3)_2$, (PVA), distilled water (H_2O), ammonia (NH_3), sodium selenosulphite (Na_2SeSO_3) and Triethalamine [$N(CH_2CH_2OH)$], which was used as complexing agent. The deposited materials were identified by X-ray diffraction. In addition, optical and morphological investigations performed revealed the morphological structure of the film. The absorbance of the film for various region of the electromagnetic spectrum was observed. The optical absorbance was found to reduce with increase in wavelength. The optical band gap a ranges from 1.26 – 2.00eV with sample $P_{(15)}$ having the lowest direct band gap.

Keywords: *Annealing temperature*, Chemical Bath Technique, Lead selenide, thin films, Optical and Solid state properties, band gaps, transmittance, wavelength.

INTRODUCTION

Metal chalcogenide thin films even their compounds have been of interest due their semiconducting nature and considerable application in the field of electronics and electro-optical devices. Based on this concept, intensive research has been performed in the past to study the fabrication and characterization of these thin films. Thus, the interest for Lead Selenide (PbSe) semi conducting thin films was motivated by its application in solar cell technology (1,2,3, 4). In the literature, a number of methods for the preparation of PbSe thin films were reported (7,8,9 10,11, 12). In laboratory, various methods of thin film deposition for production and characterization of semi conducting metal chalcogenides have been developed. Thus, the chemical deposition methodology for metal selenides such as mercury selenide (12,6), Silver selenide (13) lead selenide (11) and mercury sulphide are based on the decomposition of selenosulphite as source of selenide ions and thiosulphate as a sourse of sulfide ions precursors in an alkaline medium. The fabrication of metal oxides thin films of Fe_20_3 (13), NiO (14) and CoO are based on thermal treatment of an aqueous solution that contains the metals (15) and urea as hydroxide ions precursors and subsequent thermal conversion of the obtained hydroxide thin films to oxides.

In this paper, we present the procedure for preparing lead selenide thin films using chemical bath deposition technique on glass substrates and look at their optical and solid state properties of the samples of deposited thin film using different constituents. The structure and nature of the band gap of the films would be discussed followed by the X-ray diffraction analysis and photo micrographic data.

EXPERIMENTAL DETAILS

PbSe thin films were deposited on 76mm x 26mm x 1mm clean glass slide by chemical bath deposition (CBD) technique, (16). The 'set1' of the films($P_{(9)}$ &$P_{(14)}$) contained 5ml of 1M $Pb(NO_3)_2$ dissolved in 5ml of 1M Na_2SeS0_3, followed by the addition of 4ml of 1M sodium citrate $[C_3H_4(OH)COONa]_3.2H_20$ and 3ml of 2M Na0H as a complexing agent. The mixture was made up to the required volume with addition of 35ml of PVA (Polyvinyl Alcohol). The resulting solution was stirred for a few seconds with a glass rod stirrer. A glass slide was inserted in the reaction bath and held vertically in a synthetic foam cover. This process was repeated for different dip time in hours of: P_9 ($1^1/4$ hrs) and P_{14} ($1^1/2$hrs) at a deposition temperature of 75^0C in an oven. 'Set 2' (sample $P_{(15)}$) was deposited the same way but the deposition bath contained: solution of lead nitrate $Pb(NO_3)_2$,PVA, Distilled water (H_2O),Ammonia(NH_3),Sodium Selenosulphite (Na_2SeSO_3) and TEA $[N(CH_2H_2OH)_3$ used as complexing agent. At the end of the deposition times, the slides were taken out, rinsed with distilled water and allowed to dry in electronic oven. The slides were observed to have been coated with dark deposits. The equations of the reactions are shown below.

For set 1:

(Sample $P_{(9)}$ & $P_{(14)}$) , the reaction is:

$Pb(NO_3)_2 + 2NaOH \rightarrow Na_2Pb(OH)^{2+} + 2NO_3$
$Na_2Pb(OH)_2 \rightarrow Pb^{2+} + 2NaOH$
$Na_2SeSO_3 + OH^- \rightarrow HSe^- + Na_2SO_4$
$Pb^{2+} + OH^- + HSe \rightarrow PbSe + H_2O$ [1]

The reaction for set 2:

(sample $P_{(15)}$) is shown below:

$Pd(NO_3)_2 + TEA \rightarrow Pd(TEA)^{2+} + 2(NO_3)^{2-}$
$Pb(TEA)^{2+} \rightarrow Pb^{2+} + TEA$
$Na_2SeSO_3 + OH^- \rightarrow HSe^- + Na_2SO_4$
$Pb^{2+} + OH^- + HSe^- \rightarrow PbSe + H_2O$ [2]

They were later annealed at different temperature for one hour each as shown in the table 1. The band gaps of the films were determined by using the absorbance and transmittance measurements from Unico-UV-2102 PC spectrophotometer at normal incident of light in the wavelength range of 200-1000nm. The optical band gaps of the films would be obtained by using Tauc's Plot of $(\alpha h\upsilon)^2$ Vs $(h\upsilon)$ (17). The value of α was determined from transmittance spectra using:

$$T = I/I_0 = \exp(-\alpha x) \quad [3]$$

Where: 1_0 and I, are the incident flux and transmitted flux passing through a specimen of thickness (Xmm) with absorption coefficient (α) and transmittance (T) (18). However the fundamental absorption which corresponds to the electron excitation from the valence band to the conduction band can also be used to determine the nature and value of the optical band gap using:

$$(a\,hn)^{1/n} = \text{[illegible]}n - E_g \quad [4]$$

Where A = constant, Eg = band gap of the material and the exponent 'n' depends on the type of transition of which the values for direct allowed, indirect allowed and direct forbidden transition are n = $\frac{1}{2}$ and $^3/2$ respectively. The photon energy at the point where (α hv$)^2$ is zero represents the band gap Eg, which is determined by extrapolation.

RESULTS AND DISCUSSION

Figure 1 shows the plot of absorbance, transmittance and reflectance verses wavelength of PbSe thin films (sample $P_{(9)}$&$P_{(14)}$) deposited in this work while fig2 contains the graphs for sample $P_{(15)}$. For sample $P_{(9)}$ & $P_{(14)}$,the absorbance generally decreased with wavelength and has relatively low values in the IR region of the solar spectrum. A strong absorption was observed at wavelength range of 280-400nm, hence the film has potential application in fabrication of solar cell. The absorbance decreased as band gap decreased.

The transmittance spectra displayed in fig 1b shows downward trend in the transmittance of the films as band gap increases. The films show increase in transmittance as the wavelength increases and has over (80%) transmittance at NIR region of the spectrum of approximately 1000nm.

Fig 1c is a plot of reflectance as a function of wavelength for PbSe thin films of sample $P_{(9)}$ & $P_{(14)}$. The film shows an average reflectance of 20.5% in the wavelength rage of 300-640nm.

Fig 1d shows the refractive index of the films. Sample P_9 and P_{14} showed a sharp increase in value of 'n' from 1.5-2.3 between 1.2-1.75eV and a gentle increase of 0.2 between 1.75-4.25eV, hence it has an average refractive index 'n' of 2.3.

Table 1: **Band gap, Deposition temperature, Annealing temperature & Time of Deposition**

S/NO	PdSe films	Band gap hv (ev)	Deposition temperature (°C)	Annealing temperature (°C)	Dip Time (hrs)
1.	$P_{(9)}$	1.50	75	100	1 ¼
2.	$P_{(14)}$	2.00	75	300	1 ½
3.	$P_{(15)}$	1.26	75	300	1 ½

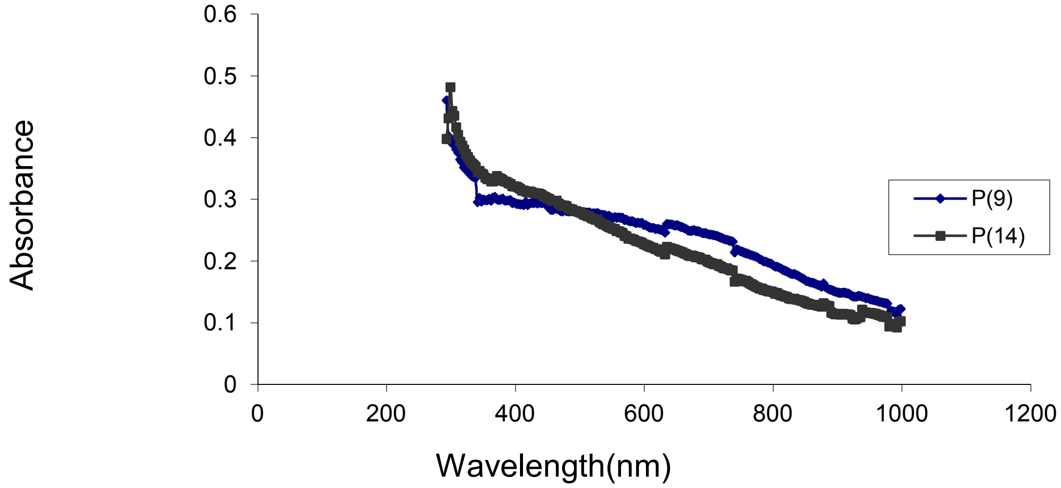


Fig 1a: Absorbance Vs Wavelength for PbSe

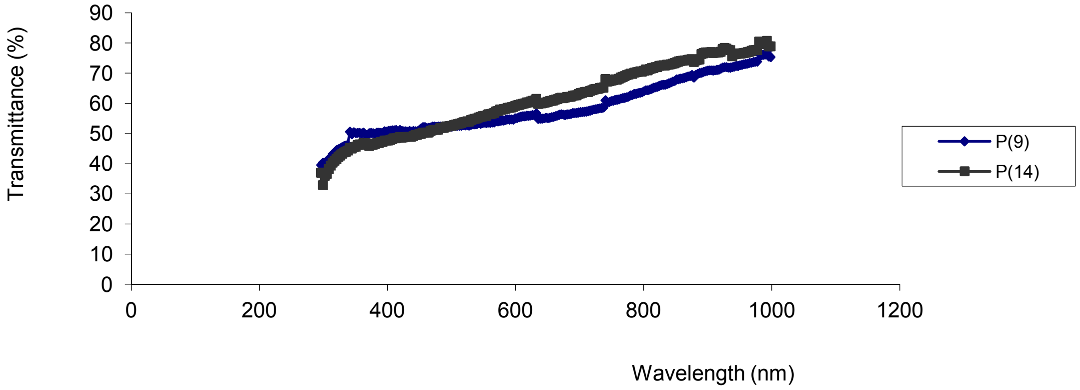


Fig:1b Transmittance vs. wavelength for PdSe

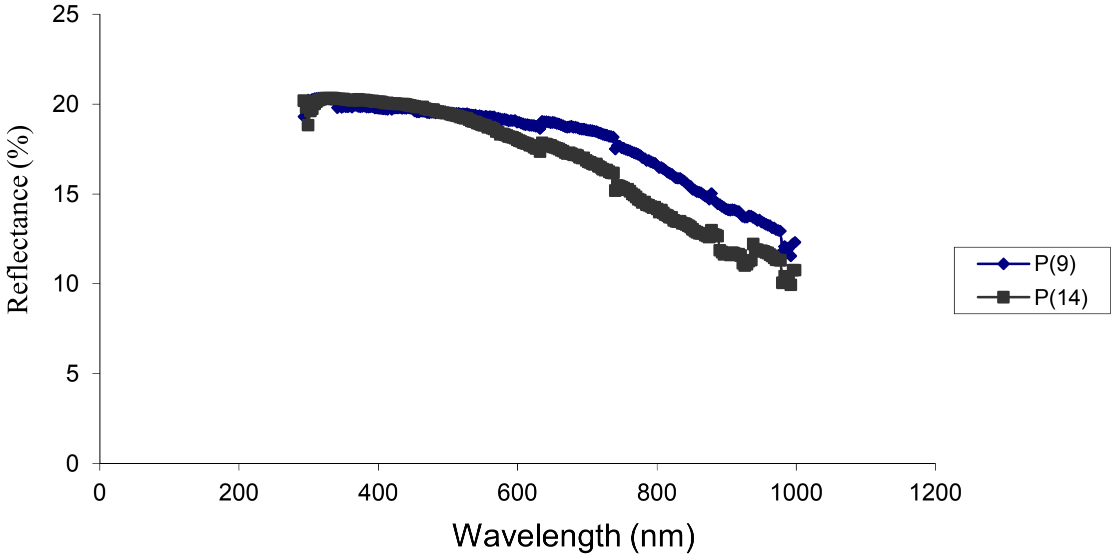


Fig 1c: Reflectance vs. wavelegth fo PdSe

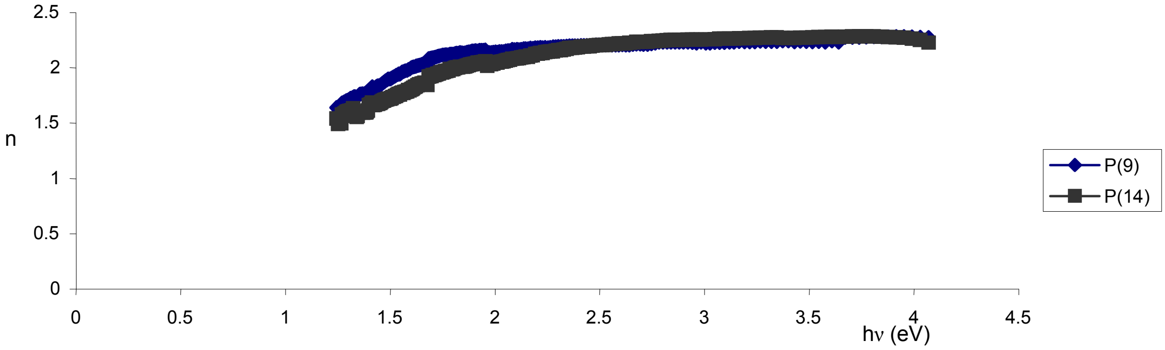


Fig 1d: Refractive index vs. Photon energy for PdSe

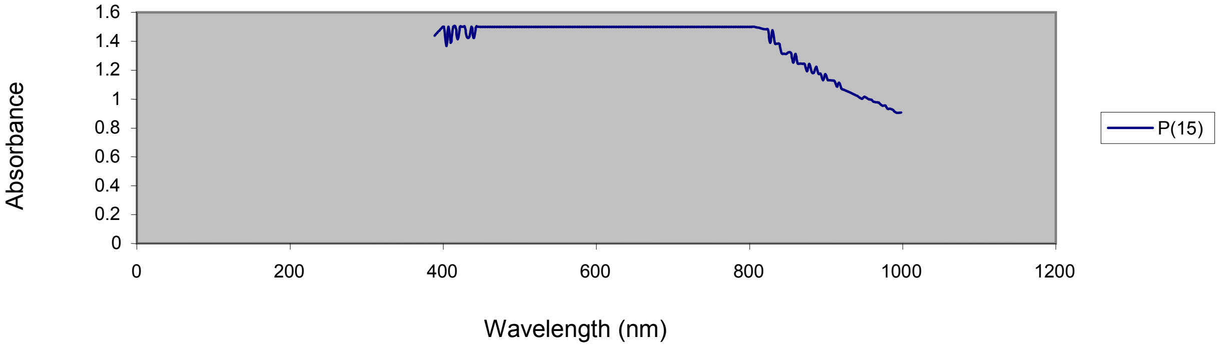


Fig 2a: Absorbance vs. wavelength P(15) PdSe

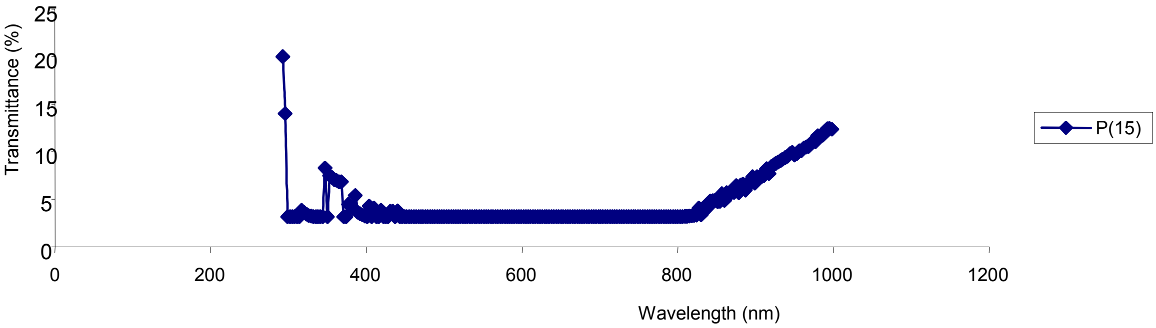


Fig 2b: Transmittance vs. wavelength P(15) PdSe

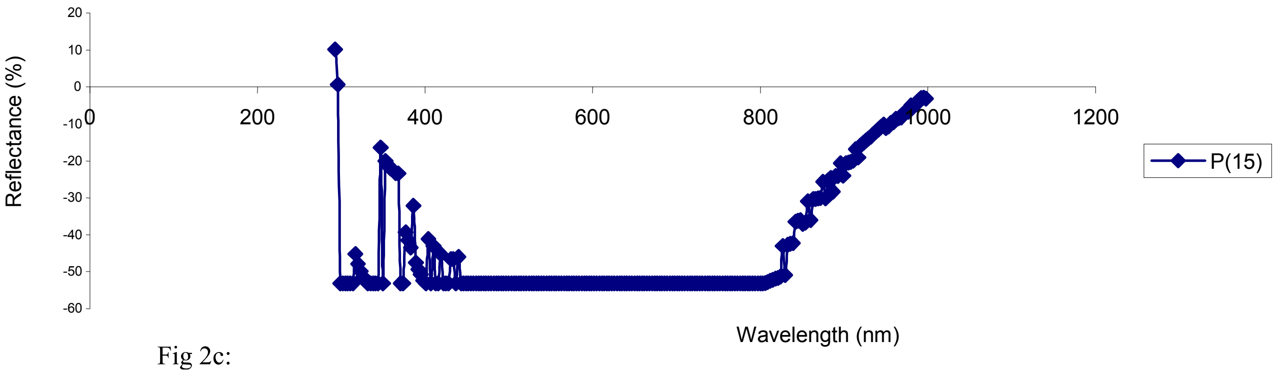


Fig 2c:

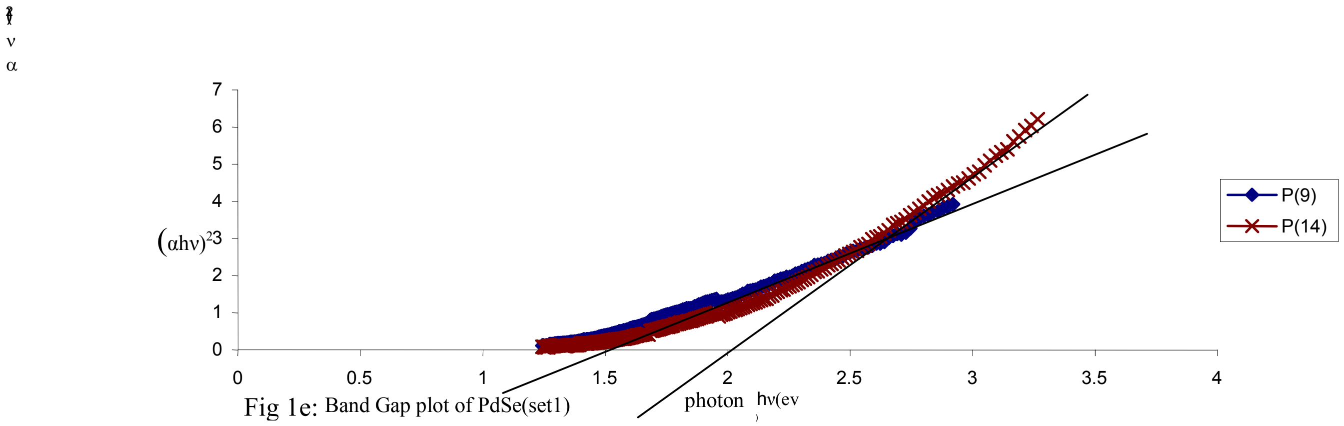


Fig 1e: Band Gap plot of PdSe(set1)

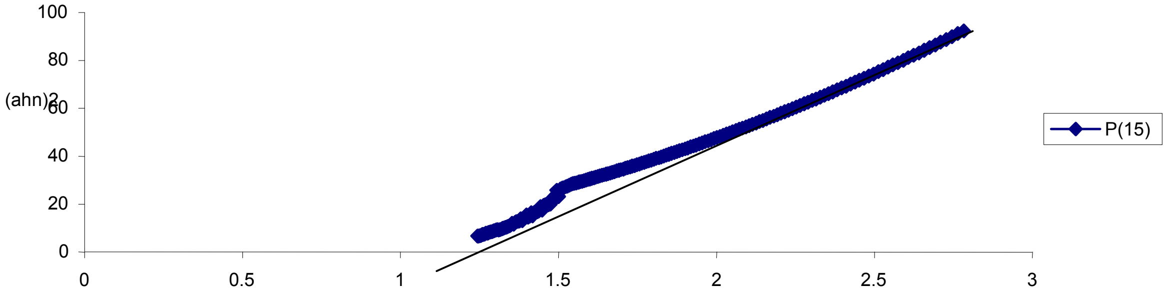


Fig 2d: Band gap plot of PdSe, P(15)

Fig2a presents a striking observation of sample $P_{(15)}$ whose constituent is completely different from the other two. The absorbance spectrum shows that it has very high and uniform absorbance of 1.5 throughout VIS and NIR regions of solar radiation. However, it has an extra ordinarily non reflectance property of -53% in the range of 300-840nm. It also has a very low transmittance of less than 5% in the same range of spectrum mentioned before. The characteristic shows that it has one of the most important properties of a thin film suitable for producing solar cell. In this respect, it is suitable for upper surface absorber of solar cell.

The values of the band gaps obtained for PbSe lie in the range of 1.26 – 2.00ev. It was observed that the band gap increased with increase in the annealing temperature which is quite different from the existing trend in literature reported elsewhere (Enriquez, 2003; Erat et al, 2007). With this range of band gap, it was observed that the band gap is generally good for opto-electronic applications.

X – Ray diffraction analysis was carried out on the chemical bath deposited PbSe thin films. The samples were grounded to below 100 meshes in an agate mortar and then loaded into a 2.5mm diameter circular cavity holder and ran on an MD 10 mini diffractometer. $\mathrm{CuK_a}$ was selected by a diffracted beam monochrometer. 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.

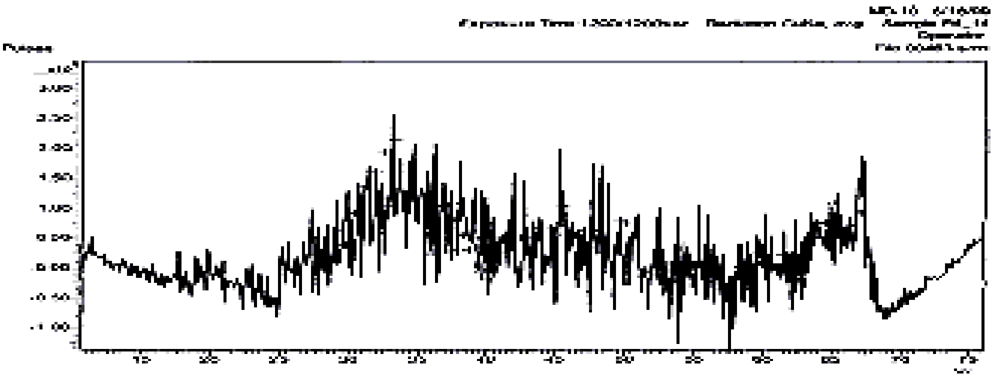
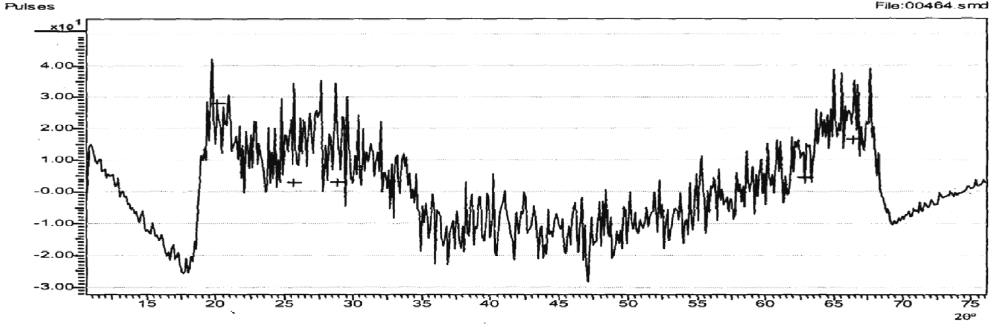


Fig.3a:XRD pattern for PbSe



	2θ°	d	I int	I max	I rel	I corr	FWHM
	20.11	4.41426	3361	36.9	32.6	41.8	1.5804
	25.67	3.47007	9160	11.7	89.0	100.0	13.929
	28.81	3.09837	3212	11.9	31.2	33.5	4.9354
	62.73	1.48114	10294	13.4	100.0	90.2	11.809
	66.32	1.40934	6903	25.5	67.1	60.1	4.1212

Fig 3b:XRD pattern for PbSe

Fig 3a displayed an XRD crystal pattern with maximum peak value of 4.25 at 2Θ value of 20.0° and 39.0 at the range of 64.5°–68.6° of 2Θ. The XRD pattern displayed in fig.3b shows several peaks at 2Θ values of around 20.11^0, 25.67^0, 28.81^0, 62.73^0 and 66.32^0. The 2Θ values of 20.11 (d = 4.41426 Å) and 62.73^0 [d = 1.48114 Å] corresponding to the diffraction lines produced by (32.9) and (100.0) planes respectively. The existence of identifiable peaks in the diffractograms suggests that the films are not amorphous but crystalline in nature (mane, et al, 1999). However the presence of several peaks suggests vibrations from impurities in the annealing oven or glass substrate used. A comparison of the observed peaks with standard JCPDS cards show that the samples posses a cubic crystal (orthorhombic in nature) of blue-gray metallic colour obtained at 19 reflections in pattern at room temperature of 25°C The calculated grain size of the thin film is about $1.91\mathrm{x}10^{-10}$ m which is approx. 2.0 Å =0.2nm.

CONCLUSION

The deposition of PbSe thin films have been successfully carried out in alkaline medium using chemical bath deposition technique. The spectral characteristics of the two sets of films showed that the effect of chemical constituents –in this case the complexing agent on the optical and solid state properties of PbSe was so conspicuous that the two sets of graphs are not related, consequently their characteristic nature. Hence the behaviour of any grown thin film depends to a large extent on the constituent of the solution from where it was deposited disregarding the environmental impurities. The deduction from the spectrophotometers showed that the band gap ranged between 1.26eV and 2.00eV and the grain size raged from 11 x 10^{-10} to 93 x 10^{-10}m.Some of the films were found to have high absorbance in the range of 280–400nm and depreciates as the wavelength increased. They had generally low transmittance and an average reflectance of 20.5% in the range of 300-640nm. The film hence has the potential for use in the solar cell fabrication, window screen and antireflection coatings while the characteristic zero reflectance of sample $P_{(15)}$ shows it potential for solar cell and solar warmer fabrication.

REFERENCE

[1] Loferski, J. J (1956). Appl J., Phys. 27, 777-784.
[2]Okimura, H. Matsumae, T. and Makabe, R (1980).., Thin Solid Films 71, 53-59.
[3] Chen, W.S. Stewart, J.M. and Mickelsen, R.A. (1985), App. Phys, Lett. 46, 1095-1097.
[4] Pejova, B. Najdoski, M. Grozdanov, I. And Dey, S. K. (1999) Mater, J., Chem. 9, 2889-2892.
[5] Mondal A. and Pramanik, P., J(1983)., Solid State Chem. 47, 81-83.
[6] Erat, S. & Metin, I P. Boyle D. S. (2007); Chemical Bath Deposition of Zinc mater.symp.proc.
[7] Padam, G. K. (1980)., Thin Solid Films 150, L89-L92 (1987).
[8] Haram, S. K. Snthanam, K. S. V. Neumann-Spallart, M. and Levy-Clement, C. (1992), Mater. Res. Bull, 27, 1185-1191.
[9] Massaccesi, S. Sanchez, S. and Vedel, J., J. (1961): Electrochem. Soc. 140 2540-2546, 19993.
[10] Thouin, L., Rouquette-Sanchez, S. and Vedel, J. (1993), J. Electrochem. Acta 38, 2387-2394.
[11] Grazdonov, I. (1994) Synthetic Mat. 63, 213-216.
[12] Levy-Clement, C. Neumann-Spallart, M. Haram, S. K. and Santhanam, K. S. V (1997)., Thin Solid Films 302, 12-16.
[13] Pejova, B. Isaliv A., Najdoski, M. (2000), Mater. Res: Bullin Press 11., 405-409.
[14]Pentia, E. Pintilie, L. Draghici V. and Lisea, M. (2003), Condensed Matt. Phys. Serbia 6, 799-802.
[15] Ezema, F. I. and Osuji R U (2007) FIZIKA, A (Zegred) 16, 107,116
[16] JCPDS- International Cetnre of Diffraction Data Set No. 08-0279 Oxford, 1997.
[17] Parkove, (1971). Optical Processes in Semiconductors. N. J. Prentice Hall, Eagle wood /Cliffs.
[18] Michels, W. C. (ed) International Dictionary of Physics and Electronics 2nd edn. (D. Van Nostrand Co., Inc., New Jersey).
Enriquez,J.P. and X.Mathew, (2003). Cells. *Solar Energy Material-Solar Cells* Vol.76.(Amsterdam:North Holland Pub.Co.),313.
Grozdanov, I. Najdoski, I. and Dey, S.K. (1999), Lett. 38, 28-32.
Najdoski, M., Grozdanov, I., Dey, S. K. and Siracevska, B., J. (1998), Mater. Chem. 8 2213-2215.
Pejova, B. Kocareva, T., Najdoski, M. and Grozdanov, I (2003)., Appl. Surface Sci. 165 271-278.

This academic article was published by The International Institute for Science, Technology and Education (IISTE). The IISTE is a pioneer in the Open Access Publishing service based in the U.S. and Europe. The aim of the institute is Accelerating Global Knowledge Sharing.

More information about the publisher can be found in the IISTE's homepage:
http://www.iiste.org

CALL FOR PAPERS

The IISTE is currently hosting more than 30 peer-reviewed academic journals and collaborating with academic institutions around the world. There's no deadline for submission. **Prospective authors of IISTE journals can find the submission instruction on the following page:** http://www.iiste.org/Journals/

The IISTE editorial team promises to the review and publish all the qualified submissions in a **fast** manner. All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Printed version of the journals is also available upon request of readers and authors.

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar