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THE OPTICAL AND SOLID STATE PROPERTIES OF LEAD SELENIDE (PbSe) THIN FILMS GROWN BY CHEMICAL BATH DEPOSITION (CBD)TECHNIQUE

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Lead selenide (PbSe) thin films were deposited on glass substrates using chemical bath deposition technique. The films' growth was based on the decomposition of lead citrate and sodium selenosulphite in the presence of sodium citrate and sodium hydroxide with Ammonia and Triethalamine acting as complexing agents and P.H stabilizers. The deposited materials were identified by X-ray diffraction. In addition, optical and morphological investigations were also performed. The as-deposited (that is unannealed) film (P_{16}) has the highest absorbance of about 0.98 while the sample P_9 has the lowest absorbance of about 0.3 in ultra-violet region. The optical absorbance generally reduced with increase in wavelength. The optical band gap shows a range of 1.58 – 2.20ev with the unannealed having the highest direct band gap.

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1. Introduction

Metal chalcogenide compounds, having a semiconductor nature, are of considerable technical interest in the field of electronics and electro-optical devices. Intensive research has been performed in the past to study the fabrication and characterization of these compounds in the form of thin films. Thus, the interest for Lead Selenide (PbSe) semi conducting thin films is motivated by its application in solar cell technology (1-4). In the literature, a number of methods for the preparation of PbSe thin films have been reported (5-12). 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 (13), Silver selenide (14), lead selenide (15) and mercury sulphide (16) 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 (17), NiO (18) and CoO are based on thermal treatment of an aqueous solution that contains the metals (19) 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. The structure and nature of the obtained films will be discussed on the basis of X-ray diffraction and photo micrographic data. The band gaps will be calculated from optical characterization reports.

2.Experimental details

PbSe thin films were deposited on 76mm x 26mm x 1mm clean glass slide by chemical bath deposition (CBD) technique, (20). 5ml of 1M $Pb(NO_3)_2$ was 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), P_{12} ($1^1/2$ hrs), P_{13} ($1^2/3$hrs), P_{14} ($1^1/2$hrs) and P_{16} (2.0hrs); at a deposition temperature of 75^0C in an oven. 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 equation of the reaction is shown below:

$$Pb(NO_3)_2 + 2\ NaOH \rightarrow Na_2Pb\ (OH)^{2+} + 2NO_3$$

$$Na_2\ Pb\ (OH)_2 \rightarrow Pb^{2+} + 2\ NaOH$$

$$Na_2\ Se\ SO_3 + OH\text{-} \rightarrow HSe\text{-} + Na_2\ SO_4$$

$$Pb^{2+} + OH^- + HSe \rightarrow PbSe + H_2O$$

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 gap of the films shown in figure2 were obtained by using Tauc's Plot of $(\alpha\ hv^2)^2$ Vs (hv) (21). The value of α is determined from transmittance spectra using:

$$T = I\ /I_0 = \exp\ (-\alpha\ x)$$

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) (22). 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:

$$(\alpha\ hv)^{I/n} = A\ (hv\text{-}Eg)$$

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 $n=^1/2$, 2 and $^3/2$ respectively. The photon energy at the point where $(\alpha\ hv)^2$ is zero represents the band gap Eg, which is determined by extrapolation.

3. Results and discussion

Fig. 1a & 1b show the plot of absorbance verses wavelength and transmittance Vs. wavelength of PbSe thin films deposited in this work. 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.

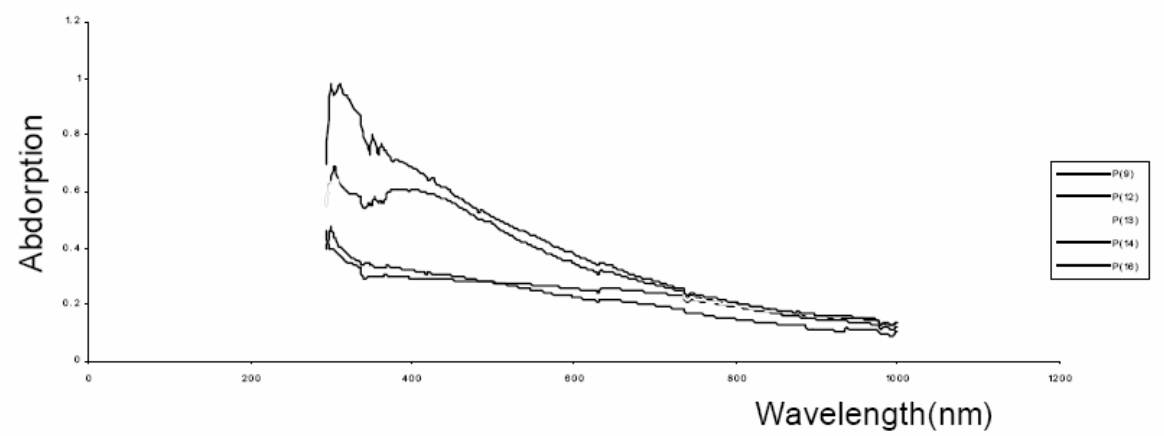

Fig. 1a. Absorption vs. wavelength for HgSe

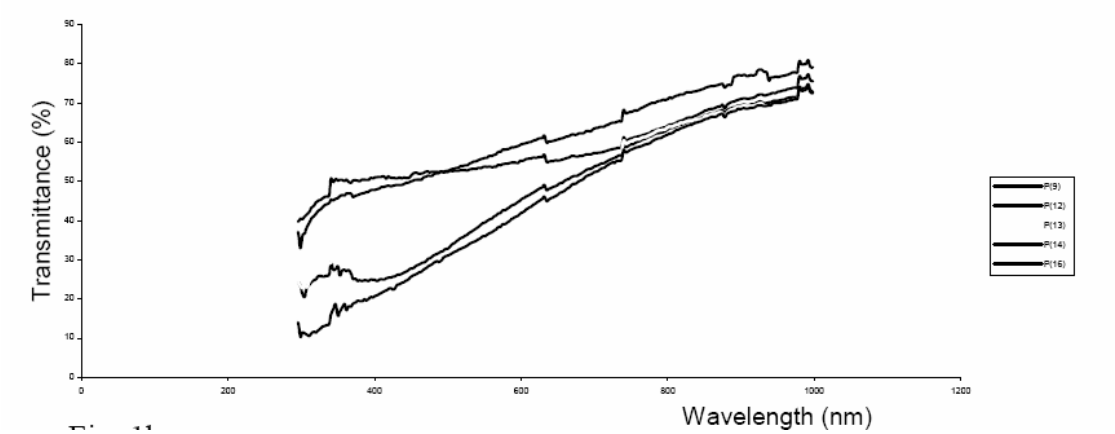

Fig. 1b. Transmittance vs. wavelength for PbSe

Fig 1c is a plot of reflectance as a function of wavelength for PbSe thin films deposited in this work. The film shows an average reflectance of 20.5% in the wavelength rage of 300-640nm.

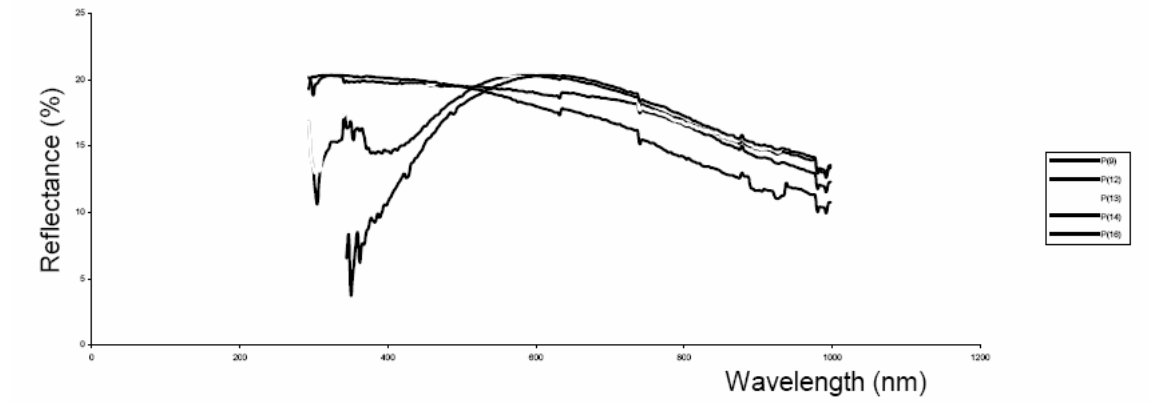

Fig. 1c. Reflectance vs. wavelength for PbSe

Fig 1d shows the refractive index of the films. Sample P_9 and P_{14} showed uniform value of 'n' throughout the whole range of the spectrum (NUV-NIR) with a refractive index 'n' of 2.3.

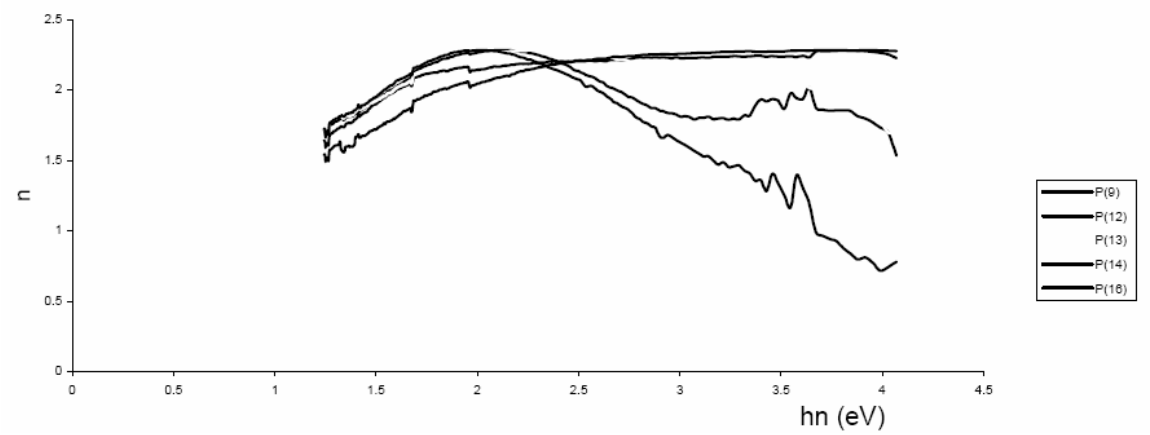

Fig. 1d. Refractive index vs. Photon energy for PbSe.

The surface microstructure of the films (shown in fig.4) were obtained by taking the photomicrograph of the films coated on the transparent glass slide with wide KPL-W10x /18 zeiss standard 14 photomicroscope with M_{35} 4760 – 9901 camera at a magnification of x200. The optical micrographs of the PbSe show uniformity in the distribution of the grains and a significant growth in grain size as the annealing temperature increased (see table 1).

Table 1.

S/NO	PdSe films	Band gap hv (eV)	Deposition temperature (^oC)	Annealing temperature (^oC)	Dip Time (hr)
1.	P (9)	1.58	75	100	1 ¼
2.	P (12)	2.10	75	400	1 1/2
3.	P (13)	2.04	75	200	1 ¾
4.	P (14)	2.00	75	300	1 ½
5.	P (15)	1.26	74	300	1 ½
6.	P (16)	2.20	75	0	2.0

The values of the band gaps obtained for PbSe lie in the range of 1.58 – 2.20 eV A close observation of figure 2 shows that the energy gap decreases from 2.20 to 1.64 as dip time increases from 1^1/4hrs to 2hrs. It was observed also that apart from the as-deposited sample $P_{(16)}$ with the largest band gap, the band gap increased with increase in the annealing temperature which is quite different from the existing trend in literature reported elsewhere (23-24)

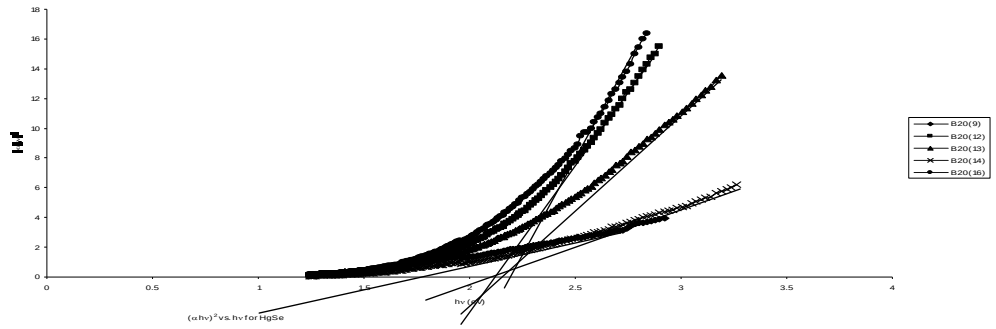

Fig 2. Band Gap of PbSe thin film

X – Ray diffraction analysis was carried out on the chemical bath deposited PbSe thin films. The samples were grounded to below 100 mesh in an agate mortar and then loaded into a 2.5mm diameter circular cavity holder and ran on an MD 10 mini diffractometer. Cuka 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.

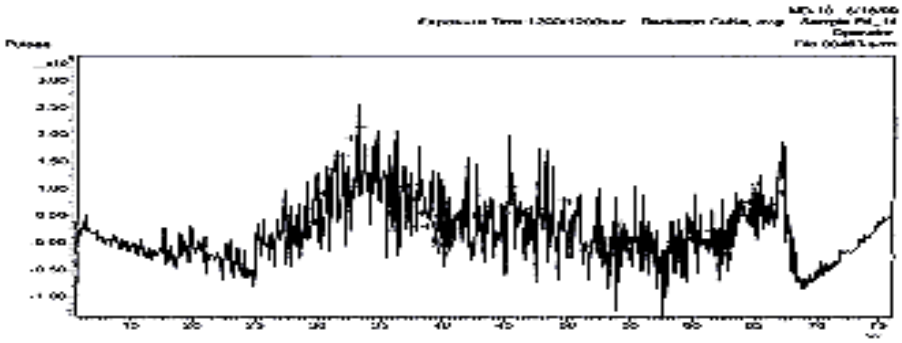

Fig.3a:XRD pattern for PbSe (P_{14})

Fig 3b:XRD pattern for PbSe P_9

Fig4a: photomicrograph for P_9 x 200

Fig 3a displayed an XRD crystal pattern with maximum peak value of 4.25 at 2Θ value of 20.0^o and 39.0 at the range of 64.5^o─68.6^o of 2Θ. The XRD pattern displayed in fig.3b show 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 ($d = 4.41426A^0$) and 62.73^0 [$d = 1.48114A^0$] corresponding to the diffraction lines produced by (32.9) and (100.0) planes respectively (mane, et al, 1999). The calculated grain size of the thin film is about $1.91x10m^{-10}$ which is approx. 2.0 Å =0.2nm.

4.Conclusion

The deposition of PbSe thin films have been successfully carried out in alkaline medium using chemical bath deposition technique. The deduction from the spectrophotometers showed that the band gap ranged between 1.58 and 2.20eV; the thickness ranged between 1.03029 and 5.7174nm while grain size raged from 11×10^{-10} to 93×10^{-10}m. 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. It showed a uniform distribution of particles as shown in the photomicrographs. The film hence has the potential for use in the solar cell fabrication, window screen and antireflection coatings.

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