STRUCTURAL, OPTICAL PROPERTIES AND APPLICATIONS OF CHEMICALLY DEPOSITED LEAD SELENIDE THIN FILMS

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Semiconductors based on selenium are important class of semiconducting systems which have been widely studied due to their fundamental electronic and optical properties. Intensive research has been performed in the past to study the fabrication and characterization of these compounds in the form of thin films. A number of methods for the preparation of PbSe thin films have been reported, but chemical bath deposition is found to be very good and low cost method to fabricate the polycrystalline PbSe thin films. We report the structural, optical properties and applications of PbSe obtained from chemical baths using $SeSO_3$ or K_2SeO_4 as a source of selenide ions. XRD studies on the films obtained from both baths suggest a clausthalite cubic structure. The optical band gap of the film is estimated to be in the range of 1.0-1.3eV.

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1. Introduction

Lead selenide (PbSe) thin films are important materials for applications such as IR detectors, photographic plates, and photo resistors (kale et al, 2006 and peitryga et al, 2004). Lead selenide film is used as a target material in infrared sensor, grating, lenses and various optoelectronic devices (Ali et al 1995). PbSe thin films have a direct band gap of 1.30 eV at room temperature. This paper reports the optical & structural properties of PbSe thin films prepared from chemical bath deposition technique and its application to solar energy.

2. Experimental details

PbSe thin films are prepared on glass substrate using the chemical bath deposition (CBD) method. The basic principle of the CBD technique consists the controlled generation of the metal and chalcogenide ions in an alkaline medium and their precipitation on the substrate in order to form a film. In the present case, the lead ion (Pb^{2+}) is generated by the decomposition of $[Pb(TEA)^{2+}]$ complex. This could be obtained by adding a Pb salt (10ml of 1M Pb $(NO_3)_2$ to 10ml of 0.5M TEA in our study) in an alkaline medium. The Se^{2-} ions are generated in alkaline medium by decomposition of the selenium precursor which is 10ml of 0.1M $SeSO_3$. The pH of the solution was adjusted by the use of 30% ammonia (NH_3).

For the sake of comparison, films were also prepared from baths containing potassium selenate (K_2SeO_4) as the source of selenide ions. The deposition bath was prepared as follows. 10 ml of 0.5 M of TEA was added to 10 ml of 0.1 M of $Pb(NO_3)_2$ in a 100 ml beaker. To this was added 10ml of 0.1M of K_2Se0_4 and the volume was made up to 100ml with distilled water. NH_3 was used for pH adjustment. The deposition was allowed to proceed at room temperature 26^oC for different pH as shown in table 1. The equations governing the reaction and deposition of PbSe films are as follow:

$$Pb(NO_3)_2 + TEA \rightleftharpoons [Pb(TEA)]^{2+} + 2NO_3$$
$$[Pb(TEA)]^{2+} \rightleftharpoons Pb^{2+} + TEA$$
$$SeSO_3 + OH^- \rightleftharpoons HSe^{2-} + SO_4^{2-}$$
$$K_2SeO_4 + OH^- \rightleftharpoons HSe^{2-} + K_2O_5$$
$$HSe- + OH^- \rightleftharpoons Se^{2-} + H_2O$$

The presence of Pb^{2+} and Se^{2-} ions lead to formation of PbSe.

$$Pb^{2+} + Se^{2-} \rightleftharpoons PbSe \downarrow$$

The above film was deposited at different conditions as specified in table 1.

Table 1 preparation of lead selenide (PbSe)

Rea-ction Bath	pH	Dip Time	$Pb(NO_3)_2$		TEA		$SeSO_3$		K_2SeO_4		NH_3	H_2O
		(hr)	MOL (M)	VOL (ml)	MOL (M)	VOL (ml)	MOL (M)	VOL (ml)	MOL (M)	VOL (ml)	VOL (ml)	VOL (ml)
T_5	10.50	20	1.0	10.0	0.5	10.0	-	-	0.1	10.0	4.0	66.0
T_{11s}	12.00	20	1.0	10.0	0.5	10.0	0.1	10.0	-	-	8.0	62.0

The lead selenide were deposited on pre-cleaned glass substrates. The deposited films were analyzed using Janway 6405 UV-VIS model of spectrophotometer to measure the optical properties of the grown films. The structural composition of the grown films was studied through the XRD analysis and optical micrograph.

3. Results, discussion and application

The thicknesses of the deposited film were measured by the optical method as described by Theye (1985) and were found to be 1.00 µm for T_5 and 1.35µm for T_{11} .

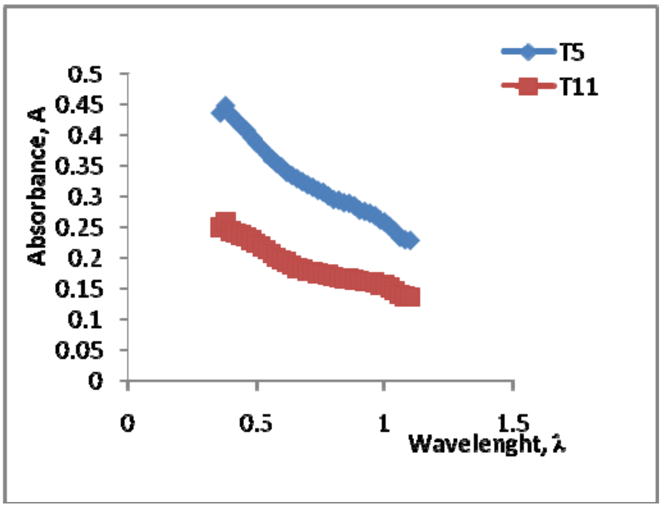


Fig. 1 spectral absorbance of PbSe for T_5 & T_{11}

Fig. 1 shows that the film T_5 which was grown in $SeSO_3$ bath absorbs better than T_{11} that was grown in K_2SeO_4 bath .The reverse is the case in the transmittance spectra where the film T_{11} transmits heavily than T_5 .

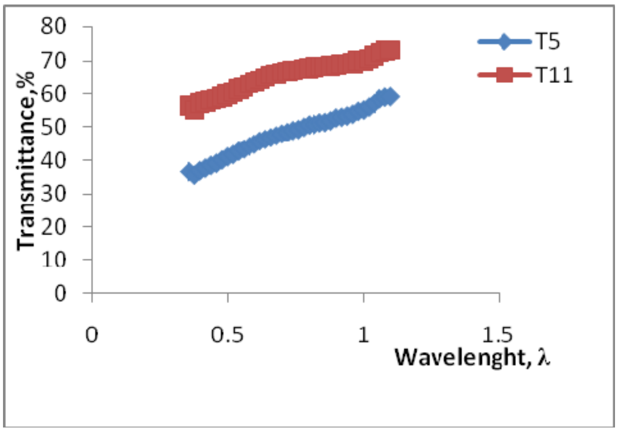


Fig. 2 Spectral transmittance of PbSe for T_5&T_{11}

Figure 1 and 2 shows the plots of absorbance and transmittance versus wavelength of PbSe thin films deposited in this work. The absorbance generally decreased with increase in wavelength and has relatively low values in the infrared region of the spectrum. A strong absorption was observed at wavelength range of 0.35 µm – 0.40 µm, hence the film has potential application in fabrication of solar cell.

The transmittance spectrum displaced in figure 2 show increase in transmittance as the wavelength increases, and has about 80% transmittance in the VIS-NIR regions for the film grown in $SeSO_3$ bath and 75% transmittance for the one grown in K_2SeO_4 bath.

The very high transmittance in the visible region makes lead selenide films useful aesthetic window glaze materials. Also, the high transmittance of the film makes it suitable for solar energy collection because if coated on the surface of the collector, it will reduce reflection of solar radiation and transmits radiation to the collector fluid.

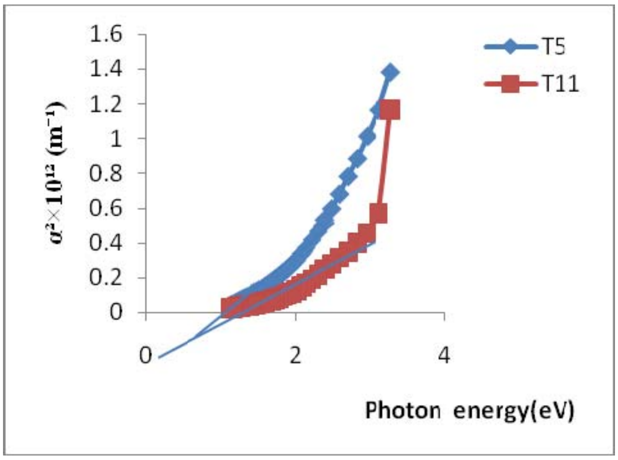
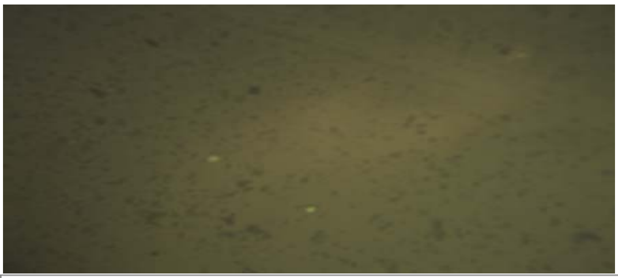


Fig. 3 Plot of α^2 Vs photon energy for T_5& T_{11}

Figure 3 shows a plot of α^2 versus photon energy (hv) of PbSe thin films. The energy gaps for these films are obtained by extrapolating the linear part of the curve to the energy axis. It is observed from the figure that PbSe thin film exhibits direct band transition and the band gap ranged from 1 eV – 1.30 eV which varies from the bulk value of 0.27 eV. Prebahar et al, (2009) reported a band gap of a vacuum evaporation deposited PbSe film ranging from 0.279 – 0.299 eV.

The anomaly with the reported value by Prebahar et al (2009) may be due to quantum size effect in a polycrystalline thin film material which blue shifts the optical spectra to that of the reported value and characteristics bulk. Secondly the variation may be due to the difference in deposition technique.

But the result is in a very close agreement with Ishiwu & Nnabuchi (2010) who reported a band gap range of 1.5eV–2.2 eV for PbSe films prepared using CBD just like in the present study.



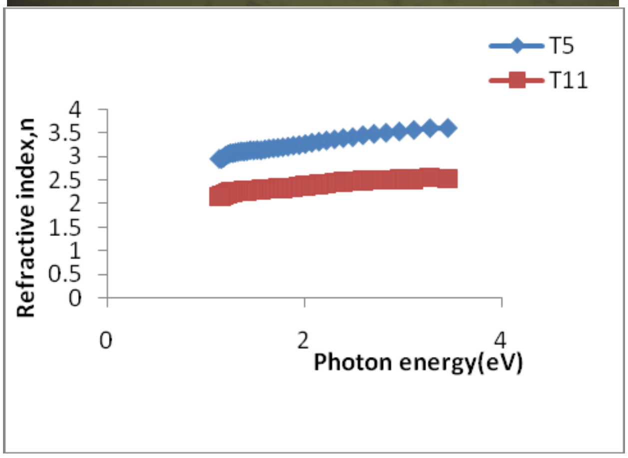


Fig. 4 Plot of refractive index Vs photon energy for T_5 & T_{11}

Fig. 4 shows a plot of refractive index (n) versus photon energy (hv) of films T_5 and T_{11}. The refractive index (n) of the films increases with the photon energy revealing a refractive index of 2.8 for the film grown in $SeSO_3$ bath (T_{11}) and 3.6 for the film grown in K_2SeO_4 bath (T_5). The result above revealed that PbSe has high refractive index. The high refractive index possessed by PbSe films made it suitable for use as anti-reflection coatings. Since T_5 which has the greatest value of refractive index (3.6) was grown in $SeSO_3$ bath, $SeSO_3$ is preferred to K_2SeO_4 as the source of cation to be able to give high value of refractive index.

3.2 surface microstructure

Fig. 5 shows the optical micrograph of PbSe film. The micrograph shows that the surfaces of the lead selenide films are dense. It shows uniformity in the distribution of the grains. This may be due to the high preferred orientation of the film in the (201) plane as was reported in the study of the structural analysis of PbSe film. Further confirmation of the structure of the grown films was carried out using the X-ray diffraction pattern in Fg 6.

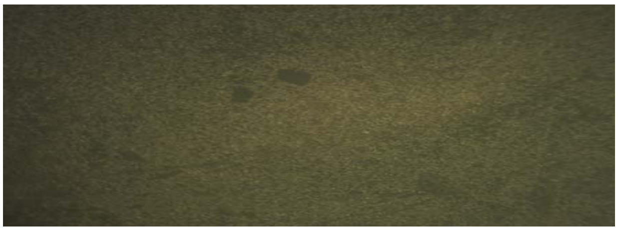


Fig. 5 Photomicrograph of PbSe prepared at 300K for T_{11}

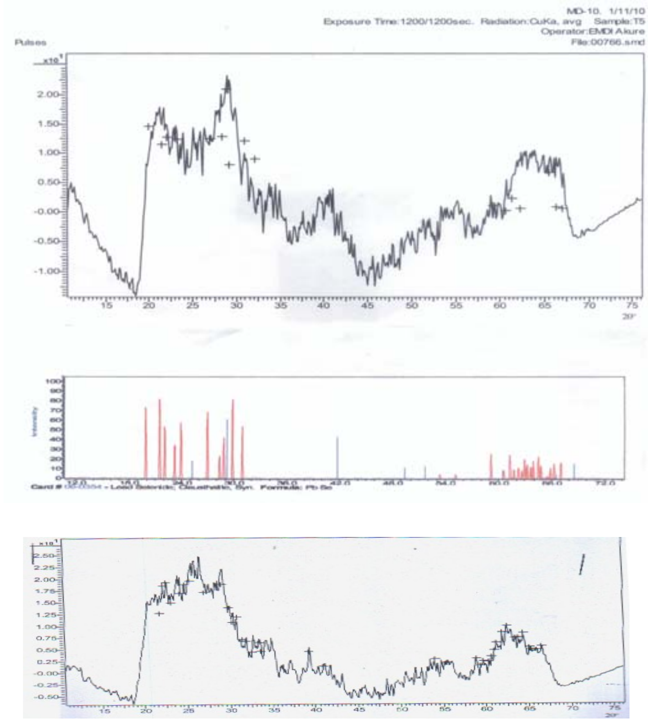


Fig. 6. X-ray diffraction patterns for PbSe

Fig. 6 shows the XRD pattern of a typical PbSe thin film prepared at substrate temperature of 300k. The 2θ peaks observed at 29.14^o, 41.68^o and 25.16^{o}give rise to the clausthalite cubic structure with lattice constant a = 6.114A^{o}which correspond to the (200), (220) and (111) planes of reflections for the films grown in $SeSO_3$ bath. These are well in agreement with the reported value by Prebahar et al (2009) who reported the dominant orientation in the (200) plane. This shows that the preferred orientation lies along the (200) plane. This confirms that PbSe films were deposited in this work. The presence of the large number of peaks indicates that the films are polycrystalline in nature (Damodara et al, 1989).

For the film grown in K_2SeO_4 bath (T_5) the observed peaks are in agreement with those due to reflections from (200) and (220) planes as shown in table 2.

The inter-planer distance (d) and lattice constants (a) as were indicated in the XRD analysis are presented in table 2. The crystallite (grain) size (D), dislocation density (ρ) and the micro strain (E) were calculated and are presented in table 2 using the expressions below:

Grain size (D) was calculated using Scherre's formular

$$D: = K\lambda / \beta \cos \theta$$

where λ is wavelength of x-ray, β is FWHM (full width half maximum), θ is the diffraction angle and K is 0.9 which varies with (hkl) and crystallite shape.

The dislocation density is

$$(\rho) = aD$$

where a is the lattice constant.

$$\text{Micro strain } (\varepsilon) = \beta\cos\theta /4 \ .$$

Table 2: Structural parameters of PbSe thin films for T_5 & T_{11} with thickness.

Reaction Bath	Thickness (μm)	hkl	2θ (deg)	2θ (rad)	d measured	Lattice constant, a (Å)	FWHM (rad)	Grain size D (Å)	Dislocation Density (ρ) X10^{-2}	Micro Stain (£) X10^{-2}
T_5	1.00	200	26.93	0.470	3.31	6.11	0.380	3.75	6.05	9.24
		220	32.17	0.561	2.78		0.381	3.78	5.93	9.15
T_{11}		200	29.14	0.509	3.06	6.12	0.380	3.77	6.00	9.19
		220	41.68	0.727	2.16		0.384	3.86	5.69	8.97
	1.35	111	25.16	0.439	3.50		0.362	3.92	5.49	8.80

The structural parameters of PbSe thin film show that the films have average crystallite size of 3.82Å. Table 2 shows that the crystal size of the film increases with film thickness, but the dislocation density and micro strain are decreasing with the increased film thickness. This may be due to the decrease in imperfections and dislocations of the films with increasing film thickness.

4. Conclusions

Lead selenide thin films have been successfully carried out using chemical bath deposited technique. Solutions of Pb $(NO_3)_2$, K_2SeO_4or $SeSO_3$, TEA and NH_3 formed the reaction bath. Good quality thin films of lead selenide of composition PbSe with clausthalite cubic structure were deposited. It showed a uniform distribution of particles as shown in photomicrograph. The average grain size is 3.82Å. The films were found to have high absorbance in the ultra violet region and depreciate as the wavelength increased. They have generally high transmittance, high refractive index. Hence, the film has potential for use in the solar cell fabrication, window screen and anti-reflection coatings.

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