Chemical Bath Deposited PbSe Thin Films: Optical and Electrical Transport Properties

Barote Maqbul A.[1], Yadav Abhijit A.[2], Surywanshi Rangrao V.[1], Deshmukh Lalasaheb P.[3], Masumdar Elahipasha U.[2]
[1]Department of Physics, Azad college, Ausa-413520, Maharashtra, INDIA
[2]Thin Film Research Laboratory, Department of Physics, Rajarshi Shahu Mahavidyalaya, Latur-413512, Maharashtra, INDIA
[3]Thin film and Solar Studies Research Lab, Dept. of Physics, Solapur University, Solapur-413 003, Maharashtra, INDIA

Abstract

A systematic study of the influence of thickness on the optical and electrical transport properties of PbSe thin films is reported in this study. The PbSe thin films were prepared on amorphous glass substrates by simple and cost effective chemical bath deposition technique at the substrate temperature 85^{0}C. The electrical resistivity measurement shows films are semiconducting and it decreases with increase in film thickness. Optical absorption studies show that the band-gap energy is decreased from 0.33 to 0.25 eV as the thickness of the film is increased from 335 to 638 nm.

Keywords: PbSe thin films, optical properties, electrical properties, carrier density.

Introduction

The polycrystalline thin film semiconductors have attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices. The technological interest in polycrystalline based devices is mainly caused by their very low production costs.

The IV–VI compounds[1-2] has been the subject of considerable attention, owing to their technological importance in the IR field. In addition, their unusual characteristics make them a preferred subject for solid state basic research. The fabrication of devices with alloys of these compounds with photo detection and injection laser capabilities has been an important recent technological development[3-4]. They have been applied in long wavelength imaging[5], diode lasers[6] and in thermo-photovoltaic energy converters[7]. The great interest is their application in the fields of gas spectroscopy and pollution control[4], remote sensing[3], thermography, chemical sensing[8]. The electrical and optical properties of PbSe thin films are studied in the present article.

Material and Methods

Preparation: Thin films of lead selenide with varying thicknesses were deposited onto ultrasonically cleaned glass substrates using AR grade chemicals. For the deposition, 10 ml (0.33 M) lead sulphate, 4 ml triethanolamine were taken in 250 ml beaker and sufficient amount of aqueous ammonia was used to get clear solution. Finally, 10 ml (0.33 M) sodium selenosulphate solution and sufficient quantity of double distilled water was added so as to make final volume 150 ml. The pH of the reaction mixture was maintained at

about 10.5 ± 0.1. Thoroughly cleaned glass substrates were mounted on a specially designed substrate holder and were rotated with a constant speed in the reaction mixture to achieve uniform and continuous stirring of the reaction solution. To obtain the good quality deposits, the time and temperature of the deposition and speed of the substrate rotation were optimized. These parameters have been selected as 70 min., 85 ^{0}C and 60 ± 2 rpm, respectively.

Characterization techniques: The thickness of 'as-deposited' thin films was determined using gravimetric weight difference method with sensitive microbalance. The samples were scanned by X-ray diffraction technique within the 2θ range from 20^0 to 80^0. The optical absorption spectra were recorded at room temperature using UV-VIS-IR spectrophotometer (NEXUS-670). The absorption coefficient energy band gap and mode of transition were determined from these studies. A d. c. two point probe press contact method was employed to measure electrical conductivity and thermo-emf of the 'as-deposited' samples in the temperature range 300-500 K. Silver paste was employed to ensure good electrical contacts.

Results and Discussion

Structural analysis: Figure 1 depicts XRD patterns of some typical thickness dependent PbSe thin film samples. All samples showed preferential orientation along (2 0 0) plane with face centered cubic structure. It is quite clear from these figures that irrespective of the thickness, the films are polycrystalline and oriented along (1 1 1), (2 0 0), (2 2 0) and (3 1 1). Presence of other orientations such as (2 2 2) and (4 2 0) have also detected, but considerably in lower intensities. These are in good agreement with earlier reported spectra on PbSe system[9].
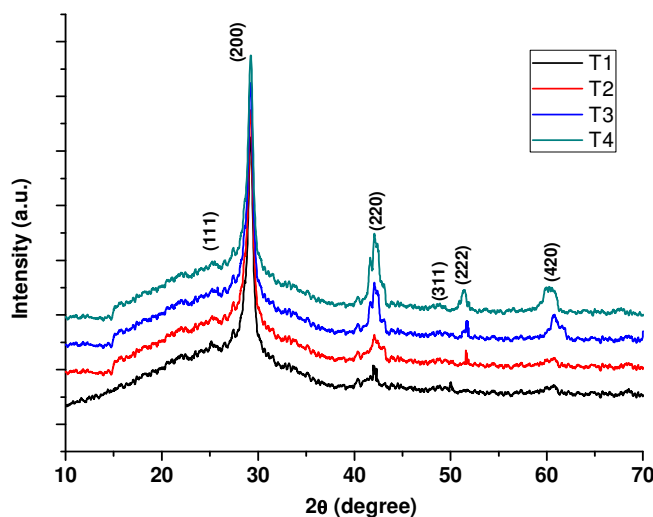
Figure - 1
XRD pattern of 'as-deposited' PbSe thin films of various thicknesses

Mean crystallite size was calculated for the (2 0 0) diffraction peak, using Scherrer's formula

$$D = \frac{0.94\lambda}{\beta Cos\theta} \qquad (1)$$

where D is the diameter of crystallites, λ the wavelength of Cu-kα line, β is full width at half maximum (FWHM) in radians and θ is Bragg's angle. The values were found to increase with increase in film thickness and are listed in table 1.

Optical characterization: The study of the materials by means of optical absorption and reflection provides a simple method for explaining features concerning the band structure and energy gap of non-metallic materials. Absorption spectra of PbSe thin films of various thicknesses were studied to evaluate the absorption coefficient (α) and band gap (Eg). Absorption coefficient can be derived from the absorbance A, which is the ratio I0/It, where I0 is the incident intensity and It is the intensity after traversing a thickness t the sample.

Absorption coefficient = optical density / thickness[10] or

$$\alpha = \left(\frac{1}{t}\right) \log \left(\frac{I_0}{I_t}\right) \qquad (2)$$

The various types of transition give rise to different frequency dependencies of absorption coefficient near the fundamental absorption edge. Absorption coefficient can also be given[11]

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (3)$$

For allowed direct transition n=1/2 and A is constant. The variation of $(\alpha h\nu)^2$ vs hν (Figure 2) is linear, which means that the mode of transition in these films is of direct nature. Extrapolating these curves on the energy axis for zero absorption gives the optical energy gap (Eg) which is given in Table 1. It is observed that the band gap is decreased after increasing the film thickness. The decrease in band gap is attributed to the improvement in crystallite size of material.

Table-1
Some of the characteristic properties of PbSe thin films

Sample Code (T)	Thickness (nm)	Grain size (nm)		Band gap E_g (eV)	Power factor (m)
		XRD	SEM		
T1	335	10.2	150	0.33	0.52
T2	468	13.5	210	0.31	0.49
T3	547	15.1	280	0.28	0.53
T4	602	16.8	315	0.27	0.47
T5	638	17.6	350	0.25	0.48

Figure-2
Plot of (αhν)^2 Vs hν for PbSe thin films of various thicknesses
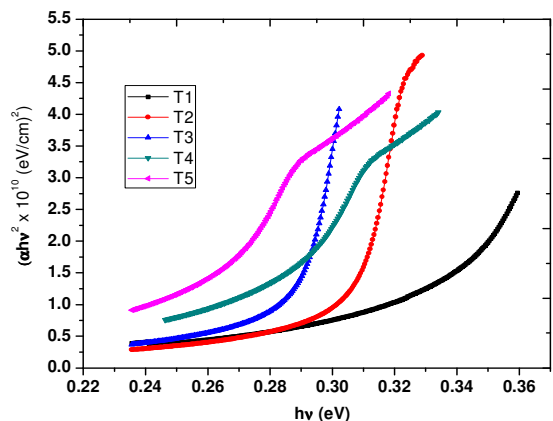
Figure-3
The variation of logρ with the reciprocal of temperature

Electrical characterization: The electrical conductivity is an important factor which reveals the important and reliable information about the transport phenomenon of the material. The electrical properties are dependent on various film and growth parameters such as film composition, thickness and substrate temperature and deposition rate. For photovoltaic application, important characterizations include electrical conductivity and the interface behavior of the semiconductor with various metals.

The d.c. electrical conductivity of a semiconductor at temperature T is given by

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \qquad (4)$$

where σ_0 is the pre-exponential factor, Ea is the activation energy for the generation process and k is the Boltzmann constant. we may write

$$\ln \sigma_{dc} = -\frac{E_a}{kT} + \ln \sigma_0$$

$$\ln \sigma_{dc} = -\left(\frac{E_a}{1000k}\right)\left(\frac{1000}{T}\right) + \ln \sigma_0 \qquad (5)$$

when we plot a graph between lnσ$_0$ and 1000/T, a straight line is obtained having slope (E$_a$/1000k) and intercept ln lnσ$_0$. Thus, the activation energy can be calculated by using the slope of the straight line.

The dark dc electrical resistivity of PbSe thin film samples of various thicknesses was measured in 300-500 K temperature range. The electrical resistance was found to be of the order of 10^2 Ω-cm and is smae as that of reported by Zingaro and Skolvin[12-13]. The conductivity of all these thin film samples increases with increase in temperature indicating the semiconducting nature. The variation of lnσ with the reciprocal of temperature is shown in figure 3. The variation
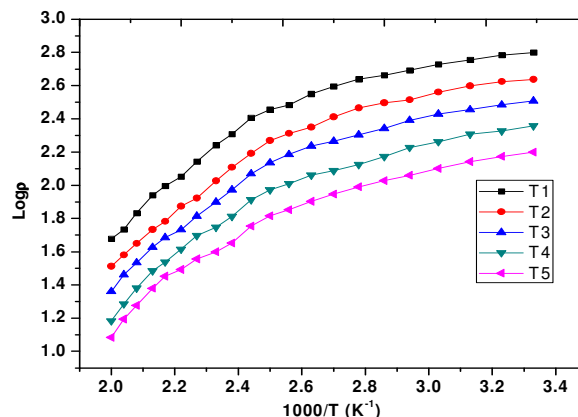
shows an Arrhenius behavior consisting of high and low temperature regions. The activation energies of electrical conduction have been determined from these plots in both the regions and are listed in table 2. It is found that the activation energy is thickness dependent and decreases with increase in thickness. This can be explained due to the polycrystalline nature of the films as explained by Seto's model[14]. The polycrystalline film material contains large number micro crystallites with grain boundaries between them. At the grain boundaries the incomplete atomic bondages can act as trap centers. These trap centers traps the charge carriers at the grain boundaries and hence a space charge impedes the transit of charge carriers from on crystallite to the other[15].

The carrier density at room temperature was determined for all samples. The variation of carrier density with composition for chemically deposited PbSe thin films is shown in figure 4. The carrier density is found to be of the order of 10^{18} cm^{-3}. The carrier density is increased with increase in thickness. The smaller carrier density is characteristic of the compensation type semiconductor involving deep donor or deep acceptors[16]. The Carrier mobility has been calculated using the standard relation,

$$\mu = \frac{\sigma}{ne} \qquad (6)$$

where μ is the electron mobility, σ is the electrical conductivity, n is the carrier density. The electron mobility is found to be a function of thickness. The calculated values of electron mobility at room temperature are listed in table 2.

The type of conductivity exhibited by chemical bath deposited PbSe thin films is determined by thermoelectric power (TEP) measurement the TEP depends on the location

of fermi energy level in the material and the type of scattering mechanism[17]. From the sign of the terminal connected towards hot end it can be deduced the sign of the predominant charge carriers. In our case the hot end is connected to the positive terminal, the film shows n-type conductivity. The vacancies and interstitials control the conductivity type, an excess of Pb causes n-type conductivity[18-19].
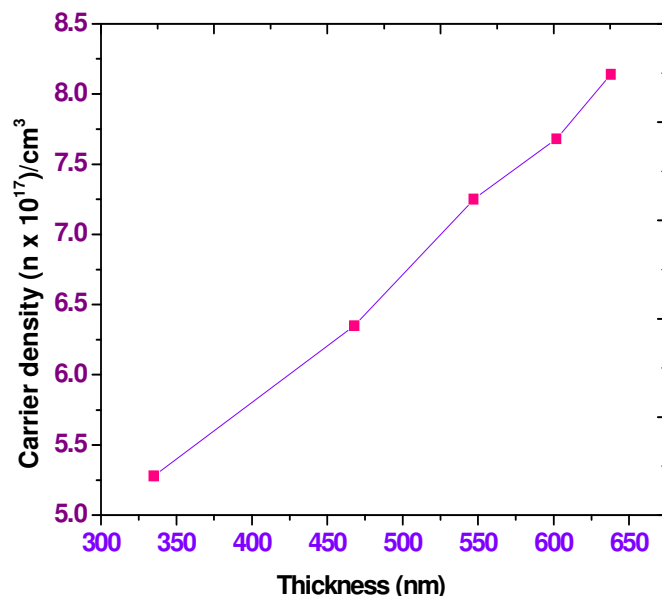

Figure-4
The variation of carrier density with thickness

Table-2
Electrical parameters of PbSe thin films

Sample code	Electrical Resistivity $(\Omega\text{-cm})^{-1}$	Barrier height Φ_b (eV)	Activation energy (eV)		Carrier Density $n \times 10^{18}/cm^3$	Mobility $\mu \times 10^{-3}$
			HT	LT		
T1	6.35×10^2	0.424	0.312	0.204	5.28	1.86
T2	4.24×10^2	0.387	0.301	0.192	6.35	2.32
T3	3.21×10^2	0.369	0.288	0.184	7.25	2.69
T4	2.05×10^2	0.352	0.268	0.179	7.68	3.97
T5	1.62×10^2	0.343	0.256	0.173	8.15	4.73

Conclusion

Lead selenide films were prepared by chemical bath deposition technique on glass substrates. Effect of thickness on the structural, optical and electrical properties of the films was systematically investigated. The X-ray diffraction studies revealed that all films had FCC crystal structure with a strong (200) preferred orientation. Optical studies indicated that the band gap decreased with increasing thickness of the films. The band gap decreased from 0.33 eV to 0.25 eV. The electrical resistance was found to be of the order of 10^2 Ω-cm. The carrier density is found to be of the order of 10^{18} cm^{-3}. Thermoelectric power (TEP) measurement showed n-type conductivity.

Acknowledgements

References

1. Yu.I. Ravich, Effimova B.A. and Smirnov I.A., Semiconducting Lead Chalcogenides, Plenum Press, New York (**1970**)

2. Zemel J.N., *Solid State Surf. Sci.*, **1,** 291 (**1969**)

3. Proc., IEEE, **63** (1) **(1975)**

4. Hesse J. and Prier H., Festkorperprobleme, **15,** 229 (**1975**)

5. Zogg H., Fach A., John J., Masek J., Muller P., Paglino C. and Buttler W., *Opt. Eng*., **33,** 1440 (**1994**)

6. Preier H., *Appl. Phys.,* **20,** 189 (**1979**)

7. Chaudhuri T.K., *Int. J. Eng. Res.,* **16,** 481 (**1992**)

8. Zemel J.N., Scott C.G. and Reed C.E. (Eds.), Surface Physics of Phosphors and Semiconductors, Academic Press, London, 523 **(1975)**

9. Barote M.A., Ingale B.D., Surywanshi R.V., Chavan T.V. and Masumdar E.U., *Res. J. Chem. Sci.,* **1(5**), 48 (**2011**)

10. Rubin K.A. and Chen M., Thin Solid Films, **181,** 1149 (**1989**)

11. Tong X.L., Jiang D.S., Hu W.B., Liu Z.M. and Luo M.Z., *Appl. Phys*., **A 84,** 143 (**2006**)

12. Fallah H.R., Ghasemi M., Hassanzadeh A. and Steki H., *Mater. Res. Bull*., **42,** 487 (**2007**)

13. Zingaro R.A. and Slolvin D.O., *J. Electrochem. Soc*., **1** 42 (**1961**)

14. W. Seto J.Y., *J. Appl. Phys*., **46,** 547 (**1975**)

15. Shahane G.S. and Deshmukh L.P., *Mater. Chem. Phys*., **70,** 112 (**2001**)

16. Rakhshani A.E., *Phys. Staus. Solidi*, **A 169,** 85 (**1998**)

17. Yadav A.A., Barote M.A. and Masumdar E.U., *Solid State Sciences*, **121,** 1173 (**2010**)

18. Saloniemi H., Academic Dissertation, VTT Pub., **423,** p-32 (**2000**)

19. Karande V.S., Mane S.H., Pujari V.B. and Deshmukh L.P., *Turk J. Phys*., **25,** 539 (**2003**)

20. Yadav A.A., Barote M.A. and Masumdar E.U., *Mater. Chem. Phys*., **121,** 53 (**2010**)

21. Rao C.N.R., Modern Aspect of Solid State Chemistry, Plenum, New York, **531, (1973)**