Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **1(9),** 37-41, Dec. **(2011)** *Res.J.Chem.Sci.*

Some Studies on Chemically Deposited n-PbSe Thin Films

Barote Maqbul A.[1], Ingale Babasaheb D.[1], Tingre Govind D.[1], Yadav Abhijit A.[2], Surywanshi Rangrao V.[1], 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, Maharashtra, INDIA

Available online at: www.isca.in
(Received 19th August 2011, revised 13th September 2011, accepted 12th October 2011)

Abstract

Thin films of PbSe of various thicknesses have been deposited onto ultrasonically clean glass substrates using simple chemical bath deposition technique. Structural investigations on these showed polycrystalline nature of the films with the presence of cubic phases. Grain size increased with increase in thickness of the film sample. Compositional analysis revealed that films are sulphur deficient. Optical absorption studies indicated a decrease of energy band gap as thickness of film increased. The electrical conductivity and thermoelectric power (TEP) measurements have been carried out in 300-500 K temperature range. The activation energy is found to be thickness dependant. TEP measurement showed n-type conduction mechanism.

Keywords: PbSe thin films, chemical bath deposition, structural characterization, optical properties.

Introduction

Lead chalcogenides are one of the basic and potential materials for modern infrared optoelectronics due to narrow band gap and high carrier motilities[1]. Lead chalcogenides have been used as sensors for infrared radiations, phototransistors, lasers, solar cells, optoelectronic devices and thermoelectric devices[2-4]. Thermoelectric devices have been used in broad areas such as refrigerators and in cooling units for fiber junctions in optical fiber communication technology[5]. The laser diodes based on lead chalcogenides are considered to be mainly utilized to an advanced measurement system for detecting hydrocarbon pollutants in atmosphere, trace gas analysis and optical fiber communication over long distances[6-7].

In recent years, there have appeared several manuscripts on IV-VI compounds by different methods such as vacuum deposition[8], electrodeposition[9], sono-chemistry[10] and chemical bath deposition (CBD)[11]. However, only few manuscripts on preparation of p-PbSe thin films by chemical bath deposition can be found, despite being one of the most common methods used for the deposition of IV-VI compound semiconductor thin films. The chemical bath deposition is on of the most convenient, reliable, simple and inexpensive methods. It is useful for large area industrial applications. This technique offers many advantages over the more established vapor phase routes, such as CVD, MBE and spray pyrolysis. Another advantage of CBD method with respect to other methods is that the films can be deposited on different kinds, shapes and sizes of substrates[12-13].

In the present investigation, we describe the deposition of n-PbSe films from alkaline medium using lead sulphate, sodium selenosulphate and triethanolamine (TEA) as a complexing agent. The preparative parameters are optimized in order to obtain good quality thin films and a growth mechanism is described. These thin films are characterized to study the structural, compositional, optical and electrical properties.

Material and Methods

Thin film 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 film thickness of the 'as-deposited' samples was measured by a gravimetric weight difference method. The thin films of PbSe were characterized for structural, morphological, optical and electrical

properties. X-ray diffraction (XRD) pattern of the film were recorded on a Philips PW-3710, X-ray diffractometer in the scanning range 10-80^0 using Cuk$_\alpha$ radiation with wavelength 1.5406 Å. The surface morphology and compositional analysis was studied by scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDAX) using JEOL-JSM-5600. To study the optical characteristics of the film, absorbance spectra was recorded in the wavelength range 2500-5000 nm by means of spectrophotometer (Model NEXUS-670), at room temperature. The resistivity measurements were done by using DC two point probe method in the temperature range 300-500 K.

Results and Discussion

Growth mechanism: The PbSe thin films were obtained from an aqueous alkaline bath containing Pb^{2+} and Se^{2-} ions. The deposition process based on slow release of Pb^{2+} and Se^{2-} ions in the solution. The concentration of lead and selenium ions has to be controlled very carefully during the film growth[14]. This is commonly achieved by using a high stability complexant and a moderately stable selenium source[15]. For deposition of lead selenide, Pb^{2+} ions, complexed with TEA, allowed to react with Se^{2-} ions, made available by decomposition of sodium selenosulphate. The mechanism of film formation can be understood from the following reactions:

$$[Pb(TEA)_n] \xrightarrow{85^0C} Pb^{2+} + n(TEA) \quad (1)$$

$$Na_2SeSO_3 + 2OH^- \xrightarrow{85^0C} Na_2SO_4 + Se^{2-} + H_2O \quad (2)$$

$$Pb^{2+} + Se^{2-} \xrightarrow{85^0C} PbSe \quad (3)$$

The deposition time was varied between 30 min. to 90 min. figure 1 shows the variation of film thickness with deposition time. Initially, PbSe film thickness was increased linearly up to 70 min. and slightly decreased for further deposition time. The maximum thickness of the PbSe film was found to be 335 nm and further film was powdery and film thickness decreased due to dissolution of film in the solution[16]. The thickness of the film is increased by retreating the samples, each time to fresh quantities of the olutions. The film thickness is tabulated in table 1.

Structural and morphological characterization: The XRD pattern of 'as-deposited' PbSe thin films on glass substrate is shown in Figure 2. The XRD analysis reveals that the obtained films are polycrystalline with face centered cubic structures. (JCPDS Data card no. 06-0354). PbSe thin films show prominent (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (4 2 0) peaks. The lattice parameter and hkl planes are in fairly good agreement with the standard values. The average grain size of the material was determined by using Scherrer's equation

$$D = \frac{0.94\,\lambda}{\beta \mathrm{Cos}\,\theta} \quad (4)$$

where λ is the wavelength of X-ray used, β is the peak width at half maximum in radian, θ is the Bragg's diffraction angle. The average grain size was found to be in the range 10.2-17.6 nm as thickness increased from 335 nm to 638 nm.

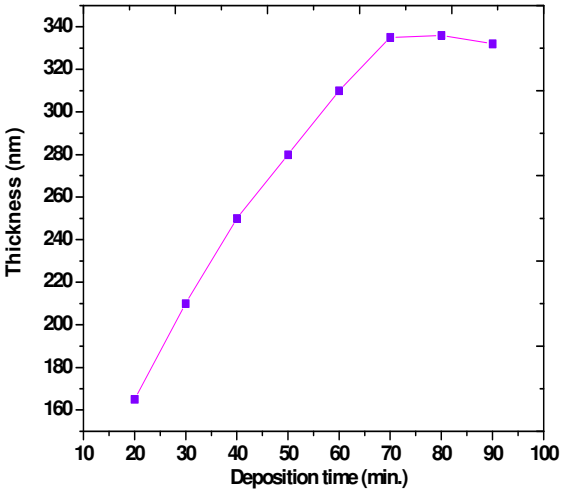


Figure-1
Variation of film thickness with deposition time

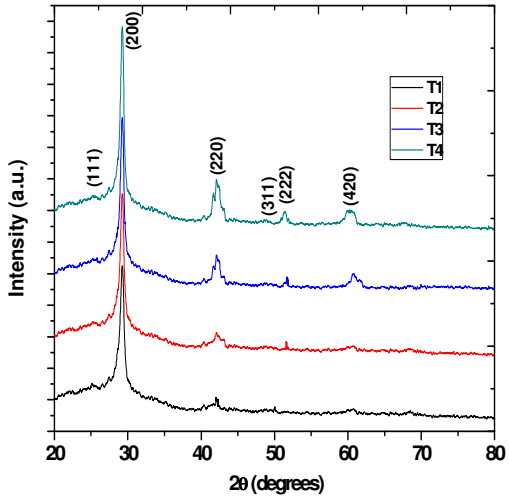
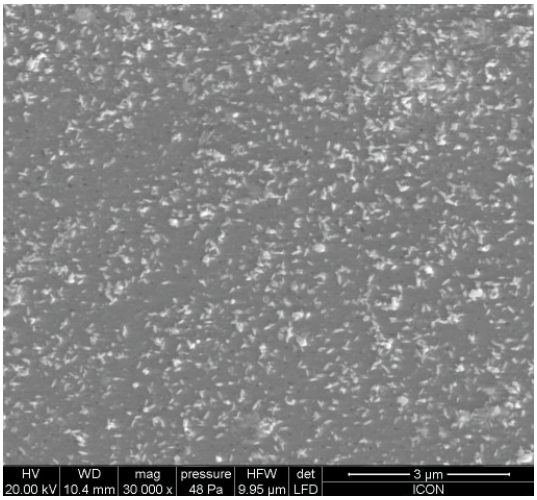
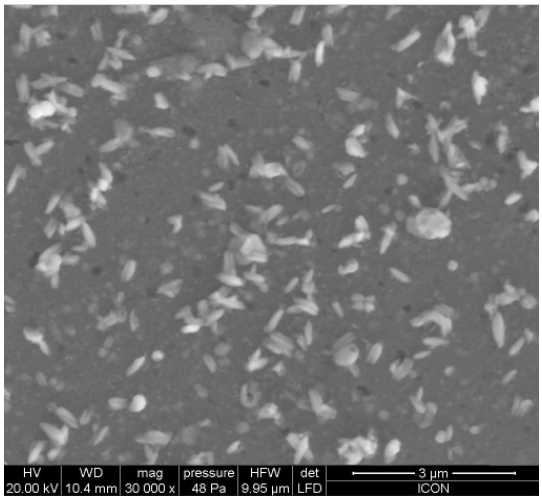


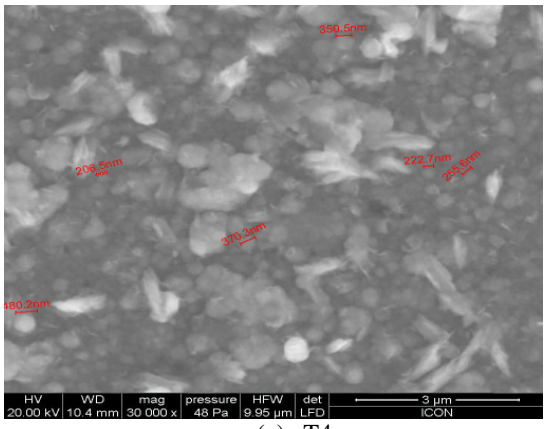
Figure-2
XRD pattern of 'as-deposited' PbSe thin films of various thicknesses



(a) T1



(b) T3



(c) T4

Figure- 3(a-c)
SEM micrographs of chemically deposited PbSe thin films of various thicknesses

The surface morphology of PbSe thin films was analyzed by SEM technique. SEM micrographs of 'as-deposited' films are shown in Figure 3. It is observed that PbSe thin films are homogeneous, without crack and it well covers the glass substrate. Form the micrographs it is clear that film composed of minute grains and grain size increases with increase in thickness. The presence of fine background is an indication of one step growth by multiple nucleations. The average grain size of PbSe films is given in Table 1. The compositional analysis using EDAX gave result as 55.99 % of Pb and 44.01 % Se, indicating that films are Pb rich (shown in Figure 4)

Optical properties: The absorption spectrum of 'as-deposited' film has been recorded with the help of FTIR spectrophotometer at room temperature without considering losses due to reflection and transmission. The absorption spectrum was used to calculate absorption coefficient (α). The absorption coefficient was found to be of the order of 10^4 cm^{-1}. The band gap energy and transition type was derived from mathematical treatment of the data obtained from the optical absorbance versus wavelength with the following relationship for near-edge absorption[17]

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \quad (5)$$

where 'A' is an energy-independent constant, 'E_g' is optical band gap of the material, 'α' is the coefficient of absorption and the exponent 'n' depends upon the type of transition. The values of 'n' for direct allowed, indirect allowed, forbidden direct or forbidden indirect transitions are n = 1/2, 2, 3/2 or 3 respectively. For allowed direct type of transitions Eq. (1) can be written as

$$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2} \quad (6)$$

Figure 5 shows the plot of $(\alpha h\nu)^2$ as a function of hν. The band gap energy (E_g) was determined from the plot of $(\alpha h\nu)^2$ versus hν by extrapolating the straight to the energy axis whose intercept to the X-axis gives the optical band gap. The linear nature of plot indicates the existence of the direct transition. It is observed that band gap energy is decreased as thickness of PbSe film is increased which agrees with earlier report[18]. The band gap values are listed in table 1.

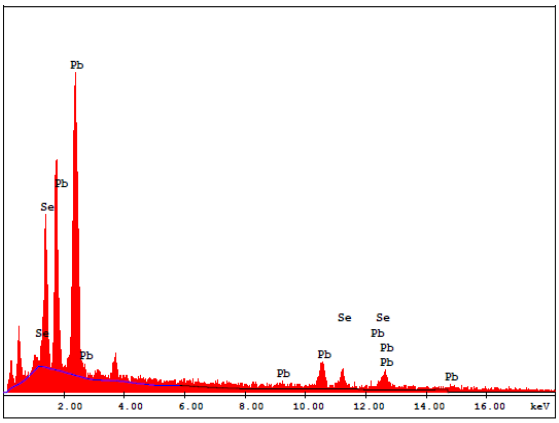


Figure- 4
EDAX pattern of PbSe thin films

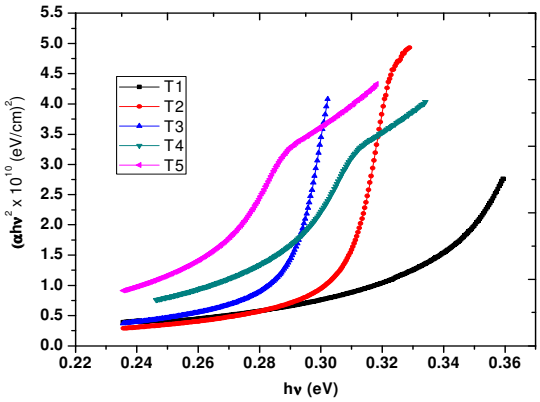


Figure-5
Plot of $(\alpha h\nu)^2$ Vs hν for PbSe thin films of various thicknesses

Electrical properties: The dark dc electrical resistivity of 'as-deposited' PbSe film samples was measured using dc two point probe method, in the temperature range 300-500 K. The electrical resistance was found to be a function of temperature. The electrical resistance was found to be of the order of 10^3 Ω-cm. A plot of inverse absolute temperature versus log (conductivity) is shown in Figure 6. An increase in magnitude of conductivity with increase in temperature confirms that PbSe thin films are semiconducting in nature. The linear variation of conductivity It is observed that the electrical conductivity increases with increase in temperature indicating that the film samples are semiconducting. The values of electrical conductivity with varying thicknesses for all the samples are given in table 1. In order to calculate the activation energy of 'as-deposited' film samples, the electrical conductivity results which are shown in Figure 6, were used. The thermal activation energies (E_a) were calculated by Arrehenious equation given by[19]

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (6)$$

where E_a is the activation energy of an electrical conduction process and other terms have their usual significance. From Fig. 6 the variation indicated two distinct temperature zones with two characteristic regions. The first region from room temperature up to 380 K is identified with low temperature region. This region is identified with the extrinsic conductivity of semiconductor due to the ionization of impurity atoms. The second region from 380 up to 500 K is identified with the transition to intrinsic conduction in semiconductor[20]. The E_a is found to be in the range between 0.204 eV to 0.173 eV in the low temperature region and 0.312 eV to 0.256 eV in the high temperature region. The activation energy results of 'as-deposited' film samples are given in Table 1.

Figure-6
Variation of log (conductivity) with inverse temperature for PbSe thin films

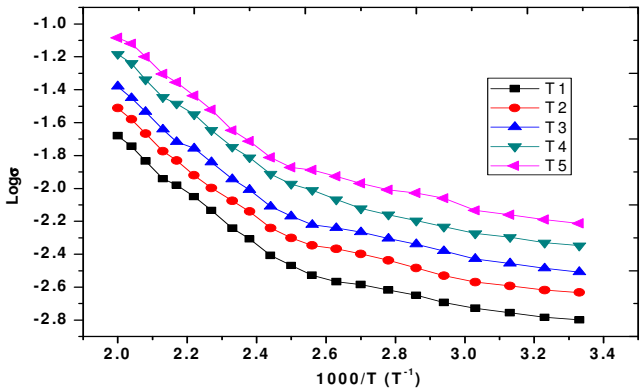


Table-1
Some important parameters of chemically deposited PbSe thin films of various thicknesses

Sample code	Thickness (nm)	Energy band gap Eg (eV)	Grain Size (nm)		Electrical conductivity $(\Omega\text{-cm})^{-1}$	Activation energy (eV)		Barrier height Φ_b (eV)
			XRD	SEM		HT	LT	
T1	335	0.33	10	150	1.57×10^{-4}	0.312	0.204	0.424
T2	468	0.31	13	210	2.36×10^{-4}	0.301	0.192	0.387
T3	547	0.28	15	280	3.12×10^{-4}	0.288	0.184	0.369
T4	602	0.27	17	315	4.88×10^{-4}	0.268	0.179	0.352
T5	638	0.25	18	350	6.17×10^{-4}	0.256	0.173	0.343

In thermoelectric power measurements, the open circuit thermo-voltage generated by the sample, when a temperature gradient is applied across a length of the sample, was measured using a digital micro-voltmeter. The temperature difference between the two ends of the sample causes transport of carriers from the hot to the cold end, thus causing creating an electric field, which gives rise to thermo-voltage across the ends. From the sign of the potentiometer terminal connected at the cold end, we can deduce the sign of predominant charge carriers. In the present study, the negative terminal was connected to the cold end, hence the sample exhibit n-type conductivity[21].

Conclusions

n-PbSe thin films can be deposited by simple and economical chemical bath method. XRD studies reveals PbSe exhibit in cubic crystal structure. Optical analysis showed direct band to band type transition and band gap was found to vary from 0.33 eV to 0.25 eV. The resistivity of the PbSe film samples is found to be of the order of 10^3 Ω-cm. TEP measurements of the sample showed n-type conduction mechanism.

Acknowledgements

One of the authors Mr. M. A. Barote is grateful to the University Grants Commission, New Delhi (West Regional Office, Pune), India for the financial assistance through the Minor Research Project No. F.47-1201/2009.

References

1. Samoylov A.M., Sharov M.K., Buchnev S.A., Khoviev A.M., and Dolgopolova E.A., *J. Cryst. Growth,* **240,** 340 (**2002**)

2. Chatterjee S., and Pal U., *Opt. Eng*., **32,** 2923 (**1993**)

3. Meca F.J., Quintas M.M., and Sanchez F.J.R., *Sensors actuators*, **84,** 45 (**2000**)

4. Dashevsky Z., Shusterman S., and Dariel M.P., *J. Appl. Phys*., **92,** 1425 (**2002**)

5. Story T., Acta *Phys. Polym*., **A 92,** 663 (**1997**)

6. Lambrecht A., Kurbel R., and Agne M., *Mater. Sci. Eng*., **21,** 217 (**1993**)

7. Agne M., Lambercht A., Schiessl U., and Tacke M., *Infrared Phys. Technol*., **35,** 47 (**1994**)

8. Das V.D., and Bhat K.S., *J. Mater. Sci*., **7,** 169 (**1990**)

9. Molin N., and Dikuskar A.I., *Thin Solid Films,* **265,** 3 (**1995**)

10. Li B., Xie Y., Huang J., and Quain Y.T., Ultrason, Sonochem., **6,** (**1999**) 217

11. Schmidt, Chem. Rev. **72,** 1709 (**1992**)

12. Barote M.A., Yadav A.A., and Masumdar E.U., *J. Non-Oxide Glasses*, **2,** 151 (**2010**)

13. Kale R.B., and Lokhande C.D., *Appl. Surf. Sci*., **252,** 929 (**2005**)

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

15. Mulik N., Rotti C.B., More B.M., Sutrave D.S., Shahane G.S., Garadkar K.M., Deshmukh L.P., and Hankare P.P., Ind. *J. Pure Appl. Phys*., **34,** 903 (**1996**)

16. Gadve K.M., and Lokhande C.D., *Thin Solid Films*, **229,** 27 (**1993**)

17. Barote M.A., Yadav A.A., and Masumdar, E.U., *Physica,* **B 406,** 1865 (**2011**)

18. Prabhakar S., Suryanarayana N., Rajasekar K., and Sikanth S., *Chal. Lett*., **6,** 203 (**2009**)

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, **1970**, pp-**531**