Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **1(5),** 48-51, Aug. **(2011)** *Res.J.Chem.Sci.*

Growth and Characterization of Chemical bath Deposited Polycrystalline n-PbSe thin films

Maqbul A. Barote[1], Babasaheb D. Ingale[1], Rangrao V. Suryawanshi[1], Tanaji v. Chavan[2], Elahipasha U[2] Masumdar[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

Available online at: www.isca.in
(Received 2nd July 2011, revised 7th July 2011, accepted 8th Augest 2011)

Abstract

Lead selenide thin films have been deposited using simple chemical bath deposition technique on amorphous glass substrate at 85^{0}C temperature. The lead sulphate and sodium selenosulphate are used as source of materials to obtain lead selenide films. The 'as-deposited' films were uniform, well adherent and dark brown in color. The films were characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), optical absorption, and electrical conductivity measurement techniques. The XRD study confirms polycrystalline nature in FCC structure. The absorption spectrum showed an exponential edge. Lead selenide films showed an optical band gap of 0.325 eV with absorption coefficient 10^4 cm^{-1}. The room temperature electrical conductivity was of the order of 10^{-3} (Ω-cm)$^{-1}$. The film exhibits n-type conductivity with activation energy of 0.153 eV.

Keywords: Chemical deposition, semiconductors, thin films, X-ray diffraction, scanning electron microscopy.

Introduction

During the last few years, a variety of binary semiconductors especially IV-VI groups of periodic table have been attracting due to their small energy gap and potential applications in solar cells. The IV-VI semiconductors have been bound to be quite useful in optoelectronic devices working in far IR region as thermoelectric transducers and solar cells[1-2]. Among these, lead chalcogenides have been the subject of considerable interest in research due to their technological importance in crystalline and polycrystalline forms as infrared radiation detectors, infrared emitters and solar control coatings[3-5], photoconductive absorbers[6], and analyzers[7]. These materials can be obtained in thin film form by various methods, including chemical bath deposition[8], vacuum deposition[9], electrodeposition[10], sono-chemistry[11] and microwave heating[12]. The chemical bath deposition is simple, economical and convenient for large area deposition of IV-VI compounds.

In this communication, an attempt is made to deposit PbSe thin films using precursors in homogenous phase at 85^{0}C. The various aspects of thin films like growth mechanism, characterization and its properties are discussed.

Material and Methods

Chemical bath deposition of PbSe thin films: The films of lead selenide were deposited onto ultrasonically cleaned glass substrates using AR grade chemicals. For the deposition 10 ml (0.33 M) lead sulphate, 4 ml triethanolamine (TEA) were taken in 250 ml beaker and sufficient amount of aqueous ammonia was added to get the clear solution. Finally 10 ml (0.33 M) sodium selenosulphate solution and sufficient quantity of double distilled water was added 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 constant speed in the reaction mixture to achieve uniform and continuous stirring of the reaction mixture. To obtain good quality deposits, the time and temperature of the deposition and speed of the substrate rotation were optimized. These parameters were selected as 70 min., 85 ^{0}C and 60 ± 2 rpm, respectively.

Characterization technique: The film thickness of the 'as-deposited' samples was measured by gravimetric weight difference method. The films of PbSe were characterized for structural, morphological, optical and electrical properties. The X-ray diffraction was recorded on Philips PW-1710 X-ray diffractometer (XRD) with C_uk_α radiation (λ = 1.5406 Å) in 2θ range from 10^0 to 80^0. The surface morphology and compositional analysis was studied with scanning electron microscopy (SEM) with JEOL-JSM-5600. The optical absorption spectra of films were recorded with spectrometer (Model NEXUS 670) at room temperature in the wavelength range from 2500-5000 nm.

Results and discussion

Growth kinetics: The lead selenide films were obtained from an aqueous alkaline bath containing Pb^{2+} and Se^{2-} ions. The rate of film growth is mostly dependent on the rate of release of Pb^{2+} ions from the complex state and the decomposition of sodium selenosulphate. For deposition of PbSe, Pb^{2+} ions complexed with TEA were allowed to react with Se^{2-} ions which were generated by decomposition of $Na_2S_2O_3$. The mechanism of film formation can be understood from the following reactions:

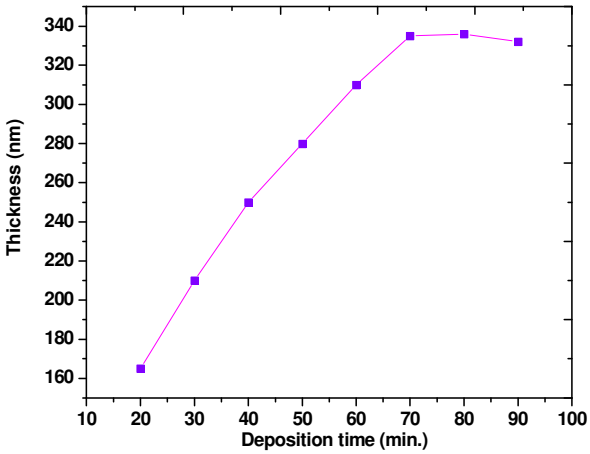
$$[Pb\ (TEA)_{n}] \xrightarrow{85^{0}C} Pb^{2+} + n\ (TEA) \quad (1)$$

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

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

The overall growth process occurs by ion-by-ion process. It is found that growth rate sensitively depends on temperature, pH of the reaction mixture, speed of substrate rotation, deposition time and initial concentration of ions. figure 1 shows a plot of thickness of the film versus time of deposition. The nature of plot indicates that film grow in two different phases firstly in quasi linear phase and second, saturation phase. The later is due to the depletion of the ions in reaction container.

Figure-1
A plot of thickness versus time for PbSe thin film



Structural properties: The XRD measurements were performed in order to investigate the structural properties of the 'as-deposited' PbSe thin films. The XRD spectrum is given in Fig. 2. The presence of several peaks in the XRD pattern revealed that 'as-deposited' film is polycrystalline in nature. The observed'd' values and respective prominent peaks corresponding to the reflection from (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2) and (4 2 0) planes coincides well with the standard JCPDS data[13]. The matching of the observed and standard'd'-values confirms that the deposited films are of PbSe with face centered cubic structure. The lattice parameter of cubic phase was calculated by using standard formula[14]. The calculated lattice parameter value 'a' for this sample is listed in Table 1. The crystallite size of PbSe thin films was calculated by using Scherrer's formula[15]. The average crystallite size was calculated by resolving the highest intense peak. It was found to be 10.2 nm. The micro strain was calculated by using formula

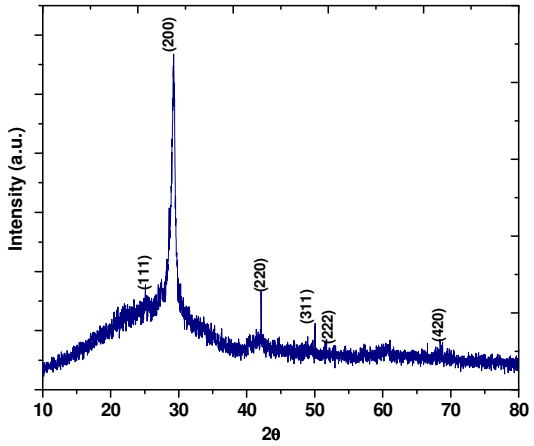
$$D = \frac{\beta \cos\theta}{4} \quad (4)$$

The micro strain was found to be 3.55×10^{-3}.

Table-1
Crystallographic parameters of chemically deposited PbSe thin film

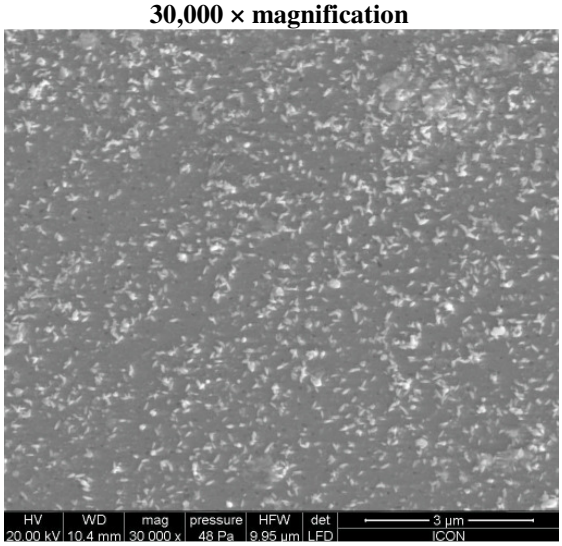
Compo.	d (Å) (standard)	d (Å) (observed)	(h k l) planes	Lattice constant (Å)
PbSe	3.5360	3.5220	1 1 1	6.0787
	3.0620	3.0538	2 0 0	
	2.1650	2.1536	2 2 0	
	1.8460	1.8184	3 1 1	
	1.7680	1.7538	2 2 2	
	1.3690	1.3566	4 2 0	

Figure-2
XRD pattern of 'as-deposited' PbSe thin film



Surface morphology: The morphological studies of the film have been carried out using SEM. The SEM micrograph of 'as-deposited' PbSe thin film at 30,000 ×magnification is shown in figure 3. The film shows smooth and uniform surface without cracks and pinholes. A compact polycrystalline texture composed of a single type of small, densely packed smaller crystallites grown over fine grained background were observed. The presence of fine grain background is an indication of one-step growth by multiple nucleations[16]. The average size of smaller grains was found to be around 150 nm.

Figure-3
The SEM micrograph of PbSe thin film at 30,000 × magnification

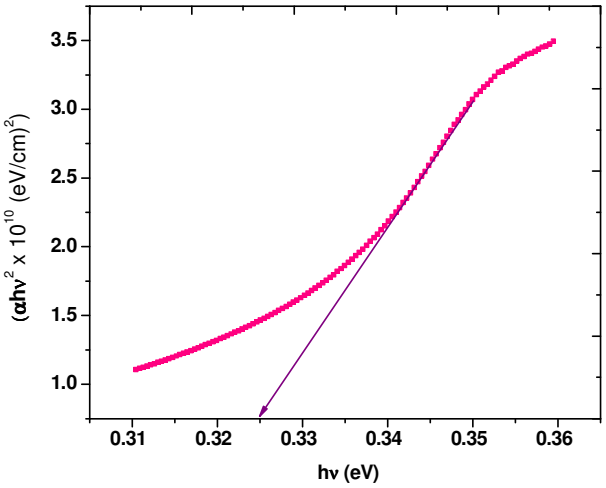


Optical properties: The optical absorption measurements were recorded in the range of 2500–5000 nm at room temperature without considering losses due to scattering and transmission. The optical band-gap and the nature of optical transitions can be obtained in dependence of absorption coefficient on photon energy. The absorption coefficient (α) and the incident photon energy (hν) is related by the following equation[17]

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

where α is absorption coefficient (cm^{-1}), hν the photon energy (eV), A and n are constants. A is complex parameter, which depends on temperature, photon energy etc. The n values are 0.5, 1.5, 2, and 3 for allowed direct, forbidden direct, allowed indirect and forbidden indirect transitions, respectively, E_g is the direct band gap energy. The optical band-gap of lead selenide film was estimated by plotting the variation of $(\alpha h\nu)^2$ versus hν and extrapolating the linear portion near the onset of absorption edge to the energy axis, which is plotted in figure 4. In the present case of PbSe thin film, the plot of $(\alpha h\nu)^2$ vs. hν (figure 4) show a linear portion indicating that the relation in equation (5) holds good for PbSe film if n = 0.5. This means that the optical transitions in the case of PbSe films are direct transitions. The linear portions of the curves were extrapolated to get the optical band gap (figure 4). The optical band gap for PbSe thin film is found to be 0.33 eV.

Figure-4
Variation of $(\alpha h\nu)^2$ versus hν for PbSe thin film

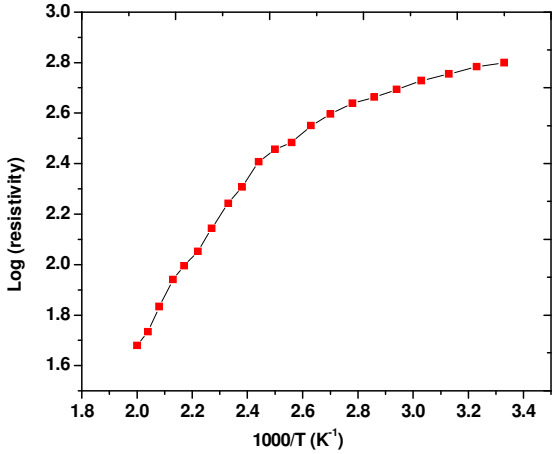


Electrical resistivity studies: The electrical resistivity of 'as-deposited' PbSe thin film sample was measured in the temperature range 300-500 K using a standard DC two point probe method under dark. A plot of inverse absolute temperature versus log (resistivity) is shown in figure 5. From figure 5 it is seen that the variation indicates two distinct temperature zones with two characteristic regions. It is observed that resistivity decreases with increase in temperature which is the indication of typical semiconductor characteristics. The room temperature electrical resistivity is found to be 6.35×10^2 Ω-cm. The activation energy of the chemical bath deposited PbSe film is calculated using the electrical resistivity result which is shown in figure 5. The value of activation energy (E_a) was calculated by equation given by[18]

$$\rho = \rho_o \exp\left(\frac{Ea}{kT}\right)$$

where ρ and ρ_o are electrical resistivity, k is Boltzmann constant and T is absolute temperature. The activation energy for low temperature region and high temperature region is found to be 0.204 eV and 0.312 eV respectively.

Figure-5
Variation of log (resistivity) vs 1/T for PbSe thin film



Thermoelectric power (TEP) measurements: The thermoelectric power is the ratio of thermally generated voltage to the temperature difference in the semiconductor, which gives the information about charge carriers in the deposited material. In thermoelectric power measurements, the open circuit thermo-voltage generated by film sample when a temperature gradient is applied across a length of a sample is measured. The type of conductivity exhibited by chemical bath deposited PbS thin film 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. These variations are found to be non-linear with n-type conduction. The non-linearity indicates non-degeneracy of the material whose thermoelectric power is proportional to n^{th} power of absolute temperature [18]. 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[19].

Conclusions

In summary, polycrystalline n-PbSe thin films have been synthesized by simple and economical chemical bath deposition technique. The structural studies indicate that the film sample is nanocrystalline in nature with cubic structure. The optical band gap of 'as-deposited' film was found to be 0.33 eV having direct band type transitions. The temperature dependence of the dc conductivity suggests that there are two types of conduction channels that contribute to the conductivity. The TEP measurement showed n-type conductivity.

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.

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