ISSN : 0974 - 7486 Volume 7 Issue 5

Materials Science

Trade Science Inc.

An Indian Journal

Full Paper

MSAIJ, 7(5), 2011 [325-330]

Structural, optical, morphological and electrical properties on PbSe bi-layer thin films

V.Arivazhagan, M.Manonmani Parvathi, S.Rajesh*

Thin Film Laboratory, Department of Physics, Karunya University, Coimbatore - 641 114, (INDIA)

E-mail: drsrajesh@karunya.edu

Received: 5th April, 2011 ; Accepted: 5th May, 2011

ABSTRACT

The bi-layer thin films of PbSe were prepared by successive coatings of Lead and Selenium layers by thermal evaporation technique. The temperature of the substrate was varied from low (0° C) to high (100°C) and its structural, optical and electrical properties were studied using XRD, UV and Hall measurement system respectively. X-ray analysis exhibits the polycrystalline nature of the prepared films with cubic structure. The relatively strongest intense peak corresponding to (2 0 0) plane for PbSe was investigated. The optical study reveals that the absorption edge starts with lower wavelength and indicates the formation and presence of PbSe nanoparticle at the interface of Lead and selenium layers. The calculated band gap values vary from 3.35 to 3.75 eV which is much larger than the bulk band gap value of PbSe material. The scanning electron microscopic images show the surface morphology of the Pb-Se bilayer films and the nano needle like structure was observed on low temperature substrate films. The carrier concentration and mobility of the films varied from $3.244X10^{11}$ cm^{-2} to $107X10^{11}$ cm^{-2} and $0.197X10^{1} cm^{2}/Vs$ to $23.17X10^{1}$cm2/Vs respectively. The sheet resistance of the films varied from 0.416 to $3.198X10^{2}\Omega$/sq and the resistivity also reported in this paper.

KEYWORDS

Pb-Se;
Bi-layer thin films;
Thermal evaporation;
Substrate temperatures.

INTRODUCTION

Thin films of semiconducting Nanocrystals are emerging as an important class of materials for electronic and optoelectronic devices such as field emission transistor, Photo detector, Thermal images, Light emitting diodes and Solar cells. Among the group IV-VI compounds, Lead Selenide (PbSe) thin films are used as a target material in infrared sensor grating, lenses and various optoelectronic devices[1-5]. Also the use of thin film polycrystalline semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices. There were interests to introduce PbSe compounds by many researchers. Many researchers reported that doping IV–VI semiconductors with variable values of elements results in appearance of a range of unusual effects that are not characterizing the undoped material[6]. Many of significant advances have taken place in the field of solid state science and technology in recent years due to the ability to prepare not only structurally and chemically pure crystals but also crystals with a controlled impurity. Lead Selenide has cubic crystal structure and a direct narrow band gap of 0.27 eV at room temperature. It does not require cooling but performs better at low temperature. Various methods are employed for depositing PbSe thin films such as Chemical vapour Deposition (CVD), Physical Vapour Deposition (PVD), Molecular Beam Epitaxial growth method etc. Among these methods Thermal evaporation is the most widely used technique for the deposition of metals, alloys and also for many compounds. In this present work, we report the effect of substrate temperature on the formation of PbSe bi-layers thin film prepared by thermal evaporation technique. The various characterizations such as structural, optical, morphological and electrical were employed and discussed.

EXPERIMENTAL

The Pb-Se bi-layer thin films were prepared by heating individual metal compound of Lead and Selenium powders. The well cleaned Silicon wafer (1 0 0), p-type and glass slide was used as the substrate. The initial compound of Lead and Selenium were placed in the Molybdenum boat (200A°) and evaporated by heating the source materials at the vacuum pressure of 10^{-6} torr. The temperature of the substrates says low (0°C), ambient (30°C) and elevated (100°C) were varied during the time of deposition. The thickness of the films is maintained at ≈500A° for Pb and ≈500A° for Se and was monitored by the Quartz Crystal thickness monitor. The constant rate of evaporation ranging 1-3A°/sec is maintained throughout the experiment. For preparing the films on low temperature substrate the cold finger was used in which the substrates were attached. The X-ray analysis of the films carried out using Shimadzu XRD-6000 X-ray Diffractometer (XRD). Here the PbSe films were exposed to Cu Kα source and the scattering angles was 10-90 degrees. The optical studies on the Pb-Se bi-layer films analyzed using UV-VIS spectrometer (Jasco-570 UV/VIS/ NIR Spectrophotometer) in the range of 200 to 2000 nm. The surface morphology and electrical characterization of the prepared films identified using the Scanning electron microscope (JSM 6390) and Hall measurement system (Ecopia HMS-3000) respectively.

RESULT AND DISCUSSION

Structural studies on Pb-Se bilayer thin films

X-ray diffraction technique was employed for studying the structural formation of the prepared Pb-Se bilayer films on Si (1 0 0) substrate. The XRD pattern of typical bi-layer films prepared at different substrate temperatures are shown in Figure 1. The prepared films oriented at (2 0 0) plane and confirms the formation of PbSe thin films. All the films exhibits the polycrystalline nature with cubic structure was also observed. The observed lattice spacing (d=6.212) values coincide with standard JCPDS (card no: 89-7105) for cubic structure. The films grown on low temperature substrate have comparatively good crystalline structure than those samples prepared at ambient and elevated temperature substrate.

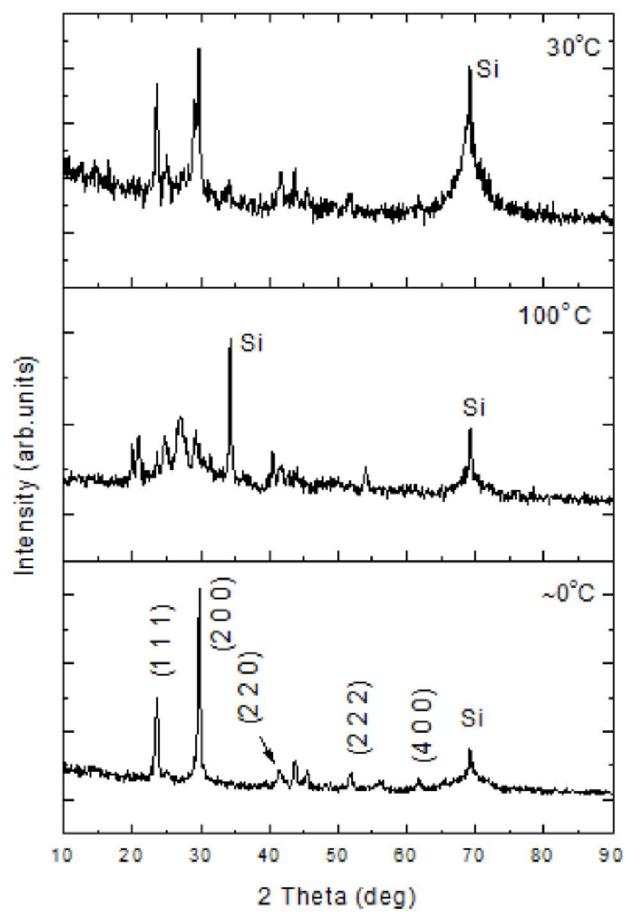

Figure 1 : XRD pattern of PbSe bi-layer film on Si substrate at different temperatures

The intensity of the films increased with decreasing the substrate temperature. M.Singh et al got the amorphous films of as deposited Zn-Se bilayer and the peaks arises when the prepared sample underwent the annealing treatment[7]. In our work we got the formation of PbSe peaks on as deposited films at room temperature substrate. The intensity of the peak corresponding to Si (1 0 0) wafer and PbSe on ambient temperature substrate is almost equal where as in low temperature substrate the PbSe peak orientated at (2 0 0) have the high intensity than the Si (1 0 0) substrate peak. This indicates that the improvement of crystallinity with deceasing substrate temperature. However the films prepared at elevated temperature substrate (100°C) not showing the well grown crystallinity of PbSe films. In this sample, the Si (1 0 0) substrate peak have the high intensity than the PbSe peak. This may happens due to the volatile nature of the Selenium which is deposited on Lead layer at the high (100°C) temperature substrate. The Crystalline size of the prepared films calculated using the Debye Scherre's formula given by[8],

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where λ is the wavelength of X-ray used (1.54 A°), β is the full width half maximum (FWHM) and 2θ is the angle between the incident and scattered X-rays. The dislocation density (δ) is defined as the length of dislocation lines per unit volume of the crystal and is given by,

$$\delta = \frac{1}{D^2} \quad (2)$$

Where D is the particle size. The origin of the strain is also related to the lattice misfit which in turn depend upon the deposition conditions. The micro strain (e) developed in the PbSe film is calculated from the relation,

$$\varepsilon = \frac{\beta \operatorname{Cos}\theta}{4} \quad (3)$$

where β is the full width half maximum of the peak. The lattice constant 'a' for cubic PbSe thin films was calculated using the formula,

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2} \quad (4)$$

Where h,k,l are the Miller indices of the lattice planes. The lattice spacing 'd' is calculated using Bragg relation,

$$d = \lambda / 2\sin\theta \quad (5)$$

All the equations (1-5) was used to study the structural parameters such as crystalline size, lattice constant, dislocation density and micro strain of the prepared PbSe thin films and tabulated in TABLE 1. From the TABLE 1, it is observed that the films prepared at room temperature have the grain size of 6 nm where as those sample prepared at high temperature and low temperature substrate have the grain size of 20 nm and 21 nm respectively. The increase in particle size on low temperature substrate will lead to the formation of good crystalline boundary at the interfaces of Lead and Selenium layers.

TABLE 1 : Structural parameters of PbSe bi-layer films at various substrate temperatures.

Substrate temperature	2θ (deg)	FWHM (A°)	Crystalline size (nm)	Lattice constant (a) A°	Dislocation density (ρ) X 10^{15} m^{-2}	Strain (ε) X10^{-3}
0°C	29.3935	1.32050	6	6.07	27	120
30°C	29.1837	0.40750	20	6.11	2.5	1.7
100°C	29.7414	0.38280	21	6.00	2.2	1.6

Surface morphology of Pb-Se bilayer films

The surface morphology of the Pb-Se bi-layer films on the formation of PbSe thin films were employed using scanning electron microscope and is illustrated in Figure 2. Inset shows the SEM images of different magnification of films. The films prepared at ambient temperature substrate have the little smooth surface than those films prepared at other substrate temperature. As discussed in XRD, the surface on elevated temperature films shows the surface profile of Si (1 0 0) wafer. Also the nano needle like structure was observed on low temperature substrate. X-ray analysis also shows the improved formation of PbSe films at low temperature on these films. This nano needle like structure formed because of the Brownian motion between the Lead and Selenium layers during the time of deposition and the also may be the vapour cooling condensation on the surface. The calculated grain size from the SEM image is high than the particle size from X-ray analysis and this is due to one grain contains many crystallite.

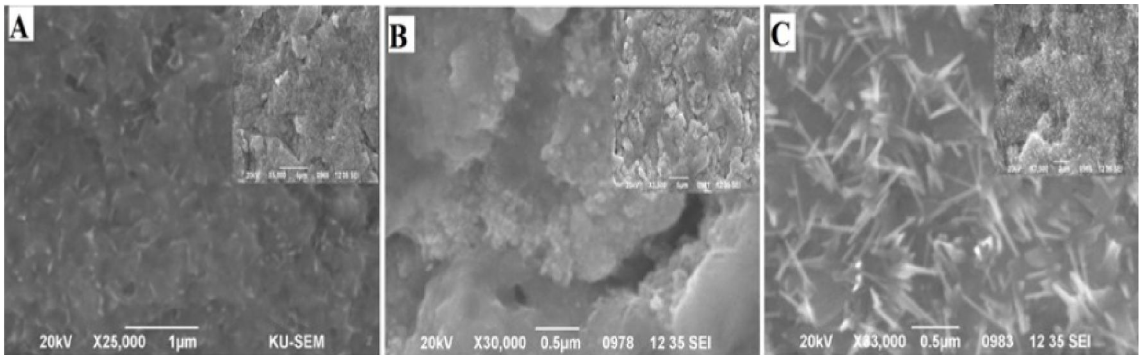

Figure 2 : SEM images of PbSe bi-layer at A) 30 °C B) 100°C and C) 0°C temperatures.

Optical studies on PbSe thin films

The optical studies of PbSe films deposited on glass substrate were employed using UV visible spectrometer in the range of 200-2500 nm (UV-vis-NIR). The optical absorption of the films shows that the edge starts with lower wavelength (blue region) and this indicates the presence of nanoparticle trapped at the interface of the Pb-Se bi-layer films. In addition, the deep raise and fall in transmittance spectra on low temperature shows the nanocrystalline effect of the films. The extinction coefficient can be calculated from the formula,

$$\mathbf{k} = \frac{\ln\left(\frac{1}{T}\right)\lambda}{4\pi\tau} \qquad (6)$$

Where 't' is the thickness of the deposited films. The absorption coefficient of the films can be calculated using the given ration,

$$\alpha = \frac{4\pi k}{\lambda} \qquad (7)$$

The nature of the transition can be investigated on the basis of the dependence of the absorption coefficient with the incident photon energy hυ. For direct and indirect allowed transitions, the theory of fundamental absorption leads to the following photon energy dependence near the absorption edge,

$$\alpha \propto (h\gamma - E_g)^m \qquad (8)$$

Where hυ and Eg are the photon and the band gap energy, respectively. In this relation, the values of m are 1/2 and 2 for direct allowed and indirect allowed transitions, respectively. Figure (3-5) shows the plot between $(\alpha h\nu)^2$ and hν for different temperature substrate. Extrapolation of the linear portion of the curve to $(\alpha h\nu)^2$ =0 gives the optical band gap value for the deposited film. The energy band gap value of 3.35 eV was calculated on the films prepared at ambient temperature substrate is shown in figure 3. The inset A and B in figure 3 shows the absorption and transmittance spectra respectively and the optically good transparency of 90% were observed. The bi-layer films prepared at elevated and low temperature substrate have the band gap value of 3.35 e V and 3.75 eV respectively (Figure 4, 5). The

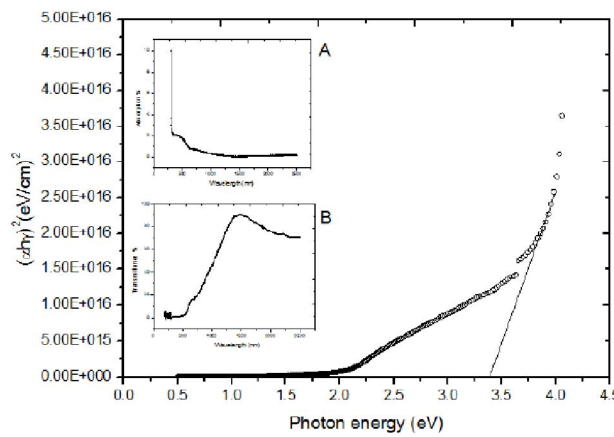

Figure 3 : Plot between hγ versus $(\alpha h\gamma)^2$. Inset A) absorption and B) Transmittance spectrum at ambient temperature substrate.

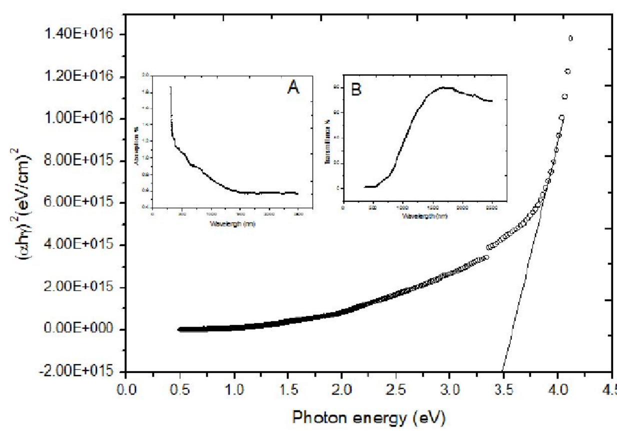

Figure 4 : Plot between hγ versus $(\alpha h\gamma)^2$. Inset A) absorption and B) Transmittance spectrum at elevated temperature substrate

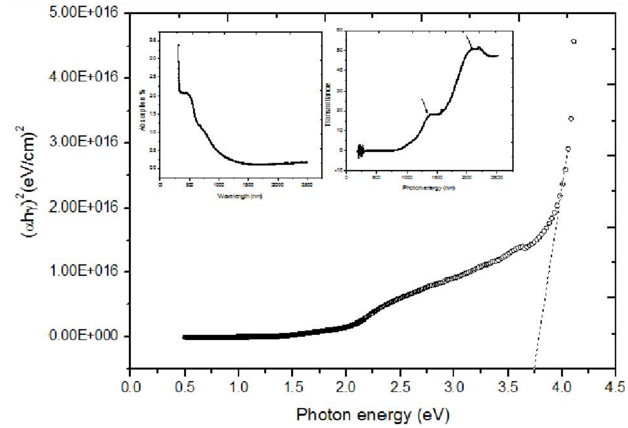

Figure 5 : Plot between hγ versus $(\alpha h\gamma)^2$. Inset A) absorption and B) Transmittance spectrum at low temperature substrate

two transmittance peak around at 1500 nm and 2250 nm indicates t the optically transparent at near IR region shown in figure 5 (inset B). The Inset A in figure 5 shows the absorption spectra of the films on low temperature substrate with steep line at absorption edge and this indicates the direct allowed transition of the prepared PbSe films. The calculated band gap values in this present work are much larger than the bulk values of PbSe material and already reported values[9,10].

Electrical studies

The electrical studies of the deposited films were carried out using the Hall measurement setup. The input current of 0.5μA and the magnetic field of 0.570 gauss were applied to study the electrical properties of the films. The p-type semiconducting natures of the deposited films are observed form the value of Hall coefficient with positive sign. The Figure 6 shows the electrical resistivity and the sheet resistance of the films at different temperature substrate.

It is observed that the sheet resistance was increased with increasing the substrate temperature. The similar effect was observed by J.H.Kim et al for films[11]. The maximum sheet resistance of 3.6×10^2 Ω/sq was observed at elevated temperature substrate. Low temperature and ambient temperature substrate have the values of 0.4×10^2 Ω/sq and 2.4×10^2 Ω/sq respectively. The electrical resistivity of the deposited films decreased from low to ambient substrate temperature and again increases with increasing the substrate temperature. The carrier concentration and mobility of the films as a function of substrate temperature are shown in Figure 7. The high carrier concentration value of 110×10^{11} cm^{-2} was observed on low temperature substrate where as the films prepared at ambient and elevated temperature substrate have the carrier concentration values of 4×10^{11} cm^{-2} and 7×10^{11} cm^{-2} respectively. The high carrier concentration on low temperature substrate is due to the un attached charge carriers freely moving due to Brownian motion. The high mobility of 230 cm^2/Vs was observed at ambient temperature substrate and is shown in figure. It is concluded that even though the electrical studies of the films prepared at ambient and elevated temperature have the better results than the low temperature prepared films, the nanocrystalline and orientation phase of PbSe films on low temperature films are found to be good from XRD, SEM and UV studies. The improved electrical properties on ambient and elevated temperature substrates are not fully the formation of PbSe but also the effect of Selenium and Si (1 0 0) substrate as described in X-ray diffractogram.

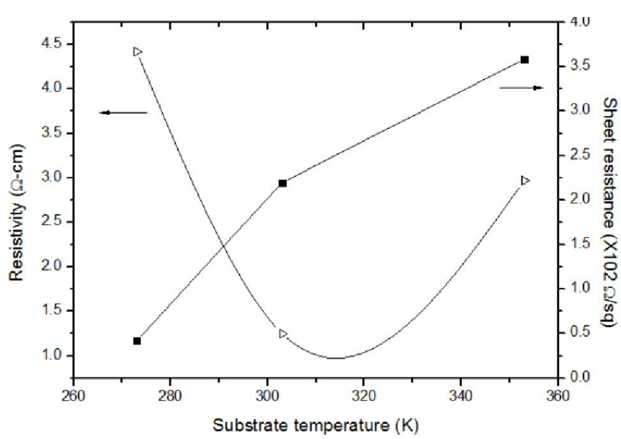

Figure 6 : Variation of electrical resistivity and sheet resistance of PbSe-bilayer with different temperature substrates.

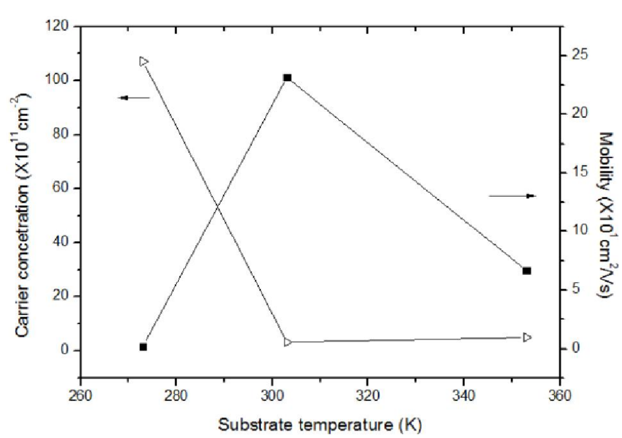

Figure 7 : Variation of carrier concentration and mobility of PbSe bi-layer at different temperature substrates

CONCLUSION

It is concluded that PbSe can be prepared by bi-layer structure of Pb and Se thin films. The formation of PbSe confirm by X-ray analysis with lattice constant (a=6.121A°) and preferred strong orientation peak at (2 0 0) plane. Also it is investigated that PbSe can perform better at low temperature substrate. The nanocrystalline effect of the films at Pb and Se interface was observed from the absorption and transmittance spectra. The nano needle like structures observed from SEM images shows the possibility to prove quantum confinement effect in the future work. The hall measurements on prepared films found to be p-type in nature.

REFERENCES

[1] I.Na.Chao, P.J.McCann, W.L.Yuan, S.Yuan; Thin Solid Films, 323, 126 **(1998)**.

[2] F.J.Meca, M.M.Quintas, F.J.R.Sanchez; Sensors Actuators, **84**, 45 **(2000)**.

[3] Z.Dashevsky, S.Shusterman, M.P.Dariel; J.Appl. Phys., **92**, 1425 **(2002)**.

[4] M.M.Ibrahim, S.A.Saleh, E.M.M.Ibrahim, A.M.Abdel Hakeem; J.Alloys Compd., **452**, 200 **(2008)**.

[5] M.M.Ibrahim, E.M.M.Ibrahim, S.A.Saleh, A.M.Abdel Hakeem; J.Alloys Compd., **429**, 19 **(2007)**.

[6] T.Story; Act.Phys.Polym.A, **94**, 189 **(1998)**.

[7] M.Singh, Y.K.Vijay; Appl.Surf.Sci., **239**, 79-86 **(2004)**.

[8] A.Guinier; X-ray Diffraction, San Francio, CA, **(1963)**.

[9] Shamshad A.Khan, Zishan H.Khan, A.A.El-Sebaii, F.M.Al-Marzouki, A.A.Al-Ghamdi; Physica B, **405**, 3384-3390 **(2010)**.

[10] E.A.Streltsov, S.K.Poznyak, N.P.Osipovich; J.Electroanal.Chem.Interfacial., **518**, 103-114 **(2002)**.

[11] R.J.Deokate, S.V.Salunkhe, G.L.Agawane, B.S.Pawar, S.M.Pawar, K.Y.Rajpure, A.V.Moholkar, J.H.Kim; J.Alloys Compd., **496**, 357-363 **(2010)**.