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COMPOSITIONAL AND ELECTRICAL RESISTIVITY STUDIES ON THERMAL EVAPORATION LEAD SELENIDE THIN FILMS

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Lead selenide films are prepared by the vacuum evaporation technique on clean glass substrates held at room temperature in a vacuum 10^{-6} torr. The thickness of the film is measured by employing quartz crystal monitor technique. EDAX analysis confirms the composition of constituent in the PbSe thin films. The electrical resistivity measurements as a function of temperature in the range 303 K - 483 K, mostly are performed using Four-Probe method. At temperature above 423 K, a sudden increase in resistivity is observed. Thermal activation energy is also calculated by varying the thickness of the films and no systematic variation of activation energy is observed.

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1. Introduction

Semiconducting thin films have been extensively studied for a long time due to their significant role in modern science and technology. Thin chalcogenide films are of particular interest for the fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensor, etc [1].Lead Chalcogenide thin films have number of applications in various opto-electronic devices [2]. Various methods employed for depositing PbSe thin films are electrochemical deposition [3, 4], chemical bath deposition [5, 6] molecular beam epitaxial growth method [7, 8] and vacuum evaporation method [9-16]. Among the various methods, vacuum evaporation method is the most widely used technique for the deposition of metals, alloys and also many compounds. This involves the evaporation for sublimation of the material in vacuum by thermal energy and allowing the vapor stream of the charge to condense on a substrate so as to form a continuous and adherent deposit of desired thickness. In a previous work we reported the structural, surface and optical studies of PbSe thin films [2].In this paper we present the results of our studies on compositional and resitivity measurements carried on PbSe thin films.

2. Experimental

PbSe thin films having different thicknesses are prepared by vacuum-evaporation method. Lead selenide with the purity of 99.99% is evaporated by resistive heating method. The powder form of PbSe is placed in a Molybdenum boat (200 amps) and is heated with high current by

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energizing transformer. The transformer capable of supplying 200 amps at 20 V is used to provide necessary current for heating the molybdenum source. Prior to evaporation, the evaporant material is carefully degassed at lower temperature for 30 minutes, with the shutter closed. The deposition of the material on the cleaned glass substrates under the pressure of 10^{-6} torr is achieved by slowly varying the current. A constant rate of evaporation ranging 1-3 Å /sec is maintained throughout the experiment. The adhesion of the films to substrates seems to be extremely good. For the preparation of hetero structure the deposited films are placed in the substrate holder with appropriate masks. The glass substrates for the film preparation are cleaned with sodium hydroxide (NaOH), with a detergent solution using a ultrasonic cleaner and finally, the substrates are cleaned with isopropyl alcohol and then heated in an oven for one hour at the temperature of 100˚C. The lateral dimensions of the films are 6 and 1 cm and the distance between the source and the substrate distance is 25 cm. The thicknesses of the films ranging 500, 1000 and 2000 Å are measured in situ using a quartz-crystal monitor. Energy dispersive x-ray analyzer confirms the composition of constituent in the PbSe thin films. The most commonly used technique in the semiconductor industry for measuring resistivity is the four point probe method. The arrangement consists of PID controlled oven (Model PID – 200, Scientific Equipment and Services, Roorkee, India) is combined to low current source, constant current source (Model LCS – 01) and digital micro voltmeter (Model DMV – 001).

3. Results and discussion

3.1 EDAX analysis of PbSe thin films

Fig. 1, Fig. 2 & Fig. 3, shows the energy dispersive X-ray spectrum of lead selenide thin films having thickness of 500 Å, 1000 Å and 2000 Å respectively.

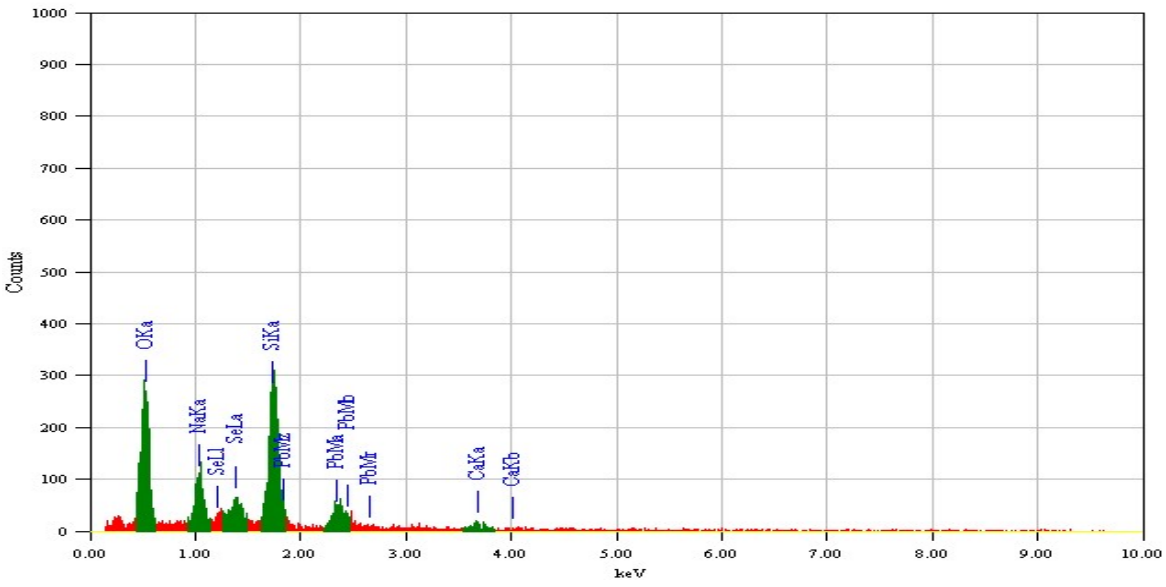

Fig. 1. EDAX spectrum of PbSe thin film of thickness 500 Å.

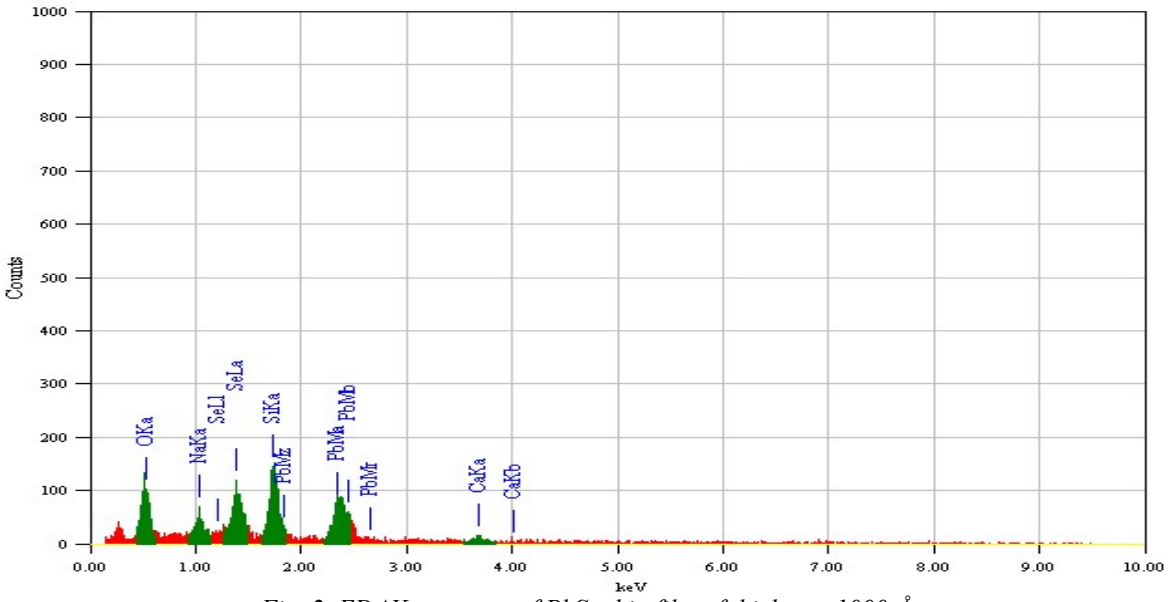

Fig. 2. EDAX spectrum of PbSe thin film of thickness 1000 Å.

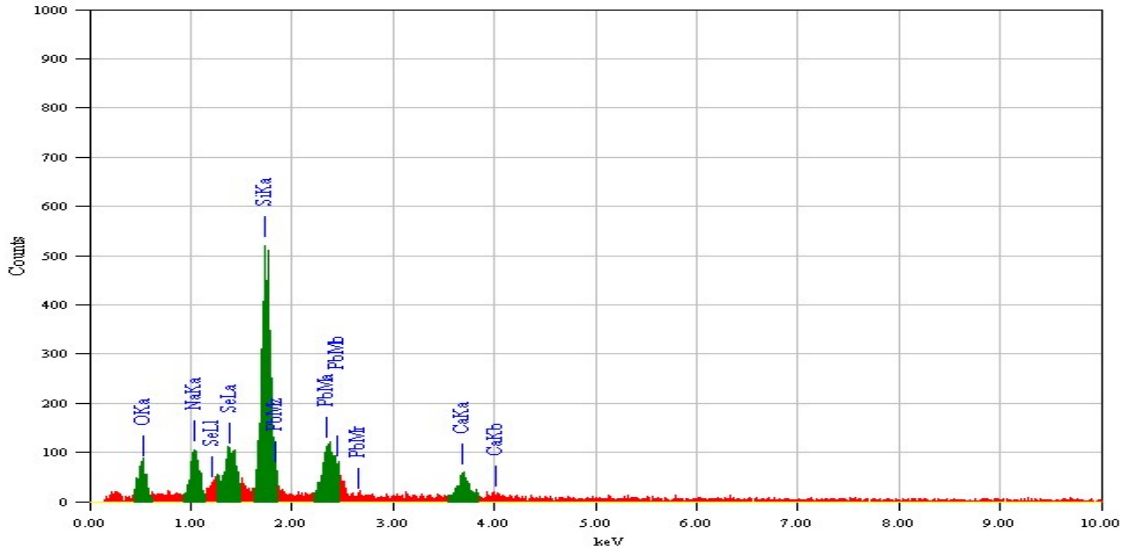

Fig. 3. EDAX spectrum of PbSe thin film of thickness 2000 Å.

The concentration is observed to be varying with film thickness, but systematic variation is not observed. The concentration of Pb and Se in 500 Å film is found to be 4.58% and 5.42% respectively which are shown in Fig.1. Increase in their concentration (Pb: 13.77%, Se: 16.97) is observed in film thickness 1000Å (Fig. 2). But on further increase in film thickness 2000Å, (Fig. 3) the concentration of constituent material elements is observed to be decreasing (Pb: 10.22%, Se: 9.58%) which requires further investigation. In the EDAX spectrum, some peaks corresponding to Si, Na and Ca are also observed. This can be attributed to the glass substrate used [17] since chalcogenide compounds including PbSe are highly sensitive to external ambient, O_2 peaks are also found in the spectra [13, 14].

3.2 Resistivity studies of PbSe thin films

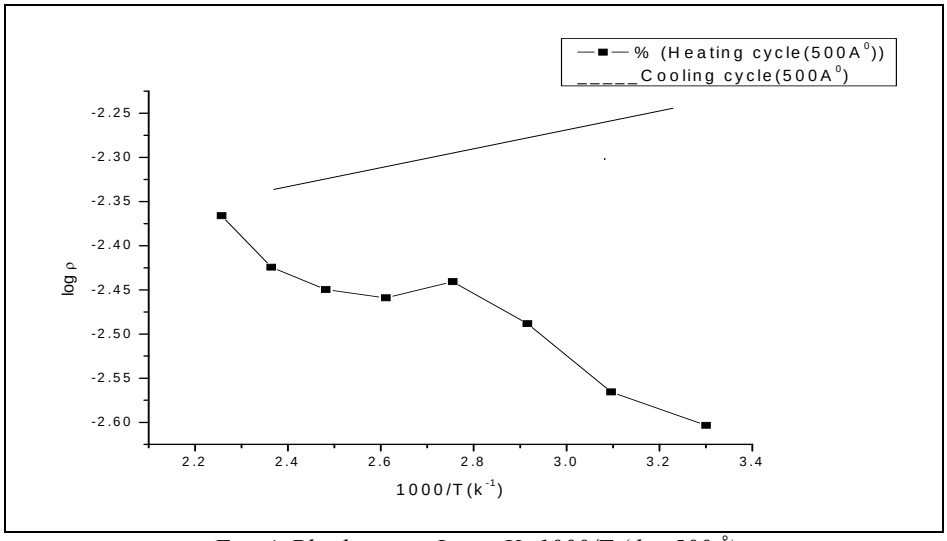

Fig. 4. Plot between Log ρ Vs 1000/T (d = 500Å)

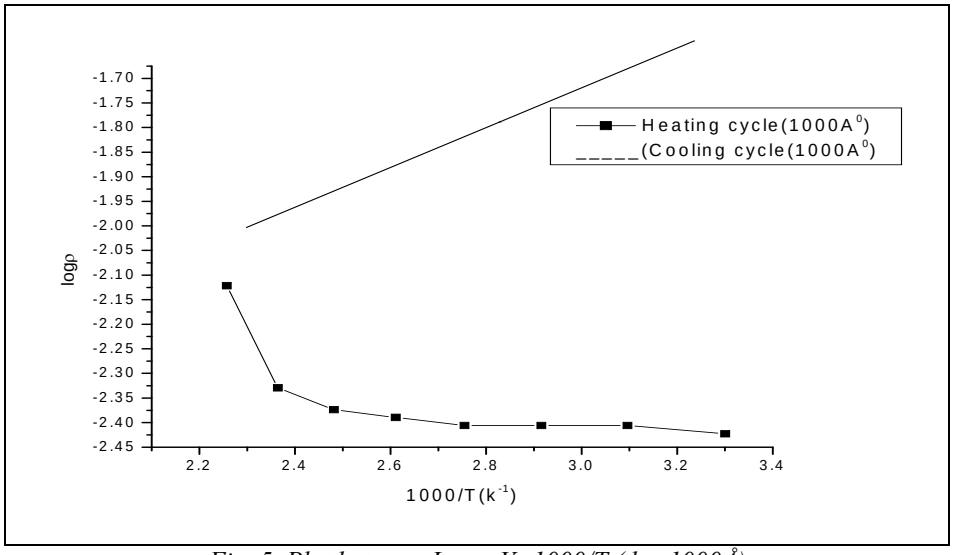

Fig. 5. Plot between Log ρ Vs 1000/T (d = 1000Å)

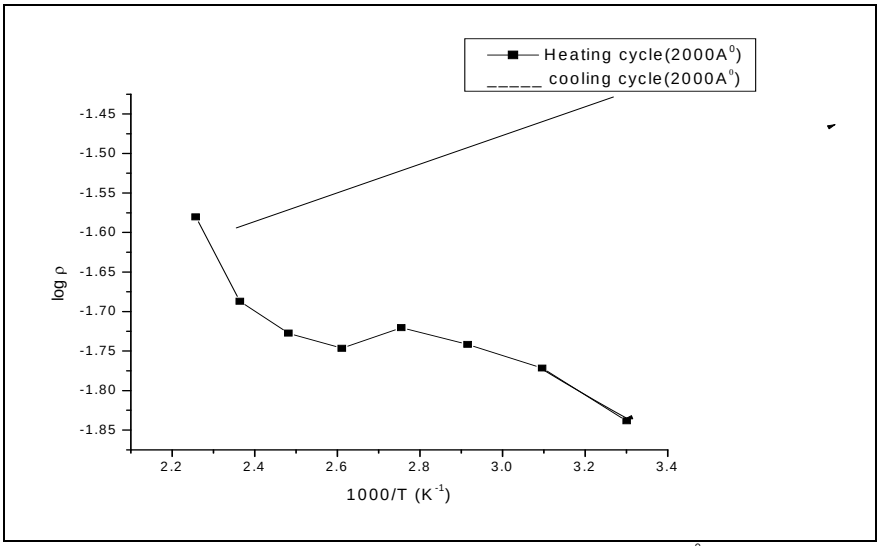

Fig. 6. Plot between Log ρ Vs 1000/T (d = 2000Å)

Fig. 4-6 shows that the resistance increases its initial heating with that of temperature. The resistance starts decreasing which is not a permanent one when a rise in resistance increases its temperature level. During the cooling cycle, it is observed that the resistance is monotonically increasing with decreasing temperature and this $\log_{10}\rho$ Vs 1000/T plot gives a linear plot. Here, in this case a straight line in the region 303 K to 483 K is observed and the activation energy in some case is lightly comparable with the energy gap. In brief the decrease in resistivity during initial heating takes place because of intrinsic conduction in PbSe thin films. But at higher temperatures (>423 K), the resistivity increases steeply when the temperature is at high level. This brings forth that some other mechanism other than intrinsic conduction is responsible for the increase in resitivity [14].

During cooling, a sharp increase of resistance is observed with decreasing temperature, which exhibits the semi conducting behavior. This is because of the hysteric nature of the thermal defects created at high temperatures. The desorbed gas molecules will not be immediately adsorbed during cooling which can also be a reason for the monotonous increase in resistance during cooling.

In this experiment, the activation energy is determined from the slopes taken from the $\log_{10}\rho$ Vs 1000/T plots of cooling cycle which is given in Table 1.

Table 1. Dependence of film thickness and activation energy

Film Thickness (Å)	**Activation Energy (eV)**
500	0.045
1000	0.162
2000	0.074

The activation energy is found to be increased when the film thickness varies from 500 Å to 1000 Å, but with further increase in film thickness the activation energy shows a lower value than the previous thickness. A systematic variation of the activation energy values with the thickness is absent and this can be attributed to the variable deposition parameters like vacuum, deposition rate etc. X.M.Fang states that the electrical conductivity of the air-exposed films does not show any systematic variation with thickness [7].

4. Conclusion

Energy dispersive x-ray analyzer confirms the composition of constituent in the PbSe thin films. PbSe thin films, during the initial heating, a slow rise in resistance is observed and followed by a slow fall. But at temperatures above 423 K, a sudden increase in resistivity is observed. On cooling, semi conducting behavior can be observed and the $\log_{10}\rho$ Vs 1000/T plots are found to be linear. No systematic variation of activation energy is found when it varies in the thickness of the film.

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