CHARACTERISTICS OF SLURRY COATED LEAD SELENIDE FILMS

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Thin lead selenide films were deposited by the slurry coating technique using the powder chemically synthesized in the laboratory. The as prepared powder exhibited cubic structure. This powder was slurry coated onto alumina substrates. The films exhibited cubic structure with peaks corresponding to single phase PbSe. The films exhibited a carrier density of 3×10^{18} cm^{-3} and mobility value of 50 cm^{2}V^{-1}s^{-1}. XPS studies indicated peaks corresponding to Pb4f$_{5/2}$ and Se3d. Laser Raman studies exhibited a peak at 135 cm^{-1}.

1. Introduction

Lead chalcogenides (PbS, PbSe and PbTe) and their alloys have been the subject of considerable research due to the technological importance of these materials, in crystalline and polycrystalline forms, as detectors of infrared radiation and more recently as infrared emitters and solar control coatings also [1–3]. the lead salts exhibit properties which are unusual and possibly unique, relative to other semiconductors, and these unusual characteristics have obviously added to the stimulated study. A particularly unusual feature of this group of materials is the relative stability of the lattice over a rather wide range of nonstoichiometry. The temperature coefficients (dE_g/dT) of the minimum energy gap E_g is positive for these compounds while it is negative for all other compound semiconductors. Lead chalcogenides and their solid solutions have generated considerable interest because of their use in long wavelength imaging [4], IR gas spectroscopy [5], thermo-photovoltaic energy converters [6]; and in photovoltaic and photoconductive detectors[7]. In particular, commercial lead salts detectors in the form of sensitized polycrystalline films have been widely used.In this work, PbSe films were deposited by the slurry coating technique using the laboratory synthesized PbSe powder and the properties are studied.

2. Experimental

High purity lead selenide powder has been prepared by the reaction of aqueous solutions of lead acetate with sodium selenosulphate solution under optimum pH conditions, of pH-10 obtained by the addition of ammonium hydroxide. Normally selenium dissolves in hot aqueous alkali metal sulphates yielding alkali selenosulphate or selenosulphites. Selenosulphate is stable under high alkaline conditions (pH=10). As the pH is decreased gradually up to 5.5 and below, selenium is precipitated out in the red form. Selenium in Selenosulphate is more easily parted as se^{2-} ion than sulphur in thiosulphate. The reaction involved may be represented as given for CdSe preparation. The reaction for PbSe preparation can be written as:

$$Na_2SO_3 \ + Se \ \text{---------} \ Na_2SeSO_3$$
$$PbAc \ + 2NH_4OH \ \text{--------------}Pb(NH_3)_2Ac \ +2H_2O$$
$$Pb(NH_3)_2Ac \ +Na_2SeSO_3 +H_2O\text{------------} \ PbSe \ +Na_2SO_4 \ +2NH_4Ac$$
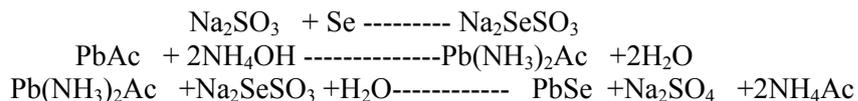
To start with sodium selenosulphate was prepared as discussed earlier.

After allowing the selenium solution to age for 20 hours, 1.8 gm of lead acetate was dissolved in 250 ml of triple distilled water and was heated for a short period. 15 ml of 15% ammonia solution was added, a white precipitate formed. 150 ml of selenosulphate solution was added to the above solution. The solution became black in colour. After 1 hour of heating 100 ml of selenosulphate solution was added. The mixture was heated for more than 2 hours. A dark black precipitate was obtained. The precipitate was then thoroughly washed with hot sodium sulphite solution to remove any trace of selenium. Washing with distilled water was continued till the filtrate was free from sulphite. Purified ethanol was used for final washing to remove moisture. The precipitate was dried in a vacuum oven.

To obtain films by the slurry coating technique, the sensitized powder was mixed with propanediol to give a consistency suitable for deposition. Cleaned steatite substrates were affixed to a cello tape 6 inches long and 1 inch wide fixed to a porcelain tile. These affixed substrates were cleaned with cotton wool dipped in acetone. The paste is applied with a doctor's blade to the polyurethane squeegee and pulled on the screen once in unidirectional, thus getting layers of uniform thickness and finish. At a time 20-30 substrates can be coated. These layers were dried in an oven at 120^0C. The thickness of the coated layers after drying was around 30 micrometers and after sintering it was around 25 micrometers. The films sintered at different temperatures in the range 400 - 500°C in air. The films were characterized by x-ray diffraction for structural studies using CuK_α radiation of Philips x-ray diffraction unit. Surface morphology of the films was studied by JSM 35 CF JEOL model SEM. X-ray photoelectron spectroscopy(XPS) studies were made using MKIII XPS system. Electrical measurements were made using evaporated gold as the ohmic contact. Photoconductivity studies were made using a 100 W tungsten halogen lamp. Laser Raman spectra were recorded using Renishaw Invia Laser Raman microscope and 633 nm He Ne laser.

3. Results and discussion

X-ray diffraction studies indicated the films to be polycrystalline in nature with peaks corresponding to the cubic phase(Fig.1). Peaks corresponding to the (111),(200), (220),(311) and (222) reflections are observed in all cases. It is also observed that the peaks increase in height and become sharper as the post heat treatment temperature increases indicating the improvement in crystallinity. The lattice parameter was calculated using the relation:

$$1/d^2 = 1/a^2(h^2 \ + \ k^2 \ + \ l^2)$$

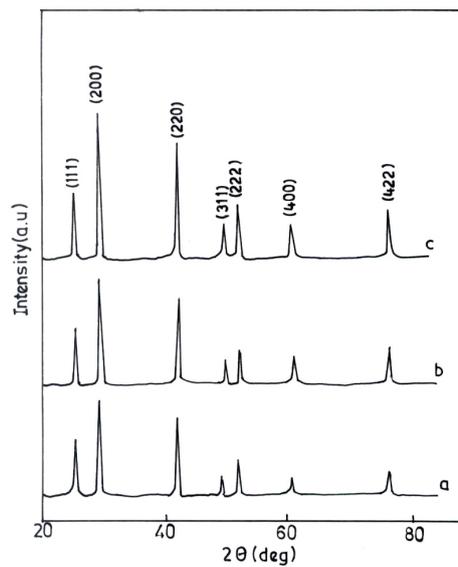where 'd' is the lattice spacing, 'a' is the lattice parameter, h,k,l are the Miller indices.

Fig. 1. X-ray Diffraction pattern of PbSe films sintered at different Temperatures (a) 400˚C (b) 450˚C (c) 500˚C.

The value of the lattice parameter is 0.611 nm. The crystallite size(D) was calculated using the Debye Scherrer equation

$$D = 0.9 \, \lambda/\beta\cos\theta$$

Where, λ is the wavelength of x-rays, β is the Full width at half maximum(FWHM) and θ is the Bragg angle. The values of the crystallite size is shown in Table-I. Dislocation density(δ) and strain(ε) were calculated using the following relations

$$\delta = 15\varepsilon/aD$$
$$\varepsilon = \beta\cos\theta/4$$

The values of dislocation density and strain are also included in Table-I. It is observed from the figure that the crystallite size increases with post heat treatment temperature.

Table 1. Crystallite size, dislocation density and strain of PbSe films sintered at different temperatures.

Sintering Temp(˚C)	Crystallite size(nm)	Dislocation density(δ) (x 10^{15} lines/m^2)	Strain (ε) (x 10^{-2})
400	83.4	13.64	4.34
450	98.05	10.30	3.69
500	108.9	8.34	3.32

It is observed from the table that the dislocation density and strain decrease with increase of sintering temperature due to the improved crystallinity.

Hall measurements of the films were made at room temperature by providing evaporated gold ohmic contacts. Table-II shows the mobility, carrier density and resistivity of the films post heated at different temperatures.

Table 2. Mobility, resistivity and carrier density with sintering temperature

Sintering Temp(°C)	Resistivity(ohm cm)	Mobility($cm^2V^{-1}s^{-1}$)	Carrier Conc(cm^{-3})
400	0.080	70	1.1×10^{18}
450	0.045	62	2.2×10^{18}
500	0.042	50	3.0×10^{18}

It is observed from the table-II, that the carrier density increases with sintering temperature, whereas the mobility and resistivity decrease.

Fig. 2 shows the X-ray photoelectron spectra of the as-prepared PbSe. The binding energies of $Pb4f_{7/2}$ and a peak of Se3d is detected and the main formation on the surface of the product is PbSe [8].
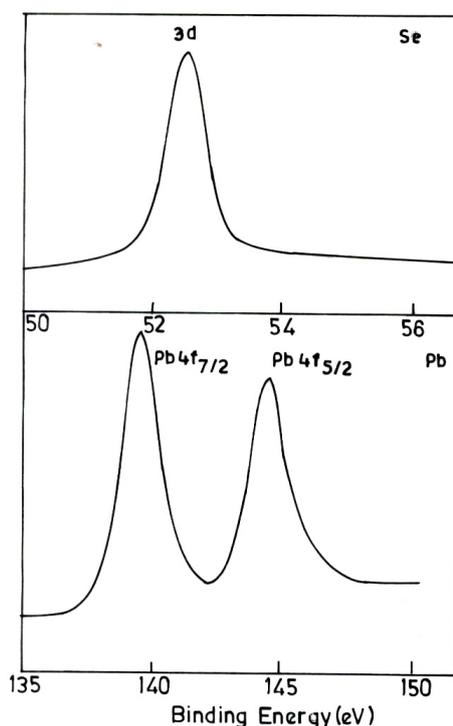

Fig. 2. XPS spectra of PbSe films sintered at 500°C

Fig.3 shows the Raman spectra of the PbSe films sintered at different temperatures. The Raman band around 135 cm^{-1} can be assigned to the lattice mode vibration of PbSe[9]. The width of the band decreases with increase of sintering temperature. This is due to improved crystallinity of the films at high temperatures. This is also supported by XRD studies, wherein the peaks become sharper at high sintering temperatures.
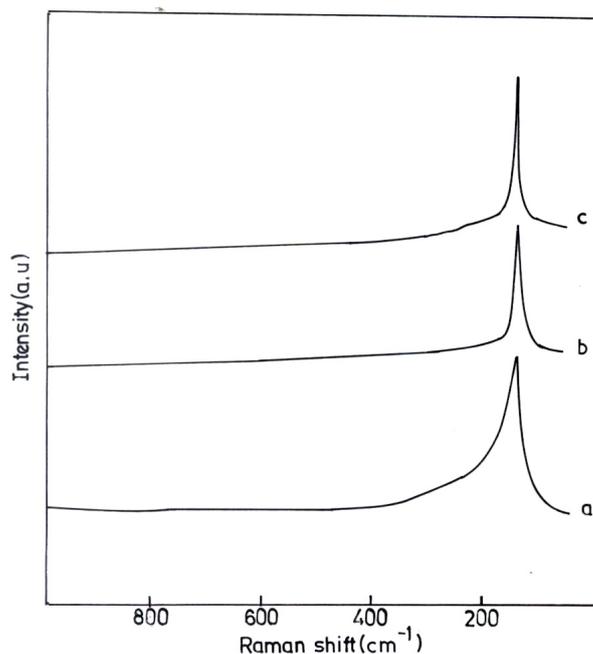
Fig.3. Raman spectra of PbSe films sintered at different Temperatures (a) 400˚C (b) 450˚C (c) 500˚C

4. Conclusion

The results of this study indicate that low resistive PbSe films with reasonable values of carrier density and mobility can be obtained with the films obtained by slurry coating the laboratory synthesized PbSe powder.

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