

Study of electrical optical and structural properties of lead selenide sulphide ternary thin films

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(Received: October 04, 2010; Accepted: November 12, 2010)

ABSTRACT

Polycrystalline Lead Selenide Sulphide thin films have been deposited on glass substrate at 300 K by thermal evaporation technique. The different sets of samples of varying composition 'x' from 0.1 to 0.9 were deposited and annealed at reduced pressure of 0.1 micron for duration of 4 hours at temp (373) K. The material parameters determined are bulk resistivity 1.450 (Ohm-cm), mean free path 2820 Å and carrier concentration 5.5×10^{12} per cm³. The estimated activation energy for heating cycles is larger as compare to cooling cycles. Fermi-energy determine from TEP study are within ranges between band gap energy and activation energy values.

Also the XRD study reveals that all the samples were polycrystalline having cubic FCC, cubic and tetragonal structure. The dependence of absorption coefficient ' α ' on photon energy has been determined. The analysis of result so that for Lead Selenide Sulphide films of different composition, direct transition occurs with band gap energy in the range of 1.0 eV to 1.4 eV. Refractive indices and extinction coefficient have been evaluated and are in the range 1.20 to 4.80 and 0.005 to 0.0245 respectively. The compositions of films were analyzed using Energy Dispersive X-ray Analysis (EDAX). Also the grain size is determined from X-ray diffraction study. Most of the grain sizes are below 300 Å indicates that the film material exhibits nano structure. The SEM analysis indicates that the film is covered with large number of star shaped microgranuals. The size of the microgranuals increases with increasing 'x'.

Key words: Thermal evaporation, optical constants, XRD, EDAX, SEM.

INTRODUCTION

A series of new materials of varying chemical and physical properties could be obtained by varying the composition of constituents of binary and ternary semiconductors; in this respect for example newer materials like $Pb_{1-x}Cd_xS$, $CuInS_2$, $CuInSe_2$, $ZnSSe/ZnSe$ and $ZnCdS$ can be used for better efficiency¹⁻⁷. Sulfide and mixed sulfide thin film coating find extensive use in number of electronic devices such as photoconductors, thin film transistors, photo-detectors, electroluminescent cells and photovoltaic devices⁸⁻¹². Lead sulfide thin films have been deposited by LP-MOCVD and AACVD, using single-source precursors of the type

$[Pb(S_2CNRR')_2]$. The same class of compounds for the preparation of nanocrystallites and thin films of PbS/Se has been studied¹³⁻¹⁵. Continuous variation of the energy gap (and other properties), which can be obtained by varying the relative concentration of constituent elements in mixed and alloyed ternary semiconductor compounds has been extensively used to tailor the spectral response of detectors for opto-electronic applications. The aim of this paper is to investigate the effect of composition of ternary solid thin films. However mixed and alloy selenides are rarely studied. Keeping this in mind thin films of $(PbSe)_x(PbS)_{1-x}$ type are prepared and characterized in the present work.

MATERIAL AND METHODS

For the preparation of ternary compound semiconductors $(\text{PbSe})_x(\text{PbS})_{1-x}$ the constituent compounds PbSe and PbS have been taken in molecular stoichiometry proportional weights and crushed and mixed homogeneously. The different sets of samples of varying compositions ($x = 0.1$ to 0.9) were deposited on to the amorphous precleaned glass substrates at room temperature 308 K . All the samples are deposited under the similar optimized conditions. The thicknesses of films were controlled by using quartz crystal thickness monitor model No. DTM-101 provided by Hind-High Vac. The deposition rate was maintained $10\text{-}15\text{ \AA}/\text{sec}$ constant throughout sample preparations. These samples were annealed at reduced pressure of 0.1 micron for the duration of 4 hours at the temperature of 373 K and maintained carefully. These samples were then used for different characterizations.

The structural characterization was done by X-ray diffractometer (Rigacu-Miniflex, Japan) with $\text{CuK}\alpha$ radiation (1.5418 \AA) and Analytical Scanning Electron Microscope (SEM) JEOL JSM 6360 (LA), with EDAX attachment. The transmittance of the films was determined at normal and near normal incidence of light in the wavelength range $200\text{ to }2600\text{ nm}$ by means of double beam spectrophotometer (Hitachi-330 model).

RESULTS AND DISCUSSION

Electrical Properties

Resistivity variation as a function of composition parameter 'x' as presented in Fig.1 Seems to be obvious as resistivity of pure material (i.e. $x = 0$) PbS and PbSe are of value $0.027\text{ }\Omega\text{-cm}$ and $0.25\text{ }\Omega\text{-cm}$ respectively. As x increases resistivity should increase and it should be maximum at $x = 0.5$, theoretically instead of this it is observed that resistivity increases slowly with x up to $x = 0.7$ and then it rapidly increases up to $x = 0.9$ For all samples $x \neq 0$ the resistivity is larger than that of pure material films of same order of thickness around 2000 \AA^{13} . Similar behavior of resistivity variation for all composition of 'x' may be due to similar processes of activation of conductivity of charge carriers may be involved. This behavior in

Table 1: Band gap energies for ternary compound $\text{PbSe}_x\text{PbS}_{1-x}$

Composition 'x'	Thickness (d) \AA	Band gap energy E_g (eV)
0.1	1200	1.16
0.2	1450	1.12
0.3	2100	1.04
0.4	1900	1.04
0.5	1850	1.16
0.6	1250	1.43
0.7	1300	1.40
0.8	1450	1.28
0.9	1520	1.16

Table 2: Range of 'n' values for the ternary compound $\text{PbSe}_x\text{PbS}_{1-x}$

Composition 'x'	Rang of 'n' of values
0.1	3.33 – 1.22
0.2	4.56 – 1.22
0.3	4.80 – 1.22
0.4	4.32 – 1.22
0.5	4.44 – 1.22
0.6	3.60 – 1.22
0.7	2.69 – 1.22
0.8	3.89 – 1.22
0.9	3.51 – 1.57

Table 3: Range of 'k' values for various compositions of the ternary compound $\text{PbSe}_x\text{PbS}_{1-x}$

Composition 'x'	Range of 'k' of values
0.1	0.0005 – 0.0245
0.2	0.0014 – 0.0150
0.3	0.0022 – 0.0157
0.4	0.0038 – 0.0164
0.5	0.0036 – 0.0149
0.6	0.0047 - 0.0176
0.7	0.0017 – 0.0169
0.8	0.0010 – 0.0177
0.9	0.0011 – 0.0164

the resistivity is supported by different structural phases involved as composition parameter 'x' increases. And similar observations have observed by Deshmukh et. al.¹⁶ In this study of (CdSe)_x–(PbS)_{1-x} composite thin films.

Material parameters evaluated approximately were bulk resistivity $\rho_0 = 1450 \times 10^{-3} \Omega\text{-cm}$, mean free path $l_0 = 2820 \text{\AA}$ and carrier concentration $n = 5.5 \times 10^{12}/\text{cm}^3$. The carrier concentration evaluated seems to be very low value as compared to the reported value of $10^{18}/\text{cm}^3$ by Fujita et.al.¹⁷ for PbS_{0.5}Se_{0.5} prepared by co-evaporated method on rock salt and PbS_xSe_{1-x} single crystal substrates.

For all compositions change in thermoelectric power at low temperature end is appreciably larger and very small changes at high temperature region except the compositions PbSe_{0.3}S_{0.7}, PbSe_{0.4}S_{0.6} and PbSe_{0.5}S_{0.5}, have appreciable thermoelectric power changes over entire temperature range may be increasing or decreasing. From the Fig. 2–3 fermi energies have been evaluated from the linear variation of thermoelectric power verses reciprocal of temperature. These values are within ranges in between band gap energy values around 1.2 eV and evaluated thermally activation energies (0.24 - 0.44) eV.

Optical Properties

The transmittance spectra have

Table 4 EDAX Data for (PbSe)_x(PbS)_{1-x} Composite thin films (x = 0.1 to 0.9) (atomic percent)

Composition 'x'	Atomic Percent Pb	Atomic Percent Se	Atomic Percent S	EDAX Composition		
				Atomic Percent Pb	Atomic Percent Se	Atomic Percent S
0.1	50	5	45	-	-	-
				-	-	-
				-	-	-
0.2	50	10	40	14.57	3.23	22.71
				16.15	8.67	18.64
				20.32	3.81	26.44
0.3	50	15	35	46.83	17.36	35.82
				46.08	17.94	35.98
				48.91	17.99	33.10
0.4	50	20	30	47.21	27.83	24.96
				46.42	27.59	25.98
				47.05	27.40	25.54
0.5	50	25	25	46.43	21.39	32.18
				48.82	21.07	30.11
				45.30	33.27	21.42
0.6	50	30	20	38.96	36.59	24.44
				38.76	25.88	35.35
				39.37	34.21	26.42
0.7	50	35	15	0.00	42.53	57.47
				6.51	23.15	70.70
				12.02	52.80	35.17
0.8	50	40	10	40.21	44.70	15.09
				39.88	44.47	15.65
				41.98	44.01	14.01
0.9	50	45	5	38.87	46.27	14.85
				38.24	46.79	14.97
				40.68	47.39	11.93

characteristic feature as a function of wavelength. Few samples are opaque below 750 nm and some of them are opaque below 950 nm. Then the transmittance increases linearly and rapidly with wavelength and attains maximum value. Also in few samples there is a well defined maxima and minima peak from the spectra. The transmittance data have been used to calculate absorption coefficients an attempt is made to plot the curves $(\alpha hn)^2$ vs hn and the curve is presented in Fig. 4. All the compositions curves shows linear variations and extended line intersects the hn axis. This intersection gives optical band gap energies. These evaluated values are presented in Table 1. These values are in the range 1.04 – 1.43 eV and varied randomly when composition parameter is less than 0.5 ($x < 0.6$).

Band gap energy 'Eg' is maximum for $x = 0.6$ and it decreases at $x > 0.6$, for these samples the thickness is also of increasing order and therefore band gap energy is also as expected goes on decreasing order. This fact is also explained for PbSe and PbS films¹⁸⁻²¹.

The observed transmittance at normal and near normal incidence and reflectance at near normal incidence data have been used to determine the optical constants refractive indices 'n' and extinction coefficient 'k'. The range of 'n' and 'k' values for all the samples of different composition of parameter 'x' are presented in Table 2 and 3 respectively and are in the range 1.20 to 4.80 and 0.005 to 0.0245 respectively.

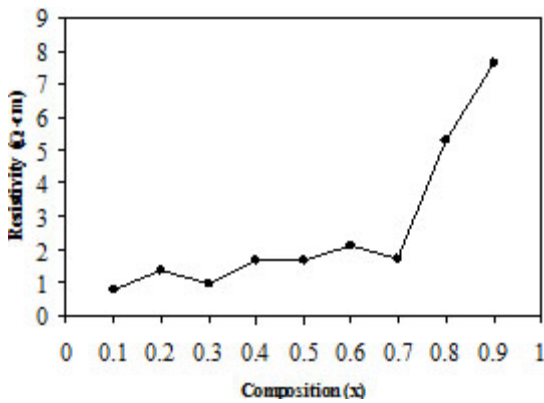


Fig. 1: Variation of Resistivity as a function of composition 'x' for $PbSe_x PbS_{1-x}$ ($x = 0.1$ to 0.9)

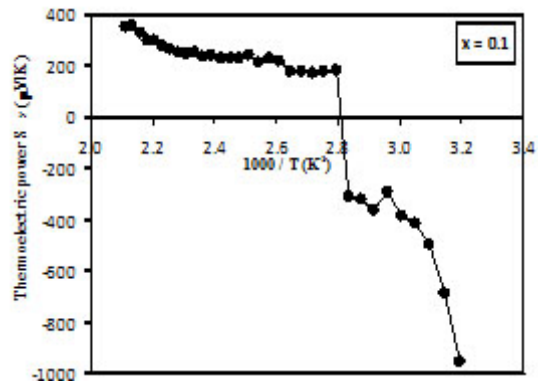


Fig. 2: Variation of TEP with reciprocal of temperature for $PbSe_x PbS_{1-x}$ thin films ($x = 0.1$)

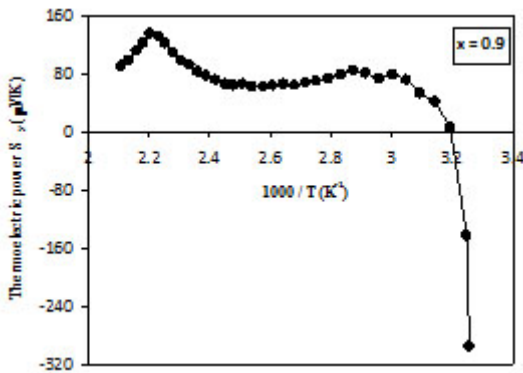


Fig. 3: Variation of TEP with reciprocal of temperature for $PbSe_x PbS_{1-x}$ thin films ($x = 0.9$)

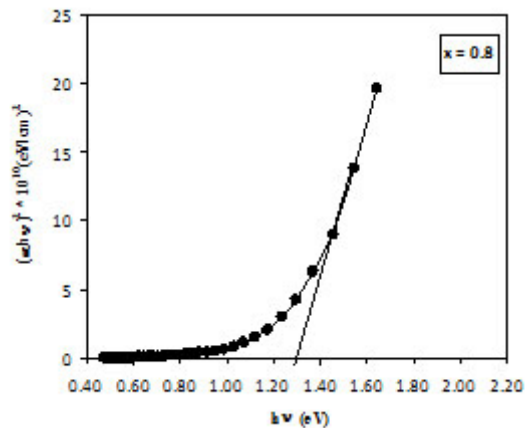


Fig. 4: Variation of $(\alpha hn)^2$ with photon energy for $PbSe_x PbS_{1-x}$ thin film ($x = 0.8$)

Structural Properties

Table 4 represents the detail EDAX analysis of the composition of starting basic ingredients and film composition comparisons. And

compares expected atomic percentage and actual atomic percentage in the film material for all the samples of all compositions 'x' varying from 0.1 to 0.9.

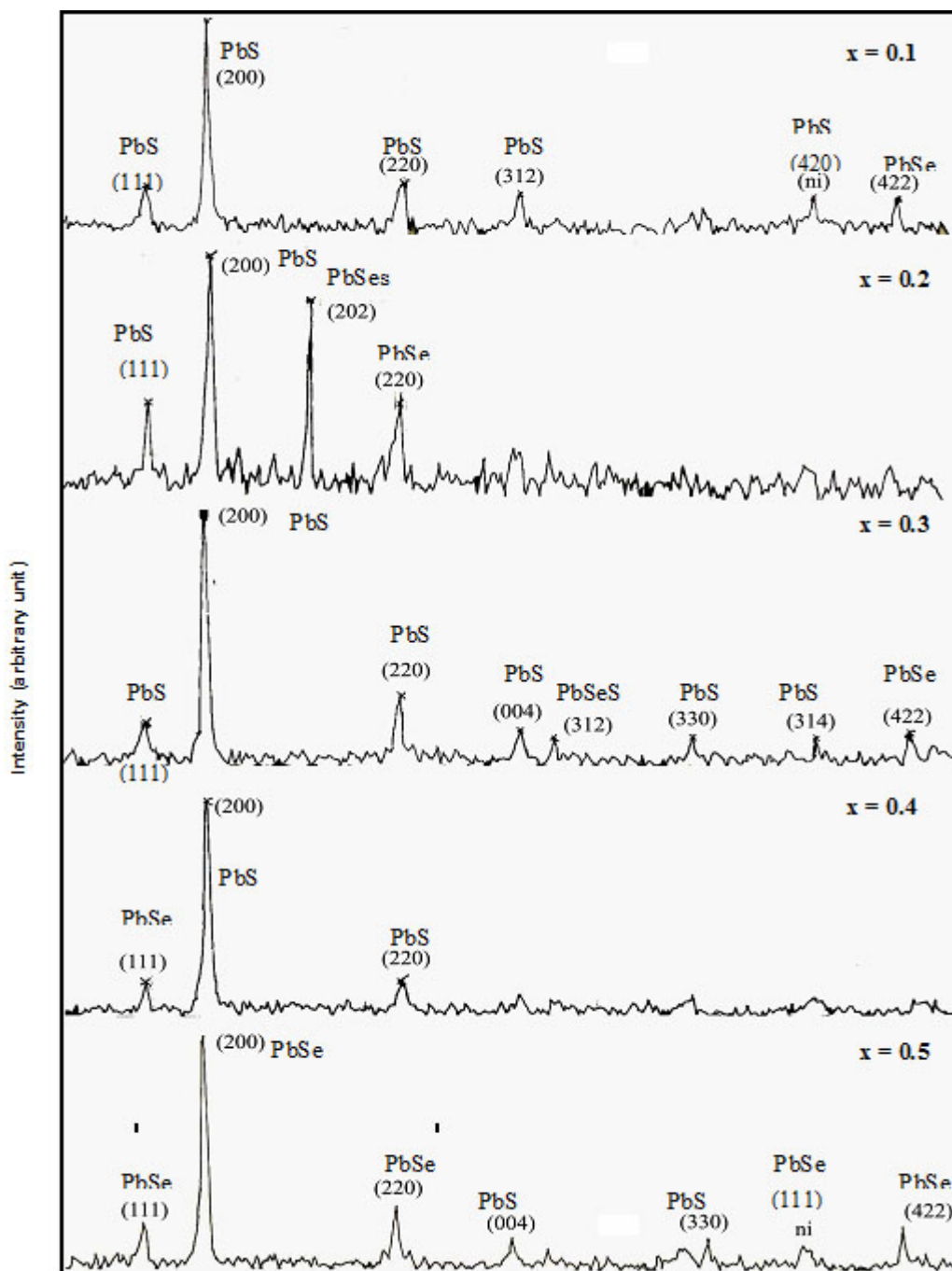


Fig. 5: X – Ray Diffractograms of various $(PbSe)_x (PbS)_{1-x}$ Structures ($x = 0.1$ to 0.5)

It is seen from this table that the samples of compositions $x = 0.3, 0.4$ and 0.5 are not much deviated from the expected atomic percentage while the samples with $x = 0.6, 0.8$ and 0.9 are comparatively more deviated than expected. While the sample of composition $x = 0.7$ is largely deviated from the expected atomic percentage.

The XRDs of all compositions ($0.1 \leq x \leq 0.5$) have been presented in Fig. 5. X-ray diffractograms differs for different compositions in relative intensities, angular positions and even relative orientations. The comparison of observed and standard diffraction parameters for three different structures of PbSeS, PbSe and PbS compounds. A detailed comparison indicates that observed and standard 'd' values very closely agree with each other for all composition parameters x varying from 0.1 to 0.9. The XRD analysis confirms that film material is polycrystalline for all compositions.

The relative intensities of prominent reflections of cubic structures of PbSe and F.C.C. structure of PbS (111) (200) and (220). From this table it is observed that, as the compositional parameter x increases, the orientation of crystallites changes from (200) of face centered cubic of PbS to (200) cubic of PbSe.

From the analysis of XRD it is found that the films are of composite structure of PbSe, PbS and PbSeS i.e. cubic face centered, cubic and tetragonal structures. In other words this analysis of different peaks indicating the presence of phases, cubic PbSe, face centered cubic of PbS as well as tetragonal of PbSeS. It is interesting to note that for $x = 0.1 - 0.2$ face centered cubic face of PbS is prominent than phases of PbSe and PbSeS. For $x = 0.4$ and 0.5 films are only phase of cubic PbSe and F.C.C. of PbS for $x = 0.6$ and 0.8 films are constituting all the three phases prominently. For $x = 0.9$, the films are constitutes tetragonal and cubic phase only, for $x = 0.7$, the film material is of prominent cubic phase of PbSe only.

In general it may be concluded that film materials of various compositions parameters are of polycrystalline, composite of different phases and having relative crystalline orientation along (200)

of cubic or F.C.C. of PbSe and PbS respectively. L.P.Deshmukh et.al.¹⁶, studied composite films of $(\text{CdS})_x (\text{PbS})_{1-x}$ grown by chemical bath deposition technique. XRD and microscopic observation show the films were composite and exhibit Phase of cubic and hexagonal (CdS) cubic (CdO) and PbS.

The grain size of crystallites for all the compositions has been evaluated. Most of the values of grain size are below 300 Å which indicates film material exhibit nano-structure.

The film with $\times 4000$ magnification for the composition $(\text{PbSe})_x (\text{PbS})_{1-x}$ ($x = 0.2$) at 25 kV accelerating voltage shows the large number of small granules as shown in Fig. 6. But the same film at the low accelerating voltage i.e. 15 kV shows the large number of microgranules, but it is interesting to point out that all the granules are star shaped which can be seen from the photographs. This star shape indicates the dendritic growth of

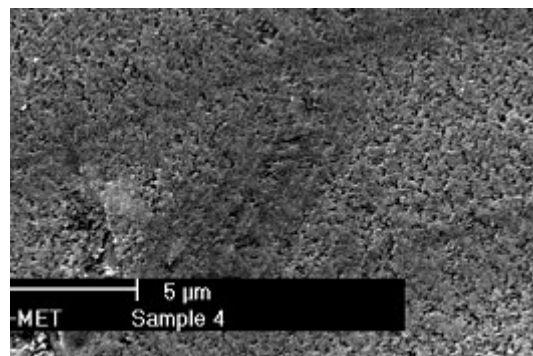


Fig. 6: Scanning electron micrograph of $\text{PbSe}_x \text{PbS}_{1-x}$ thin film ($x = 0.2$)

the samples. This may be due to the effect of WD changes from 9.3 to 9.6.

As the percentage of PbSe increases the size of the microgranules also increases without any sort of orientation and regularities. But when the concentration of PbSe is increased to 80 ($x = 0.8$) some granules are turn onto spherulitic shape with the fibers at the top of the surface. The fibers on the spheroids are clearly visible, when the x value increased from 0.8 to 0.9. The size of spheroids in some cases have been increased as compare to $x = 0.8$. But when $x = 0.8$ then numbers of spheroids

is large as compare to $x = 0.9$ and also their shape is more regular. So for the dendritic growth of the film is suitable at $x = 0.2$ ($\text{PbSe}_x \text{PbS}_{1-x}$), but when same film required at spherulitic shape then $x = 0.8$ ($\text{PbSe}_x \text{PbS}_{1-x}$) is suitable.

From this we conclude that for $x = 0.2$ gives the film of dendritic growth and for $x = 0.8$ gives the film of spherulitic shape. Both are in crystalline form and $x = 0.2$ and $x = 0.8$ both are having the good quality of the mixed ternary films.

1. Thin films of Polycrystalline Lead Selenide Sulphide were prepared by the thermal evaporation technique.
2. Estimated activation energy for heating cycles is larger as compared to cooling cycles. Also for $x < 0.5$ the activation energies are of higher magnitudes as compare to $x > 0.5$.
3. The Estimated values of Fermi-energy determined from thermo electric power study are within ranges between band gap energy and activation energy values.

4. The Band gap energy varies randomly when $x < 0.5$ and it is systematically decreases when $x > 0.6$.
5. Detailed X-ray diffraction study reveals that the films are of composite structure i.e. Cubic fcc, Cubic & Tetragonal.
6. Most of the estimated grain sizes are below 300\AA . This indicates film material exhibits nano-structure.
7. SEM analysis indicates that the film is covered with large number of star shaped microgrannuals, the size of the microgrannuals increases with increasing 'x' when $x = 0.8$ the microgrannuals are turn on to regular spherulitic shape and when $x = 0.2$ film shows dendritic growth.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. Dr. P. H. Pawar, Principal, Z. B. Patil College, Dhule. The authors are also grateful to Prof. Dr. P. P. Patil, Director and Head, Department of Physical Sciences, North Maharashtra University, Jalgaon.

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