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Polycrystalline Lead Tin Chalcogenide Thin Film Grown by Spray Pyrolysis

$PbSnS_2$ thin film has been prepared for the first time by spray pyrolysis technique on FTO substrate at 570K. The preliminary optical and structural characteristics of the film have been reported. The optical studies showed that the value of the fundamental absorption edge lies at 1.47eV and a low energy absorption band tail has been observed. The prepared film is p- type electrical conductivity, polycrystalline in nature and has an orthorhombic crystal structure. The value of an average grain size of the film is 350Å.

Keywords: PbSnS thin films, spray pyrolysis, optical properties

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1. Introduction

PbS is a narrow band gap (0.4eV) semiconductor and its thin film form has excellent solar control characteristics. It has been investigated by many researchers for photodetection and solar photothermal conversion applications (BUBE; NAIR, et al.; GARCIA et al.). The range of columns of the glazing to reflected daylight could be improved by developing ternary compounds such as, PbSnS (NAIR et al. (a)).

Doping with Sn in a lead sulfide makes deep donor level just above the valence band edge and if it is doped with acceptor impurity show high resistivity and large photoconductivity (ISHINDA et al.). PbSnS is a semiconducting material and the band gap decreases with increasing Sn concentration at small SnS content region (ISHINDA et al.). Transport properties of $Pb_{(1-x)}Sn_xS$ (x = 0 to 0.05) solid solution have been studied by Prokof'eva et al. over a wide range of temperature and the effect of variable valence of Sn on the density of carrier concentration has been analyzed (PROKOF'EVA et al.).

Novel materials are needed for thin film solar cell apart from the most extensively studied material CdTe and $CuInSe_2$. Lead tin sulfide thin film shows high absorption coefficient ($>10^4$ cm^{-1}) in the visible range. The desirable optical band gap value for thin film solar cell can be tailor made with varying the Sn composition.

Transparent conductive SnO_2:F thin films (FTO) have been used as conductive windows in the fabrication of photovoltaic devices (FEREKIDES et al.), which has led to a considerable enhancement of conversion efficiency, because of its high optical transmittance and electrical conductivity. In this study, FTO glass plates have been used as a substrate for $PbSnS_2$ thin film

Among the various thin film deposition techniques, spray pyrolysis is one of the principal methods used to produce a large area and uniform coating. On account of the numerous applications of lead tin sulfide, an attempt has been made to prepare lead tin sulfide alloy film using the spray method.

This paper contains a first report of $PbSnS_2$ thin film fabricated by the chemical spray pyrolysis technique. The preliminary results of structural and optical properties of this alloy film have been presented.

2. Experimental

$PbSnS_2$ thin coatings have been prepared on FTO coated glass substrate by a home made double nozzle sprayer. The FTO substrate has a sheet resistance of 20 Ω/sq. and was prepared in our laboratory by using the same spray method.

Spray solutions are prepared by mixing 0.1M aqueous solution of lead nitrate, $SnCl_2.2H_2O$ and thiourea in the ratio of 1:1:2. To enhance the solubility of tin chloride salt a few drops of HCl is added. Atomized spray solution is transferred to the hot substrates kept at the normalized deposition temperature of 570K with the help of carrier gas. The substrate temperature is maintained within ± 5K using a chromel-alumel thermocouple based digital temperature controller. Filtered air at a pressure of 12psi is used as carrier gas, the flow rate of which is normalized to ~7l/min. The solution flux is maintained at 5ml/min and the spray time is kept constant at one second throughout the deposition. An increase in the spray time causes thermal shock of the substrate due to excessive cooling. A 2-minute waiting time is allowed between each spraying application to maintain the substrate temperature and enable to decompose the starting material completely. The distance between the nozzle and the substrate is kept at 30cm, the spray angle is 45° and the substrates are rotated intermittently to achieve uniform deposition. After deposition, films are allowed to cool at an ambient temperature slowly. The deposited films are stable at room temperature, well adhered to the substrate and are brown in color.

Thickness measurement of the films has been carried out using JSM 35 CF JEOL Scanning Electron Microscope (SEM). The film is mounted vertically to measure the thickness directly (CHEN et al.). The measured thickness of the film is about 0.5μm. The structural properties of the films are studied by Computer controlled JEOL-JDX 8030 X-ray diffractometer using CuK_α radiation. The scanning angle 2θ is varied in the range of 10-85° in steps of 0.1°. Optical measurements are carried out using Hitachi model 3400 UV-VIS-NIR double beam spectrophotometer in the wavelength range of 450-2500nm. FTO coated glass plate is used as a reference material in the transmittance spectrum. The as prepared film shows p-type electrical conductivity, which is confirmed by the thermoelectric probe measurement.

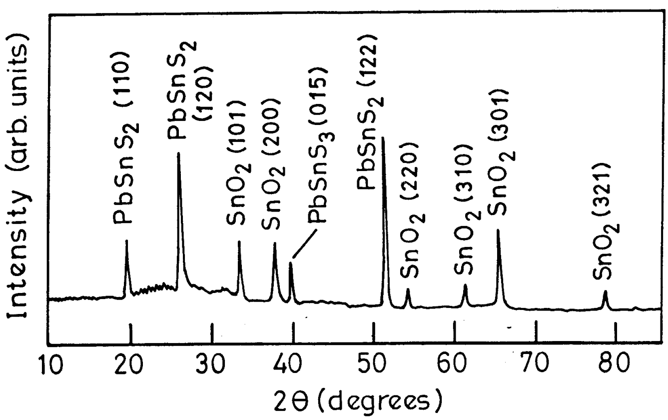

Fig. 1: XRD spectrum of lead tin sulfide on SnO_2: F coated glass substrate.

3. Results and Discussion

3.1. X-ray diffraction studies

X-ray diffraction studies have been carried out to identify the $PbSnS_2$ phase present in the film. Figure 1 Shows the XRD pattern recorded on $PbSnS_2$ film, which is coated on FTO substrate. The film is polycrystalline and has an orthorhombic crystal structure. The average grain size, calculated using the Scherrer's formula (Klug et al.), is 350Å. All the diffraction peaks that appeared in the spectrum have been identified and indexed from the known patterns of standard powder X-ray diffraction data file [JCPDS file No: $PbSnS_2$:- 14-618; $PbSnS_3$:- 25-464 & SnO_2:- 21-1250]. An impurity phase peak of $PbSnS_3$ has also been identified along with those of $PbSnS_2$. Since the thickness of the film is much smaller than the penetration depth of X-rays, thus the SnO_2 peaks are also shown in the spectrum.

3.2. Optical studies

The optical behavior of a material is generally utilized to determine its optical constants for example the absorption coefficient α. To find α from the transmittance data, the relation used is given by $\alpha = -1/t \ln T$, where T is the transmittance and t is the thickness of the film. Figure 2 shows the optical transmittance spectrum of 0.5μ thick film in the wavelength of 450-2500nm at room temperature.

The fundamental absorption edge is one of the most important features of the absorption spectrum of a semiconductor. The increased absorption near the edge is caused by the transition of electrons from the valence band to the conduction band (MILLER). Figure 3 shows the plot of absorption coefficient α against photon energy. The α exhibits a steep rise near the absorption edge and a straight line relationship is observed in the high α-region. The value of fundamental absorption edge from the intercept lies at 1.47eV and the corresponding α value is 1.88 X 10^4 cm^{-1}. The higher value of α (>10^4 cm^{-1}) shows that the transitions must correspond to a direct electronic transition and the properties of this state are important since they are responsible for electrical conduction.

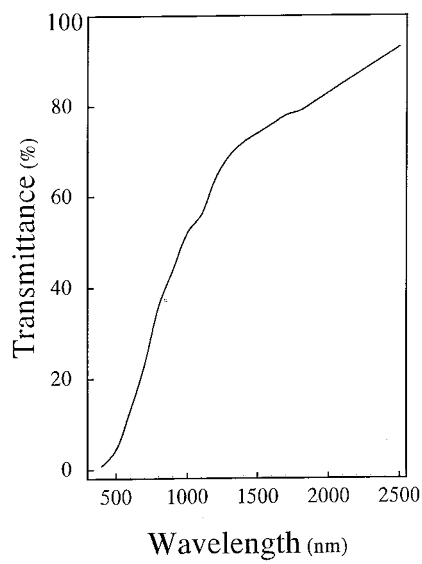

Fig. 2: Transmittance as a function of wavelength for $PbSnS_2$ thin film on FTO substrate in the VIS-NIR region.

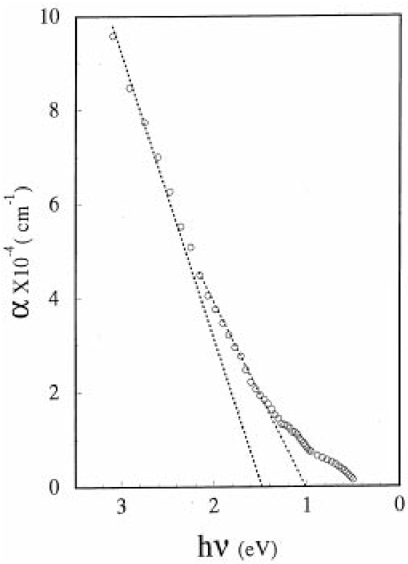

Fig. 3: Absorption coefficient (α) against photon energy.

As we move away from the absorption edge towards the low energy side, the curve exhibits low energy absorption tail at 1eV. The α value at 1eV is 8.5 X 10^3 cm^{-1}. In the low energy region (< 10^4 cm^{-1}), the absorption is generally predicted by the phonon-assisted transitions and impurity effects [10]. Although a rigorous analysis has not been done, the intercept represents E_g+E_{ph}, where E_g is the band gap energy and E_{ph} is the energy of various phonons (SMITH). In general absorption tails in polycrystalline material have been interpreted, in terms of the Dow-Redfield effect (DOW et al.) or the Urbach tail mechanism (URBACH). Since this alloy film has been investigated for the first time, comparative analysis of the present results could not be done.

4. Conclusion

Polycrystalline thin film of the solid solution $PbSnS_2$ have been prepared by a simple spray pyrolysis method. X-ray analysis revealed that the film is polycrystalline and contains a $PbSnS_3$ phase along with $PbSnS_2$. Optical studies revealed that the film fundamental absorption edge arises at 1.47eV and the low energy absorption band lies at 1eV. The former is due to the direct electronic transition and the latter may be due to the phonon-assisted transition and impurity effects. The value of 1.47eV is nearer to the optimum value of 1.5eV, the band gap required for an absorbing layer for efficient light absorption in photovoltaic application. The reported optical result gives an indication that the deposited layers may find applications in the fabrication of thin film heterojunction solar cells and photodetector.

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