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STRUCTURE AND OPTICAL PROPERTIES OF CHEMICALLY DEPOSITED TIN SELENIDE

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Tin selenide (SnSe) thin films have been prepared using chemical bath deposition technique. Deposition at various deposition conditions was studied in order to investigate the effect of these parameters on the film properties. The structural, morphological and optical properties of films were studied by using x – ray diffraction (XRD), optical microscopy (OM) and the spectrophotometer. The films prepared were found to be polycrystalline in nature. XRD studied confirms the formation of orthorhombic selenide structure with the preferred orientation along the (210) plane. The material covered the surface of the substrate completely. The optical band gap was found to be indirect, which was equal to 1.5 eV.

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Keywords: Tin selenide**,** Chemical bath**,** Structural and optical properties

1. Introduction

Tin selenide (SnSe) is one of the IV-VI semiconductors. For over a decade, IV-VI semiconductors have attracted growing interest owing to their important unique properties in optoelectronics such as light emitting diodes or laser diodes (Krause et al, 1994), memory switching devices (Subramanian et al, 1999), and infrared production and detention (Rodat M, 1975).

A number of techniques are employed in the formation of high quality thin films such as chemical vapor deposition, molecular beam epitaxy, electrochemical, evaporation and sputtering.

(Sankara et al 2003 and Guziewiez et al 2004). However there is an interest to investigate other techniques, which could be new possibilities in terms of device properties, structure. Chemical bath deposition (Wang et al 1999) belongs to these alternative techniques that could also produce high quality films of IV – VI semiconductor materials. It seems to be an inexpensive, simple, low temperature method that could produce good quality films for device application.

SnSe is considered as an important technological semiconductor having a potential solar cell material (Rodat, 1977 and Parentau et al 1990). It is a narrow band gap binary IV – VI semiconductor displaying a variety of applications as essential material in photo-electrochemical solar cells to enhance the fill factor in electrical switches and in junction devices (Sugana et al, 1996). SnSe thin film has an indirect band gap of 1.50 eV. In this paper, the structural and optical properties of SnSe thin film prepared by chemical bath deposition method were studied.

2. Experimental details

Tin selenide films were deposited onto glass substrates using CBD method at room temperature. The reagents used were tin chlorides ($SnCl_2$) as the source of cation (Sn^{2+}), potassium selenate ($K_2 SeO_4$) as the source of anion (Se^{2-}), EDTA the complexing agent which is used to

slow down the reaction in order to eliminate spontaneous precipitation which is not healthy for the growth.

To obtain the deposition of SnSe thin films 5ml 0.2M $SnCl_2$ was taken in a 50ml capacity glass beaker and EDTA was added to it with constant starring and a complex $[Sn(EDTA)]^{2+}$ was formed. To this, 5ml of 0.5M K_2SeO_4 was added.

The pH of the solution was adjusted using ammonia solution. The volume was made up to 50ml with distilled water. The cleaned substrates were attached to a holder and mounted vertically in the bath. After the deposition, the films were taken out of the bath, rinsed with distilled water, and dried in air. The deposition of SnSe thin films occurs when the ionic product of Sn^{2+} and Se^{2-} ions exceeds the solubility product of SnSe. The control of Sn^{2+} and Se^{2-} ions in the solution controls the rate of precipitation and hence the rate of film formation (Kainthala et al 1980). This is commonly achieved by using a stable complex for Sn^{2+} ions and a proper selenium ion source. The basic steps involved in the chemical deposited of a SnSe thin film are given below.

$$SnCl_2 + EDTA \rightleftharpoons [Sn(EDTA)]^{2+} + 2CL^-$$

$$[Sn\ (EDTA)]^{2+} \rightleftharpoons Sn^{2+} + EDTA$$

$$K_2\ Se\ 0_4 + OH^- \rightleftharpoons k_2\ 0_s + HSe^-$$

$$HSe^- + OH^- \longleftarrow Se^{2-} + H_20$$

$$Sn^{2+} + Se^{2-} \rightleftharpoons SnSe \downarrow$$

3. Results and discussion

3.1 Structural characterization

The structural composition of the grown film was studied through the XRD analysis and optical micrograph.

Fig.1a Micrograph for SnSe {L5}.

Fig. 1 shows the photomicrograph of the SnSe films. The films exhibit the growth of small grains distributed across the surface of the substrate.

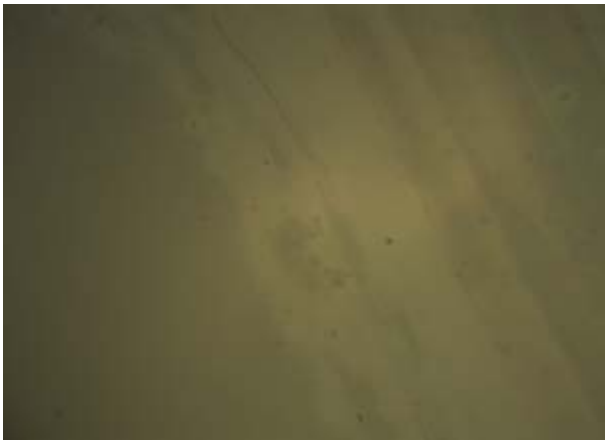

Fig.1b Micrograph for SnSe {L7}

The micrograph indicates uniform surface coverage. Further confirmation of the structure of the grown films was carried out using the x-ray diffraction pattern in Fig. 2.

(a)

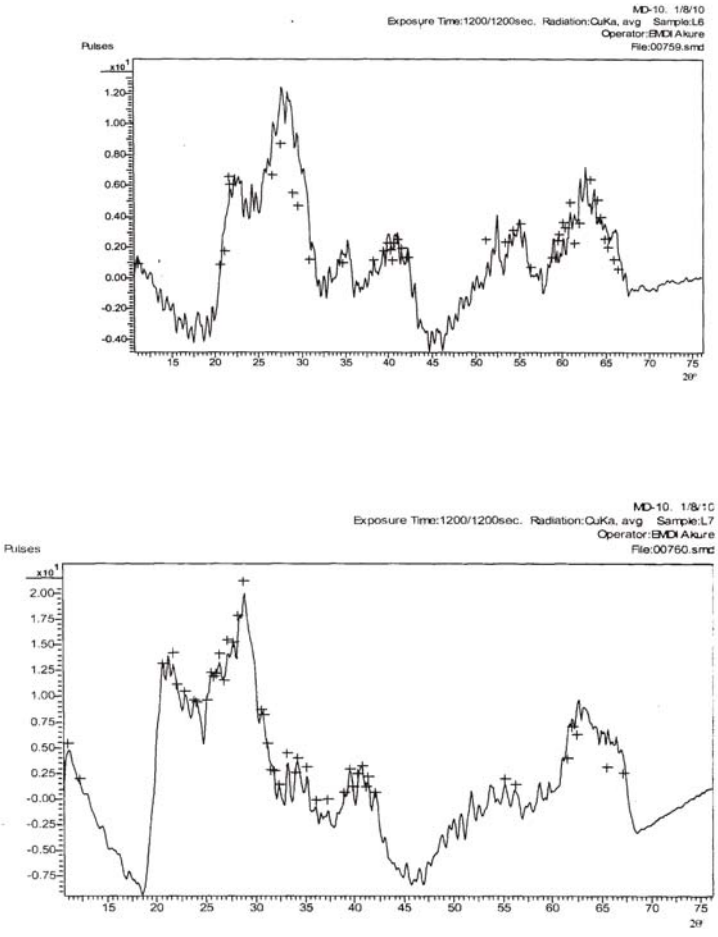

Fig 2a & b x-ray pattern of SnSe.

Fig. 2 shows the XRD pattern of a typical SnSe thin film prepared at substrate temperature of 300k. The 2θ peaks observed at 26.66^0, 28.99^0, 30.85^0 and 51.16 exhibit the formation of the orthorhombic phase of SnSe which correspond to the (201), (011), (111) and (221) planes of reflections. The inter-planar distances as were indicated in the XRD result were found to be 3.34 Å, 3.08Å, 2.89Å and 1.79Å. The presence of large number of peaks indicates that the films are polycrystalline. These results are well in agreement with the reported values by Zainal et al (2001) who reported the XRD pattern indicating an orthorhombic SnSe structure deposited by vacuum deposition techniques with (111), (400) and (311) planes Zulkanian Zainal et al (2003) obtained a film of orientation (201), (210),(011), (111), (020), (501) and (221) with the dominant orientation in the (111) plane. From the results shown above, the strongest peak for the grown films in figure 2 occurred at 2θ=26.66˚ with d = 3.34Å and 2θ=26.09˚ with d=3.41A which corresponds to (201) plane. The variation with that of Zainal may be attributed to the difference in the method of deposition. Therefore the preferred orientation lies along (201) plane for chemical bath deposited SnSe thin films which is well in agreement with the reported values by Saravanal (2004). The value of the lattice parameters obtained from the analysis of x-ray diffraction patterns are presented in Table 1.

Table 1 Result obtained from X-ray diffractogram:

Thickness	hkl		2θ	DÅ	DÅ	FWHM	Grain size, D
t(μm)		(Deg)	(rad)	Measured	Standard	(rad)	(Å)
1.62	201 011 111 221	26.66 28.99 30.85 51.16	0.465 0.506 0.538 0.893	3.34 3.08 2.90 1.79	3.52 3.05 2.95 1.80	0.381 0.381 0.381 0.377	3.74 3.76 3.78 4.08
1.64	201 011 111 221	26.09 28.32 30.56 51.58	0.455 0.494 0.533 0.900	3.41 3.15 2.93 1.75	3.52 3.05 2.95 1.80	0.381 0.384 0.381 0.369	3.74 3.77 3.78 4.12

The structural parameters of SnSe thin film show that the film has average grain size of 3.84Å for the film of thickness 1.62 μm and 3.90Å for film of thickness 1.64 μm. Table 1 shows that the grain size of the film increases with film thickness and greater thickness minimizes imperfection.

3.2 Optical properties of SnSe films

The optical absorption spectra were obtained in the 360nm-1100nm (0.36µm-1.10µm) wavelength range by employing a Janway 6405 UV-Visible model of the spectrophotometer.

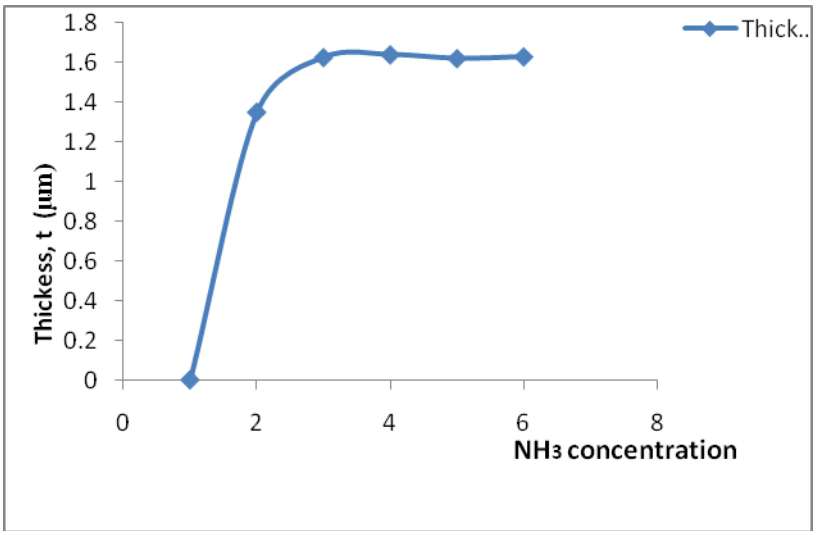

Fig 3 Variation of thickness vs vol. conc. of NH3

The thickness of the film is proportional to the volume concentration of Ammonia (NH3) used during deposition as shown in Fig. 3

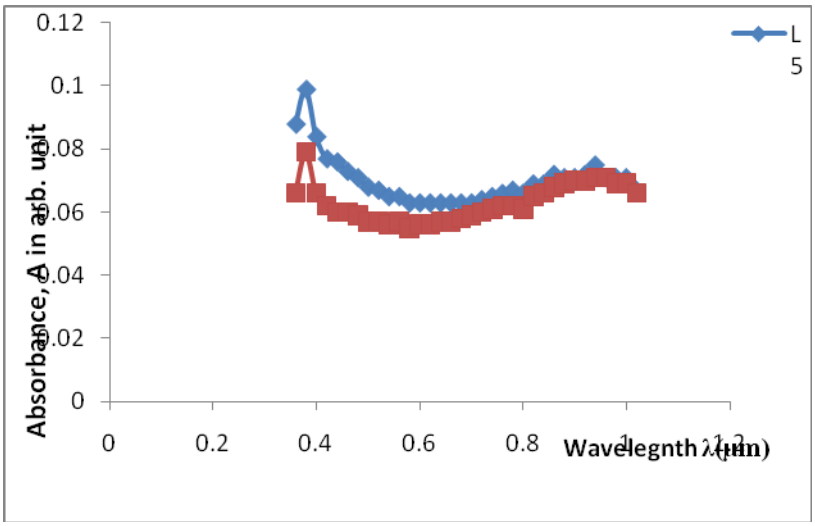

Fig. 4 Spectral absorbance of SnSe for L5 & L7

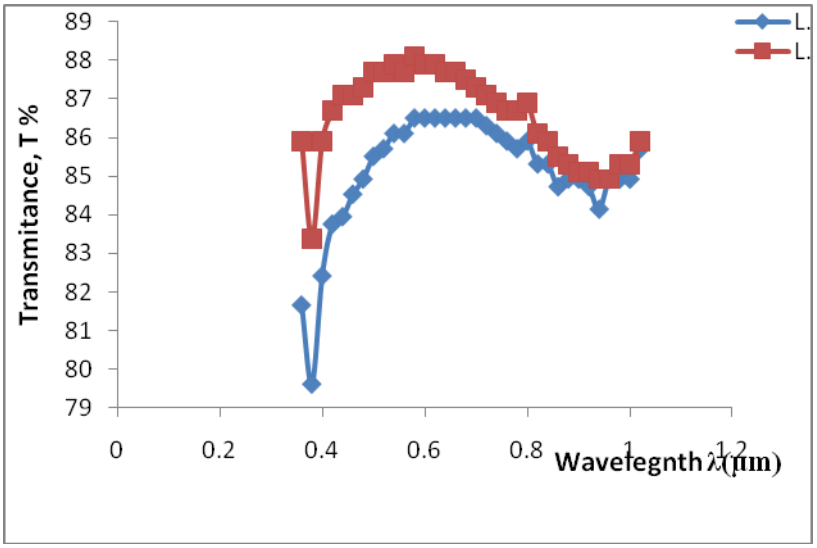

Fig. 5 Spectral transmitance of SnSe for L5 & L7

Figs. 4 and 5 show the optical absorbance and transmittance spectra of the films deposited in this work. The films absorb moderately in the UV region but show a steep decay of the absorbance with longer wavelength showing a low absorbance in VIS-NIR region of the spectrum. The high absorbance in the UV region makes the material useful in forming p-n junction solar cells with other suitable thin film materials for photovoltaic applications. The transmittance spectra displayed in figure 4 show very high transmittance in the UV-VIS-NIR regions of the electromagnetic spectrum. The very high transmittance in the visible region makes SnSe films useful aesthetic window glaze material.

The band gap energy and transition types were derived from mathematical treatment of the data obtained from the optical absorbance versus wavelength with the following relationships for near edge absorption.

$$\alpha=(hv-\varepsilon g)^{n/2}$$

Where V is the frequency, h is the Planck's constant, while n carries the value of either 1 or 4. The band gap could be obtained from a straight line plot of α^2 as a function of hv, an extrapolation of the value of α^2 to zero will give band gap. If a straight line graph is obtained from n=4, it indicates a direct transition between the states of the semiconductor, whereas the transition is indirect if a straight line graph is obtained from n=4.

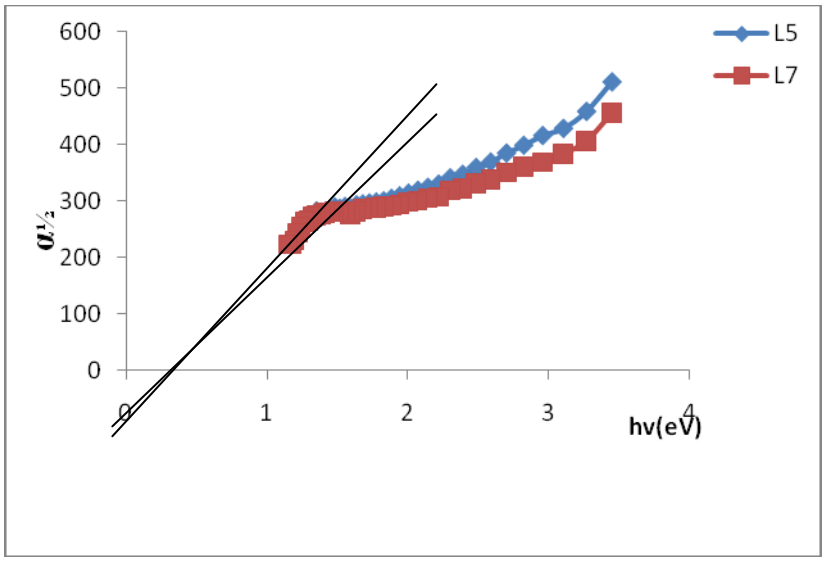

Fig.6 Plot of α² versus photon energy (hv)

For the present work, an indirect transition were obtained as shown in figure 6, and the band gap for the film is 1.5 eV. A similar band gap has been reported by other researchers.

Saravanan (2004) reported a direct band gap of 1.23 eV.

Nariya et al (2009) reported an indirect band gap value of 1.0 eV by direct vapor transport technique. Zulkarnain et al (2001) reported an indirect band gap of 1.25 eV by a combination of chemical precipitation and vacuum evaporation technique. The blue shift of 0.25 – 0.5eV were attributed to the deposition conditions for the film.

4. Conclusions

Tin selenide films have been successfully carried out using chemical bath deposition technique. Good quality films of tin selenide with orthorhombic phase of SnSe was deposited. The preferred orientation of the crystallites lies along the (201) plane. The band gap was found to be indirect and about 1.50 eV. The films were found to have high absorbance in the UV region and depreciate as the wavelength increased. They have generally high transmittance.

The film has the potential for use as aesthetic window glaze and in forming p-n junction solar cell.

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