INVESTIGATION OF pH EFFECT ON CHEMICALLY SYNTHESIZED TIN SELENIDE FILMS

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Abstract

Semiconducting thin films of tin selenide (SnSe) were chemically synthesized at room temperature by varying two different pH. X-ray diffraction data revealed that the crystallinity of SnSe films prepared at pH 11.0 slightly increased. XRD patterns of SnSe showed polycrystalline nature. The optical properties of the films were studied in the wavelength range of 0.36-1.10 μm. Optical absorption studies show that the pH has no effect on the band gap energy of the grown SnSe films; hence, the band gap remains the same as pH increases from 10.0 to 11.0.

1. Introduction

Thin films of IV–VI semiconductors are important for their applications in optoelectronic devices, such as memory switching devices, photovoltaic, and light emitting devices [1]. Since the energy band gap of SnSe film is within a range of 1.5 eV, the materials are important for solar cells. Some techniques, such as thermal evaporation [2-3], vacuum deposition [4], chemical bath deposition (CBD) [5], hot wall epitaxy [6], and flash evaporation [7], are widely used to synthesize tin selenide thin films. Among these techniques, CBD is commonly employed because it is a very simple, cost-efficient, and convenient technique, mostly used in the production of large-area devices that results in high-quality films that can compete with films obtained by more sophisticated methods. The thin films deposited by this method include PbS, SnS, CdSe, and MnS, which are thoroughly described in the literature [8-11]. This method is based on the reaction between dissolved tin and selenide ions in acidic water. In this study, films of tin selenide are deposited using CBD from an aqueous medium at different pH values. The EDTA was used as a complexing agent. This is a resultant component from a slow precipitation of the compound reducing the releasing rate of the metallic ions. Using a UV-VIS model spectrophotometer, the optical properties of the films are studied. For structural determination, the films are studied using an X-ray diffractometer.

2. Materials and Methods

Tin selenide films were deposited onto glass substrates using the CBD method at room temperature. The reagents used were tin chloride ($SnCl_2$), potassium selenate (K_2SeO_4), and EDTA. Distilled water was used as the solvent for the preparation of the solutions. During the deposition, EDTA was used as the complexing agen, while tin chloride is the source of tin ion, and potassium selenate is the source of selenide ion. In the process, 5 ml of 0.2M $SnCl_2$ was placed in a 50-ml glass beaker; EDTA was added to it under constant stirring, and complex [Sn (EDTA)] $^{2+}$ was formed. Five millilitres of 0.5M K_2SeO_4 was added to it. An ammonia solution was added to the above prepared solution in order to obtain a pH value of 10.0 and 11.0, respectively. The volume was made up to 50 ml 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 the air. The basic steps involved in the chemical deposition of a SnSe film are given below.

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

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

$$K_2\,Se\,O_4 + OH^- \leftrightharpoons K_2O_5 + HSe^-$$

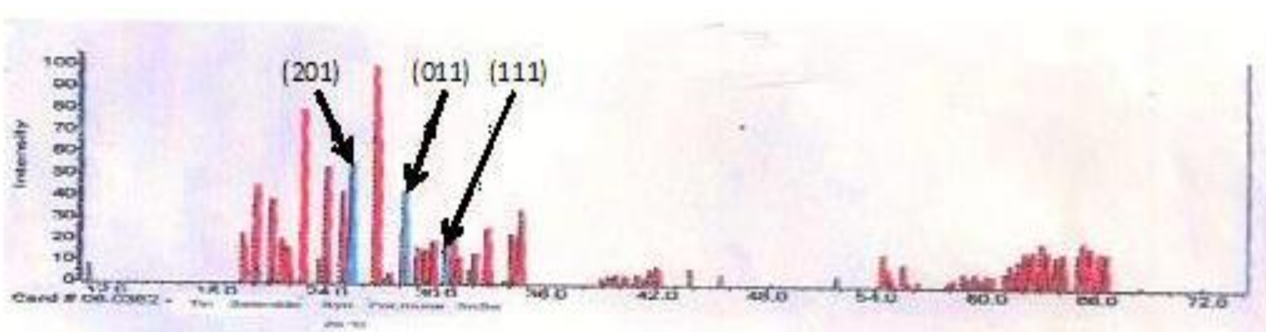
$$HSe^- + OH^- \rightleftharpoons {}^{v}Se^{2-} + H_2O$$

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

3. Results and Discussion

3.1 Structural properties of tin selenide films

The change in structure and identification of phases is studied with the help of an X-ray diffractometer using CuKα radiation ($\lambda = 1.5418$ Å). The X-ray diffraction patterns at pH 10.0 and 11.0 of SnSe thin films are shown in Fig. 1.The X-ray diffraction patterns at different pH reveal that the samples show a polycrystalline and orthorhombic nature. The diffraction angle 2Θ value is 25.66˚ with d = 3.34Å ˚ at lower pH 10.0 and has three peaks, and diffraction peaks corresponding to 2Θ = 28.99˚ and 30.85˚ with d = 3.08 and 2.90 Å are also observed. As the pH value is increased, the number and intensity of the peaks also increase corresponding to 26.09, 28.32˚, 31.00˚, and 51.58˚. The number of peaks observed at pH 11.0 is increased to four. The corresponding peaks referred to the (201), (011), (111) and (221) planes of reflections of SnSe and a number of elemental peaks for Sn and Se were observed. The observed peaks were identified by comparing the d-spacing values obtained from XRD patterns for SnSe [12]. The crystallinity also increased, as evidenced by the sharpness of the peaks.



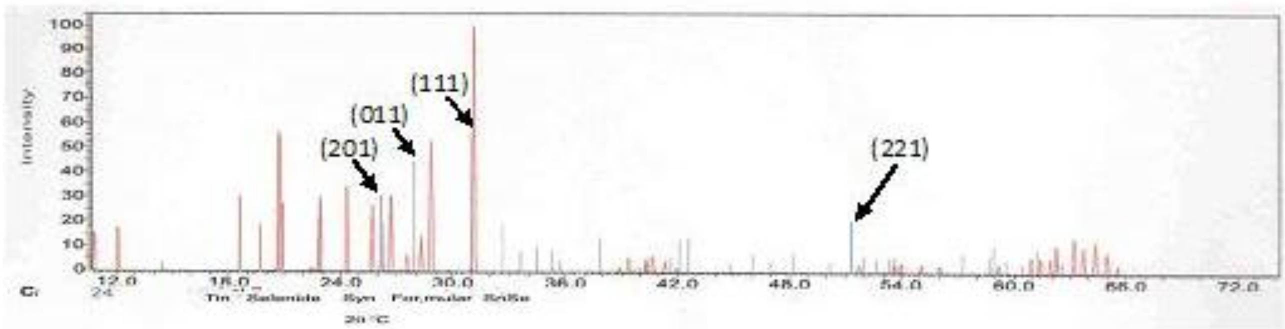


Fig. 1. X-ray patterns of SnSe thin films deposited at pH 10.0 and 11.0 .

Table 1. Structural parameters of SnSe thin films

Thickness t (μm)	h k l	2θ (deg)	d (Å) Measured	d (Å) Standard	Grain size, D (Å)
1.62	201	26.66	3.34	3.52	3.74
	011	28.99	3.08	3.05	3.76
	111	30.85	2.90	2.95	3.78
1.64	201	26.09	3.41	3.52	3.74
	011	28.32	3.15	3.05	3.77
	111	31.00	2.93	2.95	3.78
	221	51.58	1.75	1.80	4.12

Table 1 shows that the grain size of the film increases with pH likewise the film thickness, which increases as pH of the reaction bath increases and greater thickness minimizes imperfection.

3.2 Optical properties of SnSe films

The optical properties of SnSe films were studied using a Janway 6405 UV-Visible model of the spectrophotometer in a wavelength range of 0.36-1.10 μm. The relation between the absorbance and wavelength of the films at different pH is shown in Fig. 2. All the films prepared at pH 10.0 -11.0 absorb moderately in the visible region.

The transmission spectra of the SnSe thin films deposited at different pH values of the chemical bath are shown in Fig. 2. It is evident that transmission is slightly improved with increasing pH value. All deposited films exhibited transmittance between 79% and 89% in the visible region. The transmittance spectra in Fig. 3 show very high transmittance in the VIS-NIR regions of the electromagnetic spectrum.

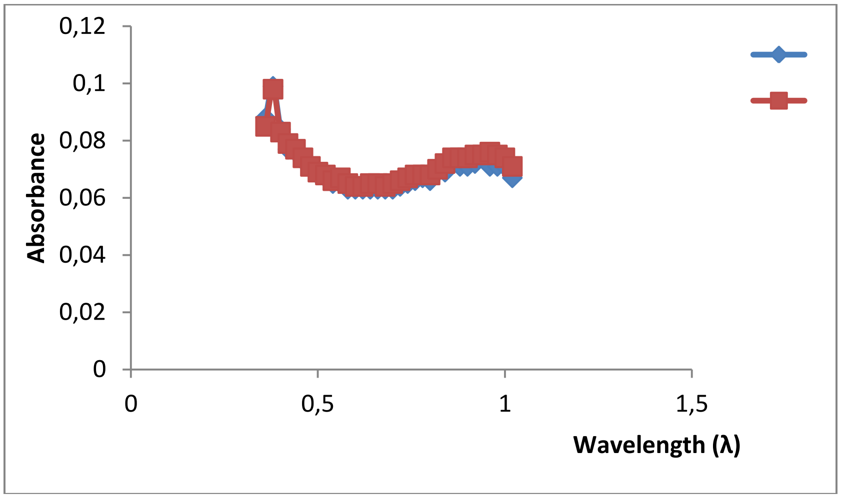


Fig. 2. Optical absorbance spectra of SnSe films deposited at pH 10.0 and 11.0.

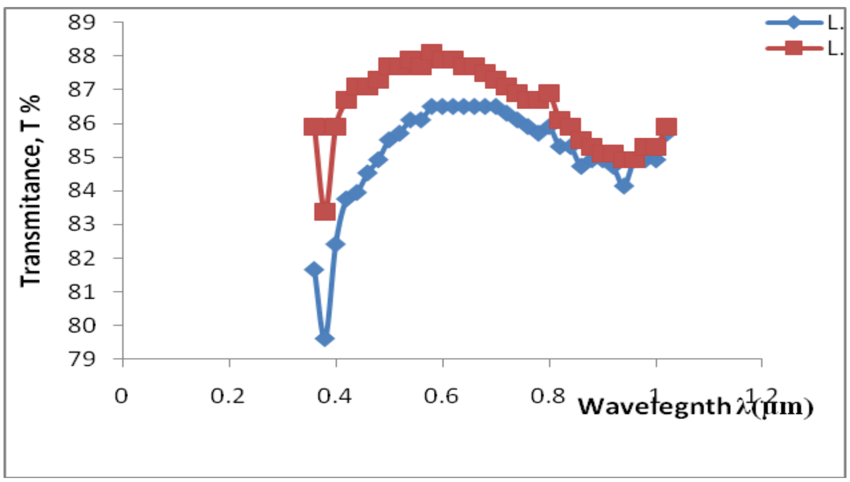


Fig. 3. Optical transmission spectra of SnSe films deposited at pH 10.0 and 11.0.

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

$$\alpha = (h\upsilon - \varepsilon_g)^{n/2},$$

where υ 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 or $\alpha^{1/2}$ as a function of hυ; an extrapolation of the value of α^2 or $\alpha^{1/2}$ to zero will give band gap. If a straight line graph is obtained from n=1, 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 as shown in Fig. 4. The pH has no significance effect on the band gap energy; hence, the band gaps remain the same (1.5 eV) as the pH value was increased from 10.0 to 11.0.

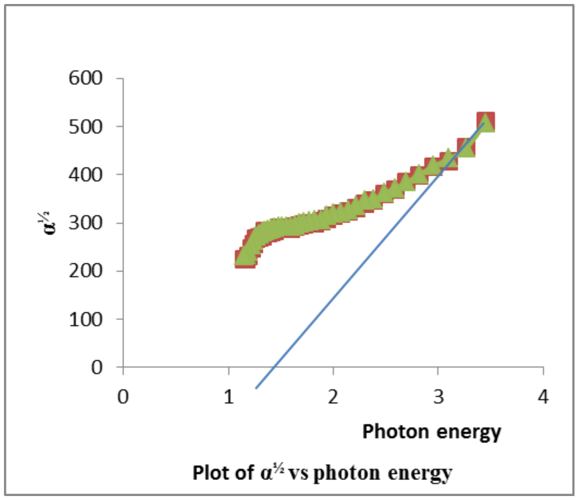


Fig. 4. Plot of $\alpha^{1/2}$ versus photon energy of the SnSe film with varied pH values of 10.0 and 11.0.

4. Conclusions

Tin selenide films have been successfully studied using the CBD technique. High-quality films of tin selenide with an orthorhombic phase were deposited. The band gap was found to be indirect and about 1.50 eV. The films were found to have moderate absorbance in the visible region. They have generally high transmittance which increases as the pH value increases. The film can be used as an aesthetic window glaze and in forming p-n junction solar cells.

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