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# Preparation, Synthesis and Optical characterization of Vacuum evaporated $Sn_xSe_y$ alloys thin films

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## Abstract

The optical characteristics properties of tin selenide compound especially in thin films plays a significance role their application especially photodetectors and storage devices, such PRAM. $Sn_xSe_y$ thin film alloys were grown by vacuum evaporation. The Ingots of Tin and Selenium have been prepared using their constituent elements synthesized in various ratios. The optical transmittance of the thin films was carried out between 450-2500 nm. The optical absorption studies indicated a direct band gap ranging from 1.27-1.94 eV. The band gap energy was found to increase with decrease in Tin concentration of the alloy.

Keywords: vacuum deposition; optical properties; tin selenide alloys; thin films

## 1. Introduction

Motivated by the potential applications of Tin chalcogenides, investigations on these compounds are becoming particularly active in the field of materials science. Tin chalcogenides offers a range of optical band gaps suitable for various optical and optoelectronic applications such as memory switching, photoelectrical cells, holographic recording systems [1-4].. These compounds are also used as sensor and laser materials, thin films polarizers and thermoelectric cooling materials SnSe is a narrow band gap binary IV–VI semiconductor exhibiting anisotropic character [5-6].

Recently, much attention has been given to find ways of reducing the cost of opto-electronic consumer products to make them affordable to everyone so that they can be socially acceptable and easily marketable. One way of achieving this is to use thin films instead of bulk single crystals for such devices [7]. The structure of the deposited thin

films strongly influences the electronic properties which are highly dependent on the preparation technique and deposition conditions. Considerable attention has been devoted by various authors to the preparation of SnSe thin films by different methods like vacuum evaporation [8].

Thin film deposition of SnSe alloys has been widely described in the literature. Chemical bath deposition, electro-deposition , solid state reactions, solvothermal, molecular beam epitaxy and pulsed laser deposition have been used to grow SnSe thin films [9]. Further, the technique adopted should be simple and cost effective. Every technique has associated with it, its own merits and demerits. Various vacuum deposition techniques have been implemented for the growth of SnSe thin films starting from single-source [10].

One of the properties of semiconductors which is very important for device applications is the band gap energy. The best values of the band gap are obtained by optical absorption. If the band gap energy is sufficiently small, thermal excitation can promote an electron from the valence band to the conduction band. If impurities are present in the band gap, thermal excitation can also be used to excite an electron from an impurity level to the conduction band [11]. In this work, the band gap energies of thin films of $Sn_xSe_y$ alloys have been studied. The thin films were deposited on microscopic glass slide substrates using single source vacuum evaporation technique.

## 2. Experimental

Ingots of $Sn_xSe_y$ have been prepared under vacuum conditions using their constituent elements of (99.999% pure) tin and selenium (obtained from M/S Aldrich, USA) weighed in molecular ratios. The powdered mixture of Sn and Se was sealed under vacuum conditions (10−3 mbar) in an ampoule and heated to 1200 K to ensure a Sn/Se solid state reaction in the melting phase of the mixture. The choice of the maximum heating temperature was determined by the highest melting temperature of the Sn–Se phases (melting temperature of the SnSe phase is 1173 K). The sealed silica tube was thoroughly agitated during heating to ensure sample homogeneity and then rapidly

cooled to room temperature. This process was repeated two to three times to ensure homogeneity of mixture before pulverizing.

The $Sn_xSe_y$ powder was evaporated using a molybdenum boat in the Edward 306 sputtering system. The composition of the powder was determined to (20±2) at.% Sn and (80±7)at.% Se for $SnSe_4$, (28±2)at.% Sn and (72±7)at.% Se for $Sn_2Se_5$, (36±3)at.% Sn and (64±6)at.% Se for $Sn_4Se_7$ and (50±3)at.% Sn and (50±1)at.% Se for SnSe respectively by Energy dispersive X-ray fluorescence (EDX).

## 2.1 Optical measurement

Optical properties of the thin film samples were determined by use of the transmission data in the range from 450 nm- 2500 nm and obtained using Shimadzu UV-VIS-NIR 3700/3700DUV spectrophotometer. The thickness of the thin film was 150 nm as-deposited and was measured using Profilometer Alpha-step IQ.

# 3 Result and Discussions

## 3.1 Transmittance

Figure 1 shows the spectral transmittance for 150 nm $Sn_xSe_y$ thin films prepared at different stoichiometric ratio as a function of wavelength. Transmission seems to vary with increase in wavelength as well as material composition. When composition of tin increased, the transmittance decreased considerably since tin is basically reflective.

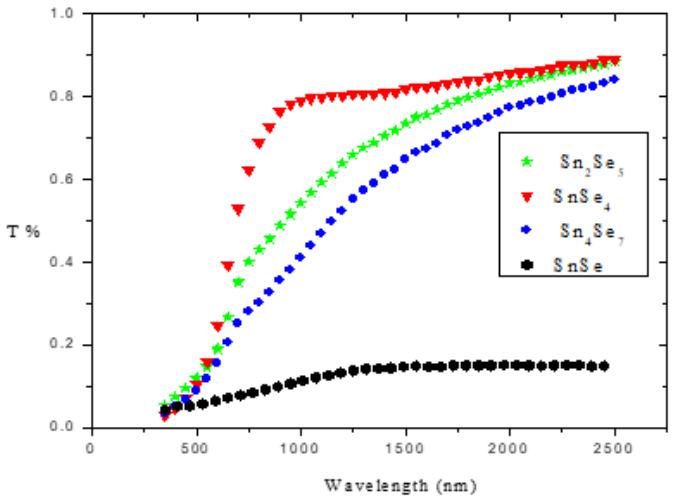


**Fig. 1:** Transmittance versus wavelength for 150 nm $Sn_xSe_y$ thin films alloys.

## 3.2 Band gap Analysis

Using equation [1], optical band gap and type of transition can be been determined.

$$(\alpha h\nu)^{n/2} = A(h\nu - E_g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[1]$$

Where A is edge width parameter, $\nu$ is the frequency, $h$ the Planck's constant, while $n$ carries the value of either *1* or *4*. The graphs in figure 2, 3, 4, 5 shows the plot of $(\alpha h\nu)^{2/n}$ as a function of $h\nu$ of the film for *n=1*. Extrapolation of the line to the base line, where the value of $(\alpha h\nu)^{2/n}$ is zero, will give an optical bandgap [12]. A straight line graph obtained for $n$ = 1, indicates a direct electron transition between the states of the semiconductor.

A plot of $(\alpha h\nu)^2$ as a function of $h\nu$ is shown in fig. 2 and it is linear in the strong absorption near the fundamental absorption edge. Since the value of $\alpha$ is in the order of $10^6$ $m^{-1}$ and the absorption coefficient is measured at room temperature, the presence of exciton bands is not likely to be possible. Therefore, the absorption is from a band to band transition and it is only due to an allowed direct transition from the top of the valence band to the bottom of the conduction band at the center of the brillouin zone. The band gap energy value obtained for the direct transition was 1.27 eV for the SnSe thin film. This energy band gap is comparable with those reported by various researchers for SnSe using different preparation techniques ,for instance, 1.25 eV reported by Zainal *et al.* [13], 1.26 eV reported by Hema *et al*. [14] and reported by Soliman *et al*. 1.27 eV [15].

The energy band gap for other alloys were given as 1.77 eV, 1.83 eV and 1.94 eV for fig. 3, 4 and 5 respectively. However, there was no reported previous research done on those alloys from these figures, a plot of $(\alpha h\nu)^2$ versus $h\nu$ indicates that there is some tailing in the band gap below the absorption edge. This indicates that there is a high concentration of impurity states in the polycrystalline thin films which can cause a perturbation of the band structure with the result that the parabolic distribution of the states will be disturbed by a prolonged tail into the energy gap [16]. The tails in the optical spectra of the films could be due to the broadening of the impurity levels due to their spatial overlap into a band. At high concentrations, the impurity band merges with the nearest intrinsic band. Due to this, the fermi level will lie inside the parabolic portion

of the appropriate band. Thus, less activation energy will be needed for the electrons to move from the Fermi level into the conduction band. The tails could also be due to ionized donors which could exert an attractive force on the conduction electrons and a repulsive force on the valence band. On a microscopic level, the nonhomogeneous distribution of the impurities to a smearing of the band edges [17].

Table 1: **Comparative data on alloys formed, percentage of tin present and its corresponding optical energy gap.**

| **Alloy** | **% of Sn** | **Energy gap** |
|---|---|---|
| SnSe | 50 | 1.27 |
| $Sn_4Se_7$ | 36 | 1.77 |
| $Sn_2Se_5$ | 28 | 1.83 |
| $SnSe_4$ | 20 | 1.94 |

From table 1, the increase in concentration of tin lowered the optical band gap, this is due to new structural units formed with lower optical threshold energy. The presence of such units, contributed to the lowering of the mean value of the bandgap in the alloys [10].

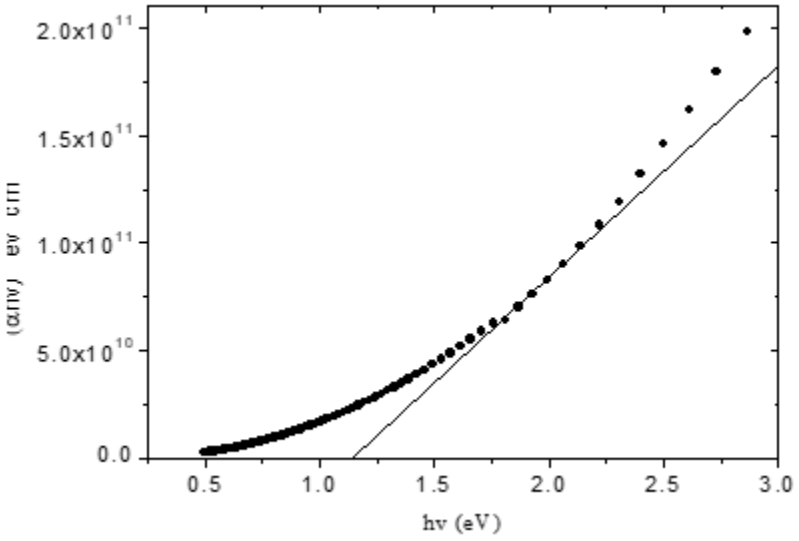


**Fig. 2**: A graph of $(\alpha hv)^2$ against energy of as -deposited 150 nm SnSe thin film.

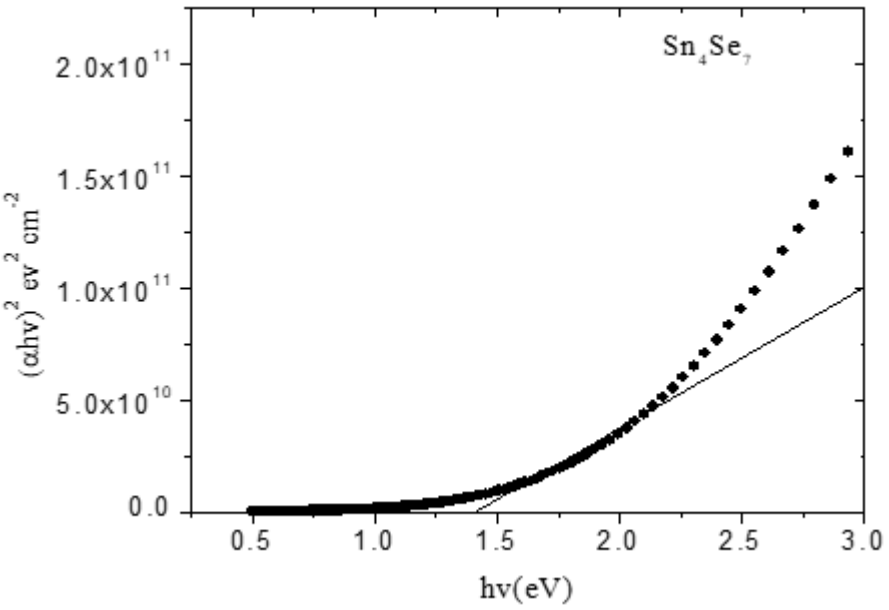


**Fig.3**: A graph of $(\alpha hv)^2$ against energy of as-deposited $Sn_4Se_7$ 150 nm film.

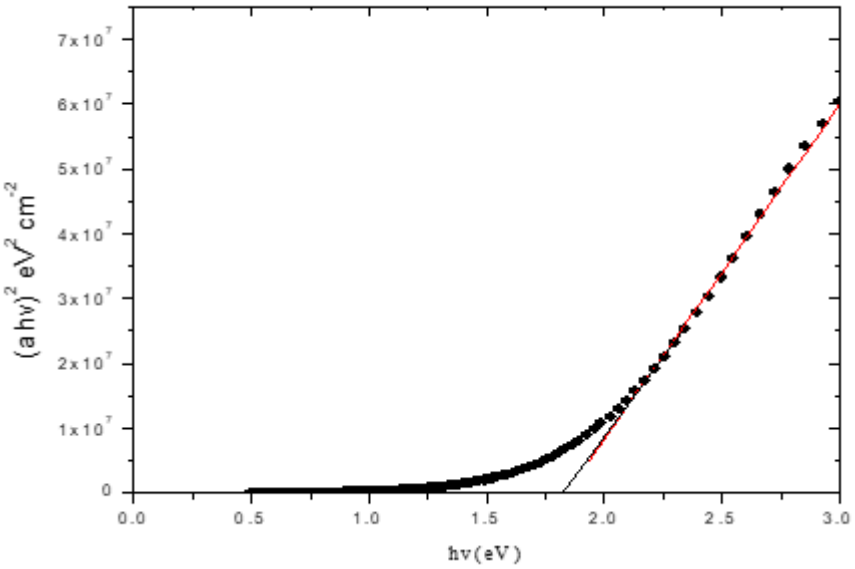


**Fig. 4**: A graph of $(\alpha hv)^2$ against energy of as-deposited $Sn_2Se_5$ 150 nm thin film.

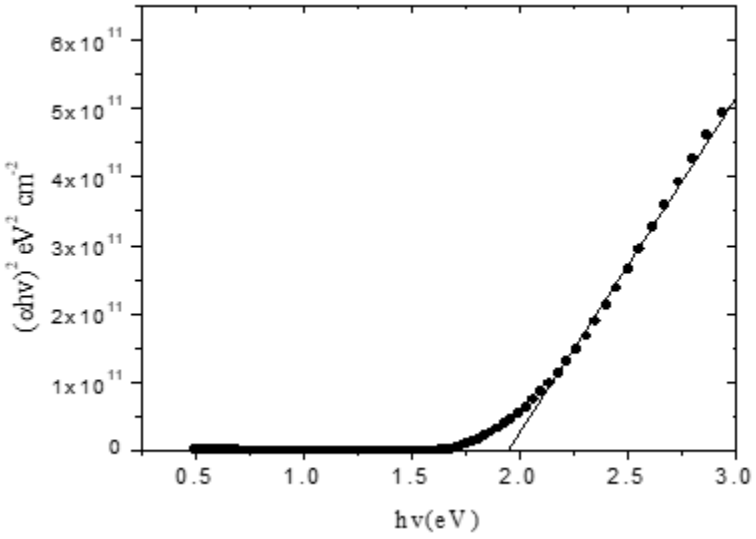


**Fig. 5**: A graph of $(\alpha h\nu)^2$ against energy of as-deposited 150 nm $SnSe_4$ thin film.

## 4. Conclusion

$Sn_xSe_y$ thin film alloys were grown by vacuum evaporation. The thickness of the films was found to be 150 nm. The transmittance of the thin films was measured from 450-2500 nm using Shimadzu UV-VIS-NIR 3700/3700DUV spectrophotometer. The optical absorption studies indicates a direct band gap ranging from 1.27-1.94 eV. The band gap energy was found to increase with decrease in tin concentration. This is due to formation of a new structural units formed with lower optical threshold energy. Metals have overlapping valency and conduction bands with no energy band gap. Hence as tin concentration increased, the energy band gap decreased. This is due to new structural units formed with lower optical threshold energy. The presence of such units, contributed to the lowering of the mean value of the bandgap in the alloy

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