

## OPTICAL PROPERTIES OF TIN-ANTIMONY-SELENIUM BASED AMORPHOUS THIN FILMS

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### ABSTRACT

Tin-Antimony-Selenium (TAS) based amorphous belongs to the ternary chalcogenide compounds of IV-V-VI group, exhibiting semiconducting properties that could be applied for optical devices in photo-conductive sensors and infrared transmission detectors. The materials were previously studied with emphasize on the structural properties separating the amorphous,  $\alpha$  and crystalline regions,  $c$ . This paper reports the optical properties of TAS measured using UV spectrophotometer observe the respective absorption spectrum over the visible and near infrared regions and determine the bang gap energies from the plot absorption edges. TAS samples were prepared from granular Sn, Sb and Se of purity 5N using a technique called solid-state reaction. In this method starting materials were thermally evaporated at a pressure of  $10^{-5}$  mbar onto glass substrate as Sn/Se/Sb/Sn stacked at a substrate temperature of 240 °C. The system employed was a vacuum coater model E306. The spectrum observed from the absorption-wavelength plots appeared to be a steady decrease in the visible region followed by a sharp drop and a further gradual declining down to near infrared at 2100 nm, with absorption coefficient,  $\alpha$  varying from  $6.21 \times 10^3$  to  $1.55 \times 10^5 \text{ cm}^{-1}$  for film thickness between 50 nm to 700 nm, respectively. The corresponding optical band gap,  $E_g$  obtained from the graph  $(\alpha h\nu)^2$  versus  $h\nu$  resulted in  $E_g$  between 1.47 eV to 1.69 eV which were dependent of film thickness. The value of other optical properties namely refractive indices, extinction coefficient, effective mass and dielectric constant was also being determined and were found to be 2.55–2.85,  $0.1 \times 10^{-2}$  –  $1.1 \times 10^{-2}$ ,  $1.42 \times 10^{-33} \text{ kg}$  and 0.006–8.094, respectively. These values varied with the film thickness.

s: Tin-Antimony-Selenium, Amorphous, Thin film.

### INTRODUCTION

Tin-Antimony-Selenium (TAS) ternary system are generally chalcogenide compounds from group IV-V-VI of the periodic table that can exist in the form of crystalline or amorphous state depending on the preparation technique. It exhibits semiconducting properties that has a quite a number of potential application in optical devices namely xerography (Kawamura, 1983), solar cells (Robert, 1998), infrared optics and switching devices (Ovshinsky, 1994). The materials were previously studied (Abdalla, 2002) with emphasize given on the structural properties separating the amorphous,  $\alpha$  and crystalline regions,  $c$  as shown in Figure 1.

Whereas in this experiment, studies would be focused on the optical properties of the TAS thin film with much consideration on the amorphous region.

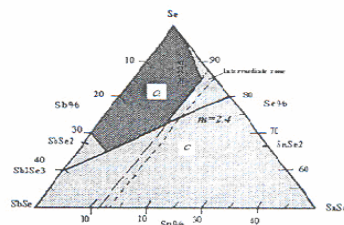


Figure 1: Triangle structure of ternary Sn-Sb-Se system, the shadowed portion represents the region that covered in this study.

## EXPERIMENTAL

The TAS samples were grown using Sn, Sb and Se granular and thermal evaporating technique. The granulated powder of Sn-Sb-Se was prepared by heating the elements (5N purity) in stoichiometric proportion in a vacuum-sealed quartz ampoule ( $<10^{-4}$  Pa) to a temperature of 650 °C for 48 hours. The ampoule was then quenched in cold water and let cool down to room temperature. The content were broken finely and put in other vacuum-sealed quartz ampoule ( $<10^{-4}$  Pa) for a second heat treatment identical to the first one. The starting materials were then thermally evaporated at a pressure of  $10^{-5}$  mbar onto Corning glass 2947 substrate as Sn/Se/Sb/Sn stacked layers at a substrate temperature of 240 °C. The system employed was a vacuum coater model E306. The thickness of the films deposited was controlled by a quartz crystal monitor and was further confirmed by a mechanical stylus pofilometer. Eight set of samples was prepared with thickness varying from 50 nm to 700 nm. The deposition parameters can be summarized in Table 1. The optical measurements of the films deposited were carried out using a Shimadzu UV-3101-PC spectrophotometer at around 300-2100 nm wavelength. Whereas the ellipsometer together with BBC Elip software were employed to obtain the refractive index and extinction coefficient of the samples.

Table 1: The deposition parameters.

Source	molybdenum boat
Vacuum	1 cm <sup>2</sup> area
Distance	10 <sup>-5</sup> mbar
(source-substrate)	25 cm
Thickness	50 to 700 nm
Substrate temperature	240 °C

## RESULT AND DISCUSSION

The optical measurements were carried out at room temperature using UV Spectrophotometer. The transmittance was measured from 300 to 2100 nm wavelength. The absorption coefficient  $\alpha$  was determined from transmission measurements  $T$ . neglecting interference effects,  $T$  is determined by (Moss, 1959)

$$T = \frac{(1-R)^2(1+k^2/n^2)}{\exp(\alpha d) - R^2 \exp(-\alpha d)} \quad (1)$$

$d$  is the sample thickness and  $R$  the reflectivity given by,

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (2)$$

where  $n$  and  $k$  are refractive index and extinction coefficient respectively.

Or  $k^2 \ll n^2$  in experiments on semiconductors so that the average transmission and reflectivity are,

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (3)$$

$$T = \frac{(1-R)^2}{\exp(\alpha d)} \quad (4)$$

In our case, the absorption coefficient,  $\alpha$  at wavelength  $\lambda$  was determined from the measured transmittivity of TAS films of different thickness,  $d$  by plotting  $\ln T$  against  $d$ . Equation (4) is simplified by considering  $R$  is small enough for  $(1-R) \approx 1$ , thus yielding,

$$T = \frac{1}{\exp(\alpha d)} \quad (5)$$

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right) \quad (6)$$

From the absorption coefficient,  $\alpha$  graph plotted against the wavelength,  $\lambda$  (as shown in Figure 2), it is observed that there is a steady decrease in the visible region followed by a sharp drop and further gradual declining down to near infrared at 2100 nm with  $\alpha$  varying from  $6.21 \times 10^3$  to  $1.55 \times 10^5 \text{ cm}^{-1}$  for film thickness between 50 nm to 700 nm, respectively. Thus in general, it can be seen that there is a high absorption for all samples at visible region. It is interesting to note that the absorption spectrum obtained can be classified into two groups which are; (1) For thicker films ( $d = 400\text{-}700 \text{ nm}$ ), the absorption coefficient,  $\alpha$  lies between  $1.20 \times 10^5 - 1.55 \times 10^5 \text{ cm}^{-1}$ , (2) For thinner film ( $d = 50\text{-}300 \text{ nm}$ )  $\alpha$  lies between  $6.21 \times 10^3 - 4.00 \times 10^4 \text{ cm}^{-1}$ . Here, the absorption coefficients of the samples tend to vary with the film thickness,  $d$ , markedly between thicker and thinner film. Absorption coefficient,  $\alpha$  of the film increases (from  $6.21 \times 10^3$  to  $1.55 \times 10^5 \text{ cm}^{-1}$ ) with the thickness increment (from 50 nm to 700 nm). This is in accordance with the results obtained by El-Nahas *et al.* (1992) where  $\alpha$  increases from  $0.9 \times 10^3 \text{ cm}^{-1} - 5.0 \times 10^5 \text{ cm}^{-1}$  as sample thickness increases.

This can be explained by referring to equation (6). When the thickness of the film increases, the color of the film tends to turn dark. This would less significantly permit the light passing through the sample. Thus transmission decreases while absorption increases. In other word, as the film gets thicker, absorption would increase and less dispersed due to drop of transmission.

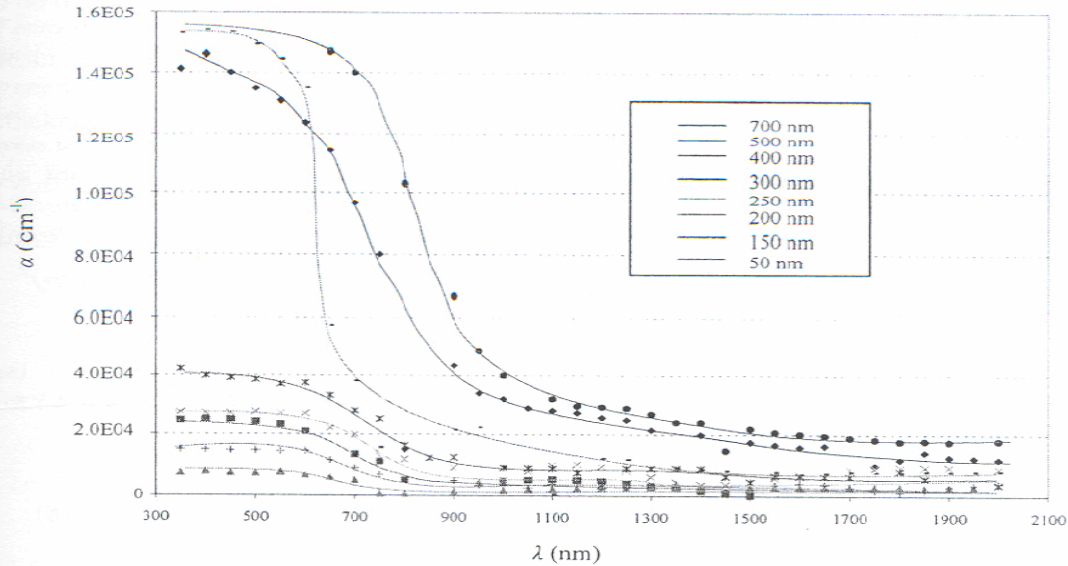


Figure 2: Spectral variation of absorption coefficient  $\alpha$  for different film thickness.



According to Tauc *et al.* (1966), for direct transition, the absorption coefficient  $\alpha$  is given by the equation

$$(\alpha h\nu) = B(h\nu - E_g)^2 \quad (7)$$

where  $h\nu$  is the photon energy and  $E_g$  is the optical band gap of the sample. From the above equation, the optical band gap can be obtained by plotting the square of the product of the absorption coefficient and the photon energy  $(\alpha h\nu)^2$  against photon energy ( $h\nu$ ). The intercept on the abscissa is obtained by extrapolating the linear portion of the plot, yielding the optical band gap,  $E_g$ .

From the graph shown in Figure 3 it is observed that as thickness of the sample increases the optical band gap was found to be decreasing from 1.69 eV to 1.47 eV. This is due to quantum size effect that generally appears on semiconducting material with its thickness nearing or smaller than the mean-free path of the collision between electrons. When thickness decreases, the optical band gap increases as a result of the quantization.

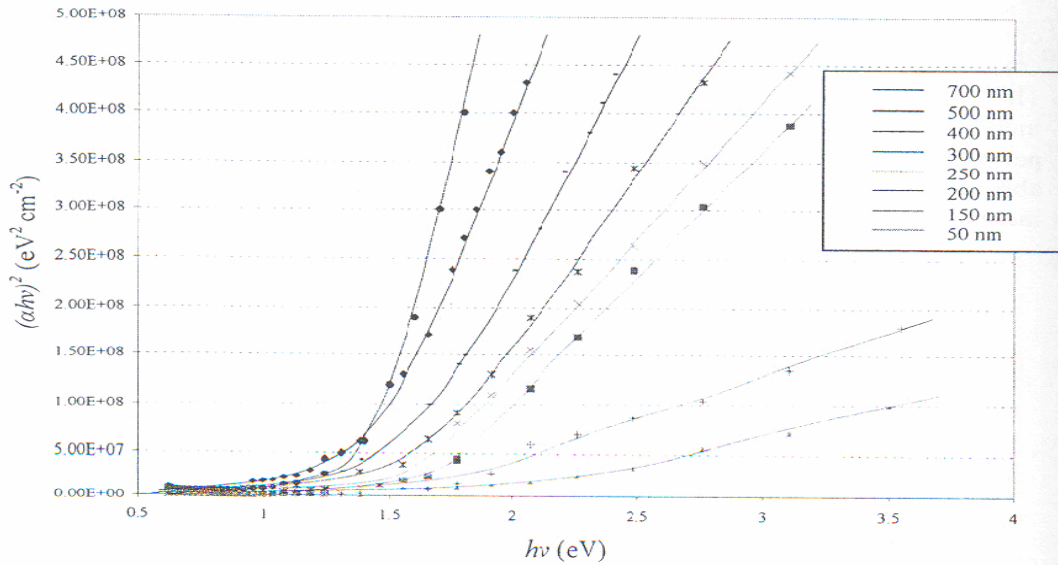


Figure 3: The absorption edge of TAS film at different thickness plotted as  $(\alpha h\nu)^2$  against photon energy.

The effective mass of the samples was obtained by plotting  $E_g$  against  $1/d^2$  (see Figure 4). The slope of the linear graph plotted was found to be  $2.4 \times 10^{-16} \text{ eV m}^{-2}$ . Using the equation,

$$\Delta E \sim \frac{h^2}{8m^*d^2} \quad (8)$$

$m^*$  - effective mass of the carriers  
 $d$  - film thickness  
 $h$  - Planck's constant

the effective mass of the carriers can be obtained which yield  $1.42 \times 10^{-33}$  kg or  $1.57 \times 10^{-3} m_o$  ( $m_o$  – rest mass of the electron).

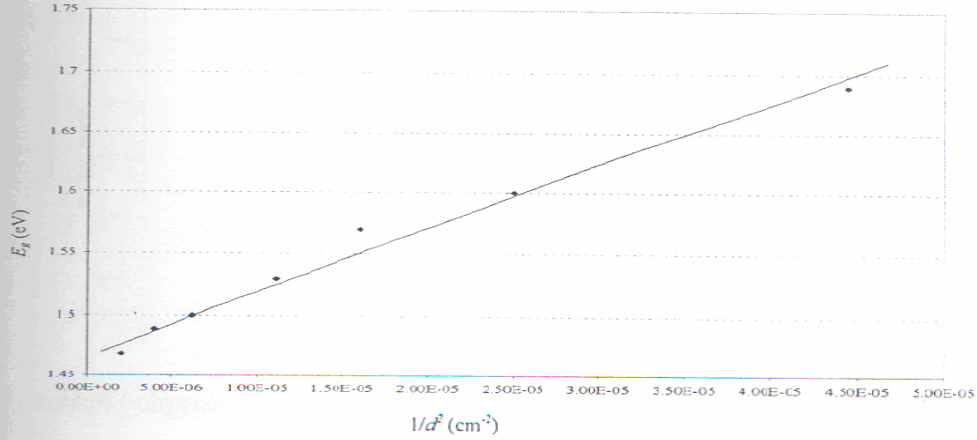


Figure 4: Optical band gap,  $E_g$  vs.  $1/d^2$

#### *Refractive Index and Extinction Coefficient*

Data obtained from ellipsometry measurement were processed using BBC Elip software to obtain the refractive index,  $n$  and extinction coefficient,  $k$  of the samples. The results ( $n, k$ ) were plotted against thickness of the samples as shown in Figure 5. From the graph plotted, it can be seen that there is an increment of refractive index from 2.55 to 2.85 for all samples as their thickness decreases. These results are generally valid since the understanding of transmittivity of films with different thickness reveals that the film becomes more opaque as it gets thicker. This would also lead to the increment of its refractive index (Sabar, 1998). As for the extinction coefficient,  $k$ , when  $k$  was plotted against thickness of the samples, it was found  $k$  increases from  $0.1 \times 10^{-2}$  to  $1.1 \times 10^{-2}$  as thickness increases from 50 nm to 400 nm (see Figure 5).

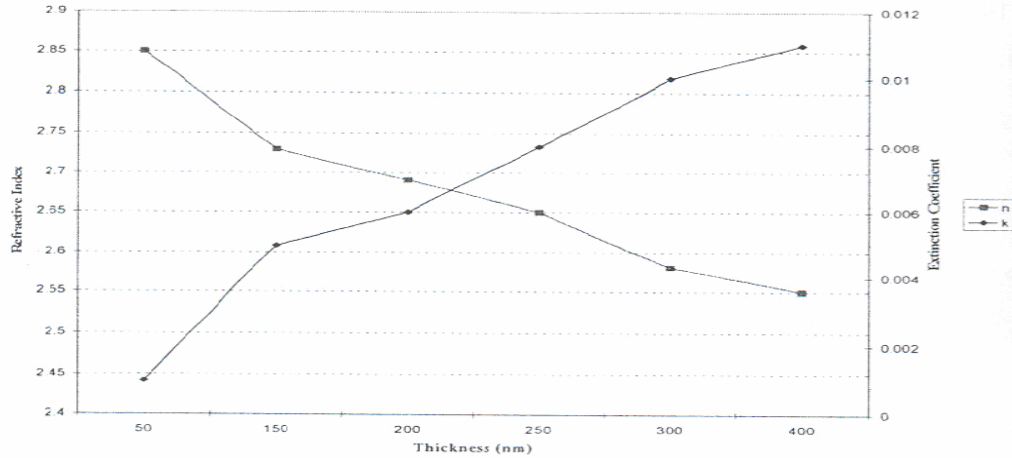


Figure 5: Refractive index,  $n$  and extinction coefficient,  $k$  vs. sample thickness,  $d$ .

An absorbing medium is characterized by a complex dielectric constant  $\varepsilon = \varepsilon_r - i\varepsilon_i$ , where  $\varepsilon_r$  – real dielectric constant,  $\varepsilon_i$  – imaginary dielectric constant, and a complex refractive index  $n - ik$ . It follows from the Maxwell equations that  $(n - ik)^2 = \varepsilon_r - i\varepsilon_i$ , so that the

$$\varepsilon_r = n^2 - k^2 \quad (9)$$

$$\varepsilon_i = 2nk \quad (10)$$

Using the equation (9) and (10) the real dielectric constant,  $\varepsilon_r$  and imaginary dielectric constant  $\varepsilon_i$  was obtained and plotted against the sample thickness as shown in Figure 6. From the graph plotted, it is obviously seen that  $\varepsilon_r$  decreases from 8.094 to 6.502 as film thickness increases from 50 nm to 400 nm. Whereas the  $\varepsilon_i$  shows an increment from 0.006 to 0.056 as the film gets thicker.

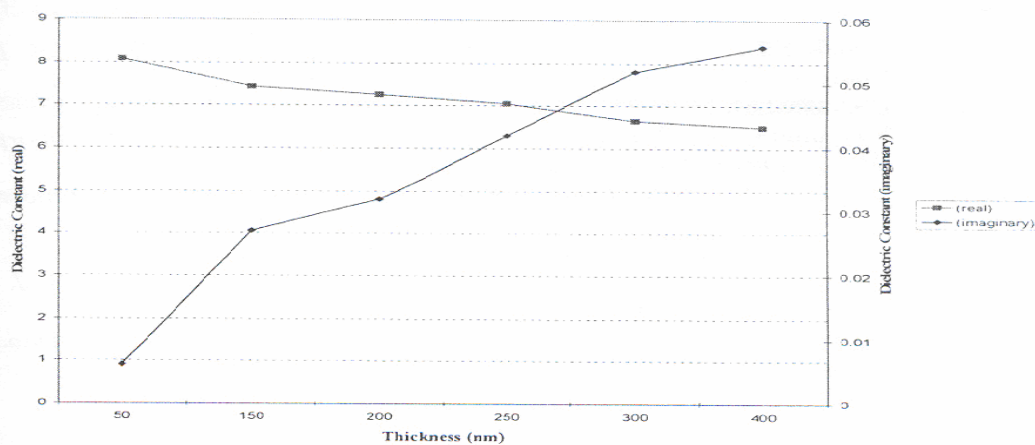


Figure 6: Dielectric constant (real and imaginary) vs. sample thickness

## CONCLUSION

The optical absorption coefficient of TAS thin films was successfully measured. The optical band gap of these films was also determined. It was found that the absorption coefficient,  $\alpha$  of the film increases (from  $6.21 \times 10^3$  to  $1.55 \times 10^5 \text{ cm}^{-1}$ ) with the thickness increment (from 50 nm to 700 nm). There is also appeared to be a steady decrease of  $\alpha$  in the visible region followed by a sharp drop and a further gradual declining down to near infrared for all samples observed. The optical band gap was found to be decreasing as thickness of the sample increases and was attributed to quantum size effect. The effective mass, refractive index and extinction coefficient of the films were also determined. There is an increment of refractive index as the thickness decreases while the extinction coefficient increases along with film thickness. The real dielectric constant  $\epsilon_r$  decreases as film thickness increases whereas the  $\epsilon_i$  shows an increment as the film gets thicker.

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