ON THE STRUCTURAL AND OPTICAL PROPERTIES
OF ANTIMONY TRISULFIDE THIN FILMS

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Thin films of antimony trisulfide were prepared by thermal vacuum evaporation technique at substrate temperatures from 300 – 498 K. At substrate temperature $T_S \leq 473$ K, the films have amorphous structure, while those prepared at $T_S = 498$ K has polycrystalline structure as identified by X – ray diffraction technique (XRD) and atomic force microscopy (AFM). Absorption coefficient, refractive index and optical band gap energy were determined from transmission spectra.

1. Introduction

Metal chalcogenides (sulfides, selenides and tellurides) are important materials for applications such as photoconducting cells, photovoltaic cells and other optoelectrical devices. Among the group V-IV compounds, antimony trisulfide (Sb_2S_3) thin film is used as a target material in television cameras, microwave devices, switching devices and various optoelectronic devices [1,2]. Antimony trisulfide has received a little attention as a potential candidate in solar energy conversion. The band gap (1.6 – 1.8 eV) covers the maximum scan the visible and near infrared ranges of the solar spectrum.

The optical and electrical studies of thin antimony trisulfide films are important both fundamentally and for applications [3, 4].

In this paper the effect of substrate temperature on the fundamental absorption edge of antimony trisulfide thin films was investigated.

2. Experimental

Antimony trisulfide thin films were prepared by thermal vacuum evaporation technique onto glass substrate, at vacuum of 5×10^{-5} torr. Antimony trisulfide powder (Merck) of purity 99,99 % was used. The experimental arrangement permitted to prepare thin films samples under various conditions: the deposition rate, $r_d = 10 - 100$ Ås^{-1}, the substrate temperature, $T_S = 300 - 498$ K and vacuum, $p = 5 \times 10^{-5} - 10^{-3}$ torr.

The film thickness, d, was measured by an interferometric method [5] and for investigated samples ranged between 0.35 and 1.25 μm.

The structural analysis of films was performed by X – ray diffraction (XRD), using the CuK$_\alpha$ radiation (λ=1.5418 Å). The surface morphology of the films was investigated by means of atomic force microscopy (AFM).

The transmission spectra, in the spectral domain 400 – 1400 nm, were recorded using a SPECORD UV – VIS M-40 double beam spectrophotometer, at room temperature.

3. Results and discussion

Diffraction analysis of thin films deposited at room temperature, or at temperatures up to 473 K, show an amorphous structure, while those deposited at T_S = 498 K have polycrystalline orthorhombic structure by using X – ray.
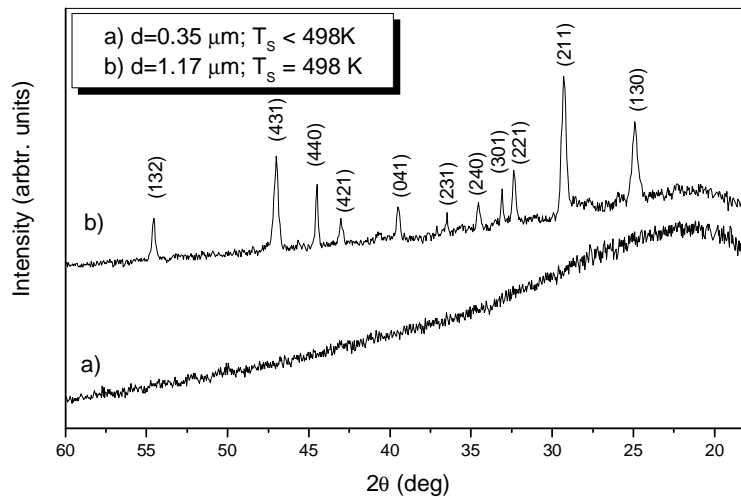

Fig. 1. X – ray diffraction pattern of Sb_2S_3 thin films.

Fig. 1 shows the characteristic peaks of antimony trisulfide. The results are in agreement with those reported by Droichi et al. [6].

Our investigations have shown that the crystallite size determined by means atomic force microscopy (AFM) ranged between 10 and 40 nm. The average size of the crystallite increases with increasing substrate temperature during film deposition. This increase is more evident for thicker films. The higher substrate temperatures determine an increase of surface mobility of adatoms during deposition [7]. These conditions favor the growth of films having crystallites with greater size.

The crystallite size also increases with increasing deposition rate. At very high deposition rates, the adatoms interact strongly with each other to become chemisorbed with little surface migration; consequently the fine – grained films were obtained.

In Fig. 2 are presented AFM images for two investigated samples deposited under different conditions. These images confirm the mentioned characteristics of film structure.
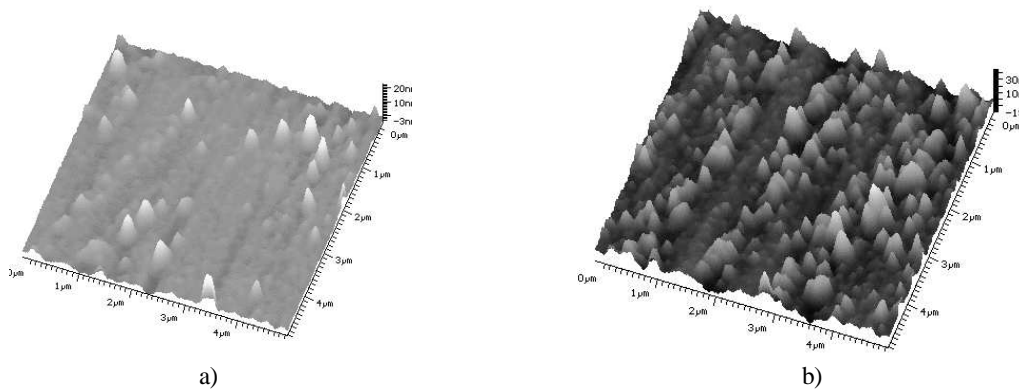

Fig. 2. AFM images (5 μm × 5 μm) for two Sb_2S_3 thin films:
a) d = 0.35 μm, T_S = 300 K, r_d = 30 Ås^{-1};
b) d = 1.17 μm, T_S = 498 K, r_d = 98 Ås^{-1}.

The optical transmission spectra as a function of wavelength in the range of 400 to 1400 nm were measured for different samples deposited at substrate temperatures from 300 to 498 K. Fig. 3 show typical transmission spectra for two investigated films.
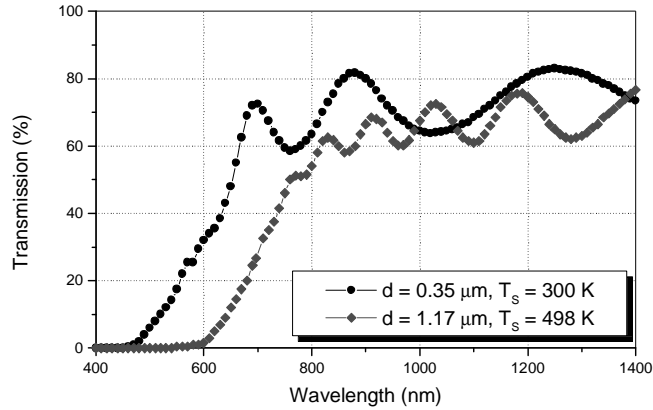

Fig. 3. Transmission spectra of Sb_2S_3 thin films.

The number of the interference fingers in the transmission curves is determined by the thickness of the films.

If the films thickness, d, is uniform, interference effects give a big number of interference fringes in the region of weak and medium absorption.

The optical constants like refractive index, n and the absorption coefficient, α of the films have been determined from the transmittance spectrum following the method of Swanepoel [8,9]. If two envelopes are drawn through the maxima and minima of the oscillating transmittance the refractive index is given as:

$$n = [\, N(\lambda) + (\, N^2(\lambda) - n_s^2 n_0^2 \,)^{1/2} \,]^{1/2}$$ (1)

where:

$$N(\lambda) = \frac{n_s^2 + n_0^2}{2} + 2 n_s n_0 \frac{T_M(\lambda) - T_m(\lambda)}{T_M(\lambda) T_m(\lambda)}$$ (2)

In relations (1) and (2) $n_s = 1.50$ is the refractive index of the glass substrate, $n_0 = 1$ is the refractive index of air and T_M and T_m are the maximum and minimum transmission in the transmission spectra.

The absorption coefficient, α, of the thin films can be calculated by the expression:

$$\alpha = \frac{1}{d} ln \frac{1}{x}$$ (3)

In the region of weak and medium absorption parameter x were calculation from the relation:

$$x = \frac{E_M - [\, E_M^2 - (\, n^2 - 1 \,)^3 (\, n^2 - n_s^4 \,)]^{1/2}}{(\, n - 1 \,)^3 (\, n - n_s^2 \,)}$$ (4)

where:

$$E_M = \frac{8n^2 n_s}{T_M} + (n^2 - 1)(n^2 - n_s^2)$$ (5)

In the region of strong absorption the values of x can be calculated using the relation:

$$x \cong \frac{(n + 1)^3 (n + n_s^2)}{16 n^2 n_s} T$$ (6)

The variation of the absorption coefficient with the incident photon energy at and near the fundamental absorption edge for Sb₂S₃ thin films of different substrate temperature is shown in Fig 4.

The film prepared at $T_S = 300$ K posses the characteristic features of the optical absorption edge of amorphous semiconductors. The film prepared at $T_S = 498$ K has a structure polycrystalline. This film shown different behavior of absorption spectra than that for amorphous films, due to the change in the structure. This behavior is probably due to the increase in the crystallite size. It is known that intercrystallite boundaries contain structural defects, impurities etc. These factors have a strong influence on the absorption processes. In films with greater crystallites the intergrain domains play a less important role in optical absorption. The absorption coefficient is slightly affected by the change of substrate temperature at lower energy values. This reflects a difference in the degree of disorder of amorphous films [10].
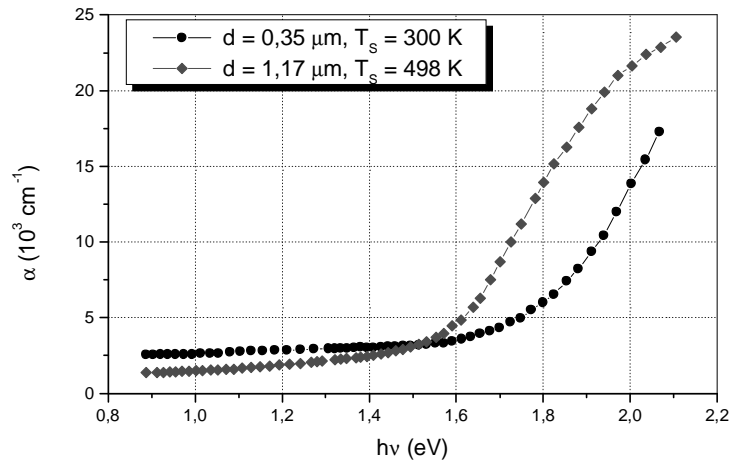

Fig. 4. Variation of the absorption coefficient with the incident photon energy for Sb₂S₃ thin films.

Optical band gap of the amorphous films were calculated from the relation:

$$(\alpha h \nu)^{1/2} = A(h \nu - E_g^i)$$ (7)

where E_g^i is the optical band gap which corresponds to indirect transition and A is a constant. Consequently, the optical band gap, E_g^i, cold be found by taking the intercept of a plot of $(\alpha h \nu)^{1/2}$ versus photon energy $h \nu$ (Fig. 5).
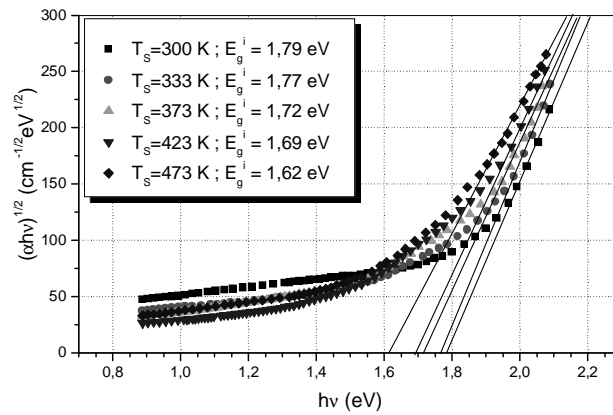
Fig. 5. Variation of $(\alpha h\nu)^{1/2}$ versus photon energy $h\nu$ for amorphous thin films.

A slight decrease in the indirect optical band gap, from 1.79 to 1.61 eV as the substrate temperature of the deposited film increases from 300 to 473 K was observed. The values of optical band gap are in agreement with that reported previously [10-13]. This feature can be related to the growth of ordered domains in the films. In general, the properties of the glasses with Sb_2S_3 component or Sb_2O_3 depend on the structure of the antimony sulfide or oxide clusters as shown by Sava [14] and Nalin et al. [15].

The optical band gap of polycrystalline film prepared at 498 K is due to the direct transition according to the relation:

$$(\alpha h\nu)^2 = A(h\nu - E_g^d)$$

(8)

where E_g^d is the direct optical band gap and B is a constant. The dependence of $(\alpha h\nu)^2$ versus photon energy $h\nu$ is represented in Fig. 6, from which the direct optical band gap is equal to 1.8 eV.
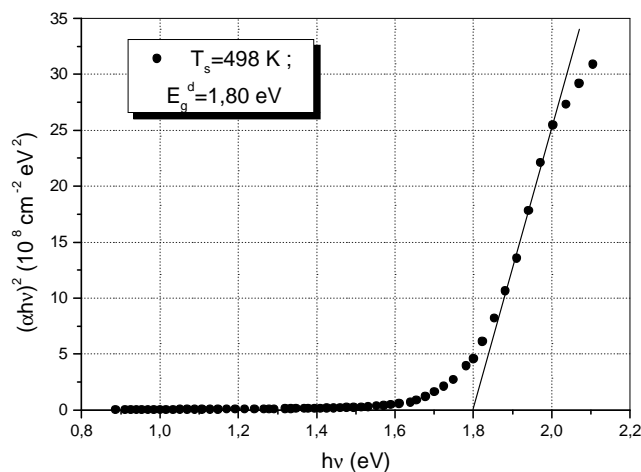

Fig. 6. Variation of $(\alpha h\nu)^2$ versus photon energy, $h\nu$, for polycrystalline thin film.

5. Conclusions

From the present study, it can be concluded that the films deposited at $T_S \leq 473$ K have amorphous structure, while those deposited at $T_S = 498$ K have polycrystalline structure as identified by X – ray diffraction analysis.

As the substrate temperature increases, the optical band gap of the amorphous films linearly decreases from 1.79 to 1.62 eV. The degree of disorder decreases with increasing the substrate temperature up to 473 K.

At $T_S = 498$ K, the optical band gap for direct transition is equal to 1.8 eV due to the structural transformation of polycrystalline.

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