Investigation of optical and thermo-electrical properties of the sulfosalt SnSb$_2$S$_4$ thin films

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SnSb$_2$S$_4$ films were grown with different thicknesses, they subsequently thermally annealed under air atmospheres from the ambient temperature to 275 °C. The SnSb$_2$S$_4$ films exhibit a polycrystalline structure and undergo drastically changes in electrical and optical properties at a transition temperature of about 150°C only for the films with thicknesses lower than 600 nm. The films show an hysteresis-like loop on accomplishing measurements of the square resistance values for the films with thicknesses higher than 600 nm. So, for the lower thicknesses this material is a good candidate as a protective material for example against high energetic laser radiation.

1. Introduction

Thin films and coatings are becoming of high interest in many different industrial applications. A variety of techniques and methods are developed for the characterization of the surface properties. A large number of studies have been reported on PbS, PbSe and PbTe and their alloys that have many applications such as detectors of infrared radiation and solar control coatings [1]. Also, Sb:SnO$_2$ films raised a high interest as protecting layers for architectural and automotive glass [2], the ZnO films are used as protective layers [3].

Sulfosalt thin films have received much attention for the last two decades due to their technological applications, namely thin film solar cells [4-6] and thermoelectric energy conversion [7]. Sulfosalt SnSb$_2$S$_4$ thin films have studied because of the interesting properties they could have, such as a low resistivity and optical transmittance with thicknesses lower than 600 nm after annealing .These properties make them good candidates for many applications as a protective material. So, in this paper the effect of both annealing temperature and the film thickness on coating's structure and properties of SnSb$_2$S$_4$ thin films were investigated.

2. Experimental procedure

2.1. Preparation of the SnSb$_2$S$_4$ ingot

Stoichiometric amounts of 99.999% pure Sn, Sb, and S were used. The mixture was sealed in vacuum in a quartz tube. The quartz tube was heated slowly (10 °C/h). A complete homogenization could be obtained by keeping the melt at 600 °C for about 48 h. The tube was then cooled at a rate of 10 °C/h, so that cracking due to thermal expansion of the melt up on solidification was avoided. X-ray analysis of the powdered material (Fig.1) showed that only a homogenous SnSb$_2$S$_4$ phase was present in the ingot [8]. A crushed powder of this ingot was used as raw material for the vacuum thermal evaporation.
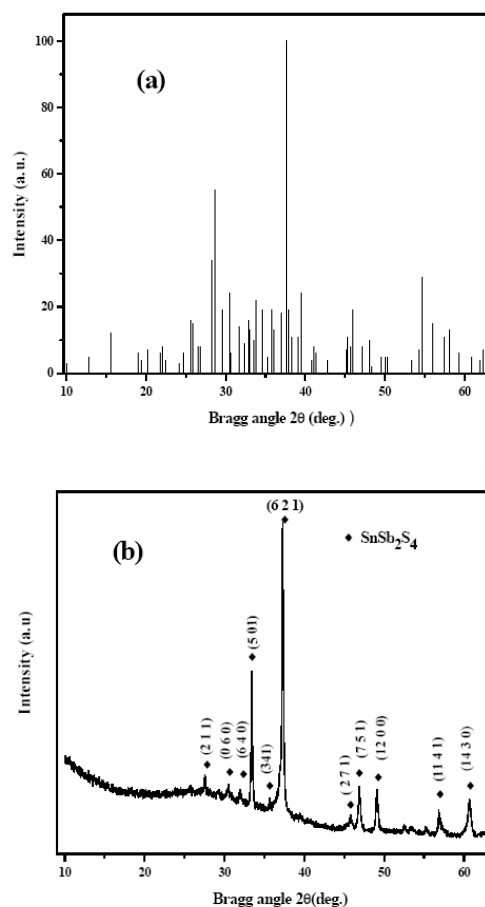

Fig. 1. .X-ray diffraction of the SnSb$_2$S$_4$ powder (a): Ref [8] and (b): our work.

2.2. Coating preparation

Before coating preparation, the glass substrate were cleaned with detergent solution, acetone and rinsed with de-ionized water, then dried in clean air. The coatings were deposited onto glass substrates by vacuum thermal evaporation. Films with various thicknesses in the range 300-800 nm were deposited. The pressure during the evaporation was maintained at 10^{-5} Torr .A chromel-alumel thermocouple monitored the substrate temperature. The deposition temperature of the films was 50°C, with heating due only to radiation from the crucible. After that, the as-deposited films were annealed for 1h in air between 25 and 275 °C.

2.3. Characterization of coatings

The structural properties were determined by X-ray diffraction (XRD) using CoK$_{\alpha1}$ radiation (λ=0.1789 nm) for vacuum evaporation coatings and scanning electron microscopy (SEM) micrographs were performed using a Philips XL30 microscope. Optical transmittance and reflectance were measured at normal incidence with a UV–visible–NIR Shimadzu 3100S spectrophotometer in the wavelength range 300–1800 nm. The coating thicknesses were measured by using a profilometer type Mitutoyo Surftest- 301. The films were thermoelectrically characterized with resistance measurements as function of the air annealing temperature in the range 25-275 °C. Hot probe method measurements were carried out in order to determine the type conductivity of the films.

3. Results and discussion

3.1. Structural properties

Typical X-ray diffraction patterns of the SnSb$_2$S$_4$ films before and after annealing in air were shown in Fig.2. The diffraction patterns have shown the films to be amorphous for all the samples before annealing. All the samples after annealing present a strong (621) preferred orientation of the SnSb$_2$S$_4$ phase in particular for the films with thicknesses higher than 500 nm. It is clear that no

secondary phases appeared in particular the metallic (Sn or Sb) or inter metallic (Sb-Sn) oxide phases. In addition, it is important to note that films with thicknesses lower than 600 nm do not exhibit a noticeable structural transition as shown for the films with high thicknesses. Understanding the phase transition processes in sulfosalt SnSb$_2$S$_4$ films between amorphous to crystalline phase is of key importance because it directly affects the quality of protective coatings.
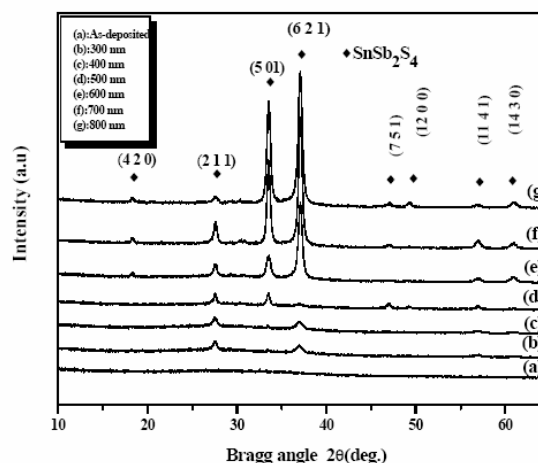

Fig. 2. X-ray diffraction patterns of as-deposited and annealed SnSb$_2$S$_4$ thin films at various thicknesses.

The investigation of the samples by scanning electron microscopy (SEM) was performed to examine the influence of the different coating thicknesses and annealing in air on the morphology of the samples. The SEM micrographs of the films having different thickness before and after the heat treatment are shown in Fig.3. As-grown films are smooth and uniform surface, the system remains amorphous. However, after annealing an increase in thickness caused the increase in the average size of the coating particles, for higher thicknesses crystallinity was improved as indicated by the appearance of defined peaks in the XRD patterns.
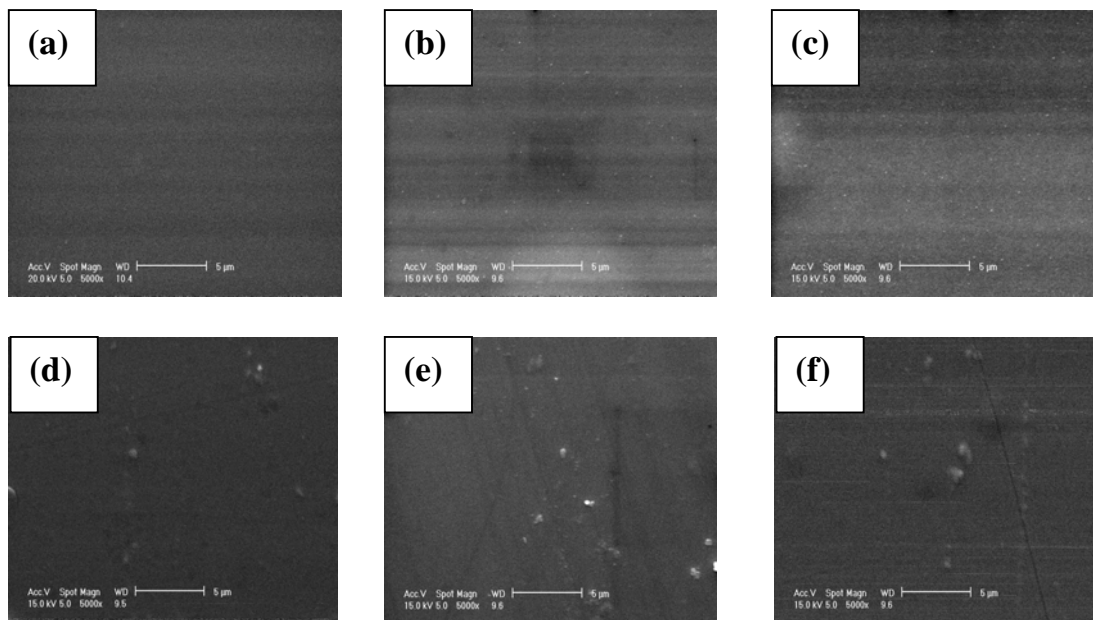
Fig. 3 .Scanning electron micrographs of the as-grown and air-annealed films at different thicknesses: As-grown:
(a) 500 nm, (b) 600 nm, (c) 700 nm, Air-annealed films: (d) 500 nm, (e) 600 nm, (f) 700 nm

3.2. Optical properties

The optical properties of $SnSb_2S_4$ films were studied. All films obtained had good adherence and covered uniformly. It can be found that the transmittances (T) are affected by the thermal treatment in air.

Fig. 4 shows the variation of the average transmittance in the range 1000-1800 nm versus the film thickness. Indeed, the films after annealing show in all cases a decrease in the transmittance values in the spectral range 1000-1800 nm between 20 and 25% before annealing to the values fewer than 5% after annealing. Alternatively the reflectance (R) decreases from 60% to 5 % by increasing the film thickness from 300 nm to 800 nm, respectively. It is clear that, the layers present an opaque aspect after annealing. Probably, the decrease of the transmittance and the reflectance values by increasing the thickness films is correlated to the change in structural properties as described in our previous work **[9]**. Indeed, from XRD results it was shown that after annealing the films have a polycrystalline structures in particular for the films with thicknesses higher than 500 nm while the films with thicknesses lower than 600 nm exhibit global amorphous structures. In addition the opacity of the films is much correlated to the heat treatment which increases by increasing the annealing temperature. The polycrystalline $SnSb_2S_4$ thin films present an opaque aspect whereas the amorphous one is much transparent.
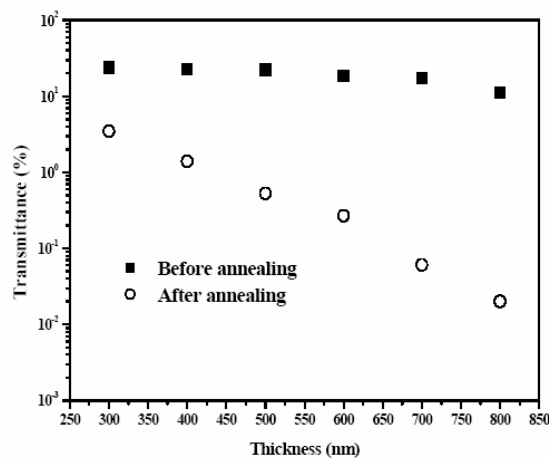

Fig .4.Variation of the average transmittance in the range 1000-1800 nm versus the film thickness.

On the other hand the absorption coefficient α is related to the energy gap E_g according to the equation:

$$\alpha h\nu = A\left(h\nu - E_g\right)^n$$

where A is a constant, h is the Planck constant and n is equal to ½ for a direct gap and 2 for an indirect gap semiconductor.

The band gap E$_g$ was determined by extrapolating the straight section of the $(\alpha h \upsilon)^2$ vs. $h\nu$ curve to the horizontal photon energy axis. Fig. 5 shows the gap energy E$_g$ as a function of the thicknesses of the films before and after annealing. It is clear that the SnSb$_2$S$_4$ films exhibit a significant change in their optical properties by decreasing the gap value. The gap energy decreases before and after annealing by increasing the thickness. So, after annealing E$_g$ is less than 1 eV which gives to the material a metallic aspect. For the films with thicknesses below than 600 nm and after annealing it is impossible to calculate the energy gap E$_g$ because the transmittances of the films are very low.

The decrease in transmittance value after annealing is correlated to the change in structural properties. Indeed, from XRD results it was shown that after annealing the films have a polycrystalline structure while the as-deposited films exhibit an amorphous structure.
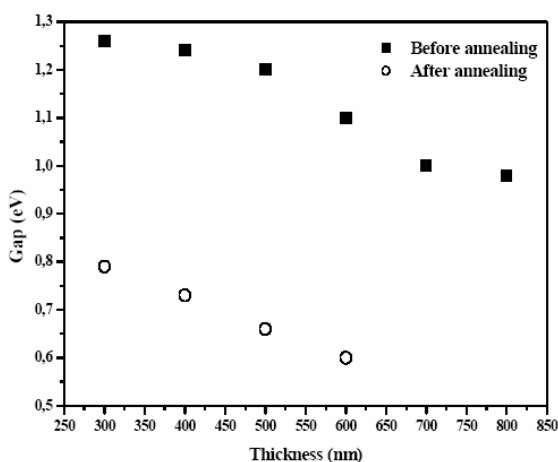

Fig . 5. Variation of direct band gap Eg with thicknesses for the SnSb$_2$S$_4$ layers.

Fig. 6 shows the refractive index, n , by taking into account the method described in [10] The same behaviour has been reported by M. Wakkad et al. [11] for Sn-Sb-Se thin films, and the extinction coefficient k (k = αλ/4π) of the as-deposited SnSb$_2$S$_4$ thin film as a function of wavelength (in the visible wavelength region). It is obvious that almost no variation is observed in both n and k values with the film thickness. Therefore, it can be concluded that both n and k are independent of the film thickness. For the films with thicknesses below than 600 nm and after annealing it is impossible to calculate the absorption coefficients and k because the transmittances of the films are very low.
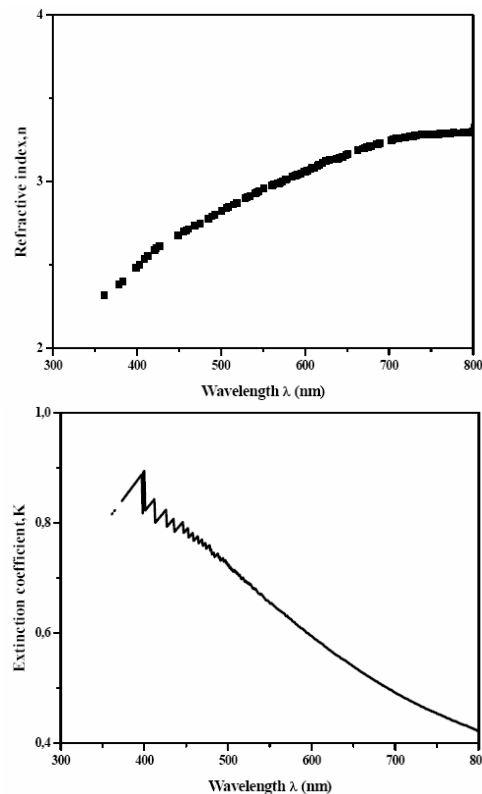

Fig. 6. Refractive index, n, and extinction coefficient, k, of SnSb$_2$S$_4$ thin films as a function of wavelength. The film with thichness at 600 nm and before annealing.

3.3. Thermo-electrical properties

The electrical resistance R of the prepared SnSb$_2$S$_4$ thin films was measured over the temperature range from 25 °C to 275 °C. Electrical contacts were made by applying previously two bands of gold with separation of about 10 mm under the film and at the edges of the substrate. Fig. 7 shows the temperature dependence of the electrical resistance of the SnSb$_2$S$_4$ thin films with various thicknesses for both the heating and the cooling cycles. From Fig. 7 it is clear that the SnSb$_2$S$_4$ thin films exhibit a remarkable change in their electrical properties at transition temperatures of about 150°C only for the films with thicknesses lower than 600 nm. For the films with higher thicknesses the behaviour of the square resistance versus the temperature is completely different and no remarkable change was observed. This is an indication of the dominance of the crystallized phase as shown by the XRD results. Indeed for the thicknesses lower than 600 nm the amorphous component is dominant. Consequently a critical thickness value of about 600 nm corresponds to a phase transition from a dominant amorphous phase to a dominant crystallized phase. On the other hand it appears that for the film thickness higher than 600 nm the heating and cooling cycles of the samples present a reversible aspect which corresponds to a lower relative variation

$\dfrac{(\rho_i - \rho_f)}{\rho_i}$ where ρ_i is the resistivity value at 50 °C

(heating cycle) and ρ_f the resistivity value at 50°C (cooling cycle) (Fig.8).
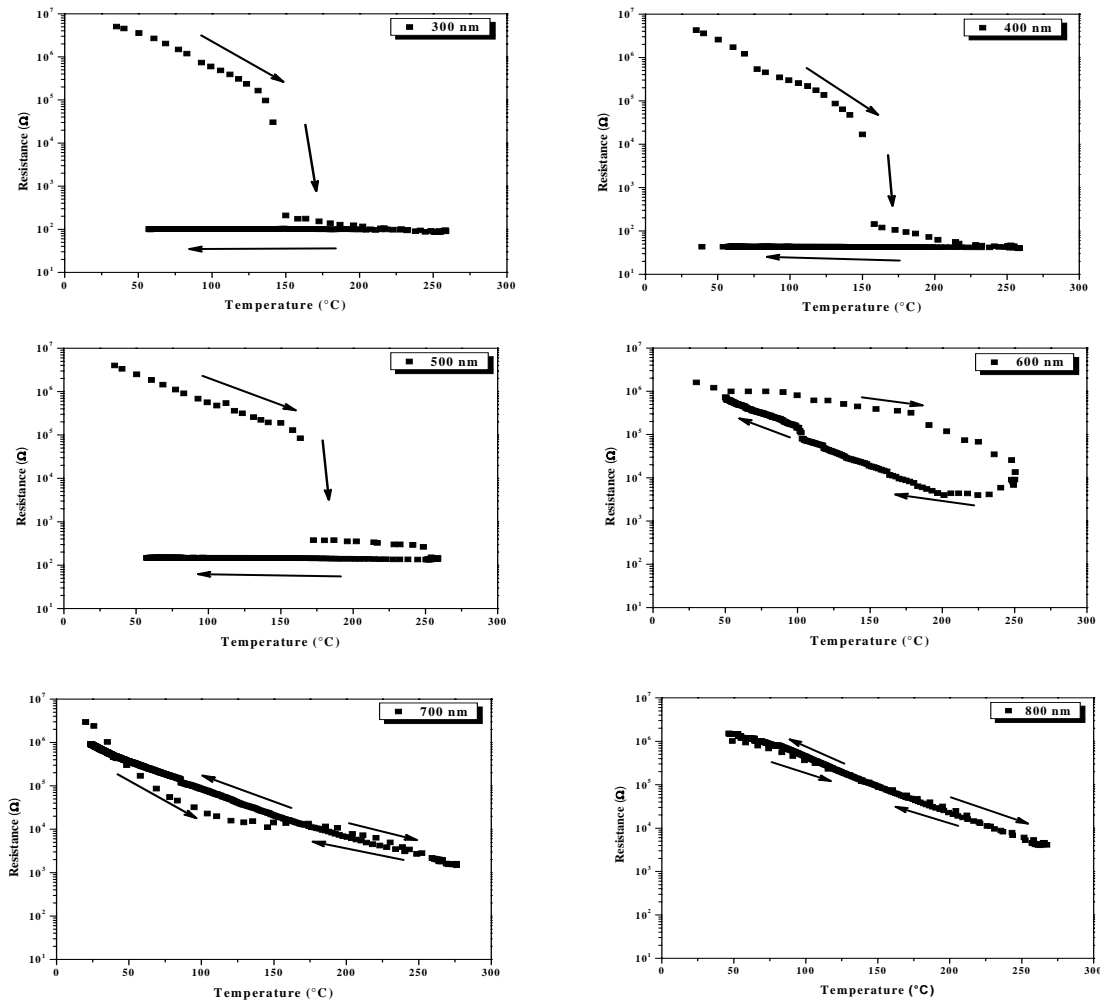

Fig. 7. Annealing temperature dependence of the resistance of the SnSb₂S₄ thin films in air for the thicknesses.

The relative variation $\dfrac{(\rho_i - \rho_f)}{\rho_i}$ of all samples decreases dramatically from the film thickness equal to 500 nm as shown in Fig. 8. The measurements of electrical resistivity suggest that the system shows "semiconducting" aspect with resistivities between 10-100 Ω cm, and "metallic" aspect with low-resistivities 10^{-2}-10^{-3} Ω cm. This statement indicated the stabilization of the sample structure in the respective temperature range, the properties of a protective due to thermal stability of the thickness less than 600 nm. The films exhibited p^+-type conductivity for the films with thicknesses lower than 600 nm and p-type conductivity for the films with higher thicknesses.
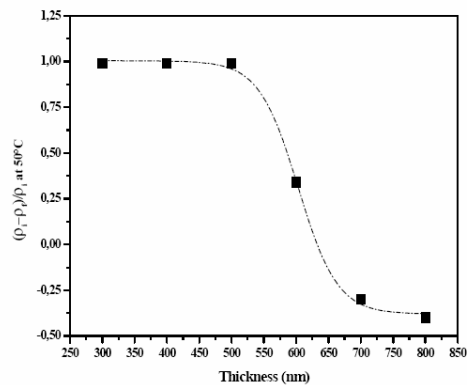

Fig. 8. Variation of $\dfrac{\sigma_i - \sigma_f}{\sigma_i}$ with thickness.

4. Conclusion

Good-quality $SnSb_2S_4$ thin films with different thicknesses have been successfully deposited on glass substrates using the vacuum thermal evaporation technique. The effect of both annealing temperature and the film thickness on coating's structure and properties of $SnSb_2S_4$ thin films were investigated. The structural analysis using XRD reveals that the films are amorphous at lower temperature and polycrystalline at higher temperature. $SnSb_2S_4$ thin films with thicknesses less than 600 nm and after annealing in air present a dramatical electrical change from smiconducting behaviour to a 'metallic' behaviour. In addition the transmittance of the films decreases considerably after the air annealing. This phenomenon has not been yet explained. The this material in film forms and with lower thicknesses may be used as a protective material for any energetic radiation.

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