COMPARATIVE STUDIES OF THE PROPERTIES OF THERMAL ANNEALED Sb_2S_3 THIN FILMS

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In the present paper, we report the growth of antimony sulphide (Sb_2S_3) thin films by thermal evaporation method and detailed characterization of these films. The films were deposited from a Sb_2S_3 powder at unheated substrates. We have analysed the structural, optical morphological and electrical properties of as deposited Sb2S3 films as well as those subjected to annealing in nitrogen atmosphere in the temperature range 100-300°C. As-deposited films are amorphous to X-ray diffraction (XRD). Polycrystalline antimony sulphide films are obtained and enhanced from the annealing temperature above 200°C. Both amorphous and polycrystalline antimony sulphide films have strong absorption coefficients in the range 10^4 -5×10^5 cm^{-1}, and have direct band gaps with band energies 2-2.2 eV for the films annealed below 200°C and 1.7-1.8 eV for the films annealed at temperatures higher than 200°C. Inside, the thermal activation energy decreased with increasing annealed temperature for thins films treated in nitrogen atmosphere.

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1. Introduction

In recent years a large number of studies have devoted to the physical proprieties of chalcogenides thin films due to their many applications: solar energy conversion, thermoelectric cooling technologies and optoelectronics in the IR region [1, 2]. Among this material, antimony trisulphide (Sb_2S_3) is the kind of semiconductor with its interesting electrical and optical proprieties. In the most recent reports, the crystalline phase, stibnite, is reported as a direct bandgap with Eg values between 1,7 to 1,8 eV. In view of the various potential applications, several methods of deposition have been employed to prepare Sb_2S_3thin films, such as chemical bath deposition [3], radio frequency sputtering [4], solvothermal reaction [5], but in this paper thin films Sb_2S_3 was deposited by thermal vacuum evaporation technique. Now, antimony sulphide Sb_2S_3 has been used in television cameras, microwave devices, switching devices, rechargeable storage cell and various optoelectronic devices [6].

2. Experimental

2.1 Synthesises of Sb_2S_3

Stoichiometric amounts of the elements of 99.999% purity Sb and S were used to prepare the initial ingot of Sb_2S_3 (figure.1). The mixture was sealed in vacuum in a quartz tube. In order to avoid explosions due to sulfur vapor pressure, the quartz tube was heated slowly (20°C/h). A complete homogenization could be obtained by keeping the melt at 650°C for about 48 h. The tube was then cooled at the rate 7 °C/h, so that cracking, due to thermal expansion of the melt on solidification, was avoided.

Fig. 1. Ingot of Sb_2S_3 after synthesized.

21.2 Film preparation

Sb_2S_3 thin films were deposited by thermal evaporation under vacuum at about 10^{-5} Torr. Thermal evaporation sources were used which can be controlled by the crucible temperature or by the source power. A chromel-alumel thermocouple monitored the substrate temperature.

3. Results and discussion

3.1 Structural properties

The X-ray diffraction (XRD) of Cu K_α radiation ($\lambda_{CuK\alpha}$ = 0.15418 nm) was used to examine the structure of the films. All the diagrams (Figure.2) revealed that the Sb_2S_3 thin films deposited at substrates temperatures of 250°C are amorphous.

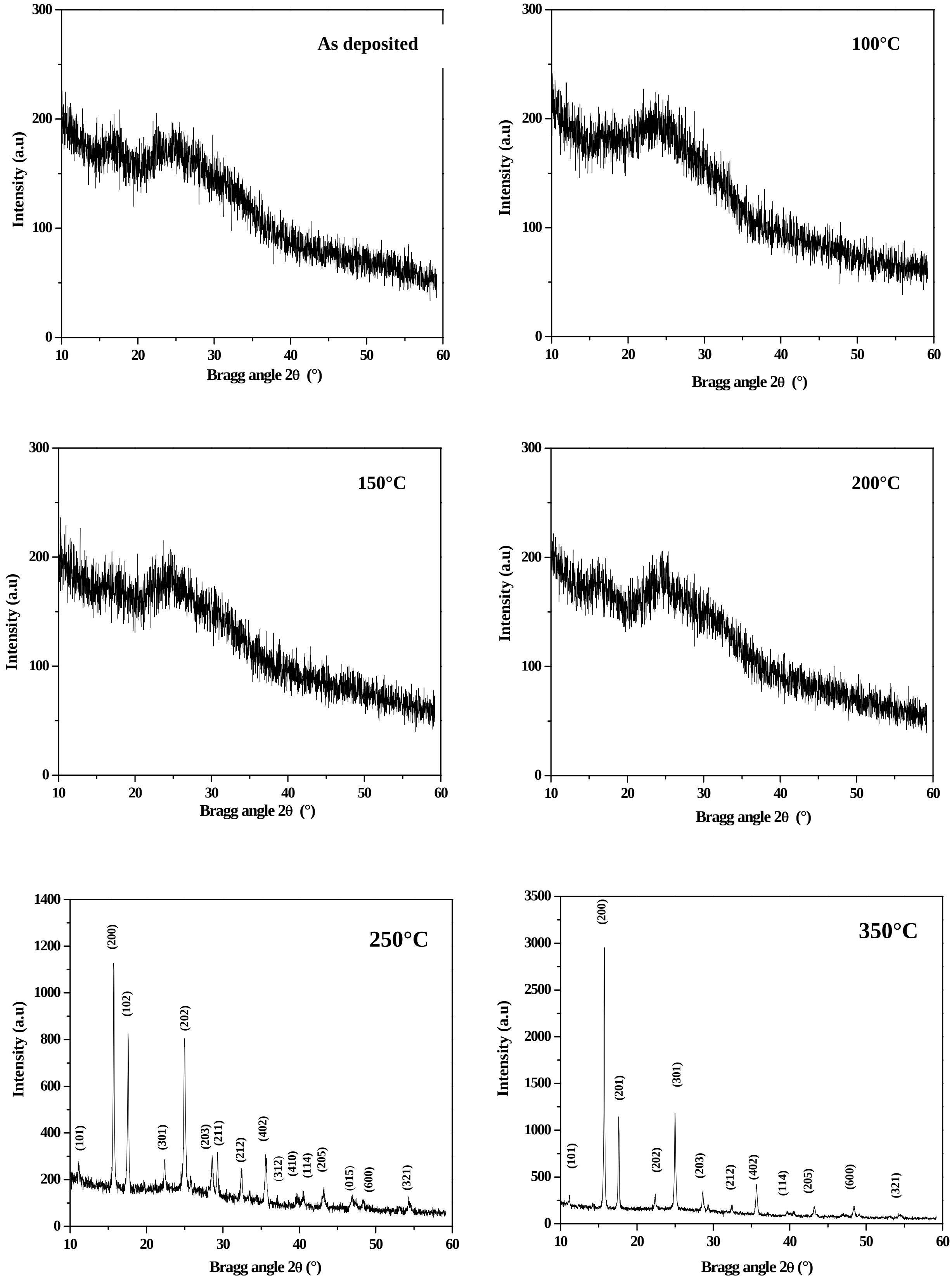

Fig.2.:The X-ray diffractograms of thin films annealed in nitrogen atmosphere: 100°C, 150°C, 200°C, 250°C, 350° C and as deposited film.

After the annealing process in nitrogen atmosphere of thin films at temperature higher than 250°C the structure of Sb_2S_3 thin film become polycrystalline. All reflections can be indexed to the orthorhombic Sb_2S_3 phase. The film presents a principal orientation along (200).

The determination of the crystallite size from the X-ray line width was done using the following Scherrer formula [7]:

$$L = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

with

$$\beta = \sqrt{B_M{}^2 + B_S{}^2} \quad (2)$$

were L is the crystalline thickness, λ the X-ray wavelength (λ=1.54056 Å), β is the width of the one of the standard diffraction peaks at half-maximum, B_M is the width in radians of the sample diffraction peaks at half-maximum, B_S is the width in radians of one of the standard diffraction peaks at half-maximum and θ is the Bragg angle of peaks [8].

The crystalline size of thin film of Sb_2S_3 treated in nitrogen atmosphere at temperature of 250°C and 350°C are grouped in theTtable.1. It is clear, when the temperature of annealing in nitrogen atmosphere increase the crystalline size increase for 53.9 to 63.7 nm.

Table 1. Crystalline size of thin films treated in nitrogen atmosphere at temperature of 250°C and 350°C.

	Thin film of Sb_2S_3 annealing at 250°C	Thin film of Sb_2S_3 annealing at 350°C
Cristalline size (nm)	53.9	63.7

3.2 Morphologies properties of Sb_2S_3 thin film

Morphologies properties of Sb_2S_3 thin film, treated in nitrogen atmosphere at different temperatures: 100; 150; 200; 250 and 350°C, were determinate by Scanning Electron Microscopy (SEM) micrographs (Fgure.3).

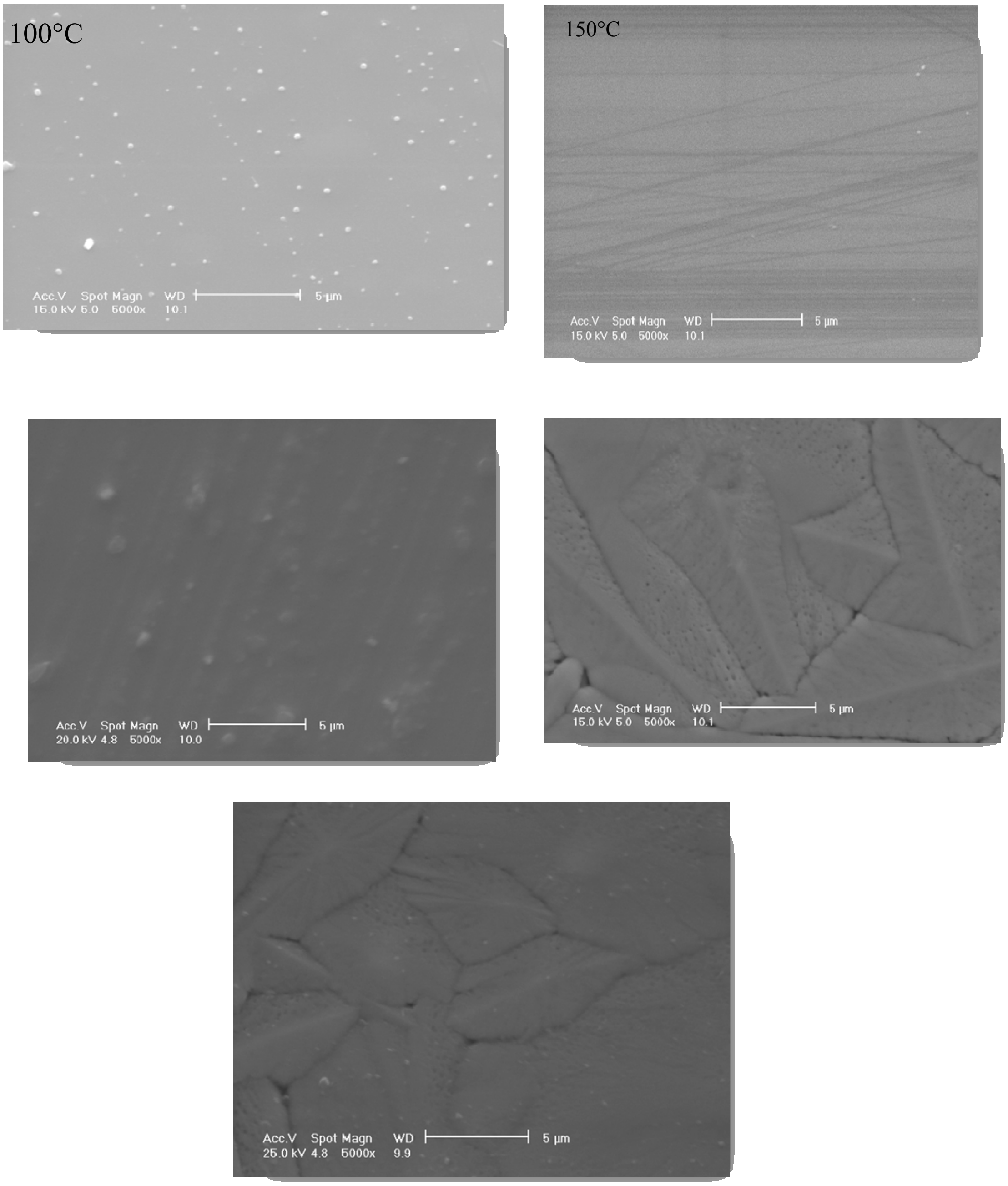

Fig..3. SEM micrographs of thin films treated in nitrogen atmosphere at different temperature.

As- deposited thin films are smooth and homogenous. The composition of Sb_2S_3 thin films of Sb_2S_3 has been determined by EDX (Table.2) and shows that the antimonbide sulphide is not deficient in sulphur compared to the ideal Sb_2S_3 stochiometry.

Table.2. Ratio in atoms of thin films treated in nitrogen atmosphere at temperature from 100°C to 350°C.

Temperature of annealing	100°C	150°C	200°C	250°C	350°C
Sulphur(S) ratio	59.30	59.47	59.14	60.66	60.07
Antimony (Sb)ratio	40.70	40.53	40.86	39.34	39.93

It is clear that the thin films of Sb_2S_3 treated at temperatures < 250°C have amorphous featureless structure but the thin films treated at temperature higher than 250°C are polycrystalline. One can see clearly many grains of different size. This result is in good agreement with the results obtained by X-ray diffraction.

3.2 Optical properties

3.2.1 Optical transmission and reflection spectrum

Transmission and reflection spectra for samples held in nitrogen atmosphere at different temperatures in the wavelength range 300-1800 nm at normal incidence for Sb_2S_3 films are shown in figure.4.

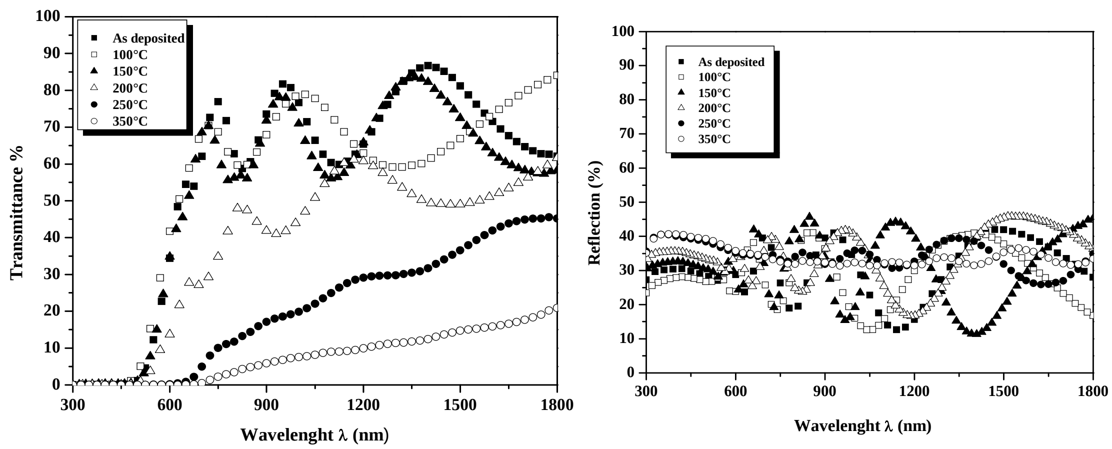

Fig. 4: Transmittances and reflections spectra of thin films treated in nitrogen atmosphere at different temperatures.

It can be seen that for annealed Sb_2S_3 thin film, the transmittance decreases when the temperature increases.This decrease becomes more important at the temperature of 350°C and this feature can be explained by an enhancement of films cristallinity and an increasing of crystallite size. However, the increase of roughness with annealed temperature can be responsible of the anomalous decrease of optical transmittance. Also, an increase of grain boundaries with annealed temperature is observed by SEM. This is at the origin of destructive interference as a consequence of the decrease of optical transmittance. Finally, this decrease can be attributed to a bulk effect because the reflections are not influences too much by the temperature.

3.2.2 Absorption coefficients

The variation of the absorption coefficient α was calculated by the following relation [9]:

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{T}\right]$$

(3)

where d is the film thickness; R and T are the reflection and transmission coefficients, respectively. The absorption coefficient α evaluated from measurements of optical transmission and reflection through the thin film is shown in figure.5.

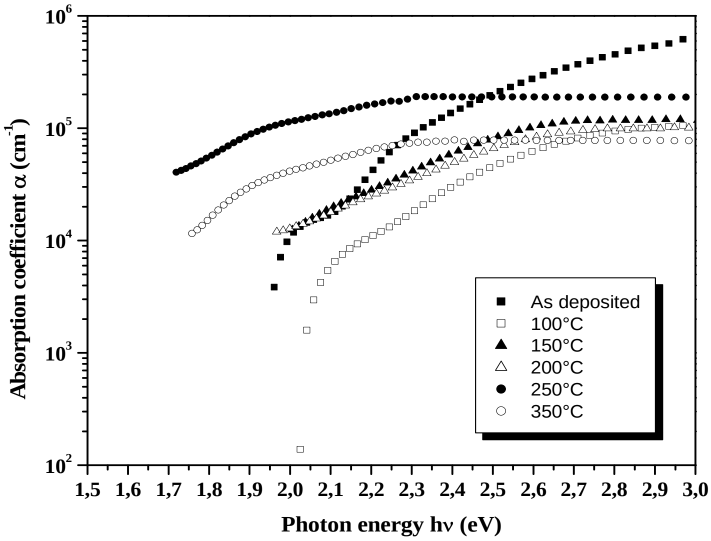

Fig. 5. Absorption coefficient spectra of thin films treated in nitrogen atmosphere at different temperatures.

The values of the absorption coefficient are situated between 10^4 and 5×10^5 cm^{-1} in the visible and near-IR spectral range. This result is very important because the spectral dependence of the absorption coefficient affects the solar conversion efficiency.

3.2.3 Energy bandgap:

The relation between the absorption coefficient α and the incident photon energy is [10]:

$$\alpha h\nu = (h\nu - E_g)^n \quad (4)$$

were A is a constant depending on the transition probability and n is equal to ½ for direct gap and 2 for indirect gap. The usual method to calculate the band gap energy is to plot the graph of $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ [9]. The bandgap value can be determined from the intercept with the photon energy axis. Figure.6a. Shows plots of $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ for the films of Sb_2S_3 annealed in nitrogen atmosphere.

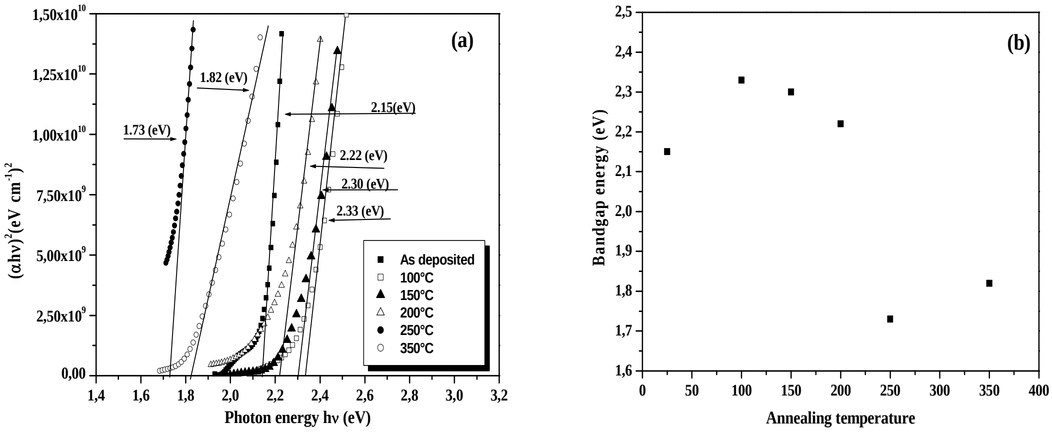

Fig. 6. (a) Energy band gaps of thin films treated in nitrogen atmosphere at different temperatures (a) Energy bandgap in function of annealed temperature (b)

Direct bandgap of amorphous and crystalline antimony sulfide films are, respectively, 2.2 eV and 1.7 eV. Such as shows in figure.6b) that bandgap energy decrease with increasing annealed temperature. This result is in good agreement with the value found in literature [11-13].

3.3 Electrical properties

The resistance was related at thermal activation energy by the following relation [14-15]:

$$R = R_0 \exp\left(\frac{-E_a}{K_B T}\right) \tag{5}$$

Fig.8.Shows the variation of $\ln(R) = f\left(\frac{10^3}{T}\right)$ of thin film deposited at ambient temperature and treated at temperatures 250°C-350°C in nitrogen atmosphere.

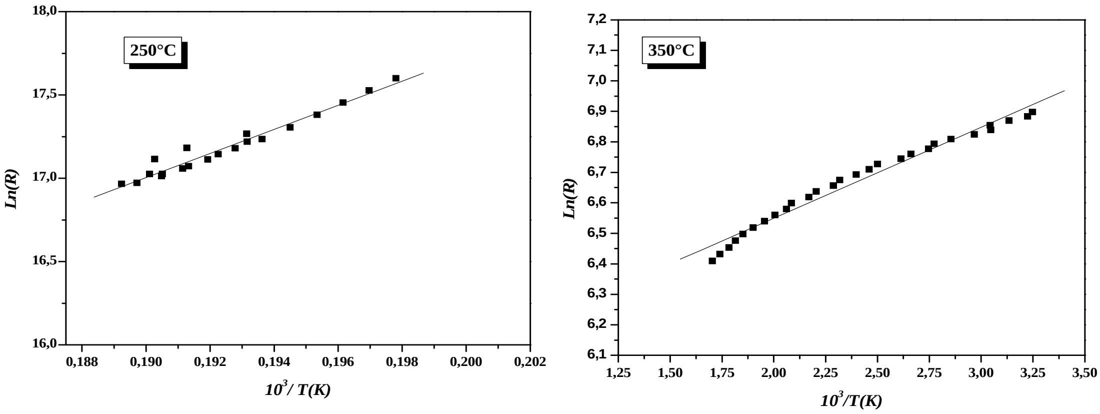

Fig. 7. Variation of Ln(R) = f(10³/T(K)) of thin films treated in nitrogen atmosphere, 250°C, 350°C.

All thin films of Sb_2S_3 elaborated at this work remain intrinsic with highly resistivity. We can concluded that the thermal activation energy decrease when the annealing temperature increase. The low values of activation energy shown in the Table 3 proves that the thin films have homogeneous character and this is in good accord with the other results.

Table.3. Activation energy of thin films treated in nitrogen atmosphere at temperature of 250°C and 350°C.

	Annealing temperature (°C)	Activation energy E_a (mV)
Thin film deposited at ambient temperature of substrate	250	76
	350	25

4. Conclusions

In summary, the antimony sulfide thin films were successfully prepared by thermal vacuum evaporation technique. Te influence of thermal annealing in nitrogen atmosphere on the structural, morphological and optical properties of antimony sulfide thin films has been investigated It was shown that the Sb_2S_3 thin films become crystalline after annealing in nitrogen atmosphere to about the temperature of 250°C. The absorption coefficient α is 5×10^5 cm^{-1}. The direct bandgap energy is 1.7 eV after annealing. These results suggest efficient applications in photovoltaic cells.

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