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Studies of the properties of thermally annealed Sb_2S_3 thin films

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Structural, optical and electrical properties of as deposited Sb_2S_3 films grown by simple source thermal evaporation method were studied. The films were annealed at temperature of 300°C in different atmosphere: vacuum, sulphur vapour, air atmosphere and nitrogen. The sulphur antimony was present structural, morphology, electrical and optical properties. Polycrystalline antimony trisulfide films are obtained by annealing at 300°C in various atmospheres. The values of some important parameters of the films as e.g. absorption coefficient and optical band gap energy are determined from transmission spectra. Polycrystalline antimony trisulfide films have strong absorption coefficients in the range 10^4 -10^5 cm−1 and the direct optical band gap was found to be 1.64-1.71 eV. The thermal activation energy of the films is determined by the temperature dependence of electrical conductivity.

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1. Introduction

Recently, the preparation of antimony trisulfide (Sb_2S_3) thin films has attracted much attention due to their wide applications in optoelectronic devices [1-4]. The binary sulphide antimony Sb_2S_3 was synthized by different methods [5-6]. One of them was of choice; it is thermal vacuum evaporation technique. This material is considerate among the most important metal chalcogenides with her interesting structural, morphology, electrical and optical properties. It covers a large applications range [7-8]. In this paper, we report on the influence of annealing in different atmosphere at 300°C on Sb_2S_3 thin films.

Crystal structures of the thin films of Sb_2S_3 were obtained by X-ray diffraction (XRD). Morphology and composition of samples treated in different atmosphere at 300°C were evaluated with emission Scanning Electron Microscopy (SEM). The transmittance and reflectance spectra were investigated between 300 nm and 1800 nm using UV-VIS spectrometer.

2. Experimental details

Stoichiometric amounts of the elements of 99.999% purity Sb and S were used to prepare the initial ingot of Sb_2S_3. The mixture was sealed in vacuum in a quartz tube. The thin films of Sb_2S_3 are deposited on glass substrate at room temperature. The samples were treated in different atmosphere: vacuum, sulphur vapour, air atmosphere and nitrogen at temperature of 300°C.

3. Results and discussion

3.1 Effect of annealing in different atmospheres at 300°C on structural and morphology properties

3.1.1 Structural properties

The X-ray diffraction (XRD) of Cu K_α radiation ($\lambda_{CuK\alpha}$ = 0.15405 nm) was used to examine the structure of the films elaborated by thermal vacuum evaporation technique and deposited on glass substrate at ambient temperature. Then, Sb_2S_3 thins films are heated at temperature of 300°C in different atmosphere: in air, in nitrogen, in sulfur vapor and in vacuum atmosphere.

Fig. 1 shows the diffraction of ray-X spectra of treated thin films of Sb_2S_3. They revealed that the preferential orientation depends on the atmosphere of annealing. The annealing in sulfur vapor didn't affect the structural proprieties of thin film of Sb_2S_3. This result proves that the thin films are not deficient in sulfur. The treatment in air introduces new plans of antimony trioxide Sb_2O_3[9].

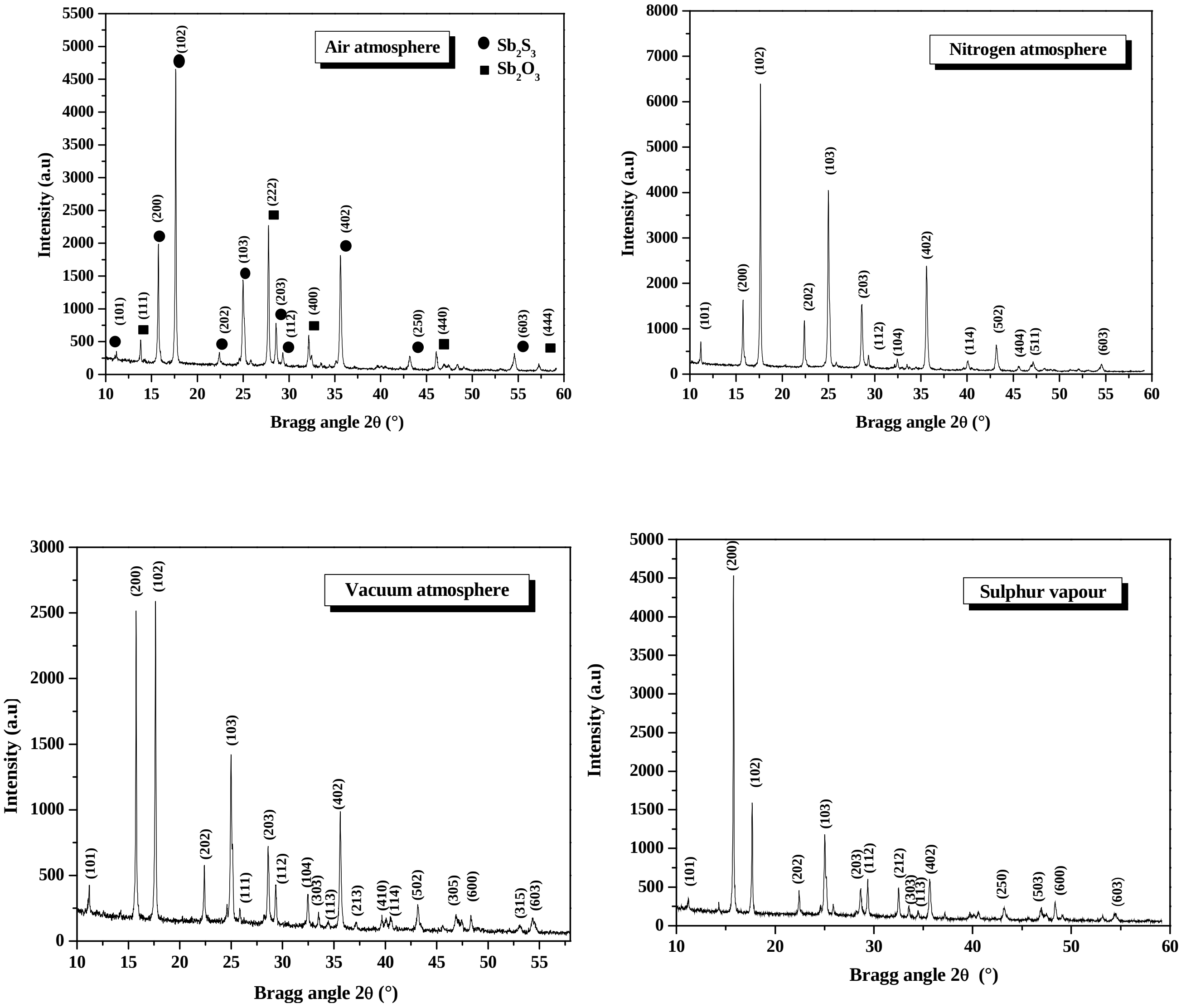

Fig.1. Diffraction X-ray in thin films treated in different atmosphere.

3.1.1 Morphology properties

The morphology of thin films of Sb_2S_3 treated in various atmospheres: air, vacuum, sulfur vapor and nitrogen atmosphere was investigated by SEM micrographs (shown in Fig. 2). The composition of samples in atoms ratio are reported in Table.1. It is clear that the antimony sulphide didn't present deficiency in the sulphur compared to the ideal Sb_2S_3 stochiometry excepting thin films annealed in air atmosphere. This can be attributed to the reaction of the antimony with air oxygen. The treatment of Sb_2S_3 thin films in air atmosphere affects the morphology and composition of samples. This result is in good agreement with the results obtained by X-ray diffraction. All thin films of Sb_2S_3 are homogenous with grain boundaries. The Table 2 shows the size of grain boundaries of all patterns. The size and number of grain boundaries depend of treatment and can degrade the properties of thin film.

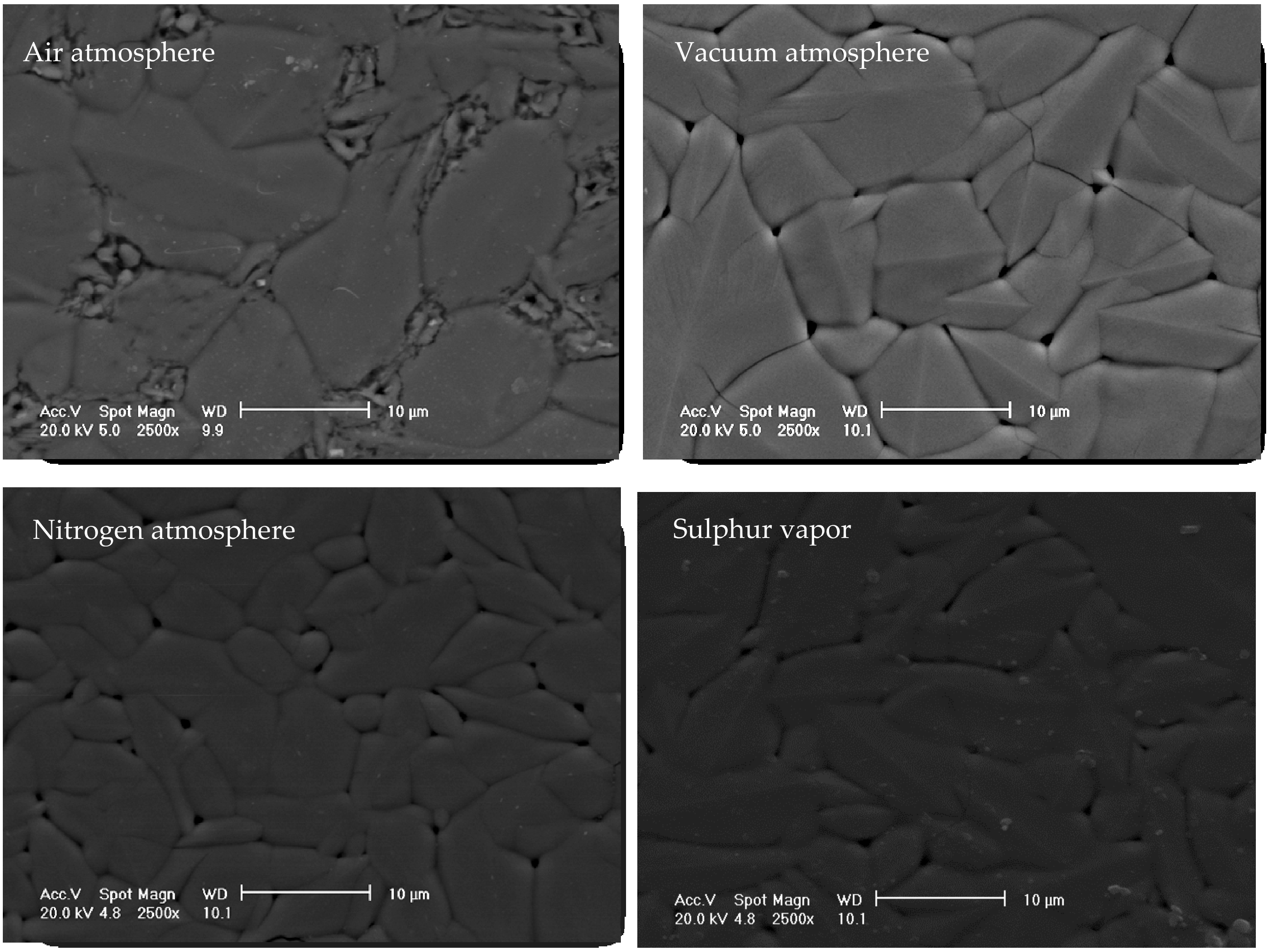

Fig. 2. SEM micrographs of thin films treated in various atmospheres at 300°C.

Table 1. Atomic ratios in films treated in different atmospheres.

Atmosphere of annealed	Vacuum	Air	Nitrogen	Sulphur vapour
Sulphur (S) ratio	60.65	53.35	60.43	60.59
Antimony (Sb)ratio	39.35	46.65	39.57	39.41

Table 2. Crystallite size of Sb_2S_3 thin film treated at temperature of 300°C in different atmospheres.

Nature of treatment	Nitrogen atmosphere	Vacuum atmosphere	Air atmosphere	Sulphur vapour
Cristalline size (nm)	73.7	66.7	63.7	82.4

3.2 Effect of annealing in different atmospheres at of 300°C on the optical proprieties

3.2.1 Transmission and reflection spectra

The transmission and reflection spectra of the samples treated in different atmospheres at temperature of 300°C are shown in Fig. 3.They revealed that the transmission spectra were affected by the atmosphere treatment especially in air atmosphere. This result can be explained by higher crystalline size at about 82.4 nm. So the treatment in different atmospheres at 300°C degrades the optical transmittance spectra.

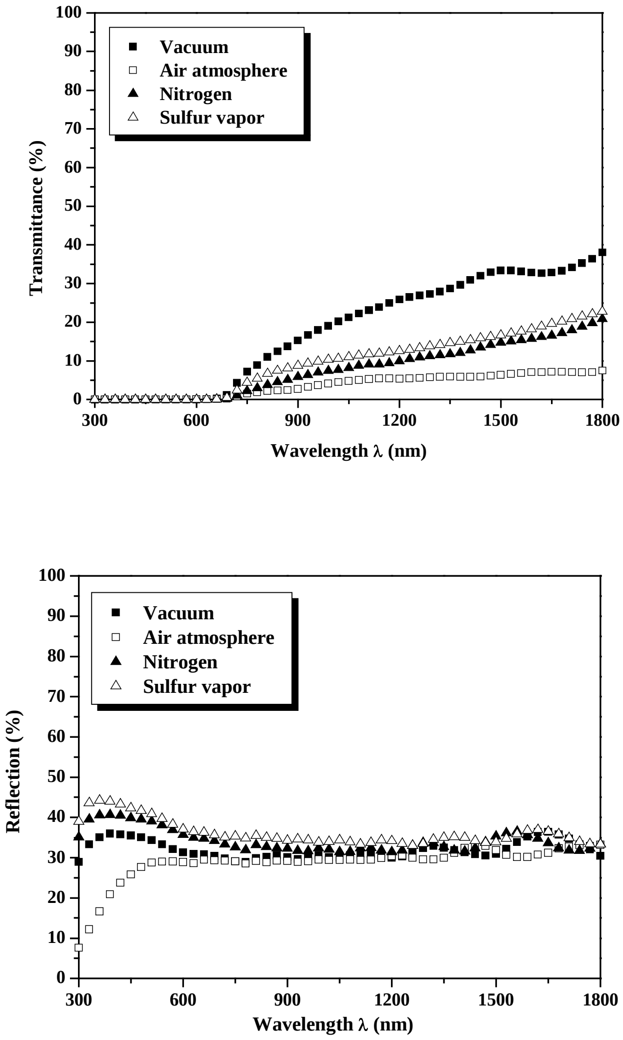

Fig. 3. Transmission and reflection spectra of thin films treated in various atmospheres.

3.2.2 Absorption coefficients

The variation of the absorption coefficient α was calculated by the following relation [10]:

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

where d is the thickness films, R and T are the reflection and transmission coefficient respectively. The absorption coefficients α of thin films are very high about 10^5 cm^{-1} excepting thin film annealing in sulfur vapor (about 10^4 cm^{-1}) (Fig. 4.). We can conclude that the treatment in sulfur vapor decreases the absorption coefficient α.

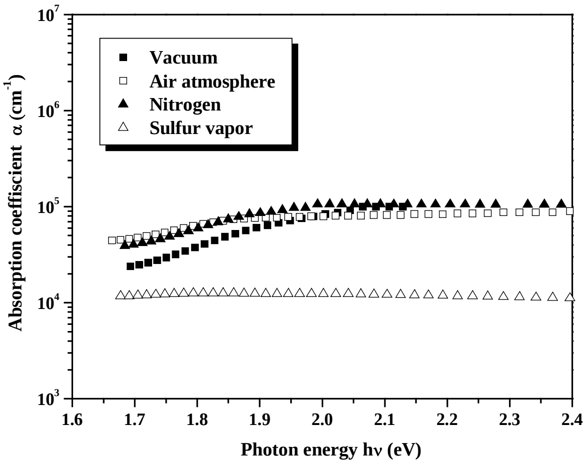

Fig. 4. Absorption coefficient spectra of thin films treated in various atmospheres.

4. Energy band gap

The relation between the absorption coefficient α and the incident photon energy is [11]:

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

where 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 a graph between $(\alpha h\nu)^2$ and photon energy $(h\nu)$ [12-13]. The band gap value can be determinate from the intercept with the photon energy axis. Direct band gap of thin films for respectively treated in sulfur vapor, nitrogen and in vacuum were 1.75eV, 1.73eV, 1.78 eV. However direct band gap for thin films annealing in air were 1.64 eV. This result is in agreement with those obtained from diffraction ray-X spectra (shown in Fig. 5).

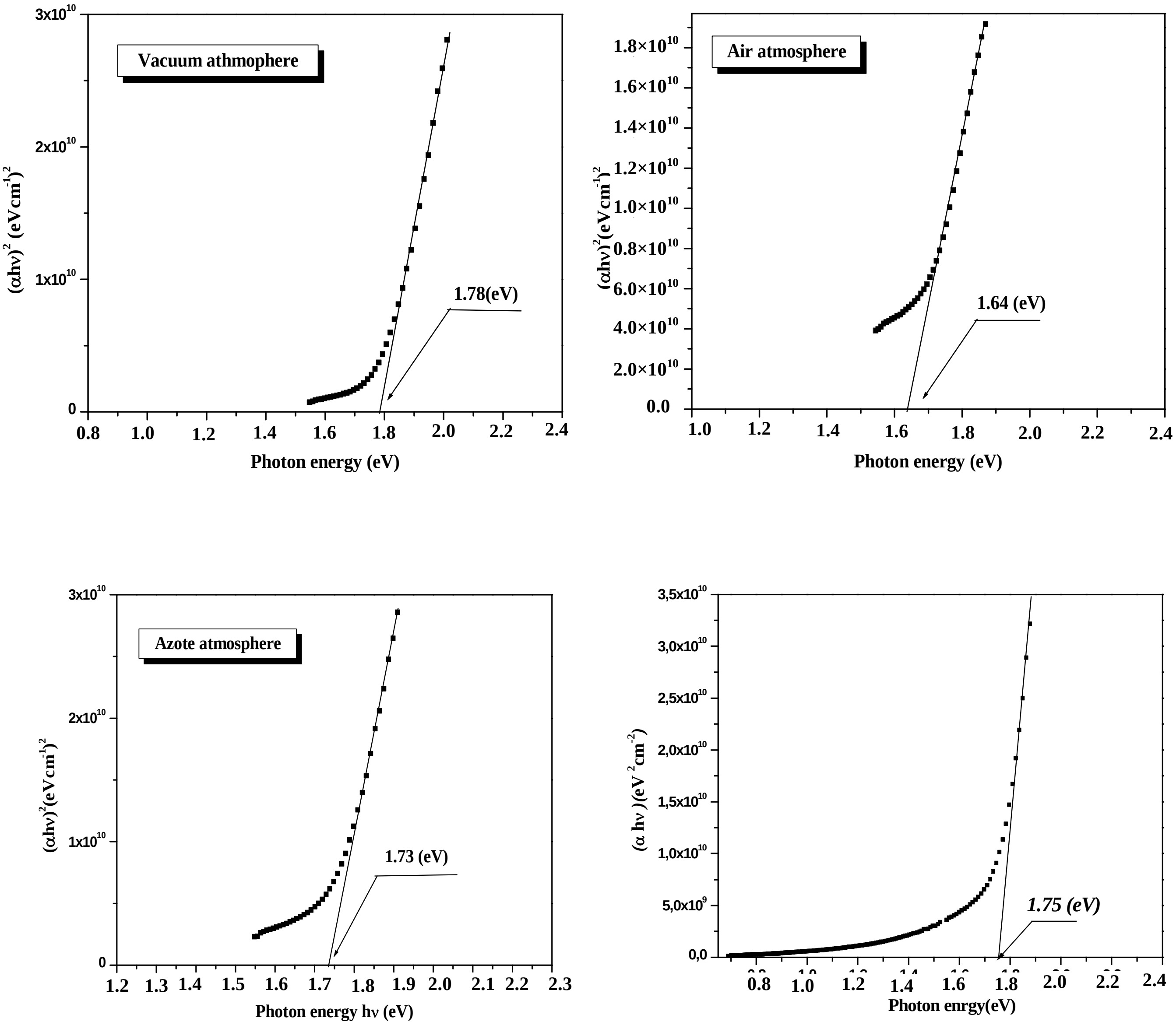

Fig. 5 Energy band gaps of thin films treated at different atmosphere.

4.1 Effect of annealing in different atmospheres at temperature of 300°C in electrical proprieties

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

$$R = R_0 exp\left(-\frac{E_a}{K_B T}\right) \qquad (3)$$

where E_a is a activation energy, K_b is a constant of Boltzmann and R_0 are the electrical resistance of the films at temperature T.

It is shown in Fig. 6 shows the variation of $ln\left(\frac{R}{R_0}\right)$ versus $\left(\frac{10^3}{T}\right)$ of thin films treated at temperature of 300°C in various atmospheres: vacuum, sulfur vapor, air, nitrogen atmospheres. For the regions in which the electrical resistance decreases with the temperature increase (in the cooling cycle) we can conclude that the activation energy depends on the nature of annealing atmosphere. Indeed, the annealing in air and in sulfur vapor increase the activation energy. This result can be explained by the presence of oxide phase observed in ray-X diffraction. All the results were collected in Table 3.

Table. 3. Activation energy of Sb_2S_3 thin film annealed at 300°C in various atmospheres.

	Different treatment		
Nature of treatment	Sulfur vapor	Air atmosphere	Nitrogen atmosphere
Annealing temperature (°C)	300	300	300
Activation energy (meV)	8	7.7	93

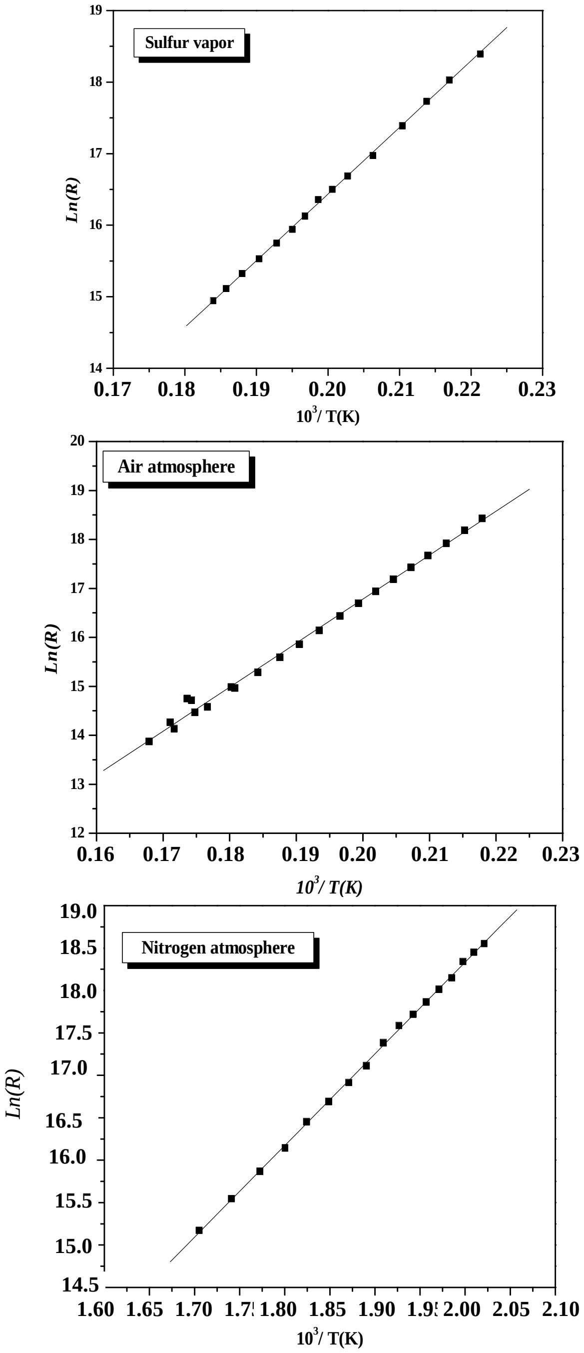

Fig. 6. $ln(R) = f\left(\frac{10^3}{T(K)}\right)$ *of thin films treated at temperature of 300°C in different atmosphere.*

5. Conclusions

Sb_2S_3 Thin film can be prepared by using vacuum evaporation method. After annealing thin films of Sb_2S_3 in different atmospheres as vacuum, sulphur vapour, normal air and nitrogen at 300°C, it can be concluded that a simple treatment in nitrogen atmosphere of Sb_2S_3 thin film can be sufficient to improve the structural, electrical and optical properties. The crystalline Sb_2S_3 thin film have high absorption coefficient α at about 10^5 cm^{-1} and bandgap energy of 1.73 eV. Although all thin films prepared and treated in this work exhibit a high electrical resistivity and remain intrinsic, this material could be used in several applications.

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