ISSN 1330–0008
CODEN FIZAE4

INFLUENCE OF HEAT TREATMENT ON THE PHYSICAL PROPERTIES OF ANTIMONY TRISULFIDE THIN FILMS

INAS K. EL ZAWAWI[a], AHMED ABD ELMOEZ[a], FATMA S. TERRA[a] and MOHAMED MOUNIR[b]

[a] *Solid State Physics Lab., National Research Centre, Tahrir St., Dokki, Cairo, Egypt*
[b] *Physics Department, Faculty of Science, Cairo University, Giza, Cairo, Egypt*

Received 15 December 1997; revised manuscript received 28 May 1998
Accepted 7 September 1998

The influence of isochronal and isothermal annealing for 0 to 180 minutes and at 27 to 250°C, respectively, on the optical and electrical properties of thin films of Sb_2S_3 have been investigated. The films deposited on glass substrate by thermal vacuum evaporation have amorphous structure, but after annealing at temperatures above 200°C for 3 hours, they change to polycrystalline structure. The optical absorption coefficient becomes higher for subgap absorption at higher annealing temperatures. The value of the optical Tauc gap and direct band gap changed with the annealing temperature. The dark electrical resistivity showed a decrease by about an order of magnitude when increasing both the isochronal and isothermal annealing treatment.

PACS numbers: 73.61.Jc, 78.66.-w UDC 538.975
Keywords: Sb_2S_3 thin films vacuum evaporated, amorphous and polycrystalline, heat treatment, optical and electrical properties

1. Introduction

Industrial applications of binary compound semiconductors stimulate the investigation of the physical properties of amorphous and crystalline systems. The relation between the physical properties and the local structure is of great interest in non-crystalline materials where the preparation techniques and composition can affect the short- and medium-range order [1]. The heat treatment affects directly the optical and electrical properties of the deposited thin films due to the changes in their structure.

Antimony trisulfide has many application in the industry such as in television camera tubes, microwaves, switching and optoelectronic devices [2-7]. The aim of the present study is to investigate the effects of post-deposition heat treatment on the optical and transport properties of Sb_2S_3 thin films.

2. *Experimental*

Thin films of Sb_2S_3 were prepared by thermal vacuum evaporation at about 10^{-3} Pa (10^{-5} Torr) from ingot powder of 99.99% purity (Merck) on glass substrates. The deposition rate was fixed at 1.2 nm/s, controlled by a quartz-oscillator thickness monitor (Modem FTM3, Edwards, England). For investigating the isochronal and isothermal annealing, we have chosen two values of film thickness, 3.67 and 4.68 μm. The film thickness was determined by measurements of interference patterns in the transmission spectra of low-energy photons [8].

The films were deposited at 27°C, and the post-deposition heat treatment was carried out in argon atmosphere at a pressure of 40 Pa (0.3 Torr) to eliminate any oxidation or contamination. The isochronal annealing effects were studied for films annealed for 180 minutes at temperatures from 27 to 250°C. The isothermal annealing effects were studied for films annealed for time intervals of 60, 120 and 180 minutes at 220°C. The structure of the films before and after the heat treatment was examined by X-ray diffraction (using X-ray analysis unit XD610 from Shimatzu, Japan). The optical data were derived from the optical transmission spectra measured by spectrophotometer Model PC3101 from Schimatzu. The films were measured in the spectral range from 200 to 2500 nm at 27°C. The DC electrical resistivity measurements were made using the four-probe method after depositing four ohmic contact electrodes of Al, made by thermal evaporation in a vacuum of about 0.001 Pa (10^{-5} Torr). The measurements were made in ambient atmosphere using electrometer Keithley Model 614 and DC precision power supply Model 1610 A.

3. *Results and discussion*

The composition of the investigated films before annealing was determined to be $Sb_{43}S_{57}$ by EDX analysis. The change of stoichiometry after annealing was not observable. It was also found by the EDX analysis in different regions of each film that the composition is the same all over the film. This confirmed the uniformity of the prepared films.

The as-deposited Sb_2S_3 films have amorphous structure as shown by X-ray diffraction technique. The films maintain their amorphous structure even after isochronal annealing for 180 minutes at temperatures lower than 200°C. Films annealed at temperatures above 200°C change from an amorphous structure of a brown colour to a polycrystalline structure of a dark-gray colour. The films have a good adherence to the glass substrate. Figure 1 shows the X-ray diffraction patterns of films of thickness 3.67 μm, annealed at 200°C (A) and 250°C (B). As determined from patterns, the structure of the films changed into polycrystalline with orthorhombic unit cell. The characteristic peaks of Sb_2S_3 and the interplanar spacing values d were calculated, and are given in Table 1 and indicated in Fig. 1. They are in agreement with the values reported by Doroichi et al. [9]. It appears that the preferred orientation of such grown polycrystalline films is [211], which is perpendicular to the substrate plane. At 250°C, as the crystallization process proceeds, the intensity of the (211) peak increases, indicating further orientation of the film crystallites in this direction.

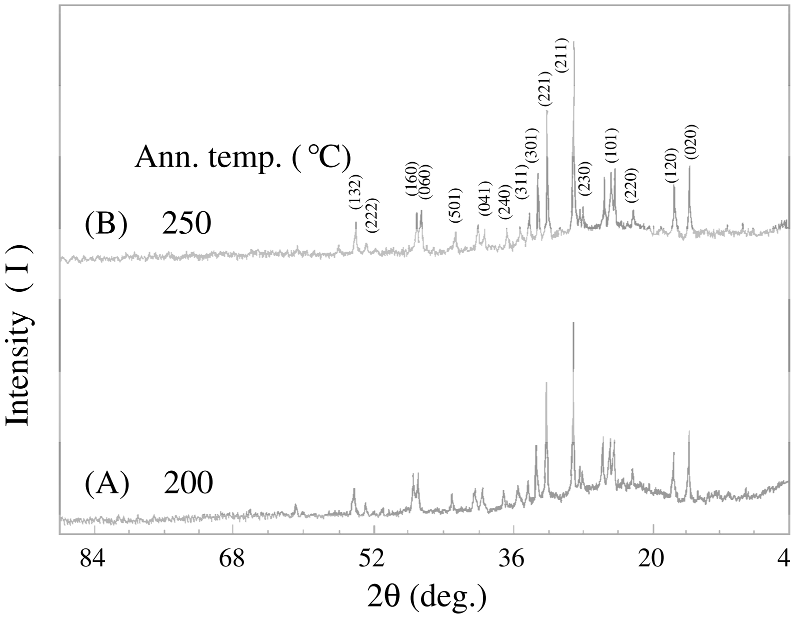

Fig. 1. X-ray diffraction pattern of Sb_2S_3 *film annealed for 180 minutes at 200°C (A) and at 250°C (B).*

Figure 2 shows the X-ray diffraction patterns for films 4.68 μm thick, which exhibit effects of isothermal annealing at 220°C for time intervals of 60, 120 and 180 minutes. It is obvious that films annealed for a time less than 180 minutes still maintain their amorphous structure. As the annealing time was increased to 180 minutes, the film structure changed to polycrystalline of orthorhombic unit cell. That is indicated by the characteristic peaks of Sb_2S_3 and interplanar spacing, calculated and shown in Fig. 2 and in Table 2. The peak of highest intensity for

TABLE 1. X-ray analysis of Sb_2S_3 *films annealed at 200°*C (A) *and at 250°*C (B) *for 180 minutes.*

This measurement (A)		This measurement (B)		JCPDS—TCDD		
d(nm)	I/I_0	d(nm)	I/I_0	d(nm)	I/I_0	hkl
0.574	50	0.571	48	0.5654	35	(020)
0.503	39	0.498	39	0.505	55	(120)
0.397	32	0.4004	26	0.3987	30	(220)
0.363	45	0.364	47	0.363	30	(101)
-	-	0.3554	45	0.3556	70	(310)
0.3172	47	0.176	44	0.3178	18	(021)
-	-	0.316	32	0.3128	35	(230)
0.3042	100	0.305	100	0.3053	95	(211)
0.2761	72	0.276	71	0.2764	100	(221)
0.268	42	0.268	44	0.268	50	(301)
0.2604	27	0.260	27	0.2609	25	(311)
0.2514	22	0.251	21	0.253	45	(240)
0.2273	21	0.2274	20	0.2277	25	(041)
0.196	20	0.1936	19	0.194	45	(501)
0.1885	30	0.1879	29	0.1885	10	(060)
0.1832	30	0.1864	28	0.1871	10	(600)
0.172	15	0.1728	23	0.1729	20	(222)
0.1687	23	0.1689	24	0.169	35	(132)

films annealed at 220°C for 180 minutes is (020), which is similar to the highest peak intensity (020) of the ingot powder used for evaporation of films (Table 2). The appearance of the highest [211] peak intensity in the case of isochronally annealed films, which is different from that of the Sb_2S_3 powder and isothermally annealed films, may be due to a slight deviation from the perpendicular orientation of the source to the substrate during the film deposition. It was reported that the (020) orientation is preferable for films prepared at substrate temperature of 220°C [10].

The optical absorption coefficients α as function of the photon energy E for the as-deposited films, and those which were isochronally annealed at 150, 200, 250°C, of thickness 3.67 μm, are shown in Fig. 3. It is clear that the absorption coefficient becomes higher for subgap absorption as the annealing temperature increased. The as-deposited films and annealed ones at 150°C have the same characteristic behaviour of the absorption coefficient in spectra of amorphous materials, i.e., the coefficient becomes slightly higher for subgap absorption. The slope of the absorption edge is slightly steeper for the as-deposited films than of the films annealed at 150°C, while the values of $\alpha < 10^3$ cm^{-1} are different. The absorption coefficients of films annealed at 200°C and 250°C have different behaviour than other samples due to the change in their structure from amorphous to polycrystalline, as indicated in Fig. 1. As the annealing temperature increased from 200 to 250°C, the absorption coefficient at lower energies increases. That is accompanied by an enhancement of crystallization of the film annealed at 250°C.

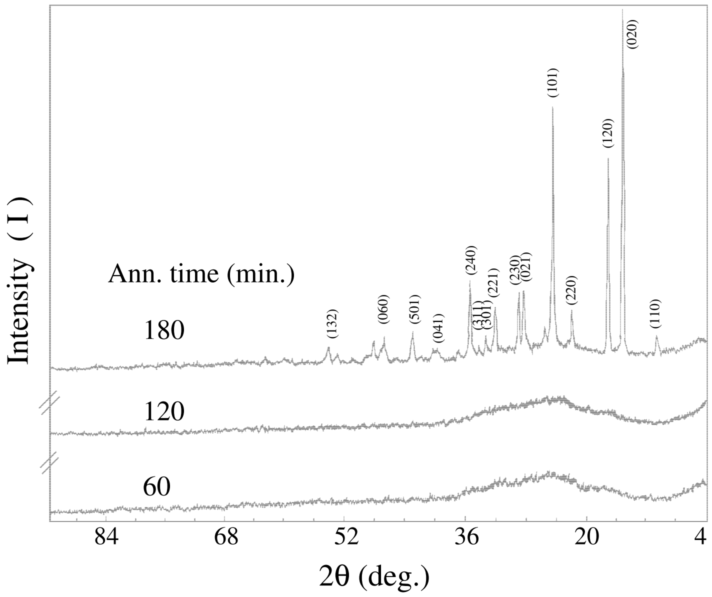

Fig. 2. X-ray diffraction pattern of Sb_2S_3 *films annealed at 220°*C *for 60, 120 and 180 minutes.*

TABLE 2. X-ray analysis of Sb_2S_3 *film, annealed for a time of 180 minutes at 220°*C*, compared with the ingot powder and the standard card data.*

This measurement, thin film		This measurement, ingot powder		JCPDS—TCDD		
d(nm)	I/I_0	d(nm)	I/I_0	d(nm)	I/I_0	hkl
0.803	10	0.804	22	0.799	16	(110)
0.577	100	0.572	100	0.565	35	(020)
0.507	59	0.512	66	0.505	55	(120)
0.397	18	0.4004	36	0.399	30	(220)
0.358	73	-	-	0.355	70	(310)
0.346	13	0.333	17	0.345	25	(111)
0.311	23	0.313	54	0.312	35	(230)
0.304	22	0.305	52	0.305	95	(211)
0.275	19	0.276	57	0.2764	100	(221)
0.268	11	0.268	31	0.268	50	(301)
0.254	26	0.252	71	0.252	45	(240)
0.209	13	0.210	41	0.2101	20	(421)
0.194	11	0.194	47	0.194	45	(501)
0.188	10	0.188	70	0.188	10	(060)
0.169	8	0.169	46	0.169	35	(132)

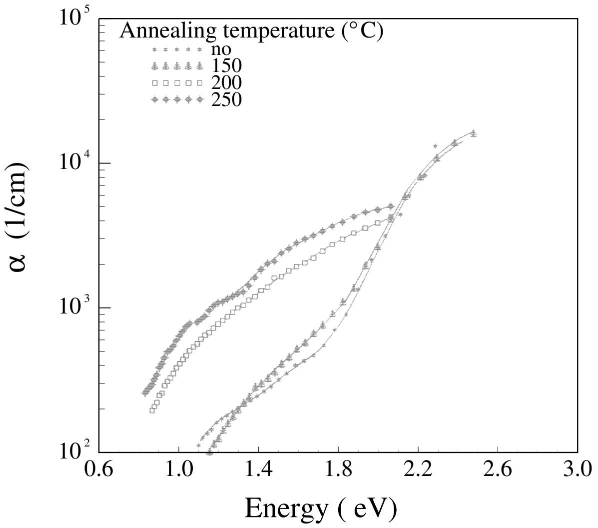

Fig. 3. Optical absorption coefficient α *as a function of photon energy* E *for* Sb_2S_3 *films as-deposited and annealed for 180 minutes at 150, 200 and 250°*C.

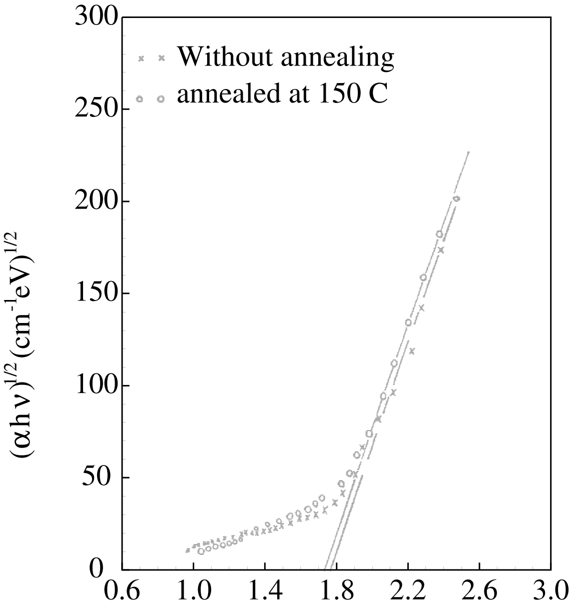

Fig. 4. Variation of $(\alpha h\nu)^{1/2}$ *with photon energy* $h\nu$ *for* Sb_2S_3 *films as-deposited and annealed at 150°*C *for 180 minutes.*

The optical gap of the as-deposited and of annealed films at 150°C, due to the indirect band to band transition in amorphous materials, was estimated from the empirical relation [11]

$$\alpha h\nu = B(h\nu - E_G)^2,$$

where E_G is the Tauc optical gap and B is a constant. Figure 4 shows the relation between $(\alpha h\nu)^{1/2}$ and the photon energy $h\nu$ for amorphous films. The extrapolation of the linear part of the curves indicates that the Tauc optical gaps have the values of 1.75 and 1.72 eV for the as-deposited films and films annealed at 150°C, respectively.

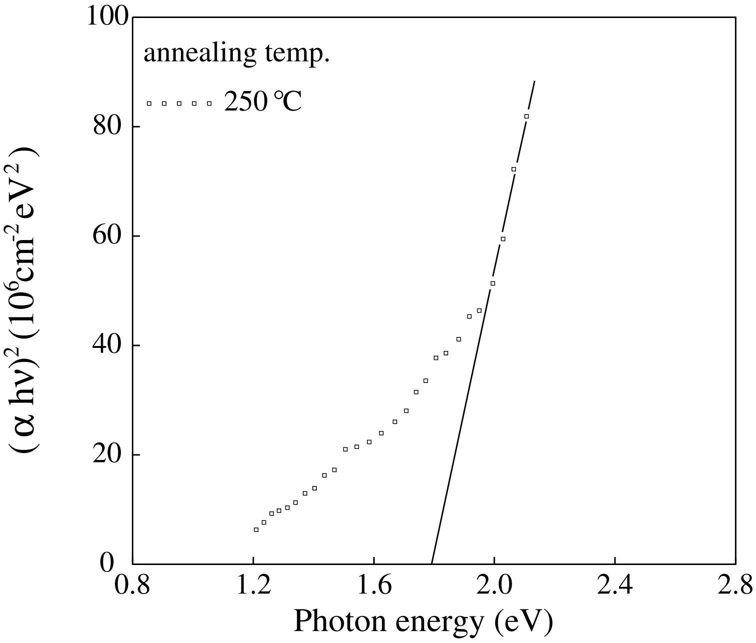

Fig. 5. Variation of $(\alpha h\nu)^2$ with photon energy E for Sb_2S_3 film annealed at 250°C for 180 minutes.

For polycrystalline films, the optical gap is estimated from the experimental data which satisfy the relation

$$\alpha h\nu = D(h\nu - E_g)^{1/2},$$

where E_g is the optical gap due to the direct transition and D is a constant. From Fig. 5, the derived value of the optical gap of polycrystalline films annealed at 250°C is 1.8 eV [12]. The material of the films annealed at 250°C represents crystalline material as the transition temperature is 214°C and the crystallization temperature is 248°C [9].

The dark electrical resistivity of the films of thickness 3.67 μm, as-deposited and annealed at 150, 200, 220 and 250°C, as a function of their isochronal annealing, is

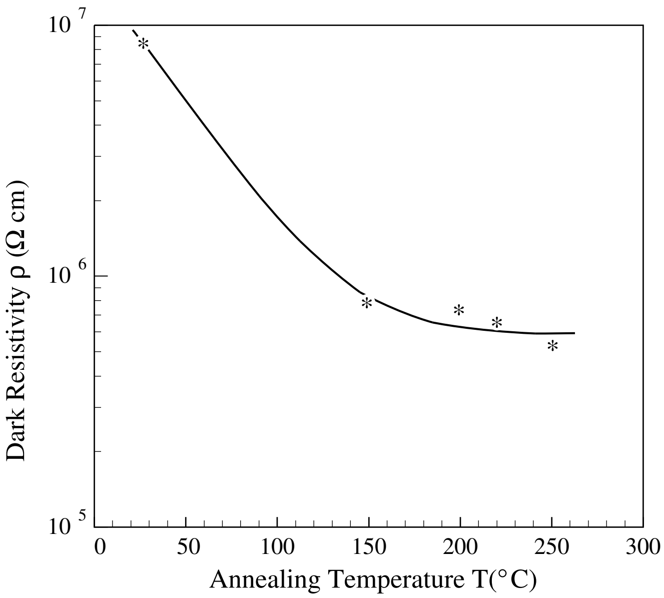

Fig. 6. Dark electrical resistivity ρ *as a function of annealing temperature T for* Sb_2S_3 *films annealed for 180 minutes.*

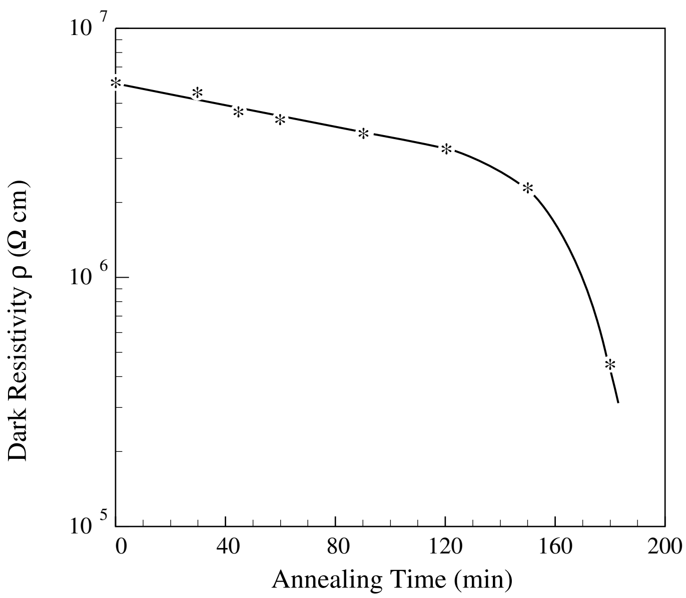

Fig. 7. Dark electrical resistivity ρ *as a function of annealing time for* Sb_2S_3 *films annealed at temperature of 220°C.*

shown in Fig. 6. It is observed that the dark electrical resistivity decreases sharply by an order of magnitude as the annealing temperature is increased from 27 to 200°C, due to the change in the structure to the polycrystalline form. The change is slow from 200 to 250°C due to an enhancement of crystallinity (see Fig. 1). The electrical resistivity tends to be stable for the crystalline form of the material. The annealing temperatures from 200 to 250°C do not play a considerable role in the dark electrical resistivity.

The dark electrical resistivity of the films of thickness 4.68 μm, annealed at 220°C, as function of their annealing time, is shown in Fig. 7. As the annealing time increases up to 120 minutes, a slight steady decrease in dark electrical resistivity occurs. This may be due to the decrease in the degree of disorder in the amorphous material. As the time of annealing increases from 120 to 180 minutes, a sharp exponential drop in the dark electrical resistivity is observed. This decrease is correlated with the change from amorphous to polycrystalline structure, as confirmed by analysis of Fig. 2. From the study of the electrical resistivity of the annealed films, it is found that in the temperature range 200 to 250°C, the important factor is the annealing time, since for 180 minutes, the resistivity decreases sharply. This is in accordance with the X-ray diffraction results, which showed that if the films are annealed at 200°C for 180 minutes, the polycrystalline films are obtained.

4. Conclusion

The isochronal and isothermal annealing treatments up to 250°C have their effects on the structure, the optical and the electrical properties of Sb_2S_3 thin films. The structure of the films changes from amorphous to polycrystalline with orthorhombic unit cell at annealing temperatures above 200°C for annealing times greater that 180 minutes. The absorption coefficient of isochronally annealed films becomes higher for subgap absorption as the annealing temperatures increase. For amorphous films, the optical gap due to the indirect transition shows a decrease to 1.72 eV for the film annealed at 150°C, while it has a slightly higher degree of disorder, as observed from the slope of the absorption edge. The films annealed at 250°C have an optical gap of 1.8 eV due to the direct transition in the polycrystalline material.

The electrical transport properties were also affected by the isochronal and isothermal annealing which is accompanied by a decrease of the dark electrical resistivity by about an order of magnitude, due to the crystallization of the films.

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UTJECAJ TOPLINSKE OBRADE NA FIZIČKA SVOJSTVA TANKIH SLOJEVA ANTIMON TRISULFIDA

Ispitivao se je utjecaj izotermičkog toplinskog otpuštanja na optička i električna svojstva tankih slojeva Sb_2S_3 na temperaturama 27 do 250°C i u vremenima od 0 do 180 minuta. Tanki slojevi dobiveni vakuumskim naparavanjem na staklenu podlogu imaju amorfnu strukturu, ali nakon otpuštanja iznad 200°C kroz 3 sata oni mijenjaju strukturu u polikristaliničnu. Optički apsorpcijski koeficijent raste za podprocijepnu apsorpciju s povišenjem temperature otpuštanja. Vrijednost optičkog Taucovog procijepa i izravni procijep mijenjali su se s temperaturom otpuštanja. Tamna električna otpornost se je smanjila za red veličine kada se je povećalo vrijeme otpuštanja i temperatura.