Journal of Ovonic Research Vol. 6, No. 6, November - December 2010, p. 259-266

STRUCTURAL AND MORPHOLOGICAL STUDIES OF Sb_2S_3 THIN FILMS

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Thin films of Sb_2S_3 with different thicknesses deposited at room temperature on pure glass and Indium Tin Oxide (ITO) coated glass substrates by thermal evaporation technique. The films are characterized for structural and morphological analyses to observe the effect of thickness on them by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman spectroscopy. Amorphous nature of the as-deposited films was evidenced from XRD, SEM and Raman spectroscopic analyses. XRD study confirms orthorhombic structure of Sb_2S_3 with lattice parameters, a = 1.12nm, b = 1.132nm and c = 0.384nm and the transition from amorphous to polycrystalline with thermal treatment. Increase of crystallite size with thickness and temperature was proved by XRD and the effect of thickness on roughness and grain size was studied by AFM.

(Received December 1, 2010; accepted December 14, 2010)

Keywords: Sb_2S_3 thin films, Thickness, Indium Tin Oxide, Thermal Evaporation Technique, Structural study, Morphological study, Lattice parameters.

1. Introduction

Thin film technology is a growing technology and it is a very developed field of microelectronics. Chalcogenides of the V-VI groups are useful semiconductors which tend to form binary compounds. Thin films of these semiconductor materials have potential applications in photoelectrochemical devices, optoelectronic devices, thermoelectric coolers and decorative coatings etc. A number of deposition techniques have been used to prepare Sb_2S_3 thin films like, chemical deposition by R. S. Mane et al.[1-2], R. F. Sputtering by Matthieu Y. Versavel et al.[3], Spray pyrolysis by C. H. Bhosale et al.[4], Flash evaporation by S. Mehanty et al.[5] and Vacuum evaporation by Z. S. El Mandouh et al. [6] and N. Tigaue et al.[7-8] . Among the various methods used for the preparation of Sb_2S_3 thin films, the deposition by thermal evaporation is simple and very convenient. The disorders and defects present in the amorphous structure change as a result of heat treatment due to transition from amorphous to crystalline state. The efficiency of the devices is determined by the structural, electrical and optical studies of the films. The present work deals with the preparation and characterization of thermally evaporated Sb_2S_3 thin films. The effect of the thickness variation on the structural and morphological properties of the films on pure glass substrate is analyzed in detail. Samples have been characterized by XRD, SEM, AFM and Raman spectroscopy. The XRD result of as-deposited antimony sulfide thin films is compared with the Sb_2S_3 thin films on Indium Tin Oxide (ITO) glass substrate.

2. Experimental

Sb_2S_3 thin films were deposited onto glass and Indium doped Tin Oxide (ITO) coated glass substrates via thermal vacuum evaporation technique from high purity polycrystalline powder (99.999% purity, Sigma-aldrich), under vacuum at 10^{-5} torr. In order to get uniformly coated films,

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the pre-cleaned substrates were placed in a rotative sample-holder at room temperature during deposition. Deposition rate and film thickness were controlled during deposition by quartz oscillator thickness monitor. Post deposition heat treatment was carried out for thin films on glass substrate in vacuum at a pressure of 10^{-6} torr for 1 hr by keeping constant temperatures at 473K and 523K. Structural characterizations of Sb_2S_3 powder and thin film samples have been done, before and after annealing, using an X-ray diffractometer with CuK_α radiation ($\lambda = 1.5406$Å) in the scanning angle (2θ) from 10^0 to 50^0 .The film surface morphology was observed by scanning electron microscope (JEOL JSM 5600) and verified by atomic force microscope in non-contact mode. The AFM investigation was utilized to measure the grain size and roughness of the surface of the film. Raman spectra were taken at room temperature with a visible Raman spectrophotometer (Jobin Yvon Horiba LABRAN-HR) and an argon ion laser operating at a wavelength of 400nm as the excitation source. The laser light was focused on the thin film sample through an optical microscope.

3. Results and discussion

3.1 Structural properties

X-ray diffractograms of the as-deposited, annealed and powder samples of Sb_2S_3 are shown in figures (1-4). It is clear from fig. (1) that all the investigated films formed at room temperature have an amorphous nature, which agrees with the previous observations reported by N. Tigau et al. [8-9]. The appearances of broad X-ray spectra suggest the amorphous nature of films. Fig. 2 illustrates that annealing temperature at 473K for 1hr cannot influence much in the amorphous nature of all the films. A similar study was reported for chemically deposited films by A. M. Salem and M. Soliman Selim [10] and for physical vapour deposition by F. Perales et al. [11] and Inas K. El Zawawi et al. [12]. To investigate the effect of annealing temperature greater than 473K on the growth of polycrystalline from amorphous phase, thin films have been annealed for 1hr at 523K and similar kind of study have been observed and presented by M. S. Droichi et al. [13]. and Inas K. El Zawawi et al. [12].

It is clear from fig. (3) that the increase of thermal treatment improves crystallinity of Sb_2S_3 films with orthorhombic unit cell. As the crystallization process proceeds with thickness at temperature 523K, the intensity of the (120) peak increases, indicating further orientation of the film crystallites in this direction. As K.Y. Rajpure and C.H. Bhosale [14] point out, annealing promotes fusion of small crystallites (agglomeration) thus reducing the grain-boundary area, which leads to an increase in diffusion length due to decrease in scattering from boundaries. This leads to an increase in crystallite size of the Sb_2S_3 particles.

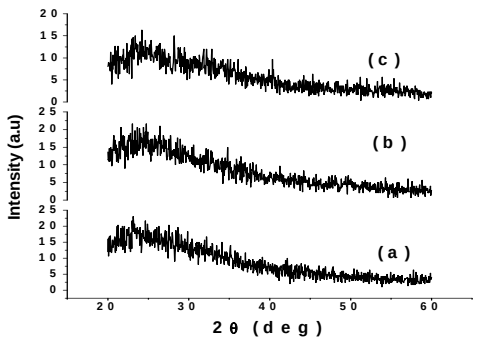


Fig. 1 XRD pattern of as-deposited Sb_2S_3 thin films of thicknesses a)17nm, b)100nm, c)300nm.

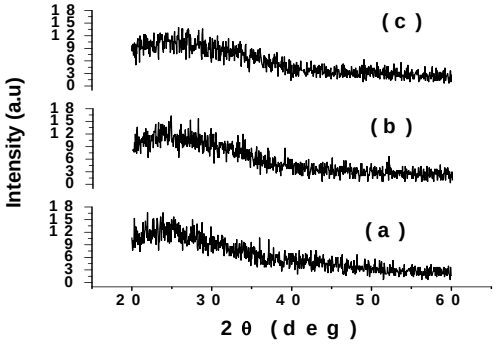


Fig. 2 XRD pattern of annealed (473K) Sb_2S_3 thin films of thicknesses a)17nm, b)100nm, c)300nm.

Fig. (4) shows the X-ray diffractogram obtained for Sb_2S_3 composition in a powder form. The orthorhombic crystal structure of Sb_2S_3 with cell parameters, a = 1.12nm, b = 1.132nm and c =

0.384nm has been found out from XRD powder data. These parameters are in good agreement with the reported results by A. A. El- Shazly et al. [15]. As it can be seen in the figs. (3 and 4), the patterns of the annealed film and powder form show a sharp diffraction peak at 2θ = 17. 54 which corresponds to (120) plane of the orthorhombic structure for Sb_2S_3. Some additional diffraction peaks appeared (fig.3b, 3c) at 2θ of about 29.24, 35.49, 43.02 and 46.81 which corresponds to diffraction from (211), (240), (250), and (501) planes to prove the increased crystallinity with higher thickness.

Using Bragg's relation [9], the inter planar spacing d_{hkl} was calculated from powder diffraction data:

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} \quad (1)$$

where λ is the X-ray wavelength, n is the order number and θ is the Bragg's angle.

Table 1 shows the calculated d_{hkl} values in comparison with the standard powder (JCPDS card No. 42-1393) and in agreement with the recorded values by A.A. El- Shazly et al. [15]. The crystallite size D can be estimated using the Sherrer's formula [9]:

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (2)$$

where K is the shape factor (0.94), β is the full width at half maximum (FWHM) of the diffraction expressed in radians. The estimated crystallite size for the annealed samples of different thicknesses is given in Table 2. Matthieu Y. Versavel et al. [3] reported that the crystallite size is smaller than 50nm. The crystallite size increases with: a) increasing film thickness and b) increasing annealing temperature [16].

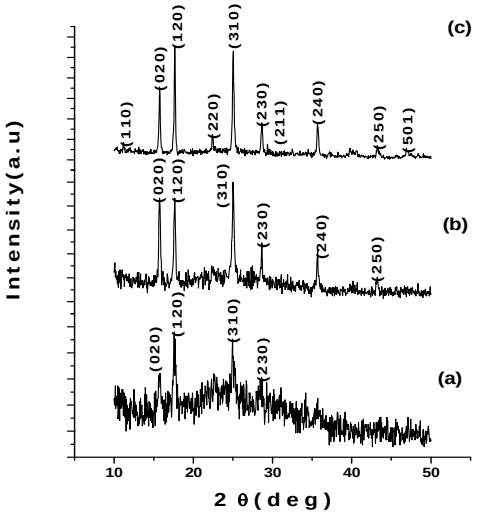


Fig. 3 XRD pattern of annealed (523K) Sb_2S_3 thin films of thicknesses a)17nm, b)100nm, c)300nm.

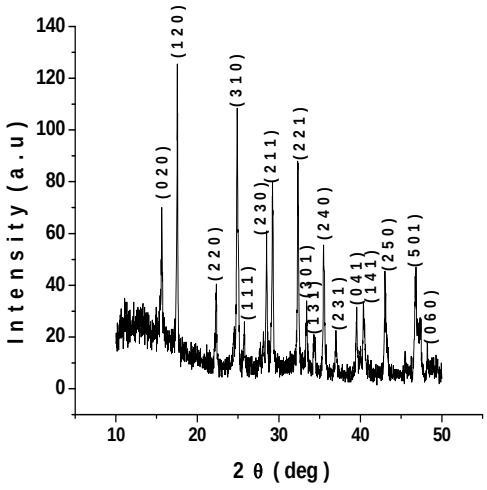


Fig. 4 XRD pattern of Sb_2S_3 powder sample

Table 1 The inter planar spacing, d, for Sb_2S_3 powder

Experimental data - d (Å)	JCPDS data-d (Å)	hkl
5.661	5.660	020
5.052	5.057	120
3.979	3.987	220
3.573	3.575	310
3.129	3.131	230
3.052	3.051	211
2.767	2.765	221
2.679	2.681	301
2.526	2.525	240
2.427	2.427	231
2.276	2.276	041
2.233	2.232	141
2.101	2.088	250
1.938	1.930	501

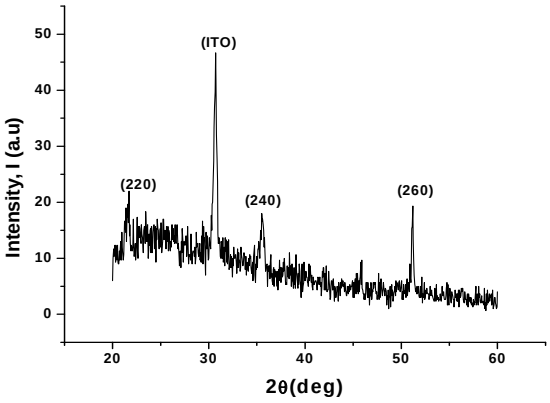


Fig. 5 XRD pattern of Sb_2S_3 thin film on ITO coated substrate

Fig.5 shows the X-ray diffractogram of as-deposited thin film of higher thickness (300 nm) on Indium Tin Oxide (ITO) coated glass substrate. Comparing with the as-deposited Sb_2S_3 thin film (t=300 m) on pure glass substrate, a new peak appeared at $2\theta = 30.7^{o}$, that proves the presence of ITO.

Table 2 The crystallite size, D, of annealed samples for three thicknesses

Thickness (nm)	Crystallite size (nm)
17	26
100	36
300	49

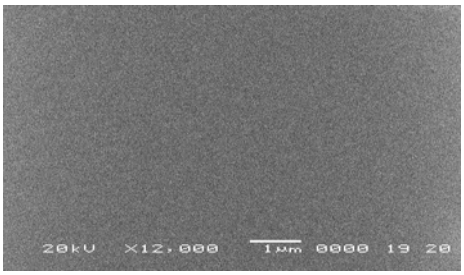
Table 3 The grain size and roughness of as-deposited samples for three thicknesses

Thickness (nm)	Grain size (nm)	Roughness (nm)
17	20	1.74
100	29	1.96
300	36	2.892

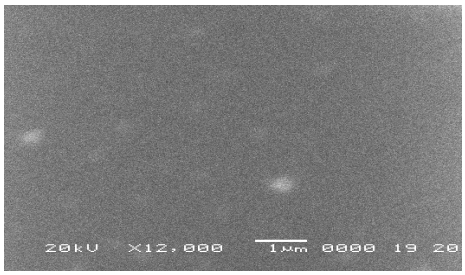
3.2. Morphological studies

The morphological characteristics of the thin film have been studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM micrographs are given in Fig.6 for as-deposited films of thicknesses 17 nm, 100 nm and 300 nm and for annealed (473K, 1hr) film of lowest thickness (17nm) respectively. The SEM images of antimony sulfide thin films are appeared as smooth, dense and homogeneous in nature. The micrographs show that the as-deposited films at room temperature have amorphous structure. After annealing for 1hr at 473 K, film structure is appeared as amorphous in nature. These results are confirmed by XRD analyses (Figs.1& 2).

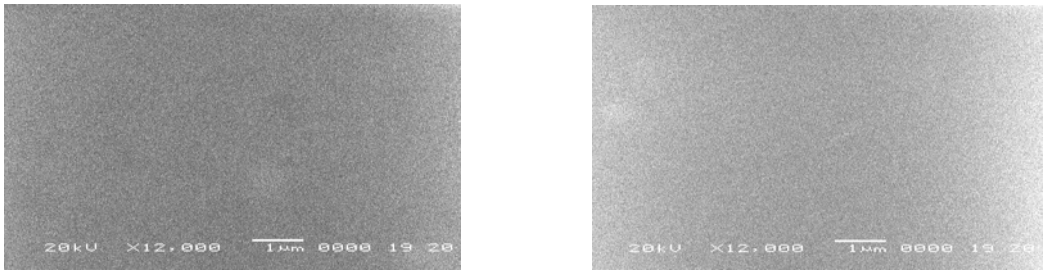
The surface topographical images recorded from atomic force microscope (AFM) for Sb_2S_3 thin films deposited at room temperature of film thicknesses 17nm, 100nm and 300nm are shown in fig.7. The measured grain size and RMS roughness are given in Table 3. As it is clear from table, the average grain size increases with increasing thickness, which is supported by N. Tigau et al. [8] and K.L. Chopra [16]. Also K. L. Chopra explains the linear increase of surface area and thus roughness factor with thickness of the film. The irregular shapes of the grains suggest that at low substrate temperature, the kinetic energy is not enough to induce the coalescence of the grains [17].



(a)



(b)



(c) (d)

Fig. 6 SEM images of as deposited, [(a), (b), (c)] and annealed (at 200^0 C) [(d)] samples

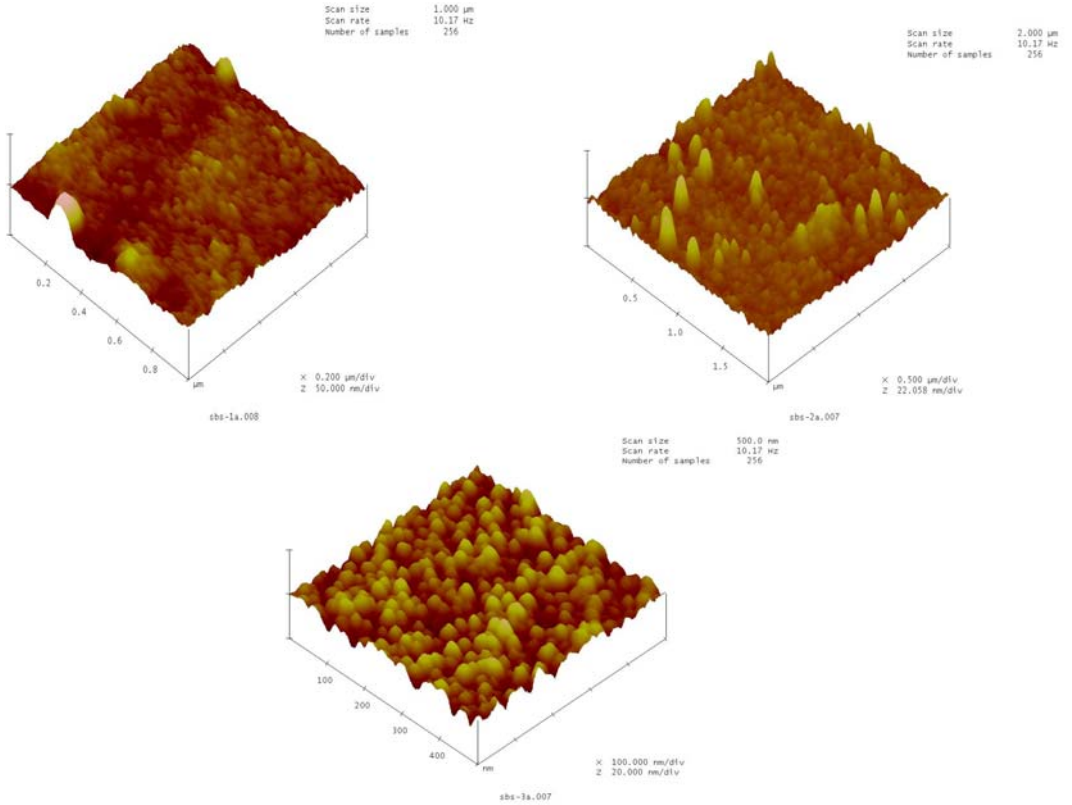


Fig. 7 AFM images of Sb_2S_3 thin films (thicknesses-17 nm, 100 nm, 300 nm)

Raman spectra of Sb_2S_3 thin films on glass substrate for different thicknesses 17 nm, 100 nm and 300 nm are shown in Fig.8. Spectra were taken at room temperature. As can be seen from this figure the spectra of as-deposited sample shows very broad modulation of intensity, indicating the amorphous phase, which is in agreement with the reported results by F. Perales et al. [11]. The amorphous nature of the as-deposited thin films is confirmed by the XRD and SEM data.

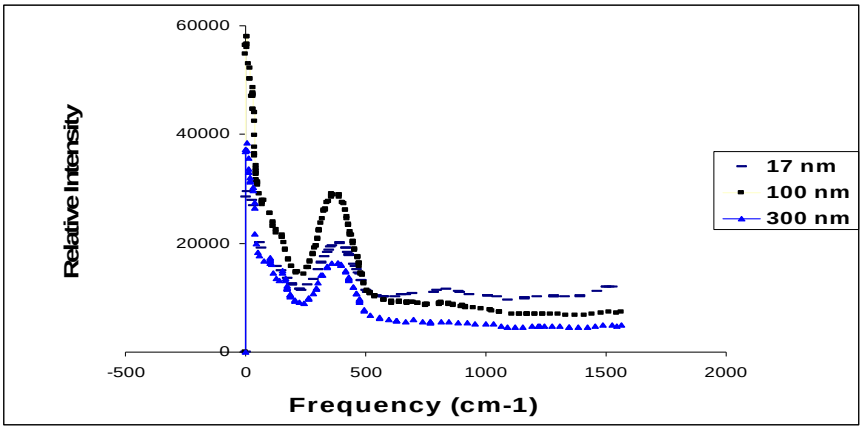


Fig. 8 Raman spectra of as-deposited Sb_2S_3 thin films (thicknesses-17nm, 100nm, 300nm)

4. Conclusions

At room temperature thermal vacuum evaporation method is employed to deposit Sb_2S_3 thin films of different thicknesses and the structural and morphological investigations have been done successfully. The orthorhombic crystal structure of Sb_2S_3 with lattice parameters and dependence of crystallite size on thickness were showed by X-ray Diffraction (XRD) measurements; dependence of roughness on thickness was proved by atomic force microscopy (AFM) photographs. XRD and SEM results confirmed the amorphous nature of as-deposited and annealed (473K) films. Raman spectra were a clear evidence of amorphous nature. The as-deposited amorphous thin films transformed to polycrystalline films during the thermal treatment at 523K.

Acknowledgement

The authors gratefully acknowledge the special support of UGC-DAE Consortium for Scientific Research, Indore, especially to Prof. Ajay Gupta- the centre Director, to carryout the measurements.

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