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Effect of annealing temperature on structure properties of SnS thin films

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ABSTRACT

SnS thin films of thickness, (300 nm ± 0.01) deposited by thermal evaporation with rate deposition (48 nm/s) on suitably cleaned glass substrates at room temperature substrate and then the films were annealed at 200°C temperature in vacuum for (2 h). The structural properties of the films are determined using x-ray diffraction, scanning electron microscopy (SEM) and atomic force microscopy (AFM). X-ray diffraction patterns indicated that the films are poly crystalline for an orthorhombic structure, with (111) preffered orientation. The values of lattice constants, grain size, microstrain and dislocation density of the deposited films were calculated and their variations with annealing. The scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies reveal good surface morphology, the average grain size and surface roughness were found to increase with annealing.

KEYWORDS

SnS;
Thin films;
Lattice constant;
Grain size;
Microstrain;
Dislocation density;
Texture coefficient;
SEM and AFM.

INTRODUCTION

Recently, a variety of binary semiconductor especially from IV-VI and among this group of semiconductor compounds, it is considered as an important material for the development of different optoelectronic devices[1-3] because of its high photosensitivity and suitable intrinsic band gap, 1.3eV[4]. In recent years special attention has been given to the investigation of optoelectronic properties of SnS thin films in order to improve the performance of devices made of it and also for finding new applications[5,6]. For preparation of SnS thin films, different growing methods have been reported[7,8]. Out of these, physical vapor deposition in its variants is often used as it offers many possibilities to modify the deposition parameters and to obtain films with pre-determined structure and suitable phototransport properties. Structure properties of semiconducting films are essential requirement for proper application in various optoelectronic devices. These properties of the films are sufficiently structure sensitive. Therefore appropriate structural characterization of the films is necessary. It may be noted that the structural parameters such as crystalline, crystal phase, lattice constant, grain size etc are strongly dependent on the deposition conditions. The structure of thermally deposited SnS thin films is likely to be governed by the degree of vacuum, rate of deposition, substrate temperature, film thickness etc. An experimental study has been undertaken in order to structurally characterize thermally evaporated SnS thin films and in this work some correlative results of different structural param-

eters with substrate temperature has been reported.

EXPERIMENTAL

Thin films of SnS thickness (300 nm ± 0.01) were deposited at room temperature and annealing with 200°C on chemically and ultrasonically cleaned glass substrates with the help of a hind high Vacuum Coating unit at a vacuum better than 10^{-5} torr. The source to substrate distance was maintained at 6.5 cm for the cases. The prepared films were annealed in vacuum at 200 °C temperature for 2h. Pure (99.99%) bulk SnS sample was used as the source material. Thin molibodum boats of proper size and shape were used as the source heater. X-ray diffractogram of SnS thin films were taken by using Philips X-ray diffract meter (Philips X'Pert-Pro) with CuKα radiations of wavelength 1.54Å.

Surface morphology of the SnS films were investigated by using scanning electron microscopy (SEM) pictures were taken using computer controlled digital scanning electron microscope model Philips XL30 ESEM.

Atomic Force Microscope (Various techniques of imagining surface and nanostructures are available but the most common ones are atomic force microscopy AFM. The AFM is useful for obtaining two and three-dimensional topographic information of insulating and conducting structures with lateral resolution down to 1.5 nm and vertical resolution down to 0.05nm. In this work, an AA 3000 Scanning Probe Microscope AFM system. The root mean square of roughness and grain size are obtained by using certain software with Imager version 4.7004, scanning probe Microscope Imager proceed software (c) 2005-2010 AA C.

RESULTS AND DISCUSSION

X-ray diffraction studies

Figure 1 shows the x- ray diffraction patterns of the as – prepared and annealed SnS films of 200°C temperature. It is clear from the figure that the films have poly crystalline structure of orthorhombic form, with small peaks at 2θ equal 31.69, 31.65 and 30.75,30.89 corresponding to planes (111) and (101) for as – prepared and annealined film respectively. The values of lattice constants a,b and c for the as prepared and annealed films are calculated using equation (1) and the calculated values are given in TABLE 1, comparing with lattice constants for orthorhombic SnS crystal given in JCPDS NO. 39 -0354 with lattice parameters a =0.4329nm, b =1.1192nm and c= 0.3984 nm, it is seen that the calculated values are in good agreement with the standered values for SnS orthorhombic strcture. From Figure 1., it is observed that the films prepared at 200°C have decreased in grain size, which attributed to the evaporation of sulpher from the film upon annealing at 200°C because of the high pressure, leaving atin-rich surface which might have reacted with the oxygen to from SnO_2 due to the low vacuum process[17].

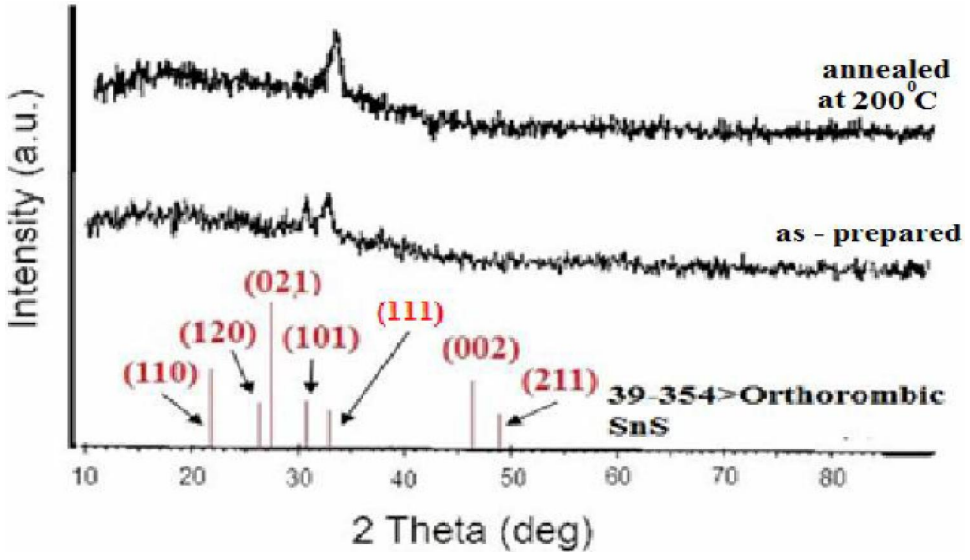

Figure 1 : X-ray diffraction pattern of SnS thin film as-prepared and annealing with 200°C for 2 h.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (1)$$

The size of crystallites is calculated using Scherrer's formulas[9], TABLE 1 :

$$D = \frac{0.94\,\lambda}{\beta \cos\theta} \quad (2)$$

Where D is the size of crystallite, λ = 1.5406 Å the wave length of x-ray used, β the broadening of diffraction line measural at half its maximum intensity in radiaus and ⊍ is the angle of diffraction. The micro strain ε is calculated using the following equation[10]

TABLE 1 : Lattic constasts of SnS thin films as prepared & 200°C

	Lattic Constants		
	a Å	b Å	c Å
ASTM	4.3291	11.1923	3.9538
As- prepared	4.5314	11.7744	3.7862
annealed	3.9103	13.0968	4.3033

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (3)$$

As can be seen from TABLE 2 as – prepared films give smaller value of strain

The dislocation density δ and number of crystalline are calculated using the following equations and usted in TABLE 2

$$\delta = \frac{1}{D^2} \quad (4)$$

$$N = \frac{t}{D^3} \quad (5)$$

Where (t) is the film thickness.

So texture coefficient was calculated for x-ray diffraction result by using the equation[11]:

$$T_{c\,(hkl)} = \frac{(I(hkl)/I_s(hkl)}{1/N\sum I(hkl)/I_s(hkl)} \quad (6)$$

Where $T_{C\,(hkl}$ is the texture coefficient of (hkl) plane, $I_{(hkl)}$ is the intensity of (hkl) plan from standard data in PDF card fitting in the x-ray diffraction and N is the total reflection number.

TABLE 2 : Structural properties of SnS thin films

Substrate Temp.(^{O}C)	2θ (deg)	hkl	Grain size (nm)	Micro strain (10)$^{-}$□	Dislocation density m^{-}² (10)^{14}	Number of Crestline (m^{-2}) ×10^{18}	$T_{C(hkl)}$
As- prepared at R.T	30.75	101	14.678	2.4655	46.415	0.0948	1.02
	31.69	111	13.1348	2.75527	57.963	0.1323	
Annealed at 200	30.89	101	14.267	2.5366	49.128	0.1033	1.4
	31.65	111	11.7804	3.072	72.128	0.1835	

Surface structural properties (AFM Analysis)

Atomic force microscopic (AFM) allows us to get microscopic information on the surface structure and topographies representing the surface relief, see TABLE 3. This technique forms digital images which allow quantitative measurement so surface features, such as root mean square roughness, RMS, or average roughness, and the analysis of images from different perspectives, including three- dimensional simulation[12-13]. In general, an AFM uses a very fine probe to scan the surface of a sample. The spectra of the surface (i.e. image) are generated by a photodiode[14,16].

Figure 2 shows the AFM image of SnS Nanocrystalline thin film deposited at a room temperature. The average grain size of Nanocrystallin SnS calculated from AFM is (nm).

Surface morphology and compositional analysis

Figure 3 show that the SEM micrograph of SnS thin film deposited at R.T. temp.and other annealed with 200 °C. SEM image revealed the growth of randomly oriented, worm-like grains, which are uniformly distributed over the surface. From the micrograph it is clearly seen that grain size is increased with annealing temp.which is clearly observed in AFM studies, the formation of

TABLE 3 : AFM data of SnS thin films as –prepared and annealing with 200°C

sample	Temp. substrate	Grain size (nm)	Roughness (nm)	r.m.s (nm)
C1	as -prepared	158	0.296	0.365
C2	Annealed at 200°C	161	0.352	0.438

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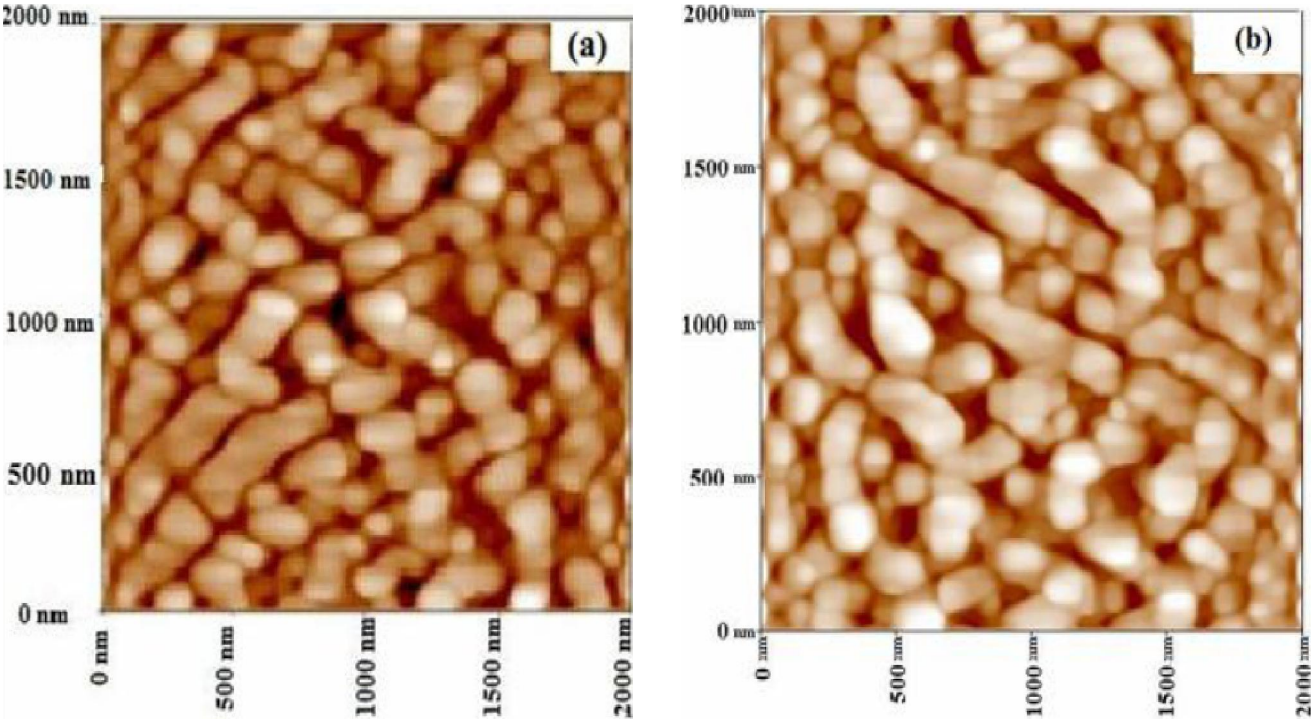

Figure 2 : AFM pictures thin films (a) as-prepared and (b) annealing with 200°C for 2 h.

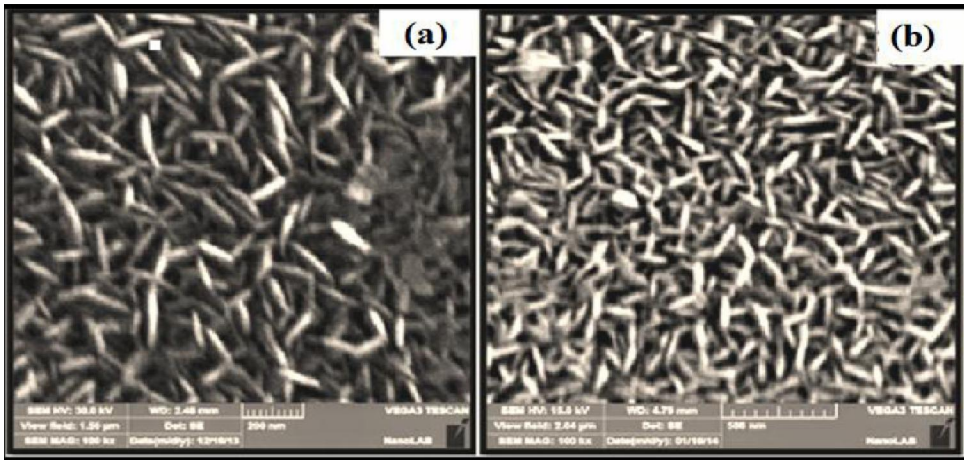

Figure 3 : SEM images of SnS thin films (a) as-prepared and (b) annealing with 200°C for 2h

bigger grains is due to coalescence of smaller grains.

CONCLUSION

Tin sulfide films were grown by a thermal evaporation technique at room temperature and annealing with 200°C on glass substrates. All the films had good adherence to the substrate and were free of worm like. Grain size was increased substantially with increase in annealing temperature; where increase in surface roughness is marginal. Films annealed at 200°C were highly crystalline, nearly stoichiometric. From XRD spectra, The microstrain and dislocation density of the deposited films were growth with increases with annealing temperature.

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