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Additional Information

Tin-mono-sulfide (SnS) Thin Films Prepared by Chemical Spray Pyrolysis with Different [S]/[Sn] Ratios

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ABSTRACT

SnS thin films were deposited by Chemical Spray Pyrolysis (CSP) using cost-effective and low-toxicity sources materials like tin (II) chloride dihydrate and thiourea as sources of tin and sulphur, respectively. We have studied the properties of sprayed SnS thin films with[S]/[Sn] ratios from 1 to 4 in steps of one in order to optimize these parameters. X-ray diffraction (XRD) was used for analyzing the films structure, Raman Spectroscopy for assessing the films quality and structure, Scanning Electron Microscope (SEM) for surface morphology and Energy Dispersive Energy (EDS) for compositional element in samples, Atomic Force Microscopy (AFM) for the topography of surfaces and optical spectroscopy for measuring transmittances and then deducing the band gap energies. All films obtained are polycrystalline with (111) as preferential direction for films with [S]/[Sn] ratio equals to one while for [S]/[Sn] ratios from 2 to 4 the main peak becomes (101) and the (111) peak decreases in intensity. Raman spectroscopy confirms the presence of only one SnS phase without any additional parasite secondary phases. SEM images revealed that films are well adhered onto glass surface with rounded grain. AFM confirms this result being films with [S]/[Sn]=1 the roughest and also with the largest grain size. EDS results show an improvement of stoichiometry with the increase of the [S]/[Sn] ratio. From optical analysis, it is inferred that the band gap energy decreases from 1.83 to 1.77 eV when the [S]/[Sn] ratio changes from 2 to 4.

Keywords: Sulfides; Tin Sulfide; Thin films; X-ray diffraction; Atomic force microscopy.

1. Introduction

There are several binary earth abundant semiconductor materials such as SnS, SnSe, Cu_2S, ZnS, etc. well suited to be used as new photovoltaic materials for making cheaper and more efficient solar cells. Tin monosulfide (SnS), which belongs to IV-VI group semiconductors, has recently focused the attention of many researchers because of its appropriate optoelectronic properties for photovoltaic applications. It has a direct band gap near to 1.3 eV [1], which is close to optimal band gap (1.5 eV) of solar cells and has high absorption coefficient ($\alpha > 10^4$ cm^{-1}) [2]. Further all components of SnS are abundant, cost-effective and less toxic compared to the cadmium of CdS or lead in the PbS thin films. SnS has also p-type electrical conductivity and it has a theoretical high efficiency greater than 24% [3]. However, nowadays despite many efforts, solar cells based on SnS absorber have only achieved conversion efficiency about 1.3 % [4]. Recent studies based on numerical simulations of SnS/CdS solar cells predicts that using the optical and electrical characteristics of SnS thin films available in the literature photoconversion efficiencies of about 10 % will be obtained [5]. This low performance in both experimental and simulated photovoltaic devices may be due to impurities and/or defects in SnS layers that result from the preparation methods used to make the thin films for cell fabrication. Even though, SnS is a potential candidate for use as absorber material in thin films photovoltaic solar cells as the optoelectronic properties of the material improves.

Tin monosulfide has been prepared using various techniques like Successive Ionic Layer Adsorption and Reaction (SILAR) [6], Chemical Bath Deposition (CBD) [7], Electrochemical Deposition (ECD)[8], Atomic Layer Deposition (ALD)[9], Chemical Spray Pyrolysis (CSP)[10] etc. Chemical Spray Pyrolyis (CSP) was used in this study because it has some advantages over the others methods to prepare semiconductor thin films because it is a simple and low cost technique. In additional it is suitable for industrial scale production.

In this study, we have prepared SnS thin films by Chemical Spray Pyrolysis technique onto simple glass substrate using different [S]/[Sn] ratios of 1-2-3 and 4. Some amount of alcohol (10%) was added to the aqueous solvent to reduce the surface tension of water. The crystalline structure, morphology, chemical composition and optical properties of CSP-deposited SnS thin films are reported.

2. Experimental details

2.1. Films preparation

Tin monosulfide (SnS) thin films were prepared onto glass substrate from aqueous solution containing tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$), thiourea ($CS(NH_2)_2$) (≥99%) and alcohol (10% in volume) to reduce the surface tension of water. The concentration of tin chloride was fixed at 0.02 M and the [S]/[In] ratio was varied from 1 to 4 in step of 1. The substrate temperature was fixed to 300 °C. The volume sprayed was 5 mL, the spray rate 1.5 mL/min, the air compressed pressure 0.7 bar and the distance between the glass substrate and nozzle was kept to 25 cm.

Glass substrates were washed in ultrasonic bath of acetone for 15 minutes, rinsed with distilled water following by washed in a bath of ethanol for 15 minutes and rinsed with distilled water before dried and used for spray.

2.2. Films characterization

Structural properties were characterized by means X-ray diffraction (XRD) measurements with a Rigaku Ultima IV diffractometer at the Bragg-Brentano (θ-2θ) configuration and using CuKα radiation (1.5418 Å). Structural properties were also characterized by Raman scattering measurements performed with a LabRAM HR UV spectrometer coupled to a Peltier-cooled CCD camera and using a 632.81 nm laser excitation line with 3 cm^{-1} spectral resolution.

The surface morphology and microanalysis using energy dispersive X-ray spectroscopy (EDS) were obtained on a Jeol-JSM6300 operating at 20 kV as well as by means of an atomic force microscopy (AFM) study was done using a Bruker Multimode 8 AFM Nanoscope V controller.

Optical properties were monitored by transmittance using a Deuterium-Halogen lamp (DT-MINI-2-GS Micro Park) in association with a 500 mm Yvon-Jobin HR460 spectrophotometer using a back-thinned Si-CCD detector (Hamamatsu) optimized for the UV-VIS range.

3. Result and Discussion

3.1. X-Ray Diffraction

The SnS thin films with different [S]/[Sn] ratios were prepared by chemical spray pyrolysis technique and the XRD spectra are presented in Figure 1. All films are SnS polycrystalline with orthorhombic structure and preferential orientation along (111) at [S]/[Sn]=1 while when the

ratios increase from 2 to 4, the main peak becomes (101) and the (111) peaks decreases. We noted also others peaks like (021) and (141) for all ratios.

The variation of crystallites size with various [S]/[Sn] ratios was calculated using the Debye-Scherrer formula. We measured the FWHM for the three most intense XRD peaks (021, 101 and 111) and then we use the average of the mentioned diffraction peaks to obtain the crystallites size. It is worth to notice that crystallites size decrease from 88 to 27 nm when the [S]/[Sn] ratios varied from 1 to 4. This reduction of crystallite size is related to the degradation of crystallinity with the augmentation of sulphur/tin ratio. Table 1 shows the variation of average crystallites size with the variation of [S]/[Sn] ratio.

3.2. Raman spectroscopy

Raman spectroscopy is very important tool for studying semiconductor films structure and was used to determine second phase like SnS_2, Sn_2S_3, SnO or SnO_2 in our films. Raman spectra of SnS thin films recorded in the range of 80-350 cm^{-1} are shown in Figure 2. Raman modes located at 88, 107, 170 and 193 cm^{-1} confirm that only the SnS phase is present in our films and any other secondary phases were observed [11-12].

3.3. Surface Morphology measured by SEM

SEM is one of the predominant techniques to survey the surface of the films. Figure 3 shows SEM micrographs of SnS thin films deposited with various ratios at a fixed substrate temperature of 300 ºC. SEM images revealed films well covered onto glass substrate with rounded uniform grains size for all ratios and size flake like particles but those deposited with [S]/[Sn]=2 seems smaller that others ratios and the same film was denser and more compact compared to others. It is possible that the difference in morphology is caused by the effect of different concentrations of sulphur.

3.4. Surface Topography measured by AFM

AFM is a technique for analyzing in order to achieve a direct insight into surface topography features of films. It was used to study the evolution and the developpement of the morphological state of the sprayed SnS thin films as a function of thiourea concentration in [S]/[Sn] ratio. It gives grain size and roughness of thin films. It is clear seen that the topography of our films changes with the variation of thiourea concentration in the initial solution. We notice that all films are rough with film prepared with [S]/[Sn] ratio of 1 the most rougher with 45nm and it has also the larger grain size evaluate at 247.35 nm than others films. When the [S]/[Sn] ratio increases from 2 to 4, ones noted that the roughness increases from 20.20 to 26.60 nm and grain

size increases significantly at the same time from 127.5nm to 222.2 nm, respectively. The reason is that the films deposited at low [S]/[Sn] ratio shows densely and compact films but while when the concentration of sulphur increases the coalescence and large grains increase grains boundaries which were the cause of the increase of the roughness. Table 2 shows the variation of grains size and roughness with the variation of [S]/[Sn] ratio.

Figure 4 shows two-dimensional AFM images of SnS thin films prepared with different [S]/[Sn] ratios. The difference between grain size given by AFM below and crystallites size given by XRD is explained by the fact that a grain was formed by several crystallites

3.5. Energy Dispersive Spectroscopy Analysis (EDS)

The Energy Dispersive X-ray Spectroscopy (EDS) is a powerful technique to analyze the chemical composition of samples based of X-ray emitted by the atoms of elements in the sample. From the Table 3 we noted that all films contain only tin (Sn) and sulphur (S) and when the ratio increases the stoichiometry improved with best S/Sn ratio in films was obtained for [S]/[Sn]=3 and [S]/[Sn]=4 in the solution, which indicates that the composition of films depend on the amount of sulphur in the initial composition of the solution.

3.6. Optical properties

Figure 5 shows the optical transmission spectra of SnS thin films with various ratios in the wavelength region of 500-1000nm. In the wavelength between 500 to 650 nm transmittance, all films exhibited very low transmittance which was close to 0% and the transmittance increases rapidly after 650 nm. The higher transmittance observed was 43%. The low transmittance in the visible region shows clearly that SnS thin films are absorber layers.

Figure 6 shows band gap energy for SnS thin films obtained from optical transmission data plotting $(Ah\nu)^2$ versus hν at various [S]/[Sn] ratios where A is the absorbance and hν is the photon energy. When the [S]/[Sn] ratio varied from 2 to 4, we observe a decrease of the band gap energy from 1.83 eV to 1.77 eV, which is higher than the gap energy of pure SnS (1.3 eV). Table 4 displays the optical band-gap values for SnS films synthesized from different [Sn]/[S] ratios.

The increase of the band gap energies of our samples, compared to pure SnS thin film which has a band gap of 1.3 eV [1], is due to the incorporation of oxygen into samples. Assuming that the variation of band gap energy of $SnS_{1-x}O_x$ increases linearly with the augmentation of oxygen content, one plot a calibration curb in order to determine the amount of oxygen contended in our samples by considering as limit values band gap energies 1.3 eV for SnS layer and 2.7 eV

(in N_2 atmosphere annealing) and 3.4 eV (in O_2 atmosphere annealing) for SnO layer [13]. According to Figure 7, the percentage of oxygen contained in SnS layers is around 23±1% and 33±2% using 3.4 eV and 2.7 eV, respectively, as band gap energy references for SnO. As SnS films are sprayed in air the presence of oxygen in the sprayed layers are unavoidable.

4. Conclusion

Tin mono-sulfide (SnS) thin films have been deposited onto simple glass substrate by chemical spray pyrolysis. All deposited films are identified to be SnS polycrystalline with orthorhombic structure with (111) preferential peak for ratio equal to one while when the ratio increases from 2 to 4 the main peak becomes (101) and the (111) peak decreases. Raman modes confirm the presence of SnS phase without any additional parasite phases such as SnS_2, Sn_2S_3, SnO or SnO_2. SEM images revealed rounded grain for all ratios and EDS analysis shows an improvement of the stoichiometry with the increase of [S]/[Sn] ratio. AFM studies revealed that an SnS thin film with [Sn]/[S] ratio equals to 1 has larger grains and higher mean roughness. The transmission in the visible region of all films was found to be very low showing the absorber character of SnS films. The band gap energies of SnS thin films prepared by chemical spray pyrolysis decrease when the [Sn]/[S] ratios increase from [S]/[Sn]=1 and 4. The difference between the measured optical band gap (1.77-1.83 eV) and the theoretical band gap can be explained by the incorporation of about 22-33% of oxygen into the sprayed SnS films. The presence of oxygen is related to the preparation method. Finally, in order to have SnS thin films with good characteristics for photovoltaic applications a [S]/[Sn] ratio close to 1 seems to be the best option.

Acknowledgments

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FIGURE CAPTIONS

Fig. 1. X-ray diffraction patterns of SnS thin films with different ratios.

Fig. 2. Raman spectroscopy analysis spectra of SnS prepared with different [S]/[Sn] ratios.

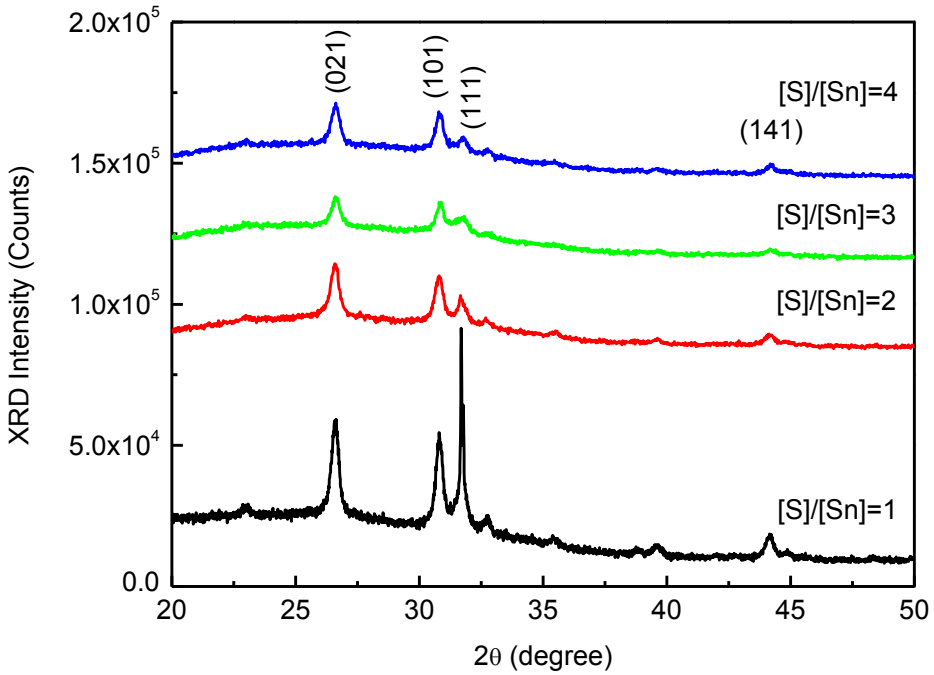
Fig. 3. SEM images of SnS samples deposited by chemical spray pyrolysis with different [S]/[Sn] ratios.

Fig. 4. Two-dimensional atomic force microscopy images of SnS prepared with various [S]/[Sn] ratios.

Fig. 5. Transmittance versus wavelength spectra of SnS prepared with different [S]/[Sn] ratios.

Fig. 6. Plot of $(Ah\nu)^2$ versus photon energy of SnS thin films prepared with different [S]/[Sn] ratios.

Fig. 7. Energy band-gap versus oxygen content in SnS thin films prepared with different [S]/[Sn] ratios.



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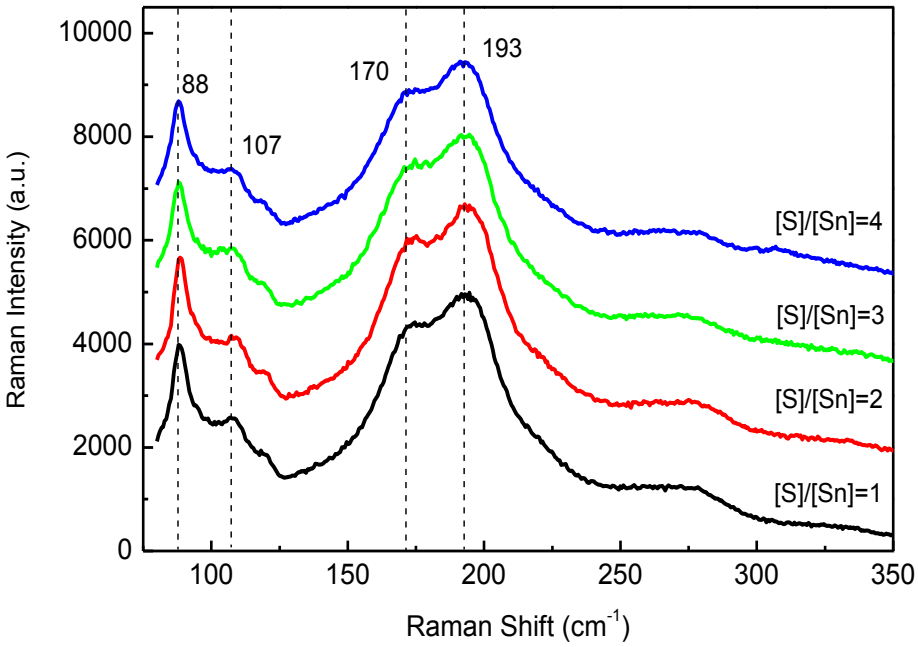

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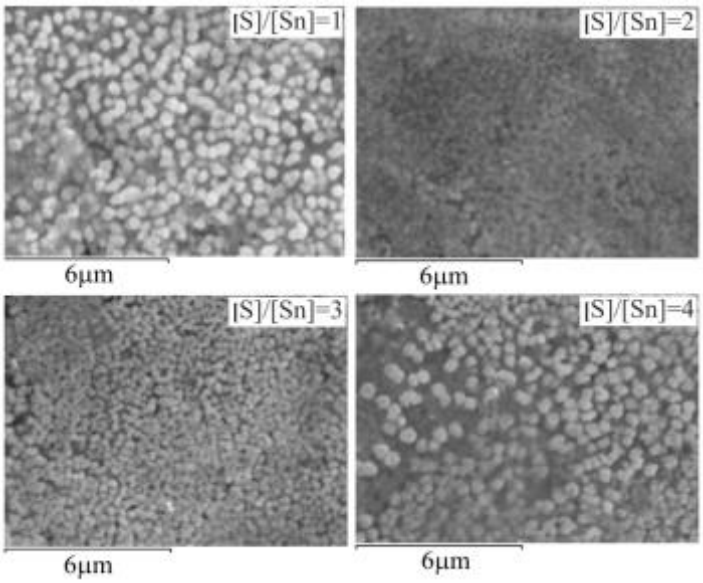

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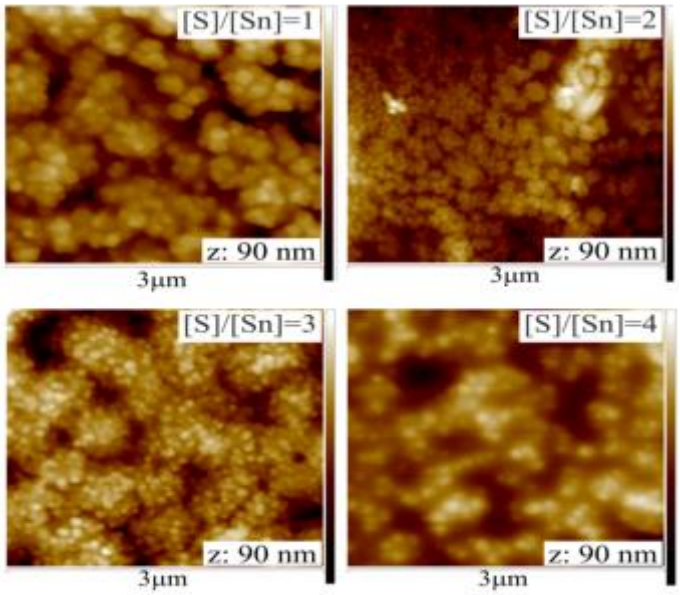

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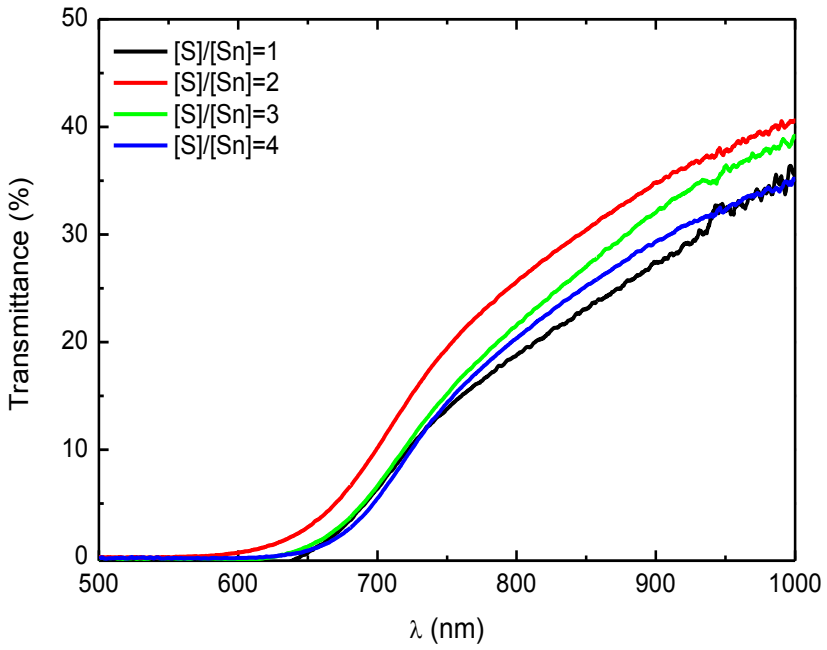

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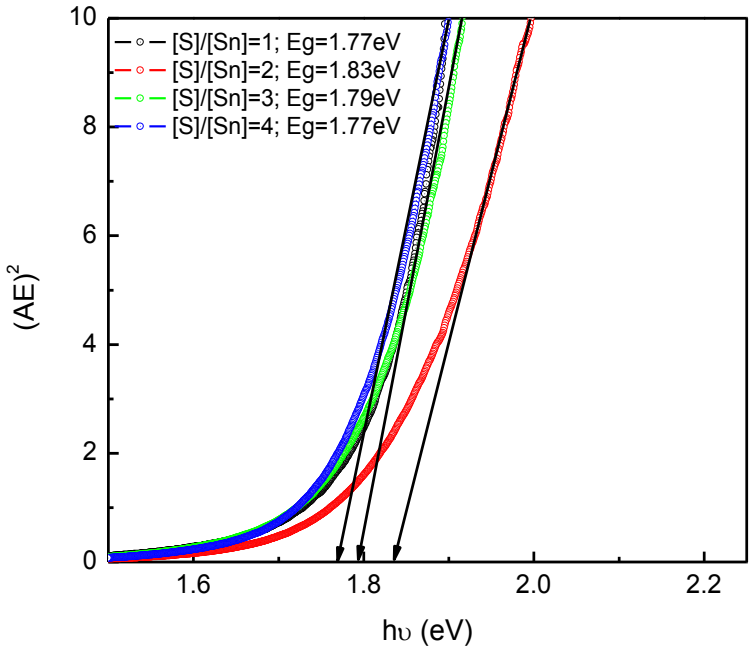

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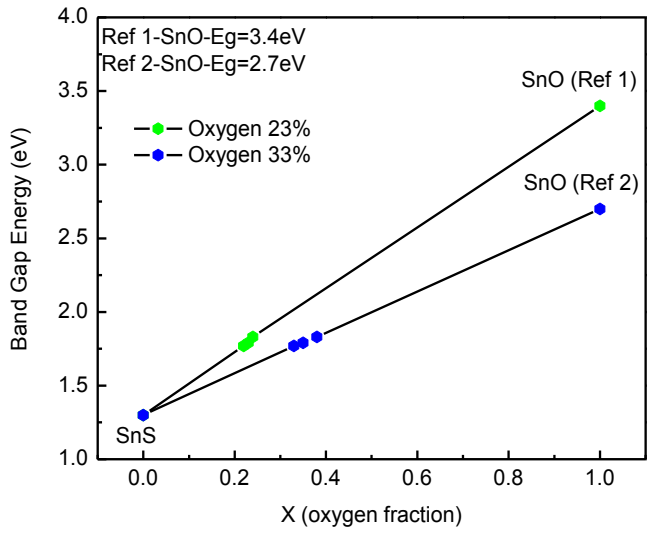

Fig. 7. Energy band-gap versus oxygen content in SnS thin films prepared with different [S]/[Sn] ratios.

TABLES

Table 1. Crystallite size of SnS thin films with different [Sn]/[S] ratios.

[S]/[Sn] ratio	D (nm)
1	88.2
2	36.7
3	30.5
4	27.0

Table 2. Roughness and grain size of sprayed SnS thin films prepared with different [Sn]/[S] ratios

[S]/[Sn] Ratio	Roughness (nm)	Grain size (nm)
1	45.0	247.4
2	20.2	127.5
3	20.9	162.4
4	26.6	222.2

Table 3. Composition of SnS thin films obtained from EDS analysis.

[S]/[Sn] Ratio	% S	% Sn	S/Sn
1	42.26	57.74	0.73
2	47.60	52.40	0.91
3	50.14	49.86	1.00
4	50.39	49.61	1.01

Table 4. Optical band gap of SnS thin films prepared with various [Sn]/[S] ratios.

[S]/[Sn] Ratio	Eg (eV)
1	1.77
2	1.83
3	1.79
4	1.77