

Preparation and Characterization of Tin Sulphide Thin Films by Spray Pyrolysis Technique in Ambient Atmosphere

M.O. Abou-Helal^{1,2} and M. Boshta¹

¹Solid State Physics Dept., National Research Center, El-Behoos str., 12311Dokki, Cairo, Egypt

²Physics Department, Faculty of Science, Jazan University, P.O. Box 2097, Jazan, Kingdom of Saudi Arabia
osamah4@hotmail.com, osamah4@tedata.net.eg, mabouhelal@mailier.scu.eun.eg, mabou-helal@jazanu.edu.sa

Abstract: Thin films of tin sulfide (SnS₂) have been prepared by spray pyrolysis on Corning 7059 glass substrates with the substrate temperatures in the range of 300–400°C, keeping the other deposition parameters constant at their optimized values, and in normal ambient atmosphere. The films were characterized to evaluate the structure and optical energy gap. X-ray diffraction (XRD) measurements revealed that the films are polycrystalline tin sulfide SnS₂. The optical band gaps for SnS₂ films vary from 1.0 to 1.25 eV depending on the experimental parameters such as deposition temperatures. Although the experimental work was done by spray pyrolysis technique in the air, and from commercial chemicals, it was possible by keeping the ratio of [S]/[Sn]=3 to control the chemical reaction, and to get tin sulfide SnS₂ films instead of tin oxide SnO₂, which is more likely in the normal ambient atmosphere (air), this lower the cost of producing tin sulfide thin films, which is very important for many applications in industry.

[M.O. Abou-Helal and M. Boshta. **Preparation and Characterization of Tin Sulphide Thin Films by Spray Pyrolysis Technique in Ambient Atmosphere.** *J Am Sci* 2012; 8(8):61-63]. (ISSN: 1545-1003).
<http://www.jofamericanscience.org>. 9

Keywords: tin sulfide, tin oxide, spray pyrolysis, structural measurements, optical measurements, cost effective thin films.

1. Introduction

The recent investigations in the field of photovoltaics are directed towards the development of cost effective and nontoxic materials that can be synthesized by a simple and robust technology for solar cell fabrication. In this direction, attention has been focused on new materials, which are abundant in nature and can be easily processed to generate device grade material without posing any environmental problems. Dittrich *et al.*[1] showed that sulpho-salts have strong potentials for photovoltaic applications. Tin sulfide (sulphide) SnS (SnS₂) is one such compound that belongs to IV–VI group with orthorhombic structure [2]. It has an optical band gap of about 1.3 eV [3–5], which is nearer to the optimum value of 1.5 eV, required for efficient absorption of solar radiation [6], which is in the range from 1.12 eV for silicon to 1.43 eV for GaAs. These films have p-type conductivity. Its electrical properties are controlled by doping with Al, Ag, N and Cl [7,8]. In addition, the elements of SnS are abundant in nature and nontoxic. These properties made SnS (SnS₂) suitable material for fabrication of heterojunction solar cells. For large-scale production of solar cells, a thin film deposition technique, which can be easily handled at low cost, is needed. The spray pyrolysis technique is very advantageous for large-scale production of thin films.

In this paper we report on the structural and optical properties of sprayed tin sulphide films deposited in air at different substrate temperatures.

2. Experimental Work

The tin sulphide films were prepared by spray pyrolysis on Corning 7059 glass substrates at temperatures (T_s) in the range of 300–400°C. The effective area of the substrates was approximately 2.5 cm². The deposition parameters such as solution flow rate; carrier gas flow rate and nozzle to substrate distance were kept constant at 6 ml/min, 8 l/min and 30 cm, respectively. The starting solution was prepared using SnCl₂·5H₂O and thiourea. Firstly, thiourea was dissolved in a minimum amount of deionized water while Tin Chloride (SnCl₂·5H₂O) was dissolved in a minimum amount of isopropyl alcohol. Secondly, both solutions were mixed and diluted with deionized water, so that the final concentration was 0.1 M., keeping the ratio = [S]/[Sn]=3 and pH=2, which were then sprayed onto the heated substrates.

The ratio = [S]/[Sn] is very crucial because if it is not well adjusted we get mostly SnO₂ instead of SnS₂, especially when the experiment is done in Air, with spray pyrolysis technique. The substrates were ultrasonically cleaned, first with trichloroethylene and then with acetone and methyl alcohol followed by rinsing in distilled water. The solution was stored in a volumetric reservoir at room temperature and connected to one side of the spray nozzle. The carrier gas, air was allowed to flow (8 l/min.) through the pressure-monitoring gauge, connected to the other side of the spray nozzle. The spray nozzle was moved in the x–y plane using the microprocessor controlled stepper motor system in order to achieve a uniform film coating. Moving the spray nozzle is just an option, so,

it is possible to work in a stationary position too with the same setup. A resistive heater system is employed to alter the temperature of the substrate, which is monitored and controlled using computerized temperature controller with an accuracy of $\pm 5^\circ\text{C}$. The structural characterization of tin sulphide (SnS_2) thin films were investigated using X-ray diffractometer. The diffraction patterns were recorded with scanning speed of $2^\circ/\text{min}$. The experimental curves of the transmittance and reflectance versus the wavelength are obtained using spectrophotometer (Jasco V-570) in spectral range (200–2500 nm).

3. Results and Discussion

3.1. XRD characterization

A clear change in the colour of the as-grown films was observed with the increase of substrate temperature (T_s). The films formed below 300°C appeared black with white spots, which indicate that this deposition temperature is not suitable for obtaining high quality SnS_2 thin films, because some of the undesirable solvents did not vaporize and remained with the films. The films were reddish yellow at substrate temperatures 300 and 350°C . However, for the substrate temperature 400°C , the films appeared reddish brown. This agrees with JCPDS (23-677). This indicates that the obtained thin films are polycrystalline SnS_2 (Fig. 1).

The X-ray diffraction (XRD) profiles of SnS_2 films at three different substrate temperatures are shown in Fig. 1. The spectra clearly show that the films formed at temperatures in the range 300– 400°C exhibit strong peak at 15° corresponding to SnS_2 phase, whereas its intensity increases as the substrate temperature increases, this is in a good agreement with JCPDS (23-677) and (21-1231), to be (001) plane reflection. This implies that the preferential orientation growth of the film is along the c-direction. This finding is in agreement with Khadraoul et al, [9].

The other phase Sn_2S_3 was detected at lower temperature (350°C), and agreed with JCPDS (14-619) as in Fig. 1. The existence or disappearance of some phases is function of the deposition temperature. This point will be discussed more clearly in section 3.2 (Optical characterization).

It is worthwhile to mention that no indication of SnO_2 peaks were found, which verify the success of obtaining SnS_2 and not SnO_2 , under the condition $[\text{S}]/[\text{Sn}]=3$.

3.2. Optical characterization

Fig. 2 shows the optical transmittance (T) and the specular reflectance (R) spectra for samples prepared at different substrate temperatures T_s . A weak change in the absorption edge is observed towards higher wavelengths as T_s increases. The transmission improves as the substrate temperature T_s increases

from $T_s=300^\circ\text{C}$ to $T_s=400^\circ\text{C}$. This improvement may be explained by the change of the film structure. These results are similar to those observed by Krunks et al. [10].

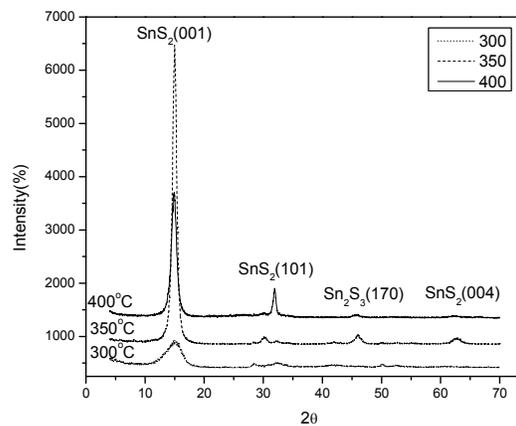


Fig. 1 XRD spectra for tin sulfide prepared at different substrate temperatures.

The absorbance coefficient (α) was calculated from the raw absorption data [11]. The variation in absorption coefficient, α , is related to the photon energy $h\nu$, for the interband transition by the relation $\alpha h\nu = A(h\nu - E_g)^n$ where $n = 2$ and $1/2$ in the case of allowed direct and indirect optical transitions, respectively, while $n = 2/3$ and $1/3$ in the case of forbidden direct and indirect optical transitions, respectively [12–13]. Therefore, the dependence of $(\alpha h\nu)$ on photon energy $(h\nu)^n$ was plotted for $n = 1/2$, which can be expressed as $(\alpha h\nu)^2$ versus $(h\nu)$, (Fig. 3). By extrapolating the linear part in the figure towards lower photon energies, the point of interception with the $h\nu$ axis exists at $(\alpha h\nu)^2 = 0$ giving the corresponding energy band gap. The tails associated to the onset edge is attributed to the photon-assisted indirect electronic transitions. Fig. 3 shows there is a shift in the energy gap in the range of 1.1–1.25 eV, as the substrate temperature increases from 300– 400°C . The optical band gap of the films varied significantly with the increase of substrate temperature, which was attributed to the presence of various phases in the films. The films formed at substrate temperature 400°C showed only single phase with an energy band gap of 1.25 eV, similar results were reported in the literature [14–17].

4. Conclusion

The present paper demonstrates that polycrystalline tin sulfide thin films with an energy band gap of 1.25 eV, can be grown by spray pyrolysis, which suitable for the fabrication of thin film heterojunction solar cells as an ‘absorber’ and many

other applications. Structural and optical studies confirmed that the obtained films are tin sulfide mostly SnS_2 , without any indication of the presence of tin oxide. The using of low cost spray pyrolysis technique, with commercial chemicals, lowers the cost of obtaining tin sulfide thin films. This result is very important for the industry, where tin sulfide has enormous applications.

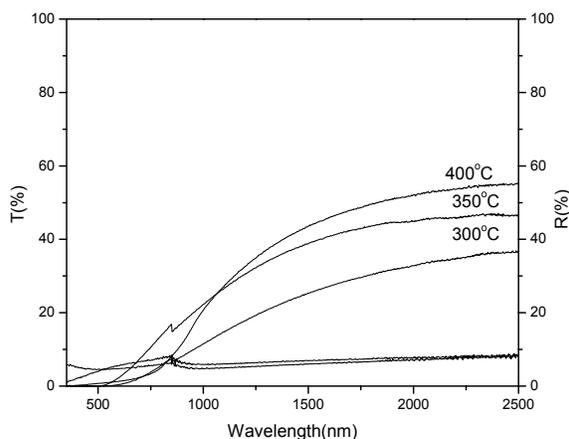


Fig. 2 Optical transmittance (T) and specular reflectance (R) spectra for samples prepared at different substrate temperatures.

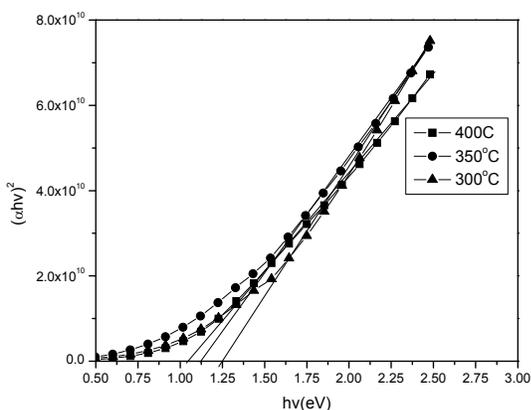


Fig. 3 The dependence of $(\alpha hv)^2$ on photon energy ($h\nu$) (direct transitions).

Corresponding author

M.O. Abou-Helal^{1,2} and M. Boshta¹

¹Solid State Physics Dept., National Research Center, El-Behoos str., 12311Dokki, Cairo, Egypt

²Physics Department, Faculty of Science, Jazan University, P.O. Box 2097, Jazan, Kingdom of Saudi Arabia

osamah4@hotmail.com, osamah4@tedata.net.eg,
mabouhelal@mailerscu.eun.edu,
mabou-helal@jazanu.edu.sa

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6/15/2012