CSM
Chemistry of Solid Materials
Vol. 2 No. 1 2014

Preparation and growth of SnS thin film deposited by spray pyrolysis technique

T. Akbari [1], S.M. Rozati [2*]
[1]MSc Student, Department of Physics, Faculty of Sciences, University of Guilan, P. O. Box: 41335-1914, Iran
[2]Professor, Department of Physics, Faculty of Sciences, University of Guilan, P. O. Box: 41335-1914, Iran
** Corresponding author's E-mail: smrozati@guilan.ac.ir*

Article history:
(Received: 29 Oct 2014, Revised: 28 Feb 2015, Accepted: 7 Mar 2015)

ABSTRACT
In this paper thin films of tin sulfide (SnS) were deposited on the glass substrates using spray pyrolysis method with the substrate temperatures in the range of 400–600℃, keeping the other deposition parameters constant. In this work the characteristic of SnS thin films investigated. The XRD pattern and optical transmittance of thin films also are discussed. With the change in concentration of thiourea, the physical properties of the thin films are also investigated.

Keywords: Tin sulfide, Spray pyrolysis, SnS thin film, Substrate temperature, Concentration.

1. INTRODUCTION

In recent years, much attention has been focused on tin sulfide (SnS) because of its potential use in the fabrication of various applications such as holographic recording systems, solar collectors and solar photovoltaic cells. SnS belongs to the IV-VI group of layered semiconductors and crystallizes in orthorhombic structure wherein the Sn and S atoms are tightly bonded by van der walls forces [1]. SnS has an absorption coefficient of $>10^4 cm^{-1}$ with an optical band gap of 1.3 eV to the optimum value of 1.5 eV, suitable for solar cell applications [1,2]. In addition, the constituent elements of this material are non-toxic and abundant in nature. Thin films have been deposited using a variety of techniques such as chemical deposition, electrochemical deposition, electro deposition, chemical vapor deposition and vacuum evaporation [1]. In this paper, SnS thin films have been deposited using spray pyrolysis. This technique is very suitable for large-scale production of thin films and the film thickness is easily controlled by the quantity of the sprayed solution [3].

2. EXPERIMENTAL

Materials and method

Thin films of SnS were prepared by spray pyrolysis using equimolar (0.1 M) solutions of tin chlorides , $SnCl_2.2H_2O$ and thiourea ($CS(NH_2)_2$) (Merck) onto glass substrates. The substrates were cleaned by HCl acid, acetone and ethanol. A mixture of 2-propanol alcohol and deionized water in the ratio 3:1 was used to prepare the starting solution [3]. The substrate temperature was kept in the range of 400-600 ℃ and the air pressure was

maintained at $2\,bar$. Compressed purified air was used as a carrier gas. The source to substrate distance was about 32 cm. The structural properties of the films were studied by X-ray diffractometer.

The optical measurements were carried out by using UV-Visible spectro-photometer. The surface morphology of deposited films is investigated by SEM analysis. Then, by changing the concentration of thiourea (M_s=0.2 and M_s=0.4), the thin film properties were studied (for this part, the optimum temperature, 500℃ was used).

3. RESULTS AND DISCUSSION

According to the XRD pattern (Figure 1), at lower substrate temperature, structure of the film is amorphous. As the temperature increases gradually, energy for crystal plates growth would be provided. At 450 ℃ substrate temperature, SnS phase would be revealed, that is in good agreement with the values of standard card [JCPDS no.01-083-1758]. With further increase in substrate temperature (500 ℃), growth of SnS films improved. By increasing the temperature, possibly presence of oxygen in the reaction and evaporation of sulfide enhances [2]. This could be the reason for the formation of binary phases other than SnS (T=550℃ and 600℃). Thus we have chosen T=500℃ as the optimum substrate temperature.

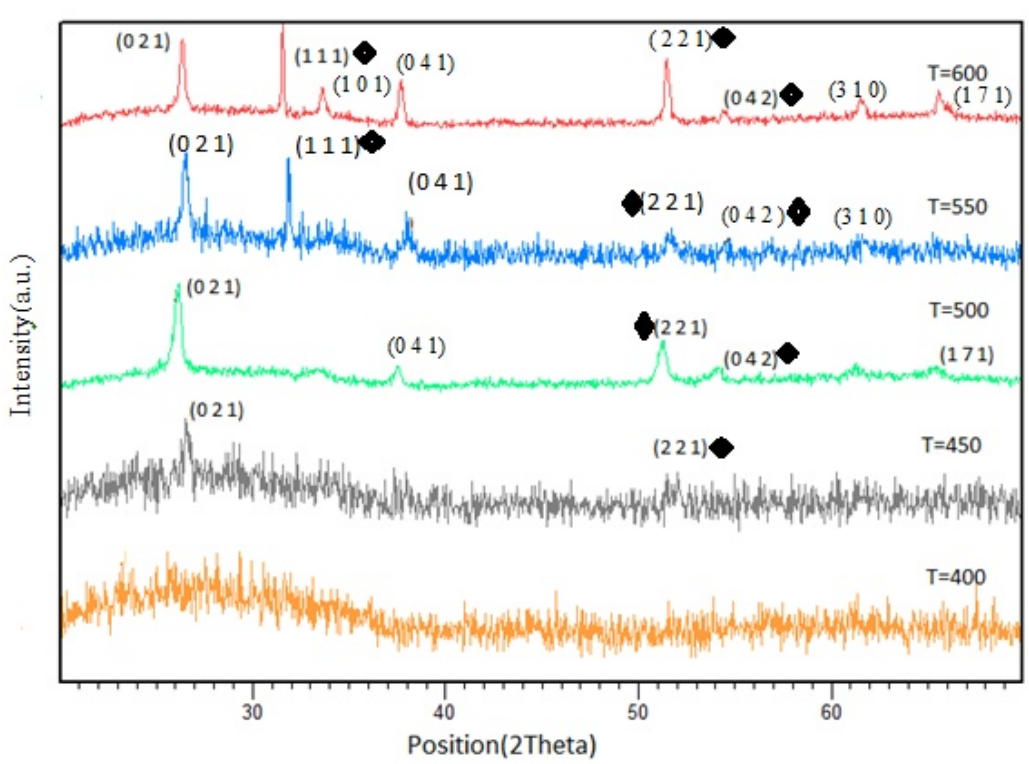

Fig. 1. XRD pattern of the prepared thin films of tin sulphide by increasing the substrate temperature**.**

Table (1) presents the change in sheet resistance, transparency and crystallite size of tin sulfide thin films with increasing substrate temperature.

Average crystallite size was estimated by the Eq (1).

$$D = K\lambda/\beta\cos\theta \qquad (1)$$

where K= 0.89 is the shape factor¸ λ is the X-ray wavelength of Cu Kα radiation (1.54 ˚A), θ is the Bragg angle and β is the experimental Full-Width at Half Maximum (FWHM) of the respective diffraction peak [4].

Table. 1. Changes of some properties in thin films of tin sulfide

Temperature (℃)	Transparence (%)	R Ω/cm^2	D(nm)
400	69	30 MΩ	_
450	72	1 MΩ	14.2
500	73	7 KΩ	23.8
550	66	37 KΩ	27.9
600	71	5 MΩ	46.1

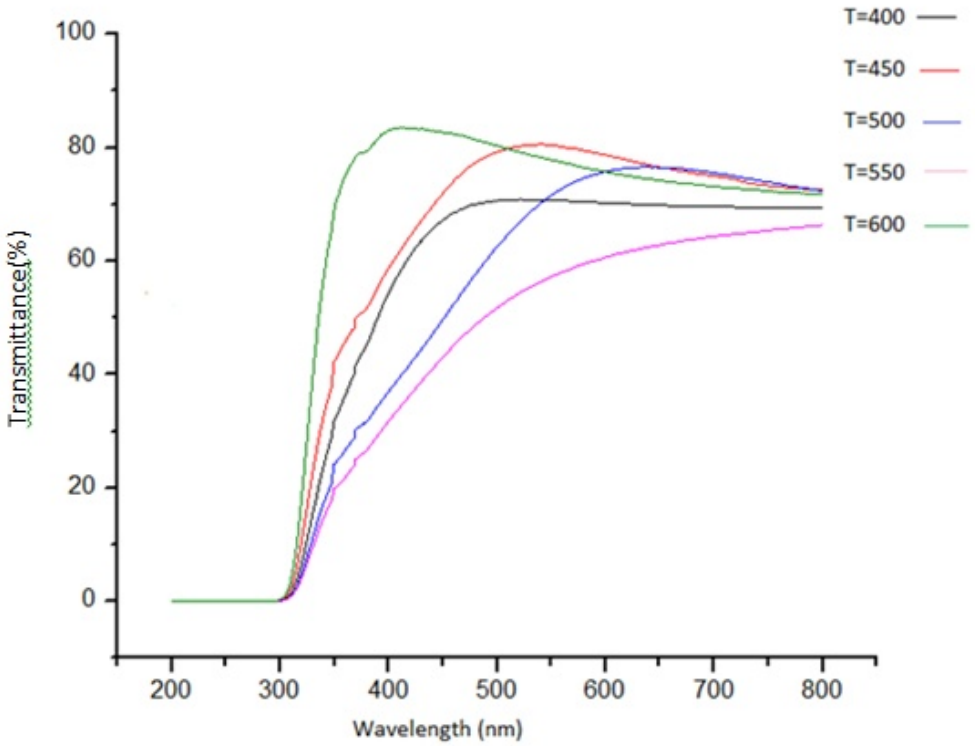

Fig. 2: Transmittance spectra of tin sulfide thin films

As shown in the table, the average crystallites size of the films increases by increasing the substrate temperature. At lower substrate temperature, high electrical resistance was caused due to the small grain size and hence crystalline structure of the film has not been formed properly. As the temperature increases to 500℃, the sheet resistance has a decreasing trend while at 550℃, it increases. By a proper bond forming, the film resistance could be improved.

Beside, with the creation of additional binary phases, the sheet resistance of the films would increase. It is also expected to observe the growth of grains with an increase in temperature. On the other hand the mobility of the prepared films would have a low value at higher substrate temperature [2].

The transparency of the thin films is shown in Figure 2. It is obvious that the transparency is about 69% at 400℃ and it changes to 73% at 500℃. However, it reduced to 66% at 550 ℃ and 71% at 600 ℃ substrate temperature. At higher temperature, the thermal energy provides bond formation thus it leads to have an increase in transparency.

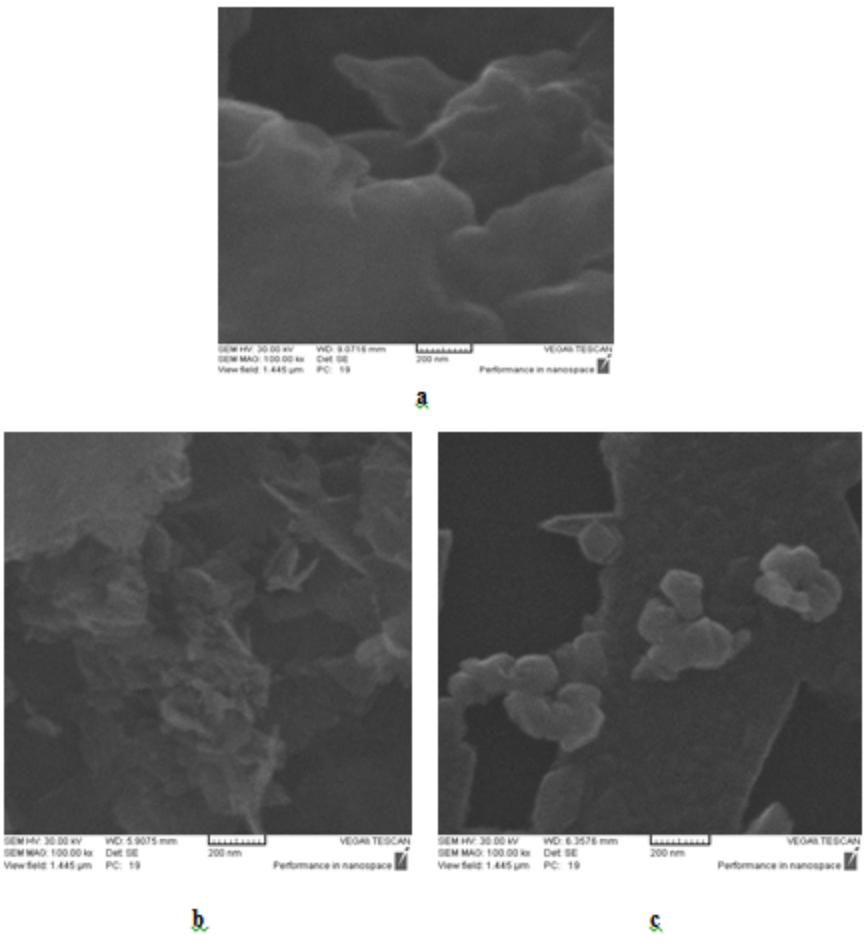

Fig. 3: The SnS Thin films picture in T=450℃(a), T=500℃ (b), T=550℃(C)

Figure 3 demonstrate the SEM morphology of SnS thin films deposited at various substrate temperatures. As shown in the figure, the process of the grain growth, film structure and the uniformity of the films are observed which could be due to the splitting of tin-sulfur bond [2, 3].

In Figure 4, the XRD pattern for thin films with increasing in concentration of thiourea is shown. According to it, with increasing the thiourea concentration, the spectrum showed a strong peak oriented along (111) that is in agreement with the results of other workers [5-7]. This can indicate that by increasing the amounts of sulfide, the reaction conditions improve. Thus, we can expect that transparency increases because the condition of formation of the films is met as in Figure 5.

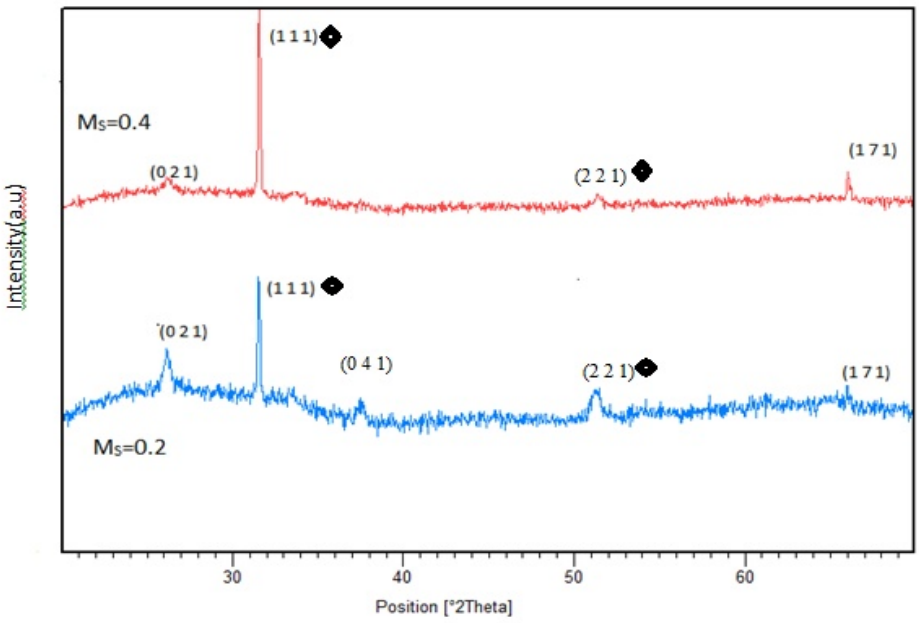

Fig. 4: The XRD pattern of the prepared thin films of tin sulphide by increasing thiourea concentration

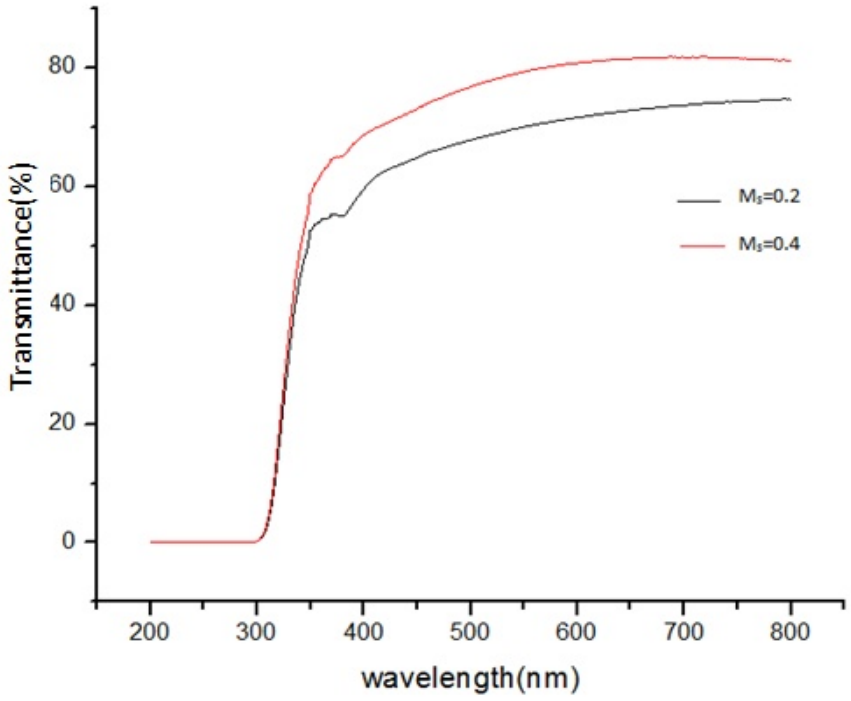

Fig. 5: Transmittance spectra of tin sulfide thin films

4. CONCLUSION

Tin sulfide polycrystalline films were deposited on glass substrates by spray pyrolysis technique. Substrate temperature and the concentration of thiourea can influences over the films structure and the optical properties. At lower substrate temperature, thin films are exhibited an amorphous structure while at higher temperature, the additional different phases such as SnS_2 and Sn_2S_3 are observed. As the substrate temperature increases to 500℃, the sheet resistance has a decreasing trend (7 KΩ/cm^2) while at 550℃, it increases to 5 MΩ /cm^2. .By changing the thiourea concentration, the films physical properties is changed. The prepared films exhibited SnS phase with strong peak at 31.9° corresponding to (111) orientation. Thus, the transparency increases due to the condition of formation of the films.

Acknowledgements

The authors gratefully acknowledge the research department of University of Guilan.

REFERENCES

[1] K .T Ramakrishna Reddy, P. Purandhara Reddy, P.K Datta, R.W. Miles, *Thin Solid Films* 403, 116 (**2002**).

[2] N. Koteeswara Reddy, K.T. Ramakrishna Reddy, *Solid State Electron*. 49, 902 (**2005**).

[3] N. Koteeswara Reddy, K.T. Ramakrishna Reddy, *Mater. Res. Bull*. 41, 414 (**2006**).

[4] B.D. Cullity, Elements of X-ray diffraction, 2nd ed. Addition-Wesley Publ. Co., Inc. **1978**.

[5] G.H. Yue, D.L. Peng , P.X. Yan , L.S. Wang, W. Wang, X.H. Luo, *J. Alloys Compd*. 468, 254 **(2009)**.

[6] M. Patel, I.Mukhopadhyay, A. Ray, *Opt. Mater*. 35, 1693 **(2013)**.

[7] N. Koteeswara Reddy, K.T. Ramakrishna Reddy, *Thin solid films* 325, 4 **(1998)**.