Scientific Journal of Frontier Chemical Development
Volume 6, 2016, PP.6-11

Preparation of the Stoichiometric SnS_2 and SnS Thin Films Using Spin-coating-pyrolysis Method at the Appropriate Pyrolysis Temperature

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Abstract

In this paper, the stoichiometric SnS_2 and SnS thin films were successfully prepared using spin-coating-pyrolysis method and the appropriate pyrolysis temperature were 260℃ of SnS_2 and 320℃ of SnS. The atomic ratios of Sn/S for SnS_2 and SnS thin films were 1:1.98 and 1:0.99. The stoichiometric SnS_2 thin film exhibited the morphology with the bilayer structure, the bottom layer was compact and the upper layer was porous.

Keywords: SnS_2; SnS; Thin Film; Spin-coating-pyrolysis Method; Pyrolysis Temperature

1 INTRODUCTION

SnS_2 and SnS are the most important semiconducting materials among binary Sn-S compound and many preparation methods have been developed such as spray pyrolysis [1,2], dip deposition [3,4], close-spaced sublimation [5], vacuum thermal evaporation [6,7], chemical vapor deposition [8,9]. The chemical composition of SnS_2 and SnS thin films strongly affect their properties and application. C. Sanjeeviraja [1] found that the tin sulphide thin film with the Sn/S ratio of 1:1.86 can be obtained using the spray pyrolysis technique at pyrolysis temperatures of 185℃. A. Attaf [10] prepared the SnS_2 thin films with the Sn/S ratio of 1:1.86 using ultrasonic spray technique at pyrolysis temperatures of 350℃. A. Voznyi [11] prepared SnS_2 thin films using close-spaced vacuum sublimation (CSS) method and obtained a Sn/S ratio of 1:1.86. I. P. Parkin [9] prepared SnS_2 thin films using chemical vapor deposition and obtained a Sn/S ratio of 1:1.88 at the deposited temperature of 400℃ and the Sn/S ratio was decreased with the increase of the deposited temperature. To the best of our knowledge, the influence of the pyrolysis temperature on the chemical composition of the tin sulphide thin film has rarely been investigated.

In this paper, SnS_2 and SnS thin films were prepared by spin-coating-pyrolysis method. The influence of the pyrolysis temperatures on the crystal phase, chemical composition, band gap, and morphology of SnS_2 and SnS thin films were investigated by X-ray diffraction (XRD), energy disperse spectroscopy (EDS), the ultraviolet-visible spectroscopy (UV-Vis), ultraviolet visible near-infrared spectrophotometer (UV-Vis-NIR), Raman spectrum and scanning electron microscope (SEM), respectively.

2 EXPERIMENTAL

2.1 Spin-coating-pyrolysis Preparation of SnS_2 and SnS Thin Films

All chemicals were commercially available and used without further purification.

SnS_2 thin films were prepared by the spin-coating-pyrolysis method using the precursor solution, which was comprised of 0.2 M $SnCl_4 \cdot 5H_2O$ and 0.6 M thiourea in methanol. 350.6 mg (1 mmol) $SnCl_4 \cdot 5H_2O$ was dissolved in 5 mL methanol, then 228.5 mg (3 mmol) thiourea was added to the solution under stirring and the pale yellow precursor solution was obtained. Subsequently, the precursor solution was spin-coated on the substrates at 3500 r. p.

m. for 20 s and the substrates were heated at 200 ℃, 260℃, 320℃ for 2 min, respectively. The above procedure was one spin-coating-pyrolysis cycle and the different spin-coating-pyrolysis cycles were applied to obtain SnS_2 thin films for the analysis of XRD, EDS, Raman, UV-Vis and SEM.

2.2 Characterization

The XRD patterns of SnS_2 and SnS thin films were measured by Cu Kα radiation (λ=0.154056 nm, 40kV and 40mA) (D/MAX2500V, Rigaku, Japan) using a scanning rate of $0.026°\cdot s^{-1}$ in the 2θ range of 5-70°. The chemical composition was analyzed by EDS (JSM-6490LV, Japan). The Raman spectra were recorded using a laser wavelength of 532 nm (Raman, Evolution, HORIBA JOBIN YVON). The absorption spectra were measured by UV-Vis (U-3900H, Hitachi, Japan) and UV-Vis-NIR (CARY 5000, Agilent, USA). The surface and cross-sectional morphology were observed using FE-SEM (Sirion200, FEI).

3 RESULTS AND DISCUSSION

3.1 SnS_2 Thin Films

FIG. 1 showed the XRD patterns of the resulting thin films at pyrolysis temperatures of 200℃, 260℃ and 320℃. The three thin films exhibited the same characteristic diffraction peaks at $2\theta = 14.60°$, corresponding to the spacing of (101) planes of SnS_2 (JCPDS NO. 01-1010). The intensity of the peak increased with the increase of the pyrolysis temperatures. The EDS analysis revealed that the atomic ratios of Sn/S at pyrolysis temperatures of 200℃, 260℃ and 320℃ were 1:2.11, 1:1.98 and 1:1.85, respectively. And the sulphur content decreased with the increase of the pyrolysis temperatures. This should be because that sulphur was easily volatile element. Combined with the result of XRD and EDS, it was found that the stoichiometric SnS_2 thin film was successfully prepared by the spin-coating-pyrolysis method at the pyrolysis temperatures of 260℃ for 2 min. Moreover, the peak at $2\theta = 26.8°$ was detected at the pyrolysis temperature of 200℃. This may be related to the residual $SnCl_4$ (JCPDS NO. 31-1394) or the complex of $SnCl_4$ and thiourea in the resulting thin films.

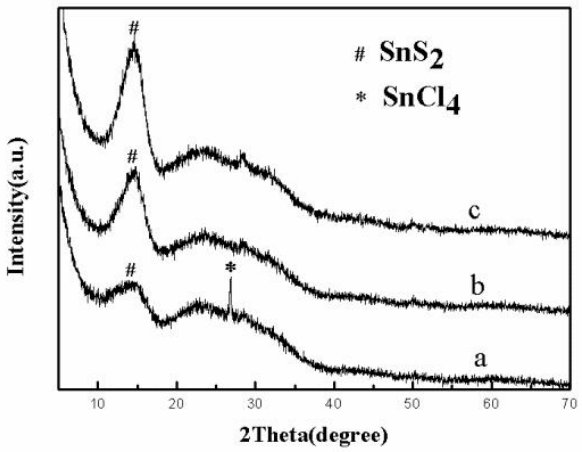

FIG. 1 X-RAY DIFFRACTION PATTERNS OF THE SnS_2 THIN FILMS AT PYROLYSIS TEMPERATURES OF 200℃(a), 260℃(b), 320℃(c) FOR 2MIN

FIG. 2 presented the Raman spectra of the resulting thin films at pyrolysis temperatures of 200℃, 260℃ and 320℃. The three thin films showed the same vibration at 315 cm^{-1}, which should be assigned to the A_{1g} mode of SnS_2 [12,13]. The result was in accordance with that of the XRD and EDS.

FIG. 3 exhibited the UV-Vis spectra of the resulting thin films at the pyrolysis temperatures of 200℃, 260℃ and 320℃. The absorption onset of the corresponding thin films was located at 485, 495 and 496 nm, and the optical band gaps were 2.55 eV, 2.50 eV and 2.50 eV, respectively.

FIG. 4 showed the cross-sectional and surface SEM images of the resulting thin films at pyrolysis temperatures of

200℃, 260℃ and 320℃. From the cross-sectional SEM images, the thickness of the three thin films was around 200 nm, and the three thin films exhibited the similar morphology with the bilayer structure, the bottom layer was compact and the upper layer was porous. From the surface SEM images, the pore sizes of the three thin films became smaller with the increase of pyrolysis temperatures.

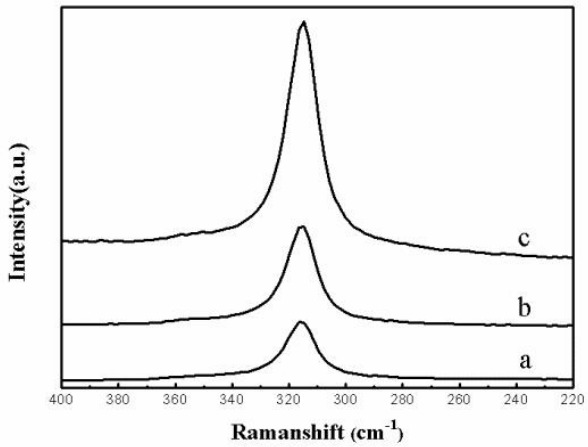

FIG. 2 RAMAN SPECTRUM OF THE SnS_2 FILMS AT PYROLYSIS TEMPERATURES OF 200℃(a), 260℃(b), 320℃(c)

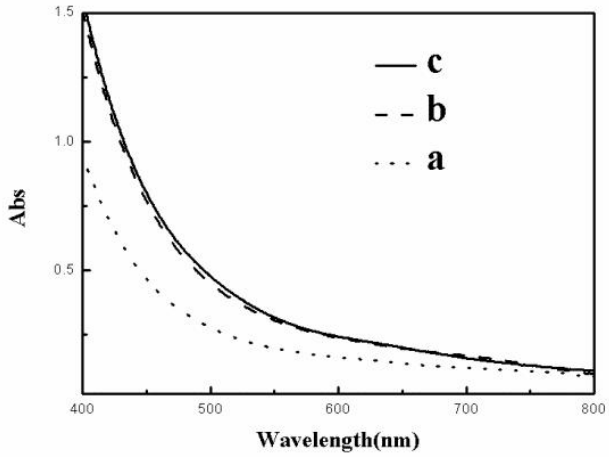

FIG. 3 ABSORPTION SPECTRA OF THE SnS_2 THIN FILMS AT PYROLYSIS TEMPERATURES OF 200℃(a), 260℃(b), 320℃(c)

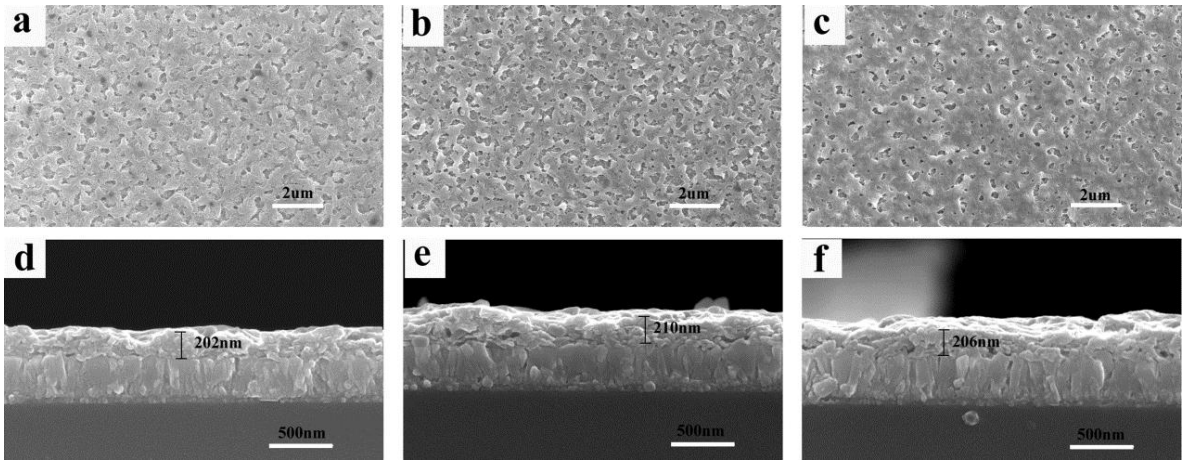

FIG. 4 THE SURFACE SEM IMAGES AND CROSS-SECTIONAL SEM IMAGES OF THE SnS_2 THIN FILMS AT PYROLYSIS TEMPERATURES OF 200℃(a, d), 260℃(b, e), 320℃(c, f)

3.2 SnS Thin Films

FIG. 5 displayed the XRD patterns of the resulting thin films at pyrolysis temperatures of 280℃, 320℃ and 360℃. It can be observed that the diffraction peaks at 2θ = 14.57°, 31.91°, corresponding to the spacing of (013), (027) planes of orthorhombic SnS (JCPDS NO. 01-0984), and a preferred orientation along (013) plane appeared. The intensity of the diffraction peak at 2θ = 14.57° increased with the increase of the pyrolysis temperatures, while the intensity of the diffraction peak at 2θ = 31.91° decreased. No diffraction peaks of any impurities can be detected. The EDS analysis revealed that the atomic ratios of Sn/S at pyrolysis temperatures of 280℃, 320℃ and 360℃ were 1:0.93, 1:0.99 and 1:0.72, respectively. Combined with the result of XRD and EDS, it was found that the stoichiometric SnS thin film was successfully prepared by the spin-coating-pyrolysis method at the pyrolysis temperature of 320℃ for 10 min.

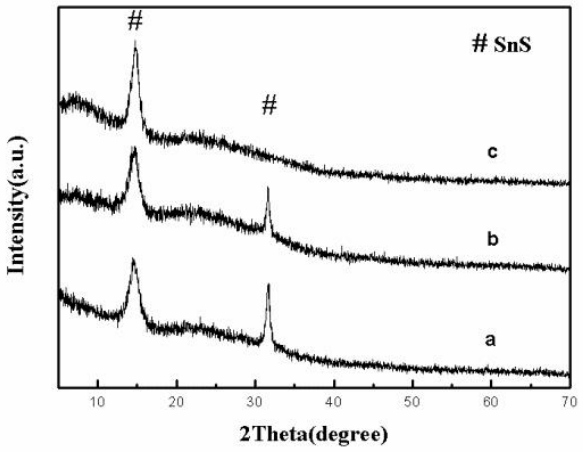

FIG. 5 X-RAY DIFFRACTION PATTERNS of the SnS THIN FILMS at PYROLYSIS TEMPERATURES of 280℃(a), 320℃(b), 360℃(c) for 10min.

FIG. 6 presented the Raman spectra of the resulting thin films at pyrolysis temperatures of 280℃, 320℃ and 360℃. The three thin films showed the same vibration at 95cm^{-1}, 154cm^{-1}, 181cm^{-1}, 229cm^{-1}, 308cm^{-1}, which should be assigned to SnS phase [14-16]. The vibration at 95 cm^{-1}, 229 cm^{-1}, 308 cm^{-1} can be assigned to the A_g mode of SnS phase, and the vibration at 181 cm^{-1} can be assigned to the B_{2g} mode of SnS phase. The vibration at 154 cm^{-1} can be assigned to the B_{3g} mode of SnS phase.

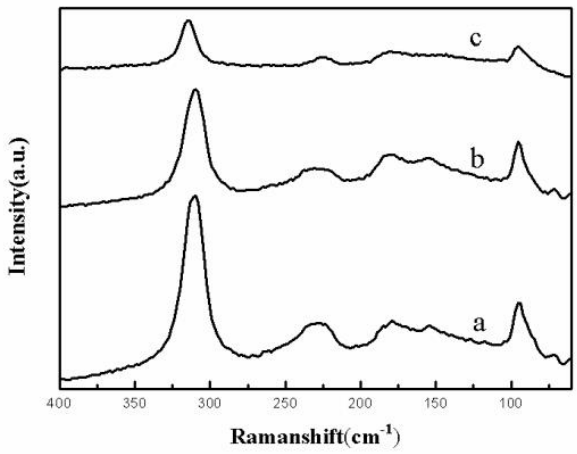

FIG. 6 RAMAN SPECTRUM OF THE SnS FILMS AT PYROLYSIS TEMPERATURES OF 280(a), 320(b), 360(c).

FIG. 7 exhibited the UV-Vis spectra of the resulting thin films at the pyrolysis temperatures of 280℃, 320℃ and

360℃. The absorption onset of the corresponding thin films was located at 850 nm, 880 nm and 740 nm, and the optical band gaps were 1.45 eV, 1.41 eV and 1.67 eV, respectively. The optical band gap at the pyrolysis temperatures of 360℃ was bigger than that of the pyrolysis temperatures of 280℃ and 320℃.This may be because that the sulphur content (Sn/S = 1:0.72) of the resulting thin films at pyrolysis temperatures of 360℃ was obviously lower than that (Sn/S = 1:0.93, 1:0.99) at pyrolysis temperatures of 280℃, 320℃.

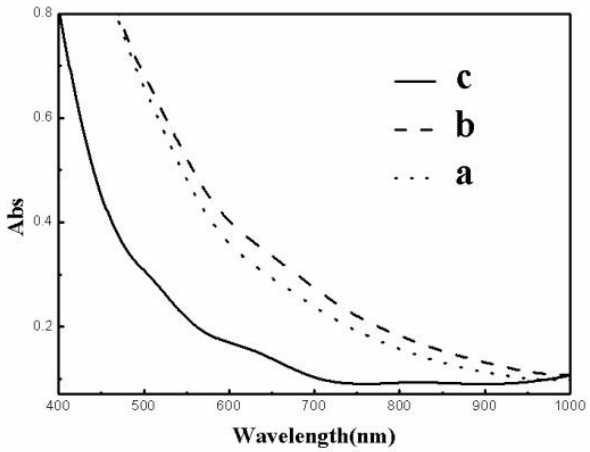

FIG. 7 ABSORPTION SPECTRA OF THE SnS THIN FILMS ATPYROLYSIS TEMPERATURES OF 280℃(a), 320℃(b), 360℃(c).

FIG. 8 showed the cross-sectional and surface SEM images of the resulting thin films at pyrolysis temperatures of 280℃, 320℃ and 360℃. The three thin films showed a sheet-appearance and were uniform and porous, and their thickness was around 80 nm.

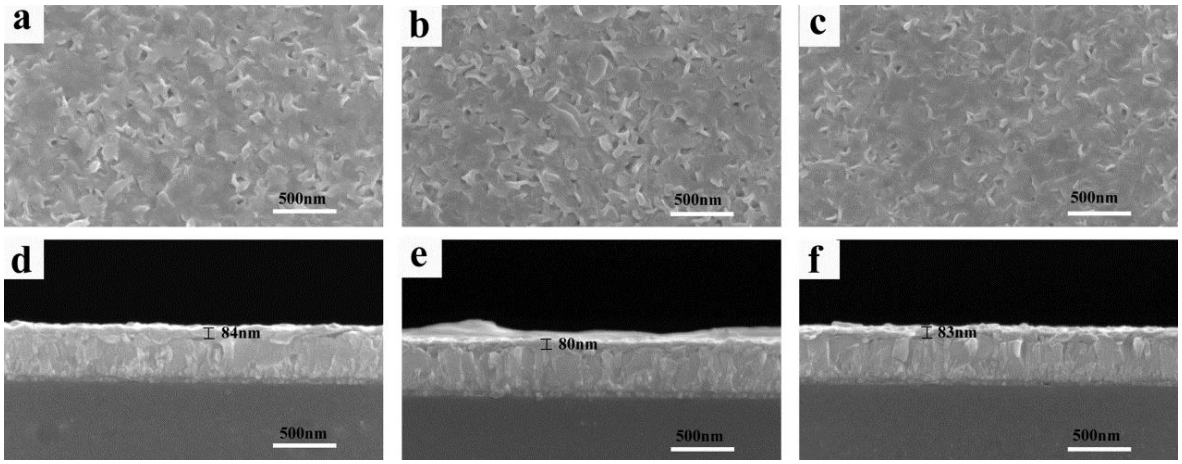

FIG. 8 THE SURFACE SEM IMAGES AND CROSS-SECTIONAL SEM IMAGES OF THE SnS THIN FILMS AT PYROLYSIS TEMPERATURES OF 280℃(a, d), 320℃(b, e), 360℃(c, f).

4 CONCLUSION

SnS_2 and SnS thin films were successfully prepared using spin-coating-pyrolysis method. The chemical composition of the precursor solution was 0.2 M $SnCl_4 \cdot 5H_2O$ and 0.6 M thiourea in methanol of SnS_2, and 0.2 M $SnCl_2 \cdot 2H_2O$ and 0.2 M thiourea in methanol of SnS. The appropriate pyrolysis temperature and time were 260℃, 2min of SnS_2 and 320℃, 10 min of SnS. The atomic ratios of Sn/S and the optical band gap for SnS_2 and SnS thin films were 1:1.98, 2.50 eV and 1:0.99, 1.41 eV.

ACKNOWLEDGEMENT

This work was financially supported by the National Natural Science Foundation of China (51272061, 51472071, 51072043).

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