Dependence of the physical properties of Sn–S film prepared by sol-gel spin-coating method on annealing temperature

Xiao-Na Zhai, Chao-Qian Liu, Nan Wang, Ting-Ting Lun, Meng-Si Song, Qing Ge, Xiao-Yang Zhang, Su-Mei Wu, Yu Zhao, Shi-Min Liu, Hua-Lin Wang, Wei-Wei Jiang and Wan-Yu Ding

1 Engineering Research Center of Optoelectronic Materials and Devices, School of Materials Science and Engineering, Dalian Jiaotong University, Dalian 116028, People’s Republic of China
2 School of Materials Science and Engineering, Dalian Jiaotong University, Dalian 116028, People’s Republic of China
3 Authors to whom any correspondence should be addressed.

E-mail: cqliu@djtu.edu.cn and yuzhao@hit.edu.cn

Keywords: sol-gel, Sn–S compounds, phase, optical property, electrical property

Abstract
Sn–S films were prepared by sol-gel method and their physical properties with annealing temperature were studied. XRD analysis showed that the dominant phase in all the films was Sn₂S₃ with cubic crystal structure. SEM images depicted that the flaky nanoparticles covered on the surfaces of the films except the film annealed at 500°C. The morphology of the film annealed at 500°C was cotton-like. The bandgaps of the films increased monotonically from 1.60 eV to 1.75 eV with the increase of annealing temperature. Moreover, the electrical properties of the films also depended on annealing temperatures.

1. Introduction
In recent years, the compounds of Sn–S system have attracted much attention because of their potential applications in photovoltaic devices and near infrared detectors [1]. Tin sulfur (mainly including SnS, SnS₂ and Sn₂S₃) thin films belong to the IV–VI family of semiconductor materials. SnS is usually a p-type semiconductor, and its optical bandgap varies from 1.0 to 1.5 eV [2], which is close to the optimal bandgap of solar cell materials. Moreover, SnS has a high absorption coefficient in the order of 10⁴ cm⁻¹. Therefore, SnS is a potential absorber candidate for thin-film solar cell [3]. SnS₂ is generally n-type semiconductor, and has wide bandgap (2.12–2.44 eV) [4]. SnS₂ can be used as n-type layer in thin-film solar cells and as the functional layer in gas sensors [5–7]. Sn₂S₃ with the bandgap of 0.95–2.2 eV has high anisotropic conductivity [8, 9], and is suitable for the application in the fields of photoconductive sensors [10–13] and gas sensors [14]. There are many methods on the preparation of Sn–S films, such as chemical vapor transport method [15], spray ultrasonic method [16], chemical bath deposition method [17] and atmospheric pressure chemical vapor deposition method [18]. It is well known that sol-gel method has the advantages of simple operation, low cost and no need of vacuum. However, it is very lacking in the study of Sn–S films prepared by sol-gel method. Up to now, we found only two related literatures. One of them reported the preparation of SnS thin films by sol-gel method, and studied the effect of sulfur content on the conductivity type of thin films [19]. Wherein, the phase of the prepared films was SnS with orthorhombic crystal structure. The other reported the effects of annealing temperature on the carrier mobility and transmittance of Sn–S film prepared by sol-gel method [20]. In this literature, the prepared films had several phases, i.e., SnS, SnS₂ and SnO₂, and had wide bandgaps (>3.6 eV). Therefore, it is necessary to further study the preparation of Sn–S films based on sol-gel method.

In the present work, the effects of annealing temperature were studied on the phase, morphology, optical and electrical properties of Sn–S films prepared by sol-gel spin-coating method.
2. Experiments

Sn–S films were prepared by sol-gel spin-coating method. Stannous chloride dihydrate (SnCl₂·2H₂O, AR grade, Aladdin), thiourea (SC(NH₂)₂, AR grade, Aladdin) and ethylene glycolmethyl ether (HOCH₂CH₂OCH₃, AR grade, Aladdin) were selected as Sn and S sources, and solvent, respectively. Glacial acetic acid (CH₃COOH, AR grade, Aladdin) was used as stabilizer. The concentration of Sn²⁺ in the precursor solution was 0.5 M, and the ion ratio of [Sn²⁺]/[S²⁻] was 1. The reagents were mixed into a 100 ml erlenmeyer flask, and were stirred in a constant temperature water bath at 75 °C for 3 h to be a transparent and uniform precursor solution. Finally, the precursor solution was aged for 24 h at room temperature.

The films were spin coated on normal glass slide whose cleaning process was the same as our previous work [21]. Each layer was spin-coated at the speed of 5500 r/min for 15 s, and then was pyrolyzed on a hot plate at 300 °C for 1 min in air atmosphere. The above process was repeated ten times for every film, and then the films were annealed respectively at 350 °C, 400 °C, 450 °C and 500 °C for 5 min in a self-made rapid thermal annealing furnace with argon atmosphere. The structure of the self-made furnace was described in our previous work [22].

The films were spin coated on normal glass slide whose cleaning process was the same as our previous work [21]. Each layer was spin-coated at the speed of 5500 r/min for 15 s, and then was pyrolyzed on a hot plate at 300 °C for 1 min in air atmosphere. The above process was repeated ten times for every film, and then the films were annealed respectively at 350 °C, 400 °C, 450 °C and 500 °C for 5 min in a self-made rapid thermal annealing furnace with argon atmosphere. The structure of the self-made furnace was described in our previous work [22].

The phase of the films was confirmed using x-ray diffractometer (XRD, Empyrean PANalytical) with CuKα radiation of wavelength λ = 1.54056 Å, where the scanning step size and the counting time of every step were 0.05° and 0.5 s respectively. The scanning electron microscopy (SEM, Germany Zeiss Ultra 55 FE-SEM, 5 kV) and energy dispersive spectroscopy (EDS, Oxford INCA, 20 kV, ×1000 magnification, 60 s acquisition time) were used to analyze the morphology and element content of the films, respectively. The optical transmittance measurement was carried out by UV–vis-NIR spectrometer (Shimadzu UV-3600) in the range of wavelength 400–1500 nm with the step size of 2 nm. Hall measurement technique (HALL8800) was employed for electrical measurements.

3. Results and discussion

3.1. Phase analysis

Figure 1 shows the x-ray diffraction patterns of the as-pyrolyzed film and the films annealed at different temperatures. Clearly, the as-pyrolyzed film had crystallized although it was not annealed at higher temperature. The dominant phase in all the films was Sn₂S₃ phase (PDF № 14–0619) with cubic crystal structure. When the annealing temperature was no more than 450 °C, the films had also a small amount of SnS₂ phase (PDF № 23–0677) with hexagonal crystal structure. At the annealing temperature of 500 °C, the diffraction peaks of SnS₂ almost disappeared, and the diffraction peaks of Sn₂S₃ could be clearly observed as well as the trace phase of SnO₂ (PDF № 41–1445). The existence of SnO₂ phase suggests that all the films containing oxygen element and Sn-O compound phase were amorphous in the films annealed at lower temperature. This should be due to the fact that the films were partially oxidized in their pyrolysis processes. Previous study indicated that mixed tin sulfide oxides-Sn₂S₃ film has potential applications in gas sensors [14]. In the literature, the sulfide films...
deposited by vacuum evaporation method were annealed designedly at 260 °C and 280 °C in ambient air to obtain the sulfide oxides-Sn$_2$S$_3$ films. Therefore, the preparation method of Sn–S films in the present work is meaningful for their application in gas sensor.

To further clarify the phase composition in the prepared films, the element contents of the films were measured by EDS, and the results are shown in table 1. When the annealing temperature was below 450 °C, the element ratio of [Sn]/[S] remains approximately 1, which equates the ion ratio of [Sn$^2+$]/[S$^2-$] in the precursor solution. That is to say, there was almost no loss of S and Sn in the preparation process of these films. The ratio of [Sn]/[S] in the film annealed at 450 °C increased slightly, but increased obviously in the film annealed at 500 °C. Obviously, the ratio of [Sn]/[S] in all films is more than 1. However, the dominant phases presented in figure 1 are Sn$_2$S$_3$, which suggests the ratio of [Sn]/[S] should be lower than 1 in all films. Therefore, the above results also suggest that Sn–O compound must exist in all films as amorphous ($\leqslant$ 450 °C) or crystal state (500 °C) and the oxidation of the films was more and more serious with increasing annealing temperature.

In addition, Sn–S compounds would lose some Sn and S elements in the form of SnS at temperature above 450 °C [23]. To confirm the loss of Sn element, the content of Si element in glass substrate as a calibration reference was also measured as shown in table 1. Obviously, the ratio of [Sn]/[Si] gradually decreased with increasing annealing temperature, which indicates that both Sn and S elements lost in the annealed films and the loss was more and more serious.

### 3.2. Surface morphology

Figure 2 depicts SEM images of the as-pyrolyzed and annealed Sn–S films. Figures 2(a)–(d) show that the surfaces of the films were covered by flaky nanoparticles. With increasing annealing temperature, the flake form of the nanoparticles was getting more obvious. Previously, some literatures [24, 25] reported the nanoparticles covered on the surfaces of Sn–S films were needle-like. Generally, sulfides grow in flake form [6, 17, 26]. Therefore, the needle-like nanoparticles in those literatures were actually the edges of flaky nanoparticles which grew upright. As shown in figure 1, the main phase was Sn$_2$S$_3$ in all the films, and there was a small amount of SnS$_2$ phase. Only when the annealing temperature reached 500 °C, did a small amount of SnO$_2$ phase appear in the film. Therefore, the morphologies of the films except the film annealed at 500 °C were very similar with each other, i.e., the surfaces of the films were covered by flaky nanoparticles. That is to say, the morphologies of the films shown in figures 2(a)–(d) are similar to those reported in the above literatures. The morphology of the film annealed at 500 °C was cotton-like as shown in figure 2(e), which is obviously different from others. This case should be due to the volatilization of Sn and S elements and the oxidation at the annealing temperature of 500 °C. The volatilization of Sn and S elements would lead to particle refinement, which therefore would destroy the flake morphology of the film. Moreover, SnO$_2$ does not grow in flake form generally, so the appearance of SnO$_2$ phase would also weaken the flake morphology of the film. In addition, it is clear that there are a lot of pores in all the annealed films, which suggests again that the annealed films are suitable for the application in gas sensor.

### 3.3. Optical properties

Figure 3 shows the optical transmission spectra of the prepared films in the wavelength range of 400 ~ 1500 nm. The relationship among the optical absorption coefficient $\alpha$, incident photon energy $h\nu$ and optical bandgap $E_g$ of a direct-bandgap semiconductor can be expressed as

$$ (a h \nu)^2 = A (h \nu - E_g), $$

where $A$ is a constant, $h \nu$ is photon energy, $E_g$ is the optical bandgap, and $\alpha$ is the absorption coefficient which is related to the thickness $d$ and transmittance $T$ of the films, i.e., $\alpha = \ln(1/T)/d$ (where the thicknesses $d$ of the films were estimated according to SEM cross-section images, and were about 600 nm, 550 nm, 600 nm and 500 nm corresponding to the annealing temperatures of 350 °C, 400 °C, 450 °C and 500 °C, respectively.).

---

**Table 1. Some elements contents in the prepared films and the glass substrate.**

| Annealing temperature (°C) | Element content (at%) | Element ratio |
|---------------------------|-----------------------|--------------|
|                           | [Sn] | [S] | [Si] | [Sn]/[S] | [Sn]/[Si] |
| As-pyrolyzed              | 42.65 | 41.75 | 15.60 | 1.02 | 2.68 |
| 350                       | 42.54 | 41.60 | 15.85 | 1.02 | 2.62 |
| 400                       | 41.61 | 40.57 | 17.82 | 1.03 | 2.28 |
| 450                       | 43.51 | 38.23 | 18.26 | 1.14 | 2.09 |
| 500                       | 50.98 | 27.66 | 21.36 | 1.84 | 1.29 |
Generally, SnS2, SnS3 and SnO2 are direct bandgap semiconductors. Therefore, the bandgaps of the films can be obtained by extrapolating the straight line part of \((ahv)^2\)\(-\)hv curve (see figure 3(b)) to \((ahv)^2 = 0\), and the results are shown in figure 3(b) as an inset. With the increase of annealing temperature, the bandgaps of the films increased monotonically from 1.60 eV to 1.75 eV. This result should be mainly due to the existence of SnO2 phase. Previous study on Cu2ZnSnS4 film with the narrow bandgap of about 1.5 eV indicated that the existence secondary phase of ZnS with the wide bandgap of about 3.7 eV could induce the increase of the bandgap of Cu2ZnSnS4 film [27]. Kumagai et al also indicated that the contamination of SnS2 or alloying with oxygen should

Figure 2. SEM images of (a) the as-pyrolyzed film and the films annealed at (b) 350 °C, (c) 400 °C, (d) 450 °C and (e) 500 °C.

Figure 3. (a) Optical transmission spectra and (b) \((ahv)^2\) versus hv plots of the films annealed at different temperatures.
increase the bandgap of Sn$_2$S$_3$. According to the phase analysis, the dominant phase in all the films was Sn$_2$S$_3$ phase. The variation of the content of the secondary phase SnS$_2$ was not obvious in the films except the film annealed at 500°C, while the secondary phase SnO$_2$ could be observed for the film annealed at 500°C. It is well known the bandgaps of both SnS$_2$ and SnO$_2$ are wider than that of Sn$_2$S$_3$. In addition, the composition analysis in the above section showed that Sn and S elements gradually lost with increasing annealing temperature. Based on the above discussion, it can be inferred that the content of secondary phase SnO$_2$ should increase in the films with increasing annealing temperature. Therefore, it is considered that the increase of the bandgaps originated from SnO$_2$.

3.4. Electrical properties

Hall measurements were performed to analyze the electrical properties of the prepared films. It found that all the films were n-type, which is consistent with the previous studies [13, 29]. Figure 4 presents the variation of carrier concentration, carrier mobility and resistivity with annealing temperature. It can be easily seen from figure 4 that, with increasing annealing temperature, the carrier concentration of the films decreased monotonically from $3.86 \times 10^{18}$ cm$^{-3}$ to $5.35 \times 10^{13}$ cm$^{-3}$ and the carrier mobility increased monotonically from 0.06 cm$^2$ V$^{-1}$s$^{-1}$ to 7.814 cm$^2$ V$^{-1}$s$^{-1}$. The factors affecting the electrical properties of the films were complex. The main factors should include the crystallization state, defect state and phase composition of the films. With increasing annealing temperature, the crystallinity would be enhanced, and then the defect concentration should be decreased. This case could induce the increase of the carrier mobility of the films with increasing annealing temperature. Moreover, the decrease of the defect concentration meant the concentration decrease of the defect that could provide carrier to the films. In fact, the major carrier in the films should be mainly provided by various point defects. Therefore, the carrier concentration of the films decreased with increasing annealing temperature. Furthermore, the content of SnO$_2$ with higher resistivity increased with increasing annealing temperature in the films according to figure 1(a), which could degrade the carrier mobility of the films. The variation of the content of SnS$_2$ was not obvious in the films except the film annealed at 500°C based on figure 1(a). Overall, the carrier mobility should be determined by the crystallization state and phase composition of the films, and the carrier concentration should be determined by the defect state.

In addition, the resistivity of the films increased with increasing annealing temperature, whose variation tendency is consistent with that of the reciprocal carrier concentration. Moreover, it is well known that resistivity is proportional to the reciprocal of the product of carrier mobility and concentration. Therefore, it can be deduced that the variation tendency of the resistivity was mainly affected by that of carrier concentration.

4. Conclusion

The Sn–S films were prepared by sol-gel spin-coating method at different annealing temperature. The dominant phase in all the films was Sn$_2$S$_3$ phase. When the annealing temperature was no more than 450°C, the films had a small amount of SnS$_2$ phase. Moreover, the trace impurity phase of SnO$_2$ was observed in the film annealed at 500°C, which indicated all the films were partially oxidized in their pyrolysis processes. In addition, both Sn and S elements lost in the annealed films, and the loss was more and more serious with increasing annealing temperature. The surface of almost all the films was covered by flaky nanoparticles. With the increase of annealing temperature, the bandgaps of the films increased monotonically from 1.60 eV to 1.75 eV. Moreover,
with increasing annealing temperature, the resistivity and carrier mobility increased, but the carrier concentration decreased. Further, it was found that the variation tendency of the resistivity was mainly affected by that of carrier concentration. In the next work, we will further optimize the preparation parameters to obtain the film with pure SnS$_2$ phase based on sol-gel spin-coating method.

**Acknowledgments**

This work was supported by Project of Department of Education of Liaoning Province, China (Grant Nos. JDL2017013/05/02/08), Natural Science Foundation of Liaoning Province, China (Grant Nos. 2015020653/191/182 and 201602120), National Natural Science Foundations of China (Grant Nos. 51002018, 51302024, 51472039, 51772038, and 61504017), Liaoning BaiQianWan Lalents Program, Program for LiaoNing Excellent Talents in University (Grant No.LJQ2012038 and LR2015010), Project of Dalian Youth Star of Science and Technology (Grant No. 2015R071).

**ORCID iDs**

Chao-Qian Liu @ https://orcid.org/0000-0002-4572-8367  
Wan-Yu Ding @ https://orcid.org/0000-0002-1186-204X

**References**

[1] Khadraoui M, Benramdane N, Miloua R, Mathieu C, Bouzidi A and Sahraoui K 2015 Physical properties of sprayed SnS$_2$ nanocrystalline thin films *International Journal of Applied Sciences and Innovation* 2 30–7
[2] Ghosh B, Das M, Banerjee P and Das S 2008 Fabrication and optical properties of SnS thin films by SILAR method *Appl. Surf. Sci.* 254 6360–40
[3] Robles V, Trigo J F, Guillen C and Herrero J 2013 Structural, chemical, and optical properties of tin sulfide thin films as controlled by the growth temperature during co-evaporation and subsequent annealing *J. Mater. Sci.* 48 3943–5
[4] Lin Y T, Shi J R, Chen Y C, Chen C J and Wu P F 2009 Synthesis and characterization of tin disulfide SnS$_2$ nanowires *Nanoscale Res. Lett.* 4 694–8
[5] Deshpande N G, Sagade A A, Gudage Y G, Lokhande C D and Sharma R 2007 Growth and characterization of tin disulfide (SnS$_2$) thin film deposited by successive ionic layer adsorption and reaction (SILAR) technique *J. Alloy. Compd.* 436 421–6
[6] Shi W D, Hsu C H, Cheng C I, Wang S H, Zhang H J, Yang J H and Wei P H 2006 Hydrothermal growth and gas sensing property of flower-shaped SnS$_2$ nanowires *Nano Research* 17 2918–24
[7] Wang Q H, Wang D W, Wu M H, Liu B X, Chen J T, Wang T M and Chen J 2011 Porous SnO$_2$ thin films with loose-packed structure: morphology conserved transformation from Sn$_2$S$_3$ precursor and application in lithium ion batteries and gas sensors *J. Phys. Chem. Solids* 72 630–6
[8] Salah H H, Bouzouita H and Rezig B 2005 Preparation and characterization of tin sulphide thin films by a spray pyrolysis technique *Thin Solid Films* 480–481 439–42
[9] Robin M B and Day P 1968 Mixed valence chemistry: A survey and classification *Advances in Inorganic Chemistry and Radiochemistry* 10 247–176
[10] Joseph I and Loferski 1956 Theoretical considerations governing the choice of the optimum semiconductor for photovoltaic solar energy conversion *J. Appl. Phys.* 27 777–84
[11] Khadraoui M, Benramdane N, Mathieu C, Bouzidi A, Miloua R, Kebbab Z, Sahraoui K and Desfeux R 2010 Optical and electrical properties of SnS$_2$ thin films grown by spray pyrolysis *Solid State Commun.* 150 297–300
[12] Lopez S, Granados S and Ortiz A 1996 Spray pyrolysis deposition of SnS$_2$ thin films *Semicond. Sci. Technol.* 11 433–6
[13] Reddy T S and Kumar M C S 2016 Effect of substrate temperature on the physical properties of co-evaporated SnS$_2$ thin films *Ceram. Int.* 42 12262–9
[14] Zaki S A, Elrahamana M I A, Sehly A A A, Shaalan M N and Hafiz M M 2018 Thermal annealing of SnS thin film induced mixed tin sulfide oxides-Sn$_x$S$_{1-x}$ for gas sensing: optical and electrical properties *Materials Science in Semiconductor Processing* 75 214–20
[15] Burton L A, Colombarda D, Abellon R D, Groziema F C, Peter L M, Savenije T J, Drenner G and Walsh A 2013 Synthesis, characterization, and electronic structure of single-crystal SnS, Sn$_n$S$_{3-n}$ and SnS$_2$ *Chem. Mater.* 25 4908–16
[16] Kherchachi I R, Attar A, Saiti H, Boudjader A, Bendjeddou Y and Arzii R 2016 Structural, optical and electrical properties of SnS$_2$ thin films grown by spray ultrasonic *J. Semicond.* 37 032001
[17] Avellaneda D, Sánchez-Orozco I, Martínez A A A, Shaji S and Krishnan B 2019 Thin films of tin sulfides: structure, composition and optoelectronic properties *Mater. Res. Express* 6 016409
[18] Price L S, Parkin I P, Hardy A M E and Clark R H 1999 Atmospheric pressure chemical vapor deposition of tin sulfides (SnS, Sn$_2$S$_3$, and Sn$_3$S$_4$) on Glass *Chem. Mater.* 11 1792–9
[19] Huang C C, Lin Y J, Chuang C Y, Liu C J and Yang Y W 2013 Conduction-type control of SnS$_3$ films prepared by the sol–gel method for different sulfur contents *J. Alloys Compd.* 553 208–11
[20] Sun J, Huang Y F, Nie S, Chen Z Q, Xu J M, Zhao L, Zhou W, Wang Q and Gong H 2016 Improved mobility of sol–gel method processed transparent tin sulfide thin films *Mater. Lett.* 178 231–4
[21] Wen B, Liu Q C and Fei W D 2014 Effect of doped boron on the properties of ZnO thin films prepared by sol–gel spin coating *Chem. Res. Chin. Unvi.* 30 509–12
[22] Wang N, Liu C Q, Wen B, Wang H L, Liu S M and Chai W P 2014 Enhanced optical and electrical properties of NiO thin films prepared by rapid radiation pyrolysis method based on the sol–gel technique *Mater. Lett.* 122 269–72
[23] Friedlmeier T M, Dittrich H and Schock H W 1997 Growth and characterization of Cu$_x$ZnSnS$_4$ and Cu$_x$ZnSnSe$_4$ thin films for photovoltaic applications *Institute of Physics Conference Series Proceedings 116th ICTMC (Salford)* 152, 345–8
[24] Prabha D, Ilangoval S, Nagarethinam V S and Balu A R 2016 Effect of solvent volume on the physical properties of spray deposited nano needle structured Sn$_2$S$_3$ thin films Mater. Res. Innovations 20 307–11
[25] Gnanamuthu S J, Jeyakumara S I, Punithavathy I K, Prabhakara P C J, Suganyab M, Usharanib K and Balu A R 2016 Properties of spray deposited nano needle structured Cu-doped Sn$_2$S$_3$ thin films towards photovoltaic applications Optik 127 3999–4003
[26] Ma J, Lei D, Mei L, Duan X C, Li Q H, Wang T H and Zheng W J 2012 Plate-like SnS$_2$ nanostructures: hydrothermal preparation, growth mechanism and excellent electrochemical properties Cite this: Cryst. Eng. Comm. 14 832–6
[27] He J, Sun L, Zhang K Z, Wang W J, Jiang J C, Chen Y, Yang P X and Chu J H 2013 Effect of post-sulfurization on the composition, structure and optical properties of Cu$_2$ZnSnS$_4$ thin films deposited by sputtering from a single quaternary target Appl. Surf. Sci. 264 133–8
[28] Kumagai Y, Burton I A, Walsh A and Oba F 2016 Electronic structure and defect physics of tin sulfides: SnS, Sn$_2$S$_3$, and SnS$_2$ Physical Review Applied 6 014009
[29] Saroja A M, Punithavathy I K, Jeyakumar S I, Gnanamuthu S J and Balu A R 2017 Substrate temperature influence on the optical and electrical properties of spray deposited Sn$_2$S$_3$ thin films Optik 130 245–54