

## Structure and properties of SnS films prepared by electro-deposition in presence of EDTA

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### ABSTRACT

SnS thin films were deposited onto indium tin oxide (ITO) glass substrates by constant potential cathodic electro-deposition from aqueous solution containing stannous sulfate, ethylenediamine tetraacetate acid and sodium thiosulfate. The co-deposited potential was explored by cyclic voltammetry and the deposition potential ( $E$ ) was roughly determined to be more negative than  $-0.70$  V (vs. saturated calomel electrode, SCE). The analysis of the composition of the as-deposited films by X-ray fluorescence spectrometer indicated that stoichiometric SnS films could be obtained under the condition of  $E = -0.95$  to  $-1.00$  V. The films deposited at  $E = -1.00$  V were characterized with X-ray diffraction (XRD), scanning electron microscope (SEM), and their transmission and reflectance spectra were measured. The as-deposited films were polycrystalline SnS compound with orthorhombic crystalline structure and the ratio of Sn and S was nearly 1. The films were uniform and compact with small grains. The direct band gap of the films was estimated to be about  $1.10$ – $1.43$  eV with an absorption coefficient near the fundamental absorption edge larger than  $4 \times 10^4$  cm<sup>-1</sup>.

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### 1. Introduction

Tin monosulphide (SnS) as a novel “absorber” layer in the fabrication of thin-film hetero-junction solar cells has attracted more attention in recent years. The reasons for that can be explained as following: (i) SnS has favorable photovoltaic properties; (ii) both Sn and S are abundant in nature and non-toxic [1]; (iii) its direct band gap and indirect band gap are respectively estimated to be  $1.2$ – $1.5$  eV and  $1.0$ – $1.1$  eV [2,3], which are suitable for the solar radiation; (iv) in theory the conversion efficiency of the solar cell fabricated with SnS thin films can reach 25% [4].

SnS films can be deposited by various methods, such as two-stage process [5], thermal evaporation [6], radio frequency (RF) sputtering [7], chemical deposition [8], electro-deposition [9] and spray pyrolysis [10]. Electro-deposition has the advantages of being economic, convenient and capable of a large area of deposition. However, the deposition velocity of Sn is faster than that of S even if the ion concentration of  $S_2O_3^{2-}$  is as four times as that of  $Sn^{2+}$  in the preparation of SnS films, thus it is not easy to co-deposit Sn and S in the ratio of 1. Because ethylenediamine tetraacetate acid (EDTA) can retard the deposition of Sn through chelation, it

is easier to obtain the stoichiometric SnS films with good quality by adding EDTA to the bath. The electro-deposition of SnS films on titanium substrates with EDTA added was first reported by Ghazali et al. [11]. The presence of complexing agents in the solution during the electro-deposition process of metal chalcogenide thin films was found to improve the lifetime of the deposition bath as well as the quality of the deposited films, such as the uniformity, crystallinity and the adhesion of the deposited film on the substrate [11]. Therefore, here the structure and properties of SnS films on the indium tin oxide (ITO) glass substrates made by electro-deposition in the presence of EDTA were investigated in order to improve the quality of the deposited films.

### 2. Experimental

The SnS films were deposited potentiostatically by a three-electrode cell. ITO coated glass substrates with the square resistance of  $100$ – $150$   $\Omega$ sq.<sup>-1</sup> were used as the working electrode for all depositions. A platinum electrode served as the counter electrode. A saturated calomel electrode (SCE) was used as a reference electrode. All the potentials mentioned in the paper are relative to SCE. The electro-deposition bath contained  $1$ – $10$  mmol L<sup>-1</sup> EDTA,  $10$  mmol L<sup>-1</sup> stannous sulfate (SnSO<sub>4</sub>) and  $40$  mmol L<sup>-1</sup> sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>). The pH value of the solution was adjusted to 2.1 by adding H<sub>2</sub>SO<sub>4</sub>. The substrates and the platinum electrode were ultrasonically cleaned with acetone and ethanol in turn, and then rinsed with distilled water prior to each deposition. The whole deposition process was performed at room temperature (25 °C). The deposition potential  $E$  was altered from  $-0.70$  to  $-1.10$  V and the deposition period  $t$  was fixed at 90 min. All the chemicals used were analytical reagents and the water used was deionized distilled water.

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The co-deposited potential of Sn and S was explored by cyclic voltammetry using CHI660B electrochemical analyzer. The composition of the deposited films was analyzed by a Philips PW2424 X-ray fluorescence spectrometer. The structure of the films was characterized by a Philips X'Pert-MPD X-ray diffraction (XRD) system with a Cu K $\alpha$  radiation source. The surface morphology was examined by a Philips XL30E scanning electron microscope (SEM) and a multimode NS3A-02NanoscopeIIla scanning probe microscopy. The transmission and reflectance spectra were examined using a CARY 500 Scan ultraviolet-visible-near infrared spectrophotometer. The thickness of the film was measured by a Veeco Dektak 6M stylus profiler.

### 3. Results and discussion

#### 3.1. Principle

In the deposition of SnS films from aqueous solution containing EDTA, the following reactions would happen.



The standard equilibrium electrode potential of reaction (2) is expressed as follows:

$$\psi^0(\text{Sn}(\text{EDTA})^{2+}/\text{Sn}) = \psi^0(\text{Sn}^{2+}/\text{Sn}) - RT \ln \left( \frac{K_{\text{Sn}(\text{EDTA})^{2+}}}{nF} \right) \quad (3)$$

Here,  $\psi^0$  is the standard equilibrium electrode potential,  $R$  the mole gas constant ( $8.314 \text{ J} (\text{K mol})^{-1}$ ),  $T$  the thermodynamic temperature ( $298 \text{ K}$ ),  $F$  the Faraday constant ( $96,485 \text{ C mol}^{-1}$ ),  $n$  the gained electronic number of the half reaction and  $K_{\text{Sn}(\text{EDTA})^{2+}}$  is the stability constant. According to Eq. (3), the value of  $\psi^0(\text{Sn}(\text{EDTA})^{2+}/\text{Sn})$  will be more negative than the value of  $\psi^0(\text{Sn}^{2+}/\text{Sn})$  because the value of  $K_{\text{Sn}(\text{EDTA})^{2+}}$  is plus.

In fact, the acidity of the bath, the chelating effect of other metal ions with EDTA and the polarization of the electrode will affect the actual process of the deposition. In practical electro-deposition, only by electro-chemical analysis and repeated experiments can the process parameters be optimized.

#### 3.2. Cyclic voltammetry

Based on studying the cyclic voltammetric behaviors of the ITO glass electrode (substrate) in the solution of  $\text{SnSO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , EDTA and their mixture, respectively, the suitable deposition potential of SnS can be obtained (see Fig. 1). Fig. 1(a) is the cyclic voltammogram of the substrate in the solution of  $40 \text{ mmol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ . The forward scan current remains at a very low value up to  $-0.51 \text{ V}$  and increases obviously at about  $-0.86 \text{ V}$ . A thin layer of yellow matter which may be S can be seen on the substrate in this process. There is no visible anodic peak in reverse scan, which proves that the reaction is irreversible. Fig. 1(b) is the cyclic voltammogram of the substrate in the solution of  $10 \text{ mmol L}^{-1} \text{ SnSO}_4$ . The forward scan current increases obviously when the potential changes to  $-0.53 \text{ V}$ , and a thin layer of gray-black matter appears very soon. An obvious anodic peak appears at  $-0.36 \text{ V}$  in the reverse scan, which marks a reversible process. From Fig. 1(a) and (b), it can be seen that the deposition current of Sn is higher than that of S at the same potential range of  $-0.50$  to  $-1.00 \text{ V}$ , namely the deposition velocity of Sn is faster than that of S. Hence the deposition of Sn is much easier than that of S. Fig. 1(c) is the cyclic voltammogram of the substrate in the mixed solution of  $0.01 \text{ mol L}^{-1} \text{ SnSO}_4$  and  $0.01 \text{ mol L}^{-1} \text{ EDTA}$ . Compared with Fig. 1(b), the separate potential of  $\text{Sn}^{2+}$  becomes more negative obviously (from  $-0.53$  to  $-0.74 \text{ V}$ ), but the anodic peak shifts reversely (from  $-0.36$  to  $-0.25 \text{ V}$ ). The deposition velocity of Sn becomes slower. Therefore, with addition of EDTA to the solution of  $\text{SnSO}_4$ , it is slower to deposit Sn, so that the deposition velocity of Sn is almost the same as that of S at the same potential range

of  $-0.70$  to  $-1.00 \text{ V}$ . Fig. 1(d) and (e) are the cyclic voltammogram of the substrate in the mixed solution of  $0.01 \text{ mol L}^{-1} \text{ SnSO}_4$  and  $0.04 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$  without EDTA and with EDTA, respectively. It can be seen that the cathodic current with EDTA is smaller than that without EDTA.

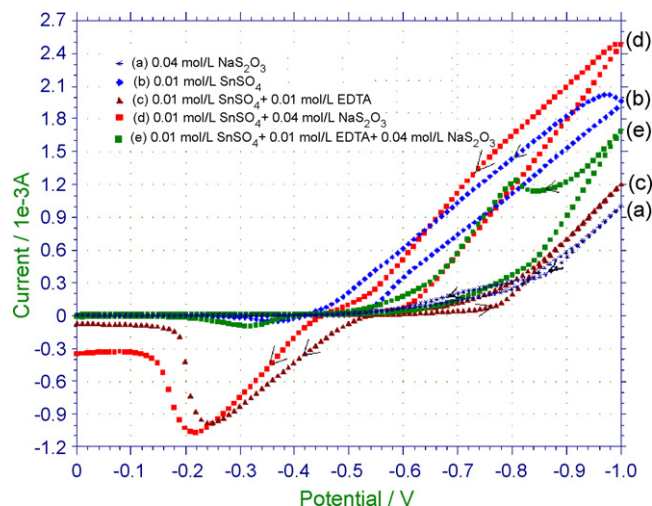
In conclusion, with the addition of EDTA, it is easier to co-deposit Sn and S and obtain stoichiometric SnS thin films favorably. The deposition potential can be ascertained to be more negative than  $-0.70 \text{ V}$ .

#### 3.3. Composition analysis

According to the results of cyclic voltammetry, the deposition potential was selected to vary from  $-0.70$  to  $-1.10 \text{ V}$ . With the change of the potential, the color of the as-deposited films changed from yellow to grey then to brown-black. By X-ray fluorescence analysis, it was found that the Sn/S ratio became larger and larger (from 0.012 to 1.1079) with the potential varying from  $-0.70$  to  $-1.10 \text{ V}$  (see Table 1). When the potential is between  $-0.95 \text{ V}$  and  $-1.00 \text{ V}$ , the Sn/S ratio is 1.0044–1.0105 and very close to the stoichiometric SnS.

We have to mention that maybe only S is deposited on the ITO glass substrate when the potential is more positive than  $-0.70 \text{ V}$  because the separate potential of Sn is more negative than  $-0.70 \text{ V}$  ( $-0.74 \text{ V}$ , see Fig. 1(c)). Thereby, the Sn/S ratio of the film deposited at  $E = -0.70 \text{ V}$  is 0.012.

So we can conclude that the composition of the films is close to stoichiometric when the deposition conditions are pH 2.1,  $\text{Sn}^{2+}:\text{EDTA}:\text{S}_2\text{O}_3^{2-} = 1:1:4$ ,  $E = -0.95$  to  $-1.00 \text{ V}$ ,  $t = 1.5 \text{ h}$ . Under the above conditions, a series of SnS thin films were deposited and



**Fig. 1.** Cyclic voltammogram on ITO glass substrates in (a)  $0.04 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ ; (b)  $0.01 \text{ mol L}^{-1} \text{ SnSO}_4$ ; (c)  $0.01 \text{ mol L}^{-1} \text{ SnSO}_4 + 0.01 \text{ mol L}^{-1} \text{ EDTA}$ ; (d)  $0.01 \text{ mol L}^{-1} \text{ SnSO}_4 + 0.04 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ ; (e)  $0.01 \text{ mol L}^{-1} \text{ SnSO}_4 + 0.01 \text{ mol L}^{-1} \text{ EDTA} + 0.04 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$ .

**Table 1**

Composition of the films prepared with potential in range of  $-0.70$  to  $-1.10 \text{ V}$

Deposition potential, $E$ (V) (vs. SCE)	Composition ratio (Sn/S)
-0.70	0.0120
-0.80	0.8160
-0.90	0.8699
-0.95	1.0044
-1.00	1.0105
-1.10	1.1079

Conditions: pH 2.1,  $\text{Sn}^{2+}:\text{EDTA}:\text{S}_2\text{O}_3^{2-} = 1:1:4$ ,  $t = 1.5 \text{ h}$ .

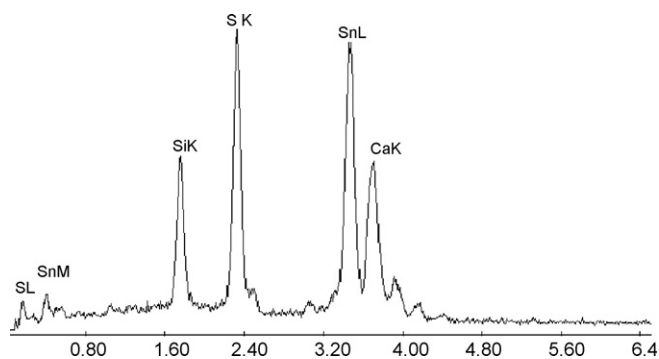


Fig. 2. The energy spectrum of the as-deposited thin film at  $E = -1.00$  V.

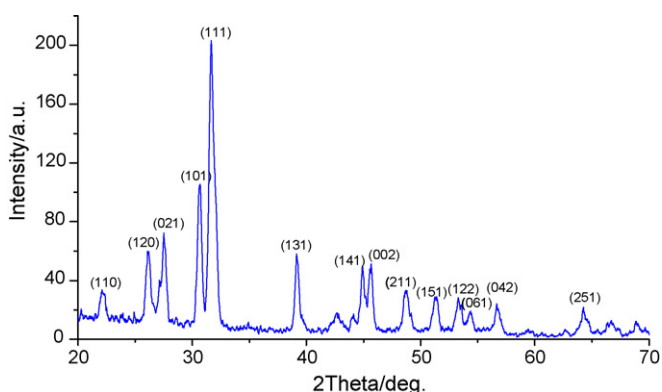


Fig. 3. The X-ray diffraction pattern of the as-deposited thin film at  $E = -1.00$  V.

characterized with XRD, SEM and AFM analysis and optical measurement. The thickness of the films is from 900 to 1000 nm depending on the preparation process.

Fig. 2 is the energy spectrum of one typical SnS thin-film deposited at  $E = -1.00$  V. The peaks of Si and Ca in the graph are the major components of the ITO glass substrate. Except the components of the ITO glass substrate, the atomic percent of Sn and S is: S-49.93 (at.%), Sn-50.07 (at.%). The Sn/S ratio was calculated to be 1.0028, which was very closed to 1.

#### 3.4. Structural characterization of SnS films

Fig. 3 is the X-ray diffractogram of the SnS thin-film deposited at  $E = -1.00$  V. There are fourteen evident XRD peaks with the  $2\theta$

angle scanning from  $20^\circ$  to  $70^\circ$ , and all of the peaks are coincident well with the corresponding diffraction peaks of orthorhombic SnS compound (referring to JCPDS 39-354). The lattice parameters of the films was calculated to be  $a = 0.43171$  nm,  $b = 1.11896$  nm and  $c = 0.39844$  nm, which are in good agreement with  $a = 0.43291$  nm,  $b = 1.11923$  nm and  $c = 0.39838$  nm from JCPDS 39-354.

It is necessary to say that there probably exists tiny S or Sn in the sample, because the strongest diffraction peak of S simple substance (referring to JCPDS13-141,  $2\theta$ :  $27.04^\circ$ ,  $d$ -space: 0.3290 nm) was almost superposed with peak (0 2 1) of the film, and similarly the strongest diffraction peak of Sn simple substance (referring to JCPDS04-0673,  $2\theta$ :  $30.64^\circ$ ,  $d$ -space: 0.2916 nm) was almost superposed with peak (1 0 1) of the film.

Fig. 4 shows the scanning electron micrograph of the SnS thin-film deposited at  $E = -1.00$  V, and the multiple of (a) and (b) is 1000 and 10,000, respectively. There are several big grains in the film, which can be explained as the conglomeration of the randomly oriented crystallites. But the images display the film is more uniform and compacter than that prepared without EDTA in our previous work [12].

Fig. 5(a) and (b) show the atomic force micrograph (AFM) of the SnS thin-film deposited at  $E = -1.00$  V, and the scan size is  $10 \mu\text{m} \times 10 \mu\text{m}$  and  $8 \mu\text{m} \times 8 \mu\text{m}$ , respectively. The 3D pictures show the presence of hills on the top of homogeneous granular surface. This indicates the roughness of the surface of the as-deposited film. The 2D picture and the roughness analysis of the film extracted from AFM are showed in Fig. 4(c), the root mean square (RMS) roughness is 62.547 nm, and the average diameter of the grain is about 270 nm.

#### 3.5. Optical properties

Fig. 6 shows the total reflection and transmission spectra of the SnS film deposited at  $E = -1.00$  V in the wavelength range of 300–2500 nm. The total reflectance varies irregularly with the wavelength, but its magnitude is small (between 11% and 20%). The transmittance is very low in the range of 300–825 nm and increases rapidly for wavelength longer than 825 nm, but it is not larger than 18% when the wavelength reaches 2500 nm. The lower transmittance at visible and near infrared waveband might be related to the fine grains, compactness and thickness of the film. The thickness of the film was measured to be 980 nm.

In terms of the formula:  $A = 1 - R - T$  ( $A$ , absorptance;  $R$ , reflectance;  $T$ , transmittance), the absorptance can be calculated approximately and it is high (much higher than 80%) at the range of visible light (not shown). In fact the visible light in the wave-

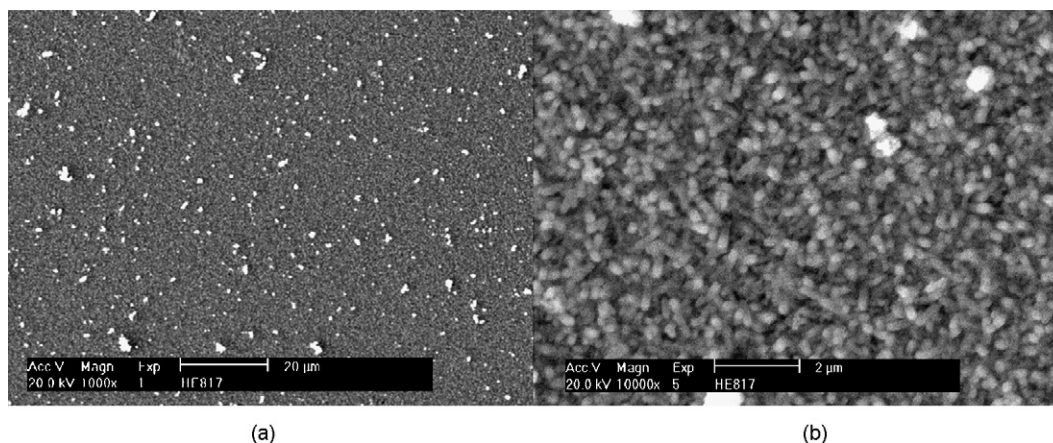


Fig. 4. The SEM micrographs of the as-deposited thin film at  $E = -1.00$  V.

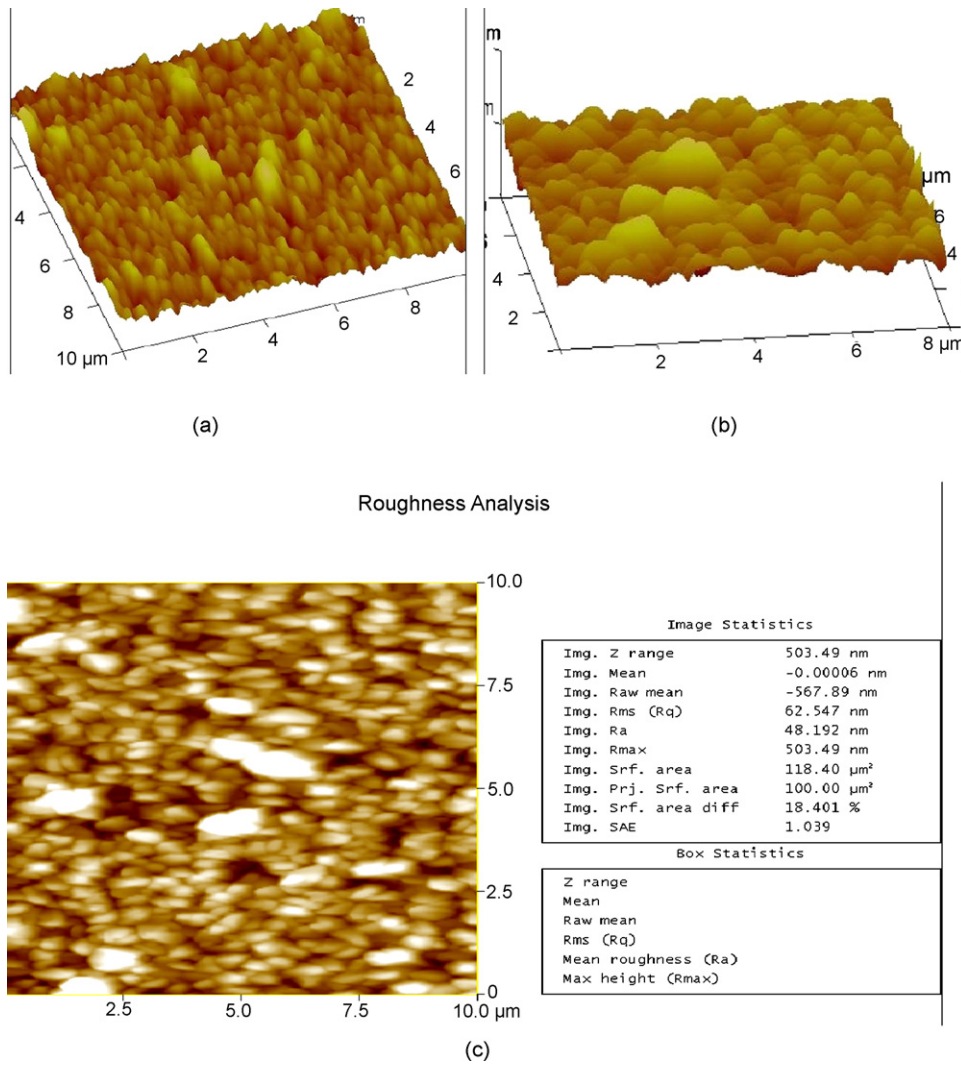


Fig. 5. The AFM micrographs of the as-deposited thin film at  $E = -1.00$  V. (a)  $10 \mu\text{m} \times 10 \mu\text{m}$ , (b)  $8 \mu\text{m} \times 8 \mu\text{m}$  and (c) the roughness analysis of the film.

length of 300–900 nm is almost completely absorbed by the film except reflection. This completely testifies the films prepared by this method are suitable to be “absorber” layer of the solar cell in theory.

According to our earlier work [12,13], the absorption coefficient ( $\alpha$ ) can be calculated from reflectance  $R$ , transmission  $T$  and thickness of the film, and it is larger than  $4 \times 10^4 \text{ cm}^{-1}$  near the fundamental absorption edge. Fig. 7 shows the  $(\alpha h\nu)^2 - h\nu$  curve of

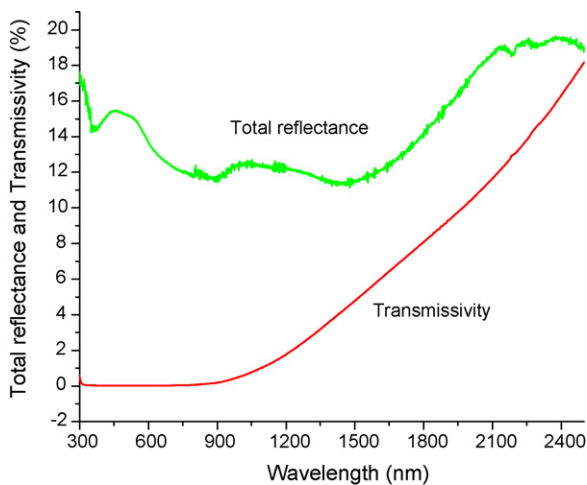


Fig. 6. The total reflection and transmission spectra of the as-deposited film at  $E = -1.00$  V.

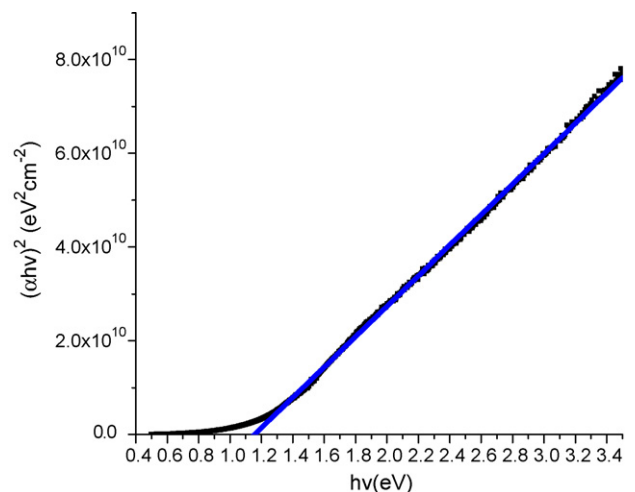


Fig. 7. The  $(\alpha h\nu)^2 - h\nu$  curve of the as-deposited film at  $E = -1.00$  V.

the same SnS thin film. From the curve, its direct band gap was estimated to be 1.16 eV, which is close to 1.10 eV in Ref. [11]. By calculating the direct band gap of some other SnS films deposited at  $E = -0.95$  to  $-1.00$  V, it is between 1.10 and 1.43 eV which is close to our previous results: 1.24–1.42 eV [12] and 1.24–1.48 eV [13].

#### 4. Conclusions

Based on studying of the co-deposition potential of Sn and S by means of cyclic voltammetry, the SnS films were deposited potentiostatically at the potential of  $-0.70$  to  $-1.10$  V in the presence of EDTA. By X-ray fluorescence, XRD and SEM analysis and optical measurement, it was indicated that the as-deposited films under the condition of  $E = -0.95$  to  $-1.00$  V (vs. SCE) were polycrystalline SnS with orthorhombic crystalline structure and the Sn/S ratio was nearly 1/1. The films were uniform and compact with small grains. The films had large absorption coefficient (larger than  $4 \times 10^4 \text{ cm}^{-1}$ ) near the fundamental absorption edge, and their direct band gaps were about 1.10–1.43 eV.

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