

Preparation of SnS : Ag Thin Films by Pulse Electrodeposition *

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Abstract: SnS:Ag thin films were deposited on ITO by pulse electro-deposition. They were characterized with X-ray diffraction spectroscopy and atomic force microscope. The as-deposited films have a new phase (Ag_xSnS_y) with good crystallization and big grain size. The conductivity of the films was measured by photoelectrochemical test. It is proved that the SnS:Ag films are p-type of semiconductor. Hall measurement shows that the carrier concentration of the films increases, while their resistivity decreases after Ag-doping.

Key words: pulse electrodeposition; SnS:Ag thin films; electrical and optical properties

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1 Introduction

Tin sulfide (SnS) is a semiconductor material with orthorhombic structure in group IV-VI. It has potential use in photovoltaic devices, which has aroused much attention from scientific community. It has an optical gap of 1.30eV that is close to the optimal optical gap 1.50eV of solar cells and a high absorption coefficient ($\alpha > 10^4 \text{cm}^{-1}$). In theory, the conversion efficiency of SnS film solar cells is up to 25%^[1,2], which is near to that of crystal Si solar cells. SnS can be used as solar cell materials due to its low cost, easy solidification and being films. Furthermore, its elements Sn and S are abundant and non-toxic in nature. Thus, it can be used as an ideal absorbing layer material in the solar cells^[3].

By far, SnS thin films studied are almost undoped. Our early investigations on SnS thin films showed that SnS films grown by pulse electrodeposition exhibited high electrical resistivity of $16.8 \sim 43.1 \Omega \cdot \text{cm}$ ^[4]. Doping in semiconductor material can improve its semiconducting properties. Therefore, it is necessary to study doped SnS thin films. It was reported that Ag-doped SnS thin films could improve the properties of p-type SnS films^[5,6], which is necessary for the films used as absorbing materials in the solar cells.

Based on our previous research, SnS : Ag thin films are deposited on ITO coated glass substrates by pulse electrodeposition, and their structure, morphology and semiconducting properties are studied so as to obtain SnS films with good quality.

2 Experiment

In the experiment, a CHI660B electrochemical analyzer was employed as power supply. A three-electrode cell was adopted. An ITO coated glass substrate was used as the working electrode for all deposition. A platinum electrode served as the counter electrode. A saturated calomel electrode (SCE) was used as a reference electrode. The electrodeposition bath contained SnSO_4 , $\text{Na}_2\text{S}_2\text{O}_3$ and AgNO_3 solution with a volume of 250mL. The pH value of the solution was adjusted to 2.7 by adding H_2SO_4 . The experiment was performed at room temperature and without stirring. The parameters of pulse electrodeposition were just as follows^[4]: $E_{\text{on}} = -0.75 \text{V}$ (vs SCE), $T_{\text{on}} = 10 \text{s}$, $E_{\text{off}} = 0.1 \text{V}$, $T_{\text{off}} = 1 \text{s}$. The other parameters were consistent with our previous research of constant current electro-deposition^[7]: $\text{pH} = 2.7$, $\text{Sn}^{2+} : \text{S}_2\text{O}_3^{2-} = 1 : 5$, deposition time $t = 1.5 \text{h}$.

The structure of the thin films was characterized by a Philips X'Pert-MPD X-ray diffraction spectroscopy (XRD) and a CSPM5000 atomic force microscope (AFM). Based on the Van der Pauw method, the electrical properties were determined by a Hall measurement system.

The light source for photoelectrochemical measurement is a xenon lamp with modulated light. Linear scan photovoltammetry of the CHI660B electrochemical analyzer was employed to record $I-V$ curve and test the photocurrent of the as-deposited thin films. 100mmol/L $\text{Na}_2\text{S}_2\text{O}_3$ was chosen as electrolyte for pre-

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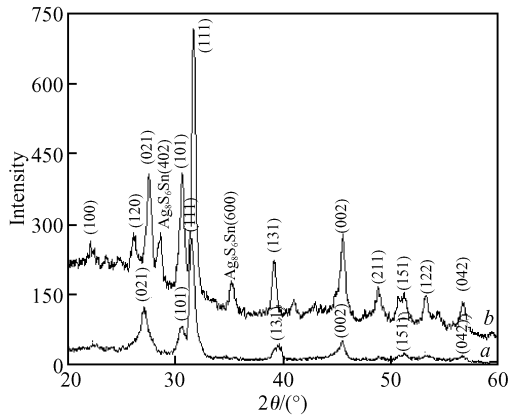


Fig.1 X-ray diffraction patterns of the SnS (a) and the SnS : Ag (b) films

venting corrosion of the semiconductor films during the photoelectrochemical test^[8].

3 Results and discussion

3.1 XRD analysis

Figures 1 (a) and 1 (b) show the XRD patterns

of the SnS and SnS:Ag films deposited on ITO substrates, respectively. It can be seen from Fig.1 (a) that the main planes with (021), (101), (111), (131), (002) (which are respectively assigned to the $2\theta = 27.10^\circ, 30.52^\circ, 31.47^\circ, 39.07^\circ, 45.56^\circ$ peaks) agree with those of SnS (JCPDS39-354). It indicates that the films have an orthorhombic crystal structure. Compared with Fig. 1 (a), the intensity of diffraction peaks in Fig. 1 (b) becomes stronger, and there appear some other peaks of SnS in Fig. 1 (b), indicating that Ag doping has a certain effect on SnS films. Simultaneously, the peaks appeared at $2\theta = 28.68^\circ$ and 35.17° are respectively assigned to the (402) and (600) planes of Ag_8Sn_6 (JCPDS38-434), which represents that there exist Ag ions in Ag_8Sn_6 phase.

In conclusion, after Ag-doping, there is a new phase (Ag_8Sn_6) in the as-deposited SnS films. At the same time, the intensity of diffraction peaks in the SnS : Ag films becomes stronger and the peaks become narrower, indicating that SnS : Ag films have better crystallization.

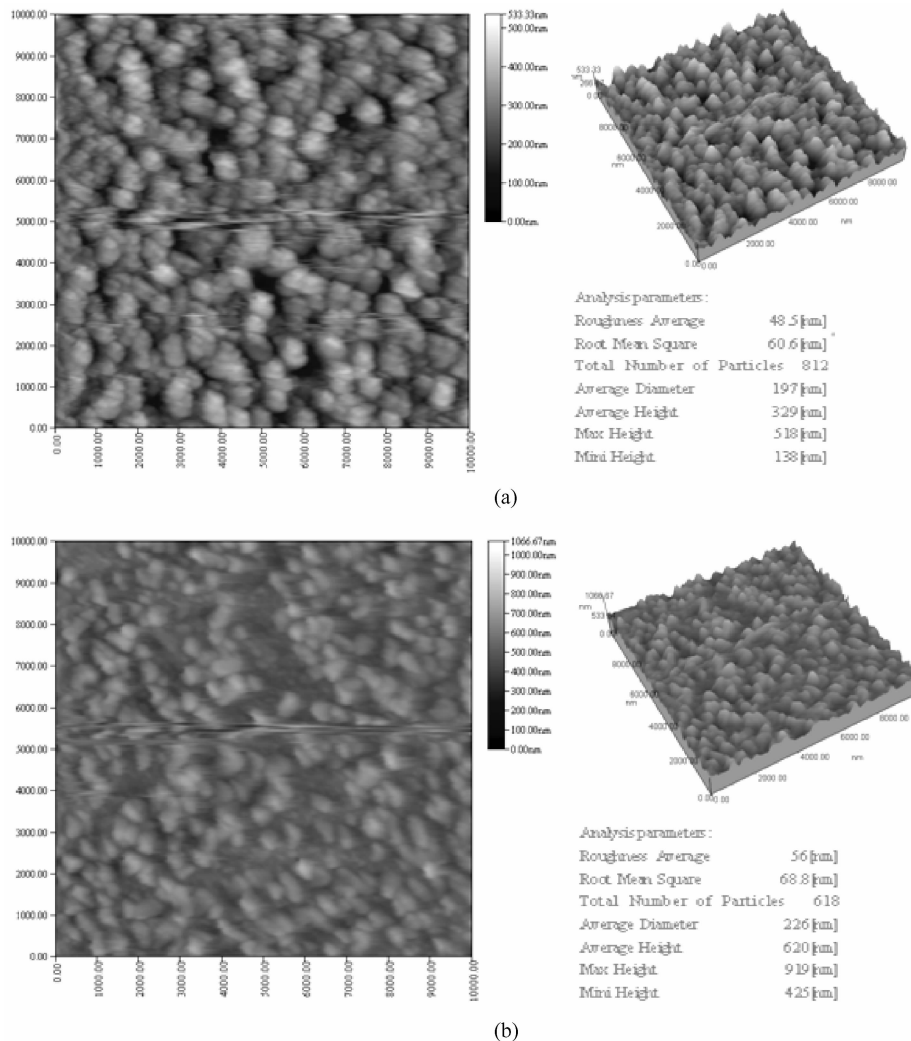


Fig.2 AFM profiles of the SnS (a) and SnS : Ag (b) films

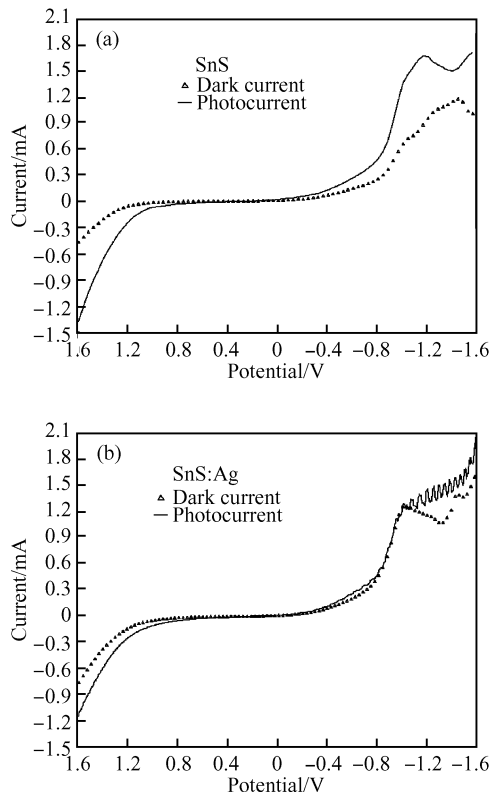


Fig.3 Current against potential linear scan photovoltammetric response of (a) the SnS and (b) SnS : Ag films

3.2 Surface analysis

Figures 2 (a) and 2 (b) show the AFM 2D and 3D micrographs of the SnS and SnS:Ag films deposited on ITO substrates, respectively. The scan size is $10\mu\text{m} \times 10\mu\text{m}$. Figure 2 shows that the two films are dense, smooth and uniform with good microstructure. The average roughness of the SnS film and the SnS : Ag film is 48.5 and 56nm, respectively, and their average diameter of the granules is 197 and 226nm, respectively. Compared with the SnS film, the surface of the SnS : Ag film is rougher and its grain size becomes bigger. In this experiment, a lot of pile-up crystal grains form island structure in the film after Ag doping. Therefore, grains of SnS : Ag films become bigger and the roughness of SnS films increases.

3.3 Photoelectrochemical test

Figures 3 (a) and 3 (b) show the $I-V$ linear scan photovoltammetric response of the SnS and SnS : Ag films deposited on ITO substrates, respectively. The dashed represents dark current and the real line shows photocurrent. Compared the two $I-V$ curves of the SnS and SnS : Ag films, the photocurrent of the SnS : Ag film is stronger than that of the SnS film. The photocurrent of SnS : Ag films is up to 2.1mA at -1.6V . Further, the photocurrent of SnS films increases as the absolute value of the negative potential

Table 1 Results of Hall measurement for the SnS and SnS : Ag films

Sample	Bulk concentration / cm^{-3}	Mobility / $(\text{cm}^2/(\text{V} \cdot \text{s}))$	Resistivity / $(\Omega \cdot \text{cm})$
SnS film	2.887×10^{16}	33.12	23.76
SnS : Ag film	7.287×10^{19}	17.54	4.885×10^{-3}

increases, but it is not affected by the chopped light. However, the photocurrent of the SnS : Ag film becomes stronger than that of the SnS film and it is affected notably by the chopped light in the vicinity of -1.0V . The photocurrent phenomenon can be explained by the fact that electrons are excited to the conduction band by xenon light illumination and holes are left in the valence band with a certain lifetime. Because energy band bends down, the electrons flow to electrolyte so that they can participate in the electrochemical reaction at the electrode/electrolyte interface^[8]. Thus it arises cathode photocurrent, which indicates the as-deposits are p-type of substance^[9]. Therefore, SnS : Ag films are p-type of semiconductor with holes as the majority carriers.

3.4 Hall measurement results

At room temperature, carrier concentration, mobility and resistivity of the films were measured by a Hall measurement system. The results are listed in Table 1. This table shows that the resistivity of SnS films decreases and the carrier concentration increases after Ag doping. The carrier concentration of the SnS : Ag films increases to 10^{19}cm^{-3} . However, the carrier concentration of the undoped film is only 10^{16}cm^{-3} .

4 Conclusion

Dense and uniform SnS : Ag thin films have been deposited by pulse electro-deposition. They are p-type of semiconductor. The above results indicate that SnS : Ag films have new phase Ag_8SnS_6 with good crystallization and big grain size. For the SnS : Ag film, the carrier concentration is up to 10^{19}cm^{-3} , and the resistivity decreases to $4.885 \times 10^{-3} \Omega \cdot \text{cm}$. In conclusion, Ag doping impacts observably on the structure, surface and semiconducting properties of SnS films. But some problems such as the best technical parameter and mechanism for preparing Ag-doped SnS films need to be further studied. It can be predicted that the investigation on SnS : Ag films can improve semiconducting properties of the films, so as to speed up the development of SnS thin film solar cells.

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脉冲法电沉积 SnS : Ag 薄膜*

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摘要: 用脉冲电沉积技术, 在 ITO 玻璃基片上制备了 SnS : Ag 薄膜. 用 X 射线衍射 (XRD) 和原子力显微镜 (AFM) 观察了薄膜的物相结构和表面形貌, 结果表明 SnS : Ag 薄膜出现了新物相 Ag_8SnS_8 , 结晶度好, 颗粒度大. 用光电流测试研究了其导电性能, 表明 SnS : Ag 薄膜是 p 型半导体材料. 霍尔测量表明掺杂后载流子浓度增大, 电阻率降低.

关键词: 脉冲电沉积; SnS : Ag 薄膜; 光电性能

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