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Effect of Duty Cycle on Properties of Pulse-electro-deposited SnS : Ag Thin Films

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Abstract: SnS : Ag thin films were deposited on ITO glasses by pulse electro-deposition. By studying the effect of duty cycle on the properties of SnS : Ag thin films, the optimum off-time(t_{off}) is obtained to be 5 s, namely, the optimal duty cycle is about 67%. The primary phase of SnS : Ag films deposited on optimum parameters condition is SnS compound with good crystallization, and the films prefer to grow towards (111) plane. The films are dense, smooth and uniform with good microstructure, and the grains in the films are densely packed together, and their direct bandgap is about 1.40 eV. In addition, the bandgap of the films first rises and then drops with the increase of the duty cycle.

Key words: duty cycle; pulse electrodeposition; SnS : Ag thin films; optical properties

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1 Introduction

Tin sulfide (SnS) can be used as an ideal absorbing layer in the solar cells[1] due to its excellent properties. It has an optical gap of 1.30 eV that is close to the optimal value 1.50 eV of solar cells and a high absorption coefficient($\alpha > 10^4$ cm^{-1}). In theory, the conversion efficiency of SnS film solar cells is up to 25%[2-3]. Furthermore, its elements Sn and S are abundant and non-toxic in nature.

By far, SnS films have been deposited by various methods such as vacuum evaporation[4], two-step process[5], spray pyrolysis[6-7], electro-deposition[8-10] and so on. Many attempts of SnS electrodepostion have been reported, mainly in the constant-current mode[8], the potentiostatic mode[9] and the pulse electro-deposition[10]. Among these modes, pulse electro-deposition is most attractive since the prepared films have the best quality. In the pulse electro-deposition, duty cycle, which is determined by on-time (t_{on}) and off-time(t_{off}), is one of the experimental parameters.

Thus, based on our previous research work, SnS : Ag thin films were deposited on ITO-coated glass substrates by pulse electro-deposition, and the effect of duty cycle on their structure, morphology and semiconducting properties were studied so as to obtain SnS : Ag thin films with good quality.

2 Experiment

In the experiment, a CHI660B electrochemical analyzer was employed as the power source. The

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experiment adopted a three-electrode cell. The ITO-coated glass substrates were used as the working electrodes 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 $SnSO_4$, $Na_2S_2O_3$ and $AgNO_3$ solution with a volume of 250 ml. 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 experiment parameters were the same with those of constant current electro-deposition in our previous paper[11]: pH=2.7, Sn^{2+} : $S_2O_3^{2-}$ = 1 : 5, deposition time t=1.5 h. The parameters of pulse electro-deposition were just as follows[10]: E_{on} = −0.75 V (vs SCE), t_{on} = 10 s, E_{off} = 0.1 V. Then the SnS : Ag films were prepared at different t_{off} (1 s, 3 s, 5 s, 10 s and 20 s, namely the duty cycles were 91%, 77%, 67%, 50% and 33%) corresponding to samples S_1, S_2, S_3, S_4 and S_5 respectively.

The structure of the thin films was characterized by a Philips X'Pert-MPD X-ray diffraction (XRD) system and a CSPM5000 Atomic Force Microscope (AFM). The reflection and transmission spectra of the SnS : Ag films were measured by a CARY500 UV-VIS-NIR spectroscopy.

3 Results and Discussion

3.1 Structure Analysis

Fig. 1 shows the XRD patterns of the SnS : Ag films deposited at different duty cycles. The main XRD peaks of the five samples are in agreement with those of SnS (JCPDS39-354). The effect of the duty cycle on the structure of the films is not obvious. However, one peak from phase Ag_8SnS_6 (JCPDS38-434) appeared in S_1, S_4 and S_5, maybe there is a new phase (Ag_8SnS_6) in the SnS : Ag films. Furthermore, the peak appeared at d = 0.336 0 nm in S_5 is closer to the strongest peak (d = 0.335 6 nm) of SnO_2 (JCPDS1-77-450), perhaps the film contains a little SnO_2. In all, the duty cycle has no much influence on their structure when $t_{off} \leqslant 10$ s. Fig. 2 shows XRD intensity of (111) plane of SnS : Ag films vs t_{off}. It can be seen that the intensity of (111) plane of the films first rises and then drops with the duty cycle increasing. The XRD peak from (111) plane of the film deposited at t_{off} = 5 s is the most intense, indicating that the crystallization of the film deposited at t_{off} = 5 s is the best. Therefore, the optimal t_{off} is 5 s, namely the duty cycle is 67%.

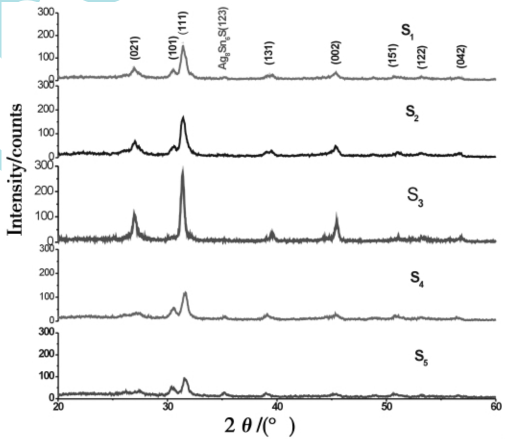

Fig. 1 X-ray diffraction patterns of SnS : Ag films prepared at different duty cycles

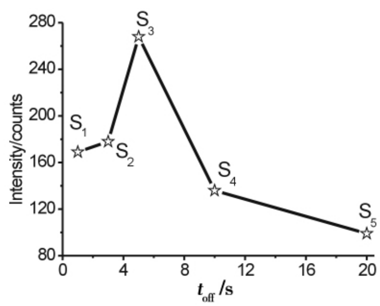

Fig. 2 XRD intensity of (111) planes of SnS : Ag films vs t_{off}

According to the data of the XRD peaks and Unit Cell software, we calculated the lattice parameters (a, b and c) of the SnS : Ag films prepared at different duty cycles. The evaluated lattice parameters of the SnS films vary slightly with a = 0.429 6 ~ 0.434 0 nm, b = 1.102 2 ~ 1.122 8 nm and c = 0.398 3 ~ 0.401 4 nm, as shown in Tab. 1. Compared with those of bulk SnS, the relative deviations of the lattice parameters a, b and c are varied in −0.99% ~ +0.25%, −0.96% ~ +0.89% and 0 ~ +0.75%, which are all within $\pm 1\%$. It can be supposed that the primary phase of the films is orthorhombic SnS and the lattice parameters are not affected obviously by t_{off}.

Tab. 1 The lattice parameters of SnS : Ag films prepared at different duty cycles

Sample	Lattice parameters/nm			Relative deviation of the lattice parameters/%		
	a	*b*	*c*	△*a*	△*b*	△*c*
Standard SnS	0.432 9	1.112 9	0.398 4	0	0	0
S_1	0.432 3	1.120 7	0.398 3	−0.14	+0.70	0
S_2	0.434 0	1.102 2	0.400 1	+0.25	−0.96	+0.43
S_3	0.432 1	1.109 5	0.398 4	−0.18	−0.31	0
S_4	0.429 9	1.122 8	0.400 3	−0.99	+0.89	+0.48
S_5	0.429 6	1.110 8	0.401 4	−0.76	−0.19	+0.75

3.2 Surface Analysis

With the increase of t_{off}, the color of the films at first becomes darker, and then lighter. That means that the thickness of the films at first becomes larger, and then smaller. Thereby the thickness of films is affected by t_{off}. Especially when $t_{off} \geqslant 10$ s, the films are brown and become thinner. The phenomenon can be explained as follows: here let's suppose that t_{on} keeps constant (i.e. $t_{on} = 10$ s). When $t_{off} < 3$ s, the metal ions brought by acquiring electrons from cathode in t_{on} time can not be supplied completely in t_{off} time due to diffusion and convection, then the concentration of metal ions decreases, leading to the pulse current density decreasing. When $t_{off} > 5$ s, maybe the metal ions brought by acquiring electrons from cathode in t_{on} can be supplied completely in $t_{off} = 5$ s and the concentration of metal ions at cathode surface exhibits stabilized state. So $t_{off} > 5$ s has no active action and only extends the cycle time (T). Based on the formula of the average pulse current density $i_m = i_p t_{on} / T$, when the peak value of current density i_p and t_{on} are fixed, the average pulse current density i_m will decrease with the increase of T, leading to the drop of deposition rate, thus the deposited SnS : Ag films are thinner.

Fig. 3 shows the AFM 3D micrographs of the SnS : Ag films deposited at different duty cycles. The scanning size is 5 μm×5 μm. All the films are dense, smooth and uniform. It can be seen from Tab. 2

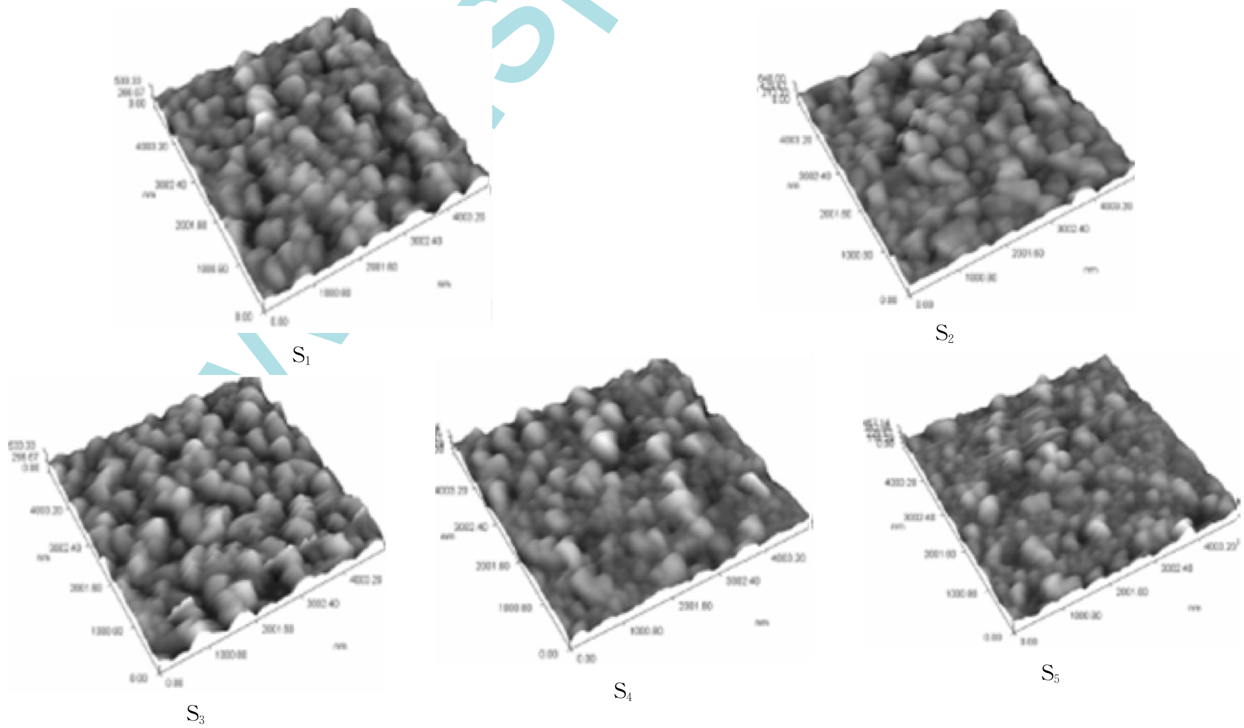

Fig. 3 AFM profiles of the SnS : Ag films prepared at different duty cycles

that the average roughness and granule diameter of S_3 are the largest among the five samples. Because the deposition rate is relatively faster when $t_{off}=5$ s, therefore the film is thicker, and the grain size of the film is greater with better crystallization, which is consistent with the results of XRD. It indicates that the optimal t_{off} is 5 s.

Tab. 2 The morphological parameters of the SnS : Ag films prepared at different duty cycles

Samples	S_1	S_2	S_3	S_4	S_5
t_{off}/s	1	3	5	10	20
Thickness/nm	600	650	680	500	430
Average Roughness/nm	53.5	56	61.4	45.1	37.3
Average Diameter of the Granules/nm	249	294	338	276	230

3.3 Optical Properties

Fig. 4(a) and (b) are plots of the total reflectance and transmittance spectra of the five samples in the wavelength (λ) range of 400～1 800 nm. Fig. 4(a) shows that those samples with $t_{off}\leqslant 5$ s have almost similar total reflectance, though they may have different magnitude in total reflectance spectra.

It can be seen from Fig. 4(b) that the transmittance of those samples with $t_{off}\leqslant 5$ s is lower at $\lambda<600$ nm and then it increases rapidly. But for the samples with $t_{off}\geqslant 10$ s, the total reflectance and transmittance are higher, since films S_4 and S_5 are thinner and smoother.

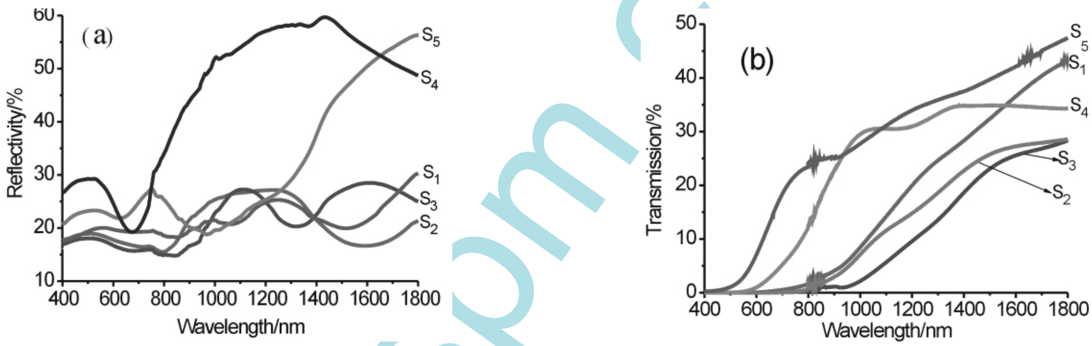

Fig. 4 The total reflectance and transmittance spectra of SnS : Ag films prepared at different duty cycles

The transmission T through an absorbing slab is related with its reflectance R, thickness d, and absorption coefficient α by

$$T=(1-R)\cdot e^{-\alpha d} \tag{1}$$

Here the thickness d of the films is about 800～1 000 nm for the five samples. Therefore, with the data of $T(\lambda)$ and $R(\lambda)$, the absorption coefficient $\alpha(\lambda)$ or $\alpha(h\nu)$ can be calculated by the above formula.

The curve $\alpha\sim h\nu$ of the five samples is shown in Fig. 5. The absorption coefficients of all these samples increase rapidly with the increasing of the photon energy and finally tend to steady values. The maximal absorption coefficients of samples $S_1\sim S_3$ are obviously greater than S_4 and S_5.

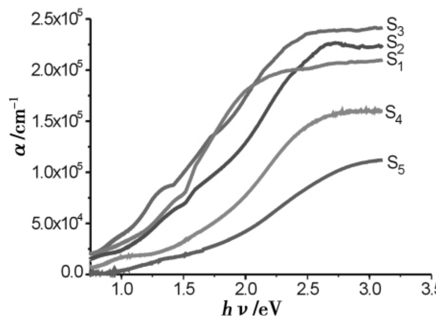

Fig. 5 The curve $\alpha\sim h\nu$ of SnS : Ag films prepared at different duty cycles

The direct bandgap and absorption edge of the five samples are listed in Tab. 3. With the increase of t_{off}, the direct bandgap E_g of the films first drops and then rises, while their absorption edge shows the contrary trend. That is to say, when $t_{off}\leqslant 5$ s, the direct bandgap decreases from 1.46 eV to 1.40 eV. When $t_{off}\geqslant 5$ s, the direct bandgap increases from 1.40 eV to 2.0 eV. Sample S_5 has a direct bandgap of about 2.00 eV, which is much greater than that of SnS due to the existence of a tiny SnO_2 (3.6～4.0 eV) in the film. From the results of the structure and surface analysis, we can conclude that the optimal t_{off} is 5 s and the prepared films have direct bandgap of 1.40 eV.

Tab. 3 The direct bandgap and absorption edge of SnS : Ag films prepared at different duty cycles

Samples	S_1	S_2	S_3	S_4	S_5
t_{off}/s	1	3	5	10	20
Bandgap E_g/eV	1.46	1.42	1.40	1.77	2.00
Absorption Edge λ_0/nm	849	873	886	700	620

4 Conclusions

By adjusting the duty cycle, the SnS : Ag thin films were prepared by pulse electrodeposition, and the effect of duty cycle on the structure, morphology and optical properties of the films were studied. When $t_{off}=5$ s (namely the duty cycles is 67%), the deposited films are dense, smooth and uniform, their primary phase is SnS, and they have the smallest relative deviation of the lattice parameters. The films have higher absorption coefficient of 9.4×10^4 cm^{-1} near the fundamental absorption edge and direct bandgap of about 1.40 eV. With the increase of t_{off}, the direct band gap E_g of the films first drops and then rises.

In conclusion, the most appropriate duty cycle is 67% for depositing SnS : Ag thin films. The SnS : Ag films prepared at this condition are suitable as absorber layers in the fabrication of thin-film heterojunction solar cells.

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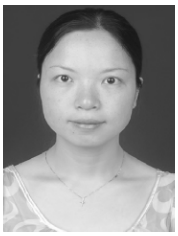
Biography:



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