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Research Article

Influence of Sulfurization Temperature on Photoelectric Properties Cu_2SnS_3 Thin Films Deposited by Magnetron Sputtering

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Cu_2SnS_3 is a narrow-band-gap semiconductor material. It has suitable optical and electrical properties which make it a potential absorber layer of solar cells. In this paper, Cu_2SnS_3 thin films were successfully obtained by sulfurizing $CuSnS_2$ thin films deposited by RF magnetron sputtering at temperatures of 350–425°C for 2 h in an atmosphere of hydrogen sulfide and nitrogen. The influence of the sulfurization temperature on the electrical and optical properties of the Cu_2SnS_3 thin films was investigated. The experimental results show that the Cu_2SnS_3 thin films sulfurized at a temperature of 425°C exhibit better properties than others. The mobility and resistivity of the Cu_2SnS_3 films are 9 $cm^2/V{\cdot}s$ and 3 $\Omega{\cdot}cm$, respectively. And its optical band gap is estimated to be about 1.77 eV.

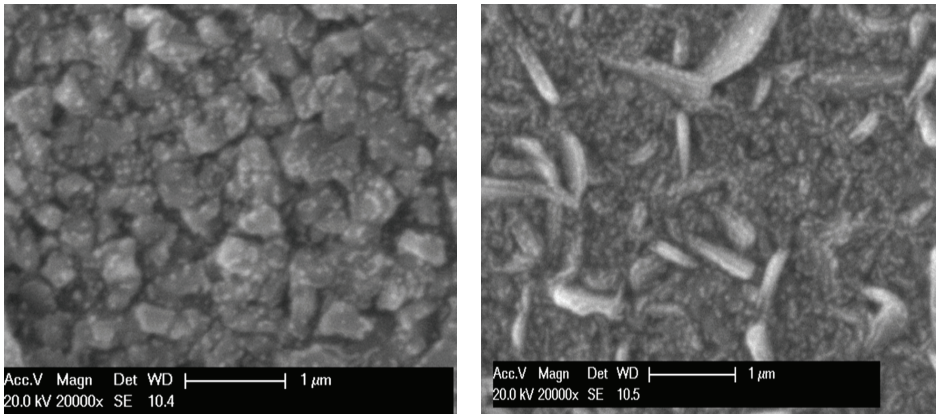
1. Introduction

Thin film solar cells with low cost and little pollution have attracted much attention. Cu_2SnS_3 (CTS) is a p-type narrow-band-gap semiconductor and its elements are abundant and nontoxic. Its band gap is ~1.1 eV and exhibits high optical absorption coefficient (>10^4 cm^{-1}) [1]. Several research groups have attempted to make use of CTS thin films as absorbers of thin film solar cells. Koike et al. reported the solar cells with CTS absorbers prepared by coelectrodeposition and showed a conversion efficiency of 2.84% [2]. Chino et al. deposited the CTS thin films by electron beam evaporation and fabricated a solar cell with an open-circuit voltage of 211 mV, a short-circuit current of 28.0 mA/cm^2, a fill factor of 0.43, and a conversion efficiency of 2.54% [3]. Therefore, CTS is a potential candidate for thin film solar cells. In this paper, we studied the electrical and optical properties of Cu_2SnS_3 thin films sulfurized at temperatures of 350–425°C in order to obtain CTS films with good properties.

2. Experimental

The glass substrates were cleaned by deionized water, acetone, ethanol, and deionized water in turn and then dried by ovens. CTS thin films were successfully prepared onto glass substrates via sulfurization of $CuSnS_2$ films deposited by an RF magnetron sputtering system. The target was $CuSnS_2$ ceramic with a purity of 99.9%. The substrates were mounted on a holder, and the distance of the target substrate was 3.5 cm. The base pressure was about 5×10^{-4} Pa. The work pressure and power were 1.5 Pa and 65 W, respectively. The flow rate of Ar (99.99%) was kept at a constant value of 60 sccm controlled by a mass flow controller. Before sputtering the $CuSnS_2$ thin films on the substrates, the target was presputtered for about 10 min with a shutter covering the target in order to remove the surface oxide layer. Thicknesses of the $CuSnS_2$ thin films were about 440 nm. The CTS thin films were obtained by sulfurizing the $CuSnS_2$ thin films at temperatures of 350–425°C for 2 h in an atmosphere of hydrogen sulfide and nitrogen. Four CTS thin films samples were fabricated by changing the sulfurization temperatures. Table 1 lists the sample names and their sulfurization conditions.

The crystalline status of the CTS thin films was characterized using an X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5406 Å). The compositions were obtained from an energy-dispersive X-ray spectrometry (EDX). The morphologies were measured by a scanning electron microscopy



(a) (b)

Figure 1: 1 SEM pictures of the CZT thin films: (a) sample CTS-3; (b) sample CTS-4.

Table 1: Sample names of the CTS thin films with different sulfurization conditions.

Samples	Sulfurization temperatures	H_2S (sccm)	N_2 (sccm)
CTS-1	350°C	2	10
CTS-2	375°C	2	10
CTS-3	400°C	2	10
CTS-4	425°C	2	10

Table 2: EDX of the Cu_2SnS_3 thin films.

Samples	Cu At %	Sn At %	S At %	Sn/Cu	S/(Sn + Cu)
CTS-3	10.87	24.94	64.19	~2.3	~1.8
CTS-4	12.67	29.29	58.05	~2.3	~1.4

(SEM) (XL30 ESEM-TMP). Film thickness was measured with a stylus surface profiler (TENCOR D100). The optical properties were measured by a spectrometer (Varian Cary 5000) in the wavelength range 400–1800 nm. The electrical properties were measured using a Hall measurement system (Ecopia HMS-3000).

3. Result and Discussion

3.1. Structure and Morphology. Figure 1 shows the SEM images of samples CTS-3 and CTS-4. On the surface of sample CTS-3, there are nubby grains with the average size of 1 μm. However the grains of sample CTS-4 present linear shape with the average length of about 1 μm. The morphology of the samples varies significantly with the sulfurization temperature. Therefore, it is obvious that the sulfurization temperature has a great influence on the morphologies of the CTS thin films. P. A. Fernandes and P. M. P. Salomé reported that the Cu_2SnS_3 thin films were sensitive to the temperature [4]. Table 2 shows the EDX of the samples (CTS-3 and CTS-4, resp.). The EDX indicates that samples CTS-3 and CTS-4 are Cu poor and S rich.

Figure 2 depicts the XRD patterns of the CTS thin films sulfurized at different temperatures. The films exhibit

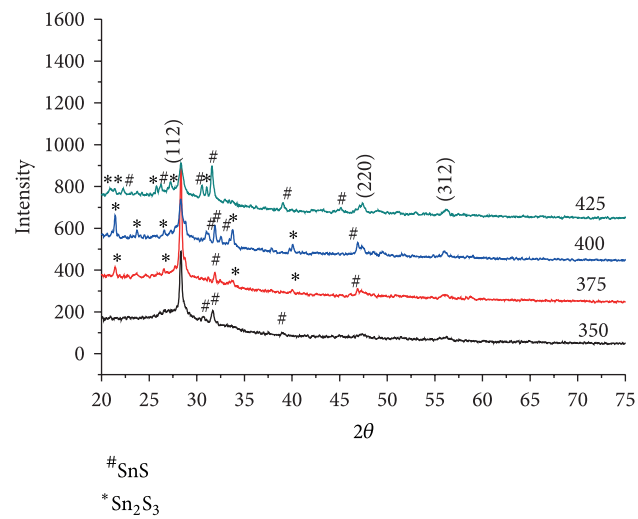


Figure 2: XRD patterns of the CTS thin films prepared at different sulfurization temperatures.

several obvious XRD peaks. Sharp and intense peak at 28.34° followed by other peaks at 47.34° and 56.03° is attributed to the diffraction of planes (112), (220), and (312) of CTS with the tetragonal structure of JCPDS 089-4714. With the increasing of the sulfurization temperature, many new peaks that do not belong to Cu_2SnS_3 appear. There are also a few weak peaks corresponding to those of Sn_2S_3 and SnS. The deterioration of the XRD peaks may be due to the diffusion of Sn atoms to the surface of the Cu_2SnS_3 thin film by high temperature [5, 6] and the reaction of Sn atoms with hydrogen sulfide.

3.2. Optical Characterization. The transmission and reflection spectra of the CTS thin films were measured in the wavelength range 400–1800 nm at room temperature. Figure 3(a) shows the plot of absorptance versus $h\nu$ of the CTS-3 thin film. At the beginning, the absorptance is rapidly increased with the increase of $h\nu$ and then it almost reaches a constant value. It indicates that the CTS thin film is a direct band gap

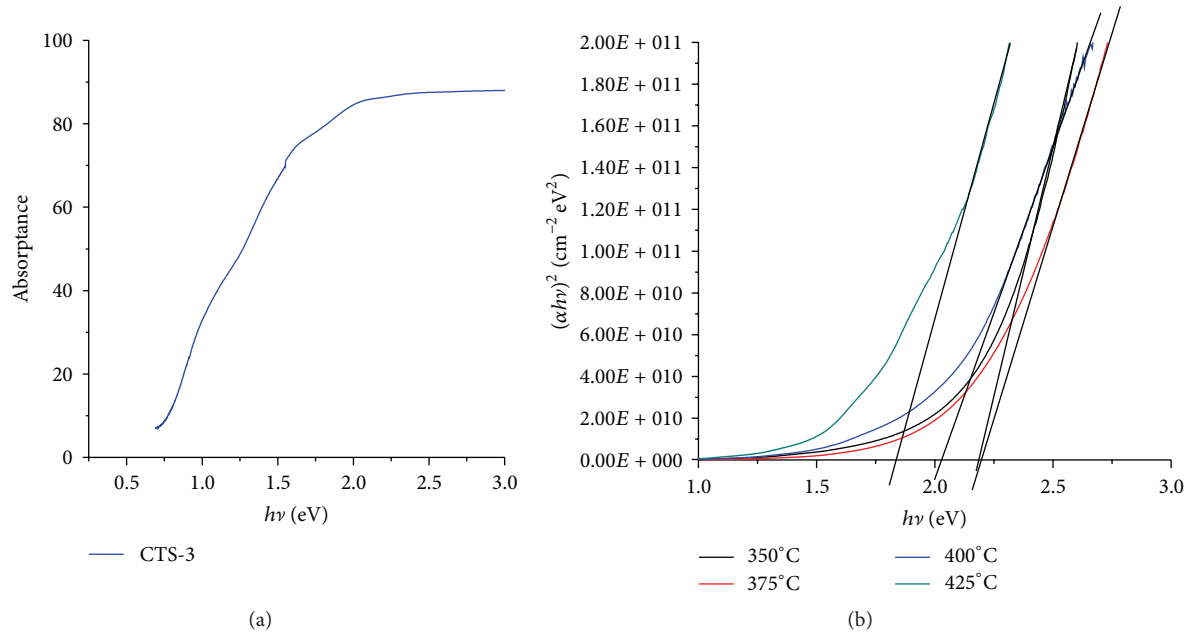


Figure 3: (a) Absorptance versus $h\nu$ plot of the CTS-3 thin film. (b) The plots of $(\alpha h\nu)^2$ versus $h\nu$ for estimating the direct band gap.

Table 3: Electrical properties of the CTS thin films sulfurized at different temperatures.

Samples	Conductive type	Carrier concentration (cm^{-3})	Mobility ($cm^2/V{\cdot}s$)	Resistivity ($\Omega{\cdot}cm$)
CTS-1	P	2.0×10^{18}	3.5×10^{-1}	8.8
CTS-2	P	7.4×10^{18}	2.8×10^{-1}	3
CTS-3	P	2.8×10^{18}	3.1×10^{-1}	7.1
CTS-4	P	2.3×10^{17}	9	3

semiconductor which is in agreement with the report of Zhai et al. [7]. The absorption coefficient of the films was estimated by the transmittance and reflectance measurements at room temperature. Figure 3(b) shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ to deduce the direct band gap of the CTS thin films. The direct band gap values of the samples (CTS-1 to CTS-4) were estimated to be 2.19 eV, 2.16 eV, 2.03 eV, and 1.77 eV, respectively. Fernandes et al. [8]. reported a direct band gap of 1.35 eV for tetragonal Cu_2SnS_3 and 0.96 eV for cubic Cu_2SnS_3. The band gap of CTS-4 thin film is close to that of the reported tetragonal Cu_2SnS_3. The band gap of the samples is reduced gradually with the increasing of the sulfurization temperature, which may be related to the existence of a secondary phase.

3.3. Electrical Properties. The electrical properties of the CTS thin films were measured by a Hall measurement system at room temperature. Table 3 exhibits the electrical properties of the CTS thin films sulfurized at different temperatures. The mobilities of the CTS thin films are varied with the increasing of the sulfurization temperature, which might attribute to the existence of the impurities. The films were not intentionally doped; therefore, it is very likely that the observed defect acceptor state is native and originated from the deviations from the ideal stoichiometry. The result of EDX indicates that the samples are S-rich and Cu-poor. The samples might contain dominant defects species: sulfur interstitials S_1, copper vacancies V_{Cu}, and Sn atoms in copper sites Sn_{Cu}. The S_1 and V_{Cu} are acceptor states, but Sn_{Cu} is a donor state. According to Hall measurement, the Cu_2SnS_3 thin films show p-type conductivity. Therefore, the Sn_{Cu} is probably the compensating donor state. The defects of S_1 and V_{Cu} play a dominant role in the Cu_2SnS_3 thin films and may form impurity band in the forbidden band. When the acceptor impurity band exists in the films, the mobility μ_p is related to the hole mobility in the valence band μ_v and the mobility in the impurity band μ_i which was reported by Emelyanenko et al. [9]. The μ_v can be related to the scattering by the ionized impurities, acoustic-lattice modes, optical-lattice modes, neutral impurities, and space-charge effects, respectively [10]. As a function of temperature, at low temperature, the μ_v increases with increasing the temperature, which is related to the scattering by the ionized impurities. However, at high temperature, the μ_v decreases with the increasing of the temperature. Therefore, it indicates that the acoustic phonon scattering is a dominant process [10]. This can be the reason why the mobilities of the CTS thin films change with increasing the sulfurization temperature. The resistivities of the CTS thin films are also varied as the sulfurization temperature increases from 350°C to 425°C, and it might attribute to the secondary phase.

4. Conclusion

The electrical and optical properties of the CTS thin films sulfurized at the temperatures of 350–425°C have been studied. It is confirmed that the electrical and optical properties

of the CTS thin films strongly depend on the sulfurization temperature. According to the requirement of photoelectrical properties of solar cell absorbers, sample CTS-4 has better properties than others. It has a band gap of ~1.77 eV and an absorption coefficient of ~10^5 cm^{-1}. The carrier concentration, mobility, and resistivity of sample CTS-4 are ~2.3×10^{17} cm^{-3}, ~9 $cm^2/V{\cdot}s$, and ~3 $\Omega{\cdot}cm$, respectively. According to those properties, the CTS thin films will be good an absorbing layers of thin film solar cells.

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