Research Article

Influence of Sulfurization Temperature on Photoelectric Properties Cu$_2$SnS$_3$ Thin Films Deposited by Magnetron Sputtering

Pengyi Zhao and Shuying Cheng

Institute of Micro/Nano Devices and Solar Cells, School of Physics & Information Engineering, Fuzhou University, Fuzhou 350108, China

Correspondence should be addressed to Shuying Cheng; sycheng@fzu.edu.cn

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Cu$_2$SnS$_3$ 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$_2$SnS$_3$ thin films were successfully obtained by sulfurizing CuSnS$_2$ thin films deposited by RF magnetron sputtering at temperatures of 350–425$^\circ$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$_2$SnS$_3$ thin films was investigated. The experimental results show that the Cu$_2$SnS$_3$ thin films sulfurized at a temperature of 425$^\circ$C exhibit better properties than others. The mobility and resistivity of the Cu$_2$SnS$_3$ films are 9 cm$^2$/V·s and 3 $\Omega$·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$_2$SnS$_3$ (CTS) is a p-type narrow-band-gap semiconductor and its elements are abundant and nontoxic. Its band gap is $\sim$1.1 eV and exhibits high optical absorption coefficient ($>$10$^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$_2$SnS$_3$ thin films sulfurized at temperatures of 350–425$^\circ$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 $\times$ 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$^\circ$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 K$_\alpha$ radiation ($\lambda = 1.5406$ Å). The compositions were obtained from an energy-dispersive X-ray spectrometry (EDX). The morphologies were measured by a scanning electron microscopy.
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 Cu₂SnS₃ 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 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 Cu₂SnS₃ appear. There are also a few weak peaks corresponding to those of Sn₂S₃ and SnS. The deterioration of the XRD peaks may be due to the diffusion of Sn atoms to the surface of the Cu₂SnS₃ 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 absorbance versus hv of the CTS-3 thin film. At the beginning, the absorbance is rapidly increased with the increase of hv and then it almost reaches a constant value. It indicates that the CTS thin film is a direct band gap
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It is confirmed that the electrical and optical properties of the CTS thin films have been studied. It is observed that the electrical and optical properties of the CTS thin films sulfurized at different temperatures vary with the increasing of 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.

### 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 $S_I$, copper vacancies $V_{Cu}$, and Sn atoms in copper sites $Sn_{Cu}$. The $S_I$ 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 $S_I$ 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 $\mu_p$ is related to the hole mobility in the valence band $\mu_{V}$ and the mobility in the impurity band $\mu_i$ which was reported by Emelyanenko et al. 

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conductive type</th>
<th>Carrier concentration ($cm^{-3}$)</th>
<th>Mobility ($cm^2/Vs$)</th>
<th>Resistivity ($\Omega\cdot cm$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTS-1</td>
<td>P</td>
<td>$2.0 \times 10^{18}$</td>
<td>$3.5 \times 10^{-1}$</td>
<td>8.8</td>
</tr>
<tr>
<td>CTS-2</td>
<td>P</td>
<td>$7.4 \times 10^{18}$</td>
<td>$2.8 \times 10^{-1}$</td>
<td>3</td>
</tr>
<tr>
<td>CTS-3</td>
<td>P</td>
<td>$2.8 \times 10^{18}$</td>
<td>$3.1 \times 10^{-1}$</td>
<td>7.1</td>
</tr>
<tr>
<td>CTS-4</td>
<td>P</td>
<td>$2.3 \times 10^{17}$</td>
<td>9</td>
<td>3</td>
</tr>
</tbody>
</table>

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.

### 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...
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 $\sim 1.77$ eV and an absorption coefficient of $\sim 10^5$ cm$^{-1}$. The carrier concentration, mobility, and resistivity of sample CTS-4 are $\sim 2.3 \times 10^{17}$ cm$^{-3}$, $\sim 9$ cm$^2$/V-s, and $\sim 3$ $\Omega$·cm, respectively. According to those properties, the CTS thin films will be good absorbing layers of thin film solar cells.

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References


