Photoelectric properties of Cu_2ZnSnS_4 thin films deposited by thermal evaporation*

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Abstract: Sn/Cu/ZnS precursor were deposited by evaporation on soda lime glass at room temperature, and then polycrystalline thin films of Cu_2ZnSnS_4 (CZTS) were produced by sulfurizing the precursors in a sulfur atmosphere at a temperature of 550 ℃ for 3 h. Fabricated CZTS thin films were characterized by X-ray diffraction, energy dispersive X-ray spectroscopy, ultraviolet-visible-near infrared spectrophotometry, the Hall effect system, and 3D optical microscopy. The experimental results show that, when the ratios of [Cu]/([Zn] + [Sn]) and [Zn]/[Sn] in the CZTS are 0.83 and 1.15, the CZTS thin films possess an absorption coefficient of larger than 4.0×10^4 cm^{-1} in the energy range 1.5–3.5 eV, and a direct band gap of about 1.47 eV. The carrier concentration, resistivity and mobility of the CZTS film are 6.98×10^{16} cm^{-3}, 6.96 Ω·cm, and 12.9 cm^2/(V·s), respectively and the conduction type is p-type. Therefore, the CZTS thin films are suitable for absorption layers of solar cells.

Key words: Cu_2ZnSnS_4; evaporation; optical properties; electrical properties
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1. Introduction

Cu_2ZnSnS_4 (CZTS) is one of the promising absorber materials in thin film solar cells because of its excellent material properties for obtaining high efficiency[1]. It has over 10^4 cm^{-1} of absorption coefficient in the visible region and a direct band gap of 1.4–1.6 eV, which is very close to the optimum bandgap value of absorber layers in solar cells[2]. Moreover, its elements are nontoxic and abundant in the crust of the earth. Owing to these properties, CZTS is considered to be a promising material for application in low cost and environmentally friendly thin film solar cells. Several research groups have attempted the fabrication of CZTS thin films by thermal evaporation of the elements and binary chalcogenides[3], a spray method[4], RF sputtering[5], among others. The conversion efficiency of 6.77% from the structure of Al/ZnO:Al/ CdS/CZTS/ Mo/soda lime glass (SLG) has been reported more recently by Katagirietal[6]. S vapour has been used successfully to sulfidize precursors in the manufacture of $CuInS_2$ thin films[7], however, there are few papers concerning CZTS films sulfurized by S vapour[9]. This is probably due to the lack of the establishment of a suitable fabrication technique for CZTS thin films, which can control the film composition precisely. Therefore, it is necessary to investigate the basic properties of CZTS films sulfurized by S vapour, such as the effect of deviation from stoichiometry on their electrical, optical, and structural properties.

The thermal evaporation technique, which is widely used for fabricating $CuInGaSe_2$ thin film solar cells, is one of the best methods to control film composition. In this paper, Sn/Cu/ZnS precursors were also deposited by evaporation on soda lime glass substrates, and then sulfurized in a sulfur atmosphere in order to obtain Cu_2ZnSnS_4 (CZTS) films with good optical, and electrical properties.

2. Experiment

The glass substrates were cleaned with deionized water, acetone, ethanol and deionized water in turn, and then dried in an oven. By using an electron-beam and thermal evaporation technique, Sn/Cu/ZnS/glass stacked layers were fabricated on the square 1.5×2 cm^2 SLG substrates at room temperature. The chamber pressure was about 5×10^{-3} Pa during deposition. The deposition rates were monitored by an FTM-V quartz oscillator. Sulfur was evaporated using a cracker source with the effusion cell. The sulfurization time and temperature were 3 h and 550 ℃, respectively.

The chemical compositions of CZTS thin films were measured by energy dispersive X-ray spectroscopy (EDX). Transmittance and reflectance spectra of the films were recorded using a Varian CARY500 Scan ultraviolet-visible-near infrared spectrophotometer in the 400–1600 nm wavelength range with an incident light perpendicular to the surface plane of the films. The electrical measurements were made using an HMS-3000 Hall measurement system. The thickness of the films was measured by a Veeco Dektak 6M stylus profiler. X-ray diffraction (XRD) patterns were recorded using a diffractometer (PANalytical, X'Pert, CuK, $\lambda = 1.5406$ Å). The surface morphological examinations were carried out by a ZETS-20 3D optical microscope.

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Table 1. Thickness of each precursor layer and the compositional ratios of CZTS films.

Sample	d_{Cu} (nm)	d_{ZnS} (nm)	d_{Sn} (nm)	$n_{Cu}/(n_{Sn}+n_{Zn})$	n_{Zn}/n_{Sn}	$n_S/(n_{Sn}+n_{Zn}+n_{Cu})$
CZTS-1	112	394	143	0.93	0.73	1.03
CZTS-2	100	394	115	1.06	0.91	1.11
CZTS-3	100	394	96	1.02	1.17	1.06
CZTS-4	86	394	82	0.97	1.42	1.15
CZTS-5	110	394	96	1.17	1.22	1.07
CZTS-6	74	394	96	0.83	1.15	1.01
CZTS-7	55	394	96	0.64	1.24	1.21

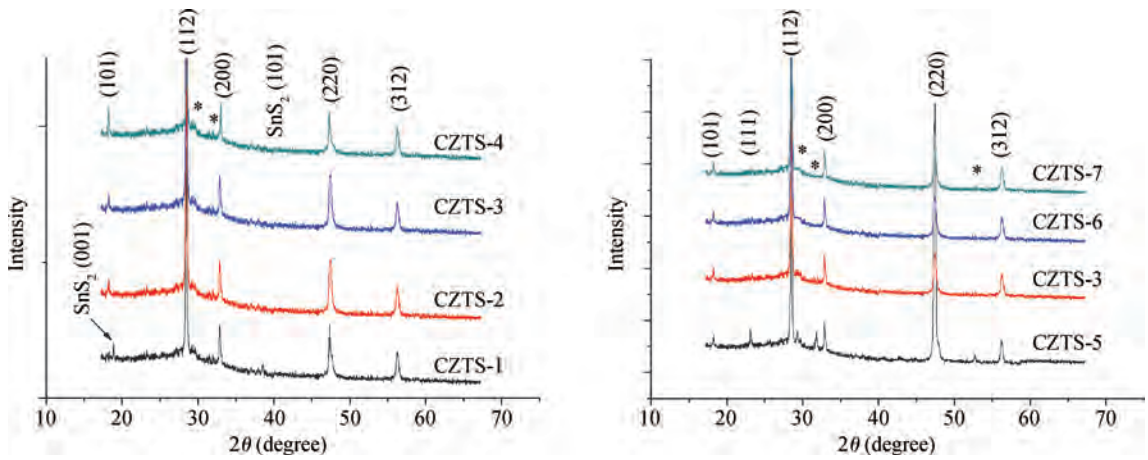

Fig. 1. X-Ray diffraction pattern of Cu_2ZnSnS_4 film.

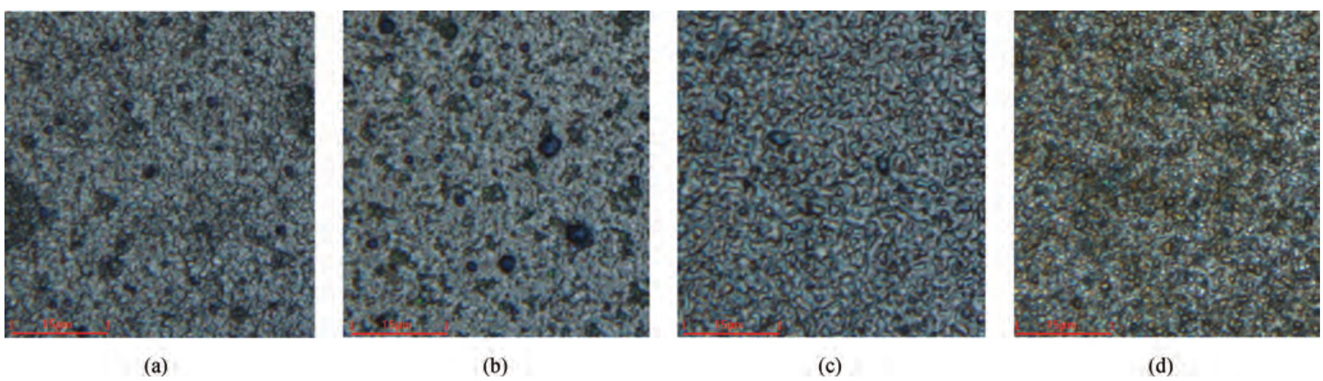

Fig. 2. 3D optical microscope images of CZTS thin films. (a) CZTS-1. (b) CZTS-5. (c) CZTS-6. (d) CZTS-7.

3. Results and discussion

3.1. Chemical composition

In the study, the thickness (d_{ZnS}) of the ZnS layer was constant at 394 nm, the thicknesses of both Cu (d_{Cu}) and Sn (d_{Sn}) layers were varied, and these precursors were named CZTS-1 to CZTS-7. The compositional ratios of [Cu]/([Zn] + [Sn]) ($n_{Cu}/(n_{Sn}+n_{Zn})$) and [Zn]/[Sn] (n_{Zn}/n_{Sn}) were determined by the thickness of copper, tin and zinc sulphide films. Table 1 lists the thickness of each precursor layer and the chemical composition of CZTS films. The chemical composition ratios of Cu (n_{Cu}), Zn (n_{Zn}), Sn (n_{Sn}) and S (n_S) in CZTS films were measured by EDX.

3.2. Structure and morphology

XRD characterization is used to analyze the crystalline phases present in the grown films. Figure 1 shows the XRD patterns of the CZTS films with different chemical compositions. All the films exhibit several obvious XRD peaks corresponding to planes (101), (111), (112), (200), (220) and (312) of CZTS with a kesterite structure (JCPDS-ICDD No.0260575). The main peak (112) is narrow, which indicates that the films have good crystallinity. Figure 1 shows XRD results of the fabricated samples, where each sample has different n_{Zn}/n_{Sn}. Besides the peaks of CZTS, there are some peaks of CuS phase (JCPDS-ICDD No. 0782391) and they are marked as "*" in Fig. 1. When $n_{Zn}/n_{Sn} = 0.73$ and $n_{Cu}/(n_{Sn}+n_{Zn}) = 0.93$, the XRD pattern shows peaks not only from CuS, but also from SnS_2. When n_{Zn}/n_{Sn} is about 1.2, and $n_{Cu}/(n_{Sn}+n_{Zn})$ is less than 1, the CuS and SnS_2 phases are not observed. In Cu-rich CZTS films, excrescent Cu migrates to the top surface during the sulfurization process and can be easily observed on the surface of the CZTS films. Because some XRD peaks of Cu_2SnS_3

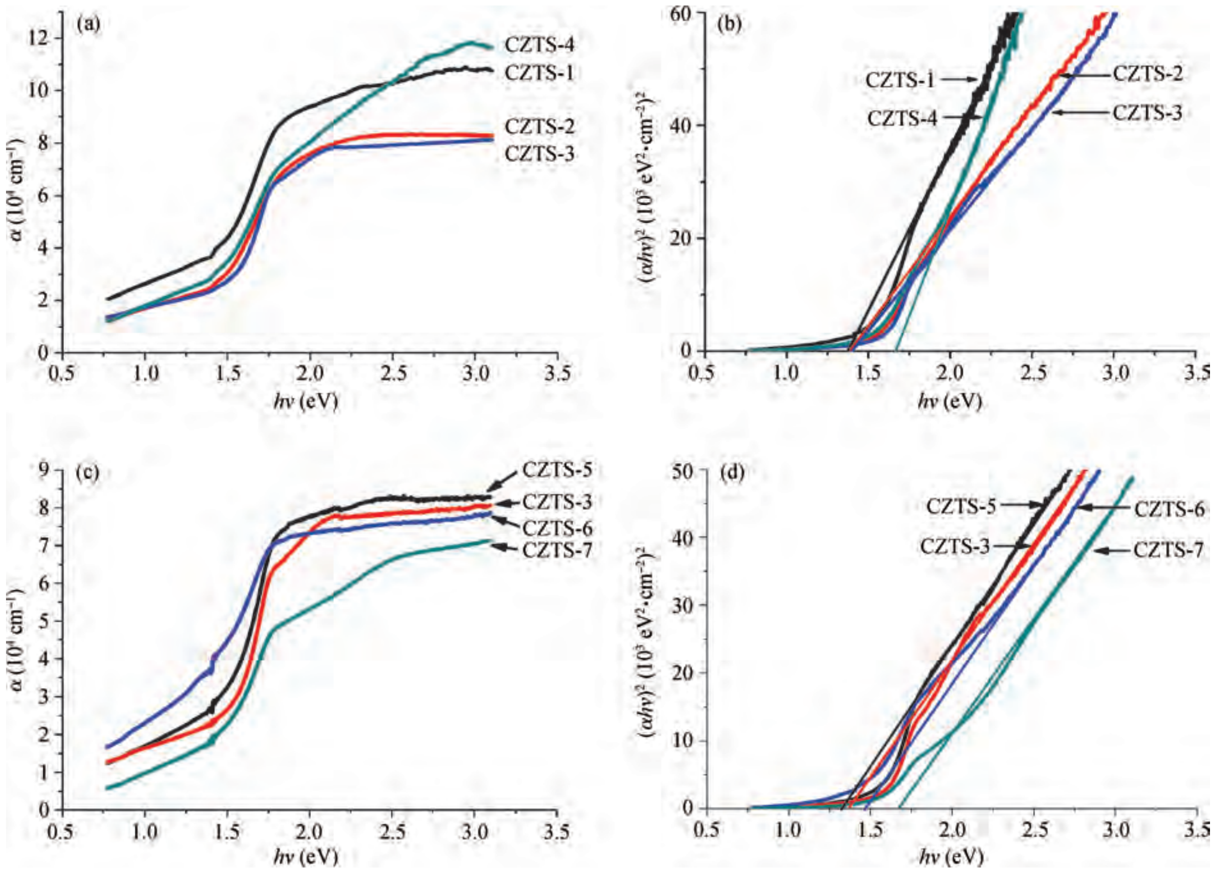

Fig. 3. Optical characteristics of the CZTS thin films.

and ZnS could be hidden under the observed kesterite and ovellite CZTS peaks due to their similar XRD peak positions, it is difficult to judge if there are ZnS or Cu_2SnS_3 phases in the films. But, we can conclude that the main phase of the films is CZTS, though perhaps there are tiny other components.

Figures 2(a)–2(d) show the 3D optical microscope images of samples CZTS-1, CZTS-5, CZTS-6 and CZTS-7 respectively. The grain size is relatively small compared with the CZTS films grown by sulfurizing the precursors in H_2S gas, whose grain size is larger than 2 μm[8]. The surface morphology of the films varies significantly with chemical composition. We can see that the surface of sample CZTS-1 is quite rough and there are many voids. There are some particles on the surface of the Cu-rich CZTS films (CZTS-5). For poor-Cu and Zn-rich films (CZTS-6), the films are smooth and dense.

3.3. Optical properties

Optical absorption coefficients of the CZTS films can be evaluated from the measured transmission and reflection spectra. Figure 3 shows the optical absorption coefficients of the CZTS thin films in the energy range 0.75–3.3 eV. It is well known that an absorption coefficient can be written in a general form as a function of incident photon energy $h\nu$

$$(\alpha h\nu)^n = A(h\nu - E_g), \quad (1)$$

where A is a constant, E_g is band gap, and n is a number related to the electron transition process. The n value is 2 and 2/3 for direct allowed and forbidden transitions, respectively, while the n value is 1/2 and 1/3 for indirect allowed and forbidden transitions.

In order to calculate the direct band gap E_g (written as E_{dir}), the curves of $(\alpha h\nu)^2$ versus $h\nu$ for the samples were plotted (see Fig. 3). All the curves tend to straight lines in the high photon energy region. By extrapolating the straight line from this linear region, E_{dir} is estimated from the interception with the energy axis ($(\alpha h\nu)^2 = 0$).

The direct band gap E_{dir} increases from 1.34 to 1.63 eV with increasing n_{Zn}/n_{Sn}, and it increases from 1.32 to 1.69 eV with decreasing $n_{Cu}/(n_{Sn} + n_{Zn})$. According to the XRD analysis of the CZTS films, there are CuS ($E_g \approx 1.26$ eV) and SnS_2 ($E_g \approx 2.4$ eV) phases in the Cu-rich and Sn-rich CZTS films, and maybe there is a small amount of ZnS ($E_g \approx 3.7$ eV) in the Zn-rich CZTS films. Therefore the direct band gap E_{dir} of the films strays from the theoretical value 1.45 eV. When n_{Zn}/n_{Sn} and $n_{Cu}/(n_{Sn} + n_{Zn})$ are 1.15 and 0.83, the E_{dir} of the CZTS films is determined as 1.47 eV which is quite close to the optimum value for a solar cell. These optical properties show that the CZTS films are suitable for absorbers of thin film solar cells.

3.4. Electrical properties

The semiconducting properties of the films were measured by the Hall measurement system at room temperature. Table 2 exhibits the electrical properties of the CZTS thin films. CZTS films with p-type conductivity are required to fabricate heterojunction solar cells with n-type transparent conductive oxide

Table 2. Optical and electrical properties of the CZTS thin films.

Sample	n (10^{17} cm^{-3})	μ (cm^2/(V·s))	ρ (Ω·cm)	E_{dir} (eV)
CZTS-1	60.8	1.49	0.69	1.34
CZTS-2	18.5	2.87	1.18	1.43
CZTS-3	2.92	6.81	3.14	1.47
CZTS-4	0.399	7.39	21.2	1.63
CZTS-5	181	0.645	0.536	1.32
CZTS-6	0.698	12.9	6.96	1.47
CZTS-7	0.348	11.8	15.3	1.69

layers as window layers. According to the result of the Hall measurement system, the positive symbol of the measured carrier concentration indicates that the films are of p-type conductivity. The resistivity (ρ) decreases as the $n_{Cu}/(n_{Sn} + n_{Zn})$ increases from 0.64 to 1.17 (the corresponding samples are CZTS-7, CZTS-6, CZTS-5), and the resistivity increases as the n_{Zn}/n_{Sn} increases from 0.73 to 1.42 (the corresponding samples are CZTS-1, CZTS-2, CZTS-3 and CZTS-4). When $n_{Zn}/n_{Sn} =$ 1.15 and $n_{Cu}/(n_{Sn} + n_{Zn}) = 0.83$, the carrier concentration (n), resistivity and mobility (μ) of the CZTS films are 6.98×10^{16} cm^{-3}, 6.96 Ω·cm, 12.9 cm^2/(V·s), respectively. These electrical properties show that the CZTS films are suitable for absorption layers of thin film solar cells. The low resistivity in Cu-rich CZTS films might be due to the presence of a CuS phase (seen in Fig. 1). The high resistivity in Zn-rich CZTS films might be due to the presence of a ZnS phase. The low Hall mobility may result from the small grain size of the film observed under the 3D optical microscope.

4. Conclusions

We fabricated several Sn/Cu/ZnS stacked films and converted them to CZTS films by a sulfurization process, where the precursor films were heated to 550 ℃ during sulfurization. When the ratios of [Zn]/[Sn] and [Cu]/([Zn] + [Sn]) are 1.15 and 0.83, the XRD analysis shows that the CZTS films grow with a strongly preferred (112) orientation and have good crystallinity, and no other phases except CZTS are found in the XRD profile. From the analysis of the UV-VIS spectrophometer and Hall measurement system, the direct band gap of the CZTS thin films is estimated to be 1.47 eV. The carrier concentration, resistivity and mobility of the CZTS films are 6.98 $\times 10^{16}$ cm^{-3}, 6.96 Ω·cm, 12.9 cm^2/(V·s), respectively. This will establish a good foundation for making CZTS thin film solar cells.

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