



Structural development and dynamic process in sulfurizing precursors to prepare $\text{Cu}_2\text{ZnSnS}_4$ absorber layer



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ABSTRACT

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) films were fabricated by sulfurizing the fabricated metal-precursor films under sulfur atmosphere. All samples prepared at different conditions were characterized by X-ray diffraction, Raman scattering measurements, scanning electron microscopy, energy dispersive X-ray spectroscopy, and UV spectrophotometer. We systematically studied the influence of sulfurization time and temperature on structures, morphologies, compositions, and optical properties, and analyzed deeply the transformation of structural phase and dynamic process during the formation process of CZTS films. Experimental results indicate that the proper sulfurization time and temperature play an important role in synthesizing pure CZTS films with high quality. Compared with the others, the prepared sample at 500 °C and 90 min shows uniform surface morphology, excellent crystal quality, and optical properties. Various growth conditions realize the modulation of structure, impurity phase, morphology and optical properties. The present research results are helpful for us to deeply understand the growth process of CZTS film and pave the way for realizing the fabrication of high quality CZTS absorption layer.

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1. Introduction

In recent years, the low-cost photovoltaic materials have attracted increasing interest. $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is one of the most promising materials for the absorber layer of low-cost thin-film solar cells because it has many advantages, such as the optimal band gap, high absorption coefficient of 10^4 cm^{-1} in visible spectrum, relative abundance and availability of the constituent elements and eco-friendly nature [1,2]. Since Ito et al. reported the photovoltaic effect of this material [1], several researchers have begun investigating its optoelectronic characteristics and tried to prepare the CZTS-based solar cell with high efficiency [2–4]. Friedlmeier et al. prepared the CZTS solar cell with 2.3% conversion efficiency in 1997 [5]. Up to now, its conversion efficiency has been improved to 9.6% [4]. Though the device performance was greatly improved, conversion efficiency of the CZTS solar cell is still greatly lower than that of $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin-film solar cell. It is necessary for us to strengthen basic knowledge on CZTS materials and realize the controllable preparation of high quality CZTS films.

An effective method for preparing stoichiometric CZTS film is to adopt two-step processes, namely precursors firstly are prepared and then sulfurized under sulfur atmosphere. Many methods,

including sol–gel methods [6], sputtering [3,7,8], electrochemical deposition [9], thermal evaporation [10], electron-beam-evaporated methods [11], electrospray method [12], and so on, were used to synthesize precursors consisting of copper, zinc, and tin, and then CZTS film was synthesized by sulfurizing precursors. Tanaka et al. prepared CZTS film by sol–gel sulfurization and researched the relationship of chemical composition ratio of $\text{Cu}/(\text{Zn} + \text{Sn})$ with conversion efficiency [6]. It is found that various tin contents could modulate the optical band gap of CZTS photovoltaic absorbers [10]. By researching the structural properties of the prepared CZTS film, Yoo et al. pointed out that the crystal quality was related with stack sequence of precursors [7]. Scragg et al. researched the differing effects of elemental sulfur and H_2S as sulfur sources on CZTS films [9]. Further study indicated that the sulfurization in sulfur vapor was more reliable than the annealing in H_2S gas for the formation of CZTS phase [8]. Marchionna et al. pointed out that Cu-poor/Zn-rich CZTS films could prevent the development of Cu_{2-x}S secondary phase [13]. During the synthesis of CZTS films, researchers gradually cognized that because of the presence of three elements in precursor, there are many possibilities for the formation of secondary phases during sulfurization, such as Cu_2SnS_3 , ZnS, CuS, and SnS [6,8,14,15]. The existence of those impurity phases will greatly affect the conversion efficiency of CZTS-based solar energy [6,7]. It is necessary for us to understand structural development and dynamic process by sulfurizing precursors to prepare CZTS absorber layer, which is helpful for us

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to modulate the appearance of secondary phases and to realize the preparation of CZTS solar cell with high efficiency. However, the related research is very limited.

In this paper, the precursors firstly were prepared by vacuum evaporation methods, and then CZTS absorption layer was synthesized by the sulfurization of the fabricated precursor films under sulfur atmosphere. We systematically studied the influence of sulfurization time and temperature on structures, morphologies, compositions, and optical properties, and deeply analyzed the transformation of structural phase and dynamic process during the formation process of CZTS films.

2. Experimental details

The preparation of CZTS films can be divided into two stages. First, soda-lime glass substrates were cut and cleaned ultrasonically in the ethanol/acetone/distilled water. The precursor films were deposited on the cleaned substrates by vacuum evaporation using the pure copper, zinc and tin powders as evaporation source. The background pressure of deposition chamber was $\sim 7 \times 10^{-4}$ Pa. Zn, Cu and Sn powders with diameters ranging from 2 to 5 μm were placed at different tungsten boats respectively, and precursor thin films were fabricated by sequential deposition of Zn, Cu and Sn. An oscillating quartz crystal microbalance was to determine the deposition rate of the different metallic layer. In the prepared precursor film, the mole ratio of Cu, Zn and Sn is 2:1:1. Second, the CZTS films were prepared by sulfuring the deposited samples at the first step under sulfur atmosphere. To avoid the oxidation of the precursor films, samples were rapidly transferred to horizontal quartz tube after they were taken out from the vacuum chamber, and a mechanical rotary pump was used to evacuate the air from quartz tube before heating. The pure sulfur powder (99.99%) of 1.0 g was placed in an alumina boat located at the center of a horizontal quartz tube, and the precursor films were placed along the downstream position of the carrier gas. Pure (99.9%) nitrogen gas was used as the carrier gas and was introduced from one end of the quartz tube at a flow rate of 400 standard cubic centimeters per minute (scm).

To investigate the effect of sulfurization time on the growth of CZTS films, we put the prepared precursor films 2 cm away from sulfur source horizontally, and heated to 500 °C at a heating rate of 5 °C/min. Samples 1, 2, 3 and 4 were prepared at the heat preservation time of 30, 60, 90, and 120 min, respectively. During the sulfurization process, the substrate temperature was also monitored at 500 °C. In addition, samples 5, 6 and 7 were prepared at 300, 400, and 550 °C, respectively, where the heat preservation time is 90 min. All the fabricated films were measured to be 1.2–1.5 μm thick after sulfurization by surface step profiler.

The morphology and structure of the synthesized samples were determined using the field-emission scanning electron microscopy (FESEM) (Philips XL30FEG) and X-ray diffraction (XRD, X'Pert Pro with Cu K α of 1.5406 Å). Raman spectra were recorded by a Jobin Yvon LabRAM HR UV-NIR micro-Raman system under 488 nm laser excitation. Transmission and reflection spectra were measured by using spectrophotometer (UV-2550).

3. Results and discussion

3.1. Effect of sulfurization time on growth process of CZTS films

Fig. 1 shows XRD pattern of samples prepared at different sulfurization times. All of samples display the relatively strong diffraction peaks at $\sim 28.44^\circ$, and the relatively weak ones at 32.89° , 47.40° , and 56.19° , respectively. Table 1 also lists main XRD peaks and orientation planes for CZTS, cubic-Cu₂SnS₃, and ZnS. It is obvious that XRD patterns of CZTS, Cu₂SnS₃ and ZnS are very similar and the difference of angle is too small to distinguish within instrument accuracy, so it is difficult to discriminate the origin of those peaks only by XRD diffraction pattern.

S1 and S2 in Fig. 1 show the XRD diffraction pattern of precursors sulfurized at 30 and 60 min, respectively. Apart from the peaks mentioned above, both of them also show the relatively weak diffraction peaks of SnS₂ [3] and CuZn (JCPDS card no. 00-026-0571), indicating that the prepared samples are incompletely sulfurized into CZTS film and should contain the impurity phases of SnS₂ and CuZn. With the increase of sulfurization time to 90 min, there is no other impurity peaks (as shown in S3 of Fig. 1), suggesting that precursors could be completely sulfurized into CZTS film at present growth condition. Further evidence will be given in the

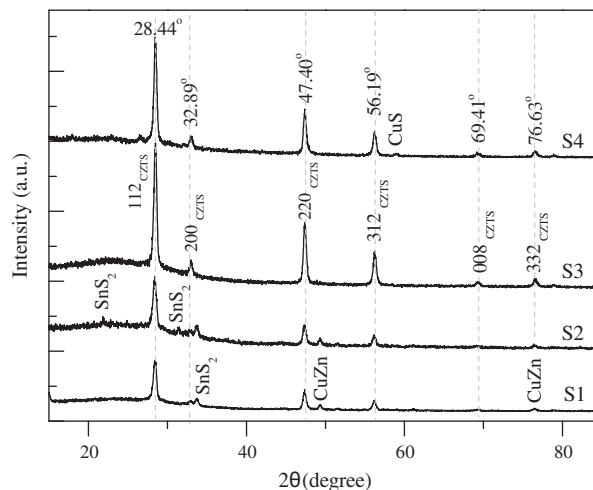


Fig. 1. XRD pattern of samples 1–4 prepared at 500 °C and different sulfurization times, where sulfurization times of S1, S2, S3, and S4 are 30, 60, 90, 120 min, respectively.

Table 1

Main XRD peaks and orientation planes for CZTS, cubic-Cu₂SnS₃, and ZnS; XRD peaks of the prepared samples 1–4.

CZTS (JCPDS card no. 01-089-4714)		Cubic-Cu ₂ SnS ₃ (JCPDS card no. 01-089-2877)		ZnS (JCPDS card no. 04-006-0807)		Samples 1,2 3 and 4	
2θ (°)	hkl	2θ (°)	hkl	2θ (°)	hkl	2θ (°)	
28.44	112	28.45	111	28.50	111	28.44	
32.93	200	32.96	200	33.03	200	32.89	
47.33	204	47.31	220	47.40	220	47.40	
56.09	312	56.13	311	56.24	311	56.19	

following analysis. In addition, the strongest (1 1 2) CZTS diffraction peaks also indicate that the sample 3 prepared at present condition has the best crystal quality. When the sulfurization time increases to 120 min, the decrease of (1 1 2) peak intensity shows that the increasing sulfurization time will lead to the decline of crystal quality. Furthermore, there is the diffraction peak of secondary phase at $2\theta = 26.5^\circ$ and 58.9° , indicating that the prolonging sulfurization time can cause the decomposition of CZTS films. The reasons of decomposition should be related to the long-term heat exposure at high temperature. As far as we know, this phenomenon has not been reported so far.

Fig. 2a shows Raman spectra of the samples prepared at different sulfurization times. All of samples show P₁, P₂, P₃, and P₄ four peaks at ~ 265 , 296, 351 and 370 cm^{-1} , respectively. Table 2 shows the list of Raman peaks' location, which is used to identify the different phase. The peaks at 351 and 371 cm^{-1} come from CZTS [3,16]. With the various sulfurization times, spectrum 3 in Fig. 2a shows the strongest P₂ and P₃ peaks, suggesting that the prepared sample 3 has the best crystal quality. This observation is consistent with XRD results. Spectrum 4 in Fig. 2a shows the weak peak at $\sim 490 \text{ cm}^{-1}$ which is assigned to the vibration mode of Cu_{2-x}S [16,17], suggesting the partial decomposition of CZTS films. It has been reported that at higher temperature (above 550 °C) CZTS phases could decompose to form Cu_{2-x}S [18,19]. The present experimental results display that prolonging heating time also can lead to the decomposition of CZTS phase to form the impurity phases. Therefore various sulfurization times are very important to modulate the secondary phase and fabricate the high quality CZTS film. In addition, Cu_{2-x}S phase was not detected by XRD pattern but revealed by Raman spectroscopy probably because Cu_{2-x}S

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