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Strategic improvement of Cu_2SnS_3 thin film by different heating rates and photoluminescence investigation

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ABSTRACT

Cu_2SnS_3 (CTS) thin films have been synthesized on molybdenum-coated soda lime glass substrates by sulfurization the Cu-Sn alloy precursors grown by radio-frequency magnetron sputtering technique. Strategic improvement has been carried out on the composition, structural, morphological and optical properties of CTS thin films sulfurized by rapid heating rate and slow heating rate. The annealing heating rate can adjust the ratio of Cu/Sn, improve the crystallinity and surface morphology. The ratio of Cu/Sn is close to the stoichiometric composition of CTS under slow heating rate with more loss of Sn. Structural characterization exhibits the CTS thin film sulfurized by slow heating rate has a better crystallinity without secondary phase. The CTS thin film obtained at slow heating rate presents a larger average grain size and smooth surface. The optical band gap of CTS thin films is at the vicinity of 0.87 eV. Photoluminescence (PL) spectroscopy has been used to study the carrier recombination mechanism and the electronic structure of CTS thin film by excitation power and temperature dependent measurements. The peak observed from PL spectra of CTS thin film conforms to the donor-acceptor pair recombination luminescence.

1. Introduction

In the environmental friendly candidate materials to replace Cu(In,Ga)Se_2 for thin film solar cell (TFSC), Cu_2ZnSnS_4 (CZTS) has present huge potential. The TFSC prepared by CZTS and its selenide derivatives have obtained a conversion efficiency of 9.5% and 12.6%, respectively [1,2]. In recent years, another potential candidate material CTS has received wide attention. The record efficiency of Cu_2SnS_3 (CTS) and doped CTS TFSC has reached 4.29% and 6.7%, respectively [3,4]. Compared with CZTS compound, CTS has less constituent elements. It means the preparation process of CTS would be simpler. Both CTS and CZTS have similar zinc blende structure. The properties between these compounds could have close relationship [5,6].

Up to now, the control of Sn content is one of the important research aspects in the growth of CTS thin film and the defect investigation still at the beginning stage. The sulfurization annealing process is the key factor to control the elemental composition. According to the various preparation methods of precursor, sulfurization temperature and sulfurization time commonly become the research subjects [7–10]. Throughout the entire sulfurization annealing process, heating rate is also a significance segment. In this paper, we would do strategic improvement about the heating rate. Comparative study of the composition, structural, morphology and optical properties of CTS thin films sulfurized by rapid heating rate and slow heating rate. Moreover, Cu-Sn alloy target was used to deposit Cu-Sn alloy precursor thin films using radio-frequency (RF) magnetron sputtering technology. Sputtering process would be simplified as one step process by using the Cu-Sn alloy target which should attribute to the less composition element of CTS compounds. At last, in order to investigate the carrier recombination mechanism in CTS thin film, photoluminescence (PL) spectroscopy was used to measure the CTS thin film based on excitation power and temperature.

2. Experimental

The CTS thin films were prepared by sulfuring the metallic alloy precursor at rapid heating rate (48 °C/min) referred as rapid thermal processing and slow heating rate (12 °C/min) referred as slow thermal processing, respectively. The precursors were fabricated on Mo-coated soda lime glass substrate by RF magnetron sputtering method using Cu-Sn alloy target with atomic ratio 2:1 (Cu:Sn) at room temperature. The sputtering power density, sputtering time and working pressure were

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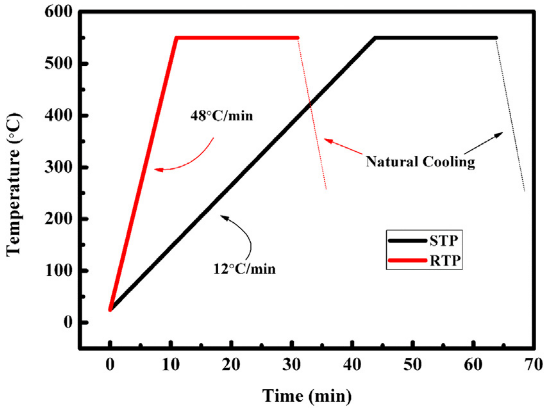

Fig. 1. Sulfurization profiles used to prepare the CTS thin films.

2.5 W/cm^2, 20 min and 0.5 Pa, respectively. The precursor was cut into two pieces, which is to increase the reliability of the experimental data, to sulfurize at different heating rates to obtain the CTS thin films. Then the precursor was put in graphite box with 0.05 g sulfur powder. The graphite box would be placed in furnace chamber under N$_2$ atmosphere with a working pressure of 1333 Pa to execute sulfurization annealing. The sulfurization annealing program was described in Fig. 1. After heating to 550 °C, the temperature was hold for 20 min. At last, the furnace was cooling down naturally. The obtained thin films are labeled as “RTP” and “STP” to indicate heating rate 48 °C/min and 18 °C/min, respectively.

X-ray diffraction (XRD) measurements were recorded by Bruker D8 Discover. Raman spectra were performed with LabRAM HR Evolution Raman spectrometer （excitation light:532 nm,0.1 mW）. The morphology of surfaces were measured with Hitachi S-4800 scanning electron microscopy (SEM). The chemical composition was analyzed by energy dispersive X-ray (EDX) spectroscopy analyzer. The optical absorption experiments were evaluated by Carry500 ultraviolet-visible-near-infrared (UV–vis–NIR) spectrophotometer attached to an integration sphere. PL spectra at different excitation power and temperature were acquired by Bruker IFS-80V fourier transform infrared spectrometer equipped with 77-K-cooled Ge detector.

3. Results and discussion

Table 1 shows the chemical composition and composition ratio for CTS thin films analyzed by EDX technique. Apparently, both STP and RTP samples exhibit Cu-poor state. Considering the Cu-Sn alloy target with atomic ratio 2:1 (Cu:Sn) used to prepare precursor, the Cu-poor state mainly attribute to the lower sputtering yield of Cu than Sn [11]. Thus, the composition ratio of Cu:Sn in thin films is lower than stoichiometric ratio in alloy target. Additionally, Cu vacancy is more easily formed in Cu-poor state [12]. It acts as accepter defect which makes the thin film with more p-type character and also could improve the performance of thin film solar cell [3,12]. Compared with RTP sample, STP sample has longer annealing time. It could lead to more loss of Sn which is volatile in SnS form [13]. This is the reason why STP has higher value of Cu content than RTP. The result also indicates our precursor has an excess of Sn. This analysis confirms that the precursor films are copper poor and tin rich. According to the literatures, the higher conversion efficiency of CTS thin film solar cell commonly has a Cu/Sn ratio in the vicinity of 1.87 [3,14]. Therefore, under this process conditions, the CTS films prepared by slow annealing rate are more suitable for the preparation of photovoltaic solar cell devices. From analysis of the above experimental results, it is necessary to use slow thermal processing to adjust the chemical composition.

Table 1
Chemical composition and composition ratio for CTS thin films.

Sample	Chemical composition (at%)			Composition ratio	
	Cu	Sn	S	Cu/Sn	Metals/S
RTP	30.46	17.63	51.91	1.73	0.93
STP	32.27	17.04	50.69	1.89	0.97

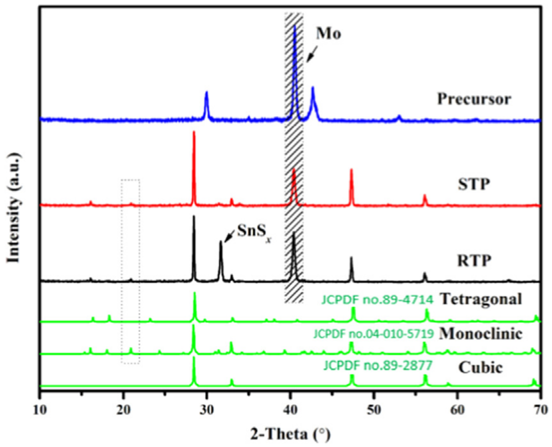

Fig. 2. XRD patterns of precursor and CTS thin films sulfurized under rapid thermal processing and slow thermal processing. Calculated diffraction patterns of tetragonal, monoclinic and cubic CTS for comparison.

Fig. 2 illustrates the XRD patterns of precursor and CTS thin films sulfurized under rapid thermal processing and slow thermal processing. The peak at the vicinity of 40° derives from the bottom Mo layer. With the growth of CTS thin film, the peak intensity of Mo decreases and the phase exhibit a transition behavior from precursor to CTS thin film. The calculated diffraction patterns of tetragonal, monoclinic and cubic phase of CTS are also presented in Fig. 2 for comparison. From the main peaks at the vicinity of 28, 47 and 56°, it is difficult to distinguish the structural phase. Cubic phase has fewest diffraction peaks and the peak at the vicinity of 21° can be used to distinguish the tetragonal and monoclinic phase [15]. As shown in Fig. 2, the weak peak marked by dot line indicates that obtained CTS thin films exhibit monoclinic phase structure. For STP and RTP samples, all observable peaks are consistent well with the monoclinic phase structure except RTP sample. A characteristic peak of SnS$_x$ appears in the XRD pattern of RTP sample. It may be originated from higher Sn content and shorter annealing time.

Fig. 3 depicts the surface images of CTS thin films under rapid heating rate and slow heating rate at different magnification. Compared with the surface morphology of RTP film, the surface of STP film is more homogeneous and dense. The reason is mainly that slow heating rate will prolong the time of sulfuration annealing, and more Sn elements will evaporate in the form of SnS. The sublimated SnS can promote the growth of grain and the film [16]. The grain of CTS film prepared by rapid heating rate can’t be fully grown, there are some large grains on the surface, and the grain size is very different, which makes the surface rougher. In addition, under the low magnification, we can find that there are some cracks on the surface of the RTP film, which will seriously affect the quality of the heterojunction in the preparation of thin film photovoltaic solar cells.

Fig. 4 presents the Raman spectra of CTS thin films sulfurized at different heating rates, which were fitted and decomposed into individual Lorentzian components to get exact peaks. There are two intense peaks at the vicinity of 290 and 350 cm^{-1} and four weak peaks at the vicinity of 223, 258, 325 and 371 cm^{-1} observed in both RTP and STP samples. Two intense modes at 290 and 350 cm^{-1} were attributed to monoclinic CTS phase [17]. The mode at 325 cm^{-1} in the films is attributed to tetragonal CTS phase present in the films [18,19]. Modes at 223 cm^{-1} and 371 cm^{-1} are also seen in the films due to a minor