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Effects of sulfurization time and H_2S concentration on electrical properties of Cu_2ZnSnS_4 films prepared by sol–gel method

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ABSTRACT

Cu_2ZnSnS_4 (CZTS) thin films have been successfully deposited by a sol–gel method and sulfurization process. The properties of the films were investigated by varying sulfurization time and H_2S concentration. X-ray diffraction and Raman spectra analyses revealed the formation of CZTS films with a tetragonal type kesterite structure. With increasing the sulfurization time and H_2S concentration, the intensity of the kesterite (1 1 2) peak became sharper. The stoichiometric ratios of the CZTS films were different from the precursors, which was due to Sn loss during the sulfurization process. The electrical resistivity and mobility of the films increased while the carrier concentration decreased with increasing the sulfurization time. The CZTS thin films sulfurized at 5% H_2S concentration for 90 min had the best opto-electrical properties with E_g of 1.41 eV, resistivity of 3.64 Ω cm, carrier concentration of 1.11×10^{18} cm^{-3} and mobility of 1.54 cm^2/(V s) at room temperature for PV application.

1. Introduction

Kesterite Cu_2ZnSnS_4 (CZTS) compound semiconductor has emerged as a promising candidate for absorber materials of thin film solar cells [1]. There are lots of reports about solar cells based on CZTS thin films which utilizes vacuum based deposition route such as sputtering, thermal evaporation, pulse laser deposition and so on [2–7]. Vacuum based deposition techniques suffer certain drawbacks like high input and low throughput. These drawbacks will hinder the realization of the goal about low-cost and sustainable conversion of energy using thin film solar cells. Sol–gel method is a very simple and low-cost process based on hydrolysis and poly-condensation reactions. Sulfide films can be directly obtained by sulfurizing oxyhydrate precursors.

In 2007, Tanaka et al. [8] reported the first sol–gel-grown CZTS films. They prepared the CZTS films by annealing oxyhydrate precursors in a $N_2 + H_2S$ gas atmosphere. In 2014, Zhang et al. fabricated the CZTS thin film solar cell with 5.7% power conversion efficiency by sulfurizing oxyhydrate precursor with sulfur power. It is the best efficiency for CZTS solar cells based on sol–gel method as far as we know [9].

During the sulfurization process, sulfurization parameters such as sulfurization temperature, sulfurization time and H_2S concentration have great influence on the properties of CZTS thin films. But in the most reported research work, researchers mainly studied the influences of the sulfurization parameters on the structural and optical properties of the CZTS films [10–12]. However, the effects of the sulfurization parameters on the electrical properties of CZTS films remain unclear.

In our study, we prepared CZTS precursors with sol–gel method and then obtained CZTS thin films by improving sulfurization process. The effects of sulfurization time and H_2S concentration on the electrical properties of the CZTS films were investigated.

2. Experimental

Cu_2ZnSnS_4 thin films were prepared by sol–gel method following sulfurization process. First, 2.5 cm × 2.5 cm floating glass (FG) substrates were treated by ultrasonic cleaning in acetone and alcohol for 15 min each. Sol–gel precursor solutions were prepared by dissolving copper(II) acetate monohydrate, zinc acetate dihydrate, tin(II) chloride dihydrate, and thiourea into 25 ml of 2-methoxyethanol and 1 ml of triethanolamine. Triethanolamine was used as a stabilizer and chelating agent to increase the stability of ion complex. Sol–gel solutions were spin-coated at 2500 rpm for 30 s on the FG substrates, which were then dried in air at 250 °C for 5 min to remove residual organic materials. The deposition process was repeated 5 times to obtain the desire film thickness (1 μm). The precursors were annealed in a $N_2 + H_2S$ gas atmosphere at 500 °C for several minutes. The sulfurization time and H_2S

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Table 1
The names of samples with different sulfurization time and H_2S concentrations.

Sample	H_2S concentration (%)	Sulfurization time (min)
T30	5	30
T60	5	60
T90	5	90
T120	5	120
T150	5	150
C03	3	90
C07	7	90
C10	10	90
C13	13	90

concentration were changed to investigate the influence on the properties of CZTS thin films. Table 1 shows the parameters of the sulfurization time and H_2S concentration during the sulfurization process.

The film thicknesses were measured by a stylus profiler (TENCOR D100). The crystallinity of the CZTS thin films was ascertained by an X-ray diffractometer with Co Kα radiation (λ = 1.78901 Å) and a Raman spectroscopy. Observation of the surface topology was carried out using a HITACHI S-4800 scanning electron microscope (SEM) with an EDAX attachment. The electrical properties of the films were evaluated using a HMS-3000Hall measurement system. The transmittance and reflectance of the samples were measured by a Varian Cary 5000 UV/VIS/NIR spectrometer with an integrating sphere accessory in the wavelength range from 400 to 2600 nm at room temperature. The obtained reflectance included direct and diffusing reflectance measured by the integrating sphere accessory. The measured transmittance excluded scattering light. The bandgap was calculated from the experimental transmission and reflection data.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows XRD patterns of the CZTS films obtained at different sulfurization times. All the XRD peaks of the CZTS films match with those of the kesterite phase (JCPDS00-026-0575: Tetragonal). Compared with the standard file, four peaks are assigned to (1 1 2), (2 0 0), (2 2 0) and (3 1 2) planes of CZTS with kesterite structure. Table 2 shows the grain sizes of the CZTS thin films with different sulfurization times. With increasing sulfurization time from 30 min to 150 min, the intensity of (1 1 2) peak becomes stronger and the crystallite size increases, but the FWHM values decrease. It indicates that the crystallinity of the CZTS thin films could be improved by increasing the sulfurization time. Since the structure of CZTS is similar to other zinc-blende structure materials such as

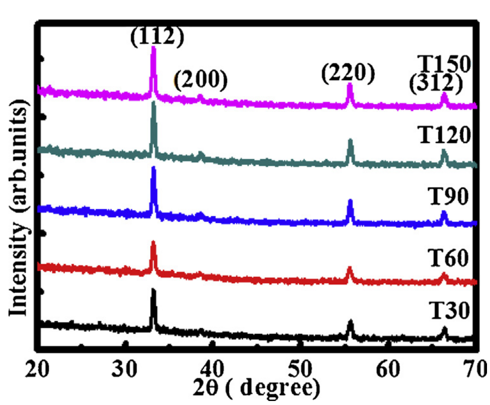

Fig. 1. The XRD patterns of CZTS thin films at different sulfurization time.

Table 2
The grain sizes of the CZTS thin films with different sulfurization time.

Sample	Sulfurization time (min)	FWHM (°)	Grain size (nm)
T30	30	0.3779	25.19
T60	60	0.2685	35.45
T90	90	0.1596	57.96
T120	120	0.1487	64.02
T150	150	0.1459	65.26

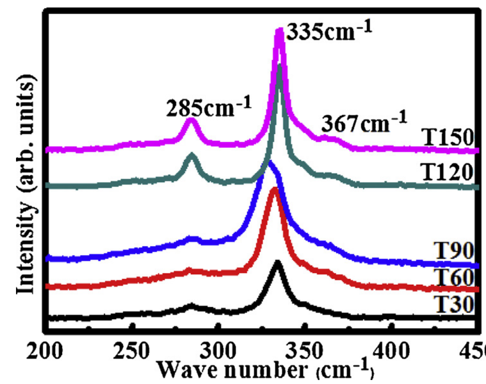

Fig. 2. The Raman spectra (532 nm excitation) of CZTS thin films at different sulfurization time.

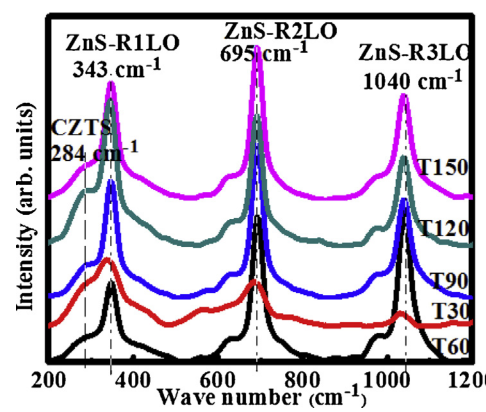

Fig. 3. The Raman spectra (325 nm excitation) of the CZTS thin films at different sulfurization time.

Cu_2SnS_3 and ZnS, the XRD patterns of all these phases have been found to be overlapping [13]. Fig. 2 shows the Raman spectra of the CZTS films with 532 nm excitation wavelength. Three peaks at

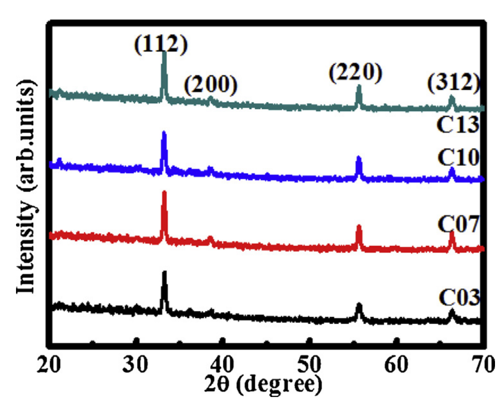

Fig. 4. The XRD patterns of CZTS thin films with different H_2S concentrations.