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Effects of sulfurization temperature on phases and opto-electrical properties of Cu_2ZnSnS_4 films prepared by sol–gel deposition

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ABSTRACT

Cu_2ZnSnS_4 (CZTS) thin films were prepared by sol–gel method and sulfurization process. The effects of the sulfurization temperature on the structural, morphological, compositional, and opto-electrical properties of the CZTS films were investigated. X-ray diffraction and Raman spectroscopy analyses confirmed the formation of CZTS films. With increasing sulfurization temperature, the crystallinity of the films was enhanced, which was accompanied by metallic deficiency, especially tin loss. When the sulfurization temperature was increased from 460 to 540 °C, the optical band-gap value decreased from 1.63 to 1.38 eV, while the resistivity and mobility increased from 1.415 to 1313 Ω·cm and from 0.372 to 7.231 $cm^2/V \cdot s$, respectively. The best CZTS film properties with a bandgap of 1.47 eV, resistivity of 581.5 Ω·cm, carrier concentration of 2.165×10^{16} cm^{-3} and mobility of 1.411 $cm^2/(V \cdot s)$ were achieved at a sulfurization temperature of 500 °C, and make the films suitable as absorbers for solar cells.

1. Introduction

Cu_2ZnSnS_4 (CZTS) is one of the most promising absorber materials for low-cost thin film solar cells due to its suitable semiconductor properties such as *p*-type conductivity, appropriate direct bandgap (about 1.5 eV) and high absorption coefficient ($\geq 10^4$ cm^{-1}) [1–3]. In addition, it can also be regarded as an alternative to $CuInS_2$ and $Cu(In,Ga)Se_2$ absorbers, in which the extremely expensive and resource limited indium is replaced by abundant and low cost zinc (Zn) and tin (Sn). To date, studies on CZTS-based solar cells are still at an early stage [4] with a highest efficiency of 9.6% under laboratory conditions [5], which is far from the theoretical efficiency of 32.2% [6]. It is necessary to develop an economical production method for fabricating solar cells with a high efficiency, which will ensure commercialization of CZTS solar cells [7]. Although several vacuum deposition methods have been developed for preparing CZTS films [8,9], vacuum equipment is normally expensive and only applicable to high-value niche markets. Therefore, development of low-cost processes for growing CZTS films is important. Sol–gel method is a viable alternative method for preparing photovoltaic materials [10]. The technique may significantly lower the cost of preparing materials without needing high vacuum systems. It has been reported that CZTS-based photovoltaic cells prepared by sol–gel technique exhibited efficiencies of more than 3% in laboratory [11], and that the highest efficiency for $Cu_2ZnSn(S,Se)_4$-based device is about 7.5% [12]. However, the relationship between the sulfurization temperature and the electrical properties of CZTS thin films was scarcely reported though it is important for manufacturing CZTS thin film solar cells. Here we prepared CZTS thin films using a sol-gel spin-coating method followed by sulfurization process and investigated the effects of the sulfurization temperature on the structural and opto-electrical properties in detail.

2. Experimental details

The CZTS precursor solution was prepared by dissolving copper (II) acetate monohydrate (0.478 M), zinc (II) acetate dihydrate (0.294 M) and tin (II) chloride (0.256 M) into 2-methoxyethanol (25 ml) and triethanolamine (2.5 ml). 2-methoxyethanol and triethanolamine were used as solvent and stabilizer, respectively. The solution was stirred at 45 °C for 1 h to dissolve metal compounds completely. Floating glass substrates of 20×20 mm^2 were treated by ultrasonic cleaning in deionized water, acetone, ethanol, deionized water in turn, then dried in the atmosphere of N_2. The sol solution was dropped onto the floating glass substrates rotating at 2500 rpm for 30 s. After deposition by spin coating, the films were dried in air at 250 °C. The coating and drying processes were repeated 5 times to obtain thick films. The precursors were annealed in the atmosphere of $N_2 + H_2S$ (5%) for 1 h at 460 °C–540 °C and the samples were named by capital letter S plus temperature, such as S460.

The film thickness was measured by a stylus profiler (TENCOR D100). And the thicknesses of the pre- and post-samples are 300 nm

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and 500 nm, respectively. 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 (RENISHAW with 532 nm and 325 nm light sources). 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 surface morphology was observed by a scanning electron microscope (SEM) (HITACHI S-4800) and the SEM analysis was operated at an electron beam acceleration of 5 kV. The composition was investigated by an energy-dispersive X-ray spectroscopy (EDS). The EDS spectra were obtained with a 15 keV electron beam. For measuring Cu and Zn contents, separate Cuk and Znk line peaks were used instead of CuL and ZnL lines, which are close to each other. For Sn and S, SnL and SK lines were used. A HMS-3000 Hall Measurement System was used to carry out the carrier concentration, mobility and resistivity of the films.

3. Results and discussion

3.1. Structural characterizations

Fig. 1 shows XRD patterns of the CZTS films obtained at different sulfurization temperatures. For the films sulfurized from 460 to 540 °C, the peaks corresponding to (112), (200), (220) and (312) planes all match very well with a tetragonal Cu_2ZnSnS_4 (JCPDS 026-0575: tetragonal, $a = b = 5.427$ nm, $c = 10.848$ nm, and I-42 m) [13,14], indicating that the formed films are polycrystalline CZTS. The size D_{hkl} of the crystallites was determined from XRD data by the Scherrer formula (1):

$$D_{hkl} = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where K is a constant, β is the FWHM (Full Width at Half Maximum) in radians, λ is the wavelength of X-ray, and θ is Bragg angle [15]. The K and λ values were taken as 0.89, 1.78901 Å for the calculation, respectively.

The FWHM values and crystallite sizes of (112) peaks of the CZTS thin films obtained at different sulfurization temperatures are listed in Table 1. The FWHM values decrease with increasing sulfurization temperature, while the crystallite size increases from 25.76 to 77.25 nm after the sulfurization temperature increased from 460 to 540 °C. It indicates that the crystallinity of the CZTS thin films could be improved by increasing the sulfurization temperature.

In the XRD patterns of ZnS (JCPDS 03-065-1691), Cu_2SnS_3 (JCPDS 01-089-2877) and some other secondary phases, there are some XRD peaks coincident with those of Cu_2ZnSnS_4. Therefore we can't affirm whether there are some other phases in our samples or not.

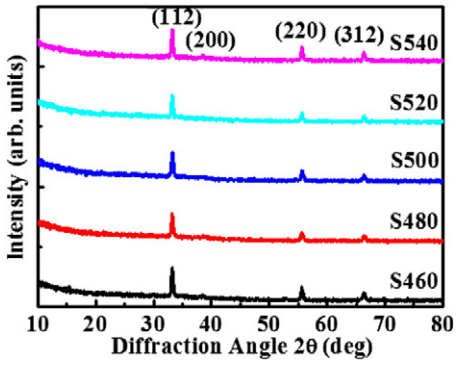

Fig. 1. The XRD patterns of the CZTS films obtained at different sulfurization temperatures.

Table 1
The FWHM values and crystallite sizes of (112) peak of the CZTS thin films obtained at different sulfurization temperatures.

Sample	Temperature (°C)	FWHM (°)	Crystallite size (nm)
S460	460	0.3542	25.76
S480	480	0.1968	46.36
S500	500	0.1574	57.96
S520	520	0.1378	66.20
S540	540	0.1181	77.25

To further detect the presence of other possible secondary phases, Raman spectroscopy analysis with a 532 nm excitation wavelength was employed to detect the samples in the range of 100–500 cm^{-1}, and the results are shown in Fig. 2. In the Raman spectra, obvious peaks at 166, 284, 335 and 367 cm^{-1} can be clearly observed. These spectral data are in good agreement with the reported Raman spectra of CZTS [16–18], hence the existence of the CZTS phase can be confirmed. With increasing sulfurization temperature from 460 to 500 °C, the intensity of the major peak (335 cm^{-1}) becomes stronger, meanwhile, the FWHM of the major peak gets narrower. In addition, at sulfurization temperatures of 460 °C and 480 °C, there is a 475 cm^{-1} peak corresponding to $Cu_{2-x}S$ [19]. When the sulfurization temperature is beyond 500 °C, the peaks of $Cu_{2-x}S$ disappear. It indicates that $Cu_{2-x}S$ will be formed at a low sulfurization temperature because of its low bond energy. Some groups reported that $Cu_{2-x}S$ was formed on the top of the CZTS thin films [20]. During the film growth, Cu tended to migrate towards the film surface and form $Cu_{2-x}S$ [21]. This can be understood in terms of vacancy diffusion mechanism discovered by Kirkendall, resulting from the interdiffusion of two species with different bulk diffusivities [22]. For sample S520, the peak arising at 308 cm^{-1} probably belongs to $Sn_{2-x}S$ phase [23]. Raman spectroscopy with a 325 nm excitation wavelength was also used to further identify the existence of ZnS, as shown in Fig. 3. The peaks at 343, 695 and 1040 cm^{-1} could be assigned to R1LO, R2LO and R3LO vibrational modes of ZnS, respectively [24]. By analyzing Raman spectra of five samples, we can find that the intensity of the ZnS Raman peaks increases with increasing sulfurization temperature, but the CZTS Raman characteristic peaks are very weak, as shown in Fig. 3, indicating that there are more ZnS on the surface of the samples.

3.2. Surface morphology and compositional analysis

Top-view SEM images of the CZTS thin films are shown in Fig. 4. It can be seen that the particle size becomes larger (from 1 to 2 μm), while the grain boundaries get smaller with increasing sulfurization temperature from 460 °C to 540 °C. It is very important for high efficiency devices to include absorbers with large grain sizes and less grain boundaries, because small grains with excess grain boundaries would lead to

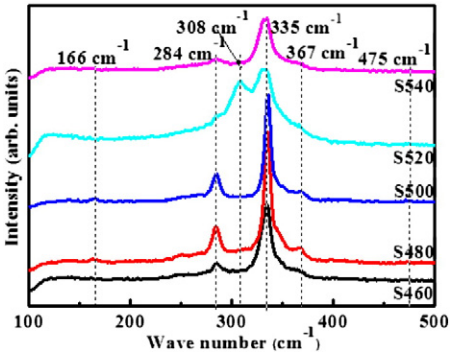

Fig. 2. The Raman spectra (532 nm excitation) of the CZTS thin films with different sulfurization temperatures.