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The role of sulphur in the sulfurization of CZTS layer prepared by DC magnetron sputtering from a single quaternary ceramic target

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ABSTRACT

The influence of sulphur vapour pressure, controlled by its mass, on the grain growth and optoelectronic properties of Cu_2ZnSnS_4 (CZTS) films prepared by a two-step procedure based on sputtering was studied. It was found that both the crystallinity and grain size of the films were promoted with the increase of the sulphur vapour pressure, indicating that the crystal growth was controlled by the sulphur vapour pressure. In addition, the crystal growth process of CZTS was investigated by analysing the microstructure and elemental composition of the sulfurized films with different masses of sulphur. It was also found that the content of Sn in the sulfurized films decreased after high-temperature annealing. However, the second phase SnS_2 was observed on the sample surface, which led to the increase of the optical band gap of the film. Moreover, we proposed the regulatory mechanism of sulphur vapour pressure in the grain growth of CZTS film. Finally, a highly crystalline p-type kieserite Cu_2ZnSnS_4 film with carrier concentration of $8.16 \times 10^{17}\ cm^{-3}$, mobility of $1.24\ cm^2/V\ s$ and optical bandgap of 1.54 eV was obtained. This CZTS layers are expected to fabricate high efficiency thin film solar cells.

1. Introduction

Photovoltaic technology is recognized as a green, sustainable energy technology that can satisfy the needs of growing energy consumption and alleviate the environmental crisis [1,2]. As far, CdTe and Cu(In, Ga)(S, Se)$_2$ (CIGS) thin film solar cell have achieved commercial production, besides crystalline-silicon solar cell that dominate the main market share [3]. Due to the low absorption coefficient, crystalline silicon (c-Si) solar cells need thicker absorbing materials and thus are subject to the high cost of materials. Nevertheless, both mentioned thin-film solar cells above require rare (In, Ga, Te) and toxic (Cd) elements [2]. Cu_2ZnSnS_4 (CZTS) is regarded as a promising solar cell absorber material to alternative to CdTe and CIGS owing to its high absorption coefficient, optimal direct band gap, and abundance and non-toxic raw materials [4]. Although a great deal of effort has been devoted to research CZTS, several challenges have not yet been addressed. For instance, the narrow range of the stable chemical potential of CZTS makes the preparation of the pure CZTS phase a difficult task [5]. In addition, a decomposition reaction occurs during high-temperature sulfurization, which in turn leads to evaporation of volatile SnS, making it tough to control the composition of the film and causing the appearance of CuS secondary phase on the surface of the film [6]. Thus the elemental control of precursors and the optimization of sulfurization conditions still deserve considerable effort to explore.

A variety of vacuum- and non-vacuum-based preparation techniques [7] have been applied to CZTS research, such as sputtering [8], thermal evaporation [9], electrodeposition [10] and hydrazine solution approach [11]. Up to now, the maximum power conversion efficiency of CZTS solar cells reaches 12.6% [12]. The solar cell is fabricated using a non-vacuum hydrazine solution method, but the method has limited application prospects due to the use of a toxic and reactive hydrazine solution. Magnetron sputtering has the potential for mass production due to its high deposition rate, good uniformity and high reproducibility. Sputtering using a single compound target is one of the most popular methods to deposit CZTS. First of all, as compared to pure metal or sulphide precursors, the reaction process of quaternary compounds as precursors is simplified, the sulfurization temperature is lower, and the control of the thin film components can be accomplished by adjusting the elemental proportions of the target [13–15]. Furthermore, highly crystalline and phase-pure CZTS films can be prepared by optimising the substrate temperature and sulfurization conditions [16–18]. In addition, another potential advantage of using quaternary compounds as reaction precursors is that preparation of CZTS thin films can be accomplished in one step by controlling the substrate

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temperature without the need for subsequent sulfurization [19].

Although the preparation of CZTS can be accomplished by a one-step process, the subsequent sulfurization is still crucial for the optimization of the crystallinity, microstructure and optoelectronic properties of the film. In the present study, a quaternary compound precursor, sputtered by a stoichiometric target, is adopted to deposit CZTS films followed by a sulfurization process. Two main technical problems remain to be determined: The first one is whether a high-performance CZTS film can be fabricated only by the reaction of the four elements (Cu, Zn, Sn, and *S*) in the precursor. The other one is the effect of sulphur vapour pressure, controlled by mass of sulphur, on the grain growth of CZTS films and optoelectronic properties.

2. Experimental

A highly pure (4 N) stoichiometric target (75 mm diameter and 4 mm thickness) was used to deposit the Cu-Zn-Sn-S precursors on a soda lime glass (SLG) substrate (2.5 cm × 3.0 cm) at room temperature via DC sputtering process. The sputtering power was 100 W, and deposition time was 60 min. The base pressure of the sputtering system was 6.0×10^{-4} Pa and the working pressure kept at 0.2, 0.6, 1.0, and 1.4 Pa sequentially. Sulfurization was accomplished at 500 °C for 20 min in a vacuum furnace without any protection atmosphere. The sulphur source was pure sulphur nanoparticle powder placed in a graphite crucible (the volume is about 2×10^{-4} m^3) along with the samples. Samples S1 (0 mg), S2 (50 mg), S3 (100 mg), and S4 (150 mg) were treated with varying amounts of sulphur, as indicated in parentheses. The samples were allowed to cool down naturally in the furnace.

The phase composition of the samples was determined by X-ray diffraction (XRD, Empyrean) analysis using Cu Kα1 radiation (λ = 1.5405 Å), in the 2θ range of 10–80° and Raman spectra with a 514 nm excitation wavelength. Scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDS) system (Quanta 400/INCA) was used to analyse the microstructure and composition contents of the films. Electrical properties of the CZTS thin films, including carrier concentration, carrier mobility and resistivity, were determined by a Hall effects measurement system (PhysTech RH2035) using the van-der-Pauw method. The measured error is < 2%. The optical transmittance spectra were determined from a UV–visible spectrophotometer (Hitachi U-4100).

3. Results and discussion

Fig. 1(a) shows the XRD spectra of the post-sulfurized CZTS thin films deposited under different pressures. Three strong peaks were located at 28°, 47°, and 56°, which are corresponded to the (112), (220) and (312) of the Kesterite-CZTS phase with preferential orientation in the plane (112) (PDF# 26-0575). The peaks' intensities show an increase tendency when the working pressure decrease, indicating the improving of crystallinity of the film. Moreover, several weak peaks corresponding to (101) and (200) appeared in the XRD pattern of the sample deposited at 0.2 Pa. No peaks of the impurity were observed for any of the samples, which confirmed the high purity of the films. Fig. 1(b) displays the curve of peak intensity and FWHM of the (112) peak versus deposition pressure. The peak intensity increased and the FWHM decreased with a decrease in the deposition pressure. Both of the curves indicate that a lower deposition pressure is beneficial for subsequent sulfurization. Because the lower depositing pressure resulted in longer mean free path of CZTS granulations when the particles transport from target to the substrate. Therefore, CZTS granulations got higher kinetic energy for microstructure rearrangement in the procedure of deposition. It is beneficial to the recrystallization of CZTS film in sequent sulfurization.

In order to further evaluate the influence of sulphur pressure, subsequent sulfurization was conducted at different sulphur concentrations. From Fig. 2(a), we can know that the diffraction peaks were sharp and intense, reflecting the crystallinity of the films were superior. Moreover, no obvious peak of secondary phase was observed in the XRD patterns, indicating a pure phase constituent of the films. The changes in the relative peak intensity of three orientation (112), (220), (312) were observed, which indicated a degree of preferential orientation of the sulfurized CZTS thin films. The degree of enhancement of a particular set of *hkl* planes is given by the texture coefficients, TC_{hkl}. It can be inferred from the following equation [19]:

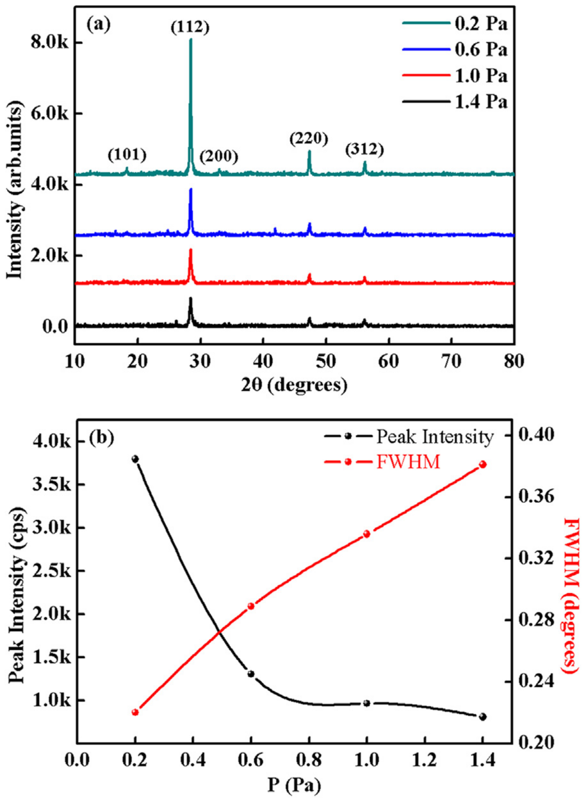

Fig. 1. Spectra of CZTS thin films deposited under different pressures and sulfurized at 500 °C: (a) XRD patterns; (b) Intensity and FWHM of the (112) peak.

$$TC_{hkl} = \frac{I_{(hkl)}/I_{0(hkl)}}{\frac{1}{n}\Sigma n I_{(hkl)}/I_{0(hkl)}} \tag{1}$$

where TC is the texture coefficient of the (*hkl*) plane, $I_{(hkl)}$ is the measured intensity of the (*hkl*) plane of interest, $I_{0(hkl)}$ is the intensity of the same peak in the reference spectrum which is considered a completely randomly oriented sample and *n* is the reflection number. Fig. 2(b) shows TC_{hkl} for selected diffracting planes. The TC along (112) orientation is larger than that of (312) and (220) orientations. Therefore, orientation along the (112) direction can be confirmed. Based on the FWHM values in the XRD pattern, Scherrer's Equation (2) can be used to infer the grain size of the film [19]:

$$D = \frac{0.9\lambda}{\beta \cdot \cos\theta} \tag{2}$$

where the grain size is defined as *D*, the wavelength of the x-ray used λ is 1.5405 Å, β is the FWHM and θ is diffraction angle. The average grain size as a function of the sulphur's mass for all specimens is presented in Fig. 2(c). It can be seen that the mass of sulphur has significant influence on the grain size of the film. The grain size calculated from (112) peak decreased from 92 nm to 49 nm as the mass of sulphur increased to 100 mg, then it increased to 96 nm when the mass was increased to 150 mg. In short, for the film annealed in sulphur atmosphere, with the