



Letter

In situ growth of $\text{Cu}_2\text{ZnSnS}_4$ thin films by reactive magnetron co-sputtering

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ABSTRACT

High-quality $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were first *in situ* grown by a reactive magnetron co-sputtering technique. Raman examination and XRD analysis indicate that the grown film shows a single CZTS phase with good crystallinity and strong preferential orientation along (1 1 2) plane. SEM analysis reveals a homogeneous, compact surface morphology and large columnar grains throughout thickness for the film. The *in situ* grown CZTS film demonstrates an optical absorption coefficient of higher than 10^4 cm^{-1} and an optical band gap of $1.52 \pm 0.01 \text{ eV}$. The carrier concentration, resistivity and mobility of the CZTS film are $3.9 \times 10^{16} \text{ cm}^{-3}$, $5.4 \Omega \text{ cm}$ and $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively and the conduction type is p-type. These optical and electrical properties are suitable for a thin film solar cell fabrication.

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1. Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a promising new material for thin film solar cell application that contains earth-abundant elements and has a near-optimum direct band gap energy of about 1.5 eV and a large absorption coefficient ($> 10^4 \text{ cm}^{-1}$) [1]. Solar cells based on CZTS absorber have achieved conversion efficiencies as high as 6.77% under AM1.5G illumination [2].

Up to now, all $\text{Cu}_2\text{ZnSnS}_4$ thin films reported are prepared by thermally activated processes like evaporation (including multi-stage [3] and co-evaporation [4,5]), which is very difficult to scale up, or sequential processing consisting of the deposition of the alloy precursors followed by post-annealing, where the precursors can be deposited by various methods such as atom beam sputtering [6], electron beam evaporation [7,8], RF sputtering [9,10], hybrid sputtering [11], pulsed laser deposition [12], photochemical deposition [13], sol-gel [14], spray pyrolysis [15–17], electrodeposition [18,19] and soft-chemistry [20]. However, for large scale production of thin film solar cells a direct one-step deposition process is needed. Fortunately, reactive magnetron co-sputtering is a well suitable technique for this task. Reactive magnetron co-sputtering can simply provide control on film composition at a relatively low cost by adjusting the ratio of the powers applied to the targets and is suitable for large-area, continuous and multicomponent film deposition. This method is already an established technique for the preparation of thin films for magnetic, optical and contact applications [21,22].

In this work, therefore, we first present a reactive magnetron co-sputtering technique for the *in situ* growth of $\text{Cu}_2\text{ZnSnS}_4$ thin films and the compositional, structural, optical and electrical properties of the films have been characterized.

2. Experimental

The depositions of the $\text{Cu}_2\text{ZnSnS}_4$ films on soda-lime glass substrates have been performed in a reactive magnetron co-sputtering system with three sputtering targets of 60 in diameter and 5 mm in thickness. Prior to film deposition, the sputter chamber was evacuated to approximately 10^{-4} Pa . The substrates were rinsed in acetone, methanol and deionized water ultrasonically, then dried with nitrogen gas and loaded in the reaction chamber. The distance between target and substrate was about 120 mm and the substrate holder rotated at a frequency of 4 rev/min. H_2S (purity: 98.0%) was solely introduced as both reactive and working gas during the sputter deposition with a flow of 40 sccm, and the sputtering pressure was controlled to 1 Pa. The sputtering source was operated using metallic copper, zinc and tin targets and the magnetron plasmas were excited independently by three dc power supplies. During the deposition, the substrate was heated to temperatures of 500 °C. The growth time was 30 min.

The surface morphology, chemical composition and crystalline properties of the films were analyzed by scanning electron microscopy (SEM, JSM-6360LV), energy dispersive X-ray spectroscopy (EDS, EDAX-GENESIS60S) and X-ray diffraction (XRD, Rigaku3014), respectively. The optical properties of the films were determined by Shimadzu UV-2450 spectrophotometer. Electrical resistivity, carrier concentration and carrier mobility of the CZTS films were measured using van der Pauw geometry

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and Hall effect measurement (HMS-3000/0.55T) at room temperature using indium ohmic contacts. The Raman spectra were taken using a Jobin-Yvon LabRAM HR800-Horiba spectrometer coupled with an Olympus metallographic microscope. Excitation was provided with the 632.8 nm line from a He–Ne laser due to the minimization of thermal effects achieved with this wavelength. The laser spot on the sample is about 1 μm and the penetration depth of this light on CZTS is estimated below 200 nm.

3. Results and discussion

The chemical composition of the deposited film determined by EDS analysis is the following: 24.69 Cu, 13.16 Zn, 12.09 Sn and 50.05 at% S. This is almost stoichiometric but slightly Zn-rich and Cu-poor composition can lead to good optoelectronic properties according to previous reports [8,23].

Fig. 1(a) illustrates the typical Raman spectrum of the CZTS film *in situ* grown on soda-lime glass by reactive magnetron co-

sputtering. From the spectrum, one can evidently observe a single peak at about 336 cm^{-1} , which corresponds to quaternary CZTS [24]. This result is in good agreement with the Raman spectrum of CZTS film reported by Fernandes et al. [25]. In addition, it is evident that there are no additional peaks related to the presence of other compounds, which means that the single phase CZTS film was obtained.

To obtain further insight into the crystalline quality, the film was characterized by XRD, as shown in Fig. 1(b). The sharp peak at $2\theta=28.48^\circ$ can be attributed to the diffraction of (1 1 2) plane of kesterite or stannite structure CZTS in combination with Raman analysis in Fig. 1(a) and its peak intensity was observed to be much greater than other peaks, revealing strong preferential orientation along (1 1 2) plane. However, it is very difficult to distinguish the structure between kesterite and stannite due to the fact that the XRD patterns of these two structures differ only slightly in the splitting of high order peaks, such as (2 2 0)/(2 0 4) and (1 1 6)/(3 1 2) resulted from a slightly different tetragonal distortion ($c/2a$) [26]. Moreover, the full width at half maximum (FWHM) of the diffraction peak is very small, which indicates that the film crystallinity is fairly good. Also, no extra phases of other compounds such as binary sulfides were observed within the detection limits of XRD analysis.

Fig. 2(a) and (b) shows the SEM micrographs of the surface morphology and cross-section of the CZTS film, respectively. In Fig. 2(a), the film shows a homogeneous, polycrystalline and extremely dense morphology without any voids, and consists of grains with uniform size of about 100 nm. From the cross-section of the film as shown in Fig. 2(b), it can be seen that film with a thickness of 800 nm and excellent crystallinity and compactness has been grown on substrate. It should be remarked that columnar grains extending from the bottom to the top of the CZTS layer were observed. This feature is similar to that of Cu(In,Ga)Se₂ (CIGS) films prepared by three-stage co-evaporation leading to the highest conversion efficiency of 19.9% [27], and beneficial to decreasing the minority carrier recombination during transport process when applied to solar cell.

Fig. 3(a) shows the optical absorption coefficient (α) of the CZTS thin films as a function of photon energy ($h\nu$). The absorption coefficient is larger than 10^4 cm^{-1} in the visible region, which is consistent with those reported in earlier published results [6,11,14,17,19,28], and therefore, the film is considered to be a suitable material for photovoltaic solar energy conversion. Based on the allowed direct interband transition, the band gap is determined to be $1.52 \pm 0.01\text{ eV}$ by extrapolating the linear $(\alpha h\nu)^2$ vs. $h\nu$ plots to $(\alpha h\nu)^2=0$, as depicted in Fig. 3(b), which is also in agreement with band gaps reported for CZTS films by other authors [6,11,14,19,28–30]. This value is quite close to the theoretical optimal value for a single-junction solar cell. Above optical characteristics indicate that the CZTS film *in situ* grown by reactive magnetron co-sputtering can be applied to the absorber layer of thin film solar cells.

The hot-probe measurement indicates that the CZTS thin film exhibits p-type conductivity. The Hall coefficient, carrier concentration, resistivity and mobility of the CZTS film tested using Van der Pauw method are $+1.6 \times 10^2\text{ cm}^3\text{ C}^{-1}$, $+3.9 \times 10^{16}\text{ cm}^{-3}$, $5.4\ \Omega\text{ cm}$ and $30\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, respectively. The result of Hall coefficient confirms the p-type conductivity of CZTS films again. The value of carrier concentration is comparable with values for device quality CIGS [31,32] and similar to those reported by Scragg et al. [18,30] and Katagiri [23] (10^{16} cm^{-3}), but lower than those found by Ito and Nakazawa [6], Tanaka et al. [11] and Zhang and Shao [33] ($10^{18}\sim 10^{19}\text{ cm}^{-3}$), who reported that the high carrier concentration might be due to the presence of Cu_xS second phase leading to the conversion film into useless degenerate semiconductor, because no second phase except for CZTS was found in our film

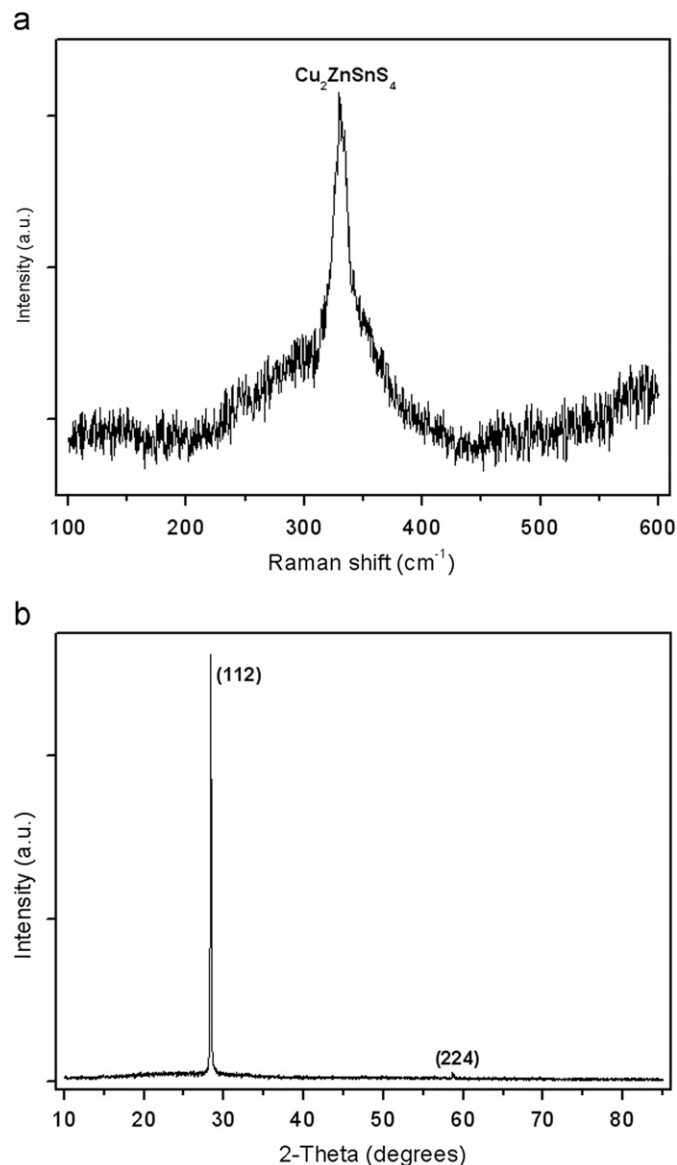


Fig. 1. (a) Raman spectrum of the CZTS film *in situ* grown by reactive magnetron co-sputtering. (b) XRD pattern of the CZTS film *in situ* grown by reactive magnetron co-sputtering.

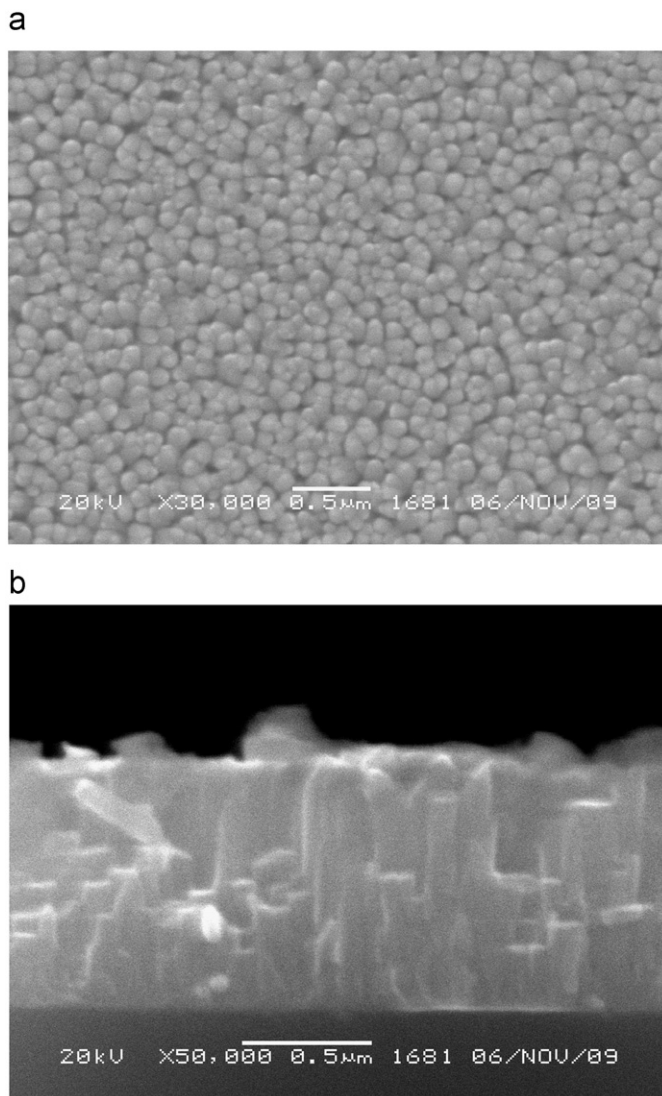


Fig. 2. SEM images of the CZTS film *in situ* grown by reactive magnetron co-sputtering showing (a) top view and (b) cross section.

from Raman and XRD data. The film shows a resistivity of a few Ω cm, in agreement with the Cu-poor and Zn-rich CZTS films prepared by sulfurization of metallic precursors [34] or spray pyrolysis [15,35]. Mobility of close to $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is higher than those reported by others [6,11,33], which may be attributed to better structural quality (such as large grain throughout the film thickness, and lower defect and dislocation density accordingly). The electrical properties of the film can meet the requirements for the applications in thin film solar cells.

4. Conclusions

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were *in situ* grown on soda-lime glass substrates by a reactive magnetron co-sputtering technique and characterized by Raman, XRD, SEM, EDS, optical transmittance and electrical measurements. The film shows a stoichiometric composition and a single CZTS phase with good crystallinity and strong preferentially oriented along (1 1 2) plane. It also has a homogeneous and dense surface morphology, large columnar grains throughout the film thickness, and an optical band gap of $1.52 \pm 0.01 \text{ eV}$. The carrier concentration, resistivity

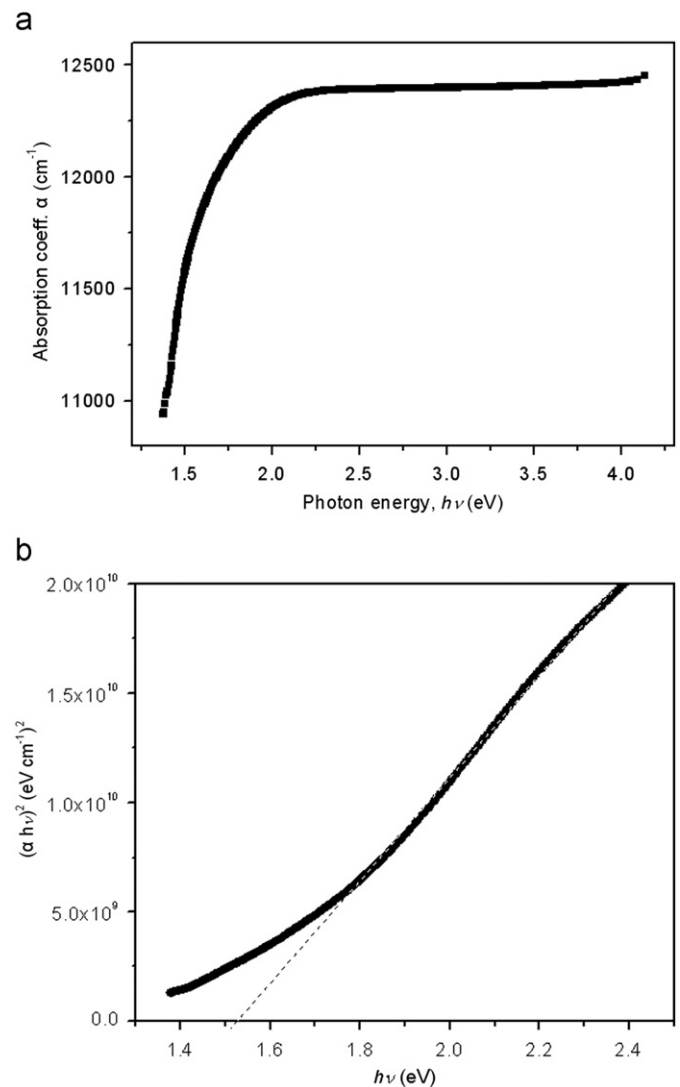


Fig. 3. (a) Optical absorption coefficient (α) of the CZTS film *in situ* grown by reactive magnetron co-sputtering. (b) $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for CZTS film *in situ* grown by reactive magnetron co-sputtering.

and mobility of the CZTS film are $3.889 \times 10^{16} \text{ cm}^{-3}$, $5.4 \Omega \text{ cm}$ and $29.75 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively and the conduction type is p-type. These optical and electrical properties are suitable for a thin film solar cell fabrication.

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