Preparing Cu_2ZnSnS_4 films using the co-electrodeposition method with ionic liquids*

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Cu_2ZnSnS_4 (CZTS) films are successfully prepared by co-electrodeposition in aqueous ionic solution and sulfurized in elemental sulfur vapor ambient at 400 °C for 30 min using nitrogen as the protective gas. It is found that the CZTS film synthesized at Cu/(Zn+Sn)=0.71 has a kesterite structure, a bandgap of about 1.51 eV, and an absorption coefficient of the order of 10^4 cm^{-1}. This indicates that the co-electrodeposition method with aqueous ionic solution is a viable process for the growth of CZTS films for application in photovoltaic devices.

Keywords: sulfurization, Cu_2ZnSnS_4, co-electrodeposition

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1. Introduction

The $CuZnSnS_4$ (CZTS)-based solar cell is currently considered to be one of the next-generation thin-film solar cells because it is free from scarce and toxic elements and has reduced cost for mass production.[1,2] It is known that CZTS has a direct bandgap between 1.45 eV and 1.6 eV and an absorption coefficient of 10^4 cm^{-1} in the visible light range. Recently, CZTS solar cells have been reported to achieve a conversion efficiency of 6.7% by using a co-sputtering process followed by annealing in H_2S.[3] For a CZTS- or copper indium gallium selenide (CIGS)-based solar cell, two advances are very important: one is the introduction of the non-vacuum deposition system, and the other the development of a way to conveniently control the element molar ratios to avoid the formation of the secondary phase. Among the feasible non-vacuum routes for preparing solar cell materials, the electrodeposition of precursor layers followed by thermal annealing has been shown to be very promising.[4–6] The carrier concentration of CZTS films formed by sequential electrodeposition of the constituent metals followed by annealing in sulfur vapor is estimated to be less than 5×10^{16} cm^{-3}, which is suitable for a thin-film absorber.[7,8] In this paper, co-electrodeposition of copper zinc tin films is performed using an aqueous choline-based ionic solution. The CZTS films are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman scattering, and ultraviolet–visible–near infrared (UV–Vis–NIR) spectrophotometer measurements.

2. Experiment

An SnO_2:F coated glass substrate was used as the working electrode (cathode), and a tin sheet was used as the counter electrode (anode). Depositions were carried out at room temperature without stirring. The solutions were prepared using deionized water and salts ($ZnCl_2$, $SnCl_2{\cdot}2H_2O$, $CuCl_2{\cdot}2H_2O$) of 4N purity. The $ZnCl_2$ and the $SnCl_2{\cdot}2H_2O$ concentrations in the solution were fixed to be 5 mmol/L, and the compositional ratio of Cu/(Zn+Sn) varied between 0.57 and 0.86. $Na_2S_2O_3$ was added into the solution to adjust the pH to 2.7, and a voltage of −1.1 V was applied during the co-electrodeposition process.

The deposited copper zinc tin films and some excess sulfur were loaded into a quartz container, which was inserted into a tube furnace. The tube was filled with nitrogen and heated at a rate of 50 °C·min^{-1} to 400 °C, which was then maintained for 30 min under a small flow of nitrogen. The system was then allowed to cool naturally.

The fabricated CZTS films were characterized

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by X-ray diffraction (XRD, X'pert Prower), scanning electron microscopy with an energy-dispersive spectrometer (SEM-EDS, JEOL-JSM-6700F/INCA-ENERGY), and Raman spectroscopy (Renishaw-2000) measurements. For the XRD measurements, θ–2θ scans were carried out from 20° to 60° at a scan rate of 3 °/min. For the Raman scattering measurement, the wavelength of the excitation light was 532 nm, and the power was 30 mW. The thicknesses of the films were estimated from micrographs of film cross sections, and the optical measurements were carried with a UV–Vis–NIR spectrophotometer.

3. Results

Figure 1 shows the XRD patterns of the samples prepared using different post-treatments. It can be found that no CZTS phase is observed in the as-deposited copper zinc tin precursor metal film obtained after the electrodeposition process. After annealing without the sulfur ambient, a CuO phase is present in the XRD spectrum, which is commonly seen among the electrodeposited films prepared using aqueous electrolytes.[9] When sulfur is used in the annealing step, CZTS film is formed by the incorporation of sulfur into the metallic precursor film during sulfurization, which then exhibits a kesterite structure with three major peaks at (112), (220), and (312), together with one other peak at (200). The results are in agreement with those reported by other groups.[4,10–12] In addition, it is important that no extra oxide phase is identified in the spectrum, which is due to the elimination reaction between S and O atoms. The secondary phase of $Cu_{2-x}S$ results from the metallic precursor film being Cu-rich.

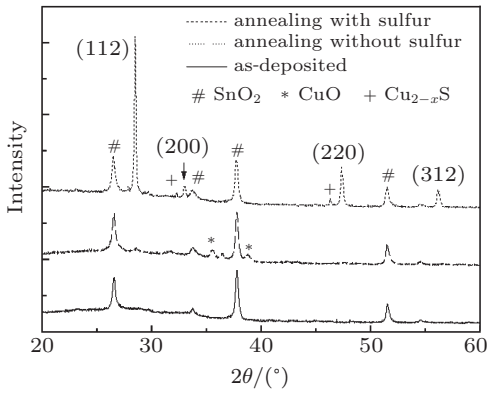


Fig. 1. X-ray diffraction patterns of samples prepared with different post-treatments. The peaks marked by # arise from the substrate.

The XRD patterns of the sulfurized CZTS films deposited at different Cu/(Zn+Sn) elemental ratios in the solutions are shown in Fig. 2. All the films are well grown with good crystallinity, and the (112)-oriented growth is observed to be dominant for all fabricated films. However, the impurity peaks from the $Cu_{2x}S$ phases are observed in the XRD results for the films prepared with higher Cu/(Zn+Sn) ratios, which results in the films being Cu-rich. This can be verified from the chemical composition ratios of the metallic precursors and CZTS shown in Table 1. The Cu/(Zn+Sn) ratio in the metal precursor film increases with the increase in Cu^{2+} concentration in the solution, and is higher than that in the solution, leading to a Cu-rich film. However, the S/metal ratio remains almost constant in all the CZTS films, so the $Cu_{2x}S$ phase is formed in the Cu-rich film. The Cu/(Zn+Sn) and the Zn/Sn ratios in the films slightly increase after sulfurization, which is caused by the evaporation of tin sulfide. It is notable that even with the existence of deviations in the Cu-ratio between the precursor films, good crystalline CZTS films with no noticeable impurity are obtained at Cu/(Zn+Sn)=0.71 after sulfurization.

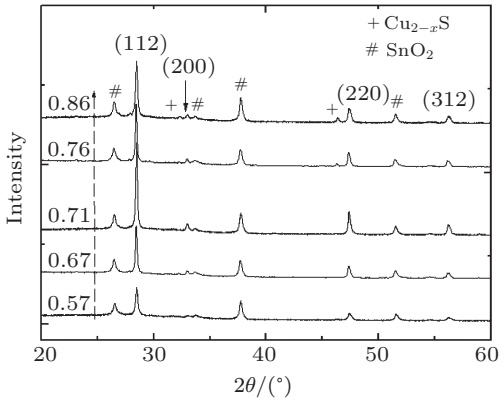


Fig. 2. X-ray diffraction patterns of Cu_2ZnSnS_4 films deposited at different Cu/(Zn+Sn) ratios. The peaks marked by # arise from the substrate.

Figure 3 shows Raman spectroscopy results for the same films used in Fig. 2. Like the XRD results, the peaks from the $Cu_{2-x}S$ phases are observed near 475–490 cm^1 for the films prepared with higher Cu/(Zn+Sn) ratios, which result in Cu-rich films. Raman peaks at $\sim$ 252 cm^1, $\sim$ 287 cm^1, $\sim$ 338 cm^1, $\sim$ 351 cm^1, and $\sim$ 368 cm^1 are reported to be from the kesterite CZTS, and the biggest peak is known to be positioned at $\sim$ 338 cm^{-1}.[13,14] For all films, the full widths at half maximum (FWHMs) for the 338 cm^{-1} peak are measured. The results are distributed between 7.8 cm^{-1} and 9.5 cm^{-1}. The minimum FWHM, 7.8 cm^{-1}, is for the CZTS film deposited at Cu/(Zn+Sn)=0.71.

Table 1. The composition ratios in metallic precursor layers and CZTS films.

Solution	Precursor metallic layer			CZTS		
Cu/(Zn+Sn)	Cu/(Zn+Sn)	Zn/Sn	Cu/Sn	Cu/(Zn+Sn)	Zn/Sn	S/metal
0.57	0.84	1.04	1.71	0.86	1.06	0.95
0.67	0.86	1.05	1.76	0.87	1.08	0.94
0.71	0.86	1.04	1.75	0.87	1.06	0.95
0.76	0.94	1.05	1.93	0.98	1.08	0.94
0.86	1.18	1.05	2.42	1.22	1.07	0.96

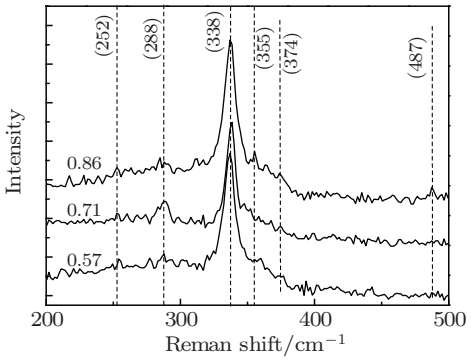


Fig. 3. Raman spectroscopy results of CZTS films deposited at different Cu/(Zn+Sn) ratios; the same films as those shown in Fig. 2 are used.

The SEM images of the CZTS films deposited at different Cu/(Zn+Sn) ratios are shown in Fig. 4. In these SEM images, we find that the grain sizes and the densities of the CZTS films increase with the increase in Cu^{2+} concentration in the solution. However, at higher Cu/(Zn+Sn) elemental ratios, massive voids are observed in the films. This result is consistent with the Raman spectroscopy result, where the CZTS films deposited at Cu/(Zn+Sn)=0.71 show the smallest FWHM.

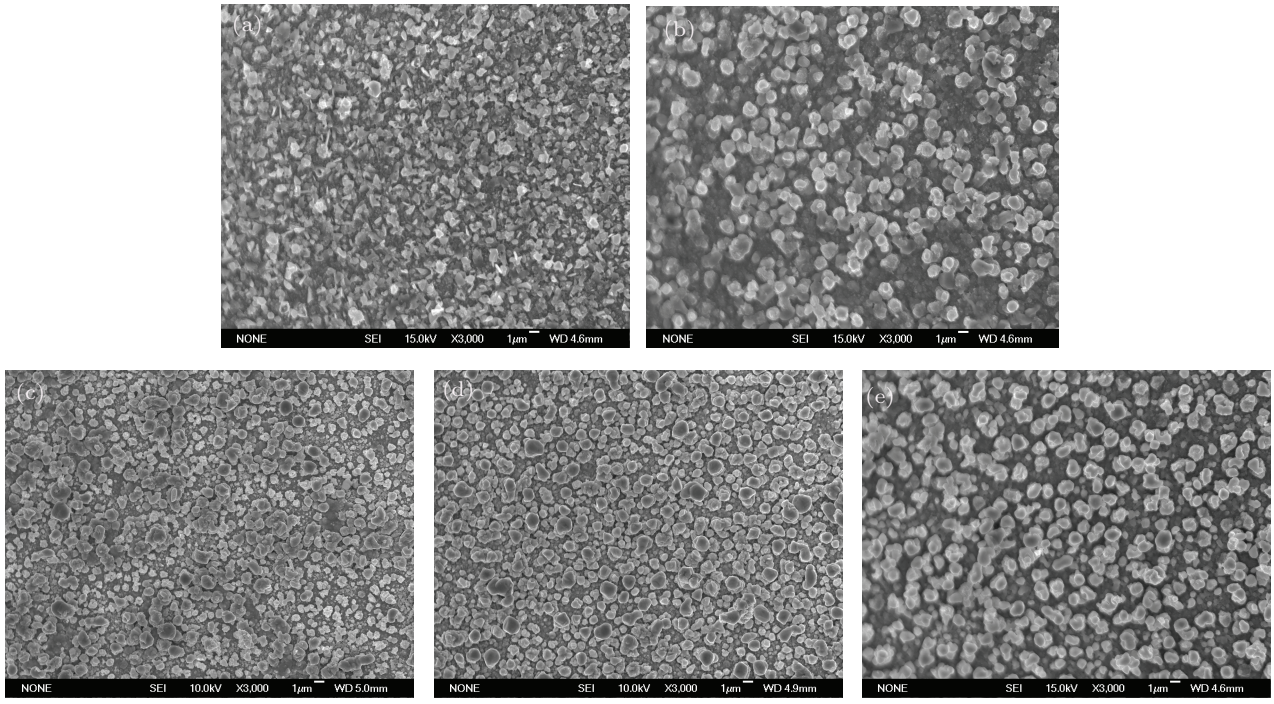


Fig. 4. SEM images of CZTS films deposited at Cu/(Zn+Sn) ratios of (a) 0.57, (b) 0.67, (c) 0.71, (d) 0.76, and (e) 0.86.

The optical transmittances of the CZTS films were measured using a tungsten lamp as the light source. The wavelength of the incident radiation ranges from 560 nm to 1040 nm. The transmitted radiation was measured using an optical power meter for the evaluation of the absorption coefficient α.[15] The experimental results for $(\alpha h\nu)^2$ versus photon energy $h\nu$ are shown in Fig. 5. The absorption coefficients

for all films in the visible region are of the order of 10^4 cm^{-1}, and are comparable to the reported results from the other research groups.[1,4,9,16] However, it is obvious that the absorption coefficient increases with the increase in the Cu/(Zn+Sn) ratio in the solution, and reaches the maximal value at the Cu/(Zn+Sn) ratio of 0.71. For a direct bandgap semiconductor, the absorption coefficient can be evaluated from expression $(\alpha h\nu)^2 \propto (h\nu - E_{\rm g})$, where $E_{\rm g}$ is the bandgap. The bandgap can be deduced from the x intercept shown in Fig. 5. We find that with the increase in the Cu/(Zn+Sn) ratio, $E_{\rm g}$ decreases from 1.52 eV to 1.47 eV. Such a bandgap shift can be related to the formation of $Cu_{2-x}S$, as shown in the XRD and Raman results, which is characterized by an absorption onset at 1.114 eV.[17] The bandgap of the CZTS film prepared with Cu/(Zn+Sn)=0.71 is found to be 1.51 eV, which is close to the theoretical optimal value for a single-junction solar cell.

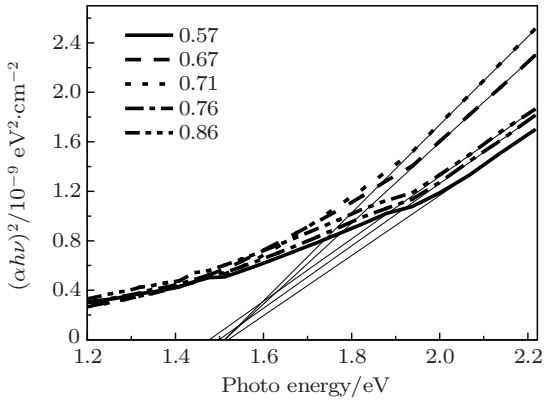


Fig. 5. Experimental results of $(\alpha h\nu)^2$ versus the incident photon energy for CZTS films prepared with different Cu/(Zn+Sn) ratios.

4. Conclusion

It is shown that the co-electrodeposition-annealing route can be used to prepare CZTS films, and that the formation of the secondary phase can be conveniently suppressed through changing the element ratio in the aqueous solution. The results also show that the oxide impurity in the film is removed by the elimination reaction between S and O atoms. The CZTS film synthesized at Cu/(Zn+Sn)=0.71 has a kesterite structure, an energy bandgap of about 1.51 eV, and an absorption coefficient of the order of 10^4 cm^{-1}. So this low-cost deposition method may be progressed and adopted for the fabrication of CZTS-based solar cells.

References

[1] Kamoun N, Bouzouita H and Rezig B 2007 *Thin Solid Films* **515** 5949

[2] Zhang K, Liu F Y, Lai Y Q, Li Y, Yan C, Zhang Z A, Li J and Liu Y X 2011 *Acta Phys. Sin.* **60** 028802 (in Chinese)

[3] Katagiri H, Jimbo K, Maw W S, Oishi K, Yamazaki M, Araki H and Takeuchi A 2009 *Thin Solid Films* **517** 2455

[4] Chan C P, Lam H and Surya C 2010 *Solar Energy Materials & Solar Cells* **94** 207

[5] Scragg J J, Dale P J and Peter L M 2009 *Thin Solid Films* **517** 2481

[6] Lincot D, Guillemoles J F, Taunier S, Guimard D, Sicx-Kurdi J, Chaumont A, Roussel O, Ramdani O, Hubert C, Fauvarque J P, Bodereau N, Parissi L, Panheleux P, Fanouillere P, Naghavi N, Grand P P, Benfarah M, Mogensen P and Kerrec O 2004 *Solar Energy* **77** 725

[7] Lincot D, Meier H G, Kessler J, Vedel J, Dimmler B and Schock H W 1990 *Sol. Energy Mater.* **20** 67

[8] Guillen C, Herrero J and Lincot D 1994 *J. Appl. Phys.* **76** 359

[9] Tanaka K, Oonuki M, Moritake N and Uchiki H 2009 *Solar Energy Materials* & Solar Cells **93** 583

[10] Scragg J J, Dale P J and Peter L M 2008 *Electrochemistry Communications* **10** 639

[11] Tanaka K, Moritake N and Uchiki H 2007 *Solar Energy Materials & Solar Cells* **91** 1199

[12] Scragg J J, Dale P J, Peter L M, Zoppi G and Forbes I 2008 *Physica Status Solidi* b **245** 1772

[13] Fernandes P A, Salomé P M P and da Cunha A F 2009 *Thin Solid Films* **517** 2519

[14] Yoo H and Kim J 2011*Solar Energy Materials & Solar Cells* **95** 239

[15] El Moctar C O, Kambas K, Marsillac S, Anagnostopoulos A, Bernède J C and Benchouck K 2000 *Thin Solid Films* **371** 195

[16] Todorov T, Kita M, Carda J and Escribano P 2009 *Thin Solid Films* **517** 2541

[17] Mulder B J 1973 *Phys. Stat. Sol.* (a) **18** 633