

Preparation of $\text{Cu}_2\text{ZnSnS}_4$ film by printing process for low-cost solar cell

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Abstract. $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) film was prepared by screen printing process with the advantages of simple, high-effective and cost-effective. The annealing effects on the screen printed CZTS films were studied. It was found that the crystallinity of the CZTS can be effectively improved by the annealing process, whereas overlong annealing can also introduce defects to the CZTS. The bandgap value of the CZTS is about 1.4 eV. The short-circuit current density, open-circuit voltage, fill factor and conversion efficiency of the best solar cell with superstrate structure of Carbon/CZTS/ In_2S_3 / TiO_2 /FTO glass (without using any vacuum conditions) are 6.20 mA/cm², 290 mV, 0.29 and 0.53%, respectively.

Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is one of the most promising absorber materials for low-cost solar cell application. It has near-optimal direct bandgap value of around 1.5 eV and large absorption coefficient ($>10^4/\text{cm}$) [1-3]. Katagiri et al [1] reported a CZTS solar cell with conversion efficiency of 6.77% from the substrate structure of Al/ZnO:Al/CdS/CZTS/Mo/soda lime glass (SLG), where the CZTS absorber layer was prepared by three sources co-sputtering process. However, the vacuum fabrication processes are rather expensive, complicated and difficult to scale-up for commercial production.

Non-vacuum solution processes such as screen printing [4], spin coating [5,6], spraying [7] and electrochemical deposition [8] are expected to fabricate cost-effective solar cells because of the low production cost. Among, screen printing is considered as a very promising commercial production process since it has the important advantages of simple, fast, low-temperature and near-100% material utilization efficiency.

In this study, we prepared the CZTS films by screen printing method. The annealing effects on the screen printed CZTS films were fully investigated by XRD, SEM and UV. In order to study the photovoltaic properties of the screen printed CZTS films, a simple superstrate structure of Carbon/CZTS/ In_2S_3 / TiO_2 /FTO glass was employed. The J-V characteristics of the screen printed CZTS films were analyzed. We aim to develop a cost-effective process for CZTS thin film solar cell.

Experimental detail

2.1 Preparation of CZTS films

2.1.1 Synthesis of CZTS precursor powder

Ball milling process was applied for the synthesis of CZTS precursor powder. Element powders Cu (99.9%, Wako Chemicals), Zn (99.9%, Wako Chemicals), Sn (99.5%, Aldrich) and S (99.9%, Kishida Chemicals) were mixed in molar ratio 2:1:1:4. The ball milling process was conducted by the planetary ball miller (M2-3F, Gokin) at various rotation speeds for 1 h to obtain single phase CZTS precursor powder. A rotation speed of 800 rpm was realized as suitable condition for this purpose.

2.1.2 Preparation of CZTS paste

The preparation scheme of CZTS paste is shown in Fig. 1. Briefly, the CZTS precursor powder was homogeneously dispersed in the viscosity controlling agent α -terpineol and ethyl-cellulose to make printable paste.

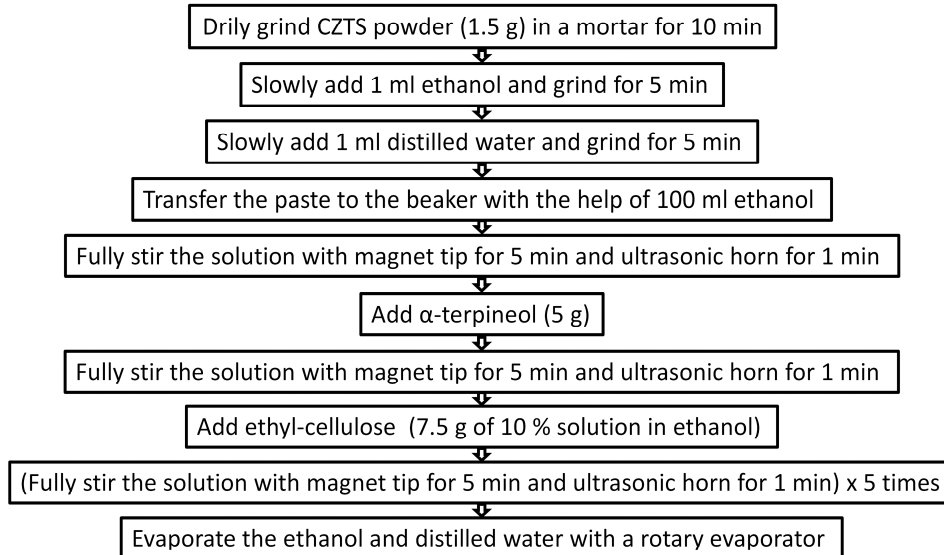


Fig. 1 Preparation scheme of CZTS paste

2.1.3 Deposition of CZTS films

In order to study the annealing effects on the screen printed CZTS, CZTS paste was deposited on glass substrates (glass/CZTS, CZTS films) by screen printing method and then annealed by Rapid Thermal Annealing (RTA) process in N_2 atmosphere (1 atm) at $600\text{ }^\circ\text{C}$ (high-temperature annealing can more effectively improve the crystallinity of the ball milled CZTS, whose particle size is rather big) for various durations. The annealed samples were characterized by XRD, SEM and UV.

2.2 Solar cell structure

For investigating the photovoltaic properties of the screen printed CZTS films, a superstrate structure of Carbon/CZTS/ In_2S_3 / TiO_2 /FTO glass was employed. The structure of the solar cell is depicted in Fig. 2. Both of compact TiO_2 window layer and In_2S_3 buffer layer were prepared by spray pyrolysis method similar to the previous reported Ref. [9,10], and their thicknesses were about 100 and 300 nm, respectively. Carbon paste was prepared in a similar way to that of the CZTS paste, where the graphite powder, Printex®L6 powder (Evonik) and TiO_2 powder (P25, Degussa) were mixed with weight ratio 2.4:3.6:0.5 to replace the CZTS precursor powder (see Fig. 1). The carbon electrode was deposited by screen printing method. The active area of the solar cell is $0.5\text{ cm} \times 0.5\text{ cm}$.

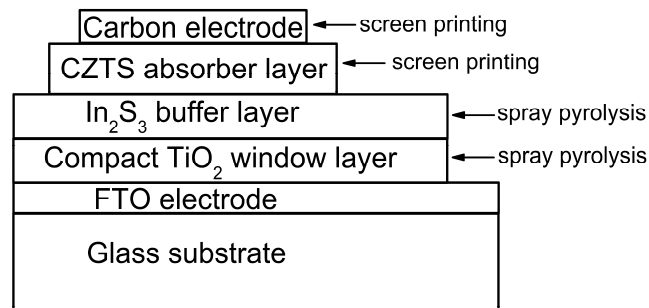


Fig. 2 Structure of the solar cell.

2.3 Characterization methods

Crystallinity and phase composition of the CZTS films were confirmed by X-ray diffraction spectrometer (XRD). Sample morphology was observed by Scanning Electron Microscope (SEM). UV spectra were recorded by UV/vis spectrophotometer (UV). J-V (short-circuit current density J_{sc} and open-circuit voltage V_{oc}) photoelectric conversion measurements of the completed solar cells were carried out under the AM 1.5 standard spectrum with 100 mW/cm^2 at room temperature.

Results and discussion

3.1 CZTS precursor powder

Figure 3 shows the XRD pattern of the CZTS precursor powder (as deposited) prepared at 800 rpm for 1 h. As shown in Fig. 3, the diffraction peaks of the precursor powder at the positions of 28.93 , 33.44 , 47.68 , 56.70 and 77° are correspondingly assigned to CZTS (112), (200), (220), (312) and (332) (PCPDF #260575). Therefore, from the XRD pattern, single phase CZTS precursor powder with preferred (112) orientation could be obtained by the simple ball milling process at 800 rpm for 1h.

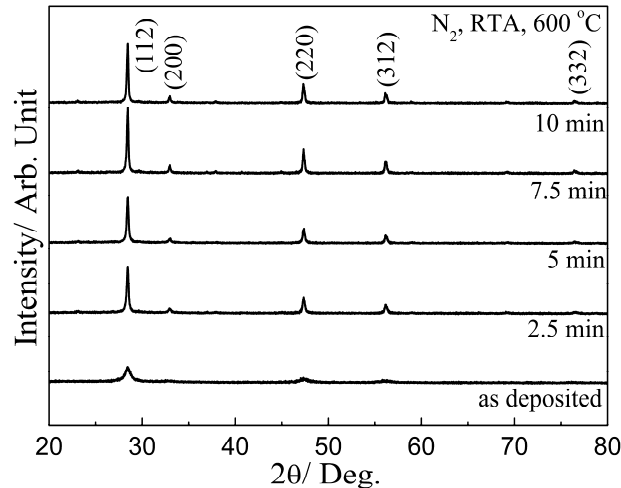


Fig. 3 XRD patterns of CZTS films prepared at various annealing durations.

Figure 4(a) shows the morphology of the CZTS precursor powder obtained by the ball milling process at 800 rpm for 1 h. The particle size of the powder was around 50 to 500 nm. Some small particles aggregated into big ones or clusters with diameter around 1 to 2 μm .

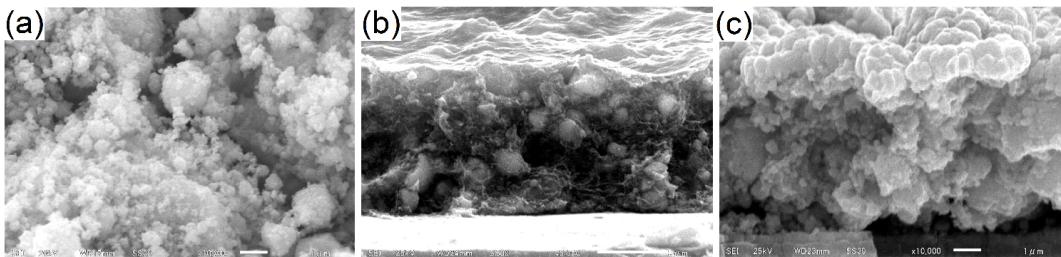


Fig. 4 SEM images of (a) CZTS precursor powder; (b) as deposited CZTS film; (c) CZTS film annealed in N_2 ambience at (600°C , 7.5 min).

3.2 Annealing effects on the screen printed CZTS films

In order to investigate the annealing effects on the properties of the screen printed CZTS, CZTS paste was deposited on glass substrates by screen printing method to prepare CZTS films (glass/CZTS). After drying treatment in air at 125°C for 5 min, the CZTS films were annealed by RTA process in N_2 ambience at 600°C for various durations.

3.2.1 XRD analysis

To confirm the crystallinity and phase composition of the CZTS films, XRD measurements were performed. Figure 3 depicts the XRD pattern of CZTS films prepared at various annealing durations. The XRD peak intensity is strongly dependent on the annealing duration. The peak intensity increases as the annealing duration increases, and reaches its maximum when annealing duration is 7.5 min. However, the peak intensity (specially the (112)) is distinctly decreased when the annealing duration is further increased to 10 min. This deterioration may be due to the evaporation of Sn and S atoms. It was reported that the evaporation of SnS occurred when annealing temperature exceeded 400 °C [11,12]. As a result, for the CZTS film, annealing duration of 7.5 min could be the optimal one.

3.2.2 UV analysis

In order to investigate the annealing effects on the optical properties of the screen printed CZTS films, we measured the UV absorption spectra (Fig. 5) of the samples annealed at different durations. As shown in Fig. 5: the as deposited film does not show clear absorption edge, possibly because of the amorphous nature of the CZTS, whereas all the annealed samples show clear absorption edges. This indicates that the crystallinity of the CZTS can be improved by the annealing process. However, in the long wavelength range (≥ 920 nm), the light absorption of the samples annealed for more than 5 min is rather high, which may be due to the existent of defects in the films after annealing at high-temperature for long duration.

In addition, from the absorption cutoff wavelengths, the calculated bandgap values of the samples annealed for 2.5, 5, 7.5 and 10 min are 1.287, 1.388, 1.407 and 1.415 eV, respectively. The bandgap value generally increases as the annealing duration increases. However, it seems that the bandgap values of the samples annealed for more than 5 min approximately keep at 1.4 eV, which is in agreement with the reported value of 1.45 eV [13].

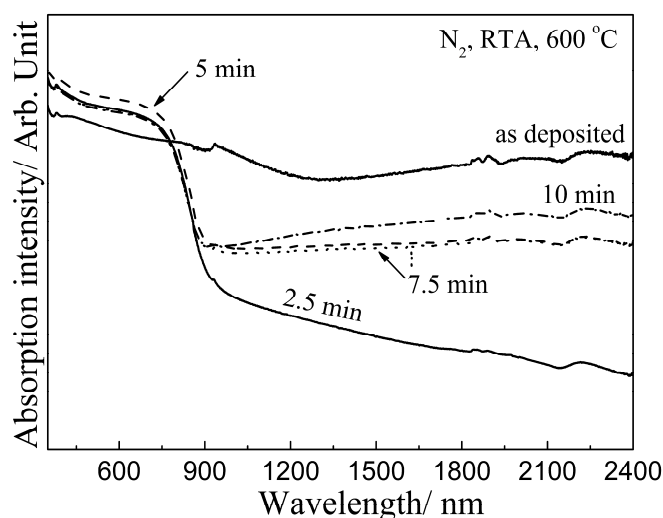


Fig.5 UV/vis absorption spectra of CZTS films prepared at various annealing durations.

3.2.3 SEM analysis

SEM images of as deposited and annealed CZTS films (for 7.5 min) are depicted in Fig. 4.

Figure 4 (b) shows the cross-section image of the as deposited CZTS film. As shown in the Fig. 4(b), the as deposited sample contains large amount of viscosity controlling agent, and the CZTS powder imbeds into them. Figure 4(c) shows the cross-section image of the sample annealed for 7.5 min. From the SEM picture, there is no visible viscosity controlling agent in the annealed CZTS film. However, there exist great morphological differences between the surface layer and deep layer of the annealed film. The surface layer turns out partly melted trace which may be due to the higher surface temperature during the annealing process, while the deep layer still shows powder-like morphology.

The annealed film does not turn out recrystallization even at such high annealing temperature of 600 °C, which may be due to the high melting point of the ball milling synthesized CZTS precursor powder. The particle size of the ball milling synthesized CZTS precursor powder is rather big, and hence its melting point is similar to that of the bulk CZTS material ~ 1000 °C. Therefore, for getting high quality CZTS absorber layer, it is necessary to synthesize low melting point CZTS nanoparticles or to add proper sintering additive into the CZTS paste [14,15].

3.2.4 J-V analysis

In order to analyze the photoelectric conversion properties of the screen printed CZTS films, completed solar cells with superstrate structure of Carbon/CZTS/In₂S₃/TiO₂/FTO glass were fabricated. Figure 6 shows the J-V characteristics of the samples annealed for various durations. As shown in Fig. 6, the J_{sc} of the solar cell increases as the annealing duration increases from 2.5 to 5 min. The increased J_{sc} may be due to the improved crystallinity of the CZTS by the annealing process. However, the J_{sc} is decreased as the annealing duration is further increased to 7.5 and 10 min. From Fig. 6, the best solar cell with 0.53% efficiency was obtained under the annealing duration of 5 min, which is not consistent with the XRD result as shown in the Fig. 3 (XRD result: for CZTS film, optimal annealing duration should be 7.5 min). It is reported that the buffer layer thickness can significantly affect the solar cell conversion efficiency [6], therefore, the shortened optimal annealing duration may have relation with the buffer layer thickness. That means, although the crystallinity of the CZTS film annealed for 7.5 min is better than that of 5 min, the buffer layer thickness after annealed for 7.5 min is too thin to be used for the solar cell. The thin buffer layer could result into leakage current and therefore decreased J_{sc}. For getting solar cell with improved efficiency, the buffer layer thickness should be optimized.

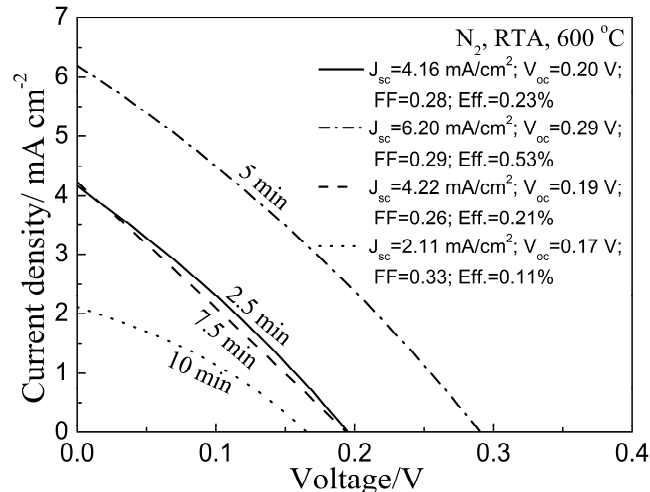


Fig.6 J-V characteristics of CZTS films prepared at various annealing durations.

4. Conclusions

CZTS films were prepared by screen printing process, and the annealing effects on the screen printed CZTS films were investigated. Experiment results indicate that: (1) Single phase CZTS precursor powder with preferred (112) orientation could be obtained by simple ball milling process; (2) Annealing parameters have strong effects on the structural, optical and morphological properties of the screen printed CZTS absorber layer; notably, annealing can also introduce defects to the CZTS; (3) The short-circuit current density, open-circuit voltage, fill factor and conversion efficiency of the best solar cell are 6.20 mA/cm², 290 mV, 0.29 and 0.53%, respectively; (4) The particle size of the ball milling synthesized CZTS precursor powder is rather big, which has high melting point and hence significantly limits the quality improvement of the solar cell absorber layer. Plans for improving the

solar cell conversion efficiency such as synthesizing low melting point CZTS nanoparticle, adding proper sintering additive into the CZTS paste or optimizing the buffer layer thickness are now under way. The screen printing process is simple, low-cost and high-speed, we believe it offers a promising way into cost-effective photovoltaic systems.

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