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Characterization of Cu$_2$ZnSnS$_4$ thin films prepared by solution-based deposition techniques

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Abstract

Cu$_2$ZnSnS$_4$ (CZTS) compound semiconductor has attracted considerable interest for use in low-cost thin-film PVs because of its earth-abundant constituents, optimal band gap, and high absorption coefficient. In this paper, CZTS thin films have been successfully prepared on soda-lime glass substrates by solution-based deposition techniques. The CZTS nanocrystals were synthesized by hot-injection method from copper (II) acetylacetone, zinc (II) acetate, tin (II) chloride and sulfide powder in an argon protection atmosphere. The as-synthesized nanocrystals were characterized by transmission electron microscopy (TEM). The structure, morphology, composition, and optical properties of the CZTS films were characterized using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectrometry, and UV-vis spectrometry. The XRD analysis demonstrated that CZTS thin films possessed a single-phase kesterite structure and no secondary phases were observed in the XRD diffraction pattern. The SEM micrographs showed the CZTS films were uniform, dense and had almost no voids. The chemical composition of CZTS films was nearly stoichiometric. The band gap was about 1.57 eV and the annealed CZTS thin films are very suitable for the absorber of solar cells.

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1. Introduction

Quaternary compound semiconductor Cu$_2$ZnSnS$_4$ (CZTS) has a direct band gap energy of 1.5 eV and high absorption coefficient >$10^4$ cm$^{-1}$ in visible wavelength region [1,2]. In particular, CZTS is inexpensive because Zn and Sn are earth-abundant elements compared with the rare metals such as In and Ga in CIGS and does not contain any toxic elements like Se [3]. From these unique features, CZTS is expected to be one of the promising materials for thin film solar cell. Therefore, if we can use CZTS film as absorber of solar cells, we will be free from both of the resource saving problem and the environmental pollution [4].

Many experimental techniques have been employed for preparing CZTS thin films: pulsed laser deposition technique [5], fast co-evaporation [6], co-sputtering technique [7]. However, these techniques involving high vacuums will bring a large capital cost. Recently, a new low cost, non-vacuum “ink”-based approaches-both from solutions and suspensions-are being developed for chalcogenide-based absorber layer deposition to replace potentially more expensive vacuum-based techniques[8]. Guo Qijie et al. [9] reported the hot-injection solution synthesis Cu$_2$ZnSn(Se,S)$_4$ nanocrystal absorber and used in the fabrication of solar cells with power conversion efficiency of 7.2%. Todorov et al [10] have reported the highest power conversion efficiency of 9.66% for Cu$_2$ZnSn(Se,S)$_4$ thin-film solar cell using the hydrazine-based solution processing. This method eliminates the need of high vacuum and high temperature, which is promising for the large scale fabrication of cost-effective solar cell absorber.

In the present work, we report on a novel fabrication process for fabricating thin films is that the semiconductor nanocrystals can be used in the form of a nanocrystal ink and a nanocrystal ink is coated on a substrate and sintered into thin film. CZTS nanocrystals prepared by hot-injection method were chosen as precursor and CZTS thin films were prepared by spin coating on soda-lime glass substrates.

2. Experiments

2.1. Synthesis of CZTS nanocrystals

All of the chemical reagents and solvents in the experiment were used as-received without further purification. In a typical synthesis of Cu$_2$ZnSnS$_4$ nanocrystals, 1 mmol of copper (II) acetylacetonate, 0.5 mmol of zinc (II) acetate dehydrate, 0.5 mmol tin (II) chloride dehydrate and 10 ml oleylamine were mixed in a 50 ml three-neck round-bottom flask connected to a Schlenk line. The mixture was heated to 130$^\circ$C under vacuum and degassed for 30 minutes and then purged with Ar. The evacuation and Ar bubbling process was repeated three times. The metallic precursor gradually turned into a brownish colored solution during this period. Meanwhile, 2 mmol of sulfur powder was sonicated in 5 ml oleylamine in another separated vial until an orange-red solution was formed. After the evacuation and Ar bubbling process, the metallic precursor was heated to 150$^\circ$C and then the sulfur-oleylamine solution was rapidly injected into it. After injection, the solution was heated to 230$^\circ$C for 1 h under an inert argon atmosphere. After the solution was cooled to room temperature, the reaction product was loaded into several 10 ml centrifuge tubes. Then 5 ml ethanol was added to each tube, and then centrifuged at 8000 rpm for 10 min. The supernatant was decanted and 2 ml toluene and 5 ml ethanol was added to the precipitate, and then centrifuged at 8000 rpm for 10 min. Finally, the CZTS nanocrystals were redispersed in toluene to form a stable nanocrystal ink for spin coating CZTS thin films.

2.2. Fabrication of CZTS thin films
The nanocrystal ink was spun coating at 4000 rpm for 30 s on soda lime glass substrate to form thin film. Then the coated wet films were transferred to a furnace for drying at 110°C for 10 min. The thickness was controlled by a multiple-coating technique. The precursor films required annealing in S vapor to form the final active layer, and sulfurizations were performed with a rapid thermal processing (RTP) system under N₂ atmosphere. The CZTS nanocrystal thin films were annealed at temperature of 450°C for 1 h.

The crystallographic properties of CZTS films were characterized by X-ray diffraction (XRD). The morphology of CZTS films was observed by scanning electron microscopy (SEM) and the compositions of CZTS thin films were measured by energy dispersive X-ray spectroscopy (EDS). The optical properties of CZTS thin films were analyzed by UV-vis spectrophotometer.

3. Results and discussion

Fig.1 shows the transmission electron microscopy (TEM) images of the as-synthesized CZTS nanocrystals. Fig.1a shows the high-resolution TEM (HRTEM) image of CZTS nanocrystals. The HRTEM image of CZTS nanocrystals reveal the interplanar spacing of the (112) plane to be 3.1Å. Fig.1b is a lower-magnification TEM image of the CZTS nanocrystals. The CZTS nanocrystals are slightly polydisperse and the crystalline size was estimated about 10-20 nm. The average size of the CZTS nanocrystals corresponds well with the crystalline size estimated from XRD analysis.

Fig. 1 The HRTEM (a) and lower-magnification TEM (b) images of CZTS nanocrystals.

Fig.2. XRD patterns of (a) as-synthesized CZTS nanocrystals coated on soda lime glass and (b) after annealing under S atmosphere at 450°C for 1 h. The intensity of the 112 diffraction line increased when the films were annealed, which indicated that CZTS thin film was preferred orientation to the 112 plane. The crystal domain size estimated from FWHM of the (112) peak by the Scherrer’s equation is about 14 nm. Diffraction peaks of the sulfurized film shifts slightly to small-angle direction due to lattice expansion after annealing. The annealed thin film shows peaks corresponding to the (112), (002), (101), (110), (200), (211), (220), (312) and (008) planes of a single kesterite CZTS phase (JCPDS card, No. 26-
0575) without secondary phases such as Cu$_2$SnS$_3$ and Cu$_{2-x}$S. Also, compared with Fig. 2a, the X-ray diffraction peaks sharpen, demonstrating that the grain size grows large after annealing.

Fig. 3a shows SEM image of as-synthesized CZTS nanocrystals coated on soda lime glass. The grains cannot be observed clearly. This may be due to the residual organic solvent like oleylamine, leading the grains to be wrapped. Fig. 3b shows the SEM image of thin film after annealing under S atmosphere at 450°C for 1 h. Compared with Fig. 3a, the crystalline size grows larger, demonstrating that annealing is in favor of grain grow. This tendency is in good agreement with the results of XRD analysis. The size of the grains in CZTS thin film with sulfurized at 450°C for 1 h was estimated to be larger than 1.0 μm, as shown in Fig. 3 (b). It is well known in general that efficiencies of polycrystalline solar cells increase with increasing grain sizes in the absorber materials. Therefore, the large grain growth in CZTS thin films is very much required for the fabrication of high-performance photovoltaic devices. The annealed thin film shows the relatively compact surface and has almost no voids. The thickness of annealed thin film approximates to 450 nm by surface profilometer.

![XRD patterns](image)

**Fig. 2** XRD patterns of as-synthesized CZTS without annealing (a) and CZTS thin film annealed under S vapor at 450°C for 1 h (b).

![SEM images](image)

**Fig. 3** Surface SEM images of the films (a) before annealing and (b) sulfurized at 450°C for 1 h.
The composition ratio of thin film annealed at 450°C for 1h was measured by energy dispersive X-ray spectroscopy (EDS). The Zn/Sn, Cu/(Zn+Sn) and S/metal ratio are about 0.87, 1.48 and 0.8, respectively. CZTS thin film annealed in atmosphere of N₂ was sulfur-deficient. The average composition is Cu₂.₅Zn₀.₈₇SnS₃.₇, indicating that the thin films deviated slightly from stoichiometric composition in comparison with the stoichiometric composition of CZTS. The slightly Zn poor deviated from stoichiometric CZTS may be due to the reactivities of different metal precursors. Further investigations are necessary to control the Cu and S content in CZTS thin films.

The UV-vis transmittance spectrum of annealed thin film is shown in Fig.4. The band gap is estimated from the \((\alpha h\nu)^2\) versus \(h\nu\) (where \(\alpha\) is absorption coefficient, \(h\nu\) is the photon energy) graph by
extrapolating the linear part of the curve. The band gap is estimated to be approximately 1.57 eV (Fig.5).

This estimated band gap energy is consistent with the literature values of 1.45–1.6 eV [11].

4. Conclusion

Cu2ZnSnS4 (CZTS) nanocrystals were synthesized by hot-injection method from copper (II) acetylacetonate, zinc (II) acetate dehydrate, tin (II) chloride dehydrate, sulfur and oleylamine. CZTS thin films were successfully prepared on SLG substrates by spin coating. The XRD analysis confirmed that the CZTS films exhibit the kesterite structure with preferential orientation along the (112) direction. The SEM micrographs showed the CZTS film was uniform, dense and had almost no voids. The chemical composition of the annealed thin film was nearly stoichiometric. The UV-vis data indicated that the CZTS thin film has an optical band gap of about 1.57 eV. The above results indicate that annealed CZTS thin films are very suitable for the absorber of solar cells. Studies on optimizing the synthesis processes and other parameters through precise control of the composition ratio of the CZTS thin films along with the fabrication of CZTS-based thin-film solar cells are currently underway.

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