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Fabrication of $Cu_2ZnSn(S,Se)_4$ absorber films by selenization of different Cu_2ZnSnS_4 nanocrystal coatings

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ABSTRACT

Kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) has been identified as one of the most promising thin film solar cell absorber candidates composed of earth-abundant elements. We demonstrate here an environmentally friendly and scalable solution-based approach to fabricating CZTSSe absorber films with Cu_2ZnSnS_4 (CZTS) nanocrystals by a selenization process. In this facile approach, phase pure and single crystal CZTS powders were synthesized with the method of molten salt reactions and dissolved in the nontoxic solution of ethanol and ethyl cellulose, forming a stable ink for depositing precursor films. It was found that the initial ink composition plays an important role in determining the properties of CZTSSe absorber films. All synthesized powders and films were analyzed with respect to their phase component, microstructure and chemical composition. The optoelectronic properties of CZTSSe absorber films investigated by UV–VIS spectrophotometer and Hall effect measurement can well meet the requirements for utilization in thin film solar cells, illustrating that the demonstrated approach has broad application prospects for CZTSSe solar cell production.

1. Introduction

$Cu(In,Ga)Se_2$ (CIGS) and related materials have attracted increasing attention for photovoltaic applications due to their unique structural and optoelectronic properties [1,2]. And the intensively investigated CIGS thin film solar cell demonstrated a world record of 22.6% photoelectric conversion efficiency (PCE) in 2016 [3]. However, the industrial production of CIGS based thin film solar cells has been hindered by the scarcity of In and Ga elements.

In recent years, thin film solar cells based on kesterite CZTS [4–7] has been widely researched as an alternative to CIGS. CZTS is a p-type semiconductor material composed of earth-abundant elements, which can compete with CIGS in terms of not only its excellent optoelectronic properties, such as high absorption coefficient ($> 10^4\ cm^{-1}$) and optimum direct band gap ($\sim$ 1.5 eV), but also its good photovoltaic performance (theoretical conversion efficiency is as high as 32.2%) [8–10]. Furthermore, the optoelectronic properties of CZTS based compound semiconductors can be tuned by forming mixed-anion alloys. For example, the substitution of Se for S, or vice versa, that occurs during a selenization or sulfurization process can be utilized to tune the band gap of CZTSSe film from 1.0 to 1.5 eV. The formation of a sulfoselenide compound leads to significant grain growth which generally benefits the device performance due to the dissolution and reformation of the anion-based lattice. The CZTSSe world record efficiency of up to 12.6% (by the IBM group) [11] is much higher than that of pure CZTS (9.2%; by Kato et al.) [12] and CZTSe (11.6%; by Lee et al.) [13] thin film solar cells.

A variety of techniques have been utilized to prepare CZTSSe absorber films, and most of the reported high efficiency CZTSSe solar cells were prepared based on a two-step procedure, namely, CZTS or CZTSe precursors deposition followed by a selenization or sulfurization treatment. The selenization of CZTS precursor films has been intensively studied by many different groups [14–18]. Wang et al. [19] presented a scalable route to fabricate CZTSSe with pure CZTSe nanocrystals by a sulfurization process for the first time. And numerous deposition methods for the preparation of CZTS or CZTSe precursor films have been reported, including vacuum-based [16,17,20,21] and solution-based [14,15,18,22] methods. Recently, much attention has been paid to solution-deposition routes since they have obvious advantages in costs associated with fabrication processes and commercial scale application compared with vacuum-based methods. CZTSSe solar cells with the highest efficiency (12.6%) [11] were typically fabricated by a solution-deposition method.

In this paper, we present an environmentally friendly, cost effective and facile colloidal solution route to prepare CZTSSe absorber films with CZTS powders by a selenization process. The overall preparation of CZTSSe absorber films involves three major steps. Firstly, phase pure and single crystal CZTS powders were prepared with the method of

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molten salt reactions instead of the frequently used hot injection [4,23]. A main advantage of molten salt reactions over the hot injection used for the preparation of CZTS powders is that it does not rely on toxic solvents. Next, ethyl cellulose, which replaced the toxic solvent of toluene, was used as a stabilizer in CZTS nanoparticles ink. The ink was subsequently coated on Mo-coated substrates by a modified blade coating method. Finally, the CZTS precursor coatings evolved into polycrystalline CZTSSe absorber films in a Se-containing environment at high temperatures. And the impact of ink composition on the properties of CZTSSe absorber films has also been studied.

2. Materials and methods

2.1. Molten salt synthesis of the kesterite CZTS powders

The source compounds of CuCl (97%, Aladdin), $C_4H_6O_4Zn$ (99%, Aladdin), $SnCl_4{\cdot}5H_2O$ (99%, Aladdin) and $Na_2S{\cdot}9H_2O$ (98%, Aladdin) were mixed and grinded in an agate mortar in the mole ratio 2:1:1:4.8. The mixture was filtered with deionized water (MilliQ, 18.2 MΩ cm) and absolute ethanol (99.5%, Aladdin) (Powder 1), and then the residue obtained was dried in an oven at 180 °C for 3 h (Powder 2). Molten salt system was composed of LiCl (99.9%, Aladdin) and KCl (99.5%, Aladdin) in the mole ratio 3:2. The weight ratio of CZTS precursors dried at 180 °C to molten salt was 0.8. Directly below that was an annealing process. The CZTS precursors and molten salt were heated to 550 °C for 1 h in a porcelain crucible under an argon atmosphere. When the reaction mixture was cooled to room temperature, the reaction product was collected and washed with deionized water to remove LiCl and KCl (Powder 3).

2.2. Preparation of CZTS precursor films by a modified blade coating method

CZTS absorber films were prepared in two stages. This was illustrated by first forming a stable blade coating ink. Approximately 200 mg as-prepared CZTS powders were dispersed in 5 ml oleylamine (85%, Aladdin) under ultrasonic processing condition. Then 5 ml absolute ethanol was injected into the solution and stirred for 2 h with 1 g of ethyl cellulose (CP, Aladdin) to afford the final ink. Ink 1, Ink 2 and Ink 3 correspond to Powder 1 (P1), Powder 2 (P2) and Powder 3 (P3), respectively. Next, CZTS precursor films were coated on bare soda lime glass substrates by a modified blade coating method. Fig. 1 shows the details on this stage. After each coating the films were annealed at 350 °C for 30 min under an argon atmosphere. This coating/sintering procedure was repeated three times to obtain the desired film thickness. Finally, CZTS absorber films were sintered into CZTSSe absorber films by exposing them under Se vapor at 550 °C for 30 min. Film 1 (F1), Film 2 (F2) and Film 3 (F3) correspond to Ink 1, Ink 2 and Ink 3, respectively.

2.3. Characterization

The crystallographic features of all powders and absorber films were characterized with a Rigaku X-ray diffraction using Cu Kα radiation (λ = 0.15405 nm). Raman spectroscopy was measured with a LabRAM HR Evolution using the argon laser with the excitation of 532 nm. The morphologies and compositional analysis of all samples were obtained on a field emission scanning electron microscope (FESEM, ZEISS SUPRA55) combined with energy-dispersive X-ray spectroscopy (EDS, Thermo-NS7). The chemical binding energy of CZTS powders was identified by high resolution X-ray photoelectron spectroscopy (XPS, AXIS ULTRA) using Al Kα ($h\nu$ = 1486.6 eV) as the exciting source. The crystallization of CZTS powders was analyzed by using a Tecnai G2 F30 at 300 kV. The optical properties of CZTSSe absorber films were determined by a UV–VIS spectrophotometer (UNICO). Carrier concentration and resistivity were measured using Hall effect measurement with van der Pauw method. Four silver point electrodes acted as the ohmic contacts were placed on the middle of each edge of the square films , and the magnetic field intensity and test current were 0.5 T and 1 μA respectively under dark testing environment.

3. Results and discussion

In order to study the growth mechanism of CZTS powders, powders at different reaction periods (P1, P2 & P3) were characterized by FESEM, XRD and Raman detectors (Fig. 2a-i). For filtered powders (P1; Fig. 2a, d & g), only three weak and wide peaks occur in its XRD spectra, but XRD alone is incapable of adequately identifying the presence of the secondary phases in a CZTS system, as different secondary phases has overlapping diffraction peaks with CZTS phase. The conclusive evidence comes from Raman spectra as it reveals typical characteristic vibrational modes for the secondary phases and CZTS phase. A sharp Raman peak assumed as the vibrational mode of $Cu_{2-x}S$ [14] at 474.4 cm^{-1} is dominant for P1, at the same time the visibly minor peaks attributed to other secondary phases are also observed. Fig. 2a presents a variety of microstructures, each microstructure corresponding to a type of phase composition. After powders were dried at 180 °C (P2; Fig. 2b, e & h), they exhibit higher and sharper XRD peaks, indicating that the crystallinity of P2 improves greatly. Besides, Raman spectra of P2 change apparently. The strength of $Cu_{2-x}S$, ZnS and Cu_3SnS_4 depending on their contents descends obviously, and the most intense peak at 337.5 cm^{-1} is assigned as the vibrational modes of CZTS phase [24]. The nanoparticles in P2 are uniform and severely agglomerated compared with those in P1. Upon completing 60 min of the molten salt reactions at 550 °C (P3; Fig. 2c, f & i), P3 shows intense peaks in XRD spectra at 23.14°, 28.44°, 29.68°, 32.95°, 47.37°, 56.15°, 58.93°, 69.17° and 76.48°, and all of them can be indexed to the (110), (112), (103), (200), (220), (312), (224), (008) and (332) planes of kesterite CZTS (JCPDS NO. 26-575), respectively. However, the minor diffraction peaks at 37.01° [(202)], 37.94° [(211)], and 44.96° [(105)] reveal the unambiguous presence of CZTS since these peaks are absent in the secondary phases (the inset in Fig. 2f). As for its Raman spectra, all of the noticeable characteristic peaks at 252.3 cm^{-1}, 287.1 cm^{-1}, 338.7 cm^{-1}, 350.0 cm^{-1} and 366.3 cm^{-1} are in accordance with the reported values for CZTS phase [24]. No peaks corresponding to the secondary phases were detected. Therefore, it could be concluded that P3 is phase pure within the detection limits of XRD and Raman characterizations. As shown in Fig. 2c, the phase transformation from sulfide nanoparticles to large CZTS grains was accompanied by grain growth up to micron level.

The growth mechanism is illustrated in Fig. 2j. During the grinding process, the most common binary and ternary metal sulfides easily formed because of their large negative formation enthalpies, in particular under room temperature conditions. Heat can be generated in partial region in the grinding process. When the chemical composition in part micro-area where heat was generated was near stoichiometric to CZTS, there was a distinct possibility that some CZTS nanoparticles formed. This phase of mixing and grinding may be referred to as the “Reaction of cationic and sulfide ions” stage. When the temperature raised up to 180 °C, the transition from binary and ternary phases to CZTS complex was accompanied by merging of metal sulfide nanoparticles. The mass transfer performance of solid state reactions was not good, so P2 still contained a small amount of the secondary phases which were not eliminated during the process. This is the reason why P2 is named as CZTS complex. We call this process as “Mergence of metal sulfide NPs”. At last P2 was transferred to the LiCl-KCl molten salt bath in which ions could migrate easily. The process of molten salt reactions comprised two steps: CZTS phase formation and grain growth. The residual secondary phases migrated together to form CZTS phase. Grain growth, in general, was driven by annihilation of high surface area and the corresponding large total surface energy. In order to prove the necessity of molten salts in the process of forming CZTS grains, P2