

Solution-based synthesis of dense, large grained $\text{CuIn}(\text{S}, \text{Se})_2$ thin films using elemental precursor

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ABSTRACT

Compared with the expensive and complicated vacuum techniques, the solution-based process to deposit I-III-VI₂ chalcogenide thin films (I=Cu, III=In or Ga, VI=S or Se) has attracted great interests due to its lower cost, higher scalable production and better application in flexible substrate. Herein, a low-toxic and high-active mixture solvent comprised of 1, 2-ethanedithiol and 1,2-ethylenediamine is utilized to dissolve elemental Cu, In and S powders at 60 °C, forming the CuInS_2 (CIS) precursor solution. After spin coating and annealing in a both Ar gas and selenium atmosphere, a dense and large-grained chalcopyrite $\text{CuIn}(\text{S}, \text{Se})_2$ (CISSe) thin films with a close-packed grain size of ~800 nm are prepared, eliminating a undesired fine fine-grained bottom layer. In addition, the selenization temperature of the CISSe thin films is also discussed, which influences the phase composition, crystallinity and morphology of CISSe thin films. Photovoltaic device of the CISSe-based thin films is fabricated, obtaining a power conversion efficiency of 6.2% with an active cell area of 0.5 cm² under AM 1.5 illumination.

1. Introduction

I-III-VI₂ chalcopyrite compounds such as CuInS_2 (CIS), CuInSe_2 (CISe), CuInGaSe_2 (CIGSe) and $\text{CuIn}(\text{S}, \text{Se})_2$ (CISSe) are promising optical-absorption materials due to their unique optical and electronic properties [1–3], such as tunable direct band gap, high absorption coefficient ($> 10^5 \text{ cm}^{-1}$), long-term excitation stability, weak-light response character and high tolerability to the defect and impurity. Up to now, the highest power conversion efficiency (PCE) of CIGSe photovoltaic (PV) device has reached 22.6% [4], which is a record among the fields of thin film PV devices. Most of the traditional fabrication methods of CISe-based PV devices with high efficiency are vacuum deposition techniques, such as three-step co-evaporation or magnetron sputtering methods [5,6]. On account of the high cost and complicated process of vacuum deposition techniques, the large-scale commercial production are inhibited [7]. Recently, a novel solution-based process to deposit I-III-VI₂ chalcogenide (I=Cu, III=In, Ga, VI=S, Se) thin films has attracted great interests due to its lower cost, higher scalable production and better application in flexible substrate [8–10], which may provide an efficient way to make the scalable production of CISe-based PV devices come true [11].

At present, many molecular-based solution processes have been utilized to prepare the high-quality I-III-VI₂ chalcopyrite thin films. For instance, Mitzi' group [12] utilized hydrazine solution to efficiently dissolve various metal sulfides and selenides (Cu_2S , In_2Se_3 , Ga_2Se_3 , Se and S) and obtained a high-quality CIGSSe thin films after selenization annealing, acquiring a PCE of 15.2%. Despite its efficiency, the large-scale production of this method is almost impossible due to the highly toxic and easily explosive properties of hydrazine. Therefore, finding a low-toxicity solvent as a substitute of the high-toxicity hydrazine is of important significance, and many efforts are working for this target. Cui et al. [13] used pyridine solution to dissolve $\text{Cu}(\text{acac})_2$, $\text{In}(\text{acac})_3$ and S and prepared the CIS thin films, fabricating a CIS-based solar cell with a PCE of 2.15%. Pan and his group [14] dissolved a number of different metal oxides in a mixed solvent of 1-butylamine and carbon disulfide (CS_2), fabricating a CIGSSe-based solar cell with a PCE of 8.8%. Brutchey and co-workers [15–17] demonstrated that a robust mixed solvent of 1, 2-ethanedithiol and 1,2-ethylenediamine can efficiently dissolve a variety of V₂VI₃ metal chalcogenides (V=As, Sb and Bi; VI=S, Se and Te), elementary chalcogens (Se and Te) and various metal oxides (Cu_2O , ZnO , CdO , Sb_2O_3 , Bi_2O_3 et al.) at room temperature in air. Recently, Wu and co-

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workers [18] developed the above mixed thiol-amine solution process to successfully fabricate CIGSe thin films using elemental Cu, In, Ga and Se powders as precursor, obtaining a PCE of 9.5% for CIGSe solar cell on a small active area of 0.19 cm^2 . However, the elemental Ga in CIGSe thin films is a rare element with a high price, which will add the cost for the future scalable production [19,20]. Comparing to CIGSe thin films, $\text{CuIn}(\text{S,Se})_2$ (CISSe) thin films considered an ideal substitute for CIGSe films not only can effectively enhance the band gap of CIGSe thin films but also have a lower raw materials cost.

Hence, in this paper, we developed the thiol-amine solution process using 1,2-ethanedithiol and 1,2-ethylenediamine as solvent and element Cu, In and S powders as precursors to prepare dense and large-grained CISSe thin films after selenization annealing, eliminating a fine-grained bottom layer. The selenized annealing temperature of the CISSe thin films was also discussed, which influenced the phase composition, crystallinity and morphology of the deposited films. Finally, the as-prepared CISSe thin film annealed at 550°C was also used to fabricate CISSe-based solar cell, and a PCE of 6.2% on an active area of 0.5 cm^2 was obtained.

2. Experiment

2.1. Materials

The materials used in this work were as follows: elemental copper powders (Cu, 99.9%, Aladdin), indium powders (In, 99.99%, Aladdin), sulfur powders (S, 99.95%, Aladdin), 1,2-ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$, $\geq 99\%$, Sigma) and 1,2-ethanedithiol ($\text{C}_2\text{H}_6\text{S}_2$, 97%, Sigma). All of the chemicals were used as received without further purification.

2.2. Solution preparation

The preparation of precursor solution was operated in a nitrogen-filled glove box in order to ensure an inert atmosphere. To obtain the anticipated stoichiometric ratio of $\text{Cu}_{0.9}\text{InS}_2$ (CIS) precursor solution, elemental Cu (0.9 mmol, 57.20 mg), In (1 mmol, 114.83 mg) and S (2 mmol, 64.15 mg) powders were added into a mixture solvent (4 ml) comprised of 1,2-ethanedithiol and 1,2-ethylenediamine with a volume ratio of 1:10, which was stirred at 60°C for several hours until all substances were absolutely dissolved.

2.3. Thin film deposition and device fabrication

The precursor thin films were obtained by spin coating the precursor solution mentioned on a Mo-coated soda-lime glass substrate at 3000 rpm for 30 s in a nitrogen-filled glovebox, followed by a drying process at 300°C on a hot plate for 5 min. The spin-coating and drying steps were repeated for several times until obtaining the desired thickness of the films. The as-deposited CIS thin films were placed in a graphite box containing a certain amount of Se powders and annealed at desired temperature (such as 525°C , 550°C and 575°C) for 30 min in a tube furnace with double temperature zone under Ar atmosphere with a pressure of 0.03 MPa. CdS buffer layer with thickness of 50 nm was deposited by chemical bath deposition (CBD). Finally, the device was coated with i-ZnO (50 nm), ITO (280 nm) by sputtering deposition, and Ni/Al grid contacts electrode ($1\text{--}2 \mu\text{m}$) by thermal evaporation. The solar cell area was defined by manual scribing to a cell area of 0.5 cm^2 .

2.4. Characterization

Thermogravimetric analysis (TGA) scans were employed using a TA Instruments SDT/Q-600 system with flowing nitrogen atmosphere and a ramp rate of $10^\circ\text{C min}^{-1}$, with a covered unsealed platinum pan. X-ray diffraction (XRD) was detected by Rigaku D/Max 2500V/PC X-ray powder diffractometer with $\text{CuK}\alpha$ radiation. FESEM morphology and

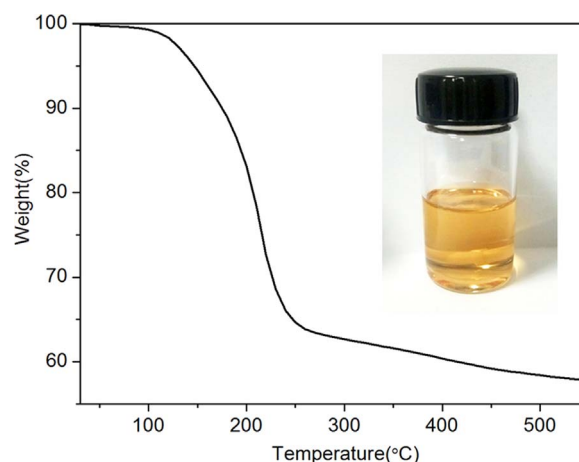


Fig. 1. TGA curve of the CIS precursor powders; the inset is a mixture solvent of 1,2-ethanedithiol and 1,2-ethylenediamine dissolving elemental Cu, In and S powders.

Energy Dispersive X-Ray spectroscopy (EDX) analyses were observed by Hatchi S-4800 field emission scanning electron microscope. Absorption spectra were recorded by UV-3600 UV-vis absorption spectrometer with spectral resolution up to 0.1 nm using optics integrating sphere. Power conversion efficiencies were done using a San-Ei Electric PV cell tester and Xenon Lamp Solar Simulator equipped with an AM1.5 filter.

3. Results and discussion

In this work, neither 1,2-ethanedithiol nor 1,2-ethylenediamine solution alone can dissolve elemental Cu, In and S powders. But a mixture solvent comprised of 1,2-ethanedithiol and 1,2-ethylenediamine can successfully dissolve elemental Cu, In and S powders together to form a clearly light yellow solution at 60°C , which is shown in the inset of Fig. 1. It is relatively important for the dissolved elemental precursor solution to recover as a solid, which can be utilized to prepare CIS thin films and used for other application. Therefore, the TGA curve was utilized to investigate the thermal decomposition process of the CIS precursor products (Fig. 1), which was realized by drying the CIS precursor solution at 100°C for 30 min under nitrogen atmosphere, followed by placing the CIS precursor powders into a Pt pan and heating from 30°C to 550°C at a speed of $10^\circ\text{C min}^{-1}$ under a flowing nitrogen environment. An obvious mass loss of about 36% could be seen from 100°C to 300°C , shown in Fig. 1, which may be attributed to the elimination and/or decomposition of the organic substances from the dried powders [15]. Further increasing the heating temperature above 300°C , the mass loss of the precursor products is almost negligible, indicating the end point of decomposition. Hence, the drying temperature for CIS precursor thin films was set at 300°C .

As can be seen in Fig. 2(a), the XRD patterns of the CIS precursor films dried at 300°C show three major broad and weak diffraction peaks, which can be assigned to the (112), (204)/(220), and (116)/(312) crystal planes of the tetragonal chalcopyrite CIS, according to the standard PDF card (JCPDS card No. 27-0159). In addition, the average crystalline size of the dried thin films calculated by the Scherrer equation is $\sim 4 \text{ nm}$, indicating the small CIS nanocrystals films can be formed using the molecular-based solution deposition after drying at low temperature. After post-selenization annealing at 550°C , the XRD patterns of the products become much stronger and sharper (Fig. 2(b)), demonstrating the increase of the crystallinity and crystal size of the selenized films. In comparison to the XRD patterns of the precursor films, the XRD patterns of the selenized films match better with the standard PDF card (No. 40-1487) of tetragonal chalcopyrite CISe, implying the phase conversion of CIS into CISe after selenization. However, comparing with the chalcopyrite CISe standard (JCPDS card

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