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Phase-controlled $CuInS_2$ nanocrystals synthesized by an ambient pressure polylol-based solution process and their photovoltaic application

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ABSTRACT

Pure-phase zincblende and wurtzite $CuInS_2$ nanocrystals were synthesized by an environment-friendly, low-cost, ambient pressure triethylene glycol based solution route. Structure, morphology, chemical stoichiometry and optical property of the synthesized nanocrystals with different crystalline structure were characterized. The average size is 11.6 nm for zincblende $CuInS_2$ nanoparticles with size distribution ranged from 5.4 nm to 19.6 nm, and a broad size distribution ranged from 20 nm to 150 nm is for wurtzite $CuInS_2$ nanoplates. Both zincblende and wurtzite $CuInS_2$ have stoichiometric composition and strong absorption over the entire visible light spectrum and near infrared region. The synthesized $CuInS_2$ nanocrystals were applied to prepare ethanol-based colloidal ink and then deposit thin films by dip-coating process. The synthesized thin films were annealed at 550 °C in a selenization atmosphere. A power conversion efficiency of ~1.02% has been achieved by using zincblende $CuInS_2$ nanocrystals as ink.

1. Introduction

I–III–IV compound, such as $CuInS_2$ (CIS), $CuInSe_2$ (CISe) or $CuInGaSe_2$ (CIGS), is one of the leading light-absorbing layer in thin film solar cells for their unique optical and electrical properties [1–4]. Recently, there have been increasing interest in developing nanocrystals-based ink technology to prepare the absorbing layer due to high fabrication cost and composition uniformity problem of vacuum deposition process [5]. Evidently, such a rout can lead to cheaper fabrication costs and ecofriendly processing technique. For this method, the morphology and crystalline structure of the nanocrystals play an important role in determining the optical and electrical properties of the materials and the final cell performance [6]. CIS, a semiconductor with a direct band gap of 1.45–1.5 eV [7], is a promising light-absorbing layer for thin film solar cell. Most of the synthesized CIS nanocrystals are tetragonal chalcopyrite crystal structure [8,9]. Several groups have reported the synthesis of metastable-phase zincblende or wurtzite CIS using hydrothermal/solvothermal [10–12] and hot-injection methods [13,14]. However, these methods are either high-pressure and time-exhausting or needing expensive solvents such as oleylamine or octadecylene [15,16]. In addition, to our best knowledge, few literatures have been reported to use zincblende and wurtzite CIS nanocrystals ink to prepare solar cells.

In this paper, we developed an environment-friendly, low-cost, ambient pressure triethylene glycol based solution route to synthesis CIS nanocrystals. By altering sulfur sources, sulphur powder and thiourea, zincblende and wurtzite CIS nanocrystals were prepared. Furthermore, the zincblende and wurtzite CIS nanocrystals were applied to prepare ink-coating thin film solar cells as light-absorbing layer followed by a selenization process. The better power conversion efficiency of ~1.02% was achieved by using zinc blende phase CIS nanocrystals.

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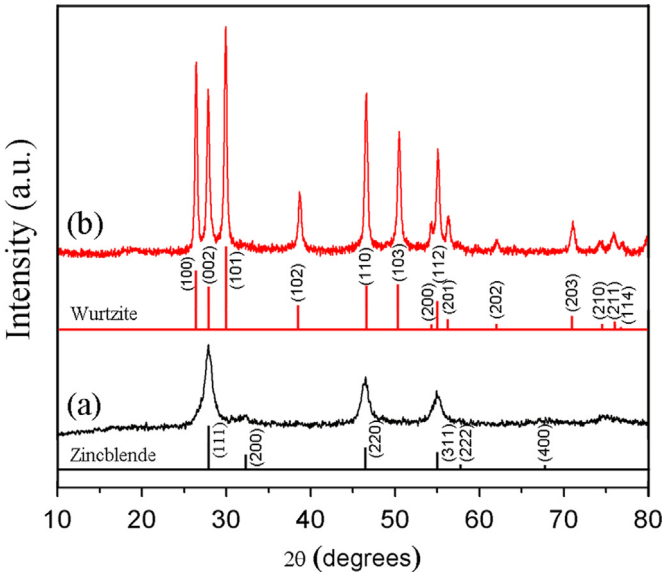

Fig. 1. XRD patterns of the CIS nanocrystals synthesized with (a) sulphur powder and (b) thiourea as S precursor.

2. Experimental

2.1. Materials

Copper(I) chloride(CuCl, 99%), indium(III) chloride($InCl_3 \cdot 4H_2O$, 99%), sulphur powder(S, 99%), thiourea($CH_4N_2O_4S$, 99%), trithylene glycol(TEG, 99%), monoethanolamine(MEA, 99%), hydrazine hydrate($N_2H_4 \cdot H_2O$, 80%), polyvinylpyrrolidone(PVP, Mr=48000), absolute ethanol(CH_3CH_2OH, 99.7%), high-purity nitrogen gas and argon gas. All chemicals were used as received.

2.2. Preparation of CIS NCs

In a typical synthesis of CIS nanocrystals, 0.5 mmol CuCl, 0.5 mmol $InCl_3 \cdot 4H_2O$ and 0.25 mL MEA were dissolved into 10 mL TEG in beaker with magnetic stirring at room temperature for 1 h to get a clear blue solution which is named Solution A. 1.0 mmol S, 0.5 mL hydrazine hydrate and 0.1 g PVP were added into 40 mL TEG in a 100 mL three-necked flask to form Solution B. The three-necked flask was attached to condenser and heated under nitrogen stream to temperature 210 °C, where Solution A was rapidly injected into Solution B in three-necked flask with vigorous stirring. The reaction solution was incubated at 210 °C for 20 min. Then the resultant solution was cooled to room temperature. The products were purified by washing with absolute ethanol and deionized water followed by centrifugation for six times. In order to obtain wurtzite-phase $CuInS_2$ nanocrystals, 1.0 mmol thiourea replaced sulphur powder as S precursor. The reaction was conducted under the same condition mentioned above.

2.3. Photovoltaic test devices

PV devices were fabricated with a conventional sandwich-types Soda-lime glass/Mo/$CuInS_2$/CdS/i-ZnO/Al-doped ZnO (AZO) configuration. The molybdenum backcontact, CdS buffer layer and i-ZnO/AZO topcontact were prepared according to the reference [17]. A thick layer of CIS thin films were deposited by layer-by-layer dip-coating method using ethanol-based colloidal ink repeatedly with several times. Then the films were annealed in Ar at 400 °C for 1 h in order to remove the organic species, followed by selenization in an Ar and Se atmosphere at 550 °C for 30 min.

2.4. Characterization

X-ray diffraction (XRD) was detected by Rigaku D/Max 2500V/PC X-ray powder diffractometer with CuKα radiation. FESEM morphology and Energy Dispersive X-Ray Fluorescence (EDX) analyses were observed by Hatchi s-4800 field emission scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed using Tecnai G2 F20 field emission transmission electron microscope. Absorption spectra were recorded by UV-3600 UV–vis absorption spectrometer with spectral resolution of 0.1 nm using optics intergrating 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

Fig. 1 presents crystal structure of the synthesized CIS nanocrystals using sulphur powder or thiourea as S precursor, respectively. The XRD pattern (Fig. 1(a)) shows that the synthesized CIS nanocrystals using sulphur powder as S precursor have zincblende structure in good agreement with the simulated zincblende pattern due to no chalcopyrite characteristic peaks of (101), (103) and (211) planes [13], and the average size calculated with Scherrer equation is 10.8 nm. Fig. 1(b) displays the synthesized CIS nanocrystals using thiourea as S precursor are single wurtzite structure which agrees well with simulated CIS wurtzite patterns [13]. No other phase is observed in Fig. 1(b). The sphalerite phase CIS (Fig. 1(a)) has a unit cell parameter of $a=5.513$ Å, while the wurtzite phase CIS (Fig. 1(b)) has unit cell parameters of $a=b=3.892$ Å and $c=6.438$ Å, which is in good agreements with the previous researches [13].

The morphologies and chemical constitution of the synthesized CIS nanocrystals were examined by SEM, TEM and EDX analysis. Fig. 2((a) and (c)) reveals that the products synthesized with the