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Well-dispersed $CuInSe_2$ nanoplates and nanoplates-ink-coated thin films for photovoltaic application by a triethylene glycol based solution process

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ABSTRACT

Single-phase and well-dispersed $CuInSe_2$ nanoplates were synthesized by a facile, ambient pressure solution chemical route using triethylene glycol as solvent, copper(II) chloride, indium(III) chloride and selenium powder as precursors, ethylenediamine as assisting agent and polyvinylpyrrolidone as capping agent. Structure and growing morphology of the products synthesized with and without polyvinylpyrrolidone addition were compared by TEM, XRD and SAED. The well-dispersed $CuInSe_2$ nanoplates were applied to prepare ethanol-based colloidal ink and then deposit flat and highly crystallographic oriented $CuInSe_2$ thin films by layer-by-layer dip-coating ink and then annealing at 500–580 °C in Ar atmosphere. *I–V* characteristics of the PV test devices with the ink-coated $CuInSe_2$ light-absorbing layers were evaluated.

1. Introduction

I–III–VI group compounds, $CuInSe_2$ (CIS) and $Cu(In,Ga)Se_2$ (CIGS), are leading light-absorbing semiconductors for thin film solar cells due to their unique photoelectronic properties [1]. However, widespread commercialization of the thin film solar cells has been restricted because of the difficulty in fabricating stable single-phase and correct stoichiometry over large device areas by conventional vapor phase deposition [2]. In the past years, there have been increasing efforts in developing non-vacuum, solution based process to fabricate CIS-based thin film solar cells for this improvement purpose [3], in which nanocrystals colloidal ink technique has been proposed [4]. Evidently, such solution based processing opens an accessible way to prepare CIS light-absorbing thin films, which may lead to cheap fabrication cost, correct stoichiometry on large substrate areas and eco-friendly process. The preparation of nanocrystals colloidal inks is an essential strategy for the scalable solution-based process to develop low-cost thin film solar cells. Up to now, several solution chemical approaches have been applied to grow CIS-based nanocrystals, such as pressure condition solvothermal process [5], microwave-assisted and ultrasonic-assisted synthesis [6,7], air-pressure solution synthesis using tri-n-octylphosphine [8], oleylamine [4] and 1-octadecene [9] solvent.

Common, cheap and green organic solvent medium synthesis under ambient pressure condition has much attraction based on consideration of processing safety and facility, inexpensive cost, less toxicity and low environmental impact, and easy extraction for nanocrystals purification. Recently, we have used triethylene glycol as the solvent to synthesize CIS nanoparticles [10] and nanoplates [11] by hot injection process. In this paper, we present new results on effective control of CIS nanoplates dispersibility by polyvinylpyrrolidone in the TEG-based solution synthesis. Furthermore, the CIS nanoplates were applied to prepare ethanol colloidal ink and deposit highly (111)/(112) oriented thin films by dip-coating colloidal ink and then annealing in Ar at 500–580 °C. Photovoltaic test devices were fabricated using the oriented nanoplates thin films, and the corresponding *I–V* characteristics were evaluated.

2. Experimental

Materials: Copper (II) chloride ($CuCl_2 \cdot 2H_2O$, 99%), indium (III) chloride ($InCl_3 \cdot 4H_2O$, 99%), selenium powder (Se, 99%), trithylene glycol (TEG, 99%), ethylenediamine (en, 99%), polyvinylpyrrolidone (PVP, Mr=10,000), absolute ethanol (CH_3CH_2OH, 99.7%), high-purity nitrogen gas and argon gas. All chemicals were used as received.

Preparation of thin films: CIS nanoplates were grown by en-assisted TEG solution injection process under ambient pressure. The details of the synthesis process were reported in Ref. [11]. Colloidal ink was prepared by ultrasonically dispersing nanoplates in ethanol for 20 min, and the solid content was 5 mg/ml. CIS thin films were deposited by layer-by-layer dip-coating colloidal ink repeatedly 60 times for the desired film thickness.

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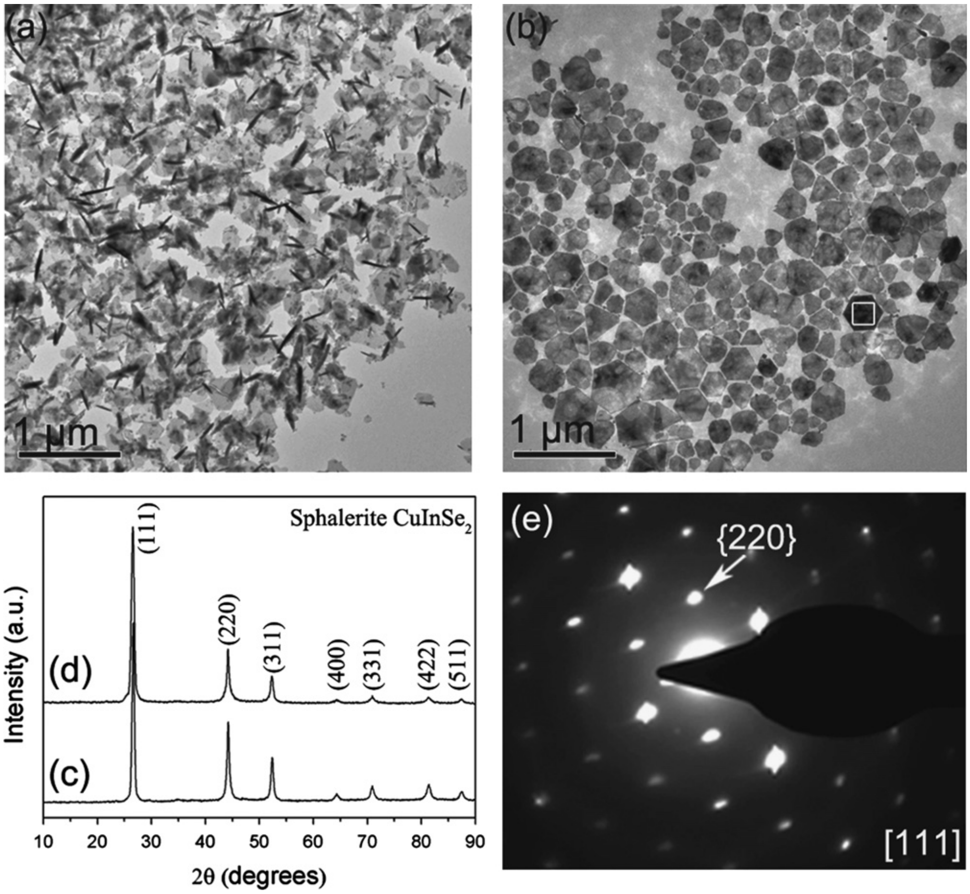

Fig. 1. TEM images and XRD patterns of CIS nanoplates synthesized with (a, c) 0 g and (b, d) 0.1 g PVP, and (e) SAED pattern of a CIS nanoplate marked in TEM image (b).

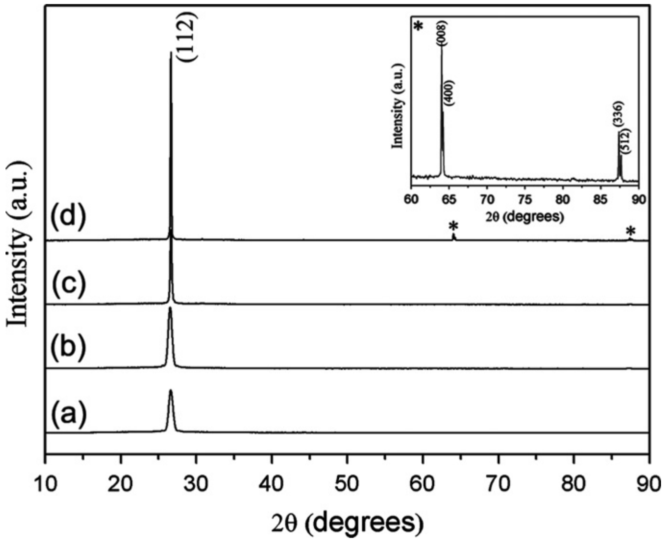

Fig. 2. XRD patterns of CIS nanoplates thin films: (a) as-coated and annealed at (b) 500 °C, (c) 550 °C and (d) 580 °C in Ar atmosphere, and the inset is a partially enlarged detail of pattern (d).

The coated substrates were settled into a light-weight alumina brick box and then annealed in a tubular oven steaming Ar at 500 °C, 550 °C and 580 °C for 30 min.

PV test devices: PV devices were fabricated with stromatolithic type glass substrate/Mo/CuInSe$_2$/CdS/i-ZnO/AZO configuration. The molybdenum backcontact, CdS buffer layer and i-ZnO/AZO topcontact were prepared according to Refs. [12,13]. The final active region of PV devices was 6 mm × 6 mm.

Characterization: XRD was detected by a Rigaku D/Max 2500 V/PC X-ray powder diffractometer with CuKα radiation. TEM and SAED were performed using a Tecnai G2 F20 field emission transmission electron microscope. FESEM morphology of thin films was observed by a Hatchi s-4800 field emission scanning electron microscope. *I–V* characteristics of PV devices were measured 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 shows the data comparison of the products synthesized with 0 and 0.1 g PVP addition in reaction solution. It is seen from TEM images (a) and (b) that the two products are all plate-shaped nanocrystals. The nanoplates without PVP addition are irregular in morphology and seriously aggregated. The well-dispersed nanoplates can be grown by PVP addition, and the size range is from 200 nm to 400 nm. The SAED pattern with incident electron beam perpendicular to nanoplate surface shows single-crystalline diffraction spots with typical hexagonal symmetry for face-centered cubic lattice (Fig. 1(e)), confirming that the nanoplates have single-crystalline structure and {111} orientation. The XRD patterns show that all the diffraction peaks of the two products can be assigned to cubic sphalerite δ-CIS, which is in agreement with the simulated pattern [1,4]. These results demonstrate that PVP is an effective capping agent to disperse CIS nanoplates well in the TEG-based solution synthesis.

Fig. 2 shows XRD patterns of the ink-coated thin films before and after annealing at different temperatures. It is seen that