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Colloidal CZTS nanoparticles and films: Preparation and characterization

Min Zhou, Yanmei Gong, Jian Xu *, Gang Fang, Qingbo Xu, Jianfeng Dong

Department of Electronic Information Science & Technology, College of Information Science and Engineering, Ningbo University, Ningbo 315211, China

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ABSTRACT

Cu_2ZnSnS_4 (CZTS) compound semiconductor has the advantage of good matching with solar radiation in optical band-gap, large absorption coefficient, non-toxic and especially large abundance ratios of elements, so that CZTS has been considered as a good absorber layer used for the thin-film solar cells with most industrialization promising and environment friendly. In the present work, colloidal CZTS nanocrystals (average size ~8–16 nm) with the band gap of ~1.5 eV were synthesized via wet-chemical processing, using oleylamine (OLA) as solvent and capping molecules. The colloids were characterized by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and UV–Vis–NIR spectroscopy. The structure and morphology of nanocrystals were influenced with the reaction temperature. The resulting nanocrystals were kesterite-phase CZTS when the reaction temperature was lower, but were wurtzite-phase CZTS when the reaction temperature above 275 °C. The CZTS films on glass substrates were prepared by drop-casting, from the colloidal 10 wt% CZTS–toluene solution where the CZTS colloids were synthesized at 260 °C with three different recipes. The resulting films with different heat-treatments were investigated by XRD, SEM and energy dispersive spectroscopy (EDS). Densified CZTS films (~5 μm in thickness) could be obtained by drying and sintering in vacuum. The CZTS films have the band-gap around 1.6–2.0 eV, due to Zn rich and S poor in the films. The dark conductivity and photoconductivity under AM 1.5 irradiation of the CZTS films on ITO glass substrates with different heat-treatments were measured by the AC impedance method.

1. Introduction

Cu_2ZnSnS_4 (CZTS), with an optimal direct band-gap of ca. 1.5 eV and a large absorption coefficient over 10^4 cm^{-1} [1,2], is one of the most promising materials as the absorber layers of thin-film solar cells. Its optical properties and crystal structure are similar to the chalcopyrite type semiconductor of $CuIn_{1-x}Ga_xSe_2$ (CIGS), one of the most successful thin-film photovoltaic materials for commercial use. However, unlike CIGS containing the expensive and toxic constituent elements such as Ga, In and Se, CZTS is composed of the earth-abundant elements: copper, zinc, tin and sulfur. All of them are nontoxic, so CZTS is considered as a future replacement for CIGS in the CIGS thin-film solar cells, to obtain the so-called CZTS thin-film solar cells. Until now, CZTS thin film solar cell have achieved the power conversion efficiency of 10.1%, using the $Cu_2ZnSn(Se,S)_4$ kesterite absorber [3].

In the last two decades, various vacuum methods have been investigated for the deposition of CZTS thin films, such as atom beam sputtering method [1], RF magnetron sputtering deposition [4,5], pulsed laser deposition method [6] and thermal evaporation of elements method [7], but all of the methods impose an additional cost on the technology. Thus, non-vacuum alternative techniques, for example, electrochemical deposition [8,9], spray pyrolysis deposition [10], the sol–gel method [11–13], and nanocrystals "ink" printing technology [14–17], have been rapidly developing. Among these methods, nanocrystals "ink" printing technology has drawn much attention, because nanocrystals "ink" could be printed, sprayed, dip-coated or roll-to-roll coated into thin films in ambient condition. Therefore, CZTS thin-film solar cells might be produced by a highly cost-effective technique using CZTS nanocrystals "ink".

In order to develop the low-cost non-vacuum method to prepare CZTS films, in this present work, colloidal CZTS nanocrystals were synthesized in oleylamine (OLA) via hot-injection processing, then the films on glass substrates were attempt to be prepared from the CZTS colloidal solution with different heat-treatments. The obtained CZTS colloids and the nanoparticles derived CZTS films were characterized by various measurements.

2. Experimental

2.1. Preparation

The precursors copper (II) acetylacetonate ($Cu(AcAc)_2$, 99.7%), zinc acetate ($Zn(OAc)_2$, 98.0%), tin (II) stannous chloride ($SnCl_2$, 98.0%), sulfur power (99.99%), oleylamine (OLA, 70%), absolute ethanol and toluene were used as received from Sinopharm.

* Corresponding author. Tel.: +86 57487600319.
E-mail address: xujian@nbu.edu.cn (J. Xu).

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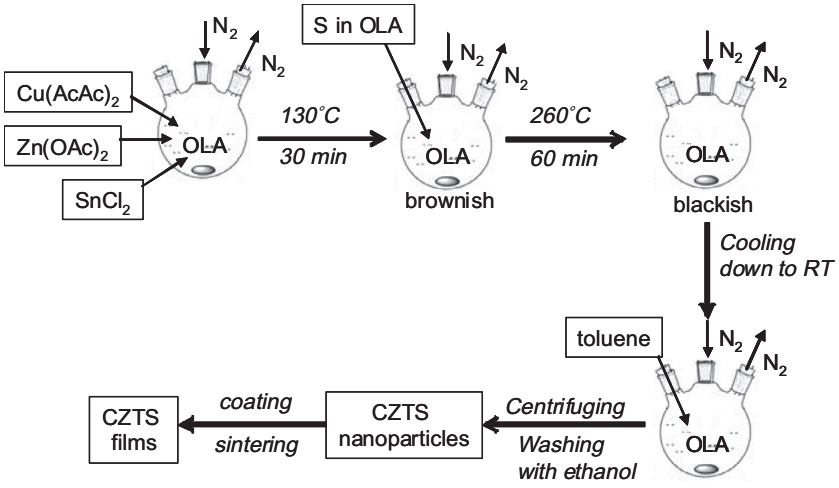

Fig. 1. Schematic flow diagram of colloidal CZTS synthesis and film preparation.

Table 1
Drop-cast CZTS film samples prepared from the colloidal CZTS nanoparticles (kesterite-phase) synthesized at 260 °C.

Sample	Cu/Zn/Sn/S (at%) in synthesis recipes	Heat-treatments	Cu/Zn/Sn/S (at%) in films by EDS	Phase structure
A1	2/1/1/4	Dried in air (RT) 100 °C in vacuum	2/0.77/1.11/2.98	Kesterite CZTS + few wurtzite ZnS
B1	2/1.53/1.09/5.64	Dried in air (RT) 40 °C in vacuum	2/1.46/1.00/4.14	–
B2		Dried in air (RT) 100 °C in vacuum	–	Kesterite CZTS + few wurtzite ZnS
B3		*Dried in vacuum (RT)* 100 °C in vacuum	2/1.45/0.98/4.06	Kesterite CZTS + few wurtzite ZnS
C1	2/1.26/1.05/4.10	Dried in air (RT) 100 °C in vacuum	2/1.02/1.12/3.66	Kesterite CZTS
C2		Dried in air (RT) 150 °C in vacuum	–	Kesterite CZTS

The schematic flowchart of colloidal CZTS synthesis and film preparation is shown in Fig. 1. The typical synthesis of CZTS nanocrystals was carried out as below. A mixture of 1.05 g (4 mmol) $Cu(AcAc)_2$, 0.44 g (2 mmol) $Zn(OAc)_2$, 0.38 g (2 mmol) $SnCl_2$, and 20 ml OLA were added into a 100 ml three-neck round-bottom reaction flask connected to a nitrogen gas cylinder. The mixture solution was always stirred vigorously in the flask purged with high pure N_2 gas (99.999%), during the whole synthesis. After heated at 130 °C for 30 min, the mixture solution became brownish. The brownish solution was injected with 8 ml of sulfur – OLA solution (1 M), then heated at the reaction temperature $T_{reaction} \sim 240–280$ °C for 1 h. When its color changed from dark brownish into blackish, the mixture solution (or product) was cooled down to room temperature (RT) and added with 15 ml of toluene for dispersing by sonication. To washing or purifying the product, 40 ml of ethanol was firstly added to let the nanoparticles flocculate and precipitate; then precipitates of nanoparticles were collected by centrifuging at 4000 rpm for 20 min and the supernatant liquid was removed; the collected precipitates were dispersed in toluene again by sonication; then ethanol was added for precipitates, new precipitates were collected again by centrifuging. The above process was repeated for three times. The final precipitates (or CZTS nanoparticles) were divided into two parts: (1) CZTS nanoparticles dispersed in toluene to form a stable ink solution and (2) CZTS power dried in a vacuum oven.

CZTS films were deposited on soda-lime glass slides by drop-casting, from the CZTS nanoparticles (10 wt%) dispersed in toluene (or the ink). In drop-casting preparation, several drops of the colloidal nanoparticles solution covered cleaned soda-lime glass substrates, where the nanoparticles could normally touch together by self-assembly with driving by capillary force during the solvent toluene evaporation. In order to prevent from cracks in the films, the colloidal films were dried in air at room temperature (RT), or at a low drying rate. Then the dried films were sintered at 40–150 °C in vacuum for densification. The film samples list in Table 1. In film preparation, only CZTS nanoparticles synthesized at 260 °C were chosen as the raw material for preparation of the CZTS films.

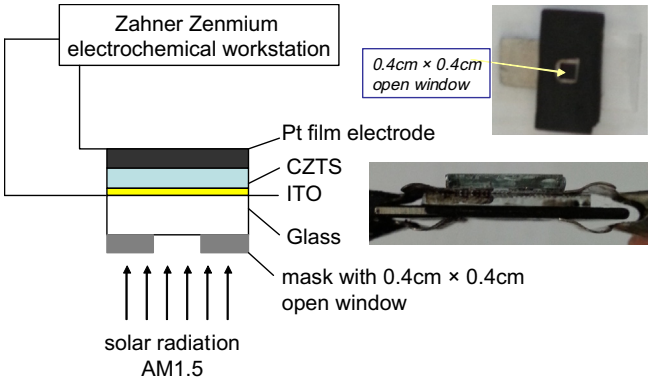

Fig. 2. Schematic diagram of the setup of measurement of CZTS film's resistances (inset shows the sample for measurement).

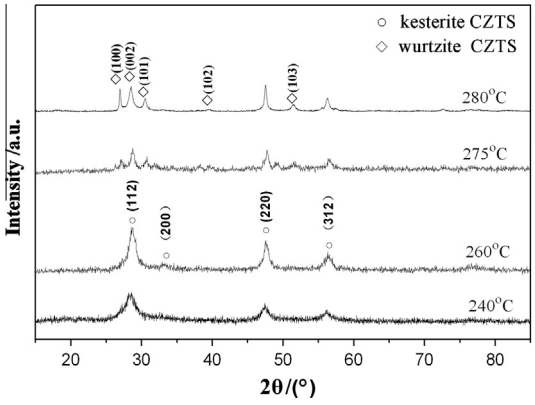

Fig. 3. XRD patterns of CZTS nanocrystals.

2.2. Characterization

X-ray diffraction (XRD) patterns of the resulting nanoparticles and films were collected with a Bruker D8 Focus X-ray diffractometer, using Cu Kα ($\lambda = 0.154056$ nm) radiation, with 0.04° steps, holding on 1 s per step. Raman spectra of the film samples were recorded with a Renishaw Microscopic Confocal Raman