



# Morphology evolution and stability of $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals in sodium halides salt solution

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## ARTICLE INFO

### Article history:

Received 12 February 2016  
Received in revised form 22 June 2016  
Accepted 19 July 2016  
Available online 20 July 2016

### Keywords:

$\text{Cu}_2\text{ZnSnS}_4$   
Nanocrystals  
Morphology evolution  
Stability  
Sodium halides

## ABSTRACT

Stability and morphology evolution of  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) films consisting of nanoparticles treated with NaX (X = I, Cl, F) based aqueous solution was investigated. It has been found that the size of the nanoparticles increased with the increase of NaI solution treatment duration. Dipping the CZTS film in NaI solution for 10 min led to the complete transformation of CZTS nanocrystals to large grains with sizes around 1–3  $\mu\text{m}$  after thermal annealing. The investigation of the material composition has revealed that NaI solution treatment resulted in significant loss of Zn. Further investigation has showed that the dissolution of Zn from CZTS is even more serious when the film of CZTS nanoparticles was soaked in NaCl and NaF solution for a short time. This is attributed to the strong complexation reaction between  $\text{Zn}^{2+}$  and the halides. X-ray diffraction measurement has confirmed that the complexation reaction led to the formation of  $\text{Na}_2\text{S}$  and Raman spectroscopy has revealed that the loss of Zn resulted in the formation of  $\text{Cu}_3\text{SnS}_4$  in the film. This work provides insights into stability and grain growth of CZTS material.

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## 1. Introduction

Semiconductor material based on  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) compound is a promising light absorber for solar cells to produce cost-effective solar electricity owing to its attractive features including abundant material source, high absorption coefficient ( $\sim 10^4 \text{ cm}^{-1}$ ) and optimal direct bandgap of 1.5 eV [1–3]. It is well known that the performance of a solar cell strongly depends on the quality of the light absorber film including the grain sizes and phase purity. Film of large grains with controlled grain boundaries, low defects and low impurities are highly desirable for high efficiency photovoltaic devices. Therefore, post-annealing treatment (sulphurisation/selenisation) is extensively employed in order to form large grains in the film [4,5].

Among the various methods that have been reported to make CZTS films, one method is based on deposition of pre-synthesised CZTS nanocrystals on Mo substrate by doctor-blading [6]. Although the CZTS nanocrystals are already composed of stoichiometric Cu, Zn, Sn and S in the material, the small particle sizes of the material mean there are large amount of grain boundaries in the corresponding light absorber film, which will form recombination centres and harm the performance of solar cells. Therefore, it is necessary to increase the grain sizes in the light absorber film. Practically, high temperature annealing is normally used to facilitate the grain growth of small particles of materials [4]. However, due to the relatively high vapour pressure of material in CZTS such as SnS and S, the high temperature annealing can cause decomposition

of the light absorber material [7,8], leading to undesired secondary phases and impurities in the CZTS film that harm the performance of solar cells. Beside the risk of decomposition of CZTS during post-annealing process, the growth of nanoparticles is also limited by carbon residue that is left from the solvent used in the CZTS paste for deposition where pre-synthesised CZTS nanocrystals are dispersed in suitable organic solvent or solvent mixture. Our previous work has showed that, even though the CZTS film was annealed at 600 °C, a certain amount of carbon residues from the organic solvents still remain in the film and form a stable coating layer on the CZTS nanoparticles that suppress the growth of nanoparticles [4]. Therefore, it is very difficult to completely transform the small nanocrystals to large grains across the whole film using only high temperature sulphurisation/selenisation. Instead, we have found large grains are mainly formed on the film surface and the majority of the film underneath the surface still consists of nanocrystals [4].

It has been reported that incorporation of alkaline ions such as sodium (Na) and potassium (K) into CZTS film can assist the grain growth and increase the material crystallinity [9]. Researchers have observed that growing CZTS on soda lime glass (SLG) leads to formation of large CZTS grains owing to the diffusion of Na ions from SLG [9–11]. Besides, evaporating a layer of Na onto CZTS surface or the substrates also increased the hole concentrations and carrier mobility in the light absorber film [12–14]. Distinct grain growth of CZTS was also perceived through treating the precursor film with an aqueous solution of  $\text{Na}_2\text{S}$  before sulphurisation [15] as well as coating Na on CZTS nanocrystals during synthesis process [16,17]. Most of the above research has been focused on the effect of alkaline cations on grain growth of CZTS and the performance of solar cells. However, little study has been reported

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about the influence of halides of sodium salt on the property of CZTS, in particular on the material stability.

Herein, we report the study of stability and morphology evolution of CZTS nanocrystals treated with NaX (X = I, Cl, F) solution. It has been found that the nanoparticles were transformed to large grains by dipping CZTS nanocrystals in NaI aqueous solution. A 10 min treatment led to formation of a film consists only large grains with size around 1–2  $\mu\text{m}$ . The investigation of the composition of the film has revealed that NaI treatment leads to partial decomposition of CZTS compound to form  $\text{Cu}_3\text{SnS}_4$ . A more serious dissolution of Zn in CZTS is found when the material was treated with NaCl and NaF solution. The mechanism underlying is discussed.

## 2. Experiments.

### 2.1. Synthesis of CZTS nanocrystals

All the chemicals used in the work were provided by Sigma Aldrich and used as received unless otherwise stated. The synthesis of Zn-rich and copper-poor CZTS nanocrystals by hydrothermal method were reported previously by us [18]. Briefly, in a typical experimental procedure, chemicals of analytical grade of copper (II) chloride dehydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 0.2 mmol), zinc chloride ( $\text{ZnCl}_2$ , 0.12 mmol, product of BDH), tin (IV) chloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 0.11 mmol), sodium sulphide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , 0.5 mmol) and thioglycolic acid (18  $\mu\text{L}$ ) were dissolved in 34 mL Milli-Q water under vigorous magnetic stirring. The solution was then transferred to a Teflon-lined stainless steel autoclave (Parr Instrument Company, 45 mL) which was then sealed and maintained at 240  $^\circ\text{C}$  for 24 h. After that, the autoclave was allowed to cool to room temperature naturally. The black precipitate was collected by centrifugation and washed with deionized water and absolute ethanol for several times to remove the ions in the product. Finally, the product of CZTS nanocrystals was vacuum-dried at 60  $^\circ\text{C}$  for 5 h. The as-synthesised material was pure CZTS with kesterite structure and did not contain secondary phases as confirmed in our previous study [6,18].

### 2.2. Fabrication of CZTS thin films

A slurry containing as-synthesised CZTS nanocrystals was prepared by dispersing the synthesised CZTS material (15%, w/w) in 1,3-propanediol (85%, w/w) and the slurry was then subject to rigorous magnetic stirring for 48 h before being deposited on cleaned Mo/soda lime glass substrate (SLG, Guardian) to make thin films by doctor-blading method. The Mo/SLG substrate was prewashed thoroughly with deionized water, acetone, and ethanol in sequence under sonication for 10 min followed by blow-dried with nitrogen gas. The as-deposited films were then pre-annealed on a hotplate at 300  $^\circ\text{C}$  for 10 min before being soaked in a sodium iodide (NaI) ethanol solution (0.2 M) for different duration (1 to 10 min). Aqueous water solution of NaCl (0.2 M) and NaF (0.2 M) was used for the stability test of CZTS films. The film was then dried on a hotplate at 80  $^\circ\text{C}$  for 5 min before being placed in a graphite box containing sulphur pieces and annealed at 600  $^\circ\text{C}$  for 2 h in a rapid thermal annealing processing (RTP) system. The heating rate of the RTP furnace was 50  $^\circ\text{C}/\text{min}$ . A constant annealing atmosphere of 0.3 atm argon gas was supplied in the RTP furnace during the annealing.

For clarity, the CZTS films treated with NaI solution with soaking time of (i) 1 min is named as CZTS-1 m; (ii) 3 min as CZTS-3 m; (iii) 5 min as CZTS-5 m; and (iv) 10 min as CZTS-10 m below.

### 2.3. Characterisation

The crystallographic structure of the synthesised samples was determined by a multi-purpose X-ray diffractometer (XRD, PANalytical XPert Pro,  $\text{Cu K}\alpha$ ,  $\lambda = 0.154056 \text{ nm}$ ). A Raman spectrometer (Renishaw

inVia Raman microscope) with a laser excitation wavelength of 785 nm was used to record Raman spectra of the materials at room temperature. The Raman spectra were collected by taking the average of 10 different spots of each sample. The morphology and composition of the samples were characterized by a field emission scanning electron microscope (FESEM, JEOL 7001F) at an acceleration voltage of 20.0 kV combined with an energy dispersive X-ray spectroscopy (EDS). The composition of the samples was carried out at an acceleration voltage of 20.0 kV for 100 s and determined by taking the average of measurement at 5 different spots. The results was determined based on standard data and the accuracy of the EDS measurement is  $\pm 1\%$ .

## 3. Results and discussion

The cross-sectional SEM image of pristine CZTS film without NaI soaking before and after sulphurisation annealing is shown in Fig. 1(a, b). It can be seen that the as-synthesised CZTS material consists of nanoparticles around 50 nm (Fig. 1(a)). After sulphurisation, a bilayer structure is formed in the film with a thin top layer of large gains (0.5  $\mu\text{m}$ ) and a thick bottom layer of nanoparticles (2.8  $\mu\text{m}$ ) (Fig. 1(b)). The top view of the film shows the grain size in the film surface varies from a few hundred nanometres to around 1  $\mu\text{m}$ . The large grains are ascribed to the grain growth driven by the tendency to reduce surface tension of small particles at high temperature according to Oswald ripening [4]. In contrast, soaking the film in NaI solution for 1 min already seems to facilitate the growth of nanocrystals. As illustrated in Fig. 2(a) and (b), the cross-sectional SEM image of the annealed CZTS-1 m film confirms that the distinct bi-layer structure still remains in the film. However, compared to the film without NaI treatment, the top layer of large grains is much thicker with thickness around 1.4  $\mu\text{m}$  and the bottom layer of fine grains is reduced to around 0.6  $\mu\text{m}$ . The surface image displayed in Fig. 2(b) indicates the close contact between the large grains to form a compact film. The particle sizes on the surface vary in the range of 1–2  $\mu\text{m}$ , which is larger than the as-synthesised nanoparticles. By increasing the NaI solution soaking time to 3 min, a similar bi-layer structure is observed in the film (Fig. 2(c)). However, the average thickness of the large grains at the top layer increases accompanied with decrease of the bottom layer nanocrystals. The thickness of small grains in some area of the bottom layer is as thin as 200 nm. The surface image exhibited in Fig. 2(d) indicates the surface of CZTS-3 m has more large grain with sizes around 2  $\mu\text{m}$  compared to that of CZTS-1 m film. When the NaI soaking duration is further extended to 5 min (CZTS-5 m film), most of the nanocrystals in the film are transformed to large-grains although a small amount of nanocrystals are still observable in some area close to the Mo substrate (Fig. 2(e)). In the meantime, the surface image of CZTS-5 m in Fig. 2(f) shows a further increment in grain size up to 3  $\mu\text{m}$ , confirming the grain growth. By further prolonging the soaking duration to 10 min, all the nanocrystals are transformed to large grains after thermal annealing according to the cross-sectional image in Fig. 2(g). The film of CZTS-10 m is mainly composed of large crystals which are closely connected with each other as illustrated in the surface image in Fig. 2(h).

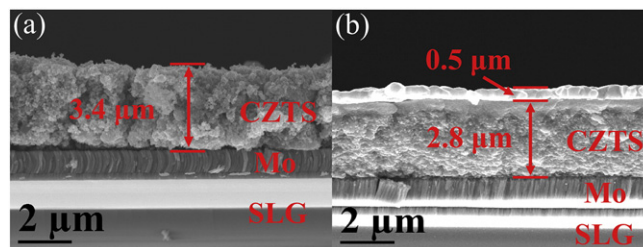


Fig. 1. Cross-sectional SEM images of CZTS films before (a) and after (b) sulfurization without NaI soaking.

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