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# Crystal size-controlled growth of $Cu_2ZnSnS_4$ films by optimizing the Na doping concentration

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ABSTRACT

Solution-based approach is a simple method to deposit $Cu_2ZnSnS_4$ (CZTS) films, which is one of the most promising materials for low-cost thin film solar cells. In this work, a novel Na-containing precursor solution using ethylene glycol as solvent was used to deposit CZTS films on Na-free substrate. Effects of various Na concentrations on the properties of CZTS films were systematically studied. The results show that the 1.0% Na-doping can well enhance the growth of particle size, has the highest crystallinity and electrical conductivity, and its band gap is 1.55 eV, which is appropriate band gap to solar cells. This Na-containing method can well control the concentration of Na and it may be used to form CZTS thin films on other flexible substrates other than soda-lime glass.



## 1. Introduction

Tin-sulphide complex compounds are very promising for optoelectronics, which is a consequence of high electron–phonon anharmonicity for the such kind of compounds [1]. In particular, $Cu_2ZnSnS_4$ (CZTS) have attracted great attention because of its optimum direct band gap energy ($\sim$1.5 eV) [2], large absorption coefficient ($\sim 10^{4-6}$ cm$^{-1}$) [3], nontoxic constituent and earth abundant elements. So far, $Cu_2ZnSnSe_4$ based solar cells using hydrazine solution approach have achieved PCE of 12.6% [4]. Other methods have also been used to fabricate CZTS thin films, such as sputtering [5], sol–gel method [6] and so on.

To fabricate CZTS based solar cells, the grain growth is one of the key points for further efficiency improvements, and doping Na metal ion into CZTS films is considered to be an effective way to achieve this purpose. CZTS films are commonly deposited on soda-lime glass. However, the main challenge is that the concentration of Na ion is difficult to control when soda-lime glass is used. So it may well make sense to use Na containing solution method and find the optimal Na doping concentration. So far, there are a few reports with regard to study on the Na-doping concentration. Carolin M etc. have studied the effect of Na on $CuZnSn(S_xSe_{1-x})_4$ films by deposited various thickness of NaF layers, using a meteorological deposition method [7].

In this work, instead of using meteorological deposition, we used a novel method of direct Na-containing solution to study the effect of Na concentration on CZTS films. CZTS films with various Na concentration were deposited on Na-free substrate by adjusting the Na concentration in precursor solution and using ethylene glycol as solvent. The results reveal that suitable Na doping benefit the formation of CZTS films. The effects of Na concentration on the properties of CZTS films were systematically studied.

## 2. Experimental

*Chemical precipitation synthesis*: The CZTS thin films were prepared by a sol–gel method. To form Na-containing CZTS precursor solution, $Cu(CH_3COO)_2 \cdot H_2O$ (1.8 mmol), $Zn(CH_3COO)_2$ (1.2 mmol), $SnCl_2$ (1.09 mol), excess amount of $SC(NH_2)_2$ (8 mmol) and NaOH were dissolved in 20 ml ethylene glycol with constant stirring. The Na/(Cu+Zn+Sn) radio is 0, 0.5%, 1.0%, 2.0%, respectively. The CZTS precursor films with different Na concentration were deposited on Na-free substrate by spin-coating method and processed an annealing treatment at 300 °C under Ar atmosphere. The spin-coating and annealing process were duplicated several times to get appropriate thickness of the CZTS films.

*Characterizations*: The surface morphologies of as-prepared samples were examined by a field emission scanning electron microscopy (FESEM, JSM-6701F). The structure of nanocrystal was analyzed by X-ray diffractometer (XRD) (SiemensD5005, Munich) with Cu $K\alpha$ radiation ($\lambda$=1.54187 Å). Micro-Raman measurements were carried out using a Horiba HR800 Raman system at room

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temperature, and a 632.8 nm line from a He–Ne laser was utilized as the excitation laser. A high resolution transmission electron microscope (HRTEM, Tecnai-G2-F30) was used to study the structure with corresponding selected area electron diffraction (SAED) pattern. The electrical conductivity was measured by the two-probe method on a Keithley 4200 SCS at room temperature in ambient air. UV–vis spectra were recorded with a UV–vis spectrophotometer (Perkin Elmer Lambda 900 spectrometer).

## 3. Results and discussion

*Surface morphology*: The SEM images of CZTS thin films with various Na concentrations (0, 0.5%, 1.0%, 2.0%) are shown in Fig. 1. As can be seen from the top view SEM images, the average diameter of particles is gradually increasing with the increasing of Na concentration from 0 to 1.0%. However, when the Na concentration increased to 2.0%, the particle sizes of the CZTS is decreased. According to the cross view of CZTS thin films (Fig. 4e), we can see that the 1.0% Na doping CZTS thin films are composed of uniform, dense and void free particles.

*Phase structure*: XRD pattern and Raman spectroscopy are utilized to obtain insight into the phase identification of the CZTS films. The XRD pattern of the samples prepared at same temperature is shown in Fig. 2a. It shows three major diffraction peaks corresponding to (1 1 2), (2 2 0) and (3 1 2), which consistent with kesterite structure of $Cu_2ZnSnS_4$ (PDF#26-0575). There are no evident characteristic diffraction peaks of other impurities appearing owing to the small concentration of Na ions that is below the detection limit of the measurement. From the peaks in Fig. 2a, we can note that the intensity of characteristic diffraction peaks such as (1 1 2) increase with the increasing of Na, but it starts to decrease when the concentration ran up to 2.0%. The mean grain size can be determined by the Debye–Scherrer formula. The mean grain size of the CZTS films with various Na concentrations (0%, 0.5%, 1.0%, 2.0%) is calculated to be about $2.63 \pm 0.05$ nm, $5.23 \pm 0.07$ nm, $6.67 \pm 0.09$ nm and $1.49 \pm 0.05$ nm, respectively. This indicates the 1.0% Na CZTS film has higher crystal quality. It was found that CZTS phase's diffraction peak also overlap with those of some binary phases of impurities such as ZnS and ternary phases such as tetragonal $Cu_2SnS_3$. Therefore, Raman spectroscopy was utilized to obtain further insight into the phase identification.

The Raman data in Fig. 2b exhibit two strong peaks at about 338 $cm^{-1}$ and 368 $cm^{-1}$, further confirming that these samples are indeed CZTS. Fig. 2c shows TEM atomic lattice image of 1.0% Na-doping CZTS. This lattice spacing is about 0.31 nm and it is belonged to (1 1 2) plane of CZTS. In Fig. 2d, SAED pattern indicates the crystal structure of the CZTS film is polycrystalline.

Fig. 3a shows the full width of half maximum (FWHM) values of (1 1 2) diffraction peak and the peak intensity ratios of $I(1\,1\,2)/I(2\,2\,0)$ for the CZTS thin films with different Na doping concentrations. The average crystallite size is inversely proportional to FWHM values basing on Scherrer formula so that the CZTS thin films with 1.0% Na doping have the highest crystal quality. All samples show the preferred orientation along the (1 1 2) plane and the $I(1\,1\,2)/I(2\,2\,0)$ of CZTS thin films with 1.0% Na doping is the highest.

*Optical property and electrical property*: Current–voltage characteristic (Fig. 3b) is measured to detect the changing of the electrical conductivity. It is evident that the current gradually

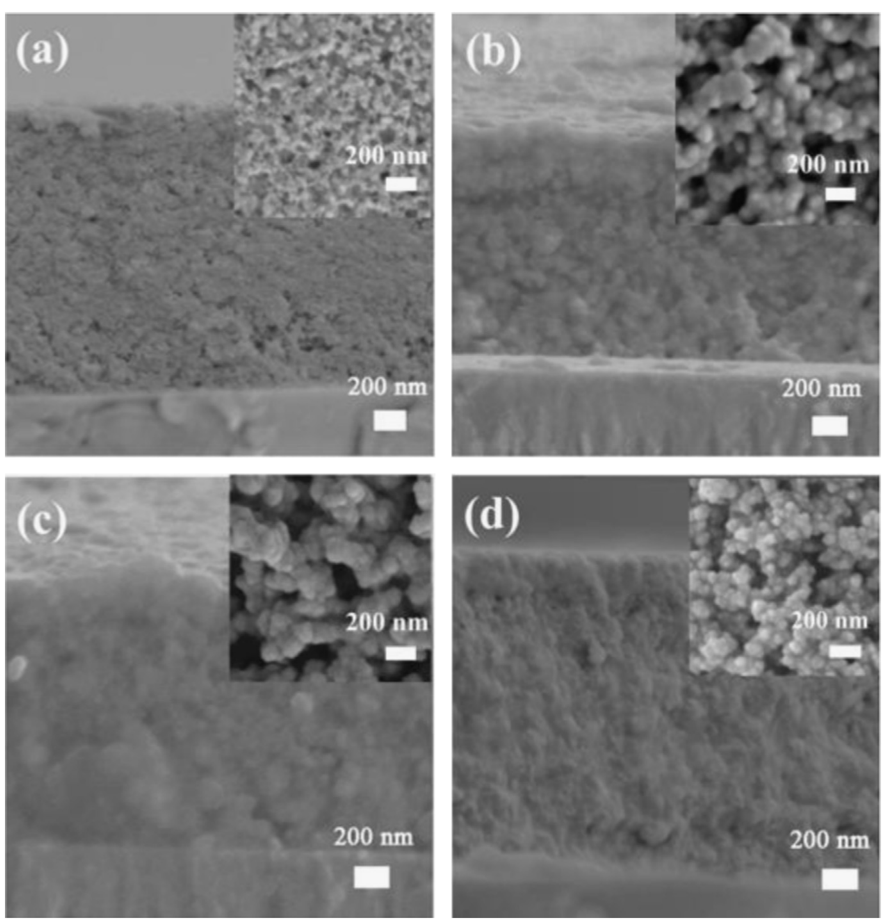


**Fig. 1.** The cross view and the top view (inset) of CZTS thin films with 0 (a), 0.5% (b), 1.0% (c), 2.0% (d) Na doping, respectively.