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A NEW MOLECULAR ISOPROPANOL-BASED SOLUTION PROCESSING FOR EARTH-ABUNDANT Cu_2ZnSnS_4 THIN FILM

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In this study, Cu_2ZnSnS_4 (CZTS) thin films were successfully synthesized by a new molecular isopropanol-based solution processing. The films were characterized by X-ray diffraction (XRD), Raman spectra, and scanning electron microscope (SEM).The effects of sodium doping on the growth of CZTS thin films and photovoltaic properties of CZTS solar cell were briefly investigated.

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1. Introduction

Kesterite structure Copper zinc tin sulfide (CZTS) have attracted considerable attention and been considered as one of the most potential substitutes material for the absorber layer of low-cost thin-film solar cells[1,2], as they have similar structures and optical properties with copper indium gallium selenide (CIGS) cells. Different synthesis methods have been reported for kesterite CZTS absorber layers. Among the various fabrication methods, solution-based processing have been drawing great interests, due to its potential low cost, high throughput production, and the ease of control film composition and volatile phases [3-6]. The fabrication of monodisperse CZTS nanocrystals can lead to binary or ternary subcomponent nanoparticles, and enables a variety of synthetic approaches to control composition and phase formation by avoiding effects of the volatile precursor at high temperature [7, 8]. Unfortunately, this approach cannot avoid some unnecessary impurities in the form of long carbon-chain ligands that stabilize the nanocrystals-based ink prerequisite to deposit uniform films in large areas. A new type of metal chalcogenide complex usually prepared form hydrazine with excess chalcogen opens the door for a chemically clean nanocrystals system without introducing unnecessary impurities[9]. Hydrazine-based slurry system by making the compromise to use particles of hydrazinium zinc chalcogenide and soluble metal chalcogenide complex of copper and tin constituent, currently holds the most successful approach to fabricate CZTS photovoltaic devices[10]. However, the formation of the slurry tends to be finicky and the stability of the complex ligands and particle systems has not been addressed. A fully dissolved molecular homogenous hydrazine-based solution capable of yielding chemically clean films is the most simple and effective way to process

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films of a multinary compound system, with each elemental component independently adjustable to control composition and phase [11]. But the reactivity and toxicity of hydrazine limit its further investigation and application in industry. Thus, it is of great importance to find a suitable solvent to form non-toxic, stable precursor solution in fabrication of low-cost and high-efficiency CZTS solar cells.

In the present study, we optimize the molecular alcohol-based solution approach for the fabrication of CZTS thin films by adopting isopropanol as solvent. Isopropanol has small molecular weight and intermediate value of physicochemical property such as viscosity, surface tension and vapor pressure, among other alcohols such as methanol, ethanol and ethylene glycol[12, 13].Importantly, the isopropanol-based precursor solution can be kept stable, which is very crucial for scalable production. Besides, the influence of sodium doping on the growth of CZTS thin films was briefly investigated.

2. Experimental

All chemical reagents were used as received without further purification. Copper (II) chloride ($CuCl_2{\cdot}2H_2O$, >99.9%), zinc (II) chloride ($ZnCl_2$, >99.9%), and tin (IV) chloride ($SnCl_2{\cdot}2H_2O$, >99.9%), thioacetamide(TAA, >99.9%), sodium fluoride (NaF, 99%), sulfur power (S, >99.9%) and isopropanolwere purchased from Sinopharm. All chemicals were of analytical grade and used without further purification. Mo-coated glass substrates with a SiO_x barrier layer were use as substrate.

The CZTS precursor complex solution consisted of $CuCl_2{\cdot}2H_2O$ (0.15 mol/ L), $ZnCl_2$ (0.102 mol/L), $SnCl_2{\cdot}5H_2O$ (0.085 mol/L), and TAA (0.0625 mol/L) dissolved in isopropanol sequentially. When adding $ZnCl_2$ and $SnCl_2{\cdot}2H_2O$ into copper precursor solution with constant stirring, the color of the ethanol solution changed from a deep green to milk-white. After adding the TAA, the color of the precursor solution changed from milk-white to transparent yellow. Finally, small amount of NaF (0.017 mol/ L) was added into the precursor solution, the doping content was controlled at 5% molar ratio.

CZTS films were deposited via dip-coating from the as-prepared transparent precursor solution on Mo-coated glass substrates. To build up the precursor layer thickness, the dip-coating process was repeated several times following an intermediate heat treatment at 150 ^oC in air for 10 min to evaporate the solvent. A final annealing was conducted in a graphite box at550^oC for 60min under S vapor in 30 torr N_2. After the heat treatment, the samples were cooled naturally to room temperature under inert atmosphere.

The CZTS absorber film was then processed into photovoltaic devices by chemical bath deposition of CdS (50 nm), RF magnetron sputtering of i-ZnO (50 nm), and indium-doped tin oxide (150 nm). Silver paint was applied to form the top contact.

The kesterite layers were analyzed by X-ray diffraction (XRD) on German Bruker AXS D8ADVANCE diffractometer (Cu K_α radiation, λ=1.5405Å). Room temperature Raman spectra were recorded using the LabRam HR800 instrument, the wavelength of laser excitation for Raman measurements was 325 nm, and the laser power was ~100 mW. The morphologies and microstructures of the films were observed using a Hitach S5200 field emission scanning electron microscope (FE-SEM). Photovoltaic devices were tested on a Karl Suss probe station and an

Agilent 4156C parameter analyzer. J-V data and power conversion efficiencies were obtained using a Keithley 2400 General Purpose Sourcemeter and a Xenon Lamp Solar Simulator (Newport) under AM1.5 (1000 W/m^2) global illumination at 25 ^{o}C.

3. Results and discussion

The XRD patterns of the two annealed CZTS thin films samples without and with Na doping are shown in Figure 1a. The XRD peaks of the two samples show three obvious diffraction peaks at 28.4°, 47.3°, and 56.1°, which can be indexed to the (112), (220), and (312) of kesterite structure of Cu_2ZnSnS_4 (JCPDS no.26-0575), with a preferred orientation in the (112) direction, and no other secondary phases are found.

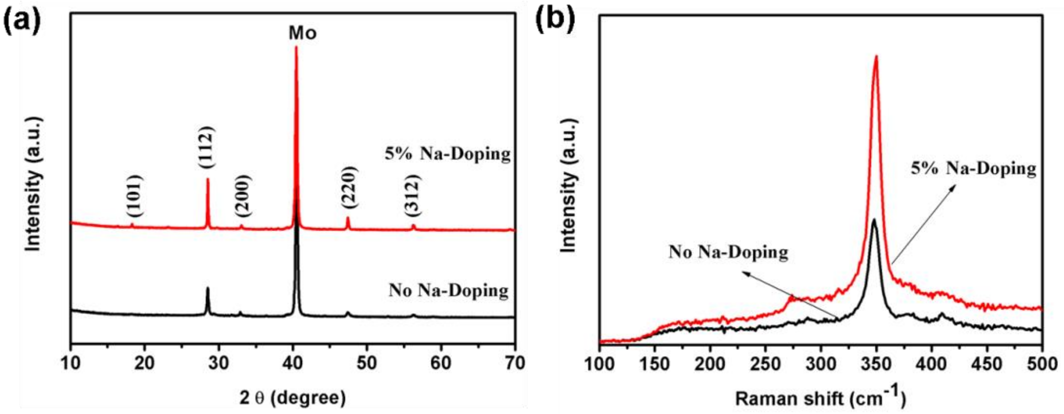

Fig. 1. (a) XRD patterns and (b) Raman spectroscopy of two CZTS thin film samples with Na doping (red) and without Na doping (black)

Compared with the thin film sample without Na doping, the thin film with Na doping has a stronger intensity and a smaller FWHM (full width at half maximum of the main peaks), indicating better crystallinity with larger grain sizes, which is essential for the improvement of the properties of the CZTS thin film. Raman scattering measurement is generally used as the auxiliary tool to analyze the structure of CZTS, since XRD pattern alone is insufficient to identify the phase purity of the product. Figure 1b shows the Raman spectra for the two CZTS thin film samples. Both samples exhibit only pure CZTS phase, since an obvious major peak at around 345 cm^{-1} can be seen, which is attributed to the CZTS A1 mode. Therefore, the results of XRD and Raman scattering indicate that the annealed two thin films consist of single phase of kesterite CZTS.

Figure 2 presents the cross-section SEM images of two annealed thin film samples without and with Na doping. These two thin film samples consist of crystallites with thickness of approximately 1.5 μm.

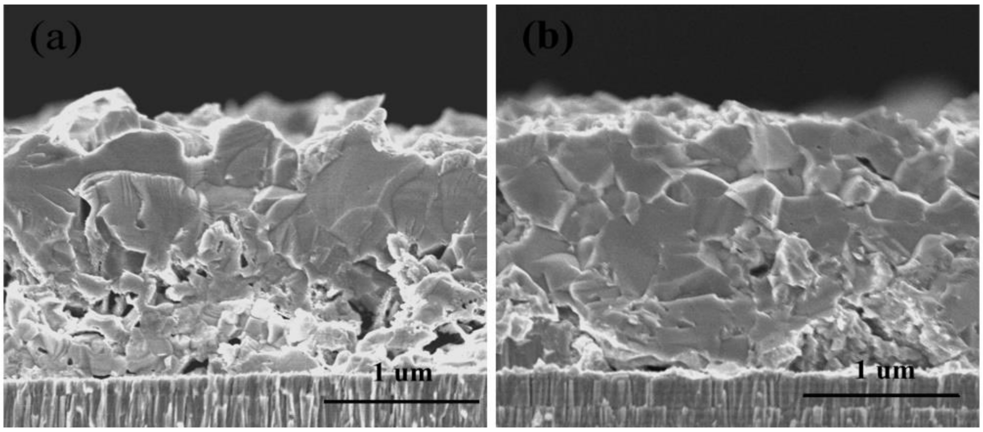

Fig. 2. The cross-section SEM images for two CZTS thin film (a) without Na doping, (b) with Na doping

It should be noticed that compared with No Na-doping sample, the resulting Na-doping thin film is composed of larger densely packed grains. It implies that the doping of Na element is beneficial to the CZTS crystal growth, which is in good agreement with XRD results. Furthermore, the doping sample exhibits better contact with the Mo back contact, indicating that doping Na element couldenhance the interface interaction between the CZTS layer and Mo coated substrate, which would be beneficialtoa better device performance.

The current density-voltage (J-V) curves of no Na-doping CZTS-based and Na-doping CZTS-based solar cells are presented in Figure 3.The no Na-doping CZTS-based cell exhibits an open-circuit voltage (V_{oc}) of 366.6 mV, which is lower than 381.3 mV for Na-doping CZTS-based cell. Meanwhile, the J_{sc} (21.8 mA/cm^2) of Na-doping CZTS-based cell is significantly improved compared with no doping cell (12.5 mA/cm^2). It is worthwhile to observe that the Na-doping CZTS cell has a better efficiency performance (2.92 %) compared with that of no Na-doping cell (1.67 %), which is expected from its larger grain size and better contact with Mo back contact.

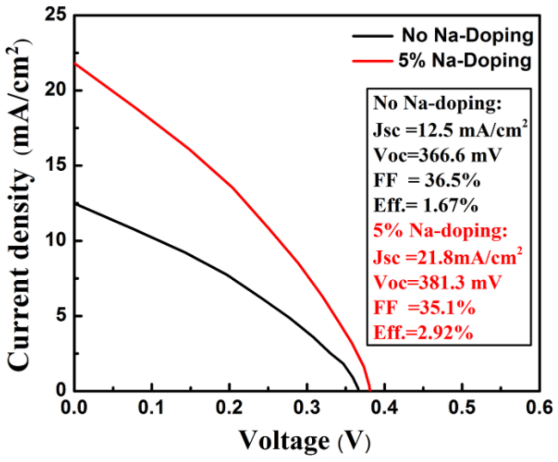

Fig. 3. Current-voltage characteristics of two CZTS devices under air mass 1.5 illumination, (a) no Na doping, (b) Na doping

4. Conclusions

We have optimized a new molecular alcohol-based solution for producing CZTS thin films. Isopropanol is used as solvent, which should reduce carbon residue and non-toxic, the same as methanol and ethanol, but more stable when forming precursor solution. XRD, Raman spectra and SEM results confirmed that the structure and composition of the as-synthesized thin films correspond to those of pure CZTS and Na-doping thin film exhibited better crystallinity, larger grain sizes, and stronger interface interaction between CZTS layer and Mo back contact, which led to higher photovoltaic properties.

Acknowledgements

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