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A general oxide-based preparation strategy for Cu_2MSnS_4 (M: Zn, Mn, Cd) thin films and relevant solar cells

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ABSTRACT

In this work, Cu_2MSnS_4 (M: Zn, Mn, Cd) thin films were successfully prepared by a low-cost and facile oxide-based route. After sulfurization of oxides precursor, the Cu_2MSnS_4 thin films with composition control exhibit good morphology, analogous crystal structure and suitable bandgaps. Finally the preliminary solar cells based on these films show proper power conversion efficiencies, which demonstrate a high potential application in low cost thin film solar cells.

1. Introduction

Recently, $Cu_2ZnSn(S, Se)_4$ (CZTSSe) thin films are being considered as ideal absorber materials for solar cells because of its proper properties such as earth abundant composition, large absorption coefficient, tunable band gap (1.0–1.5 eV), and high power conversion efficiency (12.7%) [1]. On the other hand, the derivatives Cu_2-II-IV-$(S,Se)_4$ (II = Cd, Mn, Fe, Co, Ni; IV = Si, Ge) have also received great attentions due to their analogous properties to CZTSSe. Many methods, including sputtering, evaporation, pulsed laser deposition, electrodeposition, nanoparticles (NPs) and solution processing, have been developed to prepare those thin films [2,3]. Among them, NPs-based processes is one of the successful non-vacuum approaches to chalcogenide formation, with variations employing particles composed of quaternary, blended binary/ternary and binary sulfide NPs as precursor. However, the oxide NPs process, which is regarded as an extremely promising method for the deposition of $Cu(In,Ga)Se_2$ (CIGS) and CZTSSe thin films, has rarely been used for preparing the derivatives Cu_2-II-IV-$(S,Se)_4$ thin films until now [4,5].

In this work, we extend this facile oxide-based strategy to fabricate Cu_2MSnS_4 (M: Zn, Mn, Cd) thin films and relevant devices. The crystal structure and morphology of Cu_2MSnS_4 thin films were carefully investigated. The related devices show proper photovoltaic responses. Such a low cost oxide method is also expected to prepare Cu_2MSnS_4 (M: Mg, Ba, Co, Ni) thin films.

2. Experimental

Firstly, the oxide NPs were prepared by a solvent-free method. 0.02 mol $Cu(NO_3)_2{\cdot}3H_2O$, 0.01 mol $Zn(NO_3)_2{\cdot}6H_2O$ ($Mn(CH_3COO)_2$ or $Cd(CH_3COO)_2{\cdot}2H_2O$), 0.01 mol SnC_2O_4 (Cu:M:Sn = 2:1:1) and excess ammonium bicarbonate (0.1 mol) were grinded and then baked at 380 °C. Subsequently, the obtained oxide NPs were deposited on Mo coated soda-lime glass substrate by doctor blade. Secondly, the oxide layers were sulfurized in low toxic sulfur vapor at 580 °C for 30 min, forming Cu_2MSnS_4 (M: Zn, Mn, Cd, denoted as CZTS, CMTS and CCTS respectively). Finally, after depositing the Cu_2MSnS_4 thin films on Mo coated soda-lime glass (sulfurized at 580 °C), the devices were assembled by depositing an ~80 nm thick CdS buffer layer by chemical bath deposition (CBD) approach, an ~50 nm thick i-ZnO layer via RF sputtering, an ~500 nm thick Al:ZnO layer via RF sputtering and an Ag collection grid in sequence.

The crystal structure, morphologies and compositions of the films were characterized by XRD (D/Max-rA), Raman

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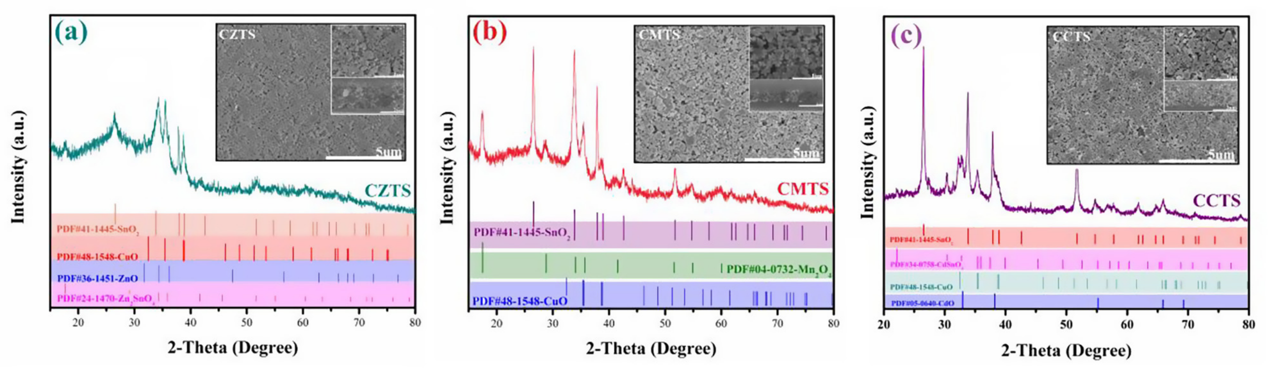

Fig. 1. XRD pattern for the precursor film of Cu_2MSnS_4: (a) Zn; (b) Mn; (c) Cd. The inset of each figure shows the SEM image of corresponding precursor film.

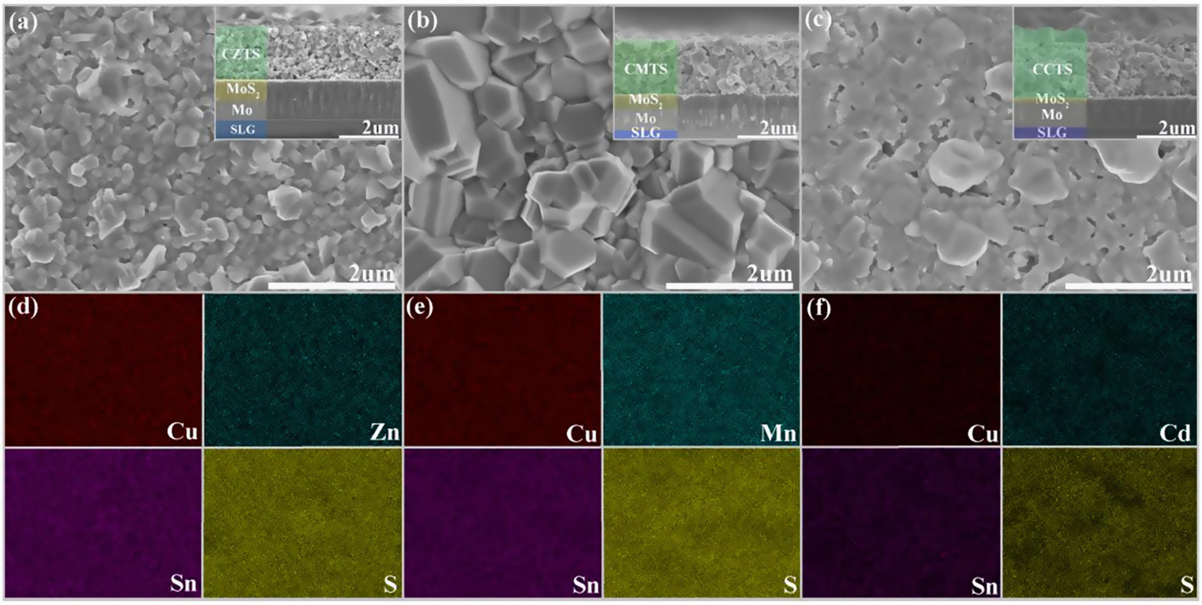

Fig. 2. SEM micrographs and related EDS mappings of Cu_2MSnS_4 : (a, d) Zn; (b, e) Mn; (c, f) Cd.

(LABRAM-HR, excitation wavelength of 532 nm) and field emission SEM with attached energy-dispersive X-rays (EDS) (FESEM, SU-8010). The solar cells were tested via using a Keithley 4200-SCS characterization system which equipped with an AAASAN-EI ELECTRIC solar simulator. The external quantum efficiency (EQE) of the devices was performed on solar cell quantum efficiency measurement system (Model QEX10).

3. Results and discussion

In this work, all precursors are consisted of the related oxides of their components, which can be shown in Fig. 1. For example, CuO (PDF#48-1548), ZnO (PDF#36-1451), SnO_2 (PDF#41-1445), Zn_2SnO_4 (PDF#24-1470) for the precursor film of CZTS, CuO (PDF#48-1548), SnO_2 (PDF#41-1445), Mn_2O_4 (PDF#04-0732) for the precursor film of CMTS and CuO (PDF#48-1548), SnO_2 (PDF#41-1445), CdO (PDF#05-0640), $CdSnO_3$ (PDF#34-0758) for the precursor film of CCTS. From the inset of SEM images of those oxide films, it is not difficult to observe that the morphologies of the films are not compact, and there are some voids exist both in the surface and the bulk of those films.

After sulfurization, it can be clearly seen that the three kinds of films are pin-hole free and smooth, as shown in Fig. 2. The grain size of CMTS films (>2 μm) are slightly larger than that of CZTS and CCTS films. Besides, the composition ratios of Cu_2MSnS_4 thin films are close to their stoichiometric ratios (Cu:M:Sn = 2:1:1) (Data not shown), which indicates good compositional control. The elemental distributions of Cu_2MSnS_4 thin films are harmonious, indicated from EDS mapping (Fig. 2(d–f)). There is no obvious segregation, which demonstrates that all the components of Cu_2MSnS_4 thin films distribute uniformly in the thin films. So the high quality Cu_2MSnS_4 thin films can be prepared by this oxide NPs method.

The crystalline structures of the annealed thin films were characterized by XRD. As shown in Fig. 3(a), all diffraction peaks can be indexed to Cu_2MSnS_4 phase (M: Zn-PDF#26-0575, Mn-PDF#51-0757, Cd-PDF#29-0537) with (1 1 2) preferential orientation. The sharp peaks indicate high crystallinity of Cu_2MSnS_4 thin films. However, XRD cannot allow us to make a clear distinction between Cu_2MSnS_4 and other possible secondary phase (e.g. MS, Cu_2SnS_3), since those secondary phases have very similar lattice parameters or analogous pattern features to Cu_2MSnS_4 phase [6]. So Raman test was further introduced for phase identification, as shown in