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Strategic improvement of Cu_2MnSnS_4 films by two distinct post-annealing processes for constructing thin film solar cells

Leilei Chen [a], Hongmei Deng [b], Jiahua Tao [a], Huiyi Cao [a], Lin Sun [a], Pingxiong Yang [a, *], Junhao Chu [a]

[a] Key Laboratory of Polar Materials and Devices, Ministry of Education, Department of Electronic Engineering, East China Normal University, Shanghai, 200241, China
[b] Laboratory for Microstructures, Shanghai University, 99 Shangda Road, Shanghai 200444, China

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ABSTRACT

The synthesis approach using a non-toxic solution-based method accompanied with special post-annealing processes demonstrates the great potential to realize industrial manufacture of earth-abundant materials for sustainable photovoltaics. Exploration of an appropriate post-annealing process is significant to gain insight into the crystallization of solar materials. The earth-abundant Cu_2MnSnS_4 (CMTS) thin films were fabricated by post-sulfuring as-prepared precursors and the results have been compared with that of directed-annealed samples. It was found that the sulfurization procedure not only can support to enhance the crystallinity but also help to obtain a nearly stoichiometric CMTS thin film which also free of SnS secondary phase. This reaction also contributes to sustainable incorporation of S into CMTS to a considerable extent and formation of notable large grains; whereas, it leads to the formation of a typical bi-layer microstructure containing large grains (500–800 nm) on the top and fine grains at the bottom. Through the sulfurization approach, the device performance is improved with the power conversion efficiency shows a 170% increase which mainly via the boost of open circuit and fill factor compared with that of direct-annealed processed. These results offers a novel research direction for preparing pure-sulfide CMTS thin film for the potential application in low-cost solar cells.

1. Introduction

Cu_2ZnSnS_4 (CZTS) is a promising material used in a variety of solar harvesting devices, such as dye-sensitized photovoltaic, solar water splitting, and thin film solar cells due to its earth abundance and nontoxic [1–4]. Therefore, materials with structures, band gaps, and absorption coefficients analogous to those of CZTS, such as Cu_2XSnS_4 (X = Mn, Co, Fe) have been recently reported for photovoltage applications [5–7]. Among these, Cu_2MnSnS_4 (CMTS) has attracted great interests because its suitable band gap, inexpensive and nontoxic elements, and high absorption coefficient ($>10^4$ cm^{-1}) in the visible spectrum range, which is optimum for a solar photovoltaic material [8–10]. Currently, CMTS thin films have been synthesized via the solution-based methods, such as solvothermal methods and hot-injection without post-sulfurization [6,9]. However, these reported methods require a complex solution phase synthesis, which involves the use of toxic organic solvents and requires special reaction conditions [11,12]. Moreover, in such processes, the final films are usually suffering from the phase impurity conditions since the narrow phase stability of quaternary CMTS makes the defects and secondary phase easy to form during the growth process [13,14]. The probably presence of those secondary phases (e.g. SnS, Cu_xS and Cu_2SnS_3) has a latent but crucial impact on the devices performance [15–17]. The Cu_xS is highly conductive and may short solar cells. And both the SnS and Cu_2SnS_3 are p-type semiconductors which exhibit band gaps close to CMTS and would affect carrier collection efficiency in the layer. These unwanted secondary phases in absorber layer will hamper the final solar cell performance. In contrast with the aforementioned technologies and vacuum-based approaches, pure direct liquid coating (DLC) method offers precursors homogeneity at a molecular scale and accordingly enables precise stoichiometric control and excellent film consistency, which are necessary for low-cost and large-

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* Corresponding author.
E-mail address: pxyang@ee.ecnu.edu.cn (P. Yang).

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scale production [18,19].

Our group previously reported using a DLC method to synthesis CMTS thin films followed by direct-annealing process [10]. The precursor solution was made of dissolving Sn, Cu, and Mn salts and thiourea (TU) in 2-methoxyethanol. TU was added into the solvent to form metal-TU and/or metal-TU-metal complexes with ions, then the complexes were thermally decomposed into CMTS films during annealing [20]. However, as mentioned in our previous report, the post-annealing approach aims to obtain high quality CMTS, then the as-prepared films were direct-annealed in an elevator furnace under an inert atmosphere (N_2) in non-vacuum processing. And there comes a problem like that, the chemical compositions are deviated from the stoichiometry, and leading to a S-poor and Cu-rich conditions which may induce the formation of more structural defects and further give inferior photovoltaic performance [16,21,22]. Similar phenomenon also has been reported in the synthesis of CZTS. This reveals that one of the major challenges to the CMTS materials are to develop impurity-free and phase-controlled thin films. To date, sulfurization plays an important role in the formation of the high-quality CZTS thin films and thereby has been investigated [4,23]. As reported, annealing with a sulfur source could decrease sulfur vacancies, improve the crystallinity and alleviate the impurity phases of the films [19,24]. Therefore, the feasibility study of the sulfurized CMTS related with structural and optical properties is a matter of primary interest. Systematic comparative experiments on CMTS should be carried out to get better understanding about the different annealing processes on the crystal growth, optical properties and structural properties, which confirm its potential for photo absorber material.

Here, we report on the fabrication of CMTS thin films using a DLC method accompanied by post-annealing processes. In order to understand the influence of distinct post-annealing paths leading to the formation of CMTS and to use this understanding to synthesize CMTS thin films with better optical properties and solar cells with better performance. The CMTS thin films were synthesized and the precursor films were processed at two different post-annealing techniques: direct-annealing and post-sulfurization. As for the sulfurization process, the sulfur source can be vaporized elemental S powder or its gaseous compound H_2S [25,26]. The disadvantage of using H_2S is that a special equipment is required to handle its toxicity, while using elemental S powders is comparatively safe and low-cost. Especially, the graphite box used in sulfurization process has an advantage of the confined chalcogen atmosphere which can decreases the loss of volatile elements, in particular SnS [21,27], and leading to the sulfur sufficient incorporated into the films which are beneficial to the devices performance. Extensive characterization of the synthesized CMTS thin films were carried out for the phase identification, morphology and band gap measurement. Further analysis suggested that the sulfur atmosphere tightly impact the quality of final layers. Compared to the direct-annealed layers with ratios of $Cu/(Mn + Sn) = 1.11$ and $S/Metals = 0.82$, the sulfurized with ratios of $Cu/(Mn + Sn) = 0.99$ and $S/Metals = 1.00$ was better to make efficient solar cells. Finally, the CMTS device made from post-sulfurization with a 170% efficiency increase was achieved.

2. Experimental

The precursor solution was prepared by dissolving $CuCl_2•2H_2O$ (7.04 mmol, 99.0%), $Mn(CH_3COO)_2•4H_2O$ (4.8 mmol, 99.0%), $SnCl_2•2H_2O$ (4.0 mmol, 98.0%) and thiourea (32 mmol, 99.0%) into 2-methoxyethanol while stirring at 50 °C for 30 min to get a yellow solution. Proper acetyl-acetone was added and stirred to avoid cracks during dip-coating. All chemical regents were used as received without any further purification. Scrupulously cleaned glass substrates were dip-coated with transparent precursor solutions. More details of the preparation procedure can be found in our previous report [5]. Then the as-prepared precursor films were annealed at two different post-annealing processes. Sample 1 (S1) was direct-annealed in an elevator furnace under a N_2 flow in non-vacuum processing. Sample 2 (S2) was sulfurized in a furnace chamber under the N_2 atmosphere with the pressure of 10 Torr. And 0.5 g sulfur powder was used as sulfur source. Both the films were heated to 560 °C maintained for 10 min, and then cooling down naturally to room temperature. In order to examine the quality of CMTS thin films synthesized utilizing different rapid thermal methods. The solar cell devices with the commonly employed structure of AZO/i-ZnO/CdS/CMTS/Mo/glass were prepared. The CdS buffer layer with approximately 50–60 nm thickness was grown by chemical bath deposition from an aqueous solution of $CdSO_4$ (1.5 mmol, 99.0%), thiourea (75 mmol, 99.0%) and ammonia (1.8 mmol) at 80 °C. Then window layers of undoped zinc oxide of about 50 nm thickness and Al-doped ZnO (AZO) of approximately 600 nm thickness were deposited by radio-frequency (RF) magnetron sputtering. Finally, a mechanical scribing step was performed to define the cell area to 0.16 cm^2.

The crystalline structures of samples were identified by X-ray diffraction (XRD, Bruker D8 Advance) using CuKα radiation. Raman scattering experiments were performed with a micro-Raman spectrometer (Jobin-Yvon LabRAM HR 800UV, 514 nm excitation). The morphologies and chemical composition were characterized by scanning electronic microscopy (SEM, FEI, S-4700) attached to an energy-dispersive X-ray spectroscope (EDS). The optical properties were determined using transmittance spectra (UV/vis Lambda 2S, Perkin–Elmer). The X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5000C ESCA System with Mg Kα source at 14.0 kV and 25 mA. All the binding energies were referenced to the contaminant C 1s peak at 284.6 eV of the surface adventitious carbon. Current-voltage (J–V) characterization for solar cells were performed using Xe-based light source solar simulator to provide simulated 1 sun AM 1.5 illumination which was calibrated with a standard Si reference cell. All measurements were performed at room temperature.

3. Results and discussion

3.1. Composition analysis

The chemical compositions of the CMTS thin films were analyzed by EDS and summarized in Table 1. Notably, despite excess thiourea (32 mmol) has been added to the precursor solution, the S1 still exhibits a much higher Cu percentage and lower S percentage ($Cu/(Mn + Sn) = 1.11$, $S/Metals = 0.82$). Interestingly, this conditions have been improved by the sulfurization process since the S/Metals ratio of S2 increases from 0.82 to 0.99 and the $Cu/(Mn + Sn)$ ratio decreases from 1.11 to 1.00. Additionally, the large atomic ratios of $Mn/Sn = 1.33$ indicates a slightly Sn-poor composition of the S1. Given the non-Sn-poor S2 ($Mn/Sn = 0.97$), this Sn deficiency in S1 can be due to the fact that the direct-annealing is processed under non-vacuum conditions which cannot prevent the

Table 1
Chemical composition and composition ratio of the direct-annealed (S1) and post-sulfurized (S2) CMTS thin films.

Samples ID	Chemical composition (at. %)				Composition ratio		
	Cu	Mn	Sn	S	Cu/(Mn+Sn)	Mn/Sn	S/Metals
S1	28.92	14.86	11.14	45.08	1.11	1.33	0.82
S2	24.93	12.41	12.71	49.95	0.99	0.97	1.00