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Fabrication of $Cu_2ZnSn(S_xSe_{1-x})_4$ solar cells by ethanol-ammonium solution process

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ABSTRACT

In this paper, $Cu_2ZnSn(S_xSe_{1-x})_4$ precursor films were produced by doctor blade process from SnS-Cu_2O-ZnS slurry. To prepare the slurry, SnS, ZnS and Cu_2O precipitates, which are outgrowths of stacked layer ZnS/Cu/SnS by CBD (chemical bath deposition)-annealing route, were dissolved in the mixture solvent of ethanol and $NH_3{\cdot}H_2O$. Synthesized precursor films were then annealed at different conditions. The post-annealed films were characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman measurements and UV–vis–NIR spectroscopy. SEM studies reveal that the rough and relatively compact absorber thin films are obtained via the sulfidation and sulfidation-selenization processes. X-ray diffraction and Raman spectrum results verify that the obtained films are composed of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ phases, which have high absorbance in visible range and direct band gap energy of 1.01–1.47 eV. The best devices yield total area power conversion efficiency of 1.99% and 2.95% corresponding to Cu_2ZnSnS_4 and $Cu_2ZnSn(S_xSe_{1-x})_4$ thin film solar cells under AM1.5 illumination without any anti-reflection layer.

1. Introduction

Chalcogenide-based thin film solar cells are expected to form the foundation of next generation photovoltaic (PV) technology [1,2]. As the typical thin film solar cells, $CuInGaSe_2$ solar cells have reached power conversion efficiency (PCE) of 21.7% particularly [3]. While due to the shortage of In and Ga elements, it is not realized to use $CuInGaSe_2$ producing cost-effective solar cells. Quaternary compound Cu_2ZnSnS_4 (CZTS) is a kind of promising candidate for the production of low-cost thin film solar cells because of their high absorption coefficient above $10^{-4}\,cm^{-1}$, optimal and direct bandgap of about 1.5 eV and abundant resources [4,5]. Various thin film deposition methods based on vacuum and non-vacuum techniques have been reported for the preparation of CZTS thin films. Shin et al. [6] reported the CZTS thin film solar cells with 8.4% power conversion efficiency (PCE) using vacuum thermal evaporation process. The 10.4% total area efficient devices were fabricated by Oueslati et al. [7] using sputtering of metal layers followed by selenization. For non-vacuum-deposition technologies, Miskin et al. [8] reported the CZTSSe thin film solar cells with a total area efficiency of 9.0% using hot-injection and spin coating followed by selenization. The best CZTSSe solar cell so far was fabricated by hydrazine slurry approach and its efficiency is beyond of 12.6% [9]. These methods have some disadvantages, such as the complicated machinery for vacuum technologies, the toxic and flammable reagents, which limit the popularization and application of these methods.

Aqueous bath process is a kind of environmentally friendly and cost-effective method and has been reported to fabricate CZTS thin films recently [10]. We reported a new process previously, namely stacked layer ZnS/Cu/SnS by CBD-annealing route and obtained the power conversion efficiency of 3.0% and 2.2% corresponding to selenization and sulfidation [11], respectively. During deposition of SnS, Cu and ZnS films on the substrate, SnS, Cu_2O and ZnS precipitates were producing in solution at the same time. In pursuit of high-efficient utilization ratio of materials and hence cost reduction, it is necessary to find out how to take advantage of these outgrowths. In this study, the outgrowths were dissolved in ethanol-ammonium solvents to form SnS-Cu_2O-ZnS slurry and then precursor films were fabricated by using doctor blade process from the slurry [12]. To form absorbed layers, the precursor films were annealed in different ways, including sulfidation, selenization and sulfidation-selenization. After annealing, $Cu_2ZnSn(S_xSe_{1-x})_4$ solar cells were fabricated with a standard structure for compound semiconductor

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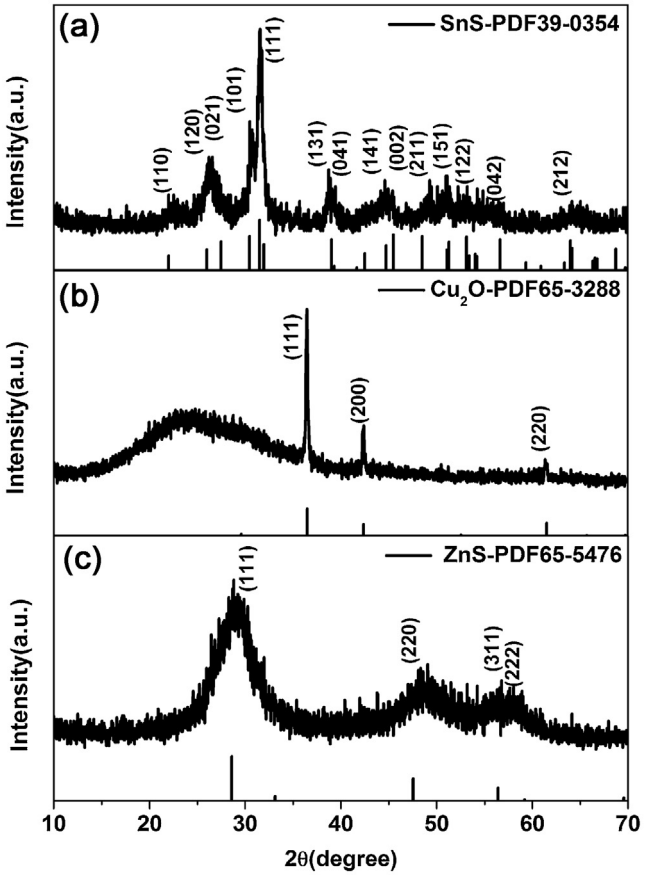

Fig. 1. XRD patterns of the resulting (a) SnS, (b) Cu_2O and (c) ZnS powders obtained from three CBD processes.

thin-film solar cells: glass/Mo/$Cu_2ZnSn(S_xSe_{1-x})_4$/CdS/i-ZnO/AZO/Al. Through process optimization, the CZTS solar cell (area 0.32 cm^2) with the PCE of nearly 2.00% and CZTSSe solar cell (area 0.35 cm^2) with the PCE of 2.95% have been achieved under AM 1.5 illumination without any anti-reflection layer.

2. Experimental

2.1. Preparation of SnS-Cu_2O-ZnS slurry

Three steps contained in stacked layer ZnS/Cu/SnS by CBD-annealing route: (1) SnS film is deposited on Mo glass; (2) Cu film is deposited on the synthesized SnS film; (3) ZnS film is deposited on the synthesized Cu film, and the details can be found in our previous work [11]. At the same time, SnS and ZnS precipitates can be obtained in the solutions by CBD method at the processes of fabrication of SnS and ZnS films, respectively. While, during the fabrication of metal Cu film on the SnS film substrate, Cu_2O precipitate rather than Cu is obtained in the solution, because Assistant Reduction Reaction ($Cu^{2+} + e^- \rightarrow Cu^+$, $Cu^+ + Sn^{2+} \rightarrow Cu + Sn^{4+}$) just occur on the surface of SnS film substrate. After the CBD coprecipitation, SnS, Cu_2O and ZnS precipitates were dissolved in ethanol and then centrifuged, respectively. Then the precipitates were dried in oven. At last, the precipitates were milled and SnS, Cu_2O and ZnS powders were obtained. Fig. 1 shows the XRD patterns of the resulting SnS, Cu_2O and ZnS powders after washing, drying and milling. All the X-ray peaks have been indexed, which are consistent with SnS (PDF No. 39-0354) [13,14], Cu_2O (PDF No. 65-3288) [15–17], and ZnS (PDF No. 65-5476) [18,19], respectively.

In a typical synthesis, 0.346 g Cu_2O, 0.400 g ZnS and 0.452 g SnS were mixed thoroughly and ground for 30 min. The as-milled powder was transferred into reagent bottle and then 1 ml of ammonium hydroxide (28%) and 1 ml of ethanol were added into it. Sequentially, the mixture was stirred for three days to form the SnS-Cu_2O-ZnS slurry. Fig. 2 shows the schematic for preparing the SnS-Cu_2O-ZnS slurry.

2.2. Preparation of absorbed layers and the final solar cells

First of all, Mo-coated glass substrates were ultrasonically cleaned with acetone followed by rinsing in methanol, isopropyl alcohol and deionized water for 5 min successively. The slurry was scraped on the molybdenum (1 μm) coated soda lime glass substrate by using doctor blade process [12] and then dried at 80 °C for an hour in oven. Posteriorly, the synthesized films were subjected to the isostatic pressing process at 12 MPa for 90 s. After the isostatic pressing process, the precursor films were annealed under different conditions. For example, the annealing processes were carried out in a sulfur-containing argon atmosphere at 600° C for 15 min, 45 min and 60 min (sulfidation); in a selenium-containing argon atmosphere at 500° C, 530° C and 550° C for 15 min (selenization) in sealed quartz tube with graphite sleeve. In order to obtain uniform, crack-free, and pinhole-free CZTSSe films, the precursor films were also annealed with elemental S at 600° C for 15 min, 45 min and 60 min first and then with elemental Se at 500° C for 15 min as a modified process (sulfidation-selenization). Finally, the annealed films were used to fabricate photovoltaic cells that had a glass/Mo/$Cu_2ZnSn(S_xSe_{1-x})_4$/CdS/i-ZnO/AZO/Al structure. CdS buffer layer (60 nm) was deposited on absorber layer by chemical bath deposition. The i-ZnO layer (50 nm) and ZnO:Al (AZO) window layer (400 nm) were then deposited by RF sputtering, and Al top electrode was deposited by vacuum evaporation [11]. Finally, the samples are mechanically scribed into individual cells.

2.3. Characterization

Morphology and EDX analysis were studied by field emission scanning electron microscopy (FE-SEM Siron 200). Phase analysis was done by X-ray diffraction (XRD) using a Bruker Advance D8 diffractometer equipped with graphite-monochromatized Cu K (radiation (λ = 1.5406 Å)). Raman measurements were performed to further confirm the secondary phase at room temperature using a LABRAM-HR micro-Raman system in the back scattering configuration with a laser source of 532 nm. X-ray photoelectron spectroscopy (XPS) spectra were carried out on thermo ESCALAB 250 spectrometer to determine the valence of elements using an Al Kα monochromatized source and a multidetection analyzer under a 10^{-8} Pa residual pressure. The optical absorbance of the deposited thin films was measured with a UV–vis–NIR spectrophotometer (SOLID 3700) in arrange 300–1600 nm. The final solar cell devices were assessed by the oriel AAA solar simulator under standard AM1.5 illumination (100 mW Cm^{-2}, 25° C).

3. Results and discussions

3.1. CZTS and CZTSSe films

Fig. 3 shows the surface and cross-section morphologies of the post-annealed CZTS and CZTSSe films. As shown in Fig. 3(a)–(c), the sulfurized CZTS films have dense and relatively smooth surfaces. With the increase of annealing time, average CZTS grain sizes/thicknesses of MoS_2 layers increase, which are 171 nm/0.58 μm, 233 nm/1.13 μm and 264 nm/1.31 μm corresponding to differently annealing time of