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SUPERSTRATE-TYPE Cu_2ZnSnS_4 SOLAR CELLS WITHOUT SULFURIZATION FABRICATED BY SPRAY PYROLYSIS

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Cu_2ZnSnS_4 is one kind of new promising material for low-cost thin film solar cells. This paper reports superstrate-type Cu_2ZnSnS_4 solar cells consisting of CdS as a buffer layer and Cu_2ZnSnS_4 as an absorber. Firstly, Cu_2ZnSnS_4 film has been fabricated using ultrasonic spray pyrolysis. A combination of XRD, Raman, UV-Vis spectroscopy and SEM-edx suggests that the Cu_2ZnSnS_4 is kesterite structure but with poor quality. Then, solar cells with superstrate structure of FTO/d-TiO_2/CdS/Cu_2ZnSnS_4/Au present a power conversion efficiency of 1.05%. The thickness of Cu_2ZnSnS_4 absorber is thin (~300nm) for the reason that thick absorber will result in poor efficiency. The key limitation factor of low efficiency is due to large series resistance (R_s) and low shunt resistance (R_{sh}), which is mainly caused by poor quality crystals and severe recombination. This work may provide a general method to achieve superstrate-type semiconductor solar cells.

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Keywords: Cu_2ZnSnS_4, Thin films, Spray pyrolysis, Superstrate-type solar cells

1. Introduction

Recently, one kind of copper system quaternary p-type compound semiconductors, namely Cu_2ZnSnS_4(CZTS) has attracted significant attention owing to its proper photoelectric properties, including earth abundant component and environmentally friendly, high absorption coefficient (>10^4 cm^{-3}), and ideal band gap of 1.5 eV, suitable for thin film solar cells [1, 2]. According to the theory of Shockley-Queisser limit, CZTS solar cells could reach a maximum efficiency of 28%[3]. So far the highest record conversion efficiencies of CZTS thin film solar cells with pure CZTS absorb layer have reached 9.2% [4] and 11.5% with cadmium alloying [5], respectively. There is still plenty of room for performance improvement in CZTS solar cells.

CZTS solar cells are mainly by fabricated with substrate structure, similar with CIGS solar cells, and CZTS film should be sulfurized in a sulfur or H_2S atmosphere to obtain high-quality crystals [6]. Compared with substrate structure, superstrate-type solar cells offer the merits of lower cost, easier processing, and could serve as top cell in tandem solar cells [7,8]. However, FTO or ITO substrate of superstrate-type CZTS solar cells will be spoiled in a sulfur or H_2S atmosphere and ruin the solar cells. It is difficult to fabricate superstrate-type CZTS solar cells similar with methods of fabricating substrate solar cells[9]. Therefore, highly efficient methods should be developed to fabricate superstrate solar cells

In this work, spray pyrolysis method has been used to fabricate CZTS thin films and corresponding devices. Composition, morphology and phases of the film were illustrated. Furthermore, superstrate-type CZTS solar cells were fabricated by spray pyrolysis without sulfurization and a total-area efficiency of 1.05% was achieved. The limitation factors of performance of solar cells were also discussed.

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2. Experimental

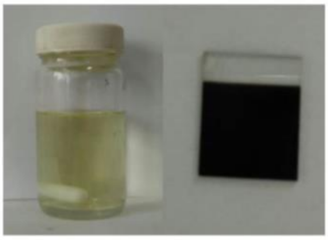
The CZTS thin films were deposited on glass substrate by spray pyrolysis method with custom-build spray system. 0.01 M $CuCl_2\cdot 2H_2O$, 0.005 M $ZnCl_2$, 0.005 M $SnCl_2$ and 0.05 M thiourea were dissolved in 60 ml methanol as precursors. The substrate temperature for the spray pyrolysis was chosen 350 °C. Before spray, the glass substrate was cleaned by acetone, ethanol and water in ultrasonic bath and then was dried in a nitrogen flow.

Cleaned fluorine-doped tin oxide (FTO, 14 Ω/sq, NSG) glass is first coated with a ~50 nm dense TiO_2 layer (d-TiO_2, as the hole-blocking layer) by spray deposition. Next, a ~50-nm-thick CdS buffer layer was prepared on d-TiO_2 by chemical bath deposition (CBD). Then Cu_2ZnSnS_4 film was deposited on CdS buffer layer and annealed in N_2 atmosphere. After that, superstrate-type device with FTO/d-TiO_2/CdS/CZTS/Au configuration was fabricated. Finally, 50 nm thick Au electrodes were deposited on top of the CZTS film through a shadow mask containing 9.07 mm^2 circular openings by thermal evaporation.

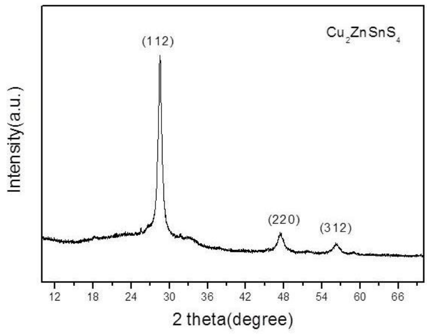
XRD patterns were measured on a Rigaku diffractometer equipped with a Cu Kα□radiation source; UV–visible absorption spectra were obtained on Shimadzu UV-2550; Raman(using 532 nm as the excitation wavelength) and UV-Raman (using 325 nm as the excitation wavelength) spectra were obtain on LabRAM HR800 (Horiba Jobin-Yvon Company); SEM images were obtained on an S-4800 microscope (Hitachi Company) with an accelerating voltage of 0.5-30 kV; J-V characteristics were measured using a Keithley 2400 source meter under illumination by a solar simulator (AM 1.5, 100 mW/cm^2, Zolix, SS150, China), and the light intensity was calibrated using a silicon solar cell. All measurements were carried out in air at room.

3. Results and discussion

$CuCl_2$, $ZnCl_2$, $SnCl_2$ and thiourea were dissolved in methanol as precursors, then light yellow transparent solution was gained, and dense and smooth film was acquired by spray pyrolysis, as shown in Fig.1(a). The XRD patterns of CZTS films synthesized is shown in Fig.1(b). As can be seen, peaks located at 28.54°, 47.56° and 56.3°, which has been indexed as the (1 1 2), (2 2 0) and (3 1 2) planes of CZTS. They are assigned to the kesterite phase with (112) preferential orientation (PDF NO.26-0575) and zinc stannate ($ZnSnO_3$) phase was not detected in XRD. The Raman spectra of the CZTS films (shown in Fig.1(c)) showed a dominant broad peak at 337cm^{-1}. The broadening of the peak suggests low crystallinity of the CZTS film and the possible existence of secondary phases, such as ZnS (350 cm^{-1}) and Cu_2SnS_3 (303cm^{-1} and 356 cm^{-1}) cannot be excluded [10]. UV-Raman spectrum was used to distinguish the phase structure of Cu_2ZnSnS_4 and ZnS [10]. Fig.1 (d) shows the UV-Raman spectrum of CZTS film, three resonant Raman lines of ZnS (R1LO, R2LO and R3LO) were not be detected, indicating the pure phase of the CZTS films prepared by spray pyrolysis.



a)



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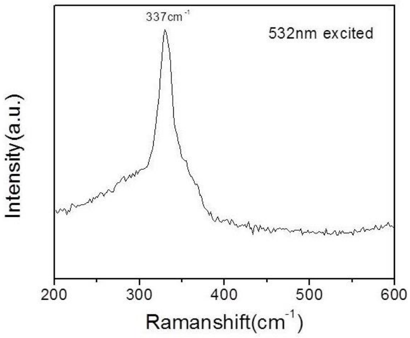

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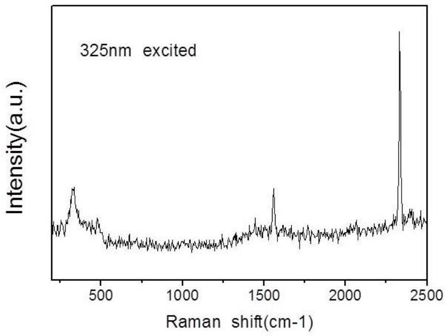
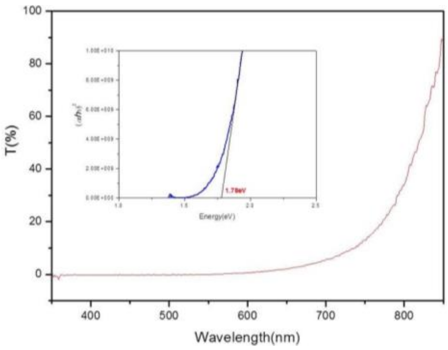


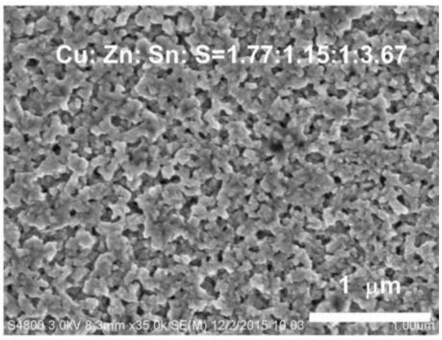
d)

Fig. 1. (a) DC photographs of CZTS precursor solution and CZTS film. (b) XRD pattern of the CZTS film prepared spray pyrolysis. (c) Raman pattern of the CZTS film prepared spray pyrolysis. (d) UV-Raman pattern of the CZTS film prepared spray pyrolysis.

The transmission spectrum for CZTS film in Fig. 2a showed a good absorption at wavelength shorter than 750 nm. By plotting $(\alpha h\nu)^2$ versus $(h\nu)$, we extrapolated the linear fitting line with the x-axis and obtained a direct bandgap of 1.72eV (Inset of Fig. 2a), which is not agreed well with the corresponding literatrues [11] for the reason that the film by spray pyrolysis is very thin (~300nm), and the thickness of film is consistent with the absorber of superstrate-type CZTS solar cell. Fig. 2b shows the SEM image of a CZTS film fabricated by spray pyrolysis, and dense structure of CZTS film can be seen, and particle size is ~100 nm, which is smaller than results in corresponding literatrues [11] because the film is not sulfurized in a sulfur or H_2S atmosphere. EDX indicates that Cu: Zn: Sn: S = 1.77: 1.15: 1: 3.67, Cu/(Zn+Sn)=0.786, and it is copper-poor and zinc-rich, which favor the formation of Cu_{Zn} and it is widely adapted literature[11]. Therefore, combining XRD, Raman, UV-Vis spectroscopy and SEM-edx suggests that the Cu_2ZnSnS_4 is kesterite structure but with poor quality.

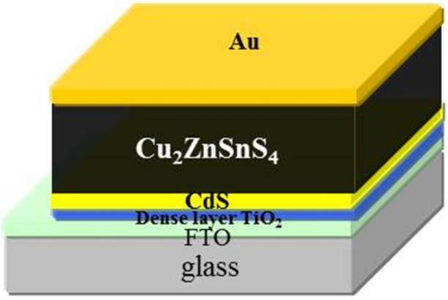


a)

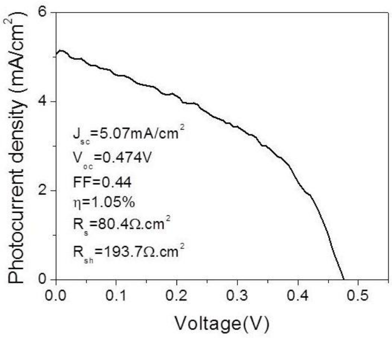


b)

Fig. 2. (a) Uv-vis spectroscopy of the CZTS film. (Inset: Tauc plot), (b) SEM image of a CZTS film



a)



b)

Fig. 3. (a) Schematic structure of a FTO/d-TiO_2/CdS/CZTS/Au superstrate solar cell(d-TiO_2, as the hole-blocking layer). (b) J–V characteristics of FTO/d-TiO_2/CdS / CZTS/Au solar cells under AM 1.5G simulated illumination (100 mW/cm^2).

Superstrate-type CZTS solar cell with structure of FTO/d-TiO_2/CdS/CZTS/Au was fabricated, as shown in Fig. 3(a). The thickness of CZTS absorber is thin (~300 nm) for the reason that thick absorber will result in sever recombination and poor efficiency (~0.1%). Current density–voltage (J–V) curves of CZTS solar cells were shown in Fig. 3(b). The solar cell showed an open-circuit voltage of 474mV, a short-circuit current density of 5.07mA/cm^2, a fill factor of 44% and a conversion efficiency of 1.05%, which is largely lower than substrate-type solar cells[4,5]. Series resistance (R_s) and shunt resistance (R_{sh}) analyzed according to the Sites's method [12]. The key limitation factor of low efficiency is due to large R_s(80.4Ω.cm^2) and low R_{sh}(193.7Ω.cm^2), which is mainly caused by poor quality of crystals and severe recombination. Furthermore, the absorber is too thin to absorb enough light for creating sufficient light-induced charges result in little photocurrent-generated. It is necessary for CZTS absorber should be sulfurized in a sulfur or H_2S atmosphere to obtain high quality crystals. The key point of sulfurized superstrate-type CZTS solar cells is to search tips to avoid spoiling FTO or ITO substrate in a sulfur or H_2S atmosphere. There is still plenty of room for performance improvement in superstrate-type CZTS solar cells.

4. Conclusions

Solar cells with superstrate structure of FTO/d-TiO_2/CdS/CZTS/Au were fabricated to explore the possibility of CZTS solar cells with easier processing and higher efficiency than substrate-type CZTS solar cells. A combination of XRD, Raman, UV-Vis spectroscopy and SEM-edx suggests that the Cu_2ZnSnS_4 absorber fabricated using ultrasonic spray pyrolysis is kesterite structure but with poor quality. The fabricated superstrate-type CZTS solar cell presents a power conversion efficiency of 1.05%, which is largely lower than substrate-type CZTS solar cells. The key limitation factor of low efficiency is due to large series resistance (R_s) and low shunt resistance (R_{sh}), which is mainly caused by poor quality crystals and severe recombination. This work may provide a general method to achieve superstrate-type solar cells with compound semiconductor as the absorbers.

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