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The fabrication of Cd-free Cu_2ZnSnS_4-Ag_2ZnSnS_4 heterojunction photovoltaic devices

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ABSTRACT

Cu_2ZnSnS_4 (CZTS) is a low cost, non-toxic material composed of earth-abundant elements with a large optical absorption coefficient. However, in CZTS solar cells, CdS buffer layers are widely used, which contain toxic elements and lead to lattice mismatch with CZTS thin films. In this paper, we have systematically investigated a I-II-IV-VI semiconductor material to replace the CdS buffer layer with a non-toxic material that offers good lattice matching with the CZTS film. For the first time, Cd-free Cu_2ZnSnS_4-Ag_2ZnSnS_4 heterojunction photovoltaic device is fabricated, where Cu_2ZnSnS_4 and Ag_2ZnSnS_4 layers are obtained by co-sputtering method. The cell exhibits a 4.51% efficiency which is higher than those of CZTS solar cells with ZnS and In_2S_3 buffer layers. This work offers the possibility to realize environmentally benign, scalable, low-cost, and high-efficiency solar cells.

1. Introduction

Chalcopyrite Cu(In,Ga)Se_2 (CIGS) and CdTe are the most promising materials for thin-film solar cells. The efficiency of solar cells based on CIGS and CdTe has already achieved 22.6% [1] and 22.1% [2], respectively. However, the high costs of gallium and indium impede the further development of CIGS, and Cd is a toxic element, which has caused serious environmental concerns [3–5]. In recent years, many efforts have been directed at finding low-cost materials with earth-abundant elements. Cu_2ZnSnS_4 (CZTS), as a potential material to substitute CIGS, is composed of earth-abundant, non-toxic elements and has attracted great interest due to its direct band gap with high absorption coefficient [6–8]. Although CZTS is a non-toxic semiconductor compound, there is an amount of toxic elements such as Cd present in the structure of CZTS solar cells, in which CdS thin films are often used as the buffer layer [9,10]. CdS layers are usually deposited by chemical bath deposition (CBD) which will cause some serious environmental problems [11–13]. Some environmentally-friendly films, such as In_2S_3, ZnS and Zn-Sn-O [14–18], have been used as the buffer layer to replace CdS.

Ag_2ZnSnS_4 (AZTS) can be an n-type semiconductor due to the high formation energy of the intrinsic point defects and composed of inexpensive, earth-abundant, non-toxic elements [19–22]. In this study, we use AZTS which has good lattice matching with CZTS film as the buffer layer instead of CdS to fabrication the CZTS/AZTS heterojunction solar cells. To the best of our knowledge, we are the first to propose the concept of an AZTS buffer layer and to successfully demonstrate a CZTS solar cell with sputtered AZTS buffer layer. An efficiency of 4.51% is obtained for CZTS/AZTS solar cells prepared by a simple co-sputtering deposition. Our results offer the possibility to realize environmentally benign, scalable, low-cost, and high-efficiency solar cells.

2. Experimental

2.1. Preparation of CZTS and AZTS films

In this work, CZTS precursor was fabricated by co-sputtering three different targets, i.e, Cu (99.99%), Sn (99.99%), and ZnS (99.99%) on a clean soda lime glass substrate. Cu and Sn were sputtered by DC magnetron sputtering with powers of 6 W and 43 W, respectively, and ZnS was sputtered using 90 W (RF magnetron) to obtain a precursor thickness of 800 nm. After sputtering, the samples were loaded into a

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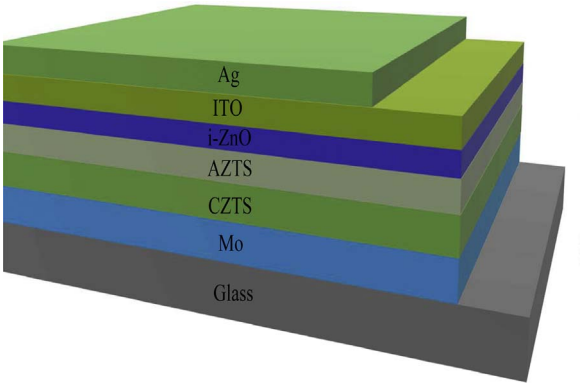

Fig. 1. The structure of CZTS/AZTS solar cells.

Table 1
The element composition of the CZTS precursor and AZTS precursor film.

Sample	Cu (Ag) (at%)	Zn% (at %)	Sn% (at %)	S% (at%)	Cu/Zn +Sn	Zn/Sn	S/metal
CZTS	31.23	16.14	39.38	13.25	0.56	0.40	0.15
AZTS	32.61	16.03	37.61	13.75	0.61	0.42	0.16

horizontal tube furnace under a H_2S atmosphere at 550 ˚C for 1 h. The ramp rate was 100 ˚C/min. Then, AZTS was fabricated under the same conditions, with Cu being replaced by Ag (99.99%), at a sputtering power of 12 W, resulting in a film thickness of 100 nm. After sputtering, the samples were loaded into a horizontal tube furnace under a H_2S atmosphere at 500 ˚C for 5 min. The ramp rate was 100 ˚C/min. After

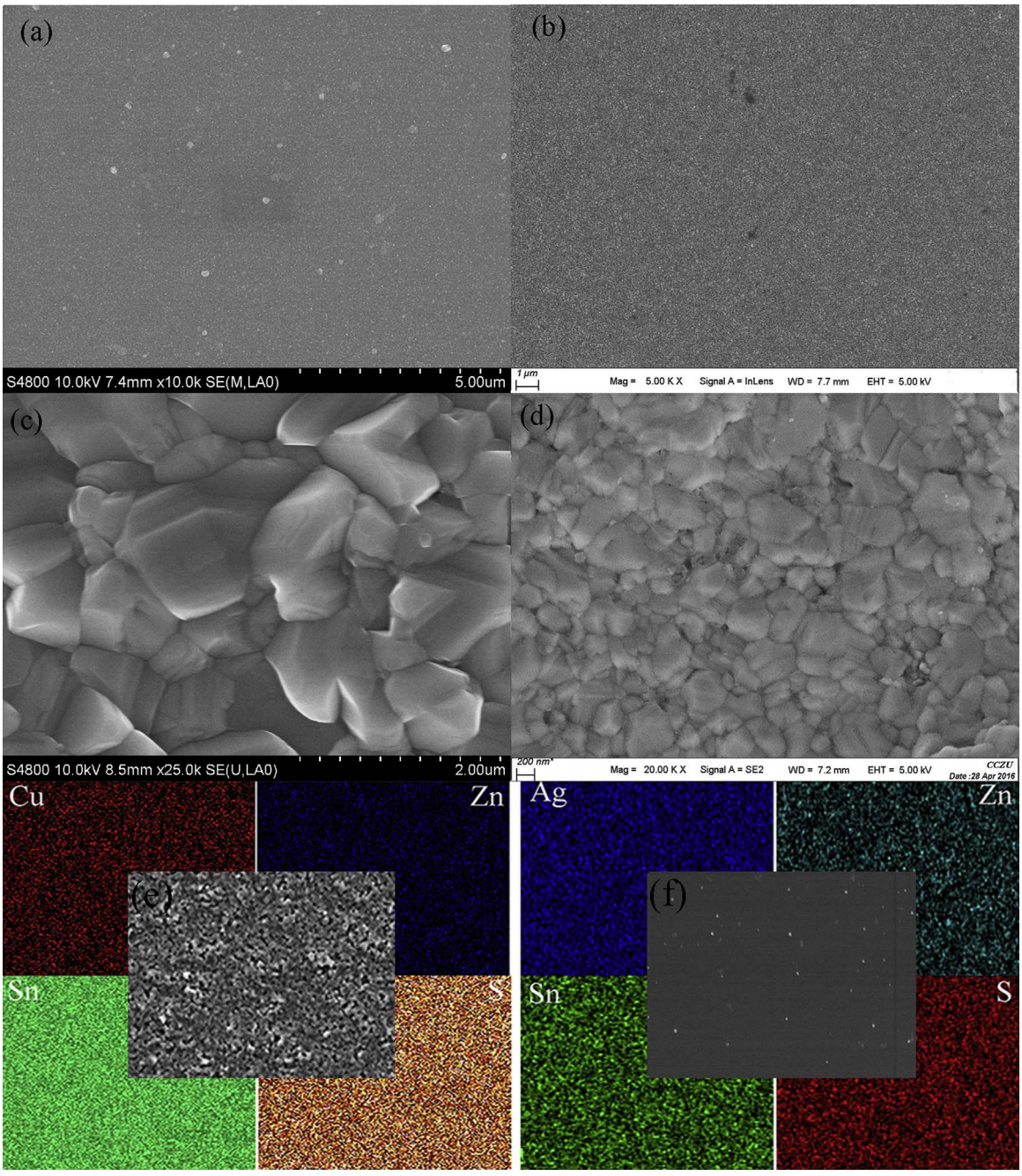

Fig. 2. (a) and (b) The SEM images of CZTS and AZTS precursor films. (c) and (d) The surface SEM image of CZTS and AZTS films, (e) and (f) EDS mapping image of CZTS and AZTS thin films.