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The effect of sulfur vapor pressure on Cu_2ZnSnS_4 thin film growth for solar cells

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ABSTRACT

The sulfurization is an essential process during the preparation of high quality Cu_2ZnSnS_4 (CZTS) absorber layers, which is controlled by the parameters such as annealing time, temperature and atmosphere, etc. The heat under different temperature not only provides energy for the samples, but also determines the sulfur vapor pressure, which affects the CZTS growth. To distinguish the effect of energy supply and sulfur vapor pressure on CZTS films, a two-temperature zone tube furnace was used, which permits independent control of the sulfur source and substrate temperature. Keeping the substrate temperature constant, the morphology and crystalline of CZTS thin films were investigated under various sulfur vapor pressure by changing sulfur temperature. Finally, the device performances have also been studied, which depended significantly on the sulfur vapor pressure. A champion PCE (2.59%) of oxide-derived CZTS device was obtained under high sulfur vapor pressure.

1. Introduction

Thin film chalcopyrite $Cu(In,Ga)Se_2$ (CIGS) and CdTe solar cells have undergone rapid developments over the past decades. The recorded efficiency of CIGS and CdTe solar cells are 22.6% and 22.1%, respectively (Jackson et al., 2016; First Solar press release, 2017). However, because of some ingredient of them are scarce (In, Ga) and toxic (Cd), these technologies cannot be widely used. Thus, it is badly in need to search for an alternative material that is non-toxic and earth-abundant. Cu_2ZnSnS_4 (CZTS) has been considered to be one of the promising alternative absorber materials. That is due to its environmental friendly, earth-abundant components, p-type conductivity, absorption coefficient of $\sim 10^4\,cm^{-1}$ and direct band gap of 1.5 eV. The recorded efficiency of CZTS and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) based solar cells are improved to 9.2% and 12.6% respectively (Kato et al., 2012; Todorov et al., 2013). Since Ito and Nakazawa found the photovoltaic effect of CZTS material in 1988, many synthesis methods have been come forth and applied to prepare CZTS thin films (Ito and Nakazawa, 1988). For example, Pravakar et al. synthesized CZTS thin films by RF magnetron sputtering approach (Pravakar et al., 2017). Rajeshmon et al. fabricated CZTS thin films by spray pyrolysis technique (Rajeshmon et al., 2011). Tanaka et al. have prepared CZTS thin films by sol-gel solution (Tanaka et al., 2007). Chan et al. synthesized CZTS thin films by electrodeposition (Chan et al., 2010) and so on.

For different methods, the heat treatment is essential for high quality CZTS thin film. There are two main heat treatment ways for the formation of CZTS thin films. One is annealing sulfur-containing precursors under sulfur-free environment. The other is annealing precursors under sulfur vapor or H_2S gas, which was known as sulfurization process. Due to the higher activity of sulfur in H_2S, the H_2S gas can make a better grain growth than the sulfur powder or sulfur pellet. However, the H_2S gas is highly toxic, which leads to the solid sulfur become an ideal source of S element for annealing (Platzer-Bjorkman et al., 2012; Emrani et al., 2013; Inamdar et al., 2013; Lee et al., 2016). For the sulfurization under solid sulfur, there are many parameters, such as sulfurization time, temperature and heating rate, etc., can affect the growth of CZTS thin films. For example, Katagiri and Fernandes et al. have studied the effects of sulfurization time on CZTS absorbers (Katagiri et al., 1997; Fernandes et al., 2013). Yao and Araki et al. have also investigated the influence of sulfurization temperatures on CZTS thin films (Yao et al., 2017; Araki et al., 2009). Consequentially, the grain and crystallinity of CZTS will be improved with the increasing of temperature, which is considered as one of key factor for CZTS growth. It is worthy note that the substrate and sulfur powder always place at same zone during conventional sulfurization,

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which play different roles in the CZTS growth. The substrate temperature provides the energy for the growth of CZTS, while the sulfur source temperature control the sulfur vapor pressure. For instance, the effects of annealing temperature on the properties of CZTS films has been studied in our previous work, in which substrate and solid sulfur source temperature change simultaneously (Chen et al., 2015). So it is hard to figure out the role of the substrate temperature or sulfur source temperature for CZTS growth.

To investigate the effect of sulfur vapor pressure on the CZTS films, a two-temperature zone tube furnace was used in this work. During the sulfurization, the sample temperature was held, while the temperature of sulfur source was varied to form different sulfur vapor pressure. This single factor model is used to illustrate influence of sulfur vapor pressure on the morphology, crystallinity and even the device performance. This refined the mechanism of sulfurization of CZTS which using solid sulfur as the sulfur source.

2. Experimental

First of all, the oxide nanoparticles were fabricated by baking the mixture at 380 °C for 30 min. Such mixture was made by mixing the Cupric nitrate ($Cu(NO_3)_2{\cdot}3H_2O$), Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), Tin(II) oxalate (SnC_2O_4) and Ammonium bicarbonate (NH_4HCO_3) then grounding until the Cu, Zn and Sn elements were blended homogenously (at least for 30 min). Next, the pre-synthesized oxide precursors for the CZTS absorber layer were deposited on the Mo layer by doctor blade method, more detailed preparation process can be seen in our previous report (Chen et al., 2015). As Fig. 1 shows, the sulfurization was conducted by using a two-temperature zone tube furnace to control the temperature of substrate and the sulfur source independently. The heating rate, holding time and substrate temperature were kept constant. While, the sulfur source temperatures were changed from 250 °C to 550 °C. After sulfurization, the tube furnace was cooled down to room temperature. In addition, the solid S (0.02 mol) was used as the sulfur source during the whole process.

CZTS thin-film solar cells were obtained through using the conventional structures (Ag/AZO/i-ZnO/CdS/CZTS/Mo/SLG), which includes a soda lime glass (SLG) substrate, a ~1 μm thick Mo layer as a back-contact layer, a CZTS absorber layer, a ~80 nm thick CdS buffer layer deposited by CBD approach, a ~50 nm thick i-ZnO layer deposited via RF sputtering and a ~600 nm thick AZO layer deposited via RF sputtering. Finally, an Ag collection grid was deposited using silver paste.

The lattice structure of the thin films were recognized by XRD method (D/Max-rA). The morphology of the films were observed by using a field emission scanning electron microscope (FESEM, JEOL-JSM-6700F). The Raman measurements were performed at room temperature using a LABRAM-HR micro-Raman system with a laser source of 514 nm. Then the solar cells were characterized using a KEITHLEY 4200-SCS semiconductor characterization system equipped with an AAA SAN-EI ELECTRIC solar simulator and a solar cell quantum efficiency measurement system model QEX10.

3. Results and discussions

It's well known that the sulfur vapor pressure is determined by sulfur source temperature, which will control the grain growth. So a series of experiments with the substrate temperature fixed and the sulfur source temperature changed was carried out to investigate the effect of sulfur vapor pressure on the CZTS thin films, as shown in Fig. 2. Basing on this point, the vapor pressure of S under diverse temperature was estimated by the Antoine Equation (Dean, 1985):

$$\log P = A - \frac{B}{t + C} \tag{1}$$

where P is the sulfur vapor pressure in mmHg, and t is the sulfur temperature in °C. A is 6.843, B is 2500.0 and C is 186.0. According to this formula, the temperature-dependent equilibrium pressure of sulfur was shown in Fig. 2. It can be clearly seen from the curve that the S vapor pressure was increased tardily under 400 °C. However, it increased rapidly as the sulfur source temperature above 400 °C.

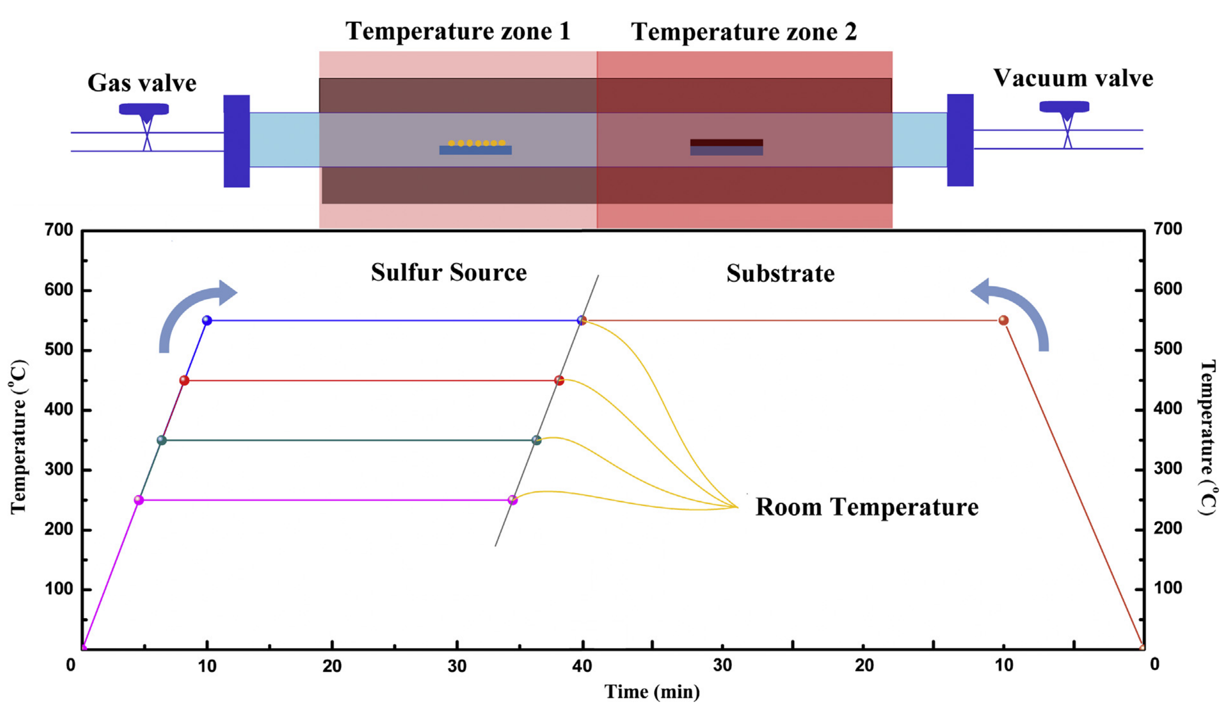

Fig. 1. Schematic diagram of sulfurization furnace profiles and a typical temperature profile of sulfurization.