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Effects of Copper Concentration on the Characteristics of Cu_2ZnSnS_4 Thin Films Prepared by Rapid Thermal Annealing

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Abstract

We report the preparation of Cu_2ZnSnS_4 (CZTS) thin films with the metallic precursor of ZnSn/Cu by a non-toxic and fast sulfurization technique. We used sulfur powders to avoid the highly toxic gas of hydrogen sulfide (H_2S) and the rapid annealing (RTA) to shorten the sulfurization process time. With different Cu concentrations [Cu/(Zn+Sn) = 0.7－1.2] in the metallic precursor of ZnSn/Cu, the crystallization of CZTS thin films would be obviously changed after sulfurization. Meanwhile, the Cu content of CZTS films appears to have rather dramatic effects on film characteristics, such as crystallization, morphology, optical and electrical properties. The diffraction peaks of (112), (220)/(204), and (312) planes observed show the kesterite structure of CZTS films. The solar cell fabricated with the CZTS film grown showed the best conversion efficiency of 5.1% for 0.45cm^2 with V_{oc}= 0.569 V, J_{sc}= 18.6 mA/cm^2, and FF= 48%.

1. Introduction

Cu2ZnSnS4 (CZTS) is one of the most promising absorber materials for low-cost thin-film solar cells due to its non-toxic and earth-abundant. CZTS has direct band gap between 1.4 and 1.56 eV that is the optimum band gap for use as an absorber layer to exploit a great magnitude of input solar irradiance from the spectrum, and a large absorption coefficient of over 10^4cm^{-1} [1－4]. The intrinsic p-type conductivity of CZTS also makes it an ideal absorber material in solar cells due to the fast transfer of photo-generated holes at the front of illuminated side [5]. All the above inherent advantages lead to inexpensive and potential CZTS solar cells have reached the power conversion efficiency of 8.4% by vacuum processing [6], and recently an efficiency of 11.1% for a mixed sulfo-selenide ($Cu_2ZnSn(S,Se)_4$) device using a hydrazine-based solution deposition [7]. These results indicate that the quaternary CZTS would be a potential candidate for solar cell applications.

The aim of this study is to adopt the non-toxic rapid sulfurization process to grow high-quality CZTS thin films. We used sulfur powders to avoid the highly toxic gas of hydrogen sulfide (H_2S) and hydrazine that are universal materials to fabricate CZTS solar cells, and the use of rapid annealing (RTA) to achieve a fast sulfurization to shorten the whole process time [8]. In aspect of RTA sulfurization process, we loaded metallic precursor into the graphite closed susceptor with sulfur powders to proceed sulfurizing.

The major concern of sulfurization is the amount of sulfur, sulfurization time, inter-diffusion, and loss extent of metals and sulfur. The graphite closed susceptor will be used to decrease the loss of sulfur and metals in sulfurization process, which means that the graphite closed-chamber will be filled with high sulfur vapor so that sulfur molecular has enough kinetic energy to diffuse into the CZTS thin film and to completely combine with metals.

The crystallization would be obviously changed after sulfurizing. Meanwhile, the Cu content of CZTS layer appears to have a rather dramatic effect on film characteristics [9], such as morphology, crystallization, and electricity. Thus, a detailed and further investigation of Cu concentration on the growth of CZTS is needed for the fabrication of smooth-surface, less second phase, and good performance of CZTS films.

2. Experimental

Deposition of the CZTS thin films consisted of a two-step process. First, metallic precursor films were deposited on Mo-coated soda-lime glass substrates by RF sputtering at room temperature (RT) using two targets of Cu and Zn/Sn (1.2:1) alloy. The metallic precursor was in form of the stacking layer with the sequence of Mo/ZnSn/Cu. The Cu metal layer on top of precursor is used to prevent the loss of Zn and Sn. The sputtering working pressure was maintained at 5 mtorr in Ar atmosphere and the sputtering power was 50 and 20 W for Cu and Zn/Sn targets, respectively. The total thickness of the metallic precursor was approximately 500 nm. The composition of CZTS thin films was adjusted by Cu layer thickness.

Next, the metallic precursor with sulfur of 400 mg was placed in a graphite closed susceptor box, which was then loaded into the RTA chamber with N_2 atmosphere. The graphite box was heated to convert the metallic precursor into CZTS thin film with full of high-pressure sulfur vapor. The CZTS thin films were prepared by sulfurizing the metallic precursors with different Cu contents (Cu/Zn+Sn = 0.7-1.2) at 570℃ for 10 min. Figures 1(a) and 1(b) show the cross section and top view of the graphite closed susceptor used for sulfurization, respectively. Temperature profile of the sulfurization process of CZTS thin film is shown in Fig. 2.

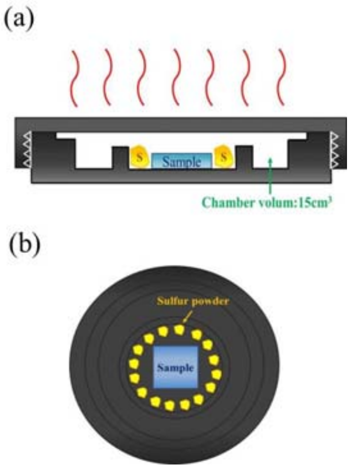

Fig. 1 (a) Cross section and (b) top view of the graphite closed-susceptor used for sulfurization by RTA.

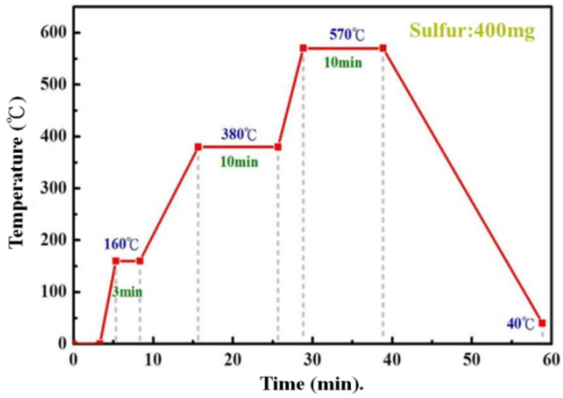

Fig. 2 Temperature profile of the sulfurization process of CZTS thin film.

3. Results and Discussion

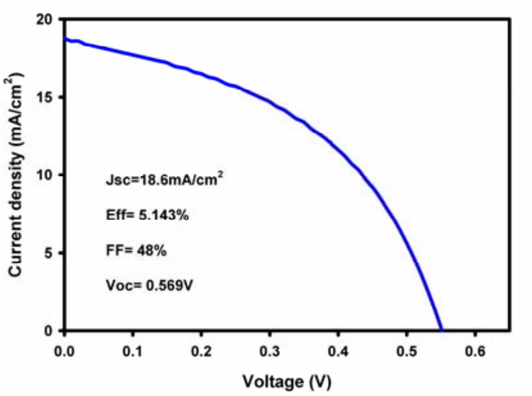

Fig. 3 Current–voltage characteristics of the solar cells fabricated with CZTS absorber grown.

Solar cells using the best CZTS films were fabricated in the Al/ ITO/ i-ZnO/ CdS/ CZTS/ Mo/ glass configuration; 70nm CdS was deposited by chemical bath deposition and 50nm intrinsic ZnO and Al doped n-ZnO were deposited by RF sputtering. Finally, Al as a top contact was deposited by evaporation using a mask. I–V measurementswereperformedon the solar cell under 1.5AM irradiation with a solar simulator. The solar cells fabricated with the film grown at Cu/(Sn+Zn)= 0.7 showed the best conversion efficiency of 5.1% for 0.45 cm^2 with an open circuit voltage of 0.569V, short circuit current density of 18.6mA/cm^2, and fill factor of 48%, as shown in the illuminated current–voltage characteristics of the solar cells in Fig. 3.

4. Conclusions

CZTS thin films were successfully deposited by non-toxic and RTA sulfurization technique. All the films are observed to be grown well with strong preferential orientation along the (112) plane by XRD analyses. The grain size become large with increasing Cu/(Zn + Sn) ratio, exhibiting an enhancement of grain growth under Cu-rich condition. Besides, Cu-rich film have roughness surface because the grains expand on the film surface and the voids appear in films. Those results obviously show that the control of Cu concentration in the metallic precursor is considered to be crucial to obtain high-quality CZTS thin films. The fabricated solar cell shows a short-circuit current density of 18.6mA/cm^2, an open-circuit voltage of 569 mV, a fill factor of 48%, and a conversion efficiency of 5.1% for the CZTS film with the ratios of Cu/(Zn+Sn) as 0.73 and Zn/Sn as 1.2. Optimizing the CdS buffer layer and i-ZnO window layer is further in progress to enhance the efficiency of CZTS solar cells.

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