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Preparation of $CuInS_2$ thin films by sulfurization using ditertiarybutylsulfide

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ABSTRACT

Sulfurization growth of single-phase chalcopyrite $CuInS_2$ (CIS) thin films was demonstrated using less hazardous liquid metal–organic ditertiarybutylsulfide [$(t\text{-}C_4H_9)_2S$: DTBS]. The effect of sulfurization temperature and DTBS flow rate on the structural and optical properties of CIS was analyzed by scanning electron microscope, X-ray diffraction, energy dispersive X-ray spectroscopy, and photoluminescence spectra. The measurement results indicated that the CIS film formed by this method was suitable as a photo-absorbing layer for CIS-based solar cells.

1. Introduction

Compounds with the chalcopyrite crystal structure $Cu(In,Ga)(S,Se)_2$ have attracted much attention as promising materials for thin film solar cells because of their high conversion efficiency, long lifetime, low cost, and light weight, as well as their application to the radiation-resistant solar cells. Among the chalcopyrite compound, $CuInS_2$ (CIS) has been theoretically predicted to have the highest conversion efficiency for a thin film solar cell [1]. This is mainly attributed to its direct optical band gap of 1.55 eV, which perfectly matches well with solar spectrum for optimizing the solar energy conversion [2], and high absorption coefficient of around 10^5 cm^{-1} [3]. In addition, non-toxic component is another advantage as an environment-friendly renewable energy semiconductor. However, the best conversion efficiency of CIS-based solar cells is still as low as 12.9% [4], the open circuit voltage(V_{OC}) is up to 879 mV [5], which is considerably less than that of other chalcopyrite-based solar cells such as $CuInSe_2$ (19.5%) [6] and $Cu(In,Ga)Se_2$ (20.3%) [7]. The main difference between $Cu(In,Ga)Se_2$ and CIS lies in the band gap energy (E_g), where $Cu(In,Ga)Se_2$ films are relatively narrow E_g materials and CIS films are a wide E_g material, and the solar cells with the wide E_g are generally governed by interface recombination, which reduces the V_{OC} in comparison with the theoretical predictions and therefore leads to lower efficiencies [8–10]. Although sulfurization of CIS using H_2S gas and elemental S vapor is the most promising way for yielding high-quality thin films, the use of H_2S is undesirable from the viewpoint of handling and safety in the manufacturing process of CIS sulfurization, because H_2S gas is very expensive and highly toxic, which is usually stored in high pressure cylinders [11]. Elemental S vapor is very difficult to control because the supply of S vapor is unstable, and the S vapor also changes the composition of films due to the loss of materials during the growth [12].

In this study, we have developed an alternative technique for the sulfurization of CIS thin films, in which a metal–organic ditertiarybutylsulfide [$(t\text{-}C_4H_9)_2S$: DTBS] was used as sulfur source. It is known that DTBS is liquid at room temperature and stored in stainless-steel cylinders under atmospheric pressure with less hazardous and very cheap price; this method is considered as a promising alternative for the massive production. In our previous studies [13–15], we have reported that CIS thin films with chalcopyrite structure were prepared by sulfurization using DTBS. In order to evaluate the properties of CIS thin films, low temperature photoluminescence (PL) measurements were performed. In the present study, we further investigate the effect of sulfurization conditions on the properties of CIS thin films. These works are aimed at optimizing the fabrication conditions for improving the performances of CIS-based solar cells.

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2. Experiments

Sequentially stacked metallic Cu/In layers were used as the starting materials, generally called precursors. They were evaporated on soda-lime glass substrates without intentional heating. The thickness and molar fraction of each layer of the precursor were controlled by in situ monitoring using a quartz crystal oscillator. The total thickness of the precursors was 670 nm and the molar Cu/In fraction was calculated to be approximately 0.76. The deposition pressure was about 1×10^{-3} Pa during evaporation.

For the sulfurization, the equipment and the process were the same as those described in our previous reports [13–15]. The precursors were sulfurized using DTBS over a temperature range of 400–575 °C for 15 min under atmospheric pressure. The supplying rate of DTBS was varied at a region of 35–100 μmol/min and the N_2 carrier gas was kept at a constant flow rate of 2 L/min. The thickness of the sulfurized CIS thin films was approximately 2.0 μm.

The crystalline structures of thin films were investigated by X-ray diffraction (XRD). XRD patterns were recorded using the Bragg–Brentano geometry on a Rigaku MiniFlex II using Cu Kα radiation ($\lambda = 0.15418$ nm) at 30 kV and 15 mA. The surface morphology of the films was examined by scanning electron microscope (SEM, Hitachi Miniscope TM-1000). The images were produced by secondary electrons by using an accelerating voltage of 15 kV. The elemental composition of samples was determined by energy dispersive X-ray spectroscopy (EDX) in a Hitachi Miniscope TM-1000 operating at 15 kV. The defect levels were evaluated by PL at low temperature using a frequency doubled quasi-cw Nd:YAG laser with a wavelength of 532 nm as the excitation source. The laser power was fixed at 60 mW and the laser was focused on the sample by a lens with a focal length of 5 cm. The luminescence was dispersed by a grating monochromator with a focal length of 50 cm and recorded by a GaAs:Cs photomultiplier and a Ge photo detector cooled by liquid N_2. The PL equipment was the same as those described in our previous reports [13–15].

3. Results and discussion

In this experiment, the precursors of the samples were deposited at the same conditions. The effect of sulfurization temperature and DTBS flow rate on the crystal properties of CIS thin films is investigated in detail. The surface SEM micrographs of CIS thin films prepared at the different sulfurization temperature are shown in Fig. 1, where the DTBS flow rate and the duration time for the sulfurization were kept at the constants of 70 μmol/min and 15 min respectively. With sulfurization process, densely packed grains in the films are formed; the typical grain size is approximately 1–2 μm for the CIS films with high sulfurization temperatures of 515–575 °C. Furthermore, the grain size increases with the sulfurization temperature at the region of 515–575 °C. Smooth surfaces without obvious grains are observed for the film sulfurized at low temperature from 400 to 460 °C, which may be not sufficient for the growth of CIS phase. These results here are in line with those reported in references [16,17]. Therefore, high sulfurization temperature is needed to obtain appropriate grains for CIS thin films.

The XRD patterns of Cu–In precursor and CIS thin films deposited at different sulfurization temperatures are shown in Fig. 2, where the DTBS flow rate was 70 μmol/min. For the In-rich Cu–In precursor, $Cu_{11}In_9$ is obtained before the sulfurization, which is in accordance with the results for the Cu–In precursors annealed at vacuum conditions [18,19], indicating that Cu and In metal formed the alloy during the evaporation. In the case of sulfurization temperature above 515 °C, single phase chalcopyrite CIS films are obtained without any extra phases such as Cu_2S, In_2S_3 formed or $Cu_{11}In_9$ precursor phase remained, and the phase separation of chalcopyrite is not confirmed. However, for the sulfurization at temperature below 460 °C, un-reacted $Cu_{11}In_9$ precursor phase is found

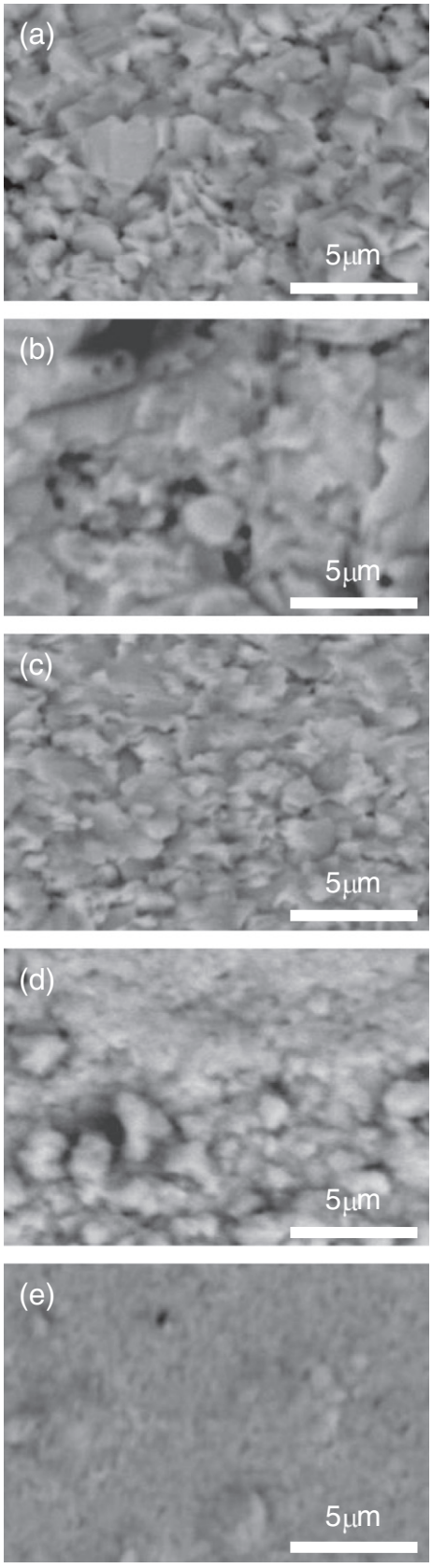

Fig. 1. The surface SEM micrographs of CIS thin films formed at different sulfurization temperatures of (a) 575 °C, (b) 545 °C, (c) 515 °C, (d) 460 °C, and (e) 400 °C. The DTBS flow rate was constant at 70 μmol/min.