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Impact of growth temperature on the properties of SnS film prepared by thermal evaporation and its photovoltaic performance

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ABSTRACT

Tin(II) sulfide (SnS) films are one of the most promising absorber materials for high efficiency solar cells without using rare metals. In this work, SnS films were deposited by the thermal evaporation on glass substrates under the variation of growth temperatures of 100–250 °C. It was revealed that the SnS thin film prepared under the temperature of 100 °C had relatively small crystal grains. On the other hand, the denser and larger crystal grains of the SnS films were obtained with the constant compositions, when the growth temperature increased to 225 °C. With the temperature of higher than 225 °C, the SnS began to be re-evaporated from the films. The highest Hall mobility of the films was obtained under the temperature of 200 °C. Ultimately, the results suggested that the optimized growth temperature of SnS by the evaporation is 200 °C, giving rise to compact and large crystal grains and the highest Hall mobility, thereby contributing to the 2.53%-efficient SnS thin-film solar cell.

1. Introduction

Recently, there are many kinds of the compound semiconductors as the absorbers of thin-film solar cells, such as CdTe [1], and Cu(In,Ga)Se_2 [2], and $Cu_2ZnSn(Se,S)_4$ [3], and etc. The CdTe and Cu(In,Ga)Se_2 can absorb sun light with the thickness of a few μm owing to their high absorption coefficients. However, In is a rare metal, and Cd and Se have detrimental impact on the environmental. In this work, we therefore concentrated on alternative Tin(II) Sulfide(VI) (SnS), which is abundant and non-harmful to the environment. The SnS is p-type II–VI compound semiconductor with high potential as an absorber of single junction solar cell because it has direct band-gap energy (E_g) of around 1.3 eV, absorption coefficient of above 10^5 cm^{-1} [4], and high carrier mobility of 90 cm^2/V s in bulk [5]. In addition, it was reported that theoretical conversion efficiency of chalcogenide thin-film solar cell with E_g of 1.3 eV is over 25% [6], and the ideal short-circuit current density (J_{SC}) is 35.5 mA/cm^2 calculated from the standard solar spectrum with E_g of 1.3 eV [7].

The SnS films as the absorbers have been prepared by various methods such as sputtering [8], electrodeposition [9,10], evaporation [11–14], spray pyrolysis [15,16], hot wall deposition [17,18], and pulsed-chemical vapor deposition [4]. The SnS thin-film solar cell with the highest conversion efficiency of around 5% has been recently obtained [19]. The thermal evaporation is the one of the most popular method to prepare the thin-film solar cell absorber (e.g. Cu(In,Ga)Se_2). In addition, this method is able to fabricate SnS absorber films with homogeneous and large grains. In this work, we therefore fabricated the SnS absorber using the thermal evaporation and investigated the effect of growth temperature of SnS film on its cell performance to improve the film quality (i.e., compact and large SnS grains), which is appropriate for the application in the solar cell.

2. Experimental methods

In this work, the SnS thin-film solar cell with the active area of 0.23 cm^2 was prepared with a structure of Al/ZnO:Al_2O_3/ZnO/CdS/SnS/Mo/soda-lime glass(SLG). The 800-nm-thick Mo layer as back electrode was first deposited on SLG substrate by radio frequency (RF) sputtering method under the pressure of 1.1 Pa in Ar atmosphere. The SnS thin film was then evaporated on Mo-coated SLG substrate using SnS powder with 99.9% purity as a material source. The wool fiber of SiO_2 was added in the crucible with SnS powder to suppress splashed SnS grain on the absorber surface. The temperature of the crucible was controlled at 575 °C. The distance between crucible and sample substrate is 20 cm. The growth temperature

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(i.e., surface temperature of substrate) was varied from 100 (not controlled) to 250 °C with deposition time of 120 min. The substrate temperature was measured by thermocouple attached on the surface of the samples. The densities of the SnS film were calculated by mass of the film divided by its volume before and after the film deposition. After the deposition, the SnS film was analyzed by scanning electron microscopy (SEM). The crystallographic structure was characterized by x-ray diffraction (XRD) with Cu Kα (λ = 1.5405 Å) radiation operated at 45 kV and 40 mA. The resulting film was moreover investigated by energy dispersive x-ray spectroscopy, Raman spectrum, and optical properties. Next, the SnS film was lifted-off from Mo-coated SLG substrate to perform Hall effect measurement [20]. The results were compared to the SnS film on Mo-coated SLG substrate.

After the preparation of SnS absorber, 50-nm-thick CdS buffer layer was deposited by chemical bath deposition. Then, ZnO as window layer with a thickness of 100 nm and ZnO:Al (Al_2O_3: 2 wt %-doped) as a transparent conductive oxide (TCO) layer with a thickness of 300 nm were deposited by RF sputtering method. Finally, the 250-nm-thick Al grid electrode was deposited as front electrode by thermal evaporation. The current density–voltage (J–V) characteristics of the SnS thin-film solar cell was measured under standard test condition (100 mW/cm^2, and air mass 1.5G illumination at 25 °C). The external quantum efficiency (EQE) of the SnS thin-film solar cells was also measured using two sources of illumination (xenon and halogen lamps) together with a conventional lock-in detection system.

3. Results and discussion

Fig. 1 demonstrates surface and cross-sectional images of SnS films prepared under the variation of the growth temperature from 100 to 225 °C. The S/Sn ratios in the figure were almost constant at about 1.04 although the phase change is observed. According to Fig. 1(a) and (b) under the growth temperature of 100 °C, the SnS films with the thickness of approximately 8 μm were observed with relatively small and flake-like crystal grains, similar to those of the films, prepared by spray pyrolysis in Ref. [16]. On the other hand, in Fig. 1(e)–(h) under the growth temperature from 200 to 225 °C, the thicknesses of resulting SnS films drastically decrease to about 2 μm, much thinner than those of the films prepared under the temperatures of 100 and 150 °C. Moreover, the SnS films with larger and non-flake-like crystal grains were observed. With further increasing the growth temperature of higher than 225 °C, the SnS film began to be re-evaporated, which will be demonstrated later.

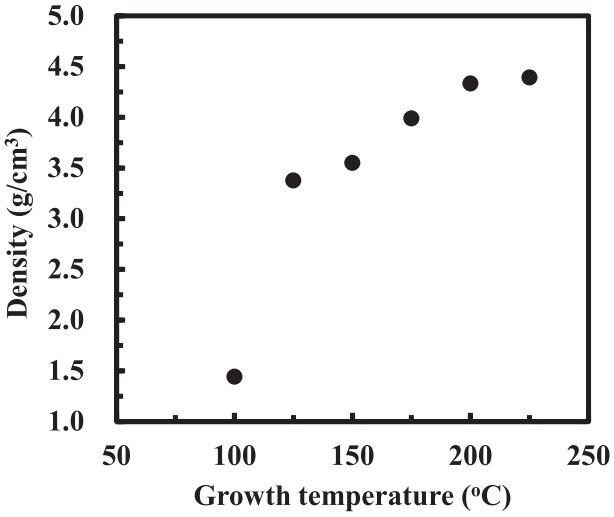

Fig. 2. Density of SnS thin films as a function of the growth temperature.

Based on the strong decrease in the thickness of the SnS film from around 8 to below 2 μm with increasing the growth temperature in Fig. 1, the film density as a function of the growth temperature was next investigated, as shown in Fig. 2. It was disclosed that the film density was increased to 4.39 g/cm^3 with enhancing the growth temperature up to 225 °C. Namely, the SnS crystal quality was improved (i.e., compact and large SnS grains). As a result, the decrease in the thickness of SnS films in Fig. 1 was not attributed to the re-evaporation of the films under increasing growth temperature, but caused by the denser films. The reported SnS densities are 4.6 g/cm^3(film) [4], 5.05 g/cm^3(bulk) [21], and 5.27 g/cm^3(bulk) [22], which shows higher density than our SnS absorber. It is however considered that the film density of our SnS (i.e., crystal qualities) can be further increased by optimizing other growth conditions such as temperature of sulfurization, which will be reported elsewhere.

Fig. 3 shows the XRD spectra of the SnS thin films under different growth temperatures. With increasing the growth temperature from 100 to 225 °C, full width at half maximum (FWHM) values of corresponding SnS peaks were decreased, implying the increase in crystal grain size of resulting films, well consistent with

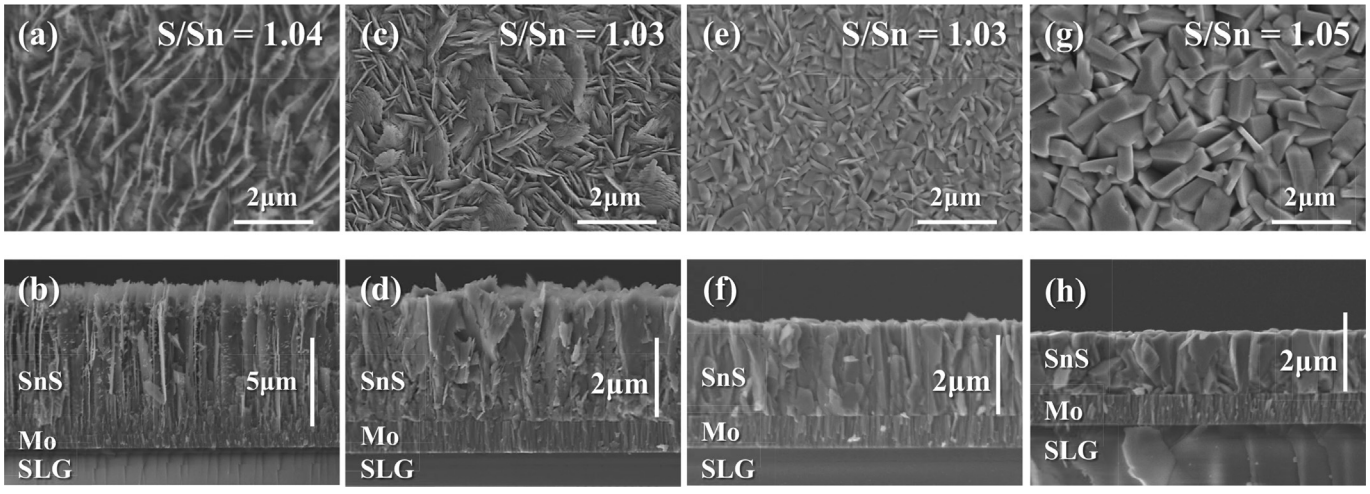

Fig. 1. Surface and cross-sectional images of SnS films prepared under the change of the growth temperatures of (a, b) 100, (c, d) 150, (e, f) 200, and (g, h) 225 °C.