Facile strategy for the formation of tin monosulfide thin films by rapid thermal annealing

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A simple but facile way to form phase-pure tin monosulfide (SnS) thin films is proposed using a rapid thermal annealing (RTA) process. SnS powder and substrate were loaded into a vacuum-sealed quartz ampoule and treated by RTA at 500 °C for 10 min. This allowed the formation of single-phase SnS films. The densely packed morphology and phase purity of the films were confirmed by scanning electron microscopy, X-ray diffraction, Raman spectroscopy, and transmission electron microscopy. A preliminary thin-film solar cell was fabricated that demonstrated the efficiency of 0.42%.

1. Introduction

Recently, significant attention has been given to tin monosulfide (SnS) as an alternative absorber for next-generation thin-film solar cells [1–4]. SnS comprises earth-abundant and inexpensive elements, which is advantageous compared to the toxic Cd used for CdTe absorbers or the expensive In used for Cu(In,Ga)Se2 absorbers. In addition, SnS has a direct bandgap of 1.3 eV, optimal for light absorption, and a high absorption coefficient exceeding 104 cm−1 [5]. The simple binary system is also beneficial for easy compositional control and eventually for the mass production of these absorbers, compared to the complex quaternary Cu(In,Ga)Se2 [6] or Cu2(Zn,Sn)(S,Se)4 [7,8] absorbers. The use of SnS thin films as alternative absorbers was reported by Reddy et al. in 2006 [1], who reported an efficiency of 1.3%. The highest efficiency of 4.36% was recorded by Sinsermsuk sakul et al. in 2014 [2]. Although the alternative material was expected to provide excellent performance, the efficiency improvement has been somewhat slow.

Several research groups have attempted the creation of large-grain SnS using multiple techniques, including spray pyrolysis [1], chemical bath deposition (CBD) [9], evaporation [3,10–13], physical vapor deposition [14,15], atomic layer deposition [16,17], electrodeposition [18], and chemical vapor deposition [2,19]. One of the most difficult obstacles to overcome is the creation of thin, pinhole-free, and phase-pure films. During the formation of SnS films, n-type Sn2S3 or SnS2 secondary phases form easily, limiting the overall efficiency of the cells [2,3,12]. In addition, the inherent layered structure of SnS promotes crystallization in thin plates, leading to frequent shunting in the fabricated cells. Therefore, morphological control of pure SnS is essential for creating high-efficiency cells.

In this letter, we propose a simple but facile way to form phase-pure SnS thin films using rapid thermal annealing (RTA). High-purity SnS powder and a substrate were loaded into a small quartz ampoule (Fig. 1(a)). Then, the ampoule was vacuum-sealed with a base pressure of 1–2 mTorr. Vacuum sealing helped to minimize the incorporation of

2. Experimental details

RTA (Ajeon Co., 12-F18) was used for the growth of SnS films. The as-received SnS powder (1 g, 99.99% purity) (iTasco Co., LT40NS312, 3–12 mm) and a glass substrate of 2 × 2 cm were inserted into a quartz ampoule (volume = 100 mL) (Fig. 1(a)). Then, the ampoule was vacuum-sealed with a base pressure of 1–2 mTorr. Vacuum sealing helped to minimize the incorporation of
impurities into the grown films and to improve the diffusion of the vaporized SnS, promoting the formation of uniform SnS films over larger areas. The annealing temperatures were set to 400 °C and 500 °C, and the ramping time for both targeted temperatures was fixed to 50 s. After heating for 10 min, the furnace was allowed to cool naturally to room temperature.

The surface morphologies and cross-sections of the grown SnS films were observed by SEM (Jeol, JSM-7500F). XRD (PANalytical, X’Pert Pro MPD) with Cu Kα radiation (λ = 1.542 Å) using a θ–2θ scan was used to investigate the phase information of the grown SnS films. In addition, Raman spectroscopy (Tokyo Instruments, Nanofinder FLEX-G) was employed to analyze the phase purity of the grown films. High-resolution TEM (Jeol, JEM-2100F) was used to confirm the crystallinities of the grown films. The samples analyzed by TEM were prepared by a focused ion beam (FEI, Helios G3 CX). A thin-film solar cell device with the structure of soda-lime glass (SLG)/Mo/SnS/CBD-CdS/i-ZnO/Al-doped ZnO/Ni/Ag was fabricated following a conventional process. Details on device fabrication can be found elsewhere [20].

3. Results and discussion

Fig. 1(a) shows the quartz ampoule loaded with SnS powder and the glass substrate. Fig. 1(b) shows the ampoule after RTA at 500 °C for 10 min. SnS is reported to evaporate congruently at elevated temperatures [3]. During the cooling of the furnace, it is believed that the SnS vapors begin condensing heterogeneously on the glass substrate, as well as on the inside wall of the ampoule. The SnS-deposited substrate was collected by breaking the ampoule and then analyzed. Upon first inspection with the naked eye, an irregular non-uniform film was observed on the sample subjected to RTA at 400 °C. Fig. 1(c) shows the surface morphology of the SnS thin film treated at 400 °C. Small millet-like grains and particle aggregates are observed in the image. Fig. 1(d) shows the low-magnification plane-view SEM image of the SnS film annealed at 500 °C. Compared to the 400 °C sample, dense and large SnS grains are observed over a wide area without large pinholes, as is further revealed in the high-magnification image of Fig. 1(e). The morphology of the SnS grown at 500 °C is comparable to that of the SnS films showing the solar cell efficiency of 2.5%, as reported by Kawano et al. when using thermal evaporation [21]. Detailed phase information was further obtained by XRD, Raman spectroscopy, and TEM, as discussed below.

XRD analysis was used to determine the phases present in the SnS films grown on the glass substrates. Fig. 2(a) shows the XRD patterns of the films grown at 400 °C and 500 °C. The bottom three patterns depict the reported powder diffraction patterns for orthorhombic SnS (#39-0354), orthorhombic Sn₂S₃ (#14-0619), and hexagonal SnS₂ (#23-0677). From the patterns, it is noted that both films mainly exhibit the orthorhombic SnS phase. No peaks match the Sn₂S₃ or SnS₂ patterns. For the film grown at 400 °C, weak SnS-related peaks are observed, except for one strong peak attributed to the (040) plane at 31.9°, indicating highly preferred (040) growth. In contrast, the pattern of the film grown at 500 °C clearly exhibits a polycrystalline SnS film with randomly oriented structures. However, preferred orientation of (040) plane remains.

Raman spectroscopy was further employed to confirm the films’ phase purity because the secondary phases would not be detected from XRD measurements if they were not crystalized well. Fig. 2(b) depicts the Raman spectra for the films grown at different
RTA temperatures. As expected, the SnS-related peaks at 51, 94, 165, 214, and 223 cm$^{-1}$ are observed for both films [21,22]. Interestingly, an additional broad peak centered at 308 cm$^{-1}$ is detected for the film grown at 400 °C. This peak can be deconvoluted into two peaks at 302 and 313 cm$^{-1}$, indicative of the secondary phases of Sn$_2$S$_3$ and SnS$_2$, respectively [21]. Although XRD detected no secondary phases for the film grown at 400 °C, it is believed that the film contains small portions of detrimental secondary phases. These secondary phases may be poorly crystallized. In addition, they may exist near the surface in small amounts, hindering their detection. Notably, no peaks from the secondary phases are detected for the SnS film grown at 500 °C. The higher temperature of 500 °C appears to be the optimum condition for the growth of phase-pure SnS film in this study.

Fig. 3(a) shows the cross-sectional TEM image of the SnS film grown at 500 °C on the glass substrate. It is seen from the figure that a ~1-μm-thick SnS thin film is formed after RTA for 10 min. Several voids near the glass substrate are seen, as expected from the SEM image of Fig. 1(d). The high-resolution image in Fig. 3(b) also supports the random orientation of the SnS grains, as indicated by the XRD pattern of Fig. 2(a). Lattice fringes with different crystal orientations are clearly seen within the circled regions in the figure. As discussed earlier, SnS forms a layered structure that increases the possibility of void formation, especially at the bottom of the interface near a substrate. Further investigation for void removal by controlling the nucleation rate is necessary.

Fig. 4 shows the current density–voltage plot for the preliminary thin-film solar cell device with the structure of SLG/Mo/500 °C-grown SnS/CdS/i-ZnO/Al-doped ZnO/Ni/Ag. The efficiency, open-circuit voltage, short-circuit current density, and fill factor are 0.42%, 91 mV, 15.6 mA/cm$^2$, and 0.297, respectively. Notably, the short-circuit current density of 15.6 mA/cm$^2$ is higher than that (9.6 mA/cm$^2$) of the 1.3%-SnS/CdS solar cell reported by Reddy et al. [1], which confirms the high quality of the RTA-grown SnS absorber. The relatively low efficiency is ascribed to
the low open-circuit voltage and fill factor [2]. We expect increases in the cell efficiency with further optimization on the densification of the SnS surface and the improvement of the interface between the absorber and buffer layer.

4. Conclusions

We propose a simple but facile method of forming phase-pure polycrystalline SnS films via RTA. By increasing the annealing temperature to 500 °C, homogeneous SnS film growth was achieved by the condensation of congruently evaporated SnS. Various analyses including SEM, XRD, Raman, and TEM revealed the phase purity of the deposited SnS films. A preliminary thin-film solar cell device was fabricated that demonstrated the efficiency of 0.42%. The proposed method may contribute to the fabrication of highly efficient SnS-based thin-film solar cells.

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