FABRICATION OF TIN MONOSULFIDE FILMS BY REACTION DIFFUSION

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1. Introduction
Tin monosulfide (SnS) is a potential absorbing material for thin film solar cells. It was reported that SnS demonstrated a p-type conductivity with the absorption coefficient of above $10^5$ cm$^{-1}$ [1]. The band-gap energy ($E_g$) of SnS is around 1.3 eV [2]. In addition, SnS consists of abundant and non-harmful elements. The highest efficiency of SnS solar cell is 4.63% [3], where the SnS absorbing layer was fabricated by atomic layer deposition (ALD) and annealed under a H$_2$S atmosphere at 400 °C for 1 hour. However, considering the chemical potential diagram of the Sn-H$_2$S$_2$ system, the partial pressure of sulfur, which is equivalent to the chemical potential of sulfur, is too large to obtain single-phase SnS ($p$(S$_2$(g)) ~ 10$^8$ atm) and SnS$_2$ ($E_g$ ~ 1.9 eV [4]) was possibly formed. In this work, we thus conceived the fabrication of SnS films with single-phase by precisely controlling the chemical potential through reaction diffusion between Sn and MoS$_2$. The chemical potential diagram of the Sn-Mo-S$_2$ system shown in Figure 1 gives the thermodynamic equilibrium between SnS and MoS$_2$, which indicates that the chemical potential of sulfur to obtain SnS can be controlled by MoS$_2$. In this work, we tried to fabricate SnS by reaction diffusion between Sn and MoS$_2$, which supplies sulfur to Sn under the controlled chemical potential.

2. Experimental methods
Mo films with the thickness of about 600 nm were prepared on soda-lime glass (SLG) substrates by DC sputtering. Then, the Mo films and sulfur powder were sealed in an evacuated quartz ampoule under the pressure below 10$^{-2}$ Pa. The ampoule was heat-treated for 2 hours to sulfurize Mo films. The temperatures of Mo films and sulfur powder were controlled to be 600 °C and 420 °C, respectively. After that, Sn films were deposited on the sulfurized films by DC sputtering. The sample with Sn/MoS$_2$/SLG were sealed in an evacuated quartz ampoule and annealed at 480-680 °C for 1 hour. For some samples, SnO$_x$ films were deposited by RF sputtering before annealing to prevent the evaporation of formed SnS because the vapor pressure of SnS was relatively high.

3. Results and discussion
SnS was identified in the XRD profile of the sample with SnO$_x$ layer annealed at 480 °C, while SnS was not confirmed in the case without SnO$_x$. This suggests that SnO$_x$ layer prevents the evaporation of formed SnS. The XRD profiles of films with SnO$_x$ before and after annealing at 580 °C for diffusion reaction are shown in Figure 2. In the sample before annealing, Mo, MoS$_2$, and Sn are identified. In the annealed sample, SnS, Mo, and MoS$_2$ are identified and the peak intensity from Sn decreases, which indicates the formation of SnS by reaction diffusion between Sn and MoS$_2$. In addition, the other tin sulfides such as SnS$_2$ are not confirmed. Therefore, the process proposed in this work is considered to be reasonable to obtain SnS. However, the sublimation of the films was observed in the sample annealed at 680 °C. The vapor pressure of tin monoxide SnO is about $10^8$ atm at 680 °C under atmospheric pressure and it is thus supposed that SnS together with SnO$_x$ evaporates during annealing. In the presentation, we are also going to discuss the experimental results of the reaction diffusion on other conditions such as temperature and period.