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Effect of Na on sulfurization growth of SnS thin films and solar cells using NaF/Sn-S precursor

Mutsumi Sugiyama *, Tsubasa Yokoi, Akihiko Henmi, Takashi Asano

Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

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ABSTRACT

The role of NaF treatment in the production of SnS thin films and solar cells was investigated. The grain size of SnS films containing Na was large (about 500 nm) compared to that of SnS films prepared by conventional sulfurization (typically 250 nm). The carrier concentration of SnS increased from 5×10^{16} to 2×10^{17} cm^{-3} by Na diffusion into the SnS film, and Na acted as an acceptor. Moreover, the NaF layer exhibited a capping effect during high-temperature sulfurization at 500 °C and suppressed the re-evaporation of SnS. The short-current density tended to increase from 1.1 to 8.8 mA/cm^2 with increasing thickness of the deposited NaF layer from 0 to 200 nm, because of the larger grain size and carrier concentration of SnS.

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1. Introduction

Tin monosulfide (SnS) is a promising candidate for solar cells using earth-abundant materials because it has a direct bandgap of 1.3 eV and a high light absorption coefficient (>10^4 cm^{-1}) [1–3]. Recent SnS-related solar cells have exhibited conversion efficiencies of 4.36% [4], which is far below the theoretical efficiency. This is because it is difficult to grow SnS films of high purity and quality, and with a low defect density.

Recently, post-deposition treatment using alkali metals such as Na or K has been employed to improve the quality of thin films and the solar cell efficiency of chalcogenide semiconductors such as Cu(In,Ga)Se_2 (CIGS) [5–7], Cu_2ZnSnS_4 (CZTS) [8], and Cu_2SnS_3 [9]. The alkali metal depletes the cation (mainly Cu) concentration in the chalcogenide film near the surface, passivates defects, and enables optical gain through a thinner CdS buffer layer. On the other hand, there are no previous reports of alkali metal effects on a SnS film, which is a Cu-free chalcogenide semiconductor.

For large-area applications, sulfurization methods, which are reactive solid-phase growth methods, are the most promising preparation techniques that yield high-quality thin films [10–12]. However, because of the relatively low melting points of Sn and S, SnS tends to re-evaporate easily [13]. As a result, only porous and small-grain SnS is obtained by this method, as opposed to that obtained using atomic layer deposition (ALD) [4,14], sputtering [15], evaporation [16,17], or chemical processes [18,19]. Therefore, understanding the effects of Na on SnS thin films grown by sulfurization, and on SnS-related solar cells, is very useful for the development of an efficient and environmentally benign solar cell. In this paper, we discuss the impact of the NaF treatment on SnS thin films and solar cells.

2. Experimental

A Sn-S precursor mixture was deposited by conventional RF sputtering (using a 3N purity SnS target, Toshima Manufacturing) on a Mo-coated soda-lime glass substrate. NaF (using 2N quality powder, Toshima Manufacturing) was deposited on the precursor by thermal evaporation and controlled the deposited NaF layer thickness. Both the layers were deposited without intentional heating. These precursors were then continuously sulfurized at 500 °C for 30–60 min using S powder (4N, Kojundo Chemical Laboratory) as the S vapor source because it is less toxic than H_2S and is easier to handle. NaF was also very easy to handle and could be removed by simply washing with deionized water after the sulfurization process. The SnS solar cells used were diverted from CIGS solar cell fabrication, and prepared using an evaporated Al electrode, RF sputtered Al-doped ZnO (ZnO:Al) as a transparent conductive oxide and undoped n-type ZnO, chemical bath deposition-processed n-type CdS, and a DC magnetron sputtered Mo back-contact. The fabricated solar cells had an Al/ZnO:Al (350 nm)/ZnO (100 nm)/CdS (50 nm)/SnS (1000 nm)/Mo (500 nm)/glass structure. A typical solar cell size was 0.30 cm^2.

Crystallographic structures and extra phases produced during fabrication were evaluated by X-ray diffraction (XRD) measurements (Rigaku, Ultima IV). Inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Seiko Instruments, SPS 7700) was used to measure

* Corresponding author.
E-mail address: mutsumi@rs.noda.tus.ac.jp (M. Sugiyama).

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the average composition of the film. The depth profile of Na in the SnS films was measured using glow discharge optical emission spectroscopy (GDOES) analysis (Horiba, JY 5000 RF). The morphology of the films was examined by scanning electron microscopy (SEM) analysis (Hitachi, S-4800). Capacitance-voltage (CV) properties were measured using an impedance analyzer (Keithley Instruments, 4200-SCS) at 100 kHz, in the dark, at room temperature. The current density–voltage (J-V) characteristics of the fabricated solar cells were measured using a solar simulator (Bunkou Keiki, Otento-Sun. II) with AM1.5 and 100 mW/cm^2 illumination at 25 °C.

3. Results and discussion

The Sn/S atomic ratios for all the sulfurized SnS thin films, without extra phases such as Sn_2S_3 [20] or SnS_2 [21], were 0.85–0.95, as measured by ICP-AES. The Sn/S atomic ratio of the as-deposited Sn-S precursor was 1.0, and some of the S atoms reacted with the precursor during sulfurization. As a result, polycrystalline, Sn-poor SnS has vacancies at the Sn sites (V_{Sn}), which act as shallow acceptors [3,22], and is an appropriate photo-absorber for solar cells.

The XRD patterns of sulfurized SnS films as a function of the thickness of the deposited NaF layer are shown in Fig. 1. In the case of sulfurized SnS films without the NaF layer, an extra phase of SnS_2 was observed as a related weak peak, and was probably formed in the presence of the excess of S used in the sulfurization process. However, the diffraction intensities of this extra phase tended to decrease with increasing thickness of the NaF layer. This indicates that the NaF layer prevented excess diffusion of S atoms between the S vapors in the sulfurization chamber and the Sn-S precursor. It is noted that the average column size estimated using Scherrer's equation was 27 ± 2 nm, and it was independent of sulfurization conditions and/or deposited NaF layer thickness (the size of the grain, which define an aggregation of columns, was mention later).

The thermal diffusion of Na was observed to investigate the carrier concentration in the SnS films. Representative depth profiles of Na along with S, Sn, and Mo atoms in the SnS film are shown in Fig. 2. There was a graded change in the number of atoms around the SnS/Mo of the film. This is caused by non-uniform film thickness and/or the irregular interface of the polycrystalline SnS, which gives rise to inhomogeneous sputtering during the GDOES measurements. However, Na atoms diffused throughout the SnS layer from the top NaF layer. Judging from the band discontinuity, carrier concentration, and Fermi level of the n-CdS/p-SnS structure, the capacitive properties provide information on the SnS layer around the pn interface and can be estimated by CV measurements. The carrier concentrations of the SnS film sulfurized without and with NaF were 5×10^{16} cm^{-3} and 2×10^{17} cm^{-3}, respectively. This difference could be attributed to the diffusion of Na from the NaF layer into the SnS layer. At the same time, NaF partly re-evaporated by decomposition and forming SF_x species which have high vapor pressures. Malone et al. reported that

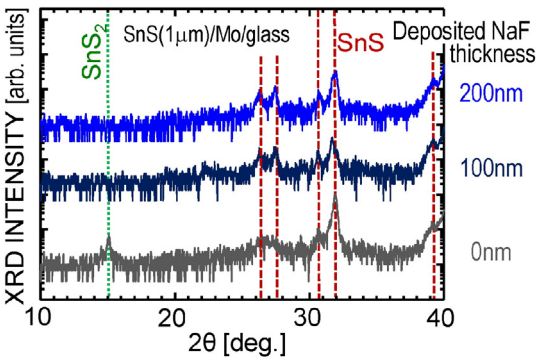

Fig. 1. XRD patterns of sulfurized SnS films as a function of deposited NaF thickness.

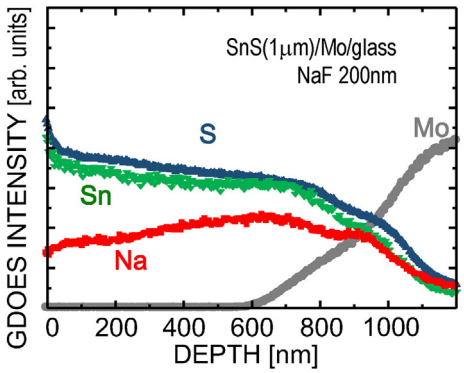

Fig. 2. Representative depth profile of Na with S, Sn and Mo atoms in the SnS film.

under *S*-rich conditions, the enthalpy of formation for Na-occupied Sn vacancies (Na_{Sn}) is small [22]. These defects then act as acceptors. Although a deeper experimental and theoretical discussion is needed, these results indicate that Na, possibly as Na_{Sn}, can act as an acceptor.

Next, the crystal morphology was investigated by SEM measurements. Fig. 3 shows representative cross-sectional SEM images of (a) the NaF/Sn-S precursor as deposited on a Mo-coated glass substrate, (b) 1.0-μm-thick precursor sulfurized for 30 min or (c) 60 min, and (d) 0.5-μm-thick precursor sulfurized for 30 min. All the sulfurized films were treated with deionized water to remove the residual NaF layer. In the *as*-deposited NaF/Sn-S film, small granular grains were packed together, as shown in Fig. 3(a). After sulfurization of the 1-μm-thick precursor for 30 min, large (300–500 nm) grains were formed in the upper half of the Sn-S layer, although small grains reflecting the initial precursor were still present around the bottom half of the Sn-S layer, as shown in Fig. 3(b). This result is due to an insufficient reaction time and/or supply of S. In addition, formation of large SnS grains tends to occur toward the top of a precursor layer. This indicates that some of the S vapor in the sulfurization chamber reacted with the Sn-S precursor by penetrating the NaF layer. A cross-sectional SEM image of the SnS film after 60 min of sulfurization is shown in Fig. 3(c). By extending the sulfurization time to 60 min, large (600–800 nm) grains were obtained. However, at the same time, small particles were observed around the SnS/Mo interface. These particles may be composed of a Mo-S alloy formed by prolonged sulfurization. To avoid prolonged sulfurization, the Sn-S precursor thickness was changed from 1.0 μm to 0.5 μm. The cross-sectional SEM image of a SnS film after 30 min sulfurization using a 0.5-μm-thick Sn-S precursor is shown in Fig. 3(d). Very large grains (1–2 μm across) were formed in this case. It is noted that the size of the grain, which define an aggregation of columns, was independent of the column size. For use in solar cells, a SnS thickness of 1–2 μm may be required as in a CIGS or CZTS solar cell, judging from the absorption coefficient of SnS. However, when changing the precursor thickness, some extra phases tended to be produced. In fact, the SnS layer thickness of the highest efficiency solar cell was about 600 nm [4]. Therefore, more thorough experimentation is needed to make the sulfurization process commercially viable including identifying the appropriate photo-absorber thickness.

In general, a higher temperature growth process, or a thermal process, would be needed to obtain higher quality films without defects. However, in the case of SnS, the vapor pressures of both S and SnS are relatively high [13], and low-temperature (300–400 °C) growth is needed because of the occurrence of thermal equilibrium processes such as evaporation or sulfurization. In other words, ALD is appropriate for high-temperature growth [4,14] because it is a non-thermal equilibrium process. In the current process, very high sulfurization temperatures such as 500 °C are possible because of the NaF "re-evaporation protection layer".

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