Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp1037-1038

Effect of post-annealing for Cu_2SnS_3 thin films prepared by sulfurization process

Mitsuki Nakashima[1], Yuki Hagiwara[1], Toshiyuki Yamaguschi[1], Junji Sasano[2] and Masanobu Izaki[2]

[1] National Institute of Technology, Wakayama College
77 Noshima, Nada-cho, Gobo-shi, Wakayama 644-0023, Japan
Phone: +81-738-29-8367 E-mail: nakashima@wakayama-nct.ac.jp
[2] Toyohashi University of Technology
1-1 Hibarigaoka, Tempaku-cho, Toyohashi-shi, Aichi 441-8580, Japan

Abstract

Cu_2SnS_3 thin films were fabricated by sulfurization process using NaF addition precursor, and applied to the photovoltaic devices. Cu_2SnS_3 thin films were post-annealed in air on a hotplate and then washed with ammonia and deionized water, thereby aiming at improvement of the interface property between the Cu_2SnS_3 active layer and the buffer layer. From EPMA analysis, the Cu/Sn mole ratios had downward trend from 2.02 to 1.53 with increasing the post-annealing temperature. XRD study showed that the thin films had a monoclinic Cu_2SnS_3 structure. The cell performances had upward trends with increasing the post-annealing temperature. The best solar cell in this study with temperature of post-annealing of 300ºC showed V_{oc} of 238mV, J_{sc} of 21.9mA/cm^2, FF of 0.412 and η of 2.14%.

1. Introduction

Cu_2SnS_3 (CTS) is a promising candidate for the solar cell materials of environmental harmony type as low-cost and non-toxic. CTS has a direct band gap energies of 0.9-1.0 eV and an absorption coefficient in order of 10^4 cm^{-1} [1-3]. In recent yaers, we achieved the conversion efficiency of 4.63% by sulfurization process using the NaF addition precursors [4]. However, this value is lower than other chalcogenide-based solar cells such as $Cu(In,Ga)Se_2$ (CIGS) [5] and Cu_2ZnSnS_4-based (CZTS-based) [6]. It is considered that one of the cause of low conversion efficiency is large $V_{oc,def}$ (E_g/q - V_{oc}, E_g is the bandgap, q is the electron charge and V_{oc} is the open-circuit voltage). The values of $V_{oc,def}$ of the CIGS and CZTS-based which achieved high conversion efficiency were 0.38V [5] and 0.58V [6], respectively. On the other hand, the value of $V_{oc,def}$ of CTS was 0.65V [4]. In this study, to obtain low $V_{oc,def}$ with improvement of V_{oc}, we performed the rinsing with the solution which added ammonia to deionized water after post-annealing, and investigated the effects of those treatments on the characteristics of thin films and solar cells.

2. Experimental

The stacked NaF/Cu/Sn precursors were deposited on a Mo/soda lime glass substrate. The mole ratio of the evaporation materials were Cu:Sn:NaF=1.0:0.6:0.075. The precursors were set in a vacuum sealed glass ampoules with elemental sulfur and tin shots. The amounts of sulfur and tin were constant at 0.062 and 0.046g, respectively. And they were crystallized by annealing in sulfur/tin mixing atmosphere for 30 min at 570ºC. Next, the fabricated thin films were annealed in air on a hotplate for 10min. In this time, the temperatures of the hotplate were changed from 100ºC to 400ºC. Then, the samples were rinsed with deionized water for 20min and rinsed for 10min with the solution which added ammonia to deionized water. The solar cells were completed by the deposition of a CdS layer of about 50nm in a chemical bath, RF sputtering of a thin intrinsic ZnO layer, DC sputtering of a 350nm thick ZnO:Ga transparent conductive layer and Al grid contact. These samples were characterized by means of EPMA, XRD, Raman, SEM and J-V characteristics.

3. Results and discussions

From EPMA, the quantity of Cu gradually decreased with increasing the post-annealing temperature, and the quantity of S gradually increased. Figure 1 shows the compositional ratio of thin films. The Cu/Sn mole ratios were in the range from 1.53 to 2.02, and it had downward trends with increasing the post-annealing temperature.

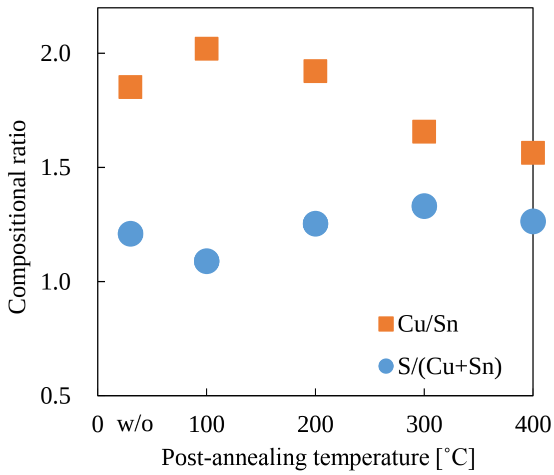


Fig. 1 Compositional ratio of the rinsed thin films.

The XRD patterns of the CTS thin films are shown in Fig. 2. In all samples, the XRD patterns showed several peaks corresponding to the diffraction line of the monoclinic CTS structure, and the peak of MoS_2 was seen with some samples. Figure 3 shows surface and cross-section SEM images of CTS thin films. The grain sizes and film thickness were approximately same in all samples. Moreover, some voids were seen between CTS layer and Mo layer in several samples.

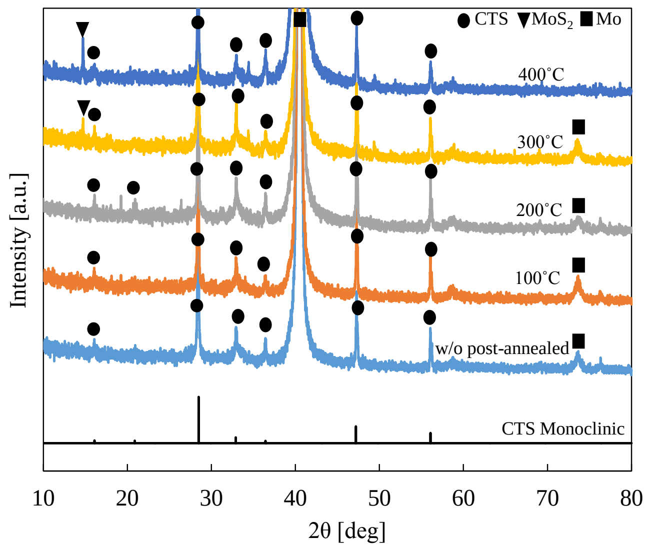
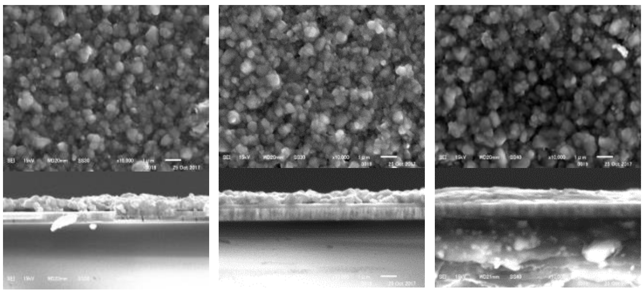


Fig. 2 XRD patterns of the rinsed thin films.



(a) w/o post-annealed (b) 200 ºC (c) 400 ºC

Fig. 3 SEM micrographs of the surface and cross-section of the rinsed thin films.

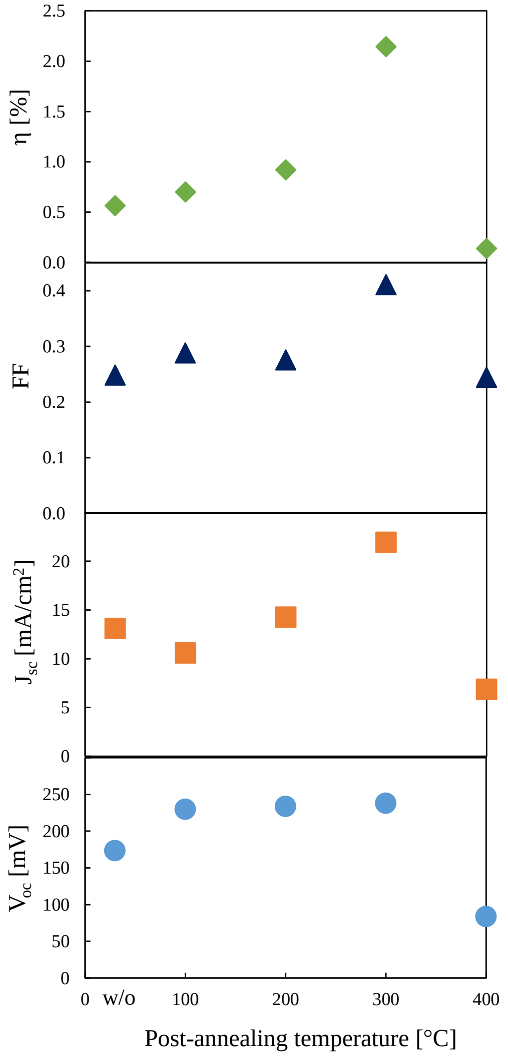


Fig. 4 V_{oc}, J_{sc}, FF and η of CTS thin film solar cells.

Figure 4 shows V_{oc}, the short-circuit current J_{sc}, the fill factor FF, and the conversion efficiency η of the CTS thin film solar cells. The values of all characteristics of the CTS thin film solar cells had upward trend with increasing the post-annealing temperature, and they had peaks at 300 ºC. The solar cell with the highest conversion efficiency in this study demonstrated V_{oc} = 238 mV, Jsc = 21.9 mA/cm^2, FF = 0.412 and η = 2.14%.

4. Conclusions

The CTS thin films were successfully fabricated by post-annealing after sulfurization. The Cu/Sn mole ratios in films had downward trends with increasing the post-annealing temperature. In addition, the CTS cell performances were improved with increasing the post-annealing temperature, and they had peaks at 300ºC. Therefore, it is considered that the post-annealing is the useful technique for improvement of the cell performances of CTS thin film solar cells.

Acknowledgements

This work was partially supported by JSPS KAKENHI Grant Number JP17K07036.

References

[1] T. A. Kuku, and O. A. Fakolujo, Sol. Energy Mater. **16**, 199 (1987).

[2] M. Bouaziz, M. Amlouk, S. Belgacem, Thin Solid Fims **517**, 2527 (2009).

[3] D. M. Berg, R. Djemour, L. Gutay, G. Zoppi, S. Siebentritt, and P. J. Dale, Thin Solid Films **520** (2012) 6291.

[4] M. Nakashima, Junya, Fujimoto, T. Yamaguchi and M. Izaki, Appl. Phy. Express **8**, 042303 (2015).

[5] P. Jackson, D. Hariskos, R. Wuerz, O. Kiowski, A. Bauer, T. M. Friedlmeier, and M. Powalla, Phys. Status Solidi: Rapid Res. Lett. **9**, 28 (2015).

[6] Y. S. Lee, T. Gershon, O. Gunawan, T. K. Todorov, T. Gokmen, Y. Virgus, and S. Guha, Adv. Energy Mater. **5**, 1401372 (2015).