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KF addition to Cu_2SnS_3 thin films prepared by sulfurization process

Mitsuki Nakashima[1], Junya Fujimoto[1], Toshiyuki Yamaguchi[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 sulferization processes using KF addition techniques, and applied to the photovoltaic devices. From EPMA analysis, the Cu/Sn mole ratios were in the range from 0.81 to 1.51. XRD study showed that the thin films had a monoclinic Cu_2SnS_3 structure. The Cu_2SnS_3 thin films using two-stage annealing had a close-packed structure and good surface morphology. The best solar cell in this study showed V_{oc} of 293mV, J_{sc} of 24.71mA/cm^2, FF of 0.41 and η of 2.93%. This value of V_{oc} surpassed early reported value.

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 0.93-1.77 eV and an absorption coefficient in order of 10^4 cm^{-1} [1-3]. Our group have been achieved the conversion efficiency of 4.63% by sulfurization process using the NaF addition precursors [4]. In recent years, the technique of alkaline metals doping is used for the improvement of the quality of thin films, and Cu(In,Ga)Se_2 (CIGS) and Cu_2ZnSnS_4 solar cells have ahieved high conversion efficiencies by this technique [5, 6]. Most recently, potassium doping helps to break the record efficiency of CIGS solar cell doped with sodium. In this study, CTS thin films were fabricated by sulfurization processes using NaF and KF, and applied to the photovoltaic devices. We carried out several KF addition experiments and investigated the effective method of KF addition to improve cell performances of CTS thin film solar cells.

2. Experimental

We have attempted three kinds of experiments. In the first experiment, the CTS thin film were fabricated by two-stage annealing process. 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. Then, KF was deposited on the crystallized thin film in the vacuum chamber at room temperature. The KF/film bilayer samples were annealed again in sulfur/tin mixing atmosphere for 30min. The amounts of sulfur and tin were same of first annealing. In this time, the KF/Cu mole ratio was 0.02 and 0.05, and the second annealing temperature was 350ºC and 500ºC. In the second experiment, the stacked KF/NaF/Cu/Sn precursors were crystallized by annealing in sulfur/tin mixing atmosphere for 30 min at 570ºC. The mole ratio of the evaporation materials were Cu:Sn:NaF:KF=1.0:0.6:0.075:x (x=0 to 0.05). In the third experiment, the CTS thin films were fabricated by same method of second experiment, and the mole ratio of the evaporation materials were Cu:Sn:NaF:KF=1.0:0.6:y:0.02 (y=0 to 0.075). 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, SEM and J-V characteristics.

3. Results and discussions

Table I shows the summary of characteristics of CTS thin films and solar cells in this study. From EPMA analysis, the Cu/Sn mole ratios were in the range from 0.81 to 1.51. In our previous research of CTS with no KF, the Cu/Sn mole ratios were range from 1.41 to 1.88 [3]. Therefore, it is considered that the content of Cu near the surface of thin film was decreased by KF addition. The XRD patterns of the CTS thin films are shown in Fig. 1. The XRD patterns showed several peaks corresponding to the diffraction line of the monoclinic CTS structure. Moreover, the peaks of Mo_xS_y were seen in some samples.

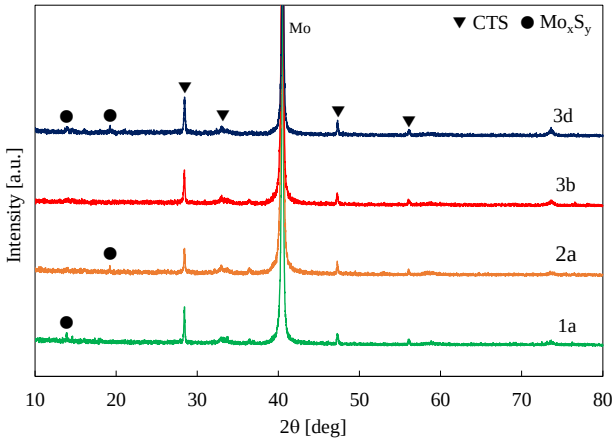
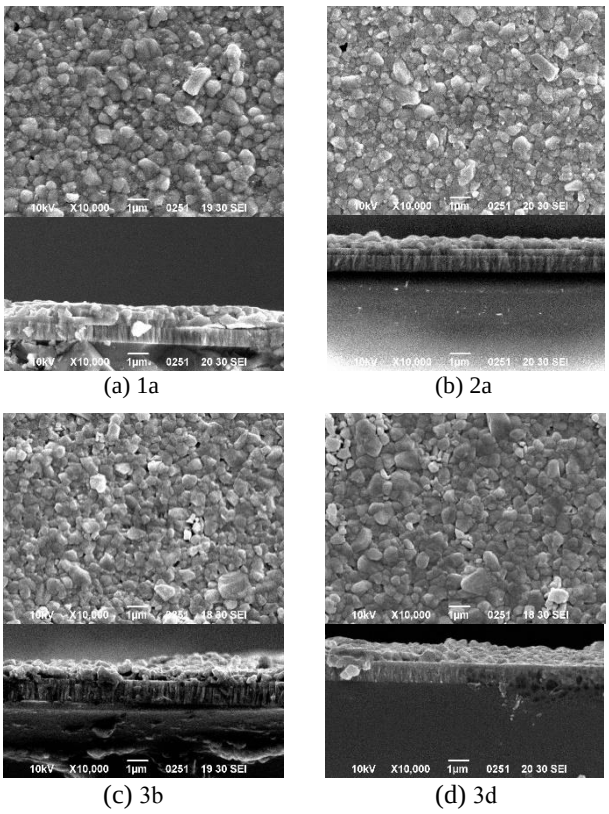


Fig. 1 XRD patterns of the CTS thin films fabricated by KF addition.

Table I Characteristics of CTS thin films and solar cells.

Experiment No.	Sample No.	NaF/Cu [%]	KF/Cu [%]	Annealing temp. $1^{st}/2^{nd}$ [°C]	Cell performance V_{oc} [mV]	J_{sc} [mA/cm^2]	FF	η [%]	Composition in film Cu [%]	Sn [%]	S [%]	Cu/Sn
1	1a	7.5	2.0	570 / 350	293	24.71	0.41	2.93	19.60	14.20	66.20	1.38
	1b			570 / 500	270	25.69	0.36	2.48	21.02	14.06	64.92	1.50
	1c		5.0	570 / 350	188	3.02	0.00	0.00	21.10	14.60	64.30	1.45
	1d			570 / 500	239	15.27	0.25	0.92	19.60	15.30	65.10	1.28
2	2a	7.5	2.0	570 / -	220	13.78	0.27	0.82	19.60	16.30	64.10	1.20
	2b		5.0		259	21.45	0.32	1.78	21.70	15.40	62.90	1.41
3	3a	0.0	2.0	570 / -	255	14.02	0.26	0.93	19.03	13.32	67.65	1.43
	3b	3.0			262	17.92	0.27	1.26	20.07	24.73	55.21	0.81
	3c	4.5			248	23.18	0.34	1.97	16.40	15.91	67.69	1.03
	3d	6.0			249	25.03	0.41	2.57	17.38	15.07	67.56	1.15
	3e	7.5			220	13.78	0.27	0.82	19.60	16.30	64.10	1.20

Fig. 2 shows surface and cross-section SEM images of CTS thin films. The grain sizes and film thickness were approximately same in all samples. As seen in Fig.3, the sample of 1a had a close-packed structure and good surface morphology in comparison with other samples.



(a) 1a (b) 2a

(c) 3b (d) 3d

Fig. 2 SEM micrographs of the surface and cross-section of CTS thin films.

Fig. 3 shows the open-circuit voltage V_{oc} of the CTS thin film solar cells. The highest value of V_{oc} was 293mV at the sample of 1a which was fabricated by two-stage annealing. This value of V_{oc} surpassed early reported value (V_{oc}=283mV [4]).

4. Conclusions

The CTS thin films were successfully fabricated by three kinds of KF addition experiments. From results of the first experiment, the cell performances had a downward trend with increasing KF/Cu mole ratio. It is considered that the quantity of addition of KF has an appropriate amount. The technique of KF addition with using two-stage annealing fabricated the thin films solar cells having good cell performances in comparison with using KF/NaF/Cu/Sn precursor. The best solar cell fabricated by two-stage annealing showed Voc=293mV, Isc=24.71mA/cm^2, FF=0.41 and η=2.93%.

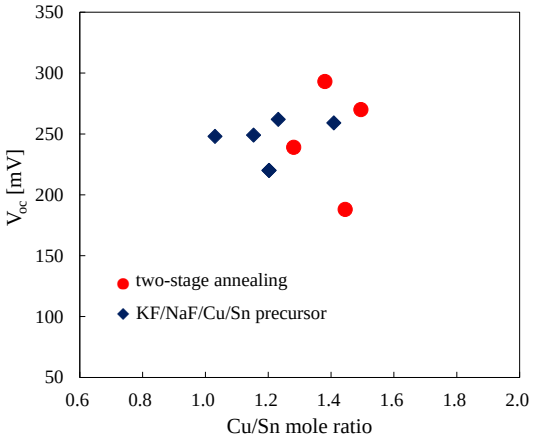


Fig. 3 V_{oc} of CTS thin film solar cells with KF addition.

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