Preparation of (Cu,Ag)$_2$SnS$_3$ Thin Films by Sulfurization and Their Application to Solar Cells

Mitsuki Nakashima$^1$, Toshiyuki Yamaguchi$^{1,*}$, Koichi Hatayama$^1$, Hideaki Araki$^2$, Shigeyuki Nakamura$^3$, Satoru Seto$^4$, Yoji Akaki$^5$, Junji Sasano$^6$ and Masanobu Izaki$^6$

$^1$National Institute of Technology, Wakayama College, Gobo-shi, 644-0023, Japan
$^2$National Institute of Technology, Nagaoka College, Nagaoka-shi, 940-0817, Japan
$^3$National Institute of Technology, Tsuyama College, Tsuyama-shi, 708-0824, Japan
$^4$National Institute of Technology, Ishikawa College, Tsubata-cho, 929-0342, Japan
$^5$National Institute of Technology, Miyakonojo College, Miyakonojo-shi, 885-8567, Japan
$^6$Toyohashi University of Technology, Toyohashi, Aichi, 441-8580, Japan

*Corresponding author

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Abstract. (Cu,Ag)$_2$SnS$_3$ (CATS) thin films and solar cells have been fabricated by sulfurization process for the first time and their properties have been investigated. In first experiment, the stacked NaF/(Ag+Cu)/Sn precursor deposited by sequential evaporation of Sn, Ag and Cu elements and NaF followed by crystallization in selenium/tin mixing atmosphere for 30 min at 570°C. The Ag/(Ag+Cu) mole ratio and the grain sizes in the thin films increased with increasing the Ag/(Ag+Cu) mole ratio in the evaporation materials. In second experiment, two kinds of precursors constructed by NaF/(Ag+Cu)/Sn (Precursor A) and NaF/Sn/(Ag+Cu) (Precursor B) were crystallized by annealing in selenium/tin mixing atmosphere for 30 min at the various temperature. The open circuit voltage $V_{oc}$ in the CATS solar cells prepared from precursor B were larger than those from precursor A. The grain growth in CATS thin films was observed with increasing the sulfurization temperature. The best performance of the CATS solar cell fabricated from precursor B at the sulfurization temperature of 530°C corresponded to an open circuit voltage of 257mV, a short circuit current density of 9.31 mA/cm$^2$, a fill factor of 0.26, and an efficiency of 0.61%, which was the first report of the photovoltaic effect for CATS thin film.

Introduction

In recent years, I$_2$-IV-VI$_3$ ternary semiconductors such as Cu$_2$SnS$_3$ (CTS) have attracted much attention as one of the promising absorber materials for application to photovoltaic devices, which consist of non-toxic and earth-abundant elements, CTS has a band gap of around 0.9-1.0 eV [1,2] and a high absorption coefficient of more than 10$^4$ cm$^{-1}$[3]. Kuku and Fakolujo reported for the first time in 1987 that CTS thin films were prepared by the direct evaporation of the synthesized compound and their solar cell showed a conversion efficiency of 0.11%, which had potential photovoltaic characteristics [4]. Many groups have fabricated CTS thin films and solar cells using several techniques like sulfurization of the metallic precursors[3,5-8], co-evaporation [9], spray pyrolysis process [10], spin coating[11,12], paste coating[13], and screen printing[14]. Up to date, the record conversion efficiency in CTS thin film solar cells increased to 4.63 % by the sulfurization of stacked NaF/Cu/Sn precursor[15]. However, the band gap of CTS is slightly below the range of the optimum conversion efficiency in a single-junction solar cell. The expansion of the band gap of the absorber layer by replacing partly the element is one of the promising approaches for obtaining more efficient solar cells. An improvement in the conversion efficiency of CTS-based thin film cells was achieved by Ge incorporation, where the fabrication of a photovoltaic device with an absorber
layer of Cu$_2$(Sn,Ge)S$_3$ (CTGS) yielded an efficiency of 6.01% [16]. On the other hand, it has been reported that Ag$_2$SnS$_3$ (ATS) which was a material substituted Cu in CTS for Ag had a band gap of 1.26 eV [17,18]. By gradual substitution of Cu for Ag, the band gap of the alloyed absorber may increase. Therefore alloyed (Cu,Ag)$_2$SnS$_3$ (CATS) is expected to give higher output voltage and more efficient solar cell than CTS thin film solar cells. Up to now, there are no reports regarding ATS solar cells, CATS thin films or CATS solar cells, though the alloyed (Cu$_{1-x}$Ag$_x$)ZnSnSe$_4$ solar cell has been reported to demonstrate a conversion efficiency of 10.2% for a device containing 10% Ag [19]. In this study, we have fabricated CATS thin films and solar cells with various Ag/(Ag+Cu) mole ratio by sulfurization process and their properties have been investigated. To the best of our knowledge, this is the first reported fabrication of CATS thin films and solar cells.

**Experimental**

We carried out two kinds of experiments. In experiment 1, the stacked NaF/(Ag+Cu)/Sn precursors were deposited on Mo/soda lime glass (SLG) substrate by sequential evaporation of Sn, Ag and Cu elements and NaF. The mole ratio of the evaporation materials were constant at (Ag+Cu):Sn:NaF = 1.0:0.6:0.075. The Ag/(Ag+Cu) mole ratio was varied from 0 to 0.5. The precursors were crystallized by annealing in selenium/tin mixing atmosphere for 30 min at 570°C. In experiment 2, two kinds of precursors were prepared on Mo/SLG substrate, which were the stacked NaF/(Ag+Cu)/Sn (Precursor A) and the stacked NaF/Sn/(Ag+Cu) (Precursor B). The mole ratio of the evaporation materials were Cu:Ag:Sn:NaF = 0.5:0.5:0.6:0.075 for the both precursors. The precursors were crystallized by annealing in selenium/tin mixing atmosphere for 30 min at T °C. The sulfurization temperature T was changed from 500°C to 570°C. We fabricated solar cells with a configuration of Al grid contact/Ga-doped ZnO transparent conducting layer/non doped ZnO/CdS buffer layer/CATS absorber layer/Mo back contact/SLG substrate using the following steps. CdS buffer layers with thicknesses of 70 nm were deposited by a chemical bath deposition technique, while i-ZnO buffer layers with thicknesses of 50 nm were produced by radio frequency magnetron sputtering. Transparent conductive ZnO:Ga films with thicknesses of 0.4 µm were subsequently deposited by direct current magnetron sputtering of 3 wt.% Ga$_2$O$_3$-doped ZnO targets at a substrate temperature of 100 °C, and Al grids for the front electrode were produced with metal masks by vacuum evaporation. The sizes of the obtained solar cells without antireflection coatings were 5 mm × 5 mm. Compositions of the obtained thin films were determined from the results of the electron probe microanalysis (EPMA) performed by energy dispersive spectrometry (EDS); their crystalline structure was examined by X-ray diffraction (XRD), while their morphologies were studied by scanning electron microscopy (SEM). Current-voltage (J-V) characteristics and quantum efficiencies (QE) of the fabricated solar cells were measured using standard 1 sun (AM1.5, 100 mW/cm$^2$) illumination.

**Results and Discussion**

For the experiment 1, the influences of the Ag/(Ag+Cu) mole ratio in the evaporation materials on the properties of the prepared thin films were investigated. Figure 1 shows the relationship between the Ag/(Cu+Ag) mole ratio in thin film and that in evaporation materials. The Ag/(Ag+Cu) mole ratio in the thin films increased with increasing the Ag/(Ag+Cu) mole ratio in the evaporation materials, which was indicative to be able to control the Ag/(Ag+Cu) mole ratio in the thin films by this sulfurization technique. The (Cu+Ag)/Sn mole ratio in the thin films were in the range of 1.29 to 1.63 for the prepared thin films, which were lower than a stoichiometric composition ratio of 2.0. For the Cu-chalcogenide based compound semiconductors such as Cu$_2$ZnSnS$_4$ (CZTS) and CTS, it was reported that their solar cells with high-efficiencies used the thin films with largely nonstoichiometric compositions of Cu/Sn [7,15,20]. The composition ratios of the thin films prepared from Ag-containing precursors were consistent with the tendency in efficient CZTS and CTS solar cells. Figure 2 shows the XRD patterns for the thin films prepared at various Ag/(Cu+Ag)
were investigated. Fig. V shows the relationship between an open circuit voltage $V_{oc}$ and the efficiency ($\eta$) of CATS thin film solar cells fabricated from precursor A and B at various sulfurization temperatures. The values of $V_{oc}$ for the sample of Ag/(Cu+Ag)=0.5 in the experiment 1 were observed in Figure 3. These peak intensities decreased with decreasing the sulfurization temperature. From the EPMA analysis and XRD study, a monoclinic CATS was considered to be formed in the sulfurized thin films. We have attempted the experiment 2 in order to improve the properties of thin films and solar cells. The fabricated thin films had the Ag/(Cu+Ag) mole ratio from 0.37 to 0.67, which values increased with increasing the sulfurization temperature regardless of the precursor structure. XRD patterns for the thin films prepared from precursor B at various sulfurization temperatures are shown in Figure 3. The same diffraction peaks from foreign phases appeared for the sample of Ag/(Cu+Ag)=0.5 in the experiment 1 were observed in Figure 3. These peak intensities decreased with decreasing the sulfurization temperature. From the EPMA analysis and XRD study, a monoclinic CATS was considered to be formed in the sulfurized thin films, although those included some foreign phases. Figure 4 shows the SEM micrographs of the surface of CATS thin films prepared from precursor A and B at various sulfurization temperatures. Although the grain size in the thin films obviously increased with increasing the sulfurization temperature, the grains were grown like an island similar to the experiment 1. On the other hand, the island shape growth was suppressed for the thin film prepared below 530°C. The photovoltaic properties of the CATS thin film solar cells were investigated. Fig. V shows the relationship between an open circuit voltage $V_{oc}$ and the efficiency ($\eta$) of CATS thin film solar cells fabricated from precursor A and B, and the sulfurization temperature. The values of $V_{oc}$ in the solar cells prepared from precursor B were larger than those from precursor A as shown in Fig. V. In this experiment, the CATS thin film solar cell prepared from precursor B had the highest value at the sulfurization temperature of 530°C. The J-V characteristic of the CATS thin film solar cell with the highest conversion efficiency in this experiment, which was fabricated at the sulfurization temperature of 530°C and had the composition ratio of Ag/(Cu+Ag)=0.42, is shown in Fig. VI. The conversion efficiency was 0.61% with $V_{oc}$ of 257 mV, $J_{sc}$ of 9.31 mA/cm$^2$, and FF of 0.26, which was the first report of the photovoltaic effect for CATS thin film to the best of our knowledge. Although the efficiency of 0.61% is considerably low compared with the reported recently values of CTS thin film solar cells [7,15], our value is slightly larger than the efficiency of 0.11% reported for CTS thin film for the first time in 1987 [4]. Figure 7 shows the quantum efficiency (QE) curves of the CATS thin film solar cell with an efficiency of 0.61% measured under the white light bias of 10 mW/cm$^2$ and the bias voltage of -0.5 V. The values of QE under the white light bias and the bias voltage were improved rather than those under the absence of both bias. The similar tendencies were reported for Cu$_2$ZnSnSe$_4$ (CZTSe) thin film solar cells fabricated by the selenization of the precursor evaporated from the CZTSe compound [22]. It is considered that the carrier trap in the crystal grain boundary was compensated by the white light bias. The QE measurement also showed a poor response in the whole wavelength region, which this incomplete carrier collection behavior has been reported for CZTSe thin film solar cells [23]. The decrease in the...
carrier collection can be due to the small minority carrier diffusion length and/or a narrow space charge region to be pointed out by Kim et al [23].

Figure 1. Relationship between Ag/(Cu+Ag) mole ratio in thin film and Ag/(Cu+Ag) mole ratio in evaporation materials.

Figure 2. XRD patterns for the thin films prepared at various Ag/(Cu+Ag) mole ratio of the evaporation materials in the experiment 1.

Figure 3. XRD patterns for the thin films prepared from precursor B at various sulfurization temperatures in the experiment 2.

Figure 4. SEM micrographs of the surface of CATS thin films prepared from precursor A and B at various sulfurization temperature.
Figure 5. Relationship between open circuit voltage $V_{oc}$ of CATS thin film solar cells fabricated from precursor A and B, and the sulfurization temperature.

Figure 6. J–V characteristics of CATS thin film solar cell fabricated from precursor B at sulfurization temperature of 530 °C.

Figure 7. QE of CATS thin film solar cell fabricated from precursor B at sulfurization temperature of 530 °C.

**Conclusion**

CATS thin films and solar cells have been fabricated by sulfurization process for the first time. The Ag/(Ag+Cu) mole ratio and the grain sizes in the thin films increased with increasing the Ag/(Ag+Cu) mole ratio in the evaporation materials. The performances in the CATS solar cells prepared from precursor B were larger than those from precursor A. The grain growth in CATS thin films was observed with increasing the sulfurization temperature. The best performance of the CATS solar cell fabricated from precursor B at the sulfurization temperature of 530 °C corresponded to $V_{oc}$ of 257 mV, $J_{sc}$ of 9.31 mA/cm$^2$, FF of 0.26, and an efficiency of 0.61%, which was the first report of the photovoltaic effect for CATS thin film. Although CATS thin film solar cells were demonstrated to be one of the promising candidates for photovoltaic devices, the solar cell performances must be further improved by investigating the fabrication conditions.

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**References**


