C-3-3 (Invited)

Development of CTS-based thin film solar cells

Hideaki Araki[1], Ayaka Kanai[1], Akiko Takeuchi[1], Kazuo Jimbo[1] and Hironori Katagiri[1]

[1] National Institute of Technology, Nagaoka College
888 Nishikatakai, Nagaoka, Niigata 940-8532, Japan
Phone: +81-258-34-9428 E-mail: h-araki@nagaoka-ct.ac.jp

Abstract

Cu_2SnS_3 (CTS) is composed solely of abundant elements and yet represents a p-type semiconductor with a monoclinic crystal structure, a high optical absorption coefficient of 10^4 cm^{-1} and a band gap energy of approximately 1 eV. It is therefore a potential solar cell absorbing material. In the present study, Cu-Sn alloy precursors with varying Cu/Sn ratios were deposited on soda lime glass or Mo-coated SLG substrates to allow evaluation of the properties of the resulting films as well as to fabricate solar cells with SLG/Mo/CTS/CdS/ ZnO:Al/Al structures. Devices made with CTS thin films having compositions that were stoichiometrically Cu-rich exhibited no photovoltaic properties, whereas relatively high photovoltaic responses were obtained in the Sn-rich composition range. This effect was attributed to the low electrical resistivity of Cu-rich samples, which in turn affected their electrical properties. Improvement of the CTS thin film morphology was attempted by co-evaporation using the shot annealing method as a means of increasing the conversion efficiency of the cells. Solar cells fabricated with CTS thin films annealed with sulfur had conversion efficiencies of over 4%.

1. Introduction

Thin film solar cells are a highly promising approach to reducing the manufacturing cost of photovoltaic power generation devices. Over the last few years, CdTe and $Cu(In,Ga)Se_2$ solar cells have accounted for an increasing share of the thin film compound semiconductor photovoltaic market, and have already gone into large-scale production. However, since In, Ga, Se and Te are relatively rare elements and Cd and Se are toxic, future mass production will depend on finding alternative materials that are cheaper, safer and more abundant.

Recently, Cu_2SnS_3 (CTS) solar cells have attracted significant attention, and the number of research reports related to these devices has also increased. The first photovoltaic cell with a CTS absorber layer was reported by Kuku and Fakolujo in 1987, who fabricated a Schottky diode with a conversion efficiency of 0.11% from a CTS film by direct evaporation [1]. More recently, Berg *et al*. reported a substrate-type CTS thin film solar cell obtained by sulfurization of electroplated Cu/Sn stacked precursors and exhibiting 0.54% conversion efficiency [2].

Our own group has also studied the development of novel, compound-based, thin film CTS solar cells optimized for large volume production. These devices make use of a sulfide-based, light-absorbing compound that is free of rare metals and toxic elements and consists entirely of copper, tin and sulfur, all of which are abundant and inexpensive. We have reported substrate-type, CTS-based thin film solar cells fabricated by sulfurization of electroplated Cu-Sn precursors and evaporated Cu/Sn stacked precursors, having conversion efficiencies of 2.84 and 2.54%, respectively [3, 4].

In the present study, the effects of the composition ratio on CTS-based, thin film solar cells and the accompanying efficiency improvements are discussed.

2. The effect of the composition ratio on CTS-based thin film solar cells

Preparation of CTS thin films and their properties

We initially deposited Cu-Sn alloy precursors having different Cu/Sn ratios onto soda lime glass (SLG) substrates by electron beam evaporation. CTS thin films were subsequently prepared by sulfurization at 560 ºC for 2 h under a flow of N_2 gas and sulfur vapor. The band gap energy of the prepared films was estimated from the measured reflectance and transmittance values. We also assessed the variations in the electrical characteristics of the films with changes in the Cu/Sn composition ratio [5].

X-ray diffraction (XRD) analyses showed that a film made using a stoichiometric composition (Cu/Sn = 2.00) exhibited only the Cu_2SnS_3 phase of the monoclinic crystal structure. However, Sn-rich CTS compositions (Cu/Sn < 2) showed a secondary $Cu_2Sn_3S_7$ phase, while a secondary $Cu_5Sn_2S_7$ phase was identified in Cu-rich films. At Cu/Sn values less than or equal to 2, the CTS films exhibited a light absorption coefficient on the order of 10^4 cm^{-1} in the visible region and were found to have relatively narrow bandgaps of the direct transition type, ranging from 0.91-0.99 eV. The effects of the Cu/Sn ratio in CTS thin films on the electrical properties were clarified based on Hall measurements. All samples exhibited p-type conductivity, and electrical resistivity values of 1.90 - 6.51 Ωcm were observed in the Sn-rich region, likely due to the high resistivity of the Sn-rich secondary phase. In contrast, the Cu-rich regions showed a sudden decrease in the electrical resistivity, to 10^{-3} Ωcm, thought to result from the low resistivity of the Cu-rich secondary phase. The carrier concentrations were 10^{17}-10^{18} and 10^{21} cm^{-3} in the Sn-rich and Cu-rich region, respectively. Finally, the Hall mobility was determined to be 0.429-3.41 cm^2/Vs in CTS thin films in which Cu/Sn was in the range of 1.6-2.4.

Fabrication of CTS solar cells

The CTS thin films were deposited on SLG/Mo substrates to fabricate solar cells with an SLG/Mo/CTS/CdS/ZnO:Al/Al structure. The CdS buffer layer was deposited on the CTS absorber layer by chemical bath deposition and a ZnO:Al transparent conductive oxide window layer was then deposited by RF sputtering. The Al top grid was deposited on the ZnO:Al window layer by thermal evaporation. The current density-voltage (*J-V*) characteristics of the solar cells were measured using a solar simulator generating an AM1.5 spectrum, at an illumination of 100 mW/cm^2. Figure 1 summarizes the effects of the Cu/Sn ratio on the photovoltaic properties of the CTS-based thin film solar cells. From these plots, it is evident that photovoltaic properties were observed in the Sn-rich region. In particular, a conversion efficiency of more than 2% was obtained for Cu/Sn ratios of 1.77-1.99, although the efficiency was less than 2% at Cu/Sn ratios below 1.66. It is believed that the series resistance was increased due to secondary phases in the Sn-rich regions, and that this increase caused both the fill factor and short-circuit current density to decrease. The open-circuit voltages and short-circuit current densities were almost zero in the Cu-rich region due to the low electrical resistivity of these compositions.

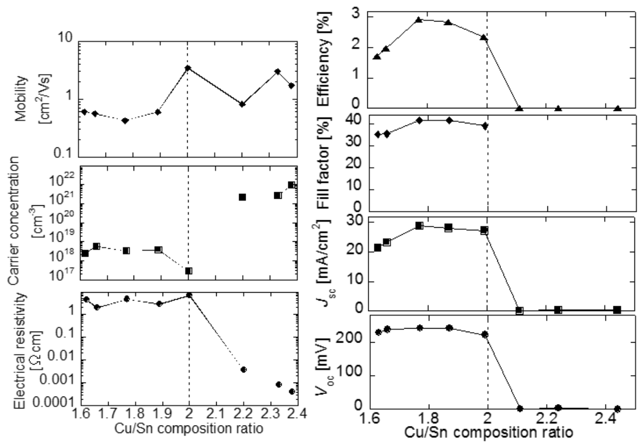

Fig. 1 The electrical properties of CTS films and the photovoltaic properties of CTS devices as functions of the Cu/Sn ratio.

3. Improvement of efficiency through using the co-evaporation method

The CTS thin films obtained by the sulfurization approach exhibited numerous voids and large pinholes due to the re-evaporation of tin sulfide. In addition, a rough surface was produced by volume expansion during sulfurization. Therefore, to increase the conversion efficiency of the CTS-based solar cells, improvements were required in the CTS thin film morphology. Consequently, a vacuum deposition process using co-evaporated Cu, Sn and S was employed, applying a shortened annealing time of several minutes rather than hours. This process was found to result in CTS-based solar cells with increased efficiencies [6,7].

In these trials, CTS thin films were grown by thermal evaporation in a vacuum system using evaporation sources for Cu, Sn and S. All three elements were co-deposited onto 1 μm thick Mo-coated SLG substrates at a substrate holder temperature of 300 °C. Following deposition, the films were annealed at 570 °C for 5 min, with or without S, in a rapid thermal processing furnace filled with N_2 gas at a pressure of 1 bar. X-ray fluorescence measurements of the as-deposited thin films showed that the Cu/Sn ratio was 1.89 and the S/(Cu+Sn) ratio was 1.12. XRD patterns of the films contained peaks only at 28.3° and 58.5°, in addition to a peak due to the Mo substrate. Based on these results, the as-deposited films were considered to consist of preferentially (-1 3 1)/(2 0 0)-plane oriented Cu_2SnS_3. Following annealing, the films were clearly identified as non-oriented monoclinic Cu_2SnS_3 on the basis of XRD data. A solar cell employing the as-deposited CTS thin film showed no photovoltaic properties. However, solar cells employing the same type of CTS thin film after annealing with sulfur exhibited good photovoltaic properties. In particular, a solar cell containing a CTS thin film with a Cu/Sn ratio of 1.87 annealed at 570 ºC with 100 mg S had the best performance among the cells examined, Using this cell, an open-circuit voltage (V_{oc}) of 258 mV, a short-circuit current density (J_{sc}) of 35.6 mA/cm^2, a fill factor (FF) of 0.467 and a power conversion efficiency of 4.29% were obtained (Fig. 2). These results suggest that Cu_2SnS_3 shows promise as a rare metal-free, compound-based light absorption material for thin film solar cells.

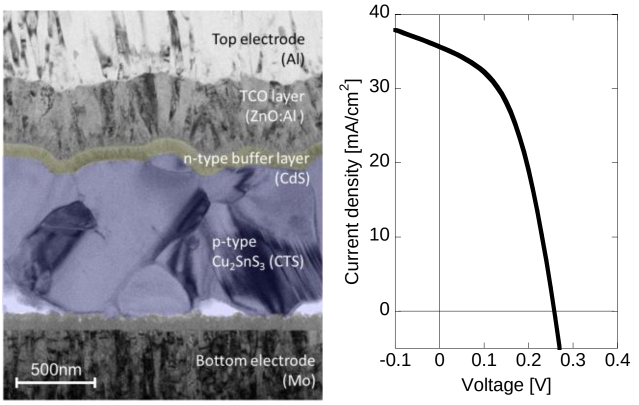

Fig. 2 Typical structure (left) and *J-V* characteristics (right) of a CTS cell showing 4.29% efficiency.

Acknowledgements

This work was supported in part by PRESTO, Japan Science and Technology Agency, Japan. The authors also wish to thank to Mr. N. Aihara for his work on composition dependence during EB evaporation.

References

[1] T. A. Kuku *et al*., Sol. Energy Mater. **16** (1987) 199.
[2] D. M. Berg *et al*., Thin Solid Films **520** (2012) 6291.
[3] J. Koike *et al*, PVSEC-21 Tech. Dig., (2011) 4D-3P-26; Jpn. J. Appl. Phys. **51** (2012) 10NC34.
[4] K. Chino *et al*., PVSEC-21 Tech. Dig. (2011) 4D-3P-27; Jpn. J. Appl. Phys. **51** (2012) 10NC35.
[5] N. Aihara *et al*., Phys. Status Solidi C **10** (2013) 1086.
[6] A. Kanai *et al*., Phys. Stat. Solid. B **252** (2014) 1239.
[7] A. Kanai *et al*., Jpn. J. Appl. Phys. (2015) in press.