Materials Science in Semiconductor Processing 85 (2018) 160–167

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

$Cu_2Sn_{1-x}Ge_xS_3$ thin film solar cells fabricated from sputtered precursors: Effects of soft-annealing process

Mingrui He[a], Jihun Kim[b], M.P. Suryawanshi[a], U.V. Ghorpade[a], Myengil Gang[a], Jin Hyeok Kim[a,*]

[a] Optoelectronics Convergence Research Center, Department of Materials Science and Engineering, Chonnam National University, Gwangju 500-757, South Korea
[b] School of Electrical Engineering and Computer Science, Gwangju Institute of Science and Technology, 123 Cheomdangwagi-ro, Buk-Gu, Gwangju 500-712, South Korea

ARTICLE INFO

Keywords:
$Cu_2Sn_{1-x}Ge_xS_3$ (CTGS)
Thin film solar cells
Soft-annealing
Sputtering

ABSTRACT

Ge-doped Cu_2SnS_3 (CTGS) thin films are promising photovoltaic materials for developing low-cost second-generation solar cells. The present work reported a soft-annealing process (annealing the as-deposited precursor without chalcogenide source) for fabricating CTGS solar cells, which is an efficient method to enhance the quality of CTGS thin films and show significant reforming on both as-deposited precursor and sulfurized film. The enlarged grain size and compact microstructure provide obvious evidence of improved efficiency. Further, the reduced defect density is attributed to using a 200 °C soft-annealed precursor. A clear increase in each performance parameter such as open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (*FF*) is observed as the soft-annealing temperature increased from 0 °C to 200 °C, whereas a limited enhancement was found at 300 °C. The CTGS solar cell prepared using the soft-annealing process showed an efficiency of 2.66%. In comparison, an efficiency of 1.93% has been achieved in cells fabricated without this process. The improved device performance indicates that further improvement in the CTGS solar cells could be achieved by adopting the soft-annealing precursor in an environmentally friendly manner.

1. Introduction

Reducing the environmental impact of fossil fuels and achieving the development of sustainable energy sources can become viable and efficient if photovoltaic (PV) systems are extensively used in various applications. Referring to low-cost and eco-friendly materials, Cu, Sn and S are required in Cu_2SnS_3 (CTS) thin film solar cells (TFSCs) for commercial applications. In a previous study, we have revealed a CTS TFSC, showing lower values of open-circuit voltage (*Voc*) (208 mV) and fill factor (*FF*) (39.7%) that are specific problems in suppressing the higher power conversion efficiency (*PCE*) [1]. For addressing the conversion efficiency of the CTS absorber layer, Ge alloying approaches have attracted considerable attention and are being studied intensively as they can enhance the quality of the absorber [2–7]. Mitsutaro Umehara et al. were the first to have reported Ge-alloyed Cu_2SnS_3, namely $Cu_2Sn_{1-x}Ge_xS_3$ (CTGS) with a high conversion efficiency of 6.0%, which was fabricated through Ge composition control (x = 0.17), revealing significant improvements in the values of both *Voc* and *FF* from 243 mV and 35.1% in CTS devices to 355 mV and 55.6% in CTGS devices, respectively [2]. Moreover, the influence of the Ge/(Ge + Sn) ratio on the photovoltaic properties of CTGS thin film has been studied, demonstrating a wide band gap from 0.86 eV to 1.53 eV with increasing Ge content in the film, which has been regarded as a promising candidate for thin film absorber materials [7]. However, few studies have been devoted to growing CTGS TFSCs. In studies related to modifying Ge doping into a CTS lattice, for example, Myo Than Htay et al. have investigated CTGS TFSCs using different Ge composition ratios as well as precursor designs [3]. A multi-stacked precursor structure with nine layers was sulfurized to exhibit noticeable enhancement of efficiency [3]. To date, the highest PCE of 6.7% for CTGS TFSCs was obtained using a graded bandgap structure, comparing the CTGS TFSCs with a non-graded structure (6.1%) [4].

According to literature, a method called “soft-annealing” has a prominent role in realizing a high-quality absorber layer [8] and it has been extensively used in the fabrication of kesterite solar cells for achieving efficient cells, particularly Se-based kesterite TFSCs [9,10]. The formation of an interfacial $MoSe_2$ layer (≈1200 nm) negatively affects the performance of CZTSe solar cells owing to its high series resistance [9]. The major role of the soft-annealing process is to form compact Cu_6Sn_5 and Cu_5Zn_8 alloys layers, which can block the diffusion of selenium and prevent its reaction with Mo at the back contact, thereby reducing the thickness of the $MoSe_2$ layer [9]. Furthermore, the utilization of soft-annealing process for kesterite solar cells is a promising method to improve the crystalline structure of the cells in

* Corresponding author.
E-mail address: jinhyeok@chonnam.ac.kr (J.H. Kim).

https://doi.org/10.1016/j.mssp.2018.05.018
Received 28 February 2018; Received in revised form 14 May 2018; Accepted 15 May 2018
Available online 20 June 2018
1369-8001/

Table 1
List of soft-annealing conditions for CTZSSe, CTZS, CZTSe and CTGS thin films.

Compound	Technique for precursor	Optimized soft-annealing temperature	Time	Annealing atmosphere	Reference
CZTSSe	Sputtering	300	10 min	N_2	10
CZTSe	Sputtering	300	20 min	Ar	9
CZTS	Electrodeposition	300	60 min	Ar	8
CZTS	Electrodeposition	310	200 min	Vacuum	11
CTGS	Sputtering	200	60 min	Ar	Present work

addition to increasing their efficiency. However, this method is not commonly used for the constituent elements of ternary Cu_2SnS_3 solar cells. Here, we summarized recent studies that focused on the soft-annealing conditions reported in the literature as compared with those used in the present work, as shown in Table 1. For selenium-based compounds, such as CZTSSe and CZTSe, the optimized soft-annealing conditions are a temperature of 300 °C with a short annealing time to form an alloyed layer for preventing Se diffusion to the Mo back contact [9,10]. On the other hand, a long soft-annealing period, which determine the purity of the phase formed and their surface morphology, might be appropriate for sulfur-based compounds (CZTS) [8,11]. To the best of knowledge, there are no specific studies on the influence of soft-annealing on CTS TFSCs. Based on our investigations, the soft-annealing process for CTS TFSCs fabricated using the sputtering method is not suitable for further improvement in the properties and device performance. In this work, it represents the demonstration of the influence of soft-annealing on Ge alloyed Cu_2SnS_3 solar cells and successfully shows the advantages and importance of this method. It thus fills a gap in the existing body of knowledge in this field.

Here, we report CTGS TFSCs prepared using sputtered precursors before soft-annealing each sample, which is a feasible, efficient, and low-cost method without using toxic H_2S gas as well as multi-stacked precursor structures that demonstrate noticeable enhancement from 1.93% to 2.66%. The improved efficiency of CTGS TFSCs is attributed to suppressing the secondary phase formation, and increased grain size using a soft-annealed precursor. Additionally, we systematically analyzed and compared different soft-annealing temperatures, giving a clear idea about the influence of the soft-annealing process on the performance of the CTGS TFSCs.

2. Experimental

2.1. Deposition of Cu-Ge-Sn precursors

In the first stage, Mo-coated soda lime glass (SLG) substrates (2.5 cm × 2.5 cm) were ultrasonically cleaned using ammonia (50%) + DI water (50%) for 2 min, as adhesion problems with as-deposited precursors frequently occur. The cleaned Mo substrates were then placed in the DC magnetron sputtering chamber for deposition of the metallic precursor. The precursor film was subsequently deposited on the Mo substrates at room temperature, following a pre-sputtering treatment for 180 s to ensure proper sputtering. In detail, the stacking of the precursors was carried out according to the following sequence: Sn (30 W, 8 mTorr, 1678 s), Ge (30 W, 8 mTorr, 350 s), and Cu (30 W, 8 mTorr, 1260 s). The Ge deposition rate is presented giving at rates of 0.57 Å/s.

2.2. Preparation of soft-annealed precursors

In the next step, the as-deposited precursors were transferred to a tube furnace for the soft-annealing process; the furnace chamber was filled with Ar gas, maintaining a pressure of approximately 400 Torr during annealing. Following this stage, the as-deposited precursors were annealed at different temperatures (100 °C, 200 °C, and 300 °C) for 60 min and were labeled A-100, A-200 and A-300, respectively. The soft-annealed precursors then cooled naturally in the tube. This process is referred to as the soft-annealing process. To investigate the influence of the soft-annealing process, one as-deposited precursor (sample A) was not subjected to the process. Instead, the sample was sulfurized directly to form an absorber layer.

2.3. Formation of CTGS absorber layers

Subsequently, the as-deposited precursor (A) and soft-annealed precursors (A-100, A-200, and A-300) were individually placed in a graphite box with 90 mg sulfur (S) powder in a rapid thermal annealing (RTA) system under a high-purity Ar gas atmosphere. The high-purity Ar gas (99.999%) was also used to remove the remaining oxygen that possibly existed in the RTA chamber. This cleaning and flushing were done using a rotary vacuum pump twice before each sulfurization process. The sulfurization reaction occurred at 550 °C for 10 min at a heating rate of 9.2 °C/s. After sulfurization, the sulfurized samples were naturally cooled, and samples A, A-100, A-200, and A-300 were renamed as samples B, B-100, B-200 and B-300, respectively.

2.4. Fabrication of CTGS thin film solar cells

The n-type part of the thin film solar cells was to start with the CdS buffer layer, which was deposited by chemical bath deposition at 80 °C for 870 s, after all samples underwent an etching process with 0.2 M potassium cyanide in an ultrasonic system for 120 s. The intrinsic ZnO (i-ZnO) and aluminum-doped ZnO (AZO) were deposited by an RF magnetron-sputtering process at a working pressure of 1 mTorr with sputtering powers of 50 W and 70 W, respectively. Finally, CTGS TFSCs were fabricated with multilateral structures of SLG/Mo/CTGS/CdS/i-ZnO/AZO/Al.

2.5. Characterization

X-ray fluorescence (XRF) spectroscopy (ZSX Primus II RIGAKU corp.) was used for quantitative analysis of the elemental compositions of the CTGS thin films. The influence of the soft-annealing process on the phase formation of the as-deposited precursor, soft-annealed samples, and sulfurized samples was investigated by utilizing high resolution X-ray diffraction (XRD, X'pert PRO, Philips, Eindhoven, Netherlands) with a scanning range of 20–60°, and the source was operated at 40 kV and 30 mA. Raman spectra were obtained using a micro-Raman spectrometer (Via Reflex UV Raman microscope, Renishaw, U.K. at KBSI Gwangju center) with a He–Ne laser source at an excitation wavelength of 488 nm and a wavenumber range of 200–450 cm^{-1}. The surface and cross-sectional morphologies of the film were characterized by scanning electron microscopy (SEM; Model: JSM-6701F, Japan). The *J-V* measurements of CTGS TFSCs annealed under different soft-annealing temperatures were performed at AM 1.5 G one-sun illumination (100 mW/cm^2) using a class AAA solar simulator (Sol31, Oriel, USA). The external quantum efficiency (*EQE*) of CTGS TFSCs was characterized using a class AAA solar simulator (WXS-155S-L2, WACOM, and Japan) at AM 1.5 G, 100 mW/cm^2, and 25 °C with an incident photon conversion efficiency measurement unit (PV measurement, Inc., USA).