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Influence of sulfurization temperature on photovoltaic properties of Ge alloyed Cu_2SnS_3 (CTGS) thin film solar cells

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ABSTRACT

Ge alloyed Cu_2SnS_3 (CTGS) thin films were prepared by annealing the sputtered deposited Cu-Ge-Sn precursor films under sulfur atmosphere at different annealing temperatures. The influence of different annealing temperatures on morphological, compositional, crystal structure of CTGS thin films were investigated. It was found that the annealing temperature of 550 °C provides a favorable sulfurization environment to promote grain growth leading to a compact thin film formation. Improved performance is ascribed to high Ge contents as evidenced from X-ray fluorescence (XRF) studies. Well incorporated Ge atoms into CTS thin film can be confirmed by X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) study provides an evidence of existence of Ge atoms where its binding energy located at 25.78 and 26.78 eV, respectively. However, the decreased performance was found at unsuitable annealing temperatures such as 500 °C, 520 °C, 580 °C and 600 °C. Finally, with annealing temperatures of 550 °C, the best power conversion efficiency (PCE) of 2.14% was attained with an open circuit voltage (V_{oc}) of 220 mV, a short circuit current density (J_{sc}) of 23.74 mA/cm^2 and a fill factor (*FF*) of 41%.

1. Introduction

Recent research in thin film solar cells (TFSCs) such as $Cu(In,Ga)Se_2$ (CIGS), CdTe and Kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) is improving significantly [1–3]. However, it is imperative to reduce the number of component elements in the TFSCs, because the cost and efficiency of solar cells are driving forces to reduce the expenditures of photovoltaic (PV) technology. Recently, ternary semiconductors Cu_2SnS_3 (CTS) TFSCs with non-toxic, low-cost and fewer elements have attracted considerable attention. The band gap of CTS is able to be tuned in a optimum range from 1.0 to −1.5 eV as photovoltaic devices [4]. Additionally, a high absorption coefficient (~ 10^4 cm^{-1}) establish the basic foundations for contributing to high conversion efficiency [5]. Several approaches such as evaporation [6], sputtering [7], pulsed laser deposition [8], electro-deposition [9] and chemical bath deposition [10] have attempted to fabricate CTS thin films as absorbers for TFSCs. Among these methods, the highest power conversion efficiency (PCE) of 4.63% have been reported for CTS TFSCs using a co-evaporation process with a stacking order of NaF/Cu/Sn under an Sn- and S-containing vapor atmosphere [6].

To improve the PCE, many researchers have reported that germanium (Ge) incorporated TFSCs can show excellent performances and have been taken into account as potential compounds for PV research. Enhancements in performance of Ge-induced Kesterite solar cell has demonstrated 11% by using nanocrystal ink precursors, and improving carrier collection and decreasing the deficit of open circuit voltage (V_{oc}) can be obtained with changing the band gap with Ge substitution [11]. Moreover, it is impressive that such small quantities of Ge significantly improve V_{oc}, fill factor (FF) and PCE and reduce the formation of the Sn_{zn} defect to some extent [12]. Recently, Umehara et al. [13] revealed that Ge-induced CTS TFSCs achieved a PCE as high as 6.7% with a graded band gap structure by using co-sputtering method showing that this compound has an excellent potential for further improvement by alloying with Ge. It should be noted that the sputtering method is highly efficient process to fabricate absorbers for TFSCs due to the deposition of fixed composition from elemental targets directly on the substrate with minimal variance in composition during each process time, and it can be also widely applied on large-scale industrial manufacturing [14]. Therefore, it is essential to investigate the sputtering method using metal targets in the preparation of Cu-Ge-Sn precursors followed by a sulfurization.

So far, studies on $Cu_2Sn_{1-x}Ge_xS_3$ (CTGS) TFSCs have recently been

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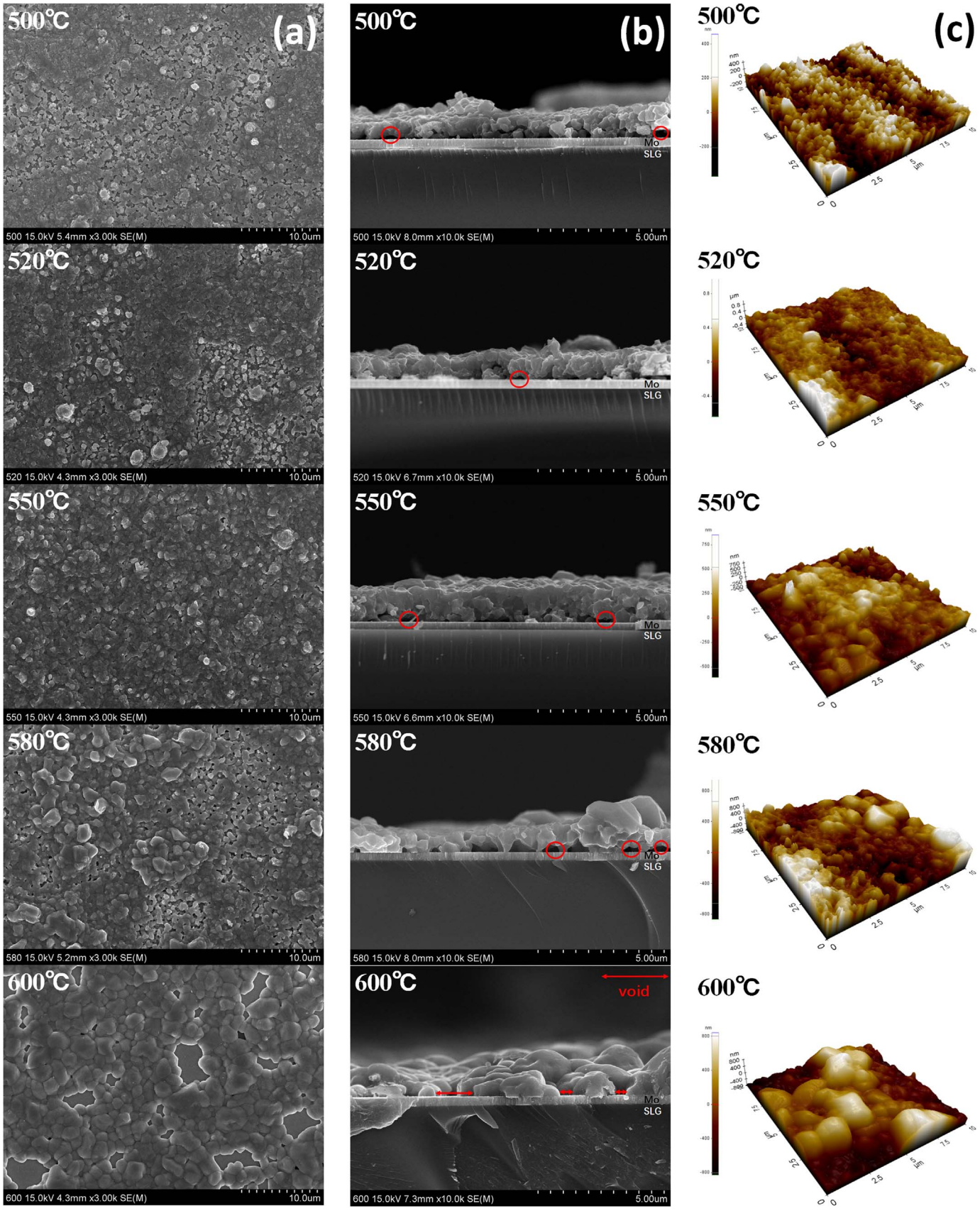

Fig. 1. (a) Surface (b) cross sectional SEM images and (c) AFM image of CTGS thin films as a function of annealing temperature.