Journal of Alloys and Compounds 689 (2016) 182–186

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Earth abundant thin film solar cells from co-evaporated Cu_2SnS_3 absorber layers

Jose A. Marquez Prieto [a], [*], Sergiu Levcenko [b], Justus Just [b], Hannes Hampel [b], Ian Forbes [a], Nicola M. Pearsall [a], Thomas Unold [b], [**]

[a] Northumbria Photovoltaic Applications Group, Department of Physics and Electrical Engineering, Northumbria University, Newcastle upon Tyne, UK
[b] Helmholtz-Zentrum Berlin for Materials and Energy, Hahn-Meitner-Platz 1, 14109, Berlin, Germany

ARTICLE INFO

Article history:
Received 14 March 2016
Received in revised form
4 July 2016
Accepted 26 July 2016
Available online 29 July 2016

Keywords:
Thin film
Solar cell
Earth abundant
Co-evaporation
Cu_2SnS_3

ABSTRACT

Cu_2SnS_3 (CTS) is starting to gain interest in the PV research community as an alternative earth abundant absorber for thin film photovoltaics. In this work, the structure, morphology and the composition of the CTS absorbers as well as their influence on the optoelectronic properties of the solar cells are analysed. The synthesis of Cu-Sn-S thin films by co-evaporation at a nominal temperature of 400 °C is presented. A combination of X-ray diffraction, Raman and UV-Vis spectroscopy suggests that the Cu_2SnS_3 is crystallising in a cubic structure with disorder in the Cu and Sn sites, leading to substantial band tailing.

The best device was fabricated from absorbers exhibiting a Cu/Sn ratio of approximately 1.7 and had an efficiency of 1.8%, a short circuit current of 28 mA cm^{-2}, and an open circuit voltage of 147 mV with a fill factor of 42.9%. From the quantum efficiency measurement, we estimate a band gap of 1.06 eV for the CTS absorber material. Capacitance-voltage measurements show charge carrier concentrations between 4 and 6×10^{16} cm^{-3}.

1. Introduction

Cu-Sn-S derived materials are increasing interest as absorber layers produced from earth abundant elements for application in thin film solar cells. Efficiencies up to 4.6% have been already achieved using the same device architecture used for Cu(In,Ga)Se_2(CIGS) and for $Cu_2ZnSn(S,Se)_4$ (CZTSSe) based solar cells [1]. In the Cu-Sn-S system, several compounds with different stoichiometry have been reported in literature, including Cu_2SnS_3 [2–8], Cu_3SnS_4 [3,6,9–11], Cu_4SnS_4 [2], $Cu_2Sn_3S_7$ [2] and $Cu_4Sn_7S_{16}$ [12]. Particularly, Cu_2SnS_3 is so far the ternary compound of the Cu-Sn-S system that has been studied most for solar cells applications.

Several synthesis approaches have been demonstrated to be suitable for producing Cu_2SnS_3 films including sputtering [6], reactive sputtering [13], electrodeposition [5,14], pulsed layer deposition [15] and several non-vacuum routes [16,17].

Cu_2SnS_3, has been reported to crystallize in several structural polytypes including a cubic (*F*-43 *m*) [3,6], a tetragonal (*I*-42 *m*) [3,6,12] and a monoclinic (*C*1*c*1) [4,5,7,8,18,19] structure depending on the temperature during synthesis. With increasing temperature, a change in the crystal structure to unit cells with higher symmetry has been predicted, changing from monoclinic to orthorhombic, then tetragonal and cubic [20]. However, experimental results in literature suggest that for synthesis process at temperatures below 550 °C, Cu_2SnS_3 adopts a cubic or a tetragonal structure [3,6] and when the synthesis temperature is above 550 °C it adopts a monoclinic structure [8,19,21]. A large discrepancy in the value of the bandgap of Cu_2SnS_3 in its different crystal structures is also found in literature. For the monoclinic form, the presence of two bandgaps was reported, one at 0.92–0.93 eV and a second one around 0.99 eV [5,8,18,19]. Fernandes et al. reported a bandgap of 1.35 eV for the tetragonal Cu_2SnS_3 and 0.96 eV for the cubic structure [3].

Most of the Cu_2SnS_3 absorber layers that have been used in solar cell devices have been synthesised in a two stage process with a reactive annealing step at temperatures higher than 550 °C under a sulphur or sulphur-tin atmosphere. This high temperature step resulted in monoclinic Cu_2SnS_3 [1,5,21]. However, it is difficult to find reports of solar cells prepared at low or moderate temperature processes, for which the Cu_2SnS_3 is not monoclinic. In addition to

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: jose.prieto@northumbria.ac.uk (J.A. Marquez Prieto), unold@helmholtz-berlin.de (T. Unold).

http://dx.doi.org/10.1016/j.jallcom.2016.07.293

the fact that in low temperature synthesis, the grain growth is more limited, the cubic CTS structure might present mid gap states and band tailing, making it difficult to make efficient solar cells out of this structure [22].

In this work, we report the synthesis of Cu-Sn-S absorber layers by a single step co-evaporation method with a nominal substrate temperature of 400 °C. Microstructural analysis of the absorber layers based on SEM, Raman spectroscopy and X-Ray diffraction is presented. It was found that Cu_2SnS_3 crystallises mostly in the cubic structure, however the presence of other Cu-Sn-S phases in the absorber layers have been identified. Solar cells fabricated from these absorber layers show a power conversion efficiency of 1.8%, mainly limited by a low value of the open circuit voltage.

2. Experimental

2.1. CTS absorber synthesis

A series of CTS absorber layers was deposited using a PVD system equipped with elemental Sn and Cu thermal evaporation sources and a sulphur evaporator with a cracking unit. The temperature of the Cu and Sn source and S cracking unit were 1285, 1295 and 500 °C respectively. 50×12.5 mm^2 molybdenum coated soda-lime glass substrates were used in this study, which were rotated during the deposition. The total pressure of the chamber during the deposition was around 1.5×10^{-3} Pa. For all the depositions the substrate temperature was set to a nominal temperature of 400 °C. Infrared reflectometry was used for in situ process control. The deposition was stopped after achieving a layer thickness of approximately 1 μm.

2.2. CTS absorber characterisation

The CTS thin films were measured with a PANalytical X'Pert MPD Pro X-ray diffractometer in Bragg-Brentano (BB) configuration using a Cu Kα radiation source ($\lambda = 0.15406$ nm). The composition of the samples was determined using a FEI Quanta 200 scanning electron microscope (SEM) equipped with an Oxford Instruments energy dispersive X-ray analyser (EDS) with an acceleration voltage of 20 kV from the top view. The cross section images of the solar cells were acquired with a Zeiss Gemini SEM. Raman scattering measurements were performed with He-Ne laser (633 nm) excitation using a CCD detector coupled to a 0.5 m spectrometer. The transmittance/reflectance of the absorber layers were measured with a Perkin-Ellmer UV-Vis setup after a lift off the films from the Mo substrate.

2.3. Device fabrication and characterisation

A CdS buffer layer of approximately 50 nm in thickness was deposited by chemical bath deposition (CBD) on the absorber layers followed by a i-ZnO/ZnO:Al window layer deposited by RF sputtering. Ni:Al metallic front contact grids were evaporated on top of the window. No etching treatment was applied before the CdS deposition. Cells of area 0.5 cm^2 were mechanically scribed. Illuminated J-V curves were measured under 100 mW/cm^2 simulated AM1.5 solar illumination calibrated with a Si reference cell and the external quantum efficiency (EQE) was measured using a lock-in amplifier combined with a 1/4 m monochromator. Capacitance-voltage (CV) measurements were performed with an HP4284 LCR meter and four-point probes.

3. Results and discussion

3.1. Microstructure and morphology of CTS absorber layers

The absorber layers showed a Cu/Sn ratio of around 1.7. Fig. 1 shows a cross sectional view of the solar cells processed for this study. The CTS absorber layer is about 1 μm thick and shows columnar like morphology suggesting that the films are highly textured. A similar morphology has been also reported for CTS samples grown by RF sputtering from Cu_2S and SnS targets heating the substrates to around 300° C [6], suggesting that this columnar growth type is typical for low temperature synthesis.

Fig. 2 shows the X-Ray Diffraction (XRD) pattern of CTS absorber layer acquired in Bragg-Brentano configuration. An intense peak appears at 28.3° that can be attributed to Cu_2SnS_3 in the cubic (F-43 m, ICSD 43532), the tetragonal (I-42 m, ICSD 50965) or the monoclinic ($C1c1$, ICSD 91762) structure. No other peaks can be observed related to this phase. Therefore, it is difficult to determine the crystal structure only based on the information provided by the XRD pattern. The single peak suggests that the films are preferentially orientated, which is consistent with the columnar growth morphology observed for the cross sectional images in Fig. 1. The inset of Fig. 2 shows a magnification of the XRD pattern between 20 and 50°. The diffractogram shows the presence of low intensity peaks at 27.4 and 30.7° that can be attributed to the presence of orthorhombic Cu_3SnS_4 [11]. The presence of Cu_3SnS_4 in films has been already reported to coexist with Cu_2SnS_3 [6,22], however the relatively low intensity of these reflexes in comparison with the strong peak attributed to Cu_2SnS_3 suggests that the amount of the Cu_3SnS_4 orthorhombic phase is rather low. No other phases have been identified with this technique.

In order to confirm the crystal structure of the CTS absorber layers Raman spectroscopy was performed on the sample and it is shown in Fig. 3. The peaks observed in the spectrum have been qualitatively fitted with Lorentzian functions to determine the position of the observed Raman modes. Two high intensity peaks at 303 and 359 cm^{-1} suggest that Cu_2SnS_3 is mainly present in the cubic structure, in accordance with the studies reported by Fernandes et al. [3,23]. Unfortunately, no calculations of the phonon spectra of the different crystal structures of Cu_2SnS_3 have been reported up to now and the assignments for the cubic Cu_2SnS_3 are made based on reported experimental data. In addition, lower intensity peaks at 319 cm^{-1} and 337-346 cm^{-1}can be observed. In the literature, peaks at these positions have been correlated with the presence of orthorhombic Cu_3SnS_4 [11,23], which agrees with its identification by XRD presented in Fig. 2. The position of the modes for the orthorhombic Cu_3SnS_4 to perform the fitting for this phase was adjusted according to the phonon spectrum calculated by Dzhagan et al. [11]. Raman measurements with $\lambda_{exc} = 633$ nm would potentially be very sensitive to the modes of Cu_3SnS_4, due to near resonant conditions [24], since a bandgap of 1.6 eV has been reported for this phase [3]. This would explain the fact that we clearly observe modes related to this phase even when its concentration in the film is low, as suggested by the low intensity peaks in the XRD patterns corresponding to Cu_3SnS_4. Also a Raman mode at 265 cm^{-1} is observed, which we are not able to attribute to a specific phase. Although calculations have predicted Raman active modes close to this frequency [11], the experimental data in literature for orthorhombic Cu_3SnS_4 does not agree with this mode being the most intense for this phase [11].

A bandgap value of 1.02 eV was calculated form the Tauc's plot generated with the optical transmission spectrum of a lifted-off CTS absorber as shown in Fig. 3b. Strong subgap absorption can be observed up to 0.85 eV, in good agreement with theoretical calculations of the density of states for the disorder cubic CTS that