Journal of Alloys and Compounds 618 (2015) 217–221

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Improved characteristics for chemically grown Cu_2SnS_3 promising solar absorbers through the use of TritonX-100® surfactant

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ARTICLE INFO

Article history:
Received 3 July 2014
Received in revised form 16 August 2014
Accepted 23 August 2014
Available online 3 September 2014

Keywords:
Cu_2SnS_3
Sol–gel spin coating
Thin film
Solar cell
Surfactant

ABSTRACT

In this paper, we report, for the first time, the results of the TritonX-100® surfactant assisted growth of Cu_2SnS_3 thin films obtained by using sol–gel spin coating method and a subsequent annealing in a sulfur atmosphere. Structural, morphological, compositional, photo-electrical investigations have been carried out. X-ray diffraction patterns of the samples matched well with the reference Cu_2SnS_3 pattern and indicated the polycrystalline nature of the films. Crystallite size of the films increased whereas surface roughness of the films decreased with increasing Triton-X100® content. The surface of the samples has been smoother with Triton-X100® inclusion. The photo-sensitivity of the n-Si/CTS structures has been confirmed through photo-transient current measurements. An increment was observed in the photo-induced current values of the samples with increasing Triton-X100® content and was attributed to transport of photo-induced electrons facilitated with decreasing recombination resulted from the surface enhancement of the films. Electrical conduction mechanism of the films was investigated with resistance–temperature measurements. It has been revealed that TritonX-100® surfactant assisted growth is a promising way to improve conversion efficiency of Cu_2SnS_3 based solar cells.

1. Introduction

Cu–Sn–S compounds are promising solar absorber materials for the production of cheaper large-scale thin film solar cells due to the abundancy of the constituents in the earth's crust [1–6]. The mineral form and photovoltaic behavior of Cu_2SnS_3 (CTS) thin films were found firstly by Kovalenker et al. [7] and by Kuku and Fakolujo [8], respectively. Semiconducting copper tin sulfides such as Cu_2SnS_3, Cu_3SnS_4 and $Cu_4Sn_7S_{16}$ could have a significant role in immediate future due to their in-free composition [9]. As a promising absorber material, Cu_2SnS_3 has an absorption coefficient of $10^4\ cm^{-1}$, an electrical conductivity of $10\ \Omega^{-1}\ cm^{-1}$, a hole mobility of $80\ cm^2\ V^{-1}\ s^{-1}$, and a hole concentration of $10^{18}\ cm^{-3}$ [1]. Its optical band gap energy has been reported in between 0.93 and 1.51 eV depending on its crystal structure type [10].

Up to now, CTS thin films have been prepared by various thin film deposition methods such as sulfurizing of electrodeposited Cu–Sn precursors [3], spray pyrolysis technique [9], dc magnetron sputtering [11,12], solid-state reaction [13], and ball milling process [14], sol–gel spin coating [15]. Among them, sol–gel method is a very simple and low-cost process that sulfide films can be directly obtained by sulfurizing oxyhydrate precursors. Furthermore, this method may also provide accurate control of film thickness, particle size and porosity by tuning different parameters such as, precursor concentrations, rotation speed, heat treatment temperature and so on [16].

It is well known that material properties such as surface morphology, crystalline structure, grain size, porosity, brightness, internal stress, pitting, corrosion behavior and even chemical composition can be tuned by using surfactants and used to improve energy conversion efficiency of thin film solar cells to some extent [17]. As a non-ionic surfactant material, Triton-X100® (namely octyl phenol ethoxylate, CAS number: 9002-93-1) exhibits both sterical and electrosterical repulsion when added in the solution [18]. Maldonado-Valdivia et al. [19] reported that the solar cell efficiency may be improved with increasing amount of Triton-X100®. The role of Triton-X100® in CTS deposition process has not been studied yet. Thus, it is of interest to us to investigate the effects of Triton-X100® on morphology, crystallographic structure, electrical properties and photovoltaic response of the Cu_2SnS_3 thin films.

Here we report, for the first time, the results of the Triton-X100® assisted preparation and characterization of CTS thin films obtained by using sol–gel spin coating method and a subsequent annealing in a sulfur atmosphere. The physical characteristics of the films were examined by means of X-ray diffraction, scanning

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http://dx.doi.org/10.1016/j.jallcom.2014.08.196
0925-8388/

electron microscopy, energy dispersive X-ray spectroscopy, photo-transient current and electrical resistivity–temperature measurement.

2. Experimental

CTS thin films were obtained on glass substrates by spinning the solution containing basically copper (II) acetate monohydrate (0.9 M, 98+%), tin (II) chloride (0.5 M, 98%) and thiourea (0.2 M, 99.0+% from Sigma Aldrich) into 2-methoxyethanol (99.8% from Sigma Aldrich). 25 µl of diethanolamine (DEA) were added slowly into the solution as a stabilizer while stirring. According to the literature reports [3,6,20] that copper concentration under stoichiometric value prevents the formation of $Cu_{2-x}S$ or other binary/ternary phases and improve the performance of the film. Therefore, we prepared the starting solution with a Cu/Sn ratio of 1.80. The solution was poured into four beakers and then 0, 1, 2 and 3 at.% of TritonX-100® (from Sigma Aldrich) were added into each solution. The final solutions were stirred at 45 °C, 1000 rpm for 1 h to dissolve all constituents completely. Glass substrates were ultrasonically cleaned in turn with detergent, nitric acid (1:4), acetone and ethanol for 10 min. To produce the CTS films, the prepared solutions were spin-coated onto glass substrates at 3000 rpm for 30 s followed by solvent-drying at 175 °C for 10 min on a hot plate. The spin-coating and solvent-drying processes were repeated 5 times. Finally, the samples were annealed under 1 atm of sulfur atmosphere for 2 h at 550 °C. The heating rate was 5 °C/min. After the annealing process, the samples were allowed to cool naturally to room temperature. The structural, morphological, compositional, optical and electrical properties of the samples were examined by X-ray diffraction (XRD, PANalytical X'Pert PRO MPD with the wavelength of 1.5418 Å Cu Kα radiation at 40 keV accelerating voltage and 35 mA current, step size of 0.05° and scan step time of 1 s), scanning electron microscopy (FEI, Quanta FEG 250), energy dispersive X-ray spectroscopy (EDXS, Oxford Instruments ISIS 300) methods. Photo-transient current of the Ag/n-Si/CTS/Ag structures were obtained at 2 V under different illuminations. The intensity of light was measured with a lux meter (Testo-540). Resistance–temperature characteristics of the samples were investigated by two point probe method in the temperature range of 300–550 K through a Keithley 6487 interfaced with computer by a Labview program.

3. Results and discussions

3.1. Structural results

Fig. 1 shows the obtained XRD patterns of the samples. From Fig. 1, all peaks observed at $2\theta = 15.02°$, 28.37°, 32.00°, 47.31°

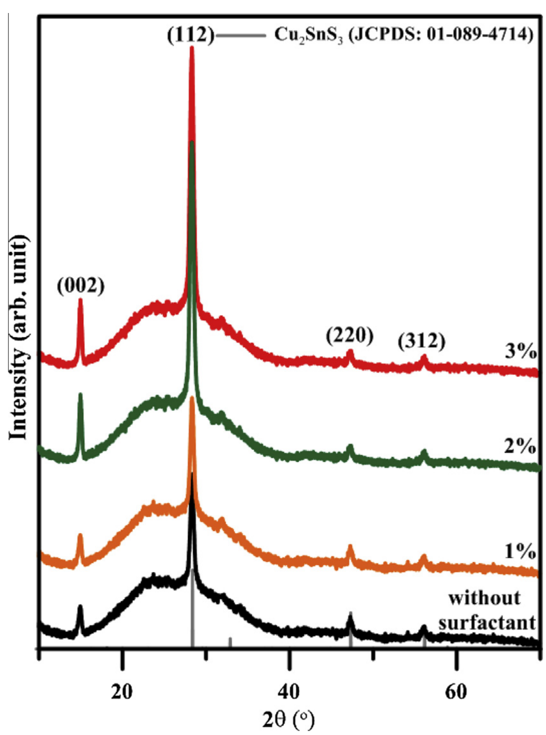

Fig. 1. Obtained X-ray diffraction patterns of the samples prepared with different TritonX-100® amounts.

and 56.22° match with those of reference Cu_2SnS_3 pattern (JCPDS 01-089-4714: Tetragonal, $a = b = 0.5413$ nm, $c = 1.0824$ nm, I-42 m). The peaks correspond to (002), (112), (200), (220) and (312) planes, respectively and they indicate the polycrystalline nature of the films. The highest peak at 28.37° corresponding to (112) plane proves the preferred crystallization. Any peak referring to other binary/ternary phases were not detected in the patterns.

As can be seen that the intensity of the peaks corresponding to (112) and (002) planes increase with increasing Triton-X100® content. It may be concluded that Triton-X100® enhances the growth of (112) and (002) oriented planes under our experimental conditions.

Through the full width half maximum (FWHM) value of an observed peak in XRD pattern, average crystallite size of a film can be calculated by using the Debye–Scherrer equation [21]:

$$D = 0.94\lambda/\beta\cos\theta \tag{1}$$

where λ is the wavelength of X-ray radiation, θ is the Bragg angle of the peak, and β is the angular width of the peak at full-width at half maximum (*FWHM*). The width of each obtained XRD peak increases because of instrumental and physical factors (crystallite size, strain and dislocation) [22]. The microstrain (ε) and dislocation density (ρ) for preferential orientation were calculated using the formulas given below [23]:

$$\varepsilon = \beta\cos\theta/4 \tag{2}$$

and

$$\rho = 15\varepsilon/aD \tag{3}$$

where a is the lattice constant. The crystallite size estimations of the films were done by taking into account all observed peaks and the estimated values are given in Table 1. According to Table 1, it can be seen that crystallite size of the films increases to some extent with Triton-X100® content. As will be discussed in photo-conversion measurement section, this trend yields an increase in photo-conversion capability of the samples (Section 3.3).

3.2. Morphological and compositional analysis

Fig. 2 shows the SEM images of the CTS films deposited by using 0%, 1%, 2% and 4% (by vol.) of Triton-X100®. From Fig. 2, it can be seen that the surface roughness of the films decreases with increasing Triton-X100® content. The surface of the sample without Triton-X100® (Fig. 2a) has porous and has agglomeration like morphology than those of the samples with Triton-X100® (Fig. 2b–d). It is also clear that, the sample prepared with 3% Triton-X100® (Fig. 2d) is more continuous and without crack than others. As a first conclusion, regarding film morphology, increasing Triton-X100® content in the sol–gel growth solution the smoother and continuous texture can be obtained. This enhancement may decrease the recombination and facilitate transport of photo-induced electrons.

Table 1
Estimated structural results of the samples.

Sample	Without surfactant	1%	2%	3%
Average crystallite size (nm)	17	18	20	23
Microstrain	2.2×10^{-3}	2.1×10^{-3}	1.9×10^{-3}	1.6×10^{-3}
Dislocation density (m^{-2})	2.6×10^{15}	2.4×10^{15}	2.1×10^{15}	1.8×10^{15}