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Sulfurization temperature dependent physical properties of Cu_2SnS_3 films grown by a two-stage process

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ABSTRACT

Cu_2SnS_3 (CTS) is a promising absorber for thin film solar cells because of its suitable opto-electronic properties. This article reports the effect of sulfurization temperature (T_s) on the physical properties of CTS thin films deposited by two-stage process. X-ray diffraction and Raman analyses revealed that sulfurized CTS films exhibited different polymorphic forms, such as triclinic structure (at T_s = 350 °C), tetragonal structure (at T_s = 400 °C), and monoclinic structure (at T_s = 450 °C). A phase change from monoclinic CTS to orthorhombic Cu_3SnS_4 was observed at T_s = 500 °C. The AFM results confirmed that the sulfurized films had the smooth surface without pinholes. The optical band gap was varied in the range, 2.34–1.49 eV with increasing sulfurization temperature from 150 °C to 500 °C. All the sulfurized films showed p-type conducting nature. The obtained results indicated that single phase CTS films prepared in the temperature range of 400–450 °C could be used as an absorber layer for the application of thin film solar cells.

1. Introduction

Currently, polycrystalline thin film photovoltaic research is directed towards the investigation on earth-abundant and environmentally benign semiconductor materials for solar cell application. In this context, Cu_2SnS_3 (CTS) material has attracted more interest because of its favorable physical properties for solar cell application. It is a p-type semiconductor with a high optical absorption coefficient ($> 10^4$ cm^{-1}) and its energy band gap (1.35 eV) is close to the optimum value of 1.5 eV for photovoltaic conversion [1–3]. Initially, the mineral form of CTS was reported by Kovalenker [4] and its photovoltaic behavior was observed by Kuku et al. [5]. Recently, a record conversion efficiency of 4.3% [6] was obtained for pure CTS solar cells, whereas, 4.8% and 6.7% for Na and Ge-doped CTS solar cells respectively [7,8].

CTS thin films have been deposited by various physical and chemical methods, such as thermal evaporation [9], electron beam evaporation [10], pulsed laser deposition [11], Two stage process (DC/RF sputtering followed by sulfurization) [12–20], spray pyrolysis [21], chemical bath deposition [22], SILAR method [23], spin coating [24], screen printing [25], sol-gel process [26] and electrodeposition [27]. Among these techniques, two-stage process is simple and cost-effective technique for the growth of homogeneous and uniform films and it can be applied for large-scale production. In fact, currently, this process has been used for the commercial production of CIGS solar modules [28].

In two-stage process, sulfurization can be carried out using a single-zone, two-zone, and three-zone annealing systems. Particularly, elemental sulfurization process required two-zone or three-zone quartz tube annealing system for continuous supply of sulfur vapor, since such process allowed controlling the total/partial pressures during the process. In the case of single-zone or graphite box sulfurization process, constant pressure maintenance is difficult that results in the formation of secondary phases during the deposition of CTS films. The presence of secondary phases in the CTS films can affect the physical characteristics and degrade the efficiency of CTS-based solar cells. Therefore, high-quality single phase CTS films are required to fabricate the high-efficiency device. Further, sulfurization was carried out using either co-sputtered Cu-Sn metallic precursors or stacked Cu/Sn layers and the related work on such process is very limited. Fernandes et al. [21] reported the sulfurization of stacked Sn/Cu metallic precursors in two-zone quartz tube furnace at various temperatures in the range of 350–520 °C using a constant vapor pressure of 0.55 mbar, while Dong et al. [26] described the sulfurization of stacked Cu/Sn layers using a graphite box under a constant (10 Torr) sulfur vapor pressure. Sulfurization of co-sputtered Cu-Sn layers showed smoother morphologies than the sequentially deposited Cu/Sn stack. Recently, Umehara et al. [23] reported a high conversion efficiency of 6.7% on Ge-doped CTS films formed by sulfurization of co-sputtered Cu-Sn metallic precursors. Till, there are no reports available in literature dealing with the

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influence of sulfurization temperature on the growth of sulfurization of co-sputtered Cu-Sn metallic precursors and their physical properties.

Therefore, in the present work, the effect of sulfurization temperature on the composition, structure, phase transformations, morphology, optical and electrical behavior of CTS films formed using co-sputtered Cu-Sn metallic layers is investigated and discussed.

2. Experimental details

2.1. Substrate cleaning

The soda lime glass substrates were cleaned initially using Teepol solution under forced tap water followed by dipping them into potassium dichromate ($K_2Cr_2O_7$) solution for 8 h. Then the substrates were subjected to ultrasonic cleaning using double deionized water for 5 min. Finally, the substrates were dried using nitrogen gas before loading them into the sputter chamber for the deposition of Cu-Sn metallic layers.

2.2. Materials

2" diameter and 0.125" thick copper (Cu) and tin (Sn) targets of 4 N purity were used for the deposition of Cu-Sn metallic precursors. Sulfur flakes of 4 N purity (Sigma Aldrich) were used for sulfurization process.

2.3. Formation of CTS films

CTS thin films were grown on soda lime glass substrates by a two-stage process. Fig. 1 shows the schematic diagram of two-stage process. In the first stage, Cu-Sn metallic precursors were co-sputtered by DC magnetron sputtering (Model: VRSU04D). In the second stage, the co-sputtered Cu-Sn metallic precursors were annealed in the sulfur atmosphere in a two-zone tubular furnace at different sulfurization temperatures varied in the range of 150–500 °C, by keeping constant reaction time of 60 min and ($N_2 + S_2$) vapor pressure of 0.6 mbar. Fig. 2 shows the temperature profile of sulfurization process.

2.4. Characterization

The elemental composition of sulfurized films was analyzed by energy dispersive X-ray spectrometer (EDS, HORIBA, Model: 7593H) attached with FE-SEM (Hitachi, Model: S-4800). The chemical states of different elements present in the sulfurized films were investigated by X-ray photoelectron spectrometer (XPS, Thermo Scientific, Model: K-ALPHA surface analysis). The XPS spectra were recorded in the binding energy range, 0–1300 eV using Al Kα source and calibrated using the C1s line. The X-ray diffraction (XRD, MPD for bulk, 3 kW, PAN analytical) with high-intensity monochromatic Cu Kα radiation (λ = 0.1546 nm) was used to analyze the crystallographic structure. Raman spectra were recorded using STR-300 confocal micro-Raman spectrometer. Ar^+ laser source (λ = 514 nm) of power 20 mW, a spot diameter of 1 µm and a 1200 lines/mm grating were used. The surface morphology of the films was examined by Field Emission Scanning Electron Microscope (FE-SEM, Hitachi, Model: S-4800). The surface topography of the films was analyzed by using atomic force microscopy (AFM, Vecco Model: Dimension V SPM) with X-Y scan range: 100 µm and Z scan range 5.5 µm. The optical absorbance spectra of the films were recorded with UV–Vis–NIR spectrophotometer (Cary 5000) in the wavelength range, 300–1500 nm. Finally, the electrical properties were measured via a Hall measurement system (Nanometrics, HL5500) at room temperature.

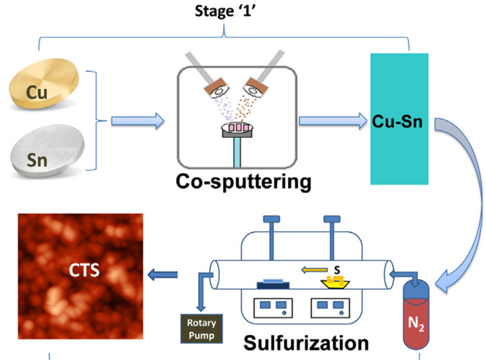

Fig. 1. Schematic diagram of two-stage process.

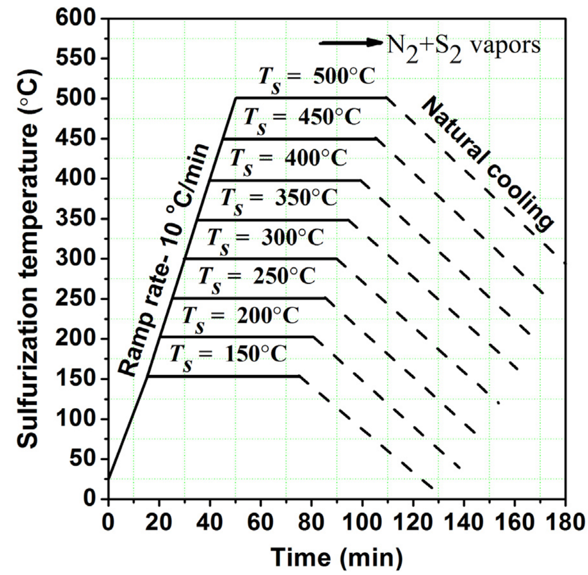

Fig. 2. The temperature profiles of sulfurization process.

3. Results and discussion

The sulfurized CTS films were uniform, pinhole free and well adherent to the substrate surface. The visual appearance of the films changed from light gray to greenish gray with increasing the sulfurization temperature.

3.1. Compositional analysis

The elemental compositions of the sulfurized films as a function of sulfurization temperature are listed in Table 1. At lower sulfurization temperatures ($T_s \leq 200$ °C), the films showed sulfur poor composition, which indicates a less incorporation of sulfur into the co-sputtered Cu-Sn metallic layers. As the sulfurization temperature was raised to 300 °C

Table 1
The composition of sulfurized films prepared at various sulfurization temperatures.

S.No.	Sulfurization temperature (°C)	Cu (at%)	Sn (at%)	S (at%)	Cu/Sn	S/ (Cu + Sn)
1	Room	65	35	–	1.85	–
2	150 °C	37.86	20.36	41.78	1.85	0.717
3	200 °C	37.46	19.28	43.26	1.94	0.762
4	250 °C	36.94	18.69	44.37	1.97	0.797
5	300 °C	35.44	18.35	46.21	1.93	0.859
6	350 °C	34.87	17.68	47.45	1.97	0.902
7	400 °C	34.26	17.11	48.63	2.00	0.946
8	450 °C	33.47	16.88	49.65	1.98	0.986
9	500 °C	35.76	14.5	49.74	2.46	0.989