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Enhanced mobility of Cu_4SnS_4 films prepared by annealing SnS–CuS stacks in a graphite box

U. Chalapathi, B. Poornaprakash, Si-Hyun Park *

Department of Electronic Engineering, Yeungnam University, Gyeongsan 38541, South Korea

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High-quality Cu_4SnS_4 thin films are prepared by annealing chemical bath-deposited SnS–CuS stacks in a graphite box. The effects of annealing temperature on the grain growth and morphology of these films are investigated in this study. Results showed that the films prepared at 500–580 °C yielded an orthorhombic crystal structure with lattice parameters $a = 1.371$ nm, $b = 0.766$ nm and $c = 0.643$ nm, a crystallite size of 260 nm, an increased grain size from 2 μm to greater than 6 μm, a direct optical band gap of 1.0 eV, and p-type electrical conductivity. The films prepared at 550 °C and 580 °C exhibited a relatively high hole mobility of 150 $cm^2V^{-1}s^{-1}$. These properties suggest that the films developed in this study can yield reasonable device efficiency when used as solar cell absorber layers.

1. Introduction

In recent years, extensive research efforts have been made to find novel and new chalcogenide thin films for solar cell applications. In following with this, the kesterite family semiconductors have shown considerable potential and they have been reported to yield a maximum conversion efficiency of 12.6% (Wang et al., 2014). Alternatively, Cu-Sn-S family semiconductors, Cu_2SnS_3 (CTS), Cu_3SnS_4, and Cu_4SnS_4, are also being considered as promising candidates because of their earth-abundant and non-toxic precursor elements. CTS, which possess a direct band gap ranging from 0.80 to 1.35 eV, high optical absorption coefficient, and p-type electrical conductivity, has been explored extensively via a variety of techniques (Becerra et al., 2014; A. Fernandes et al., 2010; Avellaneda et al., 2010b; Bouaziz et al., 2009; Chalapathi et al., 2013; M. Berg et al., 2012b; Kuku and Fakolujo, 1987). Devices implementing on CTS have attained a maximum efficiency of 6.7% using a Ge doped absorber (Umehara et al., 2016), and 4.29% using pure CTS absorber (Kanai et al., 2015). As Cu_3SnS_4 is reported to have a direct optical band gap between 1.2 and 1.7 eV, high optical absorption coefficient, and p-type electrical conductivity, it has also been explored via various deposition techniques (Bouaziz et al., 2007; A. Fernandes et al., 2010; Su et al., 2012; Guan et al., 2013; Chalapathi et al., 2014). Moreover, Cu_4SnS_4, with a reported direct optical band gap of 1.2 eV, high optical absorption coefficient ($\alpha > 10^4$ cm^{-1}), and p-type electrical conductivity, also shows promise as a solar cell absorber layer.

Although they show potential, there are few reports on the synthesis of Cu_4SnS_4 thin films. Nair et al. prepared Cu_4SnS_4 thin films for the first time by heating the chemical bath-deposited (CBD) SnS–CuS stacks at 400 °C under 300 mTorr N_2 pressure (Nair et al., 2003; Avellaneda et al., 2010a). They reported a direct band gap ranging from 1.0 to 1.2 eV, an electrical conductivity between 0.5 and 1.0 Ω^{-1} cm^{-1}, and a hole mobility of 10 $cm^2V^{-1}s^{-1}$ for these films. Additionally, Kassim et al. later employed CBD (Kassim et al., 2009), and electrodeposition (Kassim et al., 2008) techniques to prepare Cu_4SnS_4 films, subsequently reporting these films to have a direct band gap ranging from 1.68 to 1.90 eV. Vani et al. applied a co-evaporation technique to prepare Cu_4SnS_4 films at temperatures ranging between 200 and 350 °C (Vani et al., 2013b); they reported a direct optical band gap between 1.70 and 1.93 eV. Recently, Chen et al. synthesized Cu_4SnS_4 films via the doctor-blade technique and resultantly fabricated a superstrate cell with an efficiency of 2.3% (Chen et al., 2014), which is very low as compared to kesterite solar cell efficiency. Further understanding of the growth and properties of the films is quite essential for improving the quality of Cu_4SnS_4 films, and thus their applied device efficiency. Thus, with the objective of improving the quality of the Cu_4SnS_4 films, we have attempted to fabricate Cu_4SnS_4 films by annealing chemically grown SnS–CuS precursors in a graphite box at elevated temperatures ranging from 500 to 580 °C under N_2 and S_2 ambient conditions. As a result, the films prepared at temperatures ranging from 550 to 580 °C exhibited good grain growth and a higher hole mobility of 150 $cm^2V^{-1}s^{-1}$, which are

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* Corresponding author.
E-mail address: sihyun_park@ynu.ac.kr (S.-H. Park).

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two properties that are essential to improve the efficiency of the cells.

2. Experimental details

The SnS–CuS precursor layers were deposited onto chemically cleaned soda-lime glass substrates via chemical bath deposition. For the deposition of the SnS layer, we used the starting chemicals and deposition conditions similar to those optimized conditions described in our previous report (Chalapathi et al., 2016). The deposition of SnS was carried out for 3 h to obtain a thickness of 300 nm. CuS thin films were then deposited by mixing 25 ml of 0.5 M $CuSO_4{\cdot}5H_2O$, 5 ml of 0.5 M EDTA, 25 ml of 0.5 M thioacetamide, and 45 ml of DI water in a 100 ml glass beaker. The beaker containing the solution was subsequently placed in a water bath at 40 °C. The SnS thin films grown using the above procedure were dipped into this solution, and the deposition was allowed to proceed for 7 h to obtain an approximately 600 nm thick film. Following deposition, the samples were removed from the bath, washed with the DI water, and dried using N_2. The obtained SnS–CuS precursor layers were then annealed in a graphite box with approximately 500 mg of elemental S to convert the stacks into the desired Cu_4SnS_4 films. The stacks were annealed in the presence of N_2 and S_2 at temperatures ranging from 500 to 580 °C for 90 min under a 200 Torr pressure. The temperature ramping rates, and annealing conditions are similar to those implemented in our previous report (Chalapathi et al., 2017).

Glancing-indence X-ray diffraction (GIXRD) patterns of the films were recorded via an X-ray diffractometer (PANalytical) and Cu K_α radiation ($\lambda = 0.15406$ nm) at a glancing angle (ω) of 3°. Raman spectra were recorded using a confocal Raman spectrometer (Thermo Fisher Scientific, Nicolet 6700) with a 532 nm laser source. The surface morphology and cross-sections of these films were determined by using a field emission scanning electron microscope (FESEM, Hitachi, S-4100) and their elemental compositions were determined via energy dispersive X-ray spectrometer (EDS) coupled with FESEM. The transmittance curves of the films were recorded by using a double beam spectrophotometer (Cary 5000 ultraviolet–visible-near-infrared (UV–vis-NIR) spectrophotometer). Their electrical properties were measured via a Hall measurement system (Nanometrics, HL5500).

3. Results and discussion

3.1. Composition

The elemental compositions of Cu_4SnS_4 films prepared at various temperatures are listed in Table 1. The composition of each prepared film is relatively Cu-poor and Sn-rich. Because of a marginal loss of Sn, the Cu/Sn ratio of the films increases from 3.21 to 3.31, owing to increased annealing temperature.

3.2. Structural analysis

The crystal structures of the SnS–CuS stack and the films prepared at temperatures ranging from 500 to 580 °C were analyzed by recording their GIXRD patterns; the corresponding patterns are presented in Fig. 1. The XRD pattern of the SnS–CuS stack exhibits diffraction peaks due to cubic SnS (denoted by #) and CuS (denoted by $*$ symbol). The XRD pattern of the film annealed at 500 °C exhibits an intense peak at 26.72°, with low-intensity peaks at 19.16, 23.16, 27.86, 30.21, 30.98, 33.00, 33.77, 37.97, 39.01, 41.87, 43.01, 44.49, 46.74, 48.66, 50.74, 51.88, and 55.00°. These peaks are close to the reported diffraction peaks for Cu_4SnS_4 (JCPDS Card No. 29-0584). All of the prepared films are found to possess an orthorhombic crystal structure. The lattice parameters are found to be as follow: $a = 1.371$ nm, $b = 0.766$ nm, and $c = 0.643$ nm. As with the peaks, the obtained lattice parameters are comparable to the reported lattice parameters of Cu_4SnS_4 (JCPDS Card No. 29-0584). The full width at half maximum (β) of the films is found to be 0.3444° and no change in its value is observed with increasing annealing temperature. The crystallite size of the films, estimated using Scherrer's formula after correcting for the instrumental broadening, is found to be 260 nm. In these films, the possibility of either the presence or absence of monoclinic CTS, which is a possible secondary phase within this temperature range, can not be dismissed, as the intense peaks of this phase are comparable to those of Cu_4SnS_4. To distinguish the possible secondary phases in these films, Raman spectroscopy analysis was carried out.

The micro-Raman spectra of the films prepared at 500, 550, and 580 °C are shown in Fig. 2. The Raman spectra of Cu_4SnS_4 films prepared at 500 °C exhibited an intense Raman mode at 322 cm^{-1}, with two weaker modes at 292 and 355 cm^{-1}. Cheng et al. (2011) attributed Raman modes observed at 283, 318, and 377 cm^{-1} during the growth of CTS films to Cu_4SnS_4. Additionally,

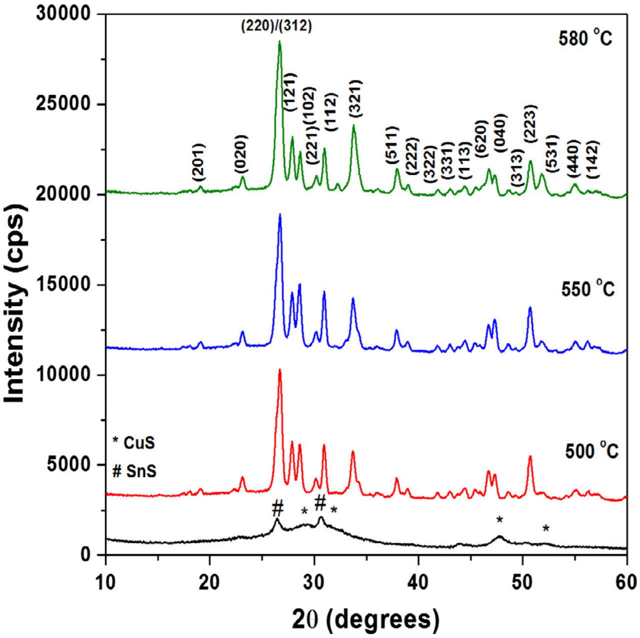

Fig. 1. GIXRD patterns of Cu_4SnS_4 films prepared at temperatures ranging from 500 to 580 °C.

Table 1
Elemental compositions of Cu_4SnS_4 films prepared at various temperatures.

Annealing temperature (°C)	Atomic percentage			Ratio	
	Cu	Sn	S	Cu/Sn	S/(Cu + Sn)
500	42.1	13.1	44.8	3.21	0.81
550	42.7	13.1	44.2	3.26	0.79
580	42.2	12.7	45.1	3.31	0.82