



Influence of selenium doping on the properties of $\text{Cu}_2\text{Sn}(\text{S}_x\text{Se}_{1-x})_3$ thin-film solar cells fabricated by sputtering



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ABSTRACT

$\text{Cu}_2\text{Sn}(\text{S}_x\text{Se}_{1-x})_3$ (CTSSe) ($0 \leq x \leq 0.03$) thin films are prepared using sputtered metal precursors. The influence of the quantity of selenium doped during an annealing process on the properties of CTSSe thin films and solar cells is investigated. The synthesized CTSSe thin films are grown in the monoclinic crystal structure with a densely packed morphology. The growth of the CTSSe thin films is successfully demonstrated by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) analyses. The band gap energy of the CTSSe thin films are extrapolated from the optical spectra of the band edge region to be 0.86 eV and 0.88 eV. A compositional analysis using X-ray fluorescence (XRF) spectroscopy shows a consistent increase in the selenium content with increase in the quantity of added selenium. This dependence is confirmed by changes in the crystallinity, composition, optical and electrical properties. CTSSe thin-film solar cells (TFSCs) were fabricated with a structure of Mo/CTSSe/CdS/i-ZnO/AZO/Al. The best efficiency of 2.49% was achieved for the fabricated CTSSe TFSC with a V_{oc} of 190.8 mV, J_{sc} of 34.6 mA/cm², and FF of 37%.

1. Introduction

Cu_2SnS_3 (CTS)-based thin-film compounds have been evaluated as a suitable material for next generation thin-film solar cells (TFSCs) because of their low cost and environmentally benign properties. In contrast with other materials for TFSCs such as CIGS, CdTe, and CZTS, CTS does not include rare metals and is a ternary compound; thus, it is a relatively low-cost material that is easy to form in the pure phase. Furthermore, CTS has an absorption coefficient ($\sim 10^4 \text{ cm}^{-1}$) and a wide, controllable band gap (0.93–1.77 eV) that are appropriate for use as an absorber layer in TFSCs [1–5]. Since the highest efficiency of 4.63% was reported for a pure CTS solar cell, many related studies have been conducted, and several promising outcomes have been achieved. Thus, the potential of CTS for next generation solar cells has been recognized [6].

In the case of kesterite CZTS, to overcome the limitations of a low J_{sc} with a high V_{oc} , selenium doping has been used to enhance the device performance. Eventually, by improving both the J_{sc} and V_{oc} , a highly efficient CZTSSe solar cell was fabricated with a power conversion efficiency (PCE) of 12.6% [7]. The addition of selenium decreased the

absorber layer's band gap, which led to a decline in the V_{oc} . Therefore, controlling the S/Se ratio in the absorber layer is very important [8–11].

Doping CTS with selenium has been reported to improve the performance of CTS-based devices as well. According to a previous report, CTSSe thin films were successfully synthesized with a controllable band gap energy (from 0.67 to 0.87 eV), and these films were suitable for full-spectrum solar cells because of their narrow band gap [12]. However, the PCE of CTSSe TFSCs has not been reported thus far.

In this study, CTSSe TFSCs were successfully fabricated using a sputtering process. The influence of the quantity of selenium incorporated during an annealing process was examined. The crystallographic, compositional, microstructural, optical and electrical properties of the $\text{Cu}_2\text{Sn}(\text{S}_x\text{Se}_{1-x})_3$ thin films with various selenium powder ($0 \leq x \leq 0.03$) and TFSCs were characterized using X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray fluorescence spectroscopy (XRF), field emission scanning electron microscopy (FE-SEM), UV-Vis/NIR spectrophotometer, and Hall measurement to better understand the CTSSe thin films. Herein, we report for the first time a cell efficiency of 2.49% for CTSSe TFSCs as measured

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by a class AAA solar simulator.

2. Experimental details

Cu–Sn ordered stack layer deposition was conducted on Mo-coated soda lime glass using a sputtering method. A sputtering power of 0.65 W/cm^2 and a working pressure of 8 mTorr was maintained during the deposition, and the deposition times for the Cu and Sn metallic layers were 2215 s and 3012 s, respectively. A conventional tube-type rapid thermal annealing (RTA) system was used to anneal the absorber layer. To dope the thin films with selenium, various quantities of selenium powder (namely, 0 mg, 2 mg, and 6 mg) and fixed sulfur powder of 90 mg were placed into graphite box in the annealing tube. The sulfurization process was conducted for 10 min at 580° in an argon (Ar) atmosphere. Cadmium sulfide (CdS) was then deposited as a buffer layer using chemical bath deposition (CBD). Next, intrinsic ZnO (i-ZnO) and Al-doped ZnO (AZO) with 2 at% of Al were successively sputtered as transparent conducting oxide layers using commercial made target. The i-ZnO and AZO were deposited in the Ar atmosphere with sputtering power of 2.46 W/cm^2 and 1.53 W/cm^2 at 0° and 400° , respectively. Finally, an Al front grid was deposited using a direct current (DC) sputtering method. Consequently, the solar cell device was fabricated with a structure of Mo/CTS/CdS/i-ZnO/AZO/Al, the active area of which is 0.31 cm^2 .

The crystal structure was analyzed by high-resolution XRD (X'pert PRO, Philips, Eindhoven, Netherlands) operated at 40 kV and 30 mA with Ni-filtered Cu-K α radiation [$\lambda = 1.54056 \text{ \AA}$]. Micro-Raman spectroscopy (Via Reflex UV Raman microscope, Renishaw, U.K. at the KBSI Gwangju Center) was carried out with an excitation wavelength of 488 nm, resolution of 1 cm^{-1} , and a He-Ne laser at a power of 15 mW in the range of $150\text{--}450 \text{ cm}^{-1}$. The morphology was analyzed by FE-SEM (JSM-6701F, JEOL, Japan). XPS (VG Multilab 2000, Thermo VG Scientific, UK) with a monochromatic Mg-K α (1253.6 eV) radiation source was used to analyze the binding energy of the thin films. XRF (ZSX primus II, RIKAKU, Japan) was used to investigate the composition. UV–Vis/NIR spectrophotometer (Lambda 1050, Perkin Elmer, USA) was used to study optical properties. The electrical properties of thin films were characterized by Hall Effect measurements in Van der Pauw configuration (M/N #7707_LVWR, Lake Shore Crytronics Inc. USA). The PCE and the detailed electrical properties were characterized using a class AAA solar simulator (Sol31, Oriel, USA).

3. Results

XRD was implemented to identify the crystal structure and crystallinity of the CTSSe thin films annealed with different quantities of added selenium. The XRD patterns as a function of the diffraction angle are shown in Fig. 1. The CTSSe thin films synthesized with 0, 2, and 6 mg of Se are denoted by CTS-0, CTSSe-2, and CTSSe-6, respectively. Diffraction peaks appeared at $2\theta = 28.44^\circ, 32.96^\circ, 47.31^\circ, 56.13^\circ, 58.86^\circ, 69.14^\circ, 76.32^\circ,$ and 78.75° , which are assigned to the (112), (200), (220), (312), (224), (400), (332), and (420) diffraction planes of CTS (JCPDS card No. 89–2877) [1,3]. The (112) diffraction plane exhibits the strongest peak, which indicates that this is the preferential growth direction. However, a shift in the CTSSe diffraction peaks due to the doped selenium can be observed in Fig. 1(b). The main diffraction peak of pure CTSSe appears at 28.2° , while that of pure CTS appears at 28.4° . Fig. 1(b) clearly shows that the diffraction peak of the (112) plane is shifted to the lower 2θ angle relative to CTS-0, while that of Mo does not shift. This indicates that the lattice ordering is modified by the substitution of sulfur with selenium because selenium has a larger ionic radius than sulfur. Lattice constant of CTSe (5.690 \AA) is slightly bigger than CTS (5.430 \AA) and, it indicates that CTSSe thin films get stressed compressively more by increasing its doping concentration [13]. Additional unknown negligibly small peaks are also observed at $21.0^\circ, 31.5^\circ$ and 44.2° . The peaks of the CTSSe samples are very similar to

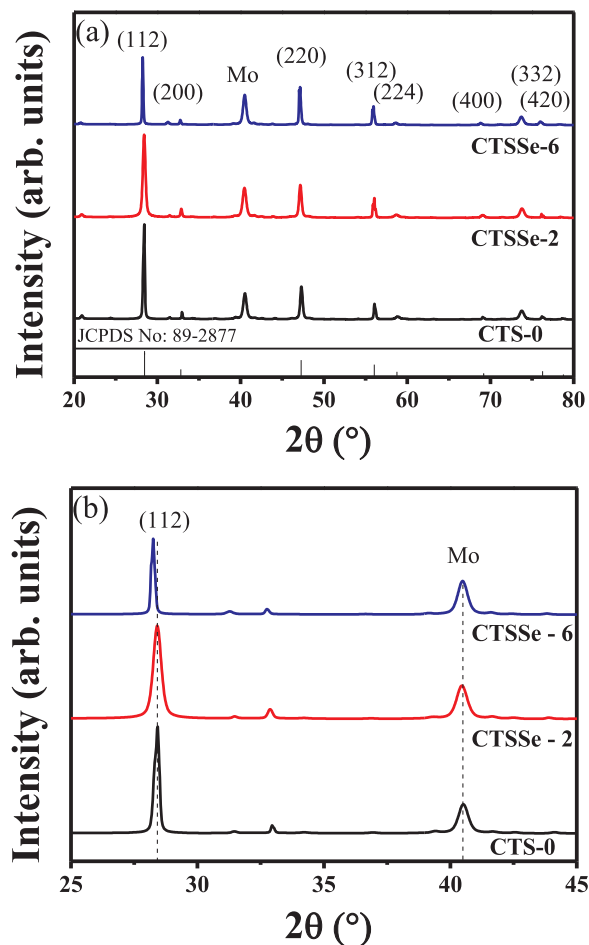


Fig. 1. (a) X-ray diffraction patterns of CTS and CTSSe thin films and (b) magnified view of (112) diffraction plane in XRD spectra.

those of the tetragonal, cubic and monoclinic crystal structures, which correspond well with the given JCPDS/ICDD data [1]. However, cubic Cu_2SnS_3 rarely forms at temperatures under 775°C , and thus, these CTSSe thin films are more likely to exhibit the monoclinic or tetragonal crystal phase [14]. Raman spectroscopy is suitable for identifying unknown crystal phases. Fig. 2 shows the Raman spectra of the CTS-0, CTSSe-2, and CTSSe-6 samples. All of the samples exhibit two obvious peaks and an additional secondary peak, which corresponds to MoS_2

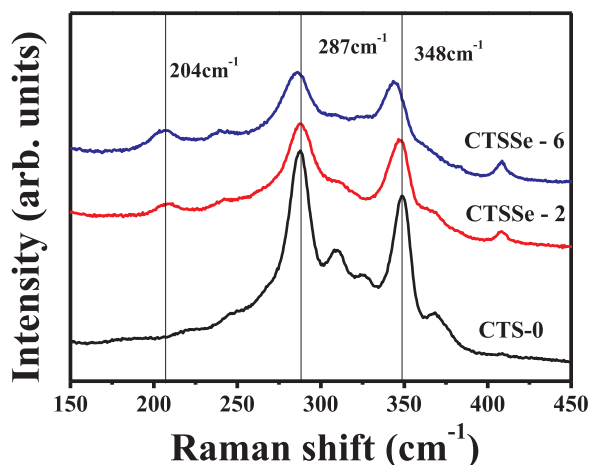


Fig. 2. Raman spectra of CTS and CTSSe thin films as a function of quantity of doped selenium.

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