

# Effects of Se/(S+Se) Ratio on $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ (CZTSSe) Thin Film Solar Cells Fabricated by Sputtering

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**ABSTRACT:** Recently,  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$  (CZTSSe) has been received a tremendous attraction as light absorber material in thin film solar cells (TFSCs), because of its earth abundance, inexpensive and non-toxic constituents and versatile material characteristics. Kesterite CZTSSe thin films were synthesized by sulfo-selenization of sputtered Cu/Sn/Zn stacked metallic precursors. The sulfo-selenization of Cu/Sn/Zn stacked metallic precursor thin films has been carried out in a graphite box using rapid thermal annealing (RTA) technique. Annealing process was done under sulfur and selenium vapor pressure using Ar gas at 520°C for 10 min. The effect of tuning Se/(S+Se) precursor composition ratio on the properties of CZTSSe films has been investigated. The XRD, Raman, FE-SEM and XRF results indicate that the properties of sulfo-selenized CZTSSe thin films strongly depends on the Se/(S+Se) composition ratio. In particular, the CZTSSe TFSCs with Se/(S+Se) = 0.37 exhibits the best power conversion efficiency of 4.83% with  $V_{oc}$  of 467 mV,  $J_{sc}$  of 18.962 mA/cm<sup>2</sup> and FF of 54%. The systematic changes observed with increasing Se/(S+Se) ratio have been discussed in detail.

**Key words:**  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$  (CZTSSe), Sputtering, Se/(S+Se) ratio, Thin film solar cells

## 1. Introduction

An efficient, low cost and proper method search has been one of the most significant technological challenges of this century. Indium and gallium-free CZTSSe is a promising candidate for high efficiency and cost effective thin film solar cells (TFSCs) due to its optimum optical band gap energy (1.0 eV-1.5 eV), high absorption coefficient ( $>10^4$  cm<sup>-1</sup>), non-toxic and earth abundant elements. The enhancement of  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) and  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) solar cells have reached efficiencies up to 8.4% and 9.6% respectively<sup>1,2)</sup>. Particularly, Kesterite CZTSSe absorber with power conversion efficiencies (PCE) of 12.7% is a promising candidate that encourages the further development in solar cell applications<sup>3)</sup>. In this regard, the interest in studying thin films with a mixture of S and Se as a possible replacement for  $\text{Cu}(\text{In,Ga})\text{Se}_2$  TFSCs have been heightened. To deposit CZTSSe absorbers with unique characteristics, selenization parameters are very crucial and important. Several techniques have been reported for Kesterite

thin film absorber preparations leading to the highly efficient cell from the hydrazine process (12.7%) and co-sputtering (9.3%) method<sup>3-4)</sup>. However, due to the high toxicity and instability of hydrazine, sputtering method is more desirable for practical application.

In this study, the effect of selenization on the stacked sputtered precursors is investigated by their structural, morphological, compositional and electrical properties using a rapid thermal annealing (RTA) technique. This method has some advantages in obtaining uniform, smooth and compact films at much shorter annealing time<sup>5)</sup>. A graphite box is artfully designed in the reaction container, in which the precursor thin films are annealed together with S and Se powder. This graphite box can reduce the elemental losses and limit the decomposition of CZTSSe at high temperature ( $> 520^\circ\text{C}$ ). CZTSSe films having different Se/(S+Se) ratio were synthesized from CZT/Mo precursor by varying the quantity of Se powder to study the effect sulfo-selenization on CZTSSe TFSCs.

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## 2. Experimental details

### 2.1 Sample preparation

The Cu/Sn/Zn precursors were consecutively deposited on Mo coated soda lime glass (SLG) by direct current (DC) sputtering system at room temperature by using Cu/Sn/Zn target. The stacked precursors were placed in a graphite box and sulfo-selenized using a RTA system at 520°C for 10 min in Ar flow, at an operating pressure of 0.03 MPa with ramp rate of 10°C/sec. The amount of Se powder is varied from 0 to 0.05 g by keeping the amount of S powder constant. CdS buffer layer was deposited by a typical chemical bath deposition (CBD) method. Before preparing the CdS buffer layer, KCN etching was done by immersing samples in an aqueous KCN solution (~5 wt%) for 1 min, followed by deionized (D.I.) water rinsing and nitrogen drying<sup>6</sup>. i-ZnO and AZO were prepared by radio frequency (RF) sputtering technique. An Al grid as a current collector was deposited using DC sputtering technique. The active area of the thin films was 0.31 cm<sup>2</sup>. Thus, CZTSSe TFSCs were fabricated with a SLG/Mo/CZTSSe/ CdS/i-ZnO/AZO/Al configuration.

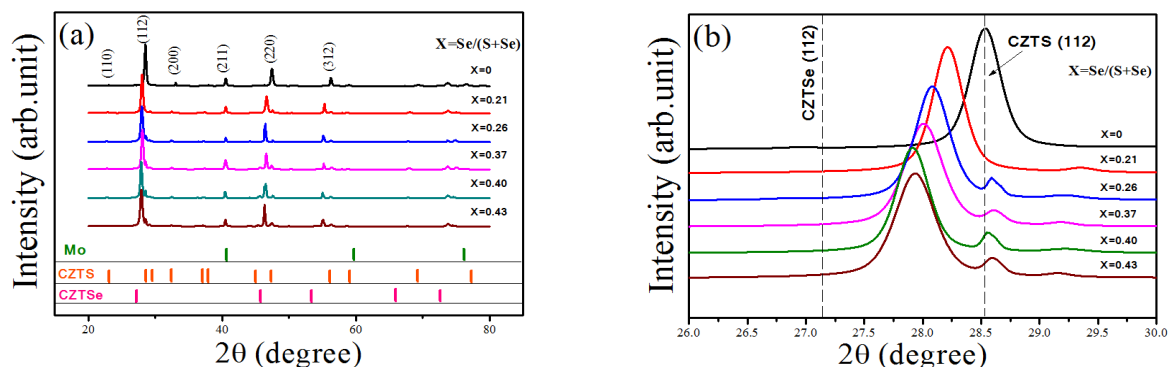
### 2.2 Sample characterization

The structural properties of CZTSSe TFSCs were measured by using high resolution X-ray diffraction (XRD, X'pert PRO, Philips, Eindhoven, Netherlands) operated at 40 kV and Raman scattering spectroscopy using a Jobin Yvon T64000 Raman scattering system with an Olympus microscope equipped with a 100X magnification lens at Korea Basic Science Institute (KBSI), Gwangju. The surface morphology was observed using field emission scanning electron microscopy (FE-SEM, Model: JSM-6701F, Japan) at Regional Innovation Center (RIC),

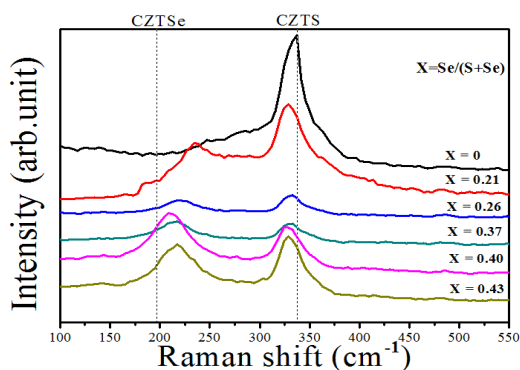
Center for Photonic Materials and Devices, Gwangju. The chemical composition was examined using an X-ray fluorescence spectrometer (XRF) (ZSX Primus II RIGAKU Corp). The power conversion efficiency (PCE) of TFSCs was characterized by a class AAA solar simulator (Sol31, Oriel, USA) and incident photon conversion efficiency measurement unit (PV measurement, Inc., USA) respectively.

## 3. Results and discussion

Fig. 1(a) shows the XRD patterns of the CZTSSe thin films with different Se/(S+Se) ratios ranging from 0 to 0.43. All samples show clearly the presence of Mo as well as a CZTS phase. The formation of CZTSSe can be seen by the presence for several kesterite peaks along (101), (110) and (211) reflections for CZTSe or CZTS. Also as seen from the XRD, prominent CZTSSe peaks are exhibited at ~27-28.53, 45-47.4, and at ~54-56.3° with presence of several peaks between CZTSe and CZTS phases. These results show the intense peaks corresponding to the (112), (220) and (312) planes of a Kesterite structure. Because of all the complex peaks, we will focus on the (112) peaks which has higher counts. A zoom of this peak is shown in Fig. 1(b). The positions of the (112) peak for CZTSe at 27.16°, and CZTS at 28.53° are shown as vertical lines with the reference of [JCPDS card No.: 26-0575 and 52-0868]. All the samples present a strong peak between the CZTSe and CZTS peaks. Therefore, it is assumed that this peak is due to a reflection from the (112) planes of the CZTSSe. It is observed that shifting of diffraction peaks to lower 2θ values takes place as Se content increases, which indicates an increase in the lattice constant due to the replacement of S and Se<sup>7</sup>. Following the above results, we can draw the conclusion that the crystal structure of the CZTSSe



**Fig. 1.** (a) The XRD patterns of the CZTSSe thin films with different ratio of Se powder i.e. 0, 0.21, 0.26, 0.37, 0.40 and 0.43. (b) (112) diffraction peak of CZTS and CZTSSe thin films



**Fig. 2.** Raman spectra of the CZTSSe films at different Se/(S+Se) ratios. The vertical lines guide to the eye corresponding to the main Raman scattering peaks of the referred structures

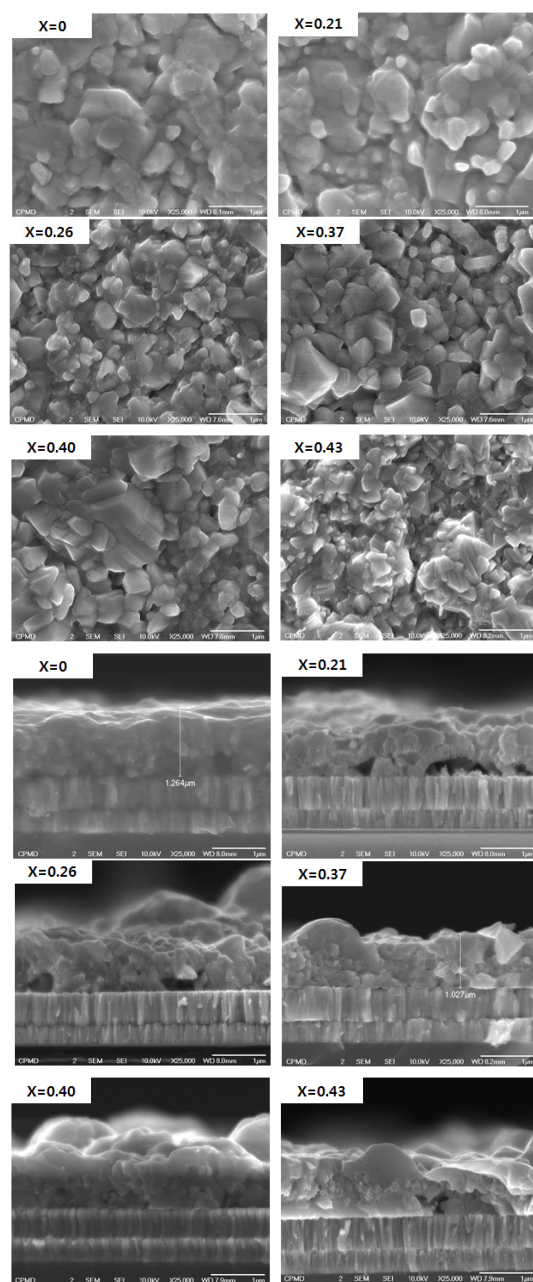
absorber appears to be same, but the entire XRD pattern shifts due to a change in the lattice parameter.

Raman scattering measurements allow a more detailed discussion regarding the origin of the XRD peak. Since surface Raman scattering analysis gives an additional information on possible secondary phases that can be obtained. In Fig. 2, the Raman spectra is presented and the literature values for the peak positions of CZTSe and CZTS are represented as vertical lines.

CZTS samples show a peak at  $338\text{ cm}^{-1}$  which matches well with literature values<sup>8,9</sup>. This peak is strongly related to CZTS since its presence is confirmed by XRD measurements, as discussed previously. All the CZTSSe samples show a peak between  $328\text{--}338\text{ cm}^{-1}$ . This peak is shifted to lower energies with respect to the CZTS peak at  $338\text{ cm}^{-1}$ . According to Grossberg *et al.*, the A1 vibration mode of the CZTS shifts to lower energies due to a substitution of Se atoms by S atoms. Considering the XRD results, the Raman peaks at  $196\text{ cm}^{-1}$  and  $226\text{ cm}^{-1}$  can be associated with a CZTSSe phase. Furthermore, no other secondary phases are seen in the Raman spectra.

The morphology of the resulting CZTSSe thin films is depicted in Fig. 3. All samples exhibit different surface morphology with the increased ratio of Se/(S+Se). The surface of the CZTSSe thin films is composed of small irregular grains spread randomly on the surface with large grains. A closely compact granular morphology is observed at lower Se/(S+Se) ratio. Additionally, well-faceted large grains are obtained in the CZTSSe absorber with increasing Se/(S+Se) ratio, which is beneficial for high efficient device.

The compact and rough morphology is depicted for the cross-section of samples at lower Se/(S+Se) ratio. The other samples share the similar structure, showing large grains at the

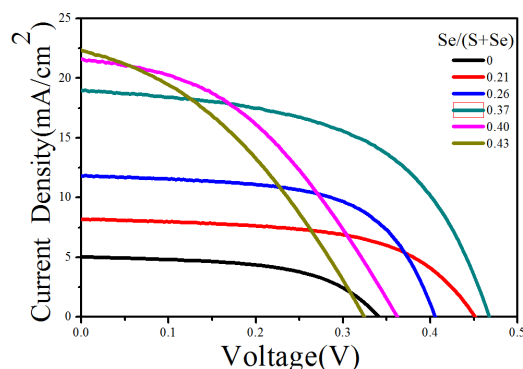


**Fig. 3.** The surface and cross-sectional FE-SEM images of the CZTSSe thin films with various Se/(S+Se) ratio, where  $x = \text{Se}/(\text{S}+\text{Se})$

top and smaller ones at the interface of Mo/CZTSSe. For the CZTSSe absorber, some voids are observed at the Mo/CZTSSe interface. For enhancing the grain growth of the absorber we mixed chalcogen sources during the growth in the annealing atmosphere. Thus, S and Se vapor mixture have higher reactivity compared to the pure vapors. Excess Se supply, in the case of  $\text{Se}/(\text{S}+\text{Se}) = 0.43$ , resulted in the deterioration of CZTSSe films with lower crystallinity and it appears to have a dissimilar layer at the top.

**Table 1.** Elemental compositional ratios of the CZTSSe absorber layers

Se/(S+Se)	Cu/Sn	Zn/Sn	(S+Se)/M
0	1.38	1.29	0.98
0.21	1.74	1.34	0.99
0.26	1.71	1.31	1.00
0.37	1.68	1.29	1.02
0.40	1.56	1.26	1.04
0.43	1.48	1.11	1.08

**Fig. 4.** J-V curves for CZTSSe films with various Se/(S+Se) ratio

X-ray fluorescence (XRF) spectroscopy gives the better quantitative information about the elemental composition of the sample, which helps in improving the quality of the device. The composition ratio of CZTS and CZTSSe absorbers is as shown in Table 1. As mentioned before in XRD data, Se/(S+Se) ratio doesn't have a significant impact on the formation of extraneous phases in CZTSSe thin films.

The solar cell performance is studied by using current-voltage (I-V) characteristics. Different Se/(S+Se) ratios exhibit a significant impact on the electronic characteristics of the device such as open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ) and also the power conversion efficiency of CZTSSe films. Fig. 4 shows the J-V curves for CZTSSe devices with different Se/(S+Se) ratio ranging from 0 to 0.43. Various solar cell parameters obtained with respect to Se/(S+Se) ratio, for all the devices

presented in Table 2. The devices exhibit the increasing values of  $J_{sc}$  corresponding to the Se/(S+Se) ratio. The solar cell device with 0.37 of Se/(S+Se) ratio shows a highest  $J_{sc}$  of 18.962 mA/cm<sup>2</sup> and  $V_{oc}$  of 467 mV having PCE of 4.83%. A relatively high fill factor (FF) of 54% caused a high PCE. The series resistance ( $R_s$ ) and shunt resistance ( $R_{sh}$ ) are of 15  $\Omega$ /cm<sup>2</sup> and 200  $\Omega$ /cm<sup>2</sup>, respectively. However excess amount of Se caused the degraded solar cell performance.

## 4. Conclusions

In this work, the CZTSSe thin films with various Se/(S+Se) ratios were synthesized from CZT/Mo precursor by sputtering method. The selenization parameters for CZTSSe thin films with different Se content were investigated and the best ratio for formation of an efficient CZTSSe thin film is evaluated from FE-SEM, XRD, Raman, XRF and J-V measurements. The device having 0.37 of Se/(S+Se) ratio exhibits the best PCE of 4.83%. It is proven that all samples show a Se graded structure for a different Se/(S+Se) ratios without the appearance of secondary phases. It is also shown that the XRD and Raman scattering peak positions shift with the quantity of Se incorporated. Although we have fabricated 4.83% efficient TFSCs, the PEC for the device is low as compare with the prime TFSCs and hence need to be enhanced.

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**Table 2.** Various solar cell parameters of CZTSSe devices with different ratio Se/(S+Se)

Se/(S+Se)	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	F.F	Eff (%)	$R_s$	$R_{sh}$
0	340	5.031	55	1.94	23	2000
0.21	451	8.193	57	2.11	33	Inf
0.26	404	11.818	60	2.89	15	2000
0.37	467	18.962	54	4.83	15	200
0.40	393	21.583	48	3.78	20	500
0.43	322	22.295	36	2.65	23	133

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