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2020

Lie, S., Li, W., Leow, S. W., Bishop, D. M., Gunawan, O., & Wong, L. H. (2020). Comparing the effect of Mn substitution in sulfide and sulfo-selenide-based kesterite solar cells. *Solar RRL*, 4(4), 1900521-. doi:10.1002/solr.201900521

<https://hdl.handle.net/10356/145743>

<https://doi.org/10.1002/solr.201900521>

This is the accepted version of the following article: Lie, S., Li, W., Leow, S. W., Bishop, D. M., Gunawan, O., & Wong, L. H. (2020). Comparing the effect of Mn substitution in sulfide and sulfo-selenide-based kesterite solar cells. *Solar RRL*, 4(4), 1900521-. doi:10.1002/solr.201900521, which has been published in final form at <https://doi.org/10.1002/solr.201900521>. This article may be used for non-commercial purposes in accordance with the Wiley Self-Archiving Policy [<https://authorservices.wiley.com/authorresources/Journal-Authors/licensing/self-archiving.html>].

Comparing the Effect of Mn Substitution in Sulfide and Sulfoselenide-Based Kesterite Solar Cells

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Cation substitution is one of the effective ways to improve $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) photovoltaic performance. However, the commonly reported substitutes, Ag and Cd, are not ideal as they detract from the earth-abundant and nontoxic motivation of CZTSSe. Herein, the role of Mn substitution in sulfide and sulfoselenide film are compared in terms of optoelectronic properties and device performance. CZT(S,Se) + CMZT(S,Se) double-layered structures are fabricated by sol-gel spin-coating method with variation in the CMZT(S,Se) layer thickness. It is found that smaller amount of Mn is required to achieve the highest photovoltaic performance in sulfoselenide film in comparison with sulfide-based film. All device parameters (particularly V_{oc} and fill factor) of the sulfoselenide films are improved as compared with the sulfide system. Using a combination of capacitance-voltage (CV), drive-level capacitance profiling (DLCP), and photoluminescence (PL), it is found that the sulfoselenide film has smaller interface defect density, higher hole mobility and PL intensity; which suggest much more effective charge separation and transport. In contrast, in double-layer sulfide film, Mn reduces the acceptor defect level of the absorber.

$\text{Cu}_2\text{ZnSnS}_{x-1}\text{Se}_{1-x}$ (CZTSSe) thin-film solar cells is an attractive replacement to copper indium gallium selenide (CIGS) due to its elemental abundance^[1] and promising optical properties such as high absorption coefficient ($\approx 10^4 \text{ cm}^{-1}$).^[2] The highest efficiency of CZTSSe solar cells is still stagnant at 12.6%,^[3] which is still well below the theoretical Shockley-Queisser power conversion efficiency due to significant V_{oc} deficit.^[4] A recent study of alloying and composition grading with Ag-substituted CZTSSe-predicted performance enhancement due to interface improvement by Cu_{Zn} antisite defects suppression near the junction and band bending formation in the absorber.^[5]

This prediction is supported by the experimental finding of interface band bending and defects elimination via Ag-graded layer $(\text{Cu},\text{Ag})_2\text{ZnSn}(\text{S},\text{Se})_4$ which exhibit significant V_{oc} increase.^[6] However, Ag is a highly valued precious metal with limited supply. It is a nonideal solution that deviates from the earth-abundant motivation in CZTS. This has led to the exploration for another earth-abundant element that can substitute in CZTS.

Several earth-abundant transition metals have been studied as substitute alternatives such as Fe, Ni, Co, and Mn.^[7] In particular, Mn has been a promising cation substitute alternative for Zn as it has higher relative abundance than Zn.^[8] Several studies have reported the photovoltaic performance in $\text{Cu}_2\text{MnSnS}_4$.^[9] Partial substitution of Zn with Mn has shown to improve the interface quality in $\text{Cu}_2(\text{Mn},\text{Zn})\text{SnS}_4$ and $\text{Cu}_2(\text{Mn},\text{Zn})\text{Sn}(\text{S},\text{Se})_4$.^[10] The device

improvement in sulfide-based device is obtained in $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ mainly from improved J_{sc} . Meanwhile, the best photovoltaic device is obtained in $\text{CM}_{0.05}\text{Z}_{0.95}\text{TSSe}$ for sulfoselenide-based device with improvements in depletion width, V_{oc} , and fill factor (FF). Both devices exhibit improvement in short wavelength collection, which indicates an improved absorber/CdS interface. In contrast, the back contact of CZT(S,Se) seems to be better than CMZT(S,Se). Therefore, double-layered structures of CZT(S,Se) as the back layer and the Mn-substituted layers as top layer should improve the interface. Even though double-layered structure of CZTS + CMZTS (15% Mn) is reported to enhance the efficiency,^[10a] this double-layer effect has not been investigated in sulfoselenide-based CZTSSe. The anion in kesterite plays an important role in determining various properties such as optical and defect properties. The substitution of sulfur with selenium is known to decrease the bandgap by lowering conduction band and increasing the valence band.^[11] In addition, selenide-based devices have shown better performances than sulfide, which many believed due to their different defect properties.^[4b,12] For example, the gap shift caused by $[\text{2Cu}_{\text{Zn}} + \text{Sn}_{\text{Zn}}]$ defects complex in CZTSe is predicted to be much smaller than in CZTS, so the charge trapping effect that limit charge separation is much weaker.^[12] The Sn_{Zn} deep defects that was proposed as the origin of persistent electron trapping/detrapping is also predicted to be less dominant in selenide-based films.^[13] Therefore, Mn substitution in both

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1 systems should be investigated as it may have different effects in
2 terms of defect properties and device performances.

3 In this study, we compared the effect of Mn in sulfide and
4 sulfoselenide kesterite solar cell. The thin films were deposited
5 with double-layered structures of CZT(S,Se) as the back layer
6 and $\text{CM}_{0.15}\text{Z}_{0.85}\text{T}(\text{S,Se})$ as the top layer using spin-coating
7 method from our previous study.^[10a] The optimum device
8 performance for sulfoselenide films was observed with a
9 thinner Mn-substituted layer compared with sulfide-based films.
10 Although improvement was observed in both systems, the
11 sulfoselenide films achieve larger increases in efficiency and
12 V_{oc} due to better junction properties. Capacitance–voltage (C–V),
13 drive-level capacitance profiling (DLCP), photoluminescence
14 (PL), Hall measurement, and temperature-dependent current–
15 voltage (IVT) measurements were also conducted to compare
16 the effect of Mn in sulfide and sulfoselenide films.

17 **Figure 1** exhibits both sulfide and sulfoselenide samples as a
18 function of Mn-substituted layers. Due to the lower bandgap of
19 sulfoselenide system, the overall J_{sc} are significantly higher
20 and the V_{oc} are less than the sulfide ones. The first difference

is that a smaller number of layers (2 layers/15% of overall thick-
ness) is needed to obtain the optimum performance. This finding
is consistent with the previous finding where smaller amount of
Mn substitution is required in the bulk for sulfoselenide (5%)
compared with sulfide (15%) film. Second, the increase in
performance of the sulfoselenide system is also accompanied
by significant increase in V_{oc} , J_{sc} , and FF, compared with only
notable J_{sc} increase in sulfide system. The V_{oc} increases by
0.1 V on average without significant bandgap changes.
Together with the large increase in FF, it infers the improved
bulk and junction properties for sulfoselenide film.

To further evaluate the differences between sulfide and sulfo-
selenide systems, diode analysis was performed for the highest
performing cell in each sample. **Figure 2** exhibits the photovol-
taic response and the quantum efficiencies for the CZTS,
CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers
of CMZTSSe. The diode parameters are extracted by Lambert-
W method in **Table 1**.^[14] The ideality factor of sulfoselenide
films are within $1 < \eta_1 < 2$, which infer the recombination
mechanism can be described as a single diode junction, whereas

Figure 1. a) Device parameters a) η , b) V_{oc} , c) J_{sc} , and d) FF as a function of either $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{SnS}_4$ or $\text{Cu}_2\text{Mn}_{0.15}\text{Zn}_{0.85}\text{Sn}(\text{S,Se})_4$ layers. (Data for each condition are taken from 16 solar cell devices.)

Figure 2. a) J - V graphs and b) EQEs of CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTSSe.

Table 1. Diode model J - V parameters for the “champion” CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTSSe cell.

Devices	Efficiency [%]	J_{sc} [mA cm ⁻²]	V_{oc} [mV]	Fill factor[%]	η_1	J_{01} [A cm ⁻²]	R_s [Ohm.cm ²]	G_{sh} [mS cm ⁻²]
CZTS	4.70	15.87	589	50.32	3.47	1.75×10^{-5}	1.57	5.21
CZTS + 4 CM _{0.15} Z _{0.85} T	5.73	17.86	600	53.27	2.81	3.41×10^{-6}	0.86	6.76
CZTSSe	6.42	28.8	385	57.80	1.88	9.57×10^{-6}	0.86	4.93
CZTSSe + 2 CM _{0.15} Z _{0.85} TSSe	8.74	31.7	471	58.57	1.50	1.33×10^{-7}	1.37	2.47

1 sulfide films have $\eta_1 > 2$, which indicate more complex recom-
2 bination mechanism.^[15] Reduced dark saturation current (J_{01}) is
3 observed in both systems, but significant decrease is observed for
4 sulfoselenide, leading to larger V_{oc} increase. In general, the
5 shunt conductance (G_{sh}) for sulfoselenide are lower than sulfide
6 film, with the lowest shunt conductance corresponding to the
7 highest performing cell. The double-layer system also further
8 enhanced the V_{oc} and J_{sc} from single-layer Mn-substituted
9 CZTSSe in the previous study.^[10b]

10 The external quantum efficiency (EQE) in Figure 2b shows
11 improvement in short wavelength (<700 nm) with constant
12 charge collection in long wavelength region in the sulfoselenide
13 films. In terms of bandgap, there are no notable changes for the
14 double-layered samples from their respective control samples.
15 The main difference between the sulfide and sulfoselenide is
16 observed in the higher absorption near the CdS region for sulfide
17 film. Even though the CdS deposition conditions are the same,
18 the sulfide samples might have a thinner CdS as a result of Cd
19 diffusion into the absorber due to the post-annealing process in
20 sulfide films. It should be noted that the double-layer structure
21 in both sulfide and sulfoselenide films shows improved charge
22 collection in the short wavelength regions, therefore confirming
23 the hypothesis that the Mn substitution improves the absorber/
24 CdS interface.

25 To assess the p-n junction quality, C-V measurements were
26 performed with +0.5 to -3 V voltage bias. **Figure 3** shows the
27 derived space-charge density from the C-V sweep as a function

Figure 3. Charge density as a function of distance from the depletion edge derived from C-V measurement for CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTSSe.

Figure 4. PL spectra (normalized) as a function of energy level (eV) for CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTS.

sulfide-based CZTS.^[12] The double-layer sulfoselenide film does not exhibit notable change in ΔE , but the PL intensity is significantly higher compared with the control sample (Figure S2, Supporting Information).

AC Hall measurement^[22] tabulated in **Table 2** reveals that all samples have comparable hole concentration. This finding is also consistent with the DLCP values at high negative bias. The double-layer sulfoselenide film has less carrier concentration and higher hole mobility than the control sample. This finding suggests the possible increase in minority carrier mobility, as the high majority carrier mobility may indirectly stipulate high minority carrier mobility.^[23] In conjunction with larger PL intensity, these findings may suggest improved diffusion length that may contribute to lesser carrier recombination and better charge transport properties for sulfoselenide film.

In terms of morphology and crystal structure, the introduction of Mn-substituted layer does not alter these properties (see Figure S3,S4, Supporting Information). Overall, this study shows that the improvement by Mn substitution near buffer interface can be optimized through double-layer structure in both sulfide and sulfoselenide films. However, the degree of improvement in the sulfoselenide film junction is higher as observed from both large V_{oc} increase and lesser interface defects. The sulfoselenide film also exhibit additional improvement in charge transport properties. This improvement in sulfoselenide films can be related to the relatively weaker charge trapping and less harmful defects as predicted in selenide films, which is further enhanced by the Mn substitution effect. In contrast, Mn substitution in sulfide films reduced the acceptor defects level.

Table 2. Hole concentration and hole mobility for CZTS, CZTS + 4 layers of CMZTS, CZTSSe and CZTSSe + 2 layers of CMZTS.

Devices	Hole concentration [cm ⁻³]	Hole mobility [cm ² V ⁻¹ s ⁻¹]
CZTS	1.71×10^{15}	0.33
CZTS + 4 CM _{0.15} Z _{0.85} T	2.65×10^{15}	0.50
CZTSSe	2.52×10^{15}	0.30
CZTSSe + 2 CM _{0.15} Z _{0.85} TSSe	9.70×10^{14}	1.41

Q5 In summary, the effect of Mn substitution by forming double-layered structure of CZT(S,Se) and $\text{CM}_{0.15}\text{Z}_{0.85}\text{T(S,Se)}$ were compared and investigated. For the sulfide, the highest efficiency of 5.73% was obtained for CZTS + 4 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TS}$ in comparison with the control samples of CZTS. In the sulfoselenide system, the highest performing cell of 8.74% is achieved using CZTSe + 2 layers of $\text{CM}_{0.15}\text{Z}_{0.85}\text{TSSe}$. In both these systems, the Mn-substituted top layer increases the depletion width and short wavelength collection, which correlates with better charge separation and collection. In double-layer sulfoselenide film, the magnitude of improvement is larger due to the better junction properties with the lowest ideality factor and dark saturation current. In addition, charge transport and lower nonradiative recombination was also suggested as observed by increase in PL intensity, CV-DLCP, and increased carrier mobility. In contrast, in double-layer sulfide film, Mn reduces the acceptor defect level. Overall, we believe that the partial Mn substitution provides an alternative pathway to improve the performance of kesterite solar cell.

20 Experimental Section

21 **Absorber Fabrication:** $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ thin films was prepared by sol-gel spin-coating technique. The precursor solutions consist of 22 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.36 M), $\text{MnCl}_2 \cdot 5\text{H}_2\text{O}/\text{ZnCl}_2$ (0.25 M), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.2 M), 23 and thiourea (1.44 M) in 3 mL of 2-methoxyethanol with ethanolamine and 24 triethanolamine as additive. All precursors were purchased from 25 Sigma-Aldrich Company. The ratio of $\text{Cu}/(\text{Zn} + \text{Mn} + \text{Sn}) = 0.8$ and 26 $(\text{Zn} + \text{Mn})/\text{Sn}$ is 1.25 with excess thiourea. The solutions were stirred 27 at 50°C for 1 h. Then the prepared solutions were spin-coated on molybdenum glass substrates at 3000 rpm for 30 s, followed by preheating at 28 280°C for 3 min on a hot plate in air. This spin-coating was repeated thir- 29 teen times (13 layers). Several layers of CZTS were spin-coated followed by 30 $\text{CMn}_{0.15}\text{Z}_{0.85}\text{TS}$, starting from the control sample of 13 layers of CZTS, 31 then proceeded by substituting 1–5 layers of CMZTS as the top layers. 32 Subsequently, the samples were annealed at 600°C for 40 min in sulfur 33 atmosphere in a two-zone furnace, where the samples were annealed 34 in one zone and sulfur powder was annealed in the other zone 35 (200°C) to act as sulfur source. For the sulfoselenide film, the films were 36 annealed with selenium atmosphere (70 mg selenium pellets) at 560°C 37 for 30 min. The selenized films had $\text{Se}/(\text{S} + \text{Se})$ ratio around 80–90% 38 based on EDS. The thickness of these samples is $\approx 1\text{--}1.3\ \mu\text{m}$. 39

40 **Device Fabrication:** Solar cell device has $\text{Mo}/\text{CZT(S,Se)} + \text{CMnZT(S,Se)}/$ 41 $\text{CdS}/\text{ITO}/\text{Ag}$ -paste configuration. CdS buffer layer (50 nm) was deposited 42 on absorber by chemical bath deposition (CBD) at 80°C for 8 min. 43 Subsequently, 200 nm SnO:In (ITO) were deposited by DC sputtering. 44 The devices were annealed at 300°C for 10 min in N_2 atmosphere. 45 Finally, silver paste was manually applied as top electrode. The samples 46 were mechanically scribed into smaller solar cell devices with an active area 47 of $0.15\ \text{cm}^2$. 48

49 **Characterizations and Analyses:** Current–voltage (I – V) under illumination 50 were performed using Xe-based light source solar simulator (VS-0852 51 and Keithley 2612A) at 1 sun AM 1.5 G (calibrated with a standard Si 52 reference cell). The EQE were measured by PVE300 (Bentham) IPCE 53 Instrument equipped with a xenon/quartz halogen light source and 54 calibrated with Si/Ge reference detectors. Temperature dependant I – V 55 measurement and C–V with DLCP measurements were conducted 56 through IBM-PVX system and an HP 4192 impedance analyzer. PL mea- 57 surements were recorded at room temperature using a 15 kHz pulsed 58 532 nm laser, a monochromator, and an InGaAs photomultiplier tube 59 detector. Hall measurements were performed by mechanically exfoliat- 60 ing the absorber and using a rotating parallel dipole line AC Hall system 61 invented by IBM.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research is partially supported by grants from the National Research Foundation, Prime Minister's Office, Singapore under its Campus of Research Excellence and Technological Enterprise (CREATE) programme and Ministry of Education (MOE) Tier 2 Project (MOE2016-T2-1-030).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

cation substitution, earth abundant, photovoltaic devices, solution processes, thin films

Received: November 18, 2019

Revised: December 5, 2019

Published online:

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