Cu₂ZnSn(S,Se)₄ kesterite solar cell with 5.1% efficiency using spray pyrolysis of aqueous precursor solution followed by selenization

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15 **Abstract**

16 Kesterite thin film solar cell has been fabricated by chemical spray pyrolysis (CSP) of an
17 aqueous solution followed by high temperature selenization. The pyrolysis formation of

Cu₂ZnSnS₄ was conducted in atmospheric condition with substrate temperature of 280 °C. X-ray diffraction and Raman spectroscopy study confirmed the formation of the single phase Cu₂ZnSn(S,Se)₄ kesterite structure after selenization without traceable secondary phases. FESEM image shows a uniform absorber layer without carbon layer formed between CZTSSe and Mo. Power conversion efficiency of 5.1% was obtained with different amounts of selenium incorporation. Power dependent and temperature dependent photoluminescence (PL) study revealed donor-to-acceptor pairs (DAP) transition at low temperature. Severe PL quenching at temperatures above 41 K is attributed to the opening of non-radiative recombination channels from the defects associated with non-stoichiometric elemental ratio. Therefore, further enhancement of power conversion efficiency can be achieved by better control of stoichiometry.

Key words: CZTS, kesterite, solar cell, spray pyrolysis, water-based precursor, photoluminescence

Introduction

Thin film chalcopyrite Cu(In,Ga)(S,Se)₂ (CIGSSe) solar cell has undergone rapid developments over the past decades. Due to its direct band gap and high absorption coefficient, the film thickness of the absorber layer can be reduced to 1-2 μm, which reduces the material and fabrication cost. Laboratory-scale CIGSe fabricated by thermal evaporation has achieved power conversion efficiency (PCE) of 20.3% and modules with efficiency of up to 16% have also been demonstrated.^[1,2] Solution processed CIGSSe solar cell based on the hydrazine method has also achieved PCE of 15.2%.^[3] However, the high cost and scarcity of indium and gallium dictate an urgent need for alternative materials.^[4]

1 Recently, kesterite $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) has drawn a lot of attention due to the utility of
2 low cost, earth abundant Zn and Sn elements to replace In and Ga. CZTSSe has a direct band gap
3 located in the same range as CIGSSe (1.0 eV to 1.45 eV) which is considered ideal for efficient
4 solar absorption.^[5] In addition, it possesses high absorption coefficient of 10^4 - 10^5 cm^{-1} . Based
5 on the calculation by Ki and Hillhouse, the highest theoretical efficiency for single junction
6 kesterite solar cell is 32.4% for CZTS and 31.0% for CZTSe.^[6]

7 CZTSe deposited by vacuum-based thermal evaporation has resulted in 9.2% efficiency.^[7]
8 However, the thermal evaporation method suffered from significant tin loss during the process
9 which made it difficult to control the final elemental ratio of the absorber. Furthermore, the high
10 substrate temperature during selenization may lead to the formation of thick MoSe_2 layer
11 resulting in low open circuit voltage (V_{oc}) and short circuit current (J_{sc}). Thus, an additional
12 TiN layer was required as a diffusion barrier to prevent the formation of MoSe_2 .^[8]

13 For non-vacuum based processes, the best performing cell with an efficiency of 11.1% was
14 demonstrated by a hydrazine based technique.^[9,10] However hydrazine is recognized as a highly
15 hepatotoxic and carcinogenic chemical which is dangerous to handle. Thin film fabricated using
16 binary and ternary nanoparticles resulted in PCE of up to 9.6% while those using CZTS
17 nanocrystals yielded a PCE of 7.2%.^[11] Furthermore, Schnabel et al has demonstrated organic
18 solution printing method using metal salts precursor dissolved in DMSO and a PCE of 7.5% has
19 been reported.^[12] However, the carbon residue, which is detrimental to grain growth and the
20 solar cell performance, is normally observed in the absorber layer for both methods.

21 Chemical spray pyrolysis (CSP) is considered a low cost and environmental friendly method.
22 It is suitable for large area deposition in ambient conditions for many functional materials
23 fabrication such as ZnO and In_2S_3 .^[13] CSP has been used for the deposition of chalcopyrite

absorber layer such as CuInS_2 and up to 6% efficiency has been reported.^[14] In terms of kesterite materials, Rajeshmon and co-workers reported a PCE of 1.5% for CZTS sprayed on ITO substrate.^[15] Since post annealing was not conducted to facilitate grain growth, the high recombination within the bulk film greatly reduced the performance of the device. Kumar and co-workers had also demonstrated CSP of CZTS with various spraying conditions, even though the photovoltaic performance was not reported.^[16] One problem of CSP technique is the poor solubility of the metal salts in aqueous condition which results in the presence of small particles on the surface of the films. This is highly detrimental to device performance as thin film PV device requires uniform coating of absorber layer on Mo substrate.

Here, we report the fabrication of kesterite thin film solar cell by solution based CSP technique with non-toxic carbon-free precursors. We had overcome the problem of uniformity and particles formation by adjusting the pH of the precursor solution to obtain a uniformly-coated absorber layer.^[15,16] We further characterized the optical and electrical properties of the CZTS_{Se} and demonstrated a solar cell with PCE of 5.1%.

Experimental

All the chemicals were purchased from Sigma-Aldrich without further purification. Precursor solution was made by dissolving copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 10 mM) zinc chloride (ZnCl_2 , 7.8 mM) and tin chloride dehydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 6.2 mM) into 160 ml water. HCl solution was added to adjust the pH value to 1.8-2.0. Thiourea was added three times above the required stoichiometric to compensate for the possible sulfur loss during the process.

After the Mo-coated glass substrates were pre-heated to 280 °C, the precursor solution was sprayed on the substrate under a rate of 3 ml/min by using N_2 as carrier gas at a pressure of 4 bars. The as-deposited CZTS film was annealed under selenium vapor at 520 °C for 12 minutes.

Subsequently, chemical bath deposition of CdS buffer layer was carried out followed by sputtering of intrinsic ZnO and ITO window layers. Finally, Al top electrode was deposited by thermal evaporation.

The morphology was observed by field emission scanning electron microscopy (FESEM). Elemental ratio of samples were determined by energy dispersive X-ray spectroscopy (EDS) and verified by secondary ion mass spectroscopy (SIMS). X-ray diffraction (XRD) and Raman spectroscopy were used to determine the material structure and phases. Light I-V curves were plotted under 1.5 AM illumination at room temperature with cell area of 0.13 cm². External quantum efficiency was obtained with light wavelength range from 300 nm to 1300 nm. Power dependent and temperature dependent photoluminescence were obtained to understand the electrical properties of the defects.

Results and discussion

Characterization of phases in kesterite absorber layer is crucial because of the high possibility of coexisting secondary phases. X-ray diffraction (XRD) and Raman spectroscopy were performed on both as-deposited and post-selenized films as shown in Fig. 1 and 2. XRD patterns show phase transformation from nearly amorphous phase to highly crystalline as a result of the high temperature selenization. The XRD pattern of the selenized CZTSSe film matches the diffraction peaks of single kesterite phase with peak positions shifting to smaller degrees because of selenium incorporation that enlarges the unit cell. The phase purity of CZTSSe film was further verified by Raman spectroscopy which clearly shows the A_1 mode shift of CZTSe at 173 cm⁻¹, 195 cm⁻¹ and 235 cm⁻¹. The small peak centered at 328 cm⁻¹ indicates that a small amount of CZTS remained after selenization, where the shift from 333 cm⁻¹ of the original position to 328 cm⁻¹ is due to the two-mode behavior which was also observed from CISSe crystals. ^[17]

1 From this spectrum, no traceable peaks from secondary phases are observed; particularly, the
2 peaks of ZnS or ZnSe peaks are absent. As the kesterite structure has a much lower formation
3 enthalpy than other secondary phases based on the first principle calculation,^[18] after high
4 temperature selenization, secondary phases apart from zinc chalcogenide can hardly exist in zinc
5 rich, copper and tin poor samples. In this case, it can be concluded the film is pure CZTSSe from
6 surface to the bulk within the Raman laser penetration depth. However, we cannot rule out the
7 presence of other secondary phase at the CZTSSe/Mo interface.^[19]

8 Due to the hydrolysis of SnCl_2 in aqueous solution, opaque precursor solution is obtained,
9 resulting in particles deposited on top of the CZTS film as shown in Fig. 3a-3b.^[16] In this case,
10 HCl was introduced to the precursor solution to adjust the pH to approximately 1.8-2.0 in order
11 to obtain a clear precursor solution. As shown in Fig. 3c, the acidic precursor solution leads to a
12 uniform and compact CZTS film after pyrolysis. This film deposited from acidic solution was
13 then chosen for subsequent selenization and device fabrication. The cross-section SEM image of
14 the control device in Fig. 3d shows that a highly crystalline absorber layer with thickness of 600
15 nm was obtained without peeling or voids at the CZTSSe/Mo interface. The grain size is
16 estimated to be 300-500 nm. It should also be noted that there is no carbon layer formed at the
17 CZTSSe/Mo interface.

18 The elemental study of post-selenized film detected by EDS indicate metal ratio of
19 $\text{Cu}/(\text{Zn}+\text{Sn}) \approx 0.75$ and $\text{Zn}/\text{Sn} \approx 1.15$. Comparing to the as-deposited CZTS ratio of $\text{Cu}/(\text{Zn}+\text{Sn})$
20 ≈ 0.7 and $\text{Zn}/\text{Sn} \approx 1.3$, moderate Zn and Sn loss is observed. This phenomenon has been reported
21 by several groups and is explained to be a consequence of elemental sublimation at high
22 temperature.^[20, 21] SIMS depth profile was used to examine the elemental distribution of the
23 absorber layer. While a uniform distributions of Cu, Sn and Se are observed across the film as

1 shown in Fig. 4, the concentrations of Zn and S increase towards the CZTSSe/Mo interface. This
2 increment indicates a high chance of Zn(S,Se) coexisting at the CZTSSe/Mo interface. However,
3 this segregated phase was not found to be detrimental to the solar cell performance.^[22] It should
4 also be noted that although thiourea was introduced as sulfur source in the precursor solution,
5 both SIMS and EDS (Supplementary Information) of the selenized film do not show any carbon
6 signals. Furthermore, our spray pyrolysis was conducted at 280 °C, which is higher than the
7 decomposition temperature ($T < 270$ °C) of metal-thiourea complexes (Cu, Zn and Sn) as
8 reported by Madarasz and co-workers^[23] Therefore, due to the absence of carbon layer as seen
9 in the cross-sectional image of CZTSSe obtained by FESEM, and the absence of carbon signals
10 from the SIMS and EDS results, it is safe to conclude that the absorber film does not contain any
11 carbon.

12 Solar cell performances from light J-V curves are presented in Fig. 5. The control device gives
13 5.1% efficiency with $V_{oc} = 370$ mV, $J_{sc} = 27.3$ mA/cm² and $FF = 50.6\%$. The relatively low
14 V_{oc} is primarily due to the low band gap of the Se-rich absorber layer. To reduce the Se content
15 in the CZTSSe layer, the amount of Se powder was reduced during the selenization step. Similar
16 performance result (5.1%) was obtained with higher $V_{oc} = 426$ mV and lower $J_{sc} = 24.2$
17 mA/cm² as compared to the control cell, which is due to the larger band gap, lower carrier
18 mobility and carrier lifetime of CZTS.^[7,24] External quantum efficiency (EQE) measurements
19 clearly show the difference at long wavelength absorption (Fig. 6a). The band gaps were
20 calculated by plotting the $[E \ln(1-EQE)]^2$ versus E in Fig. 6b. The control cell has $E_g = 1.07$ eV
21 and the low-Se-content cell has $E_g = 1.21$ eV as expected due to the selenium reduction. It is
22 worth to note that the optimized thickness for the kesterite absorber layer is around 2 μm and the
23 best reported kesterite solar cell has a $Cu/(Zn+Sn) \approx 0.8$.^[9,25] Therefore, further efficiency

improvement is expected by increasing the thickness and optimizing the Cu/(Zn+Sn) ratio of our CZTSSe absorber layer.

In order to understand the defect properties of the post-selenized CZTSSe, temperature dependent photoluminescence (PL) was conducted from 6.5 K to 120 K for the control high-Se-content CZTSSe as shown in Fig. 7a. We first focus on understanding the recombination and luminescence mechanism. No significant peak shift and peak shape change was observed from the temperature-dependent curves. This phenomenon indicates that within our detection range, the luminescence originates from the same type of radiative recombination. The peak positions are centered at 0.97 eV, which is smaller than the band gap calculated from the control cell, therefore eliminating the possibility of band-to-band transition.

In addition, it should be noted that the luminescence is not a free to bound (FB) transition but a donor-acceptor pair (DAP) type. This is because for FB transition involving valence or conduction band, the luminescence peak positions are dependent on temperature to some extent, based on the following equation^[26]:

$$h\nu = E_g - E_{D/A} + n_u k_B T$$

where E_g is the band gap, E_D and E_A are the donor and acceptor ionization energies and n_u is close to unity. For FB type transition, the peak positions should be blue-shifted as temperature increases. Since there is no obvious peak shift observed here, we can rule out the possibility of FB type transition. This PL phenomenon has also been observed for pure CZTS material because kesterite material is considered as a highly intrinsic doped and strongly compensated p-type semiconductor.^[27-29]

As the DAP transition type has been confirmed above, heavy luminescence intensity quenching effects with temperature are observed. At $T < 41$ K, the PL intensity does not decrease

significantly whereas at $T \geq 41\text{K}$, the PL intensity shows a dramatic drop as temperature increases. This quenching process can be attributed to two nonradiative channels that lead the carriers to relax or recombine in a nonradiative way. Two thermal activation energies, E_1 and E_2 , are involved in the nonradiative recombination processes. The temperature dependent PL can be fitted by the following equation^[30]

$$I(T) = I_0 \left(1 + a_1 e^{-\frac{E_1}{k_b T}} + a_2 e^{-\frac{E_2}{k_b T}} \right)^{-1}$$

Where I_0 is the PL intensity extrapolated at $T = 0\text{ K}$. The a_1 and a_2 are the coefficients that indicate the degeneracy extent of the nonradiative recombination pathways. From the fitting shown in Fig. 7b, E_1 and E_2 are calculated to be $29.6 \pm 3.7\text{ meV}$ and $6 \pm 0.6\text{ meV}$ and the calculated a_1 is two order magnitudes larger than a_2 . The mechanism can be understood that, at very low temperature $T < 41\text{ K}$, only E_2 nonradiative pathway is activated. Because of the small degeneracy factor a_2 , the quenching effect is not significant. However, when $T \geq 41\text{ K}$, E_1 pathway contributes a strong quenching effect, leading to a dramatically drop in the PL intensity. The reason for the heavy quenching can be attributed to the thermal activation of various defects in the CZTSSe originating from the non-stoichiometric composition.^[31,32]

Power dependent PL at 6.5 K was also conducted as shown in Fig. 8a, and as expected, we observe a clear PL intensity increment as excitation source power increases. The intensity has been fitted with power law following:

$$I \propto P^k$$

Where P is the excitation power and k is the coefficient.^[28] When $k \geq 1$, the transition recombination is excitonic; when $k < 1$, the transition involves defects recombination. The fitting shown in Fig. 8b delivers the k value of 0.93 ± 0.013 , indicating donor or acceptor defects are engaged in the emission, which is consistent with our statement of DAP type transition.

The defects observed from PL are recognized as the factors limiting our V_{oc} and FF . As high defect concentration reduces the lifetime of minority carriers, the charge transport across the absorber layer as well as the charge collections at the electrodes become less efficient. Therefore, both V_{oc} and FF are affected. To minimize defects recombination, optimization of the CZTS elemental ratio and grain growth during selenization can be carried out.

Conclusion

Single phase kesterite solar cells with PCE of 5.1% have been demonstrated by using chemical spray pyrolysis technique followed by high temperature selenization. Similar device performance result was observed with different S/Se ratio. Post-selenized CZTSSe film gives PL emission at low temperatures which is believed to be DAP in origin. Severe PL quenching was observed as the temperature increased which is ascribed to two thermally activated non-radiative recombination channels that are likely defect-related. It is believed that the presence of these defects in the absorber layer affects both V_{oc} and FF .

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References

- [1] P. Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Menner, W. Wischmann, and M. Powalla, New world record efficiency for Cu(In,Ga)Se₂ thin-film solar cells beyond 20%, Prog. Photovolt.: Res. Appl 19 (2011) 894-897.
- [2] Y. Chiba, S. Kijima, H. Sugimoto, Y. Kawaguchi, M. Nagahashi, T. Morimoto, T. Yagioka, T. Miyano, T. Aramoto, Y. Tanaka, H. Hakuma, S. Kuriyagawa, K. Kushiya, Achievement of 16% milestone with 30cm×30cm-sized CIS-based thin-film submodules, Proceedings of the 35th IEEE Photovoltaic Specialist Conference (2010) pp.164–168.
- [3] T.K. Todorov, O. Gunawan, T. Gokmen and D.B. Mitzi, Solution processed Cu(In,Ga)(S,Se)₂ absorber yielding a 15.2% efficient solar cell, Prog. Photovolt.: Res. Appl. 21 (2013) 82-87.
- [4] S. R. Taylor, S. M. McLennan, Blackwell Scientific Publication, Oxford, (1985) pp.1-312.
- [5] S. Chen, A. Walsh, J. Yang, X. G. Gong, L. Sun, P. Yang, J. Chu, S. Wei, Compositional dependence of structural and electronic properties of Cu₂ZnSn(S,Se)₄ alloys for thin film solar cells, Phys. Rev. B 83 (2011) 125201.
- [6] W. Ki, H.W. Hillhouse, Earth-Abundant element photovoltaics directly from soluble precursors with high yield using a non-toxic solvent, Adv. Energy Mater. 1 (2011) 732-735.
- [7] I. Repins, C. Beall, N. Vora, C. DeHart, D. Kuciauskas, P. Dippo, B. To, J. Mann, W.C. Hsu, A. Goodrich, R. Noufi, Co-evaporated Cu₂ZnSnSe₄ films and devices, Sol. Energy Mater. Sol. Cell 101 (2012) 154-159.

[8] B. Shin, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, Control of an interfacial MoSe₂ layer in Cu₂ZnSnSe₄ thin film solar cells: 8.9% power conversion efficiency with a TiN diffusion barrier, Appl. Phys. Lett. 101 (2012) 053903.

[9] T.K. Todorov, J. Tang, S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, D.B. Mizit, Beyond 11% efficiency: characteristics of state-of-the-art Cu₂ZnSn(S,Se)₄ solar cells, Adv. Energy. Mater. 3 (2013) 34-38.

[10] S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, T. K. Todorov, D.B. Mitiz, Low band gap liquid-processed CZTSe solar cell with 10.1% efficiency, Energy Environ. Sci. 5 (2012) 7060-7065.

[11] (a) Y. Cao, M.S. Denny, J.J.V. Caspar, W.E. Farneth, Q. Guo, A. S. Ionkin, L. K. Johnson, M. Lu, I. Malajovich, D. Radu, H. D. Rosenfeld, K. R. Choudhury, W. Wu, High-efficiency solution-processed Cu₂ZnSn(S,Se)₄ thin-film solar cells prepared from binary and ternary nanoparticles, J. Am. Chem. Soc. 134 (2012) 15644-15647 (b) Q. Guo, G.M. Ford, W.C. Yang, B.C. Walker, E.A. Stach, H.W. Hillhouse, R. Agrawal, Fabrication of 7.2% Efficient CZTSSe Solar Cells Using CZTS Nanocrystals, J. Am. Chem. Soc. 132 (2010) 17384-17386.

[12] T. Schnabel, M. Low, E. Ahlswede, Vacuum-free preparation of 7.5% efficiency Cu₂ZnSn(S,Se)₄ solar cells based on metal salt precursors, Sol. Energy Mater. Sol. Cell 117 (2013) 324-328.

[13] (a) G. Adamopoulos, A. Bashir, W.P. Gillin, S. Georgakopoulos, M. Shkunov, M.A. Baklar, N. Stingelin, D.D.C. Bradley and T.D. Anthopoulos, Structural and electrical characterization of ZnO films grown by spray pyrolysis and their application in thin-film

transistors, Adv. Funct. Mater. 21 (2011) 525-531 (b) W.T. Kim, C.D. Kim, Optical energy gaps of β - In_2S_3 thin films grown by spray pyrolysis, J. Appl. Phys. 60 (1986) 2631-2633.

[14] Y. Cai, J.C.W. Ho, S.K. Batabyal, W. Liu, Y. Sun, S.G. Mhaisalkar, L.H. Wong, Nanoparticle-induced grain growth of carbon-free solution-processed $\text{CuIn}(\text{S},\text{Se})_2$ solar cell with 6% Efficiency, ACS Appl. Mater. Interfaces 5 (2013) 1533-1537.

[15] (a) A.V. Sergeeva, A.V. Naumov, V.N. Semenov and Y.V. Sokolov, Phase composition and microstructure of In_3S_4 and CuInS_2 films grown on silicon by spray pyrolysis, Inorg. Mater. 43 (2007) 1046-1049. (b) T.T. John, M. Mathew, C.S. Kartha, K.P. Vijayakumar, T. Abe, Y. Kashiwaba, $\text{CuInS}_2/\text{In}_2\text{S}_3$ thin film solar cell using spray pyrolysis technique having 9.5% efficiency Sol. Energy Mater. Sol. Cell 89 (2005) 27-36.

[16] (a) Y.B.K. Kumar, G.S. Bahu, P.U. Bhaskar, V.S. Raja, Preparation and characterization of spray-deposited $\text{Cu}_2\text{ZnSnS}_4$ thin films, Sol. Energy Mater. Sol. Cell 93 (2009) 1230-1237 (b) Y.B.K. Kumar, G.S. Bahu, P.U. Bhaskar, V. S. Raja, Effect of starting-solution pH on the growth of $\text{Cu}_2\text{ZnSnS}_4$ thin films deposited by spray pyrolysis, Phys. Status Solidi A 26 (2009) 1525-1530 (c) Y.B.K. Kumar, G.S. Bahu, P.U. Bhaskar, V.S. Raja, Effect of copper salt and thiourea concentrations on the formation of $\text{Cu}_2\text{ZnSnS}_4$ thin films by spray pyrolysis, Phys. Status Solidi A 107 (2010) 149-156.

[17] (a) M. Grossberg, J. Krustok, J. Raudoja, K. Timmo, M. Altosaar, T. Raadik, Photoluminescence and Raman study of $\text{Cu}_2\text{ZnSn}(\text{Se}_x\text{S}_{1-x})_4$ monograins for photovoltaic applications Thin Solid Film 2001, 519, 7403-7406 (b) R. Bacewicz, W. Gebicki, J. Filipowicz, Raman scattering in $\text{CuInS}_{2x}\text{Se}_{2(1-x)}$ mixed crystals, J. Phys. Condens. Matter 6 (1994) L777.

[18] A. Walsh, S. Chen, S.H. Wei, X.G. Gong, Kesterite thin-film solar cells: advances in materials modelling of $\text{Cu}_2\text{ZnSnS}_4$, *Adv. Energy. Mater.* 2 (2012) 400-409.

[19] (a) B. Shin, O. Gunawan, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant $\text{Cu}_2\text{ZnSnS}_4$ absorber, *Prog. Photovolt: Res. Appl.* 21 (2013) 72-76 (b) J.J. Scragg, J.T. Watjen, M. Edoff, T. Ericson, T. Kubart, C. Platzer-Bojorkman, A detrimental reaction at the molybdenum back contact in $\text{Cu}_2\text{ZnSn(S,Se)}_4$ thin-film solar cells, *J. Am. Chem. Soc.*, 134 (2012) 19330-19333.

[20] P.A. Fernandes, P.M.P Salome, A.F. da Cunda, Growth and Raman scattering characterization of $\text{Cu}_2\text{ZnSnS}_4$ thin films, *Thin Solid Films*, 517 (2009) 2519-2523.

[21] C. Platzer-Bjorkman, J. Scragg, H. Flammersberger, T. Kubart, M. Edoff, Influence of precursor sulfur content on film formation and compositional changes in $\text{Cu}_2\text{ZnSnS}_4$ films and solar cells, *Sol. Energy Mater. Sol. Cell* 98 (2012) 110-117.

[22] W.C. Hsu, I. Repins, C. Beall, C. DeHart, G. Teeter, B. To, Y. Yang, R. Noufi, The effect of Zn excess on kesterite solar cells, *Sol. Energy Mater. Sol. Cell* 113 (2013) 160-164.

[23] J. Madarasz, P. Bombicz, M. Okuya, S. Kaneko, Thermal decomposition of thiourea complexes of Cu(I), Zn(II) and Sn(II) chlorides as precursors for the spray pyrolysis deposition of sulfide thin films, *Solid State Ionics*, 141-142 (2001) 439-446.

[24] (a) T. Washio, T. Shinji, S. Tajima, T. Fukano, T. Motohiro, K. Jimbo, H. Katagiri, 6% efficiency $\text{Cu}_2\text{ZnSnS}_4$ -based thin film solar cells using oxide precursors by open atmosphere type CVD, *J. Mater. Chem.* 22 (2012) 4021-4024 (b) M. Tsega, D.H. Kuo, Characterization and

1 electrical property of the Cu-deficient $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ bulks at different sulfur contents, J. Alloy.
2 Compd. 557 (2013) 142-146.

3 [25] K. Woo, Y. Kim, J. Moon, A non-toxic, solution-processed, earth abundant absorbing
4 layer for thin-film solar cells, Energy Environ. Sci. 5 (2012) 5340-5345.

5 [26] (a) S.R. Kodigala, $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ based thin film solar cells, 2010 (b) M. Grossberg, J.
6 Krustok, K. Timmo, M. Altosaar, Radiative recombination in $\text{Cu}_2\text{ZnSnSe}_4$ monograins studied
7 by photoluminescence spectroscopy, Thin Solid Film 517 (2009) 2489-2492.

8 [27] (a) Z. Zhou, Y. Wang, D. Xu, Y. Zhang, Fabrication of $\text{Cu}_2\text{ZnSnS}_4$ screen printed layers
9 for solar cells, Sol. Energy Mater. Sol. Cell, 94 (2010) 2042-2045 (b) H.S. Duan, W. Yang, B.
10 Bob, C.J. Hsu, B. Lei, Y. Yang, The role of sulfur in solution-processed $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ and its
11 effect on defect properties, Adv. Funct. Mater. 23 (2013) 1466-1471.

12 [28] J.P. Leitaó, N.M. Santos, P.A. Fernandes, P.M.P. Salome, A.F. da Cunha, J.C. Gonzalez,
13 G.M. Ribeiro, F.M. Matinaga, Photoluminescence and electrical study of fluctuating potentials in
14 $\text{Cu}_2\text{ZnSnS}_4$ -based thin films, Phys. Rev. B 84 (2011) 024120.

15 [29] I. Dirnstorfer, Mt. Wanger, D.M. Hofmann, M.D. Lampert, F. Karg, B.K. Meyer,
16 Characterization of $\text{CuIn}(\text{Ga})\text{Se}_2$ thin films, Phys. Status Solidi A 168 (1998) 163-175.

17 [30] G. Davies, The optical properties of luminescence centres in silicon, Phys. Rep. 176
18 (1989) 83-188.

19 [31] S.K. Zhang, H. Lu, W.B. Wang, B.B. Das, N. Okoye, M. Tamargo, R.R. Alfano,
20 Radiative and nonradiative recombination processes in $\text{ZnCdSe}/\text{ZnCdMgSe}$ multi-quantum-
21 wells, J. Appl. Phys. 101 (2007) 023111.

1 [32] S. Chen, J.H. Yang, X.G. Gong, A. Walsh, S. H. Wei, intrinsic point defects and
2 complexes in the quaternary kesterite semiconductor $\text{Cu}_2\text{ZnSnS}_4$, Phys. Rev. B 81 (2010)
3 245204.

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5 **Figures**

Figure 1 XRD curves of (a) post-selenized CZTSSe film (b) as-deposited CZTS

Figure 2 Raman spectroscopy spectra of (a) post-selenized CZTSSe film (b) as-deposited CZTS

Figure 3 FESEM imaging on (a) surface of as-deposited CZTS without HCl addition in precursor solution (b) cross-section of as-deposited CZTS without HCl addition in precursor solution (c) cross-section of as-deposited CZTS with additional HCl in precursor solution (d) cross-section of the full device on Mo coated glass

Figure 4 Elemental study of post-selenized CZTSSe film on Mo substrate by SIMS depth profiles

Figure 5 Light J-V curve of control cell (black) and low-Se-content cell (red). (Device parameter inset)

Figure 6 (a) External quantum efficiency of control cell (black) and low-Se-content cell (red) (b) band gap plots of both devices

Figure 7 (a) Temperature dependent photoluminescence (PL) of CZTSSe film
(b) PL intensity quenching fitting (fitting results illustrated inset)

Figure 8 (a) Power dependent photoluminescence (PL) of CZTSSe film measured at 6.5K (b) Power law fitting with coefficient of 0.93 ± 0.013