Silver and potassium incorporation in double-layer solution-processed Cu₂ZnSnS₄ solar cell

Ibrahim, Ahmad; Guchhait, Asim; Hadke, Shreyash; Seng, Hwee Leng; Wong, Lydia Helena

2020

Ibrahim, A., Guchhait, A., Hadke, S., Seng, H. L., & Wong, L. H. (2020). Silver and potassium incorporation in double-layer solution-processed Cu₂ZnSnS₄ solar cell. *ACS Applied Energy Materials*, 3(11), 10402–10407. doi:10.1021/acsaem.0c01165

<https://hdl.handle.net/10356/145067>

<https://doi.org/10.1021/acsaem.0c01165>

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *ACS Applied Energy Materials*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <https://doi.org/10.1021/acsaem.0c01165>

Downloaded on 26 Apr 2023 14:26:59 SGT

Silver and potassium incorporation in double-layer solution-processed $\text{Cu}_2\text{ZnSnS}_4$ solar cell

Ahmad Ibrahim¹, Asim Guchhait², Shreyash Hadke^{1,3,4}, Hwee Leng Seng⁵, Lydia Helena Wong^{1,4,6}*

¹. School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore

². Department of Physics, Prabhat Kumar College, Contai, West Bengal 721401, India

³. Interdisciplinary Graduate School, Nanyang Technological University, 637371, Singapore

⁴. Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, 637553, Singapore

⁵. Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 138634, Singapore

⁶. Campus for Research Excellence And Technological Enterprise (CREATE), 138602, Singapore

*E-mail address: lydiawong@ntu.edu.sg

ABSTRACT

Large open-circuit voltage (V_{OC}) deficit has been widely regarded as the main hindrance to realize the full potential of the low cost and environmental-friendly $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) solar cell. Alloying and doping are seen as promising pathways to reduce the harmful defects in CZTS and the V_{OC} deficit. In this study, we demonstrate the fabrication of double-layer CZTS alloyed with silver and doped with potassium (ACZTS-KCZTS). The device shows increase of V_{OC} relative to its corresponding Shockley-Queisser limit ($V_{OC}/V_{OC,SQ}$) and improvement of short-circuit current (J_{SC}) compared to the CZTS reference to realize an optimized active area device efficiency of 8.24%. The avoidance of void formation and improved carrier collection in the bulk and interface region contributed to the performance improvement. This double-layer configuration could be a viable route for co-doping using other elements.

Keywords: CZTS, kesterite, thin film, solar cell, cation substitution

INTRODUCTION

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and its sulfo-selenide counterpart, $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe), have been widely investigated as potentially low cost and environmentally-friendly photovoltaic absorbers due to their suitable bandgap and high absorption coefficient with record power conversion efficiencies ranging between 11-13% for different sulfo-selenide content.¹⁻⁴ However, this record is still far from the Shockley-Queisser (SQ) limit of about 32%. Further, the record efficiencies are lower than the expected performance of these absorbers due to the presence of bulk point defects.⁵ This discrepancy in performance is often attributed to the huge deficit of open-circuit voltage (V_{OC}) compared to its SQ-limit.⁶

Doping and alloying are considered as possible strategies to improve the efficiency of CZTS due to the success of similar strategy in $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$ solar cells.⁷ Ag alloying in CZTS (ACZTS) is known to extend depletion width while decreasing carrier concentration and reducing antisite defects.^{8,9} In case of alloying with Ag, it was also proposed that non-uniform distribution of Ag profile within the absorber would reduce the V_{OC} deficit more effectively.⁸ Kou *et. al.* reported V-shaped Ag composition grading strategy with higher Ag content towards both back and front interface side of $(\text{Cu},\text{Ag})_2\text{ZnSn}(\text{S},\text{Se})_4$ based solar cells and found significant improvement in V_{OC} .¹⁰ Previously, in view of the improvement of absorber/buffer layer band alignment, an Ag-alloyed double-layer device with Mo/CZTS/ACZTS/CdS/ITO configuration on soda-lime glass (SLG) was demonstrated to obtain 7.2% efficiency. The V_{OC} deficit was also reduced by 50 mV compared to the unalloyed CZTS.¹¹ A thin layer of Ag was also previously applied as an intermediate layer between Mo and CZTS to alleviate the formation of thick MoS_2 . It was found that during the annealing process the thin Ag layer diffused into the absorber and also helped to reduce the formation of void at Mo/absorber interface.¹² So from previous studies it is quite clear that incorporation of Ag at both interfaces

of CZTS absorber would be fruitful for the enhancement of V_{OC} . Beside Ag-alloying on different layer of CZTS, another cation substitution using Mn used similar double-layer system (Mo/CZTS/CZMnTS) resulting in better performance compared to the reference device.¹³

Regarding doping to enhance the absorber quality, K-doping in CZTS increases J_{SC} , which is attributed to a larger grain size and increased carrier concentration.^{14,15} The grain growth is facilitated by the readily available alkali element in the precursor rather than the diffusion of Na from SLG.^{16,17} Also, it has been shown that the concentration of K throughout the bulk is not as uniform as Na diffusion.¹⁸ Previously we found accumulation of K at CZTS/CdS buffer interface, allowing Cd diffusion into the absorber which is very beneficial to reduce Cu_{Zn} antisite defects at the front surface.¹⁹ Here, we aimed to exploit the advantages of both Ag and K in CZTS solar cells. For the incorporation of both Ag and K and to optimize the improvement from alloying and doping on CZTS device, it might be beneficial to have different layers with different dopants rather than only a single-layer device with two different dopants. Previously, such double CZTS layer stacks with different doping level resulted in increased V_{OC} despite the decrease of J_{SC} .²⁰

In this work, the effect of Ag alloying and K doping of CZTS was investigated by fabricating devices with a single-layer absorber consisting of the two elements (AKCZTS) and double-layer stacks absorber with two different precursor solutions of silver-alloyed CZTS (ACZTS) and potassium-doped CZTS (KCZTS). Using a double-layer absorber structure, we have found that the V_{OC} deficit could be reduced while also gaining a better J_{SC} output. The causes of performance improvement have also been investigated.

EXPERIMENTAL SECTION

The precursor solutions were prepared by dissolving $Cu(CH_3COO)_2 \cdot H_2O$ (0.52 mol L^{-1}), $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.33 mol L^{-1}), $SnCl_2 \cdot 2H_2O$ (0.27 mol L^{-1}), and thiourea (2.06 mol L^{-1})

in 2-methoxyethanol. AgNO_3 and KCl were added to obtain the precursor solution for ACZTS and KCZTS, respectively. Similar methods were used to prepare the precursor solution for AKCZTS. Ag/Cu and K/Cu ratios were maintained at 4% for Ag-alloyed and 2% for K-doped devices, respectively, and compensated accordingly for the double-layer precursor. The ratios of $(\text{Ag}+\text{K}+\text{Cu})/(\text{Zn}+\text{Sn})$ and Zn/Sn were 0.86 and 1.25, respectively. The solutions were stirred at 50 °C for 2 hours. Before spin-coating, about 0.25 ml of ethanolamine and triethanolamine were added to get stable solutions. The spin-coating process was done at 4000 rpm for 25 s followed by pre-annealing in air for 2 minutes at 280 °C. This process was repeated 14 times, while for double-layer, ACZTS and KCZTS solutions were spin-coated 7 times each. The spin-coated films were then sulfurized at 600 °C for 40 minutes in a closed-flow two-zone furnace under $\text{Ar}+\text{S}$ atmosphere.

To complete the devices, cadmium sulfide was deposited as a buffer layer using chemical bath deposition (CBD) process. Then, indium tin oxide (ITO) was sputtered on top of CdS , followed by post-annealing in Ar atmosphere at 300 °C for 10 minutes. The devices were mechanically scribed. Each device has 0.16 cm^2 area (all efficiencies are reported for 0.15 cm^2 active area) and completed with silver paste as top electrodes.

X-ray diffraction (XRD) patterns were acquired using Bruker D8 Advance. Scanning Electron Microscope (SEM) images and Energy Dispersive Spectroscopy (EDS) data were obtained using JEOL JSM-7600F FESEM. The elemental depth profile of the films was acquired using IONTOF Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) IV system with Ar^+ as sputtering ions and Bi^+ ions for analysis. Hall measurements were performed using a parallel dipole line AC Hall system on exfoliated absorber films. Photoluminescence spectra were excited at room temperature by 638 nm and 445 nm laser diodes and captured using an InGaAs detector. Current density-voltage (J-V) of the devices were measured by Keithley 2612A and

VS-0852 light source to simulate AM1.5 and 100 mW/cm², calibrated by certified Si reference cell. External Quantum Efficiency (EQE) data was collected by a Bentham PVE300 system and a certified standard Si cell reference was used for calibration. Temperature-dependant J-V measurement was performed in a liquid nitrogen-cooled chamber. Capacitance-voltage (C-V) data were obtained using Autolab PGSTAT302N.

RESULTS AND DISCUSSION

XRD patterns of the absorber films are shown in **Figure 1a**. The major peaks at 28.5° and 47.7° in the spectra are associated with (112) and (220) planes of kesterite structure, respectively. Three additional minor peaks are attributed to (101), (200), and (312), while a peak representing Mo substrate is also observed. Magnified XRD spectra at 2 θ = 27-30° is shown in **Figure 1b**. The shifting to lower diffraction angle for (112) peak is most prominent in Ag-alloyed film, including the double-layer film. This was not observed in K-doped film. The larger atomic radius of Ag compared to Cu causes an increase in the lattice parameter of the kesterite structure. Thus, the shifting indicates that Ag is incorporated in the CZTS structure, similar to previously reported study.¹¹

Figure 1. (a) XRD patterns for single-layer films (CZTS, KCZTS, ACZTS, and AKCZTS) and double-layer films (KCZTS-ACZTS and ACZTS-KCZTS). Inset illustrates the device configuration of single- and double-layer film. (b) The magnified XRD view of (112) peak

The film morphology was then compared for the double-layer film (KCZTS-ACZTS and ACZTS-KCZTS) and mixed precursor film (AKCZTS). The cross-section images of the films in **Figure 2a-d** show that all the films have a comparable thickness of $\sim 1\ \mu\text{m}$. However, a significant amount of voids exist at the bottom of the KCZTS-ACZTS film while the other double-layer ACZTS-KCZTS shows a uniform compact film. The formation of the voids can be due to the presence of high K concentration at the bottom of the film, both from the precursor and diffusion from the SLG, forming additional phases during the sulfurization step. This was not an issue for AKCZTS film because K was distributed more uniformly throughout the film, while some of KCl near the surface for ACZTS-KCZTS might be lost during spin-coating.²¹ The voids could be harmful to the device and would impede the device performance. Surface images of the film in **Figure 2e-h** show that double-layer stacks film exhibit larger grain sizes compared to the pristine film. The film morphology and the grain structure are most significant in the case of ACZTS-KCZTS double-layer stacks film. In this double-layer structure, the presence of Ag near Mo might help in obtaining better grain growth, and less void formation.¹² With this morphological study, we proceed for complete device fabrication with CZTS absorber, AKCZTS absorber, and ACZTS-KCZTS double-layer stacks absorber as it was found more promising morphologically.

Figure 2. Cross-section and surface SEM images for CZTS (a,e), AKCZTS (b,f), KCZTS-ACZTS (c,g), and ACZTS-KCZTS (d,h)

EDS was also used to evaluate the elemental composition of the films. The results in **Table S1** show that all the devices have Cu-poor and Zn-rich composition, consistent with the precursor solution. The 4% amount of Ag is well-distributed throughout the film although ACZTS precursor was spin-coated at the bottom layer as shown from the cross-section EDS results in **Table S2**. The uniform Ag distribution for both ACZTS-KCZTS and AKCZTS film is also confirmed from the elemental depth profile obtained from SIMS in **Figure S1**. The elemental depth profiles for Ag and K are corrected to the Cu concentration as the precursors were prepared using similar Cu concentration and it has similar depth profile in all the samples. For ACZTS-KCZTS film, the K concentration is lower compared to AKCZTS film. This might be due to the loss of potassium during spin-coating, which has more effect on ACZTS-KCZTS film as the KCZTS precursor was spin-coated only on the upper layers. This is also observed in other works with spin-coated precursor that contains potassium or lithium.^{17,21} In other study, no Li-thiourea complexes were observed to be formed which might facilitate the loss during spin-coating, while different loss mechanism might be responsible for K because this element can still form complexes with thiourea.²² Nevertheless, the K reduction could help avoid low

photocurrent associated with excess K concentration.²³ The increase of K for both films near absorber/Mo interface is associated with the diffusion from SLG to the Mo layer.

To study the I-V characteristics, the complete device was configured as SLG/Mo/Absorber/CdS/ITO/Ag electrode. The effect of Ag and K addition to the device characteristics is shown in **Figure 3**. All doped devices have significant V_{OC} improvement compared to the reference device and the champion ACZTS-KCZTS device shows V_{OC} of 670 mV. In regards to the V_{OC} with respect to its SQ limit ($V_{OC}/V_{OC,SQ}$), the champion ACZTS-KCZTS device has the lowest V_{OC} deficit compared to AKCZTS and reference devices as listed in **Table 1**. With Ag alloying and K doping, the improvement of V_{OC} can be considered as the result of suppression of nonradiative recombination within the absorber and efficient charge separation at the interfaces.^{10,19} The J_{SC} of ACZTS-KCZTS has the most noticeable improvement compared to both single-layer AKCZTS and CZTS reference. Enhancement of J_{SC} can be attributed to better charge separation, larger grain size, and less voids within the absorber. The improvement of J_{SC} is also consistent with the improvement observed from the EQE of the best devices in **Figure 4b**. Compared to the reference, the EQE for ACZTS-KCZTS shifts up throughout the whole wavelength range which could be attributed to reduced recombination at the back and/or front interfaces.^{24,25}

Figure 3. Device parameters V_{OC} (a), J_{SC} (b), FF (c), and Efficiency (d) for 10 devices each

Figure 4. J-V (a) and EQE (b) curve for CZTS, AKCZTS, and ACZTS-KCZTS best device

Table 1. Device parameters for the best CZTS, AKCZTS, and ACZTS-KCZTS device

Device	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	Eff (%)	E _g (eV)	V _{oc} /V _{oc,sq}
CZTS	631	18.21	59.36	6.82	1.55	0.50
AKCZTS	658	18.76	57.21	7.06	1.58	0.51
ACZTS-KCZTS	670	21.50	57.22	8.24	1.54	0.54

Room temperature steady-state photoluminescence (PL) for all the devices are shown in **Figure 5**. The measurements were repeated on three different points for each device. Despite the V_{oc} improvement for AKCZTS device compared to the reference device, the PL signal excited by 638 nm laser do not show significant difference between them. However, significant signal increase with the same laser excitation is observed for ACZTS-KCZTS device, which indicates the suppression of nonradiative recombination resulting in improved V_{oc}. The higher PL intensity upon 445 nm laser excitation (which is more surface-sensitive compared to 638 nm laser excitation) is consistent with the EQE improvement at the absorber/CdS interface of AKCZTS and ACZTS-KCZTS devices. The addition of Ag and K also do not induce a significant shift of the PL peak energy level position. This observation is similar to other works involving Ag-alloyed devices.²⁶

Figure 5. PL intensity excited by 638 nm (a) and 445 nm (b) laser diode for CZTS, AKCZTS, and ACZTS-KCZTS

The apparent carrier concentration was extracted using C-V measurement. The depletion width of all the modified devices are enhanced compared to the reference device as shown in **Figure 6**. The depletion width increases with the incorporation of Ag and K within the absorber and becomes even wider with double-layer structure. This wider depletion width yields more efficient charge separation and collection. Further, the charge density decreases with the incorporation of Ag and K. Previously, the decrease of the charge density was also demonstrated with Ag incorporation in kesterite solar cells.^{8,10} The observation from our double incorporation device could possibly mean that the suppression of Cu_{Zn} antisite caused by Ag dominates rather than the formation of compensated acceptor defects on the same antisite occupied by K which was proposed to explain the increase of carrier density for alkali metals doping.¹⁶ The ACZTS-KCZTS device has the least charge density, which along with the wider depletion width might explain the improvement of the short-circuit current. A similar trend of reduced carrier concentration was obtained by AC Hall measurement. The carrier concentration

obtained for CZTS was $4.53 \pm 2.41 \times 10^{16} \text{ cm}^{-3}$, AKCZTS was $1.37 \pm 0.31 \times 10^{16} \text{ cm}^{-3}$ and $9.60 \pm 1.34 \times 10^{15} \text{ cm}^{-3}$ for double-layer ACZTS-KCZTS device.

Figure 6. Charge density and depletion width profile obtained by C-V measurement

Temperature-dependant I-V measurement was conducted to investigate the limiting factor of the devices. The activation energy (E_A) was obtained from the intercept of the fitted V_{OC} at 0K as shown in **Figure S2**. The result from this measurement and the device performance shows a similar trend where the fitted V_{OC} at 0K were lower compared to each respective bandgap values. This indicates that the interface recombination is possibly the dominant recombination pathway, although the role of bulk effects (such as band tailing, potential fluctuations, and temperature-dependent ideality factor) on $E_g - E_A$ cannot be excluded.^{27,28}

CONCLUSION

Double-layer CZTS doped with potassium and silver with a configuration of Mo/ACZTS-KCZTS/CdS/ITO has been demonstrated to give better device performance compared to single-layer AKCZTS absorber. With double-layer ACZTS-KCZTS absorber, PL study revealed significant enhancement of PL intensity which supported the reduction of nonradiative recombination. The EQE results also supported efficient charge collection for the entire range of the photo-absorption. The improvement of the absorber quality was attributed to the avoidance of voids formation on the film and also the increase in carrier collection in the bulk and interface region. The device quality was finally inspected with C-V measurement which revealed widest depletion layer formation in case of ACZTS-KCZTS double-layer structure. As a result, the best ACZTS-KCZTS device efficiency of 8.24% was achieved not only by V_{OC} enhancement but also by the improvement of J_{SC} . Therefore, cation substitution using double-layer system could potentially be applied for other elements co-doping such as silver and manganese.

ASSOCIATED CONTENT

Supporting Information

Ag and K elemental depth profile (SIMS) for ACZTS-KCZTS and AKCZTS films corrected to the Cu concentration; Surface and cross-section EDS for CZTS, AKCZTS, and ACZTS-KCZTS; Temperature-dependant V_{OC} data points for CZTS, AKCZTS, and ACZTS-KCZTS; EQE curve for CZTS, KCZTS, and ACZTS.

ACKNOWLEDGMENTS

The authors would like to acknowledge the funding support from the CREATE Programme under the Campus for Research Excellence and Technological Enterprise (CREATE), which is

supported by the National Research Foundation, Prime Minister's Office, Singapore; and the Ministry of Education (MOE) Tier 2 Project (MOE2016-T2-1-030).

REFERENCES

- 1 Siebentritt, S.; Schorr, S. Kesterites - A Challenging Material for Solar Cells, *Prog. Photovoltaics* **2012**, *20*, 512–519.
- 2 Yan, C.; Huang J.; Sun, K.; Johnston, S.; Zhang, Y.; Sun, H.; Pu, A.; He, M.; Liu, F.; Eder, K.; Yang, L.; Cairney, J. M.; Ekins-Daukes, N. J.; Hameiri, Z.; Stride, J. A.; Chen, S.; Green, M. A.; Hao, X. Cu₂ZnSnS₄ Solar Cells with Over 10% Power Conversion Efficiency Enabled by Heterojunction Heat Treatment, *Nat. Energy* **2018**, *3*, 764–772.
- 3 Wang, W.; Winkler, M. T.; Gunawan, O.; Gokmen, T.; Todorov, T. K.; Zhu, Y.; Mitzi, D. B. Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency, *Adv. Energy Mater.* **2014**, *4*, 1–5.
- 4 Son, D. H.; Kim, S. H.; Kim, S. Y.; Kim, Y. I.; Sim, J. H.; Park, S. N.; Jeon, D. H.; Hwang, D. K.; Sung, S. J.; Kang, J. K.; Yang, K. J.; Kim, D. H. Effect of Solid-H₂S Gas Reactions on CZTSSe Thin Film Growth and Photovoltaic Properties of a 12.62% Efficiency Device, *J. Mater. Chem. A* **2019**, *7*, 25279–25289.
- 5 Kim, S.; Márquez, J. A.; Unold, T.; Walsh, A. Upper Limit to the Photovoltaic Efficiency of Imperfect Crystals from First Principles, *Energy Environ. Sci.* **2020**, *13*, 1481–1491.
- 6 Wallace, S. K.; Mitzi, D. B.; Walsh, A.; The Steady Rise of Kesterite Solar Cells, *ACS Energy Lett.* **2017**, *2*, 776–779.
- 7 Giraldo, S.; Jehl, Z.; Placidi, M.; Izquierdo-Roca, V.; Pérez-Rodríguez, A.; Saucedo, E. Progress and Perspectives of Thin Film Kesterite Photovoltaic Technology: A Critical Review, *Adv. Mater.* **2019**, *31*, 1–18.
- 8 Yuan, Z. K.; Chen, S.; Xiang, H.; Gong, X. G.; Walsh, A.; Park, J. S.; Repins, I.; Wei, S. H. Engineering Solar Cell Absorbers by Exploring the Band Alignment and Defect Disparity: The Case of Cu- and Ag-Based Kesterite Compounds, *Adv. Funct. Mater.* **2015**, *25*, 6733–6743.
- 9 Gershon, T.; Lee, Y. S.; Antunez, P.; Mankad, R.; Singh, S.; Bishop, D.; Gunawan, O.; Hopstaken, M.; Haight, R. Photovoltaic Materials and Devices Based on the Alloyed Kesterite Absorber (Ag_xCu_{1-x})₂ZnSnSe₄, *Adv. Energy Mater.* **2016**, *6*, 1–7.
- 10 Qi, Y.-F.; Kou, D.-X.; Zhou, W.-H.; Zhou, Z.-J.; Tian, Q.-W.; Meng, Y.-N.; Liu, X.-S.; Du, Z.-L.; Wu, S.-X. Engineering of Interface Band Bending and Defects Elimination via a Ag-Graded Active Layer for Efficient (Cu,Ag)₂ZnSn(S,Se)₄ Solar Cells, *Energy Environ. Sci.* **2017**, *10*, 2401–2410.
- 11 Guchhait, A.; Su, Z.; Tay, Y. F.; Shukla, S.; Li, W.; Leow, S. W.; Tan, J. M. R.; Lie, S.; Gunawan, O.; Wong, L. H. Enhancement of Open-Circuit Voltage of Solution-Processed Cu₂ZnSnS₄ Solar Cells with 7.2% Efficiency by Incorporation of Silver, *ACS Energy Lett.* **2016**, *1*, 1256–1261.
- 12 Cui, H.; Liu, X.; Liu, F.; Hao, X.; Song, N.; Yan, C. Boosting Cu₂ZnSnS₄ Solar Cells

- Efficiency by a Thin Ag Intermediate Layer between Absorber and Back Contact, *Appl. Phys. Lett.* **2014**, *104*, 041115.
- 13 Lie, S.; Sandi, M. I.; Tay, Y. F.; Li, W.; Tan, J. M. R.; Bishop, D. M.; Gunawan O.; Wong, L. H. Improving the Charge Separation and Collection at the Buffer/Absorber Interface by Double-Layered Mn-Substituted CZTS, *Sol. Energy Mater. Sol. Cells* **2018**, *185*, 351–358.
 - 14 Hsieh, Y.-T.; Han, Q.; Jiang, C.; Song, T.-B.; Chen, H.; Meng, L.; Zhou, H. Yang, Y. Efficiency Enhancement of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Solar Cells via Alkali Metals Doping, *Adv. Energy Mater.* **2016**, *6*, 1502386.
 - 15 Tong, Z.; Yan, C.; Su, Z.; Zeng, F.; Yang, J.; Li, Y.; Jiang, L.; Lai, Y.; Liu, F. Effects of Potassium Doping on Solution Processed Kesterite $\text{Cu}_2\text{ZnSnS}_4$ Thin Film Solar Cells, *Appl. Phys. Lett.* **2014**, *105*, 223903.
 - 16 Sahayaraj, S.; Brammertz, G.; Vermang, B.; Mule, A.; Schnabel, T.; Meuris, M.; Vleugels, J.; Poortmans, J. Doping of $\text{Cu}_2\text{ZnSnSe}_4$ Solar Cells with Na^+ or K^+ Alkali Ions, *J. Mater. Chem. A* **2018**, *6*, 2653–2663.
 - 17 Haass, S. G.; Andres, C.; Figi, R.; Schreiner, C.; Bürki, M.; Tiwari, A. N.; Romanyuk, Y. E. Effects of Potassium on Kesterite Solar Cells: Similarities, Differences and Synergies with Sodium, *AIP Adv.* **2018**, *8*, 015133.
 - 18 Mule, A.; Vermang, B.; Sylvester, M.; Brammertz, G.; Ranjbar, S. Schnabel, T.; Gampa, N.; Meuris, M.; Poortmans, J. Effect of Different Alkali (Li, Na, K, Rb, Cs) Metals on $\text{Cu}_2\text{ZnSnSe}_4$ Solar Cells, *Thin Solid Films* **2017**, *633*, 156–161.
 - 19 Li, W.; Su, Z.; Tan, J. M. R.; Chiam, S. Y.; Seng, H. L.; Magdassi, S. Wong, L. H.; Revealing the Role of Potassium Treatment in CZTSSe Thin Film Solar Cells, *Chem. Mater.* **2017**, *29*, 4273–4281.
 - 20 Yan, C.; Sun, K.; Liu, F.; Huang, J.; Zhou, F.; Hao, X. Boost V_{oc} of Pure Sulfide Kesterite Solar Cell via a Double CZTS Layer Stacks, *Sol. Energy Mater. Sol. Cells* **2017**, *160*, 7–11.
 - 21 Cabas-Vidani, A.; Haass, S. G.; Andres, C.; Caballero, R.; Figi, R.; Schreiner, C.; Márquez, J. A.; Hages, C.; Unold, T.; Bleiner, D.; Tiwari, A. N.; Romanyuk, Y. E. High-Efficiency $(\text{Li}_x\text{Cu}_{1-x})_2\text{ZnSn}(\text{S},\text{Se})_4$ Kesterite Solar Cells with Lithium Alloying, *Adv. Energy Mater.* **2018**, *8*, 1–8.
 - 22 Boeyens, J.; Herbstein, F. Ionic Complexes of Thiourea. II. Chemical And Crystallographic Survey and Determination of the Crystal Structures of Some Representative Complexes. *Inorg. Chem.* **1967**, *6* (7), 1408-1425.
 - 23 Haass, S.; Diethelm, M.; Andres, C.; Romanyuk, Y.; Tiwari, A. Potassium Post Deposition Treatment Of Solution-Processed Kesterite Solar Cells. *Thin Solid Films* **2017**, *633*, 131-134.
 - 24 Tay, Y. F.; Hadke, S. S.; Zhang, M.; Lim, N.; Chiam, S. Y.; Wong, L. H.; Improving the Interfacial Properties of CZTS Photocathodes by Ag Substitution, *J. Mater. Chem. A* **2020**, *8*, 8862–8867.

- 25 Hadke, S.; Levchenko, S.; Sai Gautam, G.; Hages, C. J.; Márquez, J. A.; Izquierdo-Roca, V.; Carter, E. A.; Unold, T.; Wong, L. H. Suppressed Deep Traps and Bandgap Fluctuations in $\text{Cu}_2\text{CdSnS}_4$ Solar Cells with $\approx 8\%$ Efficiency, *Adv. Energy Mater.* **2019**, *9*, 1–11.
- 26 Hadke, S.; Levchenko, S.; Lie, S.; Hages, C. J.; Márquez, J. A.; Unold, T.; Wong, L. H. Synergistic Effects of Double Cation Substitution in Solution-Processed CZTS Solar Cells with Over 10% Efficiency, *Adv. Energy Mater.* **2018**, *8*, 1–9.
- 27 Gokmen, T.; Gunawan, O.; Mitzi, D. B. Semi-Empirical Device Model for $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Solar Cells, *Appl. Phys. Lett.* **2014**, *105*, 2–7.
- 28 Hages, C. J.; Carter, N. J.; Agrawal, R.; Unold, T.; Generalized Current-Voltage Analysis and Efficiency Limitations in Non-Ideal Solar Cells: Case of $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ and $\text{Cu}_2\text{Zn}(\text{Sn}_y\text{Ge}_{1-y})(\text{S}_x\text{Se}_{1-x})_4$, *J. Appl. Phys.* **2014**, *115*, 234504.