



# Kesterite compound semiconductors for thin film solar cells

Charlotte Platzer-Björkman

Thin film solar cells based on  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ , “CZTS”, are attractive by combining high light absorption and high abundance of constituent elements. The efficiency of CZTS solar cells developed rapidly during the last decades, but significant improvements are still needed to reach commercially viable levels. This review covers the most recent trends in CZTS research; (i) alloying with new elements, (ii) exchange of CdS buffer layer with alternative materials, (iii) back contact engineering and (iv) defect studies as a function of compositional variations and annealing. Better understanding of the material and device limitations is expected to emerge from this research. In the perspective of large scale use of CZTS modules, non-toxicity and earth-abundance cannot be compromised in the view of competition with commercially mature CdTe and CIGS technologies. Large band gap kesterite derivatives for stable top cells in tandem solar cells is an interesting and less explored field meriting more attention.

## Addresses

Ångström Solar Center, Solid State Electronics, Uppsala University, Box 534, 75121 Uppsala, Sweden

Current Opinion in Green and Sustainable Chemistry 2017, 4:84–90

This review comes from a themed issue on **Novel materials**

Edited by **Susan Schorr**

<http://dx.doi.org/10.1016/j.cogsc.2017.02.010>

2452-2236/© 2017 Elsevier B.V. All rights reserved.

## Introduction

Thin film solar cells based on kesterite compounds  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ , “CZTS” have the advantage of high abundance of constituent elements which is important in view of the large volumes of PV modules needed for increased use of solar energy worldwide. After initial work by Ito [1] and pioneering work by Katagiri [2,3], efficiency records were set by Mitzi and coworkers at IBM [4,5]. The latest record of 12.6% was published in 2013 [6] and while no further efficiency improvements have been reported in more recent work,<sup>a</sup> significant advances in the understanding of kesterite materials and devices have emerged. This review provides an overview of the most recent literature covering device performance and efficiency

limitations, back- and front contact interfaces, alloying with other elements, bulk defects and correlations to composition and process conditions. This brief review complements earlier review articles on the topic [7–12].

## State of the art devices and efficiency limitations

The record 12.6% device (513 mV, 35.2 mA/cm<sup>2</sup>, 69.8% FF, band gap 1.13 eV) showed high short circuit current, but lower than expected open circuit voltage,  $V_{oc}$ , and fill factor, FF, as compared to  $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$  devices with similar band gap energy [6]. The current understanding of these  $V_{oc}$  and FF losses relate to secondary phase segregation for the Cu-poor and Zn-rich composition giving highest efficiency [13,14], strong band tailing due to potential fluctuations in bulk CZTS [15,16] and contribution from interface or grain boundary recombination [17]. One reason for strong band tailing can be high density of defects such as Cu–Zn antisites with low formation energy [18] that are expected to cluster causing compositional inhomogeneities [19] and band gap fluctuations [20]. Other defects with high concentrations have also been reported, such as  $\text{Zn}_{\text{Sn}}$  [21] for device relevant compositions. However, similar levels of defect concentrations were also measured by neutron diffraction for  $\text{CuInSe}_2$  material [22] with the exception of the extremely high concentration of the  $\text{Cu}_{\text{Zn}}\text{--}\text{Zn}_{\text{Cu}}$  anti-site defect pair in CZTS. While the high concentrations of  $\text{Cu}_{\text{Zn}}\text{--}\text{Zn}_{\text{Cu}}$  anti-site defects are problematic for CZTS devices due to contribution to potential fluctuations, it is not yet clear if other bulk defects are contributing more.

State of the art devices are believed to be limited by bulk recombination based on temperature dependent current voltage analysis. However, the general sensitivity of the heterojunction, difficulty to determine dominating recombination path [23] and lack of surface type-inversion [24] such as that seen for CIGS absorbers [25] makes significant contribution from interface recombination likely. Routes to overcome the limitations mentioned above could be alloying or doping to avoid detrimental defects, tuning of composition or annealing processes to minimize defects and interface modifications including alternative contacts. Work published during the last two years in these three topical areas is summarized below.

## Back- and front contact interfaces

Modifications of the absorber surface such as using Zn-rich surface termination in co-evaporation [26], was

<sup>a</sup> A new device record of 13.7% for CZTS was announced at the 26th PVSC in Singapore 24–28th of October 2016, but no details have been published about this device at the time of writing this review.

reported to give reduced interface recombination and improved  $V_{oc}$ . Annealing of CZTS absorbers in air can also improve device performance. The role of oxygen was studied by Kim et al. [27], where oxygen substitution of selenium was observed near grain boundaries. This could increase the band gap at grain boundaries and was suggested to contribute to grain boundary passivation and improved device performance after air annealing. Cu-depletion near grain boundaries and  $SnO_x$  formation seen from Auger Nanoprobe Spectroscopy was also correlated to enhanced performance in Ref. [28]. Selenide devices benefit from air annealing at higher temperatures than sulfide devices and the effect appears stronger for Se-rich devices [29]. One way of reducing interface recombination could be through passivation by for example  $Al_2O_3$  [30] or using band gap grading. One example of such grading employing S/Se variations was given by Yang et al. [31] where a 12.3% device was obtained.

A range of alternative buffer layers have been investigated for CZTSSe. For large band gap CZTS, several groups showed improved performance from exchanging the CdS layer with a material with larger band gap and in particular higher conduction band level matching that of the CZTS absorber. Sun et al. [32] employed a  $Zn_xCd_{1-x}S$  buffer layer deposited by a successive ion layer adsorption and reaction (SILAR) method. For  $Zn_{0.35}Cd_{0.65}S$ , a high  $V_{oc}$  of 762 mV was obtained as compared to 665 mV using CdS. Similar improvements in  $V_{oc}$  for pure sulfide CZTS were shown using atomic layer deposition (ALD)  $Zn_{1-x}Sn_xO_y$  [33,34], and for monograin CZTS solar cells by using a thin  $SnO_x$  interlayer by ALD [35]. A hybrid CdS/ $In_2S_3$  buffer layer gave improved  $V_{oc}$  for CZTSSe [36] and sulfide CZTS, partly explained by increased carrier concentration in CZTS from In diffusion [37]. For selenide CZTSe or CZTSSe, alternative buffer layers such as  $Zn(O,OH,S)$  by CBD [38,39],  $In_2S_3$  by spray pyrolysis [40] and co-evaporation [41] have been studied.

Regarding the back contact, a number of barrier layer materials have been evaluated recently with the motivation to reduce reaction of the Mo back contact in the anneal or reduce back contact recombination. These include Bi [42], thin carbon [43], TiN and TiW [44] and  $MoO_3$  [45]. Another aim is to develop transparent back contacts for bifacial solar cells or tandem top cell applications [46,47]. Reactions at the ITO/CZTS interface were studied by Ge et al. [48] showing indium diffusion into CZTS and  $SnO_x$  formation for higher temperatures.

Secondary phase segregation, preferentially at the back CZTS/ $Mo(S,Se)_2$  interface has been reported by several groups [13]. The influence of detected  $Sn(S,Se)_2$  and  $Zn(S,Se)$  phases were discussed in relation to non ohmic contacts and influence on device fill factor.

The use of other substrates than soda lime glass is motivated by lower weight, flexibility, and building integration. For CZTS, a few groups have investigated alternative substrates. Becerril-Romero et al. used commercial ceramic tiles and studied vitreous enamel for combined surface smoothing and sodium supply. A maximum efficiency of 7.5% was shown for a CZTS ceramic solar tile [49]. Todorov et al. [50] reached 11.5% efficiency on flexible zirconia substrates compatible with roll to roll processing. For CZTS on steel substrates, the influence of barrier layers, Na supply and annealing conditions have also been studied [51,52].

### Adding more elements: alloying and doping

Exchange or partial substitution of the elements in CZTS is motivated by the possibility to change the band gap energy and reduce recombination losses from band gap increase towards the front and back interface. It is also motivated by the search for ways to reduce detrimental defects and possibly reduce the strong band tailing that has been identified as a major bottleneck for CZTS. Substitution of Sn with Ge was shown to give close to linear increase in band gap energy [53–58] and Raman spectra from experimental and theoretical investigations of  $Cu_2ZnGeS_4$  was reported in Ref. [59].

Following initial work by Ford et al. [60] on substitution of Sn by Ge, several groups have shown improved device performance from partial substitution with Ge. Giraldo et al. [61,62] report improved grain growth and device improvements from adding a 10 nm Ge layer in metal precursors prior to selenisation. The addition of Ge improved long wavelength collection in quantum efficiency, QE, and  $V_{oc}$  without changing the band gap as obtained from QE cutoff. Changes in doping were reported with a possible correlation to Na as a secondary effect. While small and intermediate Ge contents are shown by several groups to improve performance [63], substitution of Sn with Ge above about 50% was shown to give worse devices [60,64,65]. The highest efficiency Ge-containing device of 12.3% was reported by Kim et al. [66]. In addition to high  $V_{oc}$ , a higher than usual fill factor of 72.7% was also reported in that study. Exchange of Sn with Si will increase the band gap energy further [67,68], but experimentally exchange with Si appears more challenging than with Ge.

Other substitutions aiming at eliminating the Cu–Zn disorder are replacing Cu with Ag and replacing Zn with Ba. Ba substitution was suggested and studied by Shin et al. [69]. A prototype of a  $BaCu_2SnS_4$  solar cell showed 1.6% efficiency, but more importantly abrupt absorption edge and sharp photoluminescence peak. A 2% device and  $V_{oc}$  around 1 V was obtained by using oxygenated CdS buffer layer [70]. The BCTSSe material crystallizes in a trigonal structure and has a tunable band gap around 1.5–2 eV from Se–S variations. The material properties

of this, and the corresponding compound with Sr, were also studied theoretically [71,72].

For Ag substitution, improved grain growth,  $V_{oc}$  and reduced antisite defect concentration was reported [73–75]. Optical analysis showed band gap increase with some bowing for increasing Ag concentration [76]. Transition from p-type to intrinsic or n-type was reported for increasing Ag substitution of Cu [77]. A reduced difference between optical absorption edge and room temperature PL peak energy was shown together with a 10.2% for a device with 10% Ag [78].

Partial substitution of Cu with Li has also been studied and shown to change band gap energy [79]. Homogeneous alloying was found for up to 30% Li exchange for Cu with increasing band gap of up to around 0.2 eV.

Substitution of Zn with Cd was studied by several authors. This results in a transition from kesterite to stannite structure and reduction of the band gap energy. Improved device performance with best device of 9.2% was reported in Ref. [80]. A combinatorial study using photoluminescence monitoring showed detrimental effect of Fe doping while Na and Cd did not have a negative effect on PL [81]. Substitution of Zn with Mn was also shown to give transition from kesterite to stannite structure and increased band gap [82].

Na supply is generally considered to come by diffusion from the glass substrate or through deliberate precursor deposition or supply at later stages in the process. However, Abzieher et al. [83] discuss the transfer of sodium from the environment during annealing as well as the resulting increase in doping density of the absorber. Improved device performance from addition of Na, Li and Rb was shown in Ref. [84]. Non-homogeneities in Na distribution was related to distribution of other elements and device performance in Ref. [85].

From density functional theory using hybrid functionals, Na and K were found to preferentially substitute for Cu in CZTS [86]. Formation energy of Na related defects were lower than for K related defects. Na interstitials had low formation energy while K interstitials are not expected to form. Another first principles study show comparable substitution energy for Na–Cu and Na–Zn, and low formation energy for Li substitution of Cu and Zn [87].

### Defects including influence from composition and annealing conditions

Compositional variations and annealing conditions have been shown to influence both optical and electrical properties. Correlation between metal composition and Raman spectra for selenide CZTSe was reported by Dimitrevska et al. [88]. Lower Cu/(Zn + Sn) content was correlated to increasing  $V_{oc}$  and band gap [89],

possibly correlated to reduced Cu–Zn antisite disorder [90]. Lang et al. [91] showed reduced difference between size of the band gap in ordered and disordered state for decreasing Cu content. A correlation between Cu substitutional defects, band gap and  $V_{oc}$  was also shown in Ref. [92] for selenide CZTSe, where  $V_{oc}$  increased with increasing band gap for intermediate compositional variations from stoichiometry. Rey [93] showed that band gap energy could be used as order parameter, but to distinguish compositional effects on band gap other measures of order parameter would be needed. Increased sub gap absorption was correlated to decreased Sn content in Ref. [94].

Regarding the size of the single phase region, In doping was reported to increase the single phase region for Zn-rich material [95]. A larger stability domain of selenide than sulfide CZTS was reported in Ref. [96].

From temperature dependent admittance measurements and photoluminescence, Levchenko et al. [97] determine an increasing depth of the dominant acceptor level as a function of increasing sulfur content in  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{S}_{1-x})_4$ . They also report a mid-gap deep defect for sulfur rich devices. A correlation between deep defects and annealing was reported by Weiss et al. [98], where a deep defect, not seen in a co-evaporated CZTSe device, appeared if annealing was performed after co-evaporation.

The order–disorder transition was studied by Rey et al. Ordering improved carrier collection and reduced effective doping but  $V_{oc}$  deficit remained the same [99]. The same result was obtained by Krammer et al. [100] and Bourdais et al. [11], where they also argue that Cu–Zn disorder is not the dominating cause for low  $V_{oc}$ . This was based on considering the potential  $V_{oc}$  loss from a maximum band gap fluctuation of about 150 meV due to disorder. Kinetic analysis of B-type sulfide CZTS allowed development of a more efficient ordering anneal, but also showed that high ordering will not be reached within practical timeframes [101]. The optical properties of sulfide CZTS thin films as a function of order–disorder were studied by Valentini et al. [102]. A band gap shift of 200 meV was observed from disordered to the most ordered state. From Monte Carlo simulations, disorder was shown to lead to cation clustering giving nanosized compositional inhomogeneities that can cause potential fluctuations [19].

Low temperature annealing has also been studied by several authors, inspired by the results from IBM, where substantial device improvements were obtained after air anneals. Xie et al. [103] studied absorber annealing in 1 atm nitrogen atmosphere at temperatures between 150 and 400 °C. A surprising trend with degraded device performance for intermediate temperatures and improved performance for high temperatures was



shown. The proposed explanation was based on the role of Na with detrimental surface accumulation at intermediate temperatures and reduced Na at higher temperatures due to Na loss to the atmosphere. Surface accumulation of Na-compounds with negative influence on CBD CdS growth was reported [104], and oxidation through air exposure shown to restore uniform CdS growth without need for KCN etching.

## Concluding remarks

CZTS based solar cells need to overcome the limitations from bulk and interface recombination that is present in today's state of the art devices. A current strong trend is investigation of alloying or substitution with new elements. It is crucial that these elements do not compromise non-toxicity and earth-abundance for CZTS to play a role in relation to commercially competitive CIGS and CdTe solar cells. Large band gap kesterite derivatives for stable top cells in tandem solar cells is an interesting and less explored field meriting more attention.

## References

- Ito K, Nakazawa T: **Electrical and optical-properties of stannite-type quaternary semiconductor thin-films.** *Jpn. J. Appl. Phys. Part 1-Regular Pap. Short Notes Rev. Pap.* 1988, **27**(11):2094–2097.
- Katagiri H, Ishigaki N, Ishida T, Saito K: **Characterization of  $\text{Cu}_2\text{ZnSnS}_4$  thin films prepared by vapor phase sulfurization.** *Jpn. J. Appl. Phys. Part 1-Regular Pap. Short Notes Rev. Pap.* 2001, **40**(2A):500–504.
- Katagiri H, Jimbo K, Yamada S, Kamimura T, Maw WS, Fukano T, Ito T, Motohiro T: **Enhanced conversion efficiencies of  $\text{Cu}_2\text{ZnSnS}_4$ -based thin film solar cells by using preferential etching technique.** *Appl. Phys. Express* 2008, **1**(4).
- Todorov T, Reuter K, Mitzi D: **High-efficiency solar cell with earth-abundant liquid-processed absorber.** *Adv. Mater.* 2010, **22**(20):E156.
- Barkhouse D, Gunawan O, Gokmen T, Todorov T, Mitzi D: **Device characteristics of a 10.1% hydrazine-processed  $\text{Cu}_2\text{ZnSn}(\text{Se,S})_4$  solar cell.** *Prog. PV Res. Appl.* 2012, **20**(1):6–11.
- Wang W, Winkler M, Gunawan O, Gokmen T, Todorov T, Zhu Y, Mitzi D: **Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency.** *Adv. Energy Mater.* 2014, **4**(7):1301465.
- Liu XL, Feng Y, Cui HT, Liu FY, Hao XJ, Conibeer G, Mitzi DB, Green M: **The current status and future prospects of kesterite solar cells: a brief review.** *Prog. Photovolt.* 2016, **24**(6):879–898.
- Kumar M, Dubey A, Adhikari N, Venkatesan S, Qiao QQ: **Strategic review of secondary phases, defects and defect-complexes in kesterite CZTS-Se solar cells.** *Energy Environ. Sci.* 2015, **8**(11):3134–3159.
- Sieberttritt S, Schorr S: **Kesterites – a challenging material for solar cells.** *Prog. Photovolt.* 2012, **20**(5):512–519.
- Polizzotti A, Repins IL, Noufi R, Wei SH, Mitzi DB: **The state and future prospects of kesterite photovoltaics.** *Energy Environ. Sci.* 2013, **6**(11):3171–3182.
- Bourdais S, Chone C, Delatouche B, Jacob A, Larramona G, Moisan C, Lafond A, Donatini F, Rey G, Sieberttritt S, Walsh A, Dennler G: **Is the Cu/Zn disorder the main culprit for the voltage deficit in kesterite solar cells?** *Adv. Energy Mater.* 2016, **6**(12).
- Altamura G, Vidal J: **Impact of minor phases on the performances of CZTSSe thin-film solar cells.** *Chem. Mater.* 2016, **28**(11):3540–3563.
- Tai KF, Gunawan O, Kuwahara M, Chen S, Mhaisalkar SG, Huan CHA, Mitzi DB: **Fill factor losses in  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$  solar cells: insights from physical and electrical characterization of devices and exfoliated films.** *Adv. Energy Mater.* 2016, **6**(3).
- Kanevce A, Repins I, Wei SH: **Impact of bulk properties and local secondary phases on the  $\text{Cu}_2(\text{Zn,Sn})\text{Se}_4$  solar cells open-circuit voltage.** *Sol. Energy Mater. Sol. Cells* 2015, **133**: 119–125.
- Gokmen T, Gunawan O, Todorov TK, Mitzi DB: **Band tailing and efficiency limitation in kesterite solar cells.** *Appl. Phys. Lett.* 2013, **103**(10).
- Sieberttritt S: **Why are kesterite solar cells not 20% efficient?** *Thin Solid Films* 2013, **535**:1–4.
- Frisk C, Ericson T, Li SY, Szaniawski P, Olsson J, Platzer-Björkman C: **Combining strong interface recombination with bandgap narrowing and short diffusion length in  $\text{Cu}_2\text{ZnSnS}_4$  device modeling.** *Sol. Energy Mater. Sol. Cells* 2016, **144**: 364–370.
- Chen SY, Yang JH, Gong XG, Walsh A, Wei SH: **Intrinsic point defects and complexes in the quaternary kesterite semiconductor  $\text{Cu}_2\text{ZnSnS}_4$ .** *Phys. Rev. B* 2010, **81**(24).
- Zawadzki P, Zakutayev A, Lany S: **Entropy-driven clustering in tetrahedrally bonded multinary materials.** *Phys. Rev. Appl.* 2015, **3**(3).
- Scragg JJS, Larsen JK, Kumar M, Persson C, Sendler J, Sieberttritt S, Björkman CP: **Cu-Zn disorder and band gap fluctuations in  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ : theoretical and experimental investigations.** *Phys. Status Solidi B-Basic Solid State Phys.* 2016, **253**(2):247–254.
- Ritscher A, Franz A, Schorr S, Lerch M: **Off-stoichiometric CZTS: neutron scattering investigations on mechanochemically synthesized powders.** *J. Alloys Compd.* 2016, **689**: 271–277.
- Stephan C, Greiner D, Schorr S, Kaufmann CA: **The influence of sodium on the point defect characteristics in off stoichiometric  $\text{CuInSe}_2$ .** *J. Phys. Chem. Solids* 2016, **98**:309–315.
- Hages CJ, Carter NJ, 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**(23).
- Bar M, Schubert BA, Marsen B, Krause S, Pookpanratana S, Unold T, Weinhardt L, Heske C, Schock HW: **Impact of KCN etching on the chemical and electronic surface structure of  $\text{Cu}_2\text{ZnSnS}_4$  thin-film solar cell absorbers.** *Appl. Phys. Lett.* 2011, **99**(15).
- Schmid D, Ruckh M, Grunwald F, Schock HW: **Chalcopyrite defect chalcopyrite heterojunctions on the basis of  $\text{CuInSe}_2$ .** *J. Appl. Phys.* 1993, **73**(6):2902–2909.
- Repins IL, Li JV, Kanevce A, Perkins CL, Steirer KX, Pankow J, Teeter G, Kuciauskas D, Beall C, Dehart C, Carapella J, Bob B, Park JS, Wei SH: **Effects of deposition termination on  $\text{Cu}_2\text{ZnSnS}_4$  device characteristics.** *Thin Solid Films* 2015, **582**:184–187.
- Kim JH, Choi SY, Choi M, Gershon T, Lee YS, Wang W, Shin B, Chung SY: **Atomic-scale observation of oxygen substitution and its correlation with hole-transport barriers in  $\text{Cu}_2\text{ZnSnSe}_4$  thin-film solar cells.** *Adv. Energy Mater.* 2016, **6**(6).
- Sardashti K, Haight R, Gokmen T, Wang W, Chang LY, Mitzi DB, Kummel AC: **Impact of nanoscale elemental distribution in high-performance kesterite solar cells.** *Adv. Energy Mater.* 2015, **5**(10).
- Larsen J, Ren Y, Ross N, Särhammar E, Li SY, Platzer-Björkman C: **Surface modification through air annealing  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  absorbers.** *Thin Solid Films* 2016, Available online: <http://dx.doi.org/10.1016/j.tsf.2016.08.030>.
- Lee YS, Gershon T, Todorov TK, Wang W, Winkler MT, Hopstaken M, Gunawan O, Kim J: **Atomic layer deposited aluminum oxide for interface passivation of**

- Cu<sub>2</sub>ZnSn(S,Se)(4) thin-film solar cells.** *Adv. Energy Mater.* 2016, **6**(12).
31. Yang KJ, Son DH, Sung SJ, Sim JH, Kim YI, Park SN, Jeon DH, Kim J, Hwang DK, Jeon CW, Nam D, Cheong H, Kang JK, Kim DH: **A band-gap-graded CZTSSe solar cell with 12.3% efficiency.** *J. Mater. Chem. A* 2016, **4**(26):10151–10158.
  32. Sun KW, Yan C, Liu FY, Huang JL, Zhou FZ, Stride JA, Green M, Hao XJ: **Over 9% efficient kesterite Cu<sub>2</sub>ZnSnS<sub>4</sub> solar cell fabricated by using Zn<sub>1-x</sub>Cd<sub>x</sub>S buffer layer.** *Adv. Energy Mater.* 2016, **6**(12).
  33. Platzer-Bjorkman C, Frisk C, Larsen JK, Ericson T, Li SY, Scragg JJS, Keller J, Larsson F, Torndahl T: **Reduced interface recombination in Cu<sub>2</sub>ZnSnS<sub>4</sub> solar cells with atomic layer deposition Zn<sub>1-x</sub>Sn<sub>x</sub>O<sub>y</sub> buffer layers.** *Appl. Phys. Lett.* 2015, **107**(24):4.
  34. Li XL, Su ZH, Venkataraj S, Batabyal SK, Wong LH: **8.6% Efficiency CZTSSe solar cell with atomic layer deposited Zn-S-O buffer layer.** *Sol. Energy Mater. Sol. Cells* 2016, **157**:101–107.
  35. Ernits K, Neubauer C, Li XL, Wong LH, Meissner D, Neisser A, IEEE: **Improvement of V-OC in Cu<sub>2</sub>ZnSnS<sub>4</sub> monograin layer solar cells with tin oxide inter-layer.** In *2015 IEEE 42nd Photovoltaic Specialist Conference*; 2015.
  36. Kim J, Hiroi H, Todorov TK, Gunawan O, Kuwahara M, Gokmen T, Nair D, Hopstaken M, Shin B, Lee YS, Wang W, Sugimoto H, Mitzi DB: **High efficiency Cu<sub>2</sub>znSn(S,Se)(4) solar cells by applying a double In<sub>2</sub>S<sub>3</sub>/CdS emitter.** *Adv. Mater.* 2014, **26**(44):7427–7431.
  37. Yan C, Liu FY, Sun KW, Song N, Stride JA, Zhou FZ, Hao XJ, Green M: **Boosting the efficiency of pure sulfide CZTS solar cells using the In/Cd-based hybrid buffers.** *Sol. Energy Mater. Sol. Cells* 2016, **144**:700–706.
  38. Neuschitzer M, Lienau K, Guc M, Barrio LC, Haass S, Prieto JM, Sanchez Y, Espindola-Rodriguez M, Romanyuk Y, Perez-Rodriguez A, Izquierdo-Roca V, Saucedo E: **Towards high performance Cd-free CZTSe solar cells with a ZnS(O,OH) buffer layer: the influence of thiourea concentration on chemical bath deposition.** *J. Phys. D-Appl. Phys.* 2016, **49**(12).
  39. Steirer KX, Garris RL, Li JV, Dzara MJ, Ndione PF, Ramanathan K, Repins I, Teeter G, Perkins CL: **Co-solvent enhanced zinc oxysulfide buffer layers in kesterite copper zinc tin selenide solar cells.** *Phys. Chem. Chem. Phys.* 2015, **17**(23):15355–15364.
  40. Khadka DB, Kim S, Kim J: **A nonvacuum approach for fabrication of Cu<sub>2</sub>ZnSnSe<sub>4</sub>/In<sub>2</sub>S<sub>3</sub> thin film solar cell and optoelectronic characterization.** *J. Phys. Chem. C* 2015, **119**(22):12226–12235.
  41. Buffiere M, Barreau N, Brammertz G, Sahayaraj S, Meuris M, Poortmans J, IEEE: **Development of co-evaporated In<sub>2</sub>S<sub>3</sub> buffer layer for Cu<sub>2</sub>ZnSnSe<sub>4</sub> thin film solar cells.** In *2015 IEEE 42nd Photovoltaic Specialist Conference*; 2015.
  42. Tong ZF, Zhang K, Sun KW, Yan C, Liu FY, Jiang LX, Lai YQ, Hao XJ, Li J: **Modification of absorber quality and Mo-back contact by a thin Bi intermediate layer for kesterite Cu<sub>2</sub>ZnSnS<sub>4</sub> solar cells.** *Sol. Energy Mater. Sol. Cells* 2016, **144**:537–543.
  43. Zhou FZ, Zeng FQ, Liu X, Liu FY, Song N, Yan C, Pu A, Park JS, Sun KW, Hao XJ: **Improvement of J(sc) in a Cu<sub>2</sub>ZnSnS<sub>4</sub> solar cell by using a thin carbon intermediate layer at the Cu<sub>2</sub>ZnSnS<sub>4</sub>/Mo interface.** *ACS Appl. Mater. Interfaces* 2015, **7**(41):22868–22873.
  44. Oueslati S, Brammertz G, Buffiere M, ElAnzeery H, Mangin D, ElDaif O, Touayar O, Koble C, Meuris M, Poortmans J: **Study of alternative back contacts for thin film Cu<sub>2</sub>ZnSnSe<sub>4</sub>-based solar cells.** *J. Phys. D-Appl. Phys.* 2015, **48**(3).
  45. Ranjbar S, Brammertz G, Vermang B, Hadipour A, Cong S, Suganuma K, Schnabel T, Meuris M, da Cunha AF, Poortmans J: **Improvement of kesterite solar cell performance by solution synthesized MoO<sub>3</sub> interfacial layer.** *Phys. Status Solidi (a)* 2016, n/a–/a.
  46. Espindola-Rodriguez M, Sanchez Y, Lopez-Marino S, Xie H, Izquierdo-Roca V, Sylla D, Neuschitzer M, Vigil-Galan O, Saucedo E, Placidi M, IEEE: **efficient bifacial Cu<sub>2</sub>ZnSnSe<sub>4</sub> solar cells.** In *2015 IEEE 42nd Photovoltaic Specialist Conference*; 2015.
  47. Ge J, Yu Y, Yan YF, IEEE: **Co-electroplated kesterite bifacial thin film solar cells.** In *2015 IEEE 42nd Photovoltaic Specialist Conference*; 2015.
  48. Ge J, Chu JH, Jiang JC, Yan YF, Yang PX: **The interfacial reaction at ITO back contact in kesterite CZTSSe bifacial solar cells.** *ACS Sustain. Chem. Eng.* 2015, **3**(12):3043–3052.
  49. Becerril-Romero I, Giraldo S, Lopez-Marino S, Placidi M, Sanchez Y, Sylla D, Perez-Rodriguez A, Saucedo E, Pistor P: **Vitreous enamel as sodium source for efficient kesterite solar cells on commercial ceramic tiles.** *Sol. Energy Mater. Sol. Cells* 2016, **154**:11–17.
  50. Todorov T, Olenick J, Olenick K, Gunawan O, Gershon T, Sturdevant C, Lee YS, Chang LY, Guha S, IEEE: **Flexible kesterite solar cells on ceramic substrates for advanced thermal processing.** In *2015 IEEE 42nd Photovoltaic Specialist Conference*; 2015.
  51. Sun KW, Liu FY, Yan C, Zhou FZ, Huang JL, Shen YS, Liu R, Hao XJ: **Influence of sodium incorporation on kesterite Cu<sub>2</sub>ZnSnS<sub>4</sub> solar cells fabricated on stainless steel substrates.** *Sol. Energy Mater. Sol. Cells* 2016, **157**:565–571.
  52. Bras P, Sterner J, Platzer-Bjorkman C: **Influence of hydrogen sulfide annealing on copper-zinc-tin-sulfide solar cells sputtered from a quaternary compound target.** *Thin Solid Films* 2015, **582**:233–238.
  53. Grossberg M, Timmo K, Raadik T, Karber E, Mikli V, Krustok J: **Study of structural and optoelectronic properties of Cu<sub>2</sub>Zn(Sn<sub>1-x</sub>Ge<sub>x</sub>)Se-4 (x = 0 to 1) alloy compounds.** *Thin Solid Films* 2015, **582**:176–179.
  54. Morihama M, Gao F, Maeda T, Wada T: **Crystallographic and optical properties of Cu<sub>2</sub>Zn(Sn<sub>1-x</sub>Ge<sub>x</sub>)Se-4 solid solution.** *Jpn. J. Appl. Phys.* 2014, **53**(4).
  55. Garcia-Llamas E, Merino JM, Serna R, Fontane X, Victorov IA, Perez-Rodriguez A, Leon M, Bodnar IV, Izquierdo-Roca V, Caballero R: **Wide band-gap tuning Cu<sub>2</sub>ZnSn<sub>1-x</sub>Ge<sub>x</sub> S<sub>4</sub> single crystals: optical and vibrational properties.** *Sol. Energy Mater. Sol. Cells* 2016, **158**:147–153.
  56. Litvinchuk AP: **Optical properties and lattice dynamics of CuZnGeSe quaternary semiconductor: a density-functional study.** *Phys. Status Solidi B-Basic Solid State Phys.* 2016, **253**(2):323–328.
  57. Choi SG, Park JS, Donohue AL, Christensen ST, To B, Beall C, Wei SH, Repins IL: **Electronic structure and optical properties of Cu<sub>2</sub>ZnGeSe<sub>4</sub>: first-principles calculations and vacuum-ultraviolet spectroscopic ellipsometric studies.** *Phys. Rev. Appl.* 2015, **4**(5).
  58. Khadka DB, Kim J: **Band gap engineering of alloyed Cu(2) ZnGe(x)Sn(1-x)Q(4) (Q = S,Se) films for solar cell.** *J. Phys. Chem. C* 2015, **119**(4):1706–1713.
  59. Valakh MY, Litvinchuk AP, Dzhegagan VM, Yukhymchuk VO, Yaremko AM, Romanyuk YA, Guc M, Bodnar IV, Perez-Rodriguez A, Zahn DRT: **Fermi resonance in the phonon spectra of quaternary chalcogenides of the type Cu<sub>2</sub>ZnGeS<sub>4</sub>.** *J. Phys.-Condens. Matter.* 2016, **28**(6).
  60. Ford GM, Guo QJ, Agrawal R, Hillhouse HW: **Earth abundant element Cu<sub>2</sub>Zn(Sn<sub>1-x</sub>Ge<sub>x</sub>)S-4 nanocrystals for tunable band gap solar cells: 6.8% efficient device fabrication.** *Chem. Mater.* 2011, **23**(10):2626–2629.
  61. Giraldo S, Neuschitzer M, Thersleff T, Lopez-Marino S, Sanchez Y, Xie HB, Colina M, Placidi M, Pistor P, Izquierdo-Roca V, Leifer K, Perez-Rodriguez A, Saucedo E: **Large efficiency improvement in Cu<sub>2</sub>ZnSnSe<sub>4</sub> solar cells by introducing a superficial Ge nanolayer.** *Adv. Energy Mater.* 2015, **5**(21):6.
  62. Giraldo S, Thersleff T, Larramona G, Neuschitzer M, Pistor P, Leifer K, Perez-Rodriguez A, Moisan C, Dennler G, Saucedo E: **Cu<sub>2</sub>ZnSnSe<sub>4</sub> solar cells with 10.6% efficiency through innovative absorber engineering with Ge superficial nanolayer.** *Prog. Photovolt.* 2016, **24**(10):1359–1367.

63. Khadka DB, Kim S, Kim J: **Effects of Ge alloying on device characteristics of kesterite-based CZTSSe thin film solar cells.** *J. Phys. Chem. C* 2016, **120**(8):4251–4258.
64. Neuschitzer M, Marquez J, Giraldo S, Dimitrievska M, Placidi M, Forbes I, Izquierdo-Roca V, Perez-Rodriguez A, Saucedo E: **V-oc boosting and grain growth enhancing Ge-doping strategy for  $\text{Cu}_2\text{ZnSnSe}_4$  photovoltaic absorbers.** *J. Phys. Chem. C* 2016, **120**(18):9661–9670.
65. Collord AD, Hillhouse HW: **Germanium alloyed kesterite solar cells with low voltage deficits.** *Chem. Mater.* 2016, **28**(7):2067–2073.
66. Kim S, Kim KM, Tampo H, Shibata H, Niki S: **Improvement of voltage deficit of Ge-incorporated kesterite solar cell with 12.3% conversion efficiency.** *Appl. Phys. Express* 2016, **9**(10).
67. Zhang XBA, Chen DG, Deng KM, Lu RF: **Band engineering of wurtzite-derived semiconductors  $\text{Cu}_2\text{ZnSiS}_4$  and  $\text{Cu}_2\text{Zn-SiSe}_4$ .** *J. Alloys Compd.* 2016, **656**:196–199.
68. Hamdi M, Lafond A, Guillot-Deudon C, Hlél F, Gargouri M, Jobic S: **Crystal chemistry and optical investigations of the  $\text{Cu}_2\text{Zn}(\text{Sn,Si})\text{S}_4$  series for photovoltaic applications.** *J. Solid State Chem.* 2014, **220**:232–237.
69. Shin D, Saparov B, Zhu T, Huhn WP, Blum V, Mitzi DB:  **$\text{BaCu}_2\text{Sn}(\text{S,Se})_4$ : earth-abundant chalcogenides for thin-film photovoltaics.** *Chem. Mater.* 2016, **28**(13):4771–4780.
70. Ge J, Koirala P, Grice C, Roland P, Yu Y, Tan X, Ellingson R, Collins R, Yan Y: **Oxygenated CdS buffer layers enabling high open-circuit voltages in earth-abundant  $\text{Cu}_2\text{BaSnS}_4$  thin-film solar cells.** *Adv. Energy Mater.* 2016, **7**(6). <http://dx.doi.org/10.1002/aenm.201601803>. Article Number: 1601803.
71. Xiao Z, Meng W, Li JV, Yan Y: **Distant-atom mutation for better earth-abundant light absorbers: a case study of  $\text{Cu}_2\text{BaSnSe}_4$ .** *ACS Energy Lett.* 2016, **29**–35.
72. Hong F, Lin WJ, Meng WW, Yan YF: **Trigonal Cu-2-II-Sn-VI4 (II = Ba, Sr and VI = S, Se) quaternary compounds for earth-abundant photovoltaics.** *Phys. Chem. Chem. Phys.* 2016, **18**(6):4828–4834.
73. Guchhait A, Su Z, Tay YF, Shukla S, Li W, Leow SW, Tan JMR, Lie S, Gunawan O, Wong LH: **Enhancement of open-circuit voltage of solution-processed  $\text{Cu}_2\text{ZnSnS}_4$  solar cells with 7.2% efficiency by incorporation of silver.** *ACS Energy Lett.* 2016:1256–1261.
74. Hages CJ, Koeper MJ, Agrawal R: **Optoelectronic and material properties of nanocrystal-based CZTSe absorbers with Ag-alloying.** *Sol. Energy Mater. Sol. Cells* 2016, **145**:342–348.
75. Chagarov E, Sardashti K, Kummel AC, Lee YS, Haight R, Gershon TS:  **$\text{Ag}_2\text{ZnSn}(\text{S,Se})_4$ : a highly promising absorber for thin film photovoltaics.** *J. Chem. Phys.* 2016, **144**(10):11.
76. Gong WY, Tabata T, Takei K, Morihama M, Maeda T, Wada T: **Crystallographic and optical properties of  $(\text{Cu, Ag})_2\text{ZnSnS}_4$  and  $(\text{Cu, Ag})_2\text{ZnSnSe}_4$  solid solutions.** *Phys. Status Solidi C: Curr. Top. Solid State Phys.* 2015, **12**(6):700–703.
77. Yuan ZK, Chen SY, Xiang HJ, Gong XG, Walsh A, Park JS, Repins I, Wei SH: **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**(43):6733–6743.
78. Gershon T, Lee YS, Antunez P, Mankad R, Singh S, Bishop D, Gunawan O, Hopstaken M, Haight R: **Photovoltaic materials and devices based on the alloyed kesterite absorber  $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnSe}_4$ .** *Adv. Energy Mater.* 2016, **6**(10).
79. Yang YC, Kang XJ, Huang LJ, Pan DC: **Tuning the band gap of  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  thin films via lithium alloying.** *ACS Appl. Mater. Interfaces* 2016, **8**(8):5308–5313.
80. Su ZH, Tan JMR, Li XL, Zeng X, Batabyal SK, Wong LH: **Cation substitution of solution-processed  $\text{Cu}_2\text{ZnSnS}_4$  thin film solar cell with over 9% efficiency.** *Adv. Energy Mater.* 2015, **5**(19).
81. Collord AD, Xin H, Hillhouse HW: **Combinatorial exploration of the effects of intrinsic and extrinsic defects in  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ .** *IEEE J. Photovolt.* 2015, **5**(1):288–298.
82. Chen LL, Deng HM, Cui JY, Tao JH, Zhou WL, Cao HY, Sun L, Yang PX, Chu JH: **Composition dependence of the structure and optical properties of  $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$  thin films.** *J. Alloys Compd.* 2015, **627**:388–392.
83. Abzieher T, Schnabel T, Hetterich M, Powalla M, Ahlswede E: **Source and effects of sodium in solution-processed kesterite solar cells.** *Phys. Status Solidi a – Appl. Mater. Sci.* 2016, **213**(4):1039–1049.
84. Altamura G, Wang MQ, Choy KL: **Influence of alkali metals (Na, Li, Rb) on the performance of electrostatic spray-assisted vapor deposited  $\text{Cu}_2\text{ZnSn}(\text{S, Se})_4$  solar cells.** *Sci. Rep.* 2016, **6**.
85. Gershon T, Hamann C, Hopstaken M, Lee YS, Shin B, Haight R: **Chemical consequences of alkali inhomogeneity in  $\text{Cu}_2\text{ZnSnS}_4$  thin-film solar cells.** *Adv. Energy Mater.* 2015, **5**(19).
86. Ghorbani E, Kiss J, Mirhosseini H, Schmidt M, Windeln J, Kuhne TD, Felser C: **Insights into intrinsic defects and the incorporation of Na and K in the  $\text{Cu}_2\text{ZnSnSe}_4$  thin-film solar cell material from hybrid-functional calculations.** *J. Phys. Chem. C* 2016, **120**(4):2064–2069.
87. Maeda T, Kawabata A, Wada T: **First-principles study on alkali-metal effect of Li, Na, and K in  $\text{Cu}_2\text{ZnSnS}_4$  and  $\text{Cu}_2\text{ZnSnSe}_4$ .** *Phys. Status Solidi C: Curr. Top. Solid State Phys.* 2015, **12**(6):631–637.
88. Dimitrievska M, Fairbrother A, Saucedo E, Perez-Rodriguez A, Izquierdo-Roca V: **Influence of compositionally induced defects on the vibrational properties of device grade  $\text{Cu}_2\text{ZnSnSe}_4$  absorbers for kesterite based solar cells.** *Appl. Phys. Lett.* 2015, **106**(7).
89. Marquez J, Neuschitzer M, Dimitrievska M, Gunder R, Haass S, Werner M, Romanyuk YE, Schorr S, Pearsall NM, Forbes I: **Systematic compositional changes and their influence on lattice and optoelectronic properties of  $\text{Cu}_2\text{ZnSnSe}_4$  kesterite solar cells.** *Sol. Energy Mater. Sol. Cells* 2016, **144**:579–585.
90. Paris M, Choubrac L, Lafond A, Guillot-Deudon C, Jobic S: **Solid-state NMR and Raman spectroscopy to address the local structure of defects and the tricky issue of the Cu/Zn disorder in Cu-poor, Zn-rich CZTS materials.** *Inorganic Chem.* 2014, **53**(16):8646–8653.
91. Lang M, Renz T, N M, Neuwirth M, Schnabel T, Kalt H, Hetterich M: **Influence of the Cu content in  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  solar cell absorbers on order-disorder related band gap changes.** *Appl. Phys. Lett.* 2016, **109**:142103.
92. Dimitrievska M, Fairbrother A, Saucedo E, Perez-Rodriguez A, Izquierdo-Roca V: **Secondary phase and Cu substitutional defect dynamics in kesterite solar cells: impact on optoelectronic properties.** *Sol. Energy Mater. Sol. Cells* 2016, **149**:304–309.
93. Rey G, Redinger A, Ler JS, Weiss TP, Thevenin M, Guennou M, El Adib B, Siebentritt S: **The band gap of  $\text{Cu}_2\text{ZnSnSe}_4$ : effect of order-disorder.** *Appl. Phys. Lett.* 2014, **105**(11).
94. Malerba C, Biccari F, Ricardo CLA, Valentini M, Chierchia R, Muller M, Santoni A, Esposito E, Mangiapane P, Scardi P, Mittiga A: **CZTS stoichiometry effects on the band gap energy.** *J. Alloys Compd.* 2014, **582**:528–534.
95. Hartnauer S, Korbel S, Marques MAL, Botti S, Pistor P, Scheer R: **Research update: stable single-phase Zn-rich  $\text{Cu}_{22}\text{nSnSe}_4$  through In doping.** *Appl. Mater.* 2016, **4**(7).
96. Choubrac L, Lafond A, Paris M, Guillot-Deudon C, Jobic P: **The stability domain of the selenide kesterite photovoltaic materials and NMR investigation of the Cu/Zn disorder in  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe).** *Phys. Chem. Chem. Phys.* 2015, **17**(23):15088–15092.
97. Levchenko S, Just J, Redinger A, Larramona G, Bourdais S, Dennler G, Jacob A, Unold T: **Deep defects in  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  solar cells with varying Se content.** *Phys. Rev. Appl.* 2016, **5**(2).
98. Weiss TP, Redinger A, Rey G, Schwarz T, Spies M, Cojocura-Miredin O, Choi PP, Siebentritt S: **Impact of annealing on electrical properties of  $\text{Cu}_2\text{ZnSnSe}_4$  absorber layers.** *J. Appl. Phys.* 2016, **120**(4).

99. Rey G, Weiss TP, Sendler J, Finger A, Spindler C, Werner F, Melchiorre M, Hala M, Guennou M, Siebentritt S: **Ordering kesterite improves solar cells: a low temperature post-deposition annealing study**. *Sol. Energy Mater. Sol. Cells* 2016, **151**:131–138.
100. Krammer C, Huber C, Schnabel T, Zimmermann C, Lang M, Ahlswede E, Kalt H, Hetterich M, IEEE: **Order-disorder related band gap changes in  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ : impact on solar cell performance**. In *2015 IEEE 42nd Photovoltaic Specialist Conference*; 2015.
101. Rudisch K, Ren Y, Platzer-Bjorkman C, Scragg J: **Order-disorder transition in B-type  $\text{Cu}_2\text{ZnSnS}_4$  and limitations of ordering through thermal treatments**. *Appl. Phys. Lett.* 2016, **108**(23).
102. Valentini M, Malerba C, Menchini F, Tedeschi D, Polimeni A, Capizzi M, Mittiga A: **Effect of the order-disorder transition on the optical properties of  $\text{Cu}_2\text{ZnSnS}_4$** . *Appl. Phys. Lett.* 2016, **108**(21).
103. Xie HB, Lopez-Marino S, Olar T, Sanchez Y, Neuschitzer M, Oliva F, Giraldo S, Izquierdo-Roca V, Lauermann I, Perez-Rodríguez A, Saucedo E: **Impact of Na dynamics at the  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4/\text{CdS}$  interface during post low temperature treatment of absorbers**. *ACS Appl. Mater. Interfaces* 2016, **8**(7): 5017–5024.
104. Ren Y, Scragg JJS, Edoff M, Larsen JK, Platzer-Bjorkman C: **Evolution of Na-S(-O) Compounds on the  $\text{Cu}_2\text{ZnSnS}_4$  absorber Surface and their effects on CdS thin film growth**. *ACS Appl. Mater. Interfaces* 2016, **8**(28):18600–18607.