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Status of materials and device modelling for kesterite solar cells

Samantha N Hood[1], **Aron Walsh**[1,2,11], **Clas Persson**[3,4], **Konstantina Iordanidou**[3], **Dan Huang**[5], **Mukesh Kumar**[6], **Zacharie Jehl**[7], **Maykel Courel**[8], **Johan Lauwaert**[9] **and Sanghyun Lee**[10]

[1] Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom
[2] Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Republic of Korea
[3] University of Oslo, Department of Physics, Oslo, 0316, Norway
[4] KTH Royal Institute of Technology, Department of Materials Science and Engineering, Stockholm, 10044, Sweden
[5] Guangxi University, School of Physical Science and Technology and Guangxi Key Laboratory of Processing for Non-Ferrous Metallic and Featured Materials, Nanning, 530004, People's Republic of China
[6] School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala, Punjab, 147004, India
[7] Institut de Recerca en Energia de Catalunya (IREC), Jardins de les Dones de Negre, 1, 2ª pl., 08930 Sant Adrià de Besòs, Barcelona, Spain
[8] Centro Universitario de los Valles (CUValles), Universidad de Guadalajara, Carretera Guadalajara-Ameca Km. 45.5, C.P. 46600, Ameca, Jalisco, Mexico
[9] Department of Electronics and Information Systems, Ghent University, Zwijnaarde B-9052, Belgium
[10] Department of Electronics and Computer Engineering Technology, Indiana State University, Terre Haute, IN, 47809, United States of America
[11] Author to whom any correspondence should be addressed.

E-mail: a.walsh@imperial.ac.uk

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Abstract

Kesterite semiconductors, derived from the mineral $Cu_2(Zn,Fe)SnS_4$, adopt superstructures of the zincblende archetype. This family of semiconductors is chemically flexible with the possibility to tune the physical properties over a large range by modifying the chemical composition, while preserving the same structural backbone. In the simplest case, three metals (e.g. Cu, Zn and Sn) occupy the cation sublattice, which gives rise to a range of competing orderings (polymorphs) and the possibility for order–disorder transitions. The rich physics of the sulphide, selenide, and mixed-anion materials make them attractive for computer simulations in order to provide deeper insights and to direct experiments to the most promising material combinations and processing regimes. This topical review assesses the status of first-principles electronic structure calculations, optical modelling, and photovoltaic device simulations of kesterite semiconductors. Recent progress is discussed, and immediate challenges are outlined, in particular towards overcoming the voltage deficit in Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ solar cells.

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1. Past, present, and future of kesterite simulations

Samantha N Hood[1] **and Aron Walsh**[1,2]
[1]Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK
[2]Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea

Building on the properties and performance of elemental and compound binary and ternary semiconductors, the extension to higher-order multi-component compounds has been of long-standing interest in the solid-state physics community. For instance, in 1964 Pamplin applied electron-counting rules to predict a range of stable semiconducting quaternary solids [1]. Wagner and Bridenbaugh succeeded in fabricating a simple photovoltaic junction from p-type Cu_2CdSnS_4 in 1977 [2]. The first Cu_2ZnSnS_4 (CZTS) solar cell was then reported in 1988 [3], which launched a line of research into earth-abundant kesterite thin-film solar cells. While the structure of these materials appears simple (figure 1(a)), there are serious issues in controlling defects and disorder in the occupancy of each element on their respective lattice sites, as well as the large number of competing compounds in their phase space (figure 1(b)).

Material modelling has become a powerful tool in material characterisation and prediction. First-principles calculations, based on solutions to the quantum mechanical Kohn–Sham equations in density functional theory, have been applied to kesterites for a diverse range of problems including polymorphism, polytypism, and defect physics, which have been the subject of extensive reviews such as those in [4] and [5]. Progress in the topic will be further explored in section 3. Optical modelling, including the application of the Beer–Lambert law and rigorous coupled-wave analysis, can be important in guiding towards higher-efficiency devices by optimising film thicknesses and morphology as covered in section 5. Finally, in section 7, models of device operation based on solutions to the semiconductor drift-diffusion equations will be discussed. The format of this topical review has been adapted from the materials by design roadmap [6].

The long-standing challenge facing kesterite solar cells is the voltage deficit [7], which is also covered in other articles in this themed issue, and that is ultimately due to non-radiative electron-hole recombination. The contributing factors can include the presence of secondary phases (e.g. small-gap Cu_2SnS_3), cation disorder (e.g. Cu–Zn antisites), deep-level defects (e.g. Sn_{Zn}), and interfacial reactions (e.g. SnS formation at the back contact). However, the relative weights of each process are still under debate and may vary between samples and by device architecture. Recent progress has been made in the quantification of deep-level defects by going beyond a simple energy-level description to calculate the capture cross-sections (figure 2(a)) for specific defects [8–10]. Unfortunately, modelling based on quantum mechanics shows that a number of defects exhibit large capture cross-sections, which can be classified as 'giant traps'. We have linked this behaviour to the redox activity of the Sn(IV) species, which can readily reduce (capture electrons) to occupy the electronic bands associated with the s^2 lone pair electrons. The accompanying large lattice distortion with lone pair formation enhances the capture rate. Such defects can give rise to rapid carrier capture even when present at low concentrations [10]. Ongoing research is focussed on finding the optimal processing regime and chemical substituents (for example, the partial substitution of Ag for Cu) that can suppress trap-mediated Shockley–Read–Hall recombination. Future opportunities in the modelling of CZTS may include high-throughput calculations of chemically substituted kesterite structures (and their competing phases) and a more detailed theoretical analysis of the effect of chemical modifications on the defect carrier capture rates.

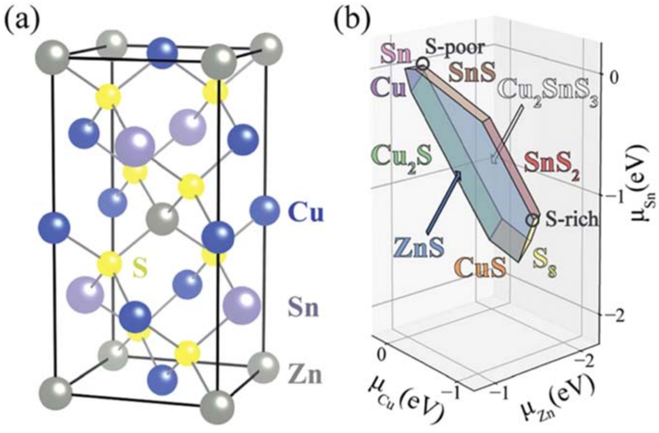

Figure 1. (a) Atomic structure and (b) phase diagram of CZTS in chemical potential space, where $\mu_i = 0$ represents element i in its standard state. Blue, grey, purple, and yellow balls represent Cu, Zn, Sn, and S atoms, respectively. Reproduced from [10].

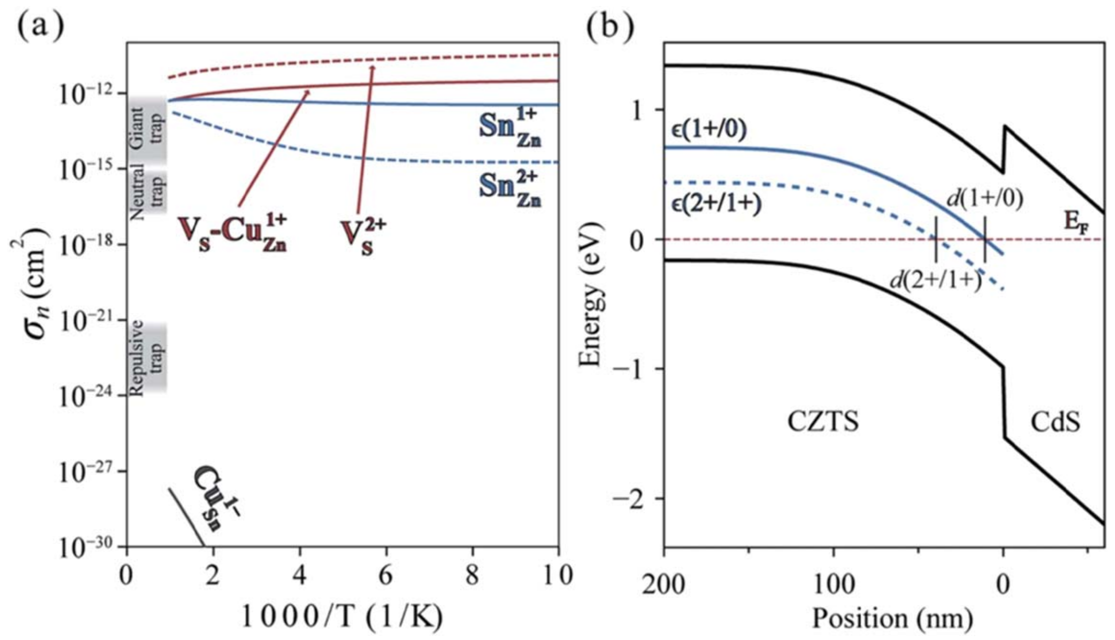

Figure 2. (a) Calculated electron capture cross-sections of V_S, V_S–Cu_{Zn} complex, Sn_{Zn}, and Cu_{Sn}. Grey shades represent the typical orders of magnitude of cross-sections of giant, neutral, and repulsive traps. (b) Band diagram of the CZTS/CdS heterojunction. The solid and dashed blue curves represent the single (1+/0) and double donor levels (2+/1+) of Sn_{Zn}, respectively. $d(q_1/q_2)$ is defined by the distance from the interface where the charge transition levels of Sn_{Zn} (q_1/q_2) equal the Fermi level E_F (red dashed line). Reproduced from [10]. CC BY 3.0.

Acknowledgments

A W thanks Su-Huai Wei for introducing him to kesterite semiconductors, and all group members that have been involved in the journey including Adam Jackson, Suzy Wallace, Jarvist Frost, Jonathan Skelton, Sunghyun Kim, and Jisang Park. The authors would also like to thank Edgardo Saucedo for bringing together this team of authors. Our research has been funded by the EU Horizon2020 Framework (STARCELL, Grant No. 720907) and the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2018R1C1B6008728).

2. Electronic structure and intrinsic defects

Clas Persson[1,2], **Konstantina Iordanidou**[1], **Dan Huang**[3], **Mukesh Kumar**[4]
[1]University of Oslo, Department of Physics, Oslo, 0316, Norway
[2]KTH Royal Institute of Technology, Department of Materials Science and Engineering, Stockholm, 10044, Sweden
[3]Guangxi University, School of Physical Science and Technology and Guangxi Key Laboratory of Processing for Non-Ferrous Metallic and Featured Materials, Nanning, 530004, China
[4]School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala, Punjab, 147004, India

Status. Kesterite-structured CZTS exhibits an electronic structure (figure 3(a)) similar to its binary counterpart zincblende ZnS. The effective electron mass of CZTS is $\sim 0.2m_0$ (twice as large as for Cu(In,Ga)Se_2) and also the hole masses of $\sim(0.2–0.5)m_0$ are reasonably small [11]. One significant character is that the fully occupied Cu d-like states are energetically distributed close to the valence band maximum (figure 3(b)), implying a strong hybridisation with the S p-like states that narrows the Γ-point direct energy gap of CZTS to $E_g \approx 1.5$ eV. This hybridisation weakens the chemical bonds, resulting in a relatively small formation energy of copper vacancies V_{Cu} [12]. Therefore, high concentrations of neutral and valence-conserving complexes are likely to be formed under normal growth conditions [13]. The Cu-poor $\{V_{Cu}^- + Zn_{Cu}^+\}^0$ and the antisite pair $\{Cu_{Zn}^- + Zn_{Cu}^+\}^0$ are often expected to distort the stoichiometry of the material. Antisite pairs make a critical contribution to band gap fluctuations (in the range of several hundred meVs) causing a large voltage deficit in CZTS solar cells [14]. This disorder transition occurs primarily within the (001) planes, but the formation of antisite pairs between adjacent planes lowers the critical temperature for disordering [15]. Moreover, the formation of these valence-conserving cation defect complexes actually implies that there is a deviation in the valence charges around the neighbouring anions. This means there is a strong correlation between two defect complexes, where the interaction originates from the octet rule imposed on the anion near the defect complex [16]. The formation energy of the $\{V_{Cu}^- + Zn_{Cu}^+\}^0$ complex is reduced if it is located next to the $\{Cu_{Zn}^- + Zn_{Cu}^+\}^0$ complex, and vice versa. Importantly, these two complexes affect the band gap energy in the opposite way: $\{V_{Cu}^- + Zn_{Cu}^+\}^0$ widens the gap while $\{Cu_{Zn}^- + Zn_{Cu}^+\}^0$ narrows the gap. The gap energy can therefore be compensated and stabilised in Cu-poor CZTS owing to the interplay between these two defect complexes.

Current and future challenges. The role of defect complexes, cluster formation, and disorder is not fully understood, but may provide a key route to improving the performance of CZTS technology. While the formation of $\{V_{Cu}^- + Zn_{Cu}^+\}^0$ and $\{Cu_{Zn}^- + Zn_{Cu}^+\}^0$ is favoured via electrostatic interactions between charged acceptors and donors, clustering occurs via minimising the deviation from the valence octet rule. In addition, isovalent and neutral point defects can form complexes with strong local bonds. Cations (often group-I Ag and alkali metals, like Na) are doped to enhance device performance of kesterite solar cells [17]. When both sodium and oxygen are present in CZTS, the formation of the complex $\{Na_{Cu}^0 + O_S^0\}^0$ dominates completely over having the constituents Na_{Cu}^0 and O_S^0 separated [18], despite the absence of long-range electrostatic interaction or deviation from the octet rule. Furthermore, theoretical modelling suggests that cation disorder can occur in CZTS via entropy-driven formation for non-ground state coordination that leads to nanometre-scale compositional inhomogeneities [18, 19].

These recent results indicate that there are major research issues and challenges to fully understand the formation of complexes and cluster formations in CZTS, but also to link the theoretical analyses to experimental characterisation of true kesterite films. From our perspective, the main challenges are: (i) to further understand theoretically how various defects diffuse, interplay, and form complexes; (ii) to describe how cluster formations on a meta- to microscopic scale impact the electronic band edges as well as the electron and hole transport; (iii) to better describe interfaces, grain boundaries, and non-equilibrium structures, and thereby explore defects located there by first-principles means; (iv) to develop accurate simulations of the defect and complex kinetics, to describe how defects diffuse and how they are captured during growth and post-processing; (v) to extend the study of high doping concentrations (i.e. alloying-like stoichiometry) and off-stoichiometric materials, especially at interfaces; and (vi) to simulate growth to guide synthesis of single-phase films of CZTS avoiding competing secondary compound formations.

Advances in science and technology to meet challenges. The advancement of infrastructure and systems for high-performance computing ensures even better modelling of material structures and configurations in the near future. Further development of first-principles computational models and methodologies is however required in order to more accurately describe the kinetics of defects. Improved accurate atomistic modelling with good scalability of system size and complexity, which can describe non-equilibrium and time-dependent systems, will

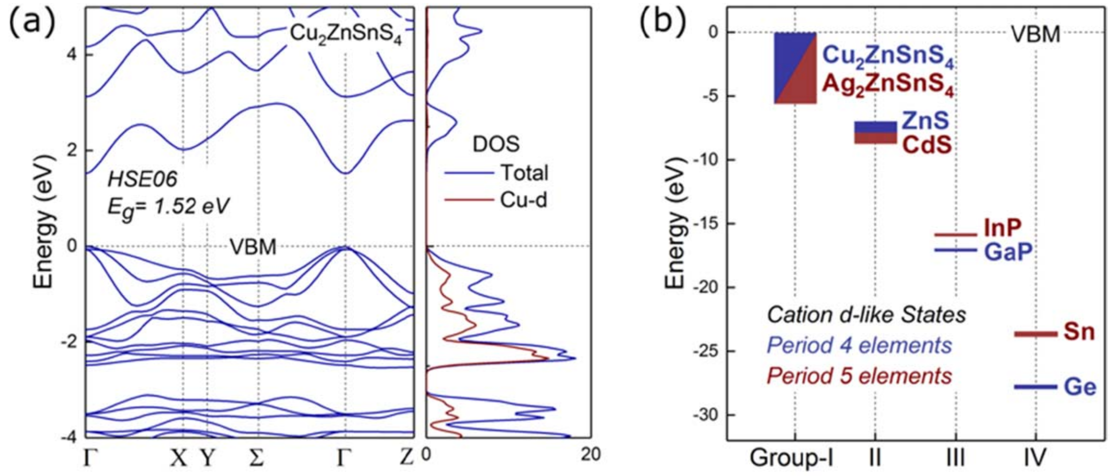

Figure 3. (a) CZTS electronic band structure and density of states (DOS in units of (eV × primitive cell)$^{-1}$). (b) The energy positions of cation d-orbital projected states in related cubic-like semiconductors. Energies refer to the valence band maximum (VBM).

be necessary to meet the challenges to study realistic CZTS structures and better connect the theoretical analyses with experimental characterisation. Computational screening of off-stoichiometric, polycrystalline, disorder, grain boundaries, and non-ground state configurations combined with full thermodynamic analyses is a necessary process in such studies. Machine learning can be a tool for such screening, although in the end it is the first-principles calculations that can describe the electronic structures and the defect physics properly.

Concluding remarks. While the native point defects in CZTS are fairly well known from a theoretical point of view, the formation and the kinetics of intrinsic complexes need to be more systematically explored, especially for the grain boundary regions. Complexes and cluster formations can locally act as defect and carrier traps, and at high concentrations they can also form electronic defect bands that directly affect the open-circuit voltage. In order to better link future theoretical analyses and predictions with experimental characterisation of realistic CZTS materials and structures, simulations of defect and complex kinetics under realistic crystalline conditions are required. This would necessitate non-equilibrium thermodynamic modelling of growth processes and of defect formation at grain boundaries and interfaces. This research direction aims towards a deeper understanding of complex defect physics, which also can provide a path to tailor-make optimised material structures and prevent degradation of solar cell performance.

Acknowledgments

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3. Optical modelling of materials and solar cells

Zacharie Jehl[1], **Maykel Courel**[2]
[1]Institut de Recerca en Energia de Catalunya (IREC), Jardins de les Dones de Negre, 1, 2ª pl., 08930 Sant Adrià de Besòs, Barcelona, Spain
[2]Centro Universitario de los Valles (CUValles), Universidad de Guadalajara, Carretera Guadalajara-Ameca Km. 45.5, C.P. 46600, Ameca, Jalisco, Mexico

Status. Reports on optical modelling of kesterite photovoltaic devices are comparatively rare, as the most glaring issue with this technology has historically been related to a larger than expected voltage deficit and is thus addressed from an electrical point of view. Moreover, having a high optical absorption coefficient and no immediate limitation from critically scarce materials, light trapping and ultrathin layers for kesterite absorbers have not been leading research pathways. The optical modelling of kesterite-based solar cells has been tackled following two main directions. Firstly, optical modelling has been used as a complement to the characterisation of relevant material properties, such as band gap, absorption coefficient, and other optical characteristics of state-of-the-art films. Secondly, the optical modelling of complete solar cell stacks was addressed mostly with the objective to increase the photocurrent by eliminating parasitic absorptions from other layers, and one-dimensional (1D) transfer matrix approaches have been the leading technique in that regard. A bulk of the research focussing on the determination of the optical properties of kesterite material was made from an experimental view point rather than through numerical analysis. In a landmark study, Raulot *et al* [20] used *ab initio* calculations to determine the properties of different kesterite compounds which are nowadays thoroughly investigated experimentally. On the other hand, optical constants of kesterites such as the complex dielectric constant and band gap bowing parameter as a function of the S/Se ratio have been reported [4, 21, 22]. Recently, the most complete optical model to date of a CZTS solar cell stack was realised to determine the optical constants of the material by spectroscopic ellipsometry [23], where the surface roughness, surface/interface segregation, and MoS_x layer for SLG/Mo/CZTS samples were identified as important features. However, additional work is required concerning solar cell simulation from an optical view point, evaluating the use of light trapping and ultrathin layers to promote device performance.

Current and future challenges. The radiative limit constitutes the simplest optical model to understand device-limiting factors, considering only losses from band-to-band transitions. An ideal buffer semiconductor is assumed and all photogenerated electron-hole pairs contribute to photocurrent density. Furthermore, contributions from series and shunt resistances and photon reflection are neglected. Figure 4 illustrates results on efficiency (η), short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (*FF*) of CZTSSe solar cells as functions of the S/(S + Se) compositional ratio considering an absorber thickness of 2 μm. Details of the calculation procedure and parameters can be found in the literature [24, 25]. Under the radiative limit, efficiency values in the range of 26.3%–29.6% are expected, markedly higher than the experimental values reported for this technology. In addition, J_{sc} values in the range of 29–48 mA cm^{-2} and V_{oc} values in the range of 0.657–1.109 V are predicted depending on the S/(S + Se) compositional ratio. For record CZTS and $Cu_2ZnSnSe_4$ (CZTSe) solar cells, J_{sc} values of 19.5 mA cm^{-2} and 40.6 mA cm^{-2} have been reported, respectively, with the use of an anti-reflection coating [26, 27]. Close to 10 mA cm^{-2} is thus lost from parasitic absorptions from other layers (mainly buffer) and photon reflection, as well as defect-related bulk and interfacial electron-hole recombination. Therefore, a buffer layer with a higher band gap than that of CdS and with good lattice-matching and band alignment with the kesterite is required for higher J_{sc} values. Another strategy could be the use of light trapping to promote J_{sc} values. On the other hand, V_{oc} values of 661 mV and 423 mV have been experimentally reported [26, 27] for CZTS and CZTSe, respectively, much lower than the values expected for these solar cells under the radiative limit. Particularly, CZTS cells suffer from a higher V_{oc} deficit, resulting from the non-ideal CdS buffer layer—cliff-like band alignment and CdS/CZTS defect formation due to lattice mismatching [25]. Finally, *FF* values of 65.8% and 67.3% have been measured for CZTS and CZTSe [26, 27], respectively, somewhat lower than the ones expected under the radiative limit (84%–89%), suggesting thereby the need to replace Mo as the back contact.

Advances in science and technology to meet challenges. As the basic optical properties of kesterite compounds have been well known for nearly two decades, modelling of complete solar cells is possible using standard numerical tools, with much of the work relying on 1D modelling. A planar model was used by Winkler *et al* [28] to simulate potential improvements of CZTSe solar cells, specifically by optimising the front layers. The method, labelled the 'scattering matrix technique', is derived from the standard transfer matrix approach including a scattering component. The authors identified optimum conditions for the CdS and ITO thicknesses maximising the current, by comparing the transmitted and reflected radiation. The minimisation of reflectivity surprisingly

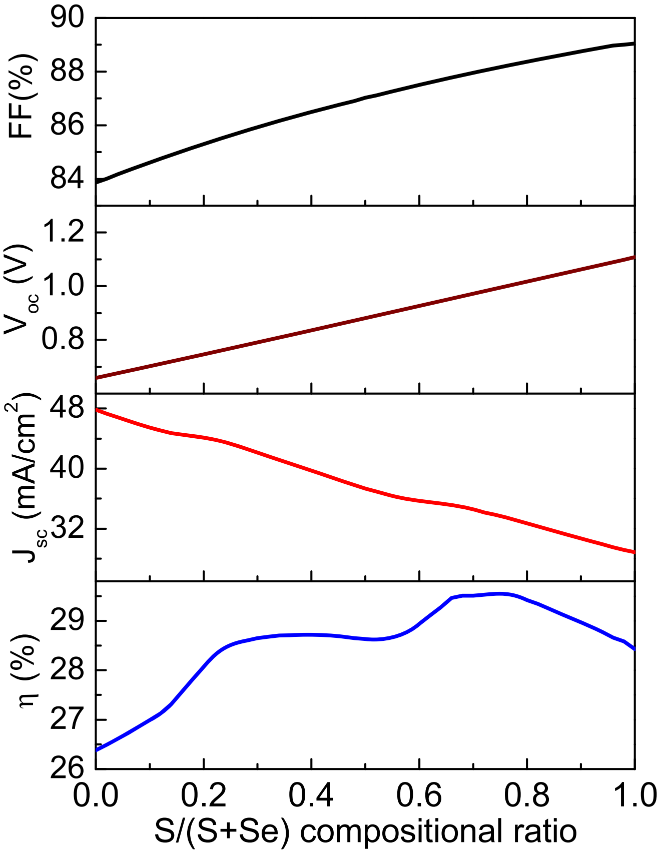

Figure 4. Efficiency (η), short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) values of CZTSSe solar cells as functions of the S/(S + Se) compositional ratio.

did not yield the highest efficiency, and the authors emphasised instead the importance of the front window transmissivity as the main lever maximising photogeneration. Another landmark work focussing on optimising the current of the cell by evaluating combinations of different thicknesses of CdS and ITO front layers using a modified transfer matrix model was published [29]. With CdS thickness becoming unrealistic to reduce below a certain threshold, the authors recommend the utilisation of a thinner and more transparent ITO layer, although they mention that it could become problematic for scaling up devices. Similar results have been obtained in the CIGS community, which led to the development of Zn-based buffer layers with a wider band gap currently holding the highest reported efficiency for this technology. Gorji [30] followed a somewhat similar approach, by quantifying the optical losses (absorption and reflection) in a CZTS solar cell. A combination of a ITO/TiO_2 nanoparticle window layer and In_2S_3 buffer layer was found to maximise the cell's current as compared to the more standard CdS/ITO stack. Again, transmission of the front layer was the critical parameter requiring optimisation rather than aiming at minimising the reflection. Other approaches consider the use of light trapping and ultrathin layers. Frisk *et al* [31] studied the influence of the absorber thickness on the photovoltaic performances and showed a current saturation for absorbers thicker than approximately 1 μm. In the ultrathin regime (less than 500 nm), efficiency and all photovoltaic parameters are affected by the back contact recombination as is established in CIGSSe technologies. More importantly, this study highlights that despite the absorption coefficient of kesterite films, thick layers (above 1 μm) are necessary to unlock the full potential of the material if an increased carrier diffusion length is achieved and interface recombination issues can be alleviated by the fabrication of higher quality materials. Hence, and if the electrical limitations of current materials are addressed, this paper brings interesting insights on optical pathways to further increase the efficiency. As light trapping could become a necessity in that context, works investigating the modelling of nanostructured CZTS could become of particular interest in the near future.

Concluding remarks. An untapped potential of 10 mA cm^{-2} short-circuit current increase still exists in kesterite solar cell technology. Particularly, buffer layer transmissivity represents in our opinion a clear pathway for improvements of the kesterite technology, and with alternative buffer layers representing the main lever to increase J_{sc}, optical modelling of alternative CZTSSe solar cell stacks will become necessary to fully evaluate the potential of this technology in a more optimised configuration. In that sense, it is in our opinion necessary for the kesterite community to follow the tracks of past research in CIGSSe absorbers as both technologies face similar issues in that regard. Additionally, light trapping, ultrathin layers, and the use of nanostructured materials are interesting pathways despite the excellent optical properties of kesterite films, and one that the technology will eventually follow to broaden its field of application.

Acknowledgments

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4. Kesterite device modelling and optimisation

Johan Lauwaert[1], **Sanghyun Lee**[2]
[1]Department of Electronics and Information Systems, Ghent University, Zwijnaarde B-9052, Belgium
[2]Department of Electronics and Computer Engineering Technology, Indiana State University, Terre Haute, IN, 47809, USA

Status. The optoelectrical device modelling of kesterite devices has been developed to optimise device parameters with predictable outputs by controlling inputs based on empirical and theoretical materials and device characteristics. Three categories are studied to elucidate the loss mechanism of devices (see figure 5): (a) a heterojunction interface recombination (CdS/CZTSSe absorber), (b) CZTSSe bulk recombination, and (c) a back contact interface recombination (Mo/$MoSe_2$/CZTSSe absorber). Foremost, the carrier recombination at the heterojunction interface severely degrades device performance. The 12.6% champion device has demonstrated a triangular shape of quantum efficiency, implying a strong carrier collection loss at the heterojunction interface. In a simulation study, the interface recombination velocity is estimated to be approximately 10^5 cm s^{-1}, based on quantum efficiency measurements [32]. Hence, extensive modelling of the heterojunction interface has been focussed on optimising the interface band offset, improving defective CdS buffer layers, and investigating alternative buffer/window layers. Another primary recombination path is CZTSSe bulk recombination, which is explored by modelling intrinsic bulk defect states and the attending increases in saturation current/diode quality factors. Even with high-efficiency devices, carrier lifetimes are extremely low (a few ns), which is an order of magnitude smaller than typical CIGSSe devices (30–100 ns) [33]. Most research focusses on modelling and characterising devices with deep defect states in the CZTSSe absorber layers, which can provide the trend of recombination in the quasi-neutral region but also give information on severe interface recombination in the space charge region, aggravated by grain boundaries and secondary phase defects. Modelling recombination at the back contact interface is done by considering a Schottky back contact associated with Mo, a $MoSe_2$ interfacial layer, and a CZTSSe absorber. Unlike CIGSSe devices, in CZTSSe these components yield thermodynamically unstable back contact interfaces.

Although modelling and characterisation by isolating each of the three categories' properties is not trivial, numerical simulators such as TCAD [32], SCAPS [34], and PC1D [35] can provide further insight with the support of empirical results. To optimise modelling and simulation results, the main characterisation methods are time-resolved photoluminescence, photoluminescence, quantum efficiency, admittance spectroscopy (AS), deep-level transient spectroscopy, capacitance-voltage, and current-voltage methods, while varying temperature, frequency, light intensity, and light/voltage biases.

Current and future challenges. Although these three categories of recombination described above are a good classification of the possible mechanisms that impact on the performance, these models contain a large number of parameters. Therefore, the main challenge is to find an adequate description for the generation and recombination profile throughout the whole solar cell structure. As for the fabrication of devices, the modelling benefits from the experience from CIGSSe devices. For the fabrication, this has resulted in similar deposition methods for the buffer and window, while for electronic modelling often optical and electronic parameters for these films (buffer, window, and back contact) can be used from the available CIGSSe models [36]. However, due to the deposition of the different absorber film the exact properties of these layers might be different. Moreover, changes in the properties are expected for production in different laboratories. The aim in modelling might therefore be to estimate these parameters based on the characterisation methods, ideally on devices, but progress can also be made on individual films or crystals [37]. On one hand, this increases the number of parameters that can be adjusted to describe the experiments but on the other hand opens the perspective to determine these parameters and optimise the back contact, buffer, and window matching the properties of the specific kesterite absorber [38]. Adequate modelling should therefore be able to mimic all the features in these characterisation methods, and estimate the uncertainty of each of the parameters. Such a methodology would lead to an understanding of which mechanism is limiting the performance, and offer the key to improve the performance of kesterite solar cells. Unfortunately, this methodology cannot be transferred from another solar cell technology. Moreover, this becomes even more challenging when more mechanisms in parallel have an impact on the solar cell performance, which is the expected situation even for the champion device of 12.6% [39]. Finding a unique model is more achievable for efficiencies close to the theoretical limit and it is therefore understandable that progress can be made by explaining experimental features based on numerical modelling.

Advances in science and technology to meet challenges. There has been some progress in understanding the back contact properties through modelling and characterisation. The unstable back contact interface near CZTSSe/Mo preferentially forms the interfacial $MoSe_2$ layer. Hence, one of the efforts to optimise a back contact interface

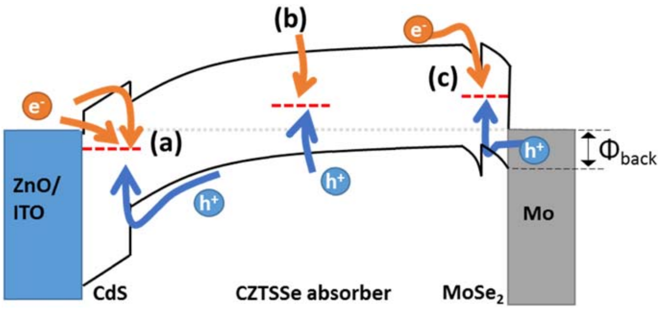

Figure 5. Three primary areas of electron-hole recombination paths in kesterite solar cells for device modelling and characterisation.

is to add a thin intentional $MoSe_2$ layer at the CZTSSe/Mo interface. A modelling study suggests that a big hole Schottky barrier (0.55 eV) is split into two small barriers (0.29 and 0.26 eV) by adding a thin $MoSe_2$ layer ($>$100 nm) due to metal workfunction and band alignment [40]. Further optimisation of back contact interfaces can be achieved through a tunnel junction of hole carriers or an electron reflector-like intermediate layer (MoO_3). To provide the interface stability, intermediate layers such as ZnO, TiN, and TiB need to be further developed and optimised.

The heterojunction interface has been extensively studied in an effort to reduce the severe interface recombination. The spike-like conduction band offset (CBO) (larger CdS electron affinity than CZTSSe) below 0.4 eV can suppress interface recombination without compromising J_{sc}. Another finding is photoconductive deep defects near the CdS/CZTSSe interface associated with Cd, which degrades CBO and causes a red-kink of the J–V response [41]. Hence, Cd-free alternative buffers such as ZnO, ZnS, In_2S_3, and (Zn,Mg)O with CBO less than 0.4 eV can minimise the interface recombination and red-kink, which also can improve the V_{oc} deficit. Regarding the optimisation of the CdS/CZTSSe interface through the absorber, a Cu replacement in the absorber such as Ag can improve V_{oc} by reducing Cu-related defects and Fermi level pinning at the interface with higher V_{oc}. From the single crystalline absorber study without grain boundary effects, interface recombination and the bulk minority carrier lifetime of the absorber are required to be improved. The bulk minority carrier lifetime is estimated to be between 2 and 7 ns with minority diffusion length 2.1 μm [32]. To improve the minority carrier lifetime and reduce bulk recombination, passivating bulk defects and associated interface defects is required. Furthermore, a systematic study of the impact of passivating bulk, grain boundary, and interface defects on device parameters is needed when the activation process is introduced to optimise the CZTSSe absorber.

Concluding remarks. Electrical modelling nowadays supports the fabrication of solar cell devices, which is mainly driven by improving the performance. Even more than other technologies, device fabrication strongly benefits from the experience researchers have gained from the development of CIGSSe. Consequently, models that propose explanations for recombination mechanisms that influence performance are in part based on existing models for CIGSSe. Although these results are extremely valuable and have given good insight into the fundamental electronic properties of the kesterite absorbers and potential recombination mechanisms, the community is still lacking a comprehensive model that can explain a sufficiently wide range of experimental observations. Such a model would offer the key understanding of which mechanism is limiting the performance and therefore be capable of optimising the buffer, window, and back contact in line with the electronic and optical properties of the kesterite absorber.

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ORCID iDs

Samantha N Hood https://orcid.org/0000-0001-9815-6289
Aron Walsh https://orcid.org/0000-0001-5460-7033
Clas Persson https://orcid.org/0000-0002-9050-5445
Mukesh Kumar https://orcid.org/0000-0003-1724-4880
Maykel Courel https://orcid.org/0000-0001-9149-3506

References

[1] Goodman C H 1964 A systematic method of deriving new semiconducting compounds by structural analogy *J. Phys. Chem. Sol.* **25** 675
[2] Wagner S and Bridenbaugh P M 1977 Multicomponent tetrahedral compounds for solar cells *J. Cryst. Growth* **39** 151
[3] Ito K and Nakazawa T 1988 Electrical and optical properties of stannite-type quaternary semiconductor thin films *Jap. J. Appl. Phys.* **27** 2094
[4] Walsh A, Chen S, Wei S-H and Gong X G 2012 Kesterite thin-film solar cells: advances in materials modelling of Cu_2ZnSnS_4 *Adv. Energy Mater.* **2** 400
[5] Park J, Kim S, Xie Z and Walsh A 2018 Point defect engineering in thin-film solar cells *Nat. Rev. Mater.* **3** 194
[6] Alberi K *et al* 2019 The 2019 materials by design roadmap *J. Phys. D: Appl. Phys.* **52** 013001
[7] Bourdais S *et al* 2016 Is the Cu/Zn disorder the main culprit for the voltage deficit in kesterite solar cells? *Adv. Energy Mater.* **6** 1502276
[8] Kim S, Park J and Walsh A 2018 Identification of killer defects in kesterite thin-film solar cells *ACS Energy Lett.* **3** 496
[9] Li J, Yuan Z, Chen S, Gong X G and Wei S-H 2019 Effective and non-effective recombination-center defects in Cu_2ZnSnS_4: significant difference in carrier-capture cross sections *Chem. Mater.* **31** 826
[10] Kim S, Park J, Hood S N and Walsh A 2019 Lone-pair effect on carrier capture in Cu_2ZnSnS_4 solar cells *J. Mater. Chem.* A **7** 2686
[11] Persson C 2010 Electronic and optical properties of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ *J. Appl. Phys.* **107** 053710
[12] Chen S, Walsh A, Gong X-G and Wei S-H 2013 Classification of lattice defects in the kesterite Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ earth-abundant solar cell absorbers *Adv. Mater.* **25** 1522
[13] Lafond A, Choubrac L, Guillot-Deudon C, Deniard P and Jobic S 2012 Crystal structures of photovoltaic chalcogenides, an intricate puzzle to solve: the cases of CIGSe and CZTS materials *Z. für Anorg. Allg. Chem.* **638** 2571
[14] Scragg J J S, Larsen J K, Kumar M, Persson C, Sendler J, Siebentritt S and Platzer-Björkman C 2016 Cu–Zn disorder and band gap fluctuations in $Cu_2ZnSn(S,Se)_4$: theoretical and experimental investigations *Phys. Status Solidi* b **253** 247
[15] Wallace S K, Frost J M and Walsh A 2019 Atomistic insights into the order-disorder transition in Cu_2ZnSnS_4 solar cells from Monte Carlo simulations *J. Mater. Chem.* A **7** 312
[16] Huang D and Persson C 2013 Band gap change induced by defect complexes in Cu_2ZnSnS_4 *Thin Solid Films* **535** 265
[17] Giraldo S, Jehl Z, Placidi M, Izquierdo-Roca V, Pérez-Rodríguez A and Saucedo E 2019 Progress and perspectives of thin film kesterite photovoltaic technology: a critical review *Adv. Mater.* 1806692
[18] Grini S, Sopiha K V, Ross N, Liu X, Bjørheim T S, Platzer-Björkman C, Persson C and Vines L 2019 *Adv. Energy Mater.* **9** 1900740
[19] Zawadzki P, Zakutayev A and Lany S 2015 Entropy-driven clustering in tetrahedrally bonded multinary materials *Phys. Rev. Appl.* **3** 034007
[20] Raulot J M, Domain C and Guillemoles J F 2005 *Ab initio* investigation of potential indium and gallium free chalcopyrite compounds for photovoltaic application *J. Phys. Chem. Solids* **66** 2019
[21] León M, Levcenko S, Serna R, Gurieva G, Nateprov A, Merino J M, Friedrich E J, Fillat U, Schorr S and Arushanov E 2010 Optical constants of Cu_2ZnGeS_4 bulk crystals *J. Appl. Phys.* **108** 093502
[22] Chen S, Walsh A, Yang J-H, Gong X G, Sun L, Yang P-X, Chu J-H and Wei S-H 2011 Compositional dependence of structural and electronic properties of $Cu_2ZnSn(S,Se)_4$ alloys for thin film solar cells *Phys. Rev.* B **83** 125201
[23] Li S-Y, Hägglund C, Ren Y, Scragg J J S, Larsen J K, Frisk C, Rudisch K, Englund S and Platzer-Björkman C 2016 Optical properties of reactively sputtered Cu_2ZnSnS_4 solar absorbers determined by spectroscopic ellipsometry and spectrophotometry *Sol. Energy Mater. Sol. Cells* **149** 170
[24] Jiménez T, Seuret-Jiménez D, Vigil-Galán O, Basurto-Pensado M A and Courel M 2018 $Sb_2(S_{1-x}Se_x)_3$ solar cells: the impact of radiative and non-radiative loss mechanisms *J. Phys. D: Appl. Phys.* **51** 435501
[25] Courel M and Vigil-Galan O 2018 Different Approaches for Thin Film Solar Cell Simulation *Advanced Ceramic and Metallic Coating and Thin Film Materials for Energy and Environmental Applications* ed J Zhang and Y G Jung (Berlin: Springer)
[26] Shin B, Gunawan O, Zhu Y, Bojarczuk N A, Chey S J and Guha S 2013 Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant Cu_2ZnSnS_4 absorber *Prog. Photovoltaics Res. Appl.* **21** 72
[27] Lee Y S, Gershon T, Gunawan O, Todorov T K, Gokmen T, Virgus Y and Guha S 2015 $Cu_2ZnSnSe_4$ thin-film solar cells by thermal Co-evaporation with 11.6% efficiency and improved minority carrier diffusion length *Adv. Energy Mater.* **5** 1401372
[28] Winkler M T, Wang W, Gunawan O, Hovel H J, Todorov T K and Mitzi D B 2014 Optical designs that improve the efficiency of $Cu_2ZnSn(S,Se)_4$ solar cells *Energy Environ. Sci.* **7** 1029
[29] Cozza D, Ruiz C M, Duché D, Giraldo S, Saucedo E, Simon J J and Escoubas L 2016 Optical modeling and optimizations of $Cu_2ZnSnSe_4$ solar cells using the modified transfer matrix method *Opt. Express* **24** A1201
[30] Gorji N E 2014 Quantitative analysis of the optical losses in CZTS thin-film semiconductors *IEEE Trans. Nanotechnol.* **13** 743
[31] Frisk C, Ren Y, Li S and Platzer-Björkman C 2015 CZTS solar cell device simulations with varying absorber thickness *2015 IEEE 42nd Photovoltaic Specialist Conf. (PVSC)* 1–3
[32] Pu A, Ma F, Yan C, Huang J, Sun K, Green M and Hao X 2017 Sentaurus modelling of 6.9% Cu_2ZnSnS_4 device based on comprehensive electrical & optical characterization *Sol. Energy Mater. Sol. Cells* **160** 372
[33] Polizzotti A, Repins I, Noufi R, Wei S and Mitzi D 2013 The state and future prospects of kesterite photovoltaics *Energy Environ. Sci.* **6** 3171
[34] Burgelman M, Nollet P and Degrave S 2000 Modelling polycrystalline semiconductor solar cells *Thin Solid Films* **361–362** 527
[35] Clugston D A and Basore P A 1997 PC1D Version 5: 32-bit solar cell modelling on personal computers *Proc. 26th IEEE Photovoltaic Specialist Conf.* (Anaheim) pp 207–10
[36] Pianezzi F, Reinhard P, Chirila A, Bissig B, Nishiwaki S, Buecheler S and Tiwari A N 2014 Unveiling the effects of post-deposition treatment with different alkaline elements on the electronic properties of CIGS thin film solar cells *Phys. Chem. Chem. Phys.* **16** 8843

[37] Hajdeu-Chicarosh E 2018 Variable-range hopping conduction in the kesterite and wurtzstannite Cu_2ZnGeS_4 single crystals *Surf. Eng. Appl. Electrochem.* **54** 279

[38] Yan C, Liu F Y, Sun K W, Song N, Stride J A, Zhou F Z, Hao X J and Green M 2016 Boosting the efficiency of pure sulphide CZTS solar cells using the In/Cd based hybrid buffers *Sol. Energy Mater. Sol. Cells* **144** 700

[39] Siebentritt S 2013 Why are kesterite solar cells not 20% efficient? *Thin Solid Films* **535** 1

[40] Cozza D, Ruiz C M, Duche D, Simon J J and Escoubas L 2016 Modeling the back contact of $Cu_2ZnSnSe_4$ solar cells *IEEE J. Photovoltaics* **6** 1292

[41] Neuschitzer M, Sanchez Y, Marino S, Xie H, Fairbrother A, Placidi M, Haass S, Roca V, Rodriguez A and Saucedo E 2015 Optimization of CdS buffer layer for high-performance $Cu_2ZnSnSe_4$ solar cells and the effects of light soaking: elimination of crossover and red kink *Prog. Photovoltaics* **23** 1660