Why are kesterite solar cells not 20% efficient?

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Although kesterite solar cells show the same range of band gaps as the related chalcopyrites, their efficiencies have so far reached only 10%, compared to 20% for the chalcopyrites. A review of the present literature indicates that several non-ideal recombination channels pose the main problem: (i) recombination at the interface between the kesterite and the CdS buffer. This is very likely due to an unfavourable cliff-like band alignment between the absorber and the buffer. However, for pure selenide absorbers, this recombination path is not dominating, which could be due to a spike-like band alignment at the absorber-buffer interface. (ii) A second major recombination becomes obvious in a photoluminescence maximum well below the band gap, even in record efficiency absorbers. This is either due to a very high density of defects, comparable to the density of states in the band, or to stannite inclusions. In view of the phase diagram, secondary phases are not likely the source of the low energy emission. Only in sulphide kesterite a non-stoichiometric SnS phase could also cause this low energy radiative recombination.

1. Kesterite solar cells

Kesterites $Cu_2ZnSnS(e)_4$ (CZTSSe) are investigated intensively as an alternative absorber material in thin film solar cells, that contains only non-toxic and Earth abundant elements. The solar cell structure is simply adapted from the related chalcopyrites $Cu(In,Ga)Se_2$ (CIGS) solar cells [1-4] with a Mo back contact, a CdS buffer layer and a ZnO window. Kesterite solar cells have reached above 10% efficiency [1], while chalcopyrites are more than 20% efficient [5]. The aim of this review is to investigate the most likely loss mechanisms in kesterite solar cells.

The best kesterite solar cell made so far is a sulphide-selenide alloy $Cu_2ZnSn(S,Se)_4$ [1] with an S/(S+Se) ratio of about 40%, a band gap, as determined by quantum efficiency measurements, of 1.15 eV and an efficiency of 10.1%. This band gap value is very close to the band gaps of the record chalcopyrite cells [5, 6]. The best pure sulphide Cu_2ZnSnS_4 cell is made like the record cell by precursor-annealing process and reaches an efficiency of 8.4% [3]. Whereas the best selenide $Cu_2ZnSnSe_4$ cell is made by a co-evaporation process and reaches an efficiency of 9.15% [2]. The photovoltaic parameters of the record cells are summarised in table 1.

2. Loss mechanisms

2.1. Comparison with the Shockley-Queisser limit

Although the Shockley-Queisser (SQ) limit [9] is an unrealistic limit for solar cell efficiencies it can be used to estimate the role of different loss mechanisms. By comparing the parameters of the solar cells with the ideal SQ parameters in table 1 it is evident that the more severe losses are in the open circuit voltage and in the fill factor than in the current. This is even more acute since one unavoidable loss in solar cells that is ignored in the SQ considerations are the optical losses, i.e. the fact that the quantum efficiency of a solar cell is smaller than 1. Optical losses in kesterite or chalcopyrite thin film solar cells contain the grid shadowing, the reflection by the ZnO window (which can be largely avoided by an antireflection coating, as was used in all solar cells listed in table 1), the absorption in the ZnO window and the CdS buffer [10]. Since these losses are very similar in CIGS solar cells, we can just assume the same ratio of optical losses for the kesterite solar cells. These are the lines labelled "SQ w/ loss" in table 1. There the current is reduced by 15% due to optical losses [11]. If optical losses were the only loss mechanism, the other parameters would hardly be influenced. The reduction by 15% regardless of the band gap overestimates the losses a bit for the higher band gaps (as in the sulphide cell) and underestimates them a bit for the lower band gaps (as in the selenide cell). As expected the current loss in CIGS solar cells can be fully attributed to the optical losses, whereas the current in all kesterite cells is further reduced. One can speculate that this can be due to further optical losses due to higher reflexion at interfaces due to different dielectric constants of kesterites and chalcopyrites which remains to be investigated. More likely are collection losses, which are evident from the quantum efficiency spectra of all three kesterite record cells [1-3]: they do not show a box-like shape with a steep increase at the band gap, but rather an almost triangular shape with a

gradual slope at the band gap. These collection losses are due to a short collection length [12], which is the sum of the space charge width and the diffusion length [13]. However, the losses in open circuit voltage and, associated with it, the fill factor are more severe. They are due to additional recombination paths. The only loss mechanism considered in the SQ model is radiative recombination in the neutral zone of the absorber. Recombination paths that reduce the efficiency, in particular the open circuit voltage and the fill factor, below the SQ values are Shockley-Read-Hall recombination in the neutral zone or in the space charge region or recombination at the interface between the absorber and the buffer or the buffer and the window. Access to the recombination mechanism is possible via the reverse saturation current j_0 [12]. The room temperature values of this parameter are also summarised in table 1. What is obvious is that the values of the kesterite solar cells are many orders of magnitude higher than the SQ values, but also still many orders of magnitude higher than the chalcopyrite solar cells, indicating that strong recombination paths are present in kesterite solar cells.

2.2. Activation energy of the recombination path

To locate where the recombination takes place one can investigate the activation energy of the reverse saturation current [12], which corresponds to the activation energy of the recombination rate of the main recombination path in the device. In most cases it is given by the band gap of the absorber, however, if the main recombination path is at the interface and if the effective band gap at the interface is lower than the absorber band gap or if Fermi level pinning occurs at the interface, than the activation energy of the reverse saturation current will be lower than the absorber band gap. The former occurs when the

conduction band minimum of the buffer is lower than the conduction band minimum of the absorber, a so called cliff configuration [12]. The activation energy can be determined from the temperature dependence of the saturation current, if the diode quality factor remains constant with temperature, or, usually more easy, from the extrapolation of the temperature dependence of the open circuit voltage to 0 K. The activation energies have been determined for a number of CZTSSe solar cells [7] with varying S/(S+Se) ratios, but all containing sulphur. In all cases was the activation energy lower than the band gap by 200 to 400 meV. The record kesterite cell also shows an activation energy lower than the band gap by 180 meV [1]. However, in a recent comparison of S-containing and S-free kesterite cells [8] it was shown, that in pure selenide cells, the activation energy equals the band gap, whereas S-containing cells show an activation energy lower than the corresponding band gap. All these observations can be easily explained by a model that assumes a cliff-like band alignment at the absorber-CdS buffer interface for sulphide and most S-containing kesterites and a spike-like band alignment for pure selenide kesterites. Currently the band alignment is somewhat disputed. Two experimental studies exist, one finds a spike in all cases independent of the S/(S+Se) ratio [14], another one finds a cliff for pure sulphide absorbers [15]. However, the former one depends on the achievement of flat-band conditions under illumination, which might not be the case and would strongly influence the results. There are also two theoretical studies: one finds a spike like configuration [16], the other one a cliff for the sulphide kesterite [17] and a spike for selenides [18]. The observed differences in the recombination path between pure selenide absorbers and S-containing ones strongly support a cliff at the interface of sulphur containing absorbers and a spike at the interface of pure selenide absorbers. If one

assumes that the cliff like configuration for the sulphide absorber is correct and if one further assumes that the conduction band minimum of the selenide compound is lower than that of the sulphide compound, because of the lower band gap, thus creating a spike configuration, then the differences between solar cells with sulphur containing absorbers and those with pure selenide absorbers can be explained. Thus, most likely, the sulphur containing absorbers have a cliff at the interface with the CdS buffer, which reduces the interface bandgap and thus lead to interface recombination with a smaller energy difference than the band gap. Whereas the pure selenide absorbers show a spike at the CdS interface, which makes interface recombination less likely and in any case leads to an activation energy of the recombination path equal to the band gap. One can thus conclude that CdS is a suitable buffer for selenide kesterites, however not the ideal choice for sulphur containing absorbers.

2.3 Bulk recombination

However, interface recombination is not the only recombination problem of kesterite absorbers. They show a radiative recombination at an energy smaller than the band gap. Room temperature photoluminescence spectra are available [1-3]. Normally in a semiconductor with a low defect density the spectral maximum of the luminescence at room temperature is slightly higher than the band gap [19, 20]. In all sulphide containing record solar cells, however, the luminescence maximum is lower than the band gap by 20 to 200 meV. Such low maximum energy of the radiative recombination indicates a high density of states at this energy, which will also limit the open circuit voltage [21]. At the moment, one can only speculate on the origin of these states: it could be electronic

defects in the band gap with a very high density of states, comparable to the effective density of states in the bands, or inclusions of secondary phases with lower band gap or inclusions of another crystal modification, namely stannite, which is predicted to have a lower band gap than kesterite [22]. If one extrapolates the QE spectrum of the selenide record cell one finds a band gap of about 0.9 eV, below the maximum of the luminescence spectrum [2]. It is interesting to note that also the pure Se absorber in ref [8] shows a PL maximum slightly above the band gap energy as determined from the QE spectrum. These two examples could indicate that the low energy radiative recombination is only a problem in sulphur containing absorbers.

Whatever the source of this low energy radiative recombination is, it will also reduce the activation energy of the radiation path in the bulk. Thus to decide whether the dominating recombination path is at the interface or in the bulk the activation energy of the recombination rate has to be compared with the maximum of the room temperature luminescence. The data needed for this comparison is only available for the record solar cell [1]. Here the activation energy of the recombination path is 180 meV below the band gap determined from the quantum efficiency spectrum, whereas the luminescence maximum energy is only 20 meV lower than the QE band gap. This still supports interface recombination as the dominating recombination path.

2.4 Comparison with the phase diagram

To investigate the possible role of secondary phases an investigation of the phase diagram can be helpful. The phase diagram in Fig. 1 is adapted from [23]. It is assumed that the phase diagram is essentially the same for the selenide and the sulphide

compounds. The kesterite existence region according to [23] and [24] is indicated by a small blue ellipse in the centre. Along the blue lines two phase regions exist: kesterite + $ZnS(e)$, kesterite + $SnS(e)_2$, kesterite + $Cu_2SnS(e)_3$, kesterite + $Cu_2S(e)$. Within the triangles in between three phases coexist. One can probe the validity of the phase diagram by summarising the secondary phases observed in the literature. This is depicted in fig. 1: green circles indicate observations of an additional $ZnS(e)$ phase [3, 25-28], blue down triangles the observation of an additional $SnS(e)_2$ phase [27, 29, 30], red up triangles the observation of a $Cu_xS(e)$ phase [25, 29-32]. Basically all these observations are in agreement with the phase diagram. $Cu_xS(e)$ phases have been observed also above the kesterite-$ZnS(e)$ tie line, in contradiction to the phase diagram, however, these observations were in films deposited at rather low temperatures [29, 31], which might be far from thermodynamic equilibrium, and are therefore not included in fig.1. $Cu_2SnS(e)_3$ has also been observed as a secondary phase [33, 34], however in these cases no over-all composition of the films was given, therefore they are not included in fig. 1. A conclusion of this literature study is that the phase diagram can be certainly used for orientation on the existence of secondary phases. It can therefore also be assumed that the $Cu_2SnS(e)_3$ phase is likely in Zn-poor material. Another phase cannot be included in the phase diagram, because it is off-stoichiometric with respect to the chalcogen: $SnS(e)$. This phase has been predicted to appear in kesterite films [35] and has been observed [30]. To judge how detrimental a secondary phase will be to the solar cell performance the band gap of the secondary phase can give a first orientation. The band gaps of the most likely secondary phases are summarised in table 2. If the secondary phase has a lower band gap than the actual absorber it will limit the open circuit voltage of the solar

cell. The presence of a material with a band gap lower by only 100 meV will reduce the maximum achievable efficiency by 8% absolute [21]. Secondary phases with band gaps lower than the corresponding kesterite phase are marked in red in table 2. In the sulphide system there are three secondary phases with lower band gap: the copper sulphide, the cupper tin sulphide and the tin monosulphide, whereas in the selenide system only one secondary phase has a lower band gap: the copper tin selenide. This could indicate that secondary phases are less detrimental in the selenide kesterite absorbers than in the sulphide kesterite absorbers. Secondary phases with higher band gaps are much less detrimental; however, they can block the transport when present in large amounts [26] or at least increase the series resistance [8]. One secondary phase to be avoided in any case is the ternary $Cu_2SnS(e)_3$. This could explain the composition range found for the best solar cells [45]. It is indicated in fig. 1 by a red ellipse. The composition of the three record solar cells is also found in this region. Following the phase diagram the most likely secondary phases in this composition region are $ZnS(e)$ and $SnS(e)_2$. The tin compound is unlikely to occur because it is volatile [46] and will evaporate in most preparation conditions. $ZnS(e)$ has a large band gap and is expected to be rather benign, if present in small amounts. The most detrimental phase, the ternary $Cu_2SnS(e)_3$ is not likely to occur in this composition region, at least according to the phase diagram. Additionally, it has been argued recently that the existence region extends into this range of compositions [47]. However, under normal preparation conditions the solar cell composition is not necessarily homogeneous, neither in depth [28, 48], nor laterally [33]. That the ternary phase can occur at the surface of Cu-poor, Zn-rich material, in

contradiction to the phase diagram, has been recently demonstrated [49]. It was also

shown that this phase can be etched from the surface by a bromine etch [49].

Having this in mind we can discuss again the likely sources of the low energy PL. It can

be concluded that the low energy luminescence is due to either defects with a very high

density of states, comparable to the effective density of states of the valence and

conduction band, or to inclusions of the stannite crystal modification or inclusions of the

$Cu_2SnS(e)_3$ phase, although the latter is unlikely according to the phase diagram. In the

sulphide kesterite it could also be caused by a SnS secondary phase, if the sulphur content

is non-stoichiometric.

3. Summary of the problems of kesterite solar cells

The efficiency of kesterite solar cells is limited by various non-ideal recombination paths.

They are manifested by an activation energy of the recombination path and the energy of

the luminescence maximum which both are smaller than the band gap. The low activation

energy of the recombination path is due to interface recombination. It occurs only in

sulphur containing kesterite solar cells, not in pure selenide devices. This difference can

be attributed to different band alignments at the kesterite-CdS interface: most likely a

cliff in the case of sulphide kesterite and a spike in the case of selenide kesterite. The low

energy of the luminescence maximum indicates a further detrimental, albeit radiative

recombination path in the bulk. This can be caused by an extremely high density of defect

states, by inclusions of the stannite crystal modification or - in the case of sulphide

kesterite only - by the presence of the non-stoichiometric secondary phase SnS.

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Figure caption:

Figure 1

Section of the phase diagram with the existence region (blue ellipse), the region where the best solar cells are made (red ellipse) and various secondary phases: $ZnS(e)$ (green circles), $Cu_2S(e)$ (red up triangles), $SnS(e)_2$ (blue down triangles)

Table captions:

Table 1

Overview of solar cell parameters of kesterite record cell and chalcopyrite record cells together with the Shockley-Queisser ideal parameters and Shockley-Queisser parameters, including optical losses

Table 2

Band gaps of the most likely secondary phases, marked in red are those phases that have smaller band gap than the corresponding kesterite compound

Table 1

Overview of solar cell parameters of kesterite record cell and chalcopyrite record cells together with the Shockley-Queisser ideal parameters and Shockley-Queisser parameters, including optical losses

cell	E_G/eV	η/%	V_{OC}/mV	j_{SC}/mAcm^{-2}	FF	j_0/Acm^{-2}
record CZTSSe	1.15	10.1	517	30.8	64	10^{-5}
SQ	1.15	32.8	887	42	89	10^{-16}
SQ w/ loss	1.15	28	887	36	89	10^{-16}
CIGS ZSW	~1.15	20.3	730	35.7	78	$4 \cdot 10^{-11}$
CIGS NREL	~1.15	20.0	690	35.5	81	$2 \cdot 10^{-12}$
sulphide CZTS	1.5	8.4	661	19.5	66	10^{-7} *
SQ	1.5	31.5	1210	29	91	10^{-22}
SQ w/ loss	1.5	27	1210	25	91	10^{-22}
selenide CZTSe	1.0	9.15	377	37.4	65	10^{-5} *
SQ	1.0	30.9	748	48	88	10^{-14}
SQ w/ loss	1.0	26	748	41	88	10^{-14}

* these values are not directly from the record devices but typical values found in literature [7, 8]

Table 2

Band gaps of the most likely secondary phases, marked in red are those phases that have

smaller band gap than the corresponding kesterite compound

compound	band gap / eV	reference
Cu_2ZnSnS_4	1.5	[22]
ZnS	3.7	e.g. [19]
SnS_2	~2.5	[36]
Cu_2SnS_3	1.0	[37]
Cu_2S	1.2	[38]
SnS	1.0 indirect, 1.3 direct	[39, 40]
$Cu_2ZnSnSe_4$	1.0	[22]
ZnSe	2.7	e.g. [19]
$SnSe_2$	1.0-1.6	[41]
Cu_2SnSe_3	0.8	[42]
Cu_2Se	1.2	[43]
SnSe	1.3	[44]

Figure 1

Section of the phase diagram with the existence region (blue ellipse), the region where
the best solar cells are made (red ellipse) and various secondary phases: ZnS(e) (green
circles), $Cu_2S(e)$ (red up triangles), $SnS(e)_2$ (blue down triangles)