Impact of Bulk Properties and Local Secondary Phases on the $\text{Cu}_2(\text{Zn},\text{Sn})\text{Se}_4$ Solar Cells Open-Circuit Voltage

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Abstract

As the development of kesterite solar cells accelerates, the bottlenecks in device performance need to be identified and ways for their circumvention defined and developed. In this work, we use 2-dimensional (2D) numerical simulations to explore possible reasons for low open-circuit voltage (V_{oc}) in $\text{Cu}_2(\text{Zn},\text{Sn})\text{Se}_4$ (CZTSe) solar cells. High defect density in the CZTSe absorber and at the CZTSe/CdS interface can be significant reasons for V_{oc} deficit, but they do not explain all of the losses observed experimentally. Local deviation from stoichiometry could create secondary phases with a lower band gap compared to the absorber. These secondary phases can be severely harmful to V_{oc} if located in the vicinity of the heterointerface and along the grain boundaries.

1. Introduction

$\text{Cu}_2(\text{Zn},\text{Sn})(\text{Se}_x\text{S}_{1-x})_4$ solar cells are Earth-abundant, promising new addition to the thin-film polycrystalline family. Several groups have reported efficiencies close to and above 10% using these materials [1-7]. In efforts to increase the conversion efficiency of kesterites, the main bottleneck is their low open-circuit voltage (V_{oc}). Figure 1 shows the voltage deficit, defined as $\Delta V = E_g/q - V_{oc}$ for $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ (CIGS) cells and $\text{Cu}_2(\text{Zn},\text{Sn})(\text{Se}_x\text{S}_{1-x})_4$ (CZTSeS) devices reported in the literature. Two trends are clearly observed: *i*) The deficit for kesterite cells is higher compared to the CIGS cells; *ii*) As the band gap increases, the V_{oc} deficit in both types of devices increases as well.

Figure 1. Voltage deficit for kesterite (solid symbols) and chalcopyrite (open symbols) solar cells from different groups. Data points a [8], b [9] and c [10] are for CIGS; data points d [11], e [12], f [13], g [14], h [15], i [16], j [7] and k [1] are for CZTSeS.

The V_{oc} of a device that has an absorber with a specific band gap is mainly determined by its carrier density and recombination. While similar hole densities have been measured for kesterites and chalcopyrites, there is a notable difference between the reported minority-carrier lifetimes [17]. Lifetimes of up to 250 ns have been reported for $\text{Cu}(\text{In,Ga})\text{Se}_2$ materials [18], whereas the best kesterite devices have reported lifetimes between 1 and 10 ns [11, 19]. This is definitely a reason for a larger V_{oc} deficit observed in kesterites, but, as will be shown below, it does not completely explain the V_{oc} losses.

This work uses numerical simulations to explore reasons for V_{oc} deficit in $\text{Cu}_2(\text{Zn,Sn})\text{Se}_4$ (CZTSe) solar cells. First, we define a set of electronic parameters describing the different layers in a CZTSe/CdS/ZnO/ZnO:Al device. The parameters for each layer are taken from experimental data where available and from theory in other cases. Sensitivity of device performance due to parameter variation is also explored. First, the absorber band gap is assumed uniform, and the impact of carrier lifetime and interface recombination on device performance is calculated. Next, the assumption of uniformity is abandoned, and local areas with band gap lower than the absorber bulk are included in the model. Such areas could be attributed to local stannite phases or compounds such as Cu_2SnSe_3 . Other compounds such as ZnSe are also observed in kesterite absorbers, but they have band gaps higher than kesterite CZTSe, and should not cause V_{oc} loss.

2. Model

The modeling was performed with a Sentaurus Device Software by Synopsys [20]. The software package solves Poisson and continuity equations. A schematic of the CZTSe device used in the calculations and a calculated equilibrium band diagram are shown in Figure 2. The device architecture is derived from a typical CZTSe device deposited in our laboratory. The device consists of a 150-nm-thick Al-doped ZnO layer, a 100-nm-thick undoped ZnO layer, a 50-nm-thick CdS layer and a 1- μm -thick CZTSe layer. The parameters used in the model are listed in Table 1.

Figure 2. a) Schematic of a CZTSe solar cell. The white areas represent secondary phases (SPs) located either at the grain boundary (GB) or within the grain, as discussed in Section 4. b) Simulated equilibrium band diagram for a CZTSe solar cell.

Table 1. Parameters used in the model

	ZnO:Al	ZnO	CdS	CZTSe
Layer thickness (nm)	150	100	50	1000
Band gap (eV)	3.3	3.3	2.4	0.96 [21]
Carrier density (cm^{-3})	$n = 10^{20}$	$n = 10^{18}$	$n = 10^{17}$	$p = 3 \times 10^{16}$ [17]
Dielectric constant ϵ/ϵ_0	9 [22]	9	8.73 [23]	10 [24]
Electron effective mass m_e^*/m_0	0.275 [23]	0.275 [23]	0.25 [23]	0.1 [25]
Hole effective mass m_h^*/m_0	0.59 [23]	0.59 [23]	0.7 [23]	0.32 [25]
Electron mobility μ_e	200 [26]	200 [26]	160 [23]	80

	(cm ² /Vs)				
Hole					
mobility μ_h	93.22	93.22	15 [23]	25.2	
(cm ² /Vs)					
Defect density	10 ¹⁷ [22]	10 ¹⁷ [22]	10 ¹⁷	1.35x10 ¹⁵	
(cm ⁻³)					
Electron					
capture					
cross section	10 ⁻¹² [22]	10 ⁻¹² [22]	10 ⁻¹⁷	10 ⁻¹⁴	
σ_e (cm ²)					
Hole capture					
cross section	10 ⁻¹⁵ [22]	10 ⁻¹⁵ [22]	10 ⁻¹³	10 ⁻¹⁴	
σ_h (cm ²)					

For the CZTSe layer, the defect density values and the capture cross sections are chosen to create a carrier lifetime of 2 ns, as measured by time-resolved photoluminescence (TRPL) [19]. The minority-carrier lifetime is calculated as [27]:

$$\tau_e = 1/(N_t \sigma_e v_{th}) ,$$

where N_t is the defect density, σ_e is the electron capture cross section, and v_{th} is the thermal velocity defined as: $v_{th} = \sqrt{\frac{3kT}{m_e^*}}$.

The conduction-band offset (CBO) at the CZTSe/CdS interface is taken to be positive (the conduction-band minimum of the CdS layer is above the conduction-band minimum of CZTSe) and equal to 0.26 eV [28]. The CBO of CdS and undoped ZnO is taken to be -0.2 eV, between the values reported by Refs. [29, 30]. The interface recombination velocity at the CZTSe/CdS interface in the baseline case is set at a low value, $S = 100$ cm/s, unless otherwise stated. The optical constants of CZTSe materials used in the model were measured by ellipsometry [31]. The optical constants for CdS are from Ref. [32], and the optical constants for ZnO are from Ref. [33]. All of the defects are assumed to have a Gaussian energetic distribution with $\Delta E = 0.1$ eV, centered in the middle of the band gap. Some of the ZnO properties are taken from previously published modeling work [22], and their impact on device performance is not significant. The CdS is assumed to be highly compensated, with n -type doping comparable to the defect density. The defects in CdS are acceptor type (the capture cross section for electrons is much smaller than for holes) [34]. The carrier mobilities in the CZTSe absorber layers were estimated based on the calculated effective masses of CZTSe.

Figure 3 shows simulated dark and light current- density- voltage (J-V) curves corresponding to the parameter choice described in Table 1(dashed and solid black lines). The red lines show J-V curve of a 9.15%-efficient CZTSe cell [13]. The curves have similar values for the short-circuit-current density (J_{sc}) and fill-factor (FF), but the model predicts higher V_{oc} by ~100 mV compared to the experiment.

Figure 3. A simulated current- density-voltage curve based on the parameters given in Table 1, and a J-V curve of a 9.15% CZTSe solar cell [13]. Parameters used to simulate the green curve, a 2D model with secondary phases (SPs), are discussed in Section 4.

In order to eliminate the incorrect choice of some electronic parameters (carrier mobility, effective mass, dielectric constant, carrier density and lifetime) as a possibility for this discrepancy between the experimental and modeled V_{oc} , we explored the sensitivity of the calculated device performance on their choice. The mobility values reported in literature vary [35-37] and depend on the deposition method. Variation of the hole mobility between $12.6 \text{ cm}^2/\text{Vs}$ [36] and $100 \text{ cm}^2/\text{Vs}$ altered the V_{oc} of the devices by only 20 mV. Low carrier mobility decreases the electron diffusion length in the absorber, and thus reduces J_{sc} and FF, that is not observed in the experiment. We have used the $\epsilon(0)$ value for the dielectric constant from theoretical prediction and similar to the experimental results [24, 31]. However, variation of the relative dielectric constant from 6 to 10 had a negligible impact on the V_{oc} , and increasing the value of effective masses by a factor of two decreased the V_{oc} by only ~25 mV. Thus, we determined that reasonable variations of the above input parameters do not explain the V_{oc} loss observed in the experiment.

3. 1D model (uniform absorber properties)

Figure 4 shows simulated contour plots of the solar cell parameters as a function of the carrier lifetime and interface recombination velocity. The experimentally observed parameters fall along the thicker lines in Fig. 4. To reproduce the experimental low V_{oc} value, the lifetime in the model needs to be lowered to ~170 ps, or the interface recombination velocity needs to be higher than $5 \times 10^7 \text{ cm/s}$. The sub-nanosecond lifetimes are not realistic because: *i*) there are various experiments that point to an order of magnitude higher lifetimes [19], and *ii*) in addition to V_{oc} losses, such short lifetimes create J_{sc} and FF losses that are not experimentally observed. Therefore, we conclude that the low lifetime is not the only cause for the low V_{oc} . Interface recombination is another suspect for V_{oc} losses. Current-density-voltage-temperature (JVT) measurements of CZTSe solar cell showed V_{oc} vs. temperature curve extrapolated to a value lower than the band gap at 0.82 eV [11]. This could be an indication of interface recombination velocity being a dominant recombination mechanism. However, interface recombination velocity of 10^7 cm/s in combination with 1-10 ns lifetimes, still creates higher V_{oc} values than experimentally observed. In addition, such high interface recombination velocity values would significantly lower the J_{sc} values as well.

For high interface recombination velocities, the interface recombination dominates the device performance, and an increase in carrier lifetime does not create a significant efficiency benefit. Similarly, for lifetimes below 1 ns, the performance losses are determined by the recombination in the absorber, and not at the interface.

The above calculations are based on the assumption of a favorable band alignment at the CdS/CZTSe interface (+0.26 eV). In a case of a lower conduction-band offset value, the interface recombination has a stronger impact on device performance, but still does not produce the experimental combination of the low V_{oc} and high FF and J_{sc} . For example, when aligned bands are assumed (CBO = 0 eV, not shown) the experimentally measured V_{oc} could be reproduced with a value of $S = 4.5 \times 10^4$ cm/s, but this device has a conversion efficiency of 7.14% due to the low J_{sc} and FF.

To explore the potential of CZTSe devices for high lifetimes, in the calculations in Fig. 4, we utilize an increased absorber thickness of 4 μm . As the lifetime in Fig. 4 increases, the diffusion length exceeds the absorber thickness of 1 μm used in our experiments and other simulations. Therefore, the recombination at the back contact becomes an important loss mechanism. For such high carrier lifetimes, steps for back contact passivation such as back-surface fields or treatments, and/or a thicker absorber should be considered. If these steps are not taken, the back-contact recombination would limit the efficiency at ~16% even with very high lifetimes [19].

Figure 4. Impact of interface recombination and carrier lifetime on CZTSe solar cell parameters. There is not a set of interface recombination velocity and lifetime value that can produce all the experimentally-observed parameters.

Evidence for band tails was found in transient photocapacitance spectroscopy measurements, and their connection to the V_{oc} deficit was suggested [37, 38]. The band tails can be included in the model as an additional defect, or if the density of the defects is high, they could create a conducting defect band, as discussed in Section 4. First, they are included as an additional defect which has an energetic distribution that decreases exponentially from the conduction band. This defect is assumed to be an electron trap and has capture cross sections of $\sigma_e = 10^{-12} \text{ cm}^2$ and $\sigma_h = 10^{-15} \text{ cm}^2$ for electrons and holes, respectively. Figure 5 shows the impact of the band-tail defect width on the device parameters.

Increase of capture cross sections for either carrier, as well as increased defect density in the tails would intensify the losses due to band-tail states. However, two trends are maintained: *i*) wider band tails have a stronger impact on the V_{oc} , which is experimentally observed [38], and *ii*) band tails are likely to lower J_{sc} , FF, and lifetime as well as V_{oc} .

Figure 5. Impact of band-tail width and defect density in the band tail on the CZTSe device performance.

4. 2D model (Nonuniform absorber properties)

In the previous section, we showed that although low lifetime, high interface recombination velocity, and the presence of band tails can cause a low V_{oc} , they also create reductions in J_{sc} and FF that are not reproduced experimentally in our devices. So, in the following section, we explore other sources of low V_{oc} that do not affect J_{sc} and FF as strongly. One source is local area that has a lower band gap, such as stannite or a secondary phase. Local stannites have been observed experimentally, and theoretical calculations have reported that stannites have a lower band gap (0.82 eV) compared to kesterites (0.96 eV) [21]. Secondary phases, such as Cu_2SnSe_3 , can also be formed in the CZTSe absorber. The experimentally reported band gap of Cu_2SnSe_3 is 0.843 eV [39]; however, a much lower value of 0.4 eV is predicted by theory [40]. In either case, this compound has a lower band gap than the CZTSe. High defect density in the band tail can create a conducting band and can act as a local lower-band-gap region. In the following, we investigate the impact of the presence of lower-band-gap regions on devices' V_{oc} , and will refer to all of them, regardless of their origin as secondary phases (SPs).

4.1. Secondary phases along the grain boundaries

The region in the vicinity of the grain boundaries (GBs) is expected to have a different structure compared to the rest of the grain. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) measurements have indicated Cu-rich grain boundary regions in kesterite devices [11, 41]. In addition, first-principle calculations have shown that cation-terminated surface of kesterites is likely to be Cu-rich [40] and that Cu-rich kesterite CZTSe, in general, should have a lower band gap because addition of Cu to CZTSe increases the energy of the valence band edge, thus decreasing the band gap. In an extreme case, in the vicinity of the interface, Cu_2SnSe_3 could form. It has been suggested [11] that the Cu-rich region in a vicinity of a GBs could play a role in V_{oc} losses in CZTSeS devices. Although the evidence mentioned above suggests decreased band gap in the vicinity of the GBs, scanning Kelvin probe force microscopy (SKPFM) measurements have shown potential barriers at the grain boundaries in an evaporated CZTSe [17] and on sputtered CZTSeS [42].

First, we analyze the impact of a lower- band- gap region in the vicinity of the GB on the device V_{oc} and efficiency. A 5-nm- thick region next to the grain boundary has a lower band gap compared to the rest of the 1- μm grain (Fig. 2a). The GBs are assumed to be columnar. The local drop in the band gap along the grain boundary can act as a weak diode and thus decrease V_{oc} of the entire device [43-47]. According to the “weak diode” analysis, the V_{oc} loss due to the weak diode is proportional to its size. Also, band-gap fluctuations have been known to affect the performance of CIGS devices [48, 49].

In addition to the formation of a “weak diode”, the local band gap decrease in the valence band can encourage recombination at the grain boundaries. This differs from CIGS materials, where the free surfaces are Cu-poor. The Cu-poor surfaces have a lower valence band, which can create a barrier for holes [50, 51]. This would make the performance of kesterites more vulnerable to recombination at the GBs compared to chalcopyrites. Figure 6 shows a contour plot of the impact of grain boundary recombination on devices' V_{oc} and efficiency, when the GB is surrounded with a different band gap region. The case of a uniform band gap $\Delta E_g = 0$ is shown with a dashed line, and the variations in the band gap in the positive direction are also shown. The calculations show that for $\Delta E_g = +0.2$ eV, as observed in CIGS, an increase on GB recombination velocity from a low value of 100 cm/s to a high value of 10^7 cm/s would decrease the V_{oc} by only 50 mV. The same increase in GB recombination in a case of a uniform band gap decreases the V_{oc} by 200 mV. If the band gap next to the grain boundary is lower, the grain-boundary recombination could be detrimental to the device performance. Even if the grain boundary recombination is low, the lower- band- gap region can severely affect device performance. For example, for $S_{GB} = 10^3$ cm/s, a device with $V_{oc} \sim 0.5$ V can become 0.3 V if only 5 nm of the 1- μm grain area has a band gap of 0.56 eV.

The calculations above assume that the grain boundaries are not charged. Charged grain boundaries would induce band bending and carrier separation at the GBs. Extensive modeling work on the effect of GB charges on the device performance and characterization has been done for CIGS [52-54].

In all the calculations, it is assumed that only the band gap is varied and not the other properties of the secondary phases, including the optical properties.

Figure 6. Contour plot of a) V_{oc} and b) conversion efficiency as a function of decreased band gap in the vicinity of the grain boundaries for different GB recombination velocities. The dashed arrows show the losses that could be expected due to the weak diode only.

4.2. Local secondary phases within the grain

The next section analyzes the impact of local secondary phases that do not stretch throughout the absorber thickness and are not necessarily connected to the GBs, but are localized at certain positions throughout the grain.

First, the secondary phases (SP) are located at the interface (white square in Fig. 2a). Three square-shaped secondary phases are assumed in a $1 \mu\text{m}$ region, and their size and band gap are varied. Figure 7a shows plots of the V_{oc} dependence as a function of the size and the band gap of SP regions next to the interface. Figure 7b shows the magnitude of the impact of interface recombination velocity on a device with three $50\text{-nm} \times 50\text{-nm}$ secondary phases. The local decrease in band gap next to the heterointerface could encourage interface recombination due to more available holes next to the heterointerface. If the decrease in band gap is in the conduction band, interface recombination velocity has a lower impact on devices' V_{oc} when the SPs create a CBO (dashed pink line in Fig. 7b) compared to the SPs that create a VBO (solid pink line in Fig. 7b), due to inversion of the absorber next to the heterointerface. If there is a variation in the conduction band larger than 0.3 eV, the secondary phases away from the interface could potentially trap the minority carriers. Our simulations have shown that this could lead to large FF losses, which are not experimentally observed. The impact of secondary phases is the strongest in the vicinity of the heterointerface, starts slowly decreasing when the secondary phases move away from it, and becomes very low outside of the space-charge region (Figure 7c).

Our investigation suggests that although we could not reproduce all of the J-V parameters with reasonable limits of parameter variation assuming spatially uniform absorber properties, once the

secondary phases were included in the model, multiple ways of reproducing experimental J-V were found. One example (not unique by any means) is shown with a dotted green line in Fig. 3 marked with SPs. In this example, in addition to all parameters listed in Table 1, there are three 50-nm×50-nm secondary phases at the CZTSe/CdS interface, with band gap $E_{g(SP)} = 0.82$ eV (stannite), and the interface recombination velocity is set to 10^5 cm/s.

Figure 7. Simulated V_{oc} as a function of the band gap of the secondary phases a) for different SP sizes, when the secondary phases are located next to the heterointerface. b) As a function of interface recombination velocity at the CZTSe/CdS interface. c) As a function of SP distance from the heterointerface (in μm), while the size is kept constant at 50-nm×50-nm.

5. Conclusions

In this manuscript, we present numerical modeling results on CZTSe/CdS/ZnO solar cells. We have collected a set of parameters from experimental data and theory, created a model for CZTSe solar cells and compared the model with experiment. We have explored how different parameters impact the device performance. Although carrier lifetime and interface recombination are the strongest sources for the V_{oc} deficit, local secondary phases can also contribute and explain the losses in V_{oc} . The magnitude of their impact depends on their size, band gap and location. Secondary phases are strong contributor to V_{oc} losses when located at the heterointerface, and they can increase the impact of interface recombination. As the lower band gap phases move away from the heterointerface, their impact on V_{oc} decreases. With the inclusion of secondary phases, 2D models can reproduce experimental J-V parameters, which was not possible for the 1D model with reasonable limits of parameter variation.

Acknowledgements

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08-GO28308 with the National Renewable Energy Laboratory. This paper is subject to government rights.

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