Sentaurus modelling of 6.9% Cu₂ZnSnS₄ device based on comprehensive electrical & optical characterization

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Abstract

In this work we perform comprehensive characterization on a 6.9% pure sulphide Cu₂ZnSnS₄ (CZTS) device and construct a 2D device model in Sentaurus TCAD to identify possible roots of performance bottlenecks. Electrical and optical parameters of the absorber from comprehensive electrical and optical characterization, together with other necessary parameters from literature, we successfully reproduce measured current density-voltage (J-V) and external quantum efficiency (EQE) curves. Absorption coefficient is extracted by fitting measured internal quantum efficiency (IQE). At the buffer/absorber interface, a surface recombination velocity of 1×10^5 cm/s is identified to adequately describe measured spectral response at the near-interface region. Furthermore, a bulk lifetime of ~29 ns is extracted from effective lifetime modelling in conjunction with [time resolved photoluminescence \(TRPL\)](#) results. The key underlying V_{oc} deficit, ~200 mV, is pinpointed to bandgap fluctuation, which is backed by the simulation study on both QE tail and steady state photoluminescence.

1. Introduction

Global photovoltaics (PV) installed capacity has been increasing steadily and continuously over the course of last decade. However, thin-film PV only shares 10% of market from recent investigation [1]. Albeit extensive research have pushed Cu(In,Ga)S₂ (CIGS) and CdTe to 22.3% and 22.1% respectively [2, 3], thin-film solar cells are still unable to compete with silicon based PV in mainstream market due to their lack of [reliability](#). Kesterite structured pure sulphide Cu₂ZnSnS₄ (CZTS), with its environmentally benign properties such as non-toxicity, earth abundance and high absorption coefficients over visible spectrums, has emerged as one of compelling alternatives to conventional chalcogenide thin-film materials. However the highest efficiency of CZTS reported up to date is 9.1% [4], which is far inferior to its thin-film counterparts. In the course of pursuing higher efficiency, better understanding of CZTS device characteristics and performance bottlenecks is the keys to approaching the target. As several researchers pointed out, the CZTS device performance is mainly constrained by large V_{oc} deficit [4-7]. Hetero-junction interface recombination [5-7] and electronic bandgap shrinkage induced by tailing states in absorber [5, 8] have been widely believed as two most popular culprits behind detrimental V_{oc} deficit. It is well known that numerical simulation can be used to explore underlying mechanisms of manifold measurement responses and to bridge the gap between theoretical hypotheses and experimental observations. In the process of comparing

experimentally measured and simulated device outputs, it is then possible to quantitatively account for them. With the aid from numerical simulation, their impacts on device Voc can be further understood.

The core parameters used in the majority of previous CZTS simulation works [5, 9, 10], were grounded in literature databases or theoretical hypothesis, while few were referenced with follow-up characterizations on device. In this work we construct a baseline computation model in Sentaurus TCAD [11] of a 6.9% efficient CZTS device based on comprehensive electrical & optical characterization. Electric-wise, depletion region width and majority carrier concentration is obtained from C-V measurement, effective minority carrier diffusion length from electron-beam-induced-current (EBIC) measurement, effective minority carrier lifetime from TRPL and majority carrier mobility from Hall effect measurement. Optic-wise, a numerical method is employed to extract modified semi-empirical absorption coefficient by fitting calculated QE with experimentally measured QE at each wavelength. By reproducing measured JV and EQE curves, quantitative analyses are carried out to probe the unknown essential properties that either lie beyond characterization detection limit or are inadequate to be interpreted only based on measurement. These include recombination at the buffer/CZTS hetero-interface and in CZTS bulk, disorder related bandgap narrowing. Interface recombination is investigated through tuning interface recombination velocity in device model so that a fraction of simulated QEs, related to photons absorbed in near-interface regions, match that of measured QEs. The comprehension of bulk lifetime from Time-resolved photoluminescence (TRPL) can often be skewed by presence of defect-populated interface [12]. Therefore we conduct an effective lifetime study under varying interface recombination velocities and bulk lifetimes. A reasonable bulk lifetime is found by linking simulation results with TRPL data. A number of simulation works have previously mentioned the tight relation between Voc deficits and bandgap narrowing [5, 8, 9]. However, it was only hypothesized that the reduced electronic bandgap of 1D simulation could be related to red-shifted room-temperature photoluminescence (RTPL) peak energy. No quantitative analysis or simulation was conducted to further explain this relationship. In this paper we examine the underlying disorder induced bandgap fluctuation by implementing Gaussian-distributed bandgap model on tail states quantum responses and RTPL spectra. Ultimately, hetero-junction interface and bandgap fluctuation are identified as the major bottlenecks of Voc. Our simulation predicts the attainable Voc could be up to 1 eV when mitigation of these two problems came to fruition.

2. Experiment and modelling setup

2.1 Device fabrication

This device was fabricated with Glass/Mo/CZTS (~900nm)/CdS (~50nm)/i-ZnO (50nm)/ITO (200nm)/Grid layers as depicted in Figure 1. The CZTS absorber was deposited by sulfurization of a co-sputtered Cu/ZnS/SnS precursor by a magnetron sputtering equipment (AJA International, Inc., model ATC-2200) on Mo-coated soda lime glass. Sulfurization step was taken in a pure sulfur atmosphere at a temperature of 560°C with a ramping rate of 10°C min⁻¹ for 3min. The Zn/Sn and Cu/(Zn+Sn) composition ratios are 1.31 and 0.8, respectively, measured from energy dispersive X-ray spectroscopy (EDS). CdS buffer layer was deposited on top of absorber by CBD method, detailed fabrication process of this layer was elaborated in our previous work [13, 14]. The window layers, intrinsic ZnO & ITO, were prepared by RF sputtering. Finally top contact was integrated by evaporation of Al grids onto ITO layer.

Figure 1. Schematic of 6.9% efficient CZTS solar cell with labelled thickness of each layer according to SEM.

2.2 Electrical and optical characterization

C-V measurements were carried out using an impedance analyser (Hewlett Packard 4194A) to evaluate bulk doping density (or free carrier concentration) and depletion region width. The reference CZTS device was tested with a DC bias voltage sweeping from -0.5 V to 0.5 V at varying AC frequencies from 1 kHz to 1 MHz. The cross-section EBIC measurements were performed on the device at the beam energy of 5keV to determine the electron carrier diffusion length in the bulk by a FEI Helios 600 NanoLab Dual-beam SEM/FIB. The electron-beam induced current was amplified by a Kleindiek nanotechnik EBIC/RCI signal amplifier. The EBIC signal is simulated using analytical method to determine diffusion length. TRPL measurements was performed on the reference device using time correlated single photon counting (TCSPC) technique with a Microtime-200 (Picoquant) system. This system is equipped with a 780-800nm detector and a 470 nm solid-state laser excitation source tuned at a repetition rate of 10 MHz with incident power of 0.18 W/cm^2 and a laser pulse width shorter than 70 picoseconds. Room-temperature PL measurement was conducted by a photoluminescence spectroscopy equipped with a 405 nm solid-state laser at 50 mW output power. Additionally, Hall-effect measurement was also employed to detect the majority carrier mobility and free carrier concentration of CZTS absorber by testing post-annealed precursor fabricated with identical processes as reference device. Each constituent layer thicknesses of the device were determined through cross-sectional morphology characterized by scanning electron microscope (SEM) using an EFI Nova NanoSEM 230 FESEM under 5 kV accelerating voltage.

Current density-voltage (J-V) curve of the device was characterized, under illumination, by utilizing a Xe-based light source solar simulator (Newport, 91160 and KEITHLEY 2400). The light spectrum of solar simulator is simulated to one Sun AM 1.5G spectrum through calibration with a standard Si reference cell from National Renewable Energy Laboratory. The external quantum efficiency (EQE) was obtained from a QEX10 spectral response system (PV measurements, Inc.), which features a monochromatized beam chopped at 120 Hz and a lock-in amplifier. The pre-measurement calibration was performed with National Institute of Standards and Technology (NIST) certified Si and Ge photodiodes.

A test sample was prepared to deposit ~900 nm CZTS film on a standard glass with identical sputtering and annealing processes in the device fabrication. Reflectance-Transmittance (R-T) data was then measured with a PelkinElmer lambda 1050 spectrometer equipped with a 150-mm integrating sphere. The raw absorption coefficient is calculated according to reference [15].

2.3 Modelling setup

In Sentaurus TCAD software packages [11], a two-dimensional device structure was constructed with four constituent layers, ITO, i-ZnO, CdS and CZTS. The top and bottom electrodes were used to extract carriers. Poisson, drift-diffusion and continuity equations were solved iteratively until reaching self-consistency. A thorough narration of parameters chosen for all window and buffer layers can be found in appendix. Based on a cliff-like 0.3 eV conduction band offset at CZTS/CdS heterointerface reported from our previous work [16], we selected a CZTS electron affinity of 3.9 eV to portray this band-alignment at the hetero-junction interface. The hetero-junction interface recombination rate was computed using the electron and hole interface recombination velocities according to the SRH model [17]. Based on C-V analysis, the doping density of CZTS layer was chosen to be $1.42 \times 10^{16} \text{ cm}^{-3}$ to obtain a ~300 nm depletion region width on absorber side in the model. Based on the measured minority carrier lifetime from TRPL and diffusion length from EBIC, we calculated the electron mobility in CZTS layer as 1.02-1.25 $\text{cm}^2/\text{V/s}$ using equation $\mu_e = \frac{L_e^2}{\tau_e} \times \frac{q}{KT}$. In the final model, 1.02 $\text{cm}^2/\text{V/s}$ was used based on an 180nm effective diffusion length within EBIC extracted range. The hole mobility in absorber layer was determined according to hall-effect measurement, 0.5-1 $\text{cm}^2/\text{V/s}$. Considering a large density of point defects inherited from synthesis processes [18], only SRH recombination was computed in the bulk using electron and hole lifetimes. Assuming identical recombination lifetime for majority and minority carriers, a single parameter, τ_{SRH} is used here to generalize bulk recombination rate due to traps distributed in forbidden bandgap. The optical bandgap of CZTS layer was determined from inflection point of measured QE data, 1.57eV. Aforementioned inputs and some of other vital electrical parameters extracted from literature can be seen in Table I.

Table I. Key electrical parameters used in CZTS layer of Sentaurus model.

CZTS layer parameters	Symbol	Value/Unit	Remark
Temperature	K	300	
Electron affinity	χ	3.9eV	Calc from CBO of [16]
Optical bandgap	$E_{g,\text{opt}}$	1.57eV	From QE
Relative dielectric constant	ϵ_r/ϵ_0	7	Reported from [19]
Conduction band density of states	N_C	$2.2 \times 10^{18} \text{ cm}^{-3}$	[5]
Valence band density of states	N_V	$1.8 \times 10^{19} \text{ cm}^{-3}$	[5]
Electron mobility	μ_e	1.02-1.25 $\text{cm}^2/\text{V/s}$	Calc from TRPL&EBIC
Hole mobility	μ_h	0.5-1 $\text{cm}^2/\text{V/s}$	Measured from hall-effect
Free Carrier concentration	N_A	$1.42 \times 10^{16} \text{ cm}^{-3}$	Measured from C-V

3. Results and discussion

3.1 Electrical characterization

C-V

The net carrier density in CZTS bulk was derived from C-V scans with different frequencies as shown in Figure 2a. Several papers have reported that in polycrystalline materials, the presence of deep level defects can well enhance the capacitance response at inappropriate low frequencies resulting in misleading interpretation of net carrier density [20-22]. When AC angular frequency is slow enough, deep level defects could have sufficient time to respond, thereby adding enormous amount of extra charge to thin film [20]. In order to exclude this adverse effect arisen from deep level defects, C-V measurements were performed at different frequencies, from 3 kHz to 700 kHz. We found that capacitance response becomes independent of AC frequency above 500 kHz, implicating deep-level-defect-free measurement. The net carrier concentration and depletion region width determined at the AC frequency of 700 kHz under zero DC bias are $1.42 \times 10^{16} \text{ cm}^{-3}$ and 300 nm, respectively. The

extracted net carrier density is in reasonably close agreement with that of previously published high efficiency CZTS solar cell with similar composition ratio [23]. The free carrier concentration is further confirmed by hall-effect measurement in which a value of $\sim 1 \times 10^{16} \text{ cm}^{-3}$ was obtained.

Figure 2. a) Frequency dependent net charge carrier profiles of the CZTS device calculated from C-V measurements. b) Time-resolved photoluminescence (TRPL) trace at an emission wavelength of 800nm obtained from the CZTS device. A fitted curve using 2 exponential decay function is also shown in red line. c) Room temperature photoluminescence (PL) spectra at an emission wavelength of 800nm obtained from the CZTS device (red curve). The black dashed line indicates the estimated optical bandgap of 1.57eV of the device based on dIQE/dλ analysis (blue curve).

EBIC

Figure 3. cross-sectional SEM image (a) and EBIC mapping (b) of the CZTS cell; (c) measured and simulated cross-sectional EBIC profiles indicated in (a) and (b).

Fig. 3 (a) and (b) show the cross-sectional SEM image of the CZTS sample and the corresponding EBIC mapping result at the same area, respectively. The EBIC line scan profile in the absorber can be described by the convolution of the collection function $f_c(x)$ and the function of the beam profile $g(x, a)$, where a is the position of the electron beam irradiation.

$$I(a) = \int_0^\infty g(x, a) f_c(x) dx \quad (1)$$

The collection function can be deduced from the continuity equation for electrons and holes under low injection condition [24]. If the electron diffusion length is smaller than the layer thickness the collection function in the EBIC measurement can be described by

$$\begin{cases} f(x_{SCR}) = 1 \\ f_c(x) = \exp(-\frac{x}{L_e}) \end{cases} \quad (2)$$

Where x_{SCR} is the position of the edge of the space charge region, L_e is electron diffusion length. We use a lateral electron-beam generation profiles $g(x)$ for different electron beam energies according to the expressions in Ref. [25] with the mass density of 4.6 g/cm³ and bandgap of 1.5eV for CZTS absorber.

Fig. 3 (c) shows the EBIC simulation result of profile marked by black and grey line in Fig.3 (a) and (b), respectively. The best fitting of this [simulation](#) gives the diffusion length of 0.16μm. To illustrate the sensitivity of the fit to different diffusion lengths, plots with half and double the best fit are also shown as grey dotted lines. Note that the simulation was done for the best fitting of the absorber layer only and the poor fitting near the buffer region is due to the different material parameters affecting the generation profile. The simulation has been performed at different areas of the cleaved device and the result of derived diffusion length is in the range of 0.13μm to 0.19μm.

TRPL

In addition to minority carrier diffusion length, effective minority carrier lifetime would provide more insights regarding recombination properties of both CZTS bulk and heterojunction. This parameter was detected by TRPL as shown in Fig. 2b. The decay profile of PL signal was fitted using bi-exponential function [26]:

$$I_{PL}(t) = A_1 \exp(-t/\tau_{fast}) + A_2 \exp(-t/\tau_{slow}) \quad (3)$$

As displayed in Fig. 2b, bi-exponential function fits reasonably well with PL signal. The mean lifetime in Equation (4) is used here to quantify effective minority carrier lifetime in CZTS bulk.

$$\tau_{mean} = \frac{A_1 \tau_{fast} + A_2 \tau_{slow}}{A_1 + A_2} \quad (4)$$

Where fast relaxation component τ_{fast} is related to the cooling time of photoexcited hot carriers that surge immediately after laser pulse, while τ_{slow} is generally ascribed to Shockley-Read-Hall (SRH) recombination. A_1 and A_2 are amplitudes of relative decay components τ_{fast} and τ_{slow} , and t the time. Nevertheless, 470 nm excitation source should inject free carriers predominantly into the region in close proximity to CdS/CZTS heterojunction. As such, the [direct](#) TRPL interpretation would be significantly affected by defect-populated interface [9, 18, 27], which in turn results in the extracted τ_{slow} to deviate from CZTS bulk recombination in device model. Therefore we adopted 12.3 ns TRPL mean lifetime as the effective absorber lifetime that is both limited by hetero-interface and defect-assisted recombination in CZTS layer. [To completely eliminate the influence from interface and determine the bulk SRH lifetime in an indirect way, the device lifetime simulation was carried out in which effective lifetime is a function of both interface recombination velocity and bulk lifetime. The bulk SRH can therefore be evaluated indirectly through matching simulated effective lifetime and measured mean TRPL lifetime.](#) Fig. 2c shows photoluminescence spectra of the reference device measured at room temperature. Firstly, a pronounced red-shift of PL peak was observed relative to optically measured bandgap. The 1.57 eV optical bandgap was determined from the inflection point of spectral derivative of IQE. Secondly, a large full width at half maximum (FWHM) can be seen around the peak of PL spectrum which consists of three bands at 1.30 eV, 1.35 eV and 1.39 eV. Both the red-shift and asymmetric bands between 1.3-1.4 eV have been reported in many PL studies. And they are most likely to be linked with disorders in the cation sub-lattice, which in turn leads to the widespread bandgap and potential fluctuation hypotheses [28-31]. In one study involving the implementation of laser intensity dependent PL technique [27], band-to-tail (BT) transition through acceptor Cu_{Zn} and

donor Zn_{Cu} has been revealed as the main recombination channel responsible for non-ideal PL spectra. The charged donor-acceptor pair (DAP) was attributed to be the root of potential fluctuation, which contributes to large Voc deficit of CZTS device. Nevertheless, in another study a contrary conclusion was obtained using the same PL analysis technique [31]. Band-to-band (BB) transition was attributed to be the prevailing pathway for radiative recombination. They pinpointed the Cu-Zn disorder induced bandgap narrowing to be the cause of this recombination mechanism. Their result is also supported by recent first-principle calculations [32], where a bandgap reduction up to 0.35 eV may exist in near-stoichiometry CZTS due to the presence of high concentration ($\text{Cu}_{\text{Zn}}^- + \text{Zn}_{\text{Cu}}^+$) and ($2\text{Cu}_{\text{Zn}}^- + \text{Sn}_{\text{Zn}}^{2+}$) defect clusters. In real CZTS film, disorder-related defects could well have spatially varying arrangement thereby giving rise to spatially varying bandgap narrowing, namely, bandgap fluctuation. Even for more matured CIGS technology, bandgap fluctuation and potential fluctuation coexist in real device as a result of spatial variation of chemical composition, stoichiometry, and charged defect density [33]. It's not aberrant to have had different PL interpretations, either potential fluctuation or bandgap fluctuation, from different research groups who prepared and fabricated their quaternary compounds using distinct methodologies. In section 3.3, quantitative analysis will be carried out to understand CZTS bulk problem and its effect on device Voc.

3.2 Optical characterization

Absorption coefficient obtained from pure optical characterization, can lead to misleading comprehension of absorber material properties. Consequently using of it in model can cause a disparity between simulation and experimental results, e.g. QE measurements [9]. It could be even worse if optical characterization is performed on single CZTS layer without accounting for its optical-modification after subsequent annealing with Mo substrate and chemical bath deposition of CdS. To circumvent this misinterpretation, we used an semi-empirical absorption coefficient for CZTS layer deduced from a 1D QE model. This model relies on preceding characterized electrical parameters in conjunction with a set of raw absorption coefficient obtained from R-T measurement, as reported in reference [34]. According to the reciprocity theorem [35], the spatial collection probability is numerically linked to minority carrier density in dark ambient divided by its thermal equilibrium value. If we assume there is no compositional gradient across whole absorber layer, namely uniform doping density used in device model, we can have a generalized form of $f_c(x)$ [36]:

$$\begin{cases} f_c(x) = 1 & 0 \leq x \leq W_d \\ f_c(x) = \frac{\cosh[(W_{\text{CZTS}} - x)/L_e] + (S_b L_e / D_e) \sinh[(W_{\text{CZTS}} - x)/L_e]}{\cosh[(W_{\text{CZTS}} - W_d)/L_e] + (S_b L_e / D_e) \sinh[(W_{\text{CZTS}} - W_d)/L_e]} & W_d \leq x \leq W_{\text{CZTS}} \end{cases} \quad (5)$$

Here we assumed a perfect depletion region where photo collection probability is unity. The depletion region width, W_d , was measured from C-V. While in quasi neutral region of absorber the collection probability profile is affected by some boundary parameters determined from aforementioned electrical characterization techniques: electron diffusion length (L_e) determined from EBIC, electron lifetime (τ_e) from TRPL hence electron diffusivity (D_e) can be calculated as $D_e = L_e^2 / \tau_e$, back surface recombination velocity (S_b) is assumed to be an extreme case of 10^7 cm/s.

Based on this QE model, we evaluated the semi-empirical absorption coefficient by fitting simulated IQE with experimentally measured IQE as shown in Fig. 4. Compared to previously published methods [9, 37], we used characterized electrical parameters like diffusion length, depletion region width and minority carrier lifetime. In this way, the gap between simulation outputs and measurement results can be diminished without sacrificing the reliability of our models.

Figure 4. Measured IQE (red dot) and simulated IQE (blue curve) of the device for the partial spectrum of light absorbed in CZTS layer only. Partial IQE spectra pertaining to space charge region (green curve) and quasi-neutral region (yellow curve) are also displayed.

3.3 Device modelling analysis

With most parameters determined from either characterization or literature, there are only three unknown parameters: interface recombination velocity, S_i , which was used to quantify recombination rate at buffer/CZTS interface; bulk SRH lifetime, τ_{SRH} , which was tuned to quantify bulk recombination rate; and effective electronic bandgap, $E_{g,eff}$, which was adjusted to account for disorder related bandgap/potential fluctuation problem. These parameters will be extracted by reproducing QE and J-V curves.

3.3.1 Interface recombination

Hetero-interface recombination has been prevalently attributed as the dominant core factor responsible for large Voc deficit in pure sulphide CZTS device [5-7]. However detailed analysis, from simulation vs. experiment perspective, has rarely appeared in previous literature. In this section we illustrate the quantitative examination of junction property as a function of S_i . QE reflects electrical characteristics of carrier recombination and collection activities. At short wavelengths, electron and hole pairs are generated near the surface region. Bulk SRH recombination has weak impact on recombination in close proximity to heterojunction, namely CdS buffer and CZTS depletion regions (CZTS- W_{dr}). Thus, QE responses at short wavelengths are directly influenced by interface recombination velocity.

The penetration depth, at which photon absorption is complete, for each wavelength of photon is plotted in Fig. 5 along with simulated and measured quantum efficiency curves. The photons with wavelength shorter than 380 nm are all absorbed before reaching CdS buffer. CdS layer collects photons in the spectral range of 380-390 nm. While CZTS depletion region picks up long wavelength photons until 700 nm. Absorption of photons with wavelength longer than this would be partially or fully attributed to quasi-neutral region of bulk. At low interface recombination velocities from 10^2 cm/s to 10^4 cm/s, simulated spectral responses at CdS region have an inflated-like shape with magnitude apparently larger than that of measured QEs. The same trend can be observed in CZTS depletion region, where simulated maximum QE of >90% can be seen for wavelength of 540 nm, apparently larger than 84% of reference device. The difference here implicates the presence of defect-

free interface in our device is nearly impossible. Simulated and measured QEs at buffer/CZTS- W_{dr} window reach agreement with reasonably small tolerance at S_i of 10^5 cm/s. Higher S_i would result in even lower QEs in interface-related window, with an average discrepancy of $\sim 4\%$ compared to the measured one. This discrepancy is believed to be triggered by plummeted collection probabilities impinged by defect-populated interface. As a result, 10^5 cm/s was selected to represent the heterojunction interface recombination in the device. This parameter leads to a V_{oc} decrement of 235 mV and J_{sc} reduction of ~ 2.1 mA/cm² comparing the case of an ideal interface.

Figure 5. At right-side y-axis, simulated EQE for different interface velocities spanning from 1E2 cm/s to 1E7 cm/s (coloured lines) is displayed as well as measured EQE on the device (red dot). At left-side y-axis, penetration depth (pink diamond), till 36% intensity, as a function of wavelength is shown. And according to this, the parts of spectrum collected by CdS buffer and CZTS depletion region are depicted in light orange and light cyan, respectively.

3.3.2 Bulk defect recombination

Similar to reference [38], we evaluate the variation of effective minority carrier lifetime (τ_{eff}) as a function of hetero-interface recombination velocity (S_i) and bulk minority carrier lifetime (τ_{SRH}) in the simulation. The excess minority carrier density was extracted from quasi-neutral bulk under the open circuit condition. The illumination wavelength and intensity were 470 nm and 0.18 W/cm² respectively, the same as those used in TRPL measurement. As shown in Fig. 6, Sentaurus lifetime modelling expounds that τ_{eff} is only subjected to bulk defect properties at the presence of benign interface with S_i range from 10^2 cm/s to 10^4 cm/s. In this condition τ_{eff} is virtually identical, in magnitude, to τ_{SRH} , both varying from 2 ns to 22 ns. Under the high injection scenario imposed by TRPL measurement condition, the dominant transport mechanism is diffusion [39] and excess electrons excited within junction could diffuse deep into CZTS bulk. Therefore the resultant effective lifetime depicts bulk recombination properties. However when interface recombination velocity is larger than 10^4 cm/s, effective lifetime becomes significantly constrained by interface. Under this condition bulk SRH lifetime variation can only make a small change between 2 ns-6 ns (with τ_{eff} at 10^6 cm/s). Here we can define the S_i of 10^4 cm/s to be the conceptual boundary between ‘good’ and ‘bad’ heterojunction interface. Previous analysis has illustrated the existence of ‘bad’ interface in CZTS device with a S_i of 10^5 cm/s. Under this fixed condition, we were able to reproduce the 12.3 ns τ_{mean} as measured from TRPL by using a τ_{SRH} of 28.8 ns in lifetime model. As this lifetime is 8 ns larger than the τ_{slow} from TRPL methodology, we may conclude that the obtained TRPL about bulk

SRH lifetime could be considerably underestimated due to the influence of ‘bad’ interface in CZTS device. In addition, first principle calculation [18] has forecasted that, with Cu poor and Zn rich composition, not only the dominant defects are replaced by shallower V_{Cu} acceptor but also the population of deep level isolated defects like Sn_{Zn}^{2+} is diminished in CZTS bulk. This theoretical conclusion is consistent with the high τ_{SRH} obtained from our lifetime modelling. One should note that the effective lifetime extracted in this model can be applied to describe τ_{mean} in TRPL and hence in turn probe the bulk recombination properties. Yet this lifetime is not equivalent to the effective lifetime in a device operating at maximum power point under full spectrum illumination. Due to the difference in the choices of spectrum and injection intensity, the simulated effective lifetime reduces to ~ 7 ns at operating condition.

Figure 6. Impact of interface velocity and CZTS bulk SRH lifetime on device effective lifetime is depicted as contour colour map. The zone of effective lifetimes as predicted by TRPL is shown between two marked lines.

3.3.3 Disorder in bulk

The poor-quality hetero-interface, with 1×10^5 cm/s SRH recombination velocity as revealed from aforementioned analysis, could only reduce device V_{oc} to 865 mV as seen in Fig. 7b. The simulated V_{oc} is still more than two hundred millivolts higher than measured 653 mV of reference device. This disparity implies that additional mechanism is required to account for the large V_{oc} deficit. Except bulk SRH recombination, Cu-Zn disorder related bulk problems such as bandgap and potential fluctuation might be the remaining causes according to aberrant PL spectra in Section 3.1. Moreover disorder related problem has already been highlighted and studied extensively in polycrystalline PV materials [40-42]. To investigate this, absorption coefficient is estimated according to Equation 6.

$$\alpha \propto \int_0^\infty \frac{1}{\sigma_g \sqrt{2\pi}} \exp\left(-\frac{1}{2} \left(\frac{E_g^{loc} - E_{g,mean}}{\sigma_g}\right)^2\right) \left(\frac{\sqrt{E_{ph} - E_g^{loc}}}{E_{ph}}\right) dE_g^{loc} \quad (6)$$

$$\alpha \propto -\ln(1 - IQE(E_{ph})) \quad (7)$$

where 2 assumptions are used in Equation (6): (i) the bandgap fluctuation can be described by Gaussian probability distribution, where σ_g defines standard deviation of spatially fluctuated bandgap and $E_{g,mean}$ defines the mean bandgap; (ii) Local density of states due to spatial variation of bandgap are assumed to be directly translated into local absorption coefficient, thereby Gaussian model of bandgap transformed into Gaussian like absorption coefficient [4, 7, 39]. Absorption coefficient can

also be approximated from IQE data [43] as presented in Equation (7). Ultimate absorption coefficient from Gaussian like bandgap fluctuation model is correlated with that obtained from IQE measurement. Presuming mean bandgap to be the optically measured 1.57 eV, we can deduce an appropriate σ_g by fitting absorption coefficients at photon-energies below optical bandgap. Similarly the amplitude of potential fluctuation, γ_{opt} from a model mentioned in [44] where $\alpha \propto \exp\left(-\frac{2}{5\sqrt{\pi}}\left(\frac{E_g - E_{ph}}{\gamma_{opt}/2}\right)^{5/4}\right)$, can be obtained using same approach as well.

Figure 7. a) Simulated RT-PL spectra (coloured lines) for different standard deviation of bandgap fluctuation from 10meV to 120meV are displayed as well as measured data (navy dot) on the device. The inset graph shows absorption coefficient vs. E_{ph} below bandgap energy for the device and fitted based on bandgap model. b) The simulated V_{oc} (green) at various electronic bandgaps. All simulated V_{oc} here are extracted from model with $1E5$ cm/s interface velocity. The measured V_{oc} from the device (red) and ideal V_{oc} (blue) without interface recombination and bandgap reduction are also shown as a comparison reference.

The plot of α vs. E_{ph} can be seen in inset of Fig. 7a. The fitting procedure yields σ_g and γ_{opt} of 120 meV and 36 meV respectively. A previous study [8] has reported these fluctuation amplitudes of 42-85 meV and 32-65 meV for CuZnSn(S,Se)_4 , and Cu(In,Ga)(S,Se)_2 solar cell, respectively. The fitted γ_{opt} falls reasonably into this range. However, the fitted σ_g is a few tens millivolts larger than their predicted values. Interestingly, for CuZnSn(S,Se)_4 , the average PL red shift is ~ 100 meV according to their study [8]. If our CZTS sample has similar level of potential fluctuation compared to that of CuZnSn(S,Se)_4 , the ~ 200 meV red shift observed from PL spectra could only be attributed to much larger bandgap fluctuation amplitude. So we propose here the dominant disorder induced problems related to PL observation could be owing to bandgap fluctuation. We then checked our hypothesis by using a theoretical model developed in reference [45]:

$$\begin{aligned} \phi_r^{glob}(E) = & \frac{\pi}{h^3 c^2} \text{erfc} \left(\frac{E_{g,mean} - E_{ph} + \beta \sigma_g^2 / KT}{\sqrt{2} \sigma_g} \right) \\ & \times E_{ph}^2 \exp \left(-\frac{E_{ph} - \mu_0 - \beta E_{g,mean}}{KT} + \frac{\beta^2 \sigma_g^2}{2(KT)^2} \right) \end{aligned} \quad (8)$$

This model was postulated to examine the impact of bandgap fluctuation (assuming a Gaussian probability distribution) on photon emission spectrum. β and μ_0 define the spatial length scale fluctuation and the chemical potential of semiconductor of interest, respectively. Fig.7a illustrates the simulated PL spectra at different bandgap fluctuation amplitudes in the case where β is comparable to minority carrier diffusion length. When σ_g is only 10 meV, a sharp peak locates at the optical bandgap. While the PL peak gradually shift to lower energy and becomes wider and flattened as σ_g is enlarged. This simulation results are in agreement with experiment observation. More importantly, the simulated PL spectra at σ_g of 120 meV overlap reasonably well with that of RTPL characterization, both showing a peak at 1.35 eV. Therefore Cu-Zn disorder induced bandgap fluctuation provides a rational way to comprehend the observed features in RTPL measurements.

When projecting CZTS bandgap fluctuation into 1D layer or uniform 2D bulk for simulation, we can use a reduced effective bandgap ($E_{g,eff}$) for flat band approximation [46]. Therefore bandgap-fluctuation induced tailing states in disordered CZTS may translate into enhanced carrier concentration and hence larger saturation current in device model where idealized semiconductor is assumed. The reduced effective bandgap of CZTS layer can be well approximated by PL peak detected from RTPL in simulation as reported in several modelling papers [5, 9]. A number of $E_{g,eff}$ values were implemented into device models based on PL peaks obtained from bandgap fluctuation model with varying σ_g as displayed in Fig. 7b. It was found that $E_{g,eff}$ of 1.35-1.37 eV, correlating with σ_g of ~120 meV, results in a ~663 mV Voc, which is consistent with J-V measurement results on the CZTS device. This result suggests that, for our fabricated CZTS, inferior hetero-interface in conjunction with bandgap fluctuation in the bulk triggered the large Voc deficit. They share nearly equal amount of contribution to voltage deficit, i.e. 235 mV, 200 mV for interface and bandgap-fluctuation respectively.

Table II Complemented parameters for final model.

CZTS layer parameters	Symbol	Value/Unit
Interface recombination velocity	S_i	10^5 cm/s
Bulk electron lifetime	τ_{SRH}	28.8 ns
Effective electronic bandgap	$E_{g,eff}$	1.37 eV

3.3.4 Completed model

Once the unknown properties were disclosed, we were able to complete the construction of our device model. A set of new parameters added into model can be found in Table II. The simulated EQE from the completed device model with appropriate bulk lifetime and interface recombination velocity, as displayed in Fig. 8a, agrees well with that from measurement. Nevertheless there are two minor discrepancies at 300-400 nm and 450-500 nm regimes. The discrepancy might arise from the difference between the used absorption coefficients for ITO and CdS layers and those actual ones. Therefore the output Jsc matches with measured one with negligible error.

Figure 8. a) Comparison of measured (red dot) and simulated (blue curve) EQE from completed Sentaurus model. b) Comparison of measured (red dot) and simulated (blue curve) J-V from completed Sentaurus model with added series resistance.

The simulated V_{oc} fits reasonably well with measured value after implementing interface recombination and narrowed effective bandgap on final model. Their detrimental effects are accumulative, contributing to ~ 440 mV V_{oc} diminutions in total. As depicted in Fig. 9a, heterojunction interface recombination and bulk disorder occupy 52.7% and 44.9% of V_{oc} loss respectively, making other loss mechanisms seemingly negligible. This observation is consistent with previous simulation work [9]. However the insignificant V_{oc} loss from bulk defect and back contact surface could only exist in the case where voltage deficit is dominantly attributed to aforementioned two aspects. According to V_{oc} loss distribution, we further used our device model to predict V_{oc} evolution by upgrading interface and bulk disorder properties, i.e. S_i and σ_g . As displayed in Fig. 9b, when interface recombination velocity was reduced from current 10^5 cm/s to 10^1 cm/s, namely from a ‘bad’ to a ‘good’ (low recombination) interface, V_{oc} could be raised up to 917 mV. Refinement of hetero-interface can be achieved in laboratory by correcting ‘cliff’ conduction band alignment via replacing CdS with more benign buffer. $Zn_{1-x}Cd_xS$ buffer can be a viable option as proved in our recent study [47]. The device using this buffer resulted in a V_{oc} value of 741 mV, which sits right in our predicted track. Therefore future improvement in interface engineering could arguably push device V_{oc} to above 900 mV. With heterojunction interface problem addressed, mitigation of bulk disorder could further eradicate another major V_{oc} bottleneck. To simulate this, we monolithically reduced σ_g , which is used in the aforementioned PL model, to find their corresponding PL peaks which were then input in device model as projected effective electronic bandgaps. Resultantly, the device V_{oc} could be boosted to a level of >1 eV when σ_g was reduced to <60 meV. The validity of simulation result is backed by recent research on CIGS solar cell. Given the low interface velocity [48] and small (<60 meV) bandgap fluctuation amplitude [8], pure sulphide CIGS (1.5 eV) has reached a V_{oc} scale of 960 mV [49]. As the chalcogenide quaternary counterpart, CZTS would potentially reach this level of high V_{oc} if bottlenecks were tackled.

Lastly we matched the measured FF in our model by introducing ad-hoc R_s of $7.5 \Omega \cdot \text{cm}^2$. Sentaurus model only takes bulk resistance into account. However extra resistors constituting the resistive network in real device are not included. Therefore the ad-hoc R_s was used to make up for these loss components in device model [5]. The J-V plots of simulated and measured CZTS device are shown in Fig. 8b, where simulated J-V curve agrees well with that of measured by sharing a nearly equal FF

around 56%. Nevertheless the shape of simulated J-V deviates from that of measured marginally at low-bias and high bias regimes. These differences might arise from device properties (like bandgap, secondary phase...etc.), variation on 2D or 3D scale and field-dependent recombination in depletion region [50]. Due to these reasons, it could be quite instrumental to extend our baseline model here to a more complicated version with 2D and 3D varying properties in the future.

Figure 9. a) Fraction of Voc loss pertain to mechanisms including heterojunction interface, bulk disorder, bulk deep level defects and back contact recombination parametrized into device model. The Voc loss is calculated comparing to that of an ideal device without any loss mechanisms. b) Device Voc evolution map predicted by improving hetero-interface and bulk disorder properties (S_i and σ_g).

4. Conclusions

In this work a reference CZTS device with 6.9% power conversion efficiency was exposed to comprehensive electrical and optical characterizations and results were then used as input into a Sentaurus TCAD device model. By reproducing the measured J-V and EQE curves in conjunction with numerical analysis, key material and device properties underlying Voc deficit, including recombination channels and disorder related bandgap narrowing, were identified and quantified.

Firstly, Heterojunction interface recombination was investigated through tuning interface recombination velocity in device model so that a fraction of simulated QEs, related to photons absorbed in near-interface regions, match that of measured QEs. This method yielded an interface recombination velocity of 10^5 cm/s suggesting the existence of defect-populated hetero-interface in CZTS device. Secondly, Effective lifetime of device model was calculated with various interface recombination velocities and bulk lifetimes at Voc bias. By matching the mean lifetime determined from TRPL, we found a bulk lifetime of 28.8 ns. Last but not least, Gaussian-distributed bandgap model was used to numerically analyse the disorder-induced tailing states in CZTS absorber through fitting QE tail and RTPL spectra. Bandgap-fluctuation amplitude of 120 meV was obtained. This, when projected into uniform 2D device, is equivalent to a narrowed bandgap of 1.37 eV.

In the ultimate device model, heterojunction interface recombination, together with disorder induced bandgap fluctuation contributed to 97% of Voc loss. Therefore we identified these two as major bottlenecks of CZTS device Voc. Our model further forecasted that, with heterojunction interface problem alone settled, the device Voc could be boosted to above 900 mV. Furthermore, device Voc could even reach to 1 eV when mitigation of these two problems comes to fruition.

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Appendix

Layer property	CdS	ZnO
Electron affinity (eV)	4.2	4.45
Optical bandgap (eV)	2.4	3.3
Relative dielectric constant	10	9
Conduction band density of states (cm ⁻³)	2.2×10^{18}	2.2×10^{18}
Valence band density of states (cm ⁻³)	1.8×10^{19}	1.8×10^{19}
Electron mobility (cm ² /V/s)	100	100
Hole mobility (cm ² /V/s)	25	25
Free Carrier concentration (cm ⁻³)	1.0×10^{18}	1.0×10^{18}

The appendix table above lists the electrical parameters inputted into buffer layer and window layer. Note that the ITO layer was only involved in optical calculation so it's "electrically transparent" in device structure.

This contour plot displays effective lifetime (Voc) variation when device is illuminated with AM1.5G spectrum, 1 SUN. Note effective lifetime reduces to ~7ns when implementing extracted bulk lifetime and interface velocity.

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