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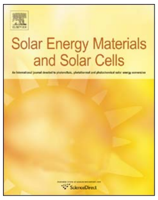

# Sentaurus modelling of 6.9% $Cu_2ZnSnS_4$ device based on comprehensive electrical & optical characterization

Aobo Pu[1], Fajun Ma[1], Chang Yan, Jialiang Huang, Kaiwen Sun, Martin Green, Xiaojing Hao*

*Australia Centre for Advanced Photovoltaics, School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney, NSW 2052, Australia*

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## ABSTRACT

In this work we perform comprehensive characterization on a 6.9% pure sulphide $Cu_2ZnSnS_4$ (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 $1\times10^5$ 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)$S_2$ (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 $Cu_2ZnSnS_4$ (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 Voc 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 Voc 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

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* Corresponding author.
*E-mail address:* xj.hao@unsw.edu.au (X. Hao).

[1] Both authors contribute equally to this work.

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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 (~900 nm)/CdS (~50 nm)/i-ZnO (50 nm)/ITO (200 nm)/Grid layers as depicted in Fig. 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 $\text{min}^{-1}$ for 3 min.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.

### 2.2. Electrical and optical characterization

C-V measurements were carried out using an impedance analyser (Hewlett Packard 4194 A) 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 −0.5V 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 5 keV 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 equiped with a 780–800 nm detector and a 470 nm solid-state laser excitation source tuned at a repetition rate of 10 MHz with incident power of 0.18 $\text{W/cm}^2$ and a laser pulse width shorter than 70 ps. 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.

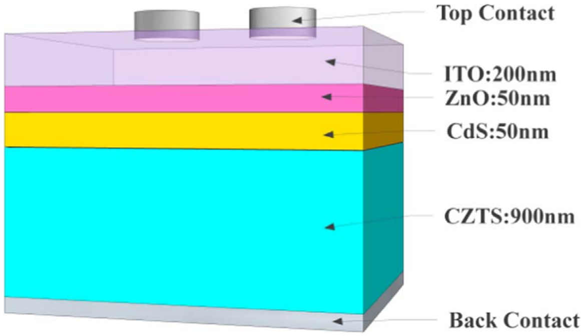

**Fig. 1.** Schematic of 6.9% efficient CZTS solar cell with labelled thickness of each layer according to SEM.

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 processess 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 coefficeint 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 A. 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 $1.42\times10^{16}/\text{cm}^3$ 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 180 nm 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, $\tau_{\text{SRH}}$ is used here to generalize bulk recombination rate due to traps distributed in forbidden bandgap. The