



(RESEARCH ARTICLE)



FULL-SPECTRUM PHOTOLUMINESCENCE ANALYSIS OF BAND TAILS AND QUASI-FERMI-LEVEL SPLITTING FOR VOLTAGE-LOSS PARTITIONING IN CIGS SOLAR CELLS

Hamidou Tangara ^{1,*}, Diakaridia Sanogo ^{1,4}, Kossi Aniya Amedome Min-Dianey ², Noé Landry Privace M'Bouana ³, Drissa Traoré ⁴ and Diouba Sacko ⁵

¹ Department of Electrical Engineering, National School of Engineering (ENI-ABT), BP 242, Bamako, Mali.

² Department of Physics, Faculty of Sciences, University of Lomé, 01BP 1515, Lomé, Togo,

³ Higher Institute of Technology, University of Bangui, B.P. 1450, Bangui, Central African Republic.

⁴ Department of Electrical Engineering, Normal School of Technical and Vocational Education (ENETP), Kabala University Campus, Building 4, Bamako, Mali,

⁵ Department of Computer Engineering and Telecommunications, National School of Engineering (ENI-ABT), BP 242, Bamako, Mali.

* Corresponding Author

GSC Advanced Research and Reviews, 2026, 28(03), 158–168

Publication history: Received on 04 August 2026; revised on 13 September 2026; accepted on 15 September 2026

Article DOI: <https://doi.org/10.30574/gscarr.2026.28.3.0234>

Copyright © 2026 Author(s) retain the copyright of this article. This article is published under the terms of the Creative Commons Attribution License 4.0

ABSTRACT

Standard Shockley–Queisser (SQ) loss analysis of CIGS solar cells assumes step-like absorptivity, ignoring both band-tail absorption and the quasi-Fermi-level splitting (QFLS). We extract the tail energy γ , QFLS $\Delta\mu$, and bandgap E_g of CIGS absorbers simultaneously from a single photoluminescence spectrum using a generalized Planck law. For two devices (18.0% and 16.9% efficiency), we obtain $\gamma = 17$ and 22 meV and $\Delta\mu = 0.76$ and 0.69 eV, consistent with EQE analysis. Including these parameters lowers the radiative-limit V_{OC} by 27 and 49 mV, reassigning part of the apparent nonradiative deficit to the tail-enhanced radiative saturation current. The corrected nonradiative losses (180 vs. 174 mV) now match the nearly identical TRPL lifetimes of the two absorbers (80 vs. 76 ns), resolving an apparent contradiction of the SQ analysis and providing a more realistic partitioning of the V_{OC} losses.

keywords: CIGS Solar Cells; Open-Circuit Voltage Losses; Quasi-Fermi-Level Splitting; Shockley–Queisser Detailed Balance.

1 INTRODUCTION

The open-circuit voltage (V_{OC}) is one of the key parameters governing the power conversion efficiency of a solar cell, and identifying the mechanisms that limit it remains a central task in photovoltaic research. The Shockley–Queisser (SQ) detailed-balance model provides the standard framework for such an analysis. From the fundamental assumption of a step-like absorption function, in which only photons with energies above the bandgap E_g are absorbed, it defines the radiative limit of the device and allows the total V_{OC} loss to be decomposed into distinct contributions. Within this idealized picture, the dark and illuminated current densities, and, in turn, the individual loss terms, can be rigorously defined. A key limitation of this approach, however, is that no real absorber possesses a step-like density of states (DOS)

and absorption coefficient. Practical photovoltaic materials, such as Cu(In, Ga)Se₂ (CIGS), exhibit an exponentially rising absorption below the bandgap, commonly referred to as the Urbach tail [1]. These tails are described by:

$$\alpha(E) = \alpha_0 \exp\left(\frac{E - E_g}{\gamma}\right), (E < E_g) \quad (1)$$

where α_0 is the absorption coefficient at the bandgap position and γ , the Urbach energy, is the characteristic energy of the tailing states. The Urbach energy reflects both the structural and thermal disorder of the material [2], and its magnitude is strongly influenced by the degree of electrostatic potential fluctuations. CIGS films, especially those grown by the three-stage co-evaporation process, exhibit pronounced spatial inhomogeneity, as confirmed by spatially resolved photoluminescence (PL) measurements. Local variations in composition give rise to fluctuations of both the local bandgap and the quasi-Fermi-level splitting (QFLS), which are directly reflected in the exponential shape of the absorption edge. Figure 1 contrasts the ideal step-like absorption edge assumed in the SQ model with that of actual samples.

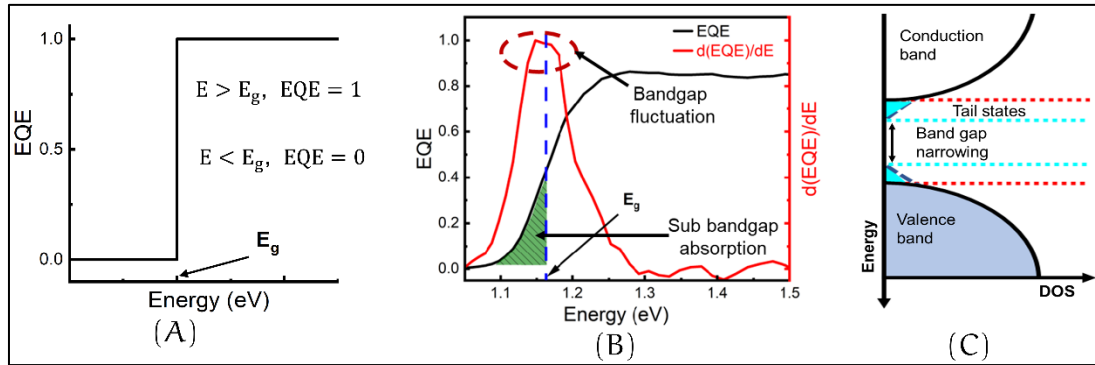


Figure 1: Schematic representation of the absorption edge of a semiconductor in (A) the SQ model where the absorptivity switches from 0 to 1 at the bandgap position E_g , (B) a real sample with an exponential shape for the DOS at the band edges. (C) Impact of the exponential tail on the DOS edges and the subsequent shrinking of the bandgap.

The impact of such band tails on photovoltaic parameters has attracted considerable attention in recent years [3,4]. Because photocurrent generation from sub-bandgap states is negligible, the influence of tail absorption concerns almost exclusively the V_{OC} . Indeed, it has been shown that V_{OC} losses increase with increasing Urbach energy across a range of solar cell materials [4-6]. Sub-bandgap absorptivity must therefore be taken into account in order to estimate realistic values of the radiative-limit and bulk-limit V_{OC} , and hence of the corresponding V_{OC} losses.

In this work, we extended the V_{OC} loss analysis of CIGS solar cells to account for the presence of exponential band tails. Specifically, we incorporated the influence of tailing states into the radiative recombination coefficient B used in the V_{OC} loss analysis. Then an expression that quantifies the additional radiative-limit V_{OC} loss, and the associated reduction of the QFLS, arising from the exponential DOS tail was derived. Finally, we compared the impact of tail states on the V_{OC} losses of CIGS absorbers prepared under different deposition conditions.

2 MATERIALS AND METHODS

2.1 Sample processing

The solar cells were fabricated on soda-lime glass (SLG) substrates coated with a 0.8 μm -thick DC sputtered Mo back contact. Besides acting as the electrical contact, the Mo layer serves as a diffusion barrier between the absorber and the glass, while the SLG substrate provides a natural source of Na incorporation into the absorber during growth, which is known to improve its electrical quality. CIGS absorbers, about 2 μm thick, were deposited by multi-source co-evaporation using the three-stage process [7]. In this growth sequence, the (In, Ga)₂Se₃ precursor is deposited in the first and third stages, while Cu and Se are co-evaporated in the intermediate second stage until Cu-rich conditions are reached, followed by a short Cu-poor finishing step. The Cu-to-group-III ratio (CGI) was controlled at 0.95 for both samples, ensuring the slightly Cu-poor composition required for efficient junction formation. Two absorbers with different deposition schemes were prepared (Table 1). For the first (high-performance) sample, the Ga-to-group-III ratio, $[\text{Ga}]/([\text{Ga}]+[\text{In}])$ (GGI) was set to 0.4 in the first stage and reduced to 0.25 in the third stage to tailor the Ga (bandgap) gradient, and the substrate temperature was 350 $^{\circ}\text{C}$ during the first stage and 550 $^{\circ}\text{C}$ during the second and third stages. The second (low-performance) sample was grown with a constant GGI of 0.3, at substrate temperatures of 400 $^{\circ}\text{C}$ and 625 $^{\circ}\text{C}$ in the corresponding stages. Apart from these growth conditions, both absorbers underwent strictly

the same processing route. After growth, both samples received an identical post-deposition treatment (PDT) at 350 °C, where KF and NaF were co-evaporated simultaneously under a Se atmosphere for 10 min. This alkali treatment passivates the absorber surface and improves the quality of the CIGS/CdS interface.

The devices were then completed by chemical bath deposition of a 35-nm-thick CdS buffer layer, followed by rf- and DC-magnetron sputtering of an undoped ZnO layer and a doped ZnO:Al layer serving as the transparent front electrode. A Ni/Al/Ni grid was deposited by evaporation to form the top contact, and a 110-nm-thick MgF₂ layer was added as an antireflection coating on top of the device to reduce reflection losses at the front surface and to enhance the short-circuit current density. The active cell area was defined by mechanical scribing of the layer stack.

Table 1: Deposition conditions for sample 1 and sample 2. Variations in the substrate temperatures ($T_{\text{sub}}(^{\circ}\text{C})$) as well as the $[\text{Ga}]/([\text{Ga}]+[\text{In}])$ at different stages are shown.

Sample 1 (high performance)				Sample 2 (low performance)			
Stage		$T_{\text{sub}}(^{\circ}\text{C})$	GGI	Stage		$T_{\text{sub}}(^{\circ}\text{C})$	GGI
1 st	In,Ga,Se	350	0.4	1 st	In,Ga,Se	400	0.3
2 nd	Cu, Se	550	-	2 nd	Cu, Se	625	0.3
3 rd	In,Ga,Se	550	0.25	3 rd	In,Ga,Se	625	0.3

2.2 Measurement setup

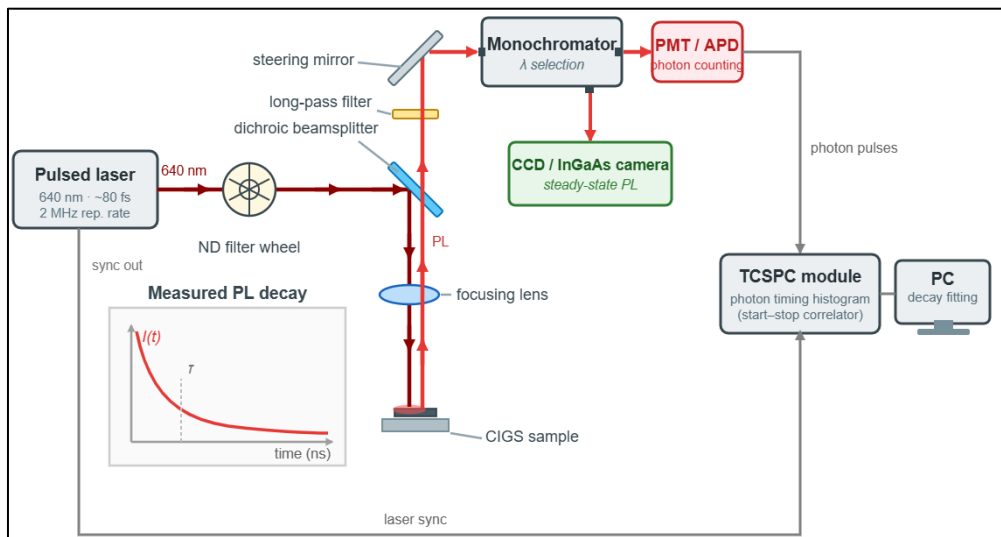


Figure 2: Steady-state PL and TCSPC-based TRPL setup for CIGS thin films.

Time-resolved photoluminescence (TRPL) measurements were performed at room temperature using a femtosecond Ti:sapphire laser operated in pulsed mode (pulse width ~80 fs, repetition rate 2 MHz) as the excitation source. The laser spot size on the sample was 40–80 μm . To record the PL transients, CIGS films covered only with CdS were used. The decay curves were recorded at the maximum energy position of the corresponding emission spectra. Emission from the narrow-gap samples was detected with an InGaAs photomultiplier tube (Hamamatsu H10330A-75), while the wide-gap samples were measured with an avalanche photodiode (IDQ ID-100, 40 ps time resolution, 300–900 nm detection range). Figure 2 shows a schematic representation of the setup.

2.3 Theoretical framework

We first outline the theoretical framework used to quantify the open-circuit voltage losses of a real device relative to an ideal device in the radiative limit (SQ model).

The SQ model defines the thermodynamic limit of photovoltaic energy conversion for a single-bandgap solar cell on the basis of the detailed-balance principle [8]. The model idealizes the cell by equating its quantum efficiency to the absorptance, $\text{EQE}(E) = a(E)$, the latter behaving as a step function of the photon energy E ; the cell is then fully characterized by its temperature T and bandgap E_g . Applying this framework to an actual device, whose absorptance is

not a step function, leads to the definition of the radiative limit [9]. Within the SQ framework, all recombination processes are assumed to be radiative. The short-circuit current density is then given by:

$$J_{SC} = q \int_0^{\infty} EQE(E) \phi_{sun}(E) dE \quad (2)$$

where q is the elementary charge, EQE the external quantum efficiency, $\phi_{sun}(E)$ the solar spectral photon flux, and E the photon energy. The radiative saturation current density follows as

$$J_0 = q \int_0^{\infty} EQE(E) \phi_{bb}(E) dE \quad (3)$$

where $\phi_{bb} = \frac{2\pi}{c^2 h^3} \frac{E^2}{[\exp(E/k_B T) - 1]}$ is the black-body spectral photon flux at temperature T , h is Planck's constant, k_B the Boltzmann constant, and c the speed of light in vacuum.

In the SQ approximation, $EQE(E) = a(E) = H(E - E_g)$, with H the Heaviside function ($H = 1$ for $E \geq E_g$, $H = 0$ for $E < E_g$). In this case J_{SC} approaches its maximum value J_{SC}^{SQ} and J_0 becomes J_0^{SQ} , and the SQ-limit open-circuit voltage is given by [10]:

$$V_{OC}^{SQ} = \frac{k_B T}{q} \ln \left(\frac{J_{SC}^{SQ}}{J_0^{SQ}} \right) \quad (4)$$

To correlate this approach with the electronic properties of actual CIGS absorbers, the V_{OC} losses due to nonradiative recombination must be evaluated. For this purpose, it is useful to express the saturation current density in the radiative limit J_0^{rad} , as well as in nonideal cases (J_0), in terms of the radiative recombination coefficient B . Following Werner et al. [11] and assuming a thin absorber (i.e., the effective minority-carrier diffusion length exceeds the sample thickness), J_0^{rad} can be written as

$$J_0^{rad} = \frac{q W n_i^2 B}{4 n_r^2} = \frac{q W n_i^2}{4 n_r^2} \left(\frac{1}{\tau_{rad} N_A} \right) \quad (5)$$

where n_r is the refractive index ($n_r = 3$), n_i the intrinsic carrier concentration, N_A the net doping density, and W the film thickness. In the low-injection regime (excess carrier density $\Delta n \ll N_A$ [12]), the ideal radiative lifetime is $\tau_{rad} = 1/(B N_A)$ [10].

Since Eq. (5) incorporates the actual absorption properties of the material, it yields a more realistic value of the radiative-limit open-circuit voltage, which is given by

$$V_{OC}^{rad} = \frac{k_B T}{q} \ln \left(\frac{J_{SC}}{J_0^{rad}} \right) \quad (6)$$

where J_{SC} is the experimental short-circuit current density. This description of V_{OC}^{rad} accounts for the impact of nonradiative recombination on J_{SC} and therefore does not represent a strict radiative limit, but it permits a more straightforward definition of the open-circuit voltage losses.

For real, non-ideal samples, the saturation current density associated with bulk nonradiative recombination, J_0^{bulk} is obtained by substituting the effective lifetime τ_{eff} for the ideal radiative lifetime τ_{rad} in Eq. (5):

$$J_0^{bulk} = \frac{q W n_i^2}{4 n_r^2} \left(\frac{1}{\tau_{eff} N_A} \right) \quad (7)$$

The effective lifetime is given by

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{nonrad}} \quad (8)$$

where τ_{nonrad} denotes the nonradiative recombination lifetime. τ_{eff} is determined from the analysis of the TRPL transients and is closely related to the density of nonradiative centers in the bulk. Note that Eq. (7) implicitly assumes that the doping density in the interfacial region varies in the same manner as the value measured in the bulk. Finally, replacing J_0^{rad} with J_0^{bulk} in Eq. (6) yields the bulk-limit open-circuit voltage V_{OC}^{bulk} , i.e., the voltage of a cell limited only by nonradiative processes in the bulk; any increase (decrease) of V_{OC}^{bulk} therefore indicates a reduction (increase) of bulk nonradiative recombination. For a systematic discussion of the origins of the voltage losses, the bulk-limit approximation assumes that nonradiative recombination is located mainly in the quasi-neutral region (QNR) and neglects recombination in the space-charge region (SCR); in reality, the SCR is subject to Shockley–Read–Hall (SRH) recombination owing to the position of the Fermi level and the presence of deep-level traps near midgap [13].

From this analysis we extract the total open-circuit voltage losses $\Delta V_{OC}^{total} = V_{OC}^{SQ}(E_g) - V_{OC}^{exp}$, together with the losses attributable to nonradiative recombination, $\Delta V_{OC}^{nonrad} = V_{OC}^{rad,sq} - V_{OC}^{exp}$ [14], where V_{OC}^{exp} is the experimental value of the open-circuit voltage.

This approach also allows the nonradiative losses to be separated into bulk ($\Delta V_{OC}^{bulk} = (V_{OC}^{SQ}(E_g) - V_{OC}^{bulk})$) and interface contributions ($\Delta V_{OC}^{inter} = \Delta V_{OC}^{total} - \Delta V_{OC}^{bulk}$).

3 RESULTS AND DISCUSSIONS

3.1 Device performance

Table 2 summarizes the photovoltaic parameters of the two devices. Both cells deliver comparable short-circuit current densities and fill factors, so their efficiency gap (18.0% vs. 16.9%) is governed mainly by the open-circuit voltage, where sample 2 lags by 26 mV (684 vs. 710 mV). In voltage-equivalent terms, the ~5% current deficit of sample 2 amounts to only ≈ 1 mV, i.e., $(k_B T/q) \ln(J_{SC}^1/J_{SC}^2)$, and is negligible (here J_{SC}^1/J_{SC}^2 represent the short-circuit currents of samples 1/2). Since both absorbers underwent strictly the same processing route apart from the growth scheme (Section 2.1), the pair constitutes a well-controlled case study for the V_{OC} loss analysis. Any meaningful decomposition of these losses, however, first requires two absorber quantities: the tail-state energy γ and the quasi-Fermi-level splitting (QFLS) $\Delta\mu$.

Table 2: Photovoltaic parameters of the two samples.

	$J_{SC}(\text{mA} \cdot \text{cm}^{-2})$	$V_{OC}(\text{mV})$	FF (%)	η (%)
Sample 1	34.6	710	74	18.0
Sample 2	33.0	684	76	16.9

3.2 Conventional extraction of $\Delta\mu$ and γ

The generalized Planck law relates the electrical properties of a photovoltaic absorber to its photoluminescence (PL) spectrum. Under quasi-equilibrium conditions, the spectral photon flux can be written as:

$$\phi_{PL}(E) = \frac{1}{4\pi^2 \hbar^3 c^2} \frac{a(E)E^2}{\exp\left(\frac{E - \Delta\mu}{k_B T}\right) - 1} \quad (9)$$

where $a(E)$ is the absorptivity. In the high-energy wing of the emission, $a(E) \approx 1$ and varies only weakly with energy, and Eq. (9) reduces to

$$\ln \left[\frac{\phi_{PL}(E)}{10^{23} E^2} \right] = - \frac{E - \Delta\mu}{k_B T} \quad (10)$$

so that $\Delta\mu$ follows from the intercept of a linear fit to the high-energy side of the semi-logarithmically plotted spectrum, while the slope yields $1/k_B T$.

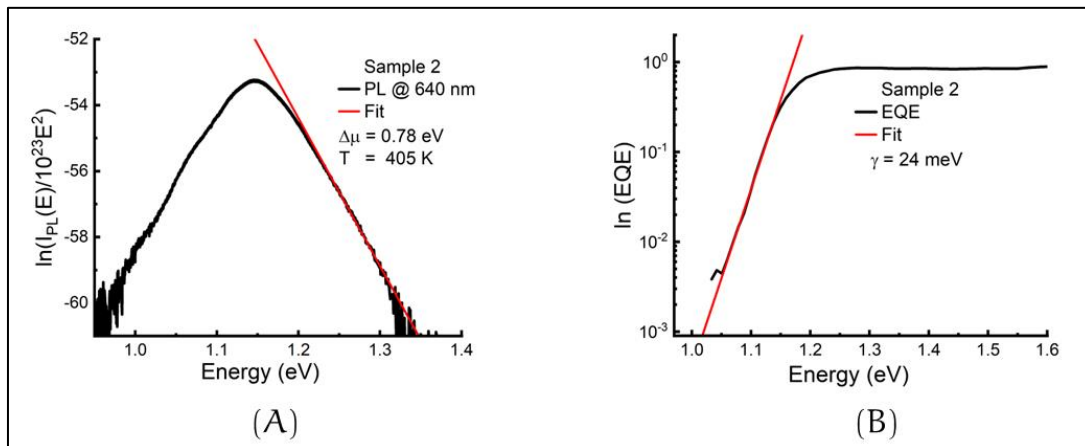


Figure 3: (A) PL spectrum of sample 2, recorded under one-sun illumination conditions showing the fit of $\Delta\mu$, the quasi-Fermi-level splitting. (B) Fit of the tail-state energy γ (Urbach energy) using the EQE spectrum of sample 2.

The PL spectrum was recorded under approximately one-sun equivalent illumination using a 640 nm laser (Figure 3(A)). Since $\Delta\mu/q$ is the maximum voltage the absorber can sustain under these conditions, it constitutes an upper bound for V_{OC} . The fit returns $\Delta\mu = 0.78$ eV, compared with an experimental $V_{OC} = 684$ mV. The tail-state energy was obtained independently by fitting the sub-bandgap region of the EQE with the Urbach relation, Eq. (1) (Figure 3(B)).

This conventional procedure, however, has several limitations. First, Eq. (10) returns a fit temperature of 405 K, which is unphysically high even when laser-induced heating is considered. Second, the extracted $\Delta\mu$ depends strongly on the spectral range chosen for the fit [15]. Third, the Urbach analysis of the EQE implicitly assumes an exponential (Urbach-like) tail and neglects other sub-bandgap absorption mechanisms. Finally, $\Delta\mu$ and γ are obtained from two separate measurements, which introduces an additional uncertainty when the two parameters are combined in the voltage-loss analysis. A more self-consistent model is therefore required.

3.3 Generalized description of sub-bandgap absorption

To this end, we adopt the model of Katahara and Hillhouse [15], which unifies the various sub-bandgap absorption mechanisms in a single functional form. Sub-bandgap absorption is conventionally written as an exponential decay of the absorption coefficient from the band edge into the gap (Figure 1(C)); in its simplest form the decay power is unity (Urbach tail). Deviations from this behavior are well documented: in the presence of charged defects the tail sharpens to a decay power of 5/4 [16]; field-assisted absorption (Franz-Keldysh effect) yields 3/2 [17]; and heavily doped semiconductors exhibit a power of 2 [18]. CIGS films grown by the three-stage process are highly disordered and strongly compensated, with charged grain boundaries [19]; a decay power exceeding unity is therefore expected, motivating a generalized treatment. Katahara and Hillhouse introduced:

$$G(\Delta E) = \exp \left[- \left(\frac{|\Delta E|}{\gamma} \right)^\theta \right] \quad (E < E_g) \quad (11)$$

where γ is the characteristic decay energy and θ the decay exponent, whose value discriminates between the mechanisms above, with $\Delta E = E - E_g$. Convolution of Eq. (11) with the band-to-band absorption of a direct-gap semiconductor yields a closed-form expression valid over the entire spectral range:

$$G(\Delta E) = \frac{1}{2\gamma\Gamma\left(1 + \frac{1}{\theta}\right)} \int_{-\infty}^{\Delta E} \exp \left[- \left(\frac{|\Delta E^*|}{\gamma} \right)^\theta \right] \sqrt{\Delta E - \Delta E^*} d\Delta E^* \quad (12)$$

where Γ is the gamma function and the prefactor is a normalization constant [20]. The absorption coefficient follows as $\alpha(E) = \alpha_0 G(E)$, and the absorbance follows from the Lambert-Beer law, $a(E) = 1 - \exp[-\alpha(E)d]$, where d is the absorber thickness. Including the occupation probabilities of the conduction and valence bands [21], the full PL spectrum becomes

$$\begin{aligned} \phi_{PL}(E) = & \frac{1}{4\pi^2\hbar^3c^2} \frac{E^2}{\exp\left(\frac{E - \Delta\mu}{k_B T}\right) - 1} \\ & \times \left\{ 1 - \exp \left[-G(\Delta E)\alpha_0 d \left(1 - \frac{2}{\exp\left(\frac{E - \Delta\mu}{2k_B T}\right) + 1} \right) \right] \right\} \end{aligned} \quad (13)$$

Fitting the complete spectrum with Eq. (13), rather than its high-energy wing alone, yields γ , $\Delta\mu$, and E_g simultaneously from a single PL measurement. Moreover, because the entire spectrum constrains the fit, the extracted parameters are independent of the chosen fitting range.

3.4 Validation of the full-spectrum fit

Figure 4 compares the bandgap and Urbach energy of sample 2, obtained from the PL fit of Eq. (13), with the values derived from the EQE.

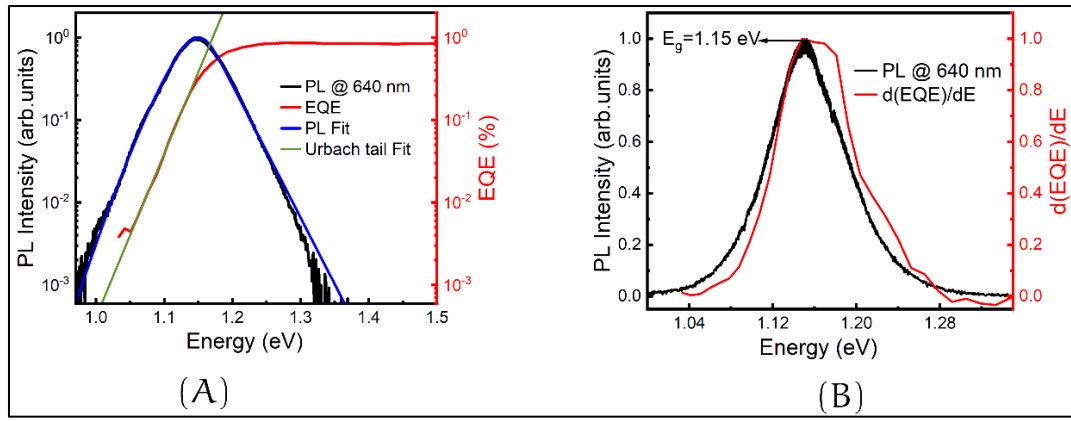


Figure 4: (A) PL spectrum fit with Eq. (13) vs. EQE. The PL fit is shown in blue and the fit of the EQE to extract γ is displayed in dark green. (B) PL spectrum vs. $d(\text{EQE})/dE$ showing the bandgap position and the peak energy position of the PL spectrum of sample 2.

Table 3 summarizes the results, together with $\Delta\mu$ and the fit temperature. The bandgaps agree within 10 meV (1.15 vs. 1.16 eV) and the tail energies within 2 meV (22 vs. 24 meV), confirming the mutual consistency of the two spectroscopies. In contrast to the high-energy fit ($\Delta\mu = 0.78$ eV at $T = 405$ K), the full-spectrum analysis returns a physically reasonable temperature (318 K); in addition, γ and $\Delta\mu$ are range-independent, and all parameters are extracted from the same measurement.

Table 3: Bandgap energy E_g , tail-state energy γ , QFLS $\Delta\mu$, and temperature extracted from the fits of the PL spectrum and the EQE of sample 2.

	E_g (eV)	γ (meV)	$\Delta\mu$ (eV)	T (K)
PL	1.15	22	0.69	318
EQE	1.16	24	-	-

3.5 Benchmark: Shockley–Queisser loss analysis

To quantify the impact of these parameters on the voltage losses, the two devices are first analyzed within the classical Shockley–Queisser (SQ) framework; the resulting values serve as benchmarks throughout this work. As described in Section 2.3, the total V_{OC} loss is defined as $\Delta V_{OC}^{total} = V_{OC}^{SQ}(E_g) - V_{OC}^{exp}$, and the loss due to nonradiative recombination as $\Delta V_{OC}^{nonrad} = V_{OC}^{rad,sq} - V_{OC}^{exp}$. Here V_{OC}^{SQ} depends exclusively on the bandgap, whereas $V_{OC}^{rad,sq}$ is further determined by the measured EQE; the bandgaps were obtained from the first derivative of the EQE with respect to energy. Table 4 lists the results. Sample 2 exhibits the larger losses, with $\Delta V_{OC}^{total} = 231$ mV and $\Delta V_{OC}^{nonrad} = 223$ mV, compared with 212 and 207 mV for sample 1.

Table 4: V_{OC} in the SQ limit (V_{OC}^{SQ}), in the radiative limit ($V_{OC}^{rad,sq}$), and experimental values (V_{OC}^{exp}) for samples 1 and 2. ΔV_{OC}^{total} and ΔV_{OC}^{nonrad} are the total V_{OC} losses and the losses due to nonradiative processes, respectively.

	$V_{OC}^{SQ}(E_g)$ (mV)	$V_{OC}^{rad,sq}$ (mV)	V_{OC}^{exp} (mV)	ΔV_{OC}^{total} (mV)	ΔV_{OC}^{nonrad} (mV)
Sample 1	922	917	710	212	207
Sample 2	915	907	684	231	223

If the nonradiative losses were governed by the minority-carrier lifetime alone, this difference should be reflected in the carrier lifetimes of the two absorbers which is not the case. As shown in Figure 5, room-temperature TRPL excited at 400 nm yields nearly identical slow decay components, $\tau_2 = 80$ ns for sample 1 and 76 ns for sample 2, both dominated by bulk recombination.

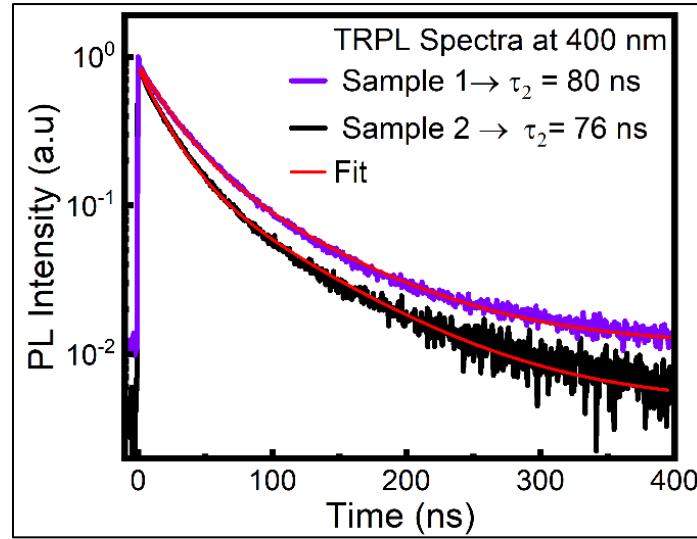


Figure 5: Room-temperature TRPL curves for Samples 1 and 2 measured with a 400 nm laser. τ_2 is the slow decay component related to bulk recombination as shown on the graph.

3.6 Tail-state analysis of both absorbers

To assess how sub-bandgap absorption affects this analysis, Eq. (13) was fitted to the PL spectra of both devices (Figure 6). Sample 1, the higher-efficiency device, exhibits both a smaller tail energy ($\gamma = 17$ vs. 22 meV) and a larger QFLS ($\Delta\mu = 0.76$ vs. 0.69 eV), indicating a lower density of structural defects and weaker electrostatic-potential fluctuations, i.e., a superior absorber quality. The remaining question is how strongly γ and $\Delta\mu$ affect the voltage losses.

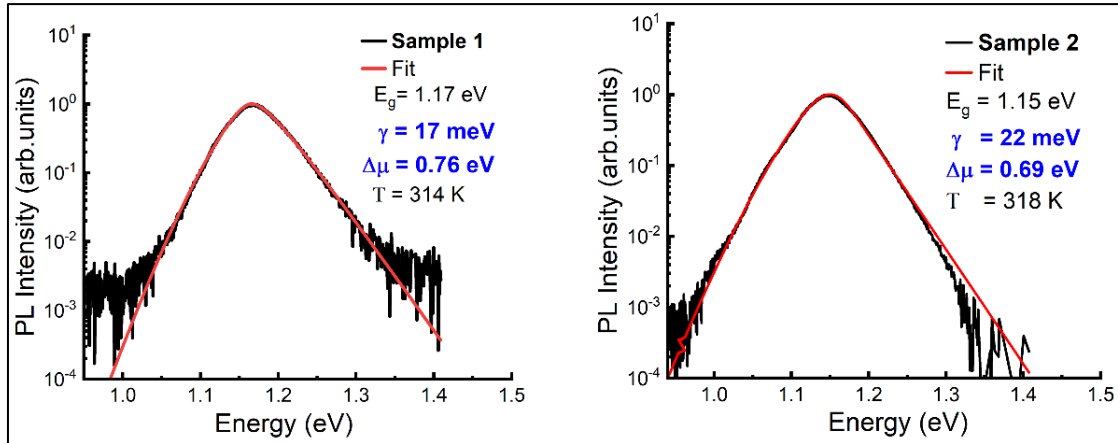


Figure 6: PL spectrum fit with Eq. (13) for samples 1 and 2. The spectra were recorded under one-sun illumination conditions with a 640 nm laser source.

3.7 Radiative limit with sub-bandgap absorptivity

Accounting for the sub-bandgap absorptivity lowers the radiative-limit V_{OC} by

$$\Delta V_{OC}^{rad} = V_{OC}^{rad} - V_{OC}^{rad,sq} \quad (14)$$

where V_{OC}^{rad} includes the tail absorption and $V_{OC}^{rad,sq}$ is the radiative limit of the SQ model. In the SQ limit, $J_0^{rad,sq}$ follows directly, since the EQE equals unity above the bandgap and small energy terms can be neglected:

$$J_0^{rad,sq} = \frac{2\pi q}{h^3 c^2} \int_{E_g}^{\infty} E^2 \exp\left(-\frac{E}{k_B T}\right) dE \approx \frac{2\pi q}{h^3 c^2} k_B T E_g^2 \exp\left(-\frac{E_g}{k_B T}\right) \quad (15)$$

With an exponential tail, the sub-bandgap EQE takes the form

$$EQE(E) = \alpha_0 \exp\left(\frac{E - E_g}{\gamma}\right) \quad (16)$$

and the additional absorption increases the radiative saturation current, $J_0^{\text{rad}} = J_0^{\text{rad,sq}} + J_0^{\text{rad,subb}}$, where $J_0^{\text{rad,subb}}$ is the sub-bandgap contribution. Neglecting the small terms and setting $a = 1$, the tail-induced change in the radiative V_{OC} is

$$\Delta V_{\text{OC}}^{\text{rad}} = \frac{k_B T}{q} \ln \left(1 - \frac{\gamma}{k_B T} \right) \quad (17)$$

When the QFLS is taken into account, the small terms can no longer be neglected and the band occupation must be included. The black-body term then reads

$$\Phi_{\text{PL}}(E) = \frac{2\pi}{h^3 c^2} \frac{E^2}{\exp \left(\frac{E - \Delta\mu}{k_B T} \right) - 1} \quad (18)$$

and the EQE acquires an occupation factor,

$$\text{EQE}(E) = \alpha_0 \exp \left(\frac{E - E_g}{\gamma} \right) \tanh \left(\frac{E - \Delta\mu}{4k_B T} \right) \quad (19)$$

The resulting change in the radiative V_{OC} is

$$\Delta V_{\text{OC}}^{\text{rad}} = \frac{k_B T}{q} \ln \left(1 + \frac{\exp \left[\left(\frac{1}{k_B T} - \frac{1}{\gamma} \right) E_g \right] I(\gamma, \Delta\mu)}{k_B T E_g^2} \right) \quad (20)$$

where $I(\gamma, \Delta\mu)$ is the van Roosbroeck-Shockley integral including both the QFLS and the sub-bandgap absorptivity [22-25]. For tail energies below the thermal energy at room temperature, Eq. (17) is recovered, with $V_{\text{OC}}^{\text{rad}}$ the radiative V_{OC} including γ and $\Delta\mu$ and $V_{\text{OC}}^{\text{rad,sq}}$ the SQ radiative limit.

Figure 7 shows $\Delta V_{\text{OC}}^{\text{rad}}$ as a function of γ . For tail energies below ≈ 26 meV, γ dominates the correction, while the QFLS contribution is minimal, which is why the two curves (sample 1, red; sample 2, black) are indistinguishable from one another in this range. Since both absorbers exhibit $\gamma < 25$ meV, including the QFLS and the sub-bandgap absorptivity lowers the radiative V_{OC} , and hence the loss attributed to nonradiative recombination, relative to the SQ benchmark, the more so the larger the tail energy.

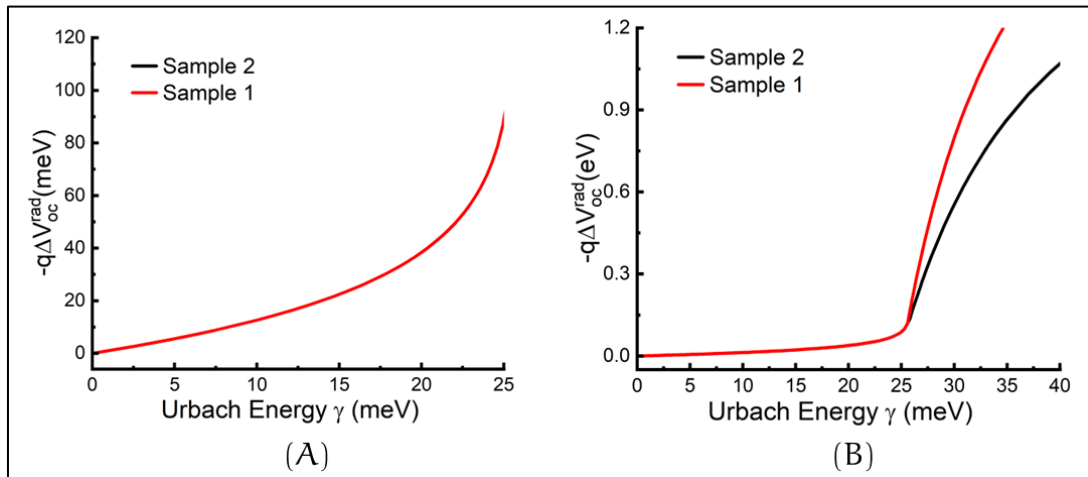


Figure 7: Radiative voltage deficit $\Delta V_{\text{OC}}^{\text{rad}}$ as a function of tail-state energy γ : (A) for $\gamma < 25$ meV, (B) where the QFLS contribution is more visible for $\gamma > 25$ meV.

3.8 Resolution of the lifetime paradox

With $\gamma = 17$ meV (sample 1) and 22 meV (sample 2), the radiative limits drop from 917 to 890 mV and from 907 to 858 mV, corresponding to $\Delta V_{\text{OC}}^{\text{rad}} = -27$ and -49 mV, respectively (Table 5). The total losses (212 and 231 mV) are of course unchanged; what the corrected model modifies is their partition.

Table 5: Tail-state energy γ , radiative-limit V_{OC} without ($V_{OC}^{rad,sq}$) and with (V_{OC}^{rad}) sub-bandgap absorptivity, and the resulting correction ΔV_{OC}^{rad} .

	$\gamma(\text{meV})$	$V_{OC}^{rad,sq}(\text{mV})$	$V_{OC}^{rad}(\text{mV})$	$\Delta V_{OC}^{rad}(\text{mV})$
Sample 1	17	917	890	-27
Sample 2	22	907	858	-49

As Table 6 shows, the nonradiative losses become 180 mV for sample 1 and 174 mV for sample 2, now nearly identical, in agreement with the nearly identical TRPL lifetimes of Figure 5. The apparent contradiction posed by the SQ analysis is thus resolved. Part of the voltage deficit attributed to nonradiative recombination under the step-like-absorption assumption in fact originates from the tail-induced increase of the radiative saturation current. Partitioning the V_{OC} losses with the QFLS- and tail-corrected radiative limit therefore provides a more accurate description of nonradiative recombination in CIGS devices.

Table 6: Summary of the V_{OC} losses analysis for samples 1 and 2.

	$V_{OC}^{SQ}(E_g)(\text{mV})$	$V_{OC}^{rad,sq}(\text{mV})$	$V_{OC}^{rad}(\text{mV})$	$V_{OC}^{exp}(\text{mV})$	$\Delta V_{OC}^{total}(\text{mV})$	$\Delta V_{OC}^{nonrad,corr}(\text{mV})$
Sample 1	922	917	890	710	212	180
Sample 2	915	907	858	684	231	174

4 CONCLUSION

In this work, we have shown that the quasi-Fermi-level splitting $\Delta\mu$ and the energy of the tail states γ of CIGS absorbers can be extracted accurately and simultaneously from a single PL measurement by fitting the full emission spectrum with the generalized Planck law, Eq. (13). The values obtained agree with those derived independently from EQE measurements, remain independent of the spectral fitting range, and return physically reasonable fit temperatures. Incorporating γ and $\Delta\mu$ into the detailed-balance analysis lowers the radiative-limit V_{OC} by 27 and 49 mV for samples 1 and 2, respectively, relative to the SQ benchmark. This correction redistributes the partitioning of the V_{OC} losses. The nonradiative losses of the two devices become nearly identical (180 vs. 174 mV), in quantitative agreement with their TRPL lifetimes, thereby resolving the apparent contradiction posed by the SQ analysis. The approach thus provides a more realistic partitioning of the open-circuit voltage losses in CIGS devices and a reliable benchmark against which the impact of performance-enhancing treatments, such as alkali post-deposition treatment and heat–light soaking, can be assessed in a more meaningful way.

STATEMENTS ON COMPLIANCE WITH ETHICAL STANDARDS

Acknowledgments

The authors acknowledge the National School of Engineering for providing the institutional infrastructure, library access, and facilities necessary to complete this research.

Disclosure of conflict of interest

The authors declare no conflicts of interest regarding this manuscript.

REFERENCES

- [1] F. Urbach, "The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids," *Physical Review* 92(5), 1324 (1953).
- [2] S. John, C. Soukoulis, M. H. Cohen, and E. N. Economou, "Theory of electron band tails and the Urbach optical-absorption edge," *Physical Review Letters* 57(14), 1777 (1986).
- [3] P. K. Nayak and D. Cahen, "Real world efficiency limits: the Shockley–Queisser model as a starting point," In: *Advanced Concepts in Photovoltaics*, RSC, pp. 547–566 (2014).

- [4] P. K. Nayak, T. S. Mahony, D. Bozyigit, M. Sponseller, J. Holovsky, M. G. Bawendi, and V. Bulović, "Radiative efficiency limit with band tailing exceeds 30% for quantum dot solar cells," *ACS Energy Letters* 2(11), 2616–2624 (2017).
- [5] P. K. Nayak, S. Mahesh, H. J. Snaith, and D. Cahen, "Photovoltaic solar cell technologies: analysing the state of the art," *Nature Reviews Materials* 4(4), 269–285 (2019).
- [6] S. De Wolf, J. Holovsky, S.-J. Moon, P. Löper, B. Niesen, M. Ledinsky, F.-J. Haug, J.-H. Yum, and C. Ballif, "Organometallic halide perovskites: sharp optical absorption edge and its relation to photovoltaic performance," *The Journal of Physical Chemistry Letters* 5(6), 1035–1039 (2014).
- [7] J. Nishinaga, T. Koida, S. Ishizuka, Y. Kamikawa, H. Takahashi, M. Iioka, H. Higuchi, Y. Ueno, H. Shibata, and S. Niki, "Effects of long-term heat–light soaking on photovoltaic efficiency limits in Cu(In,Ga)Se₂ solar cells with KF postdeposition treatment," *Applied Physics Express* 10(9), 092301 (2017).
- [8] W. Shockley and H. J. Queisser, "Detailed balance limit of efficiency of p–n junction solar cells," *Journal of Applied Physics* 32(3), 510–519 (1961).
- [9] T. Kirchartz, A. Helbig, W. Reetz, M. Reuter, J. H. Werner, and U. Rau, "Reciprocity between electroluminescence and quantum efficiency used for the characterization of silicon solar cells," *Progress in Photovoltaics: Research and Applications* 17(6), 394–402 (2009).
- [10] U. Rau, B. Blank, T. C. M. Müller, and T. Kirchartz, "Efficiency potential of photovoltaic materials and devices unveiled by detailed-balance analysis," *Physical Review Applied* 7(4), 044016 (2017).
- [11] J. H. Werner, J. Mattheis, and U. Rau, "Efficiency limitations of polycrystalline thin film solar cells: case of Cu(In,Ga)Se₂," *Thin Solid Films* 480–481, 399–409 (2005).
- [12] J. Serhan, Z. Djebbour, W. Favre, A. Migan-Dubois, A. Darga, D. Mencaraglia, N. Naghavi, G. Renou, J.-F. Guillemoles, and D. Lincot, "Investigation of the metastability behavior of CIGS-based solar cells with ZnMgO–Zn(S,O,OH) window-buffer layers," *Thin Solid Films* 519(21), 7606–7610 (2011).
- [13] A. Lafuente-Sampietro, J. Chen, S. Wang, X. Hao, M. M. Islam, T. Kato, H. Sugimoto, K. Akimoto, and T. Sakurai, "Wavelength-dependent J–V characteristics of CuIn_{1–x}Ga_x(S,Se)₂ solar cells and carrier recombination," *Applied Physics Express* 12(6), 061001 (2019).
- [14] M. He, C. Yang, J. Li, M. P. Suryawanshi, J. Kim, M. A. Green, and X. Hao, "Kesterite solar cells: insights into current strategies and challenges," *Advanced Science* 8(9), 2004313 (2021).
- [15] J. K. Katahara and H. W. Hillhouse, "Quasi-Fermi level splitting and sub-bandgap absorptivity from semiconductor photoluminescence," *Journal of Applied Physics* 116(17), 173504 (2014).
- [16] B. I. Shklovskii and A. L. Efros, "Percolation theory and conductivity of strongly inhomogeneous media," *Soviet Physics Uspekhi* 18(11), 845 (1976).
- [17] W. Franz, "Einfluss eines elektrischen Feldes auf eine optische Absorptionskante," *Zeitschrift für Naturforschung A* 13(6), 484–489 (1958).
- [18] E. O. Kane, "Thomas–Fermi approach to impure semiconductor band structure," *Physical Review* 131(1), 79 (1963).
- [19] S. Siebentritt, "What limits the efficiency of chalcopyrite solar cells?" *Solar Energy Materials and Solar Cells* 95(6), 1471–1476 (2011).
- [20] E. M. Spaans, J. de Wild, T. J. Savenije, and B. Vermang, "Unified potential fluctuations model for photoluminescence spectra at room temperature of Cu(In,Ga)Se₂ thin films," *Journal of Applied Physics* 130(12), 123103 (2021).
- [21] R. Bhattacharya, B. Pal, and B. Bansal, "On conversion of luminescence into absorption and the van Roosbroeck–Shockley relation," *Applied Physics Letters* 100(22), 222103 (2012).
- [22] J. Bisquert, "Unique curve for the radiative photovoltage deficit caused by the Urbach tail," *The Journal of Physical Chemistry Letters* 12, 7840–7845 (2021).
- [23] J. Wong, S. T. Omelchenko, and H. A. Atwater, "Impact of semiconductor band tails and band filling on photovoltaic efficiency limits," *ACS Energy Letters* 6, 52–57 (2021).
- [24] P. Würfel and U. Würfel, *Physics of Solar Cells: From Basic Principles to Advanced Concepts*, Wiley-VCH, Weinheim (2009).
- [25] P. Würfel, "The chemical potential of radiation," *Journal of Physics C: Solid State Physics* 15, 3967 (1982).