

Effect of a Band-Gap Gradient on the Radiative Losses in the Open-Circuit Voltage of Solar Cells

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The radiative open-circuit voltage loss in a solar cell occurs because the absorptance spectrum near the band gap shows a gradual increase rather than a sharp step-function-like transition. This broadening effect has been attributed to band-gap fluctuations and/or to Urbach tails. In this work, we use modeling based on Planck's generalized law to distinguish between these two effects. Our results demonstrate that Urbach tails have only a minimal effect on the absorptance-edge broadening and clarify that even an ideal direct semiconductor, with no band-gap fluctuations, shows broadening at the absorptance onset. Furthermore, state-of-the-art inorganic thin-film solar cells often incorporate a band-gap gradient across their thickness, which can further contribute to the absorptance broadening. Using Cu(In, Ga)Se₂ (CIGSe) absorbers as a case study, we perform a comprehensive analysis of voltage losses through absolute photoluminescence and electroluminescence spectroscopy, combined with photospectrometry and high-spatial-resolution cathodoluminescence measurements. This study has two main purposes: (i) to present a detailed loss analysis based on Planck's generalized law and (ii) to quantify the radiative losses arising from the band-gap gradient. We find that the loss analysis based on the combination of radiative, generation, and nonradiative losses covers the entire losses and does not leave out any other significant contribution. Samples with a graded band-gap profile show more pronounced broadening of the absorptance onset and up to 16 mV higher radiative losses compared to the samples with uniform band gap. There is also an indication that band-gap-graded samples have larger lateral band-gap inhomogeneity.

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I. INTRODUCTION

The quasi-Fermi-level splitting ($\Delta\mu$) in a photovoltaic device is analogous to the open-circuit voltage (V_{OC}) [1–5]. The Shockley-Queisser (SQ) model predicts the maximum achievable $\Delta\mu$ (denoted here as qV_{OC}^{SQ}) of an idealized solar cell with a steplike absorptance $A(E)$ spectrum [6], where $A(E)$ is zero below the band gap and one above it. On the

other hand, real solar cells exhibit a more or less gradual increase in the $A(E)$ edge [7]. Multiple factors affect the broadening of the $A(E)$ spectra; e.g., the presence of lateral band-gap fluctuations [8–10], sub-band-gap states [11], the thickness of the absorber layer [4,12], and the presence of a compositional gradient in the absorber [9,12] can all contribute to the broadening of the $A(E)$ profile. Additionally, this broadening is more pronounced in indirect semiconductors than in direct ones [7].

For a solar cell with a gradual $A(E)$ onset, the maximum attainable $\Delta\mu$, known as the radiative $\Delta\mu$ limit ($\Delta\mu^{rad}$), has lower values than the SQ limit (qV_{OC}^{SQ}) [4,7,8,13]. This difference is due to two effects: (i) increased emission, because lower-energy states contribute more strongly to the radiative emission [4] (radiative loss $\delta\Delta\mu^{rad}$), and (ii) lower generation, mostly because of insufficient absorption

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(generation loss $\delta\Delta\mu^{\text{Gen}}$). Further losses are due to non-radiative recombination (i.e., Shockley-Read-Hall [14,15] and Auger-Meitner recombination [16–18]).

The separation of the different loss mechanisms in V_{OC} was first introduced by Rau *et al.* [7]. Their approach was based on the optoelectronic reciprocity principle [19], which links the electroluminescence (EL) spectrum of any solar cell to its short-circuit-current quantum efficiency $QE(E)$ spectrum. The authors introduced the radiative V_{OC} loss ($\delta V_{\text{OC}}^{\text{rad}}$), based on the increased radiative emission due to the gradual increase of the $QE(E)$ spectrum, the short-circuit V_{OC} loss ($\delta V_{\text{OC}}^{\text{SC}}$), due to a decrease in the short-circuit current density (J_{SC}) of solar cells caused by incomplete absorption and charge-collection losses, and the nonradiative V_{OC} loss ($\delta V_{\text{OC}}^{\text{nr}}$), due to nonradiative recombination. In their approach, the nonradiative losses were determined from the difference of the measured V_{OC} and its radiative V_{OC} limit ($V_{\text{OC}}^{\text{rad}}$). However, absolute photoluminescence (PL) measurements allow us to determine nonradiative losses directly from the PL quantum efficiency (Y_{PL}). Therefore, here we analyze individual loss components and determine the final $\Delta\mu$ (analogous to V_{OC}) from PL and photospectrometric absorptance measurements. Subsequently, we compare these results to the $\Delta\mu$ values determined from a linear fit to the generalized Planck’s law [3,4,20,21].

To investigate if the loss analysis is complete and adds up, we start by describing analogies and differences between the two approaches: one based on the optoelectronic reciprocity principle and the other on the generalized Planck’s law. Subsequently, we apply the generalized Planck’s law to a couple of model systems, which allows us to separate the influence of the band-gap fluctuations and Urbach tails; these models also link real band-gap distributions to the distribution of step-function band gaps.

State-of-the-art inorganic thin-film solar cells usually incorporate a band-gap-gradient profile across the absorber thickness to minimize interface recombination. In Cu(In,Ga)Se₂ (CIGSe) solar cells, this gradient is achieved by increasing the Ga concentration toward both the front and back surfaces, resulting in a higher band gap at each end [11,22–25]. The presence of a higher Ga concentration (i.e., a higher band gap) near the back contact is essential to mitigate back-surface recombination [26,27]. Additionally, the front gradient helps to reduce front interface recombination if this interface is not ideal [26]. In Cd(Se, Te) solar cells, this band-gap engineering involves changing the Se and Te composition through the depth [28,29]. In emerging technologies, such as CuZnSn(S, Se)₄, there are also attempts to engineer the band gap along the absorber thickness. Particularly, adjustments in the S and Se concentrations across the depth has yielded efficiencies up to 13.7% by using a “V-shaped” band-gap profile [30]. The presence of a gradient further softens the absorption edge, because the region with the minimum

band gap extends only over a short depth in the absorber and therefore cannot fully absorb near-edge light.

To clarify the influence of a band-gap gradient on the radiative voltage loss, we experimentally investigate several CIGSe films and solar cells, with and without a band-gap gradient, using two approaches: one based on the generalized Planck’s law and the other on the optoelectronic reciprocity principle. We will show in the following (i) that the loss analysis introduced by Rau *et al.* [7] covers all significant losses, i.e., the losses add up to the actual $\Delta\mu$, and (ii) we quantify the additional radiative losses caused by the presence of a band-gap gradient. In particular, we show that the band-gap gradient softens the absorption edge, i.e., a gradient increases the width of the band-gap distribution by about 10–20 meV and the radiative loss by 5–16 mV.

Furthermore, by performing a meta-analysis of published CIGSe data, we demonstrate that the broadening of $A(E)$ is directly correlated with the strength of the Ga gradient throughout the depth. Our analysis reveals that when the minimum band-gap region is confined to a narrow thickness, the absorptance edge is broader compared to the cases in which the minimum band gap extends significantly through the depth of the absorber.

II. THEORY AND GENERALIZED DETAILED-BALANCE MODEL

The radiative V_{OC} loss ($\delta V_{\text{OC}}^{\text{rad}}$) was first introduced by Rau *et al.* [7]. In their study, the authors expanded the loss analysis to also include the short-circuit V_{OC} loss ($\delta V_{\text{OC}}^{\text{SC}}$) and the nonradiative V_{OC} loss ($\delta V_{\text{OC}}^{\text{nr}}$). We refer to this analysis as the “generalized detailed-balance model”. In its original version, this model is derived from the optoelectronic reciprocity principle [7,19] and relies on the optoelectronic characterization of complete solar cells by the external quantum efficiency $QE(E)$ spectrum. This model can be expanded to purely optical PL measurements for solar absorbers, without requiring a complete device structure [4]. This purely optical approach makes use of the generalized Planck’s law as the starting point. In Table I, we directly compare the formalism based on the reciprocity principle (optoelectronic measurements) to the one based on the generalized Planck’s law (optical measurements). For simplicity, all symbols and constants used in this study are listed in Appendix A. Moreover, a detailed derivation of the loss analysis based on optical characterization (i.e., using Planck’s generalized law) is presented in Appendix B.

The PL spectrum, $\Phi_{\text{PL}}(E)$, represents the photon flux density per energy interval. The generalized Planck’s law [Eq. (1)] links $\Phi_{\text{PL}}(E)$ to the absorptance spectrum $A(E)$ and $\Delta\mu$. This formalism, based on optical measurements, [Eq. (1)], allows us to generalize the detailed-balance model for non-step-like $A(E)$ spectra and determine the

TABLE I. A summary of the key equations for the generalized detailed-balance model, based on both optical and optoelectronic measurements. The symbols and constants are explained in Appendix A.

Equation to start with	Optical measurements	Optoelectronic measurements
	Generalized Planck's law:	Reciprocity principle:
	$\Phi_{\text{PL}}(E) \approx A(E)\Phi_{\text{BB}}(E) \exp\left(\frac{\Delta\mu}{k_B T}\right) \quad (1)$	$\Phi_{\text{EL}}(E) \approx QE(E)\Phi_{\text{BB}}(E) \exp\left(\frac{V_{\text{in}}}{k_B T}\right) \quad (7)$
Radiative limit	$\Delta\mu^{\text{rad}} = k_B T \ln \frac{\int_0^\infty A(E)\Phi_{\text{Sun}}(E)dE}{\int_0^\infty A(E)\Phi_{\text{BB}}(E)dE}$ $= k_B T \ln \frac{F_{\text{Gen}}^{\text{Sun}}}{F_0^{\text{rad}}} \quad (2)$	$V_{\text{OC}}^{\text{rad}} = \frac{k_B T}{q} \ln \frac{\int_0^\infty QE(E)\Phi_{\text{Sun}}(E)dE}{\int_0^\infty QE(E)\Phi_{\text{BB}}(E)dE}$ $= \frac{k_B T}{q} \ln \frac{J_{\text{SC}}}{J_0^{\text{rad}}} \quad (8)$
Radiative loss	$\delta\Delta\mu^{\text{rad}} = -k_B T \ln \left(\frac{\int_{E_g}^\infty \Phi_{\text{BB}}(E)dE}{\int_0^\infty A(E)\Phi_{\text{BB}}(E)dE} \right)$ $= -k_B T \ln \left(\frac{F_0^{\text{SQ}}}{F_0^{\text{rad}}} \right) \quad (3)$	$\delta V_{\text{OC}}^{\text{rad}} = -\frac{k_B T}{q} \ln \left(\frac{\int_{E_g}^\infty \Phi_{\text{BB}}(E)dE}{\int_0^\infty QE(E)\Phi_{\text{BB}}(E)dE} \right)$ $= -\frac{k_B T}{q} \ln \left(\frac{J_0^{\text{SQ}}}{J_0^{\text{rad}}} \right) \quad (9)$
Generation or short-circuit loss	$\delta\Delta\mu^{\text{Gen}} = -k_B T \ln \left(\frac{\int_0^\infty A(E)\Phi_{\text{Sun}}(E)dE}{\int_{E_g}^\infty \Phi_{\text{Sun}}(E)dE} \right)$ $= -k_B T \ln \left(\frac{F_{\text{Gen}}^{\text{Sun}}}{F_{\text{Gen}}^{\text{SQ}}} \right) \quad (4)$	$\delta V_{\text{OC}}^{\text{SC}} = -\frac{k_B T}{q} \ln \left(\frac{\int_0^\infty QE(E)\Phi_{\text{Sun}}(E)dE}{\int_{E_g}^\infty \Phi_{\text{Sun}}(E)dE} \right)$ $= -\frac{k_B T}{q} \ln \left(\frac{J_{\text{SC}}}{J_{\text{SC}}^{\text{SQ}}} \right) \quad (10)$
Nonradiative losses	$\delta\Delta\mu^{\text{nr}} = -k_B T \ln(Y_{\text{PL}}) \quad (5)$	$\delta V_{\text{OC}}^{\text{nr}} = -\frac{k_B T}{q} \ln(Y_{\text{EL}}) \quad (11)$
Final $\Delta\mu/V_{\text{in}}$	$\Delta\mu = \Delta\mu^{\text{rad}} - \delta\Delta\mu^{\text{nr}}$ $= qV_{\text{OC}}^{\text{SQ}} - \delta\Delta\mu^{\text{rad}} - \delta\Delta\mu^{\text{Gen}} - \delta\Delta\mu^{\text{nr}} \quad (6)$	$V_{\text{in}} = V_{\text{OC}}^{\text{rad}} - \delta V_{\text{OC}}^{\text{nr}}$ $= V_{\text{OC}}^{\text{SQ}} - \delta V_{\text{OC}}^{\text{rad}} - \delta V_{\text{OC}}^{\text{SC}} - \delta V_{\text{OC}}^{\text{nr}} \quad (12)$

$\Delta\mu^{\text{rad}}$ for an absorber material with any given $A(E)$ profile—even without finishing the solar cell [4]. This approach is completely analogous to the optoelectronic analysis based on the reciprocity principle [Eq. (7)], which links the electroluminescence spectrum $\Phi_{\text{EL}}(E)$ to the external quantum efficiency spectrum $QE(E)$ and enables to analyze the losses of the open-circuit voltage V_{OC} [19].

Furthermore, Eq. (6) describes how $\Delta\mu^{\text{rad}}$ deviates from the ideal SQ limit ($qV_{\text{OC}}^{\text{SQ}}$). Here, $\delta\Delta\mu^{\text{rad}}$ represents the

radiative $\Delta\mu$ loss [Eq. (3)], while $\delta\Delta\mu^{\text{Gen}}$ represents the generation $\Delta\mu$ loss [Eq. (4)].

The $\delta\Delta\mu^{\text{rad}}$ is due to the broadening of the absorption edge [i.e., non-step-like $A(E)$]. It depends on the radiative-saturation flux density, F_0^{rad} [see Eq. (3)]. When $A(E)$ broadens, the integral over $A(E)$ multiplied by Φ_{BB} increases due to the strong increase of the black-body spectrum Φ_{BB} toward smaller energies, leading to higher values of F_0^{rad} compared to the SQ radiative-saturation flux density (F_0^{SQ}), which is based on step-function absorption.

This trend increases $\delta\Delta\mu^{\text{rad}}$. Descriptively speaking: the radiative $\Delta\mu^{\text{rad}}$ is the quasi-Fermi-level splitting that occurs at the balance between generation flux and radiative emission flux. Because the emission flux increases when lower-energy states are involved, a lower quasi-Fermi-level splitting is needed to balance the incoming generation flux (see Ref. [4] and Appendix B).

Furthermore, the generation loss ($\delta\Delta\mu^{\text{Gen}}$) occurs due to incomplete absorption, since $A(E)$ does not reach unity for energies above the band gap due to factors such as reflection losses or insufficient thickness. Therefore, incomplete absorption reduces the Sun-generation flux ($F_{\text{Gen}}^{\text{Sun}}$) below the SQ-generation flux ($F_{\text{Gen}}^{\text{SQ}}$) [see Eq. (4)]. This loss mechanism simply means that fewer photons are absorbed, resulting in a smaller number of photogenerated charge carriers contributing to $\Delta\mu$.

Additionally, the most important loss mechanism in real absorbers is the nonradiative $\Delta\mu$ loss ($\delta\Delta\mu^{\text{nr}}$) [Eq. (5)], which reduces the final $\Delta\mu$ below the radiative limit ($\Delta\mu^{\text{rad}}$) [Eq. (6)]. This loss mechanism can be determined using the PL quantum yield (Y_{PL}) of the absorber. Y_{PL} is defined as the ratio of the emitted photon flux out of the absorber over the absorbed generation flux [4,31]:

$$Y_{\text{PL}} = \frac{\int_0^\infty \Phi_{\text{PL}}(E)dE}{F_{\text{Gen}}^{\text{Sun}}} = \frac{\int_0^\infty \Phi_{\text{PL}}(E)dE}{F_{\text{Gen}}^{\text{Laser}}}. \quad (13)$$

The second part of the equation describes the experimental measurement condition in our laboratory, where for PL measurements we use a monochromatic laser light source. Here, $F_{\text{Gen}}^{\text{Laser}} = A(E_{\text{laser}})F_{\text{inc}}^{\text{Laser}}$, where $F_{\text{inc}}^{\text{Laser}}$ is the incoming laser flux. More details regarding the calibration of PL measurements and laser fluxes are explained in Sec. VII and Note 1 in the Supplemental Material [77].

In an ideal absorber, $Y_{\text{PL}} = 1$, which translates to no nonradiative-recombination activities. However, in the real case Y_{PL} is much smaller than 1 [3].

In analogy with the generalized Planck's law of radiation [Eq. (1)], the optoelectronic reciprocity relation [Eq. (7)] makes a connection between the EL emission signal $\Phi_{\text{EL}}(E)$, the $QE(E)$ spectrum, and the internal voltage (V_{in}) of a solar cell [19]. Here, V_{in} is completely analogous to $\Delta\mu$. In general, it is different from the applied bias voltage because of transport losses at contacts and in the p - n junction [32]. Notably, the $A(E)$ and $QE(E)$ spectra are interconnected through the charge-collection function [33] (see Note 2 in the Supplemental Material [77]). In a solar cell with efficient charge collection, where all photogenerated charge carriers are extracted through the junctions, $A(E)$ would be equal to $QE(E)$.

Similar to $\Delta\mu$ losses, we define the voltage losses in Eq. (12), following the approach in Ref. [7]. Here, $\delta V_{\text{OC}}^{\text{rad}}$ arises due to $QE(E)$ -onset broadening and $\delta V_{\text{OC}}^{\text{SC}}$ is due to incomplete absorption and incomplete charge collection. Similar to Eq. (13), we can define the electroluminescence

quantum yield Y_{EL} , which is given by the ratio of the emitted flux density [i.e., $\int_0^\infty \Phi_{\text{EL}}(E)dE$] over the injected current density:

$$Y_{\text{EL}} = \frac{q \int_0^\infty \Phi_{\text{EL}}(E)dE}{J_{\text{SC}}}. \quad (14)$$

For absolute EL measurements under the 1-Sun condition, we need to inject current densities equal to the short-circuit current density (J_{SC}) [34].

III. EFFECT OF ABSORPTION-EDGE BROADENING AND URBACH TAILS ON $\delta\Delta\mu^{\text{rad}}$

The $A(E)$ -edge broadening in an absorber material can be attributed to several factors. In a polycrystalline compound semiconductor such as CIGSe, alloy disorders arising from the presence of indium and gallium, as well as fluctuations in the copper content, can introduce inhomogeneities in the band-gap energy [9,10]. These band-gap fluctuations can occur both between different grains and within every individual grain—they occur intentionally or unintentionally, in any case leading to a broadening of the $A(E)$ onset [9,10,35–37]. Moreover, electrostatic potential fluctuations, dislocations, grain boundaries, and/or strain can further contribute to the band-gap inhomogeneities and $A(E)$ broadening [9,10,12,35]. Additionally, the presence of sub-band-gap Urbach tails also plays a role in enhancing this broadening through increased sub-band-gap absorption [12]. In polycrystalline materials such as CIGSe, these factors are often interconnected and cannot be easily separated, collectively contributing to the $A(E)$ -edge broadening.

Furthermore, high-efficiency CIGSe absorbers are prepared with an intentionally graded band-gap profile within their thickness [22,23,38,39]. This gradient involves an increase in the Ga content toward the front and back surfaces. In this case, the effective absorption thickness for light near the absorption edge is confined to the narrow range of the minimum band-gap position. This small spatial extension decreases the absorptance of the near-edge photons and contributes to the broadening of the absorption edge. Moreover, the absorption coefficient $\alpha(E)$ at any given energy above the absorption edge in CIGSe absorbers decreases with increasing Ga concentration [33, 40,41]. Consequently, with the presence of a gradient, $\alpha(E)$, at any given energy above the band gap decreases toward the front and back surfaces, thereby contributing additionally to the broadening of the $A(E)$ edge [9].

In this section, by considering a Gaussian distribution of band gaps, we study the effect of lateral band-gap fluctuations and the presence of Urbach tails on the $A(E)$ -edge broadening and the radiative loss $\delta\Delta\mu^{\text{rad}}$.

Urbach tails originate from exponential decay of the valence-band and conduction-band density of states within

the band gap. They primarily have an influence on the $A(E)$ spectrum deep inside the band gap (up to approximately 200 meV below the band edge) [11,20,42]. On the other hand, band-gap fluctuations are caused by spatial inhomogeneities in the band gap within the material. These fluctuations mainly soften the absorptance spectrum at energies near the absorption onset [8,9]. Therefore, the impacts of Urbach tails and band-gap fluctuations on the $A(E)$ broadening and radiative losses are different from those of band-gap fluctuations. Importantly, we will quantify the contribution of Urbach tails and band-gap fluctuations to the radiative losses.

As proposed in earlier studies, the lateral band-gap fluctuations across the absorber can be defined as a Gaussian distribution of local band gaps (E_g^{loc}) around a mean value of the band-gap energy ($\bar{E}_g$) [8,9]:

$$P(E_g^{\text{loc}}) = \frac{1}{\sigma_g \sqrt{2\pi}} \exp\left(-\frac{(E_g^{\text{loc}} - \bar{E}_g)^2}{2\sigma_g^2}\right). \quad (15)$$

Here, σ_g is the band-gap broadening parameter, which is a measure of the degree of the band-gap inhomogeneities within the absorber.

Considering lateral fluctuation, at each point on the absorber surface, we can define the local absorptance spectrum $A^{\text{loc}}(E, E_g^{\text{loc}})$. Subsequently, the overall $A(E)$ spectrum can be obtained by integrating $A^{\text{loc}}(E, E_g^{\text{loc}})$ over the probability distribution of band gaps [8,9,34]. Thus we can write

$$A(E) = \int_0^\infty A^{\text{loc}}(E, E_g^{\text{loc}}) P(E_g^{\text{loc}}) dE_g^{\text{loc}}. \quad (16)$$

For the first approximation, we assume that at each point on the absorber surface, the local absorptance is a step function [i.e., $A^{\text{loc}}(E, E_g^{\text{loc}}) = 1$ for $E > E_g^{\text{loc}}$ and $A^{\text{loc}}(E, E_g^{\text{loc}}) = 0$ for $E < E_g^{\text{loc}}$] [8,9,34]. In this simplified model, the integration over a Gaussian distribution function would result in a complementary error function for the $A(E)$ spectrum [8,9,34]:

$$A(E) = \frac{1}{2} \text{erfc}\left(\frac{\bar{E}_g - E}{\sqrt{2}\sigma_g}\right). \quad (17)$$

For any $A(E)$ spectrum, its first derivative can be used to evaluate the $A(E)$ -edge broadening with respect to step-like band gaps [7]. Often, this derivative can be fitted by a Gaussian function with a broadening σ_A . It is obvious that for this simplified model [i.e., the error-function model in Eq. (17)], the first derivative of $A(E)$ would result in a Gaussian distribution with a broadening parameter the same as σ_g ($\sigma_A = \sigma_g$) and with a maximum peak position at the average band gap $\bar{E}_g$ [8,9]. This $\bar{E}_g$ is the band gap that we use to determine $V_{\text{OC}}^{\text{SQ}}$ (see Fig. 10 in Appendix C).

In Appendix C, we have also performed some model calculations based on this simplified model, where we have calculated $\Delta\mu^{\text{rad}}$ and $\delta\Delta\mu^{\text{rad}}$ using Eqs. (2) and (3). We show that with an increase in σ_g , $\delta\Delta\mu^{\text{rad}}$ also increases significantly. Furthermore, we have compared our numerical calculations with those reported in previous publications [8] and found that our results are consistent with them (Fig. 11 in Appendix C).

In the next section, we will show that this simplified model provides a very useful approximation for experimentally measured $A(E)$ spectra. Even though this approach is strictly valid only for lateral band-gap fluctuations, it also provides a useful analysis tool for band-gap variations in the depth of the absorber, such as in graded samples.

Although assuming the error-function-like model for $A(E)$ provides a useful and simple approximation for $A(E)$, this model does not offer any insights into the impact of Urbach tails. To address this issue, we employ a more accurate approximation for $A^{\text{loc}}(E, E_g^{\text{loc}})$, based on the absorption-coefficient behavior of a direct semiconductor for energies above the band gap, and an Urbach tail behavior for energies below the band gap. We assume at each point on the absorber, for a well-defined local band gap E_g^{loc} , that the absorption coefficient (α) is [34,42]

$$\alpha(E, E_g^{\text{loc}}) = \begin{cases} \alpha_0 \sqrt{\frac{E - E_g^{\text{loc}}}{k_B T}}, & E \geq E_g^{\text{loc}} + \frac{E_U}{2} \\ \alpha_0 \exp\left(\frac{E - E_g^{\text{loc}}}{E_U}\right) \sqrt{\frac{E_U}{2ek_B T}}, & E < E_g^{\text{loc}} + \frac{E_U}{2} \end{cases} \quad (18)$$

Here, E_U is the Urbach energy and α_0 is a constant. We use $\alpha_0 = 10^4 \text{ cm}^{-1}$, which is consistent with values reported for most inorganic direct semiconductors [33,43]. In this equation, we use a square-root behavior (SQRT) for α at energies above E_g^{loc} , which is a typical behavior of a direct semiconductor [44], and we use Urbach exponential decay for energies below it. The square-root prefactor used in the Urbach-decay term ensures continuity of the equation at the transition-energy point.

According to the Beer-Lamberts law, at each point on the absorber surface, we can define $A^{\text{loc}}(E, E_g^{\text{loc}}) = 1 - \exp(-\alpha d)$, where the d is the absorber thickness [34]. Then, as before, we integrate $A^{\text{loc}}(E, E_g^{\text{loc}})$ over a Gaussian distribution of the band gap to extract the overall $A(E)$ [Eq. (16)].

A similar approach was developed earlier by Redinger *et al.* to simulate the impact of thickness and Urbach tails on the $A(E)$ shape of a direct semiconductor [45]. However, in our simulations, we not only consider the effects

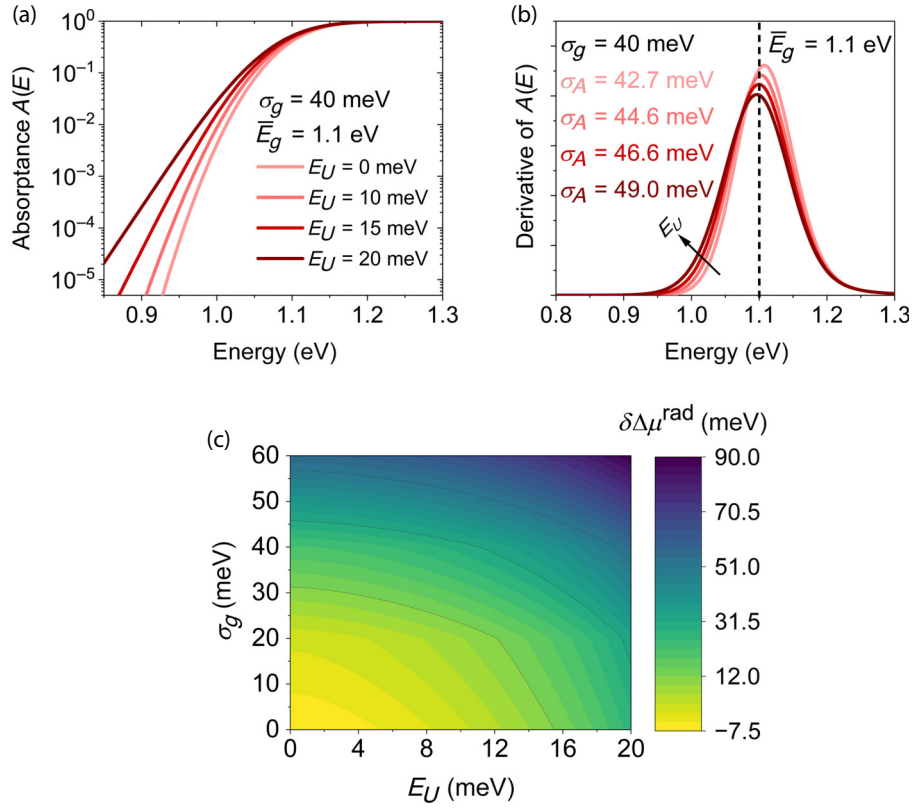


FIG. 1. (a),(b) The (a) $A(E)$ spectra and (b) first derivative of $A(E)$ for constant $\sigma_g = 40$ meV and different Urbach energies, respectively. For each E_U , a distinct color code is assigned. In (b), σ_A has been extracted from a Gaussian fit to the first derivative of $A(E)$, with the σ_A values summarized for each derivative. The direction of the arrow shows an increase in the Urbach energy. (c) The color map indicates the increase in $\delta\Delta\mu^{\text{rad}}$ with increases in both the E_U and the σ_g values. $\delta\Delta\mu^{\text{rad}}$ is calculated here using Eq. (3), with $E_g = \bar{E}_g = 1.1$ eV and $T = 296$ K.

of thickness and Urbach tails but also incorporate the influence of Gaussian band-gap fluctuations.

This combined fluctuations and tail states model [Eqs. (16) and (18)] assumes that the sample exhibits two-dimensional lateral band-gap fluctuations [34,42], with each point on the sample conceptualized as a vertical rod that absorbs light along its length. These rods have the absorption characteristics of a direct semiconductor—showing a square-root increase of $\alpha(E)$ for photon energies above the band gap and an exponential Urbach-type decay for energies below the band gap.

In Fig. 1(a), the simulated $A(E)$ spectra for $\sigma_g = 40$ meV and $d = 2$ μm are illustrated for different E_U values. In all our simulations, we have used $\bar{E}_g = 1.1$ eV and a temperature of 296 K. This $\bar{E}_g$ is the band gap that we use to determine $V_{\text{OC}}^{\text{SQ}}$.

We illustrate the derivative of the simulated spectra in Fig. 1(b). It is important to mention that the derivatives here are no longer exactly Gaussian. However, a Gaussian fit to the derivative of $A(E)$ can still be reliably used as a model to evaluate the $A(E)$ broadening (σ_A) [Fig. 1(b)]. It should be noted that in this case, σ_A is no longer the same

as σ_g . Here, σ_A is a more complex parameter, depending not only on σ_g but also on E_U and the thickness d . In Fig. 1(b), we also demonstrate the difference between the σ_g and σ_A values. Even without band tails ($E_U = 0$ meV), σ_A is larger than σ_g . To discuss this difference, we recall that the derivative of the $A(E)$ spectrum gives us the distribution of SQ steplike band gaps (i.e., the error-function approach) and thus σ_A approximates the width of the distribution of SQ-type band gaps.

It is important to note that even in the ideal case of a direct semiconductor, where the absorption coefficient shows square-root behavior above the band gap (the SQRT model), a distribution of SQ-type band gaps is needed. We demonstrate this in Fig. 12, in Appendix D. Since, for a pure SQRT-type absorptance, the derivative diverges at $\bar{E}_g$, we have added a tiny tail of $E_U = 0.1$ meV. The derivative of this particular case is not Gaussian shaped but when fitted with a Gaussian function, it results in a σ_A value of approximately 2 meV (see Fig. S2 in the Supplemental Material [77]), although there is no distribution of ideal band gaps ($\sigma_g = 0$). In Note 3 in the Supplemental Material [77], we have also discussed the effect of the thickness

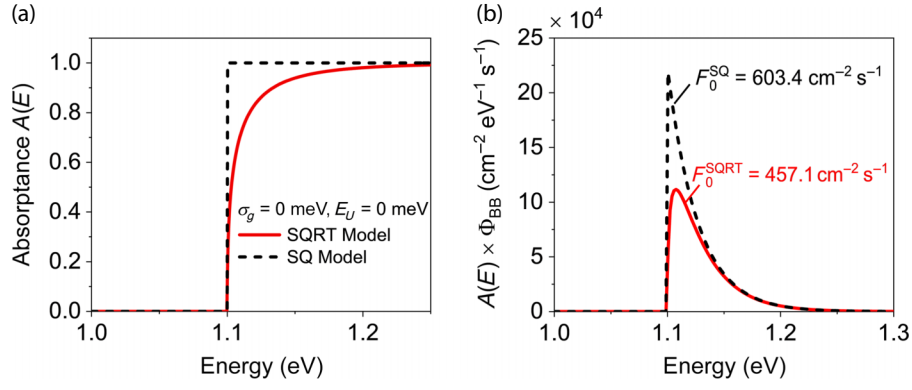


FIG. 2. (a) The $A(E)$ spectrum for an absorption coefficient with square-root behavior (SQRT) above the band gap and for a step-function (SQ) model. (b) $A(E) \times \Phi_{BB}(E)$ spectra for each $A(E)$ spectrum. The F_0^{rad} values for each $A(E)$ are calculated by extracting the area under these curves (i.e., $F_0^{\text{rad}} = \int_0^\infty A(E)\Phi_{BB}(E)dE$). F_0^{SQRT} and F_0^{SQ} are F_0^{rad} values obtained for the SQRT and SQ model, respectively. We consider an absorber thickness of $d = 2 \mu\text{m}$.

on the $A(E)$ -edge broadening. As the absorber thickness decreases, the $A(E)$ edge gets broader.

Additionally, as E_U increases, the absorption of sub-band-gap photons increases, leading to further broadening of the $A(E)$ spectrum [Fig. 1(b)]. However, the influence of increasing E_U on the broadening of the absorption edge is rather minor.

In Fig. 1(c), we have calculated $\delta\Delta\mu^{\text{rad}}$ for different values of σ_g with an increasing Urbach energy, using Eq. (3). The range of values covers those typically observed in the literature for CIGSe and other inorganic absorbers. Here, it is crucial to define the reference band-gap point (E_g) in Eq. (3) to perform our calculations. In this particular case, $\delta\Delta\mu^{\text{rad}}$ has been calculated by considering the average band gap as a reference band-gap point [i.e., $E_g = \bar{E}_g = 1.1 \text{ eV}$ in Eq. (3)]. At first glance, it is evident that, similar to the error-function model, an increase in σ_g leads to an increase in $\delta\Delta\mu^{\text{rad}}$. Moreover, as expected, Urbach tails contribute further to $\delta\Delta\mu^{\text{rad}}$. As E_U rises, $\delta\Delta\mu^{\text{rad}}$ also increases.

Based on our simulations, we can observe that band-gap fluctuations cannot be evaluated similarly to Urbach tails. Although both parameters contribute to the broadening of $A(E)$ and the increase in $\delta\Delta\mu^{\text{rad}}$, the influence of Urbach tails is more pronounced in the energy ranges deep into the band gap (around 200 meV below $\bar{E}_g$). Therefore, in the experimental measurements, it is very important to use the energy ranges very deep into the band gap—i.e., very low $\alpha(E)$ —to extract E_U [46,47]. Determining E_U at higher energies closer to the band gap would be influenced mainly by σ_g [47]. See also Appendix D for a comparison between the effect of Urbach tails and the effect of band-gap fluctuations.

CIGSe absorbers are reported to have E_U values in the range of 11–20 meV [12,20,48,49]. In Fig. 1(c), we show that within this range, the Urbach tails have minimal impact on $\delta\Delta\mu^{\text{rad}}$.

Additionally, in the case of $\sigma_g = 0 \text{ meV}$, we observe that at small E_U ranges, $\delta\Delta\mu^{\text{rad}}$ has negative values. This indicates that within this specific range, $\Delta\mu^{\text{rad}}$ has greater values than the SQ limit. Although this observation might seem surprising at first, this effect arises from the reduced absorbance above the band gap, due to the square-root increase in the absorption coefficient (α). This leads to a gradual increase in $A(E)$ for energies higher than E_g [see Fig. 2(a)]. Consequently, this specific shape of $A(E)$ reduces the integral of $A(E)$ over $\Phi_{BB}(E)$, lowering F_0^{rad} to values below F_0^{SQ} and resulting in negative values for $\delta\Delta\mu^{\text{rad}}$ [Eq. (3)]. This, in turn, means that $\Delta\mu^{\text{rad}}$ exceeds the SQ limit. To better explain this effect, in Fig. 2(a), for the case of $\sigma_g = 0 \text{ meV}$ and $E_U = 0 \text{ meV}$, we have illustrated the SQ- $A(E)$ (i.e., step function) and $A(E)$ values extracted by considering the square-root behavior of the absorption coefficient (α) above the band gap (SQRT model). Additionally, in Fig. 2(b), we compare the $A(E) \times \Phi_{BB}(E)$ and F_0^{rad} values for each emission spectrum. A lower F_0^{rad} means that a higher quasi-Fermi-level splitting is needed to balance the generation flux density with the emission flux density, i.e., negative $\delta\Delta\mu^{\text{rad}}$.

IV. MEASUREMENTS ON CIGSe ABSORBERS WITH AND WITHOUT BAND-GAP GRADIENT

A. $\Delta\mu$ losses in CIGSe absorbers deposited on glass

Up to this point, we have discussed the impact of band-gap fluctuations and Urbach tails on the broadening of the absorbance edge. In this section, we will apply this analysis to experimentally measured $A(E)$ spectra and we will quantify $\Delta\mu$ and its losses. At the beginning, we investigate five distinct samples deposited on glass (soda-lime glass, SLG). These samples cannot be used to make solar cells, since they lack the back contact, but they allow us to independently determine $A(E)$ using a photospectrometer. The name, composition as measured by energy-dispersive

TABLE II. Cu/Ga + In (CGI), Ga/Ga + In (GGI), and the presence of gradient for samples deposited on SLGs. CGI and GGI are calculated independently from EDX data. NG denotes samples without gradient and BGG samples with band-gap gradient. These samples have thicknesses of around 1–2 μm .

Sample	CGI	GGI	Gradient
A-NG	0.90	0.20	No
B-NG	0.94	0.26	No
C-BGG	0.88	0.30	Yes
D-NG	0.88	0.25	No
E-BGG	0.94	0.20	Yes

x-ray spectroscopy (EDX), and key properties of each sample are summarized in Table II. Our study includes nongraded CIGSe samples (denoted as NG) as well as band-gap-graded CIGSe samples (denoted as BGG). For selected samples, we have performed secondary-ion-mass-spectrometry (SIMS) measurements to evaluate the presence of a gradient (see Fig. S4 in the Supplemental Material [77]).

Our analysis starts with the extraction of the $A(E)$ spectrum for each sample. The $A(E)$ spectra are obtained by conducting transmittance and reflectance measurements on each absorber using a photospectrometer. From the transmittance $T(E)$ and reflectance $R(E)$ spectra, the $A(E)$ spectra can be calculated as $A(E) = 1 - R(E) - T(E)$. These measurements cover a wide range of photon energies. However, they are known to be unreliable for low absorptance values at the low-energy slope (i.e., near and below the band gap) [46]. On the other hand, PL measurements have a high sensitivity for low absorptance values, i.e., at energies below the band-gap energy [11,46,50]. Therefore, PL measurements are used to construct the low-energy part of the $A(E)$ spectra.

According to the generalized Planck's law of radiation [1] [Eq. (1)], with knowledge of the PL flux spectrum ($\Phi_{\text{PL}}(E)$) and the temperature of the absorber (here, 296 K), we can obtain the nonabsolute shape of $A(E)$ using the following relationship [1,50]:

$$A^{\text{PL}}(E) \propto \frac{\Phi_{\text{PL}}(E)}{\Phi_{\text{BB}}(E)}. \quad (19)$$

Here, $A^{\text{PL}}(E)$ denotes the $A(E)$ value extracted from PL measurements. It is nonabsolute, since at this point, we do not know $\Delta\mu$ yet, which, according to Eq. (1), enters exponentially into the proportionality factor in Eq. (19). However, in the energy ranges in which both the PL and the photospectrometry measurements are reliable, $A^{\text{PL}}(E)$ can be aligned with the absorptance spectrum measured directly from transmittance and reflectance, $A^{\text{dir}}(E)$. By rescaling the $A^{\text{PL}}(E)$ spectrum to match the one obtained from the spectrometer, we can effectively construct the full $A(E)$ spectrum across the entire energy range. Then, we

use this full range $A(E)$ spectrum to calculate the $\Delta\mu^{\text{rad}}$ and $\Delta\mu$ losses.

In Fig. 3, the top row displays the $A(E)$ spectra of samples A-NG, B-NG, and C-BGG, derived from both PL and photospectrometric (i.e., transmittance and reflectance) measurements. Additionally, the $A(E)$ spectra of samples D-NG and E-BGG can be found in Fig. S5 of the Supplemental Material [77].

To determine $\Delta\mu^{\text{rad}}$, the numerical value of the band-gap energy is not needed [see Eq. (2)]: for $\Delta\mu^{\text{rad}}$ calculations, it is sufficient to know the $A(E)$ spectrum and the absorber temperature. However, to quantify the $\Delta\mu$ losses, we need to calculate the SQ values, $F_{\text{Gen}}^{\text{SQ}}$ and F_0^{SQ} . Thus, it is necessary to know the band gap.

To determine the band-gap energy, we apply a Gaussian fit to the first derivative of the $A(E)$ spectra and we take the maximum of this fit as an average band gap $\bar{E}_g$. We use the $A^{\text{PL}}(E)$ spectra for this analysis, as the direct measurements $A^{\text{dir}}(E)$ tend to become unreliable near the absorption onset and the derivatives of $A^{\text{dir}}(E)$ are often unsuitable for accurate band-gap and broadening determination (see Fig. S6 in the Supplemental Material [77]). It is important to mention that this $\bar{E}_g$ value is a reference point for our calculations. It is evident that the determination of $\bar{E}_g$ with 1-meV accuracy can be challenging. However, small errors in $\bar{E}_g$ determination would have compensating effects on the SQ limit and $\Delta\mu$ losses in a way that the final radiative limit ($\Delta\mu^{\text{rad}}$) would not change. This is due to the fact that $\Delta\mu^{\text{rad}}$ does not depend on the defined band gap according to Eq. (2).

In Fig. 3, the bottom row illustrates the $\bar{E}_g$ and band-gap distribution obtained from the first derivative of $A^{\text{PL}}(E)$. This approach is similar to the error-function model [Eq. (17)], where the inflection point of $A(E)$ yields $\bar{E}_g$. Additionally, the broadening of the Gaussian fit gives us a degree of broadening for the edge of $A(E)$. However, it is important to mention once again that the experimental absorptance edge has a more complicated function and depends on many factors, as discussed in the previous section. Still, the Gaussian fit describes the derivative of the absorptance spectrum surprisingly well. That means that a Gaussian distribution of steplike SQ band gaps is a very suitable model with which to describe these absorptance edges. In some cases, we see that the experimental $A(E)$ derivative deviates from the Gaussian-fit model. But even in these cases, valuable information can be extracted from the Gaussian fit, enabling a comparison between the samples.

For quantifying $\Delta\mu$ and the relative losses, in the first step we quantify $qV_{\text{OC}}^{\text{SQ}}$ [i.e., $qV_{\text{OC}}^{\text{SQ}} = k_B T \ln(F_{\text{Gen}}^{\text{SQ}}/F_0^{\text{SQ}})$] using the band gap obtained from the inflection point of $A(E)$. It is worth mentioning that all our PL measurements are performed at room temperature (here, 296 K); thus, our calculations are performed considering $T = 296$ K.

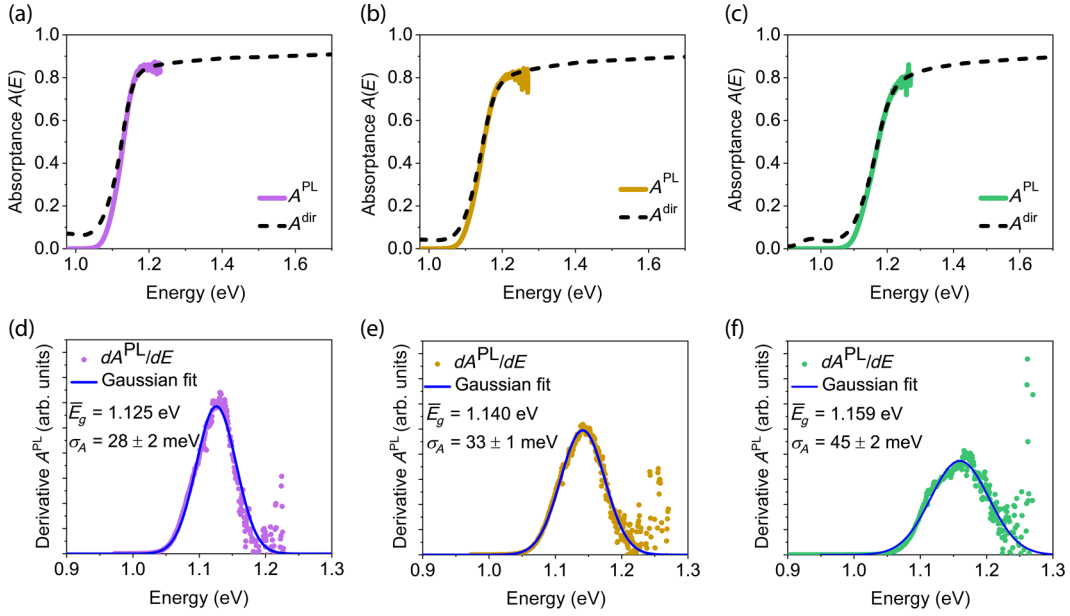


FIG. 3. (a)–(c) Absorbance $A(E)$ spectra for CIGSe samples (a) A-NG, (b) B-NG, and (c) C-BGG, respectively. A^{dir} is the (absolute) absorbance spectrum measured by photospectrometry and A^{PL} is the absorbance extracted from PL and scaled in the overlapping energy range to A^{dir} . (d)–(f) Gaussian fits to the first derivative of the absorbance spectra of samples (d) A-NG, (e) B-NG, and (f) C-BGG. To improve visualization, the first derivative here is extracted from the smoothed absorbance curves, as detailed in Sec. VII. Different fitting ranges have been used to extract σ_A and the average value is reported here with an error range of approximately 1–2 meV.

Our next step is to quantify the radiative $\Delta\mu$ loss ($\delta\Delta\mu^{\text{rad}}$) and the generation $\Delta\mu$ loss ($\delta\Delta\mu^{\text{Gen}}$), using Eqs. (3) and (4). The value of $\delta\Delta\mu^{\text{rad}}$ primarily depends on the broadening of $A(E)$. For all our samples we calculated ($\delta\Delta\mu^{\text{rad}}$), the values are summarized in Table III. As expected, with an increase in σ_A [i.e., $A(E)$ -edge broadening], $\delta\Delta\mu^{\text{rad}}$ increases [Fig. 4(a)]. On the other hand, $\delta\Delta\mu^{\text{Gen}}$ is mainly due to the incomplete absorption. In our samples, we observe that $A(E)$ nearly plateaus to values lower than 1 at energies well above $\bar{E}_g$ [see Figs. 3(a)–3(c)] and that all samples plateau to similar values. Consequently, the $\delta\Delta\mu^{\text{Gen}}$ for these samples have similar values around 3–4 meV (see Table III).

For these samples, we observe that both σ_A and $\delta\Delta\mu^{\text{rad}}$ increase with the introduction of a Ga gradient [Fig. 4(a)]. In the subsequent sections, we will discuss in more detail the effect of the band-gap gradient and compositional inhomogeneities on the broadening of the absorption edge.

Finally, in the last step, we determine the Y_{PL} for each sample and calculate the $\delta\Delta\mu^{\text{nr}}$ using Eq. (5). It is crucial to note that for CIGSe absorbers, extracting Y_{PL} under the 1-Sun illumination condition is essential. The presence of metastable defects results in nonconstant Y_{PL} values under different illumination intensities [27,51,52]. In Fig. S7 in the Supplemental Material [77], we illustrate Y_{PL} for these samples with increasing laser intensity: the Y_{PL} in CIGSe samples increases with increasing incident light intensity. In all our calculations in the previous sections, we have considered illumination under 1-Sun incident intensity. Thus, for our calculations here, the $\delta\Delta\mu^{\text{nr}}$ values are all extracted from measurements under the 1-Sun condition.

From the complete absorbance spectrum, together with Y_{PL} , we can determine $\Delta\mu^{\text{rad}}$ and quantify all $\Delta\mu$ losses, allowing us to extract the final $\Delta\mu$ value according to Eq. (6). In Fig. 5(b), we show the contribution of each loss

TABLE III. $\Delta\mu$ losses calculated with respect to the SQ limit, the $qV_{\text{OC}}^{\text{SQ}}$ and all values are calculated considering the measurement temperature $T = 296$ K. The final $\Delta\mu$ value is extracted from loss analysis in Eq. (6).

Sample	σ_A (meV)	$\bar{E}_g$ (eV)	$qV_{\text{OC}}^{\text{SQ}}$ (meV)	$\delta\Delta\mu^{\text{rad}}$ (meV)	$\delta\Delta\mu^{\text{Gen}}$ (meV)	$\Delta\mu^{\text{rad}}$ (meV)	$\delta\Delta\mu^{\text{nr}}$ (meV)	$\Delta\mu$ (meV)
A-NG	28 ± 2	1.125	885.0	13.5	2.8	868.7	207.1	661.6
B-NG	33 ± 1	1.140	898.8	13.0	3.3	882.5	220.5	662.0
C-BGG	45 ± 2	1.159	916.4	22.9	3.3	890.2	213.2	677.0
D-NG	36 ± 1	1.131	890.5	15.8	3.4	871.3	212.2	659.1
E-BGG	40 ± 2	1.109	869.9	19.0	3.8	847.1	225.6	621.5

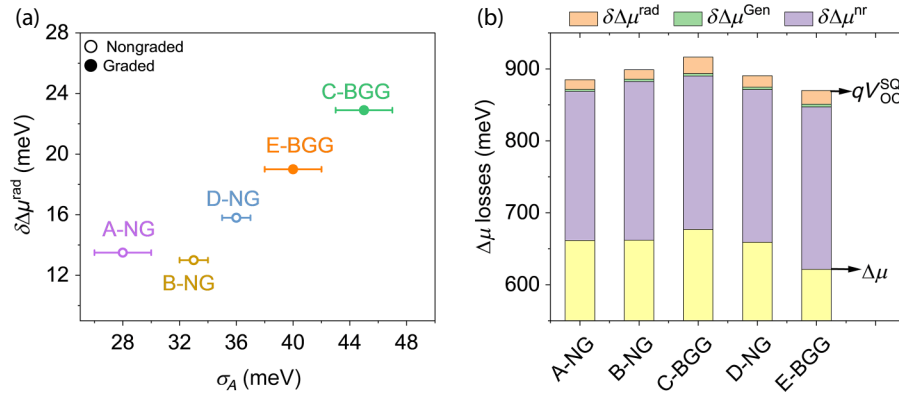


FIG. 4. (a) The increase in $\delta\Delta\mu^{\text{rad}}$ with an increase in σ_A . Different fitting ranges have been applied to extract σ_A from the Gaussian fit of $dA(E)/dE$. The average value of σ_A is represented here and the error bars denote the standard deviation. (b) The $\Delta\mu$ losses calculated for the samples deposited on SLGs. The numerical values of the $\Delta\mu$ losses are summarized in Table III.

mechanism and the resulting $\Delta\mu$ of our samples. Moreover, the values for each loss mechanism and the final $\Delta\mu$ values are summarized in Table III.

The $\Delta\mu$ values of the samples can also be extracted directly from Planck's generalized law [Eq. (1)] [3,4]. Using the Boltzmann approximation (i.e., $E - \Delta\mu \gg k_B T$), we can transform Eq. (1) into the following form [3,4]:

$$\ln\left(\frac{\Phi_{\text{PL}} h^3 c^2}{2\pi A(E) E^2}\right) = -\frac{E - \Delta\mu}{k_B T}. \quad (20)$$

Here, $\Delta\mu$ can be determined from the vertical-axis intercept of a linear fit to the high-energy wing, while the measurement temperature can be determined from the slope of this fit [4,20].

In our study, we have already determined the $A(E)$ spectra at wide energy ranges from transmittance and

reflection measurements. However, in many cases, a simple approximation for $A(E)$ can be used to extract $\Delta\mu$. In the literature, the approximation of $A(E) = 1$ for high enough energies is often used [3,4,36,53]. In our previous reports, we have already demonstrated that this assumption introduces errors of 10–20 meV [4]. In the cases in which the $A(E)$ of the samples is constant at relatively high energy ranges above the band gap, assuming a constant value for $A(E)$ [here, $A(E) = 1$] would result in the temperature extracted from this fit being the same as the measurement temperature (here, approximately 296 K) [4]. However, when the $A(E)$ spectra of the sample continue to increase and do not plateau, assuming constant values for $A(E)$ [here, $A(E) = 1$] results in extracted temperatures higher than the measurement temperature and unrealistically small $\Delta\mu$ values [4,11,20,46]. Nevertheless, by fixing the temperature to the measurement temperature, (i.e., fixing the slope), we enforce the $A(E) = 1$ condition

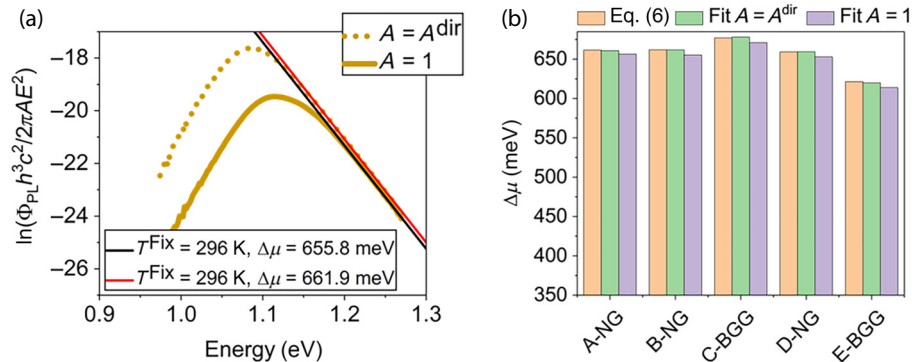


FIG. 5. (a) The linear fit to the high-energy slope of the modified Planck's generalized law [Eq. (20)] to extract $\Delta\mu$. Here, the assumptions of $A(E) = 1$ and $A(E) = A^{\text{dir}}(E)$ have been employed and in both cases $\Delta\mu$ has been extracted by fixing the temperature to 296 K (i.e., fixing the slope). More details regarding the fitting temperature can be found in Note 9 in the Supplemental Material [77]. (b) The corresponding $\Delta\mu$ values extracted from calculations based on losses [using Eq. (6)] and a linear fit to Eq. (20), with the assumptions of $A(E) = 1$ and $A(E) = A^{\text{dir}}(E)$ (the $\Delta\mu$ values from each method are summarized in Table S1 in the Supplemental Material [77]).

and enhance the accuracy of our extracted $\Delta\mu$ values [3,4,11,20,27].

In Fig. 5(a), we have performed a linear fit to the high-energy slope of Eq. (20) to determine $\Delta\mu$, considering both assumptions with $A(E) = A^{\text{dir}}(E)$ and $A(E) = 1$. [Here, $A^{\text{dir}}(E)$ is the directly measured absorptance from the spectrometer].

In our samples, when we consider $A(E) = A^{\text{dir}}(E)$ in Eq. (20), the free-slope fitted temperature is in the range of 296 ± 2 K, which aligns closely with our measured temperature of 296 K (see Note 9 in the Supplemental Material [77]). Notably, this extracted temperature from the linear fit is sensitive to the fitting range and local slope, which can be affected by the noise level in the measurements. We have tested various fitting ranges and the free-slope fit yielded a temperature with an error of ± 2 K. In Note 9 in the Supplemental Material [77], we discuss in detail the effects of local slope fluctuations and fitting ranges on the extracted temperature from the linear-fit slope. In Fig. 5, to improve consistency across all $\Delta\mu$ extractions, we have applied a fixed slope for the linear fit in all cases, setting the temperature at the measured temperature of 296 K. For comparison, the assumption of $A(E) = 1$ has also been employed and $\Delta\mu$ has been obtained under this assumption by fixing the temperature slope (i.e., fixing the temperature) of the linear fit.

In Fig. 5(b), we have summarized the $\Delta\mu$ values extracted from different methods, including calculations from losses [Eq. (6)], using a linear fit with known $A^{\text{dir}}(E)$ and a linear fit assuming that $A(E) = 1$.

We note that the assumption $A(E) = 1$ underestimates $\Delta\mu$ by 5–7 meV. This observation aligns well with our previous studies, where we have addressed the limitations of this assumption [4]. On the other hand, using the measured $A^{\text{dir}}(E)$ provides more reliable results that closely match the calculated values from losses.

The agreement between the $\Delta\mu$ determined from the combined effects of radiative, generation, and nonradiative losses and the fit to Planck's generalized law is a key observation and indicates that the model for the various $\Delta\mu$ or V_{OC} losses is complete. It is important to note that these $\Delta\mu$ values are extracted from a single point on the absorber. The aim of this analysis is to demonstrate that generalized detailed-balance model covers all essential losses and that the final $\Delta\mu$ value can be extracted by subtracting these losses from the SQ limit; therefore, to avoid any uncertainties arising from Y_{PL} inhomogeneities across the absorber, we have performed this analysis for a single point on each absorber [7]. Consequently, the $\Delta\mu$ values here are presented without statistical error bars.

B. Comparison with solar cells

Up to this point, our analysis has been based on optical absorptance and PL measurements. For solar cells, which

are generally deposited on an opaque Mo back contact, this approach is not possible. However, as highlighted in Table I, similar calculations based on the reciprocity principle can be carried out using the quantum efficiency of the short-circuit current, the $QE(E)$ spectra, to extract the relative V_{OC} losses of a photovoltaic device [7,19].

In this section, we extend our analysis to conduct a V_{OC} loss assessment for three CIGSe solar cells: sample F-BGG, which incorporates a band-gap gradient across the absorber, and samples G-NG and H-NG, both of which exhibit a uniform band gap throughout their thickness. Notably, sample H-NG is pure CuInSe_2 (CIGSe), without any Ga. On each absorber film, we prepare five or eight solar cells with areas of approximately 0.25 cm^2 . In the following, we discuss the properties of the best solar cell on each absorber. The performances of all investigated cells are given in Note 12 in the Supplemental Material [77].

In Fig. 6(a), we illustrate the J - V characteristic of the solar cell with the highest efficiency on each absorber, and corresponding device parameters, along with the composition of the absorbers, are summarized in Table IV.

In Fig. 6(b), we depict the QE spectra of these samples. Similar to the $A^{\text{dir}}(E)$ spectra, the directly measured $QE^{\text{dir}}(E)$ spectra level off at low values below the absorption edge, due to the limited sensitivity of the equipment. This limitation of direct QE measurements is commonly known in the literature [13,54].

As illustrated in Table I, the relationship between the $QE(E)$ spectrum and the EL spectrum, $\Phi_{\text{EL}}(E)$, is similar to that between the absorptance and the PL spectra, $\Phi_{\text{PL}}(E)$ [see Eqs. (1) and (7)]. Therefore, to construct the low-energy decay of the $QE(E)$ spectra, additional EL measurements have been carried out. The reciprocity relationship between the EL emission and $QE(E)$ allows us to construct the low-energy decay of the $QE(E)$ spectra from EL measurements (referred to as QE^{EL}) [see Eq. (7)] [7,13,19,54,55]. Similarly to the PL-spectra analysis, we extract a nonabsolute $QE(E)$ spectrum from the EL spectra and adjust it in the overlapping energy range to the QE^{dir} spectrum. Furthermore, we use the inflection point of the $QE(E)$ spectra to evaluate the absorption-edge broadening and $\bar{E}_g$ value [Fig. 6(c)]. Notably, in contrast to optical measurements, here both QE^{dir} and QE^{EL} can be used for this purpose [see Figs. S11(a) and S11(c) in the Supplemental Material [77]]. Both spectra give the same broadening parameter (within error of ± 2 meV). However, for simplicity, here we have just used the QE^{dir} measurements for band-gap and broadening extraction. In Fig. 6(c), we have extracted the broadening of the SQ band-gap distribution σ_{QE} from QE^{dir} measurements by again fitting a Gaussian function to the first derivative of the QE^{dir} spectrum.

As we mentioned previously, $QE(E)$ and $A(E)$ are linked through the collection function (see Note 2 in the Supplemental Material [77]) [33,34]. At energy ranges near the

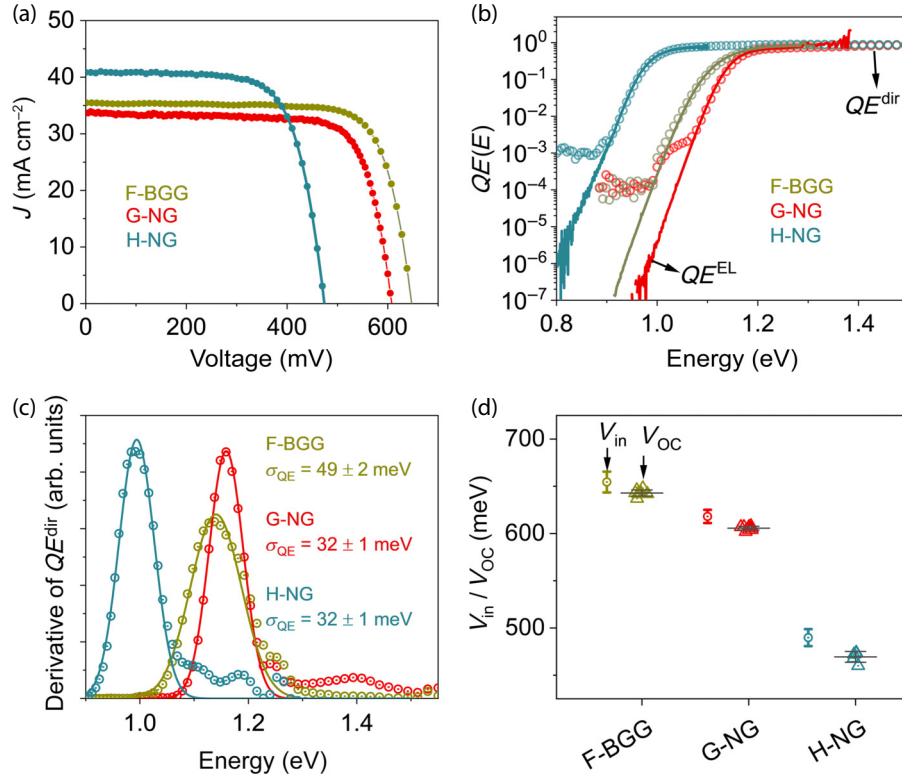


FIG. 6. (a) The J - V curve of the solar cells with the highest efficiency on each absorber. (b) The $QE(E)$ spectra extracted for samples F-BGG, G-NG, and H-NG, with a combination of direct measurements (QE^{dir}) and EL measurements (QE^{EL}). (c) The first derivative of QE^{dir} along with the σ_{QE} extracted for each sample. σ_{QE} here is extracted from a Gaussian fit to the first derivative of QE^{dir} . In (a)–(c), each sample is represented by a different color. Different fitting ranges have been employed and the average values are reported here, with the errors representing the standard deviation. (d) A comparison between V_{in} and the measured V_{OC} for each sample. The uncertainty in V_{in} is due to errors in δV_{OC}^{nr} determination (more details of the EL measurements are explained in Sec. VII).

band-gap energy and below it (i.e., with small absorption-coefficient values), the collection function can be considered as a constant factor that scales $A(E)$ values to $QE(E)$ values [34]. Thus, the $A(E)$ and $QE(E)$ spectra are expected to have the same shape in this region. Therefore, the inflection point of $QE(E)$ represents the onset of $A(E)$. Notably, in our samples, the EL and PL spectra have the same shape and the $A(E)$ and $QE(E)$ spectra are essentially identical (see Figs. S11(a) and S11(c) in the Supplemental Material [77]).

To determine the relative voltage losses, we start our calculations by obtaining V_{OC}^{SQ} from the extracted band

gap. Subsequently, we quantify the radiative voltage loss δV_{OC}^{rad} and the short-circuit voltage loss δV_{OC}^{SC} using Eqs. (9) and (10) provided in Table I and, finally, we determine the radiative voltage limit (V_{OC}^{rad}) and nonradiative voltage losses (δV_{OC}^{nr}) for each sample using Y_{EL} [see Eq. (14)].

In Fig. 6(c), we observe that sample F-BGG with a graded band-gap profile has a broader $QE(E)$ onset compared to the two other samples. Consequently, this broadening leads to increased radiative voltage loss (δV_{OC}^{rad}). Our calculations indicate that sample F-BGG with a band-gap gradient shows an approximately 16 mV higher radiative V_{OC} loss (δV_{OC}^{rad}) compared to samples G-NG and

TABLE IV. The key parameters of the solar cells investigated in this study, including the Cu/Ga + In (CGI) and Ga/Ga + In (GGI) values, along with the photovoltaic parameters of the best performing solar cell on each absorber. The J - V characteristics are shown in Fig. 6(a).

Sample	Gradient	CGI	GGI	V_{OC} (mV)	J_{SC} (mA cm ⁻²)	Fill factor (FF)	Efficiency (%)
F-BGG	Yes	0.93	0.25	648	35.5 (35.1 ^a)	76.7	17.6
G-NG	No	0.94	0.27	608	33.7 (33.4 ^a)	76.1	15.6
H-NG	No	0.99	0	474	40.8 (40.4 ^a)	71.1	13.7

^aExtracted from integration of $QE(E)$ over AM 1.5 g.

TABLE V. V_{OC} losses with respect to the SQ limit. All calculations were performed by considering a measurement temperature of $T = 296$ K. Overall, the δV_{OC}^{nr} were measured from different cells. The average value for δV_{OC}^{nr} is represented here with errors indicating the standard deviation. The errors induced in V_{in} are due to same uncertainty as in δV_{OC}^{nr} .

Sample	σ_{QE} (meV)	$\overline{E_g}$ (eV)	V_{OC}^{SQ} (mV)	δV_{OC}^{rad} (mV)	δV_{OC}^{SC} (mV)	V_{OC}^{rad} (mV)	δV_{OC}^{nr} (mV)	V_{in} (mV)
F-BGG	49 ± 2	1.140	898.8	25.8	5.1	867.9	213.4 ± 11.0	654.5 ± 11.0
G-NG	32 ± 1	1.159	916.4	10.0	5.8	900.6	282.5 ± 7.0	618.1 ± 7.0
H-NG	32 ± 1	0.994	762.8	10.0	4.6	748.2	258.4 ± 9.0	489.8 ± 9.0

H-NG. The relative voltage losses for these samples are summarized in Table V.

In the next step, we extract δV_{OC}^{SC} , analogous to $\delta \Delta \mu^{Gen}$. Notably, here both incomplete absorption and collection losses can contribute to δV_{OC}^{SC} . An increase in the collection losses can reduce $QE(E)$, lower J_{SC} , and increase δV_{OC}^{SC} . In our samples, δV_{OC}^{SC} is around 5–6 mV (see Table V). Although its overall contribution to voltage losses is still almost negligible, it is somewhat larger than the pure generation losses extracted from the absorbance (compared to Table III).

Additionally, by performing absolute EL measurement under an injected current density of J_{SC} (equivalent to the 1-Sun condition) on a complete device, we can obtain Y_{EL} and the nonradiative voltage loss [Eq. (14)]. Subsequently, we extract the internal voltage V_{in} using Eq. (12) in Table I. Here, V_{in} is completely analogous to $\Delta \mu$ and it represents the upper limit for V_{OC} . In fact, in the absence of interface voltage losses or voltage-dependent charge-collection losses, V_{in} and V_{OC} should have the same values [3,56,57].

In Fig. 6(d), we illustrate the V_{in} and the experimentally measured V_{OC} of our devices. Our analysis in Fig. 6(d) indicates that V_{in} exhibits slightly higher values (approximately 10 mV) compared to V_{OC} . This discrepancy can be attributed to additional nonradiative recombination at the interface or voltage-dependent charge-collection losses, which can reduce V_{OC} to below V_{in} [56,57].

In Table V, we observe that the primary loss mechanism remains δV_{OC}^{nr} , attributed to nonradiative-recombination channels. Notably, the nongraded samples G-NG and H-NG exhibit a higher δV_{OC}^{nr} compared to sample F-BGG, which incorporates a Ga gradient. This observation aligns with expectations, because nongraded samples suffer from backside recombination, which limits their performance [27,58]. This increase in nonradiative recombination is therefore not mainly an indication of lower absorber quality but of strong backside recombination. On the other hand, the presence of the Ga gradient in graded samples effectively passivates the back-surface recombination at the CIGSe-Mo interface, particularly when the absorbers are not sufficiently thick [27,58,59]. However, we do see that the band-gap-graded sample F-BGG suffers from approximately 16 meV higher radiative losses compared to the nongraded absorbers. While this amount of loss may be considered negligible compared to the dominant

nonradiative losses, it becomes significant in the context of state-of-the-art CIGSe technology with a V-shaped gradient, where the nonradiative loss is already reduced to less than 120 meV [60].

Once again, our experimental results confirm that the band-gap gradient can cause an additional increase in the broadening of the absorption edge and thus of the radiative loss. For a more comprehensive analysis, Sec. V includes a broadening analysis conducted on 19 samples from our laboratory. Additionally, we conduct a meta-analysis of published data from various studies to compare the absorption-edge broadening across different thin-film technologies, including state-of-the-art CIGSe technologies.

C. Microscopic analysis

To shed light on the origin of the broadening, we have performed cathodoluminescence (CL) measurements on samples F-BGG, G-NG, and H-NG, using a dedicated scanning electron microscope (SEM).

To reveal the microscopic origin of the broadening, we have carried out CL on both cross sections and surfaces of the absorbers. The SE images and panchromatic CL intensity maps can be found in Note 13 in the Supplemental Material [77]. The CL emission peak is related to the near-band-edge recombination. Therefore, the maximum CL emission peak maps allow us to access the band-gap variations from grain to grain and within a single grain. In Fig. 7(a), we illustrate the cross-section CL map of sample F-BGG with the presence of a Ga gradient. To investigate the band-gap variation across the thickness, we have performed a line scan through the depth of the absorber. We observe a continuous blue shift in the CL peak position as we move from the surface to deeper regions [Figs. 7(b) and 7(c)]. These results are in line with secondary-ion-mass-spectrometry (SIMS) measurements (see Note 4 in the Supplemental Material [77]), which show a steady increase in the Ga concentration throughout the depth. However, a smooth increase of the Ga concentration in SIMS does not necessarily indicate a smooth band-gap gradient on a microscopic scale [61]. Indeed, the shift of the CL maximum energy is not as smooth as the SIMS profile. The heat map in Fig. 7(c) shows a jump in the maximum energy around 0.35 μm depth. In contrast, for the two other samples, without a compositional gradient, we observe a

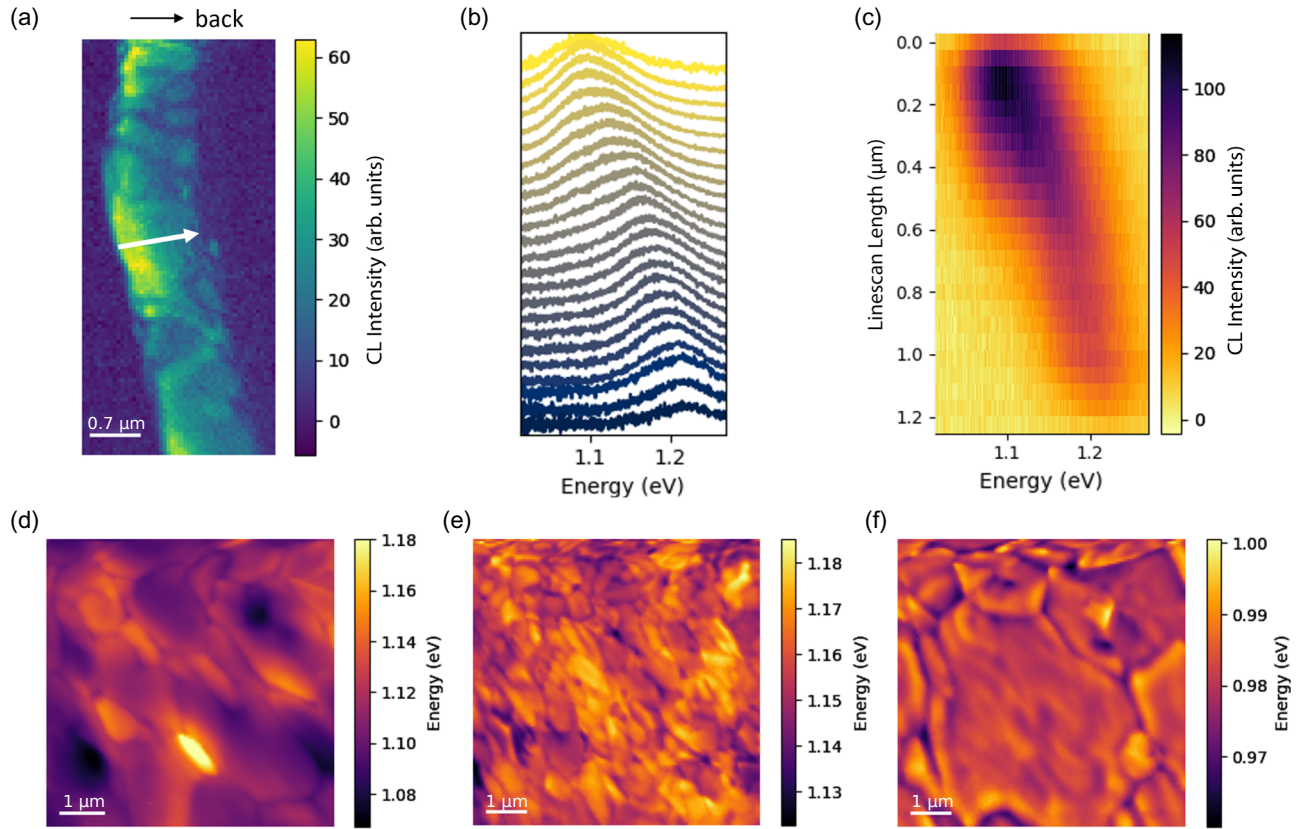


FIG. 7. (a) A panchromatic cross-section CL intensity map for sample F-BGG, with the line-scanned area shown with a white arrow. The distortion in the CL map is likely due to charging effects. (b) The evolution of the CL spectra for sample F-BGG as the line scan progresses deeper into the material. (c) A “heat map” illustrating the blue shift of the CL peak along the line scan for sample F-BGG. (d)–(f) Color maps displaying the fitted energy of the CL emission spectra at each point for samples (d) F-BGG, (e) G-NG, and (f) H-NG, respectively, along with their statistical standard deviations ($\sigma_{\text{CL}} = 16, 8.5$, and 4.5 meV, respectively), which represent the variation from the mean CL emission-energy value.

homogeneous band-gap distribution across their thickness (see Figs. S12 and S13 in the Supplemental Material [77]).

To also investigate lateral band-gap fluctuations, we have performed CL measurements on the surface of the bare absorbers. The resulting data, as shown in Figs. 7(d)–7(f), represent the fitted energy of the CL emission peak at each point across the surface. For each absorber, we have calculated the CL standard deviation (σ_{CL}) from the distribution of the fitted CL emission energies in each pixel, which indicate the fluctuations from the average CL peak emission energy. σ_{CL} serves as an indicator of the lateral band-gap fluctuations, with higher values reflecting greater inhomogeneities in the band-gap distribution across the surface of the absorbers. σ_{CL} for each absorber is summarized in Figs. 7(d)–7(f). This approach provides useful insights about the lateral variations in the band gap within the material.

We have observed that sample H-NG, which does not contain Ga, exhibits the smallest band-gap fluctuations, indicated by the lowest value of σ_{CL} . On the other hand, the introduction of Ga results in an increase in σ_{CL} to

8.5 meV for sample G-NG. Additionally, sample F-BGG, which features a Ga gradient, shows the highest σ_{CL} , indicating significantly stronger lateral band-gap fluctuations compared to the two other samples.

Our CL observations provide insight into why the F-BGG sample with a Ga gradient exhibits more significant broadening in the absorption onset compared to the other two samples. First, the effect of the depth gradient is crucial, as the absorption onset is determined by the position of the minimum band gap. In this particular sample, the minimum band-gap position is confined to a very thin region near the surface of the absorber. This reduced thickness reduces the absorptance near the minimum band gap, resulting in a wider absorption edge.

Second, this sample also displays stronger lateral band-gap fluctuations. As discussed earlier, samples with more pronounced lateral band-gap variations show increased broadening in the absorption onset. It seems that the introduction of a gradient along the sample depth also increases the lateral fluctuations. However, it cannot be determined at the moment whether this observation is specific to

this sample or is general feature of Ga-graded CIGSe samples.

V. DISCUSSION AND META-ANALYSIS

So far, we have experimentally quantified the relative $\Delta\mu$ or V_{OC} losses of our CIGSe samples. By definition, radiative losses ($\delta V_{OC}^{\text{rad}}$ and $\delta\Delta\mu^{\text{rad}}$) increase with the increase in the broadening of the $A(E)$ or $QE(E)$ onset. Moreover, we have observed that a band-gap gradient can contribute significantly to this broadening. To check the significance of these findings, we have investigated 19 samples from our laboratory (including samples in this study) to identify the primary cause of absorption-edge broadening in our CIGSe absorbers.

We would like to recall that the broadening of the absorption edge can be related to many factors, such as the Cu content (CGI), the Ga content (GGI), and Urbach tails, which are often interconnected. For instance, lower CGI and higher GGI values can increase the magnitude of electrostatic potential fluctuation, which can subsequently increase the Urbach energy and the broadening parameter [21,62].

In Fig. 8, we show the broadening-parameter values (σ_A/σ_{QE}) for different CGI, GGI, and Urbach energies

for both graded and nongraded samples from different processes. The Urbach energies are obtained from the absorption coefficient (α) extracted from PL or EL measurements, where we extract the Urbach energies from fitting the low-energy-decay part of the α spectrum (see Note 11 in the Supplemental Material [77]). In Fig. 8, we have not separated σ_A and σ_{QE} , since at the range over which we extract the broadening parameter, the EL and PL spectra have similar shapes. Therefore, the $A(E)$ spectra have an identical shape to the $QE(E)$ spectra for our samples [see Figs. S11(a) and S11(c) in the Supplemental Material [77]]. Thus, we have used these parameters interchangeably to compare our absorbers.

The Urbach energy for these samples ranges from 11 to 18 meV, which aligns well with previous reports in which the Urbach energy has been derived from PL measurements [11,20,21,48,63]. It is important to note that PL or EL measurements allow us to measure ultralow values of the absorption coefficient deep into the band gap. As we have shown previously, with EL and PL measurements, we can measure $QE(E)$ and $A(E)$ deep into the band gap, this capability enables us to determine the exponential decay of α deep into the band gap and obtain reliable Urbach energies [11] [see Fig. S11(b) in the Supplemental Material [77]].

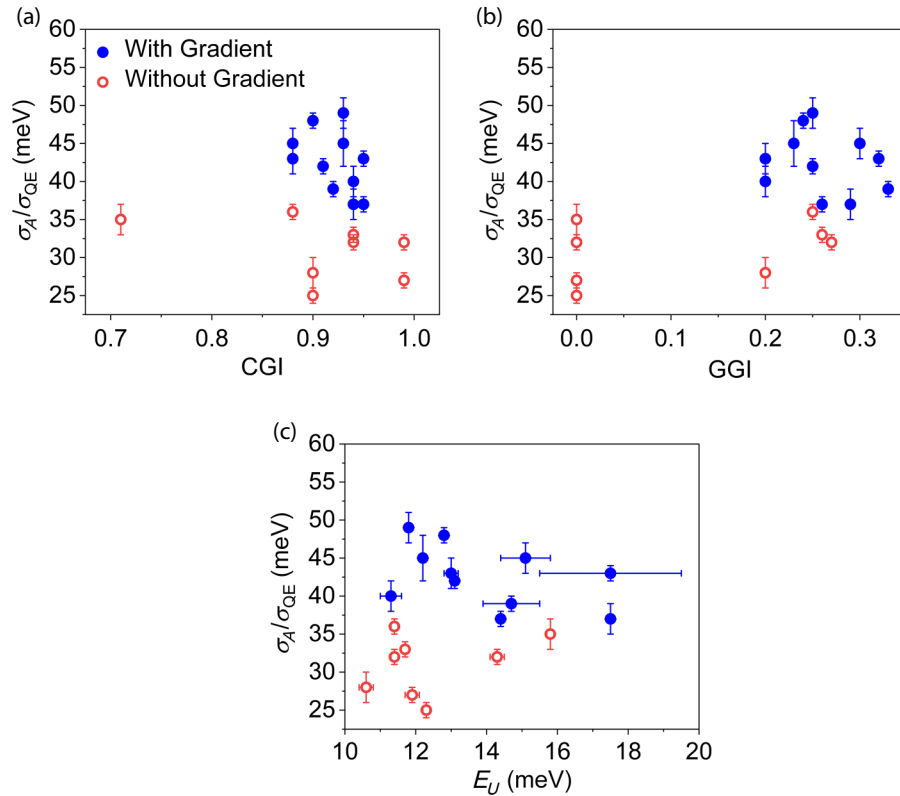


FIG. 8. The broadening parameter (σ_A/σ_{QE}) of the absorption edge plotted versus the (a) CGI, (b) GGI, and (c) Urbach energies for 19 CIGSe absorbers from different processes from our laboratory.

All samples in this study exhibit a Cu-poor composition (i.e., CGI < 1), with CGI values ranging from 0.7 to 0.99 and GGI values between 0 and 0.35.

Initially, in Figs. 8(a) and 8(b), no clear trend is observed between the variation in CGI and GGI and changes in σ_A/σ_{QE} . This does not mean that the absorption-edge broadening does not depend on the Cu or Ga content. But in this set of samples, different parameters have been varied simultaneously. It is important to note that this analysis is limited to these 19 samples. A more detailed statistical analysis would be needed to further investigate the effect of CGI or GGI on broadening, considering samples with constant CGI and varying GGI and vice versa, but here we would like to concentrate on the effect of the band-gap gradient. Moreover, we also see that the Urbach energy is almost uncorrelated to the overall broadening parameter of the samples. In both graded and nongraded samples, an increase in the Urbach energies does not necessarily lead to an increase in the broadening values. We observe some samples with higher Urbach energies that have similar broadening compared to those with lower Urbach energies.

On the other hand, we observe that in all cases, the samples that incorporate a Ga gradient show larger broadening values. This analysis indicates that the primary factor contributing to the broadening of the absorption edge in our CIGSe absorbers beyond 35 meV is the presence of the band-gap gradient throughout the thickness of the absorber.

To further investigate and understand the influence of the gradient on the broadening, we have conducted a meta-analysis and reviewed published reports to analyze the relationship between broadening and gradient profiles. The results of this analysis are summarized in Fig. 9. Additionally, data from other inorganic semiconductors, such as GaAs, CdTe, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), and Si solar cells, are also included for comparison.

In Fig. 9, the CIGSe absorbers are classified into three distinct gradient profiles: nongraded (NG) samples, characterized by a uniform band-gap distribution throughout the depth; hockey-stick-graded (HSG) samples, which exhibit a constant band gap over most of the depth, with a sharp increase near the back contact; and band-gap-graded (BGG) samples, where the band gap varies significantly over the thickness. Importantly, in both NG and HSG samples, the effective absorption thickness extends significantly across the absorber depth, while in BGG samples, this effective thickness is confined to a narrow region close to the surface.

In Fig. 9, we observe that standard graded samples (BGG) exhibit average absorption-edge-broadening values of around 45 meV. This average value decreases to approximately 30 meV for the HSG samples and is further reduced to values around 25 meV for nongraded absorbers. This trend aligns well with our findings. Among the compared technologies, GaAs stands out, with the

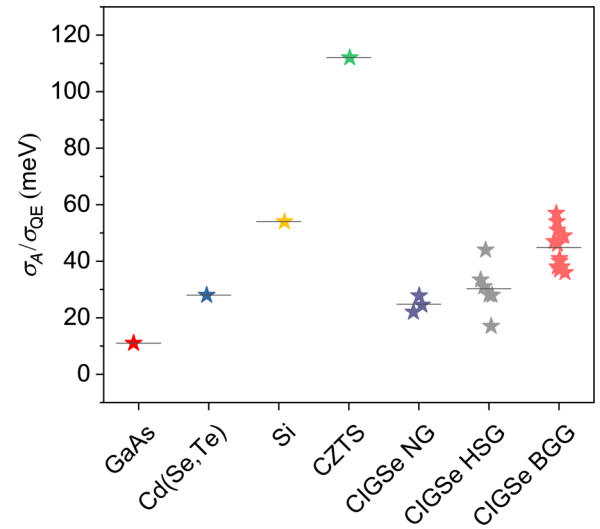


FIG. 9. A meta-analysis presenting the comparison of broadening values (σ_A/σ_{QE}) from various published studies for different solar-cell absorbers, including GaAs [64], CdTeSe [65], Si [66], CZTS [67], and CIGSe absorbers with a hockey-stick gradient (HSG) [12,38,58,68], nongraded (NG) CIGSe absorbers [58, 69], and band-gap-graded (BGG) absorbers [12,20,48,60,70]. For more details regarding the meta-analysis, see Sec. VII.

lowest broadening value of approximately 11 meV, which is 6 meV lower than the lowest reported σ_A/σ_{QE} value for CIGSe. Cd(Se, Te) technology shows broadening values comparable to those of NG and HSG CIGSe samples. Meanwhile, BGG CIGSe samples exhibit broadening as high as those observed in Si solar cells with indirect band gap. The highest value of broadening is observed in CZTS absorbers, which are well known for their strong band-gap fluctuations and significant density of states within the band gap (i.e., pronounced Urbach tails) [42,71].

Overall, investigation of our samples combined with the meta-analysis of published results highlights that the band-gap gradient is a significant factor contributing to the broadening of the $QE(E)/A(E)$ edge. We can conclude that in order to mitigate the radiative losses (δV_{OC}^{rad} and $\delta \Delta \mu^{rad}$), CIGSe absorbers with a uniform band-gap profile should be prepared. However, in this case, the passivation of the back-contact region is essential. The HSG band-gap profile has shown to be effective method to passivate the back-surface recombination [38]. Moreover, in recent years, alternative backside-passivation strategies based on selective back contact have also been developed for CIGSe absorbers. These new passivation methods can effectively mitigate the back-surface recombination without using a V-shaped Ga-gradient architecture [58,59].

The most recent record-efficiency CIGSe solar cell was prepared using an HSG band-gap profile [38]. From the

reported $QE(E)$ spectrum, we have extracted a broadening parameter of around 28 meV for this particular sample. Although nonradiative recombination remains the dominant loss mechanism in this state-of-the-art technology—with values around 100 meV—the impact of radiative losses on device performance should not be neglected. If the broadening parameter can be reduced to values comparable to those in GaAs technology (around 11 meV), an improvement in V_{OC} of approximately 15 meV is expected (see Fig. 11 in Appendix C). Such a gain is significant in the state-of-the-art devices and could translate to an increase of about 0.5% in overall power-conversion efficiency.

VI. CONCLUSIONS

In this paper, we have employed the generalized detailed-balance model to investigate the $\Delta\mu$ and voltage losses for solar-cell absorbers with and without a band-gap gradient. Our primary focus has been on the radiative losses ($\delta\Delta\mu^{\text{rad}}$ and $\delta V_{OC}^{\text{rad}}$). Initially, we have simulated the effect of band-gap fluctuations and sub-band-gap states (i.e., Urbach tails) on the radiative $\Delta\mu$ losses ($\delta\Delta\mu^{\text{rad}}$). In our simulations, we have considered the Gaussian distribution of step-function band gaps and the realistic absorption coefficient of material with a square-root increase for energies above the band gap, as well as Urbach-like decays for energies below the band-gap energy. Furthermore we have used measured $A(E)$ and $QE(E)$ spectrum to experimentally quantify losses. $A(E)$ has been obtained from a combination of photospectrometry and PL data. Our experimental results are in line with our simulation, where we have observed that $\delta\Delta\mu^{\text{rad}}$ increases with the increase in the broadening of $A(E)$ (σ_A). Additionally, using an analogy between $QE(E)$ and $A(E)$ measurement, we have quantified the V_{OC} losses for CIGSe solar cells through direct QE and absolute EL measurements. In both analyses, we have found stronger broadening and higher radiative losses in absorbers that contain a gradient. CL analysis indicates, for one sample, that the gradient might go hand in hand with stronger lateral fluctuations. We have also quantified the $\Delta\mu$ values using two different methods: a linear fit to the high-energy slope of Planck's generalized law [Eq. (20)] and adding up the overall $\Delta\mu$ losses [Eqs. (6) and (12)]. Both methods result in nearly identical values for $\Delta\mu$, indicating that the loss analysis is complete. Finally, we have investigated 19 different CIGSe samples from our laboratory. We have observed that for our samples, the dominant effect contributing to absorptance-edge broadening is the presence of a Ga gradient. Overall, our experimental results show that the presence of a Ga gradient can lead to 5–16 meV higher radiative losses compared to nongraded samples. The meta-analysis and literature review also confirm that a gradient has a dominant effect on the broadening of the $A(E)/Q(E)$ onset.

VII. EXPERIMENTAL AND METHODS

A. Sample preparation

CIGSe and graded CIGSe absorbers were prepared using the three-stage coevaporation method [22,58]. In this method, with the Se presence throughout the entire process, In and Ga were evaporated at a substrate temperature of 356 °C during the first stage. Subsequently, in the second stage, with the increase in the substrate temperature, Cu was supplied to the absorbers. At the end of second stage, the absorbers had a Cu-rich composition (CGI $\sim$ 1.2). Finally, in the last stage, the Cu flux was terminated and In and Ga were again evaporated to adjust the overall composition to be Cu poor. The maximum deposition temperature during the second and third stages was 580 °C.

For the CIGSe samples without a band-gap gradient, the Cu-rich-off (CURO) coevaporation method was employed [72]. In this method, initially In, Ga, Cu, and Se were coevaporated simultaneously at the substrate temperature of 580 °C. Cu was supplied in excess to enhance the grain size and film quality. Then in the next stage, the supply of Cu was terminated, and only In, Ga, and Se were provided to the samples, resulting in an overall Cu-poor composition.

For transmittance or reflectance analysis, samples were prepared on clean SLGs, while samples for solar-cell fabrication were prepared on Mo-coated SLG substrates.

Overall, the absorber materials prepared via these two deposition methods have thicknesses of around 1–2 μm according to SEM image. See Fig. S15 in the Supplemental Material [77].

B. Buffer-layer deposition and solar-cell fabrication

All absorbers were covered by CdS. The CdS was deposited using the chemical-bath deposition method. Details regarding the CdS deposition can be found elsewhere [27]. Subsequently, for absorbers prepared on Mo, a ZnO and Al : ZnO double layer was sequentially sputtered as a window layer and the devices were finished by evaporating Al : Ni metallic grids on the surface.

C. Photoluminescence measurements

For the absorbers deposited on SLG, the PL measurements were conducted on CdS-covered absorbers. The CdS prevents surface degradation during the PL measurements [73]. A diode laser with a wavelength of 637 nm and a beam radius of 1.3 mm was used as an excitation light source. The intensity of the incident light was calibrated to 1-Sun laser light flux. The PL signal was directed using two off-axis parabolic mirrors into fiber of 550- μm diameter, which directed the light into a spectrometer, where an InGaAs detector was used to detect the signal. For the spectral calibration, a halogen lamp with a known

light spectrum was employed. Absolute calibration was achieved by measuring the laser with both the spectrometer and a power meter. The temperature of the samples stayed at approximately 296 K and was independently measured using a thermal camera.

D. Data smoothening

To extract the broadening from the PL absorbance curve (A^{PL}), we first smoothened the absorbance (A^{PL}) spectra using the Savitzky-Golay method. We then took the derivative from the smoothed curve to obtain broadening (see Fig. S16 in the Supplemental Material [77]).

E. Electroluminescence measurements

The EL measurements were conducted on solar cells using a four-probe contact configuration. A forward voltage bias was applied to the solar cell and—in the same way as for the PL measurements—the EL emission was collected with two off-axis parabolic mirrors and detected by an InGaAs detector. The EL spectrum was subsequently spectrally corrected using the halogen lamp. Moreover, we performed absolute EL measurements to quantify Y_{EL} . The injected current under the 1-Sun condition was applied to each solar cell, which is equal to the short-circuit current density of the solar cell. The normalized EL spectra for the F-BGG, G-NG, and H-NG solar cells can be found in Fig. S10 in the Supplemental Material [77]. The EL detector has two diodes for signal detection. To minimize the impact of different sensitivity between these diodes, the data points only from single diode is used for our analysis.

F. Transmittance or reflectance measurements

A photospectrometer was used to measure the transmittance and reflectance spectra. This instrument was equipped with an integrating sphere and it covered photon wavelengths in the range of 300–1800 nm. The light from the source was passed through a monochromator and then it reached the sample. Depending on the wavelength, the light transmitted through or reflected from the absorber was detected either by InGaAs or by a photomultiplier-tube detector.

G. J – V analysis

The J – V measurements were performed using a four-probe contact configuration in a class-AAA solar simulator. The solar simulator provides a simulated AM 1.5 spectrum. All the measurements were performed at a temperature of 25 °C (298 K). The solar-cell area was independently measured using an optical microscope and the area was in the range of 0.21–0.25 cm².

H. External quantum efficiency measurements

The QE measurements were performed on complete solar cells with a four-probe contact configuration. The

QE setup was equipped with a grating monochromator using chopped illumination of a halogen and a xenon lamp. A lock-in amplifier was used to measure the current of the solar cells. Reference spectra based on calibrated Si and InGaAs detectors were used to calibrate the QE spectrum.

I. Secondary- ion-mass-spectroscopy measurements

The SIMS measurements were carried out on a CAMECA SC-Ultra instrument. The films were analyzed using a Cs⁺ low-impact energy beam (1 keV) in the depth-profiling mode. With such analytical conditions, the variation of the elemental composition was acquired across the whole thickness of the films. The intensity of the elements of interest (Cu, In, Ga and Se) was collected from a 60-μm area in diameter centered in a 250 μm × 250 μm scanned area.

J. Cathodoluminescence measurements

The CL measurements were conducted using an Atto-light Allalin 4027 dedicated CL-SEM, equipped with an Oxford Instruments iDus InGaAs 1.7 detector. All CL maps were acquired at room temperature, with an electron-beam acceleration voltage of 5 kV, a probe current of 10 nA, and a 100-μm aperture. Both plan-view and cross-section maps were captured, with a pixel exposure time of 250 ms. The open-source PYTHON packages HyperSpy [74] and LumiSpy [75] were used for processing and analyzing the CL data.

K. Meta-analysis and literature study

In Fig. 9, we present a meta-analysis of the published data, showing the broadening parameter for various absorber technologies. The broadening values were either directly extracted from reported values in previous studies or, in cases in which they were not explicitly provided, obtained through digitization of the published QE curves, followed by broadening extraction.

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S.G. (lead): writing original draft, conceptualization, visualization, formal analysis, methodology, investigation,

resources, and software. F.L.: resources, investigation, writing review and editing, and software. T.S.: investigation, visualization, and writing review and editing. T.W.: resources and writing review and editing. M.M.: investigation. N.V.: investigation, resources, and writing review and editing. J.N.: investigation. M.A.: investigation and visualization. Y.H.: investigation, visualization, and writing review and editing. G.K.: investigation, visualization, and writing review and editing. R.A.O.: resources, supervision, writing review and editing, and funding acquisition. S.S.: conceptualization, methodology, resources, supervision, project administration, funding acquisition, and writing review and editing.

DATA AVAILABILITY

The data that support the findings of this paper are openly available [78].

APPENDIX A: LIST OF SYMBOLS AND CONSTANTS

APPENDIX B: GENERALIZED DETAILED-BALANCE MODEL FOR OPTICAL MEASUREMENTS

The idea of $\Delta\mu^{\text{rad}}$ [Eq. (2)] has been already introduced in our previous work [4].

TABLE VII. List of constants.

q	Elementary charge
e	Euler's number, i.e., $\exp(1)$
h	Planck's constant
k_B	Boltzmann constant
c	Light velocity in vacuum

This $\Delta\mu^{\text{rad}}$ is the maximum attainable quasi-Fermi level-splitting limit when there is no nonradiative recombination. In this case, the photon flux density emitted from the absorber would be equal to the absorbed photon flux density (i.e., $Y_{\text{PL}} = 1$). In other words, the integrated PL emission flux density would equal the solar-generation flux density:

$$\int_0^\infty \Phi_{\text{PL}}(E) dE = F_{\text{Gen}}^{\text{Sun}}. \quad (\text{B1})$$

Thus using Planck's generalized law [Eq. (1)] and the definition of $F_{\text{Gen}}^{\text{Sun}} = \int_0^\infty A(E) \Phi_{\text{Sun}} dE$, Eq. (B1) can be transformed into

$$\int_0^\infty A(E) \Phi_{\text{BB}}(E) \exp\left(\frac{\Delta\mu^{\text{rad}}}{k_B T}\right) dE = \int_0^\infty A(E) \Phi_{\text{Sun}} dE, \quad (\text{B2})$$

which leads directly to Eq. (2).

TABLE VI. List of symbols.

Symbol	Meaning (units)	Symbol	Meaning (units)
E	Photon energy (eV)	J_0^{SQ}	SQ radiative-saturation current density (A cm^{-2})
E_g	Band-gap energy (eV)	J_{SC}	Short-circuit current density (A cm^{-2})
E_g^{loc}	Local band-gap energy (eV)	$J_{\text{SC}}^{\text{SQ}}$	SQ short-circuit current density (A cm^{-2})
$\bar{E}_g$	Mean band-gap energy (eV)	Y_{PL}	PL quantum yield
E_U	Urbach energy (eV)	Y_{EL}	EL quantum yield
$A(E)$	Absorptance spectrum	V_{OC}	Open-circuit voltage (V)
$A^{\text{PL}}(E)$	Absorptance spectrum from PL	$\Delta\mu$	Quasi-Fermi-level splitting (eV)
$A^{\text{dir}}(E)$	Absorptance spectrum from direct measurements	$V_{\text{OC}}^{\text{SQ}}$	SQ V_{OC} limit (V)
$QE(E)$	External quantum efficiency spectrum	$qV_{\text{OC}}^{\text{SQ}}$	SQ $\Delta\mu$ limit (eV)
$QE^{\text{EL}}(E)$	External quantum efficiency spectrum from EL	$\Delta\mu^{\text{rad}}$	Radiative $\Delta\mu$ limit (eV)
$QE^{\text{dir}}(E)$	External quantum efficiency spectrum from direct measurements	$\delta\Delta\mu^{\text{rad}}$	Radiative $\Delta\mu$ loss (eV)
σ_A	Absorptance-edge broadening parameter (eV)	$\delta\Delta\mu^{\text{Gen}}$	Generation $\Delta\mu$ loss (eV)
σ_g	Band-gap fluctuation (inhomogeneities) parameter (eV)	$\delta\Delta\mu^{\text{nr}}$	Nonradiative $\Delta\mu$ loss (eV)
σ_{QE}	External quantum efficiency broadening parameter (eV)	$V_{\text{OC}}^{\text{rad}}$	Radiative V_{OC} limit (V)
$\Phi_{\text{Sun}}(E)$	Sun spectrum AM 1.5 g [76] ($1 \text{ cm}^{-2} \text{ s}^{-1} \text{ eV}^{-1}$)	$\delta V_{\text{OC}}^{\text{rad}}$	Radiative V_{OC} loss (V)
$\Phi_{\text{BB}}(E)$	Black-body emission spectrum ($1 \text{ cm}^{-2} \text{ s}^{-1} \text{ eV}^{-1}$)	$\delta V_{\text{OC}}^{\text{SC}}$	Short-circuit V_{OC} loss (V)
F_0^{SQ}	SQ radiative-saturation flux density ($\text{cm}^{-2} \text{ s}^{-1}$)	$\delta V_{\text{OC}}^{\text{nr}}$	Nonradiative V_{OC} loss (V)
F_0^{rad}	Radiative-saturation flux density ($\text{cm}^{-2} \text{ s}^{-1}$)	V_{in}	Internal voltage (V)
$F_{\text{Gen}}^{\text{Sun}}$	Sun-generation flux density ($\text{cm}^{-2} \text{ s}^{-1}$)	$\Phi_{\text{PL}}(E)$	PL emission spectrum ($1 \text{ cm}^{-2} \text{ s}^{-1} \text{ eV}^{-1}$)
$F_{\text{Gen}}^{\text{SQ}}$	SQ Sun-generation flux density ($\text{cm}^{-2} \text{ s}^{-1}$)	$\Phi_{\text{EL}}(E)$	EL emission spectrum ($1 \text{ cm}^{-2} \text{ s}^{-1} \text{ eV}^{-1}$)
α	Absorption coefficient (cm^{-1})	$F_{\text{Gen}}^{\text{Laser}}$	Laser generation flux density ($\text{cm}^{-2} \text{ s}^{-1}$)
T	Temperature (K)	$F_{\text{inc}}^{\text{Laser}}$	Laser incident flux density ($\text{cm}^{-2} \text{ s}^{-1}$)
J_0^{rad}	Radiative-saturation current density (A cm^{-2})	$A(E_{\text{laser}})$	Absorptance at laser photon energy

Rau *et al.* [7] have used a mathematical expansion to calculate the V_{OC} loss components separately in the solar cells using the generalized detailed-balance limit for optoelectrical analysis. Using a similar method, we can use an optical approach based on Planck's generalized law to calculate the $\Delta\mu$ losses with respect to the SQ limit.

Starting with Eq. (2) and expanding it, we can write

$$\Delta\mu^{\text{rad}} = k_B T \ln \left(\frac{\int_{E_g}^{\infty} \Phi_{\text{Sun}}(E) dE}{\int_{E_g}^{\infty} \Phi_{\text{BB}}(E) dE} \times \frac{\int_{E_g}^{\infty} \Phi_{\text{BB}}(E) dE}{\int_0^{\infty} A(E) \Phi_{\text{BB}}(E) dE} \right. \\ \left. \times \frac{\int_0^{\infty} A(E) \Phi_{\text{Sun}}(E) dE}{\int_{E_g}^{\infty} \Phi_{\text{Sun}}(E) dE} \right) \quad (\text{B3})$$

$$= k_B T \ln \left(\frac{F_{\text{Gen}}^{\text{SQ}}}{F_0^{\text{SQ}}} \times \frac{F_0^{\text{SQ}}}{F_0^{\text{rad}}} \times \frac{F_{\text{Sun}}^{\text{SQ}}}{F_{\text{Gen}}^{\text{SQ}}} \right) \quad (\text{B4})$$

$$= qV_{OC}^{\text{SQ}} - \delta\Delta\mu^{\text{rad}} - \delta\Delta\mu^{\text{Gen}}. \quad (\text{B5})$$

Here, Eq. (B5) is the same as Eq. (6) (without the nonradiative-loss component). As explained previously, here $F_{\text{Gen}}^{\text{SQ}}$ and F_0^{SQ} are the SQ-generation flux density and the SQ-saturation flux density, respectively. The first term in the logarithm argument of Eqs. (B3) and (B4) gives us the SQ - $\Delta\mu$ limit for a defined band gap E_g . The second and third terms illustrate the relative $\Delta\mu$ losses with respect to this SQ limit.

The second term can be defined as radiative $\Delta\mu$ loss,

$$\delta\Delta\mu^{\text{rad}} = -k_B T \ln \left(\frac{F_0^{\text{SQ}}}{F_0^{\text{rad}}} \right), \quad (\text{B6})$$

and the last term as generation $\Delta\mu$ loss,

$$\delta\Delta\mu^{\text{Gen}} = -k_B T \ln \left(\frac{F_{\text{Gen}}^{\text{Sun}}}{F_{\text{Gen}}^{\text{SQ}}} \right). \quad (\text{B7})$$

$\delta\Delta\mu^{\text{Gen}}$ is due to incomplete absorption [i.e., $A(E) < 1$ for $E > E_g$], while $\delta\Delta\mu^{\text{rad}}$ is due to the broadening of the $A(E)$ spectra.

APPENDIX C: SIMULATIONS FOR ERROR-FUNCTION MODEL FOR $A(E)$

In Sec. 3, we have mentioned that the $A(E)$ spectrum can be simply modeled as an error-function-like spectrum [Eq. (17)]. In Fig. 10(a), we show the simulated $A(E)$ spectra for σ_g in the range of 0–60 meV. In Fig. 10(b), we illustrate the first derivatives of these spectra, which show a Gaussian distribution with a broadening the same as σ_g (i.e., $\sigma_g = \sigma_A$), centered at $\bar{E}_g = 1.1$ eV.

$\sigma_g = 0$ meV resembles the SQ- $A(E)$ spectrum (i.e., the step function).

Using Eq. (3), we have calculated the radiative losses ($\delta\Delta\mu^{\text{rad}}$) for the simulated spectra. The results are summarized in Fig. 10(b) (inset).

Furthermore, we also compared our calculated values with the previously published reports. Notably, Rau *et al.* have proposed the following formula to extract the $\Delta\mu^{\text{rad}}$ limit based on the definition of $A(E)$ as a complementary error function [as in Eq. (17)] [8]:

$$\Delta\mu^{\text{rad}} = \bar{E}_g - \frac{\sigma_g^2}{2k_B T} - k_B T \ln \left(\frac{J_{00}}{J_{\text{SC}}} \right), \quad (\text{C1})$$

where

$$J_{00} = \frac{2\pi q}{h^3 c^2} \left[2(2k_B T)^3 + 2(k_B T)^2 \bar{E}_g + k_B T \bar{E}_g^2 - 2\sigma_g^2 \bar{E}_g - \sigma_g^2 k_B T + \frac{\sigma_g^4}{k_B T} \right]. \quad (\text{C2})$$

Assuming $QE(E) = A(E)$, J_{SC} for this model is as follows:

$$J_{\text{SC}} = q \int_0^{\infty} A(E) \Phi_{\text{Sun}} dE. \quad (\text{C3})$$

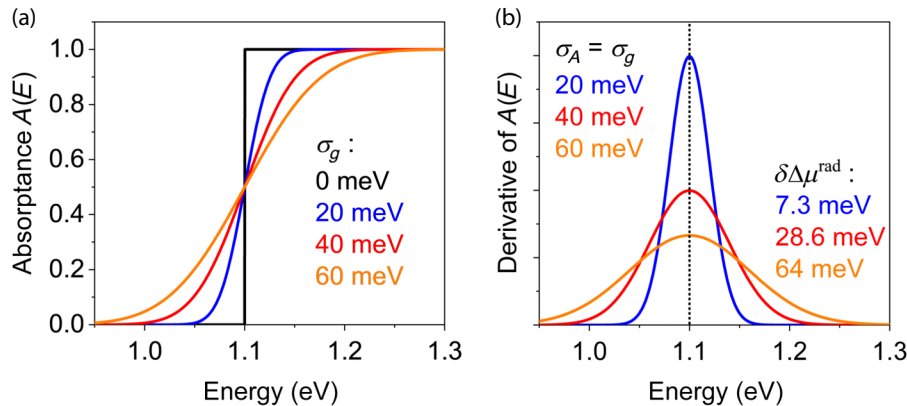


FIG. 10. (a) $A(E)$ spectra simulated using the error-function model in Eq. (17). Here, σ_g takes values of 0, 20, 40, and 60 meV. (b) The first derivative of the simulated $A(E)$ spectra along with the radiative loss ($\delta\Delta\mu^{\text{rad}}$) for each σ_g value.

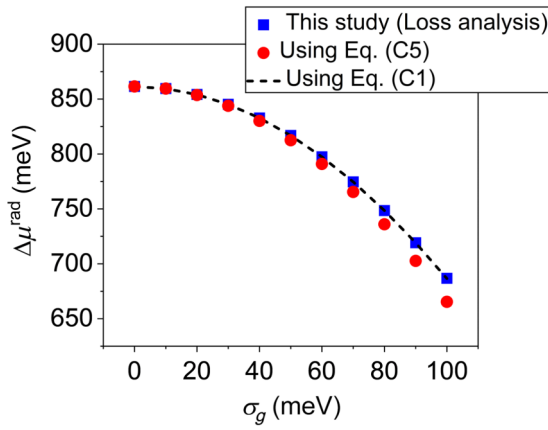


FIG. 11. The radiative limit extracted from our numerical loss analysis [Eq. (2)], from the Rau *et al.* analysis [Eq. (C1)] [8], and from approximation with Eq. (C5).

The details of the derivation of these equations can be found in Ref. [8].

Furthermore, in some reports, simplified equations are being used to estimate $\Delta\mu^{\text{rad}}$, which involves the following approximations [9,35,60]:

$$qV_{\text{OC}}^{\text{SQ}} \approx \overline{E_g} - k_B T \ln \left(\frac{J_{00}}{J_{\text{SC}}} \right). \quad (\text{C4})$$

Then, $\Delta\mu^{\text{rad}}$ would be as follows:

$$\Delta\mu^{\text{rad}} \approx qV_{\text{OC}}^{\text{SQ}} - \frac{\sigma_g^2}{2k_B T}. \quad (\text{C5})$$

In Fig. 11, we compare our $\Delta\mu^{\text{rad}}$ values [Eq. (2)] with those obtained from the Rau *et al.* method [Eq. (C1)] [8] and the simplified approximation given in Eq. (C5). It can be seen that our calculations are completely in agreement with the $\Delta\mu^{\text{rad}}$ values extracted from Eq. (C1).

Furthermore, regarding the approximation in Eq. (C5), Fig. 2(c) illustrates that this approach induces errors in $\Delta\mu^{\text{rad}}$ determination, particularly when σ_g is large. In fact, when $\sigma_g = 0$, Eq. (C1) would be same as the SQ limit.

However, as σ_g gets larger, the right-hand side of Eq. (C5) takes values higher than $qV_{\text{OC}}^{\text{SQ}}$. Therefore, simply approximating it with $qV_{\text{OC}}^{\text{SQ}}$ could result in the underestimation of $\Delta\mu^{\text{rad}}$ and an overestimation of the radiative loss.

APPENDIX D: EFFECT OF FLUCTUATION AND TAIL STATES ON $A(E)$

In Fig. 12, we present simulated $A(E)$ spectra by considering the combined contribution of band-gap fluctuations and the absorption coefficient of a direct band-gap material, which exhibits a square-root dependence above

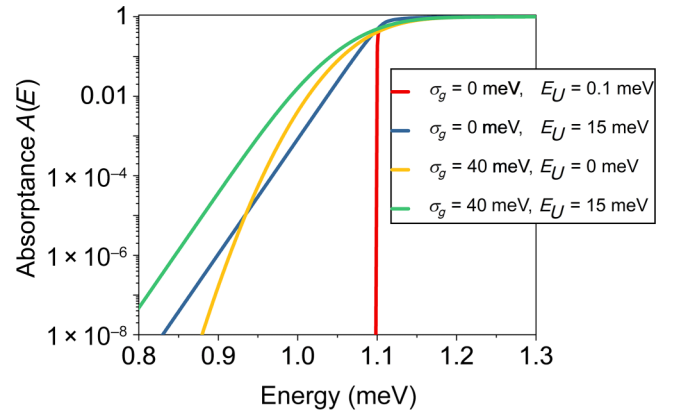


FIG. 12. $A(E)$ spectra simulated by using the absorption coefficient α of a real direct semiconductor, combined with Urbach tails and band-gap fluctuations as explained in Sec. III. The separate effects of $A(E)$ broadening and Urbach tails are clearly visible. The absorber is assumed to be 2 μm thick. For the broadening analysis, see Note 4 in the Supplemental Material [77].

the band gap and Urbach-decay behavior below it [see Eqs. (16) and (18)].

Here, we investigate four different conditions: (i) minimal Urbach tails and the absence of fluctuations, (ii) the presence of Urbach-tail effects only, (iii) fluctuations with no Urbach tails, and (iv) the combined impact of both fluctuations and Urbach tails.

In the first case, with the absence of fluctuations ($\sigma_g = 0$), the sub-band-gap $A(E)$ would be zero. This effect would cause a discontinuous derivative. To address this special case, a small $E_U = 0.1$ meV has been introduced for the simulations. The first derivatives and the corresponding broadening for each curve are discussed in Note 4 in the Supplemental Material [77].

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