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Microscopic origins of radiative performance losses in thin-film solar cells at the example of (Ag,Cu)(In,Ga)Se₂ devices

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ABSTRACT

The present work provides an overview of radiative performance losses in thin-film solar cells, focusing on those related to the open-circuit voltage, using (Ag,Cu)(In,Ga)Se₂ devices as examples. The microscopic origins of these losses are outlined, highlighting the presence of compositional variations, strain, and inhomogeneously distributed point defects on various length scales as contributors to band-gap and electrostatic potential fluctuations, which both contribute to the broadening of the absorption edge in the absorptance or quantum efficiency spectra of the semiconductor absorber layer or the completed solar-cell device. The relationship between this broadening and Urbach tails is discussed. It is shown that the photovoltaic band-gap energy as well as the broadening can be reliably determined from the arithmetic mean and standard deviation extracted from Gaussian fits to the first derivative of the absorptance or quantum efficiency spectra around the absorption edge. The more enhanced the broadening, the more the local maximum in the luminescence spectrum shifts to smaller energies with respect to the band-gap energy of the absorber layer, as verified for about 30 (Ag,Cu)(In,Ga)Se₂ solar cells.

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I. INTRODUCTION

Although photovoltaic solar-cell devices exhibit conversion efficiencies of up to 29.1% when fabricated as single junctions,¹ this value is considerably smaller than the one at the radiative “Shockley–Queisser” limit.² For any solar-cell technology, the understanding of the loss mechanisms is essential for their improvement. While the overall conversion efficiency is defined as the product of the short-circuit current density (j_{sc}), the open-circuit voltage (V_{oc}), and the fill factor (FF), the V_{oc} losses often makeup the largest fraction of all performance losses and thus require particular attention in the research and development of optoelectronic semiconductor devices.

Since the V_{oc} is strongly connected with recombination in a solar-cell device, the corresponding losses can be divided into those due to radiative and those due to nonradiative recombination. The present work focuses on radiative V_{oc} losses. While the physical background of radiative performance losses for solar cells has been discussed in various reports,^{3–6} their origins with respect to the microscopic material properties have not been treated in detail.

It was demonstrated that radiative losses in solar cells can be quantified by evaluation of the broadening of the onset in the absorptance or external quantum efficiency (EQE) spectra.³ The broadening again is a result of fluctuations in the conduction-band and valence-band edges, which can be attributed to local variations in the material properties.⁴ These fluctuations lead to a smaller effective band-gap energy of the semiconductor. The probability for radiative recombination of electron-hole pairs becomes larger for smaller (effective) band-gap energies,² and therefore, we refer to “radiative” losses.

The broadening of the absorption onset in absorptance or EQE spectra also affects the luminescence emission from the semiconductor. The more enhanced the broadening, the more shifts the local maximum in the luminescence spectrum to smaller energies with respect to the assumed band-gap energy of the semiconductor. While this phenomenon has been reported and discussed before,^{5,6} the question is whether the theoretical relationship between the

peak shift and the broadening agrees well with experimental data obtained by the evaluation of measured EQE spectra.

The present work will first provide the relationships between the broadening of the absorption onset, the fluctuations, the Urbach energy, as well as the luminescence peak shift. The microscopic origins of radiative V_{oc} losses will be discussed in detail. Moreover, the relationship between the peak shift and the broadening obtained by analyzing the EQE spectra from a large number of thin-film solar cells will be presented and compared with the theoretical relationship. It will be shown that fitting a Gaussian function to the first derivatives of absorbance or EQE spectra is an appropriate way to extract the band-gap energies and broadening values, and thus, to estimate the radiative V_{oc} losses of photovoltaic solar-cell devices.

II. THEORY OF RADIATIVE PERFORMANCE LOSSES IN SOLAR CELLS

The radiative losses in a solar cell can be divided into current and voltage losses. In order to quantify radiative losses in the open-circuit voltages V_{oc} of solar-cell devices, Rau and Werner³ suggested a Gaussian distribution of the band-gap energy E_{gap} of a semiconductor applied as an absorber in a solar cell. The mean value of this Gaussian distribution is $\bar{E}_{gap}$, and the broadening or standard deviation is σ_{gap} . The broader the Gaussian distribution or the larger σ_{gap} , the more inaccurate becomes $\bar{E}_{gap}$. This broadening and inaccuracy may be linked to fluctuations in the energy-band edges of the semiconductor. The larger σ_{gap} , the larger is the amplitude of the fluctuations. The radiative V_{oc} losses can be calculated via³

$$\Delta V_{oc,rad} = \sigma_{gap}^2 / 2ek_B T, \quad (1)$$

where e is the elemental charge, k_B is the Boltzmann constant, and T is the absolute temperature (which is 300 K throughout the present work). The nonradiative V_{oc} losses can be determined using the photoluminescence quantum yield (PLQY) via^{7,8} $\Delta V_{oc,nrad} = -k_B T / e \ln(\text{PLQY})$.

In order to obtain the distribution of the band-gap energy E_{gap} from any experimental absorbance (bare absorber) or quantum-efficiency (completed solar-cell device) spectrum, one reliable method is to calculate the first derivative of the corresponding spectrum around the absorption onset.⁹ Likewise, when deriving an expression for the theoretical absorbance a assuming a Gaussian distribution of E_{gap} , this Gaussian distribution needs to be integrated over all photon energies E_{ph} .³

$$a(E_{ph}, \bar{E}_{gap}, \sigma_{gap}) = 0.5 \operatorname{erfc}\left((\bar{E}_{gap} - E_{ph}) / \sqrt{2}\sigma_{gap}\right). \quad (2)$$

Figures 1(a) and 1(b) depict the theoretical absorbance spectra and their first derivatives for various σ_{gap} values, where 0 meV (vertical, dotted line) gives the assumed situation for the radiative (Shockley–Queisser) limit. According to Eq. (1), larger σ_{gap} lead to larger radiative V_{oc} losses. Moreover, the broadening also leads to a decrease in the short-circuit current density j_{sc} of the solar cell. This fact is not highlighted by the absorbance spectra in Fig. 1(a) since their gradients are symmetrical around the flexion

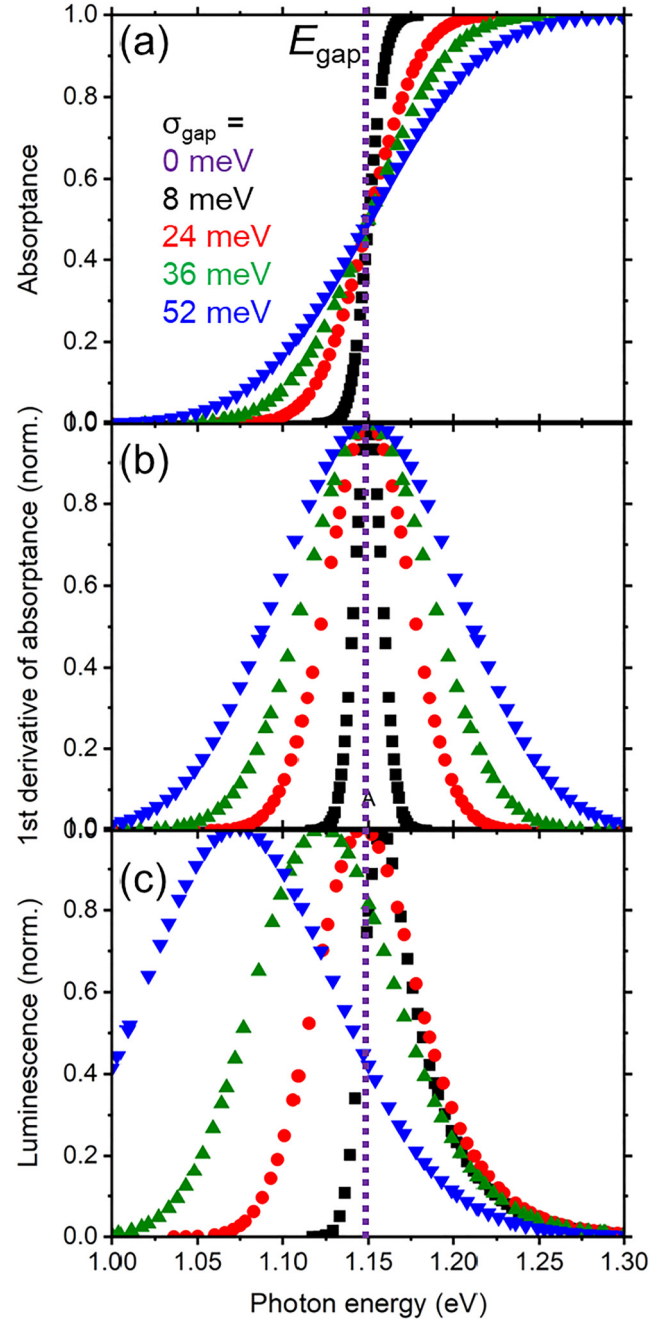


FIG. 1. (a) Simulated absorbance spectra $a(E_{ph})$ calculated using Eq. (2) and various σ_{gap} values. The dashed, vertical line represents the position of the band-gap energy (1.15 eV). At the radiative (Shockley–Queisser) limit, $\sigma_{gap} = 0$ meV, i.e., $a(E_{ph}) = 0$ for $E_{ph} < E_{gap}$ and 1 for $E_{ph} \geq E_{gap}$. Note that generally, experimental absorbance spectra are asymmetric around the inflexion point. (b) First derivatives of $a(E_{ph})$ for various σ_{gap} values. These spectra exhibit Gaussian distributions with standard deviations σ_{gap} . (c) Luminescence spectra calculated using Eq. (3) and the absorbance spectra shown in (a). Shifts between the local maxima in (b) and (c) are visible.

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point (as many photons are absorbed below E_{gap} as above, i.e., the current collected by the photovoltaic device remains the same regardless of the broadening). However, experimental $a(E_{\text{ph}})$ and $\text{EQE}(E_{\text{ph}})$ spectra exhibit asymmetric gradients (see also below), with smaller absorptance (or EQE) for $E_{\text{ph}} > E_{\text{gap}}$ than for $E_{\text{ph}} < E_{\text{gap}}$ close to the flexion point, leading to short-circuit current densities j_{sc} smaller for an enhanced broadening of the $a(E_{\text{ph}})$ or $\text{EQE}(E_{\text{ph}})$ onsets. [We note that in spite of this apparent limitation of the used model, i.e., approximating $a(E_{\text{ph}})$ by Eq. (2), this approach is appropriate for the present work since we concentrate on radiative V_{oc} losses.] Since also the FF of the solar cell becomes smaller for larger σ_{gap} values,¹⁰ the broadening leads to an overall decrease in the conversion efficiency $V_{\text{oc}} j_{\text{sc}} FF$.

Rau¹¹ provided an equation to calculate the electroluminescence (EL) spectrum from a given EQE spectrum, which expresses the reciprocity between the QE of a solar cell and the EL of a light-emitting diode. Assuming that the absorptance and EQE spectra are the same within the spectral region around the absorption onset, which is the case for high-efficiency solar cells with sufficiently large diffusion lengths and absorber thicknesses,¹² the reciprocity theorem can be written as

$$\phi_{\text{lum}} = a(E_{\text{ph}}, \bar{E}_{\text{gap}}, \sigma_{\text{gap}}) \phi_{\text{bb}} [\exp(eV/(k_B T)) - 1]. \quad (3)$$

Here, the luminescence flux from a black body $\phi_{\text{bb}}(E_{\text{ph}}) = 2\pi / h^3 c^2 \times E_{\text{ph}}^2 / [\exp(E_{\text{ph}}/k_B T) - 1]$ (h is Planck's constant and c is the speed of light) and V is the applied voltage. The luminescence spectra ϕ_{lum} calculated for various σ_{gap} are given in Fig. 1(c). It can be seen that for the absorbers with σ_{gap} between 24 and 52 meV, the shift between E_{gap} and the luminescence peak becomes larger for larger σ_{gap} .

Moreover, for $\sigma_{\text{gap}} = 8$ meV, this energetic shift is even negative. This finding can be explained by the fact that the function ϕ_{lum} in Eq. (3) depends on the product of the absorptance a and ϕ_{bb} , which are both functions of E_{ph} . If, for a certain σ_{gap} value, $a(E_{\text{ph}})$ increases more gradually than $\phi_{\text{bb}}(E_{\text{ph}})$ decreases, the local maximum of ϕ_{lum} will be at an energy larger than E_{gap} .

When evaluating the $a(E_{\text{ph}})$ spectra in Fig. 1(a) for $E_{\text{ph}} \leq E_{\text{gap}}$, assuming exponential decays of the tail-state densities from the band edges, the Urbach energies E_U can be obtained by applying^{13–15}

$$\ln[a(E_{\text{ph}})] = C + E_{\text{ph}}/E_U. \quad (4)$$

Here, C is a constant. Equation (4) describes a linear relationship between $\ln[a(E_{\text{ph}})]$ and E_{ph} with the slope E_U^{-1} . We note that the determination of E_U via Eq. (4) provides decent estimates, but, in general, overestimates the E_U values. A more accurate method to determine E_U is to calculate the absorption coefficient via $\alpha(E_{\text{ph}}) = \ln(1 - a(E_{\text{ph}}))/d$ (where d is the semiconductor film thickness) and then to extract E_U^{-1} from the slope of $\alpha(E_{\text{ph}})$. Care is advised when dealing with a semiconductor material, such as halide perovskites, for which, at room temperature, excitonic contributions to the absorption coefficient need to be taken into account.¹⁶

The Urbach energies determined from the absorptance spectra in Fig. 1(a) via Eq. (4), again for various σ_{gap} values, are given in Fig. 2. It is apparent that the larger the broadening of the absorption edge, the more extended the Urbach tails that are related to

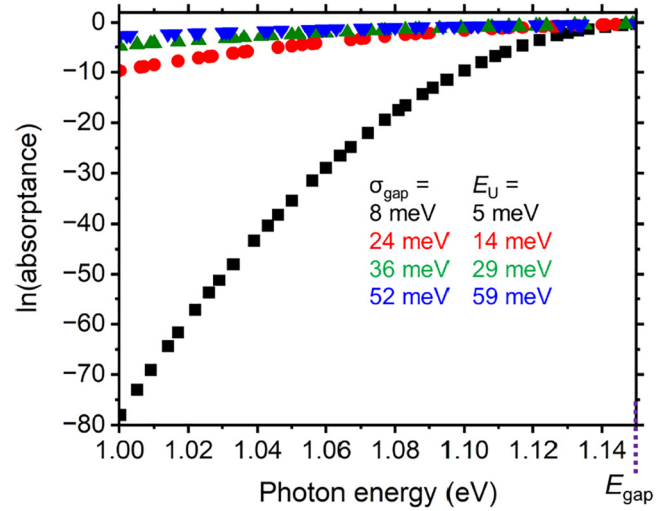


FIG. 2. Logarithms of the simulated absorptance spectra shown in Fig. 1(a), for photon energies $E_{\text{ph}} \leq E_{\text{gap}}$ and for various σ_{gap} values. Using Eq. (4), the corresponding Urbach energies were calculated (the slope was extracted over the E_{ph} range of 1.10–1.15 eV for all curves), which increased for increasing σ_{gap} values. We note that the $\ln[a(E_{\text{ph}})]$ dependencies are not straight lines, which leads to overestimated E_U values.

the density of defect states in the subgap regions. We can conclude that whatever material properties lead to a broadening of the absorption onset also cause an increase in the Urbach energy, since Urbach tails exhibit a part of the broadening. Moreover, since any broadening with $\sigma_{\text{gap}} > 0$ meV affects a radiative V_{oc} loss via Eq. (1), the same should hold also for any Urbach energy of > 0 meV. Indeed, while σ_{gap} values of 8 and 24 meV result in radiative V_{oc} losses of 2 and 22 mV via Eq. (1), similar values (6 and 20 meV) are obtained when using $k_B T / e \ln(1 - E_U/k_B T)$ ¹⁷ (only valid for $E_U < k_B T$) to calculate the V_{oc} losses from the Urbach energy E_U . In addition, Chantana *et al.*^{15,18} reported that various solar-cell technologies increased radiative V_{oc} losses for increasing E_U .

Experimental EQE data from solar cells can be evaluated to obtain the band-gap energy E_{gap} of the semiconductor absorber and the broadening of the EQE onset using the same approach as the one used for the theoretical absorptance spectra shown in Fig. 1(a). An example of such an evaluation is shown in Fig. 3, using the EQE spectrum acquired on a high-efficiency (about 21% without anti-reflection coating) Cu(In,Ga)Se₂ solar cell.¹⁹ In addition to the EQE spectrum, also the photoluminescence spectrum of the Cu(In,Ga)Se₂ absorber is given in Fig. 3, which agrees well with the luminescence flux ϕ_{lum} calculated from the EQE spectrum in Fig. 3 via Eq. (3) ($V = 0.5$ V). The value for E_{gap} of the investigated absorber is about 1.11 eV, and that for σ_{gap} about 40 meV (determined by fitting the $d\text{EQE}/dE_{\text{ph}}$ spectrum using a Gaussian). The peak shift between the luminescence and the $d\text{EQE}/dE_{\text{ph}}$ spectra is about 30 meV. Using Eq. (1), the radiative V_{oc} loss for this solar cell can be calculated to be about 30 mV.

Replacing $a(E_{\text{ph}})$ by $\text{EQE}(E_{\text{ph}})$ in Eq. (4), the Urbach energy for the data given in Fig. 3 was calculated to about 20 meV. The finding that this value is much smaller than the value of

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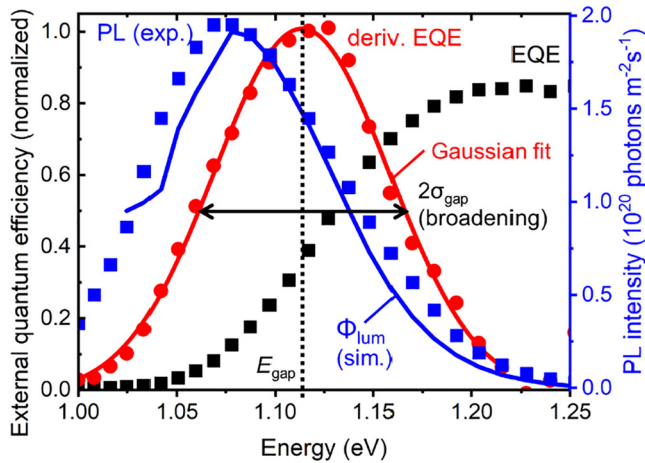


FIG. 3. Experimental EQE spectrum acquired on a high-efficiency (about 21% without anti-reflection coating) Cu(In,Ga)Se₂ solar cell (Ref. 19) (squares with label "EQE"), the first derivative of the EQE spectrum (circles with label "deriv. EQE"), its Gaussian fit (line with label "Gaussian fit"), the theoretical luminescence flux ϕ_{lum} calculated from Eq. (3) using EQE instead of the absorptance a [line with label " ϕ_{lum} (sim.)"], and the measured photoluminescence (PL) spectrum acquired on the identical solar cell [squares with label "PL (exp.)"]. The first derivative and the flux ϕ_{lum} spectrum were normalized to 1. We note a good agreement between the measured PL and the theoretical ϕ_{lum} spectra. This viewgraph is an extended version of a similar result presented in Ref. 19.

$\sigma_{\text{gap}} = 40$ meV can be explained by the fact that the experimental EQE spectrum (Fig. 3) is not symmetrical around the flexion point [in contrast to the simulated spectra shown in Fig. 1(a)], which corresponds to only a small Urbach energy in spite of a large broadening. This result also implies that in the analyzed solar cell, less photons are absorbed/electrons and holes collected in the spectral range above E_{gap} than below, which overall leads to a current loss affected by the broadening σ_{gap} .

In order to determine the fraction of the radiative V_{oc} loss with respect to the total V_{oc} loss, the V_{oc} at the radiative (Shockley–Queisser) limit needs to be calculated,² which is about 870 mV for $E_{\text{gap}} = 1.11$ eV, an AM1.5 solar spectrum and an absolute temperature of 300 K. The experimental V_{oc} of the solar cell is about 720 mV,¹⁹ i.e., the total loss ΔV_{oc} is about 150 mV. Since $\Delta V_{\text{oc,rad}}$ is 30 mV, the nonradiative loss fraction should be about 120 mV, which is indeed the same value obtained when calculating $\Delta V_{\text{oc,nrad}}$ using $-k_B T/e \ln(\text{PLQY})$ and the PLQY of 1% measured by means of absolute photoluminescence.¹⁹

It should be noted that, in general, the first derivative of the EQE spectrum of any solar cell does not exhibit a Gaussian distribution around the onset.¹² Nevertheless, it is possible to use the Gaussian fit only to extract the E_{gap} and σ_{gap} values. This type of fitting is applied to experimental EQE spectra acquired on about 30 solar cells, as discussed in Sec. IV.

III. MICROSCOPIC ORIGINS OF RADIATIVE LOSSES

The reader should be aware of the fact that in principle, all material properties leading to a broadening σ_{gap} of the absorption

onset in the absorptance or EQE spectrum of a semiconductor thin film or of a completed solar-cell device also lead to a corresponding radiative V_{oc} loss, see Eq. (1). In the present section, we will distinguish between those losses related to microscopic changes in the local crystal structure or composition, i.e., which can be attributed to band-gap fluctuations (not regarding any electrostatic properties), and those linked to electrostatic phenomena, i.e., which can be traced back to electrostatic potential fluctuations (they require discussion of changes in the charge states of point defects, the redistribution of free charge carriers, and similar phenomena). For Cu(In,Ga)Se₂ thin-film absorbers, material inhomogeneities leading to band-gap or electrostatic potential fluctuations were reviewed in Ref. 20.

A. Microscopic origins of band-gap fluctuations

Very often, band-gap fluctuations in a semiconductor are attributed only to locally varying compositions, as, e.g., alloy fluctuations on the atomic or nanometer scales or secondary phases. However, band-gap fluctuations are caused also by strain fields in the solid. When considering polycrystalline semiconductor thin films, it has to be taken into account that surfaces, interfaces with the substrate and/or other layers in a thin-film stack, as well as extended structural defects are locations with considerable compositional variations and corresponding strain fields, which need to be discussed in addition to bulk material properties. In general, changes in the crystal structure or composition in real space are related directly to variations in the density of states in reciprocal space, and thus, to fluctuations of the band edges. Consequently, any material properties varying the crystal structure or composition spatially contribute to band-gap fluctuations. Moreover, changes in composition are connected to strain fields, which may together be treated as local variations of the (mass) density.

These variations can be discussed on various length scales. On the atomic (subnanometer) scale, point defects such as vacancies, anti-site defects, or atoms/ions on interstitial sites may be present that change locally the bonding between the atoms in the lattice and, thus, introduce corresponding strain, see Fig. 4. In this respect, crystal structures with intrinsic strain caused by distorted bonds or by pseudosymmetry (e.g., solid solutions with cations or anions occupying the same lattice sites, or crystal structures with small deviations of the lattice constants to the ones of pseudocubic structures) also need to be considered. In corresponding compounds, this intrinsic strain extends across the whole material.

Surfaces and interfaces are often regions of atomic/ionic reconstructions and of interdiffusion.^{21,22} Impurities in a material tend to segregate into these regions.²³ A similar scenario can be found at extended structural defects such as stacking faults, grain boundaries, anti-phase domain boundaries, and dislocations (for example, the reader may refer to Refs. 24–27). In fact, the smaller the average grain size in a polycrystalline thin film, the larger impact have strain fields located at and around grain boundaries. The spatial extensions of such strain fields are typically on the order of several nm to several tens of nm.

Extended structural defects are often decorated by precipitates (e.g., Refs. 28 and 29). The presence of any secondary phase, with typical diameters of a few nm to several 100 nm, contributes to

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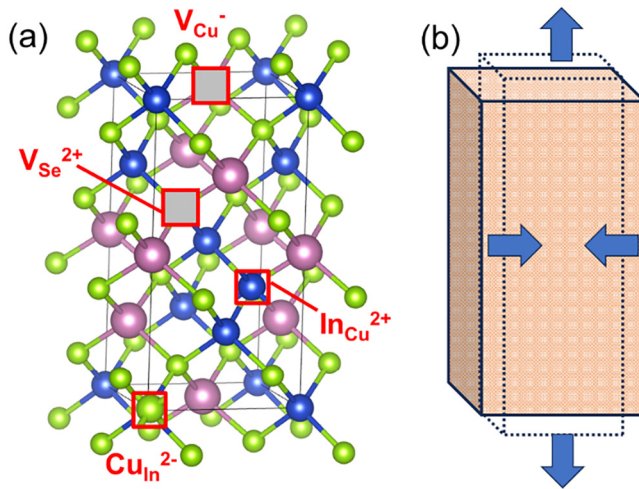


FIG. 4. (a) Unit cell of a tetragonal CuInSe₂ crystal, with the unit cell outlined by a corresponding frame. Several possible point defects are indicated. (b) Schematics of the unit-cell frame given in (a), with strain and the deformation of this unit cell highlighted by a dashed frame and arrows.

additional strain mainly at the interfaces between the matrix/bulk and the secondary phase. Finally, compositional gradients can be introduced in functional thin films (mainly in solar absorbers, as outlined, e.g., in Refs. 30–32), which provide a means to design the local band-gap energy perpendicular to the substrate or to generate a back-surface field that repels charge carriers from highly recombinative interfaces. In spite of the apparent benefit of these gradients, they contribute to additional strain (especially if the compositional gradients extend across individual grains) and, thus, to additional band-gap fluctuations extending over several 100 nm.

Band-gap fluctuations are very difficult to assess directly on the nanometer or submicrometer scales, since available techniques such as electron energy-loss spectroscopy³³ exhibit noise levels on the same order as the expected band-gap variations. However, variations in the peak-energy distributions acquired by photoluminescence⁸ or cathodoluminescence hyperspectral imaging¹² may indicate the presence and the extent of band-gap fluctuations on length scales of about 100 nm–1 μ m (we note that the peak energies detected by luminescence techniques may not be equal to the band-gap energies, see Fig. 1).

B. Microscopic origins of electrostatic potential fluctuations

In order to describe electrostatic potential fluctuations, we can turn again to the point defects in the CuInSe₂ lattice in Fig. 4(a). We can safely assume that point defects in any material system are not homogeneously distributed. In case the net-doping density is sufficiently large, the free charge carriers redistribute corresponding to the distribution of the charged, localized point defects. According to Poisson's equation, the electrostatic potential ϕ_{el} exhibits local variations corresponding to the redistribution of free

charge carriers, which translate into spatial fluctuations of the electronic energy level $-e\phi_{el}$ and, thus, also of the conduction-band and valence-band edges. We note that the charged, localized defects described here contribute to the Urbach tails if their energy levels are correspondingly close to the conduction-band or valence-band edges. Moreover, in contrast to band-gap fluctuations, a critical range exists within which the free charge-carrier concentrations cannot screen electrostatic potential fluctuations.³⁴

In a thin-film solar cell, electrostatic potential fluctuations may be found in the semiconductor absorber layer, but also in the contacts and at the absorber/contact interfaces. In order to assess the extent of these fluctuations in the absorber, scanning spreading resistance microscopy^{35–40} may be applied; this technique provides the spatial distribution of the local resistance, from which the local net-doping density can be derived assuming that the charge-carrier mobility remains constant throughout the material. The reported values of the net-doping densities acquired on Cu(In,Ga)Se₂ absorber layers³⁷ suggest that the amplitudes of electrostatic fluctuations remain within about the same order of magnitude.

When dealing with completed solar-cell devices based on *p-n* junctions, electron-beam-induced current (EBIC) measurements provide the lateral distributions of the widths of the space-charge regions along the *p-n* junction, from which variations in the charge distributions in the absorber, in the contacts, and at the interface may be estimated.⁴¹ A recent study of Cu(In,Ga)Se₂ solar cells with various n-type buffer layers⁴¹ suggests that the impact of fluctuations attributed to variations of charge densities in the Cu(In,Ga)Se₂ absorber is rather negligible (we note that this situation may change when dealing with low-efficiency solar cells or with modules).⁴² A confirmation of this result was given by two-dimensional device simulations, in which the net-doping density in neighboring grains in a Cu(In,Ga)Se₂ layer was varied within the same order of magnitude, showing no impact on the device performance.¹⁹ This finding agrees well with the scenario of an electrostatic potential landscape in which the charge carriers can move without significant perturbation as long as the variations in ϕ_{el} do not exceed a certain upper limit.

The distribution of charged point defects can be affected considerably by heating and/or illumination. This interaction of any radiation with the semiconductor material may provide the energy for electronic transitions leading to charging/decharging of defect states, which also includes metastable states. Correspondingly, again, a redistribution of the free charge carriers and a change in the spatial distribution of the electrostatic potential take place. A prominent example of the impact of light irradiation on the electrical properties of solar cells is the light soaking (or also combined heat-light soaking) applied on completed solar cells.⁴³ It was reported that this treatment can increase the j_{sc} (Ref. 44) of the device or the V_{oc} (Ref. 45) or both.⁴⁶ A microscopic insight performed by means of EBIC analyses into the material changes induced by light on Cu(In,Ga)Se₂ solar cells with various n-type buffer layers⁴¹ showed that the effects of light irradiation can be divided into the spectral ranges of the illumination. When using blue light, the lateral fluctuations of the widths of the space-charge regions along the *p-n* junction were reduced substantially, which led to a decrease in σ_{gap} and, thus, to an increase in V_{oc} according to Eq. (1). Using red light resulted in an increase in the diffusion

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length detected from the exponential decays of the EBIC signal from the edge of the space-charge region to the back contact, which increased the j_{sc} (and V_{oc}).

Another line of explanation for the light-soaking effect involves metastable defect states, as the Se–Cu divacancy complexes ($V_{Se}-V_{Cu}$) in Cu(In,Ga)Se₂ absorber layers proposed by Lany and Zunger⁴⁷ (recently,^{48,49} experimental evidence was provided for the presence of these complexes). According to these authors, metastable defect states trap effectively charge carriers in the unilluminated condition. Upon illumination, these divacancy complexes change their charge states and, thus, also change their abilities to trap charge carriers via a modified capture cross-section. The change in the charge states leads to a higher net-doping density, increasing the V_{oc} , while the changed capture cross-section results in reduced trapping, i.e., a higher V_{oc} and j_{sc} . We note that heat may have similar consequences as light irradiation. Also, depending on the absorber material and its metastable defects, light and/or heat may also have detrimental effects on the device performance of corresponding solar cells. Moreover, the effects of light and heat on the defect distributions in the contacts and at the absorber/contact interfaces also need to be taken into account.

IV. SHIFT BETWEEN PEAK ENERGY OF LUMINESCENCE EMISSION AND BAND-GAP ENERGY

The present section compares the theoretical shift between the peak energy in the luminescence spectrum and the band-gap energy extracted from the absorptance spectra (Sec. II, Fig. 1) with corresponding data calculated using the experimental EQE spectra from about 30 solar cells [all devices with (Ag,Cu)(In,Ga)Se₂ absorbers, including several previous record cells, polycrystalline as well as epitaxial, Ag-containing as well as Ag-free]. These devices were selected to provide a range of broadenings σ_{gap} from about 15 to 50 meV. From the experimental EQE spectra, the band-gap energies were determined as depicted in Fig. 3, σ_{gap} was calculated using Eq. (1), and the electroluminescence was simulated using Eq. (3) ($V = 0.5$ V). The resulting peak shift versus σ_{gap} dependencies, together with the theoretical curve, are given in Fig. 5(a). It is apparent that the theoretical curve agrees well with the experimental peak shift versus σ_{gap} data.

We can interpret the result in Fig. 5(a) in two ways. First, it is yet another confirmation for the validity of the reciprocity theorem by Rau.¹¹ Also, it means that the application of a Gaussian fit to the first derivative of the EQE spectrum around the absorption edge provides a decent way to extract the optical band-gap energy of the semiconductor absorber as well as to estimate the broadening σ_{gap} and, thus, the radiative V_{oc} loss of the corresponding solar-cell device [via Eq. (1)].

The Urbach energies versus σ_{gap} for the 30 solar cells, calculated using Eq. (4) from the corresponding EQE spectra in the spectral range of $E_{ph} < E_{gap}$, are shown in Fig. 5(b). Except for one solar cell, with a CuGaSe₂ absorber ($\sigma_{gap} = 48$ meV, $E_U = 29$ meV), the Urbach energies increase with increasing σ_{gap} . This trend is in good agreement with the one obtained by Gutzler *et al.*,⁵⁰ who recently analyzed the EQE data of more than 100 Cu(In,Ga)Se₂ and (Ag,Cu)(In,Ga)Se₂ solar cells. For most cells [Fig. 5(b)], the magnitudes of the broadening and of the Urbach energy are very

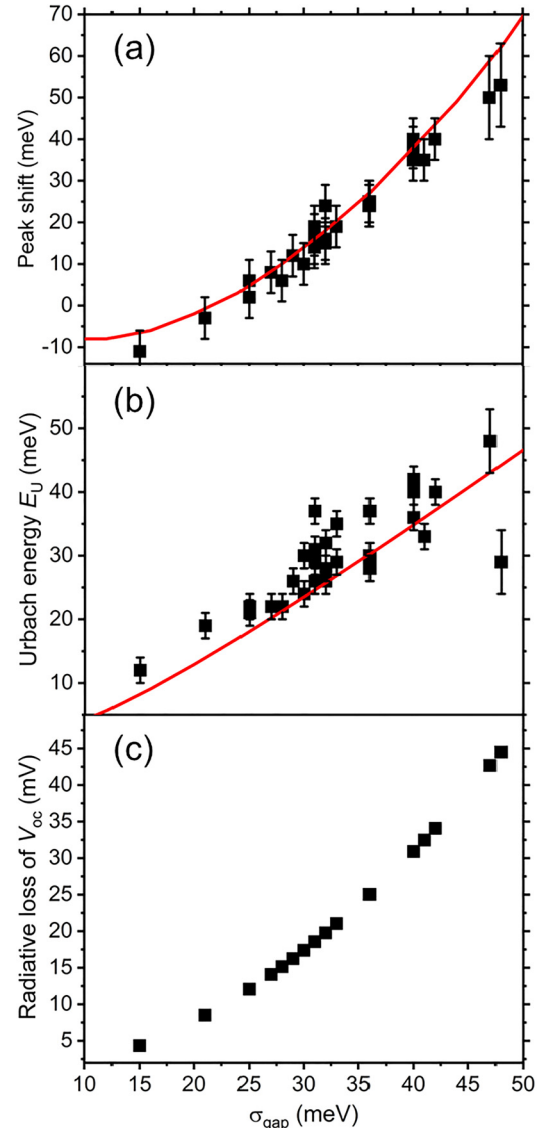


FIG. 5. Evaluation of the EQE spectra acquired on about 30 solar cells. (a) Shift between peak energy of luminescence emission and E_{gap} as a function of the broadening σ_{gap} (squares). The σ_{gap} values were determined from the EQE spectra as depicted in Fig. 3, and the electroluminescence spectra simulated (line) using Eq. (3) (for $V = 0.5$ V). The theoretical dependency (described in Sec. II, Fig. 1) agrees well with the experimental results. (b) Urbach energies calculated from the experimental EQE spectra using Eq. (4) in the spectral range of $E_{ph} < E_{gap}$ (squares) and the simulated values (line) obtained by applying Eq. (4) on theoretical absorptance spectra with various σ_{gap} values [see Fig. 1(a)]. Except for one solar cell (with CuGaSe₂ absorber, $\sigma_{gap} = 48$ meV, $E_U = 29$ meV), the Urbach energies increase roughly with increasing σ_{gap} . (c) Radiative V_{oc} loss vs broadening σ_{gap} , showing increasing V_{oc} loss with increasing broadening. The radiative V_{oc} loss was calculated in two different ways, leading to the same result: via Eq. (1) using the various σ_{gap} values of the investigated solar cells; and by the difference between the V_{oc} values at the Shockley–Queisser limit (Ref. 2) for $\sigma_{gap} = 0$ meV and for the corresponding σ_{gap} of the solar cell (following the approach in Ref. 3).

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similar. Indeed, the experimental dependency of E_U versus σ_{gap} agrees well with the theoretical curve calculated using also Eq. (4) on theoretical absorptance spectra [as the ones depicted in Fig. 1(a)]. Thus, again, we can state that, in good approximation, whatever material properties contribute to σ_{gap} also contribute to the Urbach tails. Considering that the Urbach tails are made up of shallow defect states close to the band edges, band-gap fluctuations can be attributed to compositional variations and strain, which involve point defects in the lattice, and that electrostatic potential fluctuations can be traced back to the inhomogeneous distribution of (charged) point defects, it is clear that the broadening of the absorption edge and the Urbach tail are closely linked to one another.

Figure 5(c) shows that for (Ag,Cu)(In,Ga)Se₂ solar cells with broadening values σ_{gap} ranging from about 15 to 50 meV, the radiative V_{oc} losses are between about 5 and 45 mV. These radiative V_{oc} losses were calculated in two different ways, leading to the same result: via Eq. (1) using the various σ_{gap} values of the investigated solar cells and by the difference between the V_{oc} values at the Shockley–Queisser limit² for $\sigma_{\text{gap}} = 0$ meV and for the corresponding σ_{gap} of the solar cell (following the approach in Ref. 3). The radiative V_{oc} loss increases for increasing σ_{gap} . Therefore, it is essential to reduce the broadening of the absorption onset of solar absorbers in the course of optimizing the device performance of the corresponding solar cells.

V. CONCLUSIONS

The present work gives an overview of radiative performance losses of thin-film solar cells and the microscopic origins of these losses, which mainly concern the open-circuit voltage V_{oc} . The broadening σ_{gap} of the absorption edge determined from absorptance or EQE spectra can be used to determine the radiative V_{oc} loss for any semiconductor absorber layer in a completed solar cell. Urbach tails contribute to this broadening in the spectral range of $E_{\text{ph}} < E_{\text{gap}}$. The quantities of E_{gap} and σ_{gap} can be estimated via the arithmetic mean and standard deviation from the Gaussian fitting of the first derivative of the absorptance or EQE spectrum. The broadening σ_{gap} is made up of contributions from band-gap and electrostatic potential fluctuations, which can be attributed microscopically to locally varying compositions and strain on the one hand side and to inhomogeneously distributed point defects on the other. Electrostatic potential fluctuations can be reduced considerably by light soaking and heat-light soaking treatments. Moreover, the luminescence spectra obtained from the EQE spectra using the reciprocity theorem exhibit emission peaks with energies shifted from E_{gap} corresponding to the broadening σ_{gap} , as verified for about 30 solar cells.

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AUTHOR DECLARATIONS

Conflict of interest

The author has no conflicts to disclose.

Author Contributions

Daniel Abou-Ras: Conceptualization (equal); Formal analysis (equal); Visualization (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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