Bandgap of thin film solar cell absorbers: a comparison of various determination methods

Romain Carron, Christian Andres, Enrico Avancini, Thomas Feurer, Shiro Nishiwaki, Stefano Pisoni, Fan Fu, Martina Lingg, Yaroslav E. Romanyuk, Stephan Buecheler, Ayodhya N. Tiwari

Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

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Abstract

Knowledge of the absorber bandgap is often needed for assessing the junction quality of a thin film solar cell, for example when computing the open-circuit voltage deficit. The bandgap is typically estimated from the routine measurement of the external quantum efficiency (EQE) of finished devices. However the extraction becomes ambiguous in the case of very thin absorbers, or in presence of bandgap gradients or collection issues of charge carriers. This work reviews several methods for the determination of the bandgap from EQE measurements and discusses their validity conditions. The numerical results are compared based on experimental EQE of several different thin film solar cells such as CuInGaSe₂, CuInSe₂, CdTe, CuZnSnSe and perovskite, and systematic trends are identified. Numerical simulations are also performed to illustrate the behavior of the different bandgap extraction methods in presence of a bandgap gradient and different magnitudes of the exponential tail states.

1. Introduction

The potential gain in open-circuit voltage (V_{oc}), and the quality of different solar cells is often compared using the V_{oc} deficit, best defined as $V_{oc,deficit} = V_{oc,SQ} - V_{oc}$ where $V_{oc,SQ}$ is the Shockley-Queisser voltage limit [1] (tabulated values in Ref. [2]). Its calculation requires a value for the absorber bandgap energy E_g , ideally obtained from absorption measurements. However, due to experimental difficulties and time effectiveness, typically only routine device characterization is available and the bandgap is therefore deduced from the external quantum efficiency (EQE). The bandgap may be estimated by simple models based on absorption by a direct bandgap semiconductor, leading to expressions such as $(E \cdot \ln(1 - EQE))^2$ with photon energy E as detailed later. However such approach fails for graded absorbers as reported in Ref. [3]. Variants and approximations of this expression are also commonly used.

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The determination of the bandgap is especially crucial for kesterite absorbers due to variations in composition and carrier collection issues. The derivative method applied on the internal quantum efficiency (IQE) was notably favored in Ref. [4] to determine the bandgap. In kesterite absorbers a significant contribution of tail states to the optical emission and absorption edge prompted further investigations [5, 6]. These studies suggest that the relevant bandgap might be better estimated from the photoluminescence peak energy (and the external radiative efficiency, see below), as in this disordered material the electron population mostly occupies states below the average bandgap.

An estimate of the external radiative efficiency (ERE) was proposed by Green [7] to compare solar cells of different technologies. This estimate is based on the reciprocity principle [8] and takes as inputs the EQE and the V_{oc} of the device. The expression contains an integral term in which the integrand approximates the luminescence emission peak.

In this work we review several methods to extract the bandgap from experimental EQE data and comment on their validity conditions. The numerical values are compared for absorbers with different photovoltaic technologies such as CuInGaSe₂ (CIGS), CuInSe₂ (CIS), CdTe, CuZnSnSe and perovskite, and systematic trends are identified. The extracted trends are also discussed on the basis of EQE curves obtained from optical simulations of graded CIGS solar cells, for which systematic parameters variations are conducted.

2. Bandgap extraction methods

In this section a number of methods are detailed that are used by the community to determine the bandgap of a solar cell absorber.

- The optical bandgap is in principle characterized from absorption measurements of a given layer on a transparent substrate. The absorption coefficient α of a layer with thickness d on a transparent substrate can be approximated from the reflectance R and transmittance T using :

$$\alpha = -\frac{1}{d} \ln \left(\frac{T}{1-R} \right),$$

with the underlying assumption of reflectance only occurring at the first air-layer interface. In this work a more refined data treatment was applied, taking into account the layer/substrate interface as described in Ref. [9]. The bandgap is deduced from α by a linear extrapolation in a Tauc plot ($(\alpha E)^2$ vs E for a direct bandgap semiconductor). Unfortunately most solar cells implement opaque contacts and this method is generally unsuited for routine characterization. It should be noted that the fabrication of an absorber on a transparent substrate may result in a shift in the optical bandgap, notably due to changes in the layer composition, in the composition gradients, or in the phases present in the layer.

- Extrapolation to 0 of the EQE curve: this estimate is conceptually simple but generally delivers values below those of most other methods. The choice of the fitting region is user-dependent and is sometimes not unambiguously defined, and critically affects the result.
- The peak energy of the derivative (or inflection point) of the EQE curve can be interpreted as the bandgap. The result is independent from the user. However interference fringes can shift the peak position or even create a double peak structure as shown in Figure 1(d). Processing the IQE curve instead of the EQE mitigates the negative effect of interference fringes, but requires the additional measurement of the reflectance.

- $(E \cdot \ln(1 - EQE))^2$: The light absorption at a depth z in the absorber layer can be estimated from the Beer-Lambert law $I(z) = I_0 \exp(-\alpha z)$. In a direct bandgap semiconductor the absorption coefficient α takes the form $1/E \cdot \sqrt{E - E_g}$. When neglecting the reflectance and the absorption in the window layers and assuming ideal collection of the photogenerated charge carriers it follows:

$$(E \cdot \ln(1 - EQE))^2 \sim E - E_g$$

This method is more accurate when the IQE is used instead of the EQE, i.e. when correcting for the reflectance and absorption losses in the window layers. This method is also sensitive to collection losses. It will also fail in the case of graded absorbers as the effective α of the film does not follow the assumed square root form.

- $(E \cdot EQE)^2$: This method is often used in the literature. A possible derivation of the formula is the first-order series expansion of the $(E \cdot \ln(1 - EQE))^2$ expression close to $EQE = 0$.
- ERE integrand: an estimate of the external radiative efficiency was proposed by Green [7] to compare solar cells of different technologies and reads as:

$$ERE = \frac{1}{J_{sc}} \frac{2\pi q}{h^3 c^2} \exp\left(\frac{qV_{oc}}{kT}\right) \int \frac{\overline{EQE}_{abs} E^2}{\exp(E/kT) - 1} dE$$

The integrand approximates the luminescence spectrum, and in the following its peak energy is interpreted as the bandgap. The result is independent from the user. The experimental input is the hemispheric EQE $\overline{EQE}_{abs}$ hereafter approximated by the measurement under normal incidence illumination. The V_{oc} of the device is required to compute the ERE . Large potential disorders or tail states leads to significantly lower estimates.

Figure 1(a) shows the experimental EQE of a CIGS cell, together with the best fits or curves of the methods presented above. The best fits to the $(E \cdot EQE)^2$ and $(E \cdot \ln(1 - EQE))^2$ methods are also shown in Figure 1(b)-(c) with the appropriate axis transformation. Figure 1(d) presents another CIGS cell with marked interference fringes, to the point that the derivative method fails.

3. Experimental details

The CIGS solar cells were fabricated by multistage co-evaporation at temperatures compatible with polyimide substrates, on SLG substrates coated with a SiO_x alkali diffusion barrier and a Mo back contact. Various post-deposition processes (PDT) were applied to probe the influence of absorption tails (no PDT, NaF or NaF+RbF PDT). The cells were completed with CdS deposited by chemical bath deposition (CBD), sputtered ZnO and ZnO:Al layers and evaporated Ni/Al grids. The fabrication processes is described in more details in Ref. [10].

The CIS cells were fabricated following a slightly different procedure as for CIGS. Specifically no alkali diffusion barrier was used below the Mo back contact, and the CIS deposition was performed without gallium at about 500°C substrate temperature as presented in Ref. [11]. Layers for optical characterization were delaminated from the substrate.

The CdTe cells were fabricated by depositing a sputtered Mo back contact on Corning 7059 borosilicate glass, followed by a 100 nm MoO_3 buffer layer deposited by high-vacuum evaporation (HVE). 5 μm of CdTe were deposited by HVE followed by 400 nm CdCl_2 . The stack was annealed at

435°C for 25 min in Ar/O₂ atmosphere. P-type doping was obtained by adding Cu with concentration of 10¹⁵ at/cm². Two 60 nm thick CdS layers were deposited by CBD with a CdCl₂ treatment in between. The front contact consisted of sputtered ZnO and ZnO:Al layers and evaporated Ni/Al grids. The finished cells were annealed at 210°C for 10 min in air with subsequent rapid cooling. Layers for optical characterization were directly deposited on borosilicate glass. More details on the fabrication processes can be found elsewhere [12].

Semi-transparent perovskite solar cells were grown on flexible polymer substrates. The InZnO front contact was deposited by pulsed-DC sputtering and was coated by an electron transport multilayer, polyethylenimine ethoxylated (spin coated) and C₆₀ (thermally evaporated). The perovskite absorber is obtained via a two-step deposition (thermally evaporated PbI₂ film converted into CH₃NH₃PbI₃ by spin coating of CH₃NH₃I solution in isopropyl alcohol). After annealing in a N₂ filled glovebox, a Spiro-OMeTAD solution was spin coated to act as a hole transporting layer. Then a MoO_x buffer layer was thermally evaporated and covered by an InZnO transparent electrode. Ni/Al grids were deposited by e-beam evaporation. The optical characterization was performed directly on the semi-transparent cells. Details about the fabrication methods are reported in Ref. [13].

Kesterite absorbers were fabricated by a sequential co-sputtering and rapid thermal annealing route [14]. Metallic precursor were deposited by co-sputtering of Cu, Zn, Sn and Ge and covered by a 1.15 µm thermally evaporated Se capping layer followed by a rapid thermal annealing. Devices were finished with CdS, ZnO and ZnO:Al layers and evaporated Ni/Al grids.

Reflectance and transmittance measurements were performed using a Shimadzu UV VIS 3600 spectrophotometer equipped with an integrating sphere, while correcting for the instrumental responses stemming from diffuse and specular reflections on the sample and on the reflectance standard. The EQE spectra were recorded by illuminating the sample with a chopped monochromatic light produced by a white light halogen lamp and a LOT MSH-300 monochromator, under around 0.2 sun halogen bias light. The measured current was calibrated against a certified Si solar cell.

The data treatment was performed using *grapa*, an open source software written in python proposing data processing functions for a number of experimental techniques used in the field of photovoltaics [15].

4. Comparison of bandgap extraction methods

The methods presented above have been applied to experimental EQE curves of cells of various photovoltaic (PV) technologies. Figure 2 shows the difference in the values for each method, using the $(E \cdot EQE)^2$ result as reference as with this method a value could be obtained for all analyzed EQE curves.

The $(E \cdot EQE)^2$ method systematically underestimates the bandgap as compared to the ideal absorption method by 12-25 meV. The extrapolation to 0 delivers clearly underestimates the bandgap. The slope was chosen as steep as possible: a different user may end up with significantly lower values. The derivative method delivers values in good agreement with optical measurements. The grey stripes in the CIGS column indicate samples for which interference fringes generate a double peak in the derivative. The $(E \cdot \ln(1 - EQE))^2$ method fails for graded absorbers (CIGS) as observed by Richter *et al.* [3], and for devices with collection issues (here kesterite). Otherwise the values are in reasonable agreement with the optical measurements. The ERE integrand method

underestimates the bandgap in a similar way as the $(E \cdot EQE)^2$ expression. This method fails for samples with large potential fluctuations, or with exponential decay energies close to or above 20 meV. Such discrepancy was already reported for example in Refs. [4, 5]. This aspect is analyzed in more details in the optical simulations.

Interference fringes make the bandgap evaluation more difficult for all investigated methods. A clear single peak in the EQE derivative can be shifted by more than ± 10 meV, altering the reliability of this method. In such cases the uncertainty on the $(E \cdot EQE)^2$ value is degraded by a comparable amount, but identifying problematic data is straightforward. The ERE integrand method is also affected by interference fringes, possibly to a lesser extent. This issue can be mitigated by characterizing neighboring cells with slightly different absorber thicknesses, or by measurement of the cell reflectance and extraction of the bandgap from the IQE, as this correction decreases the amplitude of the interference fringes. Investigations on a reduced number of cells showed that the use of the IQE instead of the EQE results in slightly decreased bandgap energy values (less than 10 meV difference) for all methods.

5. Optical simulations: bandgap grading and tail states

Optical simulations are performed to better understand the influence of a bandgap grading and of the tail states on the results of the different bandgap extraction methods. An experimental GGI grading with a narrow notch is chosen as a reference to better illustrate the different tendencies.

Numerical simulations of graded CIGS solar cells are performed similarly as in Ref. [16]. The optical propagation in the solar cells is simulated using the transfer matrix method implemented in the *tmm* python package [17]. The multilayer structure is as follows: 500 nm Mo, 10 nm MoSe_x, CIGS, 50 nm CdS, 70 nm ZnO, 200 nm ZnO:Al, and 105 nm MgF₂. Roughness layers are implemented as Bruggeman effective medium approximation in a 50–50% mixture of the surrounding materials. For each material, the dielectric functions determined in Ref. [16] are used, with the exception of Mo for which the values are taken from Hara *et al.* [18] to better match the average level of the experimental cell reflectance. The CIGS absorber is modelled as 25 nm-thick slices based on an experimental GGI depth profile (sample A in Ref. [16]). Close to the bandgap, the absorption coefficient is modelled with a square root dependency completed with an exponential decay (see Ref. [16]). The EQE is computed as the cumulated light absorption in each of the CIGS slices, assuming ideal collection of charge carriers. Finally, the different bandgap extraction methods are applied on the simulated EQE.

In the first set of experiments the grading is stretched or compressed by certain ratios to simulate the effect of thinner or thicker absorbers, as shown in Figure 3(a). The x2 grading can be alternatively interpreted as an ideal back-reflector. The simulated EQE are shown in Figure 3(c), and the corresponding extracted bandgaps are reported in Figure 3(d). In the second set of experiments the segment with minimum bandgap was widened by 250, 500 and 1000 nm to explore the effect the notch width on the bandgap evaluation. The last experiment focuses on the influence of the disorder, by varying the exponential decay energy U of the absorption coefficient. This implementation simplifies the reality as the fluctuations of bandgap are ignored.

The thick black lines indicate the minimum implemented bandgap and should represent the target. However, for the grading stretching experiment the notch becomes quite narrow and this value

might become insignificant. The $(E \cdot \ln(1 - EQE))^2$ method is not reported here as it is poorly suited to graded absorbers and clearly overestimates the bandgap. The extrapolation method delivers results below the minimum implemented bandgap. We observed more difference with the other methods in the cases of real solar cells than in these simulations. The other methods are in reasonable agreement. The $(E \cdot EQE)^2$ method is the most sensitive on the notch width and delivers lower values when the notch is wide. The derivative method may fail when interference fringes affect the EQE. The ERE integrand method fails for simulations with large absorption exponential decay energies. Exponential decays around 20 meV still succeed in the simulations but are observed to fail in real cases (kesterite and a few of the CIGS cells), probably because the optical model does not implement random fluctuations of the bandgap.

6. Conclusions

Different methods for the determination of the bandgap from the EQE are presented and their results are compared on a set of experimental EQE of cells of various photovoltaic technologies. Optical simulations of CIGS solar cells were also conducted to analyze the effect of a bandgap grading and of tails states below the bandgap. An open source software was released, proposing a graphical interface with a library of data treatment functions for the analysis of solar cells.

Three methods are identified which provide values in reasonable agreement with optical absorption measurements, as summarized in Table 1. The derivative method gives results in best agreement with absorption measurements. However, interference fringes disturb the numeric derivative: this method is unreliable on relatively flat samples. We recommend caution as fringes of weak amplitudes may already shift the derivative peak. This issue can be mitigated by the computation of the IQE, at the cost of an additional measurement. The $(E \cdot EQE)^2$ method is comparatively more robust and gives a reliable estimate although generally underestimated by around 20 meV. With this method values, may be overestimated for bandgap graded samples with a narrow notch. We recommend the ERE only for samples with small exponential decays and low degree of potential fluctuations. Exponential tails in the range of 20 meV are observed to result in severely underestimated bandgap values.

Finally, we recommend consistency of the chosen bandgap determination method, and the chosen determination method should always be mentioned when publishing bandgap values.

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Figure 1: (a) experimental EQE curve of a CIGS solar cell together with the best fits of the investigated methods. (b), (c): $(E \cdot EQE)^2$ and $(E \cdot \ln(1 - EQE))^2$ vs E plots illustrating the corresponding fitting ranges. (d) Experimental EQE curve of a CIGS cell showing pronounced interference fringes. Here the derivative exhibits two maxima.

Figure 2: Energy difference to the $(E \cdot EQE)^2$ method, for cells of various PV technologies. The range for most likely E_g is estimated from the absorption measurements.

Figure 3: (a), (b) Implemented bandgap gradings. (c) Simulated EQE. (d) Evaluated bandgap energies for the different methods. The minimum implemented bandgap is indicated by thick black lines.

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Table 1: Comparative summary of the different investigated methods for the determination of the bandgap from EQE measurements.

Method	Derivative / Inflection point	$(E \cdot EQE)^2$	ERE integrand	Extrapolation to 0	$(E \cdot \ln(1 - EQE))^2$
Recommended	✓	✓	(✓)	✗	✗
Unsuited for			E_g fluctuations, tails states		E_g gradients Poor carriers collection
Mathematical expression	$\frac{d}{dE}EQE$		$\frac{EQE E^2}{\exp(E/kT) - 1}$		
User- independent	✓	✗	✓	✗	✗
Avg. deviation from absorption	-5 meV	-20 meV	-20 meV	-50 meV	-10 meV
Interference fringes	Peak shift (unnoticed?)	Fitting range?	Peak shift (unnoticed?)	Large impact Fitting range?	Fitting range?

Highlights

- Comparison of different methods for the bandgap determination from EQE
 - Criteria for the choice of a method are given
 - Effects of interference fringes on the bandgap determination are discussed
 - Recommended methods: derivative (inflection point), $(E \cdot EQE)^2$ and ERE integrand
 - Open source software released for the analysis of solar cells