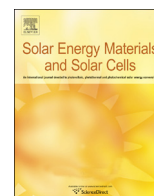




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What is the bandgap of kesterite?



Susanne Siebentritt*, Germain Rey, Ashley Finger, David Regesch, Jan Sendler, Thomas Paul Weiss, Tobias Bertram

Laboratory for Photovoltaics, Physics and Materials Science Research Unit, University of Luxembourg, 41, rue du Brill, L-4422 Belvaux, Luxembourg

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ABSTRACT

There are different ways to determine the bandgap of a semiconductor. In the case of strong tailing they lead to different results. Various versions of Tauc's plot give the gap of extended states, whereas the photoluminescence and the quantum efficiency extend into the tail states. The absorption edge in kesterite is determined by tail states therefore different methods to determine the band gap lead to different results. To decide whether the main recombination path is in the bulk or at the interface, the activation energy of the recombination rate should be compared to the energy of the radiative recombination in the bulk. This is the energy of the photoluminescence maximum and can be approximated by the linear extrapolation of the low energy edge of the quantum efficiency spectrum.

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1. Introduction

The bandgap of a semiconductor is a very fundamental material property, particularly for its use in opto-electronic devices like solar cells. The band gap of a solar cell absorber determines the maximum efficiency obtainable. This is described by the Shockly–Queisser limit, when this absorber is used in a single junction [1]. Kesterite solar cells are particularly far away from this ideal case, mostly because their open circuit voltages are about only half of what is expected from the Shockley–Queisser limit [2]. This implies that there exist strong non-ideal recombination channels in these solar cells. Repins et al. argued that interface recombination is the dominant pathway [3]. These observations were made on pure selenide absorbers, where it is expected that the band alignment to the CdS buffer is favorable [4], with a spike configuration [5,6] as opposed to a cliff configuration for the sulfide absorbers [5–8]. On the other hand, Gokmen et al. argue that the strong tailing of the states into the bandgap is responsible for the V_{OC} loss [9]. If strong tailing occurs the question arises how the bandgap should be defined and measured. It has been proposed to describe the bulk by a mobility bandgap which is lower than the optical bandgap [10]. In the following we will briefly describe the various methods used to experimentally determine the band gap energy, then compare the results of these methods for CuInSe_2 and $\text{Cu}_2\text{ZnSnSe}_4$ absorbers and draw conclusions on what method is most suitable for specific questions.

2. Experimental bandgap determination

In a perfect semiconductor the density of states near the valence band maximum and the conduction band minimum follow a square root like behavior with energy. In a direct semiconductor this translates directly into a square root like behavior of the absorption coefficient α as a function of energy E (see e.g. [11,12]). Thus, a Tauc's plot of $\alpha^2 E^2$ vs. E gives the bandgap E_G as the abscissa intercept [13]. The bandgap determined that way is the bandgap of the extended states. The absorption spectrum can be determined from a reflection–transmission (RT) measurement. Usually the model of a free standing film is used to extract the absorption coefficient. In kesterites it is essential to use the models for low absorption which take interference inside the film into account [12] since the absorption below the gap of extended states is important and can be quite weak. Other methods to determine the bandgap and other critical points in semiconductor are photo- or electroreflectance [14] or ellipsometry [15]. These methods determine the bandgap of the extended states, i.e. the same value as obtained from Tauc's plot. When dealing with solar cells the problem arises, that RT measurements need a transparent substrate, which is not the case in solar cells with a Mo backcontact. Therefore the quantum efficiency (QE) spectrum of the solar cell is often used to obtain a spectrum proportional to the absorption spectrum by taking into account that $(1 - \text{QE})$ is a measure for the transmission of the film. Ideally, one should use the internal QE spectrum after correction for reflection and absorption in the window layers. Another approach to determine the absorption spectrum is from photoluminescence (PL), using Planck's generalized law [16,17]. Because of Kirchhoff's law the luminescence spectrum contains the absorption spectrum, which can be

* Corresponding author.

E-mail address: susanne.siebentritt@uni.lu (S. Siebentritt).

extracted by first determining the quasi-Fermi level splitting from the higher energy slope of the PL spectrum and then the absorbance spectrum from the low energy slope [18] or from fitting the PL spectrum using an absorption model [19]. In an ideal semiconductor without tailing the bandgap can also be determined from the maximum of the PL spectrum, which occurs in that ideal case at $E_C + kT/2$, where k is Boltzmann's constant and T is the temperature. Since it is well known that in kesterites, as well as in $\text{Cu}(\text{In,Ga})\text{Se}_2$, tailing and thus absorption below the bandgap of extended states occurs, the linear extrapolation of the low energy edge of the QE spectrum is used to determine the absorption edge, if not the bandgap [4,20–22]. It has been argued that in the case of tailing the inflection point of the QE spectrum at the low energy slope can be used as an approach to the bandgap of extended states [9,23,24].

3. Experimental

The $\text{Cu}_2\text{ZnSnSe}_4$ and CuInSe_2 samples investigated in this study are grown by thermal co-evaporation in an MBE system on glass or on Mo coated glass [20,21]. The $\text{Cu}_2\text{ZnSnSe}_4$ samples used for the comparison of the different methods are grown in the same batch and the CuInSe_2 samples were grown in different batches of similar processes. More $\text{Cu}_2\text{ZnSnSe}_4$ films were prepared by the sequential CAPRI process [25]. Solar cells are finished by a CdS buffer, a ZnO–ZnO:Al or a ZnO-biased ZnO window [26] and a Ni–Al grid. All kesterite solar cells discussed have efficiencies between 7 and 8.4%; the CIS solar cell has an efficiency of 13.5% [27]; RT measurements are performed in a spectrophotometer on samples on glass. QE is measured on solar cells in a home built

system, using reference diodes calibrated at the German national metrology institute PTB for reference. PL is measured at room temperature and is excited by an Ar ion laser and measured in a home built system based on confocal geometry with a single monochromator equipped with a Si camera and an InGaAs diode line. The system is calibrated using a gauged lamp.

4. Comparison of different methods and of CuInSe_2 vs. $\text{Cu}_2\text{ZnSnSe}_4$

Fig. 1 shows the comparison of different methods for CuInSe_2 (a and b) and for $\text{Cu}_2\text{ZnSnSe}_4$ (c and d). QE data is external QE data. This is justified, since the absorption of the window layers is nearly negligible in the band gap region of the absorber. Tauc's plots (Fig. 1a and c) are normalized at an energy near the band gap for better comparison. For CuInSe_2 Tauc's plots obtained from the transmission–reflection measurement, the PL spectrum and the QE spectrum (Fig. 1a) agree within error and result in a band gap of 1.00 ± 0.01 eV. Since this extrapolation is based on the theoretical density of the extended band states it yields the band gap of the extended states, i.e. the band gap of the ideal semiconductor. The linear extrapolation of the QE spectrum and maximum of the PL spectrum (Fig. 1b) agree also with each other within error and are 60 meV lower than the band gap of the extended states. This effect is due to the presence of tail states which expand into the band gap. These tail states are also visible in Tauc's plots (Fig. 1a): there is clearly absorption below the band gap, i.e. there is a density of states within the band gap decaying with energetic distance from the band edges. These tail states can decay exponentially with a characteristic energy, called Urbach energy. Other

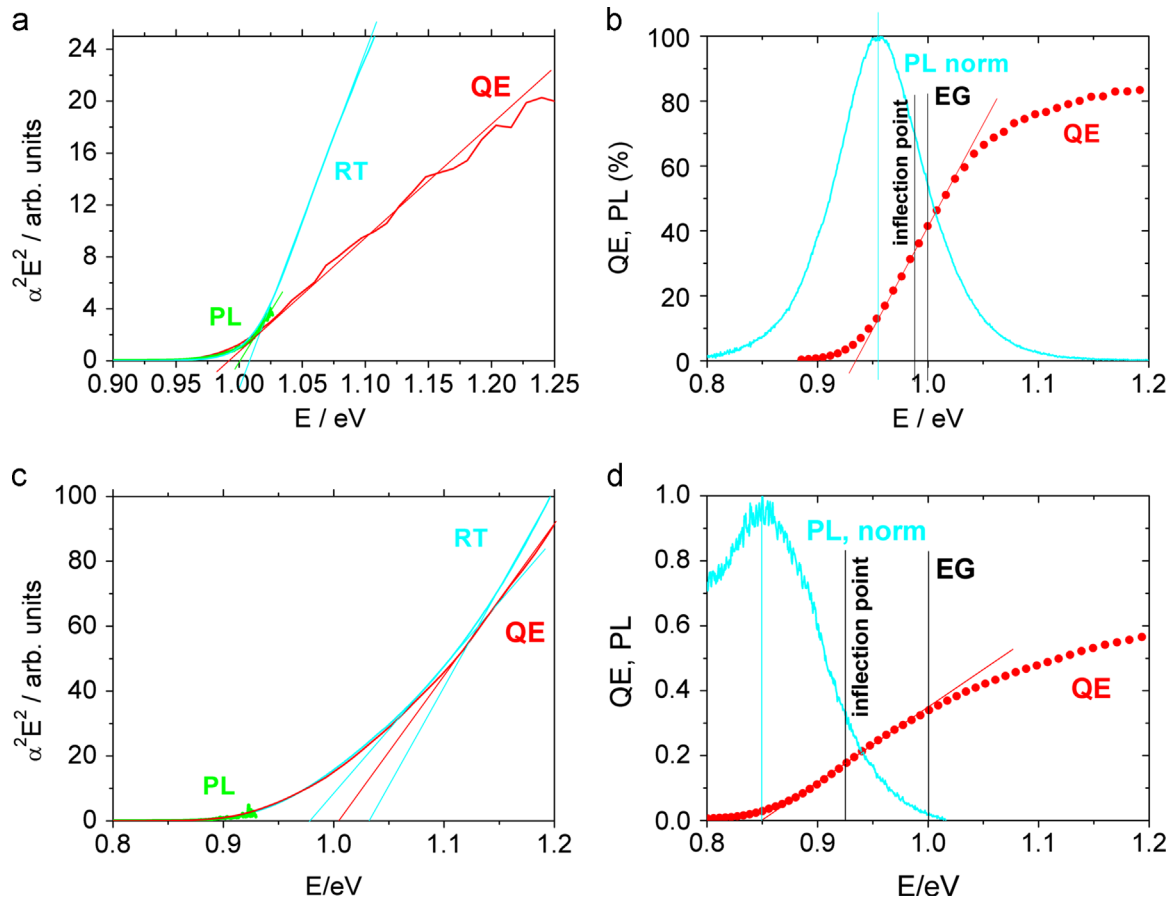


Fig. 1. Tauc's plots (a and c) and QE and PL spectra (b and d) for CuInSe_2 (a and b) and $\text{Cu}_2\text{ZnSnSe}_4$ (c and d).

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