U. Rau, B. Blank, T. C. M. Müller, and T. Kirchartz

IEK5-Photovoltaik, Forschungszentrum Jülich, 52425 Jülich, Germany

Detailed balance analysis of photovoltaic devices and materials

Abstract

The recent years have seen amazing progress in various photovoltaic technologies, like new world records for Cu (In,Ga)Se2, Si, and GaAs solar cells or the unprecedented rise of organo–metal halide materials. Furthermore, new nano-electronic and nano-photonic concepts claim to challenge traditional limits like the Shockley-Queisser-limit for the maximum power conversion efficiency or the Yablonovitch-limit for the maximum light path enhancement. In the light of the recent developments, it appears necessary to remind the community about the fundamental theories. At the same time consistent generalizations are needed that extend the description of limiting cases towards a consistent top-down approach that allows one to quantify departures from the ideal situation as well us to judge whether or not proposed concepts can really deliver what they promise. The present contribution will propose a method that allows us to measure the prospects of materials and devices with direct relation to the thermodynamic limits. The method applies to the direct experimental analysis of materials as well as to the quantification of theoretical material prospects from first principle calculations. In this way, we gain figures of merit for both the electrical and the optical quality of materials and devices.

Introduction

Traditional limits like the Shockley-Queisser-limit (SQ) [1] for the maximum photovoltaic power conversion efficiency or the Yablonovitch-limit [2] for the maximum light path enhancement in solar cells are well established and solidly based on the principle of detailed balance. However, the principle of detailed balance allows us not only to describe limiting cases but also real world devices. These more general theories result in reciprocity relations between the photovoltaic action of the devices and their electroluminescent properties [3,4]. These theories set the quantitative framework for common device analysis techniques like electroluminescence imaging [5]. Furthermore, the theories allow us to analyze the performance of solar cells and, most importantly, to quantify losses in comparison of different solar cell technologies [6,7].

The present contribution will review the theoretical and experimental progress made during the last decade in what we denote detailed balance analysis. We will further substantially extend and refine previous theories allowing for a much more detailed analysis of photovoltaic materials and devices.

Results and Discussion

In 1967, Ross [3] derived an equation for the attainable 'potential difference μ caused by a radiation field in a photochemical system'. In the notation of Ref. [4] this relation reads

$$V_{OC} = V_{OC}^{rad} + kT/q \log(Q_e^{LED}) = V_{OC}^{rad} - \Delta V_{OC}^{nonr} \quad (1)$$

where V_{oc} denotes the actual open circuit voltage of the device and V_{oc}^{rad} the open-circuit voltage that would be attained if radiative losses, i.e., *losses by photon emission* from the solar cell, were the only loss mechanism. The quantity Q_e^{LED} is the *external* luminescent (LED) quantum efficiency determining the nonradiative loss term ΔV_{oc}^{nonr}, the quantity kT is the thermal voltage, and q the elementary charge.

The second important relation is the electro-optical reciprocity [4], an equation connecting the external quantum efficiency Q_e^{pv} of a solar cell and the electroluminescence (EL)n emission ϕ_{em} via

$$\phi_{em}(E) = Q_e^{pv}(E)\phi_{bb}(E)\left[\exp\left(\frac{qV}{kT}\right)-1\right], \quad (2)$$

where ϕ_{bb} is the black body radiation at the temperature T of the device. Both Eq. (1) and Eq. (3) are reciprocity relations because they compare the same device in different operation modes. The combination of Eq. (1) and (2) provides a method to directly compare the non-radiative losses of different solar cell technologies using a combination of electroluminescence and photovoltaic quantum efficiency measurements [6] or the quantum efficiency alone [7].

An important pitfall in Eq. (1) is the fact that the radiative limit V_{oc}^{rad} is not a fixed quantity for a specific material but is dependent on the device properties such as thickness or light-trapping/light-outcoupling properties. Therefore, it is worthwhile to distinguish between the limiting V_{OC}^{SQ} in the SQ-sense, namely that one that would result from a step-function like quantum efficiency corresponding to the band gap energy E_{SQ} and the radiative V_{oc}^{rad} as obtained for the specific device.
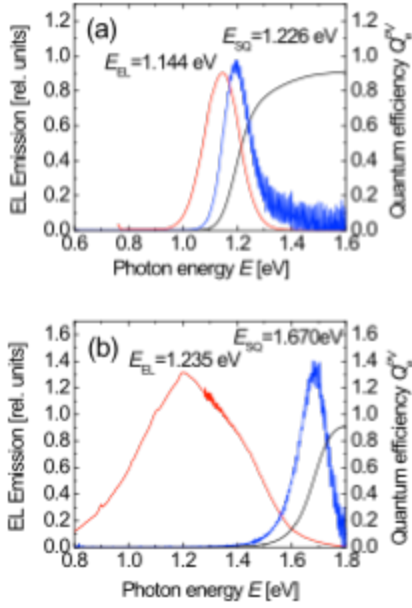
Figure 1: The distribution of SQ-gaps (blue lines) is derived from the external quantum efficiencies (black lines) for Cu(In,Ga)Se$_2$ solar cell (a) and an organic bulk-heterojunction (PBDTTTc-PC70) solar cell (b). The difference between the characteristic energies E_{SQ} (the average SQ gap) and E_{EL} (the average energy of photon emission) is 112 meV in (a) and 437 meV in (b).

We introduce here an extension of Eq. (1)

$$V_{OC} = V_{OC}^{SQ} - \Delta V_{OC}^{SC} - \Delta V_{OC}^{P} - \Delta V_{OC}^{nonr}$$
$$= V_{OC}^{SQ} - \Delta V_{OC}^{int} - \Delta V_{OC}^{SC} - \Delta V_{OC}^{em} - \Delta V_{OC}^{nonr} \quad (3)$$

that allows us to analyze real world devices by considering three loss terms (first line). As shown in Fig. 1, we interpret the external quantum efficiency as a result of a distribution $P(E_g)$ of band gap energies that leads us to the determination of the radiative loss term ΔV_{OC}^{P}.

The second line in Eq. (3) stands for a four step procedure that lead us from V_{OC}^{SQ} to the actual V_{OC} as illustrated in Fig. 2 for a simulated cell with a variation of the share p_λ

of Lambertian light-trapping [8] where $p_\lambda = 0$ represents a flat cell and $p_\lambda = 1$ a perfect Lambertian light trapping.
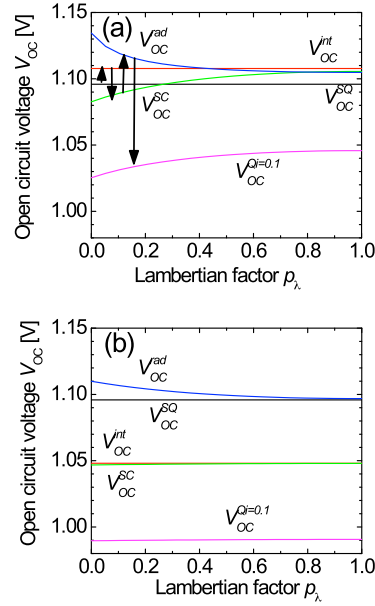
Figure 2: Loss analysis for the open circuit voltage V_{OC} of simulated devices with band gap energy $E_g = 1.35$ eV, an absorption coefficient $\alpha = \alpha_0 / kT (E - E_g)^{1/2}$ of a direct band gap with thicknesses $w = 0.05/\alpha$ (a) and $w = 0.5/\alpha$ (b). The SQ value V_{OC}^{SQ} is defined by E_g and the loss analysis is performed in 4 steps according to Eq. (3).

[1] W. Shockley and H. J. Queisser, J Appl Phys **32**, 510 (1961).
[2] E. Yablonovitch, J Opt Soc Am **72**, 899 (1982).
[3] R. T. Ross, J Chem Phys **46**, 4590 (1967).
[4] U. Rau, Phys Rev B **76** (2007).
[5] A. Gerber, V. Huhn, T. M. H. Tran, M. Siegloch, Y. Augarten, B. E. Pieters, and U. Rau, Sol Energ Mat Sol C **135**, 35 (2015).
[6] T. Kirchartz, U. Rau, M. Kurth, J. Mattheis, and J. H. Werner, Thin Solid Films **515**, 6238 (2007).
[7] M. A. Green, Prog Photovoltaics **20**, 472 (2012).
[8] U. Rau, U. W. Paetzold, and T. Kirchartz, Phys Rev B **90** (2014).