Solar Energy Materials & Solar Cells 120 (2014) 616–621

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Optical modelling of the external quantum efficiency of solar cells with luminescent down-shifting layers

R. Rothemund *

Institute for Photovoltaics and Research Center SCoPE, University of Stuttgart, Pfaffenwaldring 47, 70569 Stuttgart, Germany

ARTICLE INFO

Article history:
Received 15 September 2013
Accepted 4 October 2013
Available online 31 October 2013

Keywords:
Luminescent down-shifting
Spectral conversion
Optical model
External quantum efficiency
Solar cell
Photovoltaic module

ABSTRACT

Luminescent down-shifting (LDS) is an elegant, purely optical method to improve the short-wavelength response of photovoltaic (PV) modules by red-shifting the incident solar spectrum. This paper in a first step develops a simple optical model to investigate the effect of LDS layers on top of PV modules on their external quantum efficiency. A meaningful figure of merit is the LDS efficiency η_{LDS} which quantifies the efficiency of the LDS layer to down-shift absorbed photons and send them towards the underlying solar cell. The simplified optical model developed here, extracts LDS efficiencies from experimental quantum efficiency spectra, and thereby enables assessing the current status and future potential of LDS for various solar cell technologies. Our simplified LDS model is fast, easy-to-use and universally applicable to analyze experimental LDS results. Moreover, it is especially useful for screening candidate LDS materials.

1. Introduction

Current production-scale photovoltaic (PV) modules suffer from a reduced external quantum efficiency (*EQE*) in the short-wavelength (λ) region, e.g. $\lambda < 400$ nm for silicon solar cells. The following optical losses and recombination losses at the PV module's front side impede the efficient utilization of short$-\lambda$ photons [1]:

1. Optical losses: absorption and reflection by the front glass, by the encapsulation layer and by the anti-reflective coating; absorption in the window layer for cadmium sulphide/cadmium telluride (CdS/CdTe) heterojunction cells and CdS/Cu(In, Ga)Se_2 (CIGS) cells.
2. Recombination losses: recombination at the front surface and within the heavily doped emitter of crystalline silicon (Si) solar cells.

Luminescent down-shifting (LDS) is an elegant, purely optical approach to increase the short$-\lambda$ response of PV modules [1,2]. By absorbing short$-\lambda$ photons and re-emitting longer-λ photons, the incoming spectrum is red-shifted to better suit the PV module's spectral response. A higher number of photogenerated charge carriers increases the short-circuit current and the power conversion efficiency of the PV module. Further benefits of LDS are lower operating temperatures for the solar cells by reducing the thermalization losses, potential aesthetical improvements by colored modules and a possible transition to non-toxic Cd-free buffer layers for CIGS cells [3].

In recent years, much research work has been devoted to LDS for PV modules. Since 2011, efficiency enhancements using LDS have been reported for mono- and multicrystalline Si solar cells [4,5], as well as for CdS/CdTe [6] and CIGS [3] solar cells. LDS has been theoretically treated by ray tracing [7,8], by simulating a regular solar cell with the software PC1D [9] using a red-shifted incident spectrum [10] or by a spectral transfer matrix formalism [11]. Helpful figures of merit – photoluminescence quantum yield, spectral matching of absorption and emission, parasitic absorption, radiative overlap – have been defined to compare LDS layers [12]. Nevertheless, ray tracing usually has to be implemented to analyze LDS materials because a *combination* of the abovementioned figures of merit determine the beneficial effect of an LDS layer [12]. While ray tracing allows for the detailed theoretical investigation of luminescent materials [7], geometry effects and loss mechanisms [8], experimental *EQE* spectra were so far not fitted by theoretical models.

This paper presents a simple, analytical optical model to investigate the effect of LDS layers on PV module performance. We introduce the LDS efficiency η_{LDS} – the efficiency of down-shifting absorbed photons and sending them towards the underlying solar cell – as a meaningful figure of merit for LDS layers. By fitting *EQE* spectra of PV modules with LDS layers using the optical model developed here, their LDS efficiency is extracted. The model facilitates the analysis of experimental results and the optimization of LDS layers, and enables fast screening of LDS candidate materials.

* Tel.: +49 71168567178.
E-mail addresses: ralph.rothemund@gmail.com, ralph.rothemund@ipv.uni-stuttgart.de

0927-0248/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.solmat.2013.10.004

2. Optical processes and the simplified LDS model

This section presents a simple optical model to describe the effect of a luminescent down-shifting layer on the external quantum efficiency *EQE* of a PV module. The incoming photon flux is divided into two fractions: $f_{abs}(\lambda)$ is the fraction of photons absorbed and down-shifted by the LDS material, and $f_{trans}(\lambda)$ is the fraction transmitted through the LDS layer, preferably without any losses. Lambert–Beer's law defines both fractions by using the absorbance A and the absorbance scaling factor Λ_{abs} as

$$f_{abs}(\lambda) = (1-\Delta R_{LDS})\cdot(1-\exp[-\Lambda_{abs}\cdot A(\lambda)]), \quad (1)$$

$$\text{and } f_{trans}(\lambda) = 1-\Delta R_{LDS}-f_{abs}(\lambda). \quad (2)$$

The absorbance scaling factor Λ_{abs} is introduced to comprehensively describe the strength of absorption which is directly proportional to the concentration of luminescent particles in the LDS layer and the thickness of the LDS layer. In most cases, the additional reflectance ΔR_{LDS} due to the incorporation of LDS materials in the matrix is negligible ($\Delta R_{LDS} \approx 0$).

Fig. 1 schematically shows the optical processes occurring in LDS layers on PV modules. The LDS layer re-emits absorbed photons at longer wavelengths with a photoluminescence (PL) quantum yield η_{PL}. The down-shifted photons hit the underlying PV module either directly, via total reflection at the front-side or via re-absorption and re-emission. The fraction L_{reabs} is lost by re-absorption, while a fraction L_{esc} of down-shifted photons is lost through the front-side escape cone due to isotropic emission. The front-side escape loss for luminescence from inside a matrix with refractive index $n_{matrix} = 1.5$ towards the air interface is $L_{esc} \approx 12\%$ [13,14]. Further losses L_{other} occur due to escape through the side of the LDS layer or due to reflection at the LDS layer/solar cell interface. All losses contribute to the total luminescent down-shifting efficiency [15]

$$\eta_{LDS} = \eta_{PL}(1-L_{esc})\,(1-L_{reabs})\,(1-L_{other}). \quad (3)$$

The LDS efficiency η_{LDS} describes the fraction of absorbed photons down-shifted and transmitted into the underlying solar cell, and therefore serves as a meaningful figure of merit for LDS layers.

For enhancing the gain in short-circuit current, photons should be re-emitted at wavelengths where the solar cell converts them efficiently. Therefore, the spectral range of the emission should match the spectral range where the *EQE* of the solar cell is high. A figure of merit to characterize the suitability of LDS materials for certain solar cells is the emission spectral matching [12]

$$ESM = \frac{\int PL(\lambda')EQE_{ref}(\lambda')\,d\lambda'}{\int PL(\lambda')\,d\lambda'}, \quad (4)$$

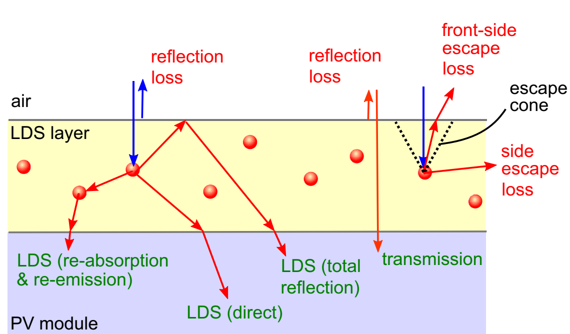

Fig. 1. Optical processes and losses for a LDS layer placed on top of a PV module. Absorbed and down-shifted photons hit the underlying PV module directly, via total reflection or via re-absorption and re-emission. Non-absorbed photons are transmitted without a change of wavelength into to the PV module. Optical losses are due to reflection at the front-side and interfaces (not shown). Due to isotropic emission, certain fractions of down-shifted photons escape through the front-side escape cone and the side of the LDS layer.

where *PL* is the photoluminescence of the LDS material and EQE_{ref} the *EQE* of the PV module without the LDS layer. The upper limit for the *ESM* is given by the maximum value of EQE_{ref}. Note that Alonso-lvarez et al. [12] used *EQE* values normalized to 100% resulting in an upper limit for the *ESM* of 100%. For the LDS model, the absolute, non-normalized *EQE* values have to be used.

Good LDS materials are characterized by both a high LDS efficiency η_{LDS} and a good *ESM* to the underlying solar cell. Using these parameters, the *EQE* of a solar cell with a LDS layer is

$$EQE_{LDS}(\lambda) = f_{abs}(\lambda)\cdot\eta_{LDS}\cdot ESM + f_{trans}(\lambda)\cdot EQE_{ref}(\lambda), \quad (5)$$

and takes into account the contributions of down-shifted as well as of transmitted photons. Eq. (5) is the core of our optical model with input from Eqs. (1) to (4). Appendix A gives a detailed derivation of Eq. (5). Integrating the *EQE* spectra of the reference cell and the LDS cell over an incident spectrum, e.g. the AM1.5G solar spectrum, yields the resulting short-circuit current density J_{SC} with and without LDS layer. Thus, the optical model is an easy-to-use tool to compare or screen different LDS materials.

The optical model uses the spectral absorption and emission of the LDS layer and the EQE_{ref} of the solar cell as experimental input data. For negligible additional reflectance ($\Delta R_{LDS} \approx 0$), the *EQE* of the PV module including the LDS layer is fully characterized by only two parameters: the absorbance scaling factor Λ_{abs} and the LDS efficiency η_{LDS}. The parameters η_{LDS}, Λ_{abs} and ΔR_{LDS} are extracted from the experimental *EQE* values using least-square fitting with the *fminsearch*-algorithm of MATLAB® [16].

3. Analyzing *EQE* spectra using the LDS model

Luminescent down-shifting has shown the potential to improve the short-circuit current density for various solar cell technologies. The optical model introduced in Section 2 is used to fit and analyze *EQE* spectra for LDS layers on monocrystalline Si (mono-Si) PV-modules, multicrystalline Si (multi-Si) solar cells, CdS/CdTe heterojunction cells, and CIGS cells. For the discussed *EQE* spectra, the research groups used Eu^{3+} complexes as the LDS specimen for mono-Si [4], a single perylene-derivative fluorescent dye for multi-Si [5] and CdS/CdTe [17] and a mixture of two perylene-derivative dyes for CIGS [3].

Fig. 2(a)–(c) presents experimental *EQE* spectra for mono-Si, multi-Si and CdS/CdTe solar cells without and with LDS layers, together with the best fit of the experimental EQE_{LDS} using the optical model according to Eq. (5). Fig. 3(a)–(c) shows the detailed analysis for CIGS cells where Klampaftis et al. [3] used a combination of two dyes. For each solar cell technology, the reasons for the decrease in short−λ *EQE* are discussed first. Second, the experimental literature results are analyzed using our optical model and η_{LDS} is extracted from the fit.

For mono-Si and multi-Si, the *EQE* is reduced for short−λ radiation due to (a) surface and emitter recombination because short−λ radiation is absorbed close to the front surface, (b) increased reflectance, and (c) increased absorbance for short−λ radiation in both the anti-reflective coating and the encapsulation material.

3.1. mono-Si

Recently, Liu et al. [4] demonstrated an efficiency enhancement by LDS from 16.05% to 16.37% using Eu^{3+} complexes in a polyvinyl acetate (PVA) coating for 156 cm^2 active area, monocrystalline Si PV-modules. Fig. 2(a) shows the short−λ *EQE* increase of their PV module with Eu^{3+}-doped PVA compared to undoped PVA. The experimental *EQE* spectra overlap in the wavelength region where the LDS specimen does not absorb light ($\lambda > 380$ nm).