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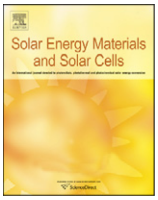

Increased efficiencies on CdTe solar cells via luminescence down-shifting with excitation energy transfer between dyes

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ABSTRACT

The external quantum efficiencies of CdTe solar cells fabricated by the atmospheric pressure metal organic chemical vapour deposition (AP–MOCVD) method have been measured with one and two dye doped luminescence down-shifting (LDS) layers on top. Excitation energy transfer between the dyes is used to extend the absorption ability of the LDS layer to $\lambda = 350$ nm and increase the external quantum efficiency (EQE) of the cells for wavelengths $\lambda < 540$ nm. The observed increase in the EQE corresponds to a rise in the short circuit current density of 1.88 mA/cm^2 under AM1.5G illumination spectra, which is equivalent to a 10% relative solar cell efficiency increase. A simple model is presented, which accounts for the absorption and photon collection efficiencies of the LDS layer.

1. Introduction

Fluorescence wavelength shifting or luminescence down-shifting (LDS) was originally proposed by Hovel et al. [1] in order to overcome the low spectral response in the blue region of the solar spectrum in some types of solar cells. The advantage of down-shifting is that it does not require extensive fabrication procedures to improve the electronic properties of the semiconductor and could be implemented on existing solar cell technologies. A recent review for luminescence down-shifting and application to different types of solar cells can be found for example in Ref. [2].

The LDS process involves the modification of the incoming spectrum by absorbing light in the short wavelength region and shifting it to longer wavelengths where the spectral response of the solar cell is more efficient. As a result, the short circuit current (I_{sc}) is increased, increasing the power conversion efficiency. The external quantum efficiencies (EQE) of cadmium telluride (CdTe) or copper indium gallium disulphide (CIGS) solar cells have a cut off in the short wavelength region $\lambda < 515$ nm of the spectrum due to absorption in the high band gap cadmium sulphide (CdS) 'window' layer [3]. In order to avoid this parasitic absorption it has been suggested that the CdS layer thickness could be reduced [4,5] or alternative window layer materials, such as ZnSe [6] or CdZnS [7], should be used. Here we suggest an alternative approach with the use of luminescence down-shifting [8–10].

Organic dyes can be used to absorb the incident solar spectrum below the cut off point in CdTe solar cells using CdS window layers. Due to the narrow absorption bands in the spectra of single dyes, several dyes could be employed together to extend their absorption and make better utilisation of the incident solar spectrum below the band gap of the CdS absorption edge. Excitation energy transfer (EET) [11,12] between the dyes in the down-shifting layer can be employed to significantly improve absorbance over single dye layers. EET is a near field interaction, which occurs during the excitation lifetime of the donor molecule and the electronic excitation energy transfer to an acceptor molecule is radiationless. A similar approach has also been applied to luminescent solar collectors [13–16].

In this paper, we evaluate the performance of a two dye doped luminescence down-shifting layer that uses excitation energy transfer between the dyes. Preliminary results are presented on improved external quantum efficiencies with the application of the LDS layer and are compared with a simple analytical model taking into account the photon collection and absorption efficiencies of the LDS layer. We observe an increase in the EQE of the cell, which corresponds to an enhancement in the short circuit current density of 1.88 mA/cm^2 when using the AM1.5G solar spectrum as the illumination source or 2.67 mA/cm^2 when using a Xenon lamp photon flux. This leads to relative power conversion efficiency increases up to 10% under AM1.5G or 17% under the Xenon lamp for the CdTe solar cells used in this study.

2. Theoretical background

The useful current collected J_{LDS}, due to the action of the down-shifting structure can be written as:

$$J_{LDS} = q\eta_{opt} < EQE_{cell} > \int_{\lambda_{min}}^{\lambda_{max}} \Phi(\lambda) d\lambda = Q_A Q_C < EQE_{cell} > J_{ideal} \qquad (1)$$

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Eq. (1) defines the optical efficiency η_{opt} of the LDS layer (equal to the number of photons reaching the solar cell surface divided by the number of incident photons) as a product of the absorption (Q_{A}) and photon collection (Q_{C}) efficiencies. The absorption efficiency Q_{A} is the fraction of the absorbed photons and the photon collection efficiency Q_{C} is the fraction of absorbed photons, which are emitted and reach the solar cell. The term $J_{\text{ideal}} = q\int_{\lambda_{\min}}^{\lambda_{\max}} \Phi(\lambda)d\lambda$ is the theoretical maximum short circuit current density, ignoring reflection losses and assuming all incident photons for $\lambda > \lambda_{\min}$ lead to current generation. The different terms in eq. (1) are defined as:

$$Q_{\text{A}} = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} \Phi(\lambda)[1-10^{-A(\lambda)}]d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} \Phi(\lambda)d\lambda} \tag{2}$$

$$Q_{\text{C}} = ET_{\text{eff}} \cdot QY_{\text{A}}^{0} \cdot LDS_{\text{eff}} \tag{3}$$

and

$$< EQE_{\text{cell}} > = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} EQE_{\text{cell}} I_{\text{f}}(\lambda)d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} I_{\text{f}}(\lambda)d\lambda} \tag{4}$$

where λ_{min} and $\lambda_{\max}$ are the minimum and maximum wavelength in the solar spectrum that are taken into consideration. In our analysis we shall take $\lambda_{\min}=300$ nm and $\lambda_{\max}=900$ nm, unless otherwise stated. $\langle EQE_{\text{cell}} \rangle$ is the average of the quantum efficiency of the bare cell weighted over the fluorescence spectrum $I_{\text{f}}(\lambda)$. $\Phi(\lambda)$ is the incident photon flux, $A(\lambda) = \varepsilon(\lambda)Cd$, is the absorbance of the LDS layer (where C is the concentration, d is the thickness of the LDS layer and $\varepsilon(\lambda)$ is the decadic extinction coefficient), ET_{eff} is the excitation energy transfer efficiency between the donor and acceptor molecules in the LDS layer, QY_{A}^{0} is the fluorescence quantum yield of the acceptor dye in the LDS layer, and LDS_{eff} is the down-shifting efficiency, which takes into account the escape cone and re-absorption losses.

The current collected by the down-shifting structure should be supplemented by the current generated from direct absorption of the solar cell calculated from the external quantum efficiency of the cell with the un-doped PMMA layer, EQE_{PMMA}:

$$J_{DIR} = q \cdot \int_{\lambda_{\min}}^{\lambda_{\max}} \Phi(\lambda) \cdot 10^{-A(\lambda)} \cdot EQE_{PMMA}(\lambda)d\lambda \tag{5}$$

The total current (J_{cell}) is then equal to the current produced from the action of the LDS layer and the current generated from un-absorbed light incident on the cell ($J_{\text{CELL}}=J_{\text{LDS}}+J_{\text{DIR}}$) and is calculated from the external quantum efficiency of cell with the LDS layer, EQE_{LDS}:

$$J_{CELL} = q \cdot \int_{\lambda_{\min}}^{\lambda_{\max}} \Phi(\lambda) \cdot EQE_{LDS}(\lambda)d\lambda \tag{6}$$

The increase in current due to the action of the LDS layer, J_{LDS}, can be estimated from the difference in J_{CELL}–J_{DIR} estimated from EQE measurements, and the photon collection efficiency of the LDS layer (Q_{C}) from measurements of the absorption and fluorescence spectra using Eq. (1).

The escape cone losses can be defined as the fraction P of untrapped photons to total photons emitted from the dye, which escape from the top of the film. Using Snell's law, the critical angle for total internal reflection,θ_c, can be given in terms of the refractive index n_{LDS} of the LDS layer as $\theta_c = \sin^{-1}(1/n_{LDS})$. The fraction $P = 1-\cos\theta_c$ is then the ratio of the solid angle of the escape cone divided by 4π and substituting θ_c it gives [15]:

$$P = \frac{1}{2}\left(1-\sqrt{1-\frac{1}{n_{\text{LDS}}^2}}\right) \tag{7}$$

For example, if we assume that all photons incident above the band gap of CdS ($\lambda=512$ nm) are absorbed by the window layer, we can place a maximum value on the available current for down-shifting. If we neglect re-absorption and reflection losses but include the escape cone losses, the maximum current available for down-shifting will be equal to $J_{\text{ideal}}{}^{*}(1\text{–}\text{P})$ with setting the upper limit of the integral J_{ideal} to 512 nm. For $n_{\text{LDS}}=1.49$ and $\text{P}=0.13$ this gives an increase of 6.3 mA/cm^2, which results in 26.3% relative increase in power conversion efficiency for CdTe solar cells under the AM1.5G [17] spectrum.

3. Materials and Methods

The dyes used in this study were the BASF Lumogen® F dyes [18] Violet 570 (V570) and Yellow 083 (Y083), which are based on naphthalimide and perylene derivatives [19]. Their absorption and emission peaks are 377/433 nm and 474/494 nm, respectively as measured in dichloromethane solution [20]. All Lumogen dyes show very high quantum yields (near 100%) in plastic plates [21], strong absorption of light, are non-toxic, and have photostability guaranteed over 10 years if shielded from UV radiation. The LDS layers were prepared by spin coating (Laurell) dye doped polymethyl methacrylate (PMMA, Microchem) solutions onto square 2×2 cm^2 glass slides (BK7).

All absorption spectra (300–600 nm) were measured directly from LDS spin coated layers on glass with a reference spin coated PMMA layer of the same thickness, using a Bentham spectrometer. The fluorescence emission and excitation spectra were measured using a Bentham spectrometer equipped with an excitation and an emission monochromator (TM300), a PMT tube (Hamamatsu R446) and a metal halide lamp (PhotoFluor, Chroma) as the excitation source. The fluorescence emission spectra were acquired with a 2 nm bandwidth resolution from 380–800 nm using an excitation wavelength of 370 nm with 4 nm bandwidth. The angle of excitation was set to 70° with respect to the sample's surface normal in order to avoid a large amount of light reflected back to the detector and to illuminate a larger area of the LDS sample [22]. All collected emission fluorescence spectra were corrected against known emission spectra standards [23].

A solar simulator (T.S. Space Systems) equipped with a Xenon lamp approximating Air Mass 1.5 (AM 1.5) spectrum and a filter selection wheel (350–1100 nm, step 50 nm) was used to measure the current-voltage (I–V) output and external quantum efficiency of the CdTe solar cells with the down-shifting layers on top coupled with an optical gel (ThorLabs). A purpose built back contact measurement stage was fabricated to allow precise and reproducible measurements for all the cells. The incident Xenon photon flux was calibrated against a silicon solar cell, which was calibrated by NREL for AM 1.5 standard test conditions (100 mW/cm^2, 25 °C). The correction of the Xenon lamp was carried out by estimating the common factor that resulted in the same short circuit current as measured by NREL.

The CdTe solar cells were deposited by atmospheric pressure metal organic chemical vapour deposition (AP–MOCVD) onto commercial aluminosilicate glass/ITO substrate, at CSER, Glyndŵr University and the methodology to deposit the device structure has been described elsewhere[7,24]. A thicker CdS layer was deposited, in this study, with a thickness of 380 nm to promote absorption of photons having higher energy than its band gap, and therefore to emphasise any effects of the down-shifting dyes. A defined area (0.5×0.5 cm^2) of the CdS/CdTe cell was always exposed to the incoming light. The thicker CdS layer resulted in lower device performance and the J–V characteristic was carried out after 10 min stabilisation under 1 sun light soaking, displaying no rollover behaviour ($J_{sc}=18.9$ mA/cm^2, $V_{oc}=687$ mV and FF=51%).