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

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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 (Isc) 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 (λ < 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/cm² when using the AM1.5G solar spectrum as the illumination source or 2.67 mA/cm² 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 JLDS, due to the action of the down-shifting structure can be written as:

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

(1)
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 \( J_{\text{cell}} = (1-P) \) with setting the upper limit of the integral \( J_{\text{ideal}} \) to 512 nm. For \( n_{\text{LDS}} = 1.49 \) and \( P = 0.13 \) 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 x 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, Glyndwr 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 x 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 roll-over behaviour (\( J_{\text{sc}} = 18.9 \) mA/cm^2, \( V_{\text{oc}} = 867 \) mV and FF = 51\%).
4. Results and discussion

The absorption and emission spectra of the LDS layers doped with the individual BASF Lumogen dyes violet (V570) and yellow (Y083) are shown in Fig. 1 together with the AM1.5G reference solar spectrum [17]. It can be seen that both dyes show high transparencies for $\lambda > 515$ nm and their combined absorption bands cover a significant portion of the incident solar spectrum at $\lambda < 515$ nm. Both dyes show a vibrational band structure in their emission spectra, which is typical of perylene dyes [25]. In addition, the emission spectrum of V570 exhibits a good overlap with the absorption spectrum of Y083, a requirement for efficient excitation energy transfer [12].

The dye concentrations of V570 and Y083 dyes were optimised for efficient energy transfer from the donor dye (V570) to the acceptor dye (Y083) in the mixed dye LDS layer. The ratio of the dyes in the layer was varied from 1:4 to 1:1 by weight (V570:Y083), whereas the total concentration was varied from 800 mg/L to 6000 mg/L in PMMA (the concentrations of the Lumogen dyes are reported in mg/L because their molecular weight is unknown). The efficiency of the energy transfer was determined from the increase of the acceptor molecule’s (Y083) fluorescence in the presence of the donor molecule (V570) according to standard methods [12]. At high dye concentrations we expect some degree of aggregate formation [25] but not necessarily significant fluorescence quenching.

The absorption and emission spectra of the LDS layer containing the two dyes (V570:Y083, 1:2, 6000 mg/L) are shown in Fig. 2 together with the EQE curve of a typical CdTe solar cell used in this study. It can be seen that all emission occurs predominantly from Y083, indicating an efficient excitation energy transfer from V570 to Y083. The excitation wavelength was set at 370 nm where Y083 does not show appreciable absorption. The excitation energy transfer was calculated to be in the range of 60%–80% for different LDS layers. Higher efficiencies of energy transfer have been reported in the literature for artificial light harvesting structures and applied to luminescent solar collectors [16,26].

The measured EQE curves of the CdTe cell with a PMMA (reference) layer and the LDS layers with one (V570) and two dyes (V570 & Y083), respectively are shown in Fig. 3. The cell performance improves significantly for $\lambda < 515$ nm because of the action of the V570 dye in the LDS layer extending the active wavelength region to $\lambda = 350$ nm and EQE values reach up to 40%. It must be emphasised that although the EQE of the CdTe cell containing the LDS layer appears to extend for $\lambda < 515$ nm, the active photons actually come from the emission of the LDS layer above the band gap of CdS, as shown in Fig. 2. The presence of the blank PMMA layer ensures that all reflection losses remain the same in measurements with and without dye doping. There is, however, a small difference in the spectral response above the band gap of CdS (515 nm) giving a small discrepancy of the short circuit current value. The cause of this small difference is currently under investigation and is not included in the EQE analysis.

The current measured due to the action of the LDS layer, $J_{\text{LDS}}$ is used to estimate the collection efficiency $Q_{\text{C}}$ of the LDS layer on the basis of the measured external quantum efficiencies. The calculated collection efficiencies ($Q_{\text{C}}$) for LDS layers containing one and two dyes are shown in Table 1. We have used the calculated $J_{\text{LDS}}=J_{\text{CELL}}-J_{\text{BASE}}$ obtained from the EQE measurements and the absorption efficiency ($Q_{\text{A}}$) obtained using Eq. (2) from the absorption spectrum of the LDS layer to estimate the LDS photon collection ($Q_{\text{C}}$) efficiencies based on eq. (1). The estimated photon collection efficiency and the relative increase in power conversion efficiency are shown in Table 1 for AM1.5G incident solar photon flux and a xenon lamp illumination source.

![Fig. 1. Normalised absorption and fluorescence spectra of the individual dyes Violet–V570 and Yellow–Y083 LDS layers spin coated on glass substrates plotted together with the AM1.5G photon flux. The excitation was 370 nm and 440 nm for V570 and Y083, respectively.](image)

![Fig. 2. Absorption and fluorescence spectra of a mixed dye down-shifting layer containing V570 and Y083 dyes. The excitation wavelength was at 370 nm. The CdTe solar cell external quantum efficiency curve is also shown.](image)

![Fig. 3. External quantum efficiency plot of CdTe cell with a PMMA layer, a single (Y083) and a two dye (V570 & Y083) mixture LDS layer. Spline curves have been fitted through the points obtained with the solar simulator.](image)
The values for $Q_A$ up to 20% show that a significant amount of the incident spectrum below the CdS band gap is absorbed in the LDS layer. The $Q_A$ calculated for the xenon lamp is higher than the AM1.5G spectrum because the xenon lamp has a higher content of “blue photons”. The $<EQE_{cell}>$ values shown are the average EQE of the CdTe cell weighted over the fluorescence emission range of each LDS layer according to eq. (4). The emission fluorescence band of the LDS layer is centred on the rising edge of the EQE curve as shown in Fig. 2. As a result, the $<EQE_{cell}>$ is less than the maximum of the cell; a feature that can be improved by shifting the emission peak further towards longer wavelengths using a mixture of different dyes (i.e. Y083 & Orange O240).

We note that the $Q_C$ values obtained are ~50%, which is near 70% of the theoretical values and indicates good photon collection with minimal losses in the LDS layers. The major losses are attributed to fluorescence quenching due to the high dye concentrations used in the fabrication of the spin coated layers. Overall, the LDS layers show a high degree of photon collection efficiencies ($Q_C$).

The observed increase in EQE due to the LDS layer with two dyes (V570 and Y083) corresponds to a rise in the short circuit current density up to 1.88 mA/cm$^2$ (AM1.5G spectrum) or 2.67 mA/cm$^2$ (xenon lamp spectrum). Relative power conversion efficiency increases up to 10% can be achieved under the AM1.5G spectrum and up to 17% with the corrected xenon lamp illumination source for the CdTe solar cells used in this study. The short circuit current deviation between the two illumination sources is due to a higher blue weighting of the Xenon spectra in comparison with the AM1.5G spectrum, leading to higher short circuit current values.

5. Conclusions

The efficiency performance of CdTe solar cells is improved by employing luminescence down-shifting layers (LDS) containing two dyes from the BASF Lumogen F series (V570 and Y083), which manifest efficient excitation energy transfer between them. The advantages of using multiple dyes in LDS layers are presented and compared to single dye LDS layers. There is an observed increase in the EQE curve of CdTe solar cells, which corresponds to 1.88 mA/cm$^2$ increase in the short circuit current density under AM1.5G illumination spectra or 2.67 mA/cm$^2$ under the blue weighted xenon spectra. The relative power conversion increase in efficiency observed for the solar cells used in this study were up to 10% under AM1.5G. Excitation energy transfer between two dyes is shown to optimise the performance of the LDS layer and also increase the absorption ability of the layer, extending into the UV region of the spectrum. A simple analytical model is presented, which allows for the different processes occurring in the LDS layer to be accounted for and the results indicate a high degree of photon collection efficiencies ($Q_C$) achieved in the LDS layers.

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