

ENHANCING THE EFFICIENCY OF PRODUCTION CdS/CdTe PV MODULES BY OVERCOMING POOR SPECTRAL RESPONSE AT SHORT WAVELENGTHS VIA LUMINESCENCE DOWN-SHIFTING

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ABSTRACT

Many commercially-produced photovoltaic (PV) modules exhibit poor external quantum efficiency (EQE) at short wavelengths (λ). However, the addition of a luminescent down-shifting (LDS) layer can absorb these short λ photons that would not have contributed towards electron-hole pair generation in the solar cell, and re-emit them at longer λ where the PV device possesses a much higher IQE. The LDS is performed via a mixture of up to four fluorescent organic dyes, which are cheap, photostable, and exhibit near-unity luminescence quantum efficiencies (LQE). Ray-tracing simulations in this paper demonstrate that an LDS layer containing three dyes can significantly enhance the short-circuit current density (J_{sc}) of cadmium sulphide/cadmium telluride (CdS/CdTe) solar cells by $\Delta J_{sc} = 3.1 \text{ mA/cm}^2$, corresponding to an increase in conversion efficiency (η) from $\eta = 9.6\%$ to $\eta = 11.2\%$ under air-mass 1.5 global (AM1.5g) solar radiation. Significantly, the application of LDS layers does not require any alteration to the structure of the solar cell.

INTRODUCTION

The performance of many PV modules manufactured in large-scale production exhibit a poor EQE at short λ , thereby reducing the amount of photocurrent that can be generated from this part of the solar spectrum. Plots of the EQE for several commercially-produced PV modules are shown in Fig. 1. In all cases, a decrease in EQE is observed at shorter wavelengths, however the origins of the lower EQE are different for each technology. For all wafer-based technologies and thin-film technologies that are deposited onto substrates (as opposed to a glass superstrate), a significant fraction of the light is absorbed in the low-iron soda-lime cover glass and the ethylene vinyl acetate (EVA) encapsulant, thus reducing the EQE of the PV module. Table 1 outlines further mechanisms that can cause a reduction in EQE in a wide variety of commercially-produced PV modules.

The most obvious approach to solving these problems that has been employed in the past is to re-design the PV device. However, design trade-offs often exist and a balance between optical and electrical performance must be achieved – otherwise it is very likely that such cost-effective improvements would have already been

implemented in production. For the cadmium sulphide/cadmium telluride (CdS/CdTe) PV modules discussed in this paper, the CdS layer is required to form a heterojunction with the CdTe layer. However, since CdS is a direct bandgap semiconductor with $E_g = 2.4 \text{ eV}$ it strongly absorbs the majority of short-wavelength (violet to blue-green) light before it can be usefully absorbed in the CdTe material. In a production environment it is difficult to reduce the thickness of the CdS layer ($\leq 0.5 \mu\text{m}$) due to:

- obtaining sufficient coverage of the rough transparent conducting oxide (TCO) layer;
- uniformity issues in thin film deposition; and
- interdiffusion of the CdS into the CdTe during a post-deposition annealing step.

Two methods have been investigated in the past to reduce the parasitic absorption in the CdS layer. Firstly, the thickness of the CdS layer can be reduced and, secondly, CdS can be replaced with a higher bandgap material [1]. While laboratory-scale devices with a high conversion efficiency ($\eta = 16.5\%$) have been fabricated [2], it remains to be seen whether these processes can be cost-effectively translated into a production environment. Therefore, the efficiency of a typical production large-area CdS/CdTe PV module remains at about 9.6% [3]. The following section discusses a new solution to the problem.

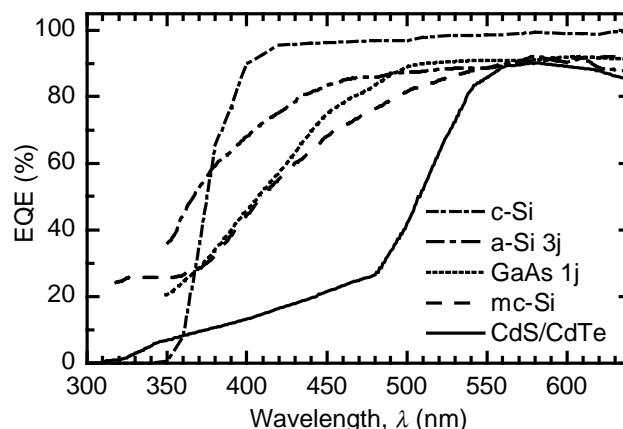


Fig. 1. IQE of different types of commercially produced PV modules. The abbreviations for the different PV technologies are given in Table 1.

Table 1. EQE loss mechanisms at short wavelengths for different PV technologies, in addition to any absorption that occurs in glass or EVA layers.

PV Technology	Major Loss Mechanisms at Short Wavelength
High-efficiency monocrystalline silicon (c-Si)	Typically exhibit the best EQEs at short wavelength. Could be improved with better surface passivation, and less absorption in antireflection (AR) coating
Screen-printed multicrystalline silicon (mc-Si)	“Dead layer” at front surface due to heavily-doped emitter, high reflectance losses, AR coating absorption
Triple-junction amorphous silicon (a-Si 3j)	Absorption in transparent conducting oxide (TCO) layer and heavily-doped a-Si layers
a-Si/c-Si heterojunction (HIT)	Absorption in TCO and heavily-doped p-type a-Si layers
Cadmium sulphide / cadmium telluride (CdS/CdTe)	Absorption in CdS and TCO layers
Cadmium sulphide / copper indium diselenide (CdS/CIGS)	Absorption in CdS and TCO layers
Single-junction gallium arsenide (GaAs 1j)	Absorption in aluminium gallium arsenide (AlGaAs) window layer

LUMINESCENCE DOWN-SHIFTING

In the late 1970s, Hovel *et al.* [4] realised that the wavelength shifting property of luminescent materials could be used to overcome the poor short λ performance of PV devices. They proposed containing luminescent materials in a luminescent down-shifting (LDS) layer that absorbs short λ photons, where PV modules have a poor EQE, and re-emit these photons at a longer λ , where the EQE of the PV device was high. During this time, the fluorescent organic dyes that were available were extremely photo-unstable, sometimes only lasting days under solar radiation [5]. Therefore, it was not until later that Maruyama *et al.* determined that the relative efficiency of mc-Si and CdS/CdTe solar cells could be increased by $\Delta\eta = 2.7\%$ and $\Delta\eta = 30\%$, respectively [6,7] by applying an LDS layer containing one or two organic dyes.

In this paper, we investigate the application of an LDS layer applied to a CdS/CdTe PV module and determining its EQE and efficiency. In addition, a wide range of dye concentrations are also investigated. This work advances on the work of Maruyama *et al.* since: i) the solar cell efficiencies examined by Maruyama *et al.* were about half that of today's commercially produced PV modules (CdS/CdTe $\eta < 5\%$) [6,7]; ii) we investigate mixtures of up to four fluorescent organic dyes in a single LDS layer, with a wide range of concentrations. The range of naphthalimide and perylene photostable dyes used for this study were manufactured by BASF (Ludwigshafen, Germany), and these exhibit near-unity luminescence quantum efficiencies (LQE) [8,9], i.e. for each higher energy photon absorbed, one lower energy photon is

emitted. These organic dyes have also been demonstrated to be photostable under sunlight for periods of years [10].

It is possible to combine multiple dyes into an acrylic – sometimes called polymethylmethacrylate (PMMA) or Perspex – sheet to attain a wide absorption band while maintaining a short emission band. Due to the high LQEs of these dyes it is also possible to mix them together into one layer, enabling broad absorption with the cascaded emission resulting from the lowest energy (longest wavelength) dye. This process is illustrated for the four dyes investigated in this work (BASF Lumogen Violet 570, Yellow 083, Orange 240 and Red 300) in Fig. 2.

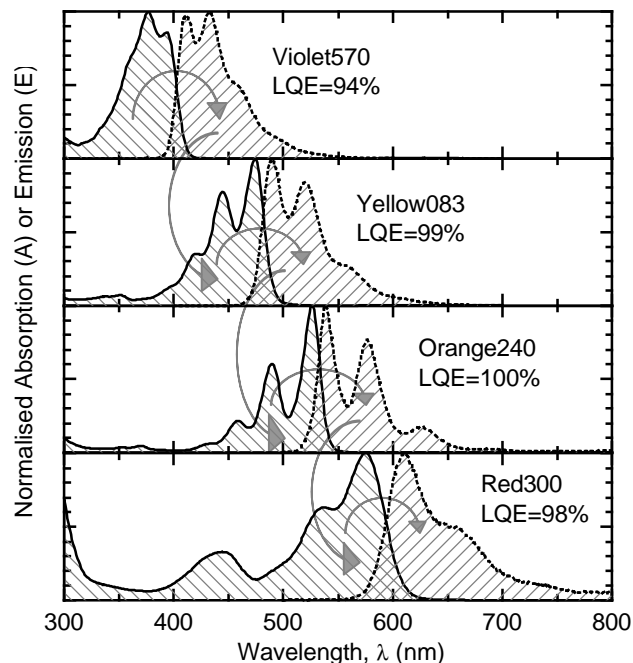


Fig. 2. Normalised absorption (solid line) and emission (dotted line) spectra for the BASF Lumogen organic dyes, which all exhibit an LQE of 94 – 100%. The horizontal arrows show the process of emission, while the vertical arrows indicate how the overlapping emission and absorption spectra result in cascaded emission from the lowest energy (longest wavelength) dye and the creation of a broadband absorber.

RAY-TRACING SIMULATIONS AND LDS LAYERS INVESTIGATED

An in-house ray-tracing program *Raylene* (described in more detail in reference [11]) was developed to accommodate LDS and used to determine how the performance of the CdS/CdTe PV module is altered by luminescent dyes. *RAYLENE* employs well known optical equations [12] to track the position, direction, wavelength and intensity of each ray as it passes through the host material, doing so until each ray's intensity decreases below a user-defined limit (typically 0.25%). Without luminescent dyes, the intensity decreases due to external

reflection at the front surface, absorption in the host material, and imperfect reflection at the internal surfaces. RAYLENE determines the fraction of rays that are absorbed by the solar cells as a function of wavelength. By converting this fraction to a density of absorbed photons, multiplying by the cell's internal quantum efficiency, and integrating over all wavelengths, the program calculates the module's output current density. We found that the simulation of 2 million rays was sufficient to produce an output current density that was repeatable to within 0.1% under the air-mass 1.5 global (AM1.5g) spectrum [13].

Table 2 summarises the different dye mixtures and concentrations that were investigated in this work. The optical density (OD) of each dye in the mixed LDS layer is given by $OD = -\log_{10} T$, where T is the internal transmittance (i.e. excluding reflection losses) of the LDS layer. The absorption range defines the wavelengths for which $OD > 0.5$, and the emission range defines the wavelengths at which the emission probability exceeds 10% of the peak emission probability. Dyes need to be selected to cover the region of poor EQE for the relevant PV device. Dyes are typically selected starting from the UV and progressing towards longer wavelengths. Once the peak emission of the longest-wavelength-emitting dye is in a region of high EQE then the optimum performance enhancement will be reached. The addition of further dyes will reduce performance. This is mostly due to the fact that when emission occurs from within PMMA or glass ($n = 1.5$), about 12.5% of the emitted rays are within the escape cone of the glass-air interface.

Ray-tracing simulations were performed, spanning all mixtures and dye concentrations outlined in Table 2. The required PV inputs for the ray-tracer are the internal quantum efficiency (IQE), reflectance (R), open-circuit voltage (V_{oc}) and fill-factor (FF). The values for a typical production CdS/CdTe PV solar cell, $V_{oc} = 784\text{mV}$ and $FF = 62.1\%$, were obtained from manufacturer's datasheets [14], while the IQE and R spectra for a production-like CdS/CdTe solar cell were provided by Colorado State University [3]. Note that any dependence of the CdS/CdTe solar cell EQE on the presence of short λ light is not included in this modelling.

PERFORMANCE OF CdS/CdTe PV MODULES WITH LDS LAYERS

The performance of a CdS/CdTe module without any LDS layer (i.e. $OD = 0$) was simulated and found an efficiency of $\eta = 9.6\%$ (as shown in Fig. 2), which is in agreement with the literature for a production module [3,14]. After the addition of an LDS layer containing any dye mixture the module efficiency increased. This is due to the light being shifted from $\lambda < 550\text{ nm}$ to $\lambda > 550\text{ nm}$, where the EQE of the CdS/CdTe device is above 90%.

The increase in performance varies greatly for the four different dye mixtures investigated. With mixture A, the violet dye is not absorbing enough of the short λ light and therefore the gain achieved via LDS is minimal. Much

Table 2. BASF dye mixtures and concentrations used in this study (host material PMMA).

Mix	Dyes	OD	Absorption range (nm)	Emission range (nm)
—	None	0	—	—
A	Violet570	0.5	—	396–502
		1	353–402	396–502
		2	339–406	396–502
		4	325–409	396–502
		8	300–412	396–502
		16	300–414	396–502
B	A + Yellow083	0.5	—	472–584
		1	353–483 [#]	472–584
		2	332–487	472–584
		4	300–490	472–584
		8	300–494	472–584
		16	300–497	472–584
C	B + Orange240	0.5	—	513–597
		1	348–525 [#]	513–597
		2	333–529	513–597
		4	300–532	513–597
		8	300–535	513–597
		16	300–539	513–597
D	C + Red300	0.5	—	566–705
		1	344–586	566–705
		2	332–594	566–705
		4	300–600	566–705
		8	300–605	566–705
		16	300–610	566–705

[#] OD is not > 0.5 over this whole absorption range.

better results are achieved for mixture B, with the inclusion of the yellow dye, due to the increased range of short wavelength light absorbed (see Table 2). The efficiency continues to increase at higher OD s, again due to the higher dye concentrations extending the absorption range slightly. The best results are achieved with mixture C, which contains the orange dye that is able to absorb all wavelengths previously affected by poor solar cell EQE. Regarding the concentration, $OD=2$ is enough to increase the efficiency of the CdS/CdTe module to $\eta = 11.2\%$. No further gains are made at higher OD s as all photons that previously experienced low IQE have now undergone LDS. The performance is worsened with the addition of the red dye in mixture D. This is because photons in the range 550–600 nm that previously experienced a high EQE are now being absorbed by the red dye and undergoing optical losses during the LDS process (primarily escape cone losses out the front surface) and these act to reduce the conversion efficiency.

The effective EQE of the CdS/CdTe PV module can also be calculated from the ray-tracing software. Plotted in Fig. 3 is the reference EQE of the CdS/CdTe PV module with no LDS, and the EQE with four different LDS layers ($OD = 4$) investigated in this work. A maximum EQE is reached with mixture C due to, firstly, the unity LQE of the Orange240 dye and, secondly, the excellent

match between its emission spectrum and the peak EQE of the CdS/CdTe solar cell.

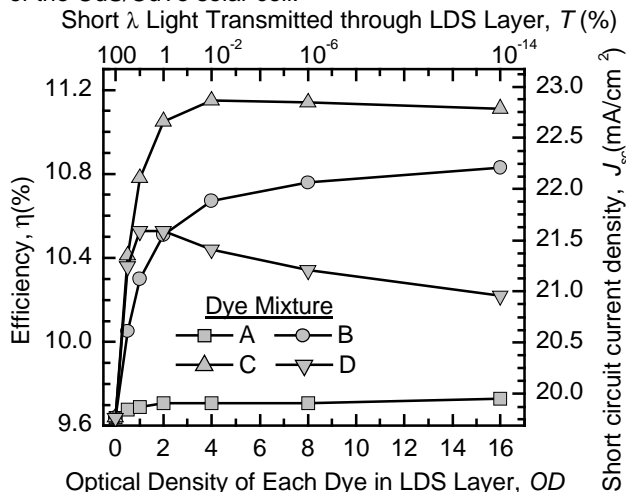


Fig. 2. Efficiency of a CdS/CdTe PV module without (OD = 0) and with LDS layers, as a function of dye OD.

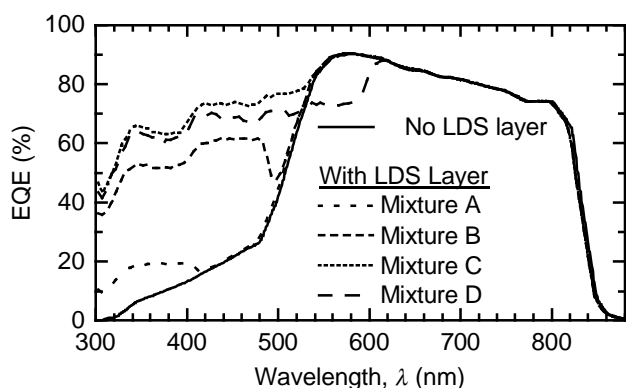


Fig. 3. Spectral response of the CdS/CdTe PV module without (reference) and with mixed LDS layers containing a peak OD of each dye of OD = 4.

CONCLUSIONS

A significant increase in module efficiency can be achieved by application of LDS layers to PV devices that exhibit a poor IQE. The ray-tracing simulations performed here demonstrate that the performance of a production-like CdS/CdTe PV module can be increased from $\eta = 9.6\%$ to $\eta = 11.2\%$ – a relative increase of nearly 17%. Note that further efficiency gains could possibly be made by improving the design of the CdS/CdTe solar cell to take advantage of the new incident spectrum, which is red-shifted compared to the AM1.5g spectrum.

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