Research

Overcoming the Poor Short Wavelength Spectral Response of CdS/CdTe Photovoltaic Modules via Luminescence Down-Shifting: Ray-Tracing Simulations

B. S. Richards* and K. R. McIntosh

Centre for Sustainable Energy Systems, The Australian National University, Canberra, ACT 0200, Australia

The short-wavelength response of cadmium sulfide/cadmium telluride (CdS/CdTe) photovoltaic (PV) modules can be improved by the application of a luminescent down-shifting (LDS) layer to the PV module. The LDS layer contains a mixture of fluorescent organic dyes that are able to absorb short-wavelength light of $\lambda < 540$ nm, nm, for which the PV module exhibited low external quantum efficiency (EQE), and re-emit it at a longer wavelength ($\lambda > 540$ nm), where the solar cell EQE is high. Ray-tracing simulations indicate that a mixed LDS layer containing three dyes could lead to an increase in the short-circuit current density from $J_{sc} = 19.8 \text{ mA/cm}^2$ to $J_{sc} = 22.9 \text{ mA/cm}^2$ for a CdS/CdTe PV module. This corresponds to an increase in conversion efficiency from 9.6% to 11.2%. This indicates that a relative increase in the performance of a production CdS/CdTe PV module of nearly 17% can be expected via the application of LDS layers, possibly without any making any alterations to the solar cell itself. Copyright © 2006 John Wiley & Sons, Ltd.

KEY WORDS: luminescence; wavelength conversion; frequency conversion; down-shifting; ray-tracing; organic dyes; CdS/CdTe

INTRODUCTION

Many photovoltaic (PV) modules, especially those produced in a production environment, exhibit a poor spectral response to short-wavelength light. This means that an appreciable fraction of the incident photons are absorbed in high recombination regions where the carriers are lost. For short wavelength light, this is at the front surface of the device. The traditional approach to rectifying such problems is to alter some of the processing steps in the device fabrication sequence to improve the electronic properties of

*Correspondence to: Dr B. S. Richards, School of Engineering and Physical Sciences, James Nasmyth Building, Heriot-Watt University, Edinburgh, HW14 4AS, UK.

E-mail: B.S.Richards@hw.ac.uk

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the front surface of the solar cell. However, there are often technical hurdles that are difficult to overcome and design trade-offs requiring a balance between optical and electrical performance.

For the cadmium sulfide/cadmium telluride (CdS/CdTe) PV modules discussed in this article, a CdS layer forms a heterojunction with the CdTe layer. Since CdS is a direct bandgap semiconductor ($E_g = 2.4$ eV), it strongly absorbs short-wavelength (violet to blue-green) light before it can be usefully absorbed in the CdTe material. It is difficult to reduce the thickness of the CdS layer (≤ 0.2 μm) in a production environment due to (i) necessary coverage of the rough transparent conducting oxide (TCO) layer, (ii) uniformity issues in thin film deposition, and (iii) interdiffusion of the S into the CdTe during a post-deposition annealing step.^{1,2} In addition, there is a tradeoff between the short wavelength external quantum efficiency (EQE)—and hence also short-circuit current density (J_{sc})—and open-circuit voltage (V_{oc}) on the CdS layer thickness. Specifically, it has been demonstrated that there can be up to a 50% reduction in V_{oc} for thin (200 nm) CdS layers as opposed to thicker (> 400 nm) CdS layers, whereas the use of thinner layers only results in a slight (5%) increase in J_{sc} .³ This is most likely due to thicker CdS layers exhibiting better junction formation and reduced interface state defect densities.³ This suggests that thicker CdS layers would achieve better performance in a production environment, especially when high yield is also desirable.

Two methods that have been investigated to reduce the parasitic absorption in the CdS layer are to, first, reduce the thickness of the CdS layer and second, replace the CdS buffer layer with a higher bandgap material.⁴ Further additional layers were employed in fabricating a laboratory-scale device with a high conversion efficiency ($\eta = 16.5\%$),⁵ however, it remains to be seen as to whether these processes can be cost-effectively translated into a production environment. Thus, the efficiency of a typical large-area CdS/CdTe PV module remains at about 9.6%.⁶

An alternative approach to improving device performance at short wavelengths ($\lambda < 540$ nm) is to modify the spectrum that is incident on the solar cells. This can be performed by placing an electronically passive luminescent down-shifting (LDS) layer in front of the solar cell. Thus, a layer of luminescent material absorbs the short-wavelength photons, where the PV module has a low IQE, and re-emits photons of a longer wavelength, where the IQE of the PV device is high. The slight energy losses in the down-shifting process are outweighed by the gains that stand to be made by converting $\lambda < 540$ nm photons into $\lambda > 540$ nm photons. A further advantage of the LDS layer is that it allows greater freedom of design and optimization of the underlying PV device. The luminescent materials may be contained in either a polymer or glass host matrix, dependent somewhat on whether they are organic or inorganic in nature.

This application of luminescent materials for overcoming the poor blue response of solar cells was first described by Hovel *et al.*⁷ in the late 1970s. When applied to gallium arsenide (GaAs) and copper sulfide (Cu_2S)/CdS solar cells, the organic LDS layers resulted in an increase in conversion efficiency from $\eta = 11.5\%$ to 13.5% and from $\eta = 3.0\%$ to 3.5%, respectively, under air mass zero (AM0) illumination.⁷ At this time, the fluorescent organic dyes that were available exhibited very poor photostability, typically lasting only days under solar illumination before photobleaching occurred.⁸ Such dyes have also been used to improve the performance of CdS/CdTe solar cells by 11%.⁹ More recently, Maruyama and Kitamura demonstrated that the efficiency of CdS/CdTe solar cells could be increased from $\eta = 5.0\%$ to $\eta = 6.8\%$ via the addition of a photostable organic dyes to the module cover plate.⁴ The single fluorescent dye was contained in a 0.38 mm-thick polymethylmethacrylate (PMMA) sheet, which was adhered to the glass cover plate with a silicone adhesive. The LDS layer contained 0.1% to 0.4% of the dye and the greatest gain was observed with the most heavily doped sheet,² when measured under air mass 1.5 direct (AM1.5D) solar radiation.

Since the solar cell efficiencies examined by Maruyama and Kitamura⁴ were significantly lower than today's commercially produced PV modules and an extensive range of photostable fluorescent dyes are now available,^{10,11} it was decided to fully investigate the potential of applying mixtures of organic dyes to modern CdS/CdTe PV modules.

MODELING

An in-house ray-tracing program (Raylene) was developed to accommodate LDS and used to determine how the performance of the CdS/CdTe PV module is altered by luminescent dyes. The resulting CdS/CdTe PV module efficiency is determined as a function of the number of dyes and the individual dye concentration.

The ray-tracer treated the module as an infinite sheet of semi-transparent host material in air, where the rear surface was coated by solar cells. Although rays could pass through the module in three dimensions, the structure of the module was one-dimensional; hence, it does not include losses associated with space between cells or with the module's edges. The incident rays were perpendicular to the front plane, reflection from the air—module interface was specular, and reflection from the cells was Lambertian. The LDS layer absorbs direct and diffuse light and its absorptive properties do not exhibit angular dependence, although front surface reflection is naturally higher for obliquely incident light.

The in-house ray tracer employs well-known optical equations^{12,13} 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 (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. The calculation of these losses requires knowing the refractive index of the host material, and the reflection, and absorption of the solar cells—all as a function of wavelength.

When luminescent dyes are included in the host medium, the ray tracer tracks absorption and re-emission events. This requires an absorption spectrum of the luminescent species in the host medium $\alpha_{\text{dye}}(\lambda)$ —see, for example, the dye spectra in Figure 1a—so that every time a ray traverses the host medium, the program

Figure 1. (a) Normalized absorption and emission spectra for the selected BASF Lumogen visible-emitting organic dyes, along with their peak absorption ($\lambda_{\text{Ab_peak}}$) and emission ($\lambda_{\text{Em_peak}}$) wavelengths and Stokes shift ($\Delta\lambda_{\text{Stokes}}$). (b) The absorption spectrum of the VYO mixture containing a peak optical density for each dye of $OD = 4$, and the emission spectrum from the lowest energy (orange) dye. Note that due to some overlap in the absorption spectra, the final peak OD for the mixed LDS layer is greater than $OD = 4$

calculates a distance to the next absorption—emission event $d_{\text{abs-em}}$. In the manner of Reisfeld *et al.*,¹³ we determine this distance from the conventional absorption equation by replacing the relative change in intensity by a random number Rnd greater than zero and less than one:

$$d_{\text{abs-em}} = -\ln(Rnd)/\alpha_{\text{dye}}(\lambda) \quad (1)$$

If $d_{\text{abs-em}}$ is less than the distance to traverse the host medium, the ray is treated as being absorbed and re-emitted by the dye molecule. This involves the determination of a new wavelength, as determined from the dye's emission spectra (see Figure 1a); a new direction, as calculated by assuming isotropic emission; and a new intensity, as determined from the dye's luminescent quantum efficiency. The ray-tracer uses the Monte Carlo approach to determine wavelength from the incident spectrum and emission spectra, and direction from Lambertian reflection and isotropic emission.

In this manner, the ray-tracer 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 two million rays was sufficient to produce an output current density that was repeatable to within 0.1% under the air-mass 1.5 global (AM1.5 g) spectrum.¹⁴

INPUT PARAMETERS

The input parameters required for ray-tracing can be divided into dye, host material, and solar cell inputs.

Dyes

The Lumogen range of perylene-based dyes used for this study were manufactured by BASF AG (Ludwigshafen, Germany).^{10,11} The Lumogen dyes exhibit a number of advantages:

- they possess a high absorption coefficient (α_{dye}), thus allowing low concentrations and thin layers to be utilized;
- they exhibit a near-unity LQE,^{10,11} that is for each higher energy photon absorbed, one lower energy photon is emitted; and,
- they are photostable under sunlight for periods of many years.^{15,16}

The organic dyes explored in this work are Lumogen Violet 570, Yellow 083, Orange 240, and Red 300.^{10,11} The absorption and emission properties of these dyes are given in Figure 1a, along with their LQE, peak absorption ($\lambda_{\text{Ab-peak}}$) and emission ($\lambda_{\text{Em-peak}}$) wavelengths, and Stokes shift ($\Delta\lambda_{\text{Stokes}}$).

There are two possibilities for increasing the range of wavelengths that a dye absorbs. First, the OD of the dye can be increased, however, this only results in a slight increase in the number of longer wavelength photons absorbed. Second, it is possible to combine multiple dyes into a single 3 mm-thick PMMA sheet to achieve wideband absorption, as demonstrated in Figure 1b. The high LQE of these dyes enables them to be mixed together in one layer, creating a broadband absorber with a high LQE, which exhibits the majority of its emission via the longest wavelength dye due the energy cascading down to the lowest energy.¹⁷

Multiple dyes need to be selected to cover the region of poor EQE for the relevant PV device due to their relatively narrow absorption band. Dyes are typically selected starting from the ultraviolet (UV) and then adding dyes that exhibit longer wavelength absorption and emission spectra. For this work, the following mixtures of Lumogen dyes contained in 3 mm-thick PMMA sheets were considered:

- V = Violet570;
- VY = Violet570 + Yellow083;
- VYO = Violet570 + Yellow083 + Orange240;
- VYOR = Violet570 + Yellow083 + Orange240 + Red300.

The concentration of each dye in the mixture is increased in steps according to its optical density ($OD = 0.5, 1, 2, 4, 8$, and 16) at the dye's peak absorption wavelength. The OD of each dye in the mixed LDS layer is defined as

$$OD = -\log_{10} T = -\log_{10}(1 - A), \quad (2)$$

where T is the internal transmittance (excluding reflection losses) and A is the absorbance within the LDS layer. It should be noted, however that due to some overlap in the dyes' absorption spectra, the final peak OD for the mixed LDS layer can be higher.

Host material

The host material chosen for this work was optical-grade PMMA, which:

- provides an excellent chemical environment for the Lumogen dyes, resulting in a high LQE;
- exhibits a very low absorption coefficient (α_{host}),¹⁸ significantly lower than α_{host} for low-iron soda-lime or borosilicate glass in the visible; and,
- has been demonstrated to be stable in desert sunlight for periods of up to 17 years.¹⁹

PV module

The required PV inputs for the ray-tracer are the internal quantum efficiency (IQE), R , V_{oc} , and fill-factor (FF). The values for a typical production CdS/CdTe PV solar cell, $V_{\text{oc}} = 784$ mV and $FF = 62.1\%$, were obtained from manufacturer's datasheets,²⁰ while the IQE and R spectra for a production-like CdS/CdTe solar cell were provided by Colorado State University.⁶ Due to the iterative nature of the ray-racing simulations, it is assumed that there is no change in V_{oc} , which is small in any case, and FF , which is less predictable.

RESULTS AND DISCUSSION

Ray-tracing simulations were performed, spanning all 24 mixtures and dye concentrations. The reference scenario was a CdS/CdTe module with an undoped PMMA coversheet (i.e., $OD = 0$), which had an efficiency of $\eta = 9.6\%$, in agreement with values from the literature for a production module.⁶ When the undoped PMMA coversheet was replaced by an LDS layer containing any dye mixture and dye concentration the module efficiency increased, as shown in Figure 2. This is due to the light being shifted from regions where the CdS/CdTe device exhibit a poor EQE ($\eta < 540$ nm) to regions where the EQE is above 90% ($\eta > 540$ nm). The trend in performance enhancement varies greatly for the four different dye mixtures investigated. With mixture V, the violet dye is not absorbing a significant fraction of the short wavelength light and most of the emission still occurs at $\eta < 540$ nm and therefore the gain achieved via LDS is minimal. Significantly better results are achieved for mixture VY, with the inclusion of the yellow dye increasing the range of short wavelength light absorbed. The efficiency continues to increase at higher ODs, again due to the higher dye concentrations extending the absorption range slightly. However, from Figure 2, it can be seen that the PV module conversion efficiency is still increasing at the highest dye concentration ($OD = 16$), which suggests that adding a third dye molecule to the mixture could further increase the performance. This is indeed the case, with the best results being achieved with mixture VYO. With this mixture, a concentration of $OD = 4$ is enough to increase the efficiency of the CdS/CdTe module to nearly $\eta = 11.2\%$ and no further gains are made at higher OD . This is because all photons that previously experienced low EQE have now undergone LDS and there is no benefit in broadening the absorption range further. This is confirmed by the performance degradation that occurs with the addition of the red dye to mixture VYOR. Incident photons in the range $\eta < 550$ – 600 nm that previously experienced a high EQE are now being absorbed by the red dye and undergoing optical losses during the LDS process, which act to reduce the conversion efficiency. The major optical loss mechanisms are the escape cone

Figure 2. The increase in short circuit current density (J_{sc}) and conversion efficiency of a CdS/CdTe PV module with an LDS layer, as a function of dye concentration, compared to the reference without an LDS layer ($OD = 0$). The peak performance is observed for the VYO mixture containing Violet570, Yellow083, and Orange240 dyes at a minimum dye $OD = 4$, corresponding to the absorption of 99.99% of short wavelength light

losses via the front surface, which for the PMMA–air interface amounts to $\sim 12\%$ of the luminescence, and the small LQE losses of less than 5%. Thus, it can be recommended that an LDS layer is advantageous to PV modules that exhibit a short-wavelength EQE of less than about 80%.

The effective EQE of the CdS/CdTe PV module can also be calculated from the ray-tracing software. Plotted in Figure 3 is the reference EQE of the CdS/CdTe PV module with no LDS, and the EQE with four different LDS

Figure 3. Spectral response of the CdS/CdTe PV module without (reference) and with an LDS layer containing a peak optical density of each dye of $OD = 4$. The short wavelength EQE is seen to increase with each additional dye, from mixtures V, to VY, to VYO. This is due to LDS enabling the short wavelength photons to be absorbed and then re-emitted in a region where the PV module exhibits a good spectral response. Once the red dye is added (VYOR) a poorer EQE results due to (i) the fractionally lower LQE of the red dye; and (ii) the red dye is now absorbing photons in a region where the solar cell possesses a high EQE (525–615 nm)

layers ($OD=4$) investigated in this work. The addition of mixture V can be seen to improve the short wavelength response slightly, however much larger improvements are realized upon the addition of further dyes to the LDS layer. A maximum EQE is reached with mixture VYO due to, first, the unity LQE of the Orange240 dye and, second, the excellent match between its emission spectrum and the peak EQE of the CdS/CdTe solar cell. This is confirmed with the addition of the Red300 dye (mixture VYOR), which reduces (i) the short wavelength performance due to its lower LQE and (ii) the EQE in the range 525–615 nm because the dye is now absorbing photons that previously were able to be effectively absorbed by the CdS/CdTe solar cell.

One issue that is not modeled in the ray-tracing simulations is effect of short wavelength light on the CdS layer. Light of energy greater than the CdS bandgap is known to increase the conductivity of the CdS layer even though these wavelengths are not directly contributing to the photocurrent.³ Current-voltage (I–V) curves measured solely under red light exhibit the same V_{oc} and J_{sc} as cells measured under white light illumination, however a significant reduction in the FF occurs.²¹ This will be examined in more detail in the future when comparing experimental results with the ray-tracing simulations. In addition, it will be interesting to determine what fraction of blue light is required for good device performance. This could be varied by simply reducing the concentration of the violet dye in the LDS layer.

CONCLUSIONS

Ray-tracing simulations indicate that a significant increase in module efficiency could be realized by application of LDS layers to PV devices that exhibit a poor IQE. In the CdS/CdTe PV modules investigated here, an increase in J_{sc} from 19.8 mA/cm² to 22.9 mA/cm² was calculated, corresponding to an increase in conversion efficiency from $\eta = 9.6\%$ to $\eta = 11.2\%$. This indicates that a relative increase in the performance of a production CdS/CdTe PV module of nearly 17% can be expected via the application of LDS layers. It should be noted that further efficiency gains might be made by optimizing the design of the CdS/CdTe solar cell to take advantage of the new incident spectrum.

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