

# Luminescent encapsulation layers for multicrystalline silicon PV modules

Bryce S. Richards & Efthymios Klampaftis, Heriot-Watt University, Edinburgh, Scotland

## ABSTRACT

This article highlights an alternative method for increasing short-wavelength external quantum efficiency (EQE) and hence overall conversion efficiency of mc-Si PV modules via luminescent down-shifting (LDS), a technique originally proposed by Hovel et al. [1] in 1979. The potential for efficiency enhancement via LDS has been either predicted or measured for a wide range of PV technologies (see [2] for a review). However, in this article, we will highlight how LDS can be incorporated into the existing encapsulation layer, avoiding any modification to well-established solar cell manufacturing processes and thus offering the potential of a production-ready technology.

## Introduction

The performance of many PV modules manufactured in large-scale production exhibit a poor response to short-wavelength ( $\lambda = 300\text{--}450\text{nm}$ ) light, thereby reducing the amount of photocurrent that can be generated from this part of the solar spectrum. In a study of the mechanisms limiting the short-wavelength response of a multicrystalline silicon (mc-Si) PV module, it was found that absorption in the ethylene vinyl acetate (EVA) encapsulant played the largest role, while absorption in and reflection from the anti-reflective coating (ARC) also contributed significantly [3]. The traditional approach to solving these problems has been to constantly improve the opto-electronic design of the PV device, particularly with regard to texturing, ARCs, and the potential of selective emitters. However, design trade-offs often exist and a balance between optical and electrical performance – as well as the potential for implementation into large-scale production – must be achieved.

## Luminescent down-shifting (LDS)

The optically active materials in the LDS layer are designed to absorb ultraviolet and blue light before it strikes the solar cell, and then emit luminescence at longer wavelengths where the underlying PV device exhibits a significantly higher EQE. In this article, the focus is on the opportunity to dope the luminescent species in the pre-existing EVA layer – as shown in Fig. 1 [4] – given that the majority of mc-Si module manufacturers use EVA encapsulation, which affords the exciting possibility of achieving LDS with no added production processes or layers to the device. In addition, the same approach can be applied to other PV technologies that rely on front-surface encapsulation, like copper indium (gallium) diselenide-based thin-film devices or indeed alternate front-surface encapsulation materials [5].

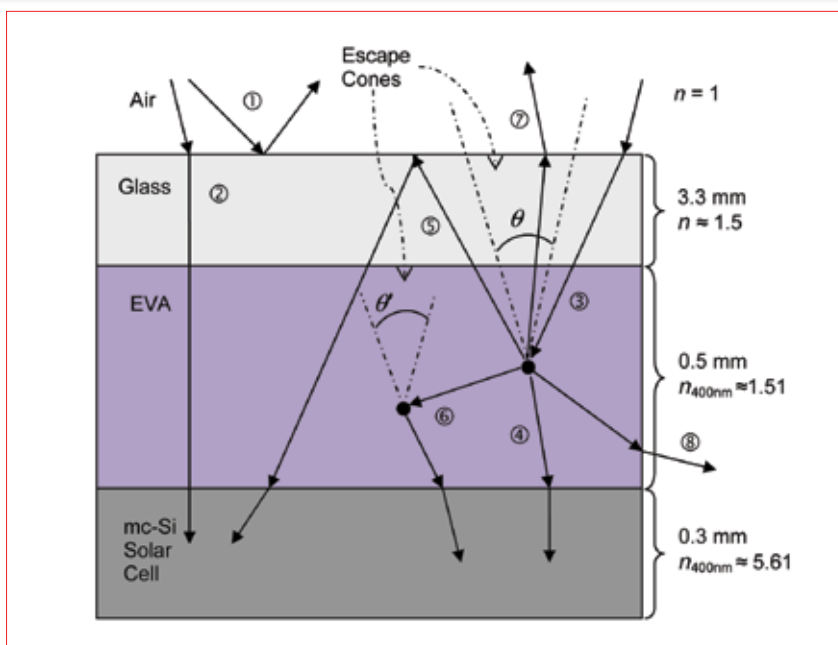


Figure 1. Possible light paths in a mc-Si PV module encapsulated with LDS EVA, with incident light ① being partially reflected by the front surface of the cover glass. Longer-wavelength light entering the module ② is transmitted to the cell without any dye interaction, while short-wavelength can be absorbed by the luminescent material ③ and re-emitted at longer wavelengths. The majority of the emitted light will reach the cell, either directly ④ or after internal reflection at the air:glass interface ⑤, or via re-absorption and re-emission by another luminescent species ⑥. A small fraction of the light can leave the module via the top plane escape cones ⑦ or through the sides ⑧, although the latter is negligible for full-size modules [4].

It has been shown that LDS EVA layers can alleviate the following loss mechanisms [1,4,6]:

- Parasitic absorption in the EVA layer is reduced as a large fraction of short-wavelength photons are now down-shifted to regions where the EVA is less absorbing.
- Absorption and reflection by the ARC can also be reduced, since the resulting red-shifted incident spectrum better matches the properties of this layer, while it is also easier to design a better ARC for the narrower spectrum that is now incident upon the solar cell.

- Recombination at the front surface can also be reduced because the down-shifted photons are more likely to be absorbed deeper into the device.

However, a trade-off remains as the implementation of LDS into a PV module also introduces certain optical losses: firstly, due to a fraction (>12.5%) of the emitted photons escaping back out of the front surface of the module; and, secondly, if the luminescent material(s) used exhibit a photoluminescence quantum yield (PLQY) of less than 100%, i.e. one photon is emitted for each photon absorbed.

## Fabrication of LDS EVA

EVA pellets (PV1650, DuPont) were used as the starting material for all experiments described in this article. The authors have produced LDS EVA layers by adding fluorescent organic dyes via two methods: mechanical mixing and sheet extrusion [4]; and dissolving the dyes in a suitable solvent (e.g. toluene), then adding to EVA, followed by baking off the solvent and using a hydraulic press to form sheets [7]. Both clear and doped EVA sheets were created, the latter containing up to four commercially-available dyes (BASF Lumogen Violet 570 [8], Yellow 083, Yellow 170 and Orange 240) as well as a europium ( $\text{Eu}^{3+}$ )-based rare-earth complex [7,9]. The Lumogen dyes were chosen because of their high absorption coefficients and PLQYs, as well as for their ease of processing with polymers, while the  $\text{Eu}^{3+}$  ion in the rare-earth complex exhibits an ideal emission wavelength and a very large Stokes shift (i.e. no overlap between absorption and emission spectra).

This article focuses on the variation of LDS performance as a function of Violet 570 dye concentration, with dye concentrations of 0.0425% w/w, 0.1305% w/w, and 0.2610% w/w being added to EVA to achieve optical densities (OD) of OD = 1, OD = 3, and OD = 6, respectively, at the dye peak absorption wavelength (375nm) and a final sheet thickness of  $d = 0.5\text{mm}$ .

**“The majority of mc-Si module manufacturers use EVA encapsulation, which affords the exciting possibility of achieving LDS with no added production processes or layers to the device.”**

The excitation and emission spectrum of each dye concentration in EVA as well as the PLQY was determined using a spectrofluorometer (Edinburgh Instruments FS920) equipped with an integrating sphere [10,11]. Quarters of full-size mc-Si solar cells were cut ( $59\text{cm}^2$  active area) and laminated in a symmetrical sandwich of EVA (doped on front, clear on rear) and borosilicate float glass. The lamination cycle was  $155^\circ\text{C}$  for five minutes under vacuum followed by five minutes under atmospheric pressure in air. Glass-glass modules were fabricated, rather than the more common glass-Tedlar construction, so that the transmittance of the PV laminate could be measured (Perkin Elmer Lambda 950 spectrophotometer). The electrical performance of the samples both before and after encapsulation was tested using a continuous solar simulator (ABET model 11044) and four current-voltage (I–V) curves were taken in each case. The EQE of these mini-modules was

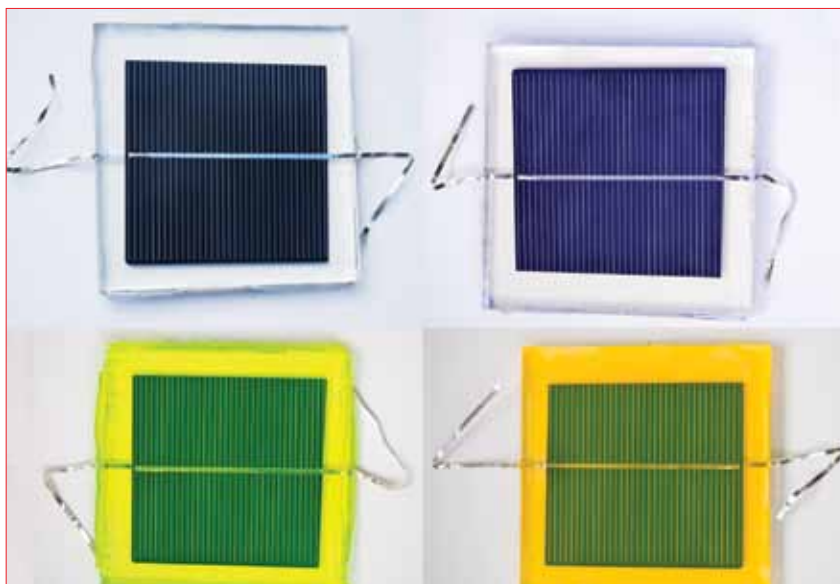


Figure 2. Four mc-Si PV mini-modules (cell area  $59\text{cm}^2$ ) fabricated with either clear EVA (top left) or luminescent EVA based on three BASF Lumogen dyes: Violet 570 (top right); Yellow 083 (bottom left) and Orange 240 (bottom right).

measured using a monochromator-based spectral response system (Bentham). Images of three different mc-Si laminates are shown in Fig. 2, one using clear EVA and two fabricated with luminescent EVA. Thus, another benefit of luminescent EVA is that it becomes a simple and cost-effective method for altering the colour of PV modules.

## Results and discussion

The absorption and emission spectra of a violet-doped EVA sheet (OD = 3) are plotted in Fig. 3, along with the EQE of the clear-EVA mini-module. The Violet 570 dye absorbs photons in the range of  $\lambda = 300\text{--}400\text{nm}$ , where the mini-module's EQE is in the range of 23–58% and emits in

the range  $\lambda = 400\text{--}570\text{nm}$ , where the mini-module's EQE is significantly higher in the range of 58–88%. The PLQY of the violet dye in EVA was determined to be  $100 \pm 10\%$  [4], which agrees with the same value measured in polymethylmethacrylate (PMMA) [10].

Comparing the transmission data for luminescent samples against the control samples (see Fig. 4) indicates that no significant scattering occurs due to the addition of the dyes to the EVA encapsulant. Fig. 4 also shows that using the solvent-based method (solid curves) to dope the sheets resulted in slightly more transparent (less scattering) material than mechanical mixing (dashed curves).

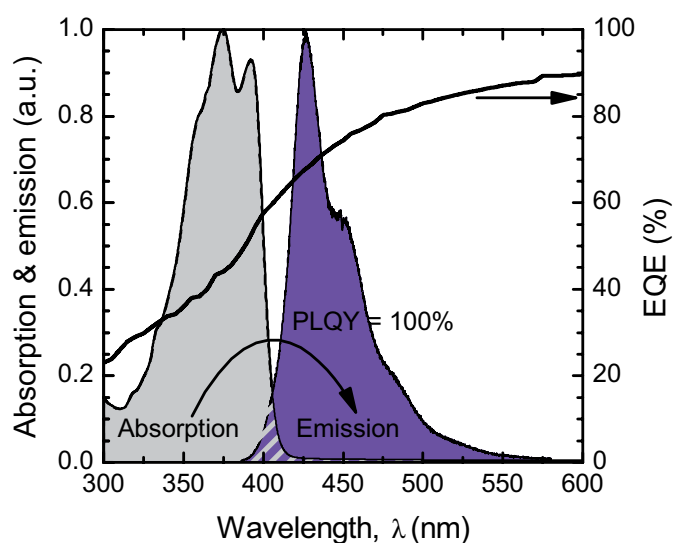


Figure 3. Normalized absorption and emission spectra of the Violet 570 dye (OD = 3) in EVA, along with the EQE of the clear-EVA mini-module to give an indication of the potential gains to be made by employing LDS in a mc-Si PV module (adapted from [4]). Note that the emission spectrum is considerably red-shifted compared to the datasheet [8] due to the high dye concentration used here.

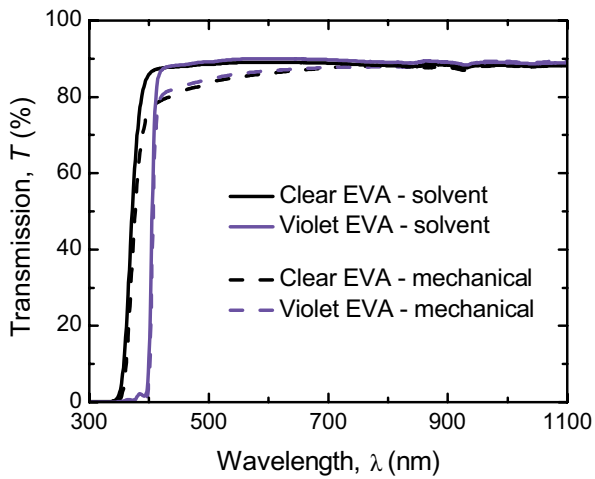


Figure 4. Transmission measurements through four of the mini-module laminates fabricated. The violet dye is seen to absorb a significant fraction of light from 350–400nm, while the use of solvent for doping the EVA resulted in a superior EVA sheet than that achieved via mechanical mixing and extruding.

The EQE curves of the four encapsulated mc-Si mini-modules are shown in Figure 5. The violet-doped-EVA laminates exhibits an increase of 10 – 20 % in EQE in the range  $\lambda = 300\text{--}400\text{nm}$ . With increasing dye concentration, a greater fraction of light is absorbed, which has the effect of broadening the width of the absorption peak centred at 375nm, while the resulting EQE increases at wavelengths less than this value.

**“If this can be achieved, then increasing mc-Si module efficiencies by 0.5% (absolute) would become possible.”**

However, at longer wavelengths, the performance is slightly worse at higher OD since there is an increased probability of re-absorption in layers with higher dye concentrations. Hence, there is an increased possibility of the emitted photons undergoing a second absorption event and being re-emitted possibly before being collected by the underlying mc-Si solar cell. However, as mentioned previously, for each emission event (assuming isotropic emission) there is a 12.5% chance of losing the emitted photons back out the front surface. These losses are compounded further during subsequent re-absorption/emission events, and for this reason luminescent materials with large Stokes shifts are of interest.

Table 1 compares the efficiency enhancement achieved via the application of LDS EVA for the series of violet-doped samples. Whilst the concentration that corresponds to OD = 3 seems to be the optimum for maximum efficiency enhancement, the OD = 1 sample yields a very similar improvement, but only using one third of the quantity of the dye. This can be important to cost analysis considerations for the technology in case of application to production scale; it is generally better to use lower concentrations if possible to avoid any risk of dye aggregation. This best result achieved to date, using the violet dye at OD = 3, translates to a 0.2% absolute gain in module efficiency.

### Cost estimate and photostability considerations

The cost of implementing an LDS layer (of OD = 3) into a mc-Si module has been presented previously [3,4]; however, the example of Violet OD = 1 is presented here to illustrate the point. To manufacture a 1m<sup>2</sup> EVA sheet of 0.5mm thickness doped with OD = 1, approximately 208mg of violet dye is required. Lumogen dyes are

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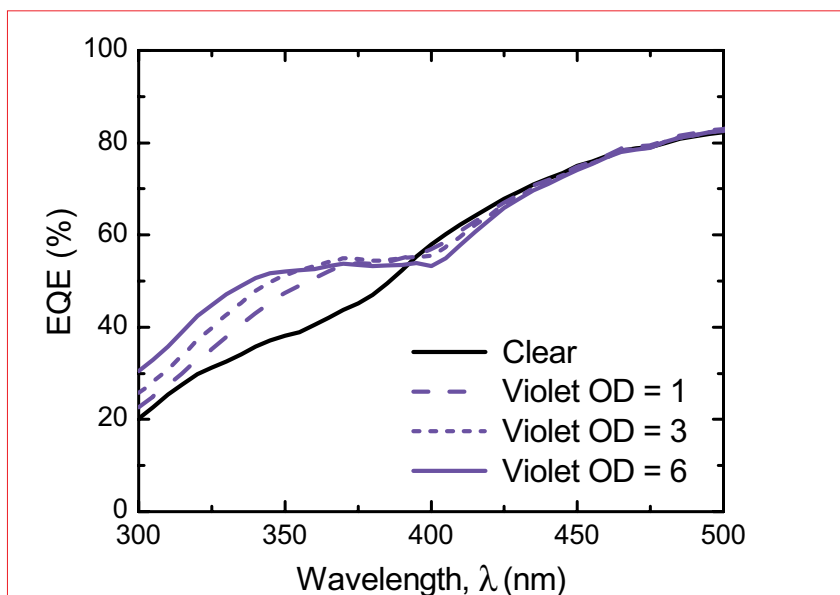


Figure 5. Impact of violet dye concentration on the EQE of a mc-Si mini-module.

EVA Type	Initial (cell) $\eta$ (% ab.)	Final (module) $\eta$ (% ab.)	$\Delta\eta$ (% rel.)	Improvement due to LDS (% rel.)
Clear	14.32	14.26	-0.39	n/a
Violet OD = 1	14.63	14.78	+1.07	+1.46
Violet OD = 3	14.26	14.42	+1.09	+1.48
Violet OD = 6	14.15	14.18	+0.24	+0.63

Table 1. Efficiency results for samples encapsulated in violet-doped EVA sheets at different concentrations. The mini-modules' efficiencies are compared to the corresponding cell efficiencies prior to encapsulation, rather than directly to each other, because the mc-Si cells had slightly different initial efficiencies. The difference between the initial and final efficiencies of the same device describes the effect  $\Delta\eta$  of the encapsulation in each case. The benefit directly attributed to LDS is calculated by subtracting from the effect of encapsulation calculated for each sample, the effect of encapsulation for the corresponding control sample.

commercially available in bulk quantities, priced at about €7,000–9,000/kg [12]. Thus, the additional cost for a 1m<sup>2</sup> module is in the range of €1.50–2.00, which is very small compared to the factory-gate price of ~€360/m<sup>2</sup> for European manufacturers of mc-Si modules [13].

Using the efficiency results presented in Table 1 and the above cost considerations, a reduction from €2.40/Wp to €2.38/Wp is estimated to be the benefit of LDS in terms of cost of photovoltaic power. Naturally, the €/Wp benefit will increase with optimized luminescent materials that exhibit a large Stokes shift and emit at  $\lambda > 600\text{nm}$ . In addition, technologies that exhibit a poorer short-wavelength performance than mc-Si, such as CI(G)S, also stand to benefit more.

For the above calculation to be really useful, this additional electricity needs to be generated over the lifetime of the mc-Si PV module. PV manufacturers typically guarantee a minimum performance over an extended period of 20–25 years and every component should meet this requirement. For

example, pure EVA exhibits inadequate photostability to UV light and requires the addition of UV-absorbers to protect the copolymer [14]. The violet dye is characterized by the manufacturer as long-term photostable, despite exhibiting UV-induced photodegradation under irradiation with light of  $\lambda < 345\text{nm}$  [15]. In experiments using acrylic (PMMA) doped with Lumogen violet dye, a 50% reduction in emission was measured after exposure to sunlight for ~two years [15]. However, in the case of LDS EVA, the doped encapsulant is beneath the glass coversheet of a PV module, which strongly absorbs light of  $\lambda < 340\text{nm}$  [3]. This, along with the presence of the UV-absorber in the EVA, will afford some additional UV protection. It is clear that extensive accelerated weathering and outdoor testing is required to adequately address this issue.

### Conclusion and future direction

This study has shown that an enhancement in the performance of mc-Si devices can be achieved without any modification to the well-established

manufacturing process of these devices and any addition to the cost of power generation. This can be done by dissolving a suitable luminescent species in the EVA encapsulation layer that is commonly used for the manufacturing of mc-Si devices. The Lumogen Violet 570 dye is reported to offer an increase of over 10% in EQE for the region of 300–400nm, which results in 0.2% higher module efficiency. Future R&D in this area needs to focus on the development of photostable luminescent materials that are able to strongly absorb light in the 300–450nm range and emit this at about 600nm with a near-unity PLQY. If this can be achieved, then increasing mc-Si module efficiencies by 0.5% (absolute) would become possible.

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#### About the Authors

**Bryce S. Richards** received his B.Sc. in physics from the Victoria University of Wellington (New Zealand) in 1994, and an M.Eng.Sc. and a Ph.D. in photovoltaic engineering from the University of New South Wales (UNSW), Australia, in 1998 and 2002, respectively. From 2002–2006 he was a postdoctoral fellow at UNSW and then at the Australian National University, and joined Heriot-Watt University in 2006, where his research focuses on the application of luminescent materials to enhancing photovoltaic devices. An author of four book chapters and proceedings, as well as 55 journal articles, Prof. Richards was the Managing Editor for *Progress in Photovoltaics* from 2006 to 2009, and is currently the Director of the Scottish Institute for Solar Energy Research (SISER).

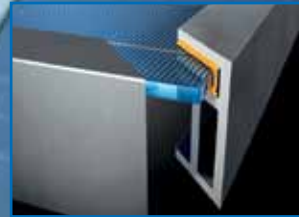
**Efthymios Klampaftis** received his degree in physics from the National and Kapodistrian University of Athens, Greece, in 2003, and in 2005, received an M.Sc. in renewable energy systems technology from Loughborough University, UK. He is currently completing his Ph.D. at Heriot-Watt University in the area of luminescent down-shifting of sunlight for improving the short-wavelength response of photovoltaic devices. He has authored or coauthored three journal articles and five conference papers to date.

#### Enquiries

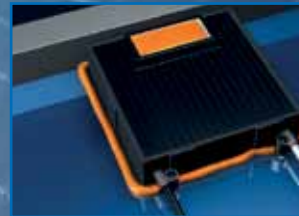
Scottish Institute for Solar Energy Research (SISER)  
School of Engineering and Physical Sciences  
James Nasmyth Building  
Heriot-Watt University  
Edinburgh EH14 4AS  
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