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Citation for published version (APA):

DOI:
10.1364/OE.18.00A536

Document status and date:
Published: 01/01/2010

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Patterned dye structures limit reabsorption in luminescent solar concentrators

Shufen Tsoi,1 Dirk J. Broer,1 Cees W. M. Bastiaansen,1,2 and Michael G. Debije1,*

1 Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
2 School of Engineering and Material Science, Queen Mary University of London, London E1 4NS, United Kingdom
*M.G.Debije@tue.nl

Abstract: This work describes a method for limiting internal losses of a luminescent solar concentrator (LSC) due to reabsorption through patterning the fluorescent dye doped coating of the LSC. By engineering the dye coating into regular line patterns with fill factors ranging from 20 - 80%, the surface coverage of the dye molecules were reduced, thereby decreasing the probability of the re-emitted light encountering another dye molecule and the probability of reabsorption. Two types of fluorescent dyes with different quantum yields were used to examine the effects of patterning on LSC performance. The effect of various dimension and geometry of the patterns on the efficiency and edge emission of LSC are presented and analyzed.

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References and links
1. Introduction

Photovoltaic (PV) solar concentrators using reflective or refractive optics coupled to a sun-tracking system are promising methods for reducing the cost of solar energy, particularly in the form of large solar farms or power plants [1]. Due to the generally large sizes of these solar concentrators and their requirement of direct, unobstructed sunlight, these solar power generators are best located in deserts or rural areas, as they are not appropriate for use in the built environment. An attractive alternative for solar concentration within metropolitan areas is the luminescent solar concentrator (LSC) [2–7]. The basic LSC consists of fluorescent dye molecules either embedded in or coated onto a plastic waveguide. Incident light is absorbed by the dye molecules and is re-emitted at longer wavelengths. Light emitted outside the escape cone of the waveguide (i.e., at an angle greater than the critical angle for total internal reflection) is directed to the edges where photovoltaic cells are attached [2, 5, 7]. Since PV cells are only attached to the edge(s) of the waveguide, the area of PV cells can be reduced >90% compared to standard PV modules, and hence the cost of the solar module and cost per unit energy (Watt Peak). Additional advantages of LSCs include low production costs and flexibility in shape and color.

The efficiency of single waveguide LSC modules is moderate ~4.6% with GaAs PV cell attach to one edge of the waveguide[8], and improvement is necessary for LSCs to become attractive for commercialization. A main factor limiting LSC efficiency is internal losses due to reabsorption of light emitted by the dye molecules. The small Stokes-shifts of the most commonly used fluorescent dyes result in an overlap between the absorption and emission spectra, and significant reabsorption of emission light. The reabsorbed photon is potentially lost in one of two main ways: 1) re-emission at angles outside the LSC waveguiding modes, or 2) transferral into heat due to <100% quantum yield of the fluorophore [9, 10]. For an LSC with a refractive index of 1.5 (typical of many polymers) it has been reported that reabsorption may account for ~25% of light loss [11]. To limit reabsorption, attempts have been made to increase the Stokes shift of the emitting material by replacing the fluorescent dyes with quantum dots [12, 13, 18, 19], lanthanide complexes [11], or by doping the dye molecules with materials such as thionin [14]. While these alternate luminophores allow better control of the Stokes shift of the luminescent material, the materials suffer from either low quantum yields or poor light absorption when compared to organic fluorescent dyes such as perylenes [15].
To exploit the advantages of the fluorescent dyes, reabsorption losses must be limited. Here, we report reduced re-absorption losses of fluorescent dye coated LSC via microstructuring of the dye layer. Surface area coverage of the dye molecules is reduced when the dye coating is deposited as line patterns separated by regions of clear waveguide. Decreasing surface area coverage reduces the probability of interaction between re-emitted photons and dye molecules, and thereby minimizing reabsorption losses (see Fig. 1 for the concept behind the patterned layers).

Fig. 1. a) Light incident on a uniformly coated LSC is absorbed and re-emitted at a longer wavelength by a dye molecule. Part of this re-emitted light propagates through the substrate in the waveguiding mode (solid light rays), and has a high probability of being reabsorbed by another dye molecule. Each time re-absorption occurs, there is a potential loss of photons due to < 100% quantum yield of the dyes and the redirecting of light. Hence the intensity of the re-emitted light from a reabsorption event decreases (dotted light rays); b) The dye layer is patterned into line structures which extend into the plane of the paper. Light re-emitted into the waveguide mode has significantly lower probability of encountering dye molecules, thereby minimizing reabsorption and energy losses as light travels across the waveguide.

2. Experiments

2.1. Substrate Preparation

B270 Glass (50 x 50 x 3 mm³) and PMMA (50 x 50 x 5 mm³) substrates were used as waveguides. A polyimide (Nissan 130 or JSR AL-1051) adhesion layer was spun onto the glass substrates at 3000 rpm for 60 s. The adhesion layer was needed to reduce the interfacial tension and prevent peeling of the dye doped polymer film during the later stages of the experiments. The polyimide coated glass substrates were baked at 90°C for 10 min in air, then placed in an oven at 190°C for 90 min under vacuum. After baking of the polyimide coated substrates, they were allowed to cool in air overnight.

2.2. Sample Fabrication

Fluorescent dye solutions were prepared using 0.5% wt of fluorescent dye molecules DFSB-K160 (Risk Reactor) or Lumogen Red 305 (BASF), and 1% photoinitiator (Irgacure184, Ciba) dissolved in a 3:1 dipentaerythritol penta-acrylate (Polysciences) and methylmethacrylate (MMA, Aldrich) blend. The dye solutions were stirred and heated at 60°C for an hour prior to spin-coating onto the substrates at 1000 rpm for 30 s. After spin-coating, all 100% covered samples were crosslinked by exposing to a high-intensity UV lamp (OmniCure S2000 UV spot curing lamp) for 80 s under nitrogen flow to form a solid film. For the fabrication of patterned LSCs, standard photolithography techniques were employed. Uniformly coated substrates were exposed to UV light through patterned shadow masks consisting of 1) 5 lines with variable widths with a period of 10 mm, 2) 10 lines with variable widths with a period of 5 mm, and 3) 90 squares of variable dimensions, arranged in a 9 × 10 rectangular pattern. Line widths...
and square sizes were varied to cover 14 to 80% of the waveguide surface. After UV exposure, ethanol was used to etch away the unexposed material on PMMA and glass substrates. The thicknesses of the fluorescent dye coatings and microstructures were measured to be 15-20 \(\mu m\) using a Sensofar Plu2300 optical imaging profiler.

2.3. Sample Characterization

Absorption spectra of most samples were measured using a Shimadzu UV-3102 PC spectrometer. Average absorbance, calculated from the peak of the absorption spectra, was found to be 0.63, 0.6, and 0.47 for the K160 doped 5 line, 10 line, and square patterned PMMA waveguides, respectively. The absorbances of the Red305 doped line and squared patterned PMMA waveguides were measured to be 0.34. Edge emission of the waveguides was measured by a SLMS 1050 integrating sphere (Labsphere) equipped with a diode array detector (RPS900, International Light). The LSC samples were placed in a custom-made sample holder, which is connected to the entry port of the integrating sphere and prevents surrounding light from entering the port. The LSCs were exposed to a collimated light source from a 300 W solar simulator with filters to approximate the 1.5 AM (global) solar spectrum (Lot-Oriel) located at a distance of 15 cm from the top surface of the waveguide. Light output spectra and intensity from all four emission edges of the LSC were measured and recorded. Total absorbed power of the 100% covered samples was calculated by multiplying its absorption spectrum with the solar simulator spectrum, and subsequently integrating it from 350 - 750 nm. The power absorbed by the dye molecules in the patterned waveguides was calculated by multiplying the integrated absorption power of the 100% covered control sample with the fractional area coverage of the patterned samples, e.g., \(0.3 \times \text{Absorption Power}_{100}\%\). Total edge emissions were determined by integrating the recorded spectra over the range of 350-750 nm. Relative efficiency of the system was determined by dividing the total edge emission (summation of all 4 edges) by the absorbed power of the sample.

3. Results and discussion

![Graph](image)

Fig. 2. Representative absorption (solid line) and edge emission (dotted line) spectra of 0.5% wt. fluorescent dye K160 (green) and Lumogen Red 305 (red) doped glass waveguides.

A series of samples were produced that consisted of ten equally spaced lines of acrylates doped with 0.5% wt. of the fluorescent dye K160 deposited on the top of clear glass and plastic waveguides. The line widths were varied to produce regular patterns that, in total, covered
from 30 to 100% of the waveguide surface. The edge emissions from all four edges of each waveguide were measured to determine the effect of dye coverage on the edge output and efficiency of the LSCs. Representative edge emission and absorption spectra of the K160 dye are given in Fig. 2. The relative efficiency of the patterned LSC system, defined as the ratio of total integrated edge emission (350-750 nm) to the total energy absorbed by the sample, increased with decreasing area of dye coverage (Fig. 3a). At 30% dye coverage, the relative light emission efficiency of the patterned LSC on glass was more than double the efficiency of the 100% covered sample. This suggests that reabsorption losses can be limited by reducing surface coverage of the dye molecules, and the efficiency of the system significantly improved. Similar trends were noted on PMMA substrates: the relative efficiency at 30% coverage on the PMMA wave-guides increased by ~70% compared with the 100% coverage control sample. To further verify the decrease in reabsorption losses as a result of the patterning, the emission spectrum from one of the waveguide edges for all waveguide coverage were plotted in Fig. 4. The emission peak of the patterned LSC is noted to red-shift with increasing coverage, which implies that reabsorption increases with coverage. This finding is similar to the measurements performed by Sholin et. al. [18] Overall, higher efficiencies are achieved with the glass waveguides than with PMMA waveguides, in general agreement with the findings of Kastelijn et al. [16]

Fig. 3. (a) Calculated relative efficiency (sum of integrated emission from all 4 edges divided by calculated total energy absorbed by the fluorescent dye molecules from 350-750 nm) and (b) measured integrated total edge emission of LSC on PMMA and glass substrates as a function of surface area covered by line structures containing 0.5% K160 dye molecules.

The absolute edge emissions of the microstructured LSCs are lower than the 100% covered LSC (Fig. 3b). The line patterns allow a considerable fraction of incident light to pass through the clear regions of the waveguide without encountering dye molecules, and this light is lost: as dye coverage decreases (that is, the line widths decrease), the amount of absorbed light also decreases, leading to a reduction in total edge emission despite the increased efficiency. It is possible to reduce these light losses by increasing light absorption through focusing incident light onto the dye regions via a microlens array. We are currently investigating this method of increasing light absorption of microstructured LSC and will present it in a future publication.

There are only small differences observed in the emissions from the two edges that are perpendicular and parallel to the lines of the microstructured LSC. Since the dye molecules in the acrylate host are isotropic, it is not surprising that the difference in edge emission of the four waveguide edges is small [17].

Possible dimensional and geometric effects on the edge emission and efficiency of the microstructured LSC were investigated by preparing a series of samples consisting of 1) five equally spaced acrylate lines, and 2) 90 squares (in a 9×10 rectangular array) doped with 0.5% wt. K160 were deposited on top of PMMA waveguides. The line widths and the area of the
squares were varied to produce regular patterns that covered 20 to 100% of the waveguide surface. The patterned samples composed of 5 and 10 lines with varying surface coverage will be referred to as 5 line and 10 line samples hereafter. Relative efficiency as a function of surface area coverage of the dye measured from the 5 line samples were similar to the 10 line (Fig. 5a), and the edge emission was the same for both systems (Fig. 5b). The slight difference (5%) in relative efficiency between the two patterned samples is likely due to a greater number of re-encounters with the dye in the broader-lined 5 line patterns. In addition, the measured absorbance of the 5 line samples (0.63) was slightly higher than the 10 line (0.6). This again suggests that reabsorption is the reason the 5 line samples exhibit the same edge emission but a greater absorbed power compared to the 10 line samples. We conclude line width variations have little effect on the edge emission or the efficiency of the LSC system.

The effect of geometry on the performance of microstructured LSCs was studied by preparing a series of samples consisting of acrylate squares arranged in a rectangular pattern doped with fluorescent dye on PMMA waveguide. The area of the squares was varied to cover 14-100% of the waveguide surface. Comparing the series of 0.5% wt K160 doped square patterned waveguides with the similarly doped 10 line system show similar trends (Fig. 5c) and values (Table 1) for relative efficiencies. Table 1 also reports integrated edge emission values as a function of waveguide surface area coverage for two different (square and 10 line) patterned LSC systems. The comparisons suggest that geometry has negligible effects on the efficiency and output of the system.

To verify that the geometry of the patterns has little effect on the output of the LSC, similar square and 10 line patterned samples doped with 0.5% wt Lumogen Red 305 were prepared. Analogous to the patterned systems doped with K160 dye, total integrated edge emissions (sum of 4 edges) of the two Red305 doped patterned LSCs were similar in both values and trend (Table 1). Again, by decreasing the dye surface area coverage of the waveguide, relative efficiencies of the patterned samples increased. Figure 5c illustrates that the relative efficiencies of the Red305 doped square patterns were comparable to both of the 10 line pattern (Red305 and K160 doped) systems. Only small differences (within measurement error) were noted for relative efficiency and edge emission of the Red305 square and 10 line patterned samples. This supports our conclusion that the geometry of the pattern has little effect on the performance of LSCs, which also implies both cylindrical and spherical lens arrays can be used for reducing
Fig. 5. a) Relative efficiency (defined as total integrated edge emission divided by the calculated energy absorbed by dye molecules from 350-750 nm) and b) total edge emission of patterned waveguides composed of equally spaced 5 and 10 lines doped with 0.5% K160 as a function of dye pattern coverage; c) relative efficiency of line and square patterned waveguides doped with 0.5% K160 and 0.5% Red305.

4. Conclusion
We have demonstrated that the relative efficiency of light emission from the edges of an LSC can be significantly improved by reducing the dye surface coverage of the waveguide via patterning. The increase in photon-photon efficiency supports our hypothesis that patterning the dye coating on a LSC limits reabsorption losses. Similar edge emission and relative efficiency were observed for both line and square patterns with similar total surface coverage doped with...
Table 1. Measurement results of different fluorescent dyes and patterned waveguides

<table>
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<tr>
<th>Dye Type</th>
<th>Pattern Type</th>
<th>Area Coverage [%]</th>
<th>Integrated Edge Emission [mW]</th>
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different fluorescent dyes. This leads to the conclusion that specific dimensions and geometry have little effect on the performance of the patterned LSC systems.

**Acknowledgements**

The authors would like to thank Senter Novem, STW VIDI grant 7940, and the National Science and Engineering Research Council of Canada for their financial support.