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Monte-Carlo Ray-Trace Modelling of Quantum Dot Solar Concentrators

Manus Kennedy

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Monte-Carlo Ray-trace Modelling of Quantum Dot Solar Concentrators

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Thesis submitted for PhD
October, 2009.

Supervised by
Professor Brian Norton
Dr. John Doran
Dr. Sarah McCormack
Abstract

Due to the finite resources of fossil fuel and nuclear reserves, renewable energy technologies must provide an increasing proportion of future energy needs, if the world’s population are to expect a secure and sustainable developed society. Quantum dot solar concentrators (QDSCs) can potentially reduce the cost of photovoltaic (PV) electrical power generation and thereby further the growth in installed PV capacity. QDSCs can concentrate both the direct and diffuse components of solar radiation which makes them particularly suitable for climates where the diffuse component is predominant.

A QDSC model has been developed based on Monte-Carlo ray-trace techniques. The model allows the multiple competing, interdependent QDSC loss mechanisms to be quantified for any given set of device parameters. The model provides an important tool for optimizing QDSC design in terms of varying geometry, PV cell configuration, matrix material, and quantum dot types. Combining the ray-trace model with solar radiation models, diurnal and seasonal variations in QDSC performance can be analysed, and devices further optimised for outdoor conditions. Model predictions show that viable QDSCs are realizable provided efficient near infra-red emitting quantum dots can be exploited.
Declaration

I certify that this thesis which I now submit for examination for the award of PhD is entirely my own work and has not been taken from the work of others, save and to the extent that such work has been cited and acknowledged within the text of my work. This thesis was prepared according to the regulations for postgraduate study by research of the Dublin Institute of Technology and has not been submitted in whole or in part for another award in any Institute. The work reported on in this thesis conforms to the principles and requirements of the Institute's guidelines for ethics in research.

The Institute has permission to keep, lend or copy this thesis in whole or in part, on condition that any such use of the material of the thesis be duly acknowledged.

Signature ___________________________ Date 17/12/09
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This thesis would not have been possible without the excellent guidance and support I have received from my supervisors Dr. Sarah McCormack, Dr. John Doran and Prof. Brian Norton. I am very grateful to them for all their dedication. It has been a pleasure working with them on this project and I look forward to future collaborations together.

I would like to express my appreciation to all my colleagues for their continued support and encouragement over the last number of years. In particular, I would like to express my deep gratitude to Dr. Brenda Rowan who fabricated the quantum dot solar concentrator samples used in this study. I am very grateful to everyone in the FOCAS institute who provided me with invaluable advice and technical instruction.

To my friends and family, who provided me with much needed diversion, and support over the course of my studies, I will always be indebted. Thank you to Maite for being there throughout.

The support of Sustainable Energy Ireland, and the Research Support Unit at the Dublin Institute of Technology is gratefully acknowledged. I would also like to acknowledge the collaboration of the Molecular Based Concepts group, part of the EU-funded FULLSPECTRUM project.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ARC</td>
<td>Anti-reflection coating</td>
</tr>
<tr>
<td>a-Si</td>
<td>Amorphous silicon</td>
</tr>
<tr>
<td>ASTM</td>
<td>American society for testing and materials</td>
</tr>
<tr>
<td>CdS</td>
<td>Cadmium sulphide</td>
</tr>
<tr>
<td>CdSe</td>
<td>Cadmium selenide</td>
</tr>
<tr>
<td>CdTe</td>
<td>Cadmium telluride</td>
</tr>
<tr>
<td>CIGS</td>
<td>Copper indium gallium selenide</td>
</tr>
<tr>
<td>CPC</td>
<td>Compound parabolic concentrator</td>
</tr>
<tr>
<td>EOT</td>
<td>Equation of time</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>FOB</td>
<td>Fibre optic bundle</td>
</tr>
<tr>
<td>FRET</td>
<td>Förster resonant energy transfer</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium arsenide</td>
</tr>
<tr>
<td>GaInP</td>
<td>Gallium indium phosphide</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
</tr>
<tr>
<td>LDS</td>
<td>Luminescent down shifting</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>LSC</td>
<td>Luminescent solar concentrator</td>
</tr>
<tr>
<td>mc-Si</td>
<td>Multicrystalline silicon</td>
</tr>
<tr>
<td>MgF₂</td>
<td>Magnesium fluoride</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infra-red</td>
</tr>
<tr>
<td>PbS</td>
<td>Lead sulphide</td>
</tr>
<tr>
<td>PbSe</td>
<td>Lead selenide</td>
</tr>
<tr>
<td>PC-LDS</td>
<td>Partially covered luminescent down shifting</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dot</td>
</tr>
<tr>
<td>QDSC</td>
<td>Quantum dot solar concentrator</td>
</tr>
<tr>
<td>QY</td>
<td>Quantum yield</td>
</tr>
<tr>
<td>RET</td>
<td>Renewable energy technology</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SSR</td>
<td>Spectrally selective reflector</td>
</tr>
<tr>
<td>TIR</td>
<td>Total internal reflection</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>W_p</td>
<td>Watt peak</td>
</tr>
<tr>
<td>ZnS</td>
<td>Zinc sulfide</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>S.I. units</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>a</td>
<td>CPC entry aperture width</td>
</tr>
<tr>
<td>a'</td>
<td>CPC exit aperture width</td>
</tr>
<tr>
<td>A_{conc}</td>
<td>LSC top surface aperture area</td>
</tr>
<tr>
<td>A_{FO, FOB}</td>
<td>Cross sectional area of fibre optic bundle</td>
</tr>
<tr>
<td>A_{PV}</td>
<td>Area of attached PV cells</td>
</tr>
<tr>
<td>A_{FO}</td>
<td>Planar area of fibre optic in solar tree system</td>
</tr>
<tr>
<td>B_h</td>
<td>Beam irradiance component on horizontal surface</td>
</tr>
<tr>
<td>B_t</td>
<td>Beam irradiance component on a tilted surface</td>
</tr>
<tr>
<td>c</td>
<td>Speed of light</td>
</tr>
<tr>
<td>C</td>
<td>Spectrally-specific solar energy concentration ratio</td>
</tr>
<tr>
<td>C_1</td>
<td>Solar energy concentration ratio of solar leaf</td>
</tr>
<tr>
<td>C_2</td>
<td>Solar energy concentration ratio of 2nd stage concentrator</td>
</tr>
<tr>
<td>C_G</td>
<td>CPC geometric concentration ratio</td>
</tr>
<tr>
<td>C_{ph}</td>
<td>Photon count concentration ratio</td>
</tr>
<tr>
<td>d</td>
<td>Distance between boundary intersection points</td>
</tr>
<tr>
<td>day_j</td>
<td>Julian day of the year</td>
</tr>
<tr>
<td>D_{es}</td>
<td>Circumsolar component of diffuse irradiance</td>
</tr>
<tr>
<td>D_h</td>
<td>Diffuse irradiance component on horizontal surface</td>
</tr>
<tr>
<td>D_{hz}</td>
<td>Horizon brightening component of diffuse irradiance</td>
</tr>
<tr>
<td>D_{iso}</td>
<td>Isotropic component of diffuse irradiance</td>
</tr>
<tr>
<td>D_t</td>
<td>Diffuse irradiance component on a tilted surface</td>
</tr>
<tr>
<td>D_t</td>
<td>Ground albedo reflected component on tilted surface</td>
</tr>
<tr>
<td>E_h</td>
<td>Extraterrestrial global horizontal irradiance</td>
</tr>
<tr>
<td>E_{in}</td>
<td>Input energy distribution</td>
</tr>
<tr>
<td>F_1</td>
<td>Circumsolar coefficient</td>
</tr>
<tr>
<td>F_2</td>
<td>Horizon brightening coefficient</td>
</tr>
<tr>
<td>f_{ij}</td>
<td>Perez coefficients</td>
</tr>
<tr>
<td>G_{geom}</td>
<td>Geometric gain</td>
</tr>
<tr>
<td>G_{h}</td>
<td>Global irradiance on horizontal surface</td>
</tr>
<tr>
<td>G_t</td>
<td>Global irradiance on a tilted surface</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>I_0</td>
<td>Solar constant</td>
</tr>
<tr>
<td>I_{sc PV}</td>
<td>Short circuit current of PV cells coplanar to concentrator</td>
</tr>
<tr>
<td>I_{sc PV_C}</td>
<td>Short circuit current of PV cell attached to concentrator</td>
</tr>
<tr>
<td>I_{sc}</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>J_{sc}</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>k_a</td>
<td>Fraction of photons exiting fibre optic bundle within CPC θ_a</td>
</tr>
<tr>
<td>k_D</td>
<td>Diffuse fraction</td>
</tr>
<tr>
<td>k_r</td>
<td>Randomly generated number in the interval [0,1]</td>
</tr>
<tr>
<td>k_T</td>
<td>Clearness index</td>
</tr>
<tr>
<td>L_{loc}</td>
<td>Location longitude in degrees west of L_{ref}</td>
</tr>
<tr>
<td>L_{ref}</td>
<td>Reference longitude</td>
</tr>
<tr>
<td>n</td>
<td>Refractive index</td>
</tr>
<tr>
<td>n_1</td>
<td>Refractive index at location of incident ray</td>
</tr>
<tr>
<td>n_2</td>
<td>Refractive index at location of refracted ray</td>
</tr>
<tr>
<td>n_{CPC}</td>
<td>Refractive index of dielectric filled CPC</td>
</tr>
</tbody>
</table>
\( N_{FO} \) Number of fibre optics in solar tree system
\( N_{in} \) Input photon distribution \( \text{photons s}^{-1} \text{m}^{-2} \text{nm}^{-1} \)
\( N_{out} \) Output photon distribution \( \text{photons s}^{-1} \text{m}^{-2} \text{nm}^{-1} \)
\( p \) Normalised surface normal vector
\( P_{\text{abs}} \) Probability of absorption event
\( R \) Probability of reflection
\( R_{||} \) Parallel polarised component of reflected light
\( R_{\perp} \) Perpendicularly polarised component of reflected light
\( R_{\text{mirror}} \) External mirror reflectivity
\( R_{PV} \) PV cell reflectivity
\( R_{\text{SSR}} \) Spectrally selective reflector reflectivity
\( \nu \) Normalised ray vector
\( \nu_{\text{reflect}} \) Reflected ray vector
\( \nu_{\text{refract}} \) Refracted ray vector
\( W_{FO} \) Width of fibre optic \( \text{m} \)
\( W_{\text{Leaf}} \) Width of solar leaf \( \text{m} \)
\( L_{\text{Leaf}} \) Length of solar leaf \( \text{m} \)
\( \alpha_{\text{mat}} \) Matrix material photon absorption coefficient \( \text{m}^{-1} \)
\( \alpha_{\text{QD}} \) Quantum dot absorption coefficient \( \text{m}^{-1} \)
\( \alpha_{\text{scat}} \) Matrix material photon scattering coefficient \( \text{m}^{-1} \)
\( \beta \) LSC surface tilt angle \( \text{degrees, radians} \)
\( \gamma_{p} \) LSC surface azimuth angle \( \text{degrees, radians} \)
\( \gamma_{s} \) Solar azimuth angle \( \text{degrees, radians} \)
\( \Delta \) Sky brightness parameter \( \text{degrees, radians} \)
\( \delta \) Solar declination \( \text{degrees, radians} \)
\( \eta \) Power conversion efficiency
\( \eta_{\text{abs}} \) Absorption efficiency
\( \eta_{\text{int opt}} \) Internal optical efficiency
\( \eta_{\text{opt}} \) Optical efficiency
\( \eta_{\text{ret}} \) Retention efficiency
\( \eta_{\text{TIR}} \) Total internal efficiency
\( \theta_{a} \) CPC acceptance angle \( \text{degrees, radians} \)
\( \theta_{\text{critical}} \) Critical angle \( \text{degrees, radians} \)
\( \theta_{\text{entry}} \) Optical concentrator entry aperture \( \text{degrees, radians} \)
\( \theta_{\text{exit}} \) Optical concentrator exit aperture \( \text{degrees, radians} \)
\( \theta_{lp} \) Angle of incidence on tilted planar surface \( \text{degrees, radians} \)
\( \theta_{s} \) Solar zenith angle \( \text{degrees, radians} \)
\( \lambda \) Wavelength \( \text{nm} \)
\( \lambda_{co} \) Spectrally selective reflector “cut-off” wavelength \( \text{nm} \)
\( \rho \) Ground surface albedo
\( \phi \) Location latitude \( \text{degrees} \)
\( \omega \) Solar hour angle \( \text{degrees, radians} \)
Table of Contents

List of Figures ............................................................................................................. 4
List of Tables ................................................................................................................ 12

1 Introduction to quantum dot (luminescent) solar concentrators ......................... 13
  1.0 The need for renewable energy sources ......................................................... 13
  1.1 Photovoltaics .................................................................................................... 15
  1.2 Optical concentrators of solar energy .............................................................. 17
    1.2.1 Compound parabolic concentrators with high acceptance angles ............ 19
    1.2.2 Flat plate optical concentrators of diffuse radiation ............................... 19
  1.3 Luminescent solar concentrators .................................................................... 21
  1.4 High efficiency LSCs and performance comparative measures ....................... 24
    1.4.1 Thin-film LSCs .......................................................................................... 27
  1.5 LSC stability and absorption range limitations ............................................... 28
  1.6 Quantum Dot Solar Concentrators ................................................................. 30
  1.7 Modelling LSCs through a Monte-Carlo ray-trace approach ........................... 31
  1.8 Research objectives .......................................................................................... 32
    1.8.1 Model development and validation; ........................................................... 32
    1.8.2 Investigation of QDSC geometries ........................................................... 32
    1.8.3 Quantifying QDSC performance for varying material properties ............ 33
    1.8.4 Outdoor modelling and annual energy yield predictions .......................... 33
    1.8.5 Quantum dot luminescent down-shifting layers ...................................... 34
  1.9 Chapter conclusions ......................................................................................... 35

1.10 References ......................................................................................................... 36

2 Ray-trace modelling of luminescent solar concentrators ..................................... 42
  2.0 Introduction ....................................................................................................... 42
  2.1 Monte-Carlo ray-trace modelling ................................................................. 44
    2.1.1 Reflection and transmission at plate boundaries ....................................... 46
    2.1.2 Finding the intersection point of a ray and a plane ................................. 48
    2.1.3 Determining boundary intersection points ............................................. 49
    2.1.4 QD photon absorption and emission ...................................................... 50
    2.1.5 Matrix material absorption and scattering ............................................. 51
    2.1.6 Concentration ratio and photovoltaic cell spectral response .................... 55
  2.2 Model Validation .............................................................................................. 57
    2.2.1 Visualization of traced rays ................................................................. 58
    2.2.2 Edge emission spectra for varying input light position ............................ 60
    2.2.3 QDSC optical efficiency with varying QD concentration ....................... 64
    2.2.4 QDSC optical efficiency with varying size and shape ............................ 67
    2.2.5 Multiple dye liquid LSCs ........................................................................ 70
    2.2.6 Comparison with analytically predicted loss mechanisms ...................... 74
    2.2.7 Comparison with predictions from other models ................................... 76
  2.3 Model assumptions, limitations, and uncertainties ......................................... 78
  2.4 Chapter conclusions ......................................................................................... 82
  2.5 References ....................................................................................................... 84
3 Device geometry

3.0 Introduction

3.0.1 QDSC geometry

3.0.2 Solar tree geometry

3.0.3 Luminescent down-shifting layer geometry

3.1 An investigation of QDSC geometry

3.1.1 Concentration ratios for varying device geometry

3.1.2 Optimum device geometry - relative costs per unit power output

3.1.3 Edge effects

3.1.4 QDSC plates with reduced thickness

3.1.5 Concentration ratios of tapered QDSC plates

3.2 Luminescent “solar tree” with 2nd stage concentrator

3.2.1 Solar tree components: Solar leaves and fibre optics

3.2.2 Solar tree 2nd stage concentrator

3.2.3 Solar tree evaluation for varying fibre optic costs and CPC θr

3.3 Luminescent Down Shifting Layers

3.3.1 LDS layers incorporating QDs

3.3.2 Partially covered LDS layers and comparison with LSCs

3.4 Chapter conclusions

3.5 References

4 Device materials

4.0 Introduction

4.1 QD optical properties

4.1.1 QDSC absorption efficiency and escape cone losses

4.1.2 Solar energy concentration ratios for varying QD quantum yield

4.2 Matrix material properties

4.3 Specular and diffuse rear reflectors types

4.4 Spectrally selective reflecting top layers

4.4.1 SSR cut-off wavelength optimisation

4.4.2 Top surface losses for varying SSR reflectivity

4.4.3 Effect of rear reflector reflectivity

4.5 Chapter conclusions

4.6 References

5 Outdoor modelling of LSCs

5.0 Introduction

5.1 Solar radiation modelling

5.1.1 Beam and diffuse horizontal irradiance

5.1.2 Solar geometry

5.1.3 Beam irradiance on tilted surface

5.1.4 Diffuse irradiance on tilted surface

5.1.5 Ground reflected irradiance

5.1.6 Spectral irradiance

5.1.7 Annual in-plane insolation

5.2 QDSC performance in outdoor conditions

5.2.1 Diurnal variation in QDSC concentration ratio

5.2.2 Monthly and annual relative energy output

5.2.3 Optimum QDSC tilt angle, β
List of Figures

Figure 1.1. Supply of global electricity by fuel type in 2006 (IEA, 2009). Renewable energy technologies accounted for ~18%, of which hydro-electric was the predominant source. Photovoltaics (PV) accounted for 0.015% of global supply. 15

Figure 1.2. Global PV production (MWp) increased annually by an average of 33% in the period 1993-2007 (Observ'ER, 2008). 16

Figure 1.3. Optical concentrator with reflective surfaces (Smestad et al., 1990). The maximum concentration ratio is given by eqn. 1.1. 17

Figure 1.4. (a) Dielectric flat-plate (Smestad and Hamill, 1984), utilising a lambertian rear reflector and (b) wedge-shaped (Maruyama and Osako, 1999) optical concentrators. In (a) and (b), incident rays may be reflected at an angle within the angular range for total internal reflection to occur and is guided to the exit aperture at plate edges. 20

Figure 1.5. Flat-plate (non-optical) luminescent solar concentrator plate without PV cells or external reflectors attached. 21

Figure 1.6. Schematic of LSC without PV cells or external reflectors attached. Incident photons may be externally reflected [1], or transmitted into the plate. Transmitted photons may be absorbed by a dye molecule [2], or transmitted through the plate [3], depending on the dye absorption coefficient and the pathlength through the plate. Energy absorbed by the dye molecule may be re-radiated at a longer wavelength within the angular range for total internal reflection to occur [4], or within the “escape-cone” of the plate [5]. An absorption event may result in no luminescence from the dye molecule [6] and the absorbed energy is converted to heat. Dye emitted photons may be absorbed within the plate (so-called “re-absorption”) [7], after which [4], [5], or [6] may ensue. Photon absorption and scattering also occur within the plate, and reflection/refraction of photons within the escape-cone occurs at plate boundaries. 22

Figure 1.7. Thin-film LSCs consist of a highly doped thin-film polymer layer supported on a transparent substrate. 27

Figure 1.8. The absorption range of current dye luminescent solar concentrators (LSC) is limited to the visible range of the solar spectrum, and therefore only a fraction of the available solar spectrum is converted to electricity. Quantum dot luminescent solar concentrators, can potentially overcome absorption range limitations (and stability limitations) of luminescent dye LSCs. 29

Figure 2.1. Ray-trace model flow diagram for ray incident on QDSC top surface. 45

Figure 2.2. An incident photon may be either reflected (ray 2) or refracted (ray 3) depending on the calculated probability of reflection which is tested against a randomly generated number in the interval [0,1]. 47
Figure 2.3. “Point b” is the intersection point of the ray vector, \( v \), and the plane defined by the three points, “Point 1”, “Point 2”, and “Point 3”.

Figure 2.4 (a) Absorption spectrum of CdSe/ZnS core-shell QDs (Evident Technologies) measured with a Perkin Elmer 900 UV/Vis/NIR spectrometer. (b) Emission spectra using range of excitation wavelengths measured with a Perkin Elmer LS55B spectrometer. The excitation line is seen as the sharp spike in each spectrum at the respective excitation wavelength.

Figure 2.5. Experimental set up for absorbance measurements using a Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer; (a) normal set up; (b) using an integrating sphere to account for scattering in the samples (Gallagher et al., 2007).

Figure 2.6. Measured absorption and scattering spectra of an epoxy matrix material sample (Gallagher et al., 2007).

Figure 2.7. (a) The weighted forward scattering probability distribution used in the model (b) An example plot of 10,000 rays scattered at angles selected at random from a weighted distribution corresponding to (a).

Figure 2.8. (a) Measured EQE, IQE and reflectivity \( R_{pv} \) at normal incidence of a mc-Si cell. (b) Extrapolated \( R_{pv} \) curves for higher angles of incidence.

Figure 2.9. A ray given a random initial angle is traced inside a non-attenuating hexagonal QDSC, assuming perfectly reflecting external mirrors at all surfaces.

Figure 2.10. Rays are traced inside a non-attenuating triangular QDSC, assuming a plate refractive index of 1.5 and no external mirrors at any surface. If \( \theta_1 > \theta_{\text{critical}} \), TIR ensues. In this example, all rays with \( \theta_1 < \theta_{\text{critical}} \) are transmitted out of the device, except a single ray which undergoes Fresnel reflection at the boundary.

Figure 2.11. Measurement of QDSC edge emission spectrum, using different input laser positions on the QDSC surface, at varying distances (5mm - 50mm) from the plate edge at which the spectrometer detector is positioned.

Figure 2.12. Measured edge emission spectra for a laser (457nm) input at seven different distances (increasing from 5mm to 50 mm) from the detector.

Figure 2.13. Predicted edge emission spectra for a laser (457nm) input at seven different distances (increasing from 5mm to 50 mm) from the detector.

Figure 2.14. (a) compares the peak wavelengths and (b) compares the relative integrated intensities of the measured and predicted edge emission spectra, shown in Figure 2.12 and Figure 2.13, respectively.

Figure 2.15. Measured absorption and emission spectra of six samples containing different concentrations of ‘488C’ CdSe/ZnS QDs.
Figure 2.16. Measured and predicted optical efficiencies ($\eta_{opt}$) of fabricated devices containing different concentrations of QDs. The predicted $\eta_{opt}$ values are calculated using a QD QY of 10%, 60% and 100%. The error bars on the predicted values indicate the $\eta_{opt}$ uncertainty due to inhomogeneous matrix material scattering in different plates.

Figure 2.17. Absorption and emission spectra of ‘Fort Orange’ QDs. Incident light spectrum from metal halide lamp.

Figure 2.18. Predicted and measured optical efficiencies from four rectangular (r1 - r4), two triangular (t1,t2) and three circular (c1 – c3) QDSCs of varying size as given Table 2.1.

Figure 2.19. A liquid LSC is pictured containing a Lumogen Orange 240 sample (left) and Lumogen Yellow 170 sample (right). A silicon PV cell is placed adjacent to one side of the liquid LSC, at right angles to the incident beam.

Figure 2.20. Normalised absorption and emission spectra of (A) Lumogen Yellow 170, (B) Lumogen Orange 240 and (C) Lumogen Red 305. The shorter wavelength emitting dye(s) overlap significantly with the longer wavelength absorbing dye(s), resulting in a large degree of re-absorption in the LSC containing multiple dyes. The spectrum of the incident light is shown in (D).

Figure 2.21. Measured and predicted relative short circuit current densities ($J_{sc}$) for the dye samples listed in Table 2.2.

Figure 2.22. Ray-trace predicted $\eta_{opt}$ and loss mechanisms with varying refractive index, $n$. Analytically predicted $\eta_{opt}$ is also shown. Ideal absorption and emission spectra with no spectral overlap, a QD QY=100%, $\alpha_{mat} = 0 \text{ cm}^{-1}$, and $R_{mirror} = 1.0$ are assumed.

Figure 2.23. The dimensions of two LSC plates containing a Bayer Fluorescent Red Coumarin dye (a) and (b), and two plates containing Fluorescent yellow Coumarin dye (c) and (d).

Figure 2.24. Percentage of photons exiting; “1”:bottom surface, “2”:top surface, “3”:two long edges, and “4”:two short edges, of four different LSC plates. Predictions are shown for the DIT ray-trace model (blue bars), the ECN ray-trace model (green bars) and the ICL Thermodynamic model (red bars). Total predicted QY and matrix absorption losses are also shown by the bars labelled “S”.

Figure 3.1. Absorption spectrum 1 is the measured photon absorption spectrum of CdSe QDs with CdS/CdZnS/ZnS multi-shell coating (fabricated at Utrecht University). Absorption spectra 2-6, corresponding to higher QD doping concentrations, are extrapolated from absorption spectrum 1.

Figure 3.2. Square, right angled triangular, hexagonal and circular devices with $A_{cone} = 256 \text{ cm}^2$. External mirrors (M) may be placed at the “non PV” sides, as indicated here, or PV may be placed at all sides of the device perimeter.
Figure 3.3. Predicted concentration ratios, $C$, for devices of varying geometry and top surface aperture area, $A_{conc}$.

Figure 3.4. Relative cost per unit power for different geometries of varying top surface aperture area ($A_{conc}$) for two PV cell configurations - (a) PV at one side only, (b) PV at all sides of the perimeter. The price of the concentrator plate per m$^2$ is assumed to be 15 times less than that of PV per m$^2$ (i.e. $cost/actor = 15$).

Figure 3.5. Relative cost per unit power for different geometries of varying top surface aperture area ($A_{conc}$) for two PV cell configurations - (a) PV at one side only, (b) PV at all sides of the perimeter. The price of the concentrator plate per m$^2$ is assumed to be 30 times less than that of PV per m$^2$ (i.e. $cost/actor = 30$).

Figure 3.6. Relative photon spatial distribution along the normalised length of one side of the square, triangular and hexagonal QDSC plates. The “edge effect” is greatest for triangular geometry.

Figure 3.7. The distribution of intersection points of rays (emitted isotropically from the circle centre) with each of the polygon sides is most non-uniform in the triangular geometry.

Figure 3.8. Square QDSC 11 x 11 cm plate with variable plate thickness and PV cells attached at one side.

Figure 3.9. (a) shows the decrease in optical efficiency for thinner plates due to lower absorption efficiency and lower internal optical efficiency. However, the increase in geometric gain, as shown in (b), results in an overall increase in $C$ for thinner plates, as shown in (c), where, $C = \eta_{opt} G_{geom}$.

Figure 3.10. QDSC device with tapered geometry. The thickness of the PV side remains constant at 0.3 cm. The thickness of side 2 is varied to investigate the effect on the concentration ratio attained at the PV side.

Figure 3.11. For tapered geometry, the angle of propagation of a QD emitted photon is altered after multiple reflections at the sloped top and bottom surfaces. Therefore, photons emitted initially inside the angular range for total internal reflection may be lost through the top surface.

Figure 3.12. Concentration ratio, $C$, for varying thickness of “side 2”. The thickness of the plate at the PV side remains constant at 0.3 cm. The side labels are illustrated in Figure 3.10. The highest $C$ is obtained for a “side 2” thickness of 0.3 cm, i.e. for a plate of uniform thickness.

Figure 3.13. Fibre optics collect light along one side of each QDSC “solar leaf”. Light is transmitted via the fibre optics, through a 2nd stage concentrator to PV cells. $C_1$ and $C_2$ are the effective concentration ratios attained by the individual leaves and the 2nd stage concentrator, respectively. $C_0$ is the ratio of the cross-sectional area of the fibre optic bundle (FOB) to the area of PV cells.
Figure 3.14. (a) $C_1$ is the concentration ratio attained by the solar leaf, for varying leaf length, $L_{\text{Leaf}}$. (b) To allow comparison of the solar tree configuration with QDSC devices, the relative cost per unit power of equivalent QDSC plate sizes is calculated.

Figure 3.15. As a first approximation, each fibre optic (FO) is assumed to have a square cross section. The width of each FO, $W_{\text{FO}}$, is equal to the thickness of the leaf.

Figure 3.16. (a) $C_G$ is the CPC geometric concentration ratio, defining the ratio of CPC entry aperture, $a$, to exit aperture, $a'$. $\theta_a$ is the CPC acceptance angle. (b) A CPC with unity transmission for all incident angles $\leq \theta_a$ is considered.

Figure 3.17. (a) Angular distribution of light exiting fibre optic bundle (FOB). (b) $C_G$ is the ratio of the cross-sectional area of the FOB to the area of PV cells, and is determined by the particular CPC acceptance angle, $\theta_a$. (c) $k_2$ is the fraction of photons exiting the FOB which are within the CPC $\theta_a$. (d) $C_2$ is the effective concentration ratio of the CPC, given the angular distribution of incident photons shown in (a).

Figure 3.18. The relative cost per unit power of the solar tree with a 2nd stage CPC, for varying CPC acceptance angle, $\theta_a$, and fibre optic (FO) cost. The relative cost per unit power for a 1mm thick single-plate QDSC is given by the black line. At fibre optic costs < €0.01/m the solar tree attains costs per unit power of the same order as the single-plate QDSC.

Figure 3.19. The luminescent down-shifting (LDS) layer transforms the wavelength of short wavelength incident photons to wavelengths better matching the EQE response of the mc-Si PV cell attached under the LDS layer.

Figure 3.20. (a) Absorption and emission spectra of Coumarin-3-Carboxylic (blue), Perylene Lumogen Yellow 170, Perylene Lumogen Red 305 dyes. Also shown are the mc-Si cell EQE, and global solar spectrum measured at air-mass 1.5. (b) Absorption and emission spectra of two QD types; green emitting CdSe/ZnS QDs, and orange emitting CdSe/ZnS QDs.

Figure 3.21. EQE of reference mc-Si cell and the cell attached to luminescent down shifting (LDS) layers.

Figure 3.22. (a) In the partially covered luminescent down-shifting layer (PC-LDS), a reduced fraction of the layer is covered by PV cell strips. (b) The PV cell $J_{sc}$ is enhanced as short wavelength photons are shifted to longer wavelengths better matching the PV cell EQE (ray 2), and longer wavelength photons not absorbed by the dye pass through the PC-LDS layer to the PV cell (ray 1). In addition, there is a geometric gain as the layer aperture area is greater than the area of PV. Hence, emitted photons (rays 3 and 4) transmitted to the PV cell via TIR increase the cell $J_{sc}$ compared to a fully covered LDS layer. (c) An LSC configuration employing the same luminescent plate, external reflector, and PV cells as used in (a).
Figure 3.23. $J_{sc}$ (of the active cell area) increases as the fraction of the LDS layer covered by PV cells decreases. The effect is greatest for the red dye, as it has the broadest absorption range of the three dyes, as shown in Figure 3.20. Luminescent QY = 98% and $\alpha_{mat} = 0.02 \text{ cm}^{-1}$ are assumed.

Figure 3.24. (a) The concentration ratio, C, quantifying the relative increase in PV cell $J_{sc}$, (b) relative cost per unit power, and (c) power conversion efficiency, $\eta$, for LSC (red) and PC-LDS (dashed black) layer of varying plate size. Luminescent QY = 98% and $\alpha_{mat} = 0.02 \text{ cm}^{-1}$ are assumed. At a relative cost per unit power of 0.8, $\eta$ for the PC-LDS layer is ~double $\eta$ for the LSC, as indicated by the blue lines.

Figure 4.1. Absorption and emission spectra of three QD types. A: Green emitting QDs: CdSe/ZnS, peak emission wavelength ($\lambda_{em}$) = 488nm, Nanoco technologies. B: Orange emitting QDs: CdSe/ZnS, $\lambda_{em} = 605$nm, Evident technologies. C: NIR emitting QDs: CdSe multi-shell coating CdS/CdZnS/ZnS, $\lambda_{em} = 690$ nm, fabricated at Utrecht University, Netherlands, and the mc-Si PV cell photo-sensitivity spectral response.

Figure 4.2. Predicted optical efficiency ($\eta_{opt}$) of 6 x 6 x 0.3 cm QDSCs containing green, orange and NIR emitting QDs. $\eta_{opt} = \eta_{abs} \times \eta_{ret}$, where the retention efficiency, $\eta_{ret} = 1$-(escape cone loss).

Figure 4.3. Predicted concentration ratios, C, of 6.0 x 6.0 x 0.3 cm QDSCs containing green, orange and NIR emitting QDs of varying quantum yield (QY). The QDSCs concentration ratio is compared with that of a high QY dye LSC.

Figure 4.4. QDSC Concentration ratio for varying plate refractive index, $n$, and matrix material absorption coefficients, $\alpha_{mat}$.

Figure 4.5. For direct normal incidence, there is an increased average pathlength using a diffuse reflector(b) compared to a specular reflector(a), resulting in a higher absorption efficiency. Moreover, there is a probability that incident light will be reflected directly onto the PV cell using a diffuse reflector(d), but not using a specular reflector(c).

Figure 4.6. Predicted C for QDSC assuming external specular (red line) and Lambertian (dashed blue line) rear reflectors for (a) direct normal, and (b) isotropic diffuse incident insolation.

Figure 4.7. A spectrally selective reflector (SSR) with angle-independent reflectivity and ideal “cut-off” between reflection and transmission wavelength regions is modelled.

Figure 4.8. Predicted QDSC concentration ratio, C, for varying spectrally selective reflector layer cut-off wavelength, $\lambda_{co}$.

Figure 4.9. (a) Variation in concentration ratio, C, with increasing spectrally selective reflector (SSR) reflectivity. (b) Top surface losses decrease with higher SSR reflectivity, however, rear reflector ($R_{Mirror} = 0.98$) losses increase.
Figure 4.10. Predicted concentration ratio, $C$, for increasing rear reflector reflectivity, $R_{\text{Mirror}}$. The QDSCs modelled assume a near-ideal spectrally selective reflector (SSR) top layer with reflectivity of 0.999. Relatively small decreases in $R_{\text{Mirror}}$ significantly affect the potential gain in $C$ attained on an SSR layer. The results highlight the importance of utilizing a highly reflective rear reflector when measuring the performance of any SSR top layer.

Figure 5.1. The measured mean hourly global horizontal irradiance, $G_h$, and predicted mean hourly horizontal beam irradiance, $B_h$, and diffuse irradiance, $D_h$, for the months January and June, 2008.

Figure 5.2. The position of the sun is defined by the solar zenith angle, $\theta_s$, and the solar azimuth angle, $\gamma_s$. A tilted planar surface has tilt angle, $\beta$, and surface azimuth angle $\gamma_p$.

Figure 5.3. The solar path, describing hourly solar elevation angle ($90^\circ - \theta_s$) and azimuth angle, $\gamma_s$, for the 15th day of months January to June, at a location latitude 53° North.

Figure 5.4. Beam irradiance on surface with varying tilt angle, $\beta$ and azimuth angle $\gamma_p$, calculated using eqn. 5.10, with a beam irradiance on the horizontal of 1000 W m$^{-2}$. The solar zenith angle, $\theta_s$, and azimuth angle, $\gamma_s$, are arbitrarily set to 60° and 180°, respectively.

Figure 5.5. The Perez model of the sky dome divided into three geometric zones; (i) the circumsolar zone, (ii) the horizon band, and (iii) the remainder of the hemispherical sky dome.

Figure 5.6. The diffuse spectral irradiance distribution (blue) is obtained by subtracting the direct normal (red) from the global (black) American Society for Testing and Materials, G-173-03, spectral irradiance.

Figure 5.7. (a) Annual in-plane insolation for varying $\gamma_p$ and $\beta$. (b) Fraction of the maximum annual in-plane insolation available at varying $\gamma_p$ and $\beta$.

Figure 5.8 Annual hourly global horizontal irradiance, $G_h$, (red + blue) measured at a location in Dublin, Ireland, and the calculated beam and diffuse components, $B_h$ (blue) and $D_h$ (red).

Figure 5.9. Diurnal variation of annual average hourly (a) $I_{nc,PV_c}$ and $I_{nc,PV}$ and (b) concentration ratio, $C$, for a QDSC inclined at 30°. The predicted $C$ for the same QDSC assuming the standard AM1.5G spectrum at normal incidence is just 2.8, indicated by the dashed black in line in (b).

Figure 5.10. Relative QDSC monthly and annual energy output with varying tilt angle, $\beta$.

Figure 5.11. Relative annual QDSC energy yield for; 1: A fixed QDSC tilt angle ($\beta=30^\circ$), 2: $\beta$ adjusted each month to the monthly optimum $\beta$, and 3: $\beta$ adjusted hourly to hourly optimum $\beta$.

Figure 5.12. Variation in QDSC relative annual energy yield with plate refractive index, $n$, and absorption coefficient, $a_{\text{mat}}$. 

10
Figure 5.13. Reflectance from MgF$_2$ thin-film anti-reflection coating on substrate of refractive index 1.7, for varying angles of incidence, $\theta$, thin-film thickness, $t_r$, and wavelength of incident light, $\lambda$.  

Figure 5.14. (a) External reflection losses (% of total incident photons) and (b) relative QDSC annual energy yield for varying MgF$_2$ thin-film ARC thickness, $t_r$.  

Figure 6.1. The cost of attached PV cells can be reduced if bi-facial cells are used, with the bi-facial cells attached to two sides of each QDSC plate of optimum dimensions. Multiple plates are packed adjacent, in a chequered configuration, to form a larger panel of required size.  

Figure 6.2. Absorption and emission spectra of PbS QDs ($\lambda_{em} = 905$ nm, Evident technologies)  

Figure 6.3. (a) Predicted C and (b) cost per W$_p$ for QDSCs of varying top surface aperture area, $A_{conc}$, and QD quantum yield (QY).  

Figure 6.4. Minimum QDSC cost per W$_p$ for varying plate costs (a), (b), and (c), varying QD quantum yield (QY), and varying bi-facial PV cell costs. A cost of €2/W$_p$ is assumed for conventional silicon PV modules.
List of Tables

Table 1.1. Power conversion efficiency, $\eta$, for LSCs of varying configurations. 26

Table 2.1. Dimensions and geometric gain ($G_{\text{geom}}$) of nine QDSCs of varying shape and size (Rowan et al., 2007). 68

Table 2.2. Luminescent dyes of varying concentrations and the dye mixes used in liquid LSC tests. 72

Table 2.3. Comparison of measured and predicted $J_{\text{sc}}$ values of the four dye LSC plates. 78
1 Introduction to quantum dot (luminescent) solar concentrators

1.0 The need for renewable energy sources

In 2007, 81% of world primary energy demand was met by coal, oil and gas resources - 26%, 34%, and 21% respectively - (International Energy Agency, 2009). Global primary energy demand continues to grow with an increasing human population and rising living standards. On average, demand increased by 2% per annum between 1971 and 2002, with higher percentage increases occurring in recent years (Goswami, 2007). Assuming a continued 2% annual increase, demand will have tripled by 2065. All proven global oil and natural gas reserves are predicted to last only until 2048 (Goswami, 2007) and 2065 (Breeze, 2005), respectively. Although coal reserves will last much longer, CO₂ emissions produced in coal-burning power stations make it an unviable option as the primary fuel for electricity generation. Nuclear power generation is one potential solution to fill the gap left by depleting fossil fuel reserves. However, finite resources of Uranium, currently the primary nuclear fuel used in reactors, mean that nuclear power is unlikely to be able to provide a significant proportion of energy needs in the near future (Kreith and Goswami, 2007). Furthermore, nuclear resources are concentrated in a limited number of regions in the world which would mean a poor security of supply for most of the world’s countries if they become overly reliant on nuclear fuels. Due to the finite resources of fossil fuel and nuclear reserves, renewable energy technologies
(RETs) must provide an increasing proportion of future energy needs\(^1\), if the world's population are to expect a secure and sustainable developed society. Furthermore, international commitments to reducing greenhouse gas emissions may mean that countries face financial penalties for failing to meet certain RET targets. For example, the European Union has set a target of 20% of primary energy demand to be met by RET by 2020, with financial penalties for member states failing to meet final and intermediate targets across each energy sector.

Electricity generation currently accounts for over 30% of global primary energy demand (Kreith and Goswami, 2007). In 2006, RETs provided 18% of electricity supply, the vast majority of which was hydro-electric, as shown in Figure 1.1 (International Energy Agency, 2009). Photovoltaic (PV) technologies supplied 0.015%. The solar energy resource available is immense, however. The solar energy received by the earth in one hour could meet the current global annual primary energy demand (Morton, 2006). Solar technologies, both direct (PV, solar thermal) and indirect (wind, wave and biomass) can meet a significant proportion of future electricity needs if expected manufacturing cost and technological developments materialise, and the political will on a global scale is present (deVries et al., 2007, Resch et al., 2008). This chapter introduces the luminescent solar concentrator (LSC), a device which can potentially reduce the cost of PV electrical power generation and, therefore, further the growth in installed PV capacity. An overview is given of the current state of development of LSCs and of quantum dot luminescent solar concentrators.

\(^1\) along with developments in energy efficiency and conservation
Figure 1.1. Supply of global electricity by fuel type in 2006 (IEA, 2009). Renewable energy technologies accounted for ~18%, of which hydro-electric was the predominant source. Photovoltaics (PV) accounted for 0.015% of global supply.

1.1 Photovoltaics

Global photovoltaic production has grown by an average of 33% per annum in the period 1993 – 2007, as shown in Figure 1.2 (Observ'ER, 2008). Silicon wafer, or “1st generation” PV technologies currently account for 90% of the market share of current PV production (Bagnall, 2008). Production costs are typically quoted per Watt peak ($W_p$) generated under standard test conditions (STC). Costs have decreased as production capacity and scale has increased and manufacturing methods improved. At an average module production cost of US$ 2.75 / $W_p$ (Margolis et al., 2006), this is too high for PV to compete with conventional energy sources in most
locations worldwide, in the absence of government capital grants or feed-in tariff subsidies. The two principal barriers prohibiting more widespread uptake of PV technology are;

(i) the low energy intensity and variation in energy supply caused by diurnally and seasonally changing solar radiation, and by changing atmospheric and air-mass conditions.

(ii) the manufacturing and installation costs of a solar panel array and balance-of-system components.

Figure 1.2. Global PV production (MWp) increased annually by an average of 33% in the period 1993-2007 (Observ'ER, 2008).

"2nd generation" PV technologies such as CdTe (Cadmium telluride) and CIGS (Copper indium gallium selenide) cells can reduce manufacturing costs, as total material costs are lower to produce these thin-film cells. For example, FirstSolar currently produce thin-film CdTe modules at ~US$ 1/Wp (FirstSolar, 2009). Another approach to reducing the cost of PV electricity is to concentrate solar energy on to a reduced area of solar cell, thereby reducing the material costs per unit power
produced. Examples of different concentrator types, which have been developed to date for use with PV cells, are outlined in section 1.2

1.2 Optical concentrators of solar energy

The theoretical maximum concentration ratio of an optical concentrator spatially receiving uniform insolation (Winston, 1976, Smestad et al., 1990) is given by:

\[ C \leq \frac{\sin^2 \theta_{\text{exit}}}{\sin^2 \theta_{\text{entry}}} = \frac{1}{\sin^2 \theta_{\text{entry}}} \quad \text{(assuming exit angle, } \theta_{\text{exit}}, = 90^\circ) \quad 1.1 \]

where \( \theta_{\text{entry}} \) and \( \theta_{\text{exit}} \) are the incident angles at the entry and exit apertures of the concentrator, respectively, as shown in Figure 1.3.

Figure 1.3. Optical concentrator with reflective surfaces (Smestad et al., 1990). The maximum concentration ratio is given by eqn. 1.1.
If the concentrator is made of a medium with refractive index \( n \), and the solar absorber at the exit aperture is immersed in the same medium, it can be shown from Snell's law that the maximum \( C \) is enhanced by a factor of \( n^2 \) (Smestad et al., 1990).

\[
C \leq n^2 \frac{\sin^2 \theta_{\text{exit}}}{\sin^2 \theta_{\text{entry}}}
\]

For \( n = 1.5 \), theoretical \( C \) of \( 10^5 \) are possible (excluding external Fresnel reflection losses), limited by the sun disk's angular size of \( \sim 0.27^\circ \).

Many reflector and lens based optical concentrators, using solar tracking devices, have been designed demonstrating very high concentration ratios. The fraction of the diffuse component of solar radiation accepted by these concentrator systems is inversely proportional to the concentration ratio. In climatic regions where overcast weather conditions are common, the diffuse component of solar radiation may be greater than the direct component. For example, as shown in section 5.1.1, the diffuse and direct components of the measured annual global insolation on a horizontal surface at a particular site in Dublin, Ireland, were 77% and 23%, respectively. Optical concentrators with a high concentration ratio, \( C \), are not practical in climates where the diffuse component is predominant. Optical concentrators with lower \( C \) can accept a higher proportion of the diffuse component. Some particular examples are described below in sections 1.2.1 and 1.2.2. It should be noted, however, that all optical concentrators are subject to the constraint given by eqn. 1.2, whereby increasing the acceptance angle (to accept diffuse light) decreases the maximum possible concentration ratio attainable by the device.
1.2.1 Compound parabolic concentrators with high acceptance angles

The compound parabolic concentrator, CPC, (Hinterberger and Winston, 1966; Winston, 1974) can be optimised, whereby lowering the CPC geometric concentration ratio results in a higher proportion of the diffuse component of incident solar radiation being accepted. A trade-off exists between increasing the geometric concentration ratio, C, and decreasing the acceptance angle. CPCs with a high angular acceptance can operate efficiently without the need for (and the additional capital and maintenance cost of) solar tracking mechanisms. Mallick et al. have demonstrated solar energy concentration ratios, C, of 1.62 and 2.01 for building-integrated, wall façade, asymmetrical CPCs with geometric concentration ratios of 2 and 2.45, respectively (Mallick et al., 2006; Mallick and Eames, 2007). The respective acceptance half angles of 50° and 37° mean that a significant proportion of the diffuse component of incident solar radiation is collected by both devices, and the direct component can be collected throughout the day without solar tracking. A reduction of 40% in cost per Wp, compared to a reference non-concentrating panel utilizing the same solar cells, is estimated for the CPC panel with acceptance half angle of 37° (Mallick and Eames, 2007).

1.2.2 Flat plate optical concentrators of diffuse radiation

As noted in section 1.2, the higher the required optical concentrator acceptance angle, the lower the possible C. From eqn. 1.2, the maximum C attainable for isotropically diffuse light (0 ≤ θ₁ ≤ 90°) is \( n^2 = 2.2 \), assuming \( n = 1.5 \). Di-
electric transparent plates with Lambertian or v-grooved rear reflecting surfaces (Smestad and Hamill, 1984, Uematsu et al., 2001) can be used as flat plate static concentrators of direct and diffuse radiation. Incident photons reflected at the rear reflector are trapped within the plate by total internal reflection and transmitted to a reduced area (relative to the concentrator entry aperture area) of PV cell, as shown in Figure 1.4(a). Measured optical efficiencies, over all angles of incidence, range from 60% to 85% for a device with a geometric concentration ratio of 2.0. Potential module costs per Wp are estimated at 15% lower than a non-concentrating PV module utilizing the same PV cells (Weber et al., 2006).

Figure 1.4. (a) Dielectric flat-plate (Smestad and Hamill, 1984), utilising a Lambertian rear reflector and (b) wedge-shaped (Maruyama and Osako, 1999) optical concentrators. In (a) and (b), incident rays may be reflected at an angle within the angular range for total internal reflection to occur and is guided to the exit aperture at plate edges.

Other static concentrator designs exist, which utilise reflection and refraction, to concentrate light over a wide incident angular range, e.g. the wedge shaped concentrator (Maruyama and Osako, 1999) shown in Figure 1.4(b). The $n^2$ concentration limit for diffuse radiation applies to all such optical concentrators. This limit does not apply, however, to luminescent solar concentrators, LSCs (Smestad et al., 1990), shown in Figure 1.5. Therefore, much higher diffuse radiation concentration ratios are possible with non-optical LSCs than is the case for optical...
concentrators. In this thesis, the potential optical performance of LSCs is analysed using ray-trace modelling.

Figure 1.5. Flat-plate luminescent (non-optical) solar concentrator without PV cells or external reflectors attached.

1.3 Luminescent solar concentrators

Luminescent solar concentrators, LSCs, (Weber and Lambe, 1976; Goetzberger and Greubel, 1977) are non-optical concentrators which can concentrate both direct and diffuse radiation. As incident insolation passes through an LSC device matrix consisting of a flat polymer plate doped with a luminescent dye, as shown in Figure 1.6, it is absorbed by the dye. Light emitted by the luminescent dye in the device matrix is transmitted by total internal reflection (TIR) to the plate edges, where PV cells are attached. The solar energy concentration effect arises as the exit aperture surface area at the plate edges is much smaller than the top surface aperture area. External reflectors may be placed adjacent and parallel to plate surfaces to reflect light that may outside the angular range for TIR.
Figure 1.6. Schematic of LSC without PV cells or external mirrors attached. Incident photons may be externally reflected [1], or transmitted into the plate. Photons may be absorbed by a dye molecule [2] in the plate, or transmitted through the plate [3], depending on the dye absorption coefficient and the pathlength through the plate. Energy absorbed by the dye molecule may be re-radiated at a longer wavelength within the angular range for total internal reflection to occur [4], or within the “escape-cone” of the plate [5]. An absorption event may result in no luminescence from the dye molecule [6] whereby the absorbed energy is converted to heat. Dye emitted photons may be absorbed by another dye molecule within the plate (so-called “re-absorption”) [7], after which [4], [5], or [6] may ensue. Photon attenuation also occurs within the plate, and photons within the escape-cone may be reflected or refracted at plate boundaries.

Advantages of luminescent solar concentrators include;

- The concentration limits of optical concentrator systems do not apply (Smestad et al., 1990). Therefore, LSCs can concentrate both the direct and diffuse components of solar radiation.
- Solar tracking is not required for LSCs to operate efficiently.
- The flat-plate structure makes them suitable for building integrated applications.
- The overall capital cost of the concentrator components is low, as shown in section 6. Richards et al. (2007) estimated LSC plate (without PV cells) production costs to be potentially as low as €24/m², ~15 times lower than
conventional crystalline silicon PV modules. Therefore, the LSC has the potential to significantly reduce the cost of PV electrical power generation.

- The cells receive light collected from a large plate area, so they are less sensitive to partial shading effects which can cause a severe decrease in PV cell power output and damage cells (Sakuta et al., 1994).

- High energy incident photons are down-shifted in the host matrix material by the luminescent species. Photons emitted by the luminescent species are better matched to the band gap energy of the attached PV cell, so thermalisation at the cell is reduced.

- Stacked layered devices may be used, where each layer collects a different part of the solar spectrum and different cells are attached to each layer (with the band-gap of the cell matched to the emission wavelength of the luminescent species in each layer), theoretically allowing higher overall power conversion efficiency than a single band-gap cell (Goetzberger and Wittwer, 1981; Goldschmidt et al., 2006).

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Down-shifting is defined distinctly from the process of down-conversion. In the former case, energy is lost in the form of heat when high energy photons are absorbed. In the latter case multiple low energy photons are emitted following the absorption of a high energy photon, i.e., there is no loss of light energy.
1.4 High efficiency LSCs and performance comparative measures

The retention efficiency of an LSC plate (i.e. the fraction of emitted photons trapped within the plate by TIR) is a function of the plate refractive index, \( n \), as is shown in section 2.2.6. A typical value of \( n \) in LSCs is \( \sim 1.5 \). It can be shown that, in this case, the retention efficiency is 75%. The overall LSC power conversion efficiency, \( \eta \), is limited by the power conversion efficiency of the attached PV cell, \( \eta_{pv} \). In an idealised LSC (assuming external reflection losses and transport losses within the plate to be zero) with a monocry stalline silicon cell attached (where \( \eta_{pv} = 20\% \)), LSC \( \eta \) could, therefore, approach 15\% (i.e., 75\% of 20\%). However, due to device loss mechanisms, which are detailed in section 1.3, real \( \eta \) are typically much lower than 15\%. High \( \eta \) LSCs reported in the literature are listed in Table 1.1. While a viable LSC device should have an acceptably high \( \eta \), it is important not to compare two devices solely by the respective \( \eta \). It is also important to consider the LSC geometric gain, which is defined as the ratio of the top surface aperture area to the area of attached solar cell. For example, consider LSC 7(a) and LSC 7(b), listed in Table 1.1, fabricated using the same plate materials and solar cells;

- LSC 7(b) has a geometric gain, \( G_{geom} \), of 2.5 and \( \eta \) is 7.1\%, the record LSC efficiency currently quoted in the literature. LSC 7(a) has \( G_{geom} \) of 10 and \( \eta \) is reduced to 4.6\%. Owing to transport losses within the plate, LSC efficiency is inversely proportional to \( G_{geom} \). However, larger LSCs have higher concentration ratios. Consequently, LSC 7(a) may be a more optimal device, despite the lower efficiency attained. Therefore, \( \eta \) is only a useful comparative measure of two LSCs if \( G_{geom} \) are approximately equivalent.

The PV cell type varies between LSCs, thereby affecting the overall \( \eta \), for example;
- LSCs 2(a) and 2(b) have $\eta$ of 2.1% and 2.5%, employing Si and GaAs cells, respectively. Currie et al. (2008) estimate that GaAs and GaInP costs could reduce to ~US$50/W_p at large scale production. This is an order of magnitude higher than silicon PV cells. LSC performance should therefore be evaluated taking into account realistic cell costs, and not only $\eta$ attained.

It is also important to take into account which external reflectors are used, for example;

- LSCs 4(a) and 4(b) are equivalent in dimensions and cell type used, but 4(b) employs a spectrally selective reflector layer to minimise escape cone losses. $\eta$ increases from 2.6% to 3.1% with the inclusion of the layer.

The general approach adopted in this research is to quantify LSC concentration ratio, $C$, as a function of device size, rather than quantify $\eta$ at a single particular device size. From $C$, the power output can be calculated and, under certain cost assumptions, the cost per $W_p$ (either relative or absolute) determined. Any two LSC configurations can thus be compared (or a given LSC compared with a conventional PV cell) by its cost per unit power output.
<table>
<thead>
<tr>
<th>Configuration</th>
<th>#</th>
<th>$G_{geom}$</th>
<th>Dye materials</th>
<th>PV cell type</th>
<th>$\eta$ (°%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-plate</td>
<td>1</td>
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<td>KF-241.</td>
<td>Si</td>
<td>2.3</td>
<td>Sidrach de Cardona et al., 1985b</td>
</tr>
<tr>
<td>single dye</td>
<td>2</td>
<td>33.3</td>
<td>Not given.</td>
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<td>2.1</td>
<td>Wittwer et al., 1984</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(b) GaAs</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>16.7</td>
<td>Lumogen Red 305.</td>
<td>Si</td>
<td>2.4</td>
<td>van Sark et al., 2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(a) BA241.</td>
<td>GaInP</td>
<td>2.6</td>
<td>Goldschmidt et al., 2009</td>
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<td></td>
<td></td>
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<td>(b) BA241+ Rugate spectrally</td>
<td>GaInP</td>
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<td>reflector top layer</td>
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<td>5</td>
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<td>DCJTP.</td>
<td>GaInP</td>
<td>5.9*</td>
<td>Currie et al., 2008</td>
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<td>(a) 10</td>
<td>Lumogen Red 305 + Coumarin</td>
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<td>Si</td>
<td>4.4†</td>
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<td>GaInP</td>
<td>5.5*</td>
<td>Currie et al., 2008</td>
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<td></td>
<td></td>
<td>(b) 45</td>
<td>Rubrene + DCJTB. FRET</td>
<td>GaInP</td>
<td>4.7*</td>
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<tr>
<td></td>
<td>10</td>
<td>16.7</td>
<td>Not given</td>
<td>GaAs</td>
<td>4.0</td>
<td>Wittwer et al., 1984</td>
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<td>GaInP</td>
<td>6.7</td>
<td>Goldschmidt et al., 2009</td>
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Table 1.1. Power conversion efficiency, $\eta$, for LSCs of varying configurations.  
†model prediction. *measured edge photon flux used to predict $\eta$ from theoretical PV cell data. FRET: Förster resonant energy transfer. DCJTB: 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran.
1.4.1 Thin-film LSCs

Thin-film LSCs, shown in Figure 1.7, consist of a highly doped thin-film (< 0.1 mm) polymer layer supported on a transparent polymer or glass substrate. One motivation for thin-film LSCs being developed was the theory that luminescence is transported to the PV cell primarily through the highly transparent substrate plate, thereby reducing re-absorption losses (Reisfeld et al., 1988c). However, photons transported by TIR still must pass through the more heavily doped thin-film layer. Assuming the probability of absorption over any distance is given by the Beer-Lambert law, re-absorption losses should be equivalent in thin-film LSC and homogeneously doped LSC plate configurations. Bose et al. (2007) showed that both configurations attained approximately equal efficiency when the absorbance was equivalent in each configuration.

![Figure 1.7. Thin-film LSCs consist of a highly doped thin-film polymer layer supported on a transparent substrate.](image)

The most interesting characteristic of thin-film LSCs, however, is that (non-radiative) Förster resonant energy transfer (FRET) may take place between different dyes if the distance between dye molecules is small (Swartz et al., 1977). This technique has been used in LSCs comprised of multiple thin-film layers, each doped with a distinct dye, on glass or polymer substrates (Bailey et al., 2007; Currie et al., 2008). These thin-film LSCs partly overcome the problem of re-absorption and associated escape-cone losses, which occur in multiple dye homogeneously doped
LSCs (Burgers et al., 2006; Richards and McIntosh, 2006; Kennedy et al., 2008b). The thin-film LSC 9 (b) listed in Table 1.1, which has an efficiency of 4.7% at a large plate size ($G_{\text{geom}}$), shows that this is a very promising approach for achieving efficient LSCs with broadband absorption of the solar spectrum.

1.5 LSC stability and absorption range limitations

For viable LSCs to be realised, dye absorbance, luminescence, and the matrix material transmittance all need to be stable, ideally over the lifetime of the attached solar cells (>20 years). A dye LSC containing a Perylene (Lumogen F Red) exhibited <3% absorbance degradation after 595 days in outdoor testing (van Sark et al., 2008). The change in electrical output of this plate over time was not measured, however. A separate Lumogen F Red 305 sample which showed almost zero degradation in absorbance after 205 days outdoor testing exhibited a decrease of ~15% in short circuit current over the same time period, showing that stability measurements of absorbance alone are not sufficient. Suggested explanations for the observed decrease in short circuit current were i) a possible decrease in the dye luminescent quantum yield, and/or ii) an increase in transport losses caused by a small increase in matrix absorption (van Sark et al., 2008). A study by Currie et al. (2008) found an 8% decrease in edge luminescence for an LSC after accelerated indoor testing, where the integrated solar flux corresponded to an equivalent of ~3 months outdoor exposure. However, the authors expected that lifetimes would approach organic LED standards of lifetime of 10 to 100 years, when samples
incorporate a UV filter as is the case with organic LED devices. Stability of dye LSCs currently remains a significant barrier to realizing viable devices.

The absorption range of current dye LSCs is limited to the visible range of the solar spectrum, as illustrated in Figure 1.8, and therefore only a fraction of the available solar spectrum is converted to electricity. Near infra-red (NIR) absorbing dyes are not suitable for inclusion in LSCs owing to low quantum yields and poor stability (Friedman and Parent, 1987; Richards and McIntosh, 2006; Rowan et al., 2008). Semiconductor nanocrystals, or quantum dots (QDs), can potentially overcome both stability and absorption range limitations of luminescent dyes as discussed in section 1.6.

![Figure 1.8](image.png)

Figure 1.8. The absorption range of current dye luminescent solar concentrators (LSC) is limited to the visible range of the solar spectrum, and therefore only a fraction of the available solar spectrum is converted to electricity. Quantum dot luminescent solar concentrators, can potentially overcome absorption range limitations (and stability limitations) of organic dye LSCs.
1.6 Quantum Dot Solar Concentrators

A Quantum Dot Solar Concentrator, QDSC, (Barnham et al., 2000; Chatten et al., 2003; Gallagher et al., 2004; Schüler et al., 2007) employs quantum dots (QDs) rather than a luminescent dye in the device matrix. One advantage of using QDs is the ability to spectrally tune a device by varying the dot size to collect specific wavelengths in the solar spectrum. Secondly, as QDs are composed of crystalline semiconductor materials, they should exhibit a greater resistance than dyes to degradation in ultra-violet light (Chatten et al., 2003). For an LSC with Si cells attached, the ideal single luminescent species would absorb light from the UV region of the solar spectrum up to ~900 nm and emit at ~950 nm, just below the band gap of silicon (Richards, 2007). PbS QDs can be tuned to exhibit the required broad absorption and NIR emission by controlling the QD size. However, commercially available PbS QDs currently have low quantum yields, QY, of ~10% (Rowan et al., 2008), where QY is defined as the ratio of photons emitted to photons absorbed by a QD.

The optical efficiency of currently fabricated QDSCs, incorporating visible-emitting QDs, has been limited by reduced QY and by large overlaps between QD emission and absorption spectra (Hyldahl et al., 2009; Rowan et al., 2008; Sholin et al., 2007). Spectral overlap results in QD-emitted photons being re-absorbed in the plate before reaching the PV cell, giving both higher escape cone losses and higher QY losses. More efficient QDSCs would result if spectral overlap could be reduced. Patanè et al. (2000) and Chatten et al. (2003) have shown that the emission spectrum

iii (The term “LSC” used within this work refers both to QDSCs and organic dye LSCs, unless specified otherwise. The term “QDSC” specifically refers to QD devices, however many results/conclusions for QDSCs given are also applicable, in general, to dye LSCs)
peak wavelength is related to the spread of QD sizes in a sample, which can be determined during the growth process. One objective of the present research is to quantify the realistic potential performance of QDSCs, incorporating current commercially-available QD types subject to the re-absorption limitations arising from spectral overlaps between QD emission and absorption spectra.

1.7 Modelling LSCs through a Monte-Carlo ray-trace approach

Monte-Carlo ray-trace modelling is used to analyse LSC performance. The advantages of adopting a ray-trace approach are a) it allows varying plate geometries to be modelled, and b) it can be combined with solar radiation models to investigate diurnal and annual variations in electrical output for varying device configurations. Within the ray-trace model, a Monte-Carlo method, detailed in section 2, is used to determine the path and eventual outcome of each incident ray vector representing an incident photon. In doing so, LSC loss mechanisms can be quantified for a given set of device parameters. Analytic, deterministic expressions have previously been derived to quantify individual LSC loss mechanisms (Goetzberger and Wittwer, 1981; El-Shaarawy et al., 2007). In QDSCs, in particular, it is critical to accurately account for re-absorption losses as large spectral overlaps exist between QD photon emission and absorption spectra, and luminescent QYs are currently significantly lower than the most efficient organic dyes. Re-absorption losses can be calculated analytically in the limit of zero matrix material absorption and scattering losses.
(Batchelder et al., 1979). A Monte-Carlo model allows all interdependent, competing loss mechanisms to be quantified for any given set of device parameters.

1.8 Research objectives

The primary research objectives are outlined below in sections 1.8.1-1.8.5.

1.8.1 Model development and validation;

The principal objectives of this section are to;

- Implement a multi-parameter LSC model using a Monte-Carlo ray-trace approach.
- Validate model predictions for varying LSC size, shape, doping concentration (of single/multiple species), and matrix material refractive index, through comparison with measurements from previously fabricated LSCs and with predictions from other modelling techniques.

1.8.2 Investigation of QDSC geometries

Quantifying the net effect of varying device geometry on QDSC solar energy concentration ratios, $C$, is a non-trivial problem owing to the multiple, interdependent, competing loss mechanisms in the device. The optimum geometry is
ultimately that which minimises the costs per unit power generated. The principal objectives of this section are to;

- Analyse the effect of varying 2-D planar geometry on C using the ray-trace model.
- Determine the optimum geometry type and optimum plate size for any given set of device parameters.
- Investigate 3-D geometries to determine whether re-absorption losses within the plate can be reduced.

1.8.3 Quantifying QDSC performance for varying material properties

The effect of varying QD, matrix material, and external reflector optical properties on QDSC performance can be analysed using the model. While maximizing QDSC efficiency ultimately remains an experimental challenge, modelling can be used to investigate under what circumstances certain goals are attainable. The principal objectives of this section are to;

- Quantify the realistic potential performance of QDSCs, incorporating current commercially-available QD types.
- Investigate QDSC performance for varying external reflector types.

1.8.4 Outdoor modelling and annual energy yield predictions

The ray-trace model can be combined with solar radiation models to investigate the outdoor performance of a QDSC. The concentration ratio of QDSCs varies diurnally
and seasonally due to variation in incident insolation spectra and in incident angle
distribution. The principal objective of this section is to;

- Analyse the effect of varying device parameters on annual energy yields and,
in particular, quantify the effect of tilt angle, plate refractive index, and external anti-reflective coating layers on device energy yield.

1.8.5 Quantum dot luminescent down-shifting layers

PV cell short circuit current, $I_{sc}$, can be enhanced through the application of a luminescent down-shifting (LDS) layer. In the literature, quoted mc-Si cell $I_{sc}$ enhancement predictions for LDS layers incorporating quantum dots are higher than that for LDS layers incorporating organic dyes. The principal objectives of this section are to;

- Investigate, using the ray-trace model, whether the optical properties of QDs make them more suitable candidates than organic dyes for incorporation in LDS layers.

- Quantify the electrical output of “partially-covered” LDS layers, of varying sizes and PV cell areas.
1.9 Chapter conclusions

- Due to the finite resources of fossil fuel and nuclear reserves, renewable energy technologies must provide an increasing proportion of future energy needs, if the world’s population are to expect a secure and sustainable developed society.

- Luminescent solar concentrators, LSCs, can potentially reduce the cost of PV electrical power generation and further the growth in installed PV capacity.

- LSCs can concentrate both the direct and diffuse components of solar radiation. Solar tracking is not required for LSCs to operate efficiently. The flat-plate structure makes them suitable for building integrated applications.

- Stability of dye LSCs currently remains a significant barrier to realizing viable devices. The absorption range of current efficient dye LSCs is limited to the visible range of the solar spectrum. Semiconductor nanocrystals, or quantum dots (QDs), can potentially overcome absorption range and stability limitations characteristic of dye LSCs.

- A validated ray-trace model can be used to investigate the effect of varying QD, geometry, and matrix material types on QDSC costs per unit power output and energy yield.
1.10 References


2 Ray-trace modelling of luminescent solar concentrators

2.0 Introduction

Modelling techniques enable LSC loss mechanisms to be quantified and optimised devices to be designed. The ray-trace modelling approach (Heidler et al., 1982; Carrascosa et al., 1983; Reisfeld et al., 1988b; Gallagher et al., 2004; Burgers et al., 2005; Bose et al., 2007; Kennedy et al., 2007b; Richards and McIntosh, 2007; Schüler et al., 2007) allows the multiple interdependent, competing LSC loss mechanisms to be accounted for, including losses arising from multiple re-absorption events. While commercial ray-trace packages are available, none can calculate absorption of traced rays by a luminescent species (at variable doping concentrations), nor trace rays emitted isotropically subsequent to an absorption event. Therefore, a Monte-Carlo ray-trace model was developed. Gallagher et al. (2004) previously developed a ray-trace model allowing the optical efficiency of rectangular QDSC devices to be quantified under varying input spectral irradiance. In the model, the plate is divided into a discrete number of zones and individual QD locations are assigned at random, in each zone, according to the specified QD doping level. Due to the computation time required for larger plate sizes the model was revised, removing the stored QD locations and introducing a background probability calculation to determine QD photon absorption events. This approach is not as computationally intensive, and allows more flexibility for device modelling, e.g. modelling of plates containing multiple luminescent species, matrix material light scattering approximation, and varying plate geometries of large sizes.
The main algorithms required to implement the model engine, i.e. ray reflection, refraction, absorption, emission, matrix material absorption and scattering, are outlined in section 0. Device concentration ratios are determined using the ray-trace model output and the attached photovoltaic (PV) cell spectral response curves. To validate the model, predictions are compared with a range of experimental measurements in section 2.2;

- Electrical output predictions are compared with measurements from fabricated QDSCs of varying size, shape, and QD doping concentration.
- Predicted spectral output for varying input light position on the QDSC top surface aperture is compared with observed spectra.
- Ray-trace predicted loss mechanisms (escape cone and external reflection losses) are compared with analytical predictions.
- Predicted photon fluxes emerging at each plate surface are compared with those of two other LSC models.

The validation tests show that the ray-trace approach provides an accurate tool for quantifying device loss mechanisms, and predicting QDSC output for any given set of material parameters. The model can be used to optimise device design in terms of geometry, luminescent species, matrix material, external reflector, and PV cell types.
2.1 Monte-Carlo ray-trace modelling

In the model, an incident photon, represented by a ray vector, is traced through the QDSC until it is lost from the system or transmitted to the PV cell. A Monte-Carlo method, described by the flow diagram in Figure 2.1, is used to determine the photon count optical efficiency ($\eta_{\text{opt}}$) and the output spectrum obtained at the PV cell, for a given monochromatic input light source at a random starting point on the top surface. Extensive MATLAB code was required to implement the model engine described in diagram in Figure 2.1.

At each branching point in the flow diagram, randomly generated numbers are tested against the respective calculated probabilities to determine whether the event ensues or not. A large number of rays of a given initial wavelength and angle are traced through the system from the same starting point, and the outcome of each ray is determined. This approach is then extended to model a non-monochromatic input light source incident on the entire QDSC top surface aperture. The algorithms behind each part of the model are described in detail in sections 2.1.1 to 2.1.6.
Reflected Ray intersects top surface. Either transmitted or reflected?

Reflect at external mirror?

Transmitted out rear/side surface

Determine next boundary intersection point

Transmitted

Reflected

Either transmitted to PV, out top surface, or out rear/side surface?

Fresnel reflection

Transmitted

Either Fresnel reflection, or transmitted at boundary?

TIR

No TIR

Transmitted to boundary or absorbed by QD, attenuated by matrix material, or scattered elastically by matrix material?

Absorbed by QD

Passed to PV or heat

Attenuated by matrix material

Photon emitted by QD?

Determine photon emission wavelength and angles.

Photon emitted

Photor not emitted, due to QD defect

Figure 2.1. Ray-trace model flow diagram for ray incident on QDSC top surface.
2.1.1 Reflection and transmission at plate boundaries

To determine if an incident ray is reflected or transmitted at a boundary, consider;

Case A: \( n_1 < n_2 \), where \( n_1 \) and \( n_2 \) are the refractive indices at the location of the incident and refracted ray, respectively. In this case the ray may be reflected or transmitted. The probability of reflection, \( R \), is given by the Fresnel equations (Hecht, 2002);

\[
R = \frac{R_1 + R_2}{2} \quad \text{where,} \quad R_1 = \left( \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2} \right)^2, R_2 = \left( \frac{n_1 \cos \theta_2 - n_2 \cos \theta_1}{n_1 \cos \theta_1 + n_2 \cos \theta_2} \right)^2
\]  

2.1

Defining the incident ray as a normalised ray vector, \( \mathbf{v} \), and the surface normal as a normalised vector, \( \mathbf{p} \), the reflected ray vector is given by;

\[
\mathbf{v}_{\text{reflect}} = \mathbf{v} - (2 \cos \theta_1) \mathbf{p} \quad \text{where,} \quad \cos \theta_1 = \mathbf{v} \cdot \mathbf{p}
\]  

2.2

If a ray is not reflected, then the transmitted refracted ray vector (Glassner, 1989) is given by;

\[
\mathbf{v}_{\text{reflect}} = \left( \frac{n_1}{n_2} \right) \mathbf{v} + \left( \cos \theta_2 - \frac{n_1}{n_2} \cos \theta_1 \right) \mathbf{p} \quad \text{where,}
\]

\[
\cos \theta_2 = \sqrt{1 - \left( \frac{n_1}{n_2} \right)^2 (1 - \cos \theta_1)^2}
\]  

2.3

A Monte-Carlo technique is used to determine whether reflection or transmission ensues at the boundary intersection point. For example, a ray vector \( \mathbf{v} = \)
[0.785  0.453  -0.423] incident on a QDSC of refractive index 1.5 at $\theta_1 = 65^\circ$, as shown in Figure 2.2, is considered. From eqn. 2.1, $R$ is calculated at 0.1205. For each incident ray, a random number, $k_r$ is then generated in the interval $[0,1]$. If $k_r < 0.1205$, the ray is reflected. If $k_r > 0.1205$, the ray is transmitted into the plate. When the number of incident rays is increased, the number of rays reflected and transmitted tends to 12.05% and 87.95%, respectively.

Figure 2.2. An incident photon may be either reflected (ray 2) or refracted (ray 3) depending on the calculated probability of reflection which is tested against a randomly generated number in the interval [0,1].

Case B: $n_1 > n_2$. The ray undergoes total internal reflection (TIR) if $\theta_1 > \theta_{\text{critical}}$. A TIR coefficient is defined by the user. If $\theta_1 < \theta_{\text{critical}}$, TIR does not occur, however the ray may still undergo Fresnel reflection at the boundary, with the probability determined by eqn. 2.1. The probability of reflection at external mirror surfaces is given by a user-defined mirror reflectivity ($R_{\text{mirror}}$).
2.1.2 Finding the intersection point of a ray and a plane

Figure 2.3. "Point b" is the intersection point of the ray vector, \( v \), and the plane defined by the three points, "Point 1", "Point 2", and "Point 3".

The equation of a plane defined by three co-planar points, "Point 1" = \((x_1, y_1, z_1)\), "Point 2" = \((x_2, y_2, z_2)\), and "Point 3" = \((x_3, y_3, z_3)\), shown in Figure 2.3, is given by:

\[
Ax + By + Cz + D = 0
\]

where the determinants \(A, B, C\) and \(D\) are given by (Bourke, 1989):

\[
A = \begin{vmatrix} 1 & y_1 & z_1 \\ 1 & y_2 & z_2 \\ 1 & y_3 & z_3 \end{vmatrix}, \quad B = \begin{vmatrix} x_1 & 1 & z_1 \\ x_2 & 1 & z_2 \\ x_3 & 1 & z_3 \end{vmatrix}, \quad C = \begin{vmatrix} x_1 & y_1 & 1 \\ x_2 & y_2 & 1 \\ x_3 & y_3 & 1 \end{vmatrix}, \quad D = -\begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix}
\]

or
\[ A = y_1 (z_2 - z_3) + y_2 (z_3 - z_1) + y_3 (z_1 - z_2) \]
\[ B = z_1 (x_2 - x_3) + z_2 (x_3 - x_1) + z_3 (x_1 - x_2) \]
\[ C = x_1 (y_2 - y_3) + x_2 (y_3 - y_1) + x_3 (y_1 - y_2) \]
\[ D = - (x_1 (y_2 z_3 - y_3 z_2) + x_2 (y_3 z_1 - y_1 z_3) + x_3 (y_1 z_2 - y_2 z_1)) \]

A ray travelling from "Point a" \((x_a, y_a, z_a)\) is defined by the direction ray vector, \(\mathbf{v} = [x_u, y_u, z_u]\). The intersection point of the ray with the plane, i.e. "Point b", is given by;

"Point b" = \((x_b, y_b, z_b) = (x_a, y_a, z_a) + u(\mathbf{v})\)

Substituting into 2.4 gives;

\[ A(x_a + u x_u) + B(y_a + u y_u) + C(z_a + u z_u) + D = 0 \]

or

\[ u = \frac{-A x_a + B y_a + C z_a + D}{A x_u + B y_u + C z_u} \]

### 2.1.3 Determining boundary intersection points

Each surface of the QDSC is represented by a plane defined by three of the four corner points. A set of intersection points of the ray vector, \(\mathbf{v}\), with each surface of the QDSC is determined using eqn. 2.7. The actual intersection point is then determined from the set of all intersection points by eliminating those points that are (i) outside the boundaries of the respective plane or (ii) in the opposite direction of the ray.
2.1.4 QD photon absorption and emission

To determine if a ray is absorbed by a QD, the QD absorption coefficient, $a_{QD}$, for the particular ray wavelength, $\lambda$, is obtained from the measured QD absorption spectrum. The total probability of an absorption event occurring between boundary intersection points, separated by distance, $d$, is determined from:

$$P_{abs} = 1 - e^{-a_{QD}d}$$

2.10

If a ray is absorbed by a QD, the probability of photon emission is given by the QD QY. The emission wavelength, $\lambda_{em}$, is assigned at random from a weighted distribution corresponding to the measured emission profile of a low QD concentration sample (Kennedy et al., 2007b). Figure 2.4 shows a series of measured emission spectra of a sample of CdSe/ZnS core-shell QDs, for varying excitation wavelengths. The ray-trace model can utilise a series of QD photon emission spectra, as proposed by Schüler et al., (2007), where the particular emission spectrum used is selected depending on the wavelength of the absorbed ray, $\lambda$. 
2.1.5 Matrix material absorption and scattering

In current low efficiency QDSC devices, where the optical efficiency < 1%, a significant fraction of light reaching the PV cell is due solely to scattering caused by the polymer matrix material\textsuperscript{iv}. Scattering events are included in the model to enable comparison of predictions with experimental measurements. A scattering spectrum for the epoxy matrix material was measured by Gallagher \textit{et al.}, (2007). The total attenuation loss (i.e. Fresnel reflection, matrix material absorption and scattering losses) of the epoxy sample was measured using a Perkin Elmer 900 UV/Vis/NIR

\textsuperscript{iv} The optical efficiency, \( \eta_{\text{opt}} \), of the fabricated QDSC devices in sections 2.2.2 - 2.2.4 is of the same order as that of a polymer plate un-seeded with QDs
spectrometer in the setup configuration illustrated in Figure 2.5(a). By locating the epoxy sample at the entry aperture to an integrating sphere within the spectrometer, as illustrated in Figure 2.5(b), scattered light is collected by the detector, thereby removing scattering losses from the measured “attenuation”. The difference between the spectra using the respective setups in (a) and (b) yields a scattering spectrum approximation for the epoxy material (Gallagher et al., 2007). The matrix scattering and absorption spectra are shown in Figure 2.6, from which the matrix material absorption coefficient, $\alpha_{\text{mat}}$, and scattering coefficient, $\alpha_{\text{scat}}$, for a particular $\lambda$ are obtained. The scattering coefficient is inversely proportional to wavelength, indicating that scattering process is Rayleigh scattering which is proportional to $\lambda^{-4}$.

Figure 2.5. Experimental set up for absorbance measurements using a Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer; (a) normal set up; (b) using an integrating sphere to account for scattering in the samples (Gallagher et al., 2007).
Figure 2.6. Measured absorption and scattering spectra of an epoxy matrix material sample (Gallagher et al., 2007).

The total probability that a ray will undergo either an absorption (by QD), a matrix material absorption or a scattering event between boundary intersection points is given by:

\[ P_{\text{total}} = 1 - e^{-(\alpha_{QD} + \alpha_{mat} + \alpha_{sca})} \]  \hspace{1cm} 2.11

A randomly generated number, in the interval \([0,1]\), is tested against \(P_{\text{total}}\) to determine if any event occurs between boundary intersection points. Assuming an event occurs, the ratio of the relative individual event probabilities over the distance, \(d\), i.e.,

\[ 1 - e^{-(\alpha_{QD}d)} : 1 - e^{-(\alpha_{sca}d)} : 1 - e^{-(\alpha_{mat}d)} \]  \hspace{1cm} 2.12
is then used to determine which particular event ensues. A ray deemed to be attenuated by the matrix material is lost (as heat in the matrix). Scattering is assumed to be elastic, and predominantly in a forward direction, based on scattering measurements carried out by Thomas et al., (1983) on a PMMA LSC plate. The weighted forward scattering angle distribution used is given in Figure 2.7(a). An illustration of 10,000 rays scattered at angles selected from this distribution is shown in Figure 2.7(b).

![Figure 2.7](image)

Figure 2.7. (a) The weighted forward scattering probability distribution used in the model (b). An example plot of 10,000 rays scattered at angles selected at random from a weighted distribution corresponding to (a).

A ray deemed not to be absorbed by a QD, nor attenuated or scattered by the matrix material is transmitted to the next intersection point where reflection/transmission ensues, as detailed in section 2.1.1.
2.1.6 Concentration ratio and photovoltaic cell spectral response

The optical efficiency, \( \eta_{\text{opt}} \), is defined as the total number of photons that are transmitted to the PV cell relative to the total incident on the top surface aperture;

\[
\eta_{\text{opt}} = \frac{\int N_{\text{out}}(\lambda) \, d\lambda}{\int N_{\text{in}}(\lambda) \, d\lambda}
\]

where, \( N_{\text{in}} \) and \( N_{\text{out}} \) are the input and output photon distributions, respectively. The geometric gain, \( G_{\text{geom}} \), is defined as the ratio between the top surface aperture area and PV cell area. The photon concentration ratio, \( C_{\text{ph}} \), is calculated as the product of \( \eta_{\text{opt}} \) and \( G_{\text{geom}} \);

\[
C_{\text{ph}} = \eta_{\text{opt}} G_{\text{geom}}
\]

The overall spectrally-specific concentration ratio (C) is given by;

\[
C = \frac{\int N_{\text{out}}(\lambda) \eta_{\text{EQE}}(\lambda) \, d\lambda}{\int N_{\text{in}}(\lambda) \eta_{\text{EQE}}(\lambda) \, d\lambda} G_{\text{geom}}
\]

where \( \eta_{\text{EQE}} \) is the measured cell external quantum efficiency, and the terms are integrated over the spectral response range of the attached PV cell. In the ray-trace model, the input spectral energy distribution, \( E_{\text{in}}(\lambda) \), is converted to a photon distribution, \( N_{\text{in}}(\lambda) \), using the relationship;
The PV cell $\eta_{EQE}$ is given by;

$$\eta_{EQE} = \eta_{IQE}(\lambda) \left(1-R_{pv}(\lambda)\right)$$

where $R_{pv}$ and $\eta_{IQE}$ are the measured PV cell reflectivity, and internal quantum efficiency, respectively. $\eta_{EQE}$, $\eta_{IQE}$ and $R_{pv}$ curves for a mc-Si cell are shown in Figure 2.8(a) (van Sark, 2008).

Figure 2.8. (a) Measured EQE, IQE and reflectivity ($R_{pv}$) at normal incidence of a mc-Si cell. (b) Extrapolated $R_{pv}$ curves for higher angles of incidence.

Using eqn. 2.1 a set of angle dependent PV reflectivity curves, $R_{pv}(\theta,\lambda)$ shown in Figure 2.8(b), are approximated from $R_{pv}$. PV cell IQE may also vary with incident angle due to the increase in pathlength through the cell. This is not accounted for by the model. However, as IQE is close to unity at typical QD emission wavelengths, variations in IQE with incidence angle will introduce only limited errors in predicted...
PV cell short circuit current. The QDSC concentration ratio, incorporating angle-dependent PV reflectivity can thus be calculated from;

\[
C = \frac{\int \frac{N_{\text{out}}(\lambda) \eta_{\text{IQE}}(\lambda) (1-R_{\text{pv}}(\theta, \lambda)))}{\int N_{\text{in}}(\lambda) \eta_{\text{IQE}}(\lambda) (1-R_{\text{pv}}(\theta, \lambda))) \, d\lambda} \, d\lambda}{G_{\text{geom}}} = \frac{I_{\text{sc,pvC}}}{I_{\text{sc, pv}}} \quad 2.18
\]

QDSC concentration ratio is defined as the ratio of the short circuit current of the PV cells attached to the concentrator, \( I_{\text{sc,pvC}} \), to the short circuit current of the same PV cells not attached to the concentrator, \( I_{\text{sc,pv}} \), oriented on the same plane as the concentrator top surface.

2.2 Model Validation

At the initial model development stage, it was found useful to plot traced rays as they propagate through non-attenuating plates, un-seeded with QDs. This provided a visual check that the geometric ray-trace algorithms had been implemented correctly. Ray-trace predicted escape cone and external reflection losses are compared with analytical predictions (calculated for simplified, idealized QDSCs), providing a further check of the geometric ray-trace algorithms.

Incorporating QD photon absorption and emission, and matrix material absorption and scattering, the model predictions are compared with measured electrical output from fabricated QDSCs of varying size, shape and QD doping concentration. Predicted and measured efficiencies are found to match for all QDSCs. Measured QDSC edge emission spectra show a variation in peak
wavelength and intensity, depending on the distance between the detector (at the plate edge) and the input laser spot position on the top surface aperture. The predicted peak wavelengths and relative intensities exhibit the same trend as the measured data. The validation checks indicate that QD absorption and emission, re-absorption of QD emitted photons, and transport losses within the plate are calculated accurately in the model.

Model predictions also match with measured electrical output from four LSC plates of varying plate dimensions, containing Coumarin luminescent dyes, which were fabricated by Chatten et al., (2005). Predictions are compared with those from two other LSC models. A high level of agreement exists between all three models, with < 1% absolute difference in the predicted photon flux magnitude emerging at each plate surface.

2.2.1 Visualization of traced rays

To check that the geometric ray-trace algorithms, i.e. the boundary intersection point and reflection/transmission algorithms, are implemented correctly, it is useful to plot the traced rays. Assuming $a_{mat}$ and $a_{scat}$ to be zero and perfectly reflecting external mirrors at all surfaces, a ray is given a random initial angle and is traced inside a hexagonal QDSC until it has intersected a boundary a given number of times. The trace, plotted in Figure 2.9, provides a visual check that the geometric ray trace algorithms are operating correctly.

Figure 2.10 shows 25 rays incident at different angles on one surface of a triangular QDSC, assuming a plate refractive index of 1.5 and no external mirrors at any surface. It can be observed that if $\theta_1 > \theta_{critical}$ TIR ensues correctly. In this
example, all rays with $\theta_1 < \theta_{\text{critical}}$ are transmitted out of the device, except a single ray which was deemed by the Monte-Carlo method employed to undergo Fresnel reflection at the boundary. A more quantitative validation check of reflection/transmission algorithms is given in section 2.2.6.

Figure 2.9. A ray given a random initial angle is traced inside a non-attenuating hexagonal QDSC, assuming perfectly reflecting external mirrors at all surfaces.
Figure 2.10. Rays are traced inside a non-attenuating triangular QDSC, assuming a plate refractive index of 1.5 and no external mirrors at any surface. If $\theta_1 > \theta_{\text{critical}}$, TIR ensues. In this example, all rays with $\theta_1 < \theta_{\text{critical}}$ are transmitted out of the device, except a single ray which undergoes Fresnel reflection at the boundary.

2.2.2 Edge emission spectra for varying input light position

Objective

The red-shift in measured edge emission spectra for varying input laser positions on the top surface aperture are compared with model predictions of the red-shift, testing whether the model accurately determines re-absorption effects and transport losses in QDSCs.

Experimental

A QDSC containing 'OMN28’ QDs (CdSe/ZnS core-shell, emission wavelength 550 nm, Nanoco Technologies) was fabricated by Rowan et al. (2007). Using a 457 nm argon-ion laser input light source, the edge emission spectrum of the QDSC was measured using seven different input laser positions on the top surface.
aperture at increasing distances from the detector. The experimental setup is illustrated in Figure 2.11. The relative intensity of the edge emission spectra should decrease for input laser spot positions further from the edge where detector is positioned, due to higher material absorption and re-absorption losses. Moreover, the edge emission spectra for input laser spot positions further from the detector should be more red-shifted, due to re-absorption of QD emitted photons (Batchelder et al., 1979; Chatten et al., 2004).

![Figure 2.11. Measurement of QDSC edge emission spectrum, using different input laser positions on the QDSC surface, at varying distances (5mm - 50mm) from the plate edge at which the spectrometer detector is positioned.](image)

**Results**

Figure 2.12 shows the measured edge emission spectra for a QDSC containing a 0.05% mass/volume 'OMN 28' QD concentration (Kennedy et al., 2007b). The measured peak at ~556 nm for the “5mm” input position is matched
closely by the predicted peak, shown in Figure 2.13. The expected red-shifting of the
dowel emission peaks for input laser positions further from the detector is observed,
matched to a large degree by the red-shifting of the predicted spectra. The measured
and predicted edge emission peak wavelengths, for each input laser position, are
shown in Figure 2.14(a). The relative integrated edge emission intensities for varying
input laser positions are shown in Figure 2.14(b). The close match indicates that
QDSC transport losses and re-absorption are calculated accurately in the ray-trace
model. There is some divergence in predicted and measured emission peaks. One
possible cause of the divergence is the uncertainty in actual matrix material
absorption and scattering. Absorption and scattering spectra of the epoxy matrix
material used in QDSCs can vary from sample to sample due to fabrication
inhomogeneities (e.g. time taken for curing which is dependent on plate dimensions,
or the mixing procedure used which can create small air-bubbles in the sample). The
epoxy attenuation spectra shown in Figure 2.6 may differ from the actual spectra of
the fabricated QDSC. In particular, a higher degree of scattering in the fabricated
QDSC would result in higher attenuation losses at shorter wavelengths, resulting in
an apparent redshift in the measured spectra. The total divergence in peak emission
wavelength is < 4 nm. This will not introduce significant errors in predicted electrical
output of a PV cell, as the cell spectral response variation is small over this
wavelength range.
Figure 2.12. Measured edge emission spectra for a laser (457nm) input at seven different distances (increasing from 5mm to 50 mm) from the detector.

Figure 2.13. Predicted edge emission spectra for a laser (457nm) input at seven different distances (increasing from 5mm to 50 mm) from the detector.
2.2.3 QDSC optical efficiency with varying QD concentration

Objective

Increasing the QD doping concentration results in higher absorption efficiency ($\eta_{\text{abs}}$). However, re-absorption of QD emitted photons also increases with higher concentrations, implying a maximum $\eta_{\text{opt}}$ should occur at a particular optimum QD concentration. A matching predicted and measured trend in $\eta_{\text{opt}}$ with varying QD concentration will indicate that QD photon absorption and re-absorption is calculated accurately in the ray-trace model.
Experimental

Six QDSC devices with increasing QD concentrations of ‘488C’ QDs (CdSe/ZnS core-shell, emission wavelength 488nm, Nanoco Technologies) were fabricated by Rowan et al. (2007). Figure 2.15 shows the absorption and emission spectra of the six QDSCs containing different QD concentrations (% mass/volume). A solely epoxy device, un-seeded with QDs, was also fabricated. Filtered light from a metal halide lamp, with the spectrum shown in Figure 2.15, was used as the incident light source. The short circuit current of a monocrystalline PV cell was used to measure the light intensity emerging at the QDSC edge. The same PV cell was employed to measure the light intensity incident on the top surface entry aperture area of the QDSCs.

![Figure 2.15. Measured absorption and emission spectra of six samples containing different concentrations of ‘488C’ CdSe/ZnS QDs.](image-url)
Results

Predicted $\eta_{\text{opt}}$, using a range of QD QYs, for each QDSC are shown in Figure 2.16 (Kennedy et al., 2007b). A QY of ~10% results in a match with the measured $\eta_{\text{opt}}$ values. The optical efficiency of the six QDSCs is of the same order as the solely epoxy device, indicating that light reaches the PV cell predominantly through scattering in all six devices. Model predictions are in agreement with the observed trend, in that no significant increase in $\eta_{\text{opt}}$ with QD concentration was observed. This indicates that QD photon absorption and re-absorption are calculated accurately in the ray-trace model for devices with varying QD doping concentration.

![Graph showing optical efficiencies](image)

Figure 2.16. Measured and predicted optical efficiencies ($\eta_{\text{opt}}$) of fabricated devices containing different concentrations of QDs. The predicted $\eta_{\text{opt}}$ values are calculated using a QD QY of 10%, 60% and 100%. The error bars on the predicted values indicate the $\eta_{\text{opt}}$ uncertainty due to inhomogeneous matrix material scattering in different plates.
Predicted errors

A single scattering spectrum (shown in Figure 2.6), representative of the epoxy matrix material, is used to model all QDSC samples. The magnitude of scattering in individual QDSCs varies from sample to sample, and therefore the model will under- or overestimate $\eta_{opt}$. The predicted error bars indicate the uncertainty in $\eta_{opt}$ which arises from this non-homogeneous matrix material scattering. Uncertainty in the other model input parameters, detailed in section 2.3, is not considered as the error introduced to the relative $\eta_{opt}$ (in these particular plates which have very low $\eta_{opt}$) is much less than the error introduced by scattering uncertainty.

2.2.4 QDSC optical efficiency with varying size and shape

Objective

Optical efficiency decreases with larger concentrator size due to increased total re-absorption losses, matrix material losses and side reflection losses. Measured optical efficiencies of four rectangular QDSCs of varying size are compared with model predictions. Varying the QDSC shape alters the mean number of reflections from side surfaces. Measured optical efficiencies of triangular and circular QDSCs are compared with model predictions. Matched observations and predictions will indicate that transport losses, i.e. matrix material losses, side reflection losses and QD re-absorption losses, are determined accurately in the ray-trace model for devices of varying size and shape.
Experimental

Nine QDSCs of varying geometries containing ‘Fort Orange’ (CdSe/ZnS core-shell, emission wavelength 605 nm, Nanoco Technologies) QDs were fabricated by Rowan et al. (2007). The dimensions of each plate are given in Table 2.1. Each plate has a thickness of 0.3 cm. The incident light spectrum used and the QD absorption and emission spectra are shown in Figure 2.17.

<table>
<thead>
<tr>
<th>Shape</th>
<th>Photo</th>
<th>Dimensions (cm)</th>
<th>Aperture Area (cm²)</th>
<th>G_gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>r1</td>
<td>![Image]</td>
<td>2 x 4.0</td>
<td>8.0</td>
<td>6.66</td>
</tr>
<tr>
<td>r2</td>
<td>![Image]</td>
<td>2.8 x 4.0</td>
<td>11.2</td>
<td>9.33</td>
</tr>
<tr>
<td>r3</td>
<td>![Image]</td>
<td>3.5 x 4.0</td>
<td>14.0</td>
<td>11.7</td>
</tr>
<tr>
<td>r4</td>
<td>![Image]</td>
<td>3.6 x 4.0</td>
<td>14.4</td>
<td>12.0</td>
</tr>
<tr>
<td>t1</td>
<td>![Image]</td>
<td>Base: 4.0&lt;br&gt;Length: 1.9</td>
<td>3.8</td>
<td>3.33</td>
</tr>
<tr>
<td>t2</td>
<td>![Image]</td>
<td>Base: 4.0&lt;br&gt;Length: 3.1</td>
<td>6.2</td>
<td>4.66</td>
</tr>
<tr>
<td>c1</td>
<td>![Image]</td>
<td>Radius: 2.0</td>
<td>6.28</td>
<td>5.23</td>
</tr>
<tr>
<td>c2</td>
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<td>26.2</td>
<td>21.8</td>
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<tr>
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<td>![Image]</td>
<td>Radius: 4.0</td>
<td>48.8</td>
<td>40.7</td>
</tr>
</tbody>
</table>

Table 2.1. Dimensions and geometric gain (G_{geom}) of nine QDSCs of varying shape and size (Rowan et al., 2007).
Figure 2.17. Absorption and emission spectra of ‘Fort Orange’ QDs. Incident light spectrum from metal halide lamp.

Results

The predicted QDSC $\eta_{opt}$, using a QD QY of 14%, given in Figure 2.18, show good agreement with measured values. The predicted error bars indicate the uncertainty due to inhomogeneous matrix material scattering. The smallest plates of each geometry type are the most efficient. The decrease in predicted $\eta_{opt}$ for larger plate sizes, matches the decrease in measured $\eta_{opt}$, indicating that transport losses are calculated accurately in the model, for QDSCs of varying size. A validation of the effect of QDSC shape, however, would require a range of many rectangular, circular and triangular plates with equal $G_{geom}$, whereas in these fabricated plates $G_{geom}$ of each geometry type are in different ranges.
Figure 2.18. Predicted and measured optical efficiencies from four rectangular (r1 – r4), two triangular (t1,t2) and three circular (c1 – c3) QDSCs of varying size as given Table 2.1.

2.2.5 Multiple dye liquid LSCs

Objective

The addition of multiple dyes in an LSC allows the absorption of the solar spectrum to be enhanced compared to a single dye LSC (Burgers et al., 2006; Richards and McIntosh, 2006; Bailey et al., 2007). However, as there may be a large degree of overlap between different dyes' absorption and emission spectra, re-absorption losses may increase significantly in a multiple dye LSC. Predictions of multiple dye LSCs are compared with measurements, to verify whether absorption and re-absorption effects in LSCs containing multiple luminescent species are calculated accurately by the ray-trace model.
Experimental

A 10 x 4 x 0.5 cm quartz cuvette was used as a liquid LSC container, as shown in Figure 2.19. A 2.0 x 0.3 cm silicon cell was placed adjacent to one side of the cuvette at a right angle to the incident beam. Three Perylene dyes (BASF Lumogen Yellow 170, Lumogen Orange 240 and Lumogen Red 305) of varying concentrations, given in Table 2.2, were prepared in chloroform solution. The absorption and emission spectra of each dye, along with the spectrum of the metal halide incident light source, are shown in Figure 2.20. Four multiple dye mixes, listed in Table 2.2, were prepared. The different dye solutions were placed into the LSC container and the resulting PV cell short circuit current density, $J_{sc}$, measured (Kennedy et al., 2008b).

Figure 2.19. A liquid LSC is pictured containing a Lumogen Orange 240 sample (left) and Lumogen Yellow 170 sample (right). A silicon PV cell is placed adjacent to one side of the liquid LSC, at right angles to the incident beam.
Figure 2.20. Normalised absorption and emission spectra of (A) Lumogen Yellow 170, (B) Lumogen Orange 240 and (C) Lumogen Red 305. The shorter wavelength emitting dye(s) overlap significantly with the longer wavelength absorbing dye(s), resulting in a large degree of re-absorption in the LSC containing multiple dyes. The spectrum of the incident light is shown in (D).

<table>
<thead>
<tr>
<th>Dye Mix</th>
<th>Abbreviation</th>
<th>Concentration x10^2 (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R4+O4</td>
<td>Mix 1</td>
<td>60</td>
</tr>
<tr>
<td>R4+O4+Y4</td>
<td>Mix 2</td>
<td>85</td>
</tr>
<tr>
<td>R2+O2+Y2</td>
<td>Mix 3</td>
<td>21</td>
</tr>
<tr>
<td>Y2+O2</td>
<td>Mix 4</td>
<td>16</td>
</tr>
<tr>
<td>Yellow 170</td>
<td>Y1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Y2</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Y3</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Y4</td>
<td>25</td>
</tr>
<tr>
<td>Orange 240</td>
<td>O1</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>O2</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>O3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>O4</td>
<td>40</td>
</tr>
<tr>
<td>Red 305</td>
<td>R1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>5</td>
</tr>
<tr>
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<td>R3</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>R4</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 2.2. Luminescent dyes of varying concentrations and the dye mixes used in liquid LSC tests.
Results

Absolute short circuit current densities ($J_{sc}$) predicted by the ray-trace model were, on average, ~30% higher than measured $J_{sc}$ for each dye sample. One surface wall of the quartz cell (10 x 0.5 cm surface) had a frosted finish. Efficient total internal reflection does not occur at this frosted surface, which may account for the higher predicted $J_{sc}$ (Kennedy et al., 2008b). The measured and predicted relative $J_{sc}$ for each single dye concentration, are shown in Figure 2.21. $J_{sc}$ is given relative to that attained for the R4 (0.2 mg/ml Lumogen red 305) sample which obtained the highest $J_{sc}$ of the single dyes. Predicted $J_{sc}$ is lowest for Y1 and R1, in agreement with the measured values. The measured and predicted $J_{sc}$ for each of the four dye mixes are also shown in Figure 2.21, each matching within the experimental error. While reasonable agreement between measurements and predictions is observed, the experimental setup requires some refinement to determine whether absolute predicted $J_{sc}$ values match measured values.
Figure 2.21. Measured and predicted relative short circuit current densities ($J_{sc}$) for the dye samples listed in Table 2.2.

### 2.2.6 Comparison with analytically predicted loss mechanisms

External top surface reflection losses, escape-cone losses, and $\eta_{opt}$ of a QDSC were calculated for varying plate refractive index, $n$, using the ray-trace model. An ideal QD QY of 100%, $\alpha_{mat}$ of 0 cm$^{-1}$ and a QD emission spectrum exhibiting zero spectral overlap were assumed. The only loss mechanisms thus remaining are initial reflection losses (proportional to $n$), and escape-cone losses (proportional to $1/n$). The variation of these loss mechanisms and $\eta_{opt}$ with $n$ is shown in Figure 2.22. With zero re-absorption and QY losses, $\eta_{opt}$ for LSCs is predicted analytically (Goetzberger and Greubel, 1977) for vertical incidence from;
Analytically and ray-trace predicted $\eta_{\text{opt}}$ match closely, as shown in Figure 2.22, thus validating the ray-trace reflection/transmission algorithms (Kennedy et al., 2007a). Figure 2.22 also shows that ~25% of QD emitted photons are lost in the escape cone for $n=1.5$, in agreement with analytical predictions (Goetzberger and Greubel, 1977; Batchelder et al., 1979).

Figure 2.22. Ray-trace predicted $\eta_{\text{opt}}$ and loss mechanisms with varying refractive index, $n$. Analytically predicted $\eta_{\text{opt}}$ is also shown. Ideal absorption and emission spectra with no spectral overlap, a QD QY=100%, $\alpha_{\text{mat}} = 0$ cm$^{-1}$, and $R_{\text{mirror}}=1.0$ are assumed.
2.2.7 Comparison with predictions from other models

Two LSC plates of different sizes containing a red Coumarin dye and two containing a yellow Coumarin dye were fabricated by Chatten et al. (2005). The plate dimensions and the labels given to each plate surface are shown in Figure 2.23. The quantum yield of both dyes was determined to be 95% (Chatten et al., 2005).

![Diagram of LSC plates with dimensions](image)

Figure 2.23. The dimensions of two LSC plates containing a Bayer Fluorescent Red Coumarin dye (a) and (b), and two plates containing Fluorescent yellow Coumarin dye (c) and (d).

**Predicted photon count emerging at plate edges**

The predicted percentage of incident photons emerging at the bottom and top surface of the plate and at the short and long edges, is shown in Figure 2.24 (Kennedy et al., 2008a). The predictions were compared with those from a ray-trace model developed at the Energy Research Centre of the Netherlands (ECN) (Burgers et al., 2005), and from a Thermodynamic model developed at Imperial College London (ICL) (Chatten et al., 2003). There is agreement between all three models, with an average absolute difference in photons emerging at all surfaces of 0.3% and a maximum absolute difference of 1.0%. The differences can be attributed to the differing absorption calculation methods used in each model.
Figure 2.24. Percentage of photons exiting; “1”: bottom surface, “2”: top surface, “3”: two long edges, and “4”: two short edges, of four different LSC plates. Predictions are shown for the DIT ray-trace model (blue bars), the ECN ray-trace model (green bars) and the ICL Thermodynamic model (red bars). Total predicted QY and matrix absorption losses are also shown by the bars labelled “5”.

(a) Large red plate
(b) Small red plate
(c) Large yellow plate
(d) Small yellow plate
**Predicted electrical output**

The short circuit current density, $J_{sc}$, of a silicon photodiode attached at the short edge of each of the four LSC plates was measured by Chatten *et al.* (2005). The photodiode spectral response and its angle dependent reflectivity are used with the predicted photon count escaping at the short edge to obtain the predicted $J_{sc}$. Table 2.3 shows the measured and predicted $J_{sc}$ from the four LSC devices. There is agreement, within experimental error, between the predicted and observed values. The error in predicted values is due to uncertainty in the incident light intensity used as model input.

<table>
<thead>
<tr>
<th>Plate</th>
<th>Measured</th>
<th>Predicted by ray-trace model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Large</td>
<td>53.2 ± 2.0</td>
<td>51.9 ± 2.59</td>
</tr>
<tr>
<td>Red Small</td>
<td>22.5 ± 2.0</td>
<td>24.9 ± 1.24</td>
</tr>
<tr>
<td>Yellow Large</td>
<td>10.4 ± 2.0</td>
<td>9.3 ± 0.46</td>
</tr>
<tr>
<td>Yellow Small</td>
<td>5.2 ± 2.0</td>
<td>5.0 ± 0.25</td>
</tr>
</tbody>
</table>

Table 2.3. Comparison of measured and predicted $J_{sc}$ values of the four dye LSC plates.

**2.3 Model assumptions, limitations, and uncertainties.**

**PV model**

In the model, PV cell short circuit current is assumed to increase linearly with $C$. In silicon PV cells open circuit voltage, $V_{oc}$, increases logarithmically with $C$. For example, an increase of ~5% in $V_{oc}$ was obtained by Sidrach de Cardona *et al.* (1985b) for an LSC with $C \approx 4$ compared to the same PV cell not attached to the LSC. In the current model $V_{oc}$ is assumed to be constant with $C$. Predicted LSC power output, therefore, underestimates the power output of a fabricated LSC.
Temperature effects have not been included in the model. Optical concentration of light on a PV cell results in a temperature increase and a resulting decrease in cell efficiency. However, light transmitted to the PV cell within a luminescent concentrator is in the wavelength region where the cell IQE is close to its maximum. Therefore, temperature increases in the PV cell attached to a luminescent concentrator would be lower compared to that in the same cell attached to an optical (non wavelength shifting) concentrator with an equivalent photon count concentration ratio.

Luminescent species emission

Discrete energy levels exist in an individual QD. Therefore, photon emission would be expected to occur at a wavelength equivalent to the absorption onset wavelength of the individual QD. In a QD ensemble, therefore, the emission spectrum should correspond to the absorption onset of the ensemble. However, the emission peak is observed at a slightly longer wavelength than the absorption onset. This redshift has been shown experimentally to be related to the QD ensemble inhomogeneous broadening linewidth (Patanè et al., 2000; Patanè et al., 2001) and the redshift tends to zero for a homogeneous (identical size) ensemble of QDs. Patanè et al. propose that carriers can thermally escape from QDs and redistribute by diffusing from high energy to lower energy dot states. This process is not inherently modelled in the ray-trace approach. Instead, a measured photon emission spectrum⁷, representative of the ensemble emission, is used as model input. The emission measurement used as model input should be taken from a very low QD doping

⁷ or, ideally, a series of spectra for varying incident wavelengths, as detailed in section 2.1.4.
concentration so as to omit effects of re-absorption and subsequent emission from the spectrum.

In all LSCs modelled, it is assumed that there is no luminescence quenching with increasing doping concentration, that the QY is independent of excitation wavelength, and that emitted light is unpolarised. While the assumptions made may over-simplify the real physical processes underlying photon absorption and emission in an LSC plate, they are sufficiently detailed to allow accurate predictions of LSC electrical and spectral output, as shown in section 2.2.

Solar radiation

To simplify the analysis in sections 3 and 4, two specific skyward angular distributions are considered - either a) isotropic, representing the diffuse component of solar radiation angular distribution, as proposed by Liu and Jordan (1960) or b) non-existent, i.e. at normal incidence only. Section 5 utilises a more detailed solar radiation model which allows for more realistic angular distributions to be simulated.

Model uncertainties

Taking the assumptions made above (i.e. those made for modelling photovoltaic energy conversion and luminescent species emission) as accurate, model predictions can still only be made to within the uncertainty in the input parameters, i.e.;

- luminescent QY,
- incident light spectral irradiance and angle,
- magnitude of matrix material absorption and scattering,
- external mirror reflectivity,
- matrix material refractive index.

The predicted error bars in any given subsection of section 2 quantify the error arising due to uncertainty in the model input parameter/s which significantly affect the relative electrical output. For example, the most significant source of error affecting the relative electrical output of the devices in sections 2.2.3 and 2.2.4, where the QD QY is very low (QY < 15%), arises from inhomogeneous matrix material scattering in different QDSC samples. At higher QYs, uncertainty due to inhomogeneous matrix material scattering is relatively less significant, as shown by Figure 2.16. The predicted error in the more efficient dye LSC plates (where the QY = 95%), detailed in section 2.2.7, is most significantly affected by the uncertainty in the incident light intensity (Chatten, 2008). Where the predicted electrical output is given without error bars, the assumption is made that model input parameters are exact. Stochastic error arises from using the Monte-Carlo approach. To reduce stochastic error and produce repeatable results, the model must be run for longer, i.e., using more input rays. The number of decimal places used for predicted results indicates the level of certainty at which the model attains repeatable results over successive programme runs.
2.4 Chapter conclusions

- The algorithms behind modelling each of the main processes in a QDSC have been detailed. Using a Monte-Carlo approach, these processes have been combined to form a multi-parameter ray-trace model of QDSCs, enabling the principal interdependent, competing loss mechanisms to be quantified.
- Visualisation of the traced rays around varying QDSC configurations provides an initial check that the geometric ray-trace algorithms have been implemented correctly. Agreement between ray-trace model and analytic predictions of top surface reflection losses and escape cone losses, with varying plate refractive index, provides a further validation.
- A matrix material scattering approximation is included in the model to enable comparison with measured $\eta_{\text{opt}}$ from fabricated QDSCs, where the QD QY was found to be very low.
- To validate the model, predictions are compared with a range of experimental measurements;
  - Predicted $\eta_{\text{opt}}$ are in good agreement with measured values from QDSCs of varying size and QD doping concentration.
  - Predicted $\eta_{\text{opt}}$ of QDSCs with varying shape match measured values, although more plates of each geometry type are required here for a validation.
  - Predicted edge emission spectra, using varying input laser spot positions on the device top surface aperture, show good agreement with measured spectra.
  - Predicted trends in electrical output of liquid LSCs containing multiple dyes of varying concentrations match measured trends.
• The results indicate that photon absorption and emission, and re-absorption of light and transport losses within the LSC plate are determined accurately by the ray-trace model.

• There is a high level of agreement between predicted and observed electrical output from four dye LSC plates, as well as between the predictions of the ray-trace and two other LSC models.

• The ray-trace approach provides a tool for quantifying device loss mechanisms and optimizing QDSC design in terms of varying geometry, luminescent species, matrix material, external reflector, and PV cell types.
2.5 References


Hecht, E., (2002). Optics, Addison-Wesley, Reading, Massachusetts, USA.


88
3 Device geometry

3.0 Introduction

3.0.1 QDSC geometry

Current fabricated QDSCs utilise a planar rectangular geometry. Quantifying the net effect of varying device geometry on QDSC solar energy concentration ratios (C) is a non-trivial problem owing to the multiple, interdependent, competing loss mechanisms in the device. The ray-trace model, described in chapter 2, provides a tool for doing so. A novel analysis of device geometry is undertaken using ray-trace predictions to calculate relative costs per unit power output of varying two-dimensional planar QDSC shapes. The analysis shows that, under certain assumptions, each two-dimensional planar geometry attains the same minimum cost per unit power, indicating that no advantage accrues from varying the plate shape.

The predictions show that the correct selection of the concentrator top surface aperture area is crucial in minimising QDSC cost per unit power output – an important criterion not previously highlighted in the research literature. For example, the predicted cost per unit power of a particular 7 x 7 cm square QDSC is 10% lower than that of an 11 x 11 cm square QDSC with the same properties, despite a higher C attained in the latter. Obtaining a 10% decrease in the cost per Wp by altering only the dimensions of the device illustrates the importance of utilizing accurate QDSC modelling techniques.

Whether PV cells are attached at (a) one side of a plate only, or (b) at all sides of the plate perimeter has multiple effects on power output and costs; (i) A higher C
is attained in case (a) due to the higher geometric gain, (ii) the power output may be lower in case (a), despite the higher C, due to the smaller area of PV cells attached, and (iii) the cost in case (a) is lower. The net effect of PV cell distribution on cost per unit power is quantified using the ray-trace model predictions.

Re-absorption losses, which increase with higher QD doping concentration levels, severely limit the potential C of QDSC devices, as is discussed in section 4.1. Current fabricated QDSCs utilise a planar geometry with plates of uniform thickness. A tapered QDSC is proposed, with the aim of reducing re-absorption losses in the device. This configuration would allow a lower QD doping concentration to be used to attain a given absorption efficiency, thereby reducing re-absorption losses. The disadvantage is that the internal optical efficiency decreases due to the sloped surfaces of the tapered devices. Ray-trace modelling is used to investigate the net effect of tapered geometry on device C. The results show an overall decrease in C for tapered devices, compared to plates of uniform thickness.

3.0.2 Solar tree geometry

A luminescent “solar tree” system is proposed in section 3.2, where fibre optics are used to transmit light exiting multiple plates, or “leaves”, to a single PV cell via a 2nd stage concentrator. Potentially, the concept allows high solar energy concentration ratios to be attained under direct or diffuse insolation conditions. However, the maximum concentration ratio of the 2nd stage concentrator, $C_2$, is limited by the angular distribution of light exiting the fibre optics. It is shown that the limitations in $C_2$, combined with the additional associated costs of the fibre optics required, result in no cost per unit power reduction for the solar tree structure.
compared with that of a single-plate QDSC. If fibre optic costs were significantly reduced compared to current levels, however, then the concept should be further evaluated.

3.0.3 Luminescent down-shifting layer geometry

Luminescent down-shifting (LDS) layers, examined in section 3.3, can enhance the short circuit current density, \( J_{sc} \), of solar cells by transforming the wavelength of incident light from short to longer wavelengths better matching the spectral response of the cell. LDS layers are modelled, to investigate whether the optical properties of QDs (i.e. broad absorption range and characteristic increased absorption in the UV and blue wavelength regions) make them a more suitable candidate than organic dyes for incorporation in LDS layers. Predictions for LDS layers containing two types of commercially available QDs show only a limited potential enhancement in \( J_{sc} \) of a mc-Si cell (-1%), and show no enhancement in \( J_{sc} \) when compared to an LDS layer incorporating particular organic dyes.

In “partially-covered” LDS (PC-LDS) layers a reduced fraction of the downshifting layer is covered with PV cells, thereby introducing a geometric concentration effect not present in an LDS layer. The performance of PC-LDS layers incorporating currently available luminescent dyes is quantified for the first time for varying device sizes. As with LSC plates, the optimum size of a PC-LDS layer, of given optical parameters, must be determined. It is shown that, for the particular dye modelled, the optimum PC-LDS configuration yields a significantly higher device power conversion efficiency compared to an optimised LSC device fabricated using the same materials.
3.1 An investigation of QDSC geometry

3.1.1 Concentration ratios for varying device geometry

Roncali and Garnier (1984) showed that, for any given concentrator top surface aperture area, $A_{\text{conc}}$, hexagonal LSCs attain higher $C$ than square or triangular shaped LSCs, resulting from the higher geometric gain, $G_{\text{geom}}$, of the hexagonal geometry. In general, $C$ increases as the number of sides in the LSC polygon increases, for any given $A_{\text{conc}}$. Circular LSCs, therefore, attain the highest $C$ as concluded by Reisfeld and Jorgensen (1982) and by Roncali and Garnier. Hexagonal geometry is preferable to circular, however, for fabricating larger panels containing multiple adjacently packed LSC plates, as it is possible to pack the plates in a honeycomb formation without gaps between individual plates (Sidrach de Cardona et al., 1985a). As the concentration ratio attained for hexagonal geometry is close to that of circular geometry, hexagonal geometry was proposed as the optimum. In terms of cost per Wp, hexagonal geometry may not be advantageous, however. To investigate this, and to compare with previous findings of Roncali and Garnier, $C$ are determined for varying geometry types using the ray-trace model.

Using QD photon absorption spectrum 5 and the QD emission spectrum, shown in Figure 3.1, $C$ is calculated for 0.3 cm thick QDSC plates, of varying geometry type and size, using eqn. 2.14. Square, right-angled triangular, hexagonal and “circular” geometries are considered. Two specific PV cell configurations are considered – a) PV is placed at one side only and external mirrors at the other sides, as shown in Figure 3.2, and b) PV is placed around the full perimeter of each device. The circular devices modelled have a single PV cell attached, where the length of the
cell is equal to the radius of the circle. A QD quantum yield of 100%, matrix material absorption coefficient, $\alpha_{\text{mat}}$, of 0.02 cm$^{-1}$, and refractive index of 1.5, and external mirror reflectivity, $R_{\text{mirror}}$, of 0.94 are assumed in the analysis.

![Absorption spectra](image1)

Figure 3.1. Absorption spectrum 1 is the measured photon absorption spectrum of CdSe QDs with CdS/CdZnS/ZnS multi-shell coating (fabricated at Utrecht University). Absorption spectra 2-6, corresponding to higher QD doping concentrations, are extrapolated from absorption spectrum 1.

![Device diagrams](image2)

Figure 3.2. Square, right angled triangular, hexagonal and circular devices with $A_{\text{conc}} = 256\text{cm}^2$. External mirrors (M) may be placed at the “non PV” sides, as indicated here, or PV may be placed at all sides of the device perimeter.
The predicted C are given in Figure 3.3. The circular geometry attains the highest C for the range of \( A_{\text{conc}} \) considered, matched closely by the hexagonal geometry as was found by Roncali and Garnier (1984). With PV placed at one side only of each device, predicted C are higher than those assuming PV around all sides of the perimeter. This is due to the decreased area of attached PV, \( A_{\text{pv}} \), and the resulting higher \( G_{\text{geom}} \). However, the geometry which attains the highest C is not necessarily the optimum in terms of the cost per unit power output. This is investigated, under certain material capital cost assumptions, in section 3.1.2.

Figure 3.3. Predicted concentration ratios, C, for devices of varying geometry and top surface aperture area, \( A_{\text{conc}} \).
3.1.2 Optimum device geometry - relative costs per unit power output

In section 3.1.1, hexagonal geometry was found to attain higher C than rectangular or triangular geometries, for the range of $A_{\text{conc}}$ considered. However, the aim of the LSC is to reduce the cost per Watt peak ($W_p$) of photovoltaic generated power, not to maximise C. A new approach is undertaken to determine the optimum QDSC geometry type, whereby the relative cost per unit power output is calculated for each of the shapes and sizes considered in section 3.1.1. Circular geometry is excluded due to the difficulty, previously outlined, in packing multiple plates efficiently onto a larger panel.

For each particular device shape and size, the relative power output is assumed to be proportional to the product of $A_{\text{pv}}$ and the resulting device C;

$$\text{relative power} = A_{\text{pv}}C$$  \hspace{1cm} (3.1)

The relative total production cost of a device is assumed to be proportional to the quantity of materials required, and is calculated using $A_{\text{conc}}$ and $A_{\text{pv}}$;

$$\text{relative cost} = (A_{\text{pv}}) + \left( \frac{A_{\text{conc}}}{\text{costfactor}} \right)$$  \hspace{1cm} (3.2)

The variable costfactor, defining the cost of the concentrator plate relative to the cost of PV per unit area, is given by;

$$\text{costfactor} = \frac{\text{cost of PV per unit area}}{\text{cost of concentrator plate per unit area}}$$  \hspace{1cm} (3.3)

95
A cost factor of 15 is considered. Taking the cost of PV to be €450/m², then the cost of the concentrator plate in this case would be €30/m², similar to that estimated for a LSC plate containing a dye (Meyer, 2007). The relative cost per unit power output for each particular shape and size can thus be calculated from:

\[
\frac{\text{relative cost per unit power}}{\text{relative power}} = \frac{1}{C} + \frac{A_{\text{conc}}}{CA_p \text{ costfactor}} = \frac{1}{C} + \frac{G_{\text{geom}}}{C \text{ costfactor}}
\]

Figure 3.4 (a) and (b) show the relative cost per unit power assuming a cost factor of 15. The minimum relative cost per unit power is ~0.8, which corresponds to a 20% decrease in the production cost per W_p compared to that of the mc-Si cells used. Hexagonal, square, and triangular geometry all attain the same minimum cost per unit power, indicating that there is no advantage in using any specific 2-D planar geometry. Significantly, approximately the same minimum cost per unit power is achieved whether PV is placed at one side only, or at all sides of the device perimeter.

The model predictions do show, however, that the correct selection of \( A_{\text{conc}} \) is crucial in minimising QDSC cost per unit power output – an important criterion not highlighted in the literature. For example, (assuming PV is placed at one side only) the predicted cost per unit power of the 7 x 7 cm square QDSC is 10% lower than that of the 11 x 11 cm QDSC. Obtaining a 10% decrease in the cost per W_p solely by altering the dimensions of the device illustrates the importance of utilizing accurate QDSC modelling techniques.
Figure 3.4. Relative cost per unit power for different geometries of varying top surface aperture area ($A_{\text{conc}}$) for two PV cell configurations - (a) PV at one side only, (b) PV at all sides of the perimeter. The price of the concentrator plate per m$^2$ is assumed to be 15 times less than that of PV per m$^2$ (i.e. $\text{costfactor} = 15$).

Figure 3.5 (a) and (b) show the relative cost per unit power assuming a $\text{costfactor}$ of 30. The increase in $\text{costfactor}$, compared to that in Figure 3.4, results in a lower QDSC minimum relative cost per unit power, and the optimum plate size of each geometry type shift to larger $A_{\text{conc}}$. Each geometry type, however, still attains the same minimum cost per unit power as the other geometry types. A more detailed cost optimization is presented in section 6, however, the analysis here shows that varying the geometry type does not offer any significant reduction in relative cost per unit power, but that the choice of device size is critical.
Figure 3.5. Relative cost per unit power for different geometries of varying top surface aperture area ($A_{conc}$) for two PV cell configurations - (a) PV at one side only, (b) PV at all sides of the perimeter. The price of the concentrator plate per m² is assumed to be 30 times less than that of PV per m² (i.e. costfactor = 30).

3.1.3 Edge effects

It is noted that only the total photon count reaching the PV cell has been considered in section 3.1.2, and not the spatial distribution of photons along the PV cell. An uneven photon spatial distribution affects the overall fill factor of an individual PV cell (Smyth et al., 1999) attached at that side. If multiple PV cells were connected in series along one side subject to an uneven incident photon spatial distribution, the overall current would be limited by the cell generating the lowest current. Figure 3.6 shows the predicted spatial distribution of photons along the normalised length of one side of the hexagonal, square, and triangular QDSC plates. The so-called “edge-effect” is less pronounced for hexagonal geometry, as was previously shown by Sidrach de Cardona et al. (1985a). For this reason, hexagonal
geometry may offer an advantage over square or triangular shaped plates. The non-uniformity in the photon spatial distribution is easily explained with reference to the two-dimensional LSCs illustrated in Figure 3.7. Isotropic emission is represented by rays originating from the centre of the circle at angular separation intervals of 10°. It is observed that the spatial distribution of rays intersecting each of the three triangle sides is more weighted to the centre of each side. For the hexagon, the distribution is more uniform along each side, and for the circle a uniform distribution is obtained.

Figure 3.6. Relative photon spatial distribution along the normalised length of one side of the square, triangular and hexagonal QDSC plates. The "edge effect" is greatest for triangular geometry.

Figure 3.7. The distribution of intersection points of rays (emitted isotropically from the circle centre) with each of the polygon sides is most non-uniform in the triangular geometry.
3.1.4 QDSC plates with reduced thickness

LSC concentration ratio, C, increases with reduced plate thickness (Carrascosa et al., 1983; Roncali and Garnier, 1984). Decreasing the thickness has a two-fold effect – (i) \( G_{\text{geom}} \) increases, but (ii) the absorption efficiency, \( \eta_{\text{abs}} \), is reduced. By increasing the QD doping concentration \( \eta_{\text{abs}} \) can be increased but, in doing so, the internal optical efficiency, \( \eta_{\text{int}_{\text{opt}}} \), is reduced due to higher re-absorption losses in the plate. Hence, an optimum QD concentration exists for each particular plate thickness. The net effect of varying plate thickness on C is examined using the ray-trace model. Square devices of dimensions 11 x 11 cm and of varying plate thickness are modelled, assuming PV cells attached to one side only, as illustrated in Figure 3.8. The QD photon absorption spectra shown in Figure 3.1, corresponding to a range of QD doping concentrations, are used in the model, with the optimum concentration for each plate thickness selected. Predicted \( \eta_{\text{opt}} \) decreases with thinner plates, due to a combination of lower \( \eta_{\text{abs}} \) and lower \( \eta_{\text{int}_{\text{opt}}} \), as shown in Figure 3.9(a). However, the increase in \( G_{\text{geom}} \) with thinner plates, as shown in Figure 3.9(b), results in an overall increase in C, indicating significant potential reductions in cost per Wp are realizable with thinner QDSC devices.

![Figure 3.8. Square QDSC 11 x 11 cm plate with variable plate thickness and PV cells attached at one side.](image-url)
Figure 3.9. (a) shows the decrease in optical efficiency for thinner plates due to lower absorption efficiency and lower internal optical efficiency. However, the increase in geometric gain, as shown in (b), results in an overall increase in C for thinner plates, as shown in (c), where \( C = \eta_{\text{opt}} G_{\text{geom}} \).
3.1.5 Concentration ratios of tapered QDSC plates

In this section, a tapered QDSC device is proposed with the aim of reducing re-absorption losses in the QDSC, thereby attaining higher solar energy concentration ratios compared to plates of uniform thickness.

Current fabricated devices utilise a planar geometry with plates of uniform thickness. Re-absorption losses, which increase with higher QD doping concentration levels, severely limit the potential $C$ of QDSC devices. A tapered QDSC device, shown in Figure 3.10, is proposed with the aim of reducing re-absorption losses in the QDSC. The thickness of the device is increased on one side, which allows a lower QD doping concentration to be used, thereby reducing re-absorption losses in the plate. The side where the PV is attached remains at a thickness of 0.3 cm, thereby maintaining a high $G_{geom}$. In the tapered device, however, the angle of propagation of emitted photons is altered by multiple reflections at the sloped top and bottom surface. This causes some photons, emitted initially inside the angular range for TIR, to be lost through the top surface, as illustrated in Figure 3.11. The ray-trace model is used to determine if the net effect is an increase or decrease in $C$, compared to a device of uniform thickness. Using the optimum QD concentration, from the range of QD concentrations shown in Figure 3.1, $C$ was calculated for varying “side 2” thickness, where “side 2” is indicated in Figure 3.10. The tapered devices do not attain a higher $C$ than the device of uniform thickness, as is shown in Figure 3.12.
Figure 3.10. QDSC device with tapered geometry. The thickness of the PV side remains constant at 0.3 cm. The thickness of side 2 is varied to investigate the effect on the concentration ratio attained at the PV side.

Figure 3.11. For tapered geometry, the angle of propagation of a QD emitted photon is altered after multiple reflections at the sloped top and bottom surfaces. Therefore, photons emitted initially inside the angular range for total internal reflection may be lost through the top surface.

Figure 3.12. Concentration ratio, C, for varying thickness of “side 2”. The thickness of the plate at the PV side remains constant at 0.3 cm. The side labels are illustrated in Figure 3.10. The highest C is obtained for a “side 2” thickness of 0.3 cm, i.e. for a plate of uniform thickness.
3.2 Luminescent “solar tree” with 2\textsuperscript{nd} stage concentrator

Figure 3.13 illustrates the concept of the luminescent “solar tree”, where fibre optics are used to transmit light exiting multiple plates, or “leaves”, to a single PV cell via a 2\textsuperscript{nd} stage concentrator. The concept is investigated to determine whether;

a) A higher concentration ratio compared to a single-plate QDSC is attained.

b) The cost per unit power generated is lower than a single-plate QDSC.

The concentration ratio of the 2\textsuperscript{nd} stage concentrator, $C_2$, is limited by the angular distribution of light exiting the fibre optics. The angular distribution can be determined from the ray-trace model.

Figure 3.13. Fibre optics collect light along one side of each QDSC “solar leaf”. Light is transmitted via the fibre optics, through a 2\textsuperscript{nd} stage concentrator to PV cells. $C_1$ and $C_2$ are the effective concentration ratios attained by the individual leaves and the 2\textsuperscript{nd} stage concentrator, respectively. $C_G$ is the ratio of the cross-sectional area of the fibre optic bundle (FOB) to the area of PV cells.

$C_G = \frac{A_{cs, FOB}}{A_{pv}}$

$A_{cs, FOB}$: Cross-sectional area of fibre optic bundle

$A_{pv}$: Area of PV

$C_1 = I_2/I_1$

$C_2 = I_1/I_2$
3.2.1 Solar tree components: Solar leaves and fibre optics

Solar leaves

The concentration ratio of a 0.1 cm thick solar leaf is calculated using QD photon absorption spectrum 6 and the photon emission spectrum shown in Figure 3.1. A range of leaf lengths, \(L_{\text{leaf}}\), are considered, with the leaf width, \(W_{\text{Leaf}}\), a constant 10.0 cm. The other device parameters assumed, e.g. QD QY, \(n_2\), \(\alpha_{\text{mat}}\), \(R_{\text{mirror}}\), are as given for the QDSC plates in section 3.1.1. The concentration ratio attained by the leaf, \(C_1\), is shown in Figure 3.14(a) for varying \(L_{\text{leaf}}\). The relative cost per unit power of QDSC plates of equivalent dimensions to each particular solar leaf is also calculated, to allow comparison of the solar tree configuration performance with that of single-plate QDSC devices. The QDSC relative cost per unit power is calculated from eqn. 3.4, and is shown in Figure 3.14(b).

![Figure 3.14](image)

Figure 3.14. (a) \(C_1\) is the concentration ratio attained by the solar leaf, for varying leaf length, \(L_{\text{leaf}}\). (b) To allow comparison of the solar tree configuration with QDSC devices, the relative cost per unit power of equivalent QDSC plate sizes is calculated.
Solar tree fibre optics

To investigate the performance of the solar tree configuration, the following idealistic fibre optic (FO) characteristics are assumed;

- All photons transmitted to the leaf edge and impinging on the FO entrance aperture are within the acceptance angle of the FO, and no reflection occurs at the FO-leaf interface.
- There are no transmission losses in the FOs and no reflection occurs at the FO exit aperture.
- The thickness of the FO cladding is zero.
- To simplify the calculations, FOs have a square cross-section with a width, \( W_{\text{FO}} \), equal to the thickness of the solar leaf, as illustrated in Figure 3.15.

![Figure 3.15](image)

Figure 3.15. As a first approximation, each fibre optic (FO) is assumed to have a square cross section. The width of each FO, \( W_{\text{FO}} \), is equal to the thickness of the leaf.

Whether the solar tree components’ idealised optical and physical properties are completely realisable or not is not the principal objective in this section. The main aim is to calculate a 1st approximation of the theoretical upper limit of scaleable\(^\text{vi}\) solar tree system concentration ratio and cost per unit power output.

\[^{\text{vi}}\text{ i.e., solar tree systems of varying collector area to PV area ratio}\]
3.2.2 Solar tree 2\textsuperscript{nd} stage concentrator

A compound parabolic concentrator, CPC, (Hinterberger and Winston, 1966; Winston, 1974) may be utilised as the 2\textsuperscript{nd} stage concentrator indicated in Figure 3.13. In an ideal CPC, incident light within the concentrator acceptance angle, $\theta_a$, shown in Figure 3.16(a), is transmitted to the exit aperture. $C_G$ is the CPC geometric concentration ratio, defining the ratio of CPC entry to exit apertures. An ideal CPC transmission curve, as shown in Figure 3.16 (b), is assumed in order to simplify initial analysis, however, fabricated CPCs have been shown to achieve close to the ideal transmission curve (Welford and Winston, 1989).

For a 3-D CPC, $C_G$ is less than or equal to;

$$C_G \leq \frac{1}{\sin^2 \theta_a}$$  \hspace{1cm} 3.5

For a dielectric-filled CPC (Winston, 1976), $C_G$ is enhanced by a factor corresponding to the refractive index of the CPC medium, $n_{CPC}$ squared;
\[ C_G \leq \frac{n_{\text{CPC}}^2}{\sin^2 \theta_a} \]  \hspace{1cm} (3.6)

\( C_G \), shown in Figure 3.17(b) for varying CPC \( \theta_a \) is the maximum possible concentration ratio of the CPC, assuming all photons entering the ideal CPC are within \( \theta_a \), and assuming \( n_{\text{CPC}} \) of 1.5. \( C_2 \) is defined as the effective concentration ratio of a particular CPC receiving light from the fibre optic bundle (FOB), a proportion of which may be outside \( \theta_a \). The angular distribution of photons exiting the FOB, shown in Figure 3.17(a), is determined from the ray-trace model. The fraction of photons incident on the CPC entry aperture which are within \( \theta_a \), termed \( k_a \), is shown in Figure 3.17(c). \( C_2 \) is thus defined as:

\[ C_2 = C_G k_a \]  \hspace{1cm} (3.7)

CPC \( \theta_a \) is inversely proportional to \( C_2 \), as shown in Figure 3.17(d). The total system efficiency decreases with higher \( C_2 \) due to reduced \( k_a \). More leaves and more FOs would therefore be required to attain a given power output. The relative cost per unit power output of the solar tree system, with varying CPC \( \theta_a \), is calculated in section 3.2.3.
Figure 3.17. (a) Angular distribution of light exiting fibre optic bundle (FOB). (b) $C_G$ is the ratio of the cross-sectional area of the FOB to the area of PV cells, and is determined by the particular CPC acceptance angle, $\theta_a$. (c) $k_a$ is the fraction of photons exiting the FOB which are within the CPC $\theta_a$. (d) $C_2$ is the effective concentration ratio of the CPC, given the angular distribution of incident photons shown in (a).

3.2.3 Solar tree evaluation for varying fibre optic costs and CPC $\theta_a$

The relative cost per unit power of the solar tree, for varying $\theta_a$ and FO cost per unit length is determined by;

$$\text{rel. cost/power} = \frac{1}{C_1C_2} + \frac{L_{\text{Leaf}} C_G}{C_1C_2W_{\text{FO}} \text{costfactor}_1} + \frac{L_{\text{FO}} C_G}{C_1C_2W_{\text{FO}} \text{costfactor}_2} \quad 3.8$$

where, costfactor$_1$ and costfactor$_2$ relate the cost of the leaves and FO, respectively, to the cost of the PV per unit area, as detailed in Appendix A. Calculating the cost
per unit power allows a comparison to be made with single-plate QDSCs with equivalent optical properties to those of the individual solar leaves. The following parameter values and assumptions are made:

- $C_1$ is determined in section 3.2.1 as a function of leaf length, $L_{\text{Leaf}}$, where the optimum length is determined to be $\sim 4.0$ cm for a plate thickness of 0.1 cm. A $\text{costfactor}_1$ of 45 is considered here, i.e., the relative cost per unit area of the 0.1 cm thick leaves is assumed to be three times less than the 0.3 cm thick plates detailed in section 3.1.2.

- The FO width, $W_{\text{FO}}$, is equal to the thickness of the leaves, i.e., 0.1 cm. The average length of each FO, $L_{\text{FO}}$, is assumed to be (a minimum of) 0.1 m.

- The FO cost per unit length is varied from €1.00/m to €0.001/m, which correspond to $\text{costfactor}_2$ values of 0.45 and 450 respectively, for the particular $W_{\text{FO}}$.

- The CPC geometric concentration ratio, $C_G$, and overall effective 2$\text{nd}$ stage concentration ratio, $C_2$, for a range of CPC acceptance angles, $\theta_a$ are given in Figure 3.17 (b) and (d), respectively.

The predicted relative costs per unit power for the idealised solar tree system are shown in Figure 3.18, showing that FO costs must be significantly less than €0.01/m for the solar tree to attain a lower cost per unit power than an equivalent single-plate QDSC. However, commercial bulk FO prices are currently much higher, ranging from €0.50/m to €5.00/m (OceanOptics, 2009; AnchorOptics, 2009; Kandilli and Ulgen, 2009), depending on the transmission grade, core diameter and material used. It is also noted that, to simplify the initial analysis of the solar tree system, the
cost of the multiple CPCs required is assumed to be zero, and hence the predictions underestimate the solar tree cost per unit power output\textsuperscript{vii}.

The analysis shows that the solar tree configuration does not result in a reduction in cost per unit power output, compared to that of a QDSC due to (i) the concentration effect of the 2\textsuperscript{nd} stage concentrator being limited by the angular distribution of photons exiting the FOs, and (ii) the associated costs of the additional system components. FO costs need to be \(< €0.01\) per metre for the solar tree system to have manufacturing costs per W\textsubscript{p} of the same order as single-plate QDSCs.

![Figure 3.18](image)

Figure 3.18. The relative cost per unit power of the solar tree with a 2\textsuperscript{nd} stage CPC, for varying CPC acceptance angle, \(\theta_a\), and fibre optic (FO) cost. The relative cost per unit power for a 1mm thick single-plate QDSC is given by the black line. At fibre optic costs \(< €0.01/m\) the solar tree attains costs per unit power of the same order as the single-plate QDSC.

\textsuperscript{vii} Fibre optic transmission losses and the cladding thickness are also assumed to be zero, in order to simplify the analysis.
3.3 Luminescent Down Shifting Layers

A luminescent down-shifting (LDS) layer (Hovel et al., 1979) can enhance the short circuit current density, \( J_{sc} \), of solar cells by transforming the wavelength of incident light from short to longer wavelengths better matching the spectral response of the cell, as shown by the schematic in Figure 3.19. For mc-Si cells, \( \sim2\% \) relative increase in \( J_{sc} \) is predicted by Klampaftis et al. (2008), using a LDS layer incorporating the optimum combination (at the optimum doping concentration) of the particular organic dyes investigated. A larger increase of 7.5 - 10\% is predicted by van Sark et al. (2005) using a LDS layer incorporating QDs, however. The LSC ray-trace model, described in section 2, is modified to predict the \( J_{sc} \) of a mc-Si solar cell attached to a LDS layer. The model is used to investigate whether the optical properties of QDs (i.e. broad absorption range and characteristic increased absorption in the UV and blue wavelength regions) make them a better potential candidate for incorporation in LDS layers than organic dyes. The American Society for Testing and Materials (ASTM, 2003) G-173-03 standard global hemispherical solar spectrum corresponding to air-mass 1.5 (AM 1.5g) is used as the input solar irradiance, following the normal standard for solar cell power conversion efficiency characterization.

Although the results presented here in section 3.3 are for mc-Si cells, it is important to note that LDS layers have been proven to enhance overall conversion efficiencies more significantly with other solar cell types. For example, a 16\% increase in efficiency was measured by Richards and McIntosh (2007) for a CdS/CdTe cell. Maruyama and Kitamura (2001) obtained a 36\% increase for a CdS/CdTe cell, but with a poorer quality cell with lower EQE in the blue region.
LDS layers have been shown to increase overall conversion efficiencies of organic solar cells (Koepe et al., 2007), and dye-sensitised solar cells (Liu et al., 2006). Up-converting layers could also be used to convert sub band-gap energy to photons at wavelengths above the PV cell band-gap. However, the efficiency and stability of up-conversion species are not sufficient to realise significant gains in PV cell electrical output.

The main aims of this section are (i) to investigate whether the optical properties of QDs (i.e. broad absorption range and characteristic increased absorption in the UV and blue wavelength regions) make them a more suitable candidate than organic dyes for incorporation in LDS layers, and (ii) to quantify the increase in PV cell power output, using a “partially-covered” LDS layer.

Figure 3.19. The luminescent down-shifting (LDS) layer transforms the wavelength of short wavelength incident photons to wavelengths better matching the EQE response of the mc-Si PV cell attached under the LDS layer.
3.3.1 LDS layers incorporating QDs.

The EQE of a mc-Si solar cell is shown in Figure 3.20. The lower EQE at short wavelengths results from higher emitter recombination in the cell, and higher reflection and absorption of the anti-reflective (AR) coating which is optimised for longer wavelengths (Klampaftis et al., 2009).

![Figure 3.20](image-url)

Figure 3.20. (a) Absorption and emission spectra of Coumarin-3-Carboxylic (blue), Perylene Lumogen Yellow 170, Perylene Lumogen Red 305 dyes. Also shown are the mc-Si cell EQE, and global solar spectrum measured at air-mass 1.5. (b) Absorption and emission spectra of two QD types; green emitting CdSe/ZnS QDs, and orange emitting CdSe/ZnS QDs.

LDS layers containing blue Coumarin, yellow Perylene, and red Perylene dyes, and layers containing CdSe/ZnS green-emitting and CdSe/ZnS orange-emitting quantum
dots were simulated using the ray-trace model. The doping concentration of each species can be varied in the model. The optimum absorption spectra and emission spectra of each luminescent species are shown in Figure 3.20. The same luminescent QY (98%) was assumed for each species, in order to compare the near maximum potential of each.

The enhancement in the mc-Si cell $J_{sc}$ using the blue, yellow and red dye doped LDS layers, compared to the reference cell covered with an undoped layer, is 1.01, 1.00, and 0.98, respectively. The enhancement using the green and orange QDs is 1.01 in both cases. The cell EQE for each LDS layer is shown in Figure 3.21. The device EQE is improved by the LDS layers at short incident wavelengths, resulting from incident photons being shifted to wavelengths better matching the cell EQE. The device EQE decreases at longer incident wavelengths, however, as the losses within the layer are greater than the gain attained by shifting the incident photon wavelength. The predicted enhancement of $\leq 1\%$ attained using the QD LDS layers is significantly lower than that predicted analytically (van Sark et al., 2005) for similar QD LDS layers (7.5 - 10% enhancement). The van Sark model uses QD absorption and emission spectra, and the incident light spectrum to determine a modified spectrum incident on the PV cell attached underneath the LDS layer. Re-absorption effects are not calculated in the analytic approach, however, thereby overestimating the PV cell short circuit current enhancement (van Sark et al., 2005). The ray-trace approach used here does incorporate the effects of photon re-absorption, and therefore allows a more accurate modified spectrum to be determined. The PV model, as described in section 2.3 is a less detailed model than that used by van Sark et al., which also calculates variation in open-circuit voltage and cell fill-factor. However, the short-circuit current enhancement is primarily
determined by the modified spectrum and the cell spectral response as given by 2.17. The different PV models used, therefore, are unlikely to account for the differing predictions.

![Graph](image)

Figure 3.21. EQE of reference mc-Si cell and the cell attached to luminescent down shifting (LDS) layers.

### 3.3.2 Partially covered LDS layers and comparison with LSCs

A geometric gain is added to the LDS layer, by reducing the area of PV cells attached to the LDS layer, as illustrated in Figure 3.22. The $J_{sc}$ of the active area of PV is enhanced as short wavelength photons are shifted to longer wavelengths better matching the PV cell spectral response. In addition, there is a light concentration effect as photons are transmitted to the cells (from areas of the layer not covered by
PV) via TIR, as shown in Figure 3.22. The configuration has previously been described by Sakuta et al. (1994) and Rau et al. (2005). Rau’s simulated device utilised a photonic structure acting as a spectrally selective reflector (SSR) on the top surface aperture. The devices considered here assume no SSR top layer.

Figure 3.22. (a) In the partially covered luminescent down-shifting layer (PC-LDS), a reduced fraction of the layer is covered by PV cell strips. (b) The PV cell $J_{sc}$ is enhanced as short wavelength photons are shifted to longer wavelengths better matching the PV cell EQE (ray 2), and longer wavelength photons not absorbed by the dye pass through the PC-LDS layer to the PV cell (ray 1). In addition, there is a geometric gain as the layer aperture area is greater than the area of PV. Hence, emitted photons (rays 3 and 4) transmitted to the PV cell via TIR increase the cell $J_{sc}$ compared to a fully covered LDS layer. (c) An LSC configuration employing the same luminescent plate, external reflector, and PV cells as used in (a).

The increase in mc-Si cell $J_{sc}$ using a 10x10 cm “partially covered” luminescent down-shifting (PC-LDS) layer is shown as a function of decreasing coverage fraction for varying luminescent dye types in Figure 3.23. The increase is greatest for the red dye, as it has the broadest absorption range of the three dyes, and, therefore, the light concentration effect is greatest. Reducing the coverage fraction to 10% results in an increase in cell $J_{sc}$ from 30.8 mA/cm$^2$ to 70 mA/cm$^2$. The short
circuit current is determined from eqn. 2.15 in this analysis, i.e., reflection at the PV cell is independent from the angle of incidence at the PV surface.

\[ \text{cell } J_{sc} (\text{mA/cm}^2) \text{ with blue PC-LDS layer} \]
\[ \text{cell } J_{sc} (\text{mA/cm}^2) \text{ with yellow PC-LDS layer} \]
\[ \text{cell } J_{sc} (\text{mA/cm}^2) \text{ with red PC-LDS layer} \]

Figure 3.23. \( J_{sc} \) (of the active cell area) increases as the fraction of the LDS layer covered by PV cells decreases. The effect is greatest for the red dye, as it has the broadest absorption range of the three dyes, as shown in Figure 3.20. Luminescent QY = 98% and \( \alpha_{\text{mat}} = 0.02 \text{ cm}^{-1} \) are assumed.

The PC-LDS devices are comprised of the same materials as an LSC, with the PV cells positioned at the bottom surface rather than at the side surfaces, as illustrated in Figure 3.22 (a) and (c). However, the electrical output of the attached PV cells in each configuration may differ. For example, assuming a normally incident AM 1.5 input spectrum, the predicted C for an 8 x 8 cm LSC containing Red 305 dye, with PV cells attached at the four sides, is 1.4. In the PC-LDS configuration, the four PV cells are attached to the bottom of the plate and the predicted concentration ratio increases from 1.4 to 1.9 due to longer wavelength incident photons being transmitted to the cells in the latter case. The material costs
are approximately the same in both the LSC and PC-LDS configurations, however C is \(~30\%\) higher in the PC-LDS for these particular dimensions.

C is shown for both the LSC and PC-LDS layer for increasing device size in Figure 3.24(a). For a given top surface aperture area, an equal area of PV cell is used in both device configurations. For smaller plate sizes, predicted C is higher for the PC-LDS configuration. The average pathlength of emitted photons to the PV cells is higher in the PC-LDS layer than in the LSC. Therefore, at larger plate sizes the advantage of using the PC-LDS is counteracted by increased matrix absorption losses and re-absorption losses, and higher C results for the LSC as shown in Figure 3.24(a).

The relative cost per unit power, calculated as in section 3.1.2, is shown in Figure 3.24(b) for both configurations. Both the LSC and PC-LDS layer attain approximately the same minimum relative cost per unit power of \(~0.7\), which corresponds to a \(30\%\) reduction in the cost per W, compared to the mc-Si cells.

Overall device power conversion efficiency, \(\eta\), decreases for larger LSC and PC-LDS layer plate sizes. Predicted \(\eta\), shown in Figure 3.24 (c), is significantly higher for the PC-LDS layer than the LSC, at device sizes corresponding to equivalent costs per unit power. For example, to attain a relative cost per unit power of 0.8, \(\eta\) for the PC-LDS layer is 7.1\%, compared to just 3.6\% for the LSC, as shown in Figure 3.24(c). This is significant as current single-plate LSCs utilizing mc-Si cells, have low power conversion efficiencies, \(\eta\), of \(~2.5\% - 3.5\%\) (depending on \(G_{gain}\)) under standard test conditions (van Sark et al., 2008; Slooff et al., 2008; Pravettoni et al., 2009a), with optimised plates predicted to attain \(\eta\), of 3.8\% for \(G_{gain}\)

\(^{viii}\) Efficiency of LSCs is not a useful comparative measure unless the geometric gain (or concentration ratio attained) is specified, as LSC efficiency is highly dependent on the plate dimensions and number of attached solar cells.
The ray-trace predictions show that employing the same PV cells and matrix materials in the PC-LDS layer configuration would significantly increase $\eta$, as compared to the LSC configuration. It should be noted that if the band-gap of the attached cell was matched better to the spectral range of the absorbing species, the benefit accruing from the PC-LDS layer would diminish. This is because the efficiency increase in PC-LDS layers is primarily due to longer wavelength light, not absorbed by the dye, being transmitted to the PV cells attached underneath.

![Figure 3.24](image)

Figure 3.24. (a) The concentration ratio, C, quantifying the relative increase in PV cell $J_{sc}$, (b) relative cost per unit power, and (c) power conversion efficiency, $\eta$, for LSC (red) and PC-LDS (dashed black) layer of varying plate size. Luminescent QY = 98% and $a_{mat} = 0.02$ cm$^{-1}$ are assumed. At a relative cost per unit power of 0.8, $\eta$ for the PC-LDS layer is ~double $\eta$ for the LSC, as indicated by the blue lines.
3.4 Chapter conclusions

The effect of varying device geometry and PV cell configurations was investigated using the ray-trace model, concluding that;

- For any given $A_{\text{conc}}$, hexagonal geometries attain higher $C$ than square or triangular geometry.

- Factoring in approximate relative costs of PV cells and QDSC plate material, the relative cost per unit power, for varying geometry type and $A_{\text{conc}}$, can be determined.

- The various geometry types all attain the same minimum cost per unit power if the correct $A_{\text{conc}}$ for that particular geometry is selected.

- The correct selection of $A_{\text{conc}}$ is critical for attaining the lowest possible cost per Wp. Ray-trace modelling provides an important tool for doing so.

- A non-uniform photon distribution along the QDSC plate edge would result in (1) reduced current through PV cells connected in series along any one plate edge, and/or (2) reduced fill factor for an individual cell attached at that edge. Hexagonal QDSC plates yield a more uniform spatial distribution of photons along the plate edges than rectangular or triangular plates.

- Whether PV cells are (a) attached at all sides of the device, or (b) attached at one side only with external mirrors at other sides, does not affect the minimum cost per unit power. This analysis, however, does not take into account the costs of additional mirrored surfaces required in case (b). Therefore, case (a) is, in fact, a marginally more optimal configuration.

- Higher QD doping concentrations are required for thinner QDSC plates to attain a given $\eta_{\text{abs}}$, and total re-absorption losses consequently increase. Despite the
increased re-absorption losses, the net effect of thinner QDSC plates is a significant increase in $C$.

- A tapered plate was proposed in an attempt to reduce QDSC re-absorption losses. The tapered device allows a lower QD doping concentration to be used to attain a given absorption efficiency while maintaining a high geometric gain. The tapered device does not result in higher $C$, due to an increase in top surface losses.

- A solar tree system, utilizing fibre optics to transmit light from multiple luminescent plates to a single PV cell via a 2nd stage concentrator, was proposed and the relative cost per unit power compared to that of a QDSC. The solar tree does not provide a reduction in relative cost per unit power output, due to the gain of the 2nd stage concentrator being limited by the angular distribution of photons emerging from the fibre optics, and due to the associated costs of the additional system components. If fibre optic costs were significantly reduced compared to current levels, however, then the concept should be further evaluated.

- An increase in mc-Si cell $J_{sc}$ of $\leq 1\%$ is predicted, using a quantum dot luminescent down-shifting (LDS) layer. The predicted increase is significantly lower than analytical predictions for quantum dot LDS layers in the literature.

- The minimum relative cost per unit power of a partially covered LDS layer is approximately the same as that attained for a LSC device. Power conversion efficiencies, $\eta$, of PC-LDS layers were quantified. It was shown that $\eta$ attained by the PC-LDS layer is greater than that attained by the LSC, at the respective optimum device sizes. This is significant as current LSC $\eta$ utilizing mc-Si cells under standard test conditions are low (c. 3% at a geometric gain of 10). Employing the same device materials that are used in an LSC in a PC-LDS layer configuration, would significantly increase $\eta$ without any additional costs.
3.5 References


http://www.anchoroptics.com/catalog/product.cfm?id=354 (last accessed 20/9/09)


123


125
van Sark, W.G.J.H.M., Meijerink, A., Schropp, R.E.I., van Roosmalen, J.A.M.,

Press, San Diego, USA.

Energy, 16, 89-95.

15, 2, 291-2.
4 Device materials

4.0 Introduction

This chapter investigates the effect of varying QD, matrix material, and external reflector optical properties on QDSC performance. While maximizing QDSC efficiency ultimately remains a materials challenge, modelling can be used to investigate under what circumstances certain goals are possible. For example, what is the minimum quantum yield required for a QDSC to attain a particular concentration ratio or particular power output. Moreover, gains that ensue from changes to device materials in currently realizable QDSCs may not ensue to the same degree in future higher efficiency QDSCs. For example, the solar energy concentration ratio, C, of current fabricated low efficiency QDSCs increases by a factor of two with the addition of a diffuse rear reflector in place of a specular rear reflector. Ray-trace modelling was used to show what increase is attained by the inclusion of a diffuse reflector in a higher efficiency QDSC.

The ray-trace model was used to determine the effect of varying QD optical properties on concentration ratios. Low QD luminescent quantum yields have limited concentration ratios attained in devices fabricated to-date. QDs with ideal luminescent quantum yields (QY) were modelled to quantify the potential performance of QDSCs, subject to re-absorption limitations arising from spectral overlaps between QD emission and absorption spectra. The analysis shows that escape-cone losses account for up to 58% of photons absorbed in a QDSC containing green-emitting QDs, – much higher than the minimum 25% escape cone losses.
predicted for a luminescent species with no spectral overlaps in the same plate with a plate refractive index of 1.5\textsuperscript{ix}. Higher matrix material refractive index, $n$, results in reduced escape cone losses but increased external reflection losses. The ray-trace model was used to examine the net effect of varying $n$ and matrix material absorption coefficient, $\alpha_{\text{mat}}$, on QDSC concentration ratios.

Utilizing rear reflectors with diffuse angular reflection results in significantly enhanced $C$ compared to specular reflector types. The effect of varying the external rear reflector type on $C$ is analysed for varying insolation angular distributions. The predictions indicate that the actual reflectivity of the reflector used, along with its cost, are the most important considerations for a viable QDSC reflector, and not the type of reflector used.

A spectrally selective reflector (SSR) top layer, e.g., a thin-film dielectric mirror, can reduce escape-cone losses in the device by reflecting QD emitted light within the angular range of the escape cone, while allowing incident light in the QD absorption range to enter the device. The modelling predictions illustrate why only limited gains have been obtained to date with SSR top layers. Owing to the multiple reflections at the SSR layer, even a small decrease in SSR reflectivity results in significant top surface losses. The ray-trace analysis also demonstrates the critical importance of utilizing a highly reflective rear reflector when measuring the performance of any SSR top layer.

\textsuperscript{ix} The refractive index of materials typically used in QDSCs fabricated to-date is ~1.5 in the visible wavelength range (400 – 700 nm).
4.1 QD optical properties

One advantage of using QDs over an organic luminescent dye, as the device luminescent species, is the ability to tune a device by varying the quantum dot size to collect specific wavelengths in the solar spectrum (Barnham et al., 2000; Chatten et al., 2003). The optical efficiency ($\eta_{\text{opt}}$) of currently fabricated QDSCs, however, has been limited by low luminescent quantum yields (QY) and large overlaps between QD emission and absorption spectra (Hyldahl et al., 2009; Rowan et al., 2008; Sholin et al., 2007). Spectral overlap results in QD-emitted photons being re-absorbed in the plate before reaching the PV cell, giving both higher escape cone losses and higher QY losses.

Re-absorption losses in QDSCs containing commercially-available green emitting and orange emitting (CdSe/CdS core-shell) QDs, and laboratory (CdSe CdS/CdZnS/ZnS multi-shell) near infra-red emitting QDs, are quantified. The absorption and emission spectra of the three QD types are shown Figure 4.1. To analyse re-absorption effects solely in terms of escape cone losses, and hence investigate the potential performance of QDSCs subject to spectral overlap limitations, particular device parameters are assumed (Kennedy et al., 2009);

- an ideal QD QY of 100%
- no matrix material absorption or scattering of light emitted by the QD
- perfectly reflecting external mirrors

Model parameter values also assumed are;

- a matrix material refractive index of 1.5
- an incident insolation spectrum corresponding to air-mass 1.5
- a QDSC plate size of 6 x 6 x 0.3 cm
- the spectral response, given in Figure 4.1, of the attached mc-Si solar cell.

![Absorption and emission spectra of three QD types. A: Green emitting QDs: CdSe/ZnS, peak emission wavelength ($\lambda_{\text{em}}$) = 488 nm, Nanoco technologies. B: Orange emitting QDs: CdSe/ZnS, $\lambda_{\text{em}}$ = 605 nm, Evident technologies. C: NIR emitting QDs: CdSe multi-shell coating CdS/CdZnS/ZnS, $\lambda_{\text{em}}$ = 690 nm, fabricated at Utrecht University, Netherlands, and the mc-Si PV cell photo-sensitivity spectral response.](image)

Figure 4.1. Absorption and emission spectra of three QD types. A: Green emitting QDs: CdSe/ZnS, peak emission wavelength ($\lambda_{\text{em}}$) = 488 nm, Nanoco technologies. B: Orange emitting QDs: CdSe/ZnS, $\lambda_{\text{em}}$ = 605 nm, Evident technologies. C: NIR emitting QDs: CdSe multi-shell coating CdS/CdZnS/ZnS, $\lambda_{\text{em}}$ = 690 nm, fabricated at Utrecht University, Netherlands, and the mc-Si PV cell photo-sensitivity spectral response.

4.1.1 QDSC absorption efficiency and escape cone losses

The absorption efficiency ($\eta_{\text{abs}}$) is defined as the fraction of incident photons absorbed on a double-pass through the plate. Predicted $\eta_{\text{abs}}$ of the green, orange and near infra-red (NIR) QDSCs are 11.6%, 21.7% and 23.1%, respectively, as shown in Figure 4.2. $\eta_{\text{abs}}$ is highest in the NIR QDSC due to the broad absorption range. From Figure 4.1, it is noted that the NIR QD absorption coefficient ($\alpha_{\text{QD}}$) at the NIR peak emission wavelength is significantly lower than the orange $\alpha_{\text{QD}}$ and green $\alpha_{\text{QD}}$ at their respective peak emission wavelengths. A consequence should be comparatively lower re-absorption and associated escape cone losses in the NIR QDSC. In the green, orange and NIR QDSCs, escape cone losses account for, respectively, 58%
±5\%^x, 57\% ±4\%^x, and 43\% ±1\%^x of incident photons absorbed in the plate. These losses are much higher than the ~25\% minimum escape cone loss predicted for no spectral overlaps, also in a plate of refractive index 1.5 (Batchelder et al., 1979). However, escape cone losses are significantly lower for the NIR QDSC when compared to the green and orange QDSCs. The retention efficiency ($\eta_{\text{ret}}$) is defined as the fraction of QD emitted photons transmitted to the PV cell. The predicted optical efficiency ($\eta_{\text{opt}}$), in this ideal case, is thus given by;

$$\eta_{\text{opt}} = \eta_{\text{abs}} \eta_{\text{ret}}$$  \hspace{1cm} (4.1)

$\eta_{\text{opt}}$ of the green, orange and NIR QDSCs is 5.0\%, 9.3\% and 13.2\%, respectively, as shown in Figure 4.3. The higher $\eta_{\text{opt}}$ of the NIR QDSC, compared to the orange QDSC, is due partly to the slightly higher $\eta_{\text{abs}}$ but more significantly due to lower re-absorption and associated escape cone losses.

![Figure 4.2](image)

Figure 4.2. Predicted optical efficiency ($\eta_{\text{opt}}$) of 6 x 6 x 0.3 cm QDSCs containing green, orange and NIR emitting QDs. $\eta_{\text{opt}} = \eta_{\text{abs}} x \eta_{\text{ret}}$, where the retention efficiency, $\eta_{\text{ret}} = 1$-(escape cone loss).

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* Measured QD emission spectra vary in their peak wavelength, depending on the excitation energy used. The uncertainty in the predicted escape cone losses, arise from the use of only a single emission spectrum in the model.
4.1.2 Solar energy concentration ratios for varying QD quantum yield

Ideal QYs were assumed in section 4.1.1 to analyse re-absorption effects solely in terms of escape cone losses and, hence, investigate the potential performance of QDSCs, subject to spectral overlap limitations. Commercially-available QDs have significantly lower QYs of 30%-50% (Nanonco Technologies, UK; Evident Technologies, USA), however, QD QYs > 85% have been demonstrated (Rogach, 2008). The effect of decreasing QY on predicted concentration ratios, C, is shown in Figure 4.3. Lower QYs have a less detrimental effect on the NIR QDSC, than on the green and orange QDSCs, due to lower re-absorption.

The predicted values of C are compared with that of an efficient organic dye (Lumogen Red305) LSC in Figure 4.3. The Red305 dye has a broad absorption range (from 400 to 600 nm) and a QY of 98% (Boehm, 2008). The estimated QY of these particular NIR CdSe QDs is ~50% (Koole, 2007), yielding a predicted device concentration ratio only 1/3 of that attained by the Red305 dye LSC.
Figure 4.3. Predicted concentration ratios, C, of 6.0 x 6.0 x 0.3 cm QDSCs containing green, orange and NIR emitting QDs of varying quantum yield (QY). The QDSCs concentration ratio is compared with that of a high QY dye LSC.

The results indicate that, even allowing for ideal QD QYs, homogeneously doped single-plate QDSCs containing current commercially-available visible-emitting QDs are unlikely to result in practical devices, due to the large spectral overlaps. The NIR emitting QDs have lower re-absorption losses owing to the shape of the absorption cross-section. Coupled with the broader absorption range, NIR emitting QDs remain potential candidates for viable QDSCs provided higher luminescent QYs are attained.
4.2 Matrix material properties

Multiple characteristics are required for a suitable QDSC matrix material (Gallagher et al., 2007), i.e., low absorption coefficient, solubility with QDs, high luminescence when cast with QDs, chemical durability, non-toxicity, and low cost. The effect of varying the matrix material absorption coefficient, $\alpha_{\text{mat}}$, can be analysed using the ray-trace model. An epoxy resin used in previously fabricated QDSCs has $\alpha_{\text{mat}}$ of $\sim0.04$ cm$^{-1}$ across the wavelength range 400-800 nm (Gallagher et al., 2007). Various $\alpha_{\text{mat}}$ for dye doped LSC plates are quoted in the literature, ranging from 0.04 cm$^{-1}$ (Burgers et al., 2006), to 0.005 cm$^{-1}$ (Thomas et al., 1983, van Sark et al., 2008). Matrix material absorption is wavelength dependent, with increased absorption at UV wavelengths. PMMA, for example, also shows increases at narrow bands in the NIR region due to harmonic vibrations involving the hydrogen atom. (Thomas et al., 1983), For this analysis, $\alpha_{\text{mat}}$ is assumed to be wavelength independent over the spectral response range of the attached solar cell (e.g. 300-1200 nm for crystalline silicon solar cells).

The refractive index of the plate, $n$, is an important parameter in relation to QDSC efficiency. The refractive index of polymer materials commonly used in LSCs is $\sim1.48$ - 1.6. Optical glass with refractive indices up to 1.82 have been used as substrates in thin-film LSCs (Mulder et al., 2009, Currie et al., 2008). Higher $n$ results in higher retention efficiency, $\eta_{\text{reis}}$, as escape cone losses are diminished. External reflection losses are increased, however, with higher $n$. The ray-trace model is used to examine the net effect of varying $n$ (and $\alpha_{\text{mat}}$) on QDSC concentration ratios. Figure 4.4 shows predicted concentration ratios for the QDSC detailed in section 4.1, with varying $n$ and $\alpha_{\text{mat}}$. Increasing the refractive index from 1.5 to 1.7
would increase C by 10% (assuming \( \alpha_{\text{mat}} = 0.01 \text{ cm}^{-1} \)). Employing a matrix material with \( \alpha_{\text{mat}} = 0.04 \text{ cm}^{-1} \) would decrease C by 35%, compared to a QDSC with \( \alpha_{\text{mat}} = 0.01 \text{ cm}^{-1} \) (assuming \( n = 1.5 \)).

Figure 4.4. QDSC Concentration ratio for varying plate refractive index, \( n \), and matrix material absorption coefficients, \( \alpha_{\text{mat}} \).

The results clearly highlight the importance of maintaining \( \alpha_{\text{mat}} \) as low as possible, with significant gains achievable with lower \( \alpha_{\text{mat}} \). Attempts to increase device efficiency by increasing \( n \) must consider the effect of any variation in \( \alpha_{\text{mat}} \). It is noted that C has been predicted for normal incidence. While the variation in C (and hence, in device power conversion efficiency ratings) are representative of those attainable under standard test conditions, realistic external reflection losses would be higher in outdoor conditions with increased insolation incident angles. Therefore, the effect of varying \( n \) on outdoor annual energy yields is examined in section 5 using more realistic solar radiation modelling.
4.3 Specular and diffuse rear reflectors types

In this section, the effect of rear reflector type (i.e., whether the reflector type is diffuse or specular) on $C$ is analysed using the ray-trace model. Under normally incident light, device $C$ may increase with the inclusion of a diffuse reflector through two mechanisms (Kennedy et al., 2007);

(a) With a diffuse reflector, the initial pathlength of normally incident light on a double-pass through the plate is increased, as illustrated in Figure 4.5, resulting in a higher absorption efficiency.

(b) Normally incident light not absorbed in the plate may be reflected onto the attached PV cell when a diffuse rear reflector is utilised, whereas utilizing a specular reflector this does not occur.

Varying relative increases are reported in the literature. Rowan et al. (2007) observed more than 100% increases in $C$, whereas Burgers et al. (2005) measured an increase of $\sim 25\%$ for an LSC employing a diffuse reflector, compared to the same device with a specular reflector.

![Figure 4.5](image)

Figure 4.5. For direct normal incidence, there is an increased average pathlength using a diffuse reflector(b) compared to a specular reflector(a), resulting in a higher absorption efficiency. Moreover, there is a probability that incident light will be reflected directly onto the PV cell using a diffuse reflector(d), but not using a specular reflector(c).
C is calculated for the NIR QDSC, described in section 4.1, assuming a diffuse rear reflector in place of the specular rear reflector used therein. A Lambertian angular distribution, with an ideal reflectivity, is assumed for the diffuse reflector. Two insolation incident angular distributions are considered - (i) direct normal to the QDSC top surface, and (ii) isotropic diffuse insolation. An air-gap is assumed to exist between the plate and external reflectors allowing TIR to occur at this boundary. Higher device efficiencies ensue with an air-gap, as $\eta_{\text{TIR}}$ is greater than the reflector reflectivity (Debije et al., 2009).

As shown by the ray-trace predictions in Figure 4.6(a), the potential increase in C from a diffuse rear reflector depends on the QD QY. Assuming a QD QY of 20%, for example, the diffuse reflector results in a 60% relative increase in predicted C. Assuming a QD QY of 90%, however, only a 15% relative increase in C ensues. This explains the varying results presented in the literature with lower relative increases accruing in more efficient devices. In overcast outdoor conditions the sky undertakes the role of the diffuser, negating the advantages of the diffuse reflector outlined above for normally incident light (Sidrach de Cardona et al., 1985b). There is no significant difference in predicted C assuming isotropic diffuse insolation, as shown in Figure 4.6(b). These results indicate that the actual reflectivity of the reflector used, along with its cost, are the most important considerations for a viable QDSC reflector, and not the type of reflector used.
Figure 4.6. Predicted C for QDSC assuming external specular (red line) and Lambertian (dashed blue line) rear reflectors for (a) direct normal, and (b) isotropic diffuse incident insolation.
4.4 Spectrally selective reflecting top layers

Spectrally selective reflector (SSR) top layers can reduce the escape-cone losses in the device by reflecting QD emitted light within the angular range of the escape cone, while allowing light in the QD absorption range to enter the device (Smestad et al., 1990). With a perfectly reflecting SSR, Rau et al. (2005) have shown that LSC efficiency can approach that of the maximum possible for a single junction solar cell. “Hot mirrors” were proposed as SSR layers by Richards et al. (2004), but no increase in overall efficiency was observed with the particular hot mirror used. Rugate filters (Goldschmidt et al., 2006) resulted in an 11% increase in LSC internal optical efficiency due to the reduction in escape-cone losses. However, the gains were negated by partial transmission losses, reflection of short wavelength incident light, and scattering at the filter surface. More recent prototypes have demonstrated a 20% increase in device efficiency with the inclusion of a Rugate filter (Goldschmidt et al., 2009). Cholesteric liquid crystal coatings have also been proposed (Chatten et al., 2007), however no significant increase (within the experimental error) was found using the cholesteric reflector on two dye LSC plates, compared to control samples without the cholesteric reflector, due to reflection of short wavelength light negating the advantage of reduced escape cone losses.

In section 4.4.1, the cut-off wavelength of the SSR modelled is optimised for the particular luminescent species used. An ideal cut-off and zero transmission losses are assumed for the SSR. Emitted photons exiting the device through the escape-cone are reflected by the SSR layer. However, multiple reflections are required at the SSR layer interface (and at the rear reflector) before the photon is transmitted to the plate edges and, therefore, even a small decrease in SSR reflectivity, $R_{SSR}$, may result in a
significant overall top surface losses. In sections 4.4.2 and 4.4.3, the ray-trace model is used to investigate the effect of reduced $R_{SSR}$ and rear reflector reflectivity on device concentration ratios.

4.4.1 SSR cut-off wavelength optimisation

Assuming a diffuse rear reflector with a reflectivity of 0.98, a concentration ratio of 3.8 is predicted for the 6 x 6 x 0.3 cm QDSC detailed in section 4.3. Top surface escape cone losses account for 41% of incident photons absorbed in the QDSC. A SSR top layer with a reflectivity of 0.999 is incorporated into the ray-trace model of the QDSC. An-air gap is assumed between the SSR layer and the QDSC top surface, which allows TIR to occur for incident light within the angular range. To simplify calculations, transmission losses through the SSR layer are assumed to be zero. In SSR layers the reflectivity is found to blue-shift with higher angles of incidence (Richards et al., 2004). However, for this preliminary analysis, reflectivity is assumed to be angle independent.

The SSR reflection/transmission cut-off wavelength ($\lambda_{co}$), shown in Figure 4.7, is varied and the resulting device concentration ratio calculated. Using a shorter $\lambda_{co}$, more QD emitted light escaping the top surface is reflected, but a larger fraction of the incident light is also reflected from the device. With a longer $\lambda_{co}$, less QD emitted light is reflected, but more of the incident light enters the device. Predicted C for varying $\lambda_{co}$ is shown in Figure 4.8, with an optimum $\lambda_{co}$ of 655 nm predicted for this particular QDSC. The analysis shows that it is critical to optimise $\lambda_{co}$ for the particular optical properties of the luminescent species used.
Figure 4.7. A spectrally selective reflector (SSR) with angle-independent reflectivity and ideal "cut-off" between reflection and transmission wavelength regions is modelled.

Figure 4.8. Predicted QDSC concentration ratio, C, for varying spectrally selective reflector layer cut-off wavelength, $\lambda_{co}$. 
4.4.2 Top surface losses for varying SSR reflectivity

As shown in Figure 4.9(a), a concentration ratio of 5.0 is predicted for the particular QDSC assuming an $R_{SSR}$ of 0.999. The top surface losses are reduced from 41% (without an SSR) to 2%. The effect of reduced $R_{SSR}$ on top surface losses is shown in Figure 4.9(b). For example, assuming reduced $R_{SSR}$ of 0.95 and 0.85, the total top surface losses increase (from 2%) to 19% and 29%, respectively. The modelling predictions partly explain why only limited gains have been obtained to date with many SSR top layers. Owing to the multiple reflections at the SSR layer, even a small decrease in $R_{SSR}$ results in significant overall top surface losses.

![Figure 4.9](image.png)

Figure 4.9. (a) Variation in concentration ratio, C, with increasing spectrally selective reflector (SSR) reflectivity. (b) Top surface losses decrease with higher SSR reflectivity, however, rear reflector ($R_{Mirror}=0.98$) losses increase.

142
4.4.3 Effect of rear reflector reflectivity

Figure 4.10 shows the effect of variation in *rear reflector* reflectivity, $R_{\text{Mirror}}$, on $C$ of QDSCs\(^{xi}\) with, and without, a near-ideal SSR top layer with $R_{\text{SSR}}$ of 0.999. Relatively small decreases in $R_{\text{Mirror}}$ significantly affect the potential gain in $C$. Even though $R_{\text{SSR}}$ is close to ideal, the multiple reflections required at the rear reflector before photons are transmitted to the plate edges results in significant reductions in $C$ when $R_{\text{Mirror}} < 1.0$. The results highlight the importance of utilizing a highly reflective *rear* reflector when measuring the performance of any SSR top layer.

![Figure 4.10](image)

Figure 4.10. Predicted concentration ratio, $C$, for increasing rear reflector reflectivity, $R_{\text{Mirror}}$. The QDSCs modelled assume a near-ideal spectrally selective reflector (SSR) top layer with reflectivity of 0.999. Relatively small decreases in $R_{\text{Mirror}}$ significantly affect the potential gain in $C$ attained an SSR layer. The results highlight the importance of utilizing a highly reflective *rear* reflector when measuring the performance of any SSR top layer.

\(^{xi}\) The other QDSC parameters are as detailed above in section 4.1.
4.5 Chapter conclusions

While maximizing QDSC efficiency ultimately remains a materials challenge, modelling can be used to investigate under what circumstances certain goals are possible. The effect of varying QD, matrix material, and external reflector optical properties on QDSC performance has been investigated.

- Escape cone losses account for 58% and 57% of incident photons absorbed in the green and orange QDSCs modelled, respectively. This is much higher than the ~25% minimum escape cone loss assuming a luminescent species with no spectral overlaps in the same plate. Predicted escape cone losses are reduced to 43% for the QDSC incorporating NIR QDs.

- Even allowing for ideal QYs, commercially-available visible-emitting QDs are not suitable candidates for inclusion in viable QDSCs, due to spectral overlaps and the resulting re-absorption losses. The NIR emitting QDs have lower re-absorption losses owing to the shape of the absorption cross-section. Coupled with the broader absorption range, NIR emitting QDs remain potential candidates for viable QDSCs, provided higher luminescent QYs are attained.

- Higher matrix material refractive index, \( n \), results in reduced escape cone losses but increased external reflection losses. The ray-trace model was used to examine the net effect of varying \( n \) and matrix material absorption coefficient, \( \alpha_{\text{mat}} \), on C of a particular 6 x 6 x 0.3 cm QDSC. For example, increasing \( n \) from 1.5 to 1.7 would increase C by 10% (assuming \( \alpha_{\text{mat}} = 0.01 \text{ cm}^{-1} \)). Employing a matrix material with \( \alpha_{\text{mat}} = 0.04 \text{ cm}^{-1} \) would decrease C by 35%, compared to a QDSC with \( \alpha_{\text{mat}} = 0.01 \text{ cm}^{-1} \). The results clearly highlight the importance of maintaining \( \alpha_{\text{mat}} \) as low as possible, with significant gains achievable with lower \( \alpha_{\text{mat}} \). Attempts
to increase device efficiency by increasing \( n \) must consider the effect of any variation in \( \alpha_{\text{mat}} \).

- Under direct normal insolation, the advantage of employing a diffuse rear reflector reduces with more efficient QDSCs. There is no significant difference in predicted \( C \) assuming isotropic diffuse insolation. The results indicate that the actual reflectivity of the reflector, and its cost, are the most important considerations for a viable QDSC reflector, and not the reflector type.

- The ray-trace model is an important tool for determining the optimum cut-off wavelength of a spectrally selective reflector (SSR) top layer.

- The effect of reduced SSR reflectivity, \( R_{\text{SSR}} \), and rear reflector reflectivity on device concentration ratios was analysed. The modelling predictions partly explain why limited gains have been obtained experimentally to date with many SSR top layers. Owing to the multiple reflections at the SSR layer interface, even a small decrease in \( R_{\text{SSR}} \) results in significant top surface losses. For the same reason, it is of critical importance to utilise a highly reflective rear reflector when measuring the performance of any SSR top layer.
4.6 References


Mulder, C.L., Theogarajan, L., Currie, M., Mapel, J.K., Baldo, M.A., Vaughn, M.,
Luminescent solar concentrators employing phycobilisomes. *Advanced
Materials*, 21, 1-5.


assembly, spectroscopy*. Springer-Verlag/Wien, Austria.

Concentrator. School of Physics, Dublin Institute of Technology, Dublin.

Rowan, B.C., Wilson, L.R., Richards, B.S., (2008). Advanced material concepts for
luminescent solar concentrators. *IEEE Journal of Selected Topics In
Quantum Electronics*, 14, 5, 1312-22.

dots in luminescent solar concentrators for solar energy harvesting. *Journal of

Outdoor evaluation of luminescent solar concentrator prototypes. *Applied
Optics*, 24, 13, 2028-32.


5 Outdoor modelling of LSCs

5.0 Introduction

The performance of LSCs can vary over the course of a given day due to variation in:

- the incident insolation spectrum due to changes in air mass and atmospheric conditions;
- the diffuse fraction of total incident insolation;
- the skyward distribution of the diffuse insolation component;
- albedo radiation, from the ground or from adjacent buildings, which may be incident on the LSC plane.

Mansour et al. (2002) and El-Shaarawy et al. (2007) obtained higher efficiencies and concentration ratios for fixed plate LSCs in morning and evening times, compared to those obtained at mid-day. This was attributed to the higher diffuse component of the insolation available at those times (Mansour et al., 2002). The effect of varying tilt angle was also found to have a significant effect on overall power output. El-Shaarawy et al. found the optimum LSC tilt angle to be 16° during summer testing at a particular location in Egypt (latitude 31°). In a year long LSC outdoor field trial also at a location in Egypt, Salem et al. (2000) determined the relative seasonal increase in average power output for LSCs employing two-axis tracking compared to an LSC at varying fixed tilt angles, concluding that tracking was not beneficial for LSC systems due to the additional capital and operational costs. Pravettoni et al. (2009b) measured the diurnal variation in LSC electrical output over two separate
days at a location in Italy. Increases in efficiency were noted a) when the diffuse component increased due to short-term cloud cover, and b) at morning and evening times when light was incident at higher angles. Indoor testing has also demonstrated higher efficiencies at higher incidence angles (Pravettoni et al., 2009a).

The ray-trace model was used to investigate the outdoor performance of a QDSC in a climate with a large diffuse component of insolation at a location in Dublin, Ireland (53°N). Monthly averaged hourly spectral irradiance and incident angle distributions on a tilted QDSC plate were determined from horizontal irradiance measurements. Using the hourly data as input to the ray-trace model the following were investigated;

- the diurnal variation in QDSC concentration ratio,
- the effect of tilt angle and solar tracking on QDSC outdoor performance,
- the effect of varying the QDSC plate refractive index on annual energy yield,
- the effect of an anti-reflective coating in minimizing external reflection losses and increasing annual energy yield.

5.1 Solar radiation modelling

Variation of the global irradiance on a tilted surface, $G_t$, is required to model the outdoor performance of a QDSC. $G_t$ is given by the sum of the beam, $B_t$, diffuse, $D_t$, and ground albedo reflected, $R_t$, irradiance components;

$$G_t = B_t + D_t + R_t$$

5.1
Global horizontal irradiance, $G_h$, from which $B_t$, $D_b$ and $R_t$ can be determined, was measured at the Dublin Institute of Technology, Ireland (53° N, 6° W), at five minute intervals over the year January to December, 2008. A diffuse-global correlation model (Mondol et al., 2008) is used to predict the horizontal diffuse and beam irradiance components, $D_h$ and $B_h$, from $G_h$. The beam and ground reflected components on a tilted surface, $B_t$ and $R_t$ are easily determined from $B_h$ and $G_h$, respectively, with knowledge of the solar geometry and the plane tilt and orientation.

Determining $D_t$ is less straightforward as, ideally, an accurate angular distribution of the diffuse component is required to determine the diffuse irradiance on any given tilted surface. The semi-empirical Perez slope irradiance model (Perez et al., 1987; Perez et al., 1990) is used to predict $D_t$ from $D_h$. Sections 5.1.1 - 5.1.6 detail the methods used to obtain the spectral irradiance on a tilted surface, required as ray-trace model input. All solar irradiance data and results are presented in solar time. Solar time describes the angular motion of the sun across the sky at a particular location, with solar noon occurring when the sun reaches maximum altitude as observed from that location. Appendix B details how to convert from local standard time to solar time.

### 5.1.1 Beam and diffuse horizontal irradiance

Extraterrestrial global horizontal irradiance, $E_h$, is the irradiance a horizontal surface would receive in the absence of any clouds or atmosphere around the earth and is given by:

$$E_h = I_0 \cos \theta_s$$  \hspace{1cm}  \text{(5.2)}
where $I_0$ is the solar constant. $I_0$, measured outside the earth’s atmosphere, varies slightly throughout the year and instrumentation uncertainty is also a factor in determining $I_0$ (Liou, 2002). An annual average value of $1366 \pm 3\text{W/m}^2$ is quoted by Lean and Rind (1998) for $I_0$. A constant value of $1366\text{ W/m}^2$ is assumed for irradiance calculations.

The clearness index, $k_T$, an indicator of the relative clearness of the atmosphere is given by;

$$k_T = \frac{G_h}{E_h}$$  \hspace{1cm} 5.3

Increased cloud cover and/or sky turbidity xii decreases the measured global irradiance, $G_h$, yielding a lower clearness index. The diffuse fraction, $k_D$, of hourly irradiance is correlated with $k_T$, and can therefore be determined from measured hourly $G_h$ data. The Mondol diffuse-global correlation model (Mondol et al., 2008) is given by;

\begin{align*}
  k_D &= 0.98 \\
  k_D &= 0.61092 + 3.6259k_T - 10.171k_T^2 + 6.338k_T^3 \\
  k_D &= 0.672 - 0.474k_T \\
\end{align*}

for $k_T \leq 0.2$  \hspace{1cm} 5.4

for $0.2 < k_T \leq 0.7$  \hspace{1cm} 5.4

for $k_T > 0.7$  \hspace{1cm} 5.4

The Mondol model was found to predict $k_D$ more accurately than two other diffuse-global correlation models (Erbs et al., 1982; Reindl et al., 1990) when compared with measurements taken over a 33 month period at a location in Northern Ireland at latitude 54° N (Mondol et al., 2008). Mean hourly $D_h$ (and $B_h$) were calculated for

\text{xii} due to absorption of solar irradiance by water vapour or scattering by aerosol particles
each calendar month of 2008. Predictions for January and July are shown in Figure 5.1. \( D_h \) is significantly greater than \( B_h \) in both months. The total annual horizontal diffuse fraction at the location (Dublin, Ireland), was 0.77. LSCs, with limited absorption ranges, operate more efficiently in diffuse light conditions as a higher fraction of the incident irradiance is within the absorption range (Goetzberger, 1978).

![Figure 5.1](image)

**Figure 5.1.** The measured mean hourly global horizontal irradiance, \( G_h \), and predicted mean hourly horizontal beam irradiance, \( B_h \), and diffuse irradiance, \( D_h \), for the months January and June, 2008.

### 5.1.2 Solar geometry

The position of the sun is defined by the solar zenith angle, \( \theta_s \), and the solar azimuth angle, \( \gamma_s \), as shown in Figure 5.2. The 15th day of each calendar month is taken as an approximate "mean day", representative of the solar path of all days in that month. The solar path, describing hourly \( \theta_s \) and \( \gamma_s \), for the mean day of months January to June, at a location 53° N, is shown in Figure 5.3.
Figure 5.2. The position of the sun is defined by the solar zenith angle, $\theta_s$, and the solar azimuth angle, $\phi_s$. A tilted planar surface has tilt angle, $\beta$, and surface azimuth angle $\gamma_p$.

Figure 5.3. The solar path, describing hourly solar elevation angle $(90^\circ - \theta_s)$ and azimuth angle, $\gamma_s$, for the 15th day of months January to June, at a location latitude 53° North.
The solar angles $\theta_s$ and $\gamma_s$ are given (Sproul, 2007) by:

$$\theta_s = \cos^{-1}(\sin \delta \sin \phi + \cos \delta \cos \phi \cos \omega)$$

$$\gamma_s = \cos^{-1}\left(\frac{\cos \phi \sin \delta - \cos \delta \sin \phi \cos \omega}{\cos\left(\frac{\pi}{2} - \theta_s\right)}\right)$$

if $\omega > 0$, $\gamma_s = 2\pi - \gamma_s$

where, $\Phi$ is the location latitude, north (positive) or south (negative) of the equator, $\delta$ is the solar declination, i.e., the angular position of the sun with respect to the plane of the earth’s equator, given (Duffie and Beckman, 1990) by;

$$\delta_{\text{degrees}} = 23.45 \sin\left(360 \frac{284 + \text{day}_j}{365}\right)$$

and $\omega$ is the hour angle, i.e., the angular displacement of the sun to the east (negative) or west (positive) of the local meridian, given by;

$$\omega = 15(\text{solar hour-12})\pi/180$$

**5.1.3 Beam irradiance on tilted surface**

For a surface with tilt angle, $\beta$, oriented at a planar azimuth angle, $\gamma_p$, as shown in Figure 5.2, the beam irradiance on a tilted surface, $B_b$, is given (Drif et al., 2008) by;
where $\theta_p$ is the angle of incidence on the tilted planar surface given (Sproul, 2007) by;

$$\cos \theta_p = \cos \beta \cos \theta_s + \sin \beta \sin \theta_s \cos (\gamma_p - \gamma_s)$$ \hspace{1cm} 5.10

If the sun is located behind the tilted surface plane, the beam irradiance on the tilted surface, $B_t$, is zero, as is shown by the graph in Figure 5.4.

![Graph showing beam irradiance on tilted surface](image)

**Figure 5.4.** Beam irradiance on surface with varying tilt angle, $\beta$ and azimuth angle $\gamma_p$, calculated using eqn. 5.10, for an arbitrary beam irradiance on the horizontal of 1000 W m$^{-2}$. The solar zenith angle, $\theta_s$, and azimuth angle, $\gamma_s$, are arbitrarily set to 60° and 180°, respectively.
5.1.4 Diffuse irradiance on tilted surface

The simplest model for calculating $D_t$ is to assume that solar diffuse radiation is isotropic (Liu and Jordan, 1960), however, this model leads to an underestimation of $D_t$ (Drif et al., 2008). The Perez slope irradiance model is an anisotropic model which divides the sky dome into three geometric zones; (i) the circumsolar zone, (ii) the horizon band, and (iii) the remainder of the hemispherical sky dome, as illustrated in Figure 5.5. (Perez et al., 1987; Perez et al., 1990). In a two year study comparing predicted and measured hourly $D_t$ on sloped surfaces at two sites in France (Perez et al., 1987), the root mean squared errors in predicted $D_t$ were 16.3%, 9.3%, 6.5% and 8.7% for North, South, East and West facing vertical surfaces, respectively.

![Figure 5.5. The Perez model of the sky dome divided into three geometric zones; (i) the circumsolar zone, (ii) the horizon band, and (iii) the remainder of the hemispherical sky dome.](image)

The point-source Perez model for calculating diffuse irradiance on a tilted surface, $D_h$, is given by;

$$D_t = D_{cs} + D_{hz} + D_{iso}$$

where the circumsolar, horizon brightening and isotropic diffuse components, $D_{cs}$, $D_{hz}$, and $D_{iso}$ are given by;
\[
D_{cs} = D_h F_1 \frac{\cos \theta_i}{\cos \theta_s}
\]
\[
D_{he} = D_h F_2 \sin \beta
\]
\[
D_{iso} = D_h (1 - F_1) \frac{1 + \cos \beta}{2}
\]

The circumsolar and horizon brightening coefficients, \( F_1 \) and \( F_2 \), are given by;

\[
F_1 = \max[0, (f_{i1} + f_{i2} \Delta + f_{i3} \theta_s)]
\]
\[
F_2 = f_{21} + f_{22} \Delta + f_{23} \theta_s
\]

where, \( f_{ij} \) and \( f_{2j} \) (\( j=1\rightarrow3 \)) depend on the "sky clearness", and are obtained from the lookup table given in Appendix B. The sky brightness parameter, \( \Delta \), is defined as;

\[
\Delta = mD_h / I_0
\]

where \( m \) is the air-mass given (Kasten and Young, 1989) by;

\[
m = \frac{1}{(\cos \theta_s \text{ (degrees)} + 0.50572(96.07995 - \theta_s \text{ (degrees)})^{-1.6364}}
\]

5.1.5 Ground reflected irradiance

Ground reflectance is assumed to be isotropic from a horizontal ground surface. The ground reflected irradiance, \( R_g \), depends on \( \beta \) and the ground surface albedo, \( \rho \) (Duffie and Beckman, 1990);
Ground surface albedo, $\rho$, varies depending on the environment and also on the solar zenith angle. If the value of $\rho$ is unknown, it is common to consider that $\rho = 0.2$ (Drif et al.).

5.1.6 Spectral irradiance

The average photon energy of solar insolation varies depending on air-mass and atmospheric conditions, with the transmitted spectrum being more “blue rich” in overcast conditions. Using a single standard spectrum, such as the American Society for Testing and Materials (ASTM, 2003) G-173-03 global hemispherical solar spectrum for air-mass 1.5 (AM 1.5g), will therefore underestimate QDSC power output in diffuse insolation conditions. Therefore, approximate beam and diffuse spectral irradiance are determined for use in the QDSC ray-trace model. The standard direct normal irradiance at air-mass 1.5 (AM 1.5d), shown in Figure 5.6, is normalised and then weighted by $B_t$ to simulate the beam spectral irradiance component. Subtracting the AM 1.5d from the AM 1.5g irradiance, normalizing the result, and weighting by $D_t$ yields the diffuse spectral irradiance component approximation. A useful study would be to compare the hourly spectral irradiance with measured spectral irradiance data, to quantify the error arising from using the approximated spectra. Comparisons could also be made with spectral irradiance models, such as the parameterised semi-empirical SPCTRL2 (Bird and Riordan, 1986) and SEDES2 (Nann and Riordan, 1991; Nann and Emery, 1992; Houshyani, 2007).
Figure 5.6. The diffuse spectral irradiance distribution (blue) is obtained by subtracting the direct normal (red) from the global (black) American Society for Testing and Materials, G-173-03, spectral irradiance.

5.1.7 Annual in-plane insolation

Total insolation (J/m²) on a tilted surface is calculated by integrating $G_i$ over a given time period. The total annual insolation on a tilted surface for the year 2008 at the Dublin location\(\text{\textsuperscript{xiii}}\) is shown in Figure 5.7, with a broad maximum occurring at a tilt angle, $\beta$, of $\sim$30°. Insolation levels $\geq$ 95% of the maximum are obtained over a wide range of $\beta$ ($<10^\circ \leq \beta <55^\circ$).

The optimum QDSC tilt angle may not necessarily correlate exactly with the maximum in-plane insolation, however, due to spectral effects and surface reflection

\(\text{\textsuperscript{xiii}}\) assuming a surface albedo, $\rho = 0.2$
losses. Relative QDSC annual energy yields for varying tilt angles are determined in section 5.2.2.

Figure 5.7. (a) Annual in-plane insolation for varying $\gamma_p$ and $\beta$. (b) Fraction of the maximum annual in-plane insolation available at varying $\gamma_p$ and $\beta$.

Figure 5.8 Annual hourly global horizontal irradiance, $G_h$, (red + blue) measured at a location in Dublin, Ireland, and the calculated beam and diffuse components, $B_h$ (blue) and $D_h$ (red).
5.2 QDSC performance in outdoor conditions

5.2.1 Diurnal variation in QDSC concentration ratio

The hourly concentration ratio of a 20 x 20 x 0.3 cm QDSC is determined for the mean day of each calendar month under the following assumptions;

- Fixed QDSC plate at $\beta=30^\circ$ and $\gamma_p=180^\circ$.
- QD QY = 100%,
- $a_{mat} = 0.02 \text{ cm}^{-1}$,
- $n_2 = 1.5$,
- $\rho = 0.2$,
- 20 x 0.3 cm mc-Si cells, characterised by the IQE and $R_{p}$ curves shown in Figure 2.6, are attached at each of the four QDSC edges.

QDSC concentration ratio is equivalent to the ratio of the short circuit current of the PV cells attached to the concentrator, $I_{sc,pv_c}$, to the short circuit current of the same PV cells not attached to the concentrator, $I_{sc,pv}$, oriented on the same plane as the concentrator top surface, i.e.;

$$ C = \frac{I_{sc,pv_c}}{I_{sc,pv}} \quad 5.17 $$

Using the irradiance data from the Dublin location, average hourly $I_{sc,pv}$ and $I_{sc,pv_c}$ are predicted for the mean day of each month from eqn. 2.22. The annual hourly average $I_{sc,pv}$ and $I_{sc,pv_c}$ are shown in Figure 5.9. The concentration ratio, $C$, is
higher in mornings and evenings than at mid-day, due to an increase in QDSC $\eta_{\text{abs}}$ at these times arising from;

i) An increase in pathlength of the direct component of the solar radiation on a double pass through the QDSC plate.

ii) A higher mean photon energy of the global irradiance, as hourly $k_D$ is higher in mornings and evenings at this location, as shown in Figure 5.8.

![Graphs showing diurnal variation of annual average hourly (a) $I_{sc, PVc}$ and $I_{sc, PV}$ and (b) concentration ratio, C, for a QDSC inclined at 30°. The predicted C for the same QDSC assuming the standard AM1.5G spectrum at normal incidence is just 2.8, indicated by the dashed black line in line in (b).]

Higher C at times when global irradiance is low is a further advantage of LSC devices, in that the useful daily operating time of the PV cells is extended. The predicted C for the same QDSC assuming the standard AM1.5G spectrum at normal incidence is just 2.8. In outdoor simulations, however, $3.7 < C < 4.2$ is attained on an
annual average. Therefore, comparing QDSCs to crystalline silicon PV cells using STC does not give a realistic reflection on the relative power output of the two technologies in outdoor conditions, particularly in climates where the diffuse component of solar radiation is predominant\(^{xiv}\). The results highlight the advantage of using QDSCs in such climates.

### 5.2.2 Monthly and annual relative energy output.

Hourly short circuit current of the attached PV cells, \(I_{sc, PV}\), are calculated for the QDSC described in section 5.2.1, for varying \(\beta\) (\(0^\circ \leq \beta \leq 90^\circ\)) over the duration of each calendar month’s “mean” day. QDSC power output is assumed to be directly proportional to \(I_{sc, PV}\). The relative monthly energy yield is assumed to be proportional to the sum of the predicted hourly \(I_{sc, PV}\) over the duration of the mean day of each month;

\[
\text{relative monthly energy output } \propto \sum_{\text{hour}=1}^{24} I_{sc, PV} \tag{5.18}
\]

The relative annual energy yield is proportional to the sum of the twelve predicted monthly yields;

\[
\text{relative annual energy output } \propto \sum_{\text{month}=1}^{12} \sum_{\text{hour}=1}^{24} I_{sc, PV} \tag{5.19}
\]

\(^{xiv}\) As the absorption range of the LSC extends towards the band-gap of the attached solar cell, the difference between AM 1.5G and outdoor predicted C diminishes.
5.2.3 Optimum QDSC tilt angle, $\beta$

Relative monthly energy yields are calculated for varying tilt angle, $\beta$, to determine the optimum QDSC $\beta$ for the given location. Optimal $\beta$ in terms of a tilted surface receiving the maximum insolation, can be determined without ray-trace modelling by calculating hourly $G_t$ and summing over a given time period (see section 5.1.7). However, the optimum $\beta$ in terms of the maximum energy yield may not necessarily match the maximum in-plane insolation, due to a) spectral effects, e.g., it may be more beneficial to fix the QDSC tilt angle to receive more diffuse insolation, as the device is more efficient at shorter wavelengths, and b) reflection losses.

Monthly and annual energy yields for varying $\beta$ are shown in Figure 5.10. The predicted monthly optimum $\beta$ varies from $\sim 15^\circ$ in summer to $\sim 80^\circ$ in winter months. A broad annual optimum exists between $20^\circ$ and $30^\circ$. The predicted variation in annual energy yield is very similar to the variation in received in-plane insolation, as shown in Figure 5.10.

QDSCs with one-axis tracking

Compared to a QDSC fixed at $\beta = 30^\circ$, only a 13% increase is obtained if $\beta$ is varied hourly to the particular hourly optimum $\beta$ angle (i.e. utilizing one-axis tracking with the axis oriented east-west), as shown in Figure 5.11. QDSCs as low cost devices are, therefore, unlikely to benefit from utilization of solar tracking due to the additional associated installation, operational, and maintenance costs of tracking devices. Monthly adjustments in $\beta$ to the monthly optimum $\beta$ angle would result in only a 5% increase in annual energy yield.
Figure 5.10. Relative QDSC monthly and annual energy output with varying tilt angle, $\beta$.

Figure 5.11. Relative annual QDSC energy yield for; 1: A fixed QDSC tilt angle ($\beta=30^\circ$), 2: $\beta$ adjusted each month to the monthly optimum $\beta$, and 3: $\beta$ adjusted hourly to hourly optimum $\beta$. 
5.2.4 Annual energy yield for varying matrix material properties

As discussed in chapter 4, increasing the plate refractive index, \( n \), reduces escape cone losses but increases external top surface reflection losses. Assuming a QD QY of 80%, the relative annual energy yield is predicted for the QDSC detailed in section 5.2.1. The results for varying \( n \) are shown in Figure 5.12. In section 4.2, a 10% increase in device concentration ratio was attained, under direct normal insolation, with an increase in \( n \) from 1.5 to 1.7. However, there is only \( \sim 5\% \) increase in annual outdoor QDSC energy yield with an identical increase in \( n \) from 1.5 to 1.7. The relatively smaller increase under outdoor conditions is due to larger external top surface reflection losses than is the case under direct normal insolation.

![Figure 5.12. Variation in QDSC relative annual energy yield with plate refractive index, \( n \), and absorption coefficient, \( \alpha_{\text{mat}} \).](image)

Figure 5.12. Variation in QDSC relative annual energy yield with plate refractive index, \( n \), and absorption coefficient, \( \alpha_{\text{mat}} \).
5.3 Anti-reflection coatings

Annual reflection losses total 13% of photons incident on the QDSC modelled in section 5.2.4 with plate refractive index of 1.7. Anti-reflective coatings (ARCs) can reduce reflection losses. The effectiveness of an ARC on annual energy yields differs to the effect on power output under direct normal incidence (Wohlgemuth et al., 2005), as reflectance depends on the angle of incidence, $\theta_1$, and the wavelength of the incident light, $\lambda_1$. MgF$_2$, a common thin-film ARC material, has a refractive index of 1.38 (at 550 nm). Reflectance from the QDSC with a MgF$_2$ ARC is determined from the set of equations in Appendix D for varying $\theta_1$, $\lambda_1$, and thin-film thickness, $t_f$, and is shown in Figure 5.13. A thicker thin-film results in the minimum reflectance shifting to longer wavelengths. The ARC does not have an effect on the total internal reflection efficiency within the QDSC plate (Petrova-Koch et al., 2008)

![Figure 5.13](image-url)

Figure 5.13. Reflectance from MgF$_2$ thin-film anti-reflection coating on substrate of refractive index 1.7, for varying angles of incidence, $\theta_1$, thin-film thickness, $t_f$, and wavelength of incident light, $\lambda_1$. 

169
5.3.1 Effect of ARC on QDSC annual energy yield

Annual energy yields are determined assuming a thin-film ARC deposited on the QDSC of plate refractive index of 1.7 modelled in section 5.2.4. Optimising thin-film thicknesses, $t_f$, to minimise total reflection losses does not necessarily maximise QDSC energy yield, as reflection ought to be reduced in wavelength regions where the QDSC is most efficient. Four values of $t_f$ are assumed for the analysis - 80, 100, 120, and 140 nm - and external reflection losses are calculated as in Appendix D. An optimum ARC thickness, $t_f$, of 120 nm results in an increase in QDSC energy yield of 8% compared to the same QDSC with no ARC, as shown in Figure 5.14. A thickness of 140 nm minimises total reflection losses but doesn’t maximise the energy yield. While more accurate spectral irradiance data would be required to fully optimise ARC thickness, the results do show that significant gains in QDSC annual energy yields are realizable through the inclusion of an optimised ARC.

![Figure 5.14](image_url)

Figure 5.14. (a) External reflection losses (% of total incident photons) and (b) relative QDSC annual energy yield for varying MgF$_2$ thin-film ARC thickness, $t_f$. 
5.4 Chapter conclusions

- Measured horizontal irradiance data from a location in Dublin, Ireland, were used as ray-trace model input. Combined with the Mondol diffuse-global correlation model and the Perez slope irradiance model, monthly averaged hourly spectral irradiance and incident angle distributions on tilted QDSC plates were determined.

- Predicted QDSC concentration ratio, C, is higher in mornings and evenings than at mid-day, due to a higher diffuse component at those times. Higher C at times when global irradiance is low is a further advantage of QDSC devices, in that the useful daily operating time of the PV cells is extended.

- The predicted C for a particular QDSC under the standard AM1.5G spectrum at normal incidence is just 2.8. In outdoor simulations, however, 3.7 < C < 4.2 is attained on an annual hourly average for the same QDSC. The results highlight the advantage of using QDSCs in climates where the diffuse component of solar radiation is predominant.

- The predicted monthly optimum tilt angle, $\beta$, varies from $\sim 15^\circ$ in summer months to $\sim 80^\circ$ in winter, with a broad annual optimum between 20$^\circ$ and 30$^\circ$.

- Compared to a QDSC fixed at $\beta = 30^\circ$, a 13% increase in annual energy yield is attained if $\beta$ is varied hourly to the particular hourly optimum $\beta$ (i.e., assuming one-axis tracking with the axis oriented east-west). QDSCs as low cost devices are, therefore, unlikely to benefit from utilization of solar tracking due to the additional associated installation and maintenance costs of tracking devices.

- A 5% increase in annual QDSC energy yield is attained with an increase in QDSC plate refractive index, $n$, from 1.5 to 1.7. This is significantly lower than the predicted increases observed under direct normal insolation, due to larger external
top surface reflection losses in outdoor conditions than is the case under direct normal insolation.

- Annual external reflection losses account for 13% of total photons incident on a QDSC, of refractive index 1.7, fixed at $\beta = 30^\circ$. The ray-trace model can be used to optimize anti-reflective coating (ARC) thickness in order to minimize reflection losses in the spectral range where the QDSC is more efficient. A potential 8% increase in QDSC annual energy yield is predicted using an optimized anti-reflective coating with the QDSC of refractive index 1.7.
5.5 References


Towards a viable QDSC.

6.0 Introduction

Crystalline silicon technologies currently represent over 90% of PV module market share (Bagnall, 2008). As global silicon PV module manufacturing capacity and scale has increased, average manufacturing costs have decreased from US$6/Wp in 1992 to US$2.75/Wp in 2005 (Margolis et al., 2006). The rate of reduction was greatest in the period 1992-2000. The reduction in average costs slowed significantly after 2000 when the cost per Wp was already as low as $2.75/Wp. In the next 20 years, total costs per Wp of "1st generation" silicon PV technologies are predicted to fall by less than 30% (Bagnall, 2008). QDSC costs per Wp are determined to analyse the potential for (stable) devices to compete with crystalline silicon technologies. The QD QY required to do so, under varying QDSC cost scenarios, is quantified.
6.1 QDSC manufacturing costs

Minimum QDSC manufacturing costs can be estimated from the total cost of the principal components, i.e., the matrix materials and quantum dots;

**Matrix materials**

The price of bulk-purchased PMMA is < €3/kg (ICIS, 2009). A 1m² plate of 0.3 cm thickness would require ~3.5 kg of PMMA, assuming a specific density of 1.16 (Sane et al., 2001), which equates to ~€10/m².

**Quantum Dots**

Using the ray-trace model, the optimum concentration (mass/volume) of PbS QDs in a 3mm thick QDSC incorporating a rear reflector was determined to be ~0.05 mg/ml. For a 1 m² plate, therefore, ~0.15 g of the particular PbS QDs are required. Current prices of PbS QDs from commercial suppliers are ~€15,000/g (Evident Technologies, USA), equivalent to ~€2,000/m² of QDSC plate – costs which would need to be reduced by two to three orders of magnitude for QDs to be considered viable candidates for LSC devices. Cademartiri et al. (2006) estimate the total cost of materials required in the production process of their PbS QDs, however, to be < €10/g. It is estimated that with a very large scale production process, QDs could be produced for as little as €3/g (Barnham, 2008), whereby QD costs would be negligible compared to the other materials required for a QDSC.
6.1.1 QDSC manufacturing costs per Watt peak calculations

The potential QDSC manufacturing cost per Wp is compared with that of crystalline silicon modules. The manufacturing cost of a QDSC is assumed to be proportional to the area of concentrator plate, $A_{\text{conc}}$, and PV cells, $A_{\text{pv}}$, required;

$$\text{relative cost} = \left( \frac{A_{\text{pv}}}{\text{costfactor}_{\text{pv}}} \right) + \left( \frac{A_{\text{conc}}}{\text{costfactor}} \right)$$

where the variable costfactor, defines the cost of the concentrator plate relative to the cost of (single-sided) crystalline silicon PV per unit area;

$$\text{costfactor} = \frac{\text{cost of PV per unit area}}{\text{cost of concentrator plate per unit area}}$$

The QDSC relative power output is determined from eqn. 3.4. Bende et al. (2008) proposed the use of bi-facial PV cells on LSCs, with cells attached to two edges of each individual LSC plate (of optimum size), and multiple plates configured onto a larger module so that each of the four LSC edges is in contact with one side of a bi-facial cell, as illustrated in Figure 6.1. In this configuration, costs per Wp can be reduced providing that the cost of bi-facial cells, per m$^2$ active area, is less than twice that of single sided cells of equivalent efficiency, $\eta$. The variable costfactor$_{\text{pv}}$ in eqn. 6.1 defines the cost of the bi-facial cells;

$$\text{costfactor}_{\text{pv}} = \frac{\text{cost of single-sided PV per unit active area}}{\text{cost of bi-facial cells per unit active area}}$$
Figure 6.1. The cost of attached PV cells can be reduced if bi-facial cells are used, with the bi-facial cells attached to two sides of each QDSC plate of optimum dimensions. Multiple plates are packed adjacently, in a chequered configuration, to form a larger panel of required size.

At €2/W_p manufacturing costs, a PV module with $\eta = 18\%$ equates to €360/m^2. Richards et al. (2007) estimated the potential dye LSC plate costs (including PMMA, dyes, glass cover, and framing) to be potentially as low as €24/m^2, equating to a costfactor of 15. A costfactor of 15 is also used in the cost optimisation analysis of Bende et al. (2008), based on estimated LSC material costs^xv.

Assuming the current cost of PMMA and potentially low cost of QDs outlined in section 6.1, a QDSC cost of $\sim$€22/m^2 (costfactor = 16) seems reasonable. However, Smestad (2008) estimates that $\sim$€70/m^2 of actual production costs of thin film silicon PV modules, fabricated in a large scale production facility (20MW_p/ year), is attributed to the moisture barrier, framing, electrical interconnections, encapsulant and sealant materials required. Arguably, all these materials would be

^xv Bende et al. include the cost of attached PV cells in estimated “plate” costs, whereas the analysis above excludes the cost of the PV cells in the “plate” cost, treating them as an additional separate cost. The relative cost factor of 15, assumed by Bende et al. (2008), is actually equivalent to a costfactor, as defined in eqn. 6.2, of $\sim$16.5.
required for a QDSC module, resulting in significantly greater manufacturing costs per m². A cost factor of 4 (i.e. €90/m² QDSC) is considered below, to account for this higher QDSC manufacturing cost scenario.

From eqn 2.15, concentration ratios, C, are predicted for a QDSC of varying top surface aperture area, $A_{\text{conc}}$, with the following assumptions;

- an incident insolation spectrum corresponding to air-mass 1.5
- a plate refractive index of 1.5
- a matrix material absorption coefficient of $0.01 \text{ cm}^{-1}$
- the QD photon absorption and emission spectra shown in Figure 6.2.
- a diffuse rear reflector with reflectivity 0.97
- PV cells attached at all four QDSC sides

![Figure 6.2. Absorption and emission spectra of PbS QDs ($\lambda_{\text{em}} = 905 \text{ nm}$, Evident technologies)](image)

Figure 6.2. Absorption and emission spectra of PbS QDs ($\lambda_{\text{em}} = 905 \text{ nm}$, Evident technologies)
6.1.2 QD quantum yields required for a viable QDSC

C are predicted for QDSCs of varying top surface aperture area, $A_{\text{conc}}$, to determine what QD QY is required for the QDSC to compete with conventional PV module manufacturing costs per unit power output. A *manufacturing* cost of €2/W$_p$ is assumed for current crystalline silicon technologies. Figure 6.3 (a) shows the predicted C for varying $A_{\text{conc}}$ and QD QY. Assuming a *cost factor* of 16, the cost per unit power for varying $A_{\text{conc}}$ is given in Figure 6.3 (b). A QD QY of 50% is required for this particular QDSC to attain a manufacturing cost per unit power < €2/W$_p$.

![Figure 6.3](image)  
(a) Predicted C and (b) cost per W$_p$ for QDSCs of varying top surface aperture area, $A_{\text{conc}}$, and QD quantum yield (QY).

A *cost factor* of 16 may underestimate the realistic manufacturing costs of QDSCs, when the framing, sealing and interconnection costs are included, as discussed above. Therefore, reduced *cost factor* of 8 and 4 are considered below. Three bi-facial PV cell costs are assumed in the analysis – (i) 360, (ii) 240, and (iii)
€180/m² active area. The maximum bi-facial cell cost of €360/m² active area would be equivalent to using two single-sided PV cells, of equivalent η, back-to-back.

The optimised cost per unit power output attained using each of the three QDSC cost scenarios (i.e. costfactor of 16, 8, and 4), and for each of the three bi-facial cost approximations, is shown in Figure 6.4. At a costfactor of 8, QD QYs of 70 – 80 % would yield QDSC manufacturing cost < €2/W_p. At a costfactor of 4, QD QYs > 95% are required. Bi-facial PV cells could reduce optimised QDSC cost per W_p by up to 25% compared to using single-sided cells.

As discussed in section 1.1 the production cost of CdTe thin-film PV modules is now estimated to be < €0.75/W_p. Only in the lowest QDSC cost assumptions, i.e. Figure 6.4(a), does this particular QDSC attain comparable cost per unit power to the CdTe modules. Clearly, the total module costs including framing etc., need to be minimised if QDSCs are to compete with newer emerging PV technologies, such as CdTe thin-film PV.

![Figure 6.4](image.png)

Figure 6.4. Minimum QDSC cost per W_p for varying plate costs (a), (b), and (c), varying QD quantum yield (QY), and varying bi-facial PV cell costs. A cost of €2/W_p is assumed for conventional silicon PV modules.
6.2 Chapter conclusions

- QDSC cost per $W_p$ is a function of top surface aperture area. Optimised minimum QDSC cost per $W_p$ have been quantified for varying QD QY under different cost scenarios.
- The QDSC high cost scenario assumes equivalent module sealing, framing, moisture barrier, encapsulant and interconnection costs as are incurred in current large-scale production of PV modules. In this case, the estimated QDSC cost is ~€90/m$^2$ (excluding PV cell costs). Even in the high cost scenario, QDSCs utilizing PbS near infra-red emitting QDs, can compete with “1st generation” silicon PV costs per $W_p$, provided efficient QDs can be exploited.
- Bi-facial PV cells can reduce optimised QDSC cost per $W_p$ by up to 25%.
- Total QDSC module costs, including framing etc., need to be minimised if QDSCs are to compete with newer emerging PV technologies such as CdTe thin-film PV.
6.3 References


Commercially available visible-emitting QDs have been used by many groups to date in thin-film and homogeneously doped QDSC plates (Gallagher et al., 2007; Bose et al., 2007; Sholin et al., 2007; Rowan et al., 2008). However, QDSC plates which increase the attached PV cell power output under standard test conditions (i.e. concentration ratio > 1) have not been reported. The low concentration ratios attained have been attributed to low luminescent QYs and large spectral overlaps between QD photon emission and absorption spectra. Initial motivation for developing the QDSC ray-trace model was to investigate the realistic potential performance of QDSCs (subject to the spectral overlap limitations), assuming efficient QDs could be encapsulated in suitable matrix materials whilst preserving high luminescent QY. Adopting a ray-trace approach allows the effect of varying geometry, and varying (multiple) luminescent species type on device performance to be analysed. A Monte-Carlo ray-trace approach allows the multiple competing, interdependent QDSC loss mechanisms to be quantified (including those losses arising from re-absorption of QD emitted light) for a given set of device parameters. Scattering of QD emitted light has, for the first time, been included in a QDSC ray-trace model. The model has been extensively validated through comparison with a range of electrical and spectral experimental measurements, and with predictions of other numerical models. Ray-trace modelling of QDSCs has, for the first time, been combined with outdoor solar radiation models. A novel analysis of diurnal and seasonal variations in QDSC electrical output in outdoor conditions for different QDSC configurations has been completed.
7.1 QDSC optimisation using the ray-trace approach

7.1.1 The effect of varying geometry on QDSC performance

2-D planar geometry

The net effect of varying device geometry on QDSC solar energy concentration ratios, C, was investigated using the ray-trace model. A novel analysis of device geometry was undertaken using the ray-trace predictions to calculate relative costs per unit power output of varying two-dimensional planar QDSC shapes. The analysis shows that, under certain assumptions\textsuperscript{xvi}, all geometries attain the same minimum cost per unit power, indicating that no advantage accrues from varying the plate shape. The model predictions show that the correct selection of concentrator top surface aperture area is crucial in minimising QDSC cost per unit power output. PV cells should be attached at all plate perimeter sides. Bi-facial PV cells could result in up to 25% decrease in the cost per W\textsubscript{p} of an optimised QDSC.

Tapered geometry

Re-absorption losses, which increase with higher QD doping concentration levels, severely limit the potential C of QDSC devices. Current fabricated devices utilise a planar geometry with plates of uniform thickness. A novel tapered QDSC device was proposed with the aim of reducing re-absorption losses in the QDSC. Tapered plates, with one PV cell attached to the thin end, allow a lower QD doping concentration to be used to attain a given absorption efficiency, without decreasing

\textsuperscript{xvi} i.e. assuming a uniform spatial distribution of photons incident on attached PV cells
the geometric gain of the device. With the lower QD doping concentration, re-absorption losses in the plate are reduced. The disadvantage, however, is that the internal optical efficiency decreases due to the sloped top and rear surfaces of the tapered device. Ray-trace modelling was used to investigate the net effect on device C. The results show an overall decrease in C for tapered devices, compared to plates of uniform thickness.

7.1.2 QD and matrix material optical properties.

QD optical properties

Escape cone losses in QDSCs have been quantified for the first time using ray-trace modelling. Predicted escape cone losses accounted for 58% of incident photons absorbed in one particular QDSC containing visible-emitting QDs. This is much higher than the ~25% minimum escape cone loss, assuming a luminescent species with no spectral overlaps in the same plate. Therefore, even allowing for ideal QYs, the commercially-available visible-emitting QDs are unlikely to be suitable candidates for inclusion in viable QDSCs, due to spectral overlaps and the resulting re-absorption losses. Re-absorption losses vary considerably between different QD types. The NIR emitting QDs modelled have significantly lower re-absorption losses owing to the profile of their absorption cross-section. Coupled with the broader absorption range, NIR emitting QDs remain potential candidates for viable QDSCs provided higher luminescent QYs are attained.
Matrix materials

Higher matrix material refractive index, \( n \), results in reduced escape cone losses but increased external reflection losses. The ray-trace model is used to determine device concentration ratios for any particular matrix material parameters (i.e., \( n \) and absorption coefficient, \( \alpha_{\text{mat}} \)). The analysis shows that attempts to increase device efficiency by increasing \( n \), must consider the possibly greater negative effect of any variation in \( \alpha_{\text{mat}} \). The primary experimental objective should be to reduce (and stabilise) matrix material light absorption. Higher refractive index materials should be used only if this criterion is fulfilled.

7.1.3 External reflectors

Specular/diffuse rear reflectors

Research in the literature has shown that utilizing a rear reflector with a diffuse angular reflection distribution results in increased device \( C \) under normally incident direct light. This analysis has quantified, for the first time, the increase in \( C \) as a function of luminescent QY, and has shown that the advantage of employing a diffuse rear reflector reduces with more efficient QDSCs. Assuming a diffuse insolation angular distribution, there is no significant difference in predicted \( C \) for devices utilizing either reflector type. It is concluded, therefore, that the reflectivity of the reflector, and its cost, that are the most important considerations for a viable QDSC rear reflector, and not the reflector type.
Spectrally selective reflector top layers

Spectrally selective reflector (SSR) top layers can reduce escape-cone losses in the device by reflecting QD emitted light within the angular range of the escape cone, while transmitting incident light in the QD absorption range into the device. It has been shown that the ray-trace model provides a useful tool for optimizing the SSR cut-off wavelength for any particular luminescent species.

The modelling predictions of SSR top layers can partly explain why limited gains have been obtained to date utilizing such layers. Photons reflected by the SSR layer re-enter the device at a small angle, and therefore multiple reflections are required at the SSR interface (and at the rear reflector) before the photon is transmitted to the plate edges. Therefore, even a small decrease in SSR reflectivity results in significant reflection losses. For the same reason, it is of critical importance to utilise a highly reflective rear reflector when measuring the performance of any SSR top layer, a criterion which has not previously been emphasised in the research work carried out on SSRs in LSCs.

7.1.4 QDSC outdoor performance predictions

Ray-trace modelling of QDSCs has, for the first time, been combined with solar radiation models allowing a novel analysis of QDSC electrical output in outdoor conditions for different QDSC configurations. Diurnal and seasonal variations in QDSC performance on a tilted plane were analysed.

Predicted QDSC concentration ratio, C, is higher in mornings and evenings than at mid-day. There is a higher diffuse component at those times, which results in a higher QDSC absorption efficiency due to (i) a more blue-rich spectrum better
matching the QD absorption spectrum, and (ii) larger angles of incidence and, hence, a longer pathlength on a double pass through the QDSC plate. Higher C at times when global irradiance is low is a further advantage of QDSC devices, in that the useful daily operating time of the PV cells is extended. The predicted C for a particular QDSC, under the standard AM1.5G spectrum at normal incidence, is 2.8. In outdoor simulations annual average C of the same QDSC is much higher - varying between 3.7 and 4.2 throughout the day. The results highlight the advantage of using QDSCs in climates where the diffuse component of solar radiation is predominant. It also highlights the need to determine device annual energy yields, and not only power output under STCs, when comparing LSC performance with that of conventional PV cells.

The predicted monthly optimum tilt angle, $\beta$, at the Dublin location varies from $\sim 15^\circ$ in summer months to $\sim 80^\circ$ in winter, with a broad annual optimum between 20° and 30°. Compared to a QDSC fixed at $\beta = 30^\circ$, a 13% increase in annual energy yield is predicted assuming one-axis tracking with the axis oriented east-west. QDSCs as low cost devices are, therefore, unlikely to benefit from utilization of solar tracking due to the additional associated installation and maintenance costs of tracking devices.

A 5% increase in annual QDSC energy yield is predicted with an increase in QDSC plate refractive index, $n$, from 1.5 to 1.7. This is significantly lower than the predicted increases observed under direct normal insolation (i.e. 10%), due to larger external top surface reflection losses in outdoor conditions. The results further highlight that the primary experimental research, regarding matrix materials, should be to reduce (and stabilise) light absorption. Higher refractive index materials should be used only if this criterion is fulfilled.
Annual external reflection losses account for 13% of total photons incident on a particular QDSC fixed at $\beta = 30^\circ$. Utilizing an anti-reflective coating (ARC), reflection losses can be significantly reduced at particular wavelengths. The outdoor modelling predictions show that the ARC thickness needs to be optimised to maximise QDSC output and not to minimise total reflection losses. A potential 8% increase in QDSC annual energy yield is predicted using an external ARC. Gains would need to be evaluated in terms of the relative increase in costs of applying a robust ARC to a low-cost QDSC module.

7.1.5 QDSC cost analysis

QDSC cost per $W_p$ is a function of top surface aperture area. Optimised QDSC cost per $W_p$ have been quantified for varying QD QY under different cost scenarios. The results show that, even in the high cost scenario, QDSCs utilizing PbS near infra-red emitting QDs, can compete with “1st generation” silicon PV costs per $W_p$, provided high QYs can be exploited.

The low $C$ attained by QDSCs fabricated to-date have been attributed to low QYs and large spectral overlaps between QD photon emission and absorption spectra. Initial motivation for developing the QDSC ray-trace model was to investigate the realistic potential performance of QDSCs (subject to the spectral overlap limitations), assuming QDs with high QY could be encapsulated in suitable matrix materials. The predictions show that viable QDSCs are realizable without the need for a spectrally selective reflector top layer, providing efficient NIR emitting QDs can be exploited. The ray-trace model now developed provides an important
tool for optimizing device design for outdoor conditions, and minimizing the costs per unit energy produced.

7.2 Luminescent down shifting layers

Luminescent down-shifting (LDS) layers can enhance the short circuit current density, $J_{sc}$, of solar cells by transforming the wavelength of incident light from short to longer wavelengths better matching the spectral response of the cell. LDS layers were modelled, to investigate whether the optical properties of QDs (i.e. broad absorption range and characteristic increased absorption in the UV and blue wavelength regions) make them a more suitable candidate than organic dyes for incorporation in LDS layers. Predictions for LDS layers containing two types of commercially available QDs show that only a limited potential enhancement in mc-Si cell $J_{sc}$ (1% relative increase) is attained$^{xvii}$. This is significantly lower than analytical predictions in the research literature which yielded 7.5 % - 10% relative increase in $J_{sc}$.

7.2.1 Partially covered luminescent down shifting layers

In “partially-covered” LDS (PC-LDS) layers a reduced fraction of the down-shifting layer is covered with PV cells, thereby introducing a geometric concentration effect not present in an LDS layer. The performance of PC-LDS layers incorporating currently available luminescent dyes has been quantified for the first

$xvii$ even assuming a near ideal QD QY of 98%
time for varying plate size and coverage fractions. As with LSC plates, the optimum size of a PC-LDS layer, of given parameters, must be determined.

Current single-plate LSCs, utilising mc-Si cells, have power conversion efficiencies, $\eta$, of 2.5 – 3.8% (depending on the geometric gain) under standard test conditions. The ray-trace predictions show that employing the same PV cells and matrix materials in the $PC-LDS$ layer configuration could increase $\eta$ significantly, as compared to the LSC device. As the absorption range of LSCs extends towards the attached PV cell band gap, the magnitude of the potential increase in $\eta$ diminishes. However, it is a simple effective method to further increase $\eta$, in what are currently the most efficient LSCs utilising mc-Si cells.

7.3 Luminescent “solar tree”

A luminescent “solar tree” system was proposed, where fibre optics are used to transmit light exiting multiple plates, or “solar leaves”, to a single PV cell via a 2nd stage concentrator. Potentially, the concept allows high concentration ratios to be attained under direct or diffuse insolation conditions. However, the maximum concentration ratio of the 2nd stage concentrator, $C_2$, is limited by the angular distribution of light exiting the fibre optics. It is shown that the limitations in $C_2$, combined with the additional associated costs of the fibre optics required, result in no cost per unit power reduction for the solar tree structure compared with that of a single-plate QDSC.
7.4 Future direction of model development

7.4.1 Spectral irradiance modelling

The spectral irradiance approximations, detailed in section 5.1.6, should be compared with measured spectral irradiance data to quantify the error arising from using the approximated spectra in outdoor modelling predictions. Comparisons could also be made with spectral irradiance models, such as the parameterised semi-empirical SPCTRL2 (Bird and Riordan, 1986) and SEDES2 (Nann and Riordan, 1991; Nann and Emery, 1992) models.

7.4.2 PV cell modelling

Currently the model calculates the PV cell short circuit current using the edge emission spectrum and measured cell IQE and reflectivity data. Angular dependent reflectivity curves are approximated from the optical properties of the cell material. A more detailed PV model could quantify the variation in cell internal resistance, open circuit voltage, and fill factor, under varying light intensity, spectra, and temperature. Modelling the cell temperature would be complex as it would also depend on the heat transfer to/from the polymer plate. The plate temperature would need to be calculated taking into account non-radiative recombination of absorbed solar energy by the luminescent species, matrix material photon absorption, ambient temperature and temperature increases in the cell.
7.5 References


Appendix A

Solar tree relative cost per unit power

In this section, the relative cost per unit power output of the scalable solar tree system, described in section 3.2, is determined;

Positioning all FOs used in the system adjacently, as illustrated in Figure A.1, the total planar 'area' of FOs, $A_{FO}$, is defined by;

$$A_{FO} = L_{FO} W_{FO} N_{FO} \tag{A.1}$$

where, $L_{FO}$ is the average FO length and $N_{FO}$ is the total number of FOs. Expressing the quantity of FO in units of planar area allows the dimensionless variable $costfactor_2$ to approximate the cost of the FO relative to the cost of a unit area of PV.

![Diagram](image)

Figure A.1. The total 'area' of FO, $A_{FO}$, is equal to the product of the average FO length, times the FO 'width', times the total number of FOs.
Relative cost

The relative cost of a particular sized solar tree system, excluding the cost of the 2nd stage concentrator, is dependent on (i) $A_{pv}$, (ii) the number of leaves, $N_{Leaf}$, and the leaf dimensions, $W_{Leaf}$ and $L_{Leaf}$, and (iii) the 'area' of fibre optics, $A_{FO}$;

$$\text{cost} = A_{pv} + \frac{W_{Leaf}L_{Leaf}N_{Leaf}}{\text{costfactor}_1} + \frac{A_{FO}}{\text{costfactor}_2}$$

$$\text{cost} = A_{pv} + \frac{W_{Leaf}L_{Leaf}N_{Leaf}}{\text{costfactor}_1} + \frac{L_{FO}W_{FO}N_{FO}}{\text{costfactor}_2}$$  \hspace{1cm} \text{A.2}

where, $\text{costfactor}_1$ and $\text{costfactor}_2$ relate the cost of the leaves and FO, respectively, to the cost of the PV per unit area;

$$\text{costfactor}_1 = \frac{\text{cost of PV cells per m}^2}{\text{cost of solar leaf per m}^2}$$

$$\text{costfactor}_2 = \frac{\text{cost of PV cells per m}^2}{\text{cost of fibre optic per m}^2}$$  \hspace{1cm} \text{A.3}

The number of leaves used, $N_{Leaf}$, in a particular tree system can be expressed relative to the area of PV cell used as follows;

In a scaleable solar tree system $N_{FO}$ is related to $N_{Leaf}$ by;

$$N_{FO} = N_{Leaf} \frac{W_{Leaf}}{W_{FO}}$$  \hspace{1cm} \text{A.4}

where, $W_{FO}$ is the 'width' of each FO. From Figure 3.14, the total cross-sectional area of the FOB, $A_{cs\_FOB}$, is related to $A_{pv}$ by;

200
C_G = \frac{A_{sz\_FOR}}{A_{pv}} = \frac{W_{FO}^2 N_{FO}}{A_{pv}} \quad \text{(A.5)}

substituting A.4 into A.5;

C_G = \frac{W_{FO}^2 N_{Leaf} W_{Leaf}}{A_{pv} W_{FO}} \quad \text{(A.6)}

N_{Leaf}, \text{ in a scalable solar tree system, is therefore related to } A_{pv} \text{ by;}

N_{Leaf} = \frac{C_G A_{pv}}{W_{FO} W_{Leaf}} \quad \text{(A.7)}

substituting eqns. A.4 and A.7 into eqn. A.2, the total relative cost is given by;

\text{rel. cost} = A_{pv} + \frac{L_{Leaf} C_G A_{pv}}{W_{FO} \text{ costfactor}_1} + \frac{L_{FO} C_G A_{pv}}{W_{FO} \text{ costfactor}_2} \quad \text{(A.8)}

\textbf{Relative power}

The relative power of a scalable solar tree system is determined by the area of PV, C_1, and C_2;

\text{rel. power} = A_{pv} C_1 C_2 \quad \text{(A.9)}

\textbf{Relative cost per unit power}

Dividing eqn. A.8 by eqn. A.9 yields the lower bound relative cost per unit power of the solar tree;
rel. cost/power = \frac{1}{C_1C_2} + \frac{L_{\text{cond}} C_G}{C_1C_2 W_{P0,\text{costfactor}_{1}}} + \frac{L_{\text{RO}} C_G}{C_1C_2 W_{P0,\text{costfactor}_{2}}}

A.10
Appendix B

The measured horizontal global irradiance data in section 5.1 are converted from local standard time to “Solar time”. Solar time describes the angular motion of the sun across the sky at a particular location, with solar noon occurring when the sun reaches maximum altitude as observed from that location. The sun takes 1 hour to traverse 15° of longitude, i.e., solar time lags local standard time by 4 minutes for every one degree west of the reference longitude. The rate of the earth’s rotation on its own axis varies throughout the year. The variation is described by the equation of time. The equation of time (EOT), as a function of the Julian day of the year (\(day_J\)), is shown in Figure B.1 and is given (Duffie and Beckman, 1990) by:

\[
EOT = 9.87 \sin 2B - 7.53 \cos B - 1.5 \sin B ,
\]

where;

\[
B(\text{degrees}) = \frac{360(day_J - 81)}{364}
\]

Solar time at a particular longitude is related to local standard time\(^{xviii}\) by;

\[
\text{solar time} = \text{local standard time} + 4(L_{\text{ref}} - L_{\text{loc}}) + EOT
\]

where, \(L_{\text{loc}}\) is the location longitude in degrees west of the reference longitude, \(L_{\text{ref}}\).

\(^{xviii}\) Local standard time remains at Winter Time all year and does not change forward one hour in Summer Time.
Figure B.1. The equation of time (EOT), given by eqn. B.1, accounting for the variation about the mean of the earth’s rotation time on its own axis.
Appendix C

The sky clearness parameter, $\varepsilon$, used in eqn. 5.13 to determine the Perez circumsolar and horizon brightening coefficients, increases as sky conditions change from heavy overcast to a low turbidity clear sky and is defined as;

$$\varepsilon = \left( \frac{D_h + B_n}{D_h + \kappa \theta^2} \right) \left( 1 + \kappa \theta^2 \right)^3$$

with the dimensionless constant $\kappa = 1.041$ and the other parameters defined in section 5.

The Perez coefficients, $f_{ij}$, are dependent on $\varepsilon$ and are given in Table C.1.

<table>
<thead>
<tr>
<th>$\varepsilon$</th>
<th>$\varepsilon$ bin</th>
<th>$f_{11}$</th>
<th>$f_{12}$</th>
<th>$f_{13}$</th>
<th>$f_{21}$</th>
<th>$f_{22}$</th>
<th>$f_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon &lt; 1.065$</td>
<td>1</td>
<td>-0.008</td>
<td>0.588</td>
<td>-0.062</td>
<td>-0.060</td>
<td>0.072</td>
<td>-0.022</td>
</tr>
<tr>
<td>$1.065 \leq \varepsilon &lt; 1.23$</td>
<td>2</td>
<td>0.130</td>
<td>0.683</td>
<td>-0.151</td>
<td>-0.019</td>
<td>0.066</td>
<td>-0.029</td>
</tr>
<tr>
<td>$1.23 \leq \varepsilon &lt; 1.50$</td>
<td>3</td>
<td>0.330</td>
<td>0.487</td>
<td>-0.221</td>
<td>0.055</td>
<td>-0.064</td>
<td>-0.026</td>
</tr>
<tr>
<td>$1.5 \leq \varepsilon &lt; 1.95$</td>
<td>4</td>
<td>0.568</td>
<td>0.187</td>
<td>-0.295</td>
<td>0.109</td>
<td>-0.152</td>
<td>-0.014</td>
</tr>
<tr>
<td>$1.95 \leq \varepsilon &lt; 2.80$</td>
<td>5</td>
<td>0.873</td>
<td>-0.392</td>
<td>-0.362</td>
<td>0.226</td>
<td>-0.462</td>
<td>0.001</td>
</tr>
<tr>
<td>$2.80 \leq \varepsilon &lt; 4.50$</td>
<td>6</td>
<td>1.132</td>
<td>-1.237</td>
<td>-0.412</td>
<td>0.288</td>
<td>-0.823</td>
<td>0.056</td>
</tr>
<tr>
<td>$4.50 \leq \varepsilon &lt; 6.20$</td>
<td>7</td>
<td>1.060</td>
<td>-1.600</td>
<td>-0.359</td>
<td>0.264</td>
<td>-1.127</td>
<td>0.131</td>
</tr>
<tr>
<td>$6.20 \leq \varepsilon$</td>
<td>8</td>
<td>0.678</td>
<td>-0.327</td>
<td>-0.250</td>
<td>0.156</td>
<td>-1.377</td>
<td>0.251</td>
</tr>
</tbody>
</table>

Table C.1. Perez coefficients, $f_{ij}$
Appendix D

The reflectance from the anti-reflective coatings, $R$, simulated in section 5.3 is determined below. $R$ depends on the angle of incidence, $\theta_1$, the wavelength of the incident light, $\lambda_1$ and the thickness of the thin-film, $t_f$;

$$R = \frac{R_p + R_s}{2}, \text{ where}$$

$$R_p = \frac{r_{12p}^2 + r_{23p}^2 + 2r_{12p}r_{23p} \cos 2\beta}{1 + r_{12p}^2 + r_{23p}^2 + 2r_{12p}r_{23p} \cos 2\beta} \quad \text{and} \quad R_s = \frac{r_{12s}^2 + r_{23s}^2 + 2r_{12s}r_{23s} \cos 2\beta}{1 + r_{12s}^2 + r_{23s}^2 + 2r_{12s}r_{23s} \cos 2\beta}$$

where $\beta$ is the phase difference, in the external medium, between waves reflected from the first and second surfaces of the coating;

$$\beta = \frac{2\pi}{\lambda_1} n_3 t_f \cos \theta_2$$

The amplitude reflectance coefficients at the interface between the external medium and the ARC are given by;

$$r_{12p} = \frac{n_2 \cos \theta_1 - n_1 \cos \theta_2}{n_2 \cos \theta_1 + n_1 \cos \theta_2} \quad \text{and} \quad r_{12s} = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2}$$

and the amplitude reflectance coefficients at the interface between the ARC and the substrate (LSC plate) are given by;

$$r_{23p} = \frac{n_3 \cos \theta_2 - n_2 \cos \theta_3}{n_3 \cos \theta_2 + n_2 \cos \theta_3} \quad \text{and} \quad r_{23s} = \frac{n_2 \cos \theta_2 - n_3 \cos \theta_3}{n_2 \cos \theta_2 + n_3 \cos \theta_3}$$

where $n_1, n_2$, and $n_3$ are the refractive indices of the external medium, ARC, and substrate, respectively.
List of Publications

Journal publications


Conference publications


