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Winter College on Optics and Energy

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Luminescent solar concentrator

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Luminescent solar concentrator

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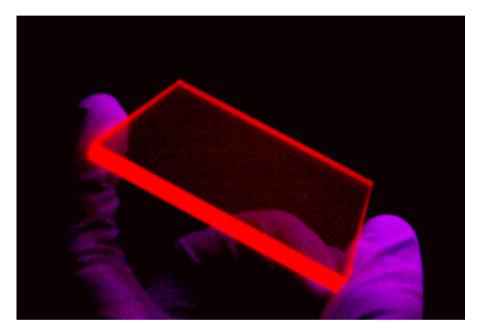
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Winter College on Optics and Energy ICTP, Triest, Italy,16 February 2010



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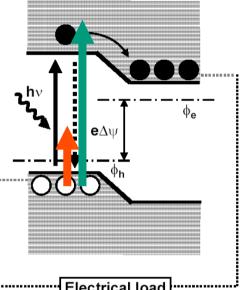


Introduction



Introduction

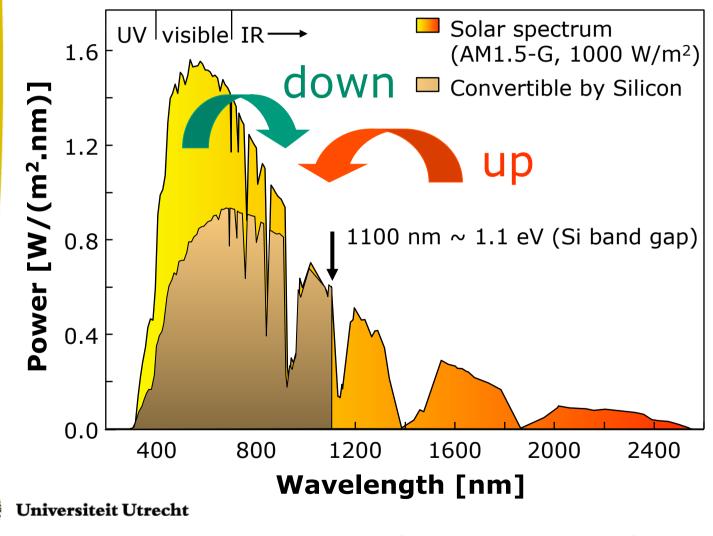
- Solar cell efficiency limited to 30% on thermodynamic grounds
 - pn junction optimal for monochromatic light
- Fundamental loss terms (Si)
 - Spectral (50% loss)
 - No absorption for $E_{ph} < E_g$



- Partial use of energy when $E_{ph} > E_g$
- Practical limit presently ~15% (mc-Si)
- Challenge: use **complete** solar spectrum



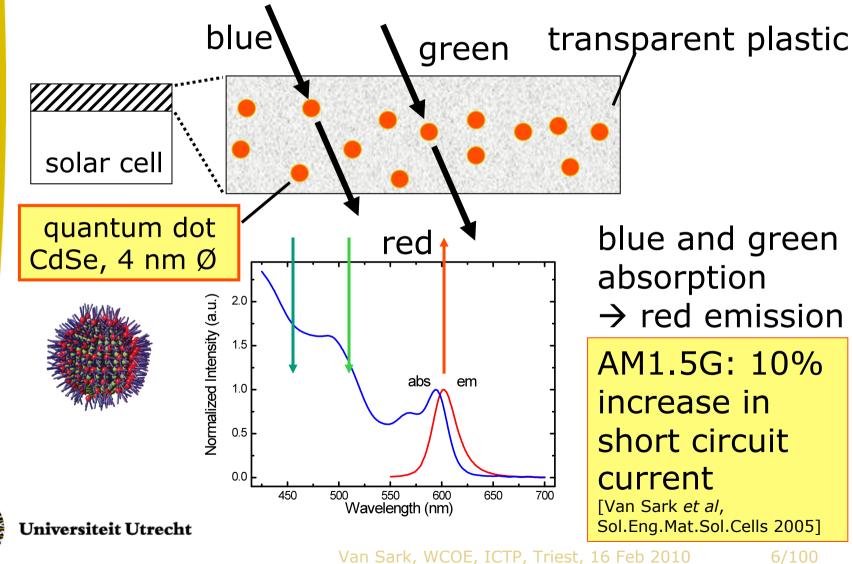
Spectral down/up conversion



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Example: spectral down shifter

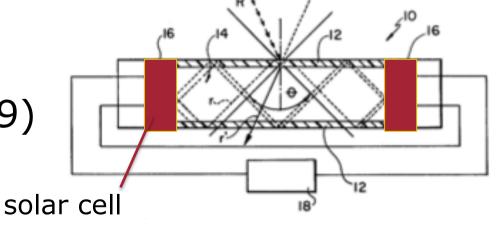




Introduction

- Luminescent solar concentrator (LSC) proposed as possible low-cost alternative for high-cost photovoltaic cells (Goetzberger, 1970s)
- LSC employs spectral down shifters/ converters

US patent (1979)
4,149,902

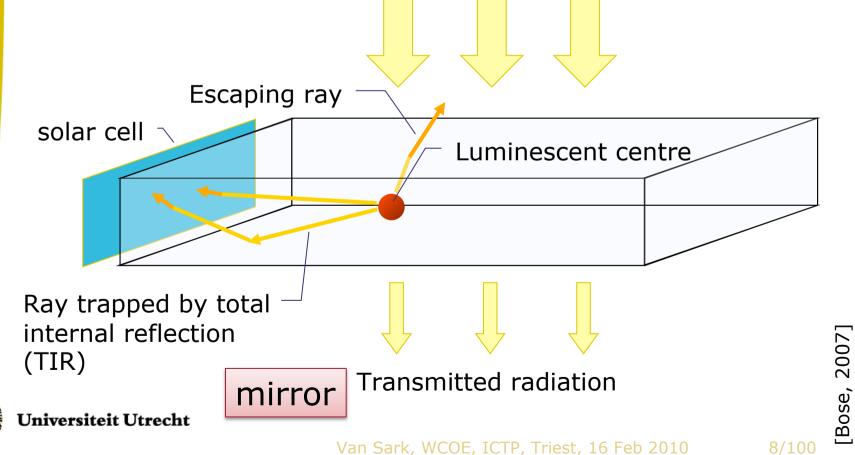






Luminescent Solar Concentrator

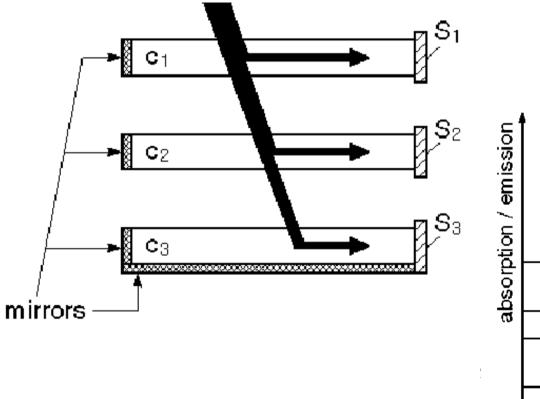
Incident radiation





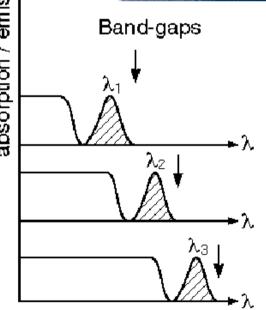
Stacks

Similar to triple-junction solar cells



[Goetzberger, 1970s]





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Introduction

- Diffuse solar irradiation constitutes half of irradiation at higher latitude → no conventional optical concentrators
- Polymer based materials "capture" diffuse irradiation due to low index of refraction, trapping efficiency ~75%
- Collects direct and diffuse light
 - In the UK over 7× as much solar energy falls on buildings as is consumed inside and about half of this is diffuse [Chatten, 2008]



LSC advantages

- Concentration ratio 5-10X
- <u>Non-tracking</u> concentrator!
- Present efficiency record: 7.1%
- Reduce the costs of PV electricity
 - Large area cheap plastic
 - Small area not-so-cheap solar cell
- Ideally suited to building integration



Basic principles



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Basic principles

- Efficiency of LSC $\eta_{LSC} = \eta_{opt} \eta_{PV}$
- Optical efficiency η_{opt} ; PV efficiency η_{PV}
- Note: at 1.0 emission mc-Si GaAs 0.8 wavelength, InGaP dye emission PV efficiency 0.6 is high 0.4 0.2 0.0 400 600 800 1000 1200 Wavelength (nm)





$$\eta_{opt} = \left(1 - R\right) \eta_{abs} \eta_{LQE} \eta_{S} \eta_{trap} \eta_{mat} \left(1 - \eta_{self}\right) \eta_{TIR}$$

- *R* reflection coefficient
- $\eta_{\rm abs}$ absorption efficiency
- $\eta_{\rm \tiny LQE}$ luminescent quantum efficiency
- $\eta_{\rm S}$ Stokes' efficiency
- $\eta_{\rm trap}$ trapping efficiency
- $\eta_{\rm mat}$ transmission efficiency through matrix
- $\eta_{\rm self}\,$ efficiency of self absorption
- $\eta_{\rm TIR}$ total internal reflection efficiency



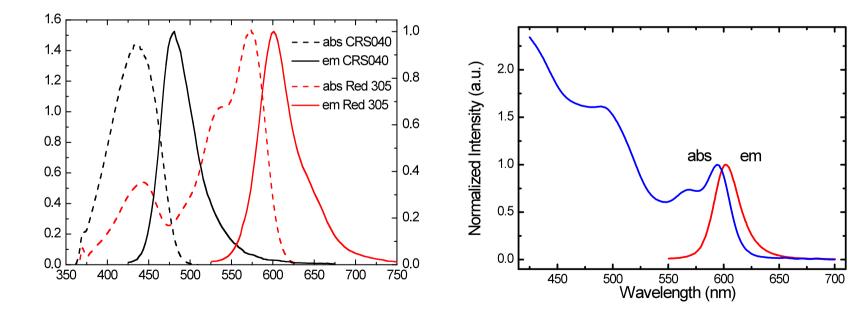
• Surface reflection loss (Fresnel)

$$1 - R = \left(\frac{n-1}{n+1}\right)^2$$

- Polymethylmethacrylate (PMMA): n = 1.49 1-R = 3.9%
- Can be lowered using anti-reflection coating



- Absorption efficiency $\eta_{\rm abs}$
- Depends on luminescent species:
 - Organic dyes, narrow absorption bands
 - Nanocrystals, broad absorption bands





- Luminescent quantum efficiency $\eta_{\scriptscriptstyle LQE}$
- Depends on luminescent species:
 - Organic dyes: 90-95%
 - Nanocrystals: 20-80%
- Stokes' efficiency $\eta_{\rm S}$
 - Must be small for low energy loss
 - Must be large for low self-absorption



• Trapping efficiency

$$\eta_{trap} = rac{\sqrt{n^2 - 1}}{n}$$

- For PMMA: $\eta_{trap} = 0.741$
- Can be enhanced by selective mirrors (dichroic/photonic)

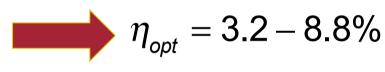


- \bullet Transmission through material efficiency $\eta_{\rm mat}$
- Depends on scattering in the matrix
 - Absorption coefficient $\sim 1 \text{ m}^{-1}$
 - Lambert-Beer $I = I_o \exp(-\alpha x)$
- Self absorption depends on species, and leads to red shift of emission
- Total internal reflection depends on surface quality





1-R reflection 96% $\eta_{\rm abs}$ absorption 15-20% $\eta_{\rm LQE} ~{\rm LQE}$ 95% Stokes' 85-95% η_{s} trapping 74% η_{trap} transmission 85-95% $\eta_{\scriptscriptstyle mat}$ selfabsorption 50-80% $\eta_{\scriptscriptstyle self}$ 90% TIR $\eta_{\scriptscriptstyle TIR}$





Concentration

 Maximum concentration depends strongly on Stokes' shift [Yablonovitch, 1980]

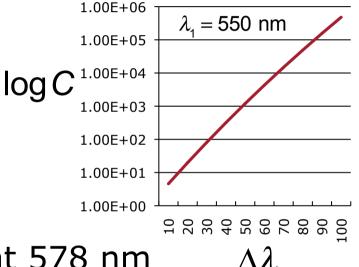
$$C \leq \left(\frac{v_2}{v_1}\right)^2 \exp\left(-\frac{h\Delta v}{k_B T}\right)$$

- Lumogen F Red dye:
 - Absorption maximum at 578 nm
 - Emission maximum at 613 nm
 - →C=119

(order of magnitude larger than obtained in practice!)

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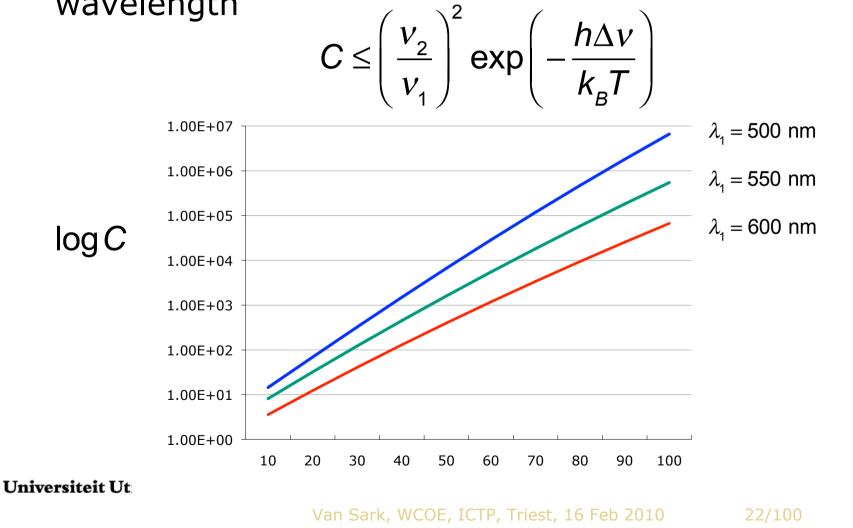
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Concentration

Dependence on absorption maximum wavelength





Modelling

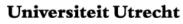


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Modelling

- Two models
- Thermodynamic model
 - Based on radiative energy transfer between points (of a mesh) in the concentrator
- Ray-trace model
 - Every incoming photon is tracked and its fate is determined using Monte Carlo principles





Thermodynamic model

- Yablonovitch [1980] was the first to develop a thermodynamic model
 - applying a detailed balance argument to relate the absorbed light to the spontaneous emission
 - 1D model: obtain the photon chemical potential as f(x) only
- Not accounted for
 - absorption of incident flux by matrix
 - spectral overlap of the incident radiation with the luminescence
 - re-absorption of radiation emitted into the escape cone
 - reflection at surfaces
 - losses owing to absorption in the host
- Chatten [2004] developed self-consistent 3D flux model, considering reflection and transmission at the surfaces





Thermodynamic model

 Brightness B of radiation field in equilibrium with electronic degrees of freedom of absorbing species

$$B(v) = \frac{8\pi n^2 v^2}{c^2} \frac{1}{e^{(hv-\mu)\beta} - 1}$$

n = refractive index $\beta = 1/kT$ $\mu = chemical potential$

> [Yablonovitch, 1980] [Chatten, 2004]

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Thermodynamic model

 Applying the principle of detailed balance within the absorber leads to:

 σ_e = absorption cross section

 $W_c = escape cone$ $W_2 = 4\pi - 2$

 W_c totally internally reflected solid angle in 1D z = D

[Chatten, 2004]

W_c

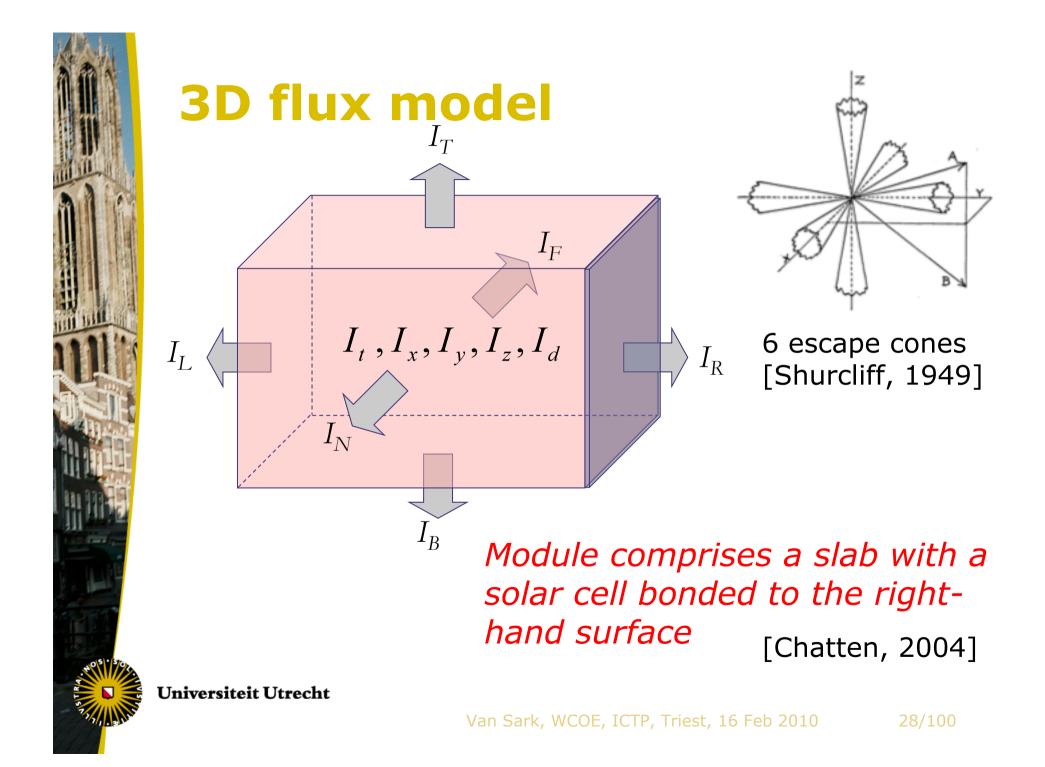
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Yablonovitch, 1980

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- 1. integrating the differential equations for the fluxes
- 2. evaluating the resulting expressions at the surfaces
- applying appropriate boundary conditions considering reflection and transmission at the surfaces

derive the trapped and escaping

intensities within the slab and fluxes exiting the surfaces

(thin plates: analytically)

[Chatten, 2004]



- 4. Chandrasekhar's general threedimensional radiative transfer equation
- Schwarzschild and Milne, detailed angular dependence of the radiative intensity is ignored; radiation is either forward (+) or backward (-) streams
- 6. Treat the escaping photons (q <q_c) and the trapped photons (q >q_c) as separate streams

[see for details: Chatten, 2004]





• Escaping intensity in x-direction:

$$I_{x}(x,y,z) = \frac{\Omega_{c}\lambda_{e}\cosh\left(\lambda_{a}x + \frac{\alpha_{L}}{2}\right)}{2\pi\sinh\left(\lambda_{a}L + \alpha_{LR}\right)}\int_{0}^{L}dx'\cosh\left[\lambda_{a}(L-x') + \frac{\alpha_{R}}{2}\right]B(x',y,z)$$
$$-\frac{\Omega_{c}\lambda_{e}}{2\pi}\int_{0}^{x}dx'\sinh\left[\lambda_{a}(x-x')\right]B(x',y,z)$$

Trapped intensity

$$I_{t}(x,y,z) = \frac{\Omega_{6}\lambda_{et}\cosh(\lambda_{at}x)}{4\pi\sinh(\lambda_{at}L + \frac{\alpha_{t}}{2})}\int_{0}^{L}dx'\cosh\left[\lambda_{at}(L-x') + \frac{\alpha_{t}}{2}\right]B(x',y,z)$$
$$-\frac{\Omega_{6}\lambda_{et}}{4\pi}\int_{0}^{x}dx'\sinh\left[\lambda_{at}(x-x')\right]B(x',y,z)$$
[Chatten, 2004]

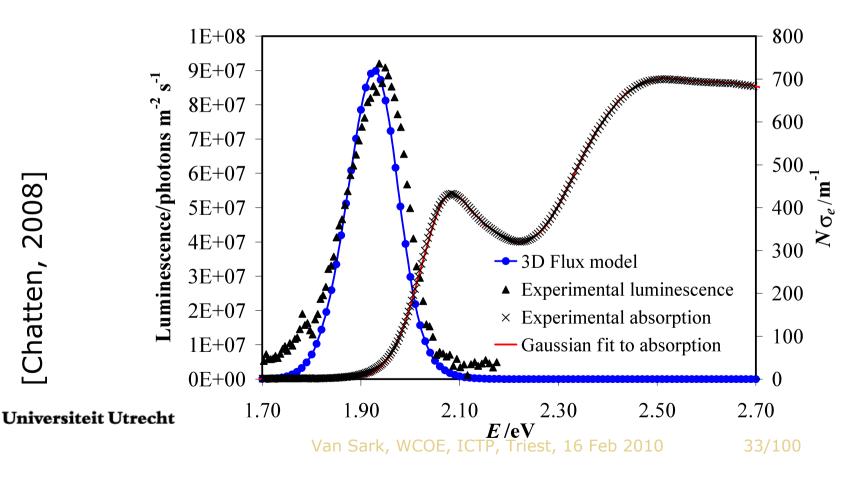


• Flux exiting on to the solar cell: $I_{R}(y,z) = \frac{\Omega_{c}\lambda_{e}}{2\pi} \frac{e^{-\alpha_{LR}}e^{-\lambda_{a}L}\sinh\left(\frac{\alpha_{R}}{2}\right)}{\sinh\left(\lambda L + \alpha_{LR}\right)} \int_{0}^{L} dx' \cosh\left[\lambda_{a}\left(L - x'\right) + \frac{\alpha_{B}}{2}\right] B(x',y,z)$ $+\frac{\Omega_{c}\lambda_{e}e^{-\frac{\alpha_{R}}{2}}\sinh\left(\frac{\alpha_{R}}{2}\right)}{2}\int_{-\infty}^{L}dx'e^{-\lambda_{a}(L-x')}B(x',y,z)$ $+\frac{\Omega_{6}\lambda_{et}}{8\pi}\frac{e^{-\frac{\alpha_{t}}{2}}e^{-\lambda_{at}L}\sinh\left(\frac{\alpha_{t}}{2}\right)}{\sinh\left(\lambda_{at}L+\frac{\alpha_{t}}{2}\right)}\int_{0}^{L}dx'\cosh\left[\lambda_{at}\left(L-x'\right)+\frac{\alpha_{t}}{2}\right]B(x',y,z)$ $+\frac{\Omega_{6}\lambda_{et}e^{-\frac{\alpha_{t}}{2}}\sinh\left(\frac{\alpha_{t}}{2}\right)}{2}\int_{0}^{L}dx'e^{-\lambda_{at}(L-x')}B(x',y,z)$ [Chatten, 2004]



3D flux model - results

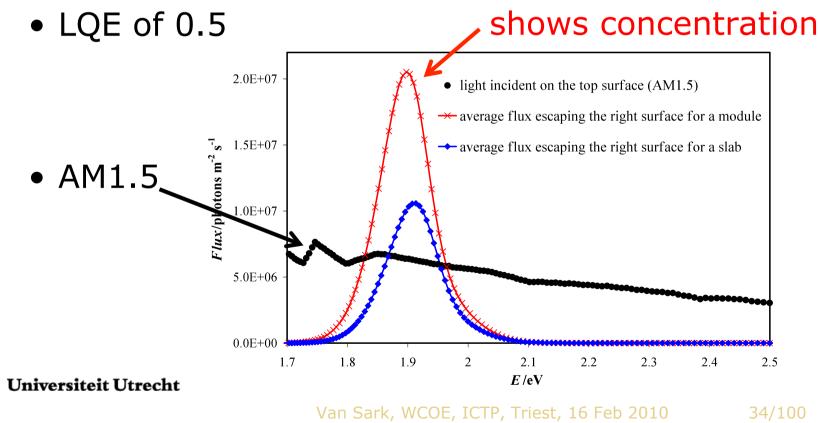
 Modelled and measured luminescence for a 1cm thick sample of CdSe/CdS core-shell dots in acrylic illuminated by a 530 nm laser





3D flux model – predicted fluxes

- Predicted fluxes escaping right hand side
- $L \times W \times D = 42 \times 10 \times 5 \text{ mm}^3 \text{ slab}$
- CdSe/CdS QDs in acrylic, connected to cell

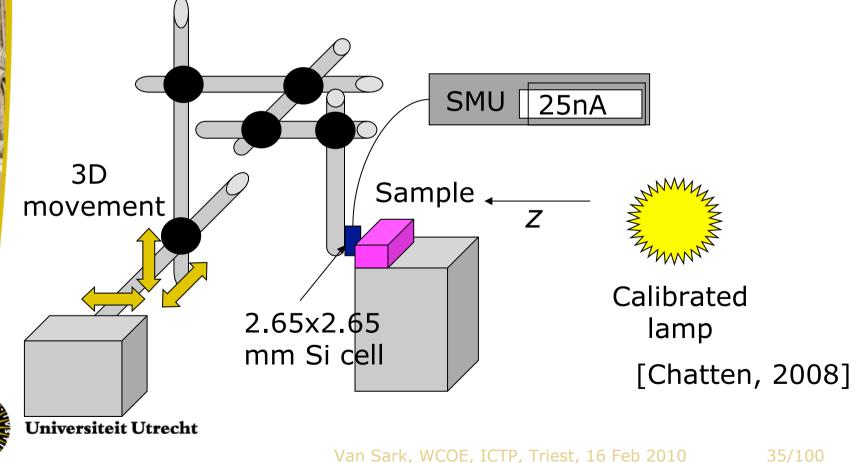


[Chatten, 2008]



3D flux model - results

• Measure short circuit current $I_{\rm sc}$ of cell bonded to the right-hand surface for modules, or of 2.65mm cell flush to the right-hand surface for slabs





3D Flux model - results

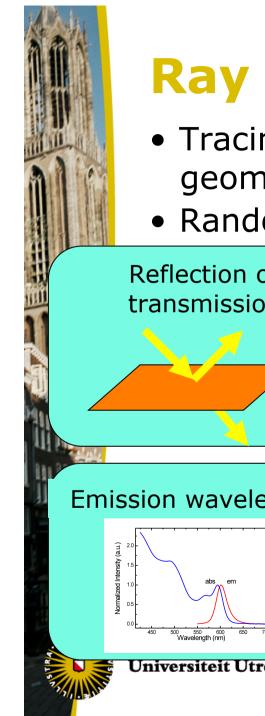
• Measured and predicted short circuit currents, J_{sc} , for the slabs and module investigated \rightarrow good agreement

Slab/Module	Slab Size	Q_e	$J_{sc}/mA m^{-2} @ x =$	
	(mm)	Ī	Ехр	Pred
CdSe/CdS QD slab	42×10×5	0.50	11.1±2.0	10.0 ± 1.4
Red dye slab	40×15×3	0.95	20.1±2.0	22.1±1.7
Mirrored red dye slab	40×15×3	0.95	26.0±2.0	26.2±2.6
Red dye module	40×15×3	0.95	31.1±2.0	29.3±2.8

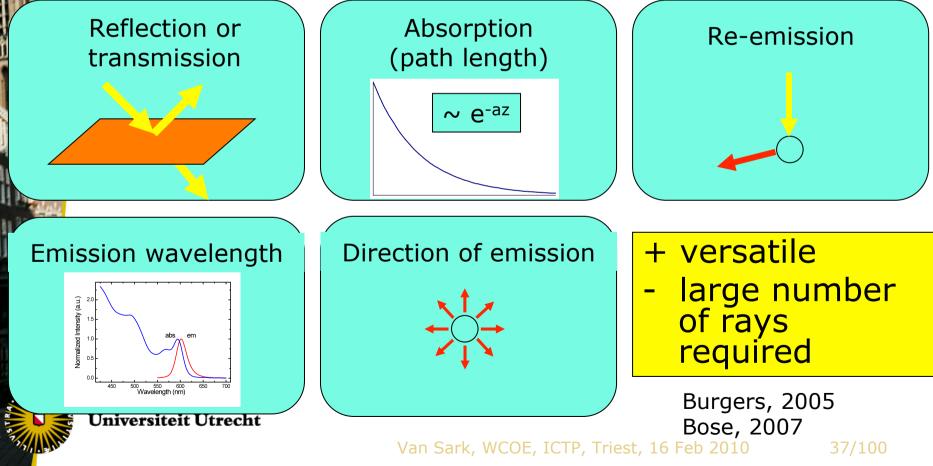
• Evaporated AI mirrors

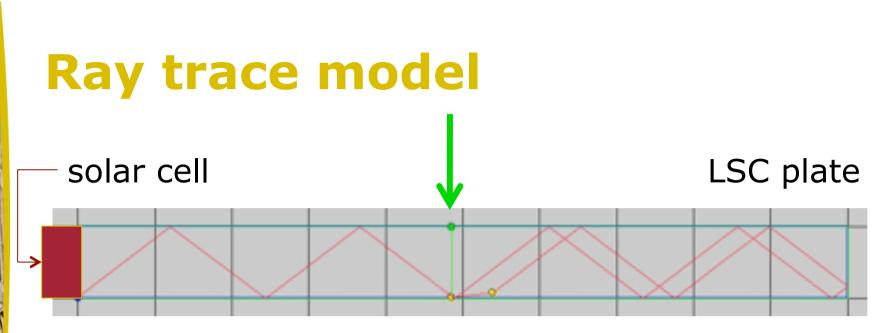
[Chatten, 2008]

• BP Si concentrator cell on RHS



- Tracing photons of specific wavelength using geometrical optics
- Random numbers determine outcome





Example path of the fate of an individual ray incident at the top of the LSC

- A green photon enters the LSC perpendicularly (centre)
- It is emitted as a red photon close to the bottom of the LSC
- It subsequently undergoes several internal reflections to finally arrive at the left side of the LSC where it is absorbed by the solar cell

[Gallagher, 2004; Burgers, 2005]



Models compared

- Thermodynamic model requires minimum of input data, and runs quickly, but limited to square geometries and single, homogenously doped with luminescent species
- Ray-trace approach is more flexible allowing multiple dopant dyes, thinfilms and different geometries
- Do they yield similar results?





Models compared

- four Plexit slabs
- different sizes
- different dyes
 - Red and Yellow Coumarin

edicted J _{sc} (mA/m ²) ay-trace
51.9
24.9
9.3
5.0
2005]

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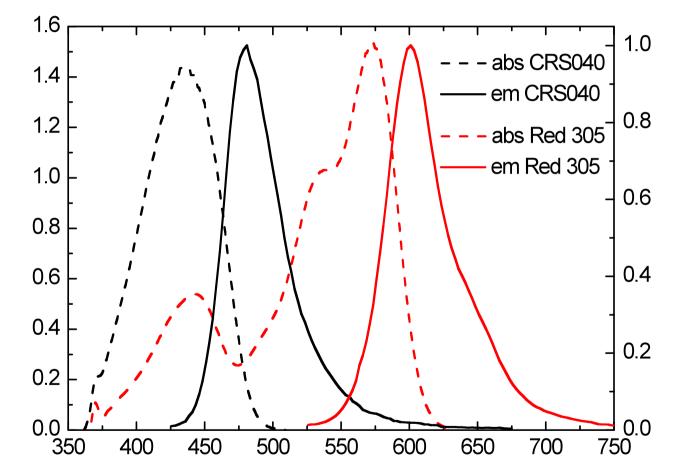
- Parametric study
 - Mirror configuration
 - Polymer background absorption
 - Solar cell type
 - Infrared dyes
 - Wavelength selective mirrors
 - Geometry
 - Nanoparticles
- PMMA (n=1.49, abs 1.5 m⁻¹)
- 5x5x0.5 cm³, Si solar cell on one side
- CRS040 and Lumogen F Red dye (next slide)
- Modeled efficiency <u>2.45</u>%

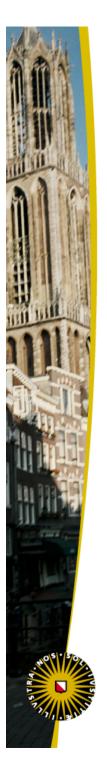
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[Van Sark , 2008]

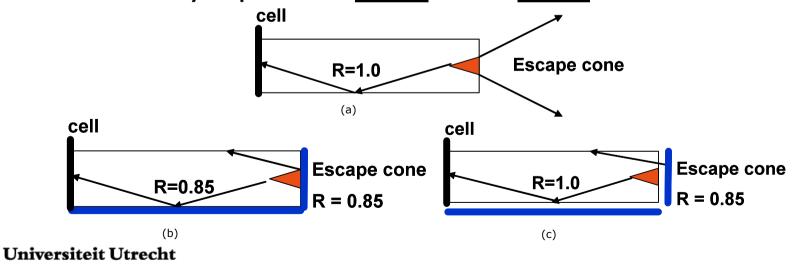


• CRS040 and Lumogen F Red dye (LQE 95%)





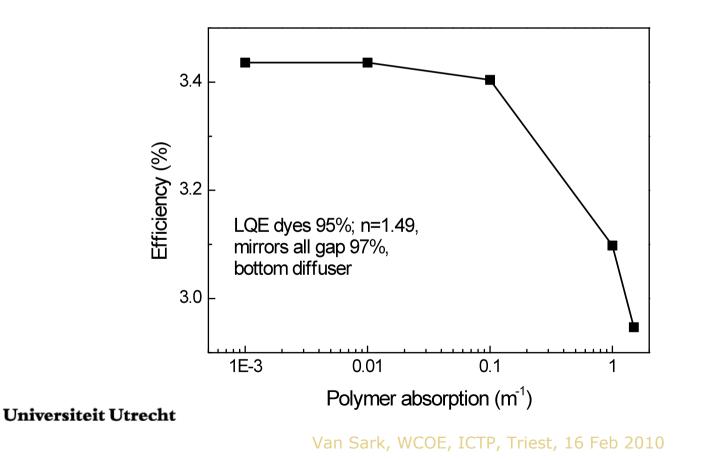
- Parametric study: Mirror configuration
- Adding mirrors directly to sides removes TIR, reflection coefficient of mirror
- Air gap restores TIR
- Lambertian bottom Mirror (R=97%)
- 3M adhesive silver foil on sides (R=97%)
- Efficiency up from <u>2.45</u>% to <u>2.97</u>%



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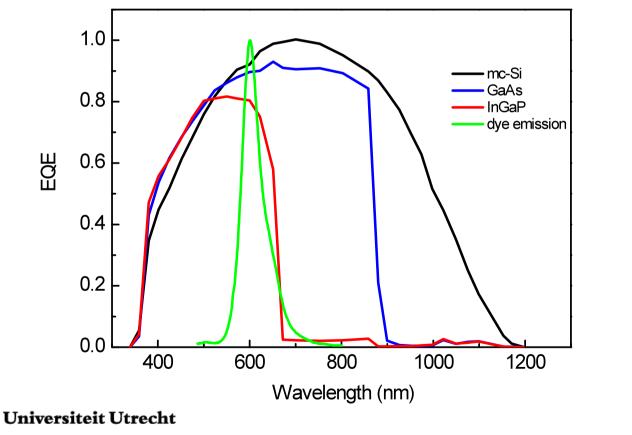


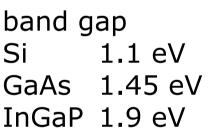
- Parametric study: background absorption
- Efficiency further up from <u>2.97</u>% to <u>3.42</u>% (with n=1.7, efficiency would be 3.8%)





- Parametric study: solar cell type
- Si cells not optimized for emission dyes
- 650-1050 nm spectral range not used





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- Parametric study: solar cell type
- The higher the band gap, the higher efficiency

mc-Si	GaAs	InGaP	Parameters
2.4	4.2	5.9	fixed mirrors, 85% reflectivity, dyes with 95%
			LQE
2.9 5.1	5 1	7.1	97% reflectivity "air-gap mirrors" on sides, and
	5.1		97% reflectivity Lambertian mirror at bottom
3.4 5.9	5 0	8.3	reduce background absorption of polymer matrix
	5.9		from 1.5 m ⁻¹ to 10 ⁻³ m ⁻¹
3.8	6.5	9.1	increase of refractive index from 1.49 to 1.7
1 1 0 /	$1/15 $ 1	100	V hand dan

1.1 eV 1.45 eV 1.9 eV band gap



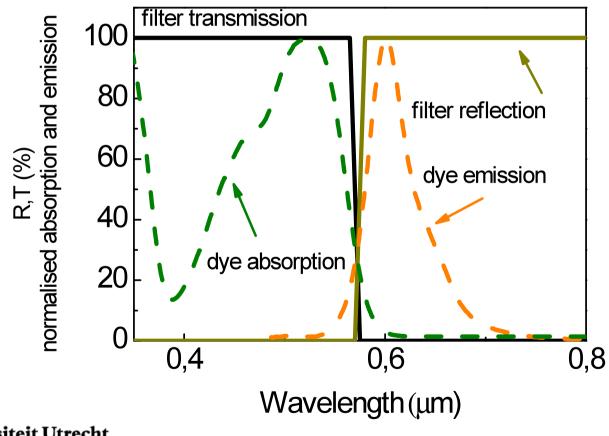
- Parametric study: IR dyes
- Not yet available at high LQE (model 50%)
- Stacks: similar to tandem solar cells

	efficiency
dye // cell combination	(%)
single plate Red305+CRS040 // 1 c-Si solar cell	3.8
single plate Red305+CRS040+IR dye // 1 c-Si solar cell	2.3
stack Red305+CRS040 top/IR dye bottom // 2 c-Si solar cells	4.5
stack IR dye top/Red305+CRS040 bottom // 2 c-Si solar cells	4.3

If LQE would be 95% → efficiency 5.4% (in single plate)



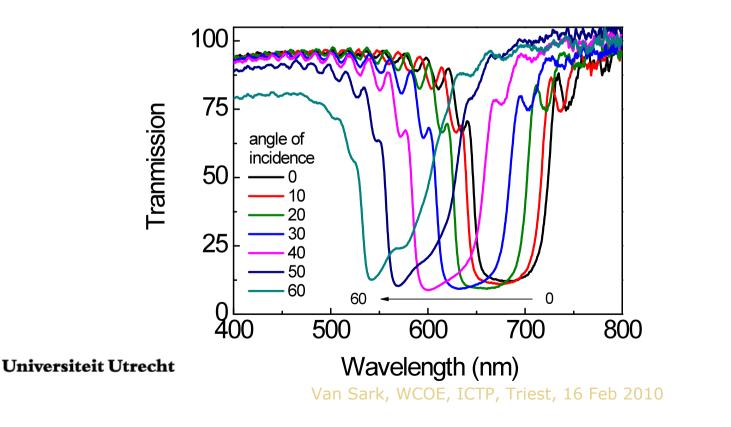
• Parametric study: Wavelength selective mirrors to reduce top escape losses





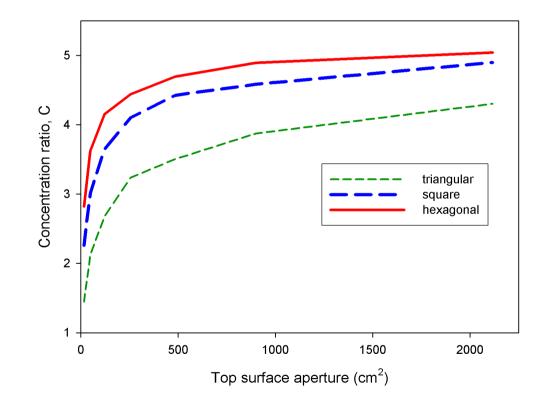


- Parametric study: Wavelength selective mirrors: cholesteric mirrors [Debije, 2006]
- Low transmission in dye emission range
- However, depends on angle of incidence





- Parametric study: geometry
- Square, triangular, hexagonal shapes, but in terms of cost per unit of power no difference



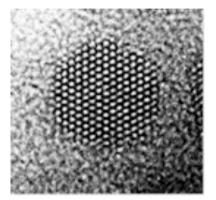




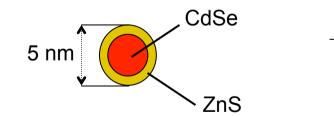
- Parametric study: nanoparticles
- Broad absorption
- Stable
- Tunable
- Example: [Kennedy, 2008]
- Three types of quantum dots
 - Green, 488 nm (commercial)
 - Orange, 605 nm (commercial)
 - Infrared, 690 nm (UU-research)
- QD Intermezzo

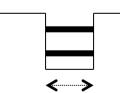
Intermezzo: quantum dots

- semiconductor nanocrystals
 - CdSe/ZnS
- quantum confinement
 - exciton is "particle-in-a-box"

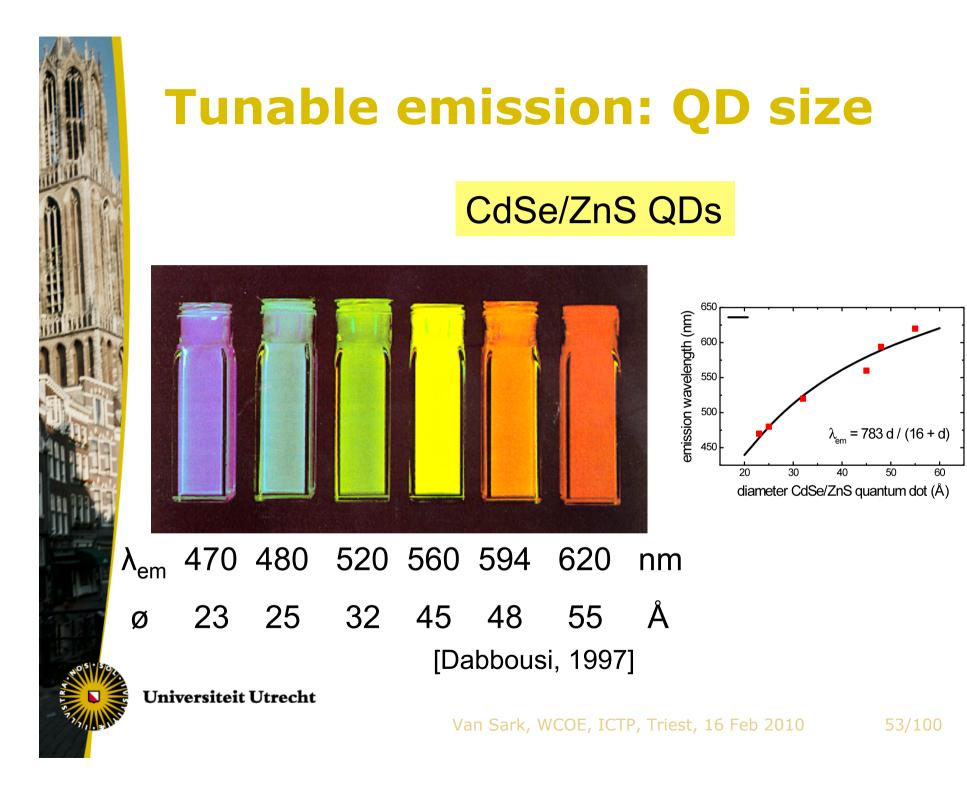


- radius smaller than exciton Bohr radius
- used as fluorescent probes
 - tunable emission as a function of size



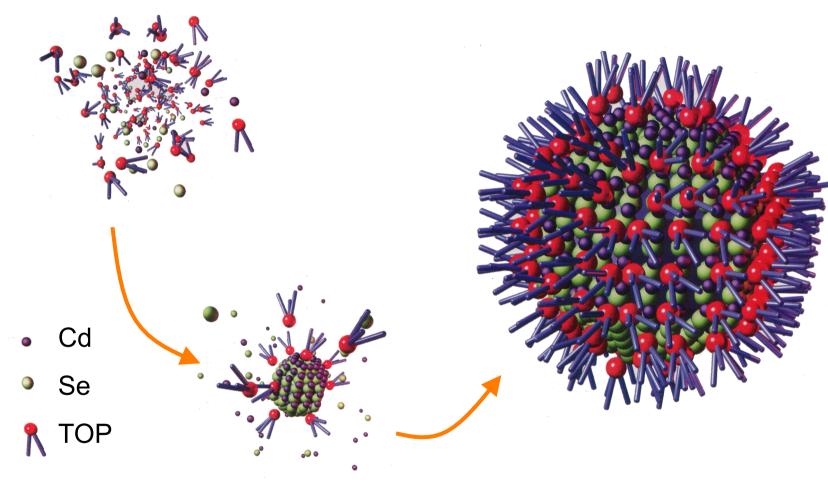








CdSe quantum dot assembly



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Scientific American, sept 2001 Van Sark, WCOE, ICTP, Triest, 16 Feb 2010



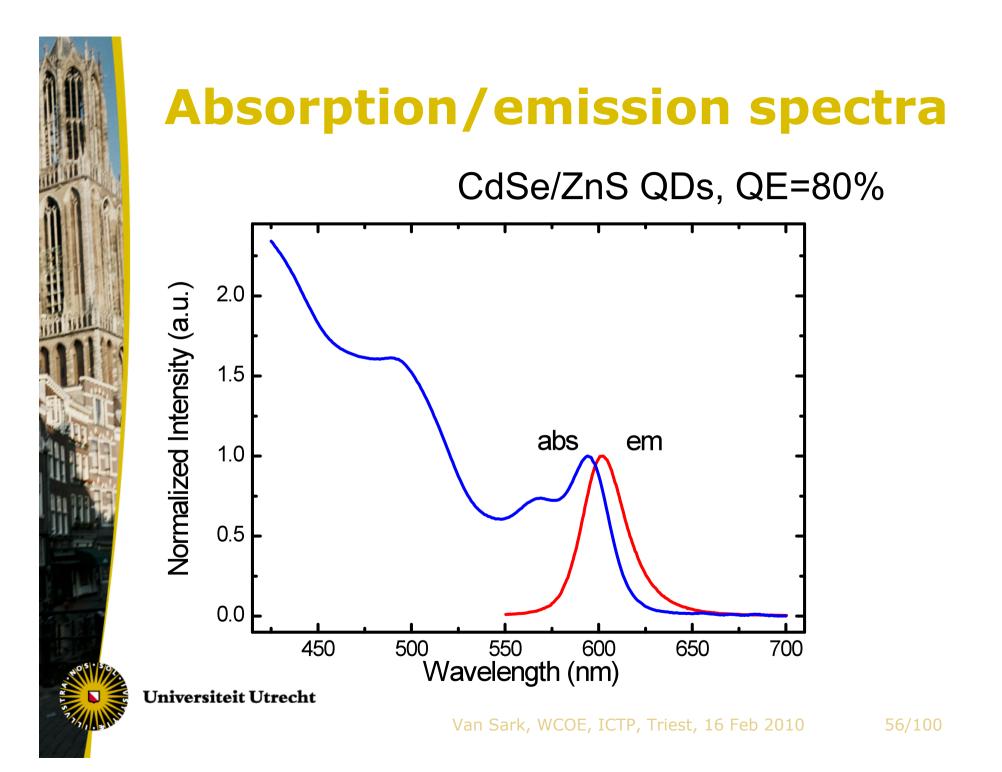
CdSe synthesis at UU

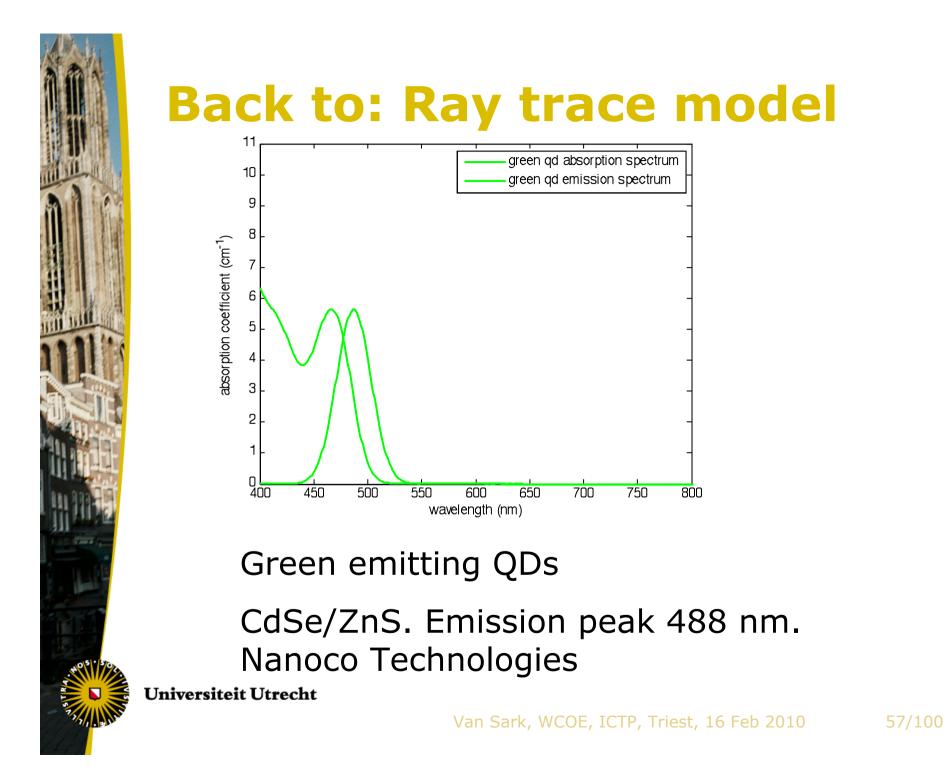


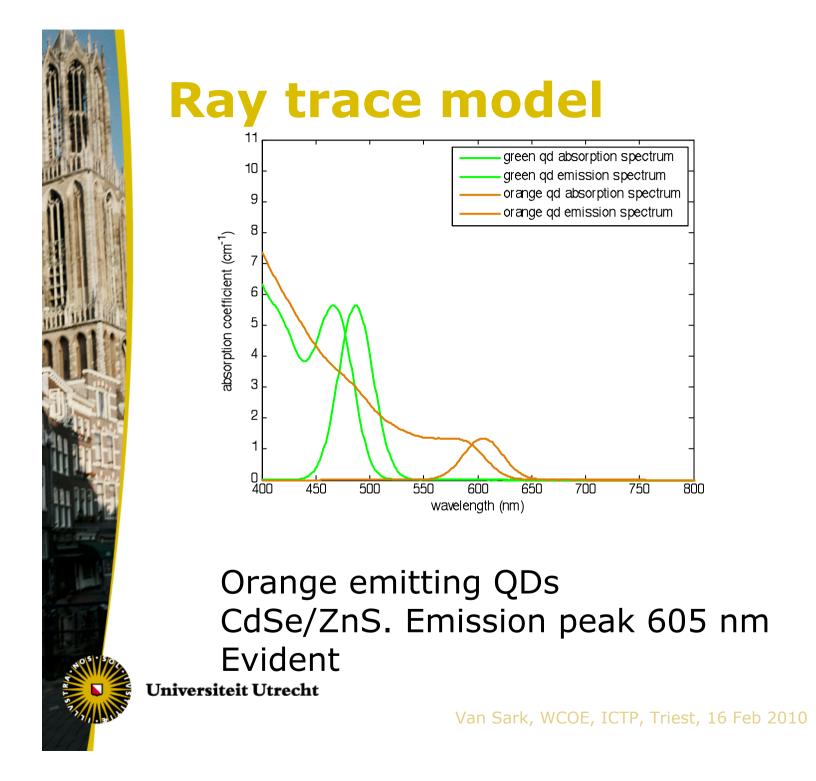
- in glovebox
- mix 100 ml heptane and 3 g surfactant (igepal)
- add 50 ml 1M Cd(ClO₄)₂ stir
- inject (TMS)₂Se stir

Courtesy of Freek Suyver and Sander Wuister (Debye Institute, Condensed Matter and Interfaces, Utrecht University)

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green qd absorption spectrum

green qd emission spectrum orange qd absorption spectrum

orange gd emission spectrum

600

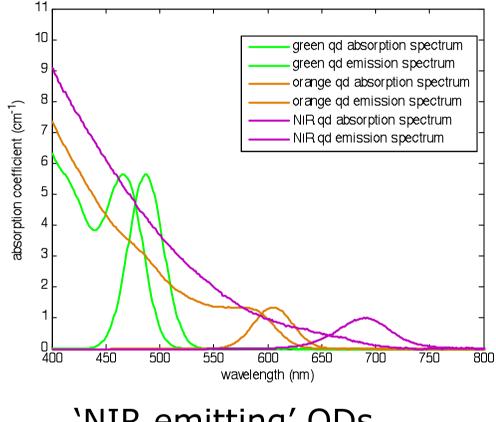
650

700

750

800





'NIR emitting' QDs

CdSe/CdS/CdZnS/ZnS (SYN1CSS, UU)





absorption efficiency (η_{abs}) fraction of incident photons absorbed by QDs

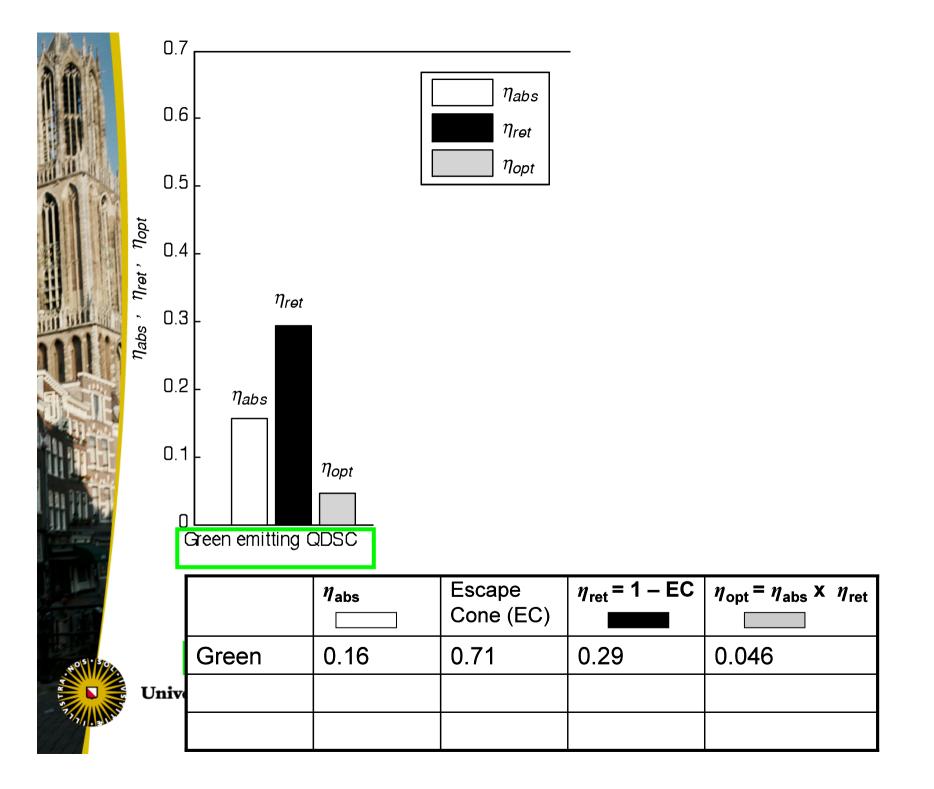
All absorbed photons are emitted (QD QY=100%)

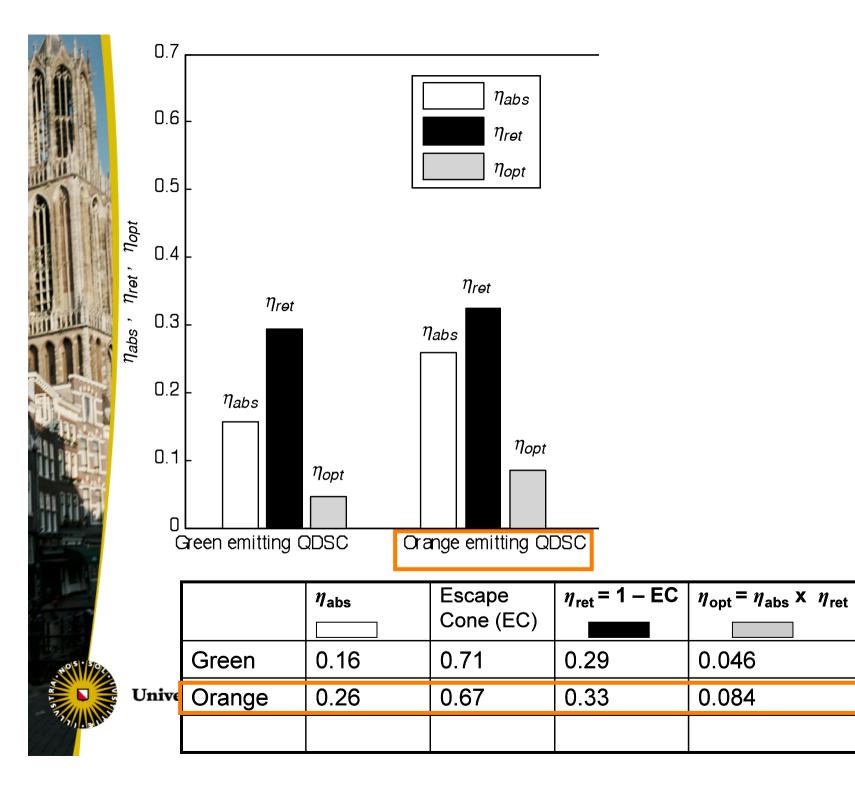
Only (internal) loss mechanism is escape cone loss

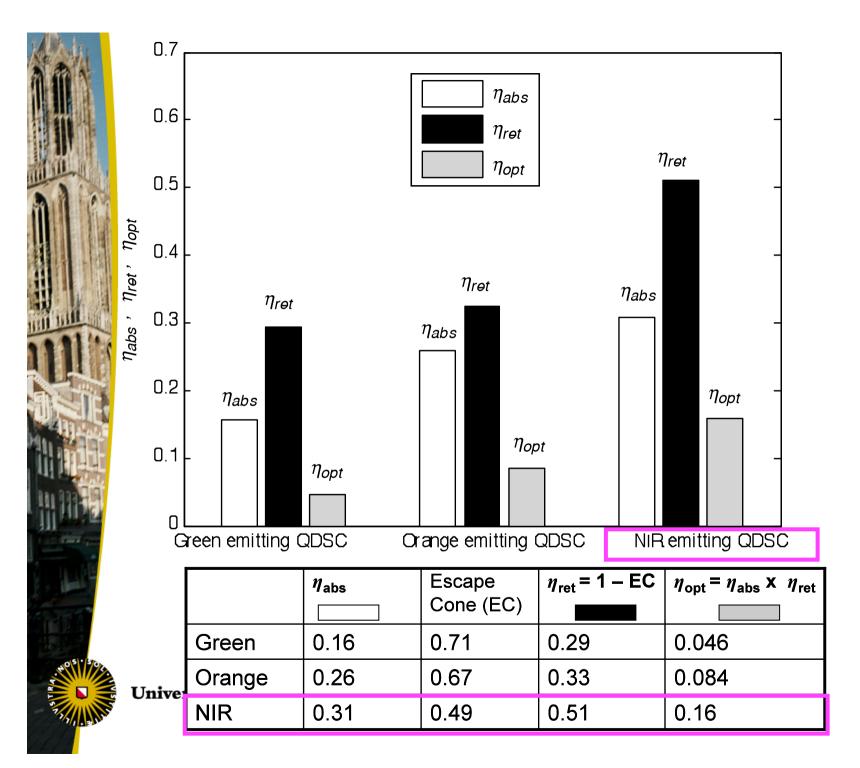
retention efficiency $(\eta_{ret}) = 1$ -total escape cone loss

optical efficiency (η_{opt}): fraction of incident photons transmitted to PV

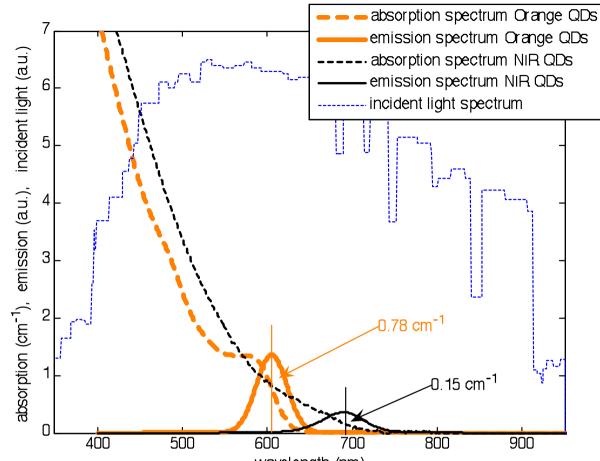
 $\eta_{opt} = \eta_{abs} \times \eta_{ret}$





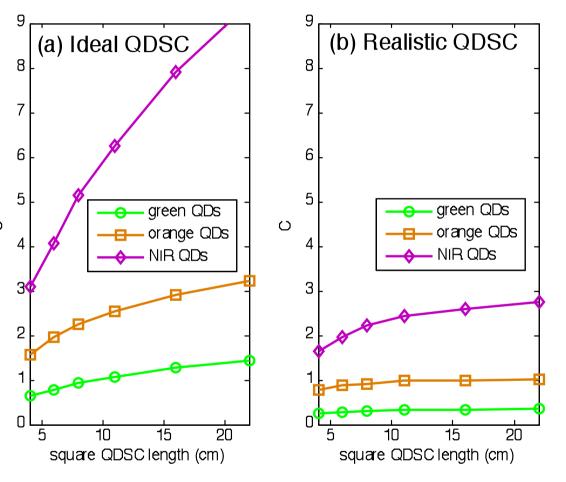






Optical efficiencies are much higher for NIR QDs than commercially-available visible emitting QDs -partly due to broader absorption range -more significantly due to lower re-absorption losses





Predicted Concentration Ratios using same QDs and more realistic parameters:

attenuation coefficient; 4 m^{-1}

Mirror reflectance: 0.94

QD QY: 85%

Re-absorption is less detrimental in NIR QDSC



Experiments

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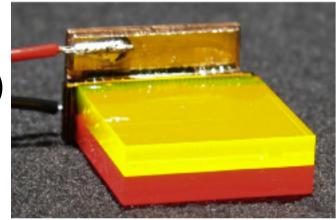
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Experimental LSCs

- Early work (Goetzberger's group): 4% for 40x40 cm²
- Goldschmidt [2009]: stack of plates (2x2 cm²) two different dyes InGaP solar cells → 6.7%

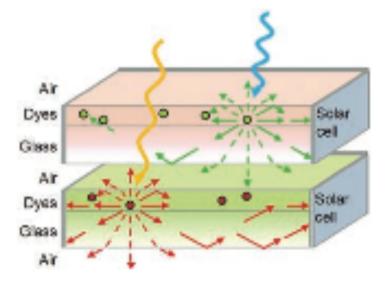


• When spectral range could be extended to infrared, 13.5% would be possible



Experimental LSCs

- Currie [2008]:
- stack of plates (2.5x2.5 cm²)
- films of organic dyes on glass
- GaAs solar cell
- Efficiency 6.8%
- Projected 12-14.5% for CdTe or Cu(In,Ga)Se₂ solar cells

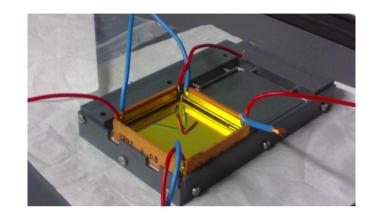


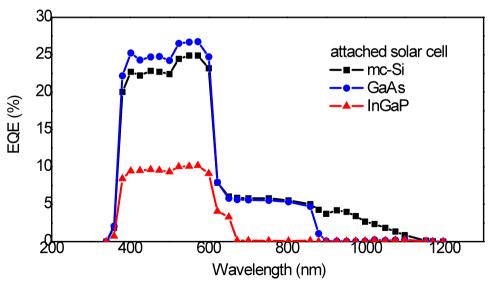




Experimental LSCs

- Slooff [2008]:
- Single plate (5x5 cm²)
- Lumogen F Red 305
- Yellow CRS040
- PMMA (Plexit)
- 4 GaAs cells
- Efficiency 7.1%







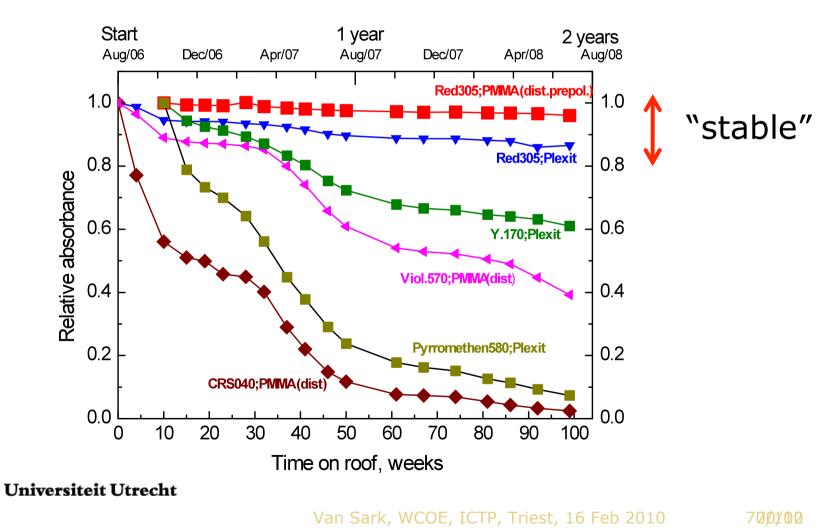
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Stability

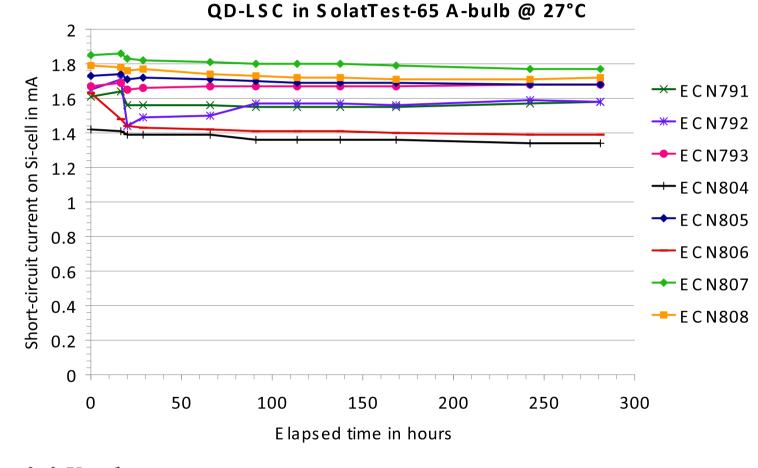
• Outdoor test, dye doped LSCs





Stability

• Outdoor test, quantum dot concentrators



Outdoor performance

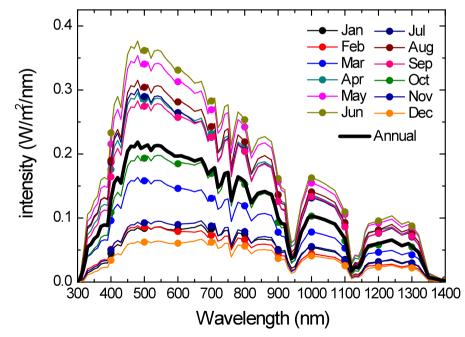
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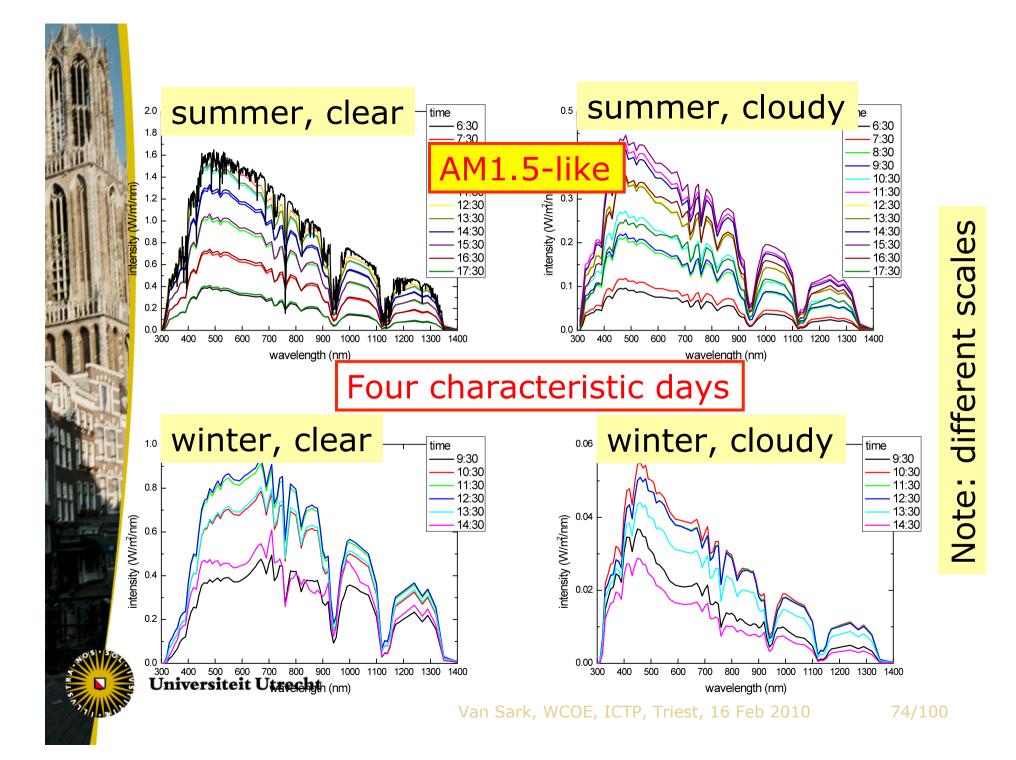
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Outdoor performance

- Ray trace model
- 23x23 cm plate, 1 mm thickness
- Use actual spectra (modeled based on irradiation data, SEDES2), for the Netherlands







0.3

0.2

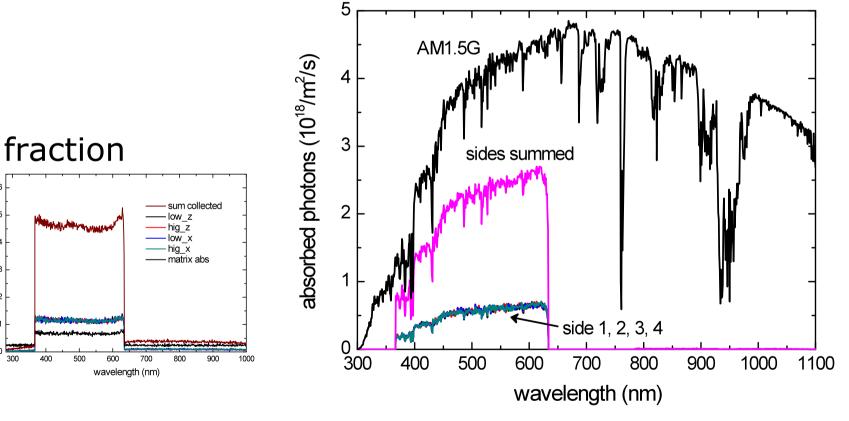
0.1

0.0 두

300

Outdoor performance

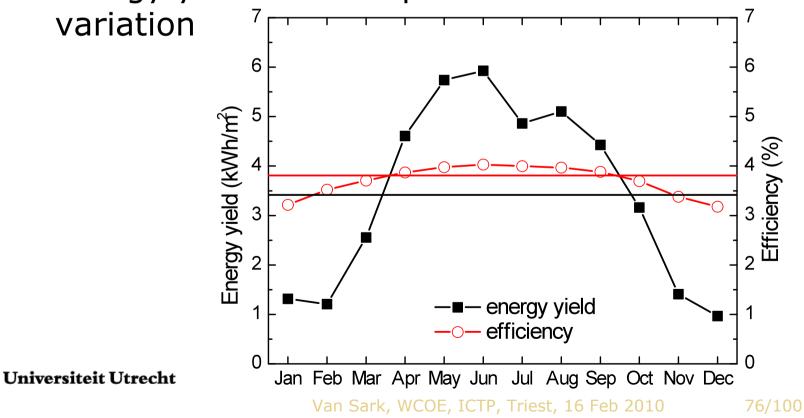
• Collected photons





Outdoor performance

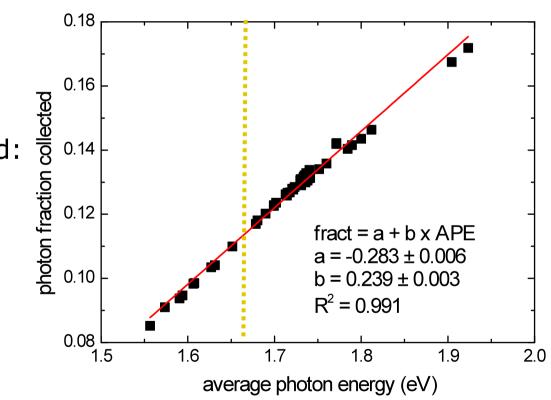
- efficiency
 - lower than AM1.5G efficiency (4.2%)
 - varies between 3% and 4 %
- energy yield follows spectral irradiance





Outdoor performance

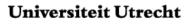
- Collected photon fraction linearly dependent on average photon energy
- The bluer the spectrum (diffuse) the more photons are collected
- APE AM1.5G: 1.714 eV
- Annual energy yield: 41.3 kWh/m²
- Si: ~120 kWh/m²
- Cost?









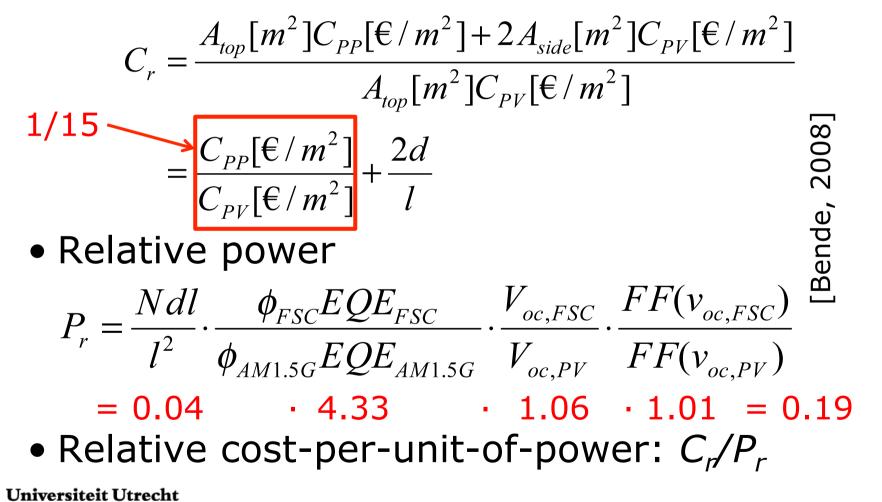


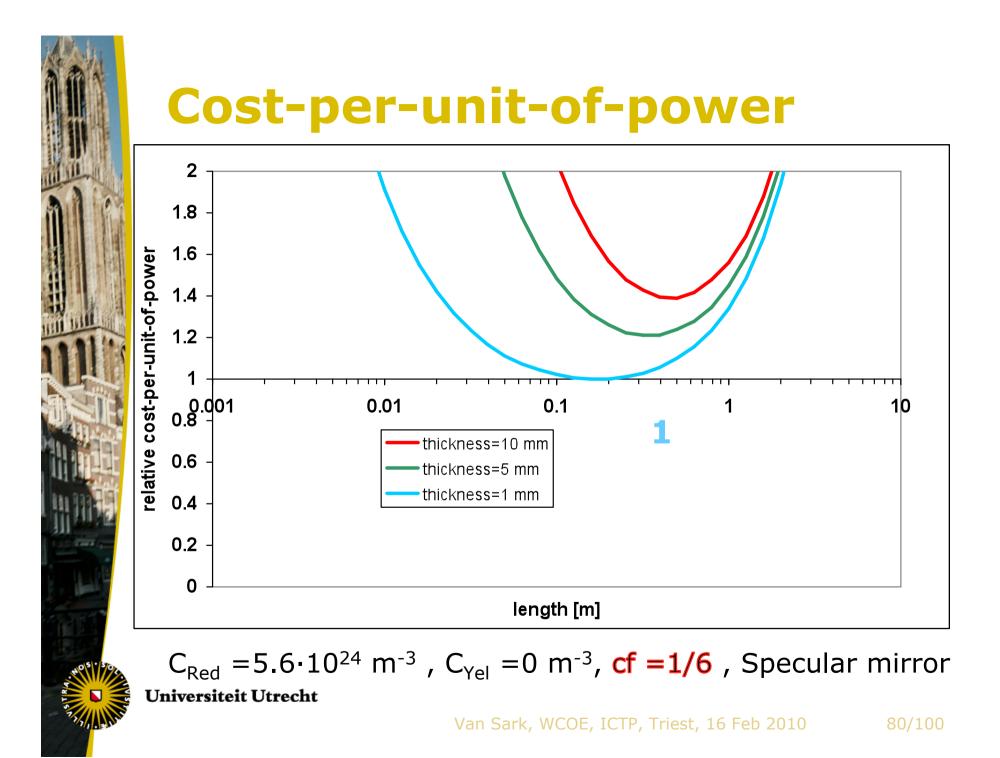
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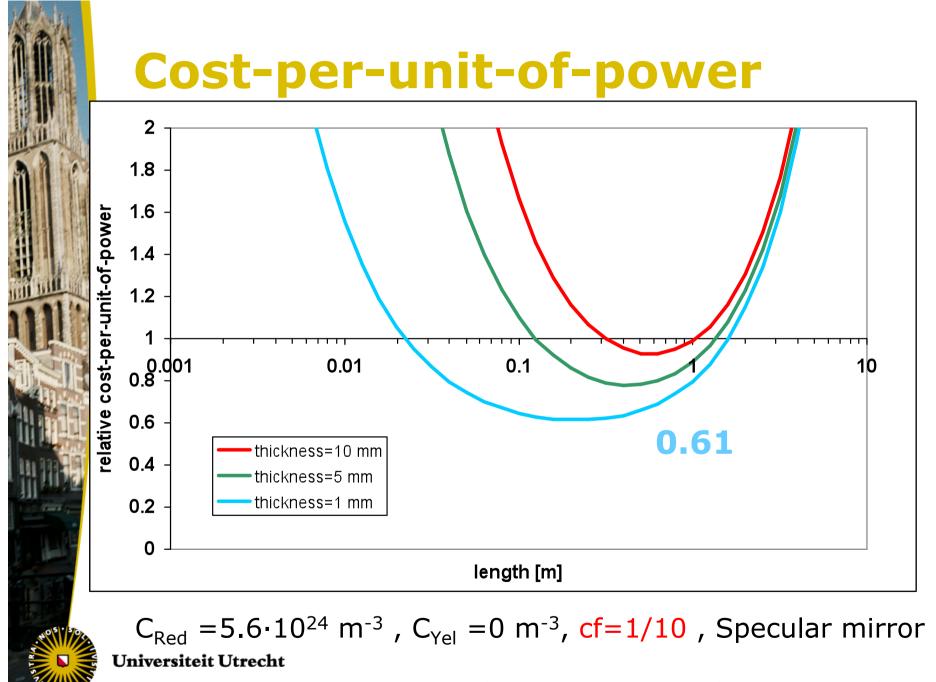


Cost calculations

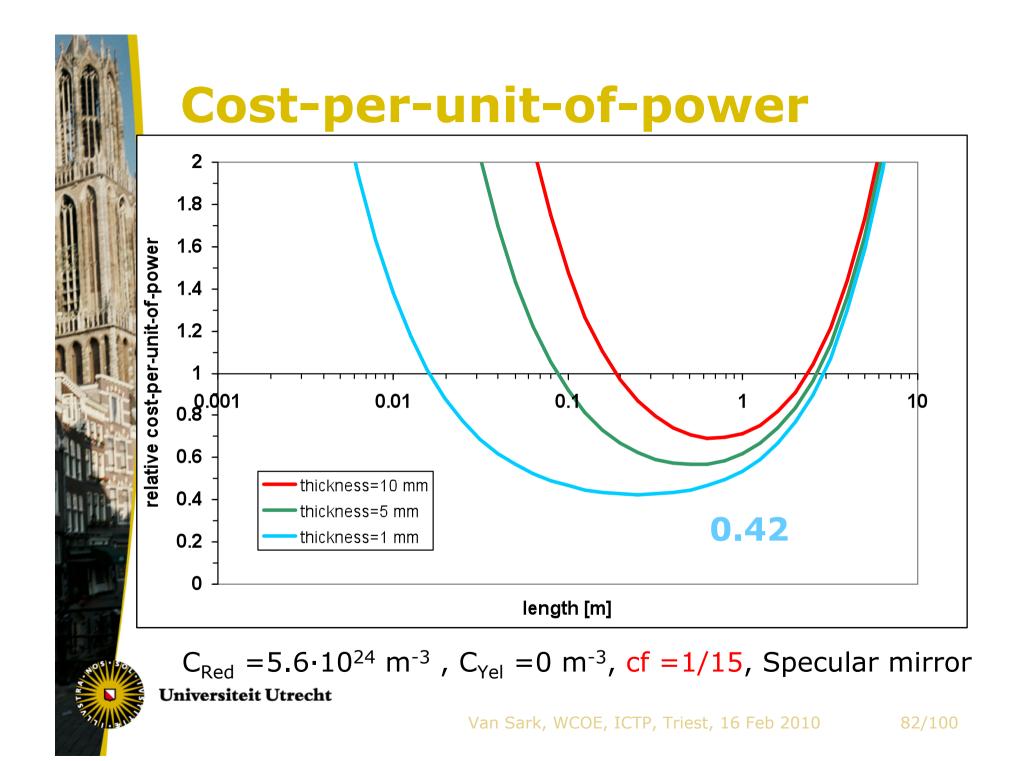
• Relative cost

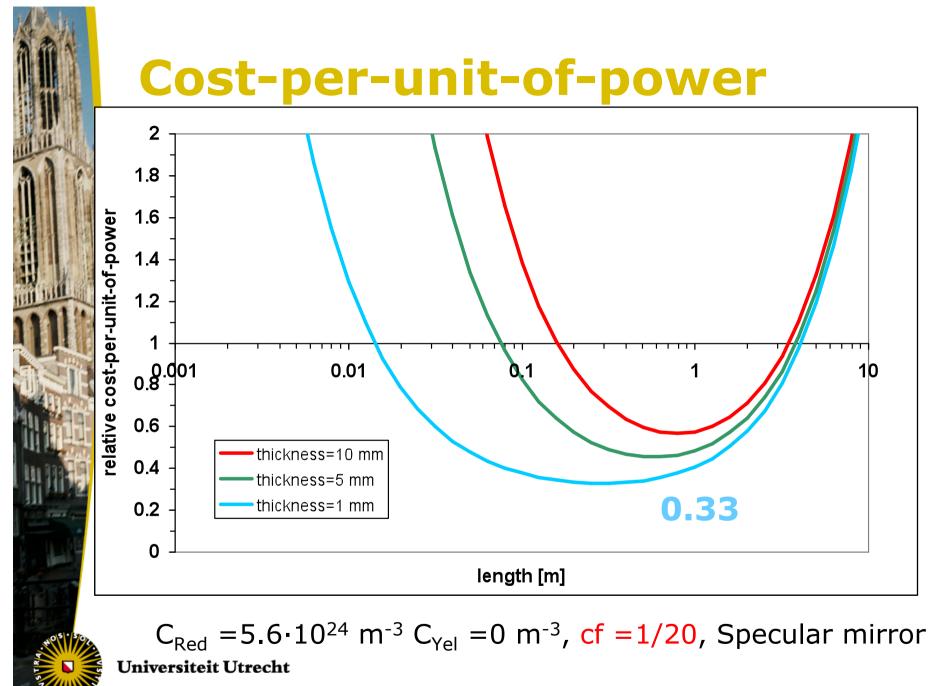






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Outlook

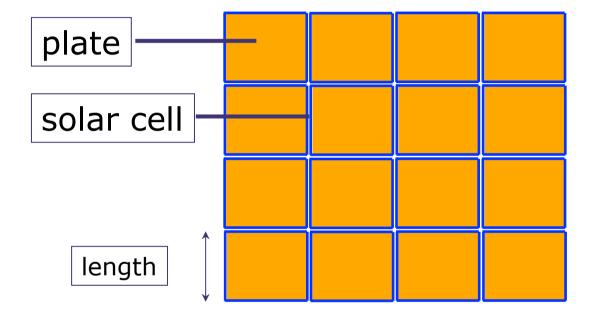
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Possible LSC structure

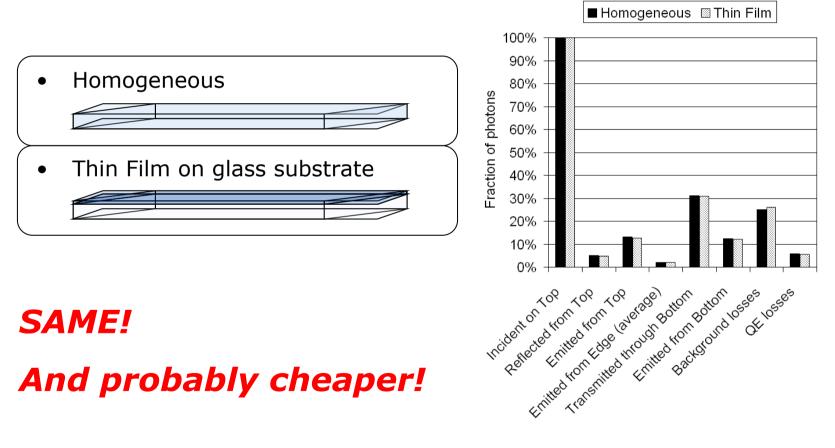


- Length 10-100 cm
- Thickness 1-5 mm



Thin film LSC

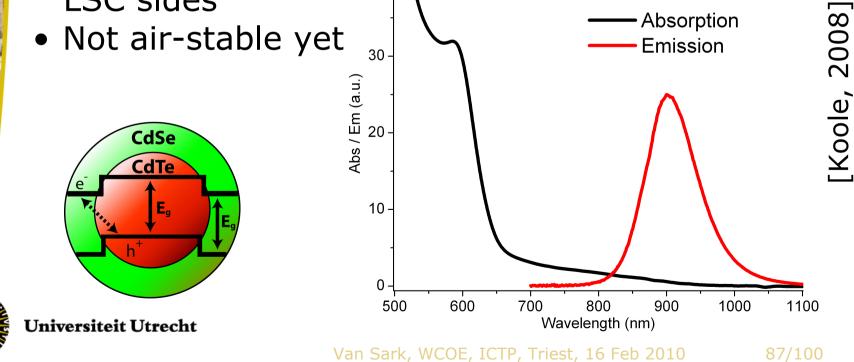
- Proposed to minimize re-absorption losses [Rapp, 1978]
- Thermodynamic modeling [Bose, 2007]





Large Stokes' shift QDs

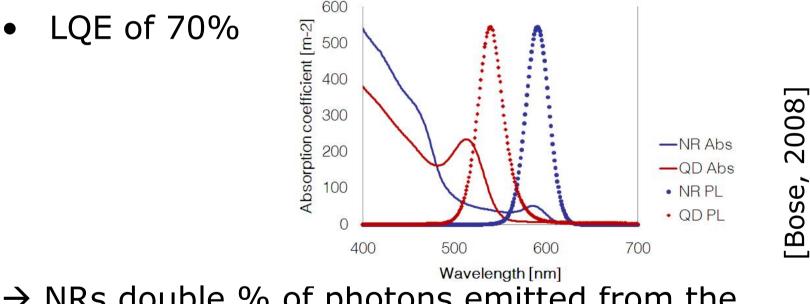
- Synthesis of type II CdTe/CdSe core/shell QDs with a large Stokes'-shift, high QE, and NIR emission (>900nm)
- Large Stokes' shift prevents re-absorption
- Emission 900 nm perfect for Si cells attached to LSC sides





Nanorods

- CdSe/CdS nanorods provided by CNR-INFM and UCB
- Reduce reabsorption losses

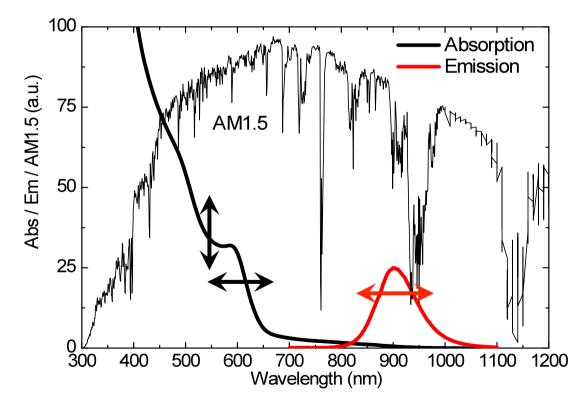


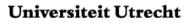
→ NRs double % of photons emitted from the LSC edges



Matching emission with band gap

- Type II QDs with a-Si:H solar cells
- Tuning emission and tuning band gap
- Find optimum combination, project started at UU

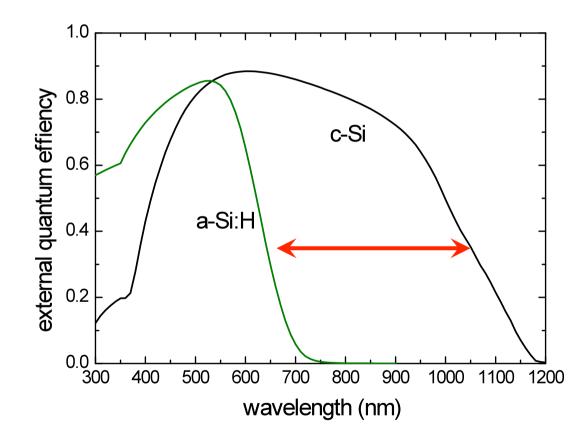






Matching emission with band gap

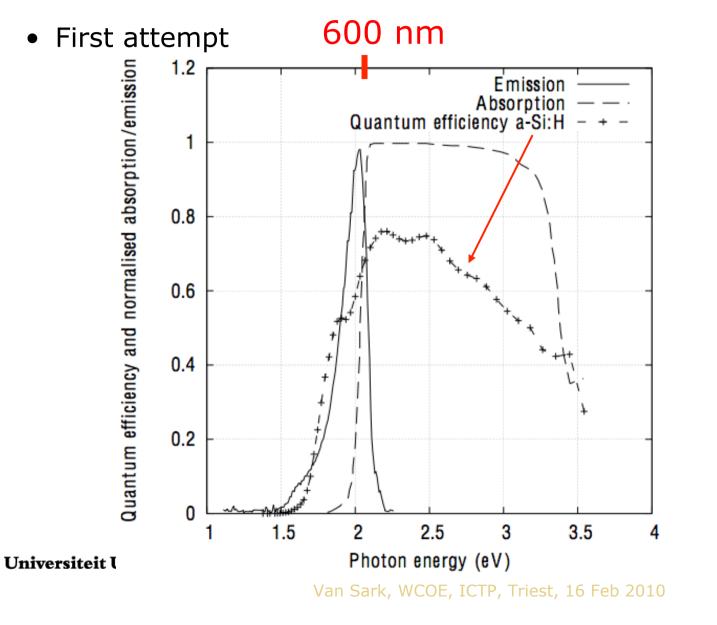
• Band gap variation 1.1 – 1.8 eV







LSC/a-Si:H



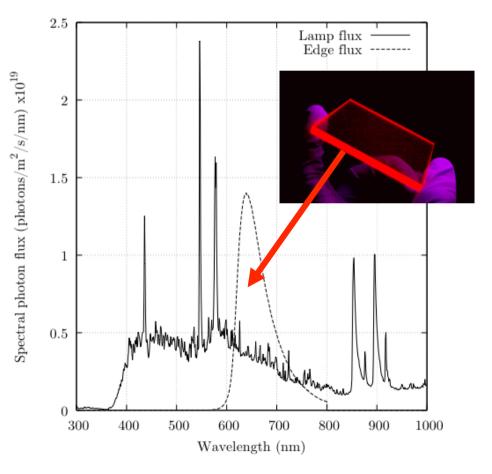
91/100



LSC/a-Si:H

Spectral photon flux (#/m²/s/nm)

- Solar simulator
- Incident 693 W/m²
- Edge 321 W/m²
- Concentration effect: higher flux in same wavelength region

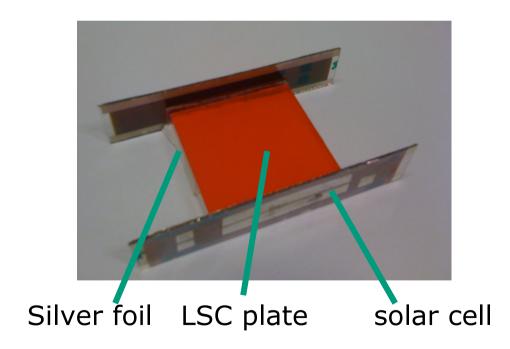






LSC/a-Si:H

- State-of-the-art a-Si:H cells (8%)
- 5x0.5 cm2, on 2 LSC edges
- 3M silver foil on other 2 edges
- Efficiency 1% [Van Sark, 2010]







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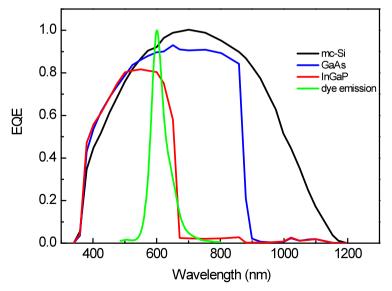
- Luminescent Solar Concentrator is a very good option to harvest cheap solar power, also at higher latitudes
- Modeling allows for parametric studies to find optimum design
- Many luminescent species available, nanoparticles are promising







- LSC present drawbacks
 - Spectral sensitivity
 - Organic dyes available with high QE only for wavelengths < 600 nm (2 eV)
 - Using c-Si (Eg=1.1 eV) leaves large part of spectral range (600-1100 nm) unused
 - Stability
 - Absorption matrix
 - Nanoparticles too expensive



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- LSC challenges
 - Need of full spectrum absorbers and NIR emitters, perhaps cascaded
 - Stability of luminescent species in matrix
 - Very low absorption matrix
 - Low cost (nano) materials
 - Abundant materials







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 - Solaronix: Andy Meier, Toby Meier

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Further reading

- Van Sark et al. Optics Express 16 (2008) 21773.
- Barnham *et al.* Luminescent Solar Concentrators, in *Nanoparticles for Solar Spectrum Conversion"*, Tsakalakos (Ed.) Taylor&Francis, Spring 2010.
- Van Sark *et al.* Nanoparticles for Solar Spectrum Conversion, in "Nanotechnology for Photovoltaics", Tsakalakos (Ed.) Taylor&Francis, Spring 2010.
- Van Sark *et al.* Luminescent Solar Concentrator, in "*Physics of Nanostructured Solar Cells*", Badescu, Paulescu (Eds.) Nova Science, Spring 2010.



