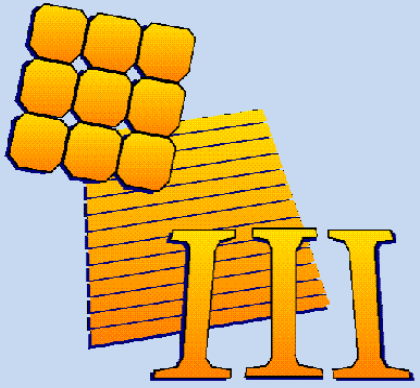
Up-conversion for Crystalline Silicon Photovoltaics:

Realistic Efficiency Limits and Enhancement in Photonic Structures

Craig Johnson



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Presentation outline

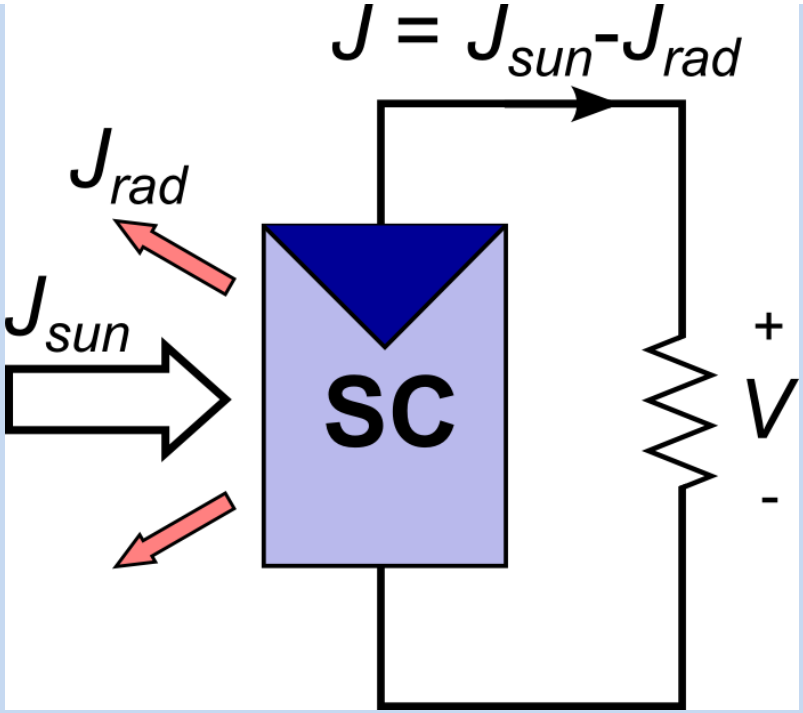
- Solar cell efficiency limits
- Up-conversion (UC) for Third-Generation PV
- UC efficiency limits
- UC model with *generalised* ‘realistic’ c-Si solar cell
- UC model with generalised ‘realistic’ UC material
- Implications for experimental study
- UC enhancement in multilayer photonic structures
- Erbium-doped porous Si as a UC material

Detailed balance analysis

Shockley-Queisser insight:
perfect solar cell at steady state is a black body emitter obeying Planck's (generalised) law

$$J_{rad} = \frac{q\varepsilon_c}{4\pi^3 h^3 c^2} \int_{E_g}^{\infty} \frac{E^2}{\exp\left(\frac{E-qV}{kT_c}\right) - 1} dE$$

For a known solar flux J_{sun}/q, limiting photocurrent may be found for any applied voltage V:

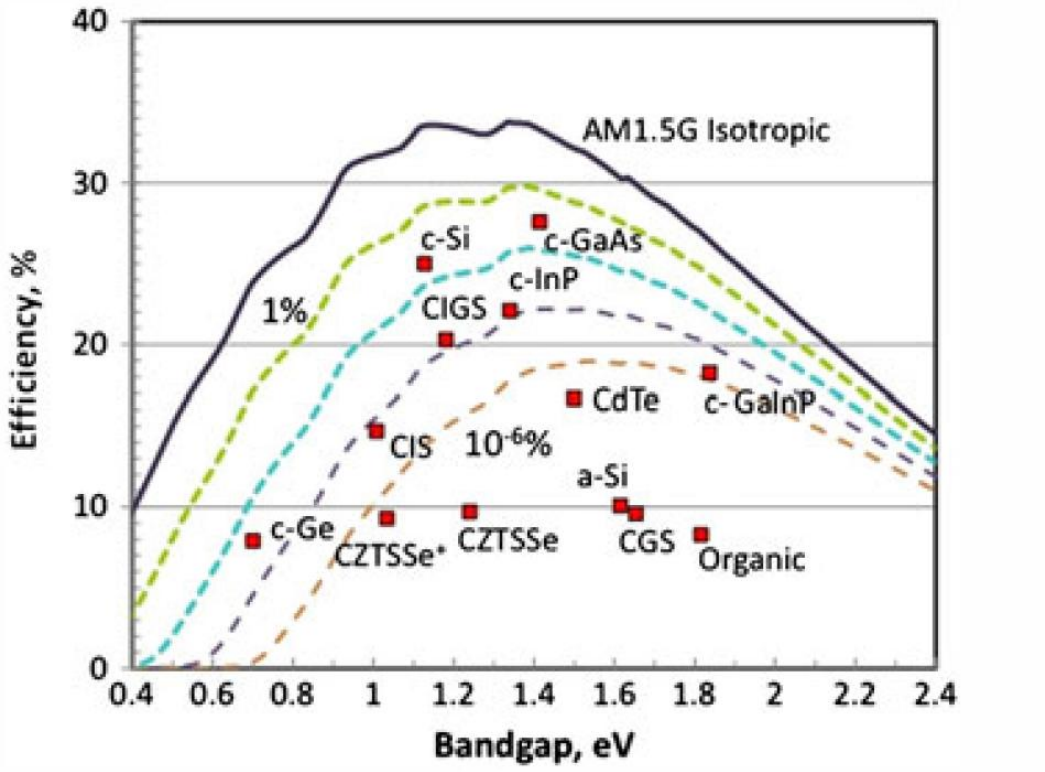


Overall limiting efficiency η_{SQ} is given by $J_{mpp}V_{mpp}/P_{in}$

AM1.5G limiting efficiency

Perfect cell: sharp absorption cutoff at E_g.

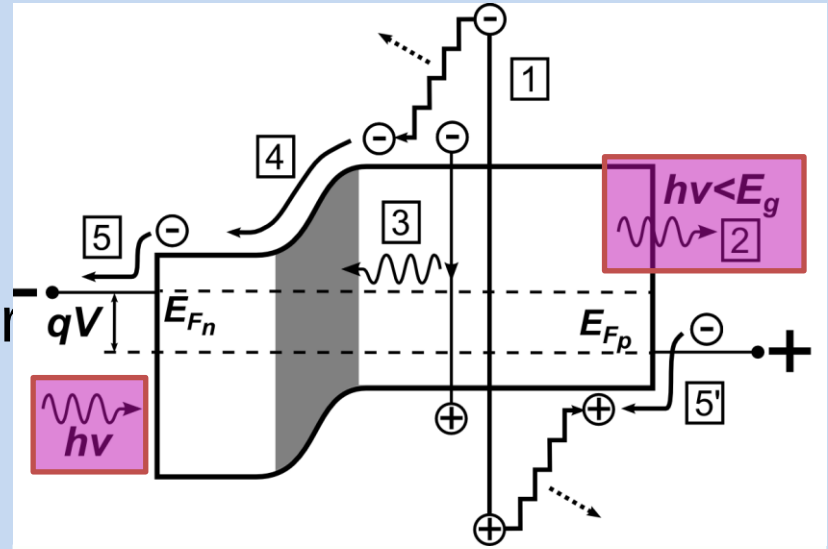
Assuming cell is at ambient temperature with non-degenerate doping, $\eta_{SQ} = f(E_g)$.

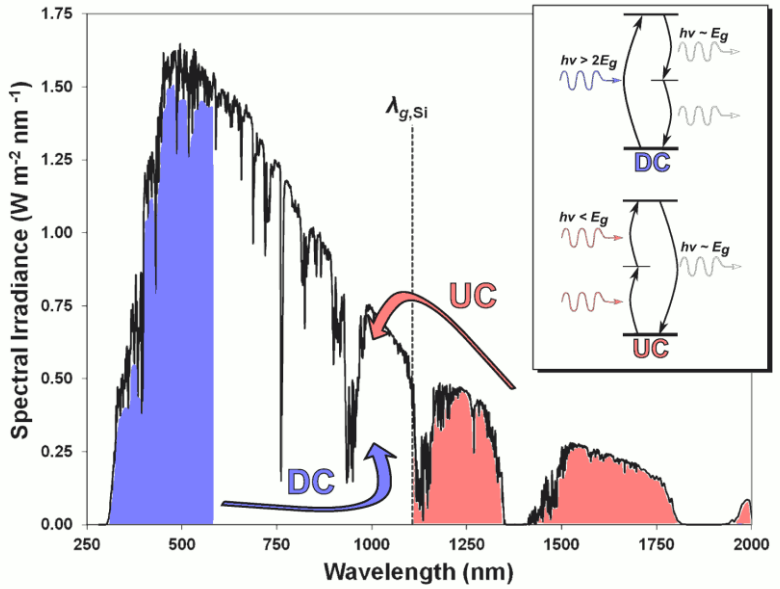


From Green, *PIP* 2011 (DOI 10.1002/pip.1156)

UC for Third Generation PV

- *Sub-band-gap transmission* major contributor to efficiency suppression
- c-Si: **19.1%** loss of solar power density in AM1.5G spectrum
- Lowering band gap to collect more photons reduces V_{oc}
- Si band gap nearly ideal (η_{SQ} ~ 33%)
- **Up-conversion (UC)**: modify incident spectrum to convert sub-band-gap photons into absorbable photons





Up-conversion concept

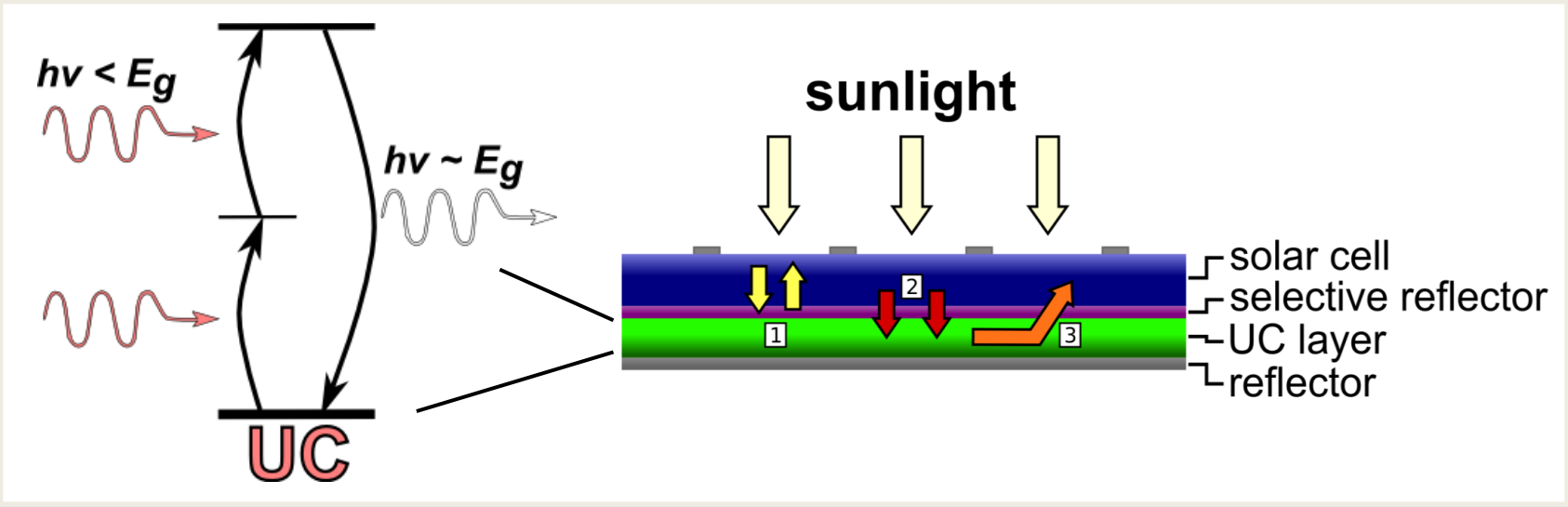
Exploit sub-band-gap spectrum: break SQ limit

Extend SC spectral response without altering voltage

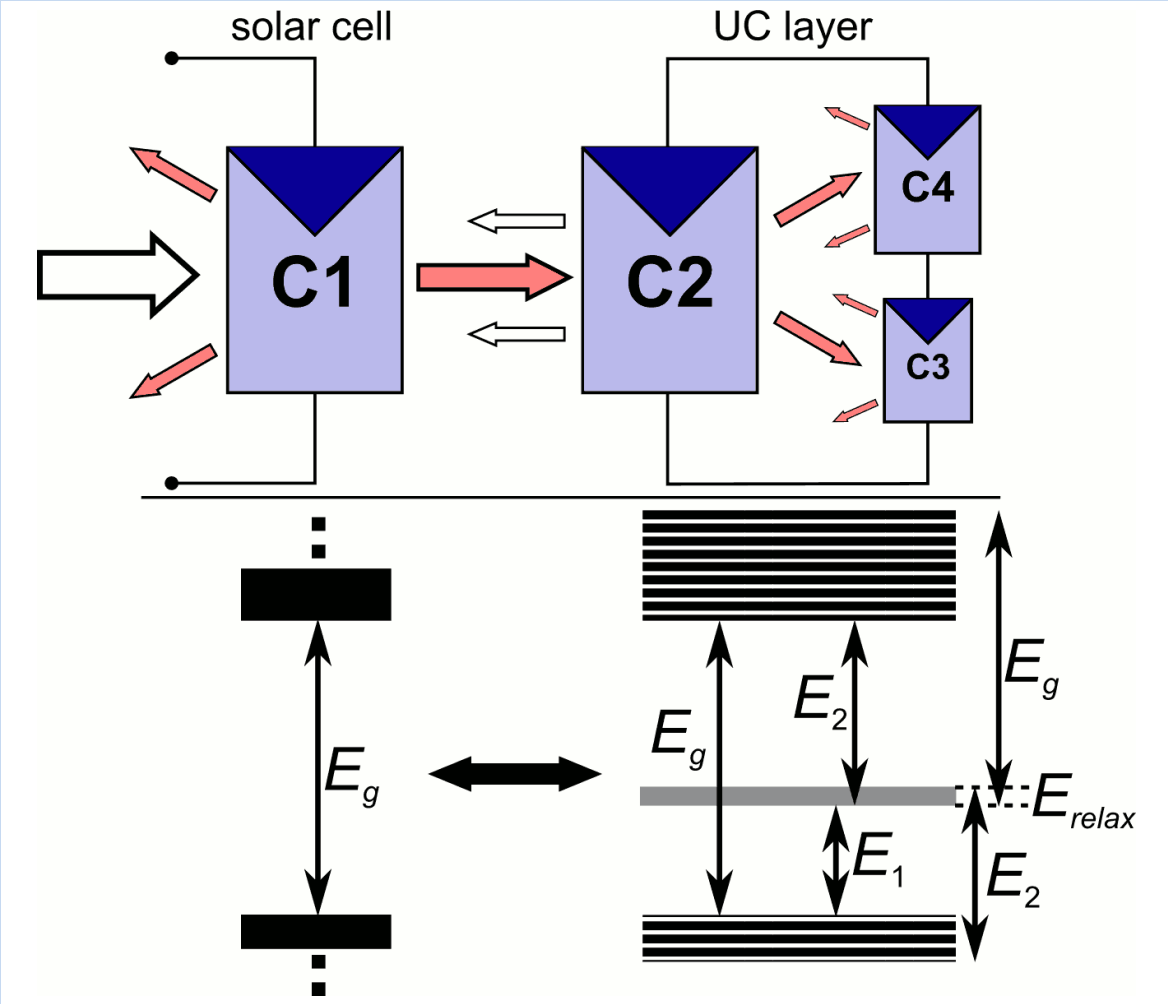
Luminescent layer behind conventional SC

Two-photon absorption leads to single photon emission (e.g., rare earth ions, metallorganic dyes)

Advantage: device based on ‘standard’ commercial SC!



Ideal UC-PV eq. ckt. model
(after Trupke, 2002)

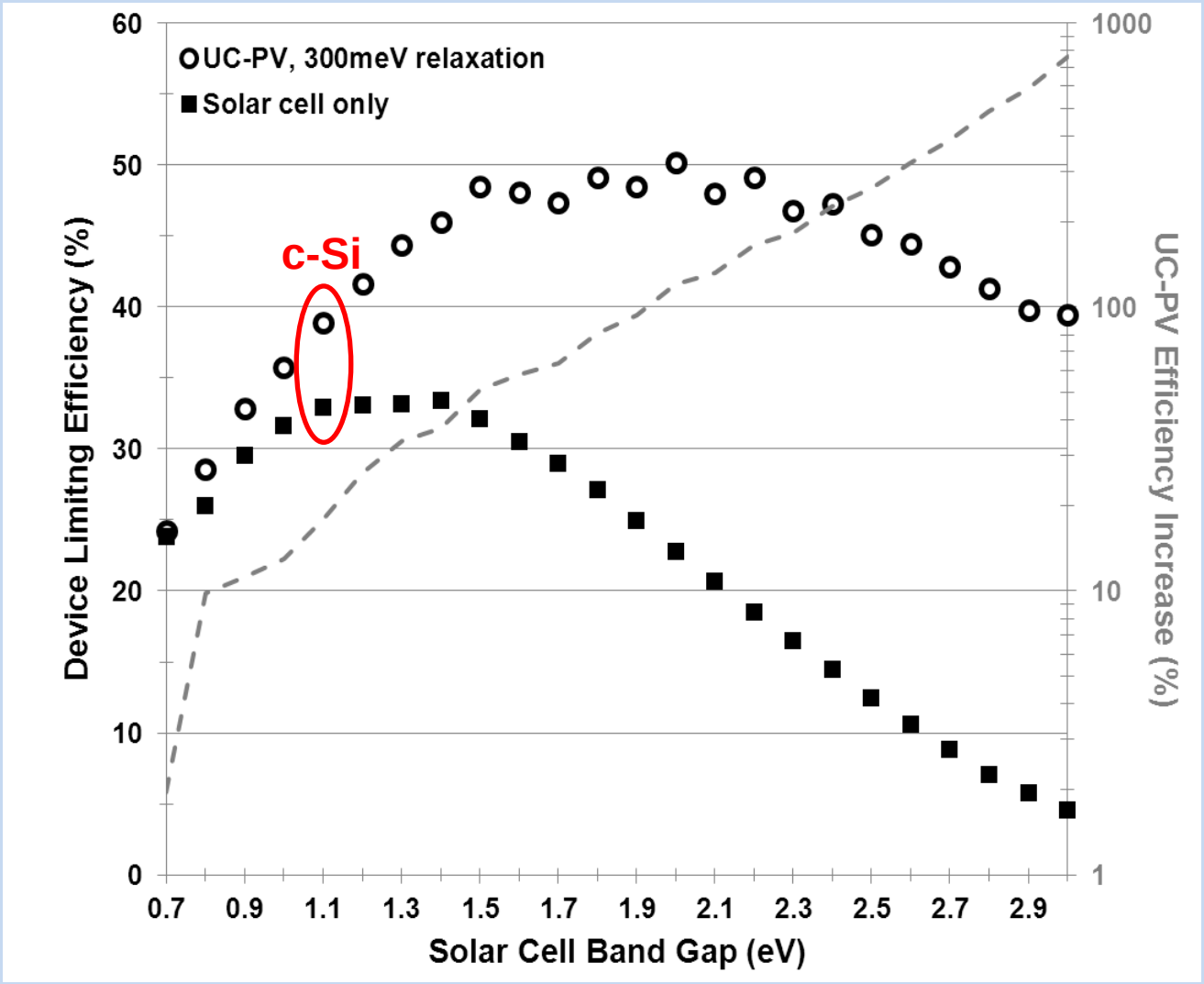


Four single-threshold ‘solar cells’ acting as black-body converters (from SQ model)

Current and voltage are constrained in equivalent circuit

Energy band diagram of system above

Ideal UC-PV efficiency



c-Si SC limiting efficiency increases from **33%** to almost **40%** under AM1.5G

Standard assumptions

Extension of SQ analysis to four-diode model:

1. Solar cell absorption is perfect
   (1 for $E > E_{g,i}$ and 0 for $E < E_{g,i}$)
2. Perfect radiative efficiency of all components
3. UC layer absorbs over entire sub-band-gap region
4. Absorption of two small-band-gap cells is selective
   (non-overlapping)

Real solar cells do not behave according to 1 and 2… what is impact of ‘non-ideal’ absorption as seen in real device?

Optical properties of Si

Tabulated complex refractive index for planar intrinsic Si linked to absorption via Fresnel equations:

$$r(\lambda) = \frac{1-[n_{Si}(\lambda)-i\kappa_{Si}(\lambda)]}{1+[n_{Si}(\lambda)-i\kappa_{Si}(\lambda)]};$$

$$R(\lambda) = \left|r(\lambda)^2\right|$$

$$\alpha(\lambda) = \frac{4\pi\kappa_{Si}(\lambda)}{\lambda}$$

$$A(\lambda) = [1-R(\lambda)](1-e^{-\alpha(\lambda)\cdot d})$$

Refractive index data from Green and Keevers, 1995.

Realistic generalised solar cell absorption

Absorption expression can be modified to account for:

- Relevant wafer thickness: 250 μm
- ‘Reasonable’ broadband ARC properties (modify *R*)
- ‘Weak’ surface texturing/light trapping—allows transmission of NIR light (modify *d*)
- Free-carrier absorption for 10^{17} cm^{-3} doping (i.e., absorption that does not contribute to photocurrent)

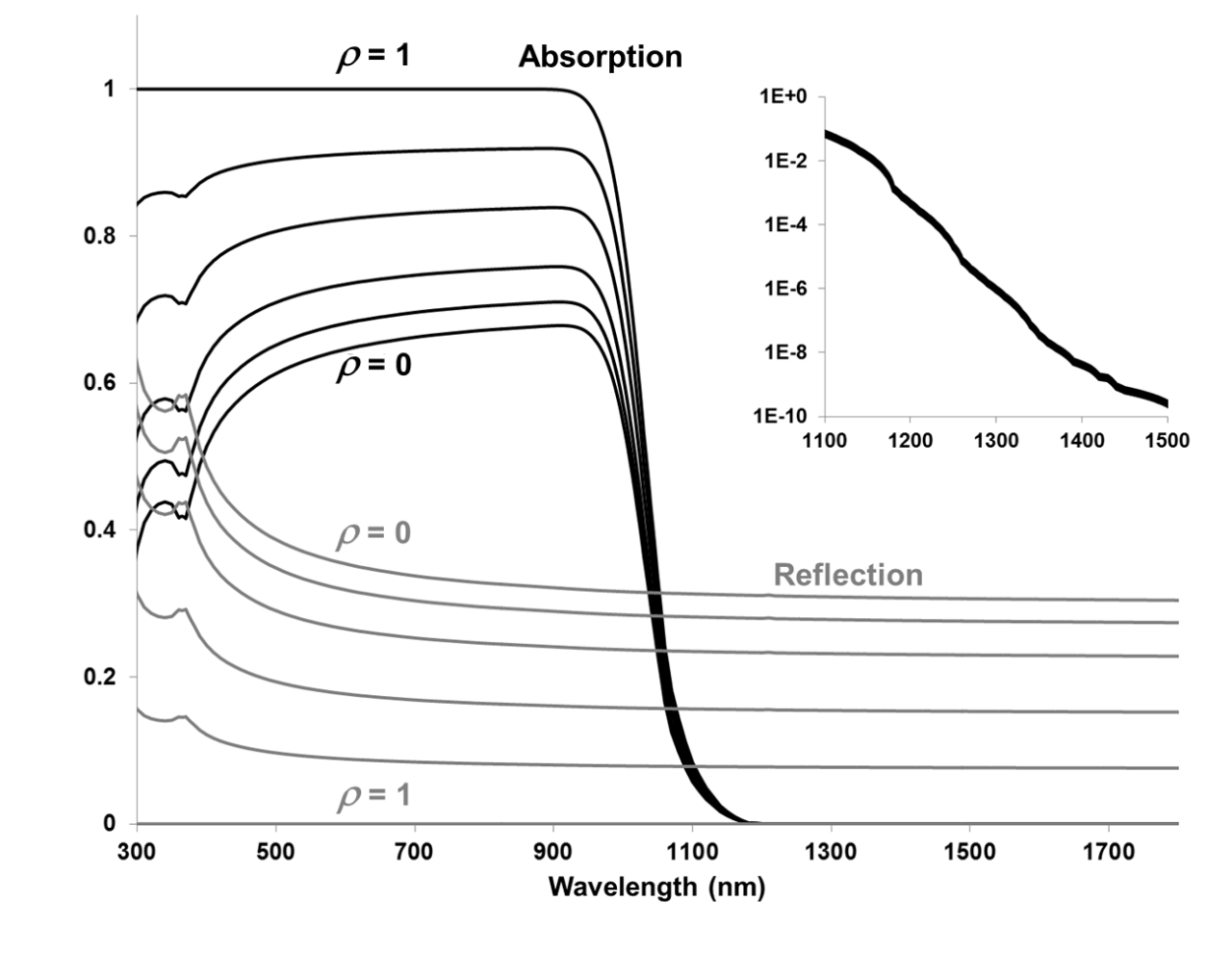
$$A = [1 - R](1 - e^{-(\alpha + \alpha_{fc})d})$$

$$\alpha_{fc} = \kappa_{fc} \lambda^2 N$$

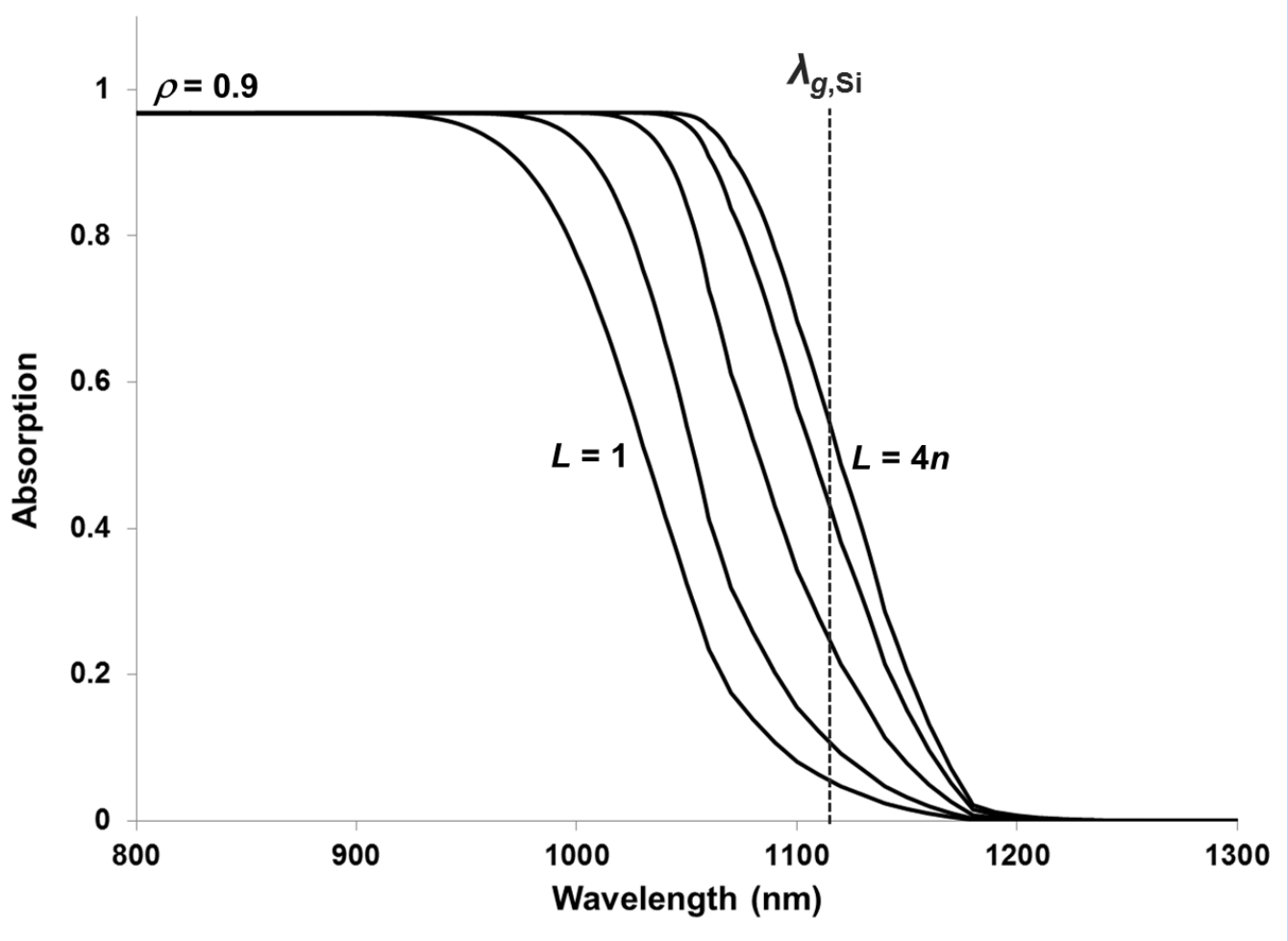
$=3.3\times10^{-18}$ $cm^2/\mu m^2$
(Kerestes *et al*., 2011)

ARC effect

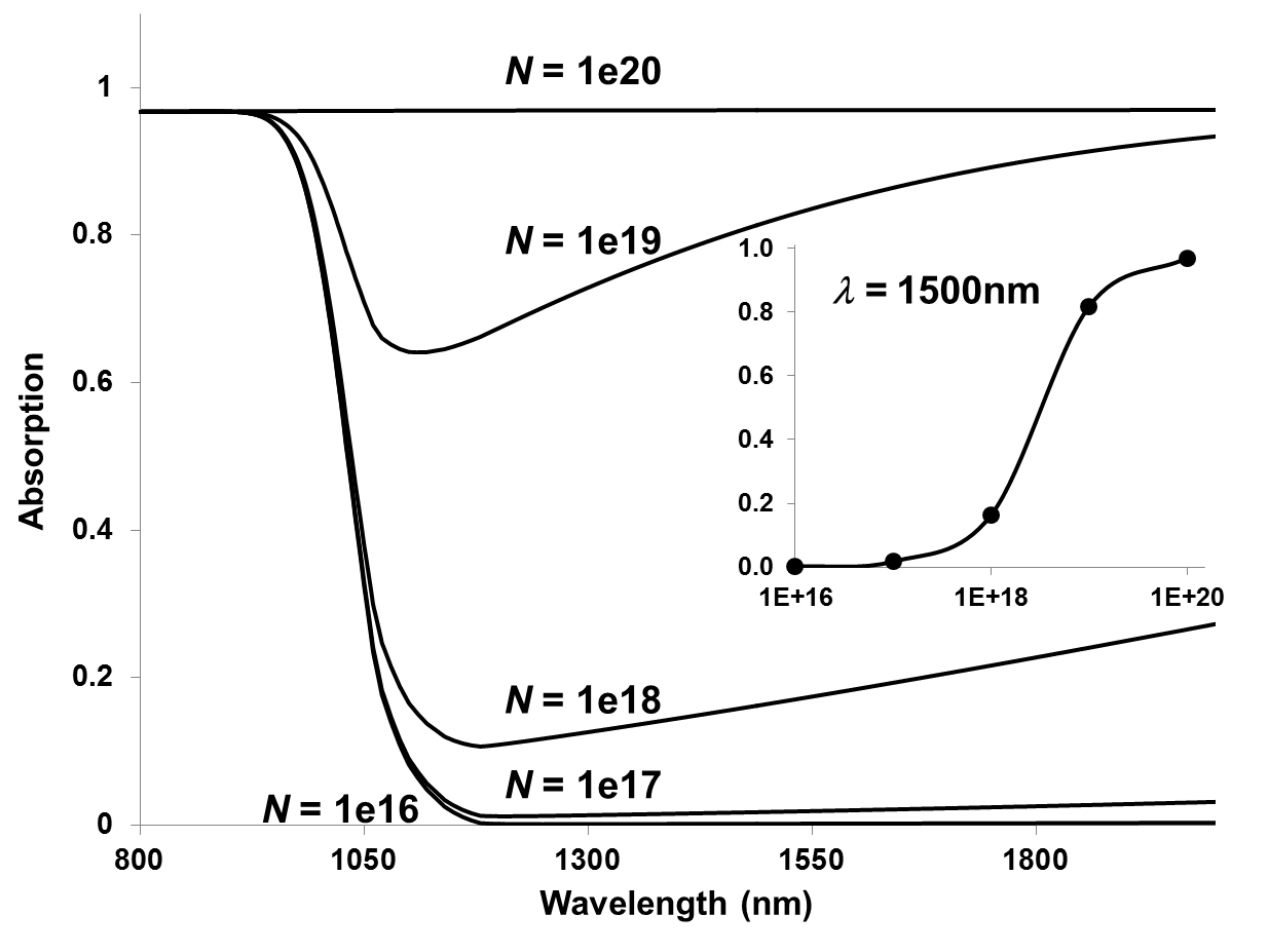
Broadband scaling of R by a factor ρ simulates ARC



Light trapping
(no FCA, ρ = 0.9, d = 250μm)

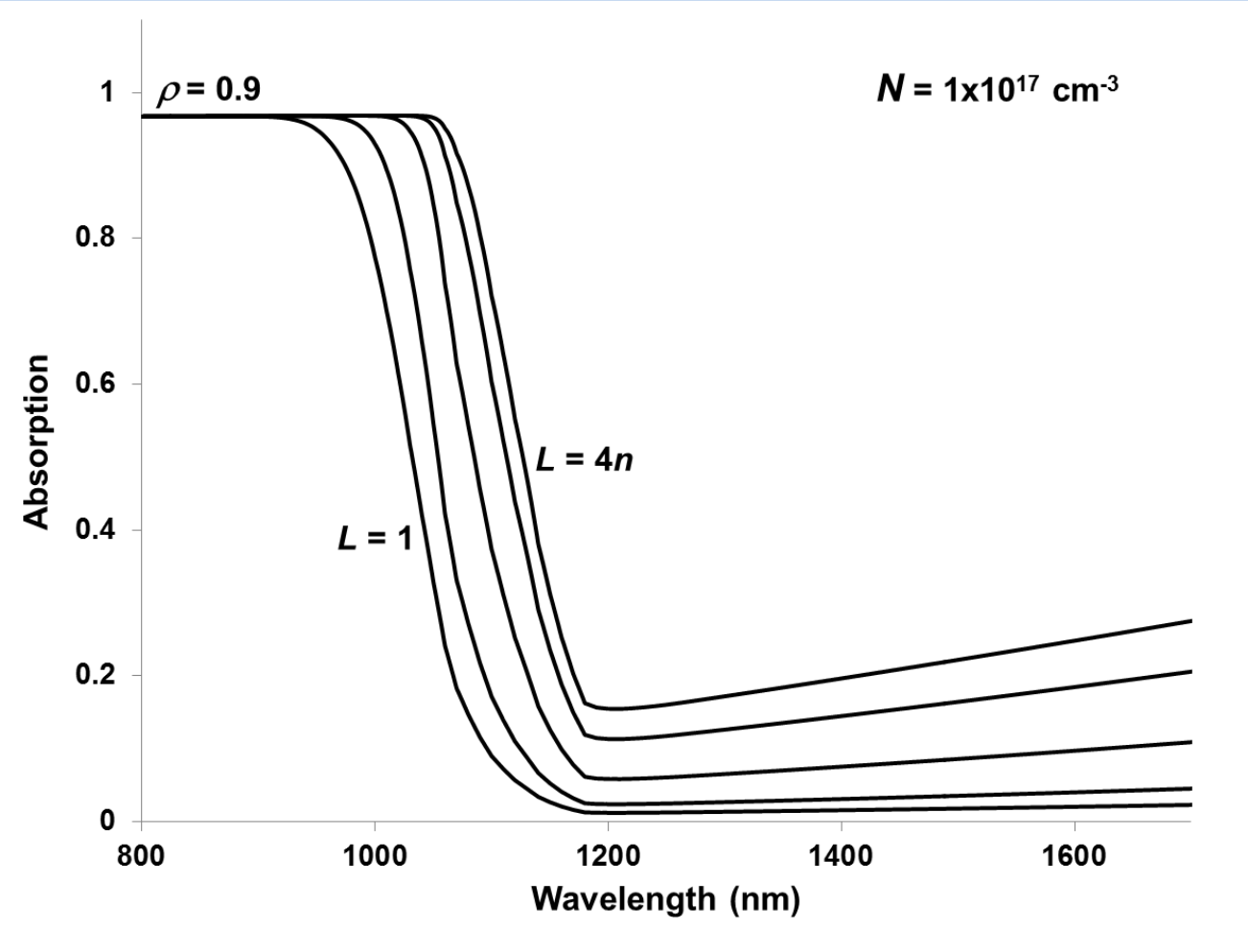


Free carrier absorption



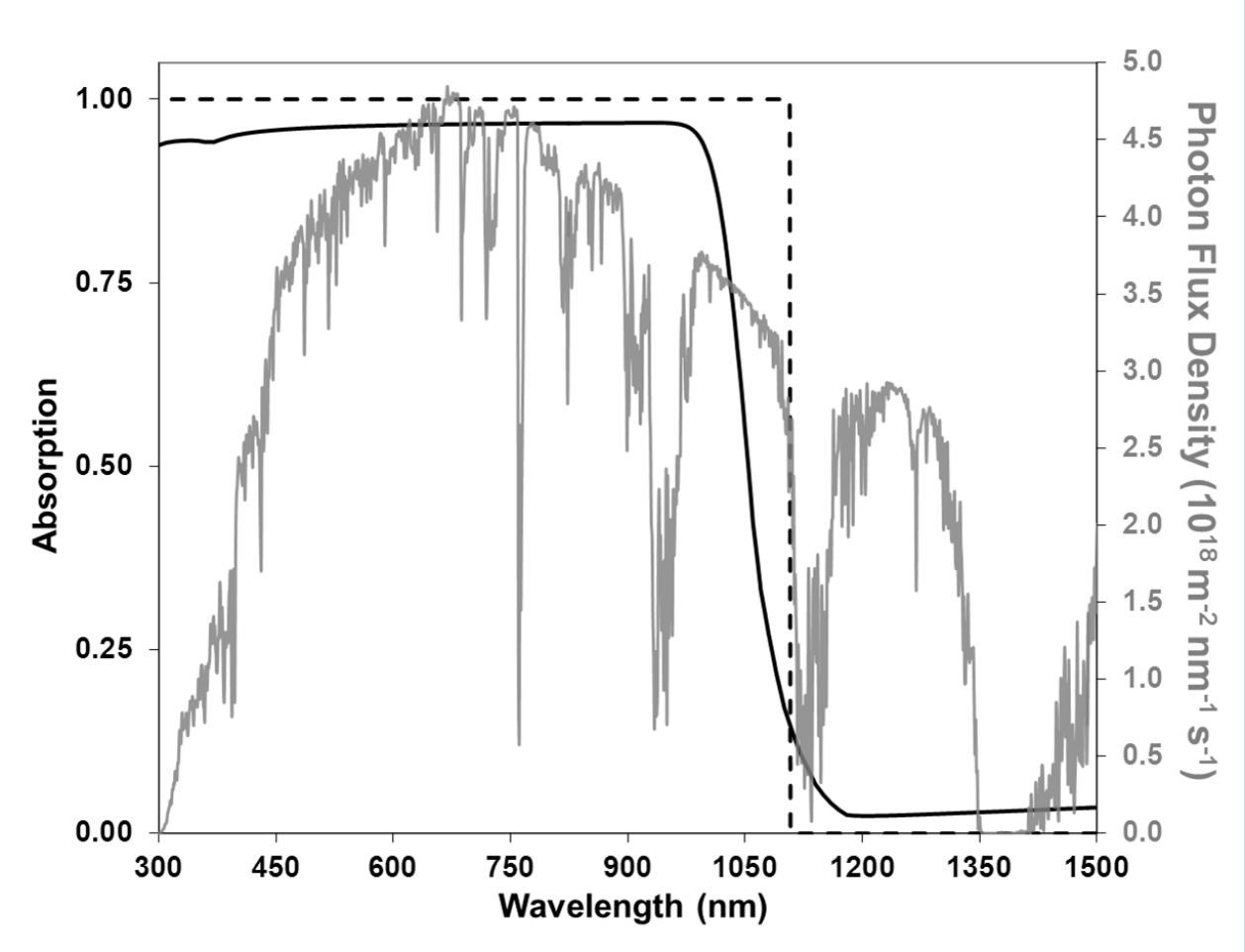
FCA will have major impact on UC-PV efficiency if base doping is high!

Light trapping/FCA interaction



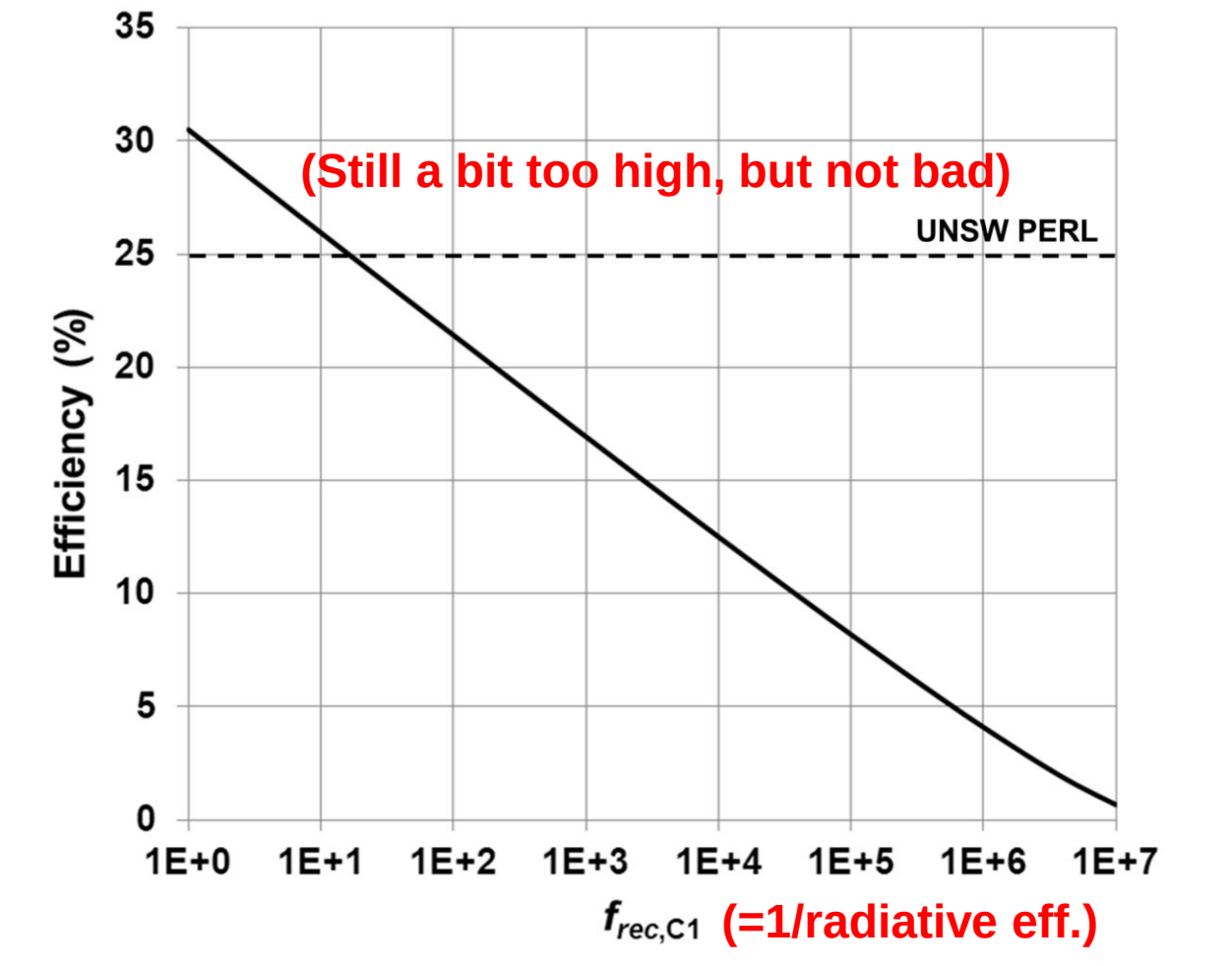
Even for moderate base doping FCA is considerable when path length is long

Absorption spectra compared



How does model stack up?

η_{SQ} of generalised realistic cell vs. radiative efficiency



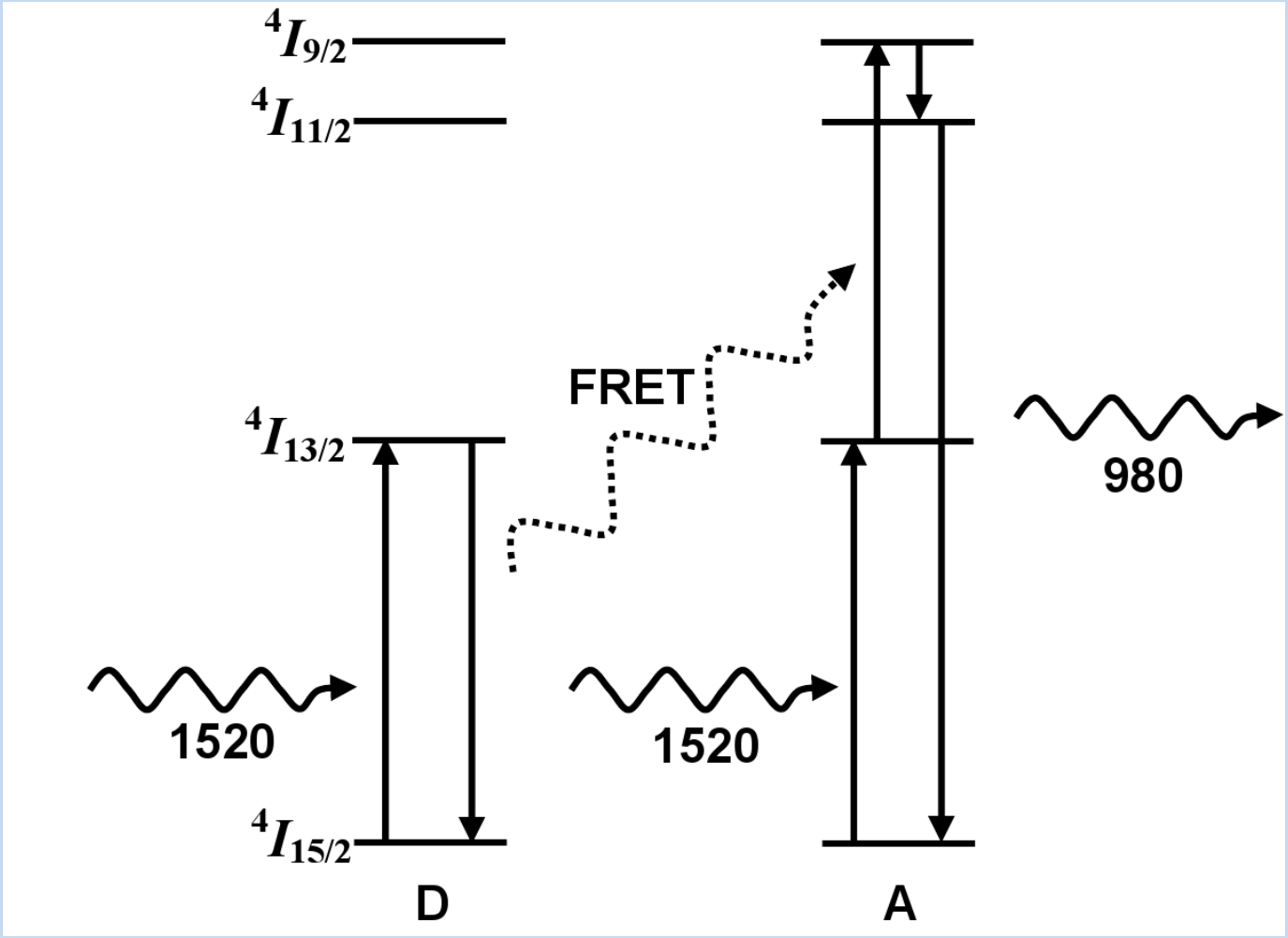
Results

Ideal Si SC, Ideal UC	
Solar cell peak efficiency	33%
UC-PV peak efficiency	40%
Relative increase	21%

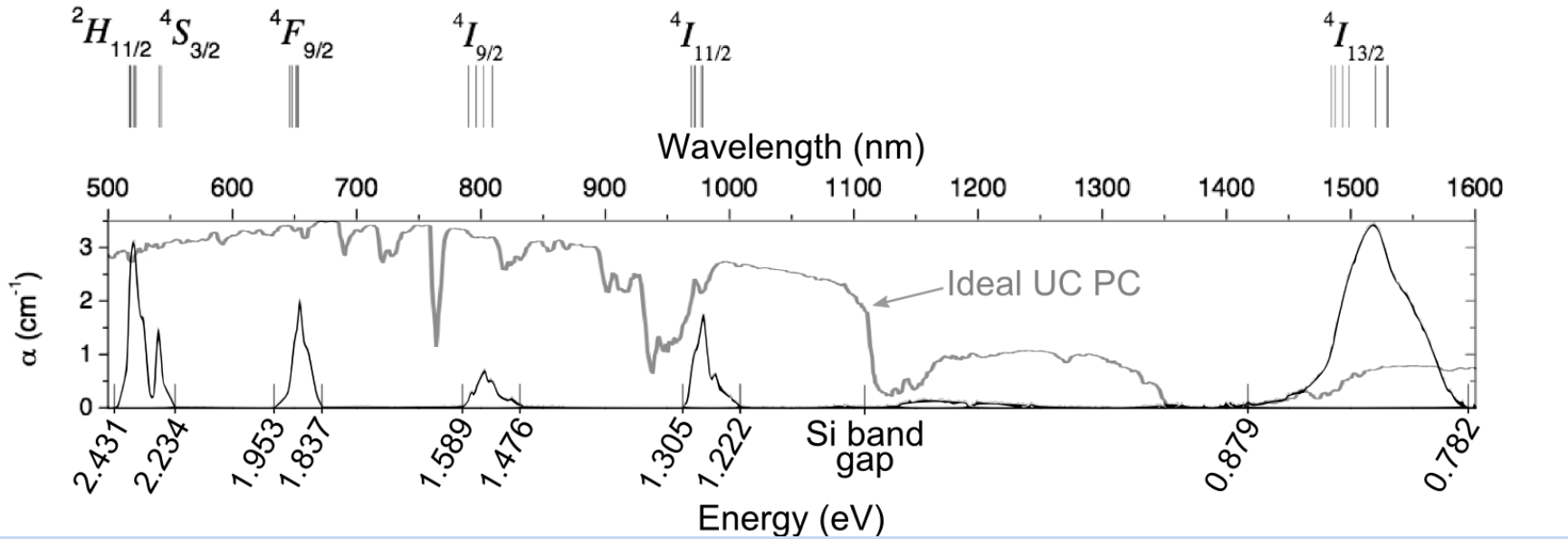
Realistic Si SC, Ideal UC SC radiative eff. = 100%	
Solar cell peak efficiency	30.5%
UC-PV peak efficiency	38.5%
Relative increase	26%

Realistic Si SC, Ideal UC SC radiative eff. = 10%	
Solar cell peak efficiency	26%
UC-PV peak efficiency	32%
Relative increase	23%

Realistic UC layers: Erbium-based UC



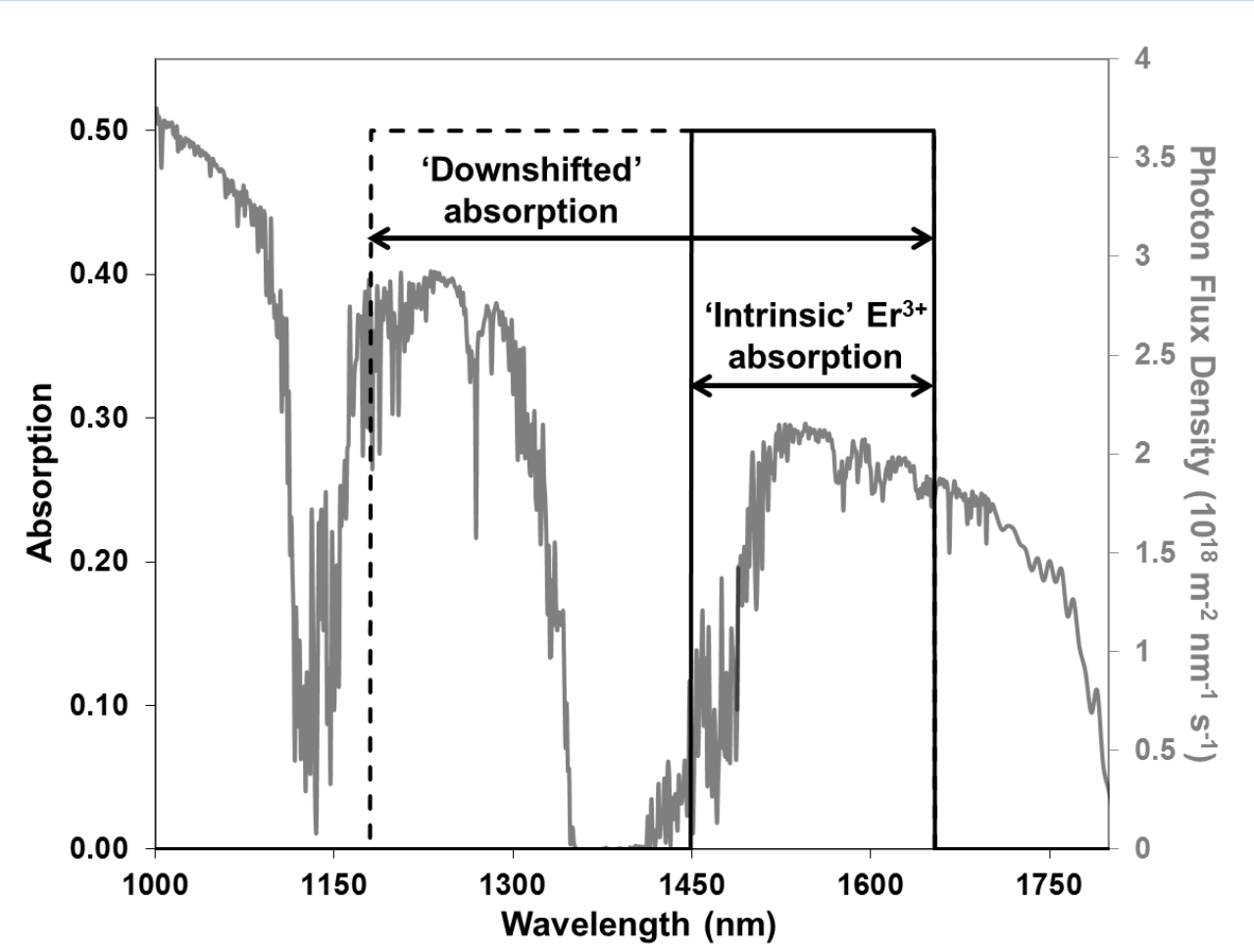
Erbium-based UC



Er-based UC is:

- not broad band
- not selective
- not complete

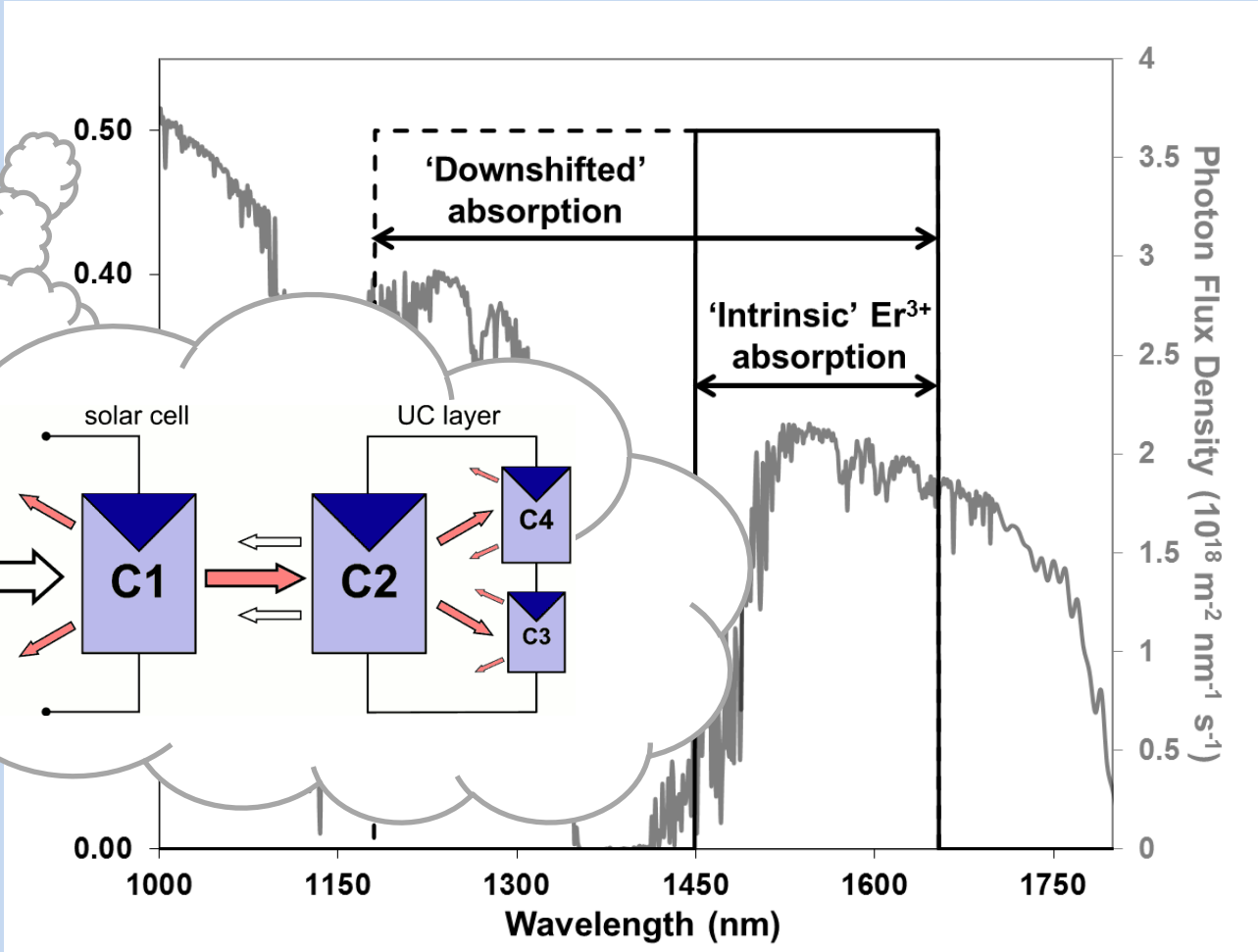
Idealised Er absorption (per ion)



For A = 0.5 per ion, all photons in Er range absorbed.

Value represents an average over these wavelengths.

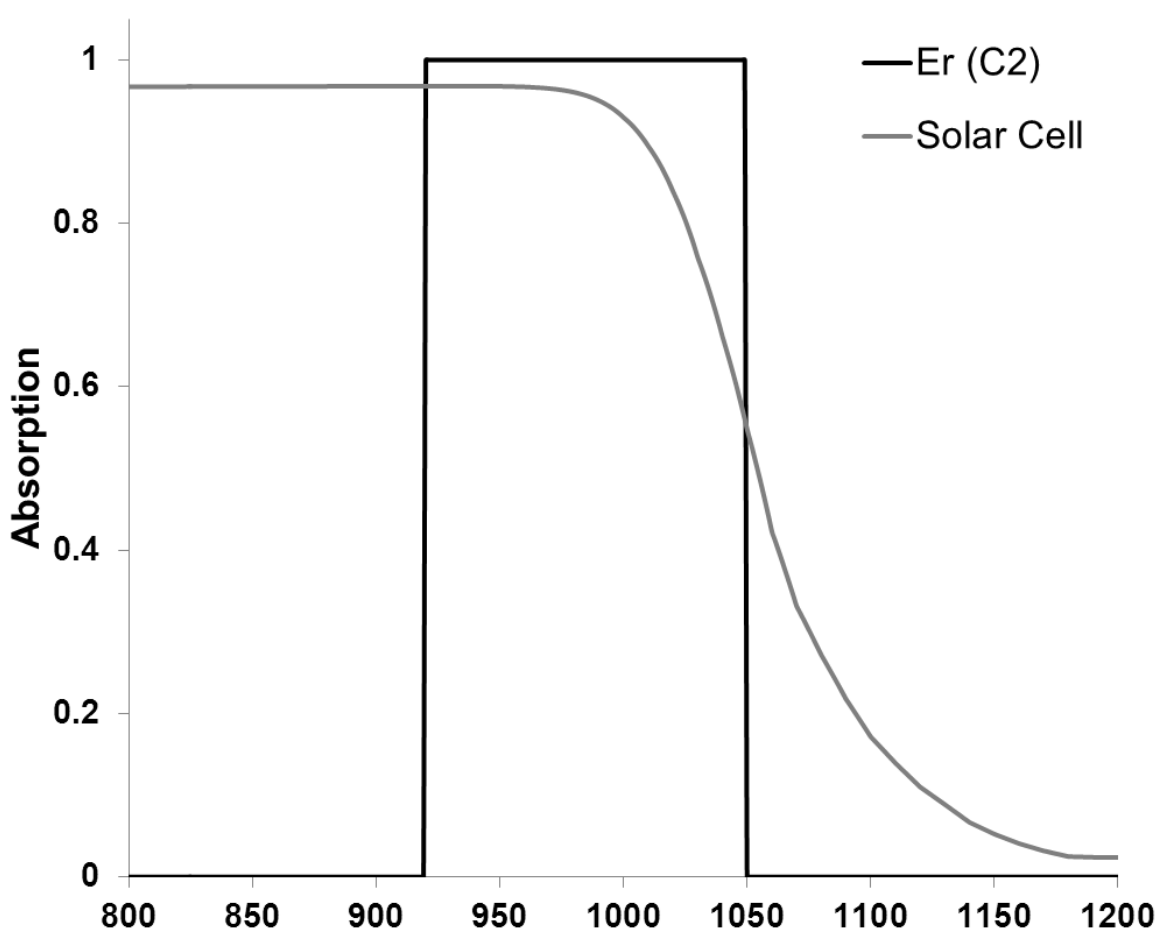
Idealised Er absorption (per ion)



For A = 0.5 per ion, all photons in Er range absorbed.

Value represents an average over these wavelengths.

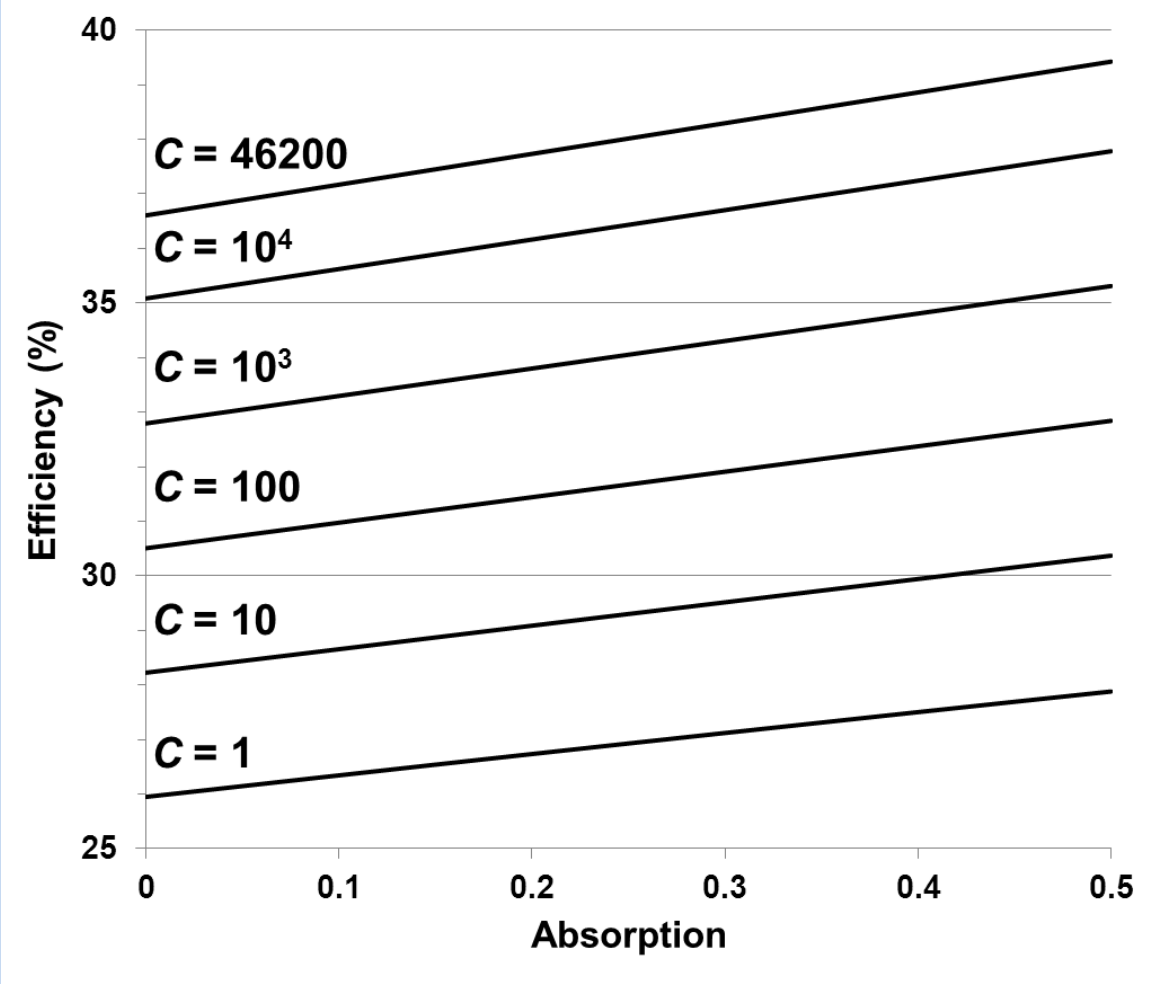
Idealised Er emission



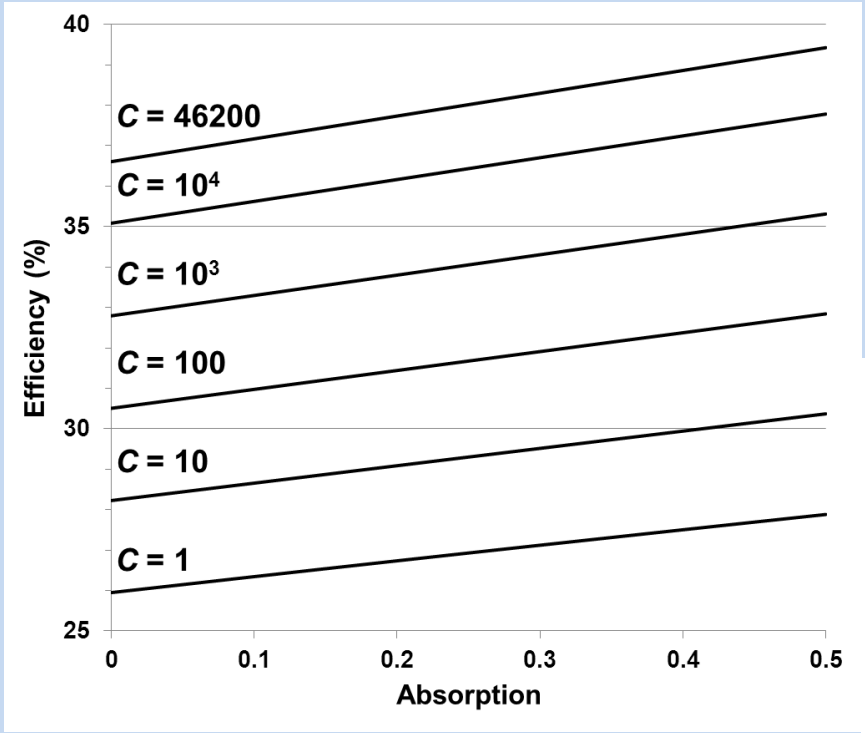
Emissivity is taken to be twice the absorptivity of each Er ion.

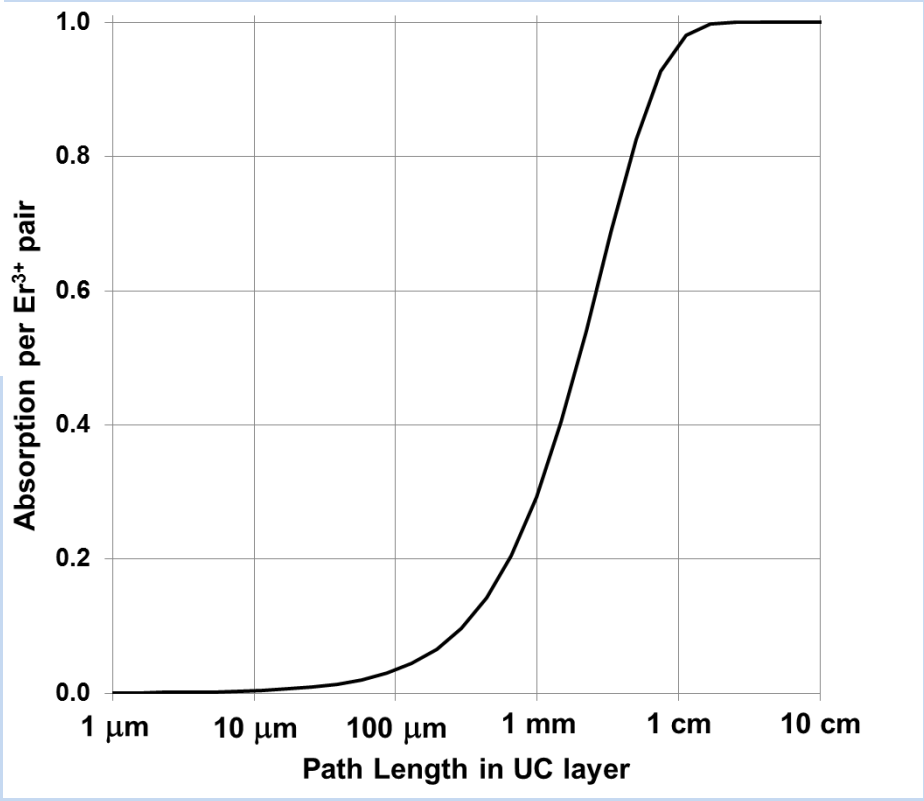
All other detailed balance constraints still enforced.

Modified result, all concentration ratios
(SC rad. eff. = 10%, UC system rad. eff. = 100%)

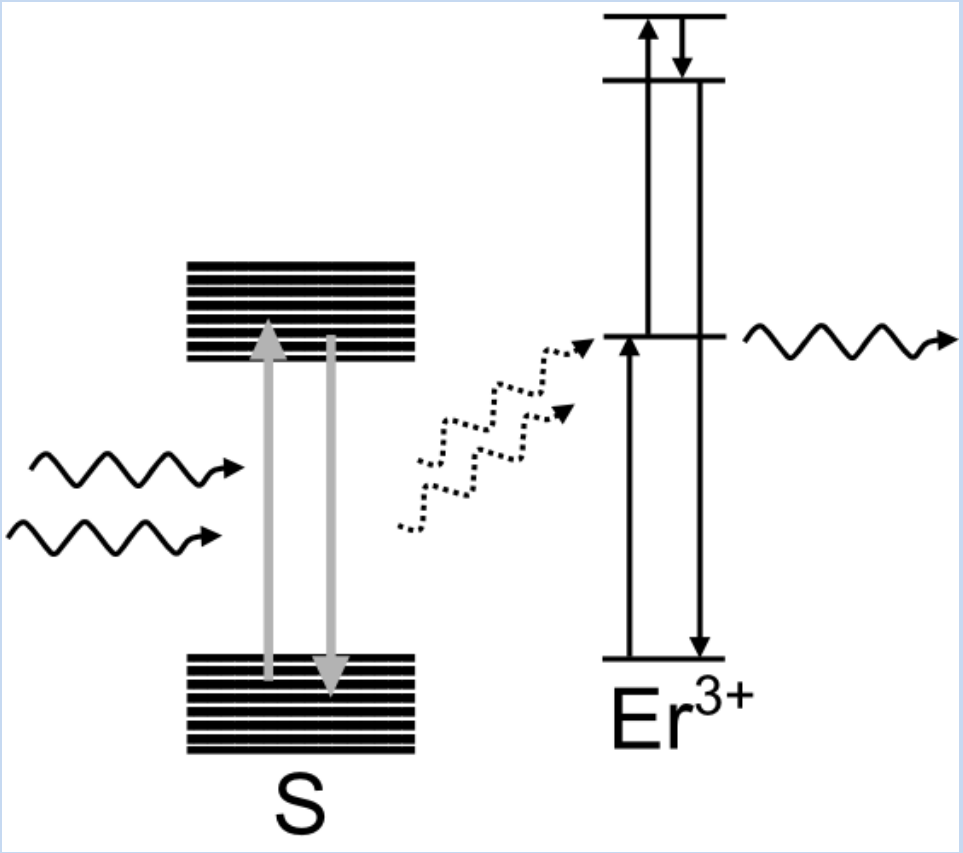


Absorption in $NaYF_4$:Er



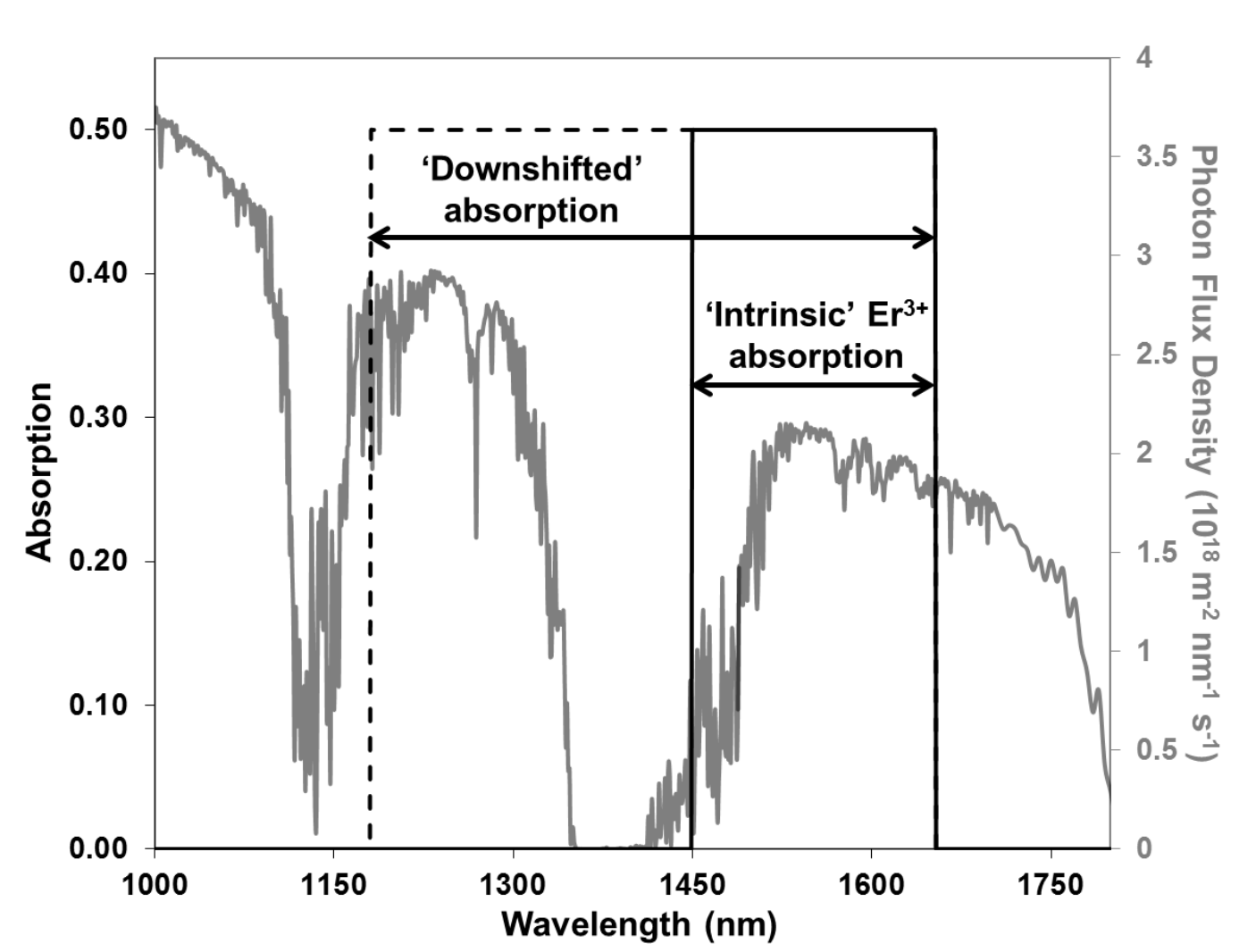


Downshifting/Sensitisation

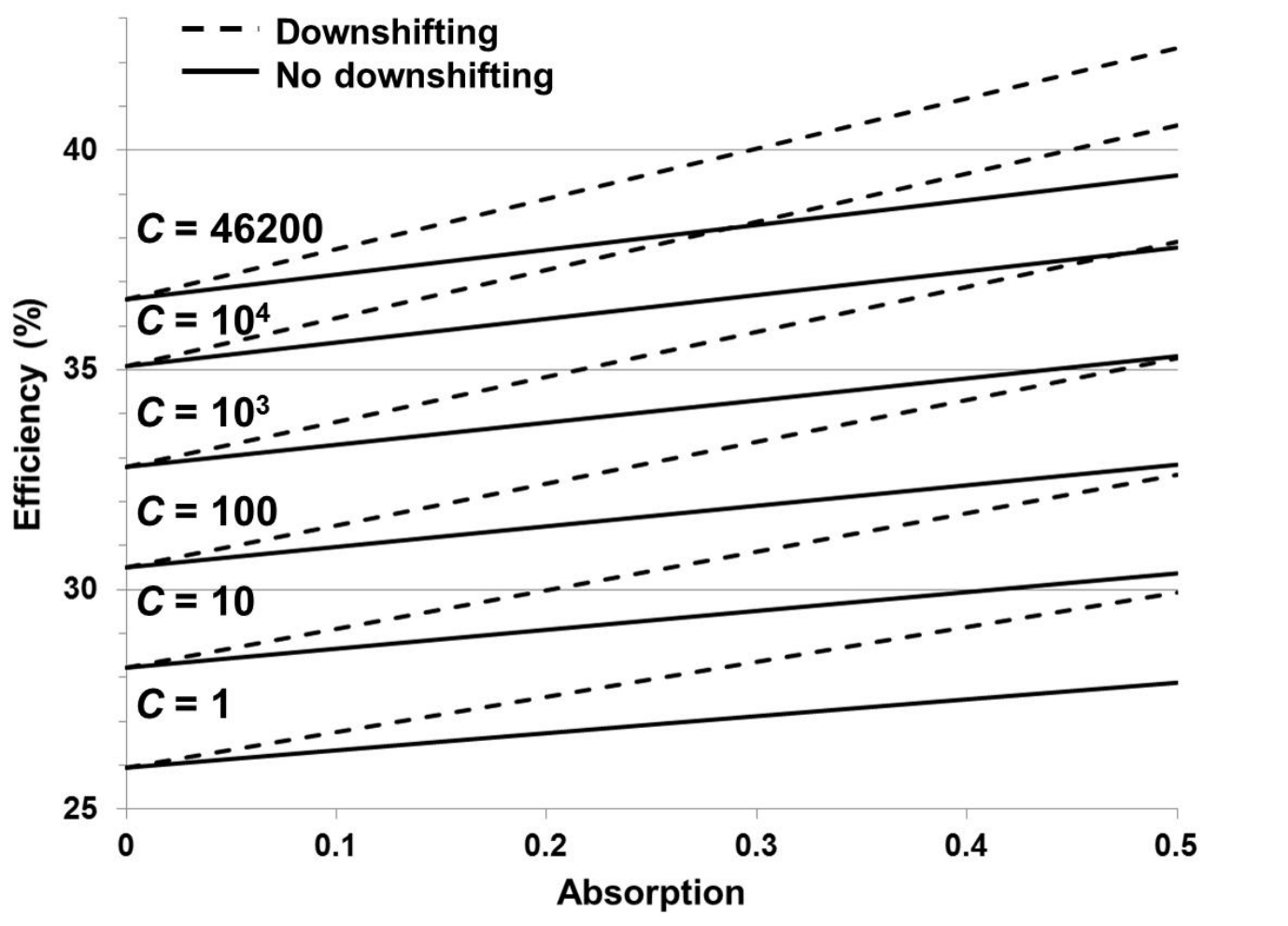


e.g., PbS QDs: see Liu *et al*., 2008.

Broadened absorption spectrum (per Er/sensitiser chromophore)



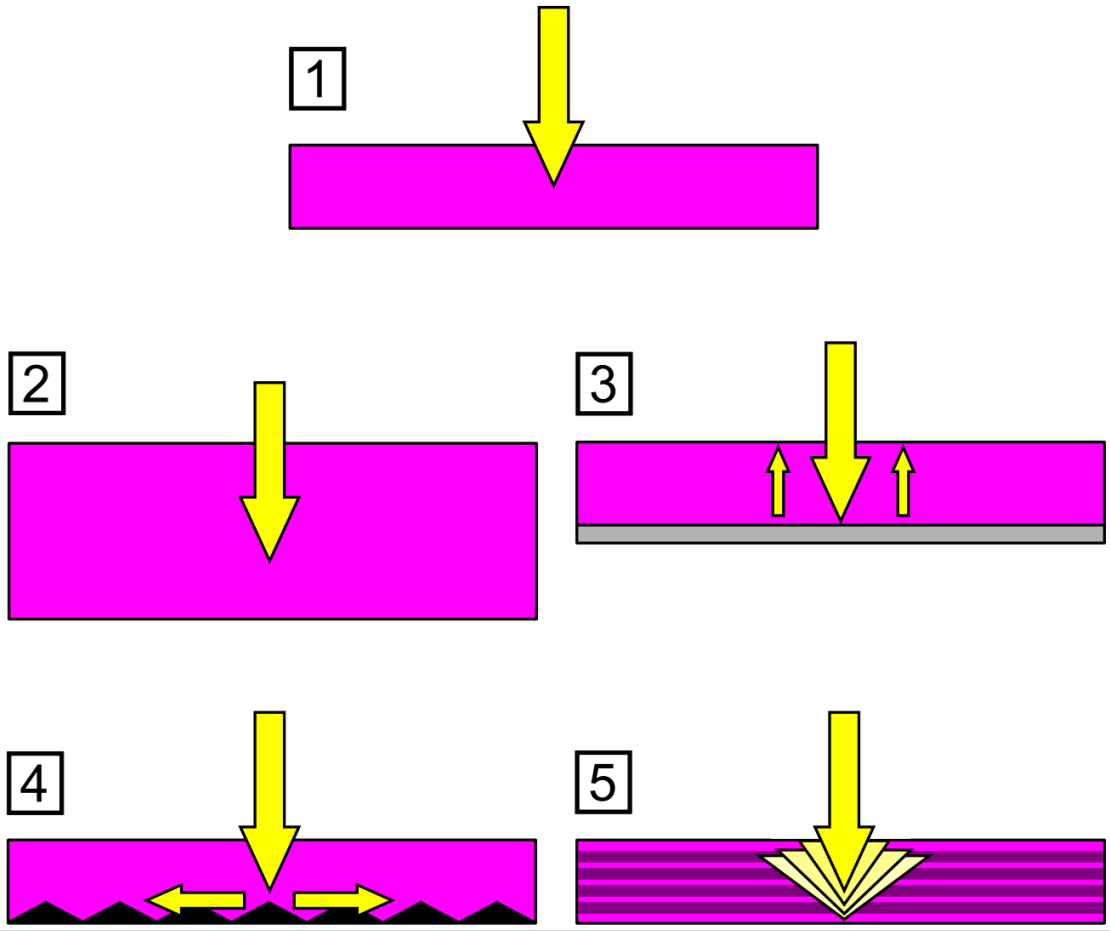
Modified result, all *C*, downshifting
(SC rad. eff. = 10%, UC system rad. eff. = 100%)



Summary

- No reports of increased c-Si SC efficiency from Er-based UC-PV: Modified detailed balance model illustrates why
- Modest one-sun limits resulting from this model:
  - ~1.5% absolute increase for 100% QE, perfectly-absorbing UC layer (no downshifting)
  - ~4% absolute increase for layer w/ perfect downshifting
- Full-concentration limits:
  - No downshifting: UC benefit same for all concentrations (for 100% EQE)
  - Downshifting: benefit improves to ~5.5% absolute (compare to ~6% for ideal c-Si UC-PV, non-ideal SC)
- Effective UC-PV design for c-Si must incorporate **absorption enhancement**, photon downshifting
- (Situation even worse for realistic radiative properties!)

Methods of absorption enhancement



Erbium-doped porous silicon (PSi:Er^{3+})

Experimental basis for UC measurements

Formed from c-Si by anodic etching in HF

Porous but stable c-Si skeleton with large internal surface area

Pore diameter ~ 100nm

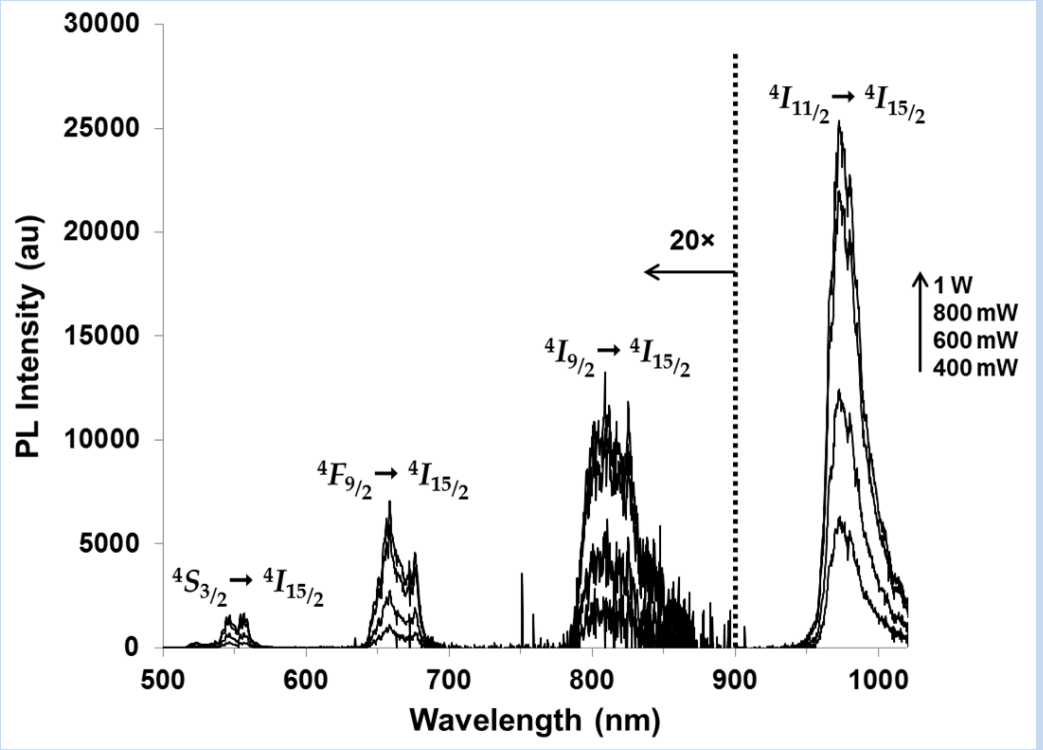
PSi offers:

- tunable refractive index (inv. prop. to porosity)
- formation of high-quality, uniform, thick layers
- fabrication of stacked multilayer films
- host for electromigration of dopant species
- speedy, simple prototyping (room temp., no vacuum)

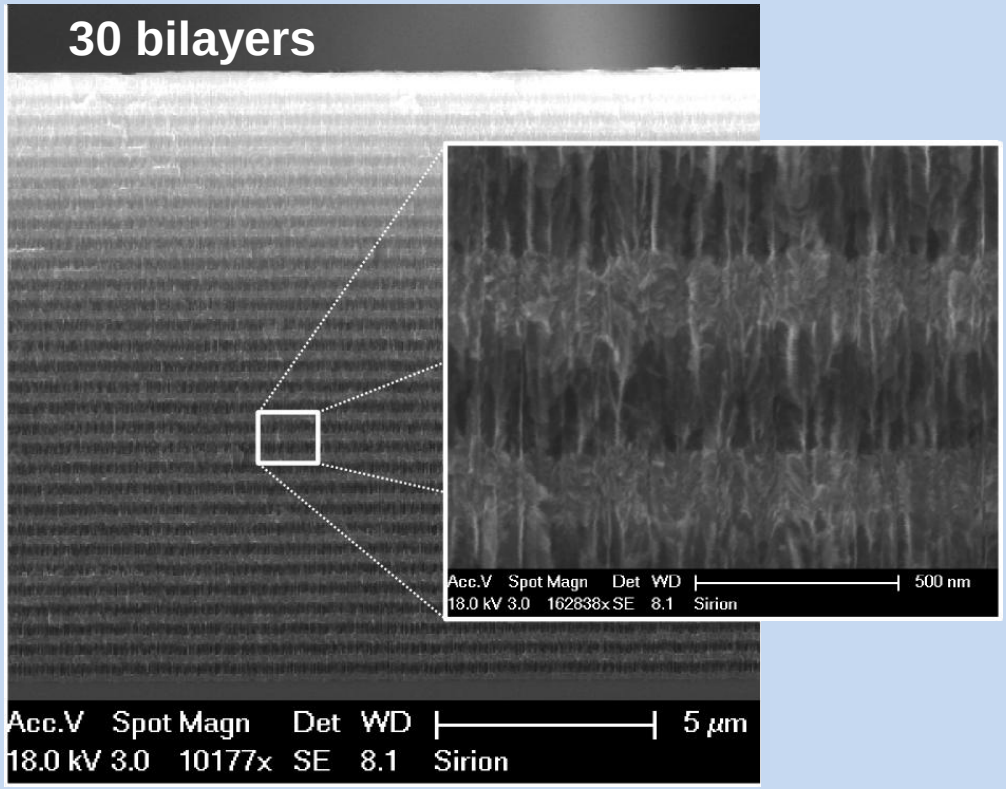
PSi:Er UC-PL results

- Electroplating from saturated $ErCl_3$/ethanol solution into single thick PSi layer (43% porous, 5.5µm thick)
- Annealed 30 min at 900°C in O_2:N_2, 20 min at 1100°C in N_2
- Distinctive Er UC emission spectrum for 1550-nm excitation
- RBS shows high Er concentration in similar films (not all active)

While not very efficient, a basis for investigating photonic UC enhancement

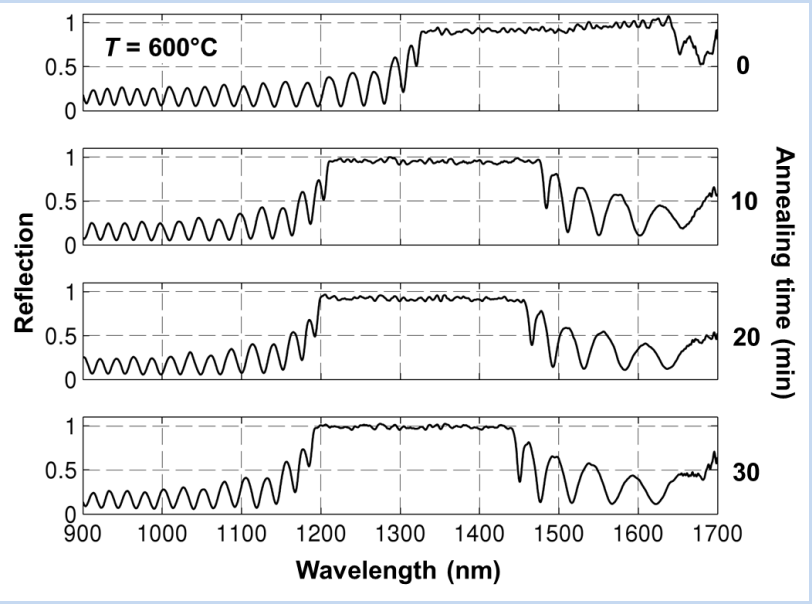


PSi Distributed Bragg Reflector



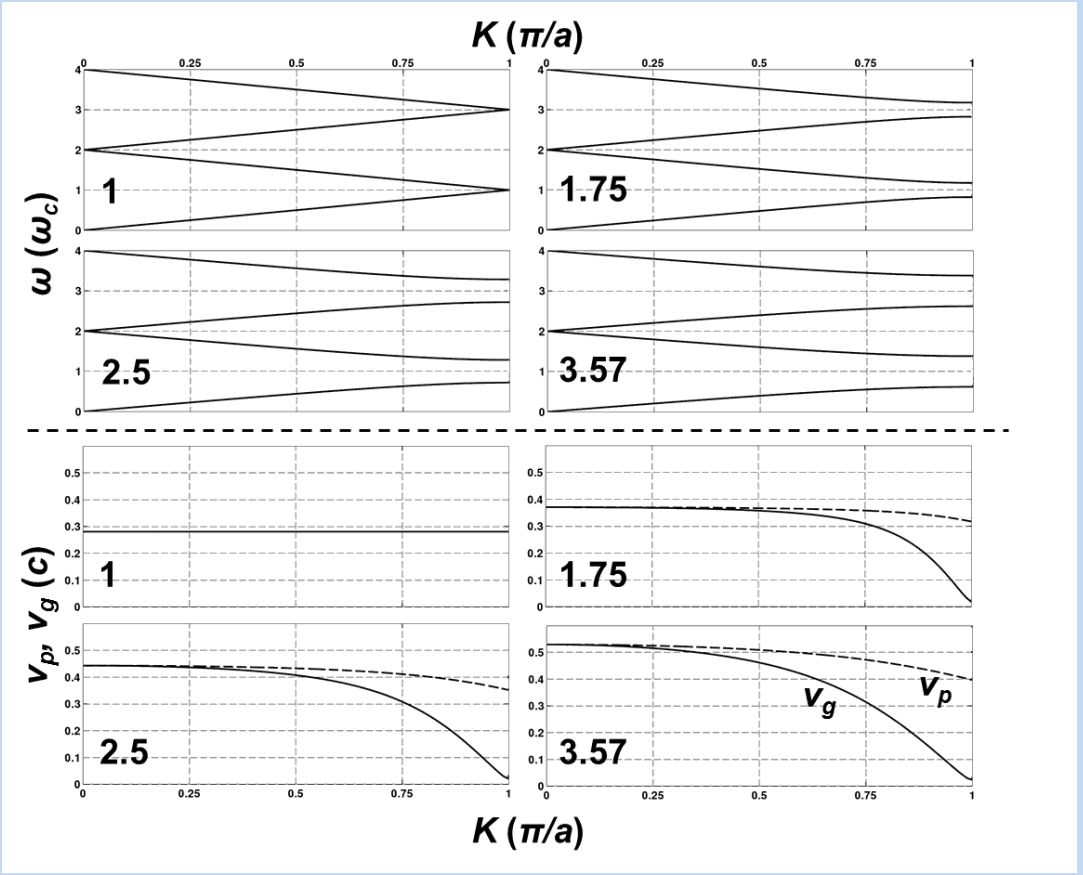
- High-quality optical structures (dielectric mirrors, microcavities etc.) may be fabricated by temporal modulation of etching current
- Periodic porosity
  → periodic refractive index

- Optical properties also tunable by post-fab treatment, e.g., oxidation.
- Design of structures relies on suitable effective medium approximations.



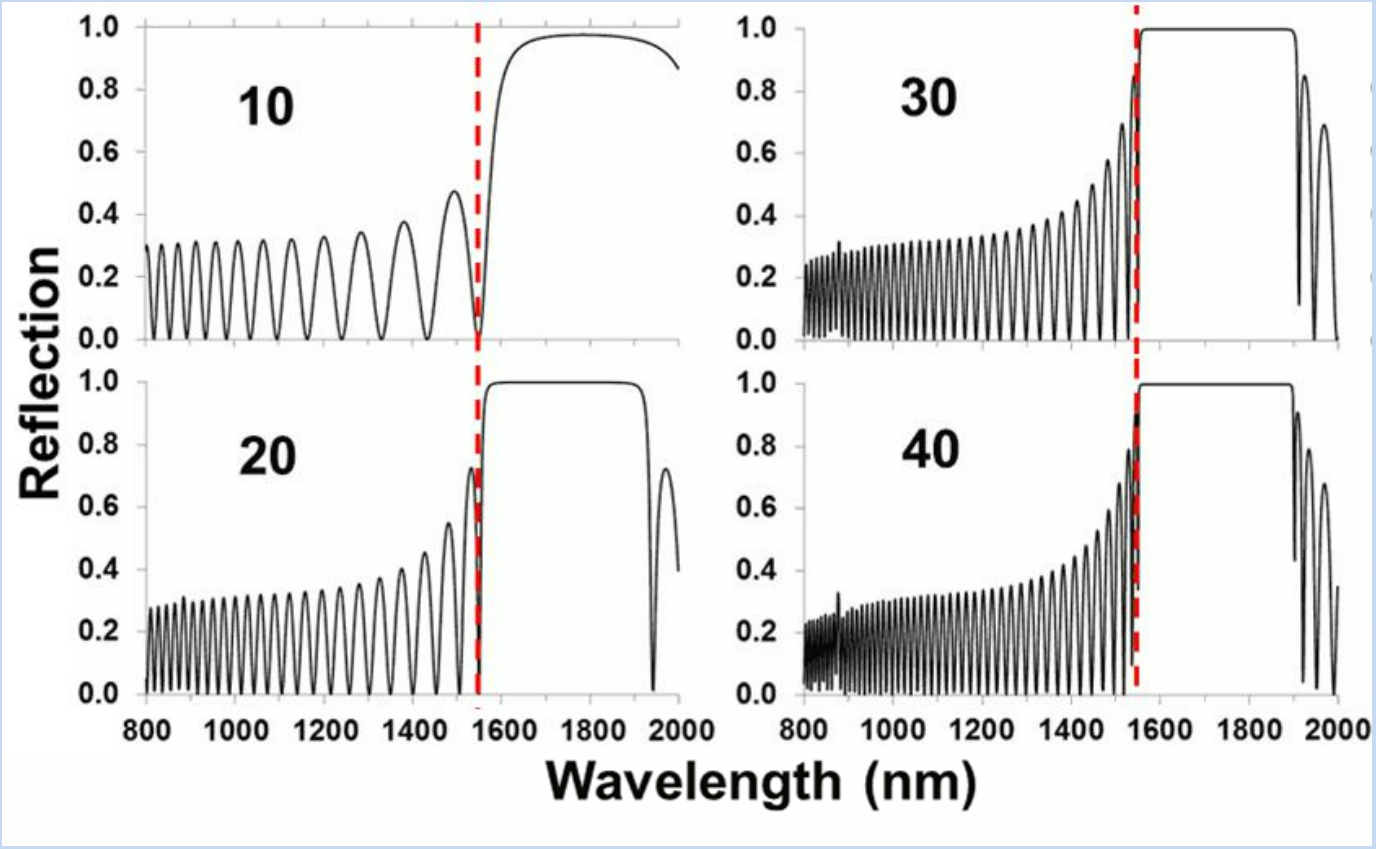
Band structure of dielectric multilayers (infinite DBRs)

- Bragg reflector is a 1D photonic crystal—has a ‘band structure’
- Refractive index contrast gives rise to photonic band gap
- Near edge of BZ, group velocity $v_g = d\omega/dk$ approaches zero



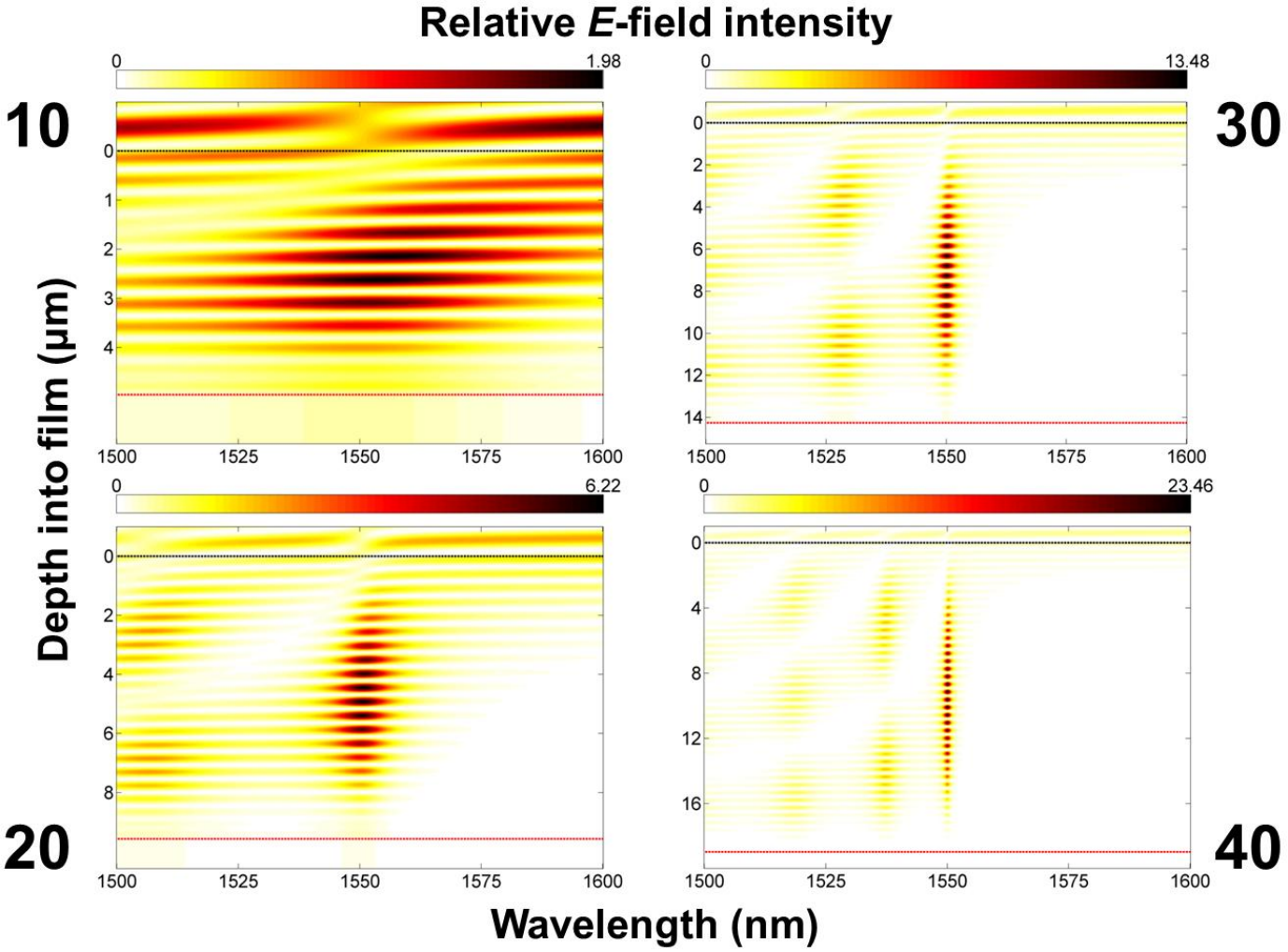
Finite DBRs

- Reflectivity spectra simulated for PSi DBRs with 0.5/0.7, band edge at 1550 nm: strong Er absorption line
- Transfer matrix electromagnetic calculation (Yeh 1988)



Field enhancement

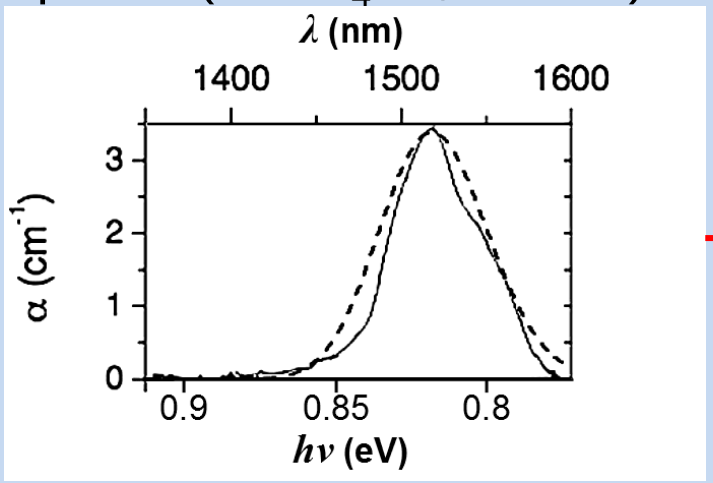
What happens to electric field near band edge, i.e., for low v_g?



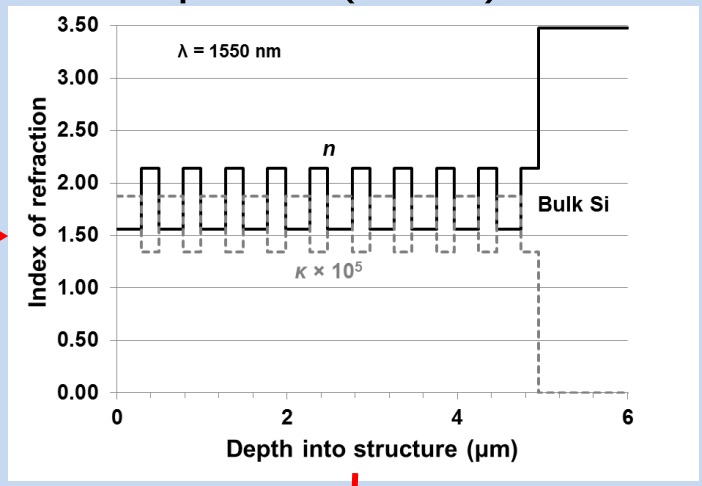
'Squeezing' of the mode results in intense standing wave!

Modelling Er in DBR slow modes

Gaussian fit to empirical Er α profile ($NaYF_4$:Er, Shalav)

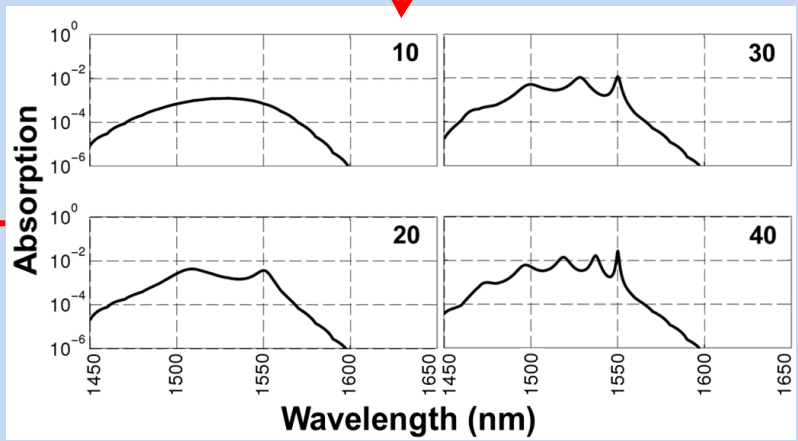


Modified refractive index profile (N=10)



$$\alpha_{eff} = \frac{\ln(1 - A')}{D}$$

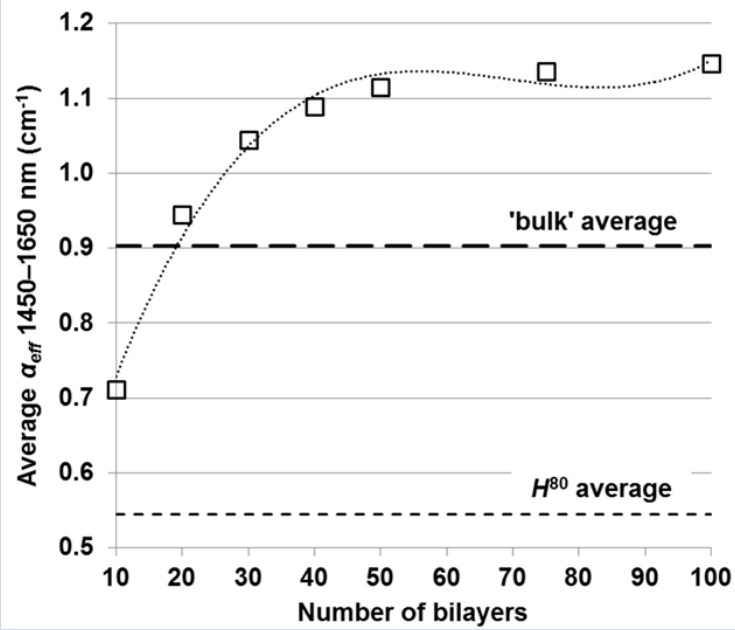
'Effective absorption coefficient'



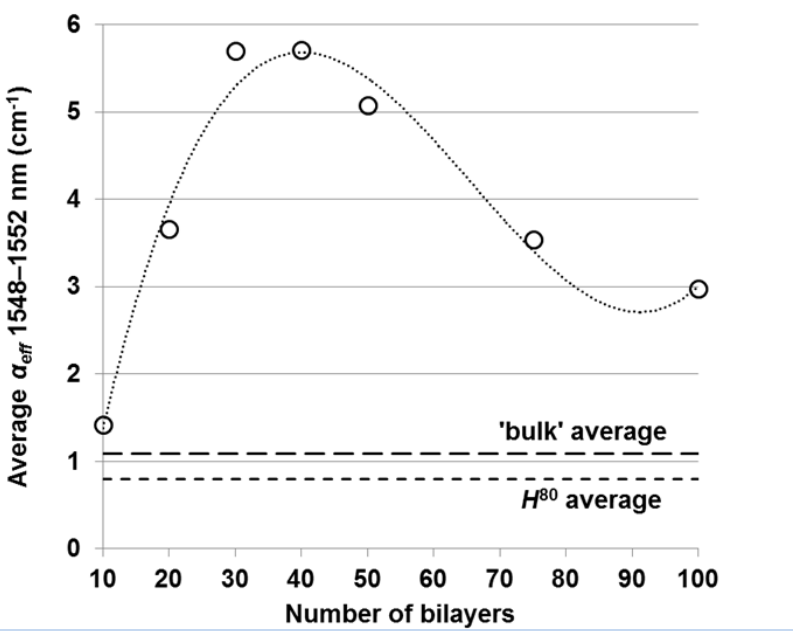
Absorption spectrum

Effective absorption coefficient

Broad band average



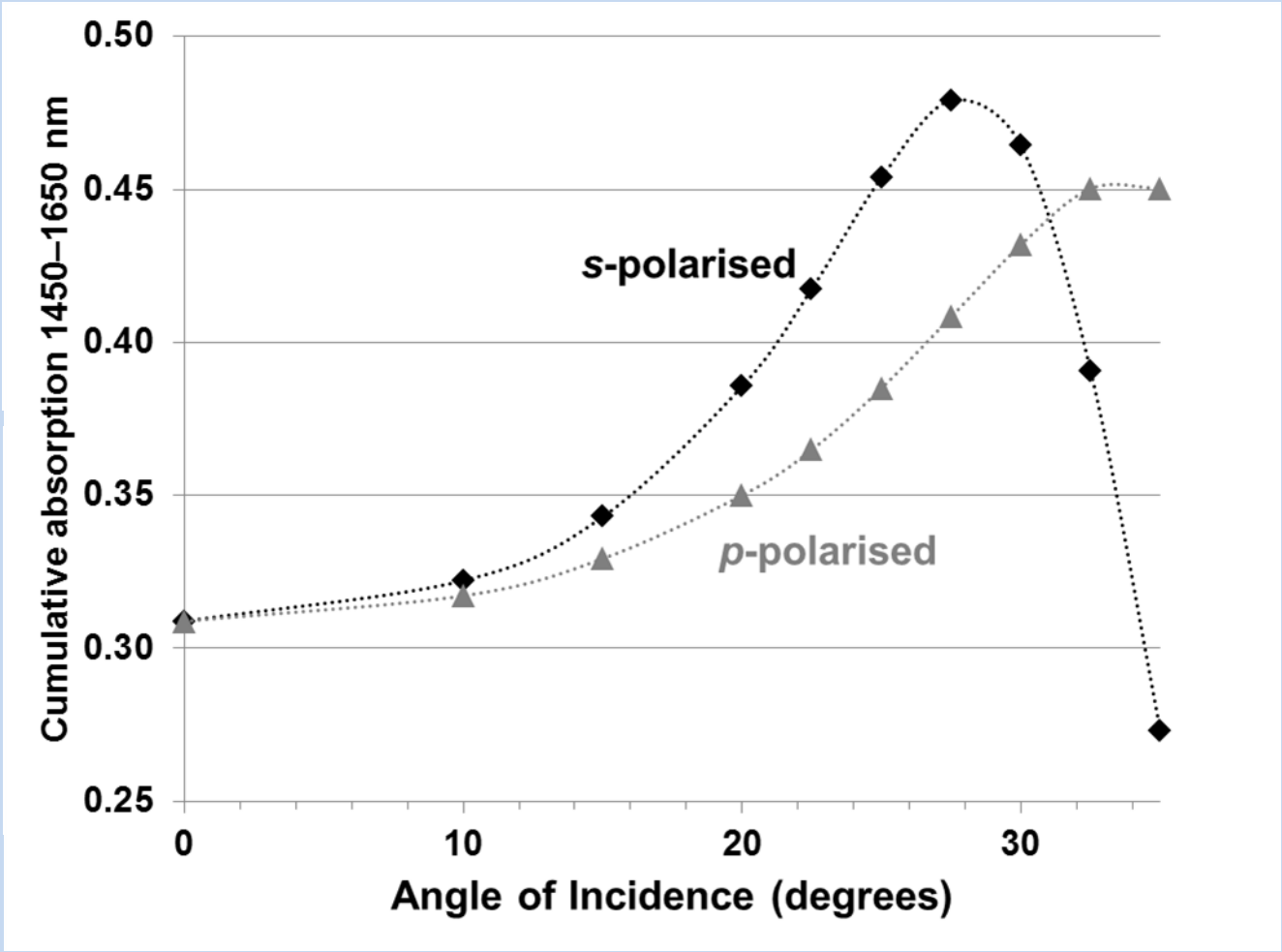
Narrow band average



Effect of band edge position

How do optical properties vary as incident angle changes?

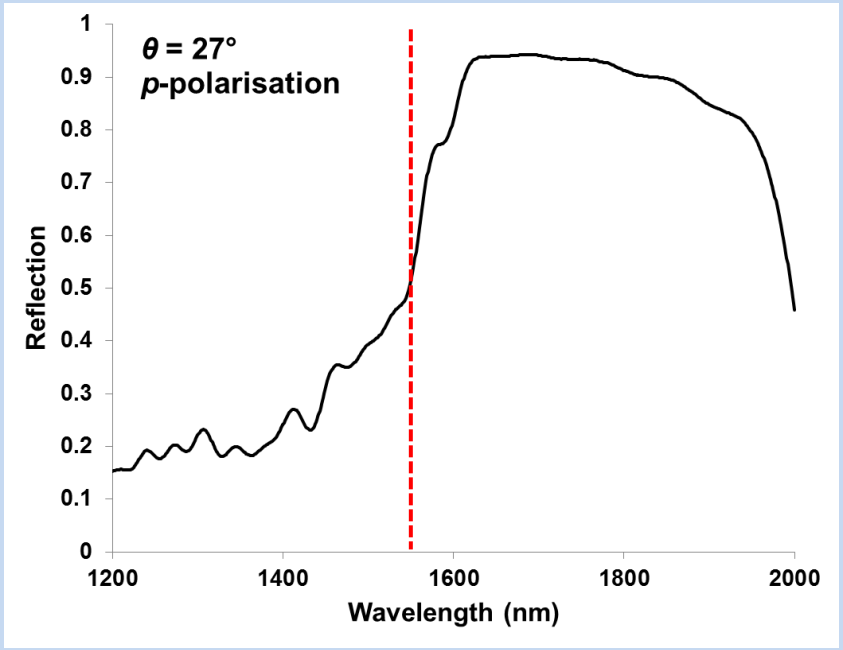
- Blue shift in interference features/band edge position
- Broad region of enhanced absorption
- Polarisation splitting
- Tradeoff between slow-light enhancement and suppression in band gap



Fabrication of PSi:Er DBR

What is the effect of pumping Er near band edge of real structure?

- Trial-and-error fabrication to position band edge near 1550nm (laser wavelength, Er absorption line)
- Major challenge: oxidation, annealing required to activate Er, suppress refractive index
- These steps severely degrade structure!



'DBR42N':

- Etched from 1.5–2-mΩ-cm *p*-type (B-doped) <100> Si wafer
- Room temperature, 25% HF
- Etching currents 5.6mA and 99.75mA → 50%- and 70%-porous layers
- Layer etching times 58.878s and 9.4s
- 30 bilayers

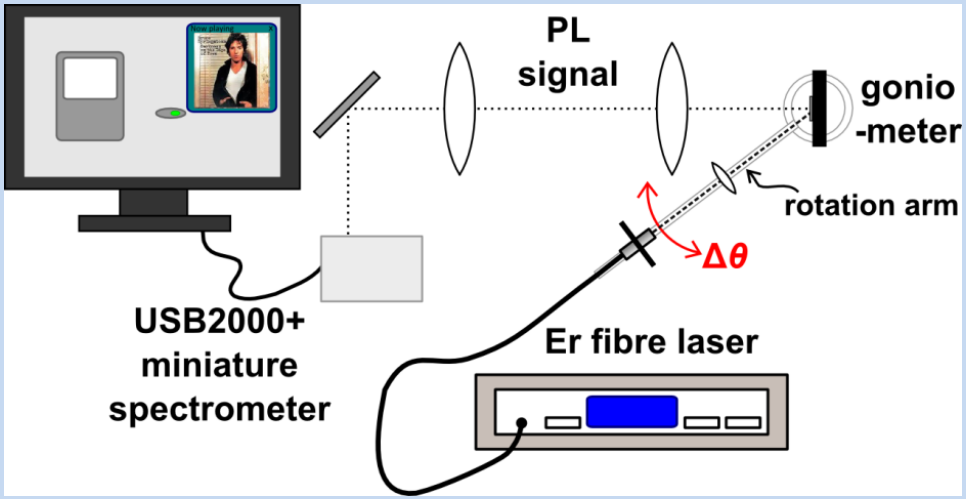
Angular-dependent UC-PL

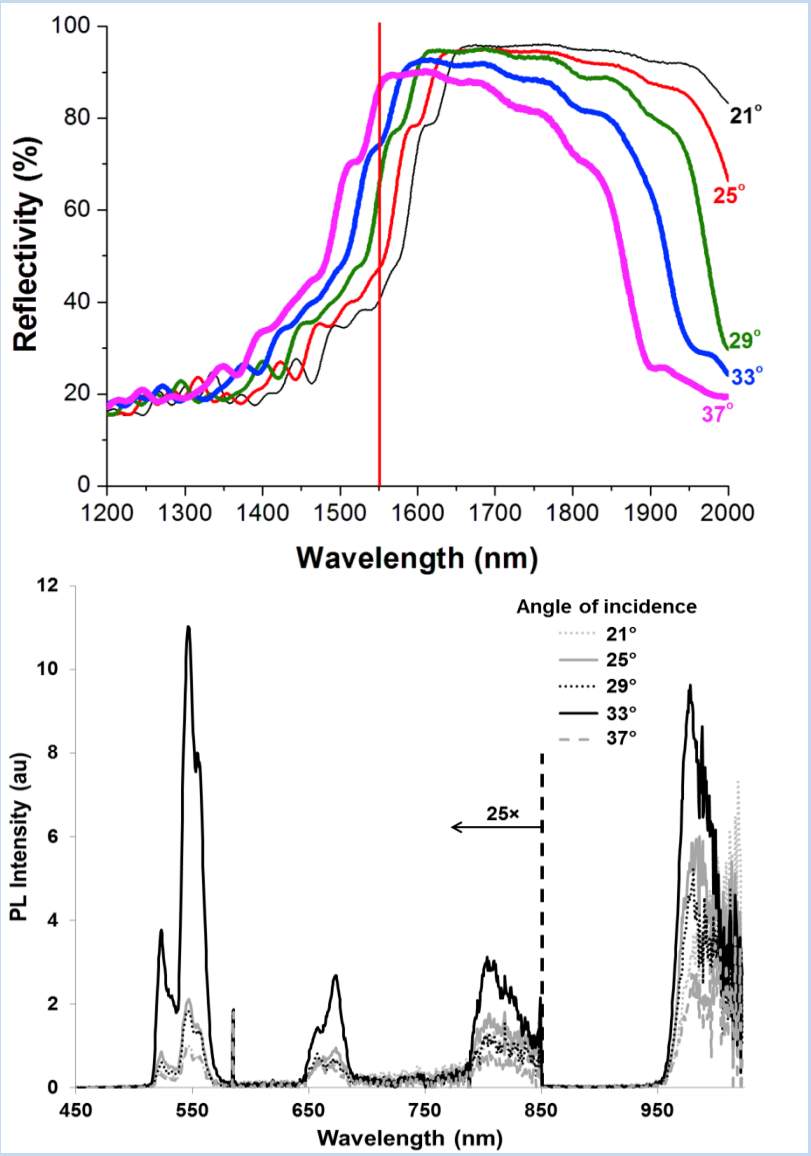
Vary angle of excitation

→ vary effective band edge position

→ variation in UC-PL intensity?

→ agrees w/ expected absorption variation?

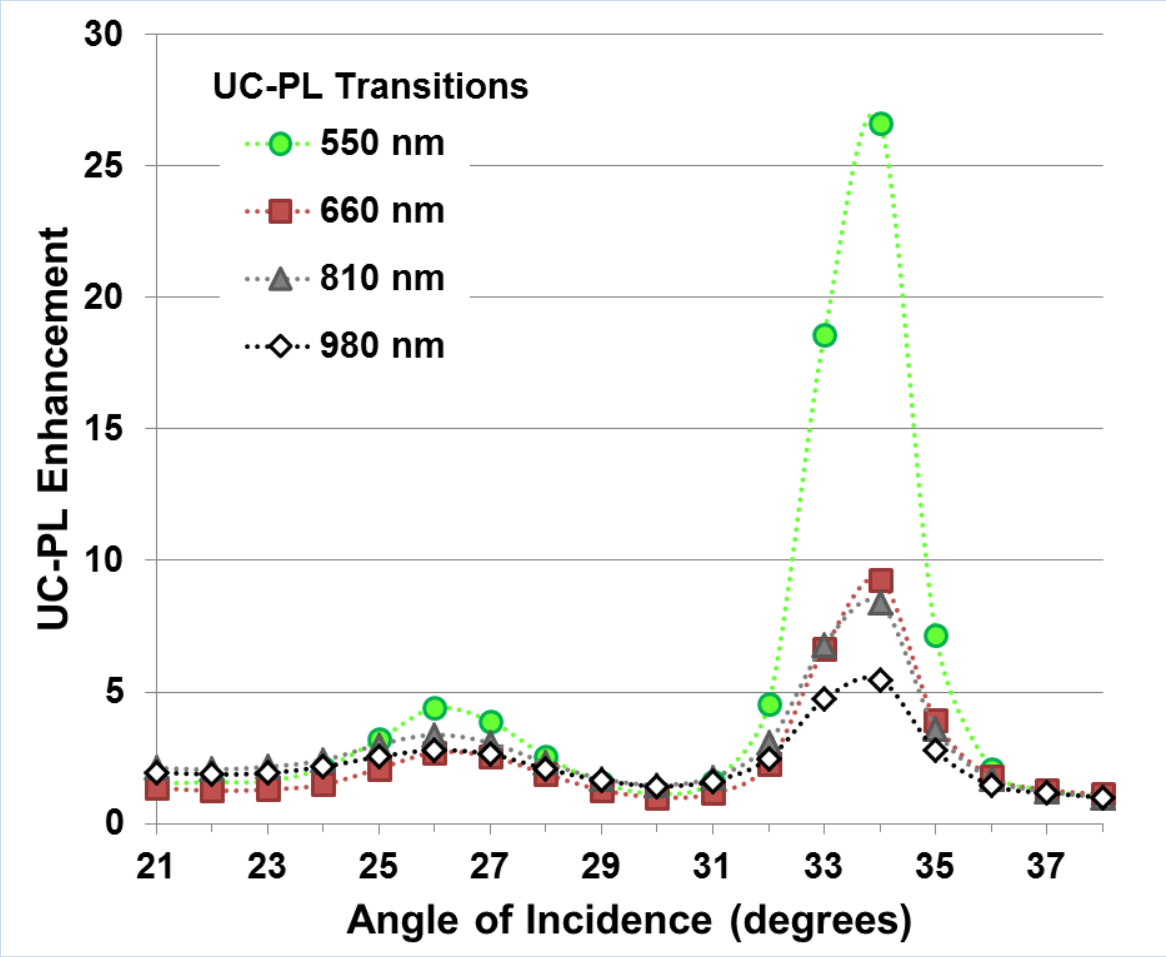




- UC-PL at same angles shown above
- λ_{ex} = 1550nm, P = 200mW
- Single spot, av. of 5×2.5-s acquisitions
- Note relative intensity of 980-nm peak
- Peak also cut off

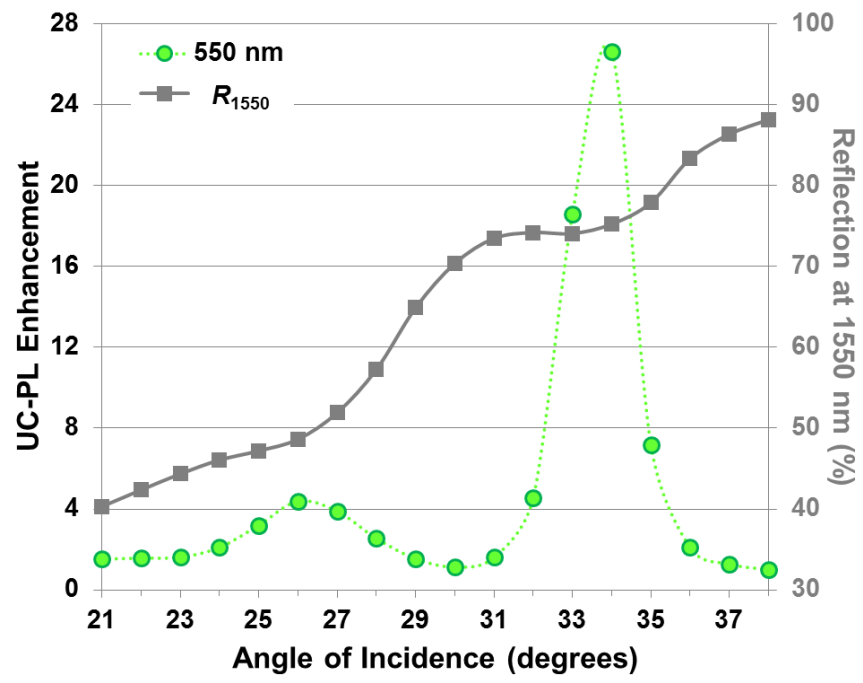
Normalised UC-PL variation

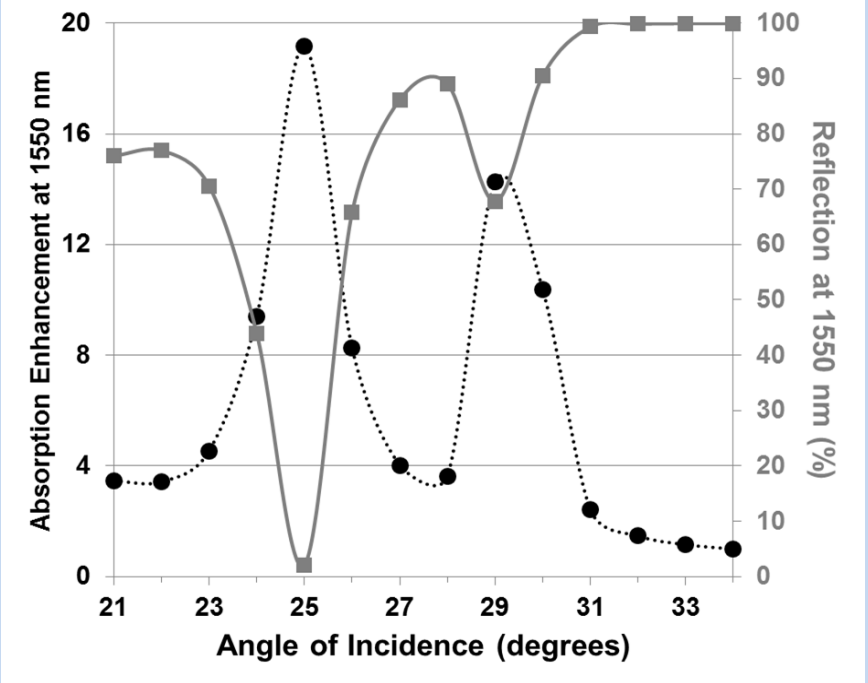
- Average of 5 spots 0.5mm apart
- PL trend tracked per PL peak
- Each trend normalised to weakest PL = 1 (38°)



Correspondence with model?

Consider strong 550-nm peak:





- Model shows absorption peaks for reflectivity troughs (makes sense)
- BUT absorption clearly not only dependent on *R*
- Experimental results show similar trend but *R* ‘smeared out’
- Laser samples sub-mm point while reflectivity samples large area

Conclusions I

- Detailed balance analysis not the best means for predicting exact operational characteristics of real devices…
- …but placing simple non-ideal constraints on DB model allows straightforward comparison to ideal case.
- Extended classic ‘Trupkean’ UC DB analysis to new AM1.5G spectrum, generalised non-ideal c-Si solar cell (ARC, LT, FCA)
- Ideal UC: relatively bigger bang for buck for ‘realistic’ c-Si (26%/23% vs. 21%)

But ‘realistic’ c-Si must have poor LT properties… false economy?

Conclusions II

- Idealised UC in DB model vastly different to real UC material
- Er-based UC phosphors: narrow-band, poor absorbers
- These properties can be approximately incorporated into DB model
- Limiting efficiency of realistic c-Si cell only boosted by ~1.5% by *perfectly absorbing, perfect QE* Er-like UC material (regardless of *C*)
- Improves to 4% (*C*=1) or 5.5% (*C*=46200) with downshifting
- No wonder there are no reports of c-Si UC-PV enhancement!
- Want impressive results? Use bad thin-film SCs!

Conclusions III

- Substantial absorption enhancement achievable in principle in 1D photonic crystals
- Band-edge modes where $v_g \rightarrow 0$ produce high internal field intensity (tens of times)
- Average effective Er absorption coefficient may be increased over bulk value
- Attempts to fabricate real structures: non-monotonic UC-PL intensity with variation in band edge position
- Promising for narrow-band enhancement, but still inconclusive!

Thank you!

References

A. Atre and J. Dionne, *Journal of Applied Physics* 110, 034505, 2011.

M. A. Green, *Progress in Photovoltaics* 2011, DOI: 10.1002/pip.1156

M. A. Green and M. J. Keevers, *Progress in Photovoltaics* 3, 189–192, 1995.

C. Kerestes *et al*., *Progress in Photovoltaics* 2012, DOI: 10.1002/pip.1232

C. Liu *et al*., *Journal of Non-Crystalline Solids* 354, 2–9, pp. 618–623, 2008.

T. Trupke *et al*., *Journal of Applied Physics* 92, 4117–4122, 2002.

P. Yeh, *Optical Waves in Layered Media*, Wiley 1988.