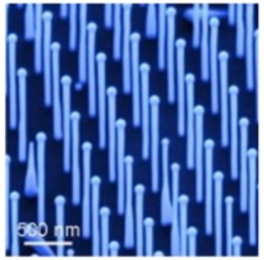


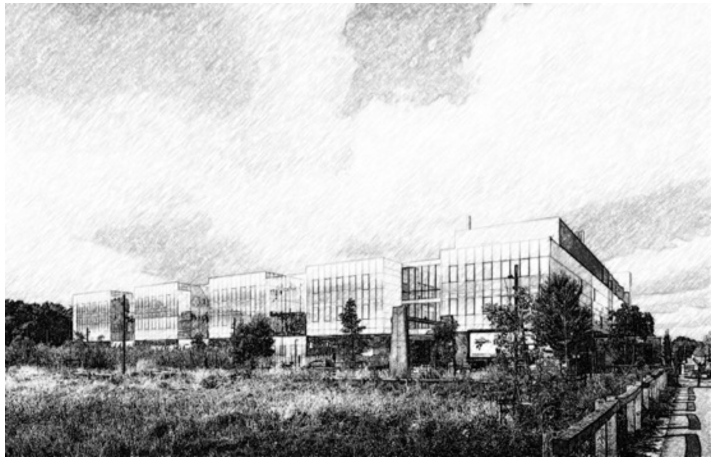
ELaboration of NANOmaterials for the recovery, conversion, transport and storage of energy

11-16 Jun 2023 Aussois (73500) (France)

Nanostructures for light trapping in ultra-thin solar cells

Andrea Cattoni

Physics Department, Politecnico di Milano, Milano, Italy
Previously: C2N, CNRS, Paris-Saclay University & IPVF, Palaiseau, France



15th June 2023

Outline

POLITECNICO
MILANO 1863

- Introduction on photovoltaics and the Shockley-Queisser model
- Solar cell operation, designs and structures
- Ultra-thin solar cells, benchmark (Si, CIGS, GaAs), notable examples
- Low-cost nanofabrication techniques and Nanoimprint Lithography
- Outlook

News from 8th World Conference on Photovoltaic Energy Conversion

26 - 30 September 2022 in the Milano

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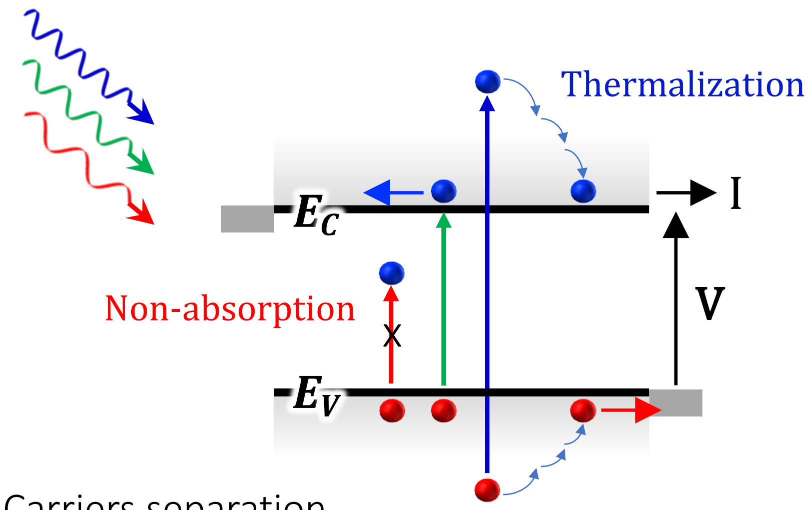
Global PV installation	1st Terawatt by fall 2022 (60 years). 2nd Terawatt expected in 3 years [1]
PV share, 100% RE (2050)	60-63% (anyway > 50*%)* [2]
Market share (2021)	95% Si-wafer based PV [3] (5% CIGS & CdTe)
Energy Payback Time	0.9/1.1 years (north/south Europe) [3]
Production costs (today)	19.9 $ct/Wp in India / 25 $ct/Wp EU (high) [4]

[1] Pierre Verlinden, Trina Solar, WCPEC-8, 26 September 2022
[2] Christian Breyer, Finland University), 5EP.1.3, WCPEC-8, 30 September 2022
[3] PHOTOVOLTAICS REPORT, Fraunhofer ISE, 22 September 2022
[4] Peter Fath, RCT-Solutions, 26 September 2022

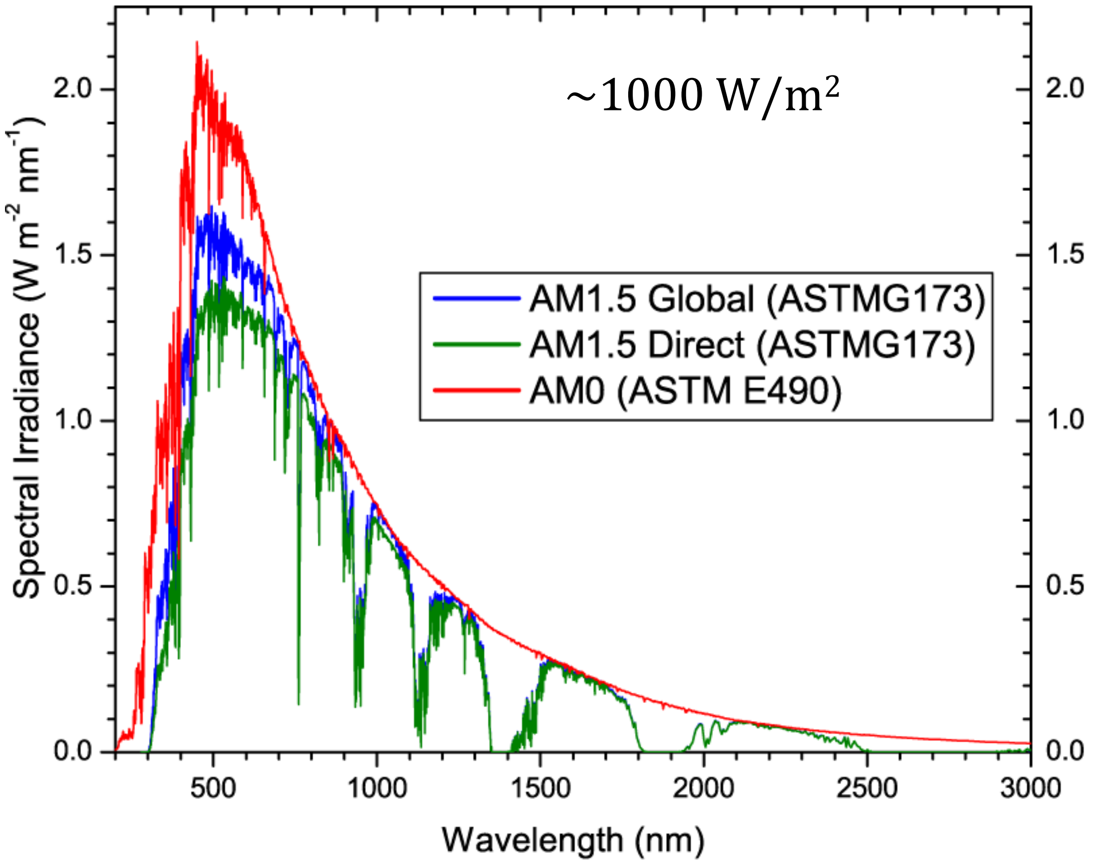
Shockley-Queisser model for solar cells

Energy loss processes:



(Carriers separation
requires a built-in asymmetry)

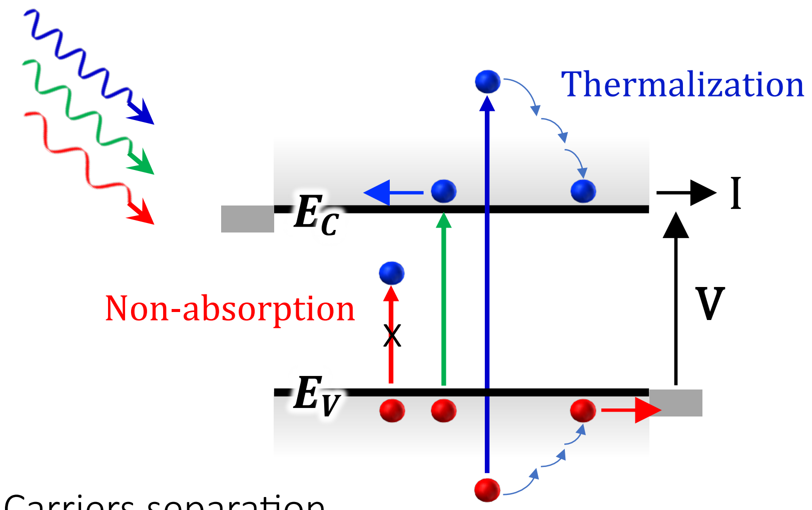
$$P = V \times I$$



Best bandgap to maximize converted **power** (1-J):
compromise between high current and voltage

Shockley-Queisser model for solar cells

Energy loss processes:



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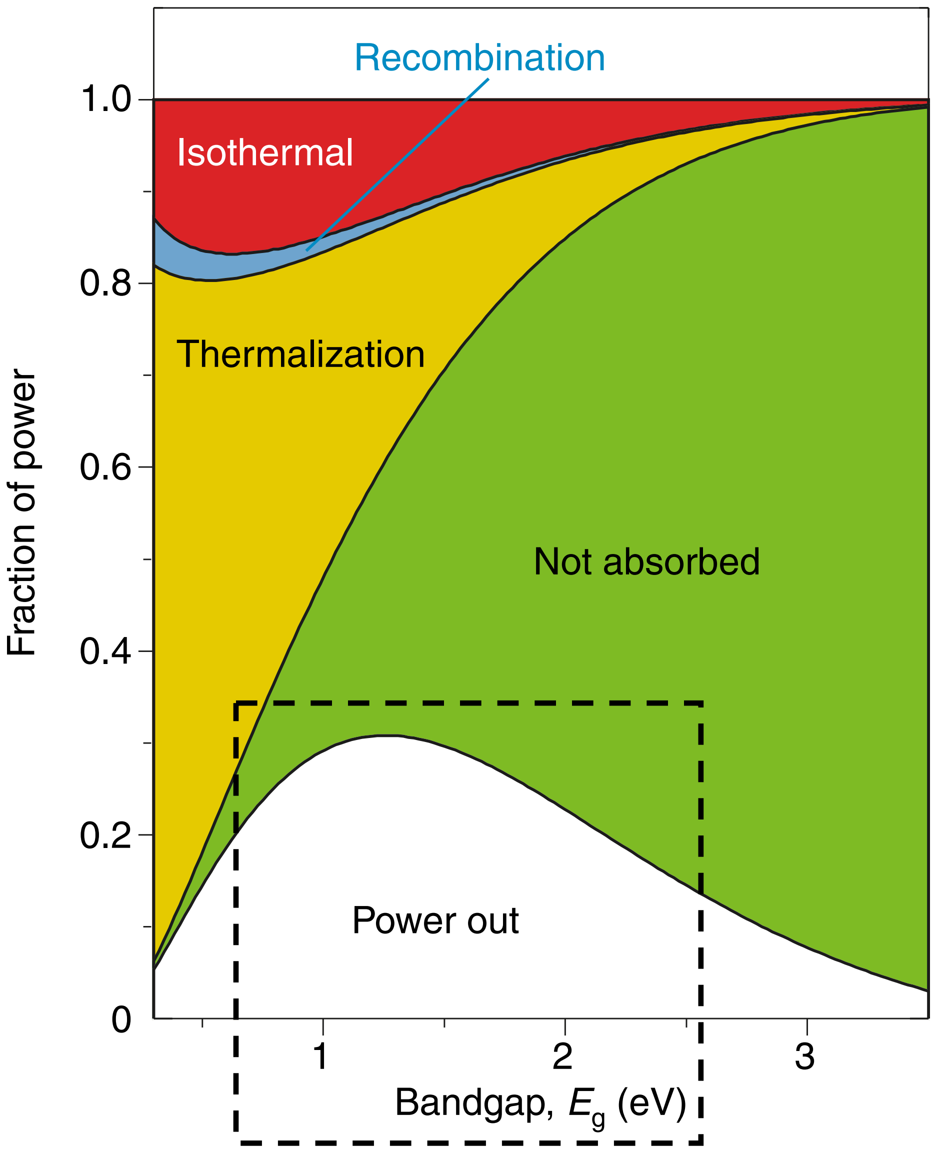
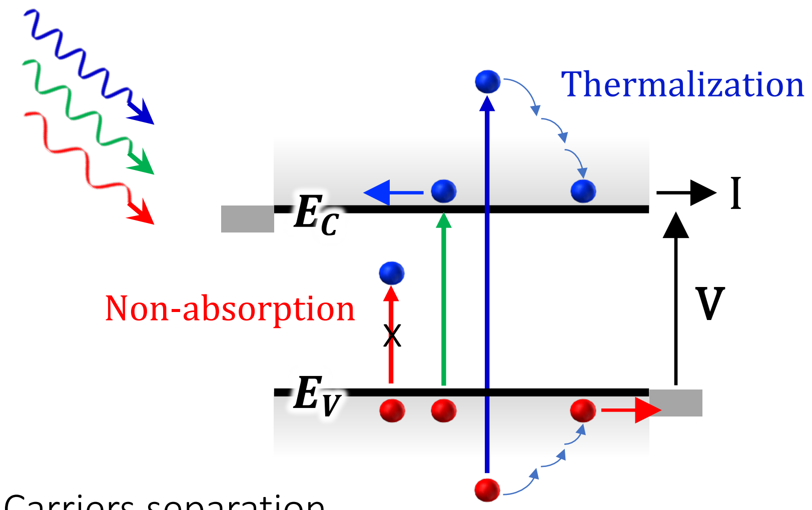


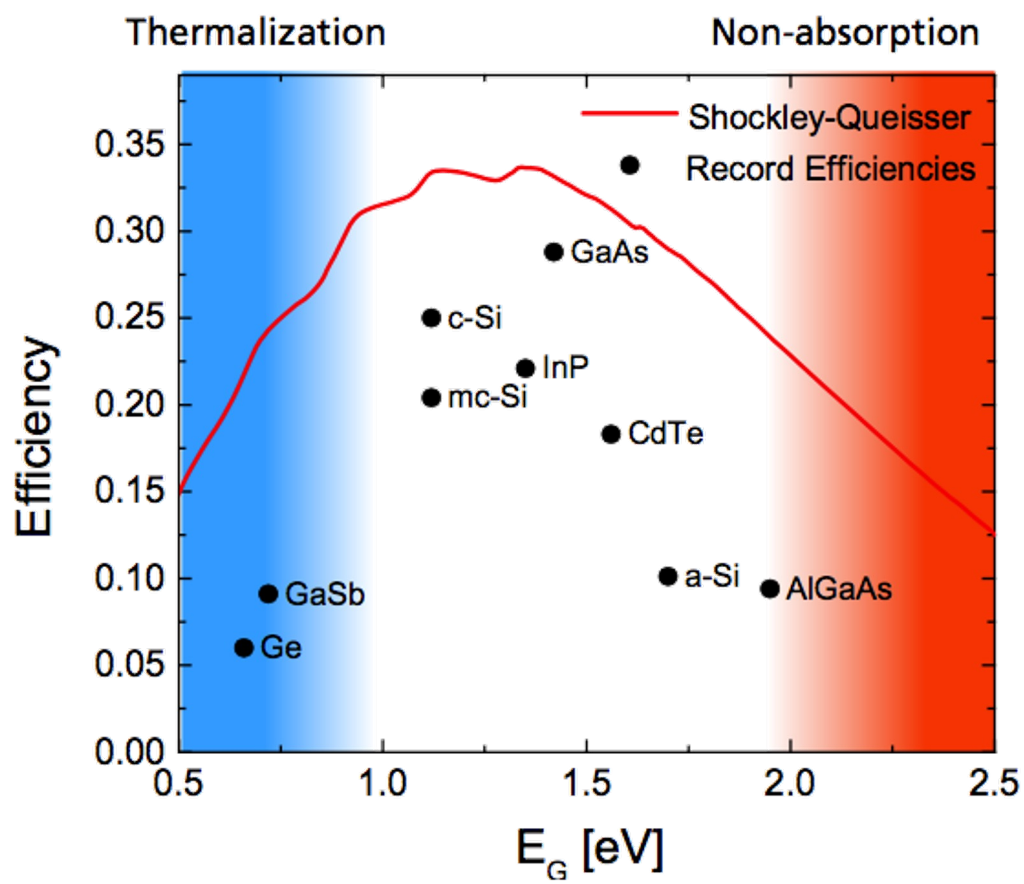
Shockley-Queisser model for solar cells

Energy loss processes:



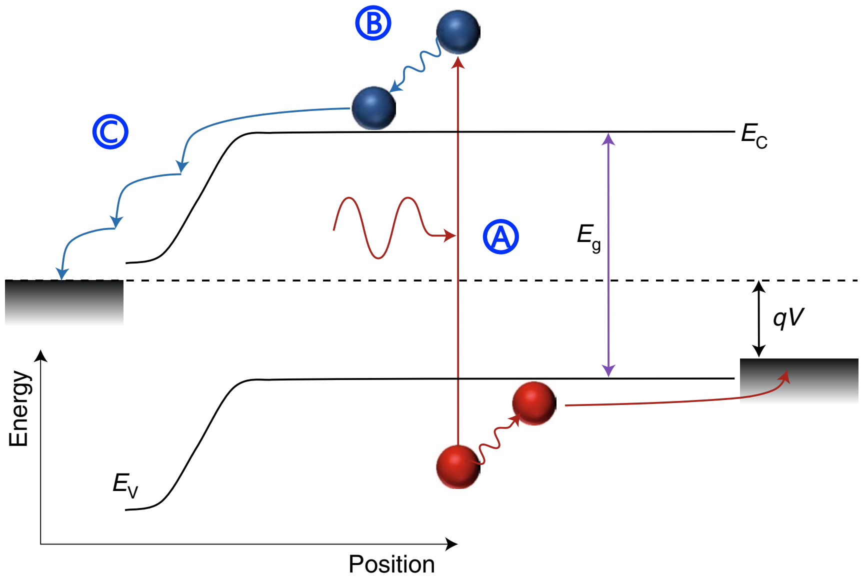
(Carriers separation
requires a built-in asymmetry)

$$P = V \times I$$



Best bandgap to maximize converted **power** (1-J):
compromise between high current and voltage

Assumptions of the Shockley-Queisser



Ⓐ Optical

1) At Eg, absorptivity of photons in the absorber switches from 0 to 1.

2) One electron–hole pair per absorbed photon. Each pair is collected at short circuit.

Ⓑ Thermal

3) Heat extraction from the carrier system such that the carrier temperature equals the cell and ambient temperature.

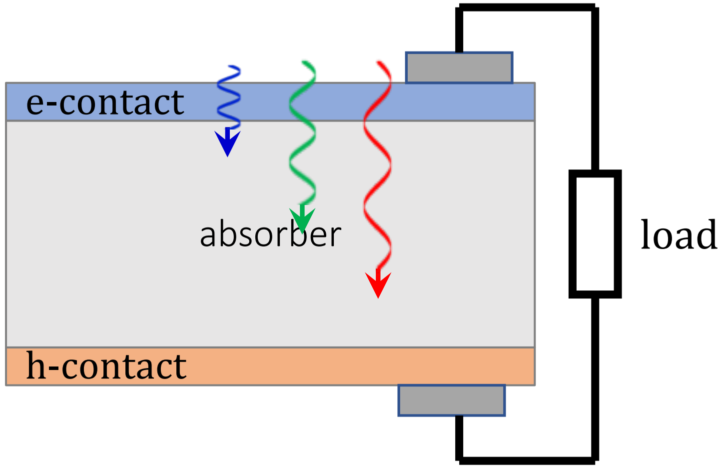
Ⓒ Electronic

4) Electron–hole recombination is only radiative.

5) No ohmic losses, contacts are perfectly selective.

« Guide for the perplexed to the Shockley– Queisser model for solar cells », Nature Photonics 13, 501 (2019)

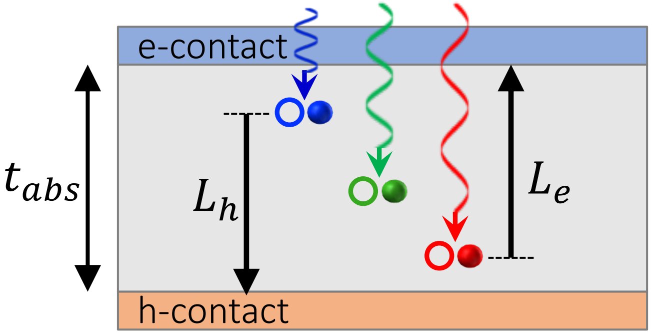
In real life: solar cell efficiency is governed by the αμτ product



Photovoltaic absorber material:

- Light absorption (α)
- Charge-carrier transport (μ)
- Charge-carrier recombination (τ)

$\boldsymbol{\alpha\mu\tau}$ the higher the better!



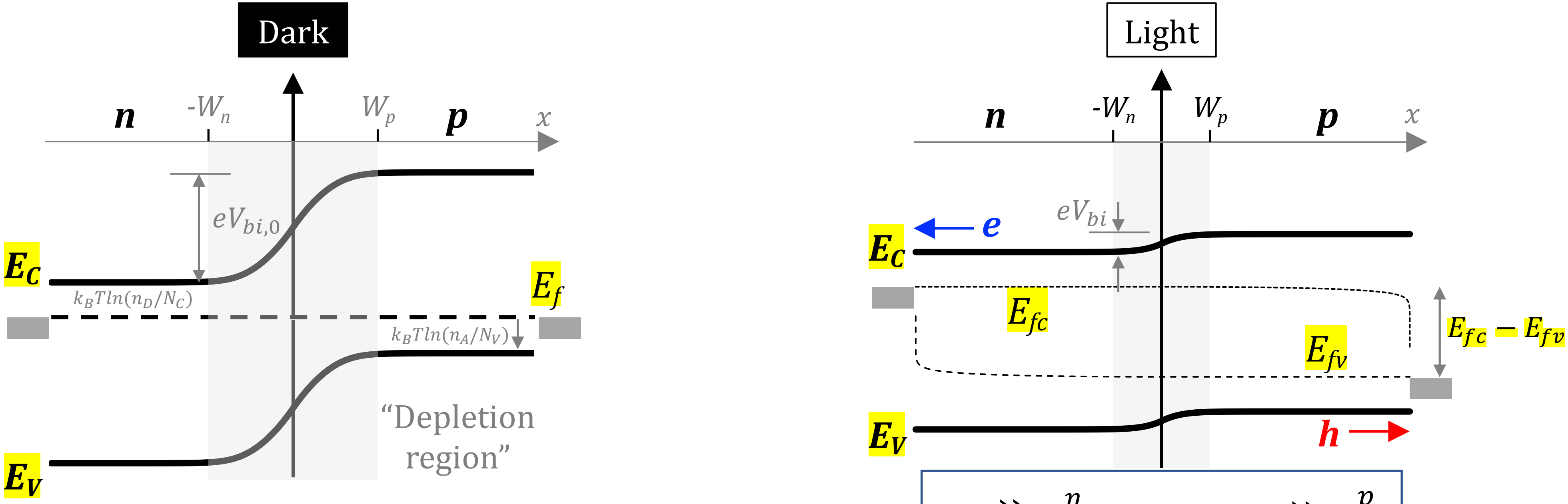
Typical requirements:

Absorption: $t_{abs} \gg$ Penetration depth ($1/\boldsymbol{\alpha}$)

Collection: $t_{abs} \ll$ Diffusion/Drift lengths ($\boldsymbol{\mu}$&$\boldsymbol{\tau}$)

Physical Review Research **2**, 023109 (2020)

The pn junction



$n_D \gg n_h^n$ $\quad$ $n_A \gg n_e^p$

E_{fi} : Quasi − Fermi level (or Electrochemical Potential)

$$J = \frac{\sigma_e}{e}\nabla E_{fc} + \frac{\sigma_h}{e}\nabla E_{fv}$$

☛ Electron/holes are charged particles and the electrical force ($\propto \nabla\varphi$) and the chemical force ($\propto \nabla n$) act on them simultaneously.

$$\sigma = e(n_e\mu_e + n_h\mu_h)$$

Drift and Diffusion currents

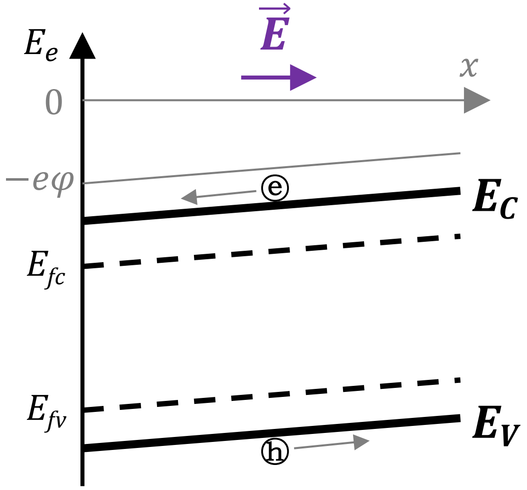
Mathematically - if you like - we can consider the two contributions separately and express:

Only Field (Drift) current

$n_e(x) = const.$

$n_h(x) = const.$

$E \neq 0$



$$J_i^{Drift} = \sigma_i E = -\sigma_i \nabla\varphi$$

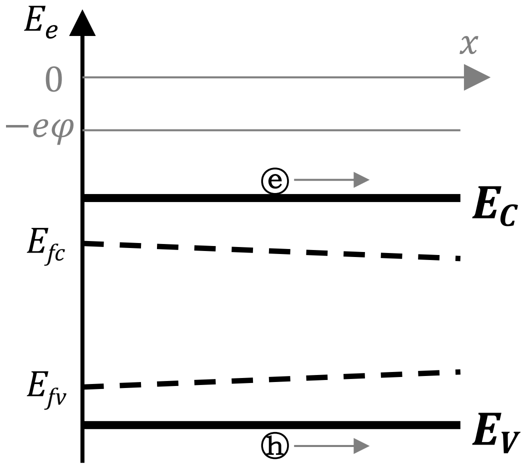
$$\sigma = e(n_e\mu_e + n_h\mu_h)$$

Only Diffusion current

$\nabla n_e(x)$

$\nabla n_h(x)$

$E = 0$



$$J_i^{Diff} = -qD_i \nabla n_i(x)$$

$$D_i = \frac{k_B T \mu_i}{q}$$

but the 2 current components lack a real physical meaning!
Only the total current originating from the total driving force ($\propto \nabla E_{fi}$) is a real physical quantity.

Diffusion and Drift lengths

The carrier diffusion length is the mean path length for the charge carrier diffusion during its lifetime (τ_i):

$$L_i^{Diff} = \sqrt{D_i \tau_i}$$

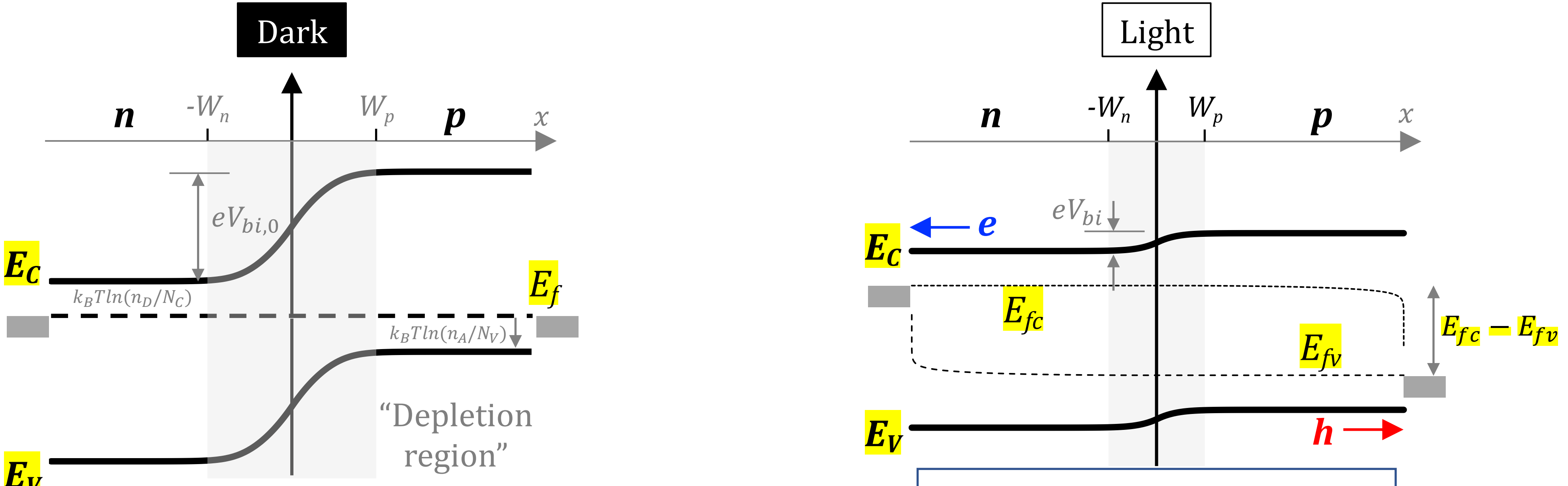
Similarly, the carrier drift length is the mean path length for the charge carrier drift during its lifetime (τ_i):

$$L_i^{Drift} = \mu_i \tau_i E$$

μ_i and τ_i strongly depend on densities of defects and impurities

	Si	**GaAs**
m_e^*/m_e	1.08	0.067
m_h^*/m_e	0.55	0.47
μ_e (V^{-1}s^{-1})	1400	8500
μ_h(V^{-1}s^{-1})	450	400
D_e (cm^{2}s^{-1})	36	200
D_h (cm^{2}s^{-1})	12	10
$\tau_{e/h}$ (sec)	up to ms	up to µs
$L_{e/h}^{Diff}$ (cm)	100-300 µm	10-50 µm

The pn junction



$n_D \gg n_h^n$ $n_A \gg n_e^p$

Selective carrier transport can only result from different conductivities of electrons and holes on the way toward "their" contacts!

$$J = \frac{\sigma_e}{e}\nabla E_{fc} + \frac{\sigma_h}{e}\nabla E_{fv}$$

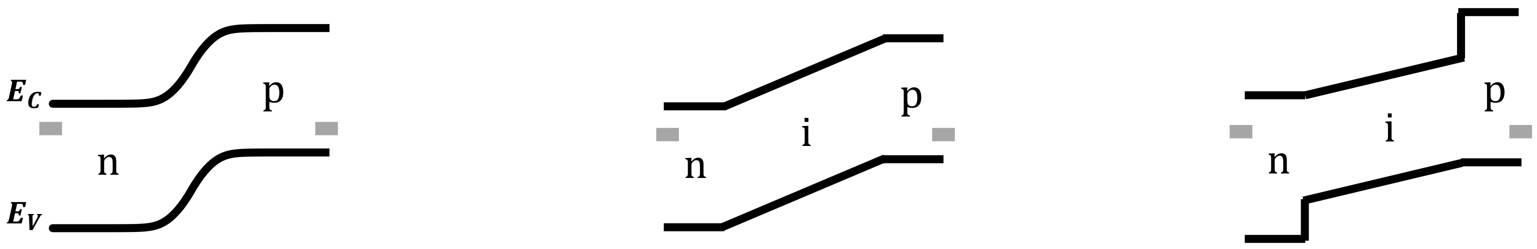
$$\sigma = e(n_e\mu_e + n_h\mu_h)$$

IEEE J. of PV 5, NO. 1, 461 (2015)
Peter Würfel and Uli Würfel , «Physics of Solar Cells», Wiley VCH

Solar cell structure and design

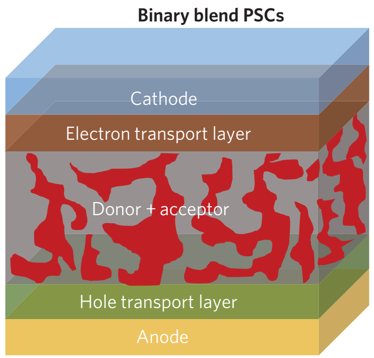
Must be adapted to $\boldsymbol{\alpha\mu\tau}$!

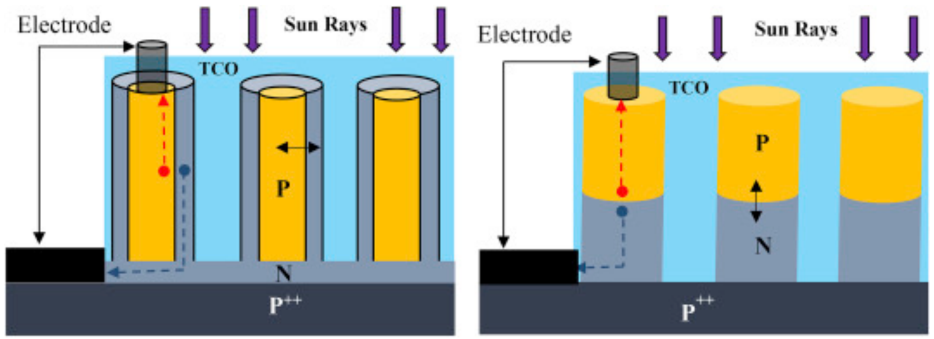
In the « Energy space »: different **(band) structures** are more/less suitable/possible depending on material and its $\boldsymbol{\alpha\mu\tau}$



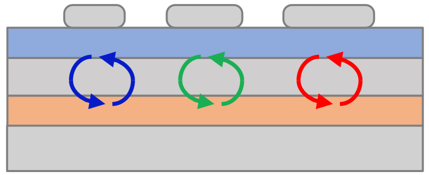
In the **« Real space »:** different **(geometrical) designs** can compensate for some material "weaknesses"

We need enough material, how it is arranged is not important!



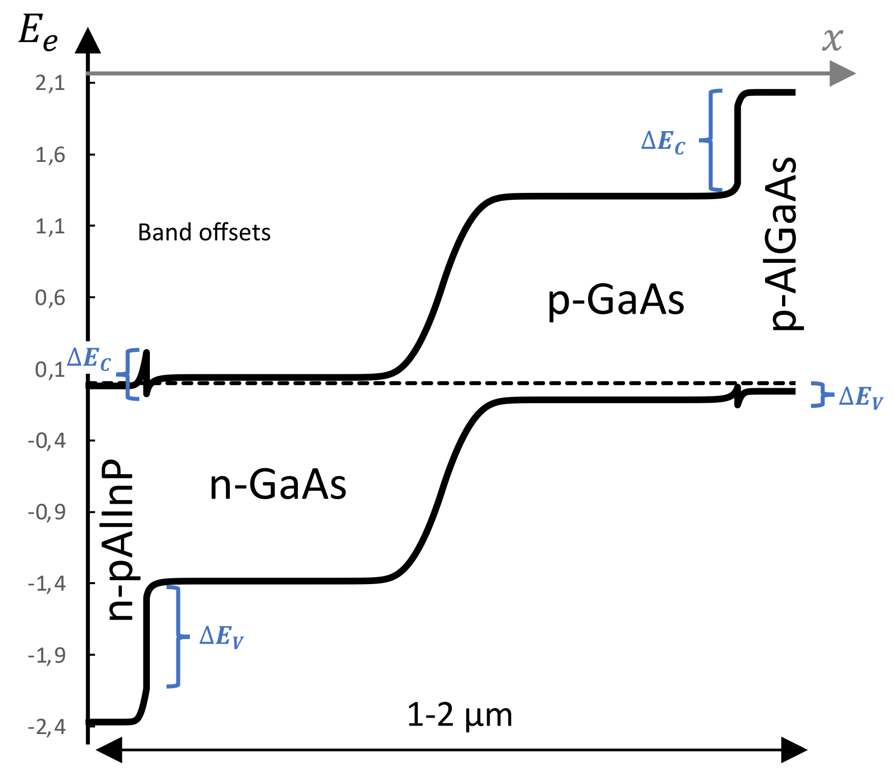


Otherwise, let's bend the light instead of the absorber!



GaAs (and III-V) solar cells

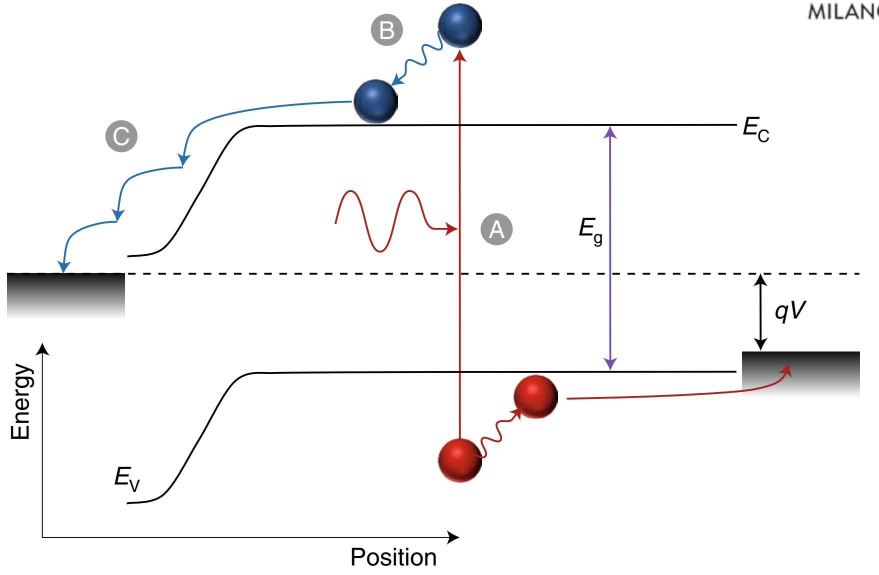
- Monocrystalline, high crystal quality, low defects
- High absorption coefficient (**α**), direct E_g ($t^{absorber}$~2 µm)
- Long lifetimes (**τ**), very high mobilities (**µ**), long diffusion lengths
- Doping possible
- Chemical passivation possible (wide-bandgap III-V)
- Hetero-contacts possible and much more!



Material	E_g (eV)	χ (eV)	Interface	ΔE_C (eV)	ΔE_V (eV)
GaAs	1.42 [18]	4.07 [18]	GaAs/GaInP	0.06	0.375
$Ga_{0.52}In_{0.48}P$	1.85 [19]	4.01 [21]	GaAs/AlInP	0.3	0.63
$Al_{0.53}In_{0.47}P$	2.35 [20]	3.78 [21]	GaInP/AlInP	0.23	0.27
$Al_{0.8}Ga_{0.2}As$	2.09 [13]	3.53 [22]	GaAs/AlGaAs	0.54	0.13
			GaInP/AlGaAs	0.48	0.24

c-Si solar cells

- Monocrystalline, high crystal quality, low defects
- Low absorption coefficient (**α**), indirect bandgap ($t^{absorber}$~200 μm)
- Very long lifetimes (**τ**), high mobilities (**μ**), very long diffusion lengths
- Doping possible
- Chemical passivation possible: SiO_2, hydrogenated a-Si (a-Si:H)
- Hetero-contacts possible: a-Si:H/doped-a-Si + TOPCon and others
- + doped microcrystalline Si (μc-Si)



Many band structures and architectures, but in general:

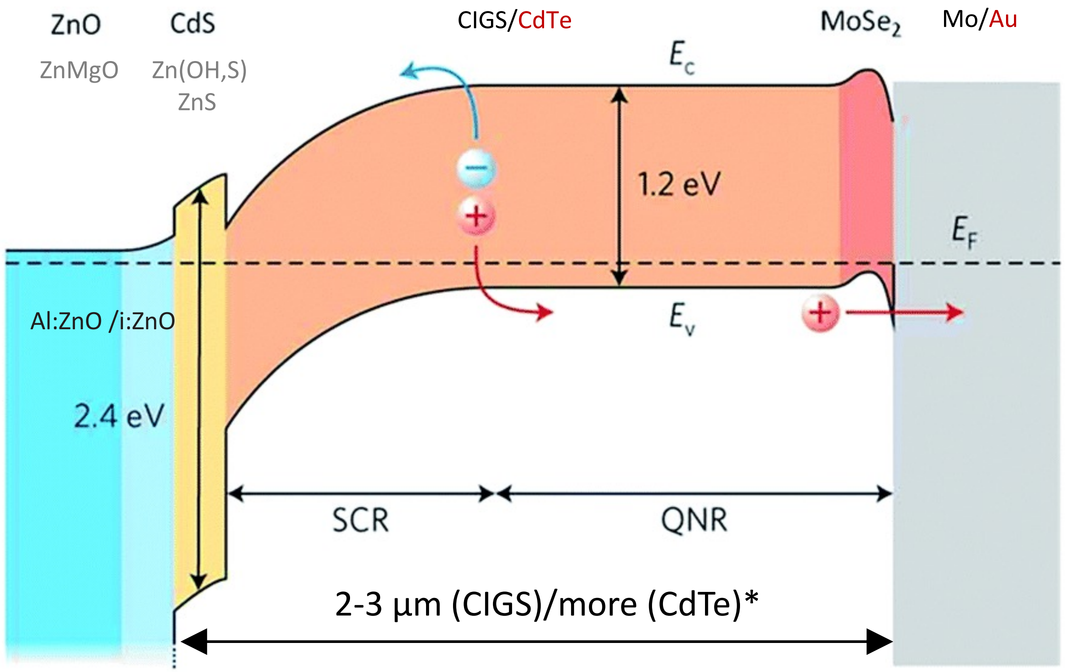
p-n: 100-300 μm thick p-type silicon wafer base, poorly doped + thin n-type emitter highly doped

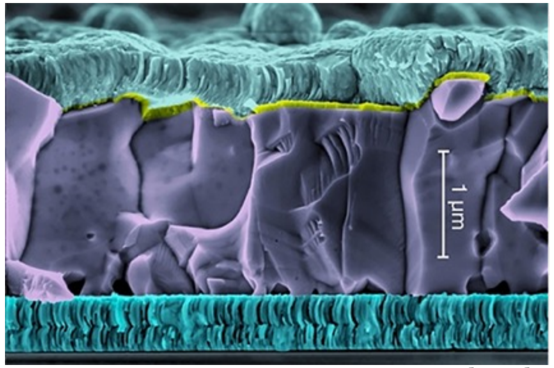
Heterojunction: Si wafers + passivated contacts hydrognated amorphous silicon (a-Si:H) + doped nanocrystalline silicon (nc-Si:H) or doped silicon oxide (nc-SiO_x:H)

TOPCon: Si wafers + SiO_2 passivation + doped microcrystalline Si (μc-Si)

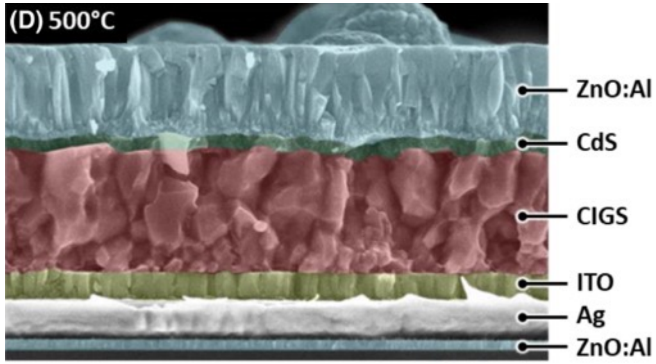
Cu(In,Ga)Se_2 & CdTe solar cells

- Polycrystalline, defects → Passivation of grain boundaries required with Alkali-metals (CIGS) or annealing in $CdCl_2$ atmosphere (CdTe)
- (Very) High (CdTe) absorption coefficient (α), direct E_g ($t^{absorber}$~4 μm)
- Poor lifetimes (τ), mobilities (μ), diffusion lengths (compare to Si and III-V)
- Doping not possible, slightly p-type (Cu vacancies), compensated
- Chemical passivation not possible, few attempt to passivate the p-type contact with charged dielectrics (CIGS)
- Hetero-contacts possible using CdS (intrinsically n-type)





www.zsw-bw.de



PPR Appl. 29, 212 (2021)

I-V Characterization (Dark/Light)

$$\eta = \frac{V_{MPP} J_{MPP}}{P_{inc}} = \frac{J_{SC}\, V_{OC}\, FF}{P_{inc}}$$

J_{SC} : *short circuit current*

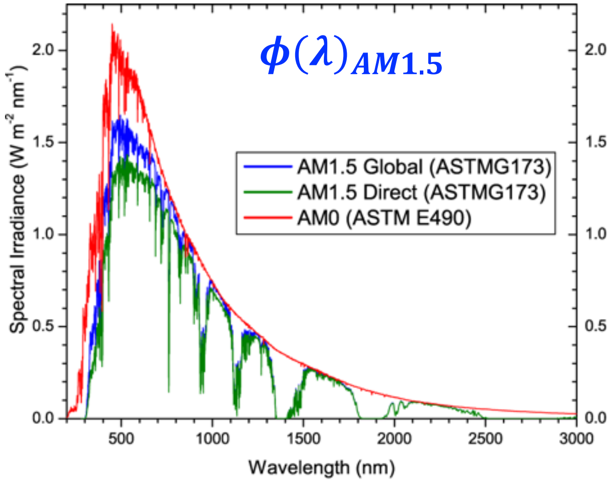
V_{OC} : *open circuit voltage*

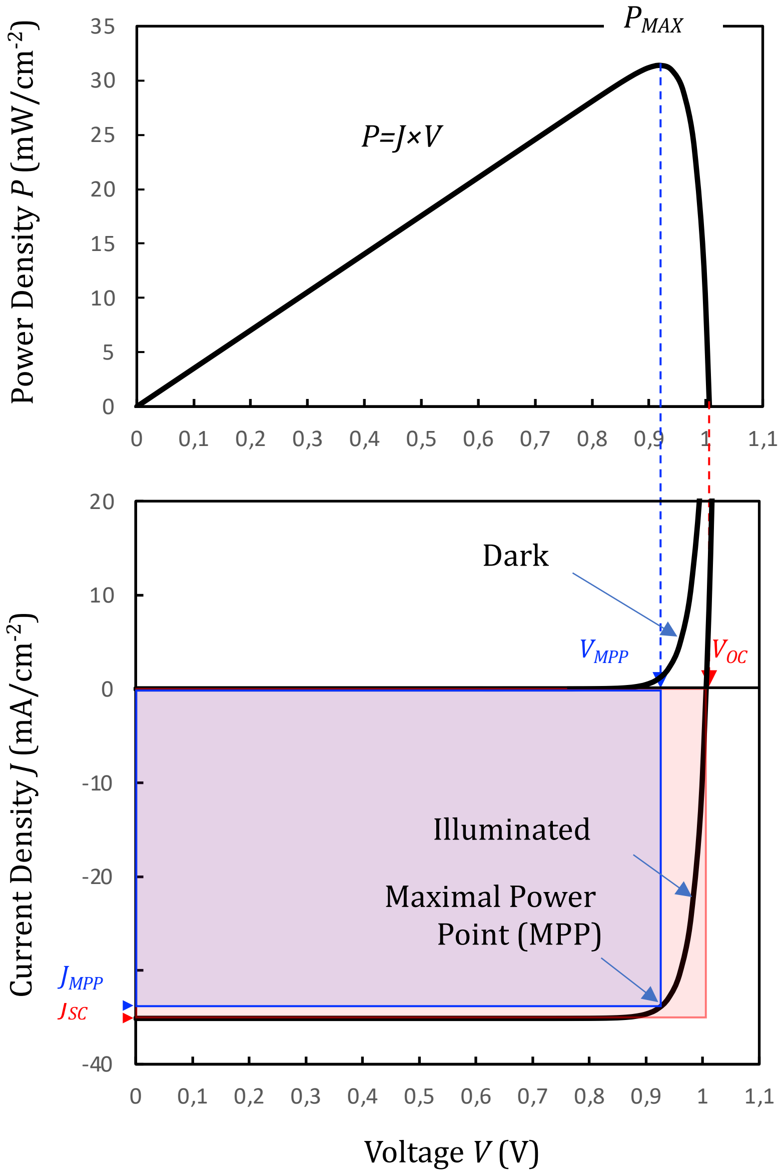
$$FF = \frac{V_{MPP}\, J_{MPP}}{V_{OC}\, J_{SC}}$$

In the following we will assume:

$$J_{SC}\,(d) = q \int \boldsymbol{A}(\boldsymbol{\lambda})\, \phi(\lambda)_{AM1.5} d\lambda$$

Absorptivity

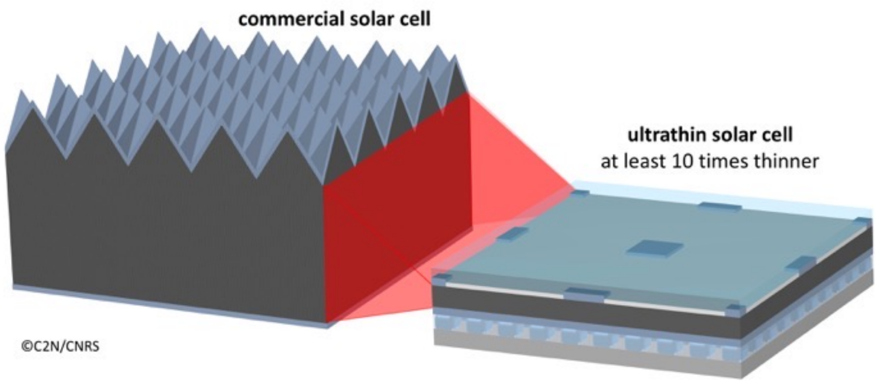




Ultra-thin solar cells

- State of the art single-junction solar cells today are very close to the "Schottky-Queisser limit"

GaAs	33.5%th	29.1%^{Exp}	(1-2 µm thick)
c-Si	29.4%th	26.7%^{Exp}	(165 µm-thick)



- They operate (essentially) at the single-pass absorption
- Conversion efficiency could be retained in ultrathin absorbers (1/10th) using light-trapping

Does light trapping in solar cell make sense?

The enthusiastic:

- Completely change the fabrication absorber process (Si)
- Reduce costs (materials) and improve throughput (CIGS)
- Improve lifetime (III-V for space)
- Increased power production by preventing heating
- Improve carrier collection in defective/degraded absorber materials (potential for new/cheaper absorber materials)

The Skeptical:

→ It may be too late for 1-J Si, maybe for Tandem

→ Yes, but CIGS market < 5%

→ Yes, but we need light-trapping in 2-J, 3-J

→ Yes, a flat mirror will suffice

→ Silicon is unbeatable.

How thin can we go? (1/2)

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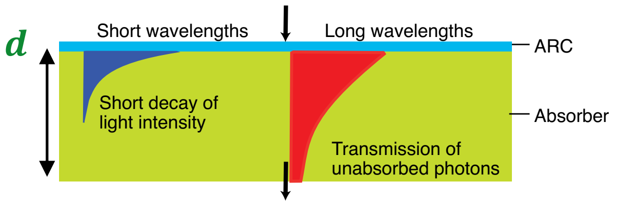
The optical path can be enhanced by light trapping
to compensate for the low absorption in ultrathin layers by a factor $\boldsymbol{F}$

Optical thickness: $\boldsymbol{F} \times \boldsymbol{d}\ (absorber\ thickness)$

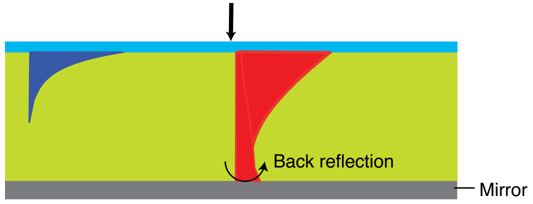
(Hyperuniform)

Single-pass
$\boldsymbol{F = 1}$



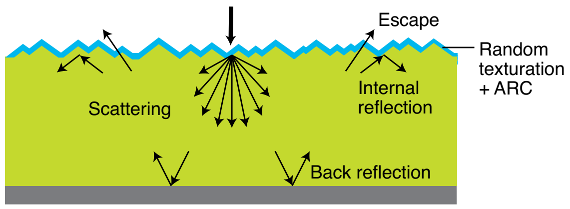
Perfect ARC

Double-pass
$\boldsymbol{F = 2}$



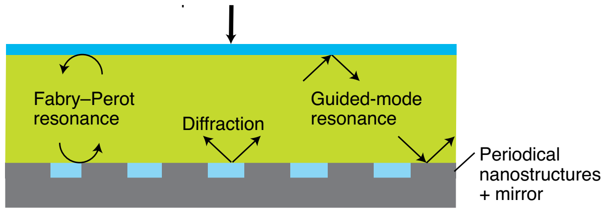
Perfect ARC + Mirror

Lambertian scattering
$\boldsymbol{F = 4\pi n^2}$ **[1]**



Incoherent scattering + Mirror

« Multi-resonant »



Coherent scattering + Mirror

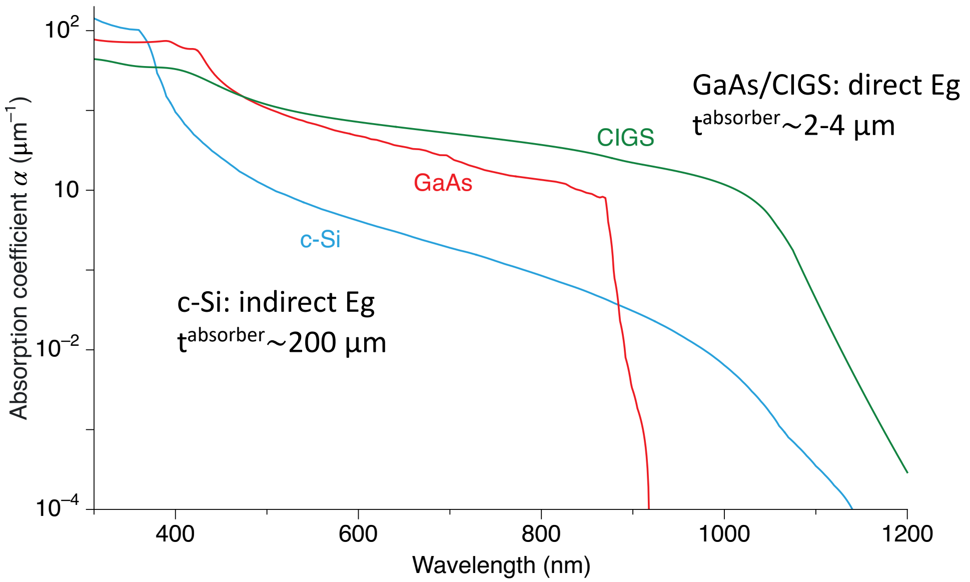
$$\mathrm{A}(\lambda) = 1 - e^{-F\alpha d}$$

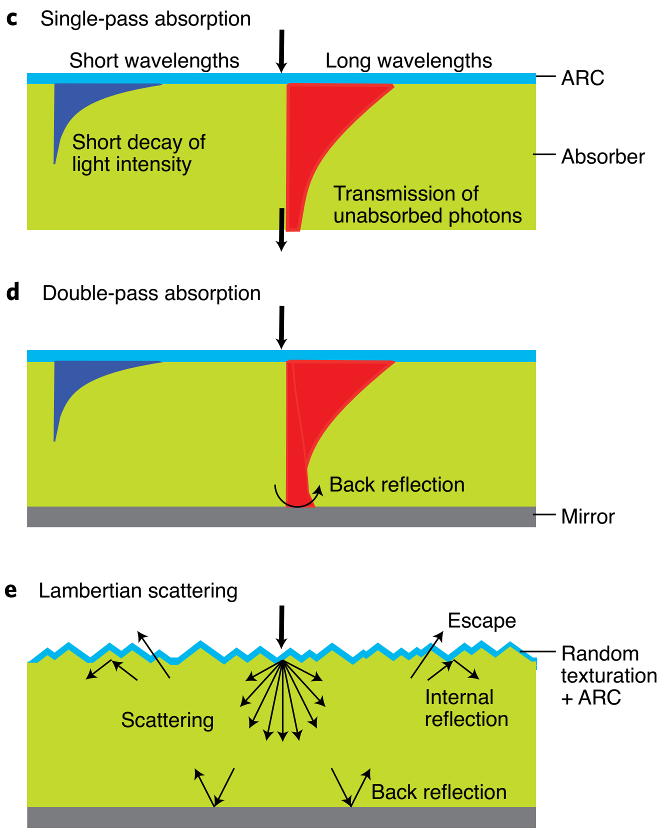
$$\mathrm{A}(\lambda) = \frac{\alpha d}{\alpha d + {}^{1}/_{F}} \quad [2]$$

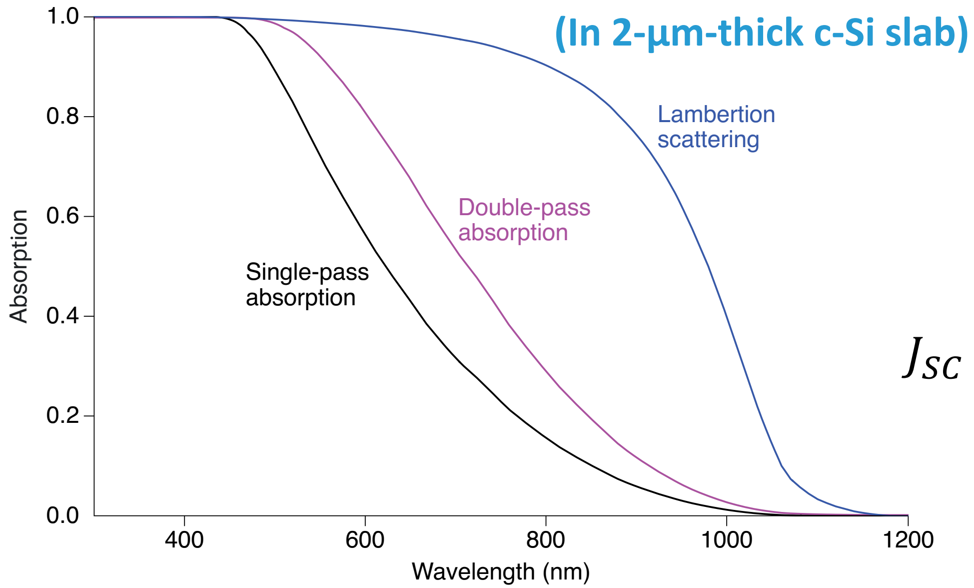
[1] E. Yablonovitch, J OPT SOC AM B 71, 899 (1982)

[2] M. Green, *Prog. Photovolt: Res. Appl.* 10, 235 (2002)

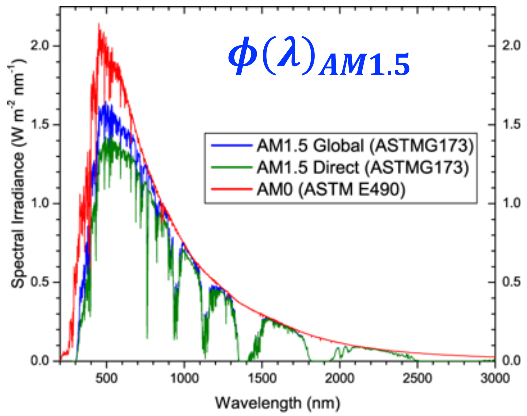
How thin can we go? (2/2)





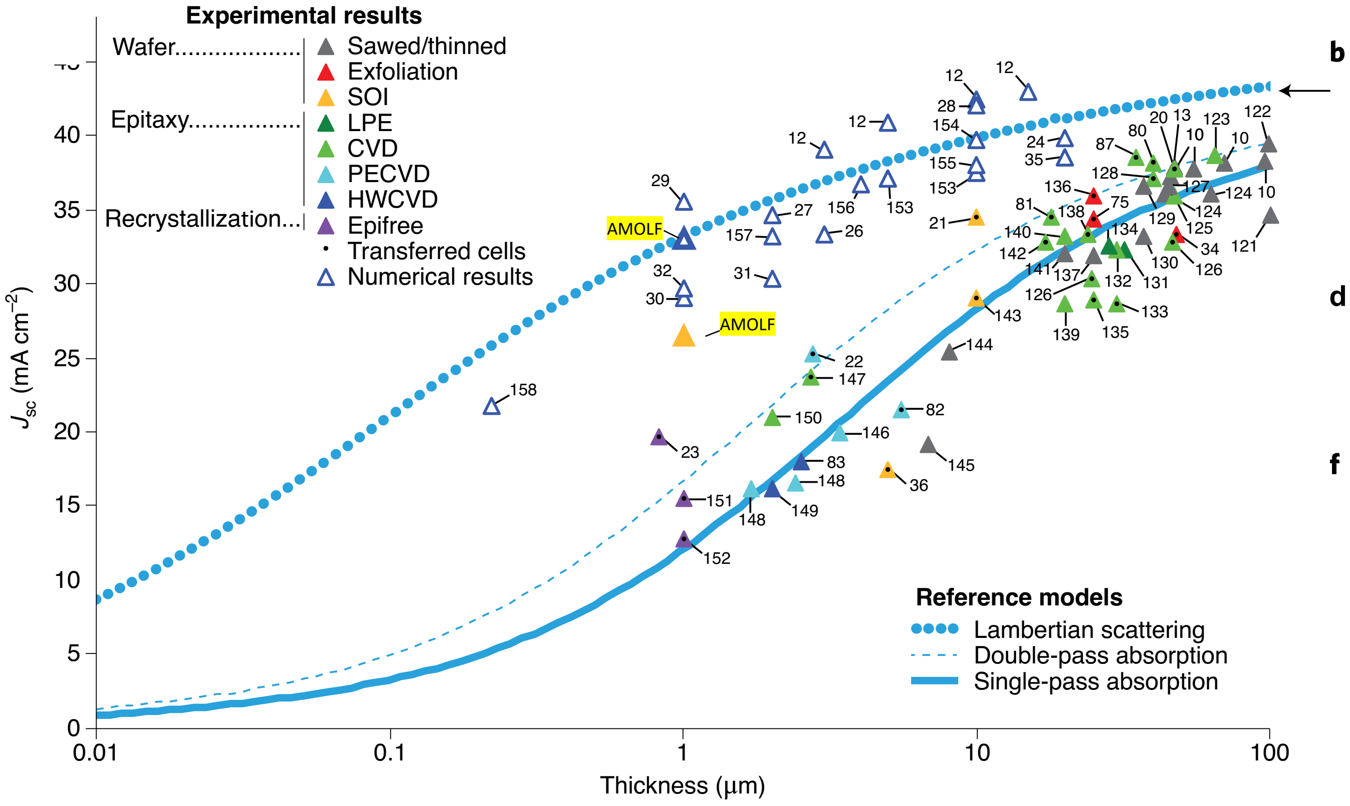


$$J_{SC}\,(\mathrm{d}) = q \int \boldsymbol{A(\lambda)}\; \boldsymbol{\phi(\lambda)_{AM1.5}} d\lambda$$

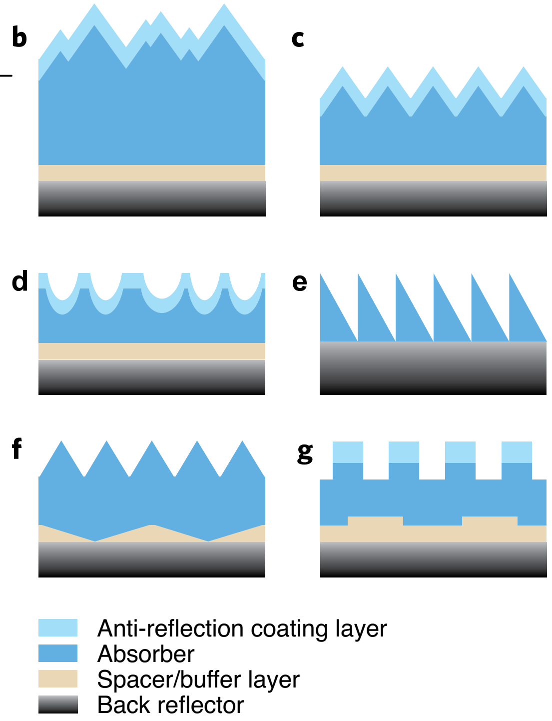


Benchmark for c-Si

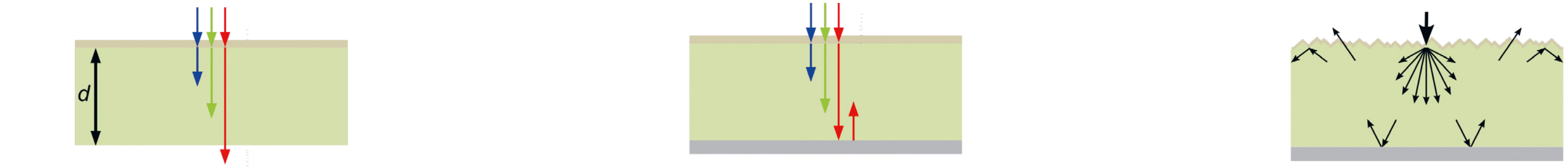
Adapted from : Massiot, Cattoni, Collin Nat. Energy **5**, 959 (2020)



Record Si cell (Kaneka: 180 µm, 42.65 mA/cm²



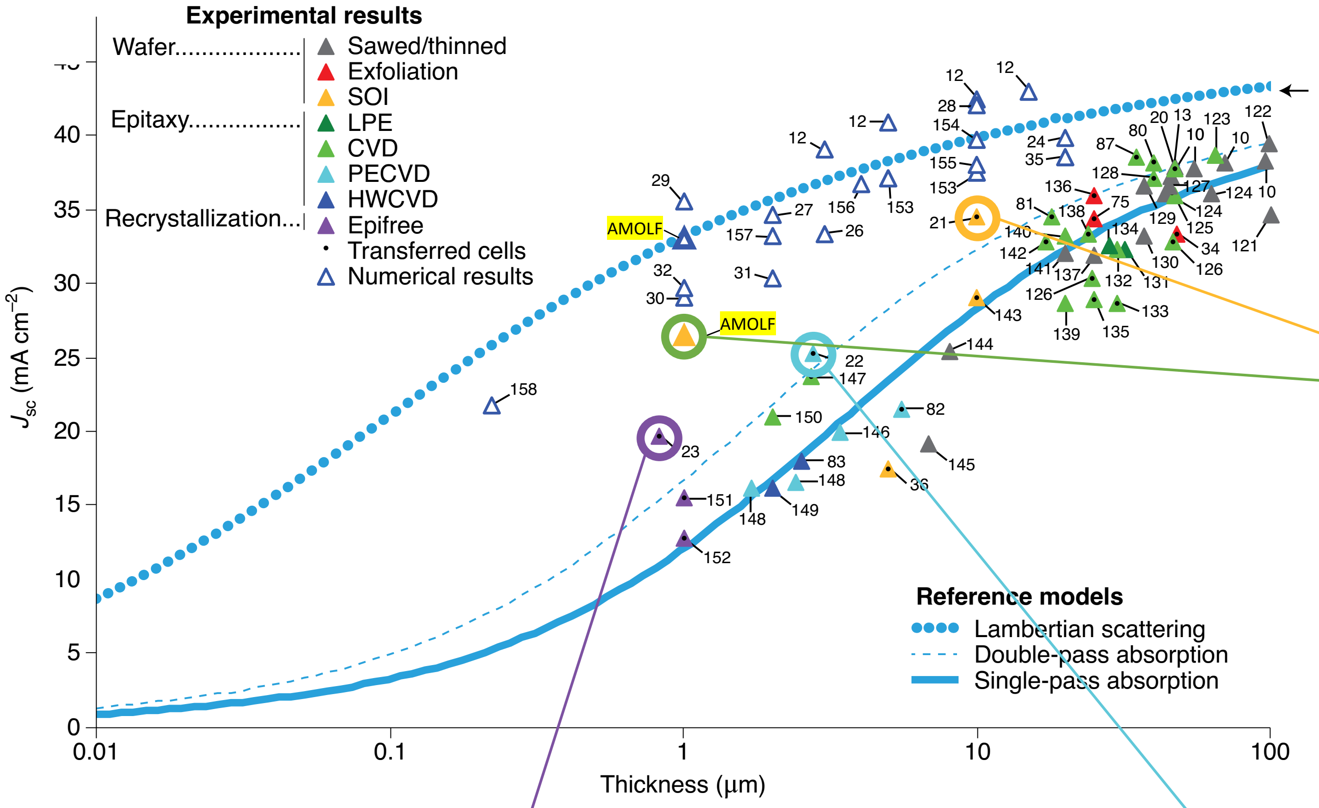
Single-pass abs. (F=1) | Double-pass abs. (F=2) | Lambertian scattering (F=4n²)



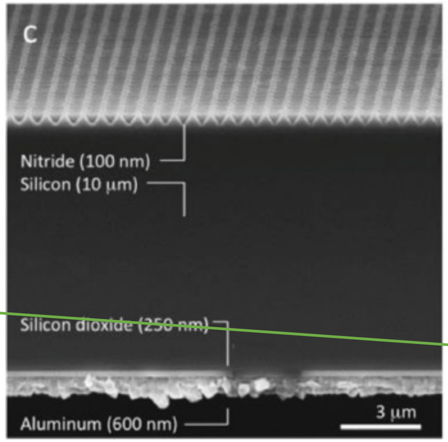
- **Si directly textured (simple to etch/passivate)**
- **Sim. can exceed $4n^2$**
- **Not all Sim. take into account complete cell**

Notable examples (Exp.)

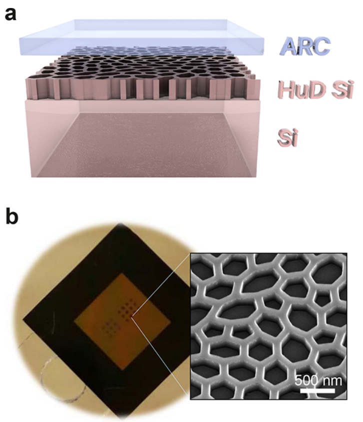
Adapted from : Massiot, Cattoni, Collin Nat. Energy **5**, 959 (2020)



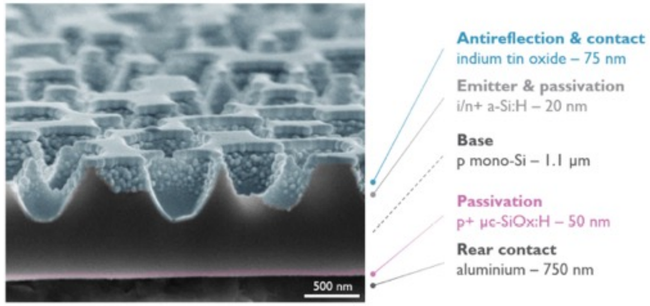
Low cost Si synthesis/texturing mandatory!



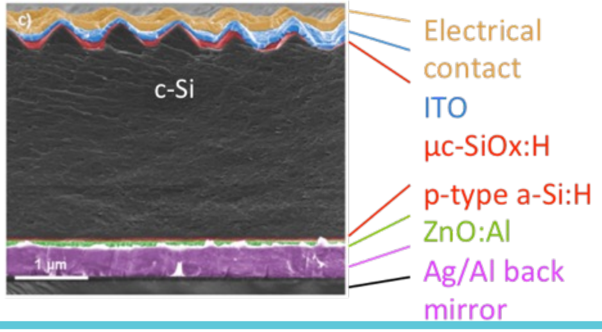
MIT
e-beam litho + wet etching
SOI
10 µm nm, 34.5 mA/cm²
Adv. Mater. **27**, 2182 (2015)



AMOLF
e-beam litho + dry etching
Si membrane
1 µm nm, 26.3 mA/cm² (**Eq.**)
ACS Photonics **9**, 1206 (2022)



IMEC
Sparse Nanospheres + Dry Etching
Epi-free
900 nm 24.8 mA/cm²
Nano Futures **1**, 021001 (2017)

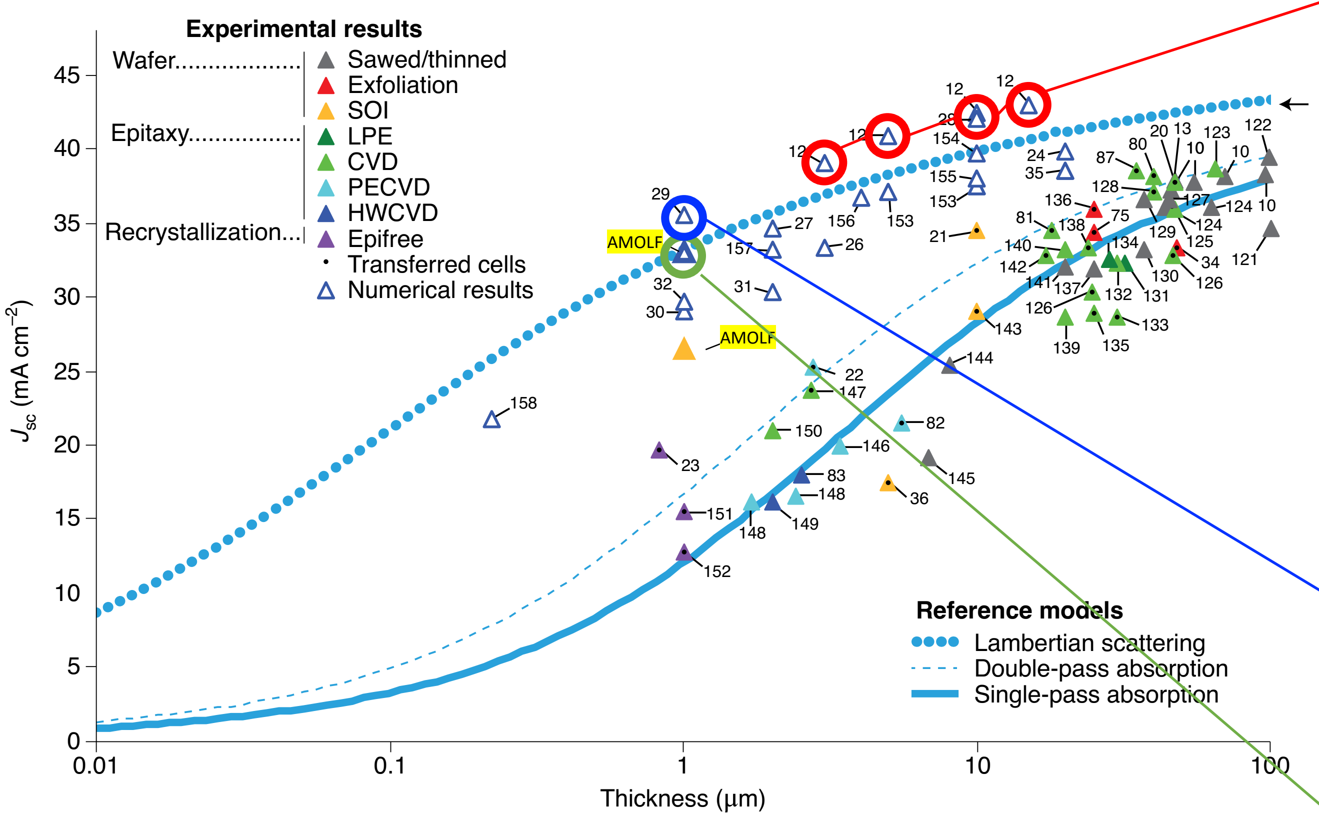


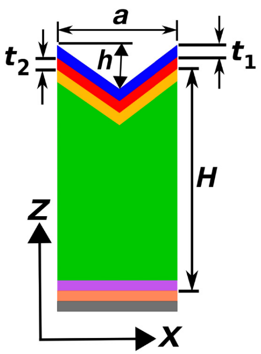
C2N-CNRS / Ecole Polyt.
Soft NIL + wet etching
Low Temperature PECVD
3 µm nm, 25.3 mA/cm²
Nano Lett., **16**, 5358 (2016)

POLITECNICO MILANO 1863

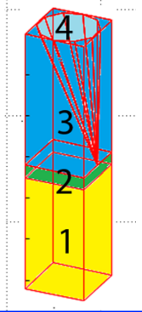
Notable examples (Sim.)

Adapted from : Massiot, Cattoni, Collin Nat. Energy **5**, 959 (2020)

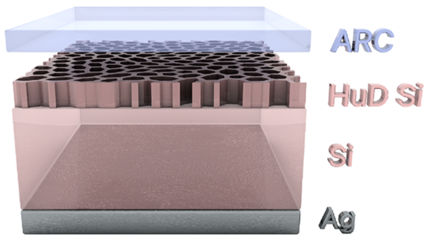




University of Toronto
Array of inverted pyramids
10 μm, 42.4 mA/cm²
Phys. Rev. Appl. 11, 014005 (2019)



University of Toronto
Array of slatend cones
1 μm, 35.5 mA/cm²
J. Appl. Phys. 113, 154315 (2013)



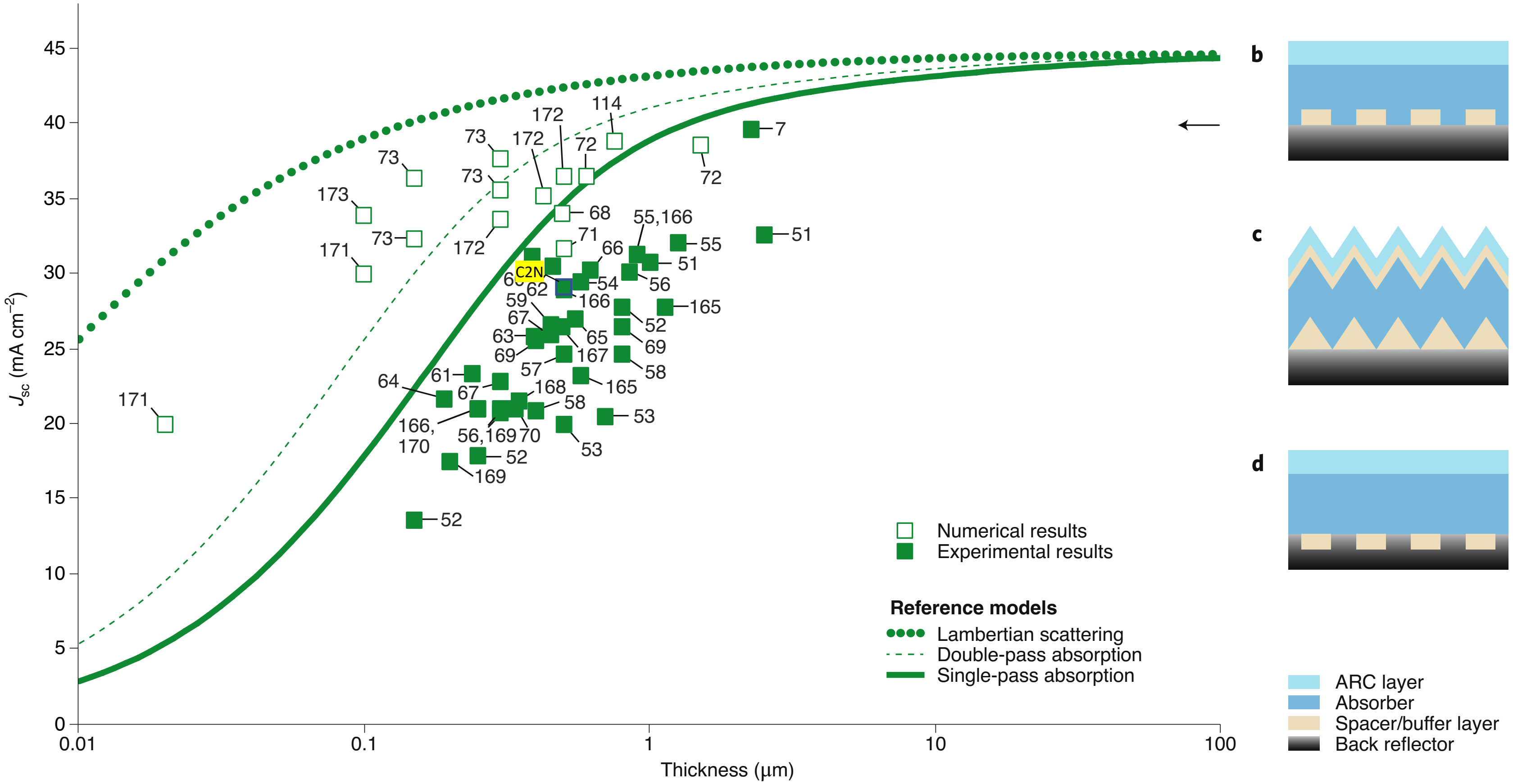
AMOLF
Hyperuniform
1 μm, 33.8 mA/cm² (**Abs.**)
ACS Photonics **9**, 1206 (2022)

- **Breaking the symmetry pays off**
- **Yet, low cost fabrication is more sensible**

Benchmark for $Cu(In,Ga)(S,Se)_2$

Adapted from : Massiot, Cattoni, Collin Nat. Energy **5**, 959 (2020)

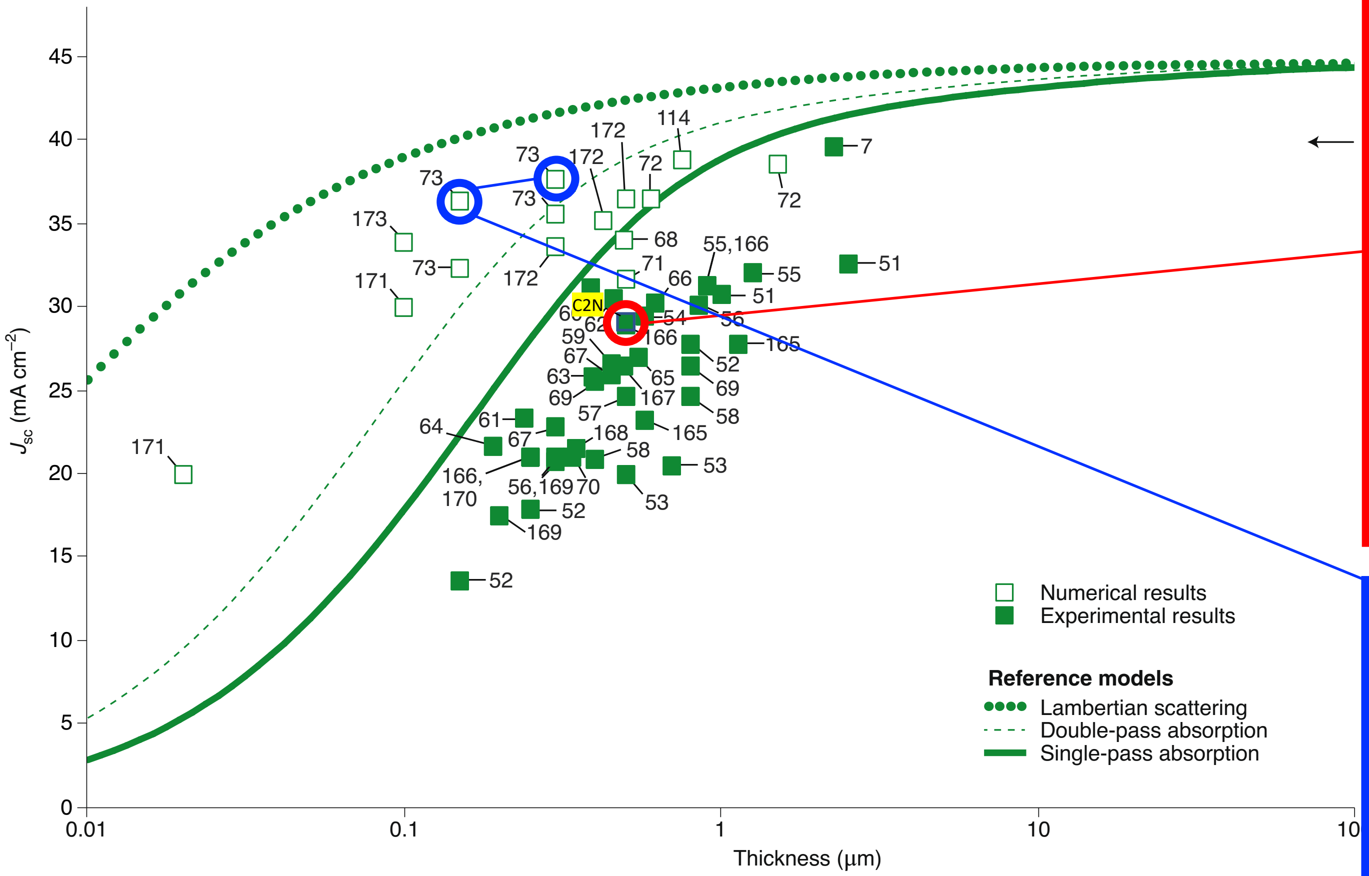
Record CIGS cell (Solar Frontier)
2.25 µm, 39.58 mA/cm²

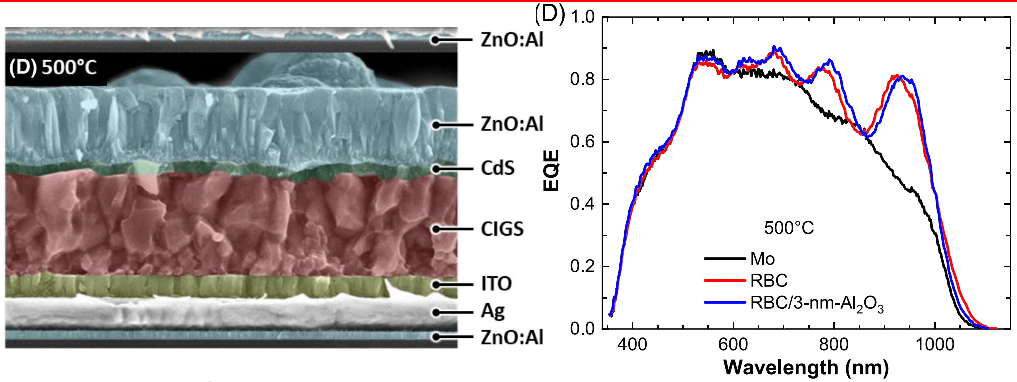


- **Exp. well under the single-pass**
- **We need to replace the Mo back contact first!**

Benchmark for $Cu(In,Ga)(S,Se)_2$ (Exp. & Sim.)

Adapted from : Massiot, Cattoni, Collin Nat. Energy **5**, 959 (2020)



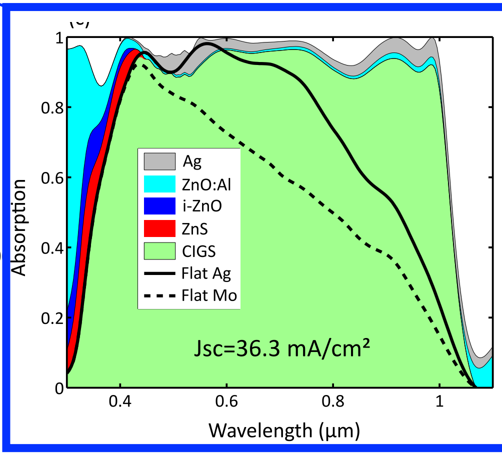


C2N-CNRS / Uppsala University

Flat Al_2O_3/ITO/Ag mirror

500 nm, 28.9 mA/cm²

Prog Photovolt Res Appl. 1, 10 (2020)



C2N-CNRS

Textured Ag mirror (2D grating)

150 nm, 36.3 mA/cm²

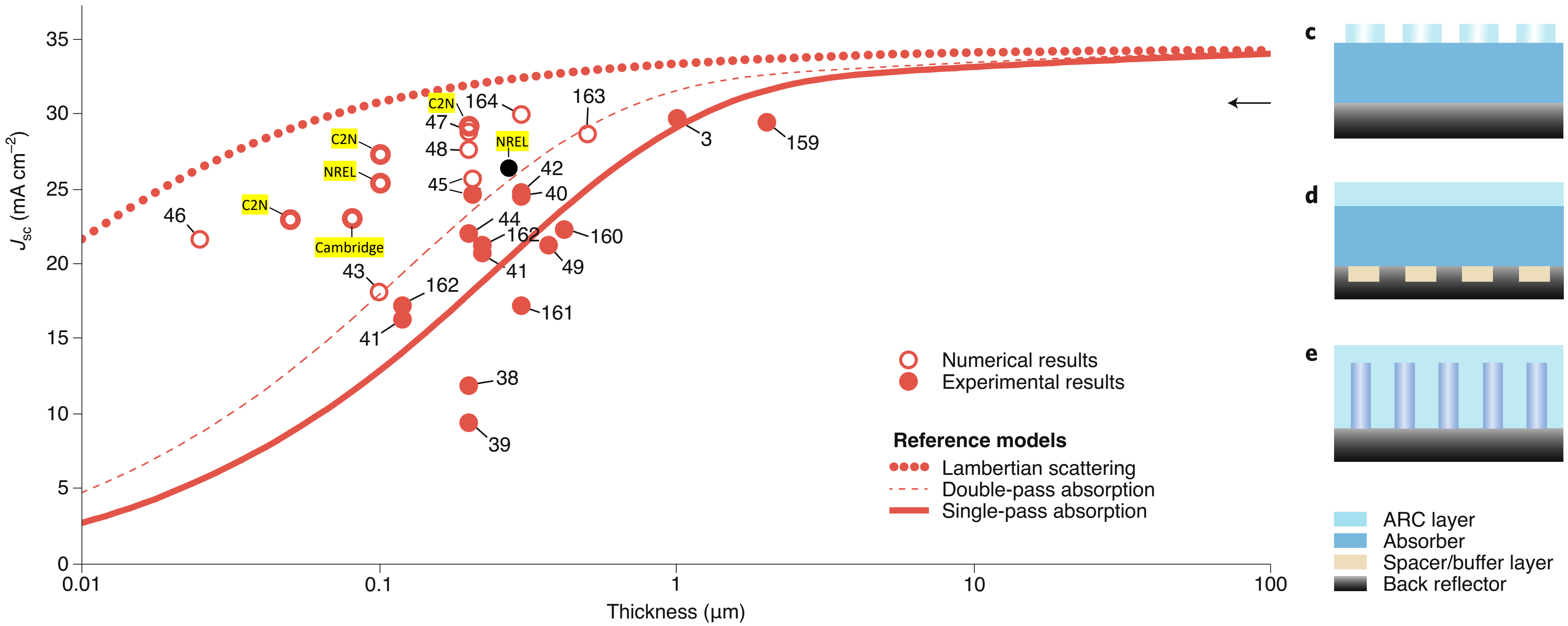
IEEE J. of PV, 7, 1433 (2017)

- **Exp. well under the single-pass**
- **We need to replace the Mo back contact first!**

Benchmark for GaAs

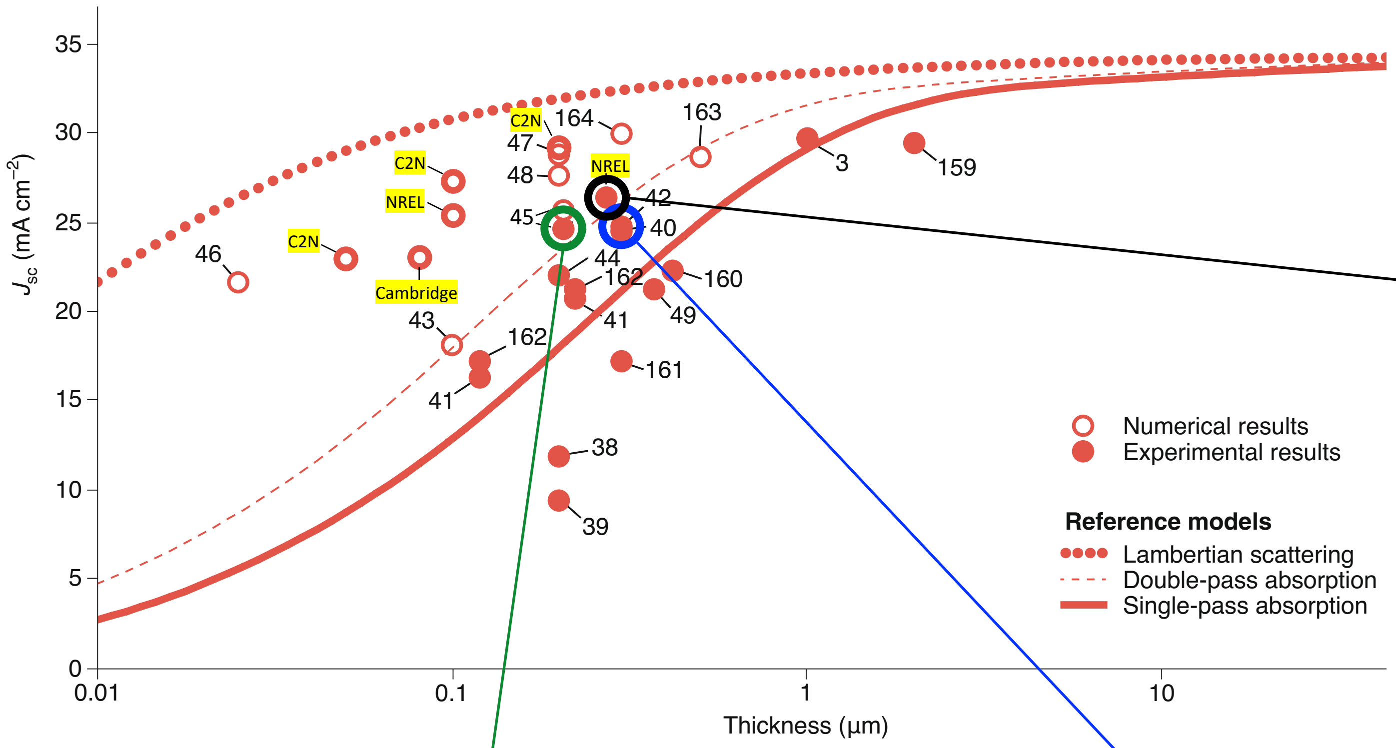
Adapted from : Massiot, Cattoni, Collin Nat. Energy **5**, 959 (2020)

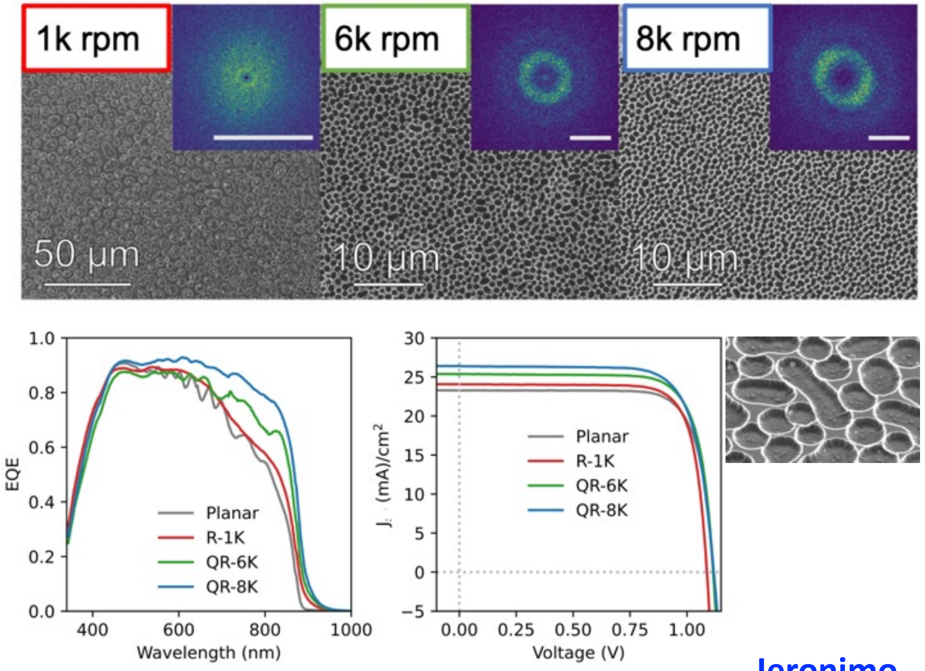
Record GaAs cell (Alta Devices)
1-2 µm (?), 29.78 mA/cm²



Benchmark for GaAs (Exp.)

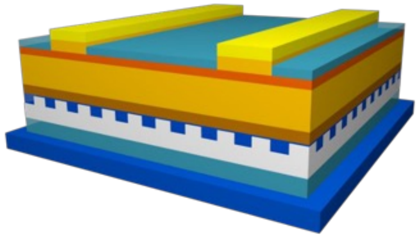
Adapted from : Massiot, Cattoni, Collin Nat. Energy **5**, 959 (2020)



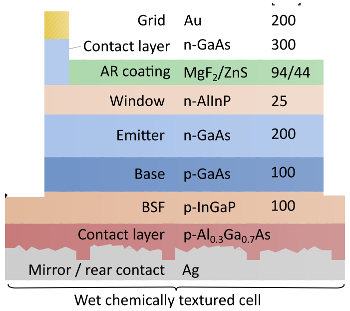


NREL (22.4 %)
Hyperuniform AlGaAs BSF + flat Ag mirror
Polymer-blend lithography + wet etching
260 nm, 26.4 mA/cm²
Nano Energy 96, 107080 (2022)

Jeronimo Buencuerpo



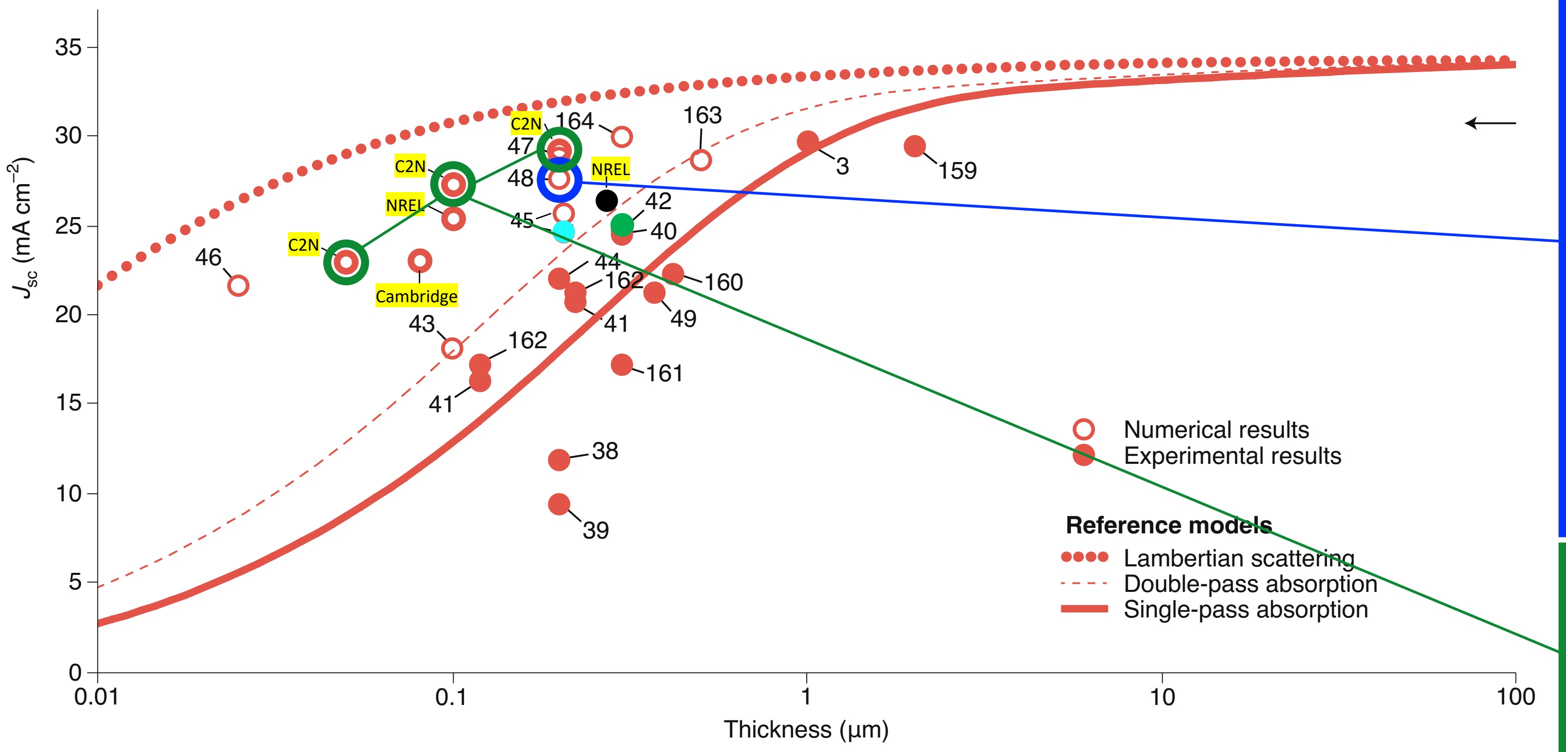
C2N-CNRS, Fraunhofer ISE (19.9 %)
Nanostructured TiO_2/Ag mirror
Nanoimprint of TiO_2 sol-gel
200 nm, 24.64 mA/cm²
Nature Energy, 4, 761 (2019)

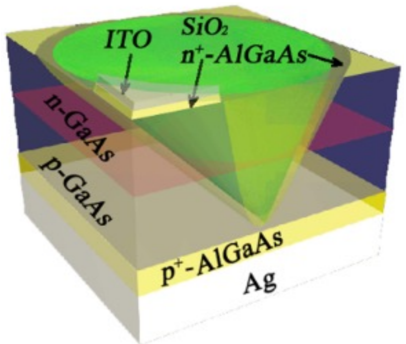


Radboud University (21.4%)
Rough p-AlGaAs contact + rough Ag mirror
Wet etching
300 nm, 24.8 mA/cm²
Prog. Phot. Res. Appl. 28, 200 (2020)

Benchmark for GaAs (Sim.)

Adapted from : Massiot, Cattoni, Collin Nat. Energy **5**, 959 (2020)



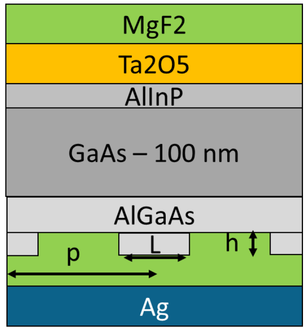


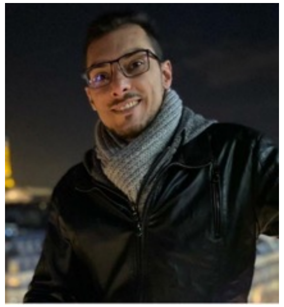
University of Toronto

Inverted pyramids array in GaAs + flat Ag mirror

200 nm, 27.6 mA/cm^2

Scientific Report 6, 1 (2016)





Daniel Micha

C2N-CNRS

2D grating in AlGaAs BSF + flat Ag mirror

100 nm, 27.2 mA/cm^2

200 nm, 28.9 mA/cm^2

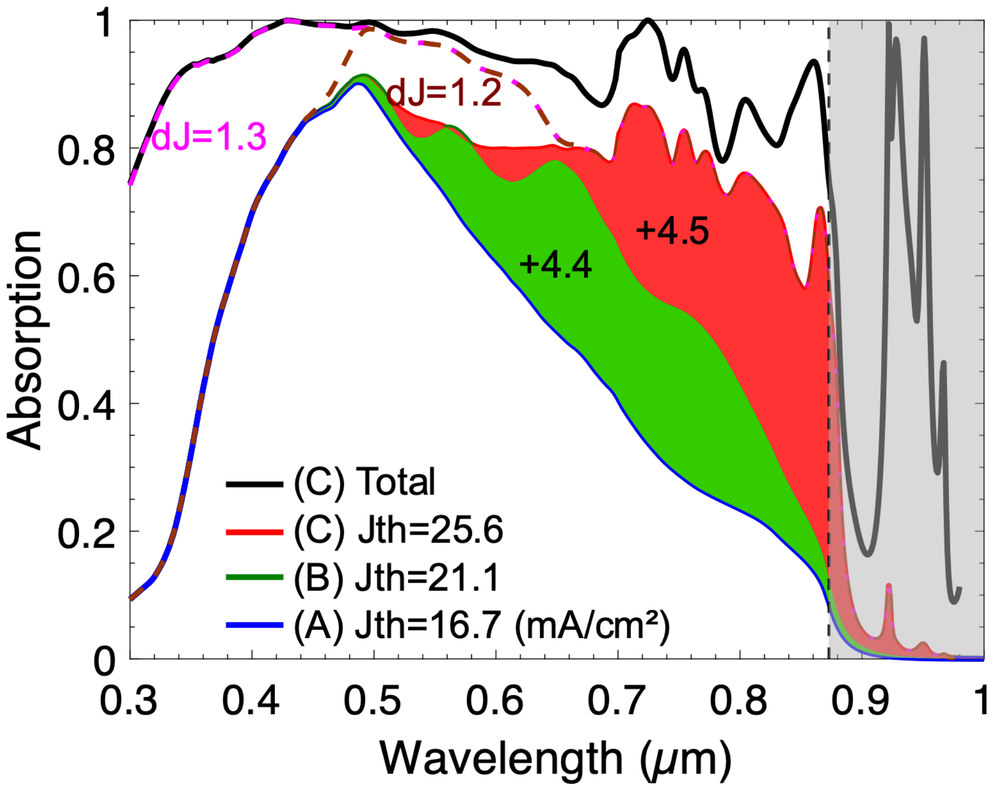
SPIE OPTO, WCPEC-8

- **Window layer & BSF introduce more losses than in Si**
  → No Sim. Results exceeding Lamb. Model
- **Flat Ag mirror (+ spacer) mandatory to reduce its losses**

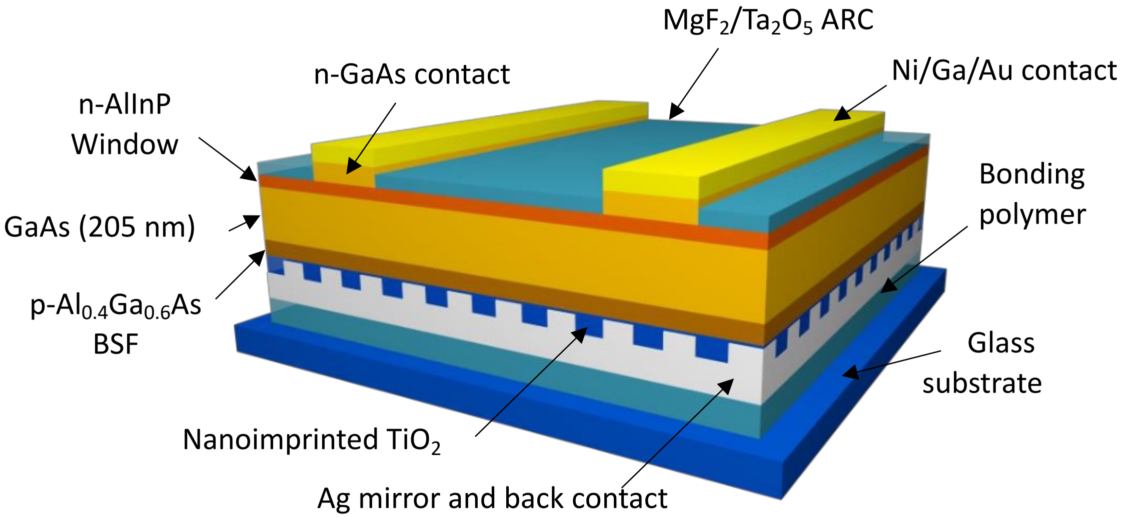
Ultra-thin (205 nm) GaAs solar cell: design

Electromagnetic simulations (RCWA) of:

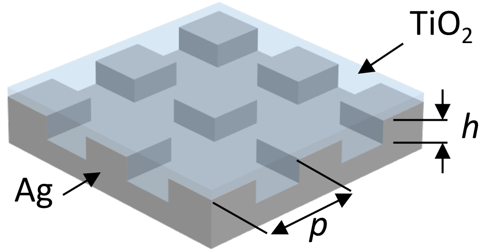
- Non-transferred solar cell (single-pass)
- Transferred on flat Ag mirror (double-pass)
- Transferred on nanostructured TiO_2/Ag mirror (multi-resonant absorption)



Design of the Solar cell with nanostructured TiO2/Ag mirror



Detail of the TiO_2/Ag mirror



a-TiO_2 n=1.9
p = 700 nm
h = 120 nm
d = 420 nm

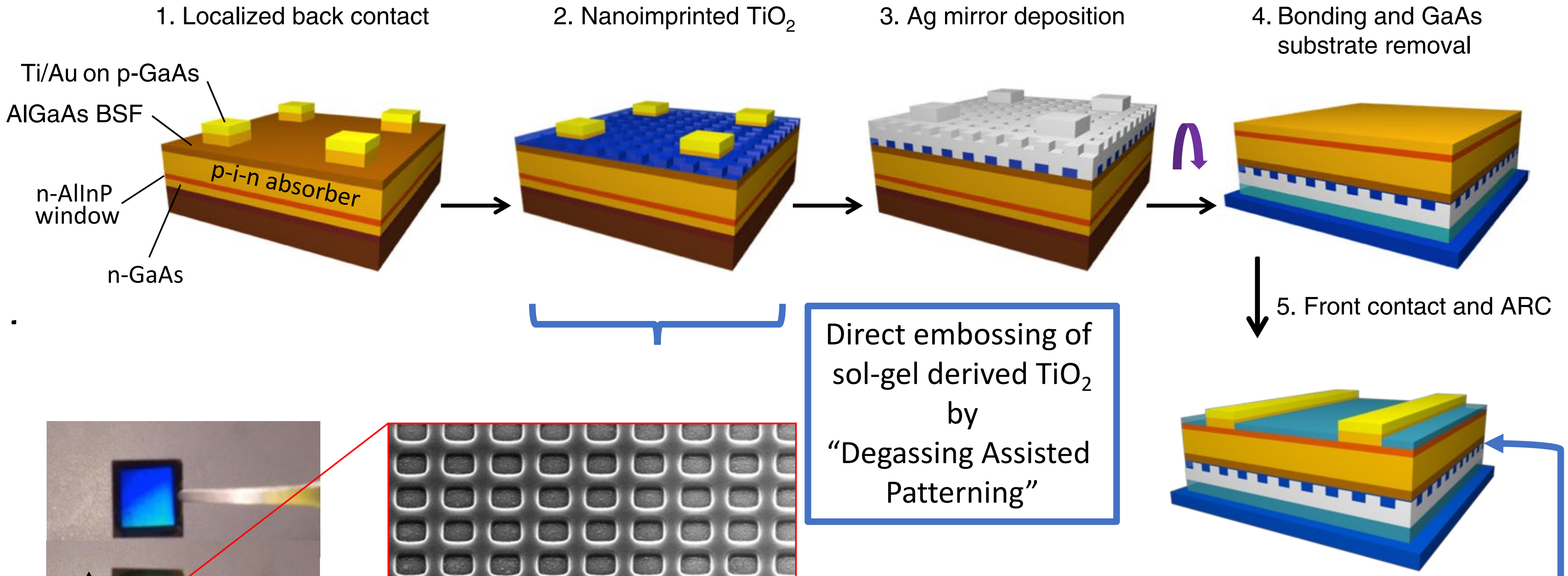
Nature Energy, 4, 761 (2019)

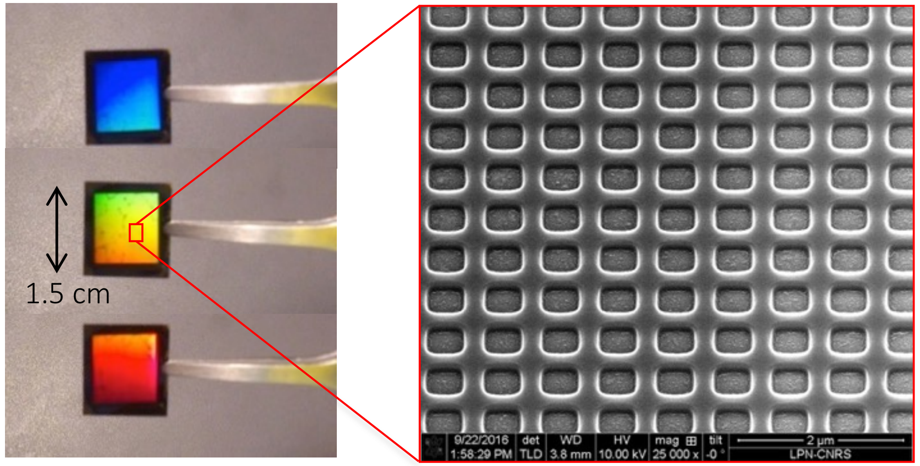
Ultra-thin GaAs solar cell: fabrication process

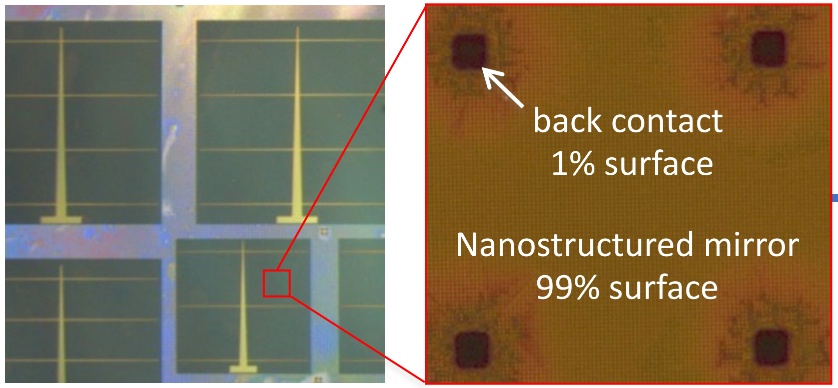
Solar cell epitaxially grown upside-down at

Fraunhofer ISE

Material	Function
p-GaAs	Contact layer
p-$Al_{0.4}Ga_{0.6}As$	BSF
p-GaAs	Base
i-GaAs	
n-GaAs	Emitter
n-AlInP	Window
n-$Ga_{0.87}In_{0.13}As$	Cap (Si) layer
n-GaAs	Cap (Si) layer
n-AlGaAs	Etch stop
n-GaAs	Buffer

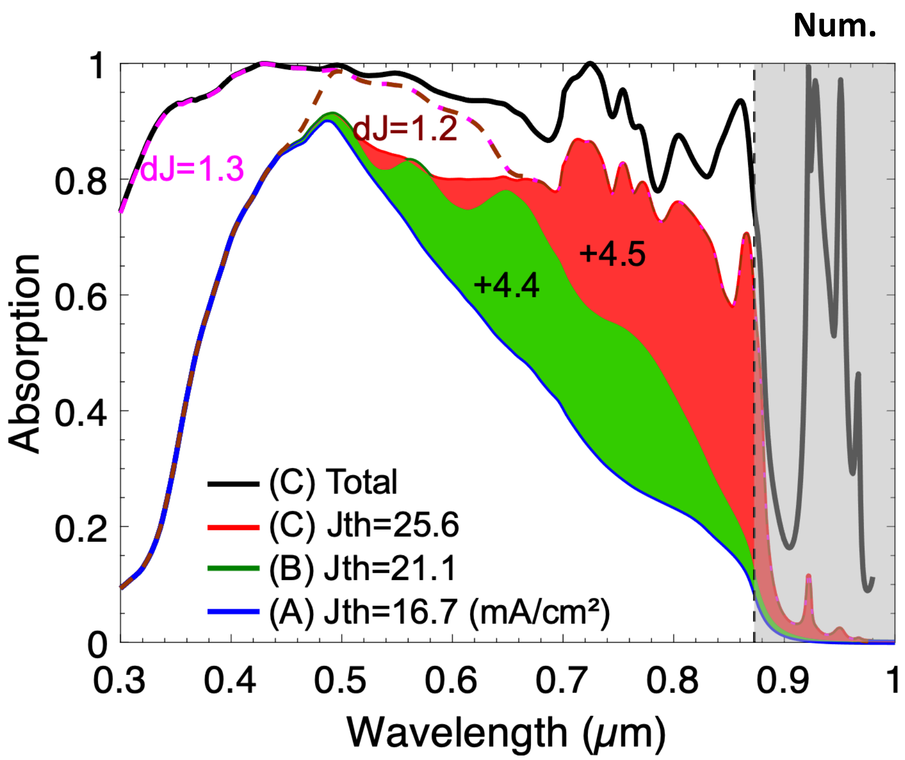


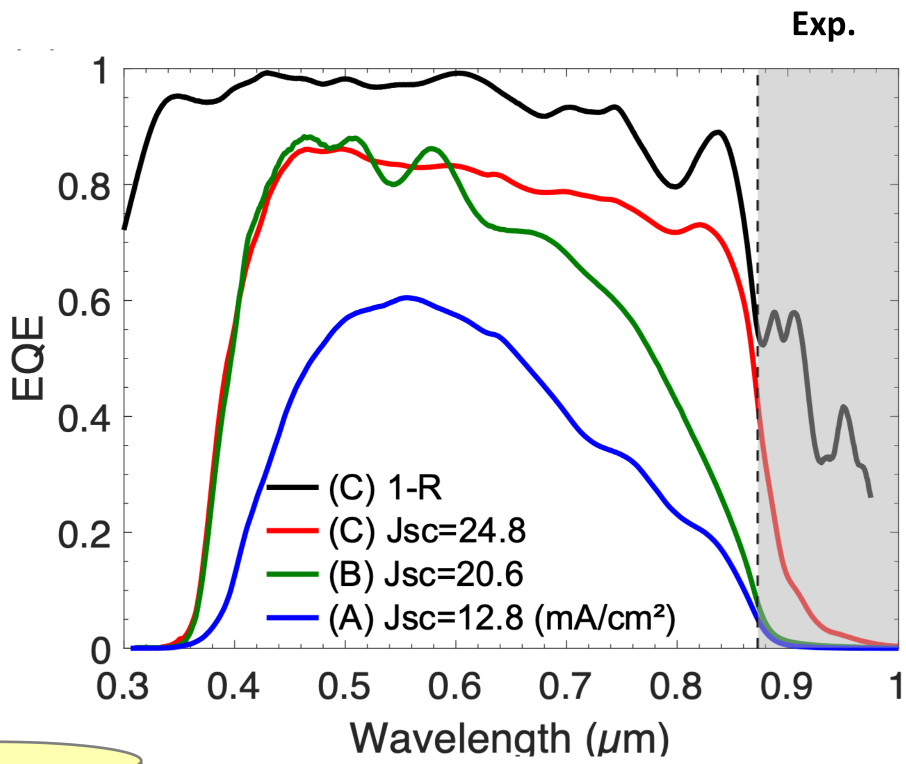




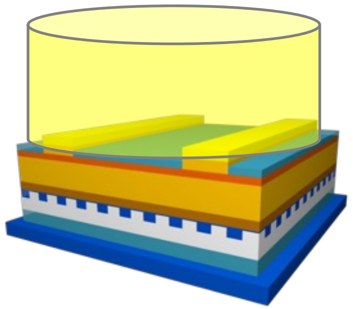
Nature Energy, 4, 761 (2019)

EQE – Num. vs Exp.



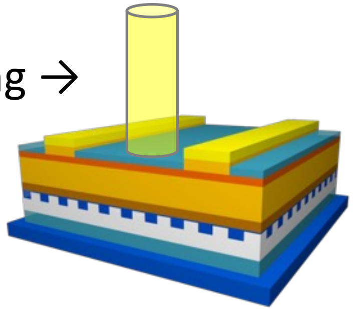


Predicted J_{SC}^{th}= 25.6 mA/cm^2

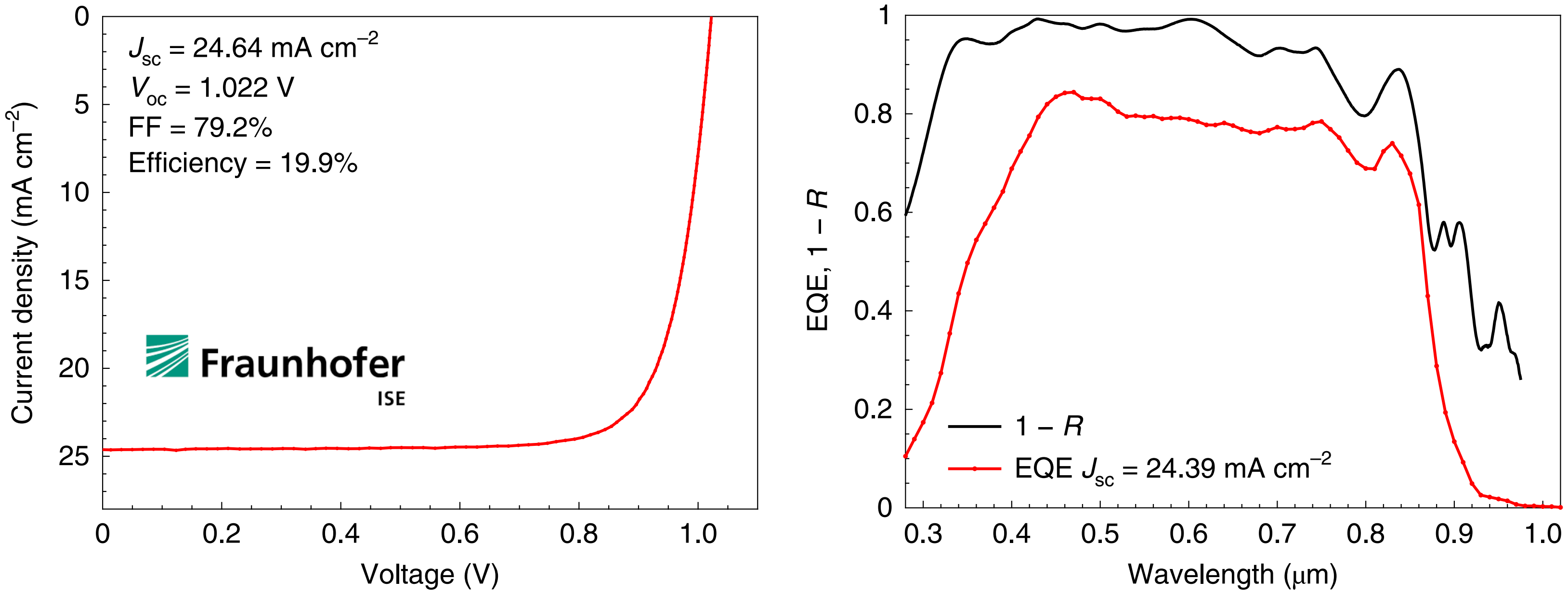


← Exp. J_{SC}^{exp} = 24.8 mA/cm^2

Exp. no "fingers" shadowing →
J_{SC}^{epx}= 25.2 mA/cm^2



I-V, EQE



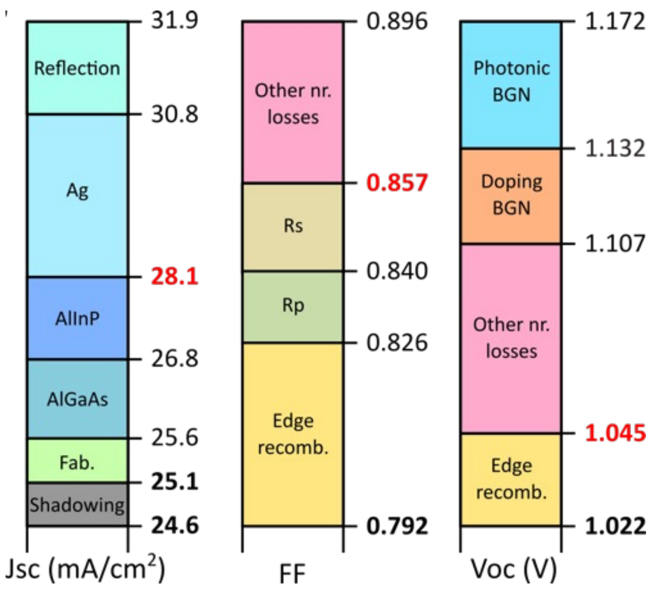
$J_{SC}{}^{th}$= 25.6 mA/cm² (num.) $J_{SC}{}^{exp.}$= 24.64 mA/cm² (Exp.) **ΔJ_{SC} = -0.8 mA/cm²**

+ 11.9 mA/cm² (48%) compared single-pass abs.

+ 3.6 mA/cm² (15%) compared flat Ag mirror

H.L. Chen, A. Cattoni et al., Nature Energy, 4, 761 (2019)

Detailed loss analysis and path to 25%



- Lowering parasitic absorption in Ag mirror (↑ J_{SC})
- Optimized front contact design (↑ J_{SC}, FF)
- Larger surface area: 3 × 3 → 10 × 10 mm (↑ V_{OC})

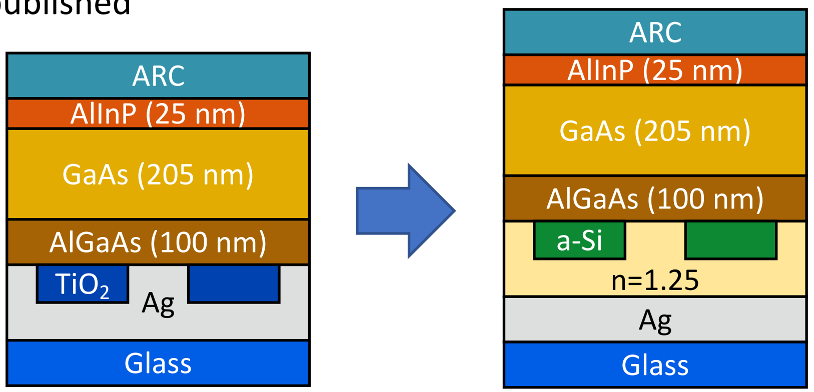
J_{SC}= 24.64 → 28 mA/cm^2

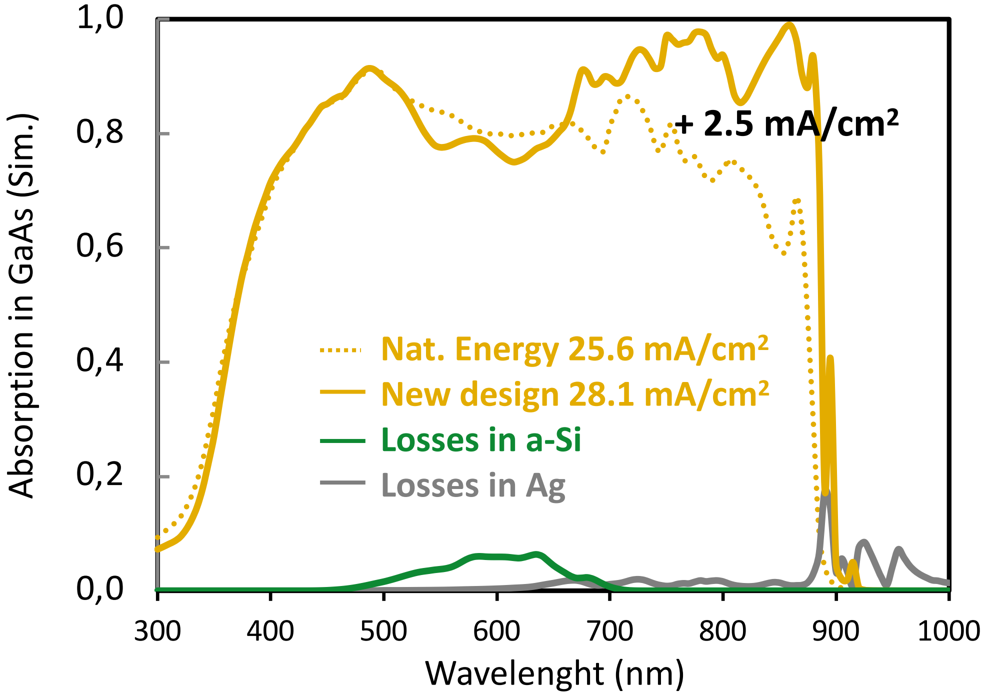
FF = 0.792 → 0.857

V_{OC} = 1.022 → 1.045 V

η^{th} = 25.1%

unpublished



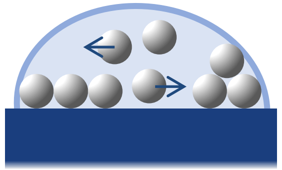


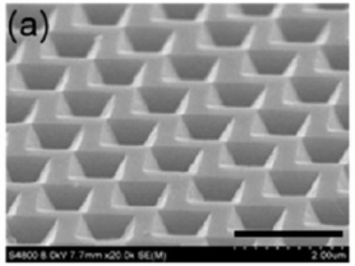
H.L. Chen, A. Cattoni et al., Nature Energy, 4, 761 (2019)

Unpublished

Low-cost nano-structuration

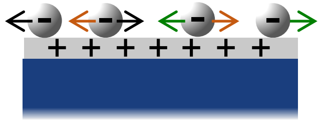
Nanospheres lithography

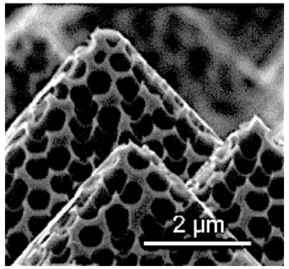




Gao et al., *Nano Letters* **15**, 4591 (2015)

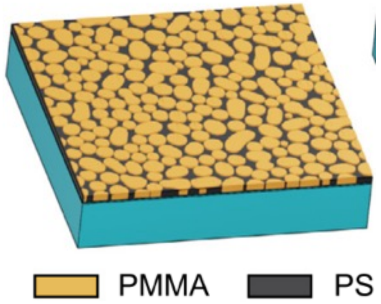
Sparse Nanospheres lithography

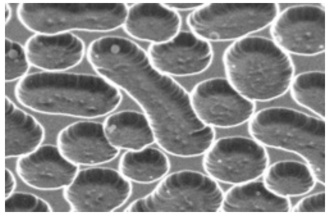




Massiot et al., *Nanoscale **8**, 11461 (2016)*
Piechulla, Adv. Optical Mater. 6, 1701272 (2018)

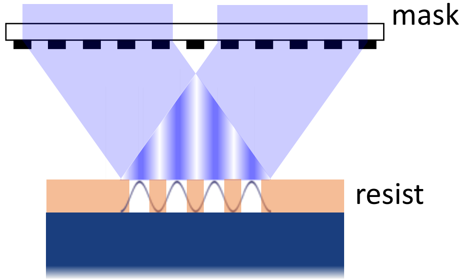
Polymer blend lithography

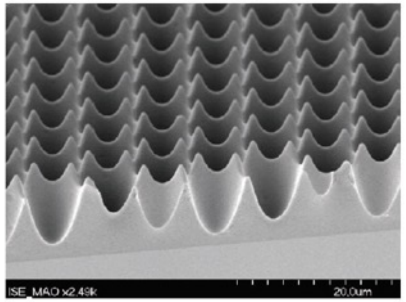




Buencuerpo et al., Nano Energy 96, 107080 (2022)

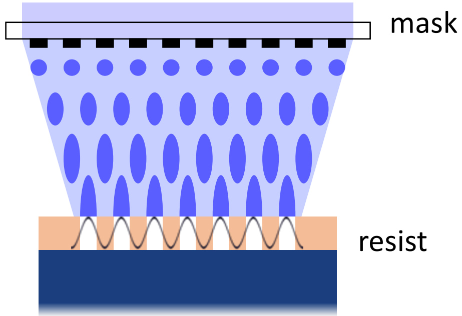
Interference Lithography

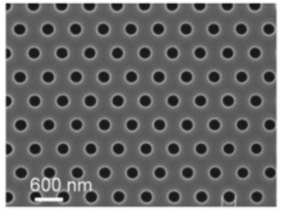


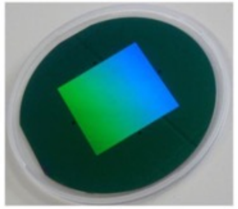


Wolf et al., *Microelectr. Engineer.* **98**, 293 (2012)
Blasi et al., Energy Procedia 8, 712 (2011)

Talbot Lithography







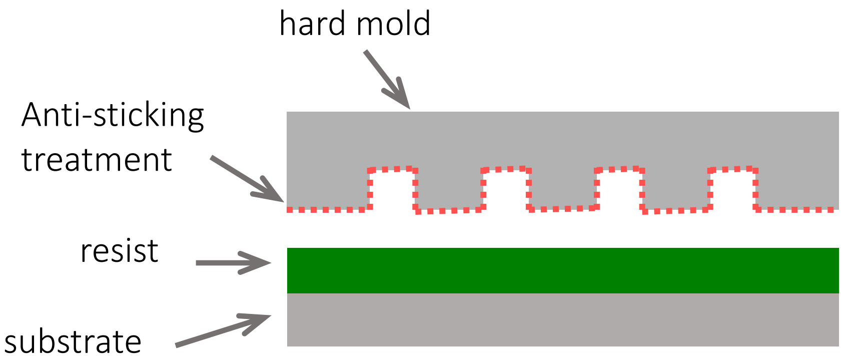
Fan et al., *Microelectr. Engineer.* **155**, 55 (2016)
Solak et al., *Opt. Express* **19**, 10686 (2011)

Nanoimprint lithography

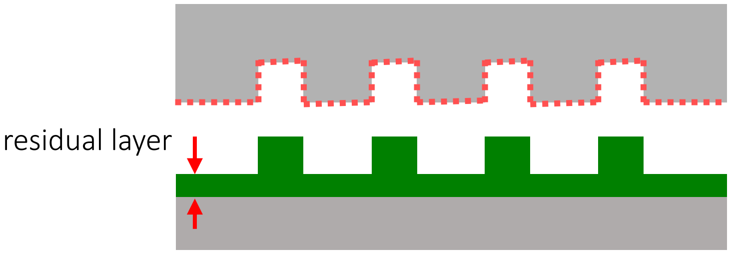
Roll-to-plate Nanoimprint

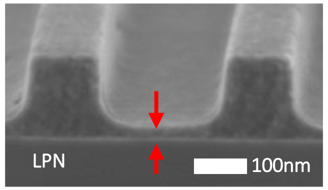
Nanopatterning by Replication

Nanoimprint Lithography (NIL)

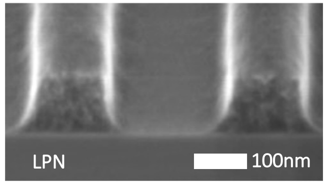


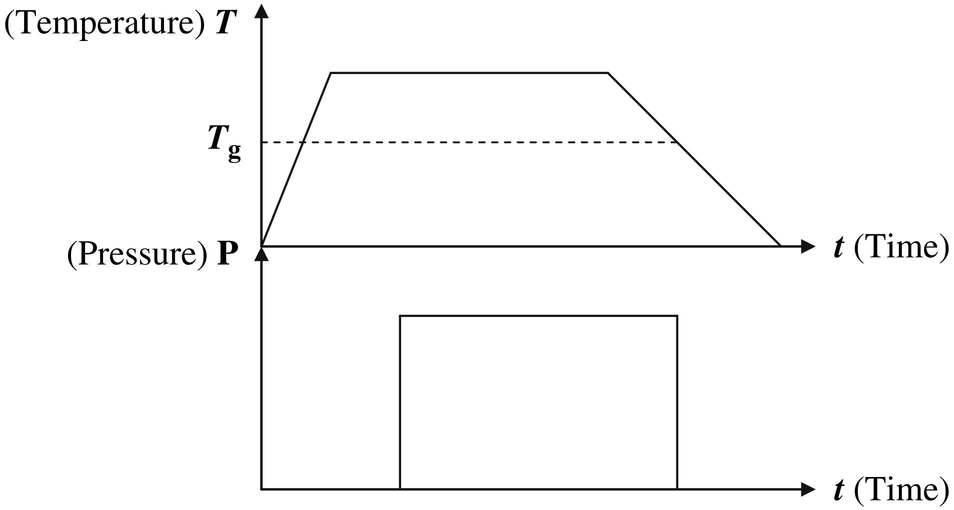
1) Imprinting at high pressure and temperature





2) Pattern Transfer by Reactive Ion Etching





- **Hight Temperature:** T > glass transition temperature of the thermoplastic resist
- **High Pressure:** in order to have conformal adhesion and homogeneous residual layer)

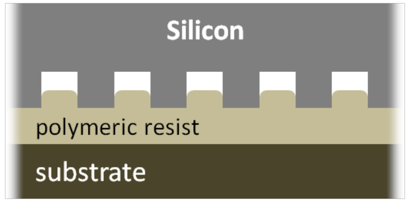
- Parallel process (like optical lithography)
- No diffraction-limited
- No proximity effects

S.Y. Chou et al., APL **67**, 3114 (1995)

Nanoimprint Lithography: variations on a Theme

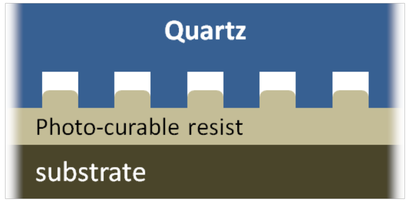
POLITECNICO
MILANO 1863

T NIL



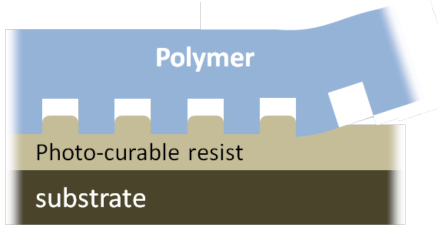
- High Pressure
- Hight Temperature

UV NIL / Step&Flash

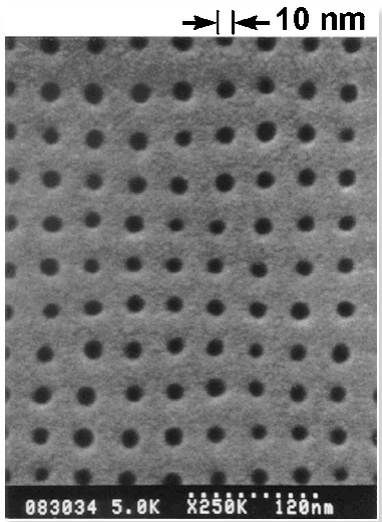


- Lower Pressure
- Room Temperature

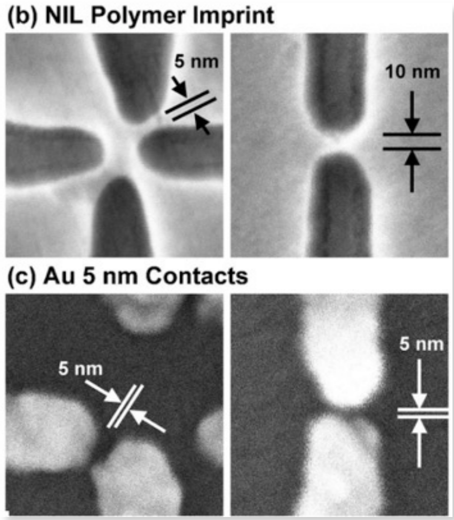
Soft UV NIL



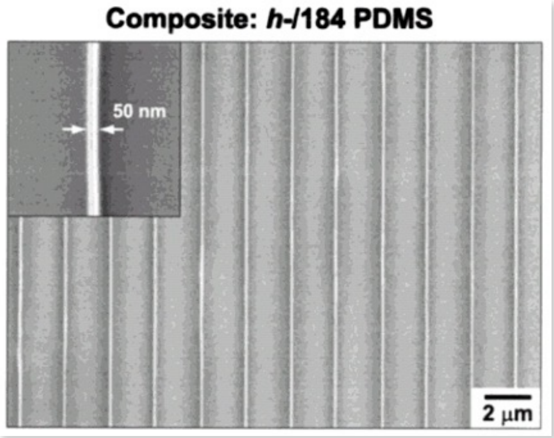
- Low Pressure (< 1 atm)
- Room Temperature
- Cheap
- Flexible/curved substr.



J. Vac. Sci. Tech. B **15**, 2897 (1997)



APL **84**, 5299 (2004)

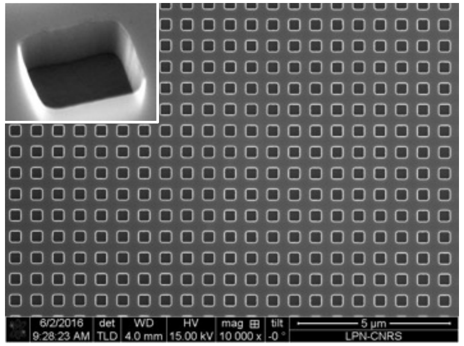


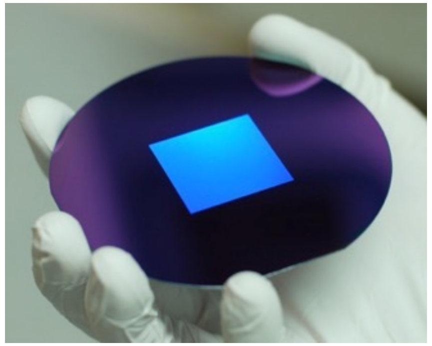
Langmuir **18**, 5314 (2000)

Soft UV Nanoimprint Lithography (Soft-UV NiL)

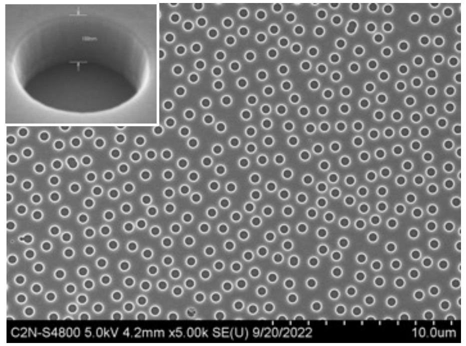
1) Silicon master mold fabricated by a “low-cost” patterning method

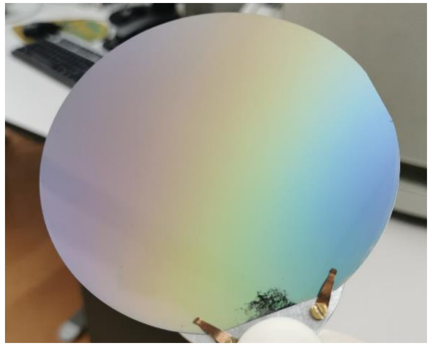
E-beam lithograpphy and RIE





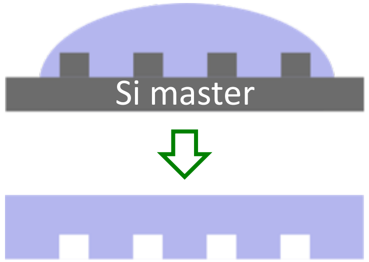
Sparse nano-spheres lithograpphy and RIE

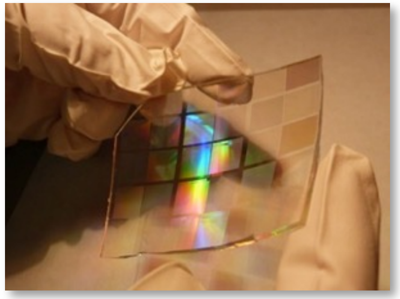




2) Replica in a cheap and flexible polymeric stamp

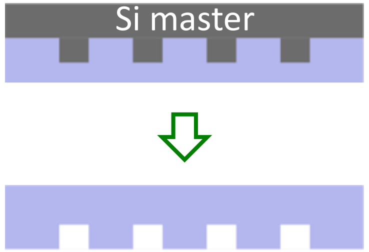
1) Pour of pre-polymer PDSM on Si master
2) Thermal curing & peel-off of the PDMS stamp

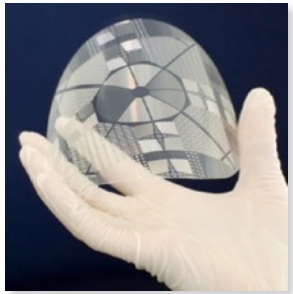




hard-PDMS/PDMS stamp (LPN)

1) T-NIL in flexible polymer foil
2) Peel-off of the polymer foil

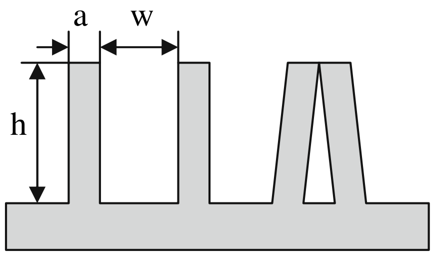




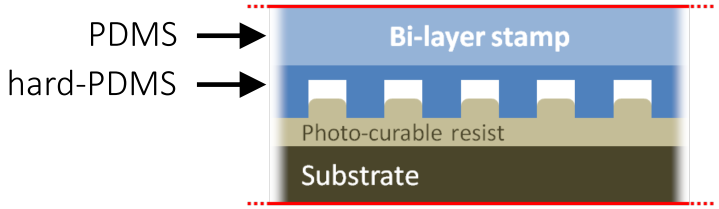
IPS Polimer (Obducat)

Poly(dimethylsiloxane) (PDMS)

- Elastomer: conformal contact with a (non)planar surface on without applying any pressure
- Low surface energy (22 mJ m–2): simple peel off (large surface area)
- Chemically inert
- Optically transparent (UV curing)
- Low Young's modulus (≈2 MPa) → Structure collapse if h/a is too large
  → Fails to replicate sub-100 nm structures



→ « Hard-PDMS »/PDMS bi-lauyer stamp

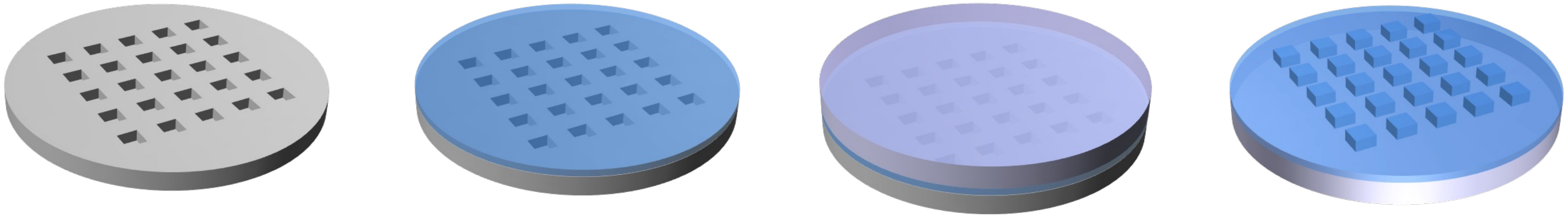


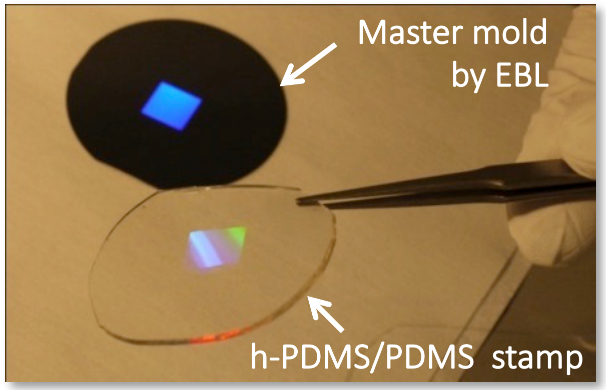
1) Si master mold by EBL and dry-etching

2) Spin-coating of pre-polymer hard-PDMS

3) Casting of PDMS, soft baking 60 ° C

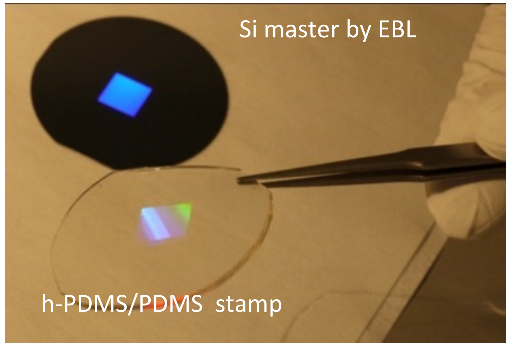
4) Demolding, anti-sticking treatment



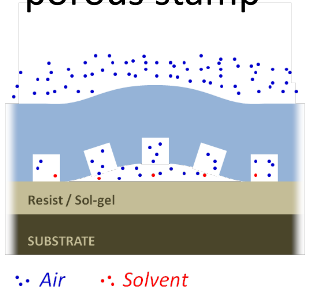


Odom et al, Langmuir 18, 5314 (2000)
"Soft UV Nanoimprint Lithography: a versatile tool for nanostructuration at the 20 nm scale" A. Cattoni, et al., in "Recent advances in Nanofabrication Techniques and Application" edited by Bo Cui, Intech (2011).

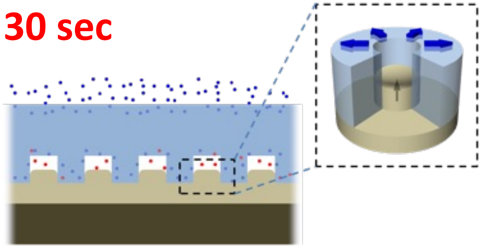
Degassing Assisted Patterning (DAP)



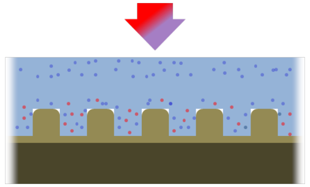
Degassing
porous stamp



Molding
ΔP → air/solvents/ resist
30 sec



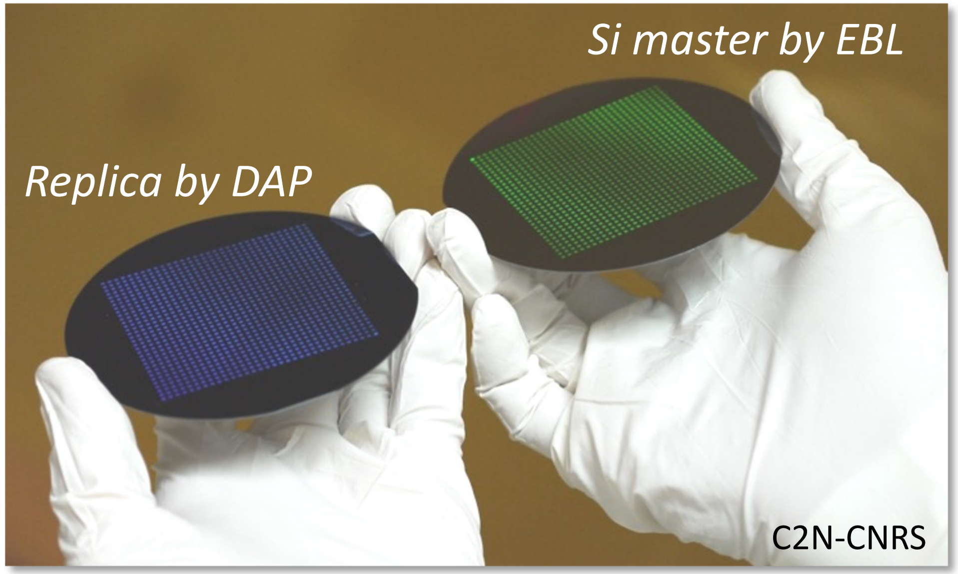
Sol-gel tabilization
T = 100 °C
2 min



Sol-gel crystallization
T = 450 °C
5 min

(TiO2 Anatase)

- No imprinter machine
- No pressure → no deformations
- Bubble-defects-free
- UV-curable commercial resist & dense/porous sol-gel derived films (TiO_2, SiO_2, Al_2O_3, IrO_2…)
- Large area imprint

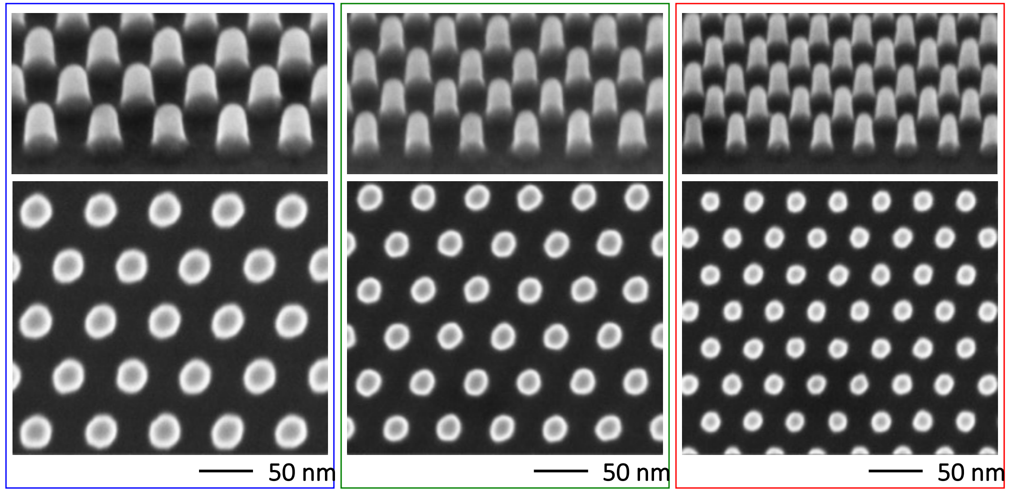


Cattoni 36th MNE (2010) / Biotech. & Bioengineer. 105, 854 (2010) / Adv. Funct. Mat. 26, 81 (2016)

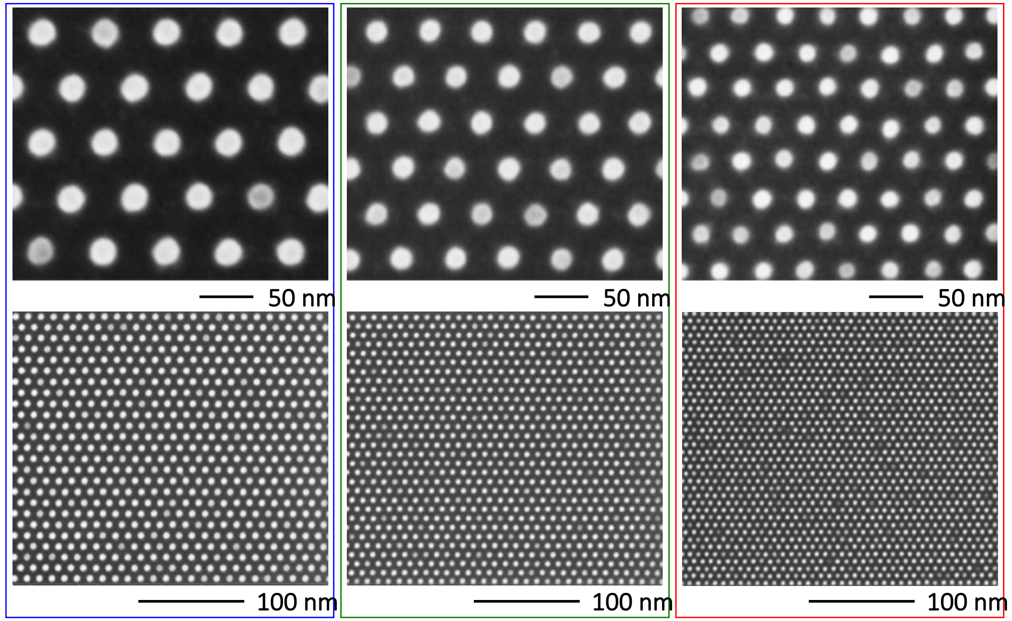
Degassing Assisted Patterning (DAP)

Si master

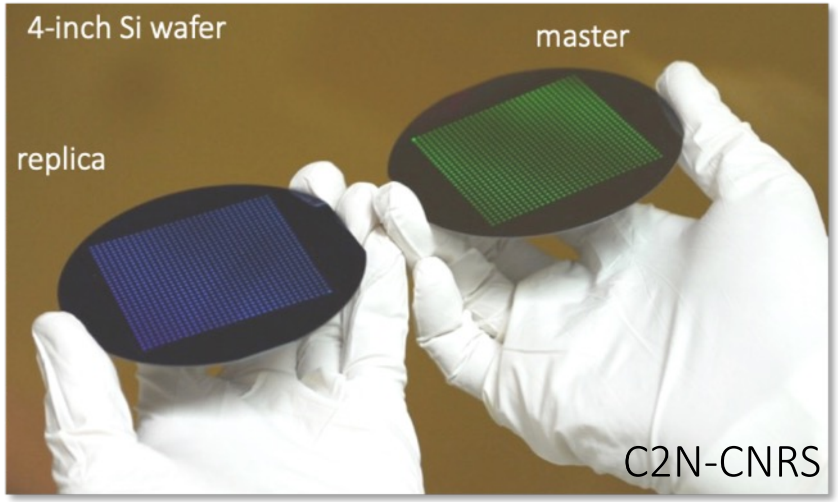
60 nm pitch, μ =32 nm | 50 nm pitch, μ =25 nm | 40 nm pitch, μ =19 nm



Replica by DAP



- Higher resolution as compare conventional Soft UV Nanoimprint (up to 20 nm)
- No imprinter machine (dessicator + pump + UV lamp = 1 K$ vs. 200 K$ and more for S&F)
- No pressure → no deformations
- Bubble-defects-free
- Large area imprint



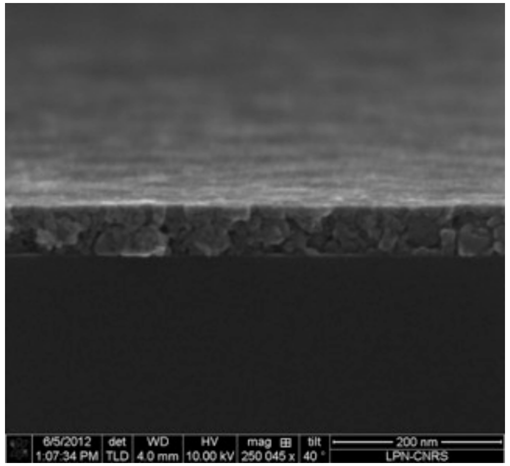
DAP for direct embossing of sol-gel derived films (TiO_2)

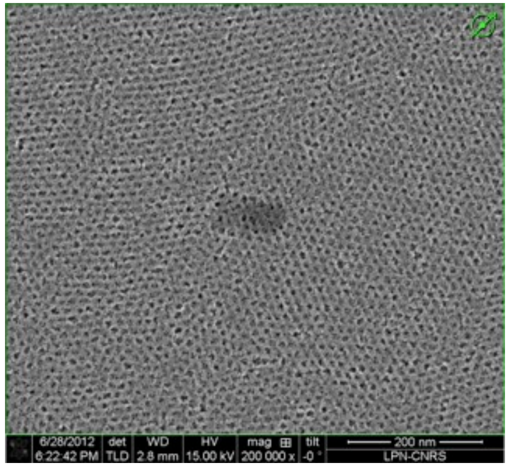
POLITECNICO MILANO 1863

TiO_2 Sol-gel by hydrolysis of Ti alkoxide precursors:

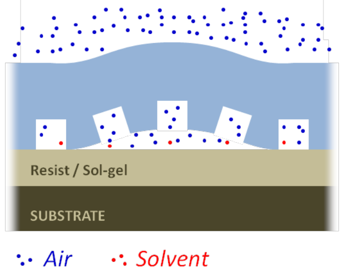
- Titanium alkoxide
- Ethanol
- Water
- (surfactants → porosity)

Spin or dip-coating → amorphous film
Thermal processing (450 ° C) → crystal phase (TiO_2 Anatase)

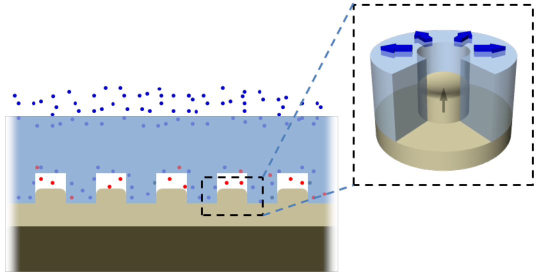




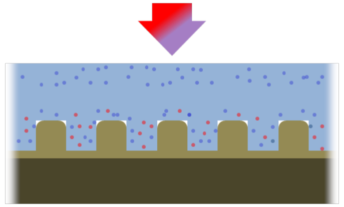
1) PDMS stamp degassing
(τ ≈ 5 min)
2) Sol-gel spin-coating
3) PDMS stamp molding



4) ΔP → air/resist/solvents
(**1 min**)



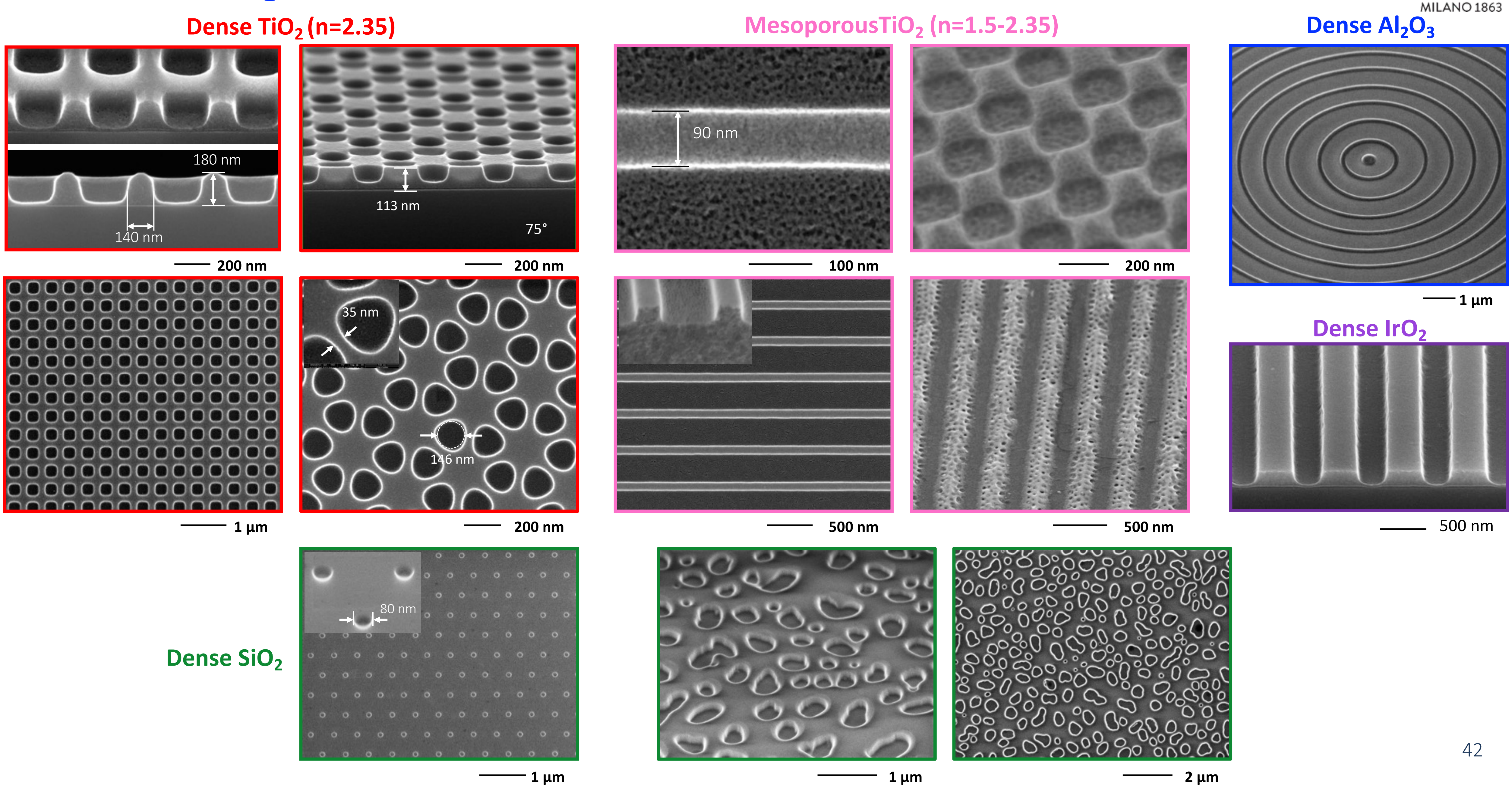
5) Sol-gel stabilization
(T = 110 °C, **3 min**)



6) Sol-gel crystallization
(T = 450 °C)

(Anatase, n = 1.8 ⟶ 2.4)

DAP of sol-gel derived films



Outlook

- TODAY > Solar cell efficiency close to Schottky-Queisser
  > Solar cell thickness far from Lambertian model

- At least 1/10 thickness reduction possible for all technologies. Advantages:

  > Reduce fabrication process and/or increase throughput

  > Improve lifetime and power production by preventing heating

  > Improve carrier collection in defective/degraded absorber materials → new/cheaper absorber materials

- Coherent or incoherent scattering? Coherent! (symmetry, hyperuniform, etc.)

- We need cheap nano-structuration technologies: NIL is a good option