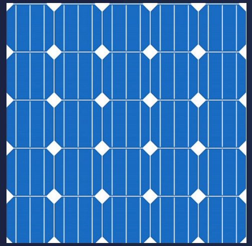


Modern light harvesting

Latest techniques in Photovoltaics

Leonardo Lucchesi

DEPARTMENT OF PHYSICS "ENRICO FERMI"

IN SUPREMÆ DIGNITATIS · 1343 ·
UNIVERSITÀ DI PISA

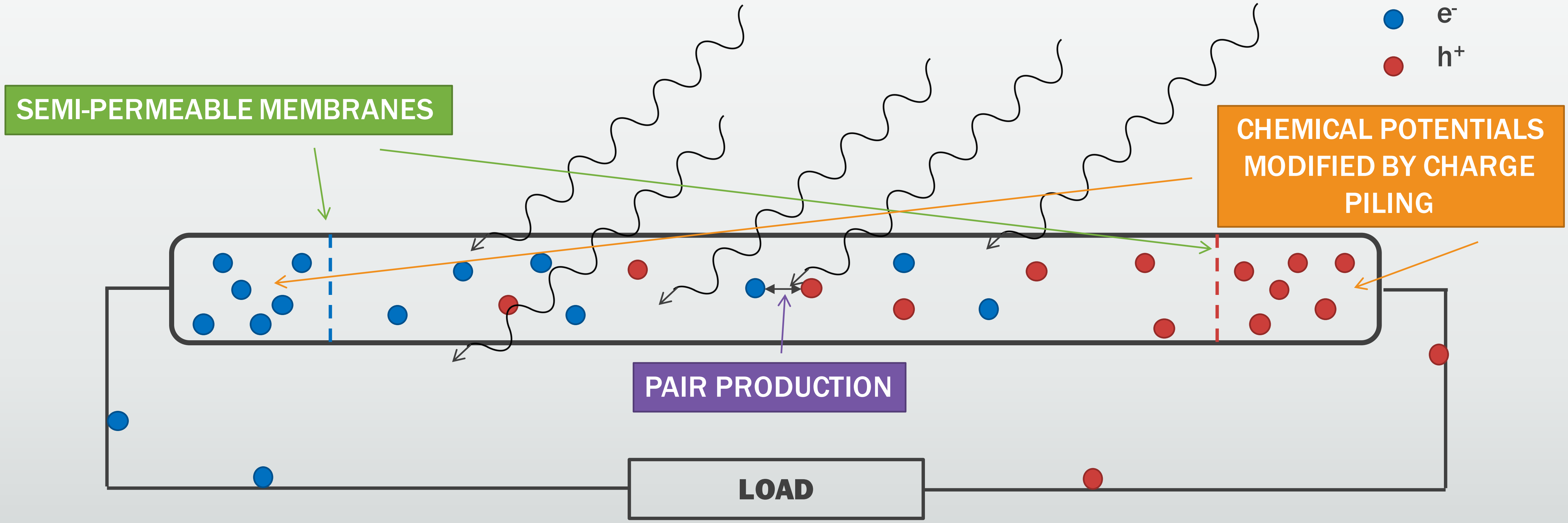
PRESENTATION OUTLINE

1. Introduction & Motivation
2. Solar cell processes
3. Overview on existing technology
4. Latest techniques & outlooks

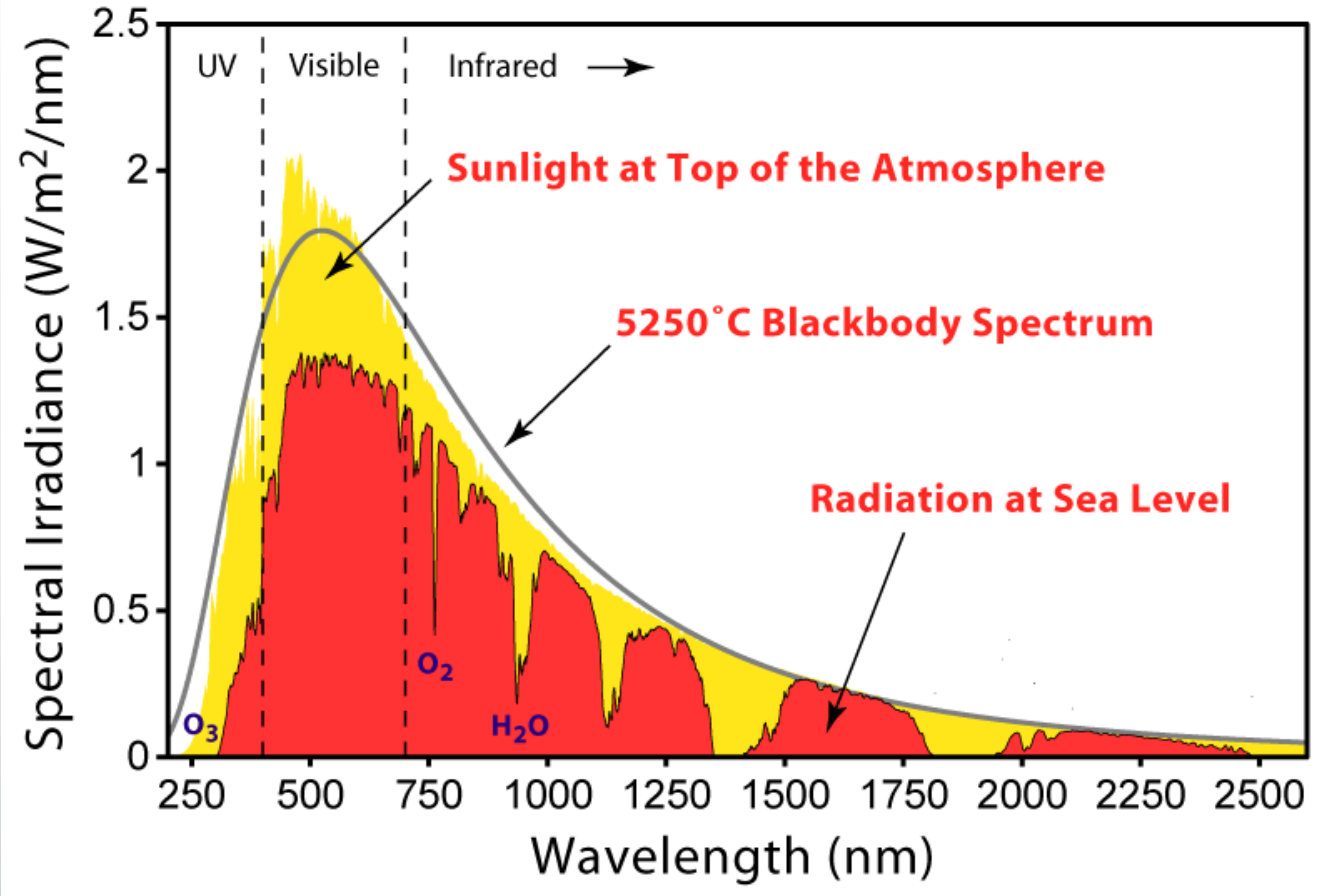
Introduction & Motivation

A GENERAL SOLAR CELL

or the shortest explanation of a solar cell I can think about



THE SOLAR SPECTRUM



Varies quite strongly with position on Earth

AVERAGE POWER
~ 1 kW/m²

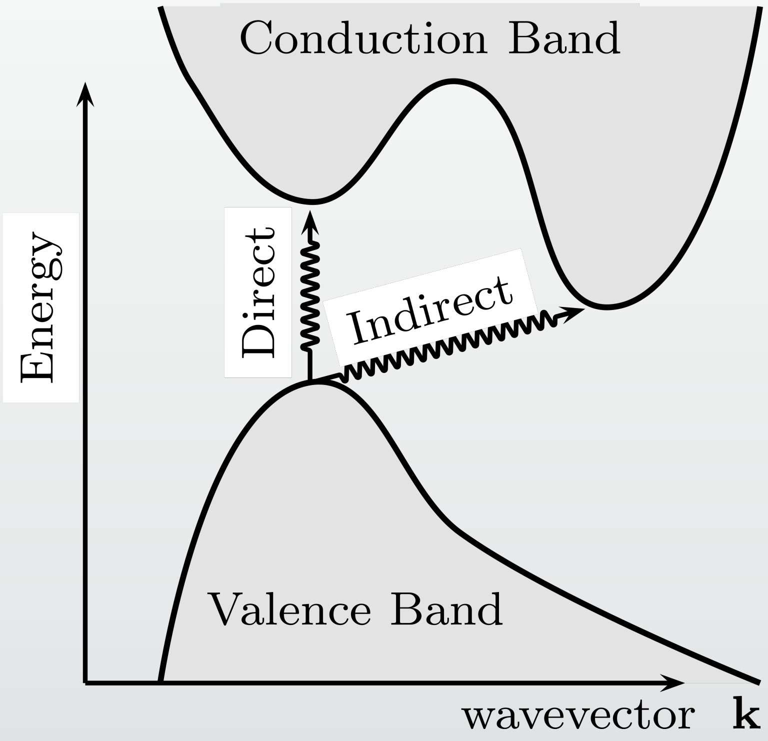
Solar cell processes

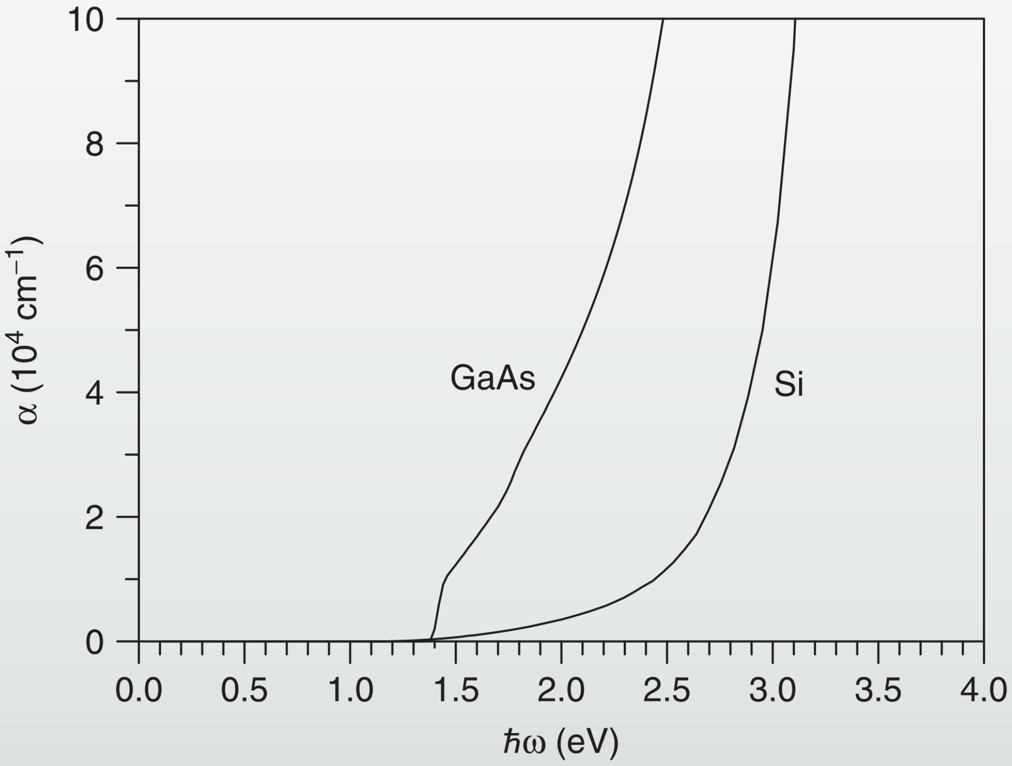
Efficiency & Shockley-Queisser (SQ) limit

adapted from P. Würfel & U. Würfel, *Physics of Solar Cells* , Wiley-VCH, 2010

LIGHT ABSORPTION

Photons are absorbed by causing a transition from valence to conduction band, creating an electron-hole couple





$\tau \sim$ 1-10 fs

DIRECT

$$\hbar\omega = \varepsilon_G + \frac{p^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) = \varepsilon_G + \frac{p^2}{2m_{comb}}$$

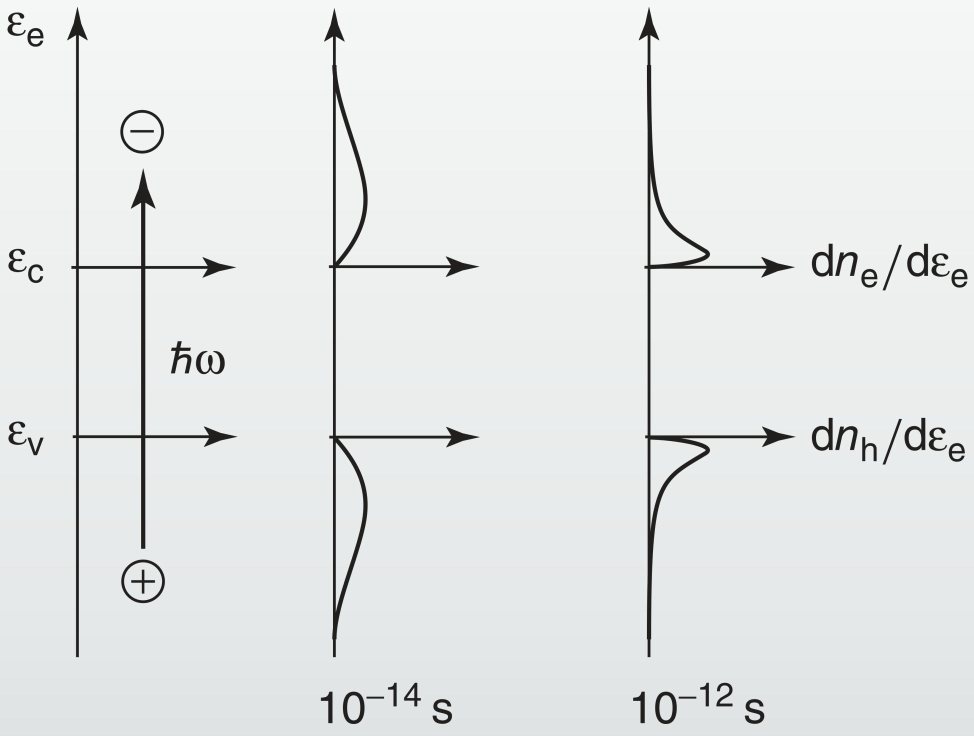
$$\alpha(\hbar\omega) \propto D_{comb}(\hbar\omega) = \frac{4\pi}{h^3}(2m_{comb})^{3/2}(\hbar\omega - \varepsilon_G)^{1/2}$$

INDIRECT

$$\alpha(\hbar\omega) \propto \int_0^{\hbar\omega \pm \hbar\Omega - \varepsilon_G} D_C(\varepsilon_{e,kin}) D_V(\hbar\omega \pm \hbar\Omega - \varepsilon_G - \varepsilon_{e,kin})\, d\varepsilon_{e,kin}$$

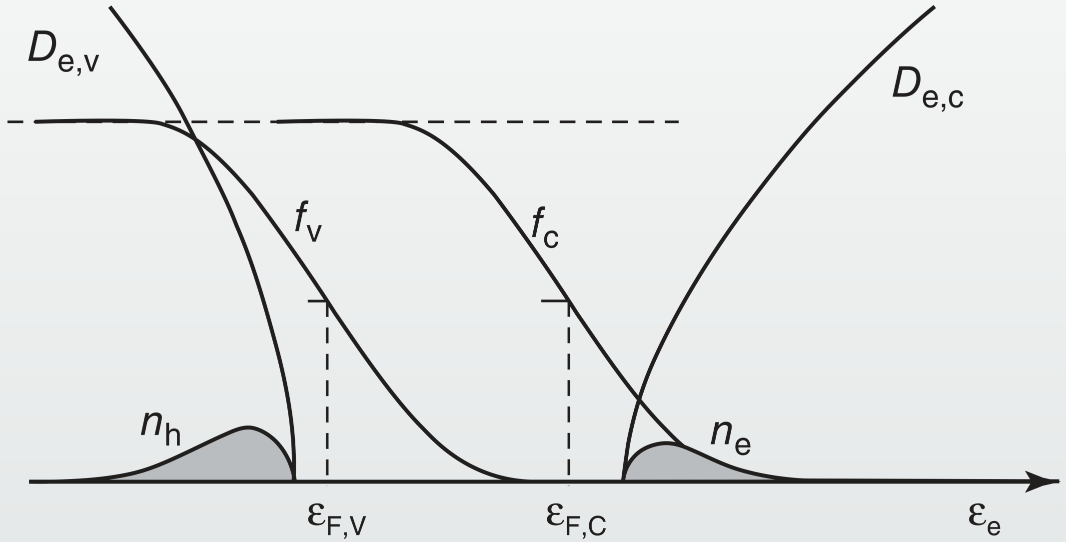
THERMALIZATION

Electron and holes separate and thermalize via phonon scattering



$\tau \sim 0.1\text{-}10$ ps

Quasi-Fermi distributions



Distribution of electrons in valence band states described by different distribution function than conduction band states. They differ only in their chemical potential μ

f is DISCONTINUOUS

CARRIER EXTRACTION

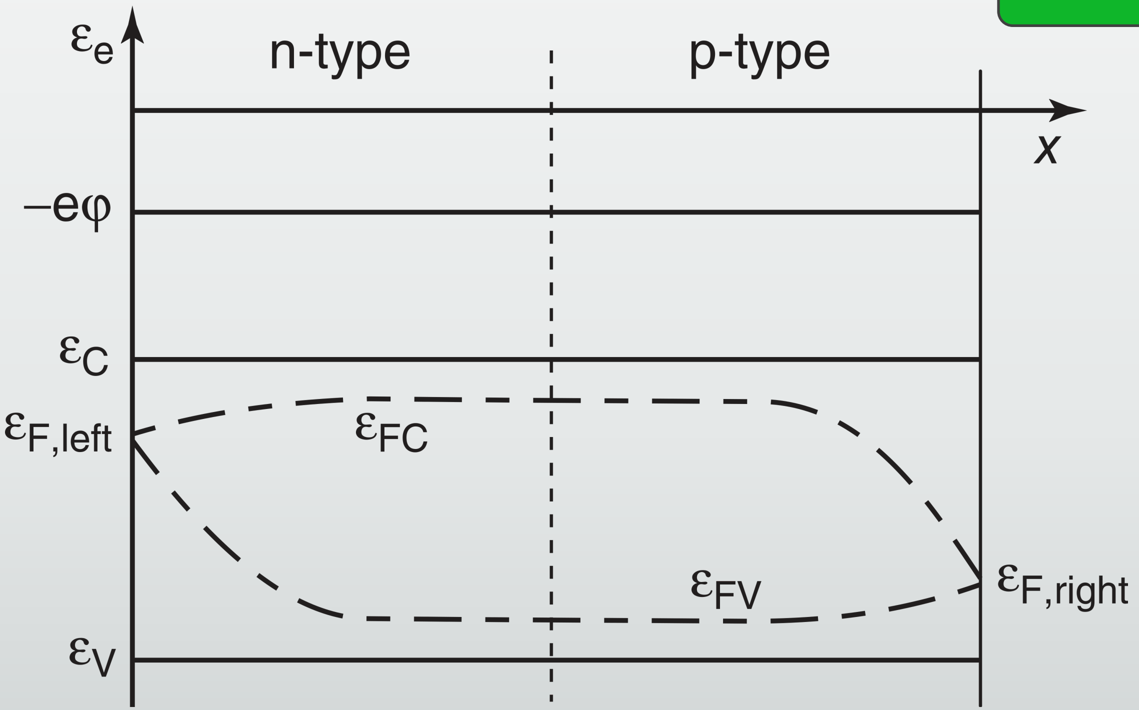
Electrons and holes diffuse through semi-permeable media, creating 2 regions with different chemical potentials

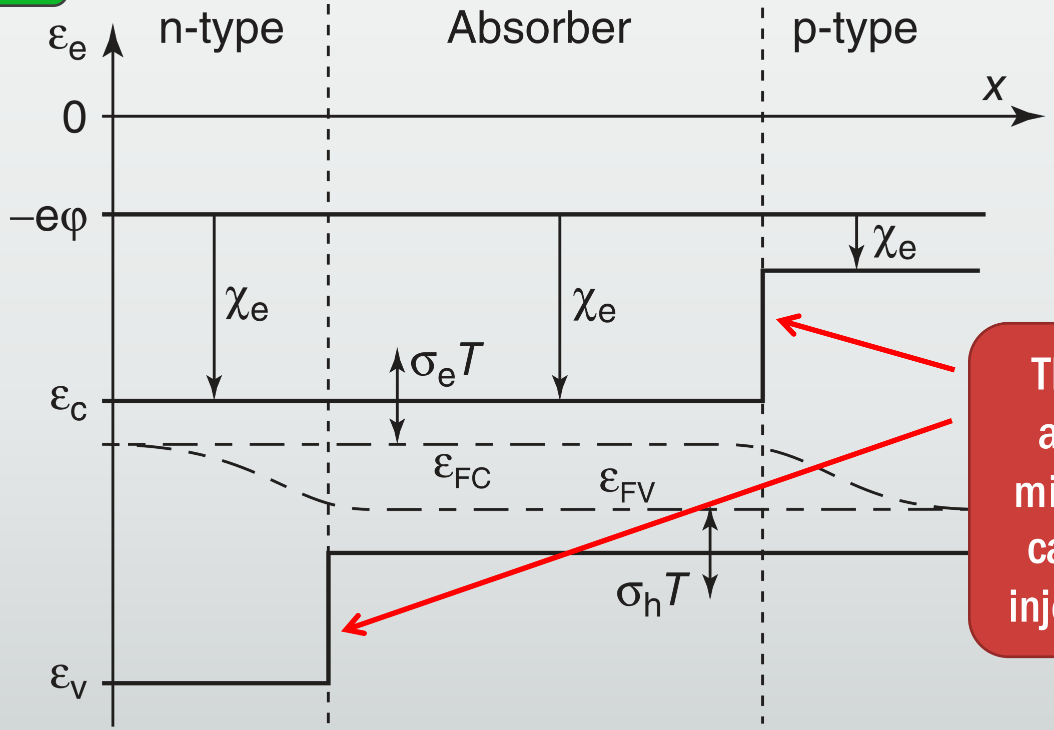
FIELD-DIFFUSION EQUATIONS

$$j_{Q,i} = -\frac{\sigma_i}{z_i e}\left\{\mathrm{grad}\,\mu_i + \mathrm{grad}\,(z_i e \varphi)\right\} = \frac{\sigma_i}{e}\mathrm{grad}\,\varepsilon_{Fi}$$

$$\sigma_i = z_i^2 e^2 n_i \tau_{c,i} / m_i^*$$

$\tau \sim 0.1$-10 ns





These avoid minority carrier injection

RADIATIVE RECOMBINATION

Absorption inverse process: electron and hole annihilate into a photon

Direct solution is complicated, involves **quantum open systems** physics.

Shockley - Queisser → DETAILED BALANCE can provide a solution

"QUASI-EQUILIBRIUM" PICTURE → Recombination rate proportional to product of carrier densities

$$G_\gamma = R_e = R_h = B n_e n_h$$

At equilibrium conditions (with 300 K black body radiation), DETAILED BALANCE principle imposes

$R_e^0 = G_e^0 = B n_e^0 n_h^0$ with $n_e^0 n_h^0 = n_i^2$ intrinsic concentration of carriers

but generation of pairs is equal to the absorbed radiation

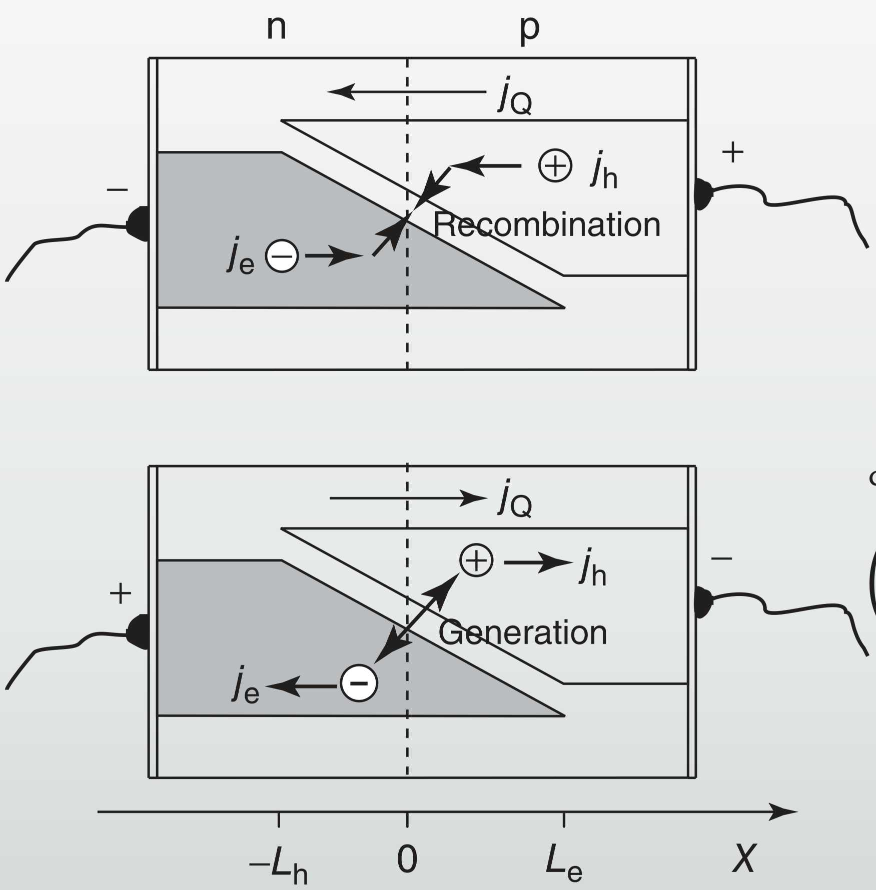
$$G_e^0 = \frac{\Omega}{4\pi^3 \hbar^3 c^2} \int_0^\infty \frac{\alpha(\hbar\omega)(\hbar\omega)^2}{\exp\left(\frac{\hbar\omega}{kT_0}\right) - 1} \, d\hbar\omega$$

with $\alpha(\hbar\omega)$ being the absorption coefficient

$\tau \sim 1$ - 1000 ns

SOLAR CELL ELECTRONICS

The maximum power needs to be a compromise between extraction (j) and generated voltage bias (V)



$$j_Q = -e\int_{-L_h}^{L_e} \mathrm{div}\, j_h \, dx$$

$$\mathrm{div}\, j_h = G_h^0 + \Delta G_h - R_h$$

$$R_h = R_h^0 \frac{n_e n_h}{n_i^2} = R_h^0 \exp\left(\frac{\varepsilon_{FC}-\varepsilon_{FV}}{kT}\right)$$

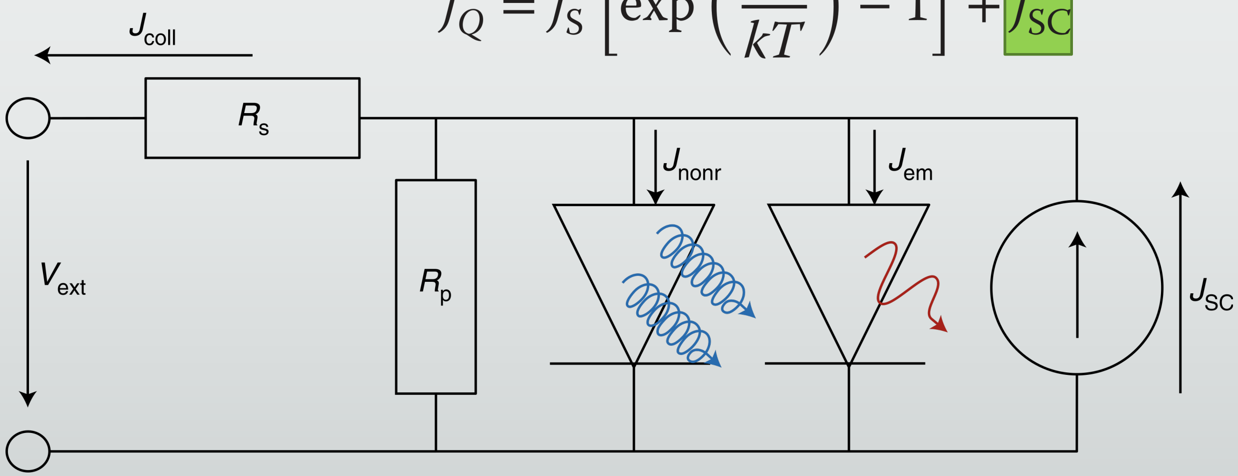
$$j_Q = -e\int_{-L_h}^{L_e} \left\{ G_h^0 \left[1 - \exp\left(\frac{\varepsilon_{FC}-\varepsilon_{FV}}{kT}\right)\right] + \Delta G_h \right\} dx$$

$$j_Q = j_S \left[\exp\left(\frac{eV}{kT}\right) - 1\right] + j_{SC}$$

$$d(j_Q V) = dj_Q V + j_Q dV = 0$$

$$\left(\frac{dj_Q}{dV}\right)_{mp} = -\left(\frac{j_Q}{V}\right)_{mp}$$

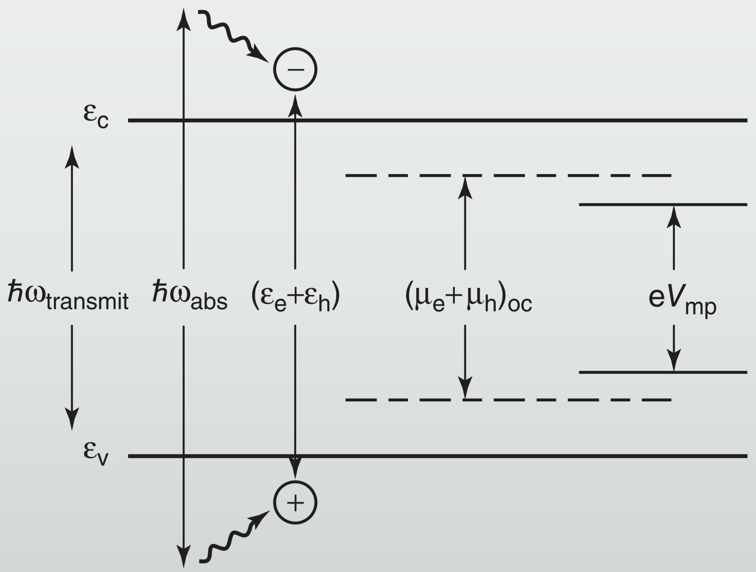
$$FF = \frac{j_{mp} V_{mp}}{j_{sc} V_{oc}}$$



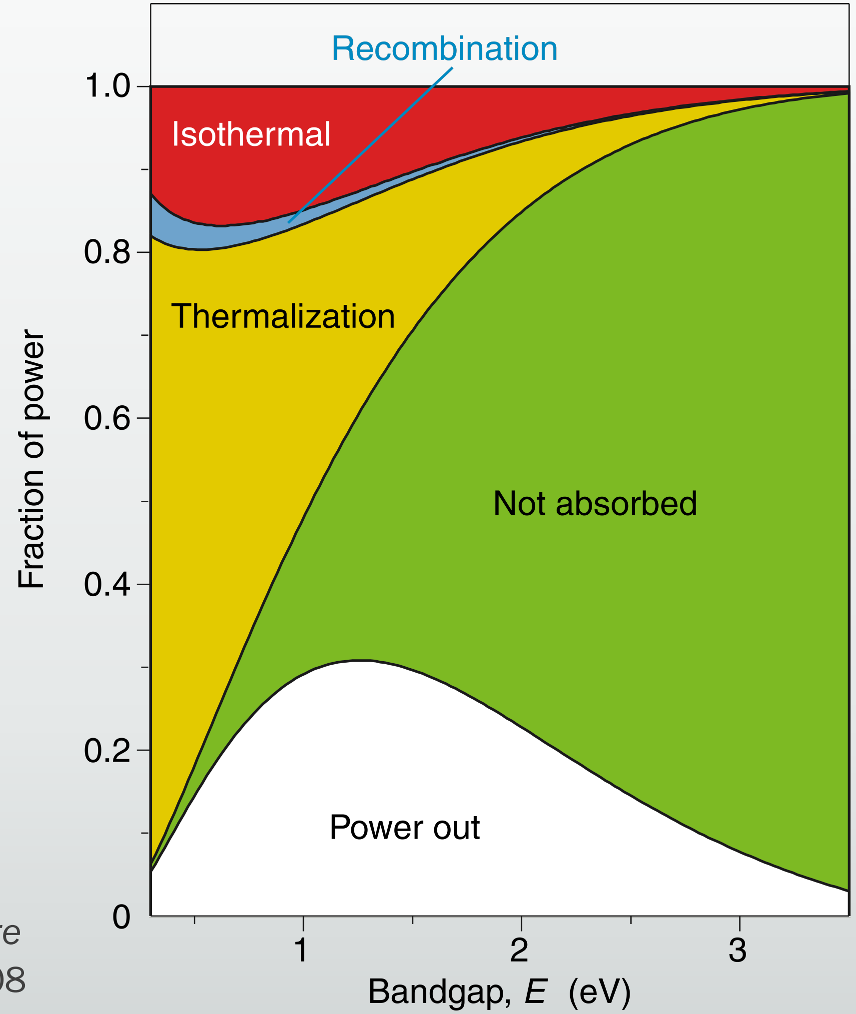
THE SHOCKLEY-QUEISSER LIMIT

ASSUMPTIONS

1. Absorption coefficient switches from 0 to 1 at bandgap
2. Each photon creates ONE pair
3. Thermalization is instantaneous
4. Carrier extraction is instantaneous
5. Only RADIATIVE recombination
6. No Ohmic losses



Max efficiency ~ 33 %
$E_g \approx 1.1$ eV



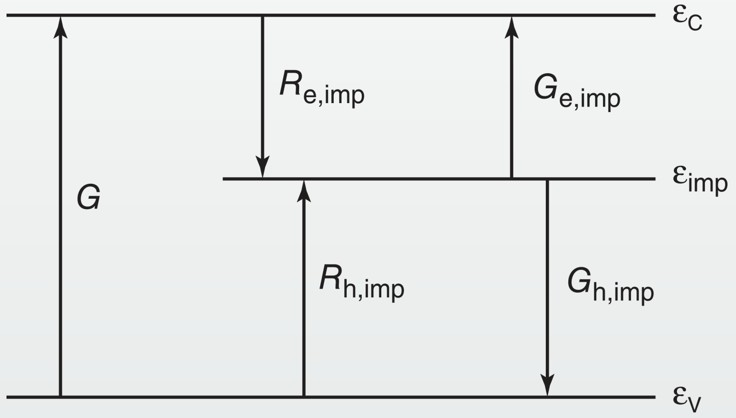
[1]

[1] J.-F. Guillemoles et al., *Nature Photonics* 13, Aug 2019, 501-508

NONRADIATIVE RECOMBINATION

Presence of states in the forbidden gap or carrier-carrier interaction can cause recombination

IMPURITY RECOMBINATION



$$R_{e,\,imp} = \sigma_e v_e n_e n_{h,\,imp}$$

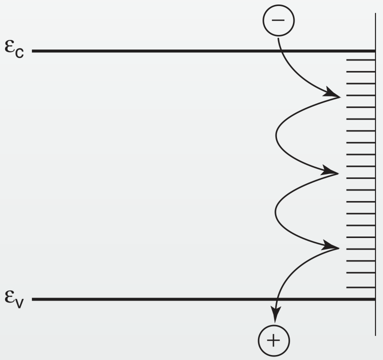
Impurity capture approximation
Usually most important source

Mostly effective when impurity is in the **middle of the gap**

↓

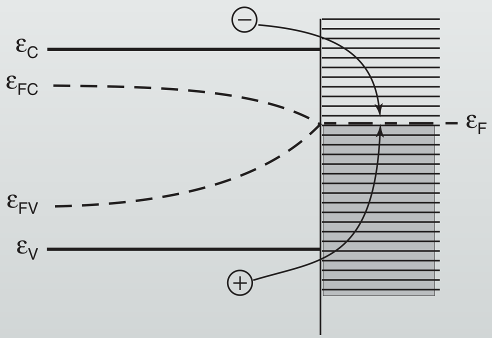
Acceptor/donor impurities are **not** very effective

SURFACE RECOMBINATION

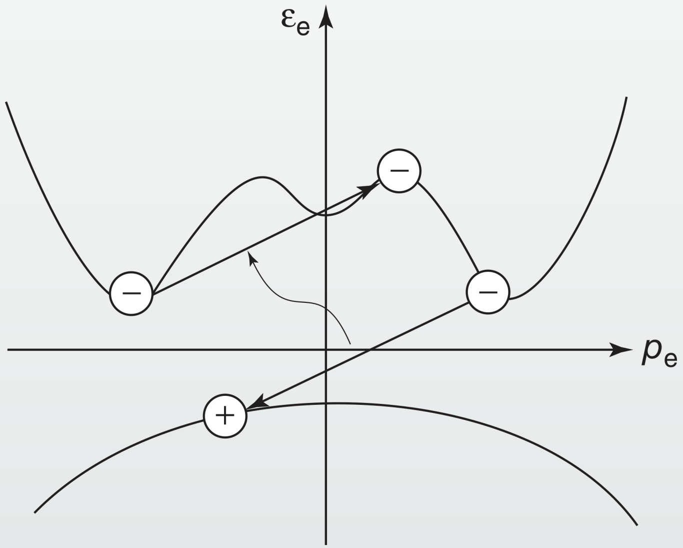


$$R_{s,e} = \sigma_{s,e} v_e n_{s,h} n_e$$

SEMICONDUCTOR-METAL



AUGER RECOMBINATION



$$R_{Aug} = C_e n_e^2 n_h + C_h n_e n_h^2$$

Very effective in strongly doped systems

Existing techniques

an overview

Si p-n JUNCTION

SILICON IS (ALMOST) PERFECT

PROS
- Abundant on Earth
- Gap is 1.12 eV (just perfect)
- Contact with air forms protective oxide film
- Oxide-Si interface has low surface state density (good for avoiding recombination)
- Both dopings possible (**p** and **n**)

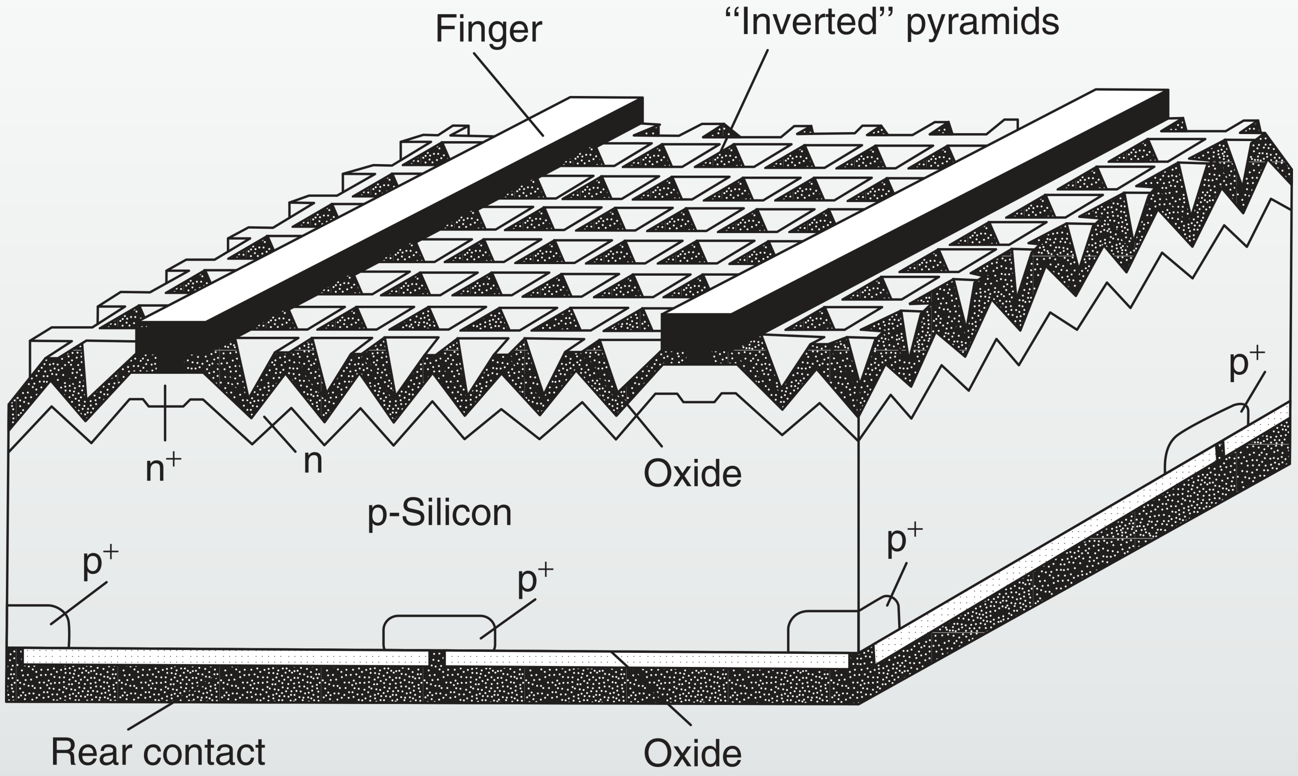
CONS
- **Weak absorption** due to **indirect bandgap**

THIS IS BAD

LARGE PENETRATION DEPTH

MOST GENERATED CARRIERS ARE FAR FROM CONTACTS

LONG LIFETIMES REQUIRED (HIGH QUALITY CRYSTAL)



RECORD EFFICIENCY

RESEARCH	monocrystal **25.3%**	polycrystal **21.9%**
COMMERCIAL	monocrystal **22.8%**	polycrystal **17.1%**

THIN FILM CELLS

Broad family, including every inorganic solar cell using an absorbing material with direct bandgap

HIGH ABSORPTION COEFFICIENTS → THIN ABSORBING MEDIUM → TOLERANCE OF IMPURITY → LESS ORDER REQUIRED

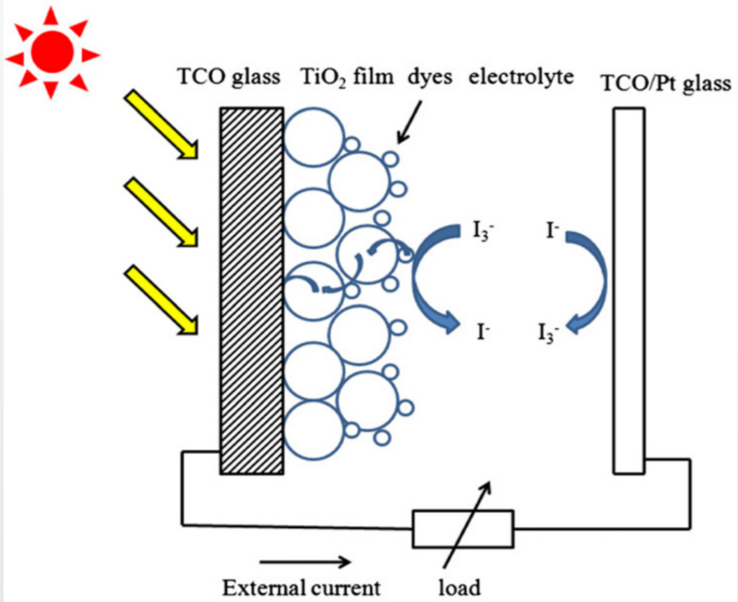
MATERIALS

	RECORD EFFICIENCY
Cadmium Telluride : good efficiency, easy production, Telluride rare&expensive	R 22.1% C 14%
Copper Indium Gallium Selenide : good efficiency, easy production requires heat	R 22.6% C 14%
Amorphous Silicon : dangling bonds passivated with H, decaying efficiency	R 12.1% C 8%
Gallium Arsenide : easily tunable bandgap, p&n doping, Ga rare&expensive	R 28.8% C 25%
Perovskites: cheap, low temperature process, very efficient, highly unstable, Pb & Au	R 22.1% C 11%

"Photovoltaics Report". Fraunhofer ISE. July 28, 2014 NREL, Best-Research Cell Efficiency Chart

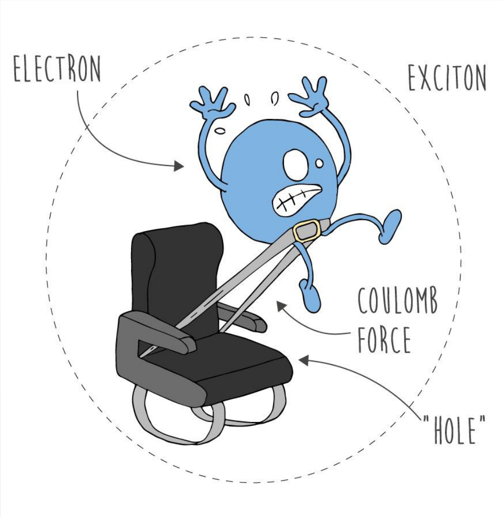
ORGANIC SOLAR CELLS

DYE-SENSITIZED



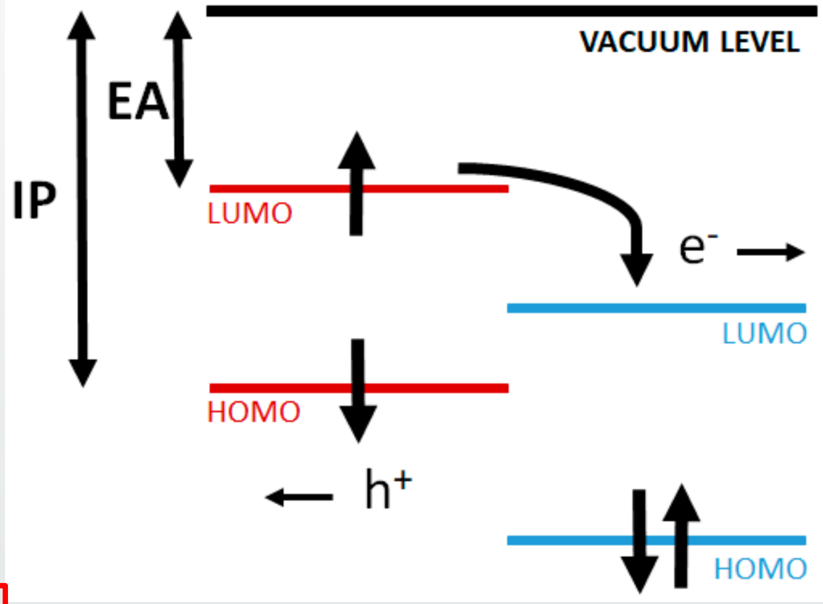
[1]

STRONG EXCITONS



$$\varepsilon_{exc} = \frac{m_{red}\, e^4}{2(4\pi\epsilon\epsilon_0)^2\hbar^2} \approx 1\text{-}10 \text{ eV}$$

POLYMER-BASED



[1]

PROS : Cheap, energy inexpensive, easy to tandem

CONS : Poor conductivity, exciton breaking required

11%	RECORD EFFICIENCY	10% (tandem)

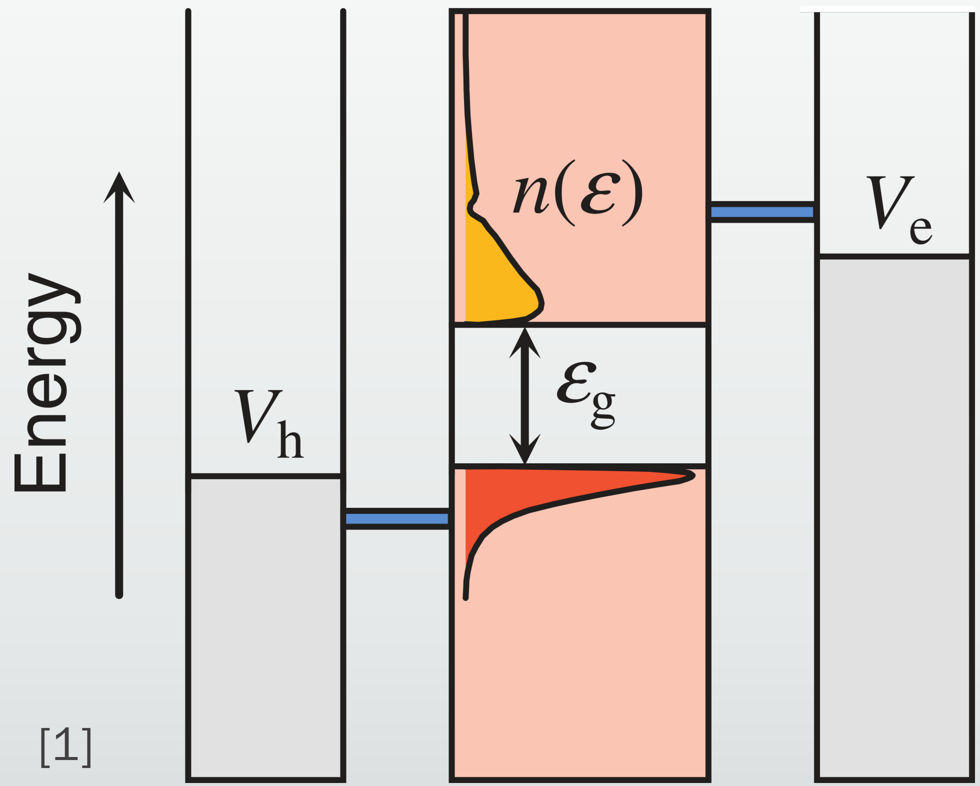
[1] J.A. Luceño-Sánchez *Int. J. Mol. Sci.* 2019, 20, 976

Proposals & Outlooks

latest ideas in photovoltaics

HOT CARRIER EXTRACTION

Extracting carriers before thermalization avoids thermalization losses. Energy selection avoids entropy generation.



$$\Delta S = \frac{\Delta Q_L}{T_L} + \frac{\Delta Q_R}{T_R} = \frac{-(\varepsilon - \mu_L)}{T_L} + \frac{(\varepsilon - \mu_R)}{T_R}$$

$$\varepsilon_S \equiv \frac{\mu_L T_R - \mu_R T_L}{T_R - T_L}$$ [2]

CARRIER-CARRIER INTERACTION ENSURES TEMPERATURE EXISTENCE & REPLENISHMENT

Thermalization time needs to be very long $\tau \approx 1$ ns, currently obtainable only in clean samples of GaAs. [1]

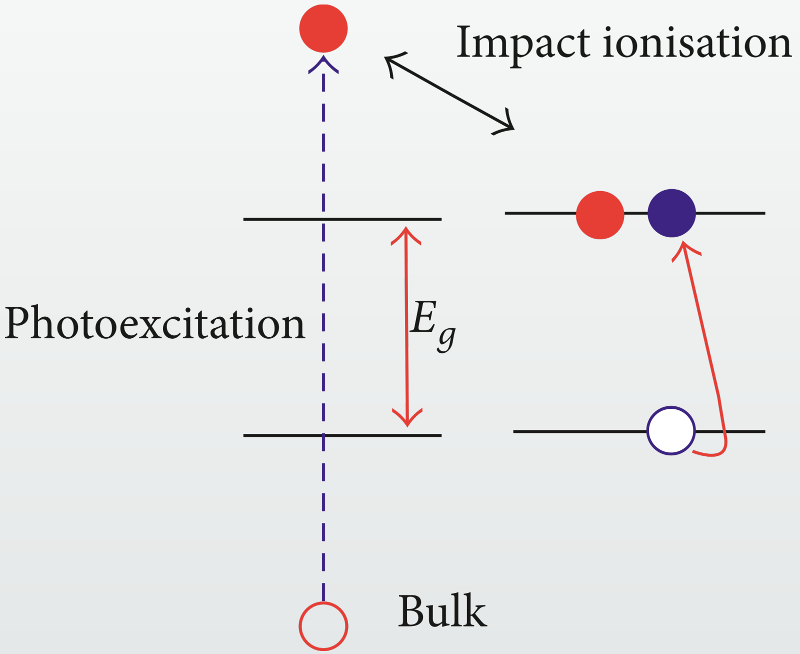
Use of resonant tunneling diodes has been proposed for energy selection.

Theoretical max efficiency ~ 66%
dependence on times computed [3]

[1] Y. Takeda et al. , Appl. Phys. Exp. 3, 104301 (2010)
[2] T. E. Humphrey et al. , Phys. Rev. Lett. 89 (2002) 116801
[3] K. Kamide et al., Phys. Rev. Appl. 10, 044069 (2018)

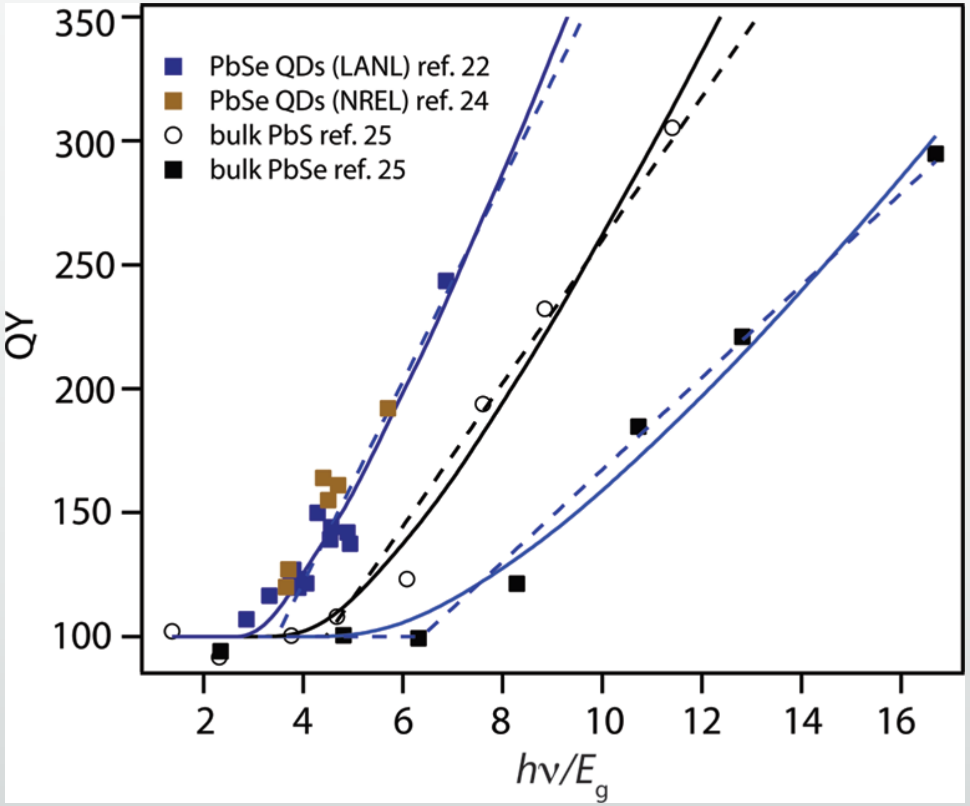
MULTIPLE EXCITON GENERATION

High energy photons contain enough energy for multiple pair formation. Impact ionisation can multiply pairs.



[1]

Impact ionisation due to Coulomb interaction

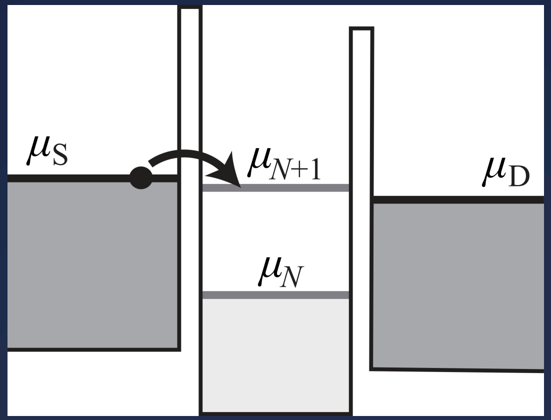


[2]

QY : QUANTUM YIELD : $\dfrac{\text{\# generated pairs}}{\text{\# photons absorbed}}$

[1] N. Siemons & A.Serafini, *J. of Nanotech.* , 7285483 (2018)

[2] M.C. Beard et al. , *Nano Lett.* 10, 3019–3027 (2010)



Quantum Dots

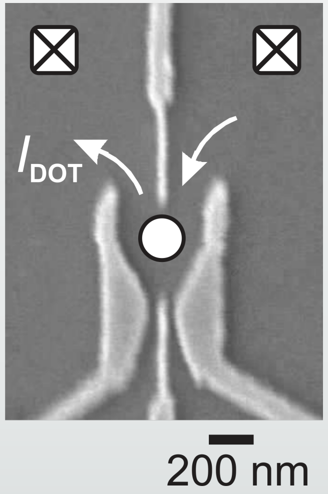
a brief introduction

Quantum system confined in every spatial direction (zero-dimensional)

Energy quantization becomes appreciable, levels becomes **spaced**.

Level spacing is dictated by **size** of quantum confinement & **Coulomb** interaction if particles are charged. It can resist a **weak** interaction with external environment.

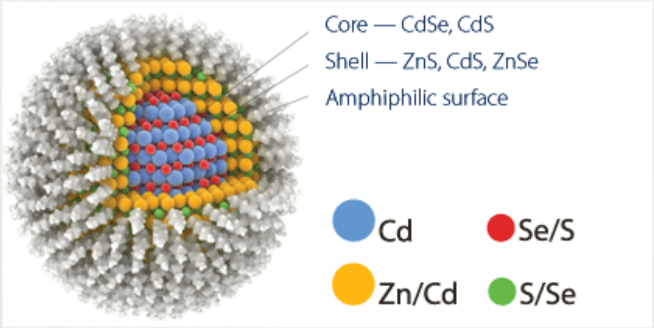
SOLID-STATE QD (2DEG)



REAL TIME
ENERGY & COUPLING CONTROL

SMALL SPACING (~ 1 meV)

COLLOIDAL QD



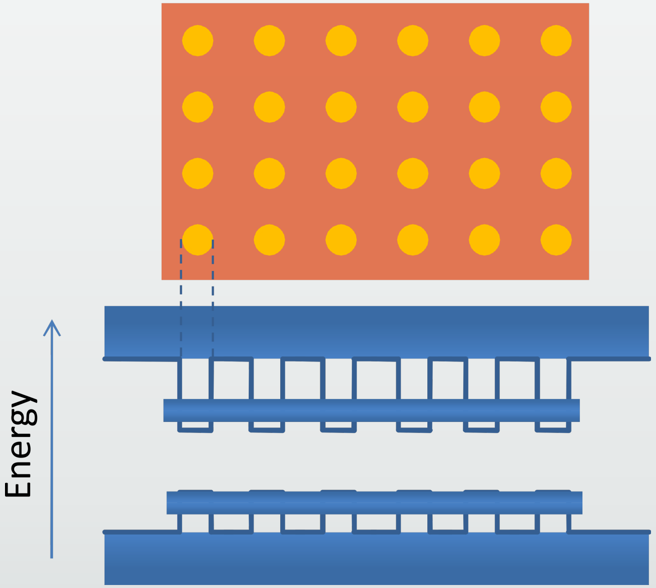
LARGE SPACING (~ 1-10 eV)
ROOM TEMPERATURE

FIXED PROPERTIES

QUANTUM DOT SOLAR CELLS

Quantum dots are easily tunable in bandgap. If regularly spaced they form superlattices.

INTERMEDIATE BAND (SUPERLATTICE)



GOOD CONDUCTIVITY

IMPURITY-LIKE RECOMBINATION
EXPENSIVE

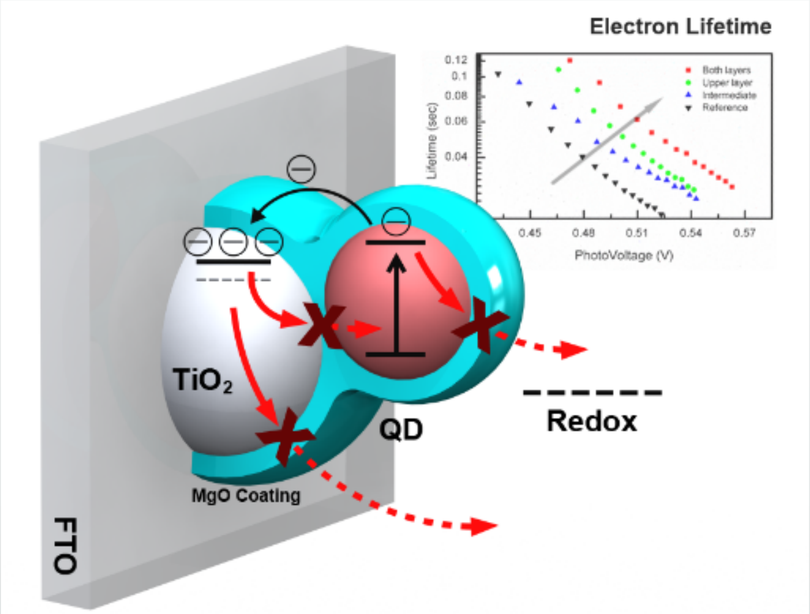
HOT CARRIER EXTRACTION

MULTIPLE EXCITON GENERATION

MULTIJUNCTION

ARE POSSIBLE !

COLLOIDAL QD ABSORBERS



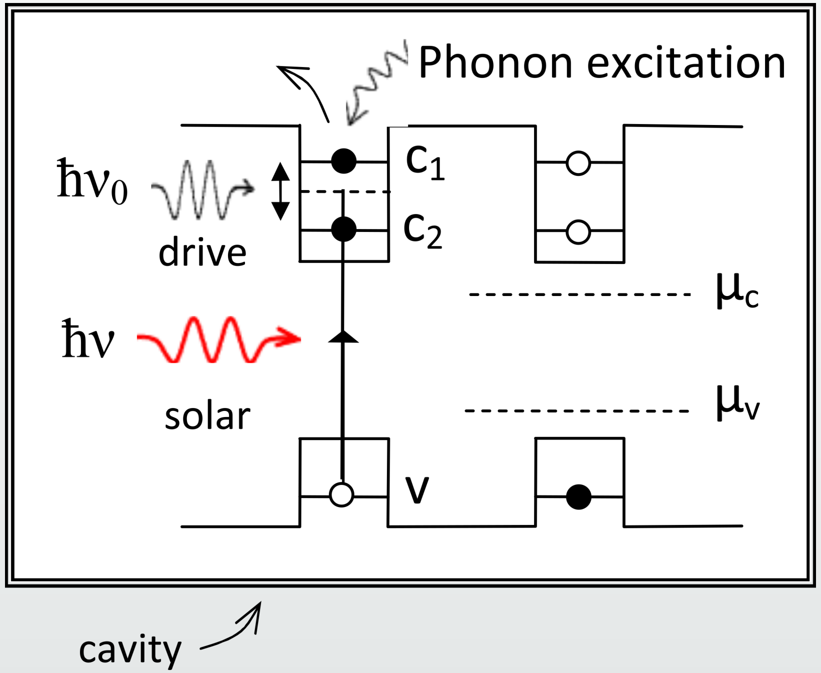
TUNABLE ABSORPTION
INEXPENSIVE SUBSTRATES

UNSTABLE TO AIR EXPOSITION

SCULLY'S QUANTUM PHOTOCELL [1]

Use of quantum interference can favor absorption to radiative recombination, an inverse of inversionless lasers

PROPOSAL INVOLVES USE OF CAVITY TO PROVIDE COHERENCE BETWEEN CONDUCTION BAND STATES



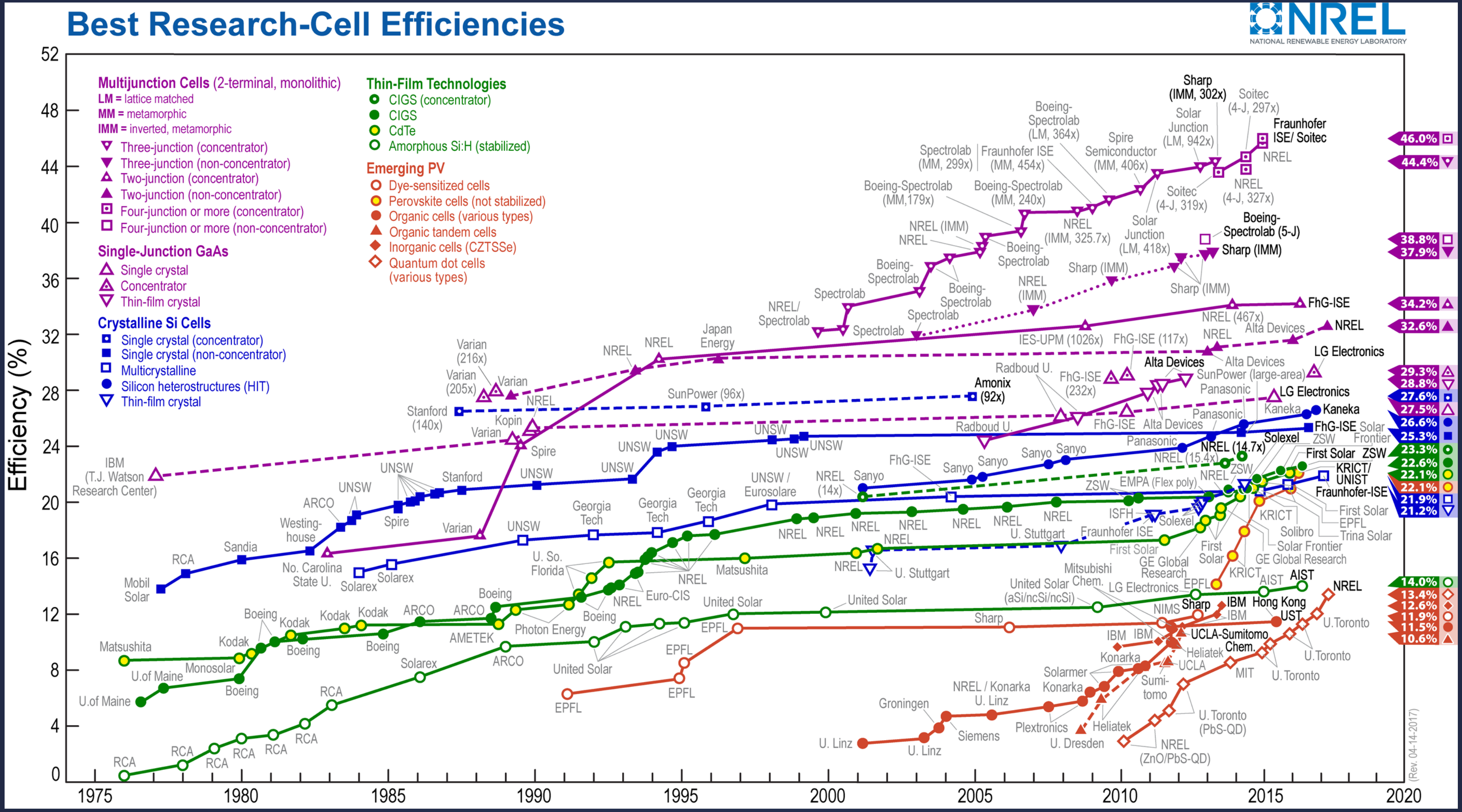
SIMILAR MECHANISM PROVEN UNDER MANY OBSERVED PHENOMENA
LWI, LIT, ETC.

MOST INTERESTING PROPOSAL IS USE OF FANO INTERFERENCE INSTEAD OF CAVITY DRIVING, LIKE IN LWI [2].
IT MIGHT BE A BYPRODUCT OF COUPLING WITH EXTERNAL ENVIRONMENT OR ENSEMBLE OF SURFACE STATES.

[1] M. Scully, *Phys. Rev. Lett.* 104, 207701 (2010)

[2] S. E. Harris, *Phys. Rev. Lett.* 62, vol. 9 (1989), 1033

THANK YOU FOR YOUR ATTENTION



email : leonardo.lucchesi1@phd.unipi.it