Imperial College London

Yonsei University Graduate Class

Energy Materials: Design, Discovery and Data

Solar Energy Conversion

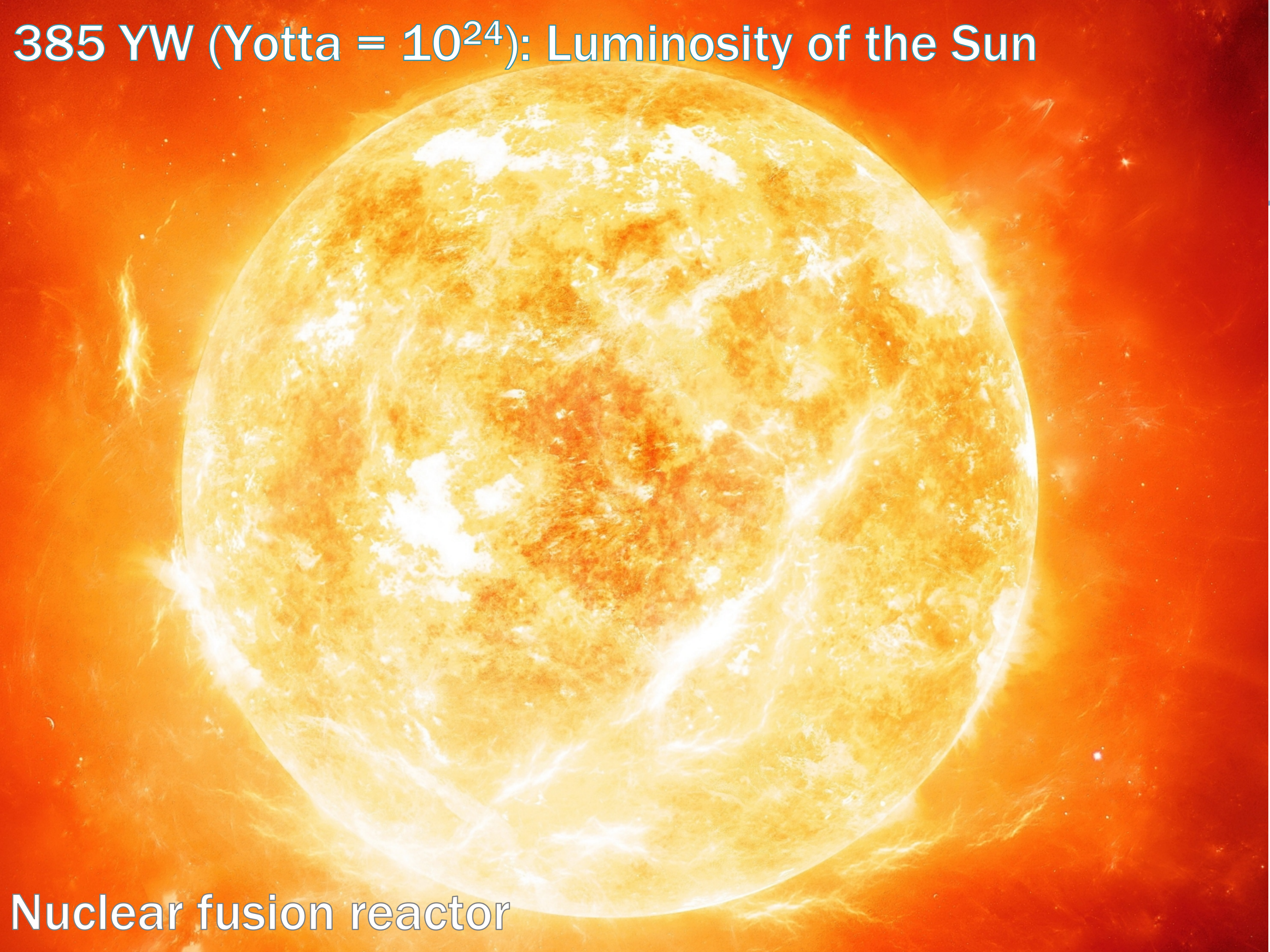
Prof. Aron Walsh

Department of Materials

Imperial College London

https://wmd-group.github.io @lonepair

385 YW (Yotta = 10^{24}): Luminosity of the Sun



Nuclear fusion reactor

385 YW (Yotta = 10^{24}): Luminosity of the Sun

174 PW (Peta = 10^{15}): Power reaching Earth

Blackbody emission at ~ 5800 K


385 YW (Yotta = 10^{24}): Luminosity of the Sun
174 PW (Peta = 10^{15}): Power reaching Earth
15 TW (Tera = 10^{12}): Power usage on Earth
20% electricity consumption on lighting

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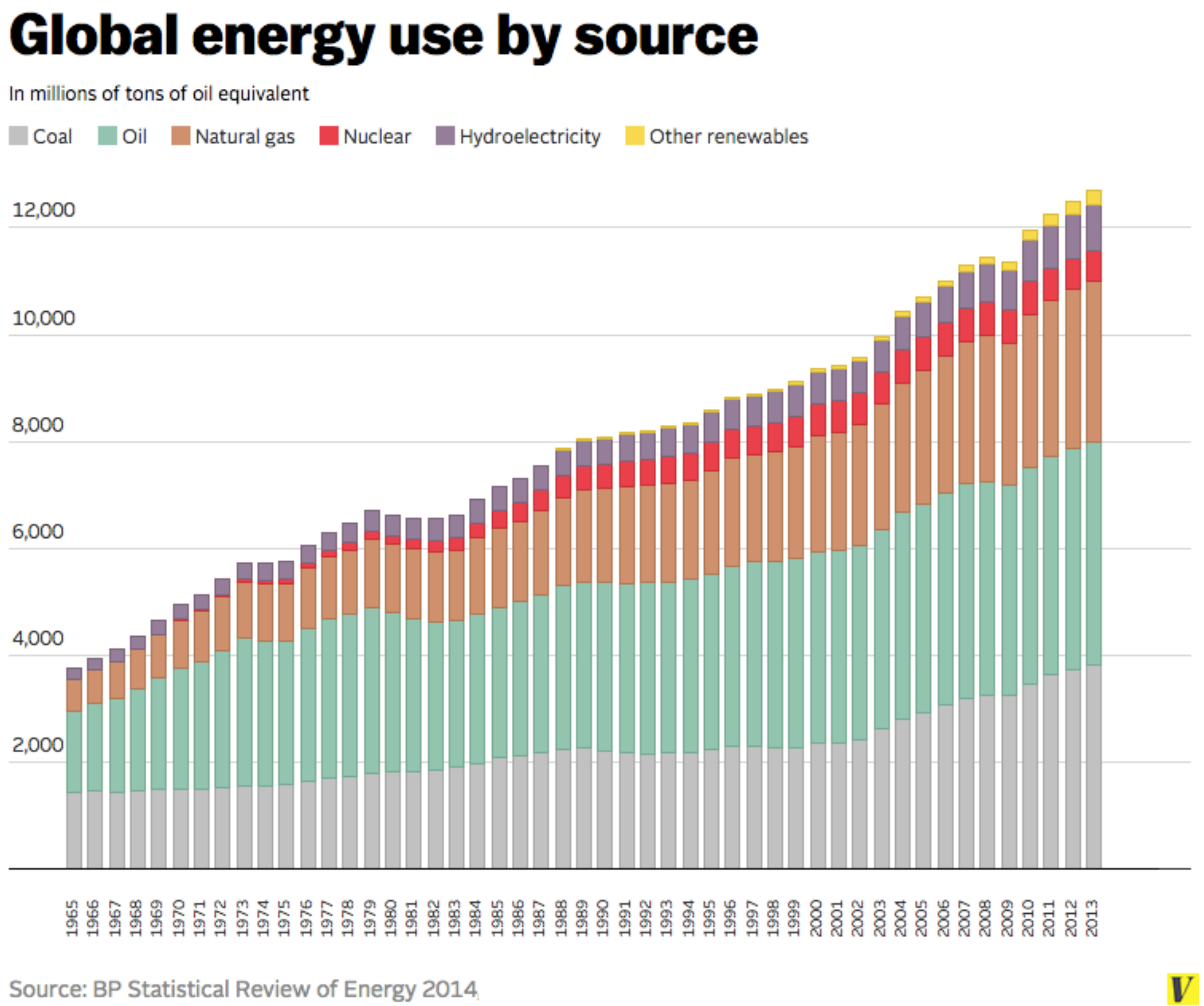
Global Trend – Total Energy



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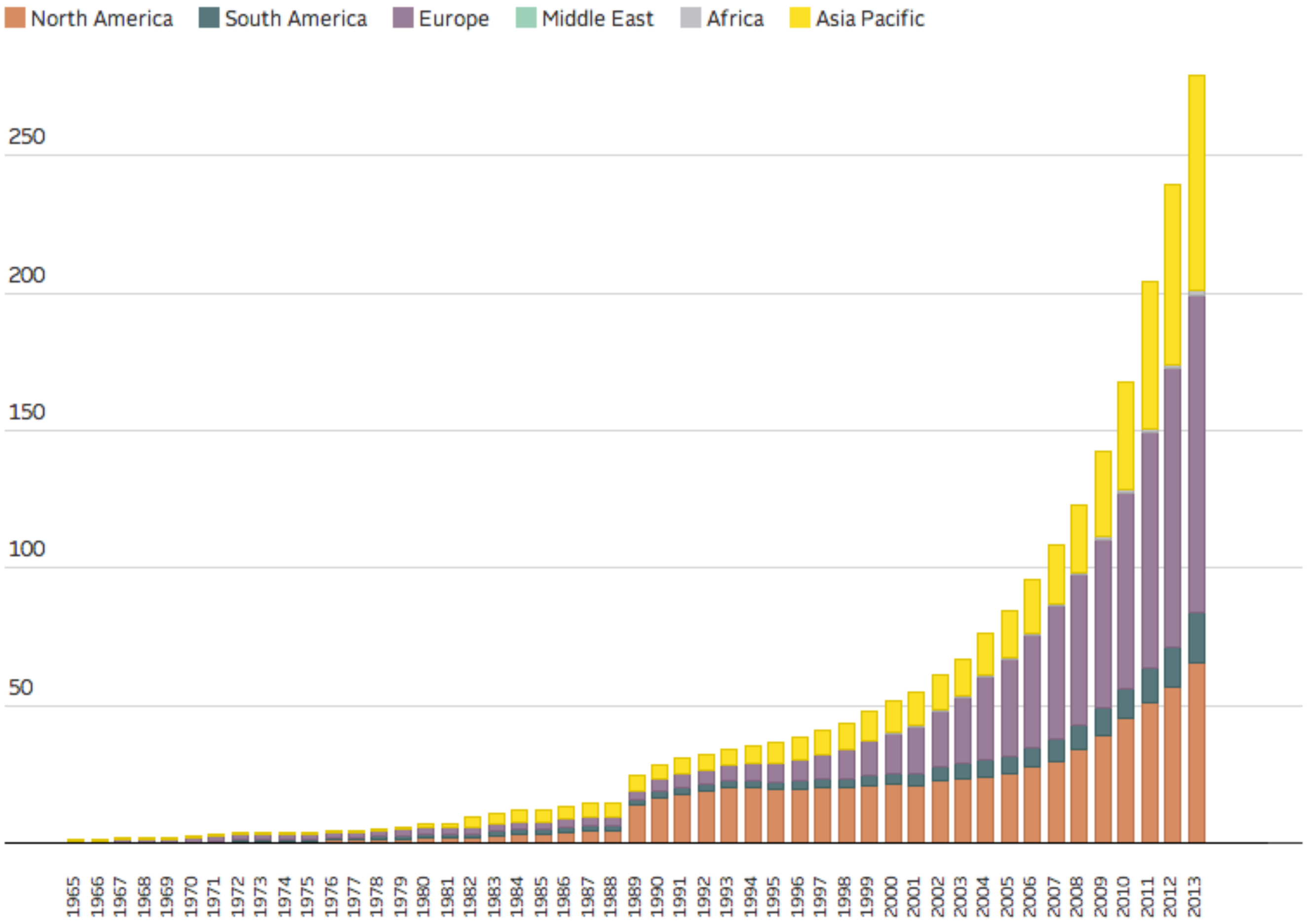
Global Trend – Renewable Energy

Global renewable energy consumption

Excluding hydropower. In million tons of oil equivalent.



Source: BP Statistical Review of World Energy 2014

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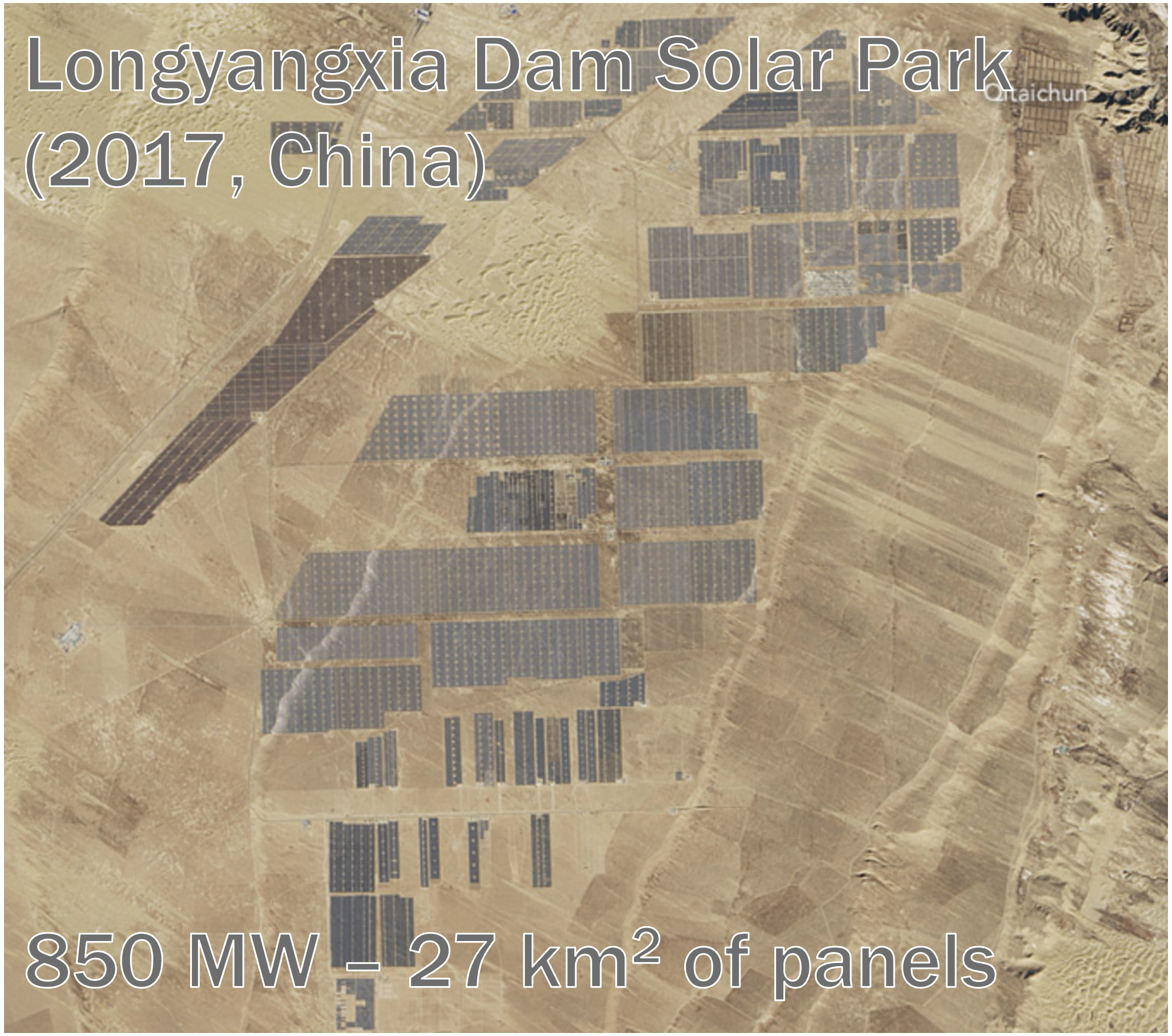
Solar Energy Future

Solar Energy Future

Latest Developments



http://earthobservatory.nasa.gov/IOTD/view.php?id=89668

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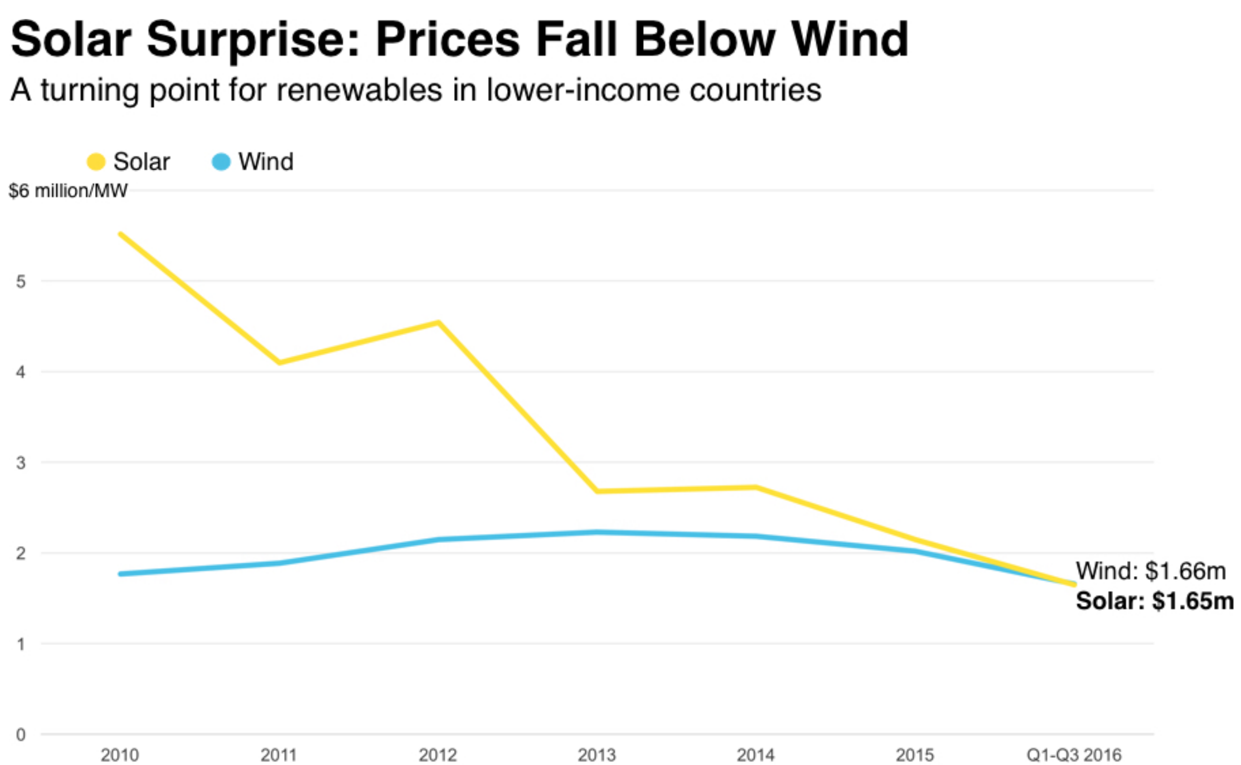
Latest Developments

"Renewables are robustly entering the era of undercutting fossil fuel prices"



Bloomberg Finance Report: http://bloom.bg/2h3nZf3

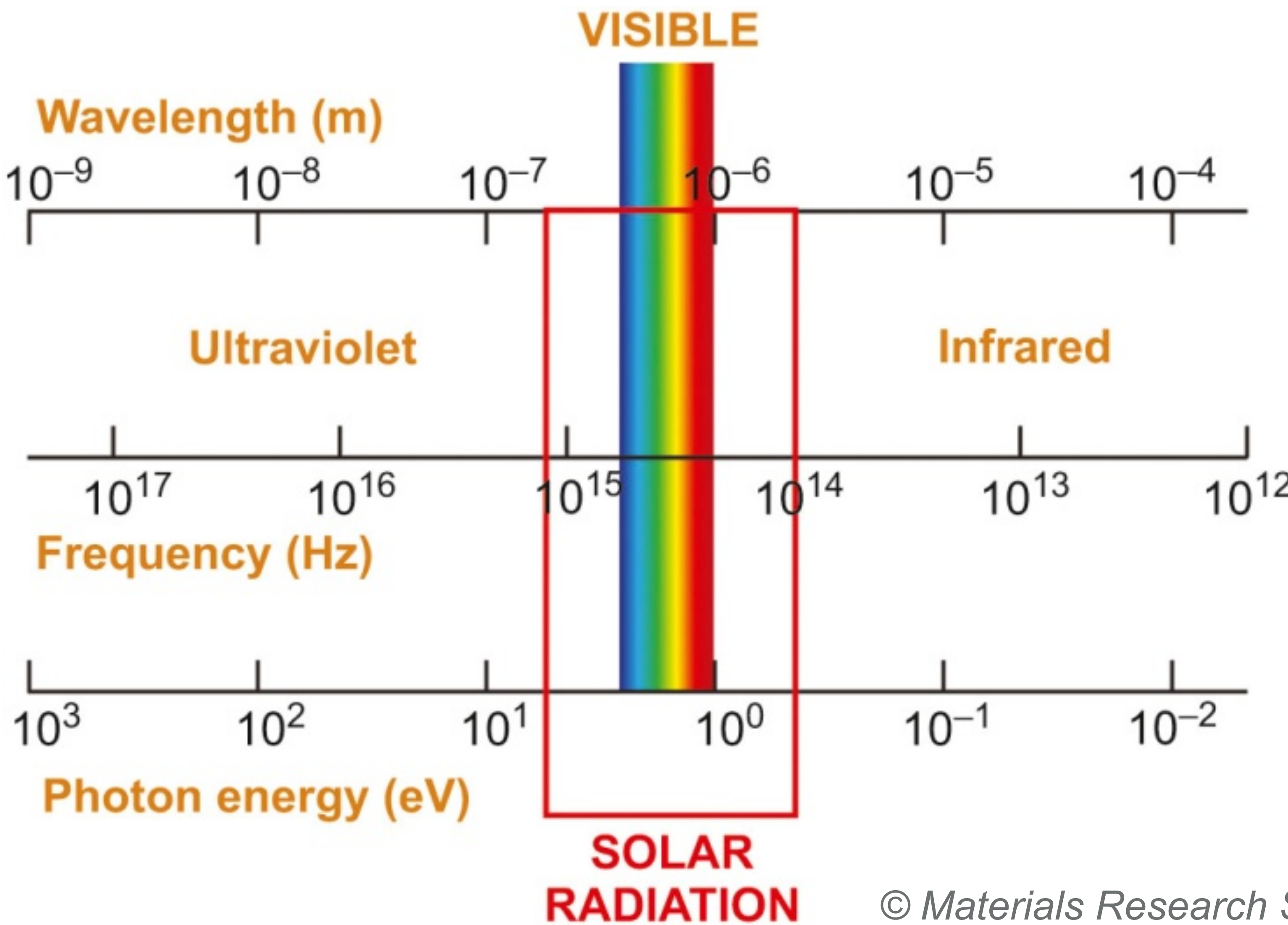
Class Question

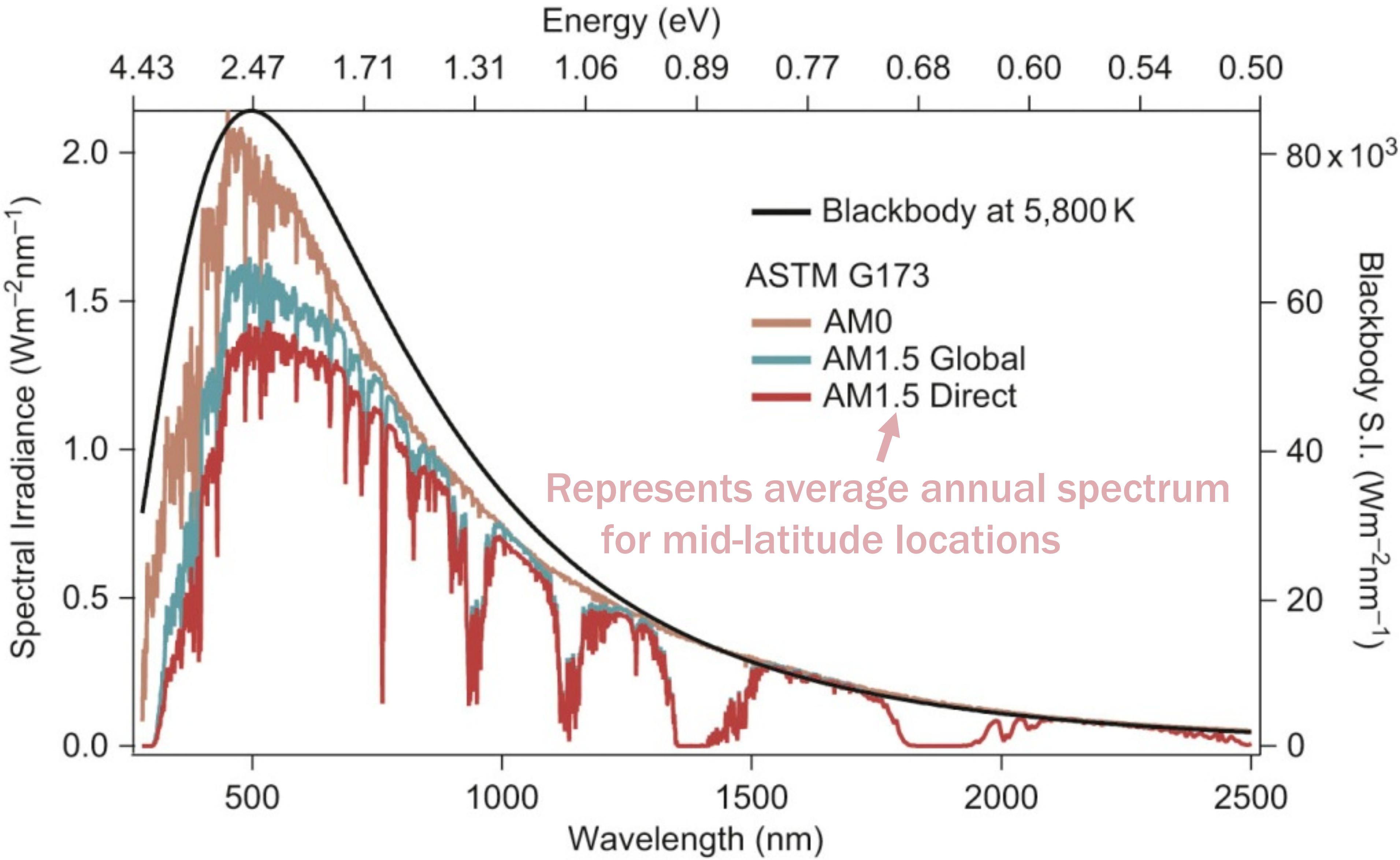
How is South Korea's electricity generated?

Talk Outline: Solar Energy

1. Solar Energy Fundamentals
2. Current Photovoltaic Technologies
3. Case Study: Hybrid Perovskites

Solar Spectrum





Data: http://rredc.nrel.gov/solar/spectra/am1.5

Class Question

How to convert sunlight to electricity?

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Solar Energy Timeline

Archimedes Death Ray (212 BC)

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London

Solar Energy Timeline

LA LUMIÈRE

SES CAUSES ET SES EFFETS

PAR

M. EDMOND BECQUEREL

DE L'ACADÉMIE DES SCIENCES

DE L'INSTITUT DE FRANCE

PROFESSEUR AU CONSERVATOIRE IMPÉRIAL DES ARTS ET MÉTIERS, ETC., ETC.

TOME PREMIER

SOURCES DE LUMIÈRE

	MATIÈRES placées dans la flamme du chalumeau à gaz oxygène et hydrogène.	PHOTOMÈTRE. Angle observé.	PHOTOMÈTRE. Logarithme de I.	PHOTOMÈTRE. Intensité lumineuse I.	TEMPÉRATURE calculée.
Expériences de décembre 1862.	Chaux vive....	1°18'	3,2884330	»	1566,9
	Magnésie	1.19	3,2766000	»	1564,6
	Platine.........................	2.22	2,7682170	»	1463,2
	Palladium......................	4.12	2,2705248	»	1364,0
	Fer...... { Effets lumineux variables; éclats par instants.	5.44	2,0008810	»	»
	Cuivre... { Effets lumineux très-variables d'intensité.	25.32	0,7309726	»	»

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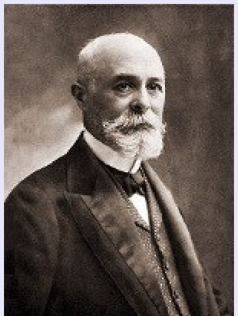
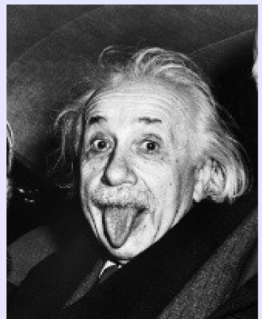
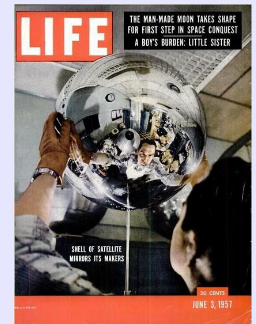
Solar Energy Timeline







1839:
Edmund Bequerel discovers photovoltaic effect in electrolytic cell

1873:
Willoughby Smith observes photoconductivity in Selenium

1905:
Einstein publishes paper on photoelectric effect (not photovoltaic effect!)

1954:
First PV cell made at Bell Labs, USA. Used to power telephone repeaters – 4% efficient.
Daryl Chapin, Calvin Fuller, Gerald Pearson.
.

1958:
First PV cell in space. Vanguard Satellite. Max power 1W!
Followed Explorer VI and VII satellities (1959)

1960:
Hoffman Electronics achieves **14%** PV cells!

https://www1.eere.energy.gov/solar/pdfs/solar_timeline.pdf
http://jongertner.net/idea-factory/

http://www.cdt-pv.org/training

EPSRC
Engineering and Physical Sciences Research Council

Solar Energy Timeline

1977:
U.S. DOE launches Solar Energy Research Institute. Now NREL.
Total PV manufacturing capacity exceeds 500 kW

1982:
First MW capacity solar plant goes online. Hisperia, California

1992:
CdTe solar cell 15.9% efficient Univ. South Florida.

1994:
GaAs solar cells > 30%
NREL

First Solar®

2000:
First Solar starts production

2008:
Peak in Si cost as production of SC grade Si slows.
Thin film gets excited

2010:
Global installed PV capacity reaches 40GW

2012:
Emergence of high-efficiency perovskite cells.


REVIEW ARTICLE
PUBLISHED ONLINE: XX JULY 2014 | DOI: 10.1038/NPHOTON.2014.134
nature photonics

The emergence of perovskite solar cells

Martin A. Green[1]*, Anita Ho-Baillie[1] and Henry J. Snaith[2]

EPSRC
Engineering and Physical Sciences Research Council

Imperial College London

Solar Electricity and Fuel

Fusion Reactor

174,000 Terawatts reaches the Earth's surface

Electricity

Solar Cells

High efficiency (20 – 50%)

Chemical Energy

Solar Fuels

Low efficiency (< 5%)

Physics (electron–hole separation) is easier than chemistry (oxidation/reduction reactions)

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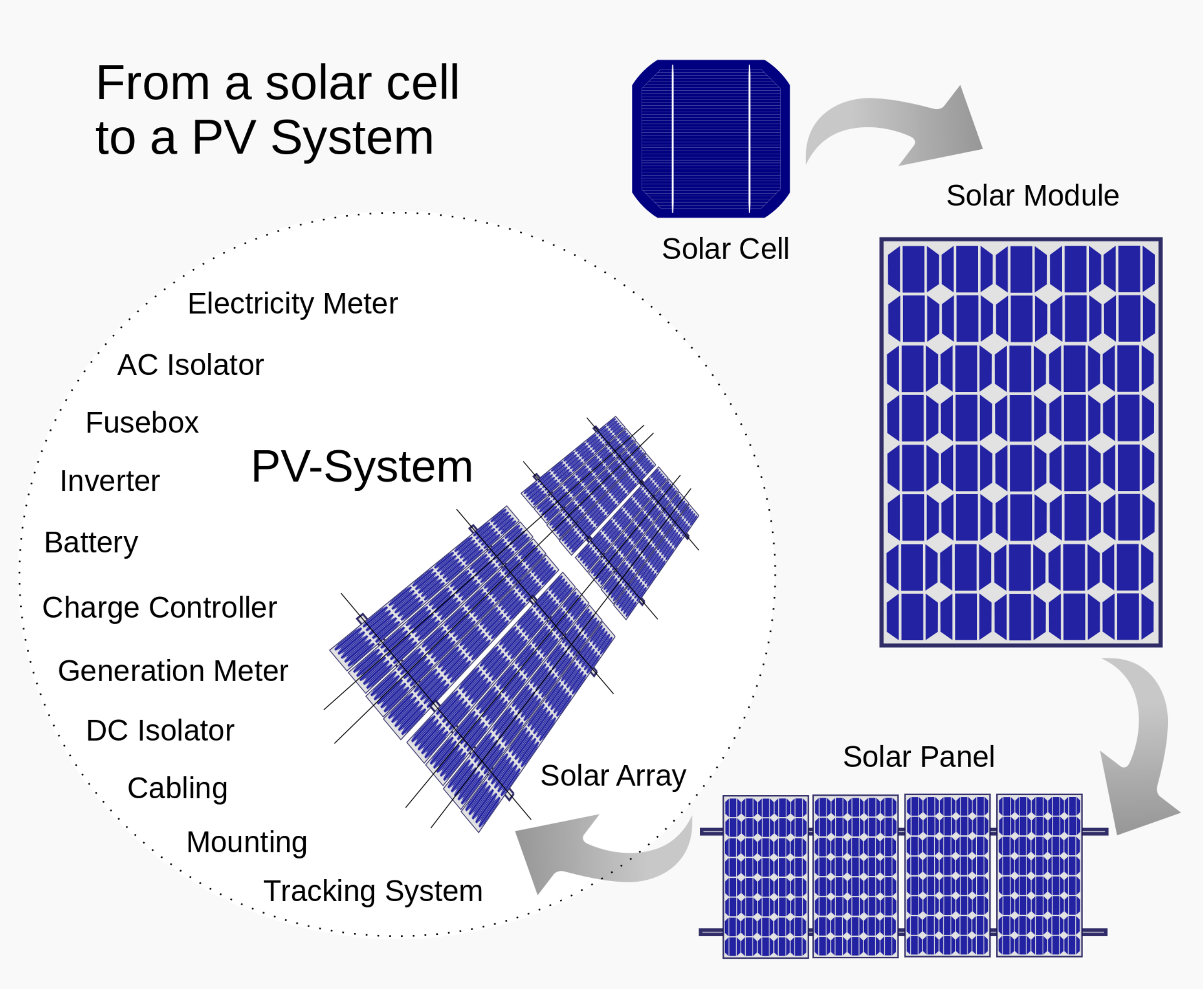
Our Focus: Solar Cells



https://en.wikipedia.org/wiki/Solar_panel

Our Focus: Semiconductors

- **Optical Materials** – light collection and trapping, spectral up / down conversion
- **Electronic Materials** – primary light absorption and light-to-electricity conversion. Electrical contacts
- **Thermal Materials** – heat conversion and collection, e.g. thermoelectrics, thermionic emission, thermophotovoltaics

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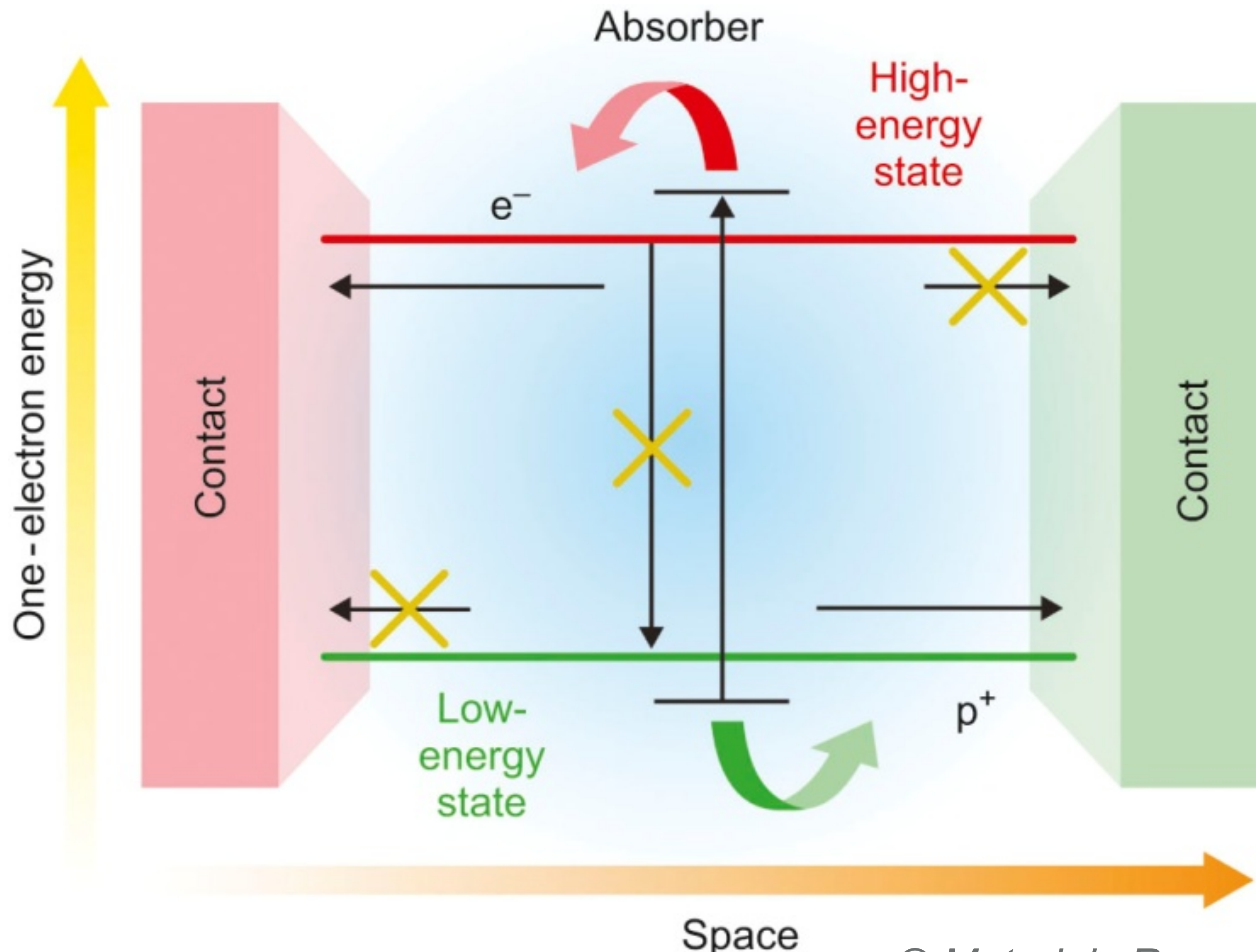
Single Junction Solar Cell



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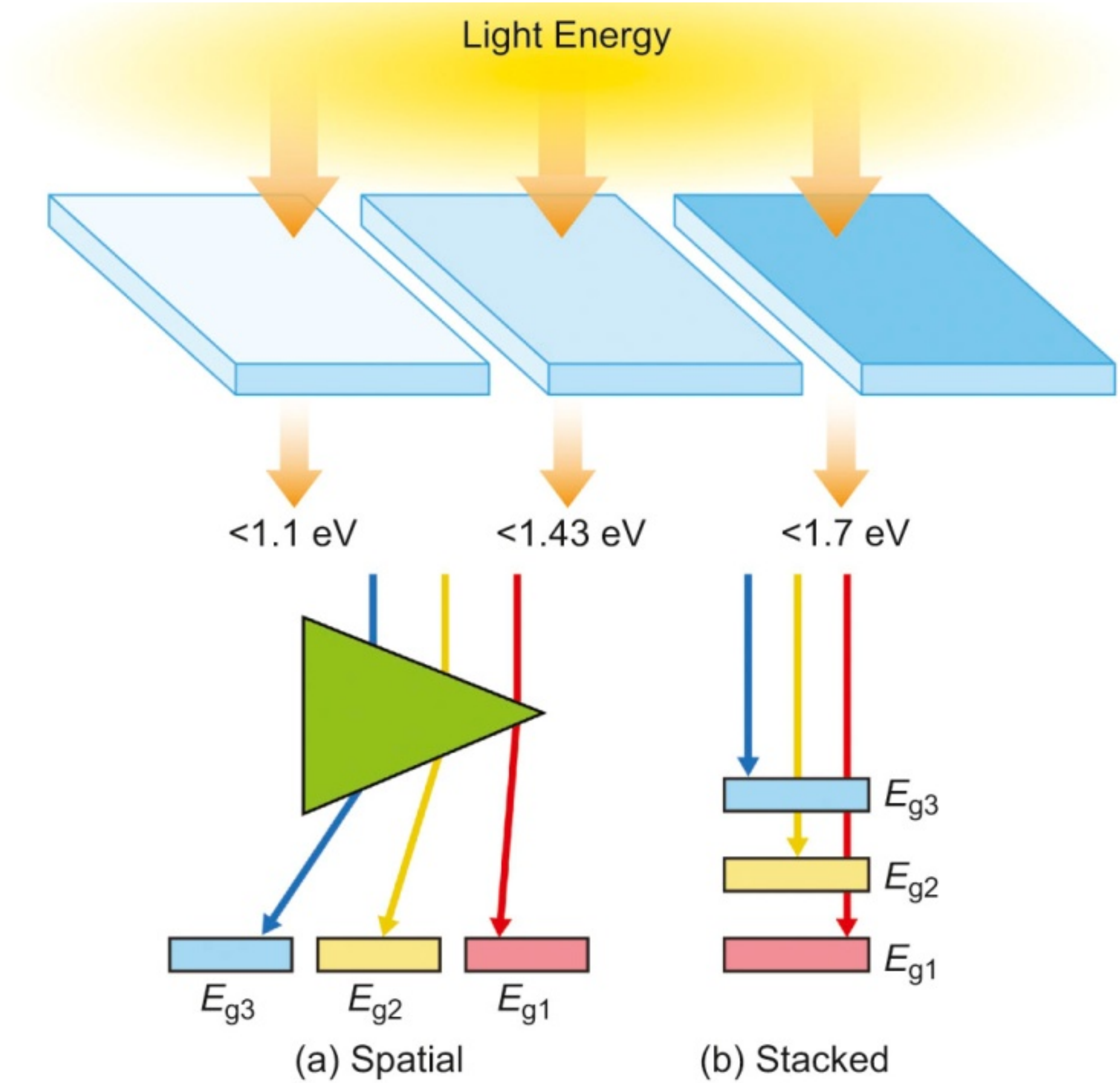
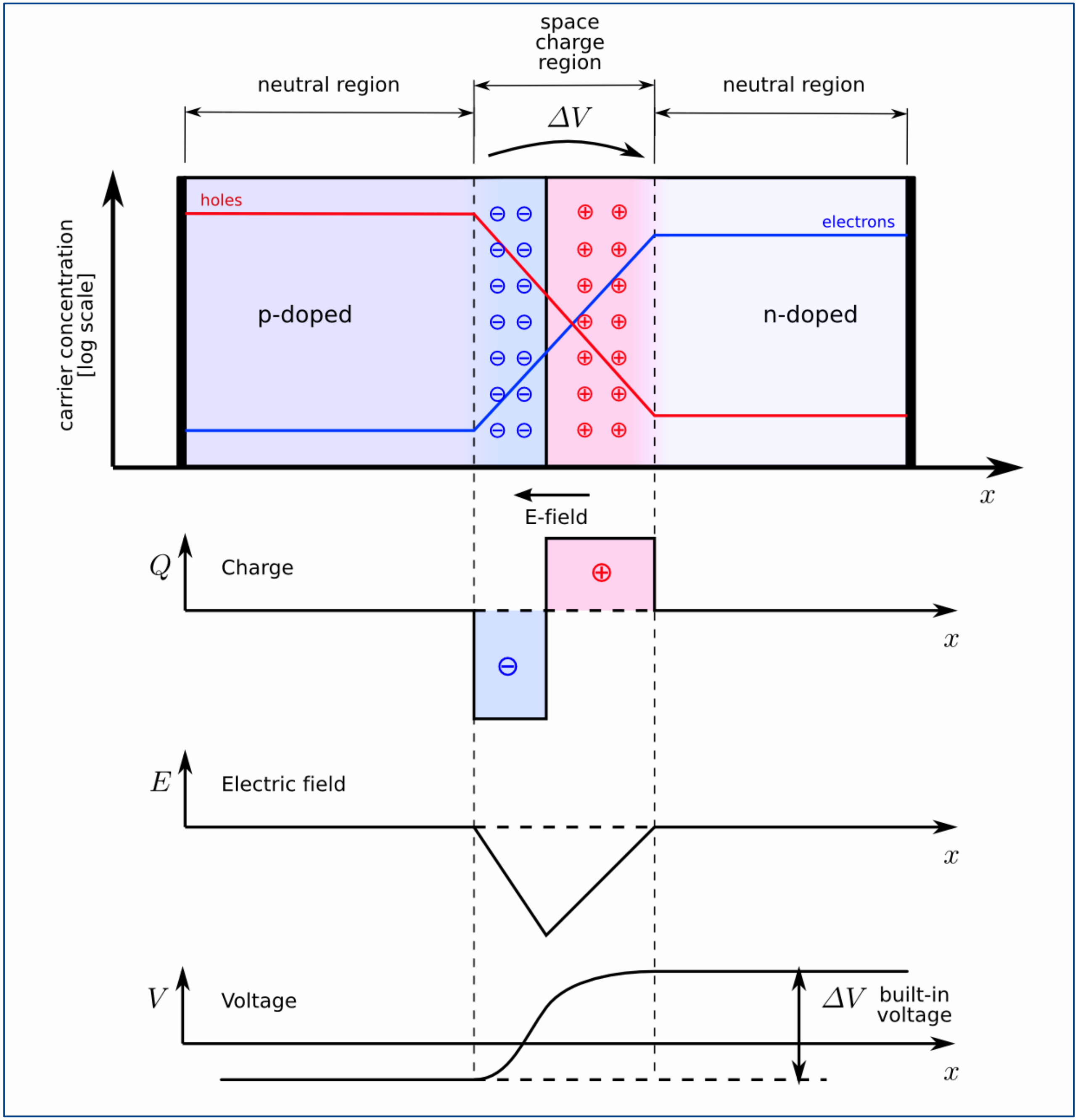
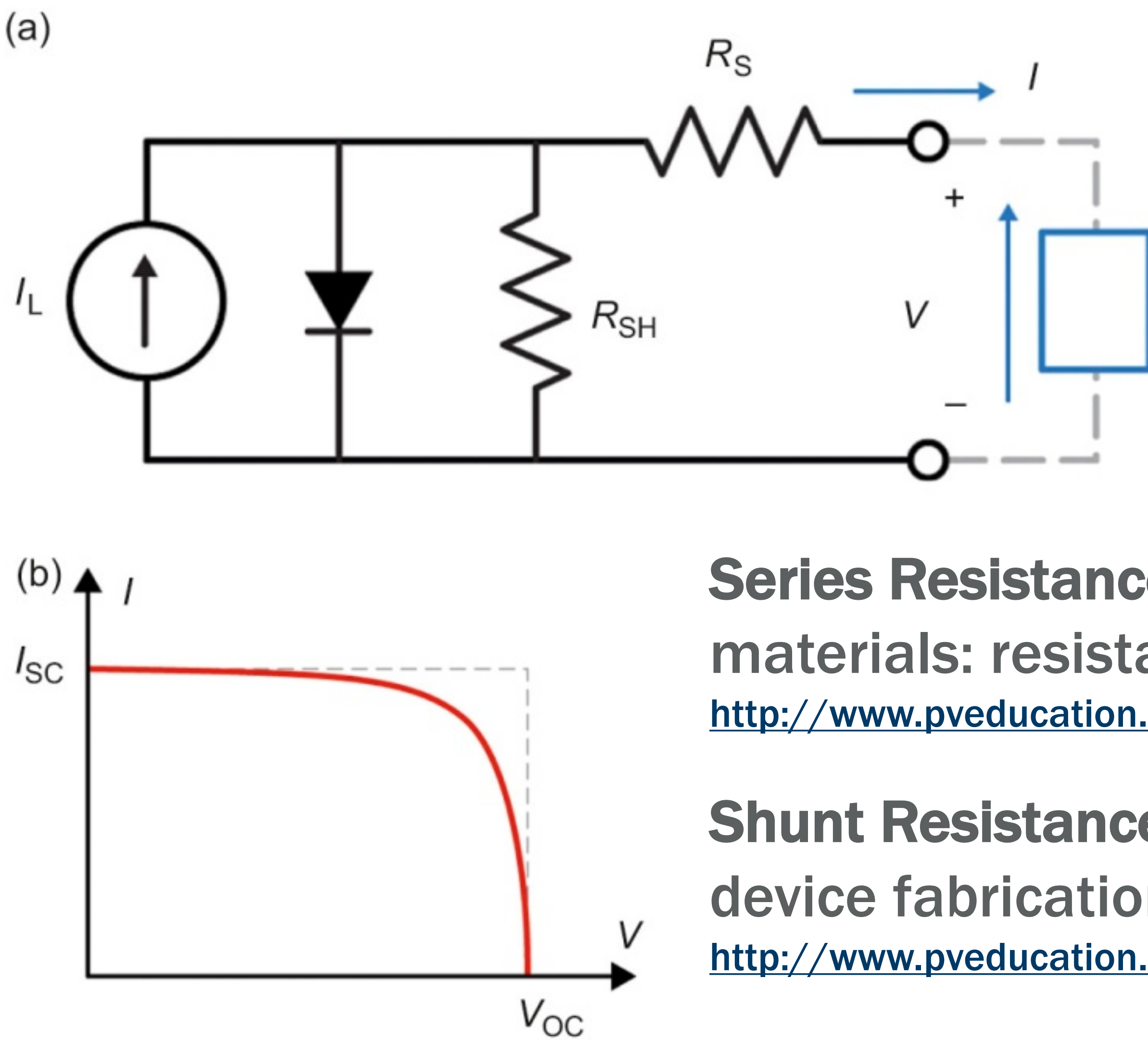
Multi Junction Solar Cell





https://en.wikipedia.org/wiki/p–n_junction

Equivalent Electric Circuit



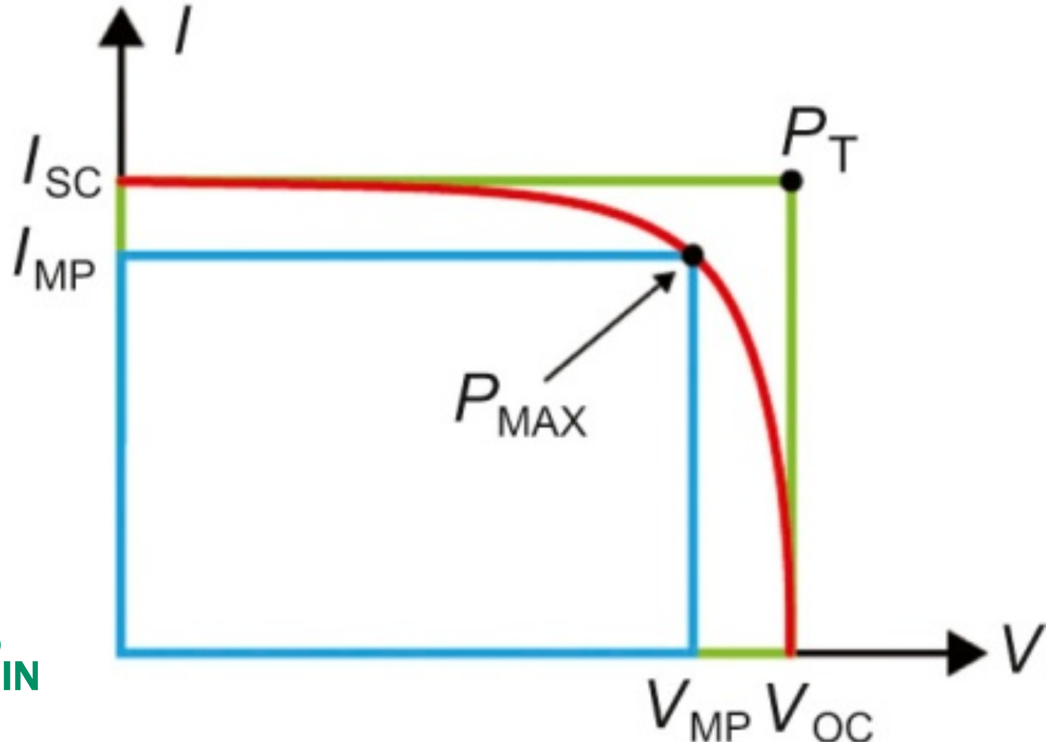
Series Resistance (R_S) – limitation of real materials: resistance at interfaces + bulk
http://www.pveducation.org/pvcdrom/series-resistance

Shunt Resistance (R_{SH}) – limitation of device fabrication: short circuit pathways
http://www.pveducation.org/pvcdrom/shunt-resistance

Fill Factor and Photovoltaic Efficiency

$$FF = \frac{P_{MAX}}{P_T} = \frac{\boxed{I_{MP} \cdot V_{MP}}}{\boxed{I_{SC} \cdot V_{OC}}}$$

Fill Factor



Device Efficiency: $\eta = P_{MAX} / P_{IN}$

External Quantum Efficiency: **EQE(λ)**

Efficiency of photons to e-h pairs

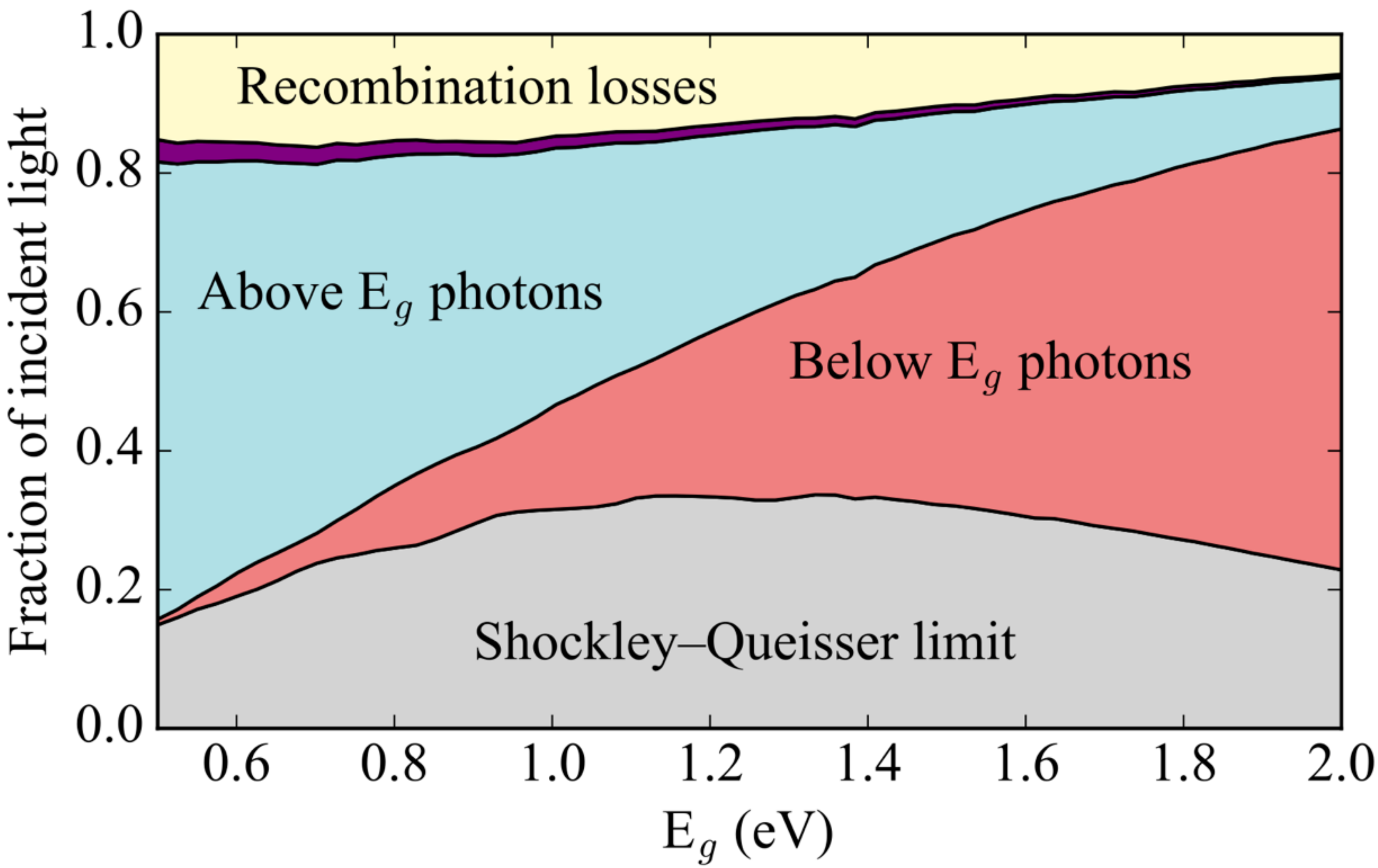
Internal Quantum Efficiency: **IQE(λ)**

Exclude reflectance and transmission

Class Question

What is the maximum efficiency that can be achieved?

pyExample in Jupyter Notebook

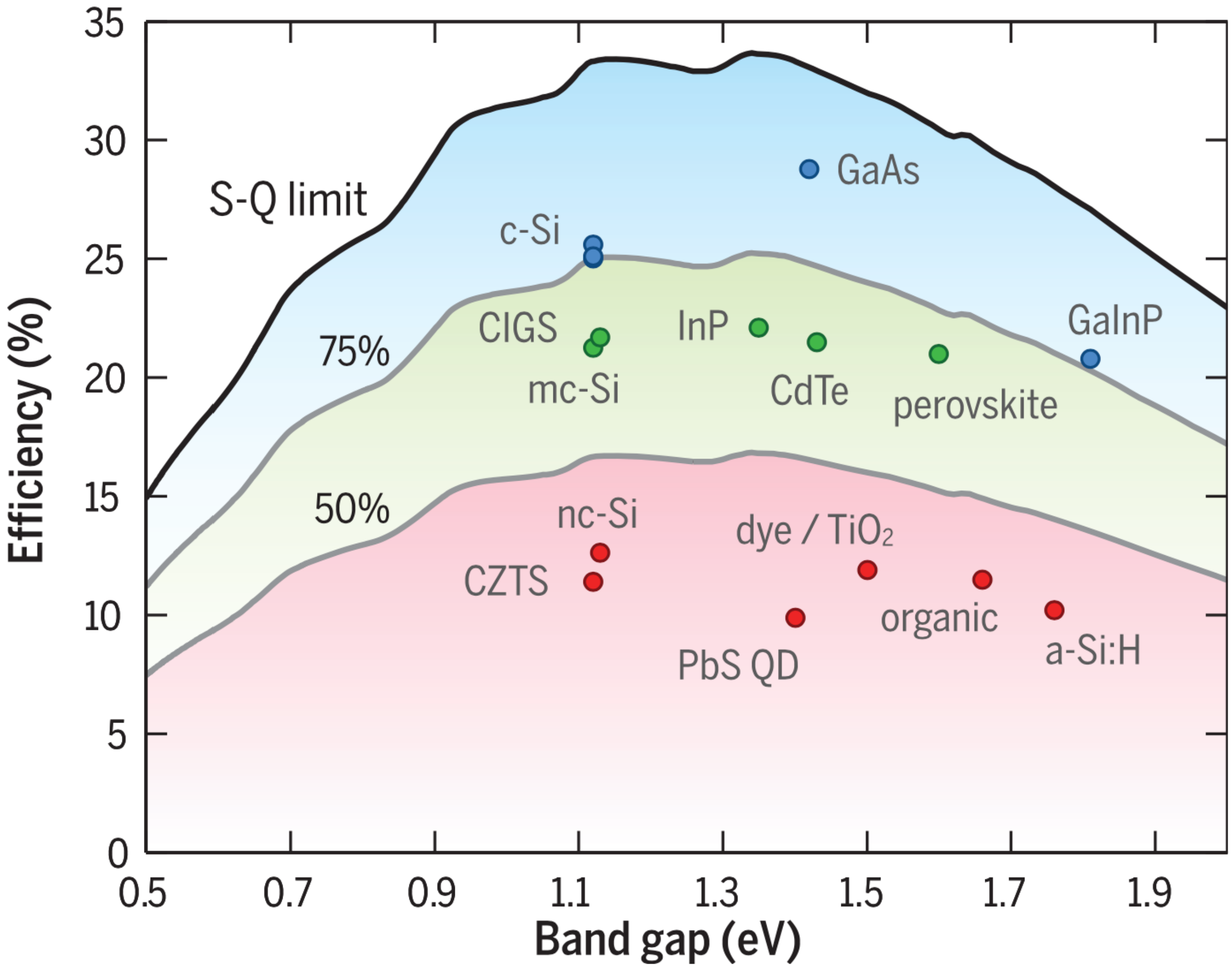


https://github.com/WMD-group/yonsei17

Talk Outline: Solar Energy

1. Solar Energy Fundamentals
2. Current Photovoltaic Technologies
3. Case Study: Hybrid Perovskites

Many Materials and Technologies



A. Polman et al, Science 352, 307 (2016)

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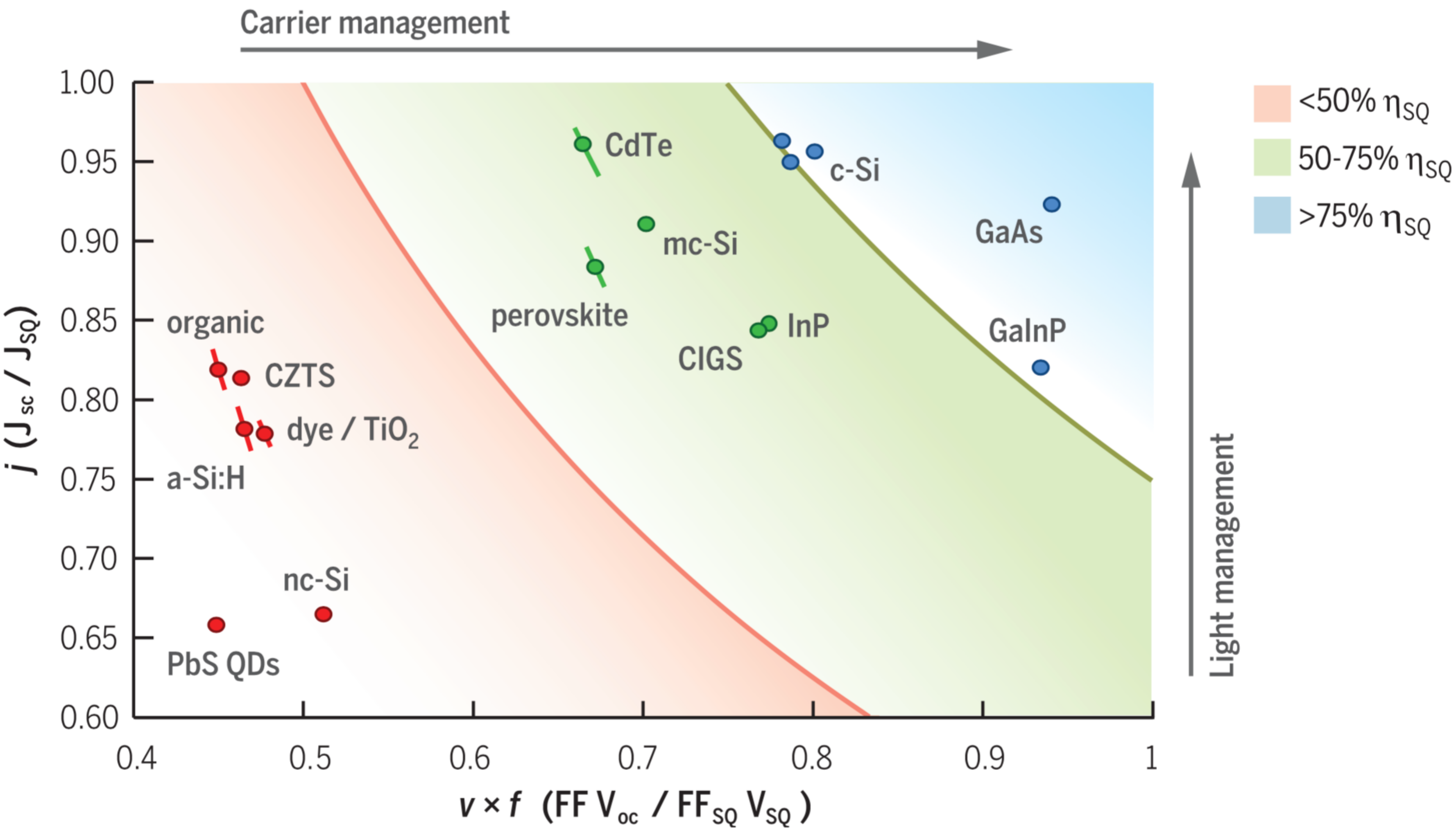
Efficiency Bottlenecks



A. Polman et al, Science 352, 307 (2016)

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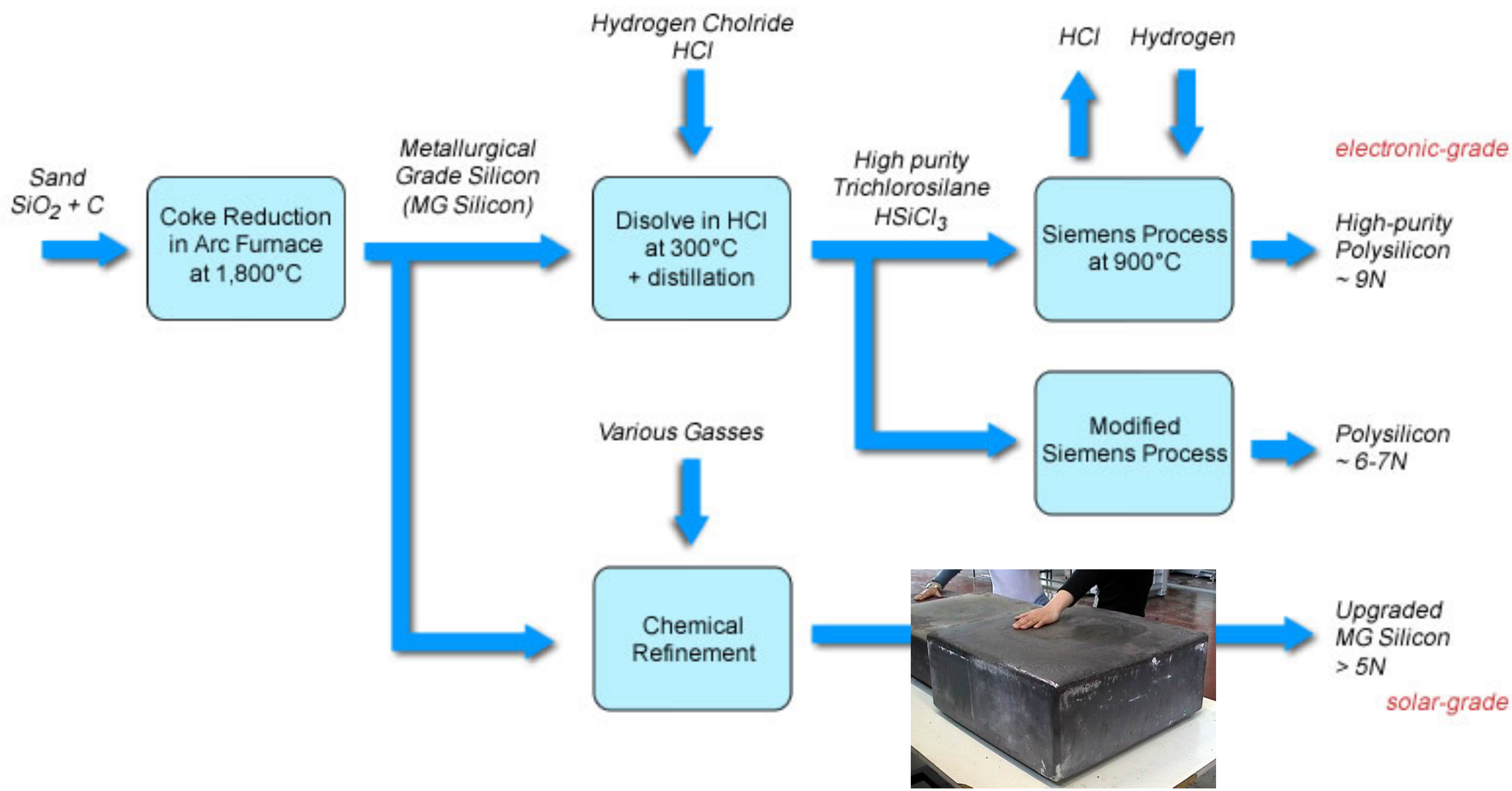
Silicon: Energy Intensive Processing



http://www.greenrhinoenergy.com/solar

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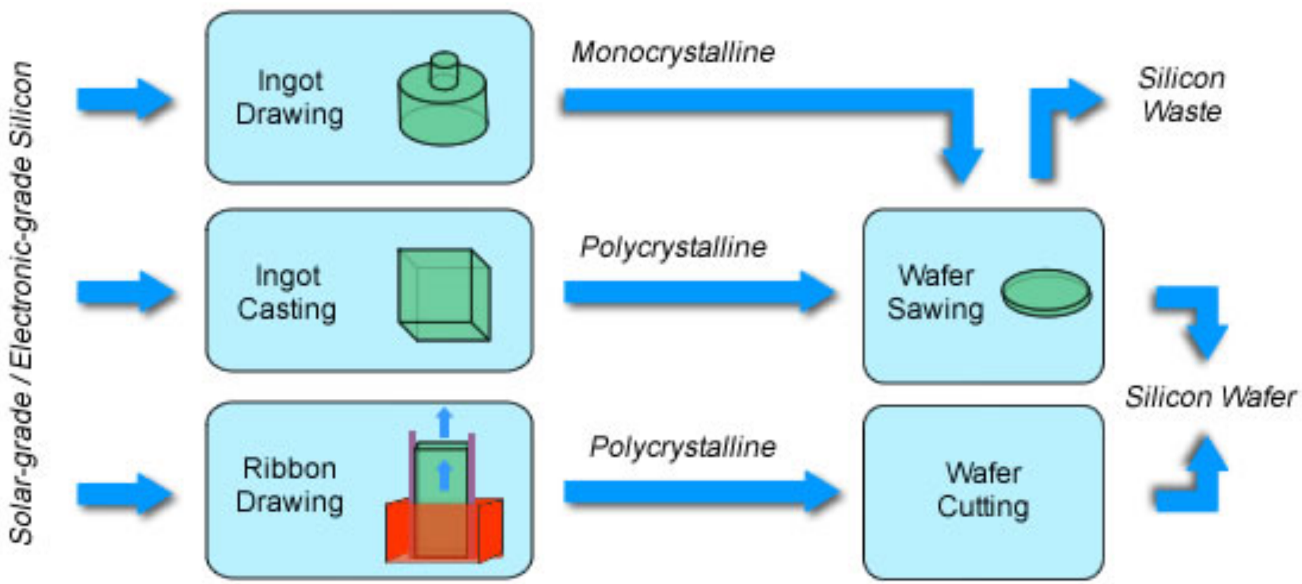
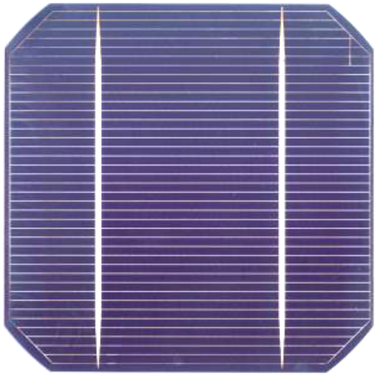
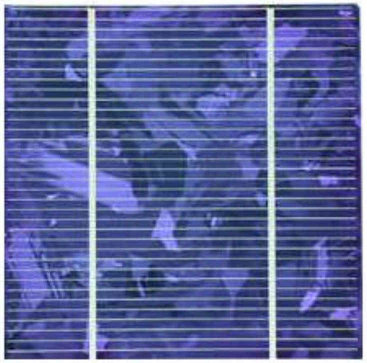
Silicon: Energy Intensive Processing







http://www.greenrhinoenergy.com/solar

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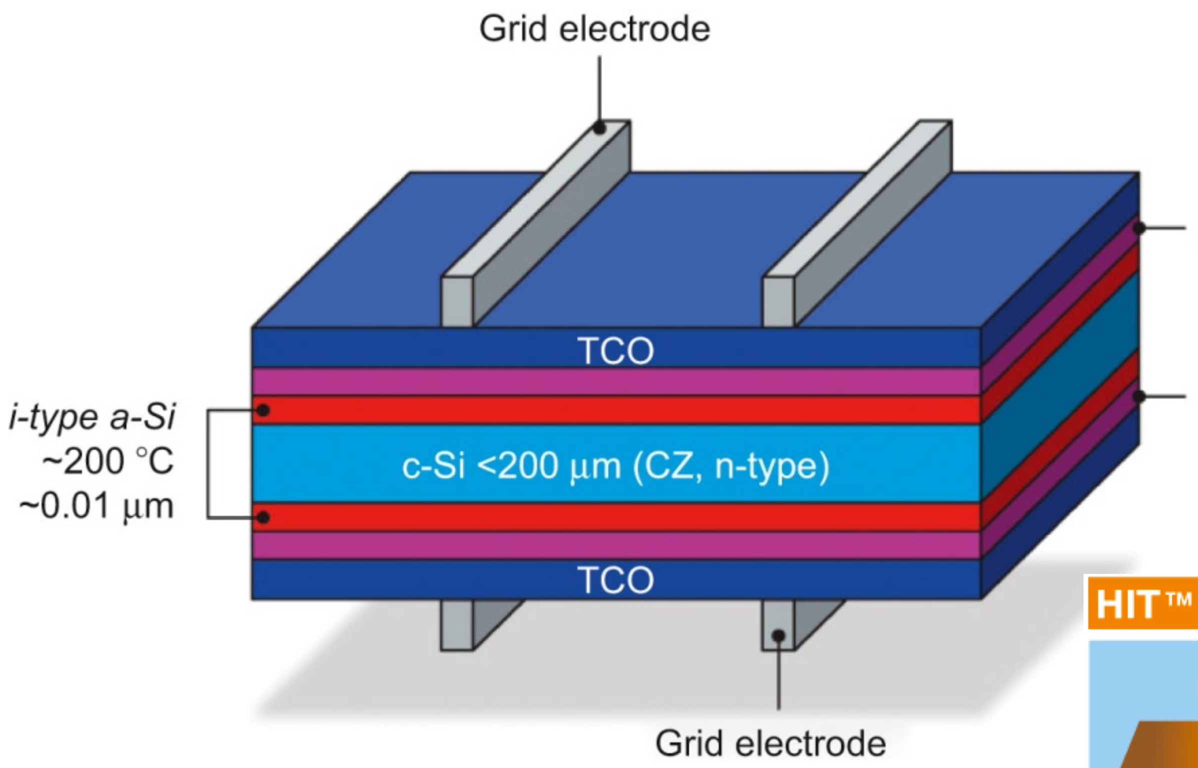
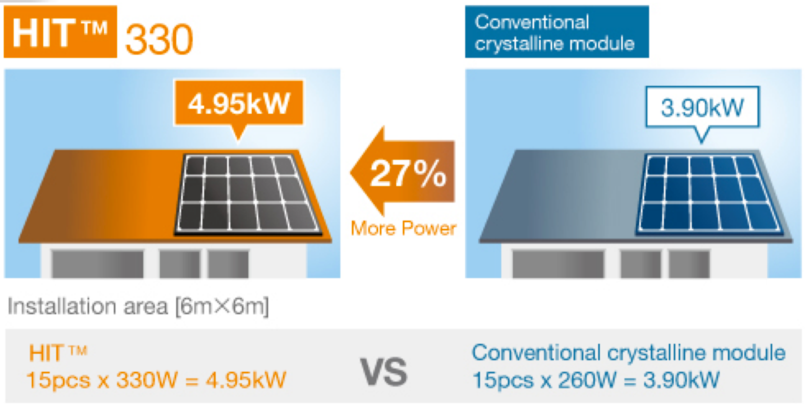
Silicon: Robust Technology



HIT cell: 25.6% (144 cm^2)

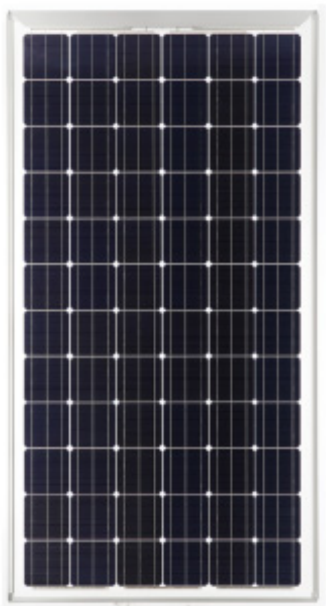


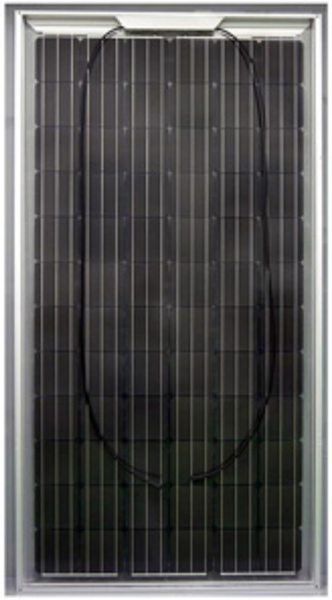
Si 'Heterojunction with Intrinsic Thin layer'

http://panasonic.net/ecosolutions/solar/hit/

Silicon: Robust Technology

HIT Double
Photovoltaic Module


Front surface


Back surface

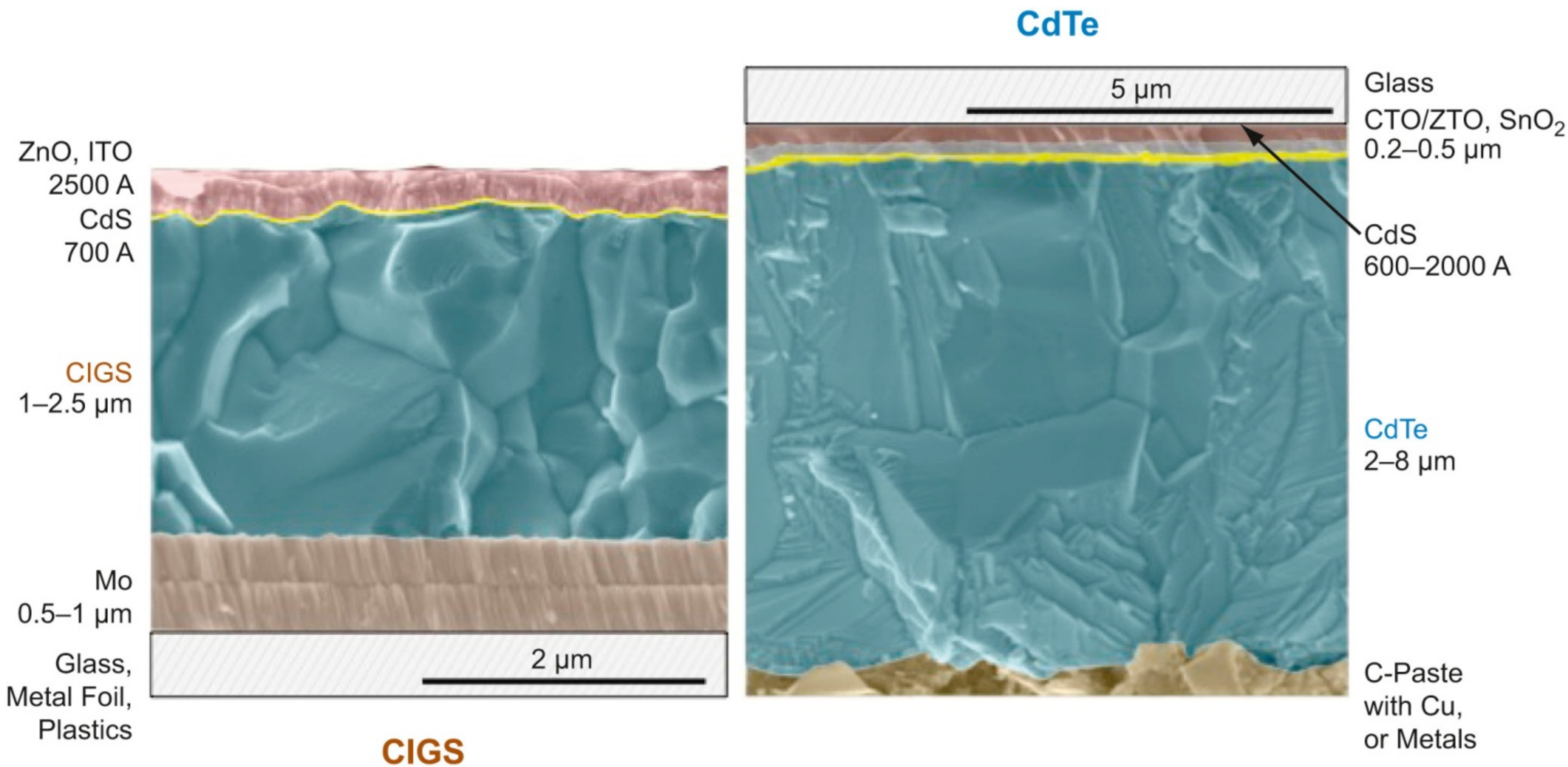

Patio Awning: 1.4kW
Solar Living Design Lakewood, CO


Canopy: 11.9kW
Acme International Services, Inc. Cayman Islands.


Canopy: 10.4kW
New American Home, Las Vegas, NV.

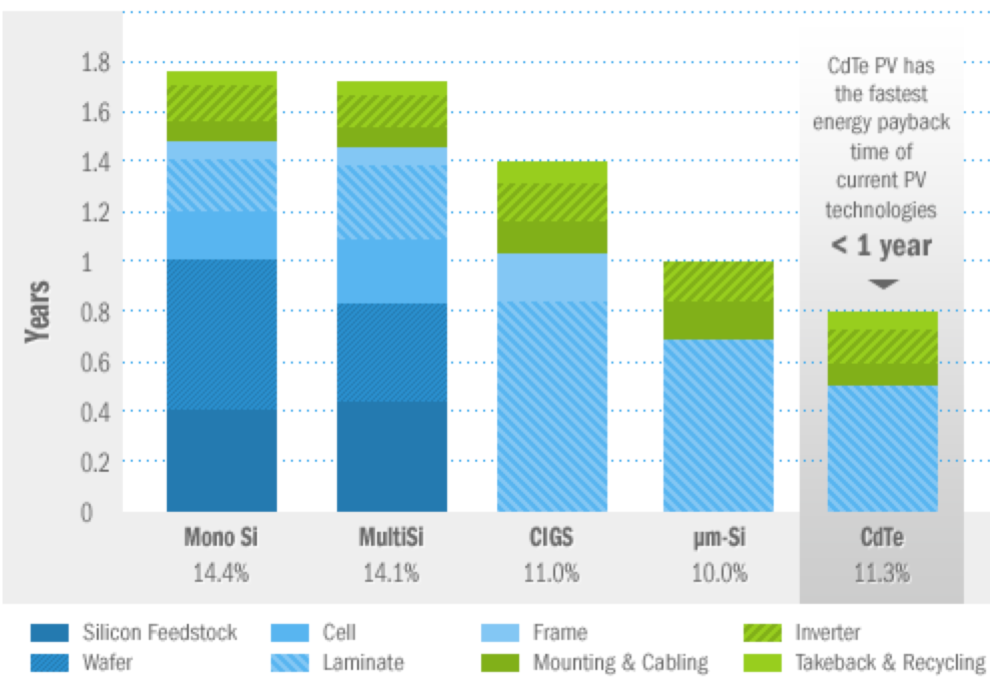
http://panasonic.net/ecosolutions/solar/hit/

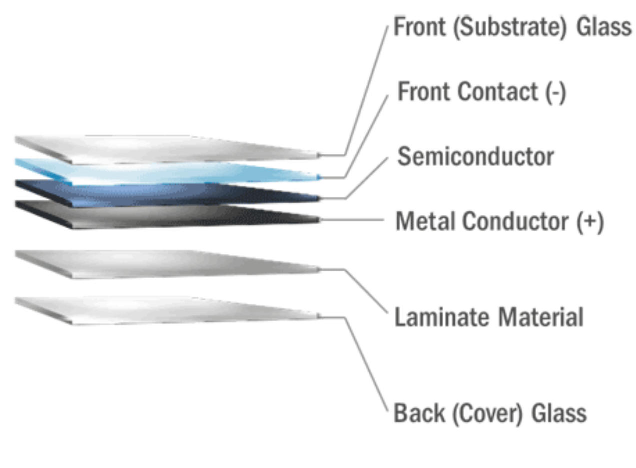
Thin Films: Indirect to Direct Band Gap



Thin Films: Rapid Energy Payback

$$\text{EPBT} = E_{input} / (E_{output} / yr)$$





First Solar's Series 4 CdTe Thin Film Module

http://www.firstsolar.com

Thin Films: Many New Materials

Discovering and optimising new candidate materials is an active research field

Cu_2O	SnS	$SnZrS_2$	$CdTe$	Cu_3N	$ZnSnP_2$
$BiFeO_3$	$CuInS_2$	$CuSbS_2$	WSe_3	$CuTaN_2$	Cu_3PS_4
$CuTaS_4$	Cu_2ZnSnS_4	$CuBiS_2$	Sb_2Se_3	$LiZnN$	$FeSi_2$
Fe_2SiS_4	Cu_2S	Zn_3N_2	$AgSbS_2$	$FeSe_2$	FeS_2
$CsPbI_3$	$CH_3NH_3PbI_3$	$CsSnI_3$	$CuTaN_2$	Bi_2S_3	Sb_2S_3

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Talk Outline: Solar Energy

1. Solar Energy Fundamentals
2. Current Photovoltaic Technologies
3. Case Study: Hybrid Perovskites

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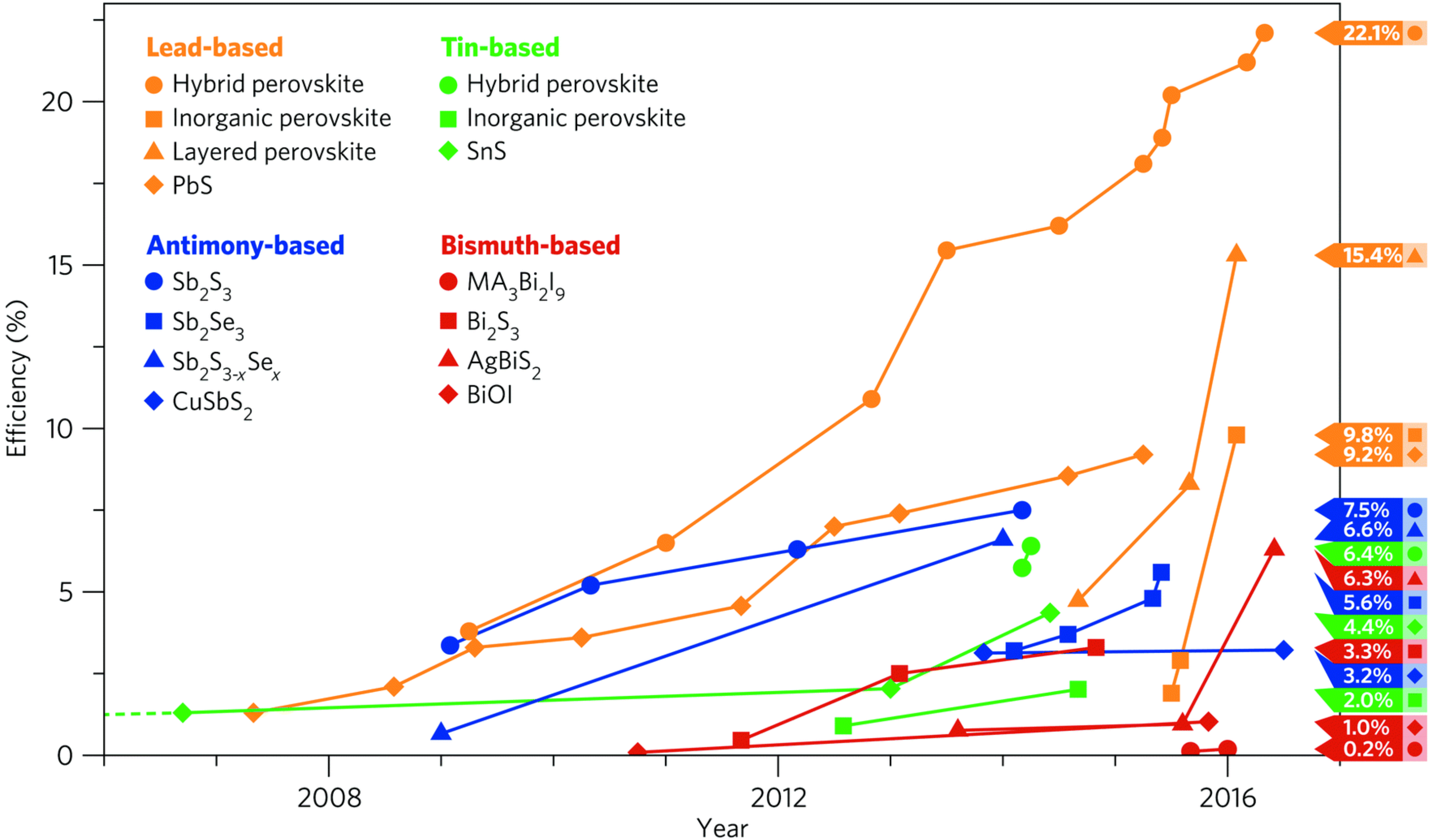
Rise of Perovskite Solar Cells



A. M. Ganose et al, Chem. Comm. 53, 20 (2017)

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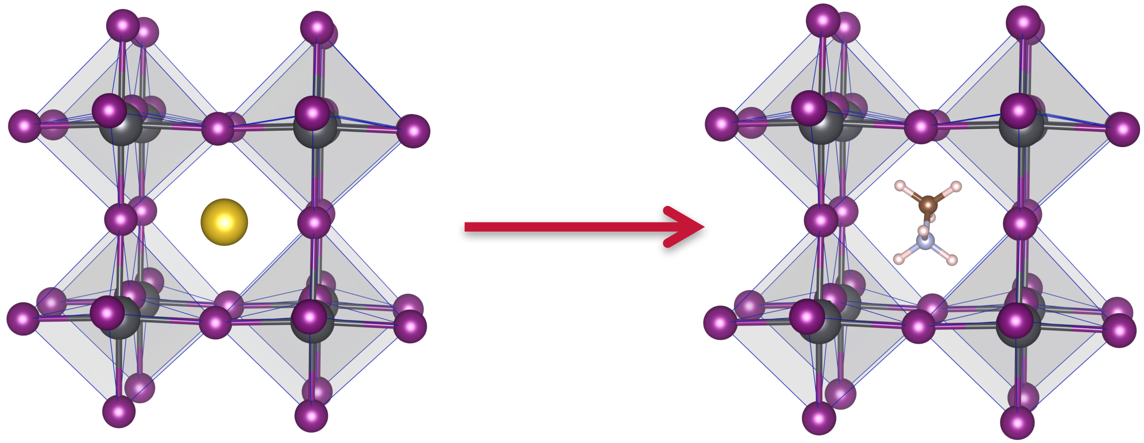
Hybrid Organic–Inorganic Perovskites

Inorganic
$CsPbI_3$



Hybrid
$CH_3NH_3PbI_3$
or MAPI

Brief History

(1958) – Photoconductivity in $CsPbI_3$ (Møller)
(1978) – Synthesis of $CH_3NH_3PbI_3$ (Weber)
(1994) – Metallic transition in $CH_3NH_3SnI_3$ (Mitzi)
(2009) – Perovskite dye cell (Miyasaka)
(2013) – Planar thin-film solar cell (Snaith)

Why Hybrid Perovskites?

Essentials for Solar Cells

- Strong optical absorption (E_g ~ *1.6 eV*)
- Light electron and hole masses (*conductive*)
- Easy to synthesise (*cheap and scalable*)

Advanced Features

- Large dielectric constants: carrier separation (*weak excitons*) and transport (*low scattering*)
- Slow *e-h* recombination: low losses, large V_{oc}
  - Relativistic effects – spin-orbit coupling
  - Ferroelectricity – dynamic fluctuations

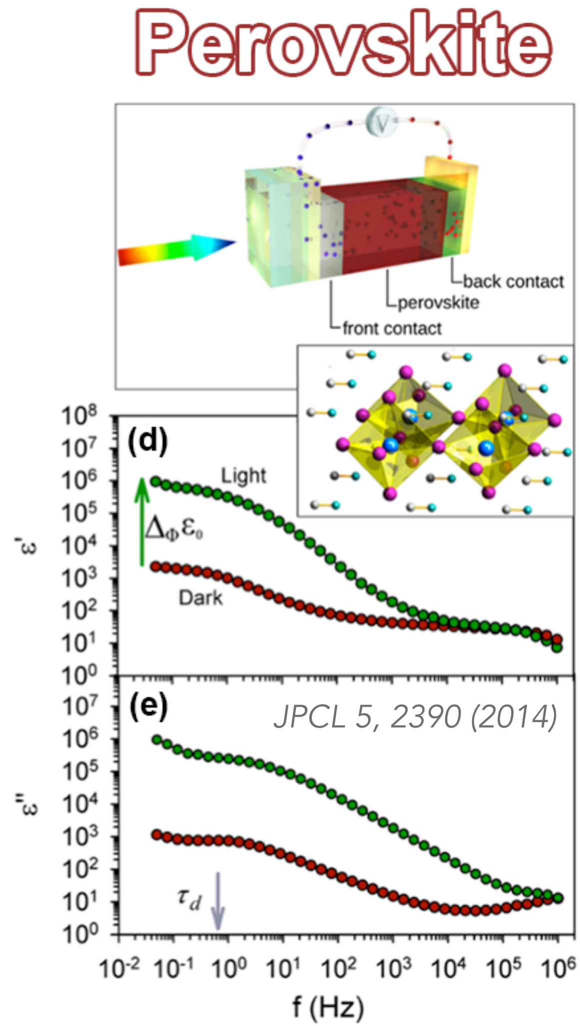
Dielectric Response

$$\overbrace{\underbrace{\epsilon_0 = \epsilon_\infty + \epsilon_{ionic}}_{\text{Standard Inorganic Dielectric}} + \epsilon_{rotation}}^{\text{Organic-Inorganic Dielectrics}} + \underbrace{\epsilon_{other}}_{\substack{\text{Microstructure} \\ \text{Conductivity} \\ \text{Contacts}}}$$

CdTe	$CuInSe_2$	Cu_2ZnSnS_4	$CH_3NH_3PbI_3$
$\epsilon_0 \sim 10$	$\epsilon_0 \sim 13$	$\epsilon_0 \sim 13$	$\epsilon_0 \sim 34$
$\epsilon_\infty \sim 7$	$\epsilon_\infty \sim 8$	$\epsilon_\infty \sim 7$	$\epsilon_\infty \sim 5$
$\epsilon_{ionic} \sim 3$	$\epsilon_{ionic} \sim 5$	$\epsilon_{ionic} \sim 6$	$\epsilon_{ionic} \sim 20$
			$\epsilon_{rotation} \sim 9(300\mathrm{K})$

Frost and Walsh, Acc. Chem. Res. 49, 528 (2016)

“Giant Dielectric Constant”



Frost and Walsh, Acc. Chem. Res. 49, 528 (2016)

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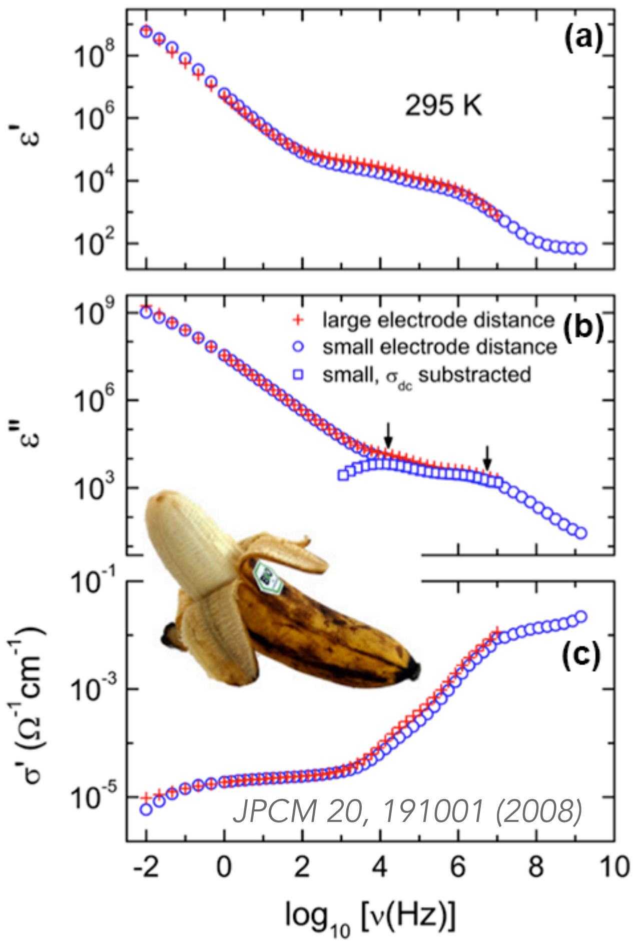
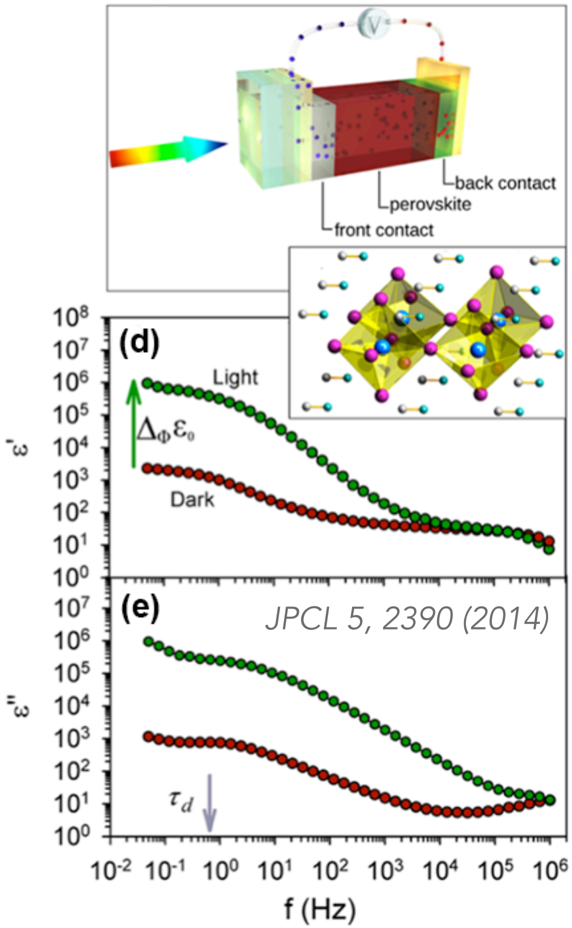
"Giant Dielectric Constant"

Banana



Perovskite



Frost and Walsh, Acc. Chem. Res. 49, 528 (2016)

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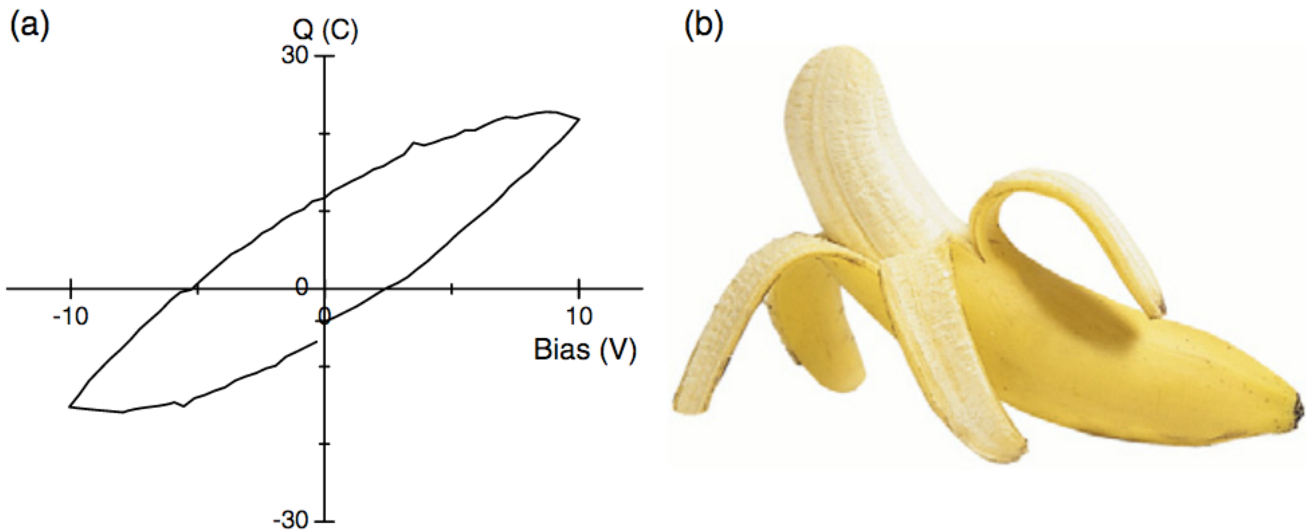
Bananas are Lossy Dielectrics



Conclusions

If your ‘hysteresis loops’ look like figure 1(a), please do not publish them. Publish data that are saturated and have a region in Q versus V that is concave. Bananas are not ferroelectric, and it is easy to be misled by closed $Q(V)$ loops.

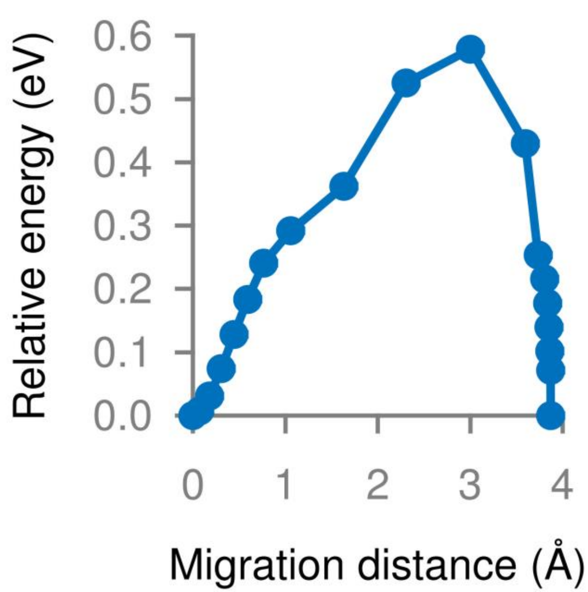
J. F. Scott, J. Phys. Conden. Matter 20, 2 (2007)

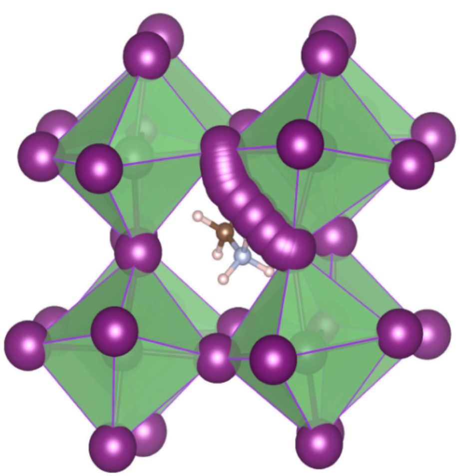
Mixed Ionic–Electronic Conductors

Reservoir of charged point defects (site vacancies) in thermodynamic equilibrium: V^{-}_{MA}, V^{2-}_{Pb}, V^{+}_{I}

Angewandte Chemie 54, 1791 (2015)

Vacancy	E_a (eV)
$CH_3NH_3^+$	0.8
Pb^{2+}	2.3
I^-	0.6





$D \sim 10^{-12} cm^2 s^{-1}$
at T = 300 K

C. Eames et al, Nature Comm. 6, 8497 (2015)

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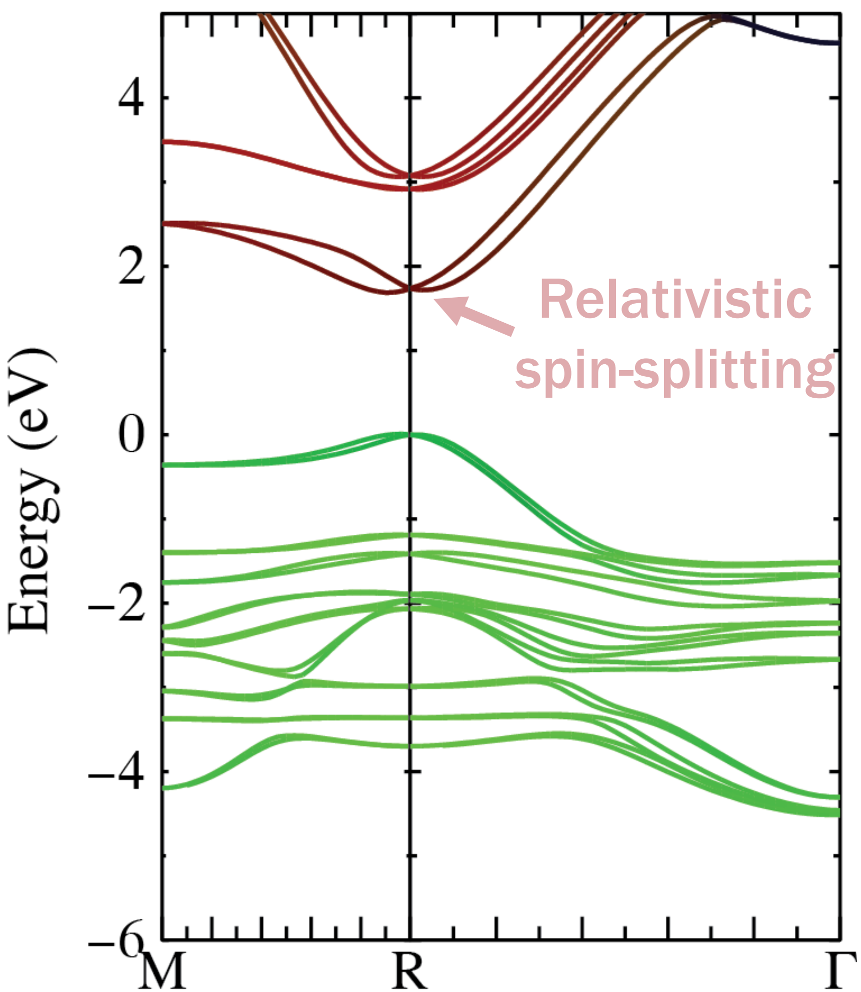
Electronic Band Structure (MAPI)



Degeneracy removed by Δ_{CF} and Δ_{SOC}

Conduction Band — Pb $6p^0$

E_g^{QSGW} = 2.7 eV → 1.7 eV (SOC)

Valence Band — I $5p^6$, Pb $6s^2$

[QS*GW* with M. van Schilfgaarde, KCL] Physical Review B 89, 155204 (2014)

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Band Gap Engineering: Principles

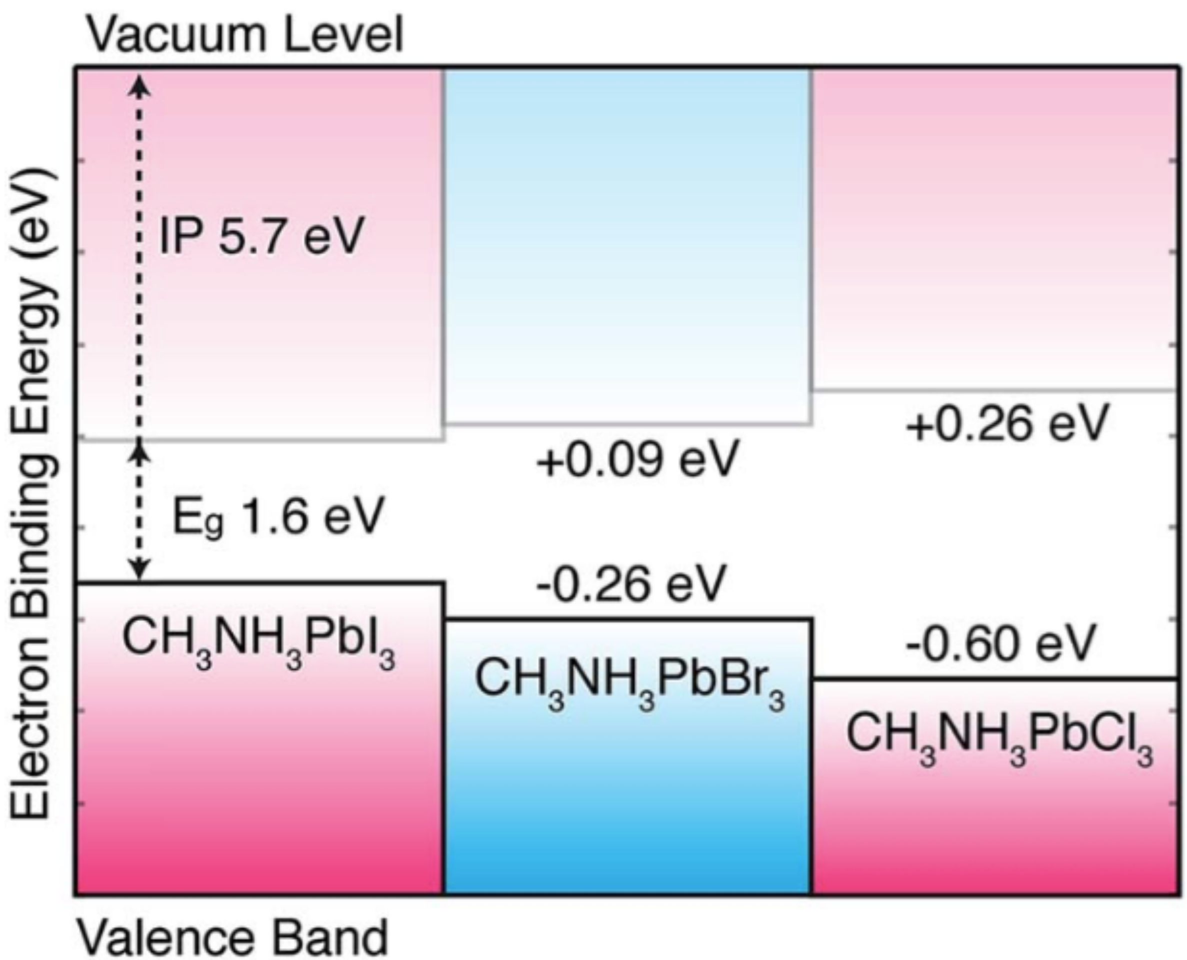
A site: Usually electronically inactive, but can change structure (volume and tilting pattern)

B site: Forms lower conduction band (Pb is key for electron affinity and transport)

X site: Forms upper valence band (I is key for ionisation potential and hole transport)

A. Walsh, J. Phys. Chem. C 119, 5755 (2015)

Band Gap Engineering: Halides



Band offsets from heterojunction core level alignments: HSE06+SOC

K. T. Butler et al, Materials Horizons 2, 228 (2015)

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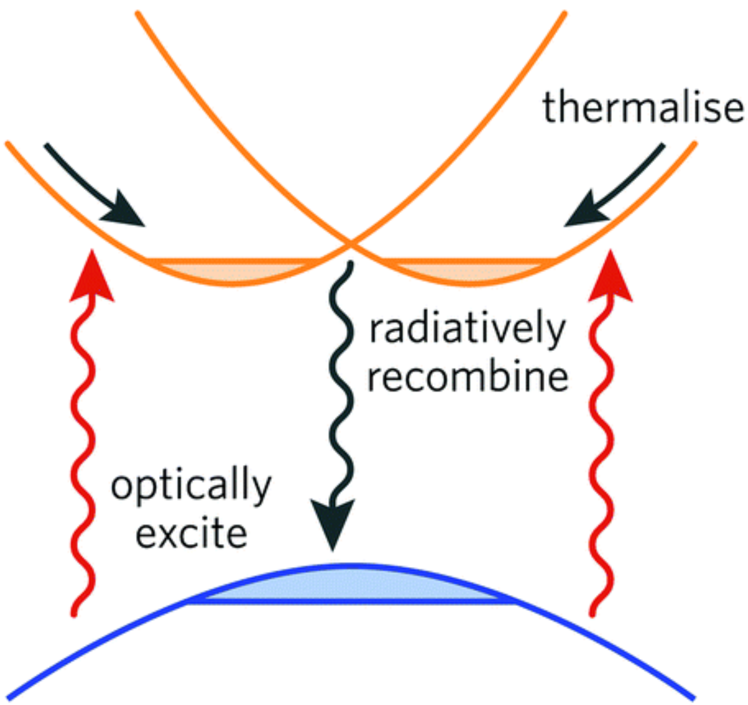
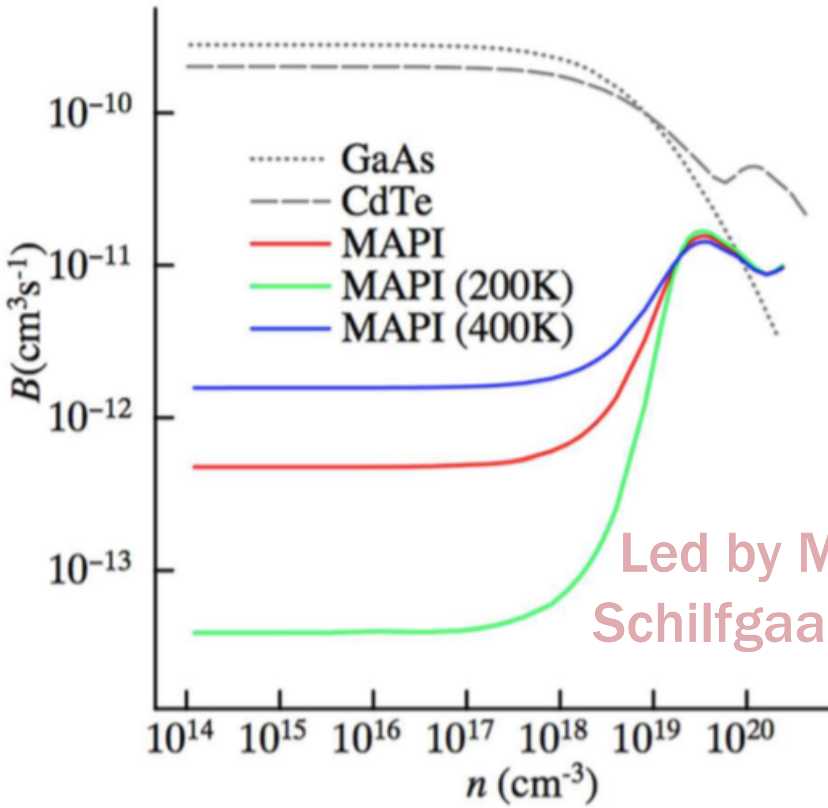
Rashba and Radiative Recombination

Rashba splitting of conduction band reduces radiative recombination at low fluence





Led by Mark van Schilfgaarde (KCL)

[First-principles recombination rates] APL Materials 4, 091501 (2016)

Support for Weakly Indirect Gap

Validation from experiment is growing

Indirect to direct band gap transition under pressure

Led by Bruno Ehrler (AMOLF); Energy. Environ. Science (2017); DOI: 10.1039/c6ee03474h

Indirect to direct band gap transition with fluence

Led by Sam Stranks (Cambridge); Nature Materials (2016); DOI: 10.1038/nmat4765

Giant Rashba splitting in $MAPbBr_3$ with ARPES

Led by Thomas Fauster (Erlangen); Physical Review Letters (2016); DOI: 10.1103/PhysRevLett.117.126401

Perovskites: Challenges & Opportunities

Local Structure – correlation lengths

Dynamic Disorder – connection to optoelectronics

Ionic Conductivity – how to limit

Electrical Conductivity – control p-type and n-type

Chemical Stability – breakdown with O_2 and H_2O

Surfaces & Interfaces – poor understanding

Alloys –thermodynamics and photo-stability

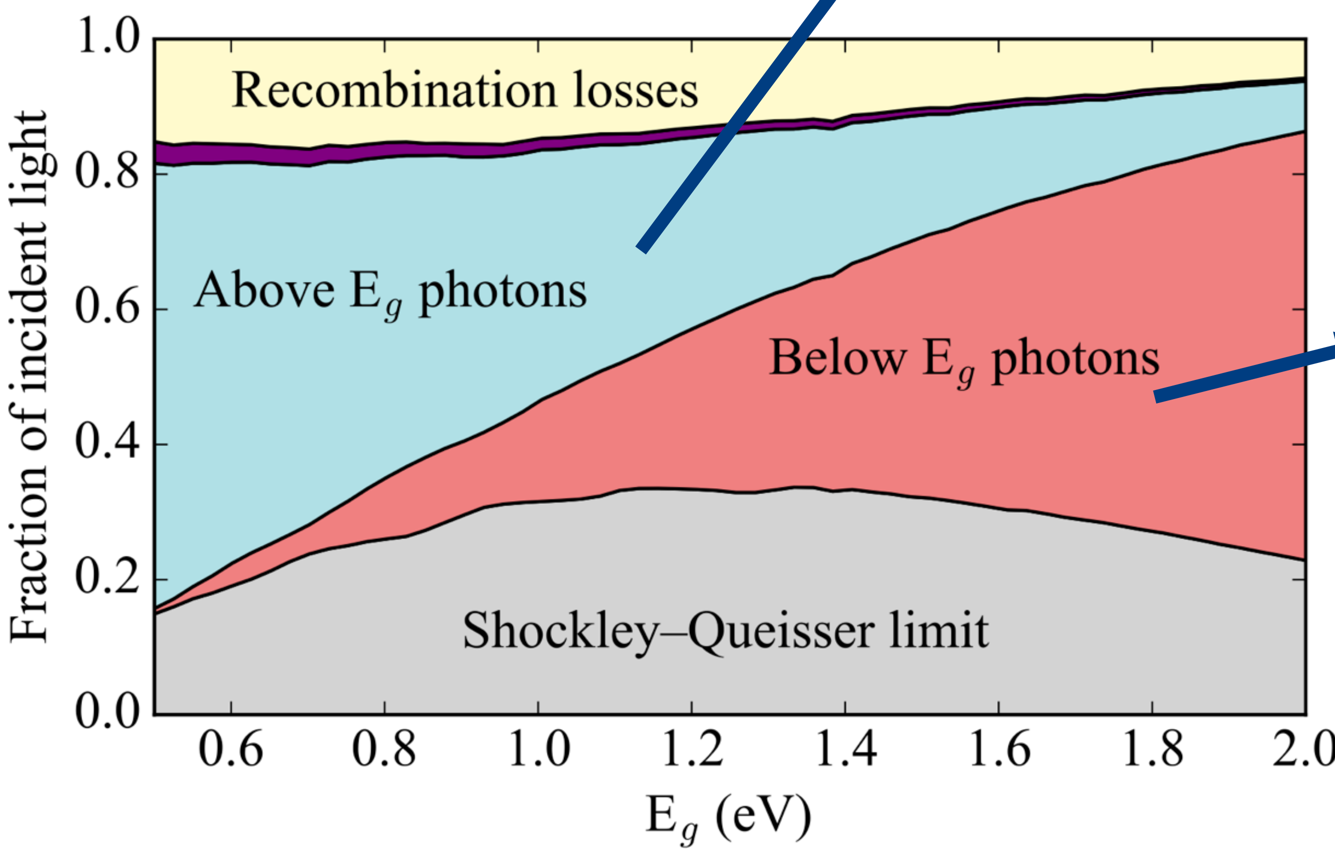
Hysteresis – how to eliminate

Beyond 3D – 2D and 1D hybrid perovskites

Beyond Pb – alternative non-toxic metals

Beyond S-Q Limit (> 30% Efficiency)

Hot carrier solar cells



Intermediate band solar cells

Summary – Key Points

- Motivation and basic science of solar energy harvesting
- Fundamental limits for light to electricity conversion
- Effective materials for photovoltaics are semiconductors that absorb sunlight and transport charges
- Halide perovskites have the potential to displace existing technologies