

# *Tomorrow's Photovoltaic Solar Cells*

John C. Bean

## Outline

Quick review of PV science / NREL's scorecard on Best Research PV Cells

Thin-film cells: Potentially low cost, but now often less efficient OR shorter-lived OR toxic

Multi-junction / Tandem cells: Using different parts to absorb different colors of sunlight

Layering multiple solar cells atop on another: The more common approach

Tuning different quantum-dots to different colors: An emerging approach

Luminescent Solar Concentrators: Capturing / converting sunlight into one PV-friendly color?

Via quantum-dots or dye molecules embedded in thin transparent plastic layers

The possibility of skimming off unwanted colors trying to pass through windows

Such as unwanted infrared (i.e., summer heat) and/or destructive ultraviolet

Thermophotovoltaics: Converting waste heat from engines, factories . . . into PV power?

Using weird manmade "metamaterials," including "photonic crystals"

*(Written / Revised: November 2019)*

# *Tomorrow's Photovoltaic Solar Cells*

**Today's Solar Cells** ([pptx](#) / [pdf](#) / [key](#)) introduced the science of PV solar cells

And then described the materials & types of cells producing today's PV power

This note set instead explores a **long list** of contenders for **PV cell of tomorrow**

Some seek cost reduction through the use of **cheaper materials**

Many strive for more efficient conversion of sunlight's **full range of colors**

Motivating the latter: SINGLE photons give ALL of their energy to SINGLE electrons

Each electron liberates itself with some of that energy (=> PV electricity)

But it uses any excess energy to whiz about, ricocheting off atoms,

kicking them into vibration, wasting that excess photon energy as heat

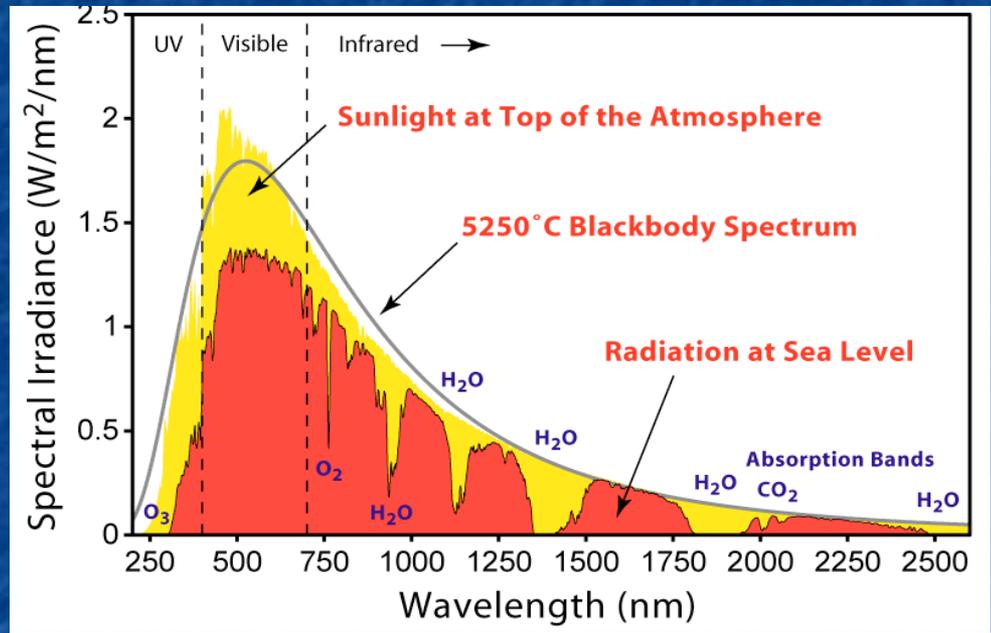
To fully appreciate these challenges, a review of my earlier PV note set is in order

## *A Review of Solar Cell Science in 10 Slides*

(See the my **Today's Solar Cells** ([pptx](#) / [pdf](#) / [key](#)) note set for greater / more palatable detail)

# PV cells TRY to efficiently convert sunlight of ALL colors into electricity

Here are plots of sunlight intensity (as power flow / area / increment of wavelength)  
at both the top and bottom of the earth's atmosphere:



Wavelength →

← Photon Energy 5 eV 2 eV 1 eV 0.5 eV



*Those colors interact **very differently** with matter:*

Infrared



Vibrates a few atoms

But most light just passes right through

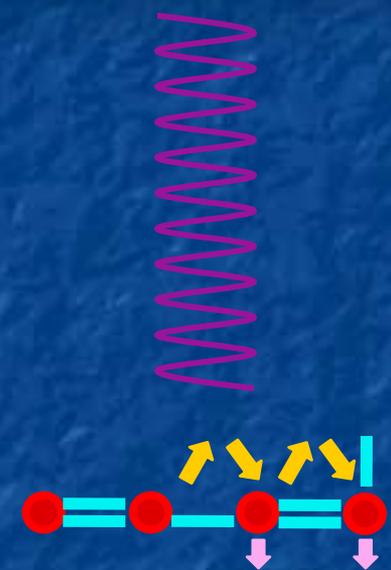
Visible



Liberates electrons from bonds

IFF the material has an electron liberation energy  $\leq$  light energy

UV



Liberates electrons from bonds  
but gives them so much **excess energy** that they ricochet all around

Excess energy is lost as struck atoms start to vibrate (=heat)

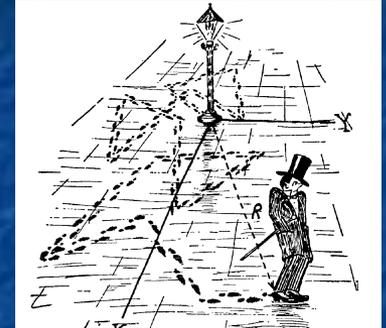
## *But mere liberation of electrons is not enough!*

Liberated electrons (leaving behind "holes" in bonds) are subject to no driving force

And thus wander randomly = **Diffusion**

Diffusion is analogous to "**the drunkard's walk**"

Depicted here, a drunk bouncing off light posts:



But PV cells have **two types of wandering drunks: electrons and (bond) holes**

And these unique types of drunks can "annihilate" one another

That is, a wandering electron can just fill the hole (in a bond) => zip!

To create a net flow (=> electricity) a photovoltaic cell **MUST** include a **cliff**

Over which the "electron drunks" will fall (and the "hole drunks" ascend)

Or the way I was first taught it:      **Electrons ~ Ball bearings (which fall DOWN)**

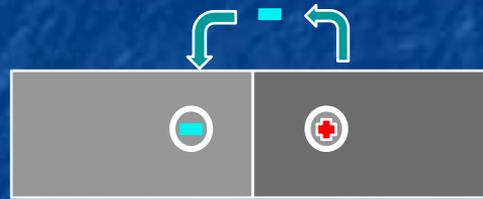
**Holes ~ bubbles (which FLOAT up)**

*The solar cell's selective "cliff" is provided by an electric field*

Which WE do NOT have to create by applying an external battery or power supply!

Instead, **electric fields** are naturally generated at the junction between two materials

But only if electrons choose to shift from one material to the another



THIS OCCURS WHEN: Material at right has electrons in energy levels higher than empty levels in material at left => Electron moves to new lower energy home!



**Negative charge displacement ALSO creates an electric field at the junction**

*Which, via careful materials selection, gets us to this point:*



The **Electric Field** sorts things out, pushing holes left & electrons right => "electricity"

But **only** if drunkard's walk of light-liberated holes & electrons GETS them to the electric field BEFORE they have recombined with one another!

If they recombine first, their energy is instead lost as heat (a.k.a. vibrating atoms)

**So why use a thick layer that puts the field (cliff) so far away? (!)**

Because light is not all absorbed (and converted to electrons + holes) at the surface

**Strong light absorption requires tenths to tens of microns of material**

*With that necessarily thick layer, situation is more like this :*



It is then **REALLY IMPORTANT** that freed electrons & holes do NOT recombine before reaching the sorting electric field at the junction between the layers

Their average random walking **survival distance** is called their **diffusion length**

Diffusion length depends on the structure and purity of the material because:

Electrons & holes are drawn to **impurities and flawed crystal bonds**

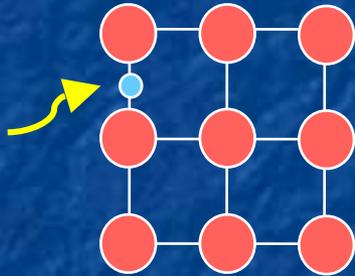
Once together at such **TRAPS**, electrons & holes can easily recombine

So the purity and perfection of PV crystals is extremely important!

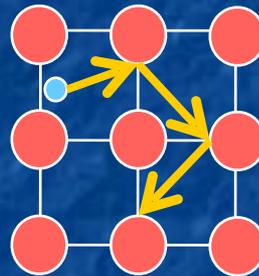
*But looking more closely at the light photon's absorption by an electron:*

Different cell materials have different electron liberation energies (= "**Bandgaps**")

1) Absorbing photon's energy, electron uses "bandgap" of it to climb out of a bond:



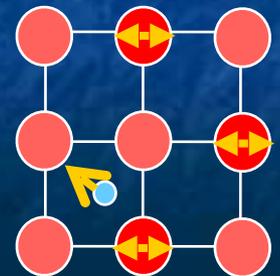
2) Any leftover energy propels electron madly through PV cell (=> "**Butt-Kicking**")



3) Struck atoms absorb that Butt-Kicking kinetic energy:

=> Atomic vibrations (= Heat) + Slowed down electron

**Heat energy is NOT converted to electrical power!**



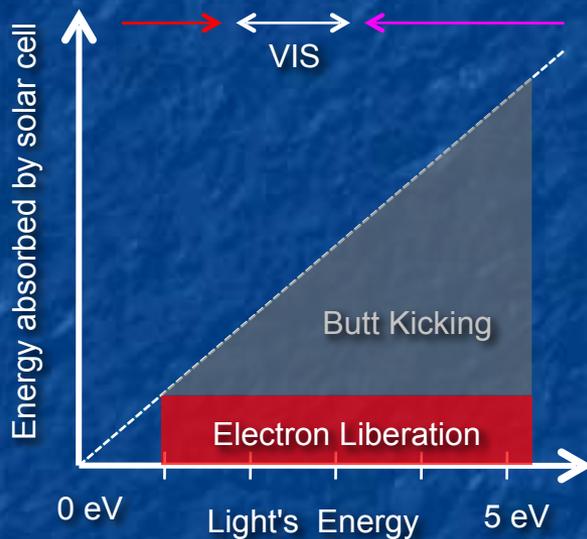
# Fate of absorbed light energy in materials having different bandgaps:

$\text{Energy}_{\text{photon}} < \text{Material's bandgap}$ : Minimal absorption, zero electron liberation

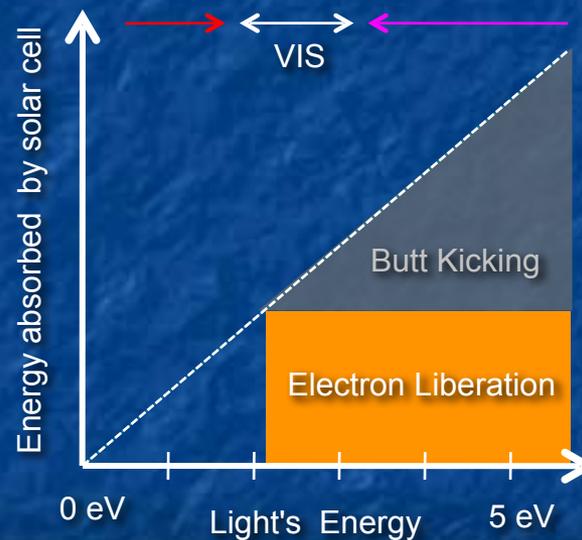
$\text{Energy}_{\text{photon}} = \text{Material's bandgap}$ : All of energy goes into electron liberation

$\text{Energy}_{\text{photon}} > \text{Material's bandgap}$ : More & more energy wasted on Butt-Kicking

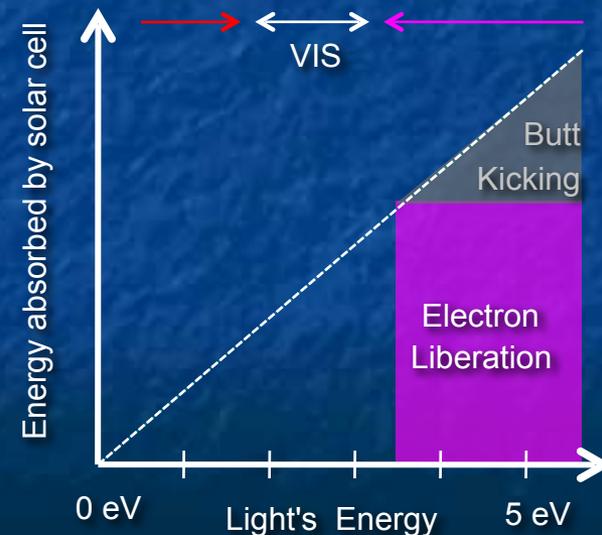
## Cell with small "bandgap"



## Cell with medium "bandgap"



## Cell with large "bandgap"



**Gray Triangles => Energy lost to heating of the cell**

# *Electron liberation energy, alone, is reclaimable as PV electric output*

Working out possible power output for a PV cell **above** the earth's atmosphere:

Full available sunlight power = **Area under yellow curve**

Net electron liberation power absorbed by small bandgap cell = **Area under red curve**

Net electron liberation power absorbed by medium bandgap cell = **Area under orange curve**

Net electron liberation power absorbed by large bandgap cell = **Area under violet curve**

**<= Light's Energy (eV)**

5 eV

2

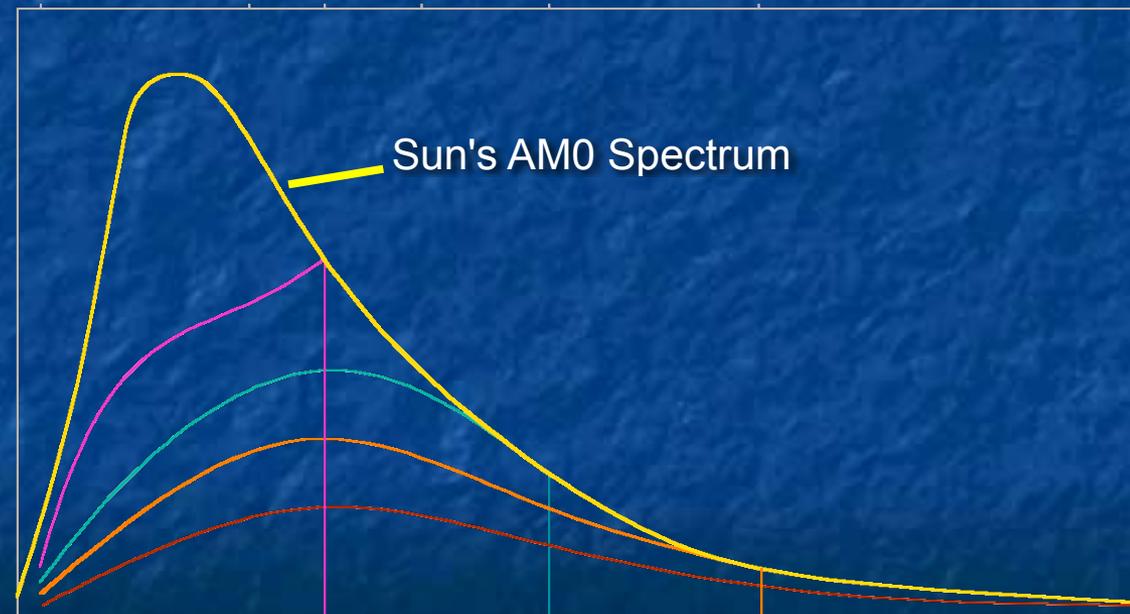
1.5

1.25

1 eV

0.75 eV

0.5 eV



Sun's AM0 Spectrum

**Light's Wavelength (nm) =>**

250

500

750

1000

1500

2000

2500

*Larger the area under a curve => Larger the possible electrical output*

BIGGEST area comes between the curves for cells made of 1 eV & 1.5 eV materials

Material with a 1.3 eV bandgap could capture & convert ~ 35% of Sun's energy

This is called the **Shockley-Queisser Limit** after William Shockley & Hans Queisser

This ~ 35% efficiency limit is NOT due to poor solar cell engineering!

It is instead because:

**We can ONLY CAPTURE that part of light energy liberating electron from bond,**

**REST of light energy is wasted giving that liberated electron a kick in the butt**

**All because a photon insists on giving ALL of its energy to a single electron**

**(even photons with enough energy to liberate multiple electrons!)**

*What are **today's** PV cells?*

*What **emerging** cells seek to replace them?*

*The U.S. National Renewable Energy Lab (NREL) tracks this via their annual:*

## **Best Research Cell Efficiencies** chart

As the name suggests, the chart records results achieved ONLY in a lab

Even if only ONE lab in the whole world has ever achieved these results!

Meaning that many of these cells are not (and may never become) commercially viable

But the chart **does** try to plot all credible contenders & their R&D progress

**Here is the 2018 chart in its full (and decidedly gory) glory: <sup>1</sup>**

*1) In the summer of 2018 I downloaded the following (then current) version of the NREL chart at:*

<https://www.nrel.gov/pv/assets/pdfs/pv-efficiencies-07-17-2018.pdf>

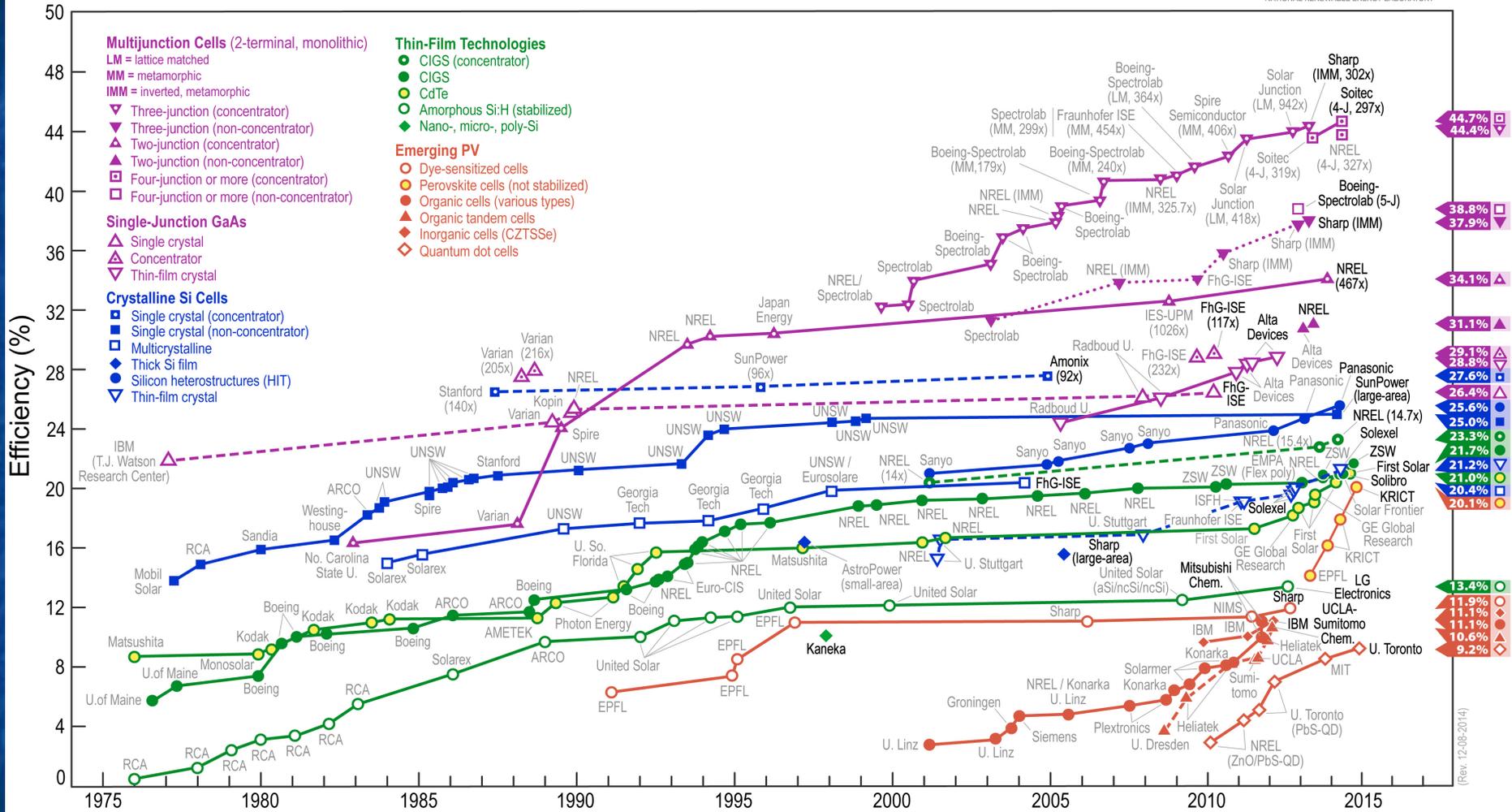
*This link has since died (as MANY U.S. Government links to renewable energy data have died under the Trump administration)*

*This alternative link was still functional as of late February 2019:*

<https://www.energy.gov/eere/solar/downloads/research-cell-efficiency-records>

# The full (high-resolution version) of the 2018 NREL chart:

## Best Research-Cell Efficiencies



This chart's file is HUGE, starting out more than four times the size of a PowerPoint slide

So I will only use this high-resolution version here (and you may have come back to magnify its details)

Today's mature & commercialized cells fall in the chart's center

This note set's featured emerging cells are at the top & lower right:

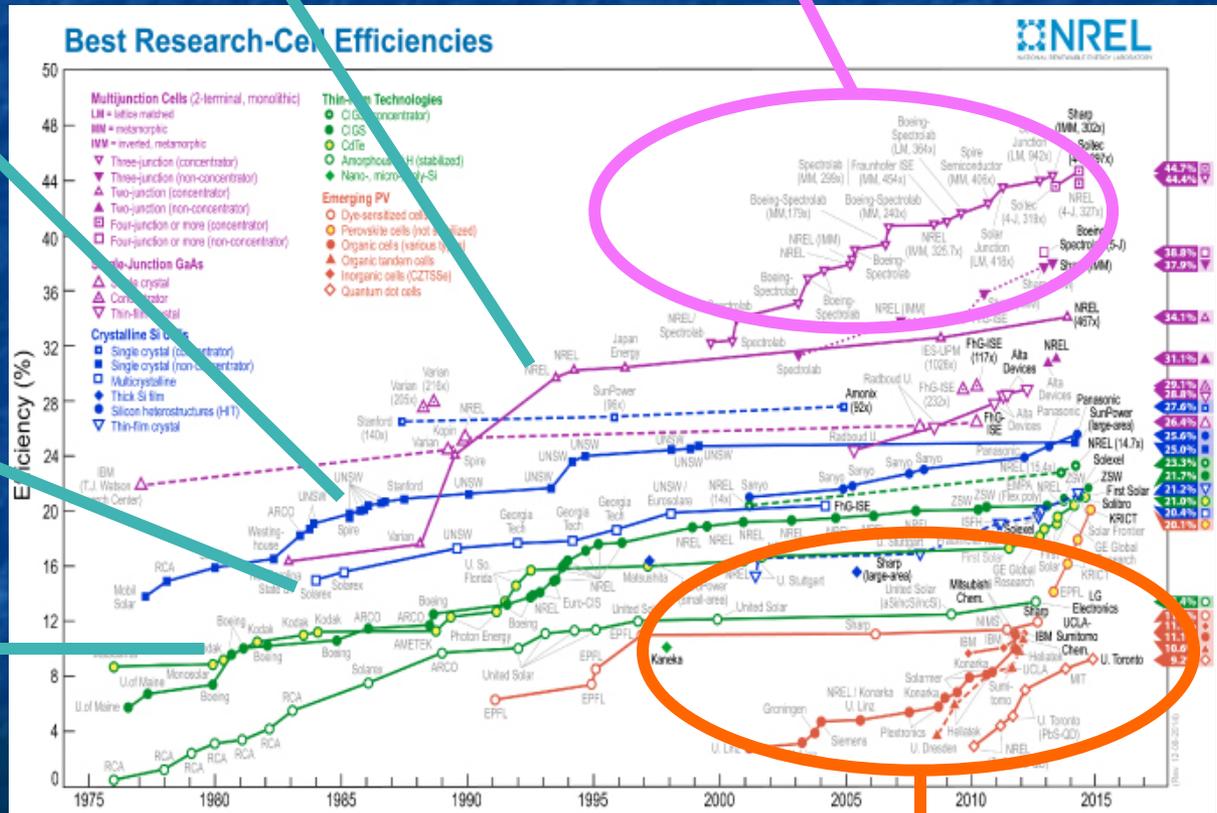
Emerging Multi-junction / Tandem PV

Single crystal GaAs PV

Single crystal Si PV

Polycrystal Si PV

Amorphous Si PV



Emerging Thin-Film PV

# Research on "thin-film" PV cells targets cost reduction

As their name suggests, these cells use only very thin sunlight-absorbing layers

Generally sprayed or painted on cheaper substrates such as sheet metal

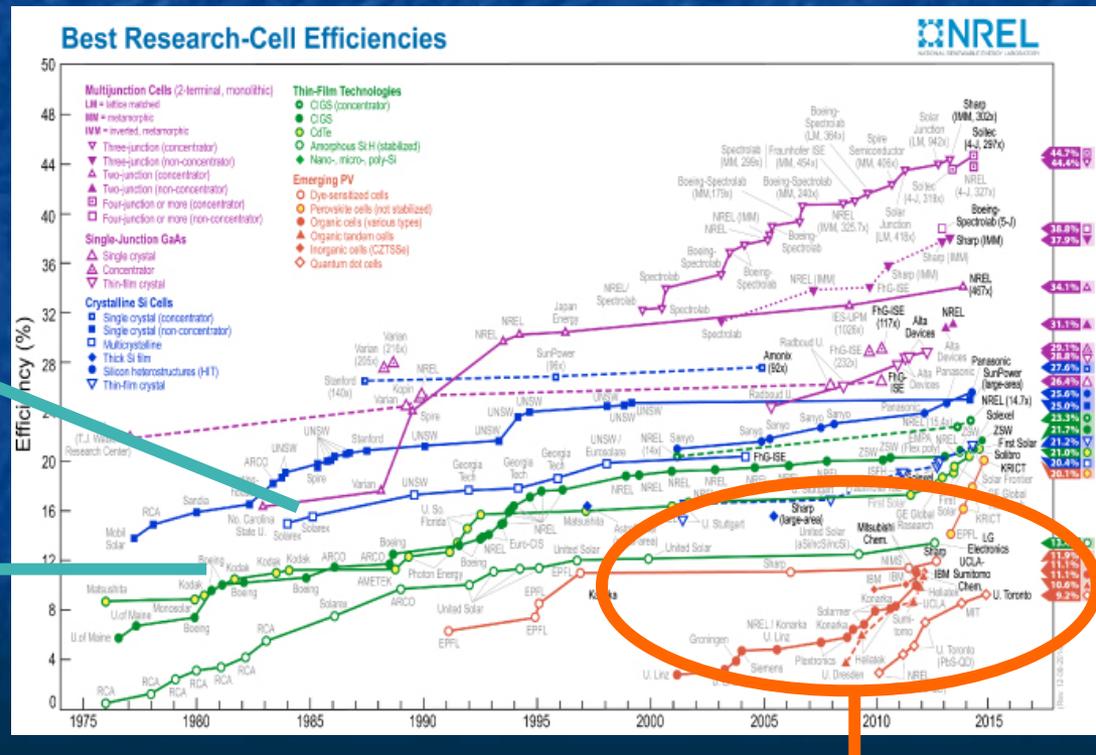
Thinner light-absorbing layers reduce cost . . . but they can also reduce cell efficiency

One reason thin-films fall in the lower-efficiency bottom half of the chart

Established Thin Film PV:

Polycrystal Si

Amorphous Si



Emerging Thin-Film PV

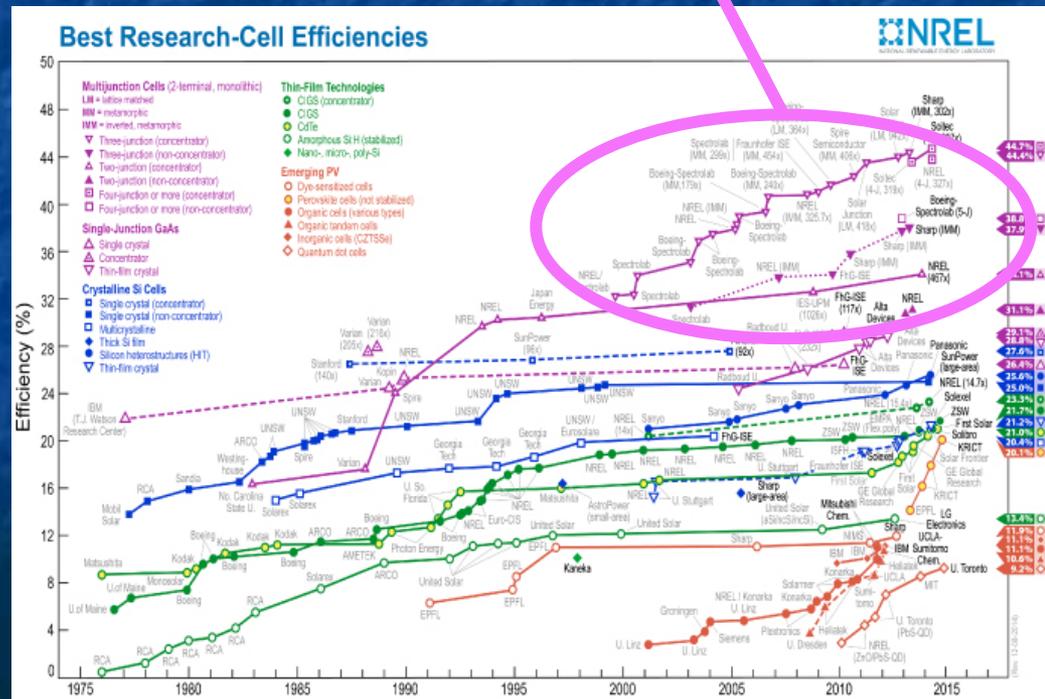
# Research on "multi-junction" / "tandem" PV cells targets improved efficiency

Which is achieved by merging together **several different PV cells**

Each targeting only that **part** of the sun's spectrum that their chosen material most efficiently absorbs and converts (by minimizing Butt-Kicking)

The challenge: Can such a large increase in complexity ever yield **affordable** PV?

## Emerging Multi-junction / Tandem PV



## *Thin Film Photovoltaic Solar Cells:*

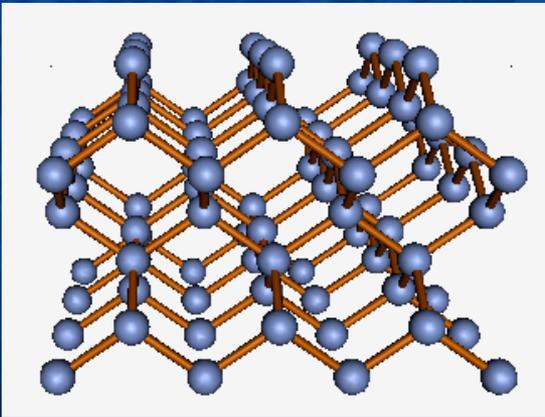
*Light-liberated electrons MUST reach the cell's charge-sorting electric field*



Which may NOT occur if they instead get hung up at those black blobs (**traps**)

These are generally faulty crystal bonds, or certain deadly impurities

The dominant "Crystalline Si" PV technology avoids such "traps" through its use of:



Almost flawless ( $\sim 1$  atom in  $10^{15}$  out of place)

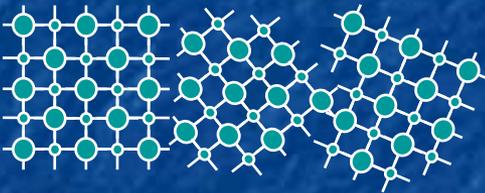
hyper-pure ( $\sim 1$  impurity per trillion atoms)

silicon crystals - **Which are thus quite expensive!**

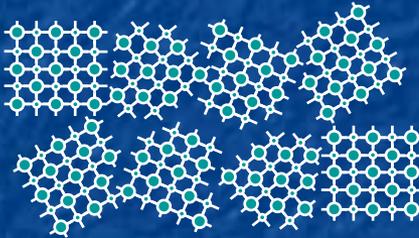
*Flawed or completely disordered silicon is a heck of a lot cheaper!*

Other possible silicon structures (in simplified 2D representations):

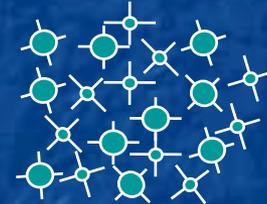
Multi-crystalline:



Poly/microcrystalline:



Amorphous:



The wealth of flawed, broken or missing crystal bonds creates myriad electron traps

But if a large quantity of **hydrogen** is added to such structures,

IT attaches to the traps, rendering **most** ineffective (i.e., "**passivating**" them)

Which is exploited in commercial **thin-film poly-Si** & **thin film amorphous-Si** PV cells

Which ARE much cheaper, but also less efficient (not **all** traps are passivated),

and shorter-lived (because the hydrogen can gradually escape)

*Is hydrogen also the salvation of "Emerging Thin Film" PV cells?*

*No, most of these instead rely on what I call **mushy**\* semiconductors*

The exceptional strength of Si-Si bonds facilitates growth of its extraordinary crystals

But it also means that, once grown into crystals, Si atoms can't move around

And that includes not moving to fix any flaws grown into that crystal

Thus, from the outset, Si PV crystals must be extremely pure and perfect!

But in far less stable, low melting point semiconductors, atoms CAN move around

Meaning that (at least to some extent) these materials CAN **self-heal**

And much poorer starting crystals (or polycrystals) often work well for PV!

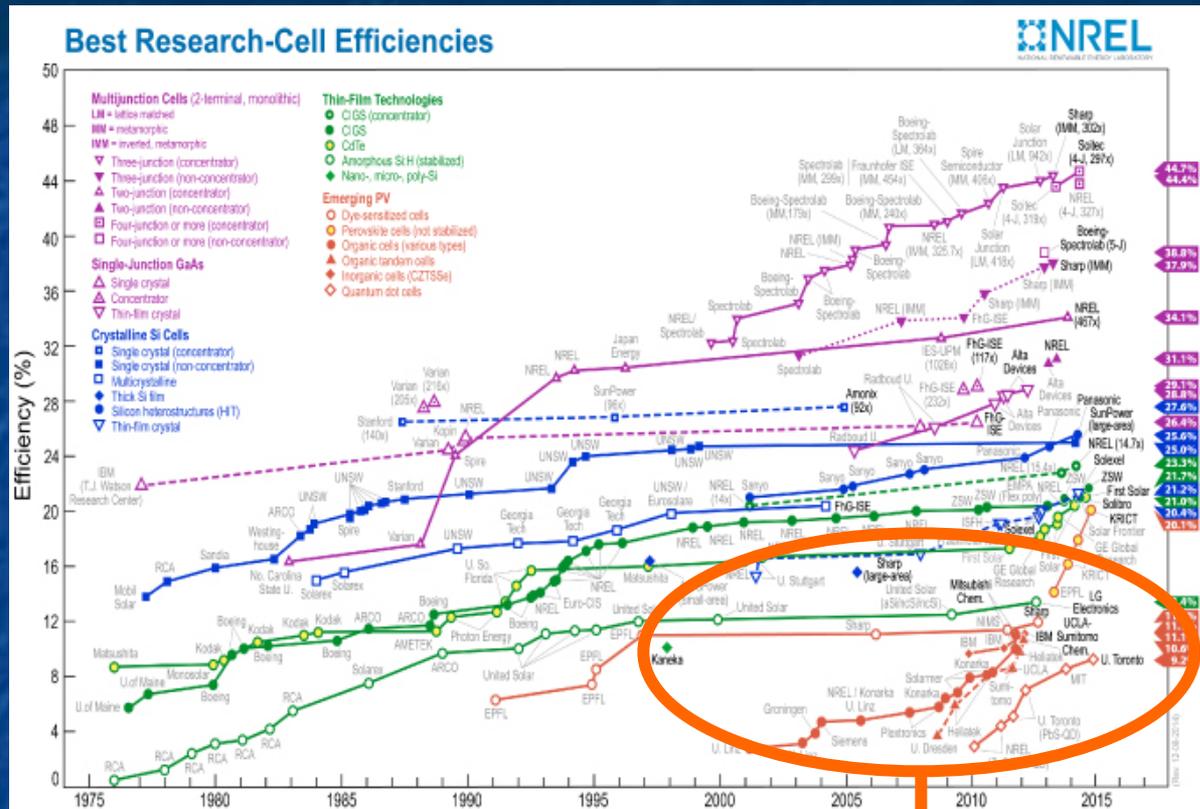
**But there is also a down side:** Low T semiconductors ARE less stable

So their PV cells often readily degrade (accelerated by moisture & **UV sunlight**)

Further, breaking down, they can release their often **toxic components**

*\* As a career PV researcher ([link](#)), I reserve my right to make up descriptive (if somewhat silly) technical terms*

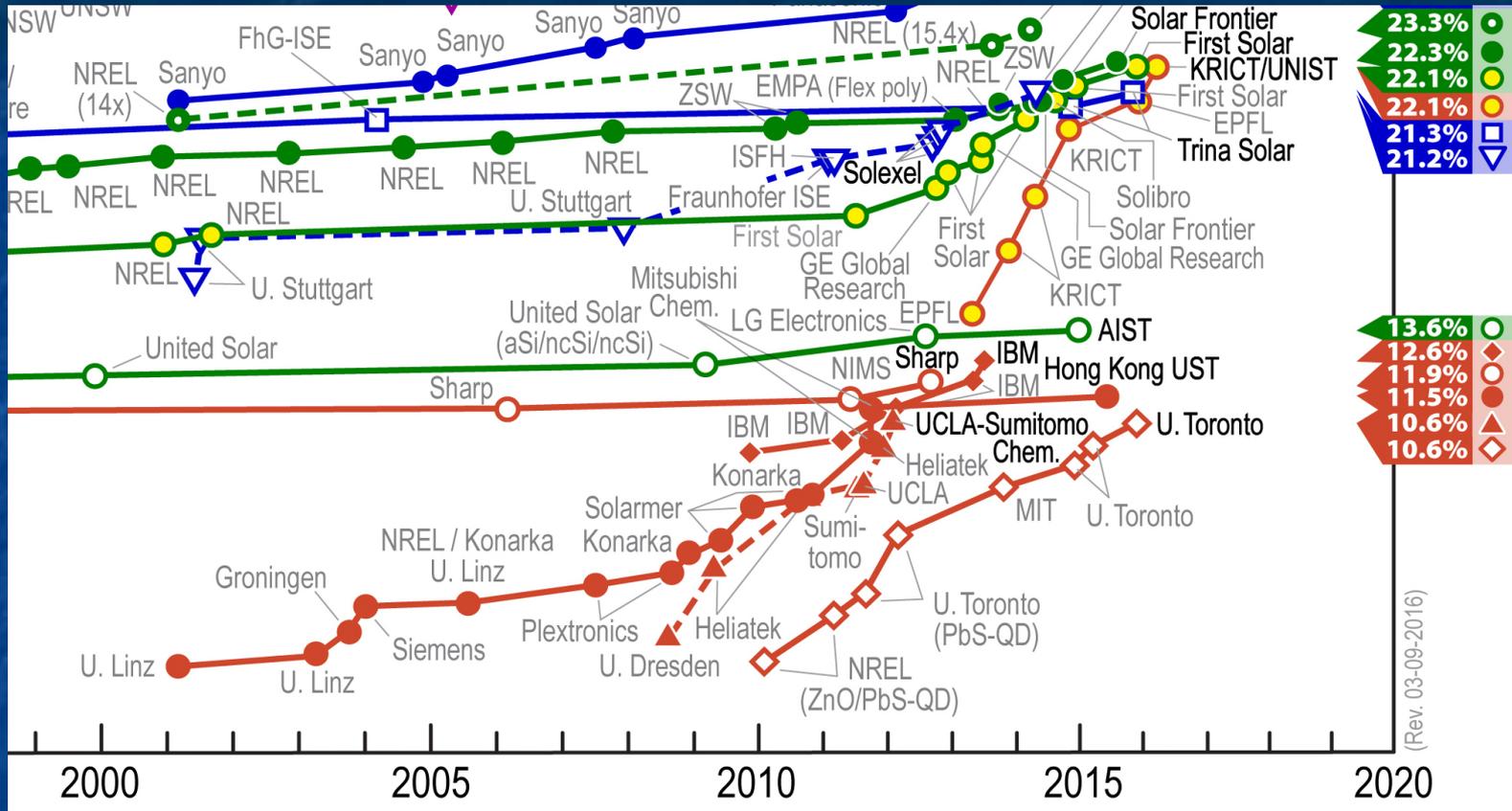
# What are those mushy "Emerging Thin Film" alternatives to Silicon?



Emerging Thin-Film PV

We'll need to enlarge this corner of the NREL chart:

# That corner (and its explanatory keys):



Efficiency of light to electric power conversion

- Thin-Film Technologies**
- CIGS (concentrator)
  - CIGS
  - CdTe
  - Amorphous Si:H (stabilized)

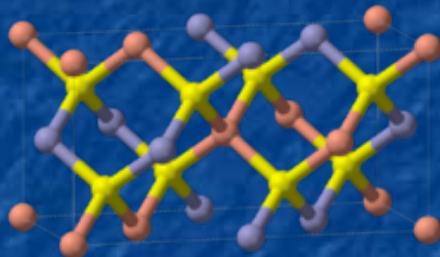
- Emerging PV**
- Dye-sensitized cells
  - Perovskite cells (not stabilized)
  - Organic cells (various types)
  - ▲ Organic tandem cells
  - ◆ Inorganic cells (CZTSSe)
  - ◆ Quantum dot cells

(Established & commercialized)

## *Starting with the older thin film technologies:*

Being more mature, they tend toward higher but more slowly improving efficiencies

No longer considered "emerging" is Copper Indium Gallium Selenide =  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$



[http://en.wikipedia.org/wiki/Copper\\_indium\\_gallium\\_selenide](http://en.wikipedia.org/wiki/Copper_indium_gallium_selenide)

In its structure **Cu** takes one site, either **In** or **Ga** takes the next, and **Se** takes the last:

Which makes "**CIGS**" an **alloy** of two **compounds**

(x in formula = the **In** fraction, remainder 1-x = the **Ga** fraction)

The two (fixed stoichiometry) compounds:

**CuInSe<sub>2</sub>** with an electron liberation energy (bandgap) of 1.0 eV, and

**CuGaSe<sub>2</sub>** with an electron liberation energy (bandgap) of 1.7 eV

Thus for  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ , as x changes from 0 to 1, CIGS bandgap goes 1.7 to 1 eV

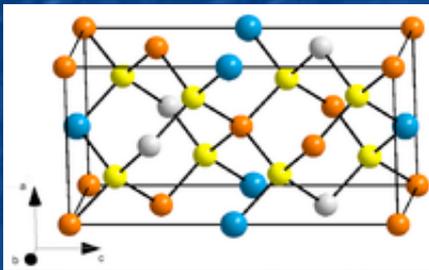
So you can **TUNE** a CIGS cell to the maximum Shockley-Quiesser efficiency

*Closely related to CIGS but still "emerging" are thin film CZTS & CZTSe*

Standing for copper zinc tin sulfide ( $\text{Cu}_2\text{ZnSnS}_4$ ) & copper zinc tin selenide ( $\text{Cu}_2\text{ZnSnSe}_4$ )

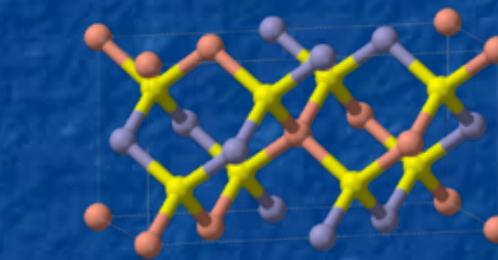
Which can be alloyed together as CZTSSe (more precisely:  $\text{CZTS}_{4x}\text{Se}_{4(x-1)}$ )

CZTS and CZTSSe crystal structure:



With color coding of **Cu**, **Zn**, **Sn**, **S or Se**

Versus the CIGS crystal structure of:



Versus **Cu**, **In or Ga**, **Se**

While not identical, these are all very, very similar, as are their solar cell properties

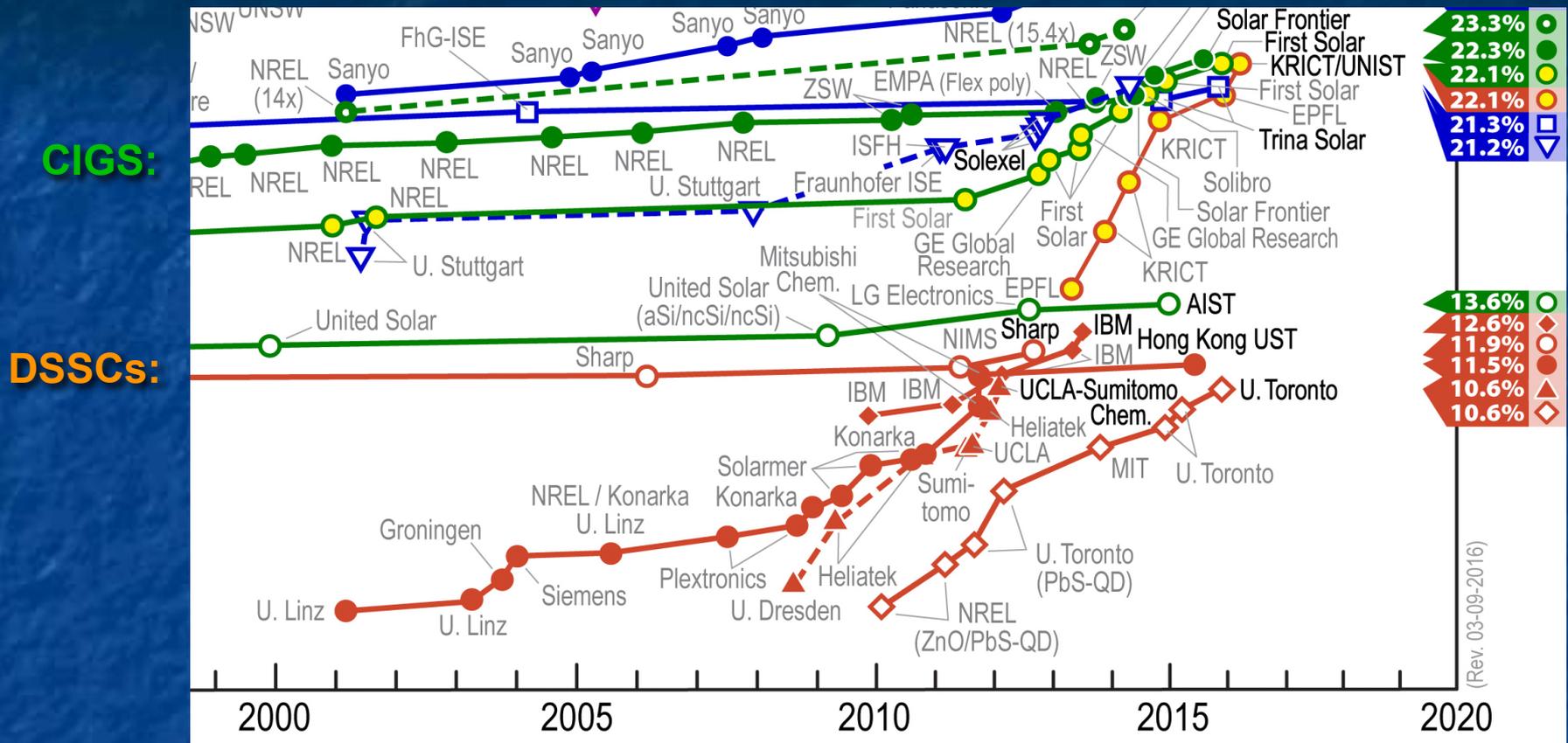
**The big difference is that CZTS eliminates toxic Se in favor of more abundant, less toxic, S**

**CZTS should** be more environmentally friendly

And its use of more abundant **S could** make it cheaper

**But at this point CIGS cells are still ~ 2X more efficient (22.3% vs. 12.6%)**

# Similar to CIGS in maturity are "Dye-sensitized solar cells" (DSSCs):



Efficiency of light to electric power conversion

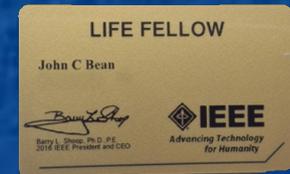
(Rev. 03-09-2016)

## *Explanation of DSSC's requires delving into terminology:*

Most of the preceding cells come from the **physics & electrical engineering world**

Known as the "Device Physics Community"

Of which, yes, I am a card-carrying member:



DSSC's were instead developed by **chemists** (or even the occasional **biologist**)

**The science is essentially similar**

But the terminology is fiercely different, as is the researcher's approach:

- Physicists focus on atomic scale mechanisms (getting vague at larger scales)
- Chemists focus on macroscopic properties (getting vague at the atomic scale)

**So what follows is my attempt at both bridge-building AND translation**

## Chemistry speak vs. Physics speak:

Papers on DSSC's (and the organic cells to follow) talk about three things:

1) **Dyes** or **photo-sensitizers** in which light produces unbonded electrons & holes

Using my 1<sup>st</sup> solar lecture key of ● = atomic cores, — = electrons:



Thus: Chemist's "Dye / photo-sensitizer" = Physicist's "semiconductor"

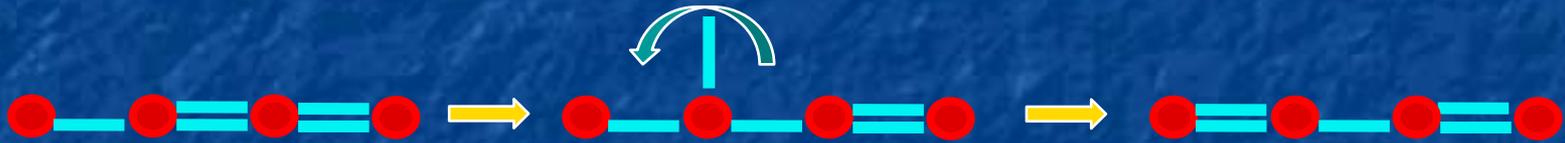
2) **Hole transport materials** (or layers) in which **ONLY** holes can move:



## Only holes move? But weren't electrons really moving?

Yes, but the subtle distinction is as follows:

A single hole move = valence electron slithering from one bond to an adjacent one:



But it really doesn't have to jump as it's actually a quantum mechanical cloud

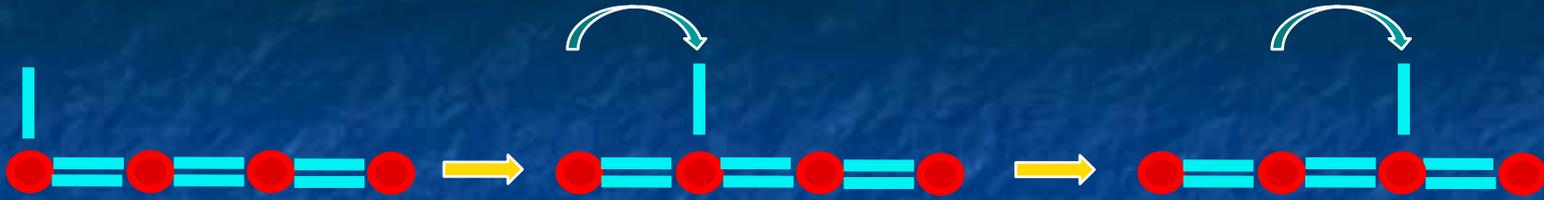
Which can just ooze around the atom's core from one bond to another:



That oozing requires very little additional energy

- In Physics speak: This electron remains in the "**valence band**"
- In Chem speak: It's in the "**HOMO**" = Highest (normally) Occupied Molecular Orbital

*As opposed to the movement of a truly unbonded electron:*



This electron **cannot** just ooze from one side of an atomic core to the other:

Because it's **outside** the atomic core (which is already fully packed w/ electrons)

So it's at a much higher energy - Physicist: it's in the "**conduction band**"

Chemist: It's in the "**LUMO**" = Lowest (normally) Unoccupied Molecular Orbital

Which, also in Chem-speak, makes the material above an:

3) **Electron Transport Material** (or layer)

In their preferred liquid environment, Chemists can simplify things further:

Electron Transport Material (wet) => Solution with negative ions (anions)

Hole Transport Material (wet) => Solution with positive ions (cations)

*All **three** things occur in the physicist's classic semiconductor solar cell*

Why **wouldn't** all three things happen in ANY single material?

1) If bonds are too strong (the "**bandgap**" is too large), light **won't** be absorbed,

=> Electrons will not be liberated from bonds

2) If bonds are too strong, any loose electrons won't **stay** liberated,

=> Killing off (unbonded) electron transport

3) If material's bonds are oriented or separated differently, result might be that

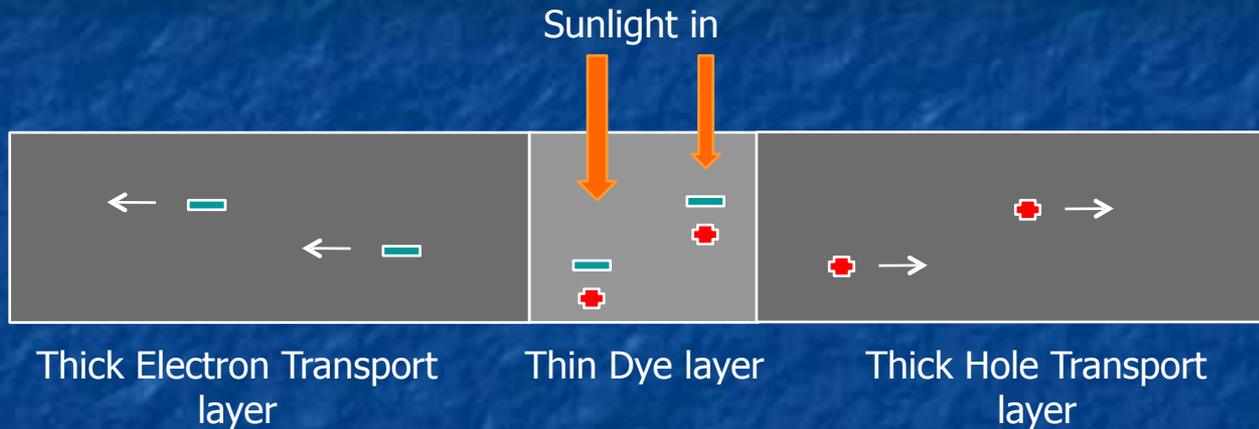
Quantum Mechanical "oozing" of electrons between bonds is far less likely

=> Killing off valence band hole transport

**Chemists like to divide the three functions between different materials**

## Chemist's DSSC (or organic) solar cell:

Which divides the three phenomena / functions between three different layers



The actual geometry is more complex:

With light coming in **through** either the Electron or Hole transport layer

And instead of flat planes, a much more convoluted 3D geometry is used

**This structure SEEMS to do required job of sorting electrons from holes**

Sending them in opposite directions to form an "electrical current"

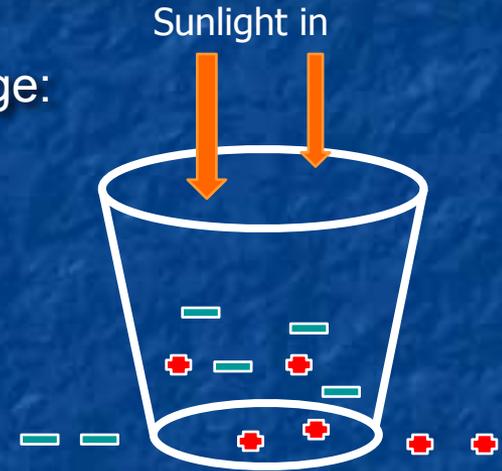
*But hold it: There is no "push" => No power!*

**Electrical Power = Flow x Pressure = Current (I) x Voltage (V)**

Above scheme shows no way of producing the pressure/voltage:

It's not yet a pump!

It's just bucket leaking electrons left & holes right:



To be a bit more technical:

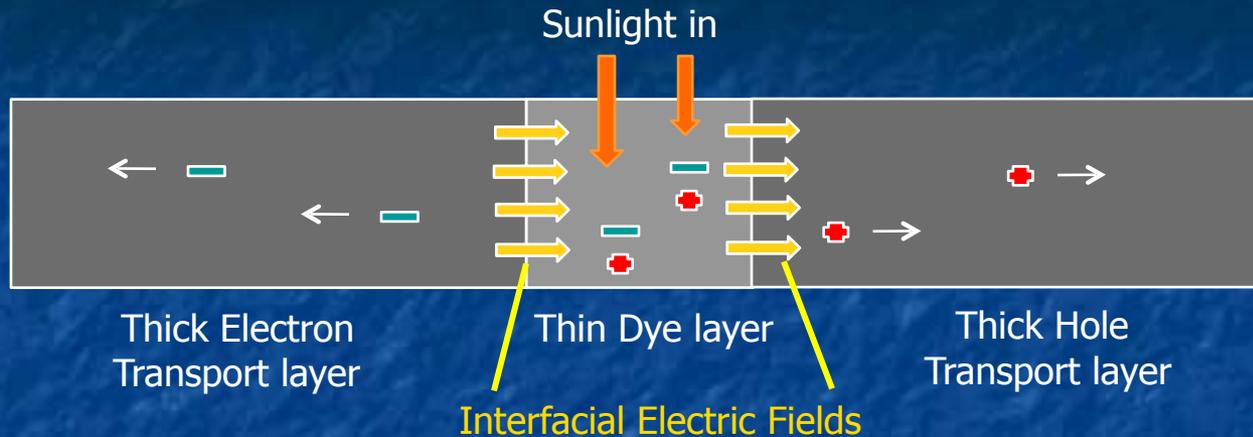
While it's "**short circuit current**" (unopposed **flow**) might be finite

It's "**open circuit voltage**" (electrical **force**) would be ~ zero

Thus, while papers on DSSC's and Organic Solar Cells seldom mention it,

**There has got to be something MORE going on!**

There must be at least one **pushing Electric Field**:



Material of the **electron transport layer** CANNOT ONLY transport electrons

Line up of its energy levels vs. those of the the Dye layer

MUST promote electron transfer across that interface ( $\Rightarrow$  E field)

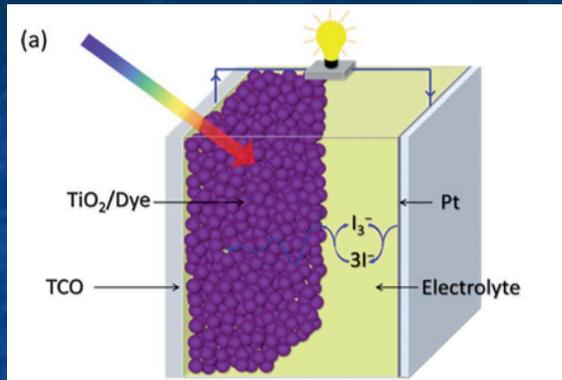
AND/OR material of the **hole transport layer** CANNOT ONLY transport holes

Line up of its energy levels vs. those of the Dye layer

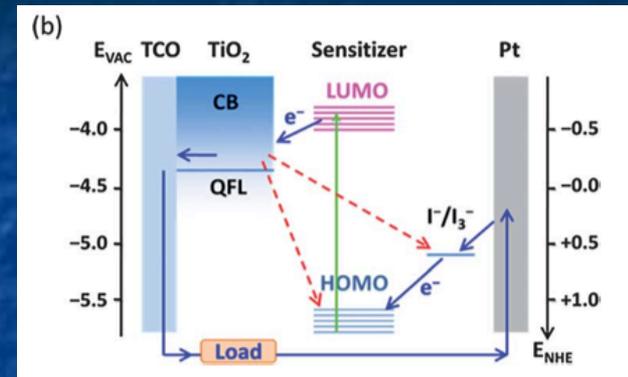
MUST promote electron transfer across that interface ( $\Rightarrow$  E field)

# Finally moving on to **actual** DSSC configurations:

Geometry:



Corresponding energy levels:



**Dye/Sensitizer** coats surfaces of TiO<sub>2</sub> particles

**Electrons** photo-generated in the dye move into the TiO<sub>2</sub> electron transport layer

**Holes** in dye layer are then filled by electrons from I<sup>-</sup> ions arriving in the electrolyte

By absorbing holes, this serves the role of a hole transport layer

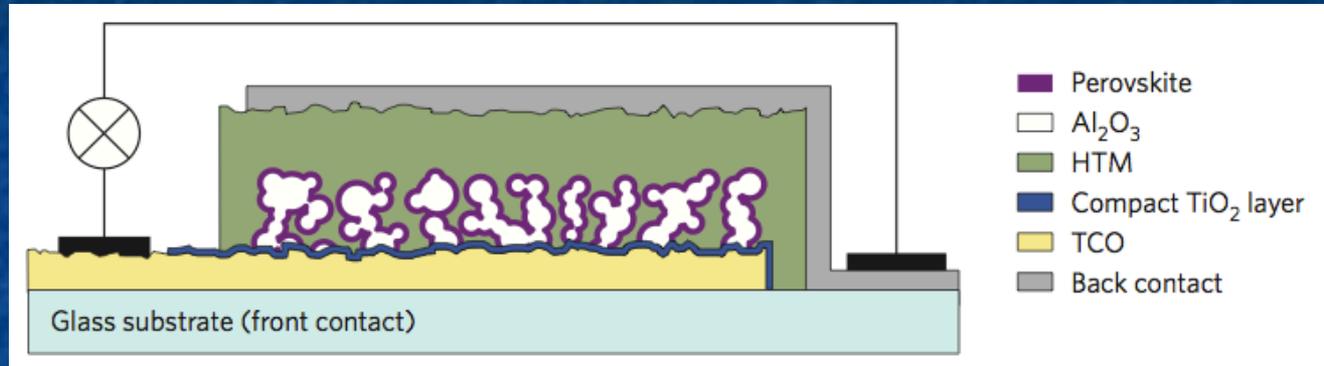
(with I<sup>-</sup> ions then regenerated at far right Pt electrode)

Energy levels are indeed **carefully chosen** to promote interfacial electron transfer

Thereby supplying (even if never mentioned) the **pushing electric fields**

*Or getting rid of liquids and moving to all solid state:*

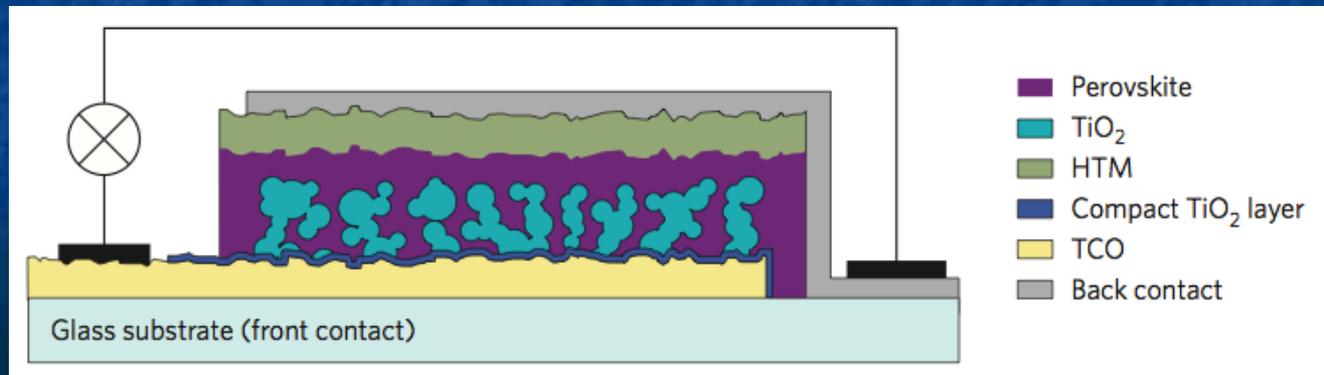
THIN Perovskite Dye (light absorber) on  $\text{Al}_2\text{O}_3$  particles (electron transporter)



(HTM = hole transport material, TCO = top contact transparent oxide)

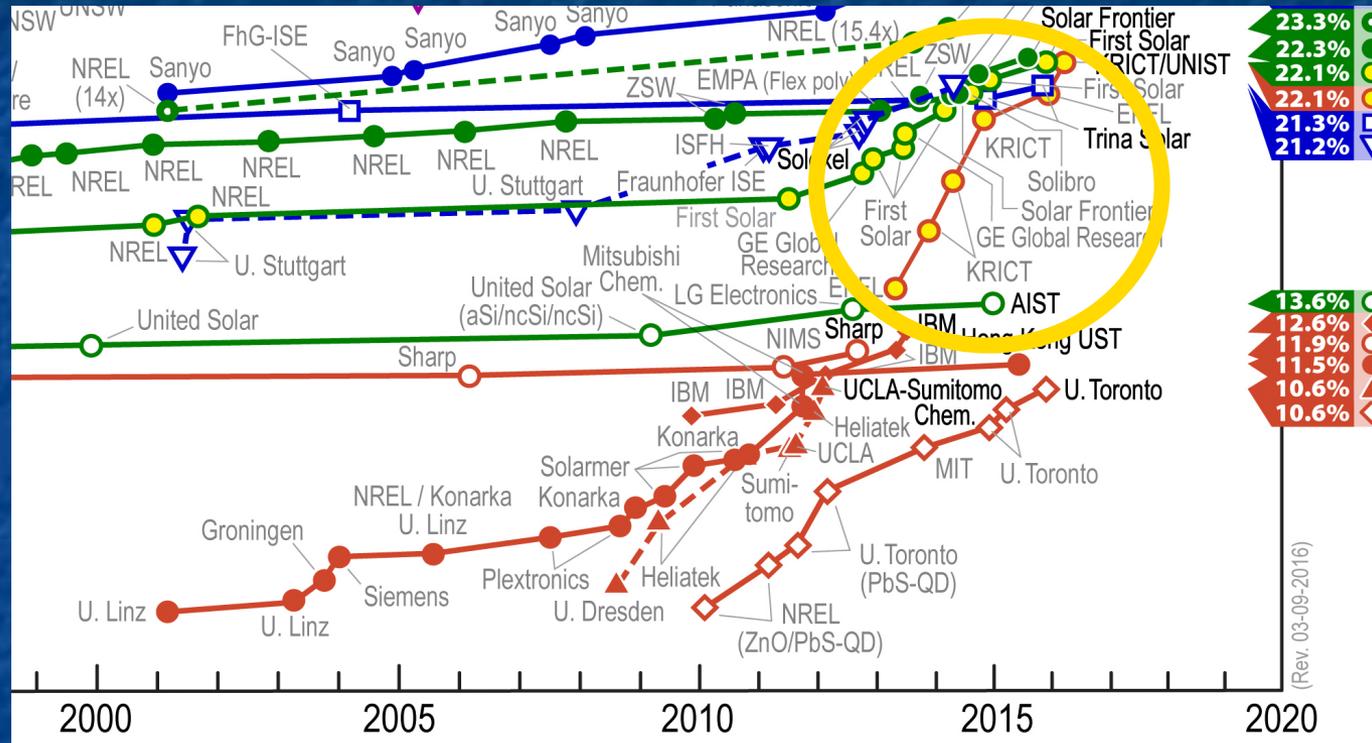
ALTERNATE more strongly sunlight-absorbing structure:

THICK Perovskite Dye (light absorber) on  $\text{TiO}_2$  particles (electron transporter)



# Where I just snuck in Perovskite thin film solar cells

Which have been **rocketing** up the NREL chart:



**Perovskites**

Which is attributed to BOTH electrons & holes moving REALLY well in perovskites:

=> LONG electron/hole diffusion lengths due to very few and/or ineffective traps

Perovskites = "Mushy" less stable but **remarkably** self-healing semiconductors

## The Perovskite family structure and formula:

Take as the basic repeating crystal building block ("unit cell"):

**The CUBE with fat gray B's in its corners**

**A** = Organic or inorganic cations (+) = green: **1 per cell**

**B** = Metal cations (+) = gray: **1 per cell**

8 corner atoms x (1/8 of each inside our cube) = 1 inside each unit cell

**X** = Anion (-), frequently halide = purple: **3 per cell**

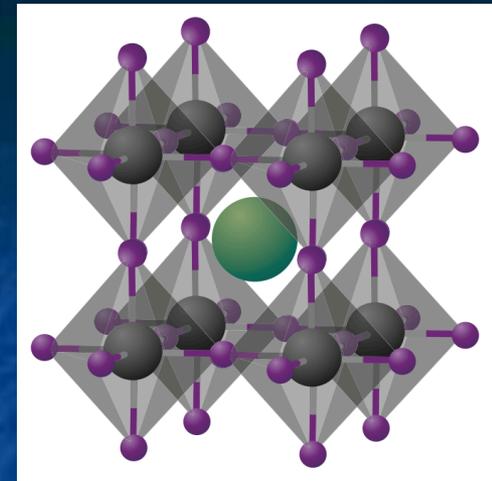
Don't count any atoms outside of the gray atom bounded cube

Every gray cube **edge** (12 of them) has a purple X atom at its center

But only  $\frac{1}{4}$  of each of those purple X atoms is inside our cube (i.e.  $\oplus$ )

Thus X count = 12 edge atoms x (1/4 of each inside or cube) = 1

**So general formula of repeating perovskite unit cell is:  $ABX_3$**



*For Perovskites used in solar cells:*

**ABX<sub>3</sub> is made up of:**

**A** organic cation = **Methylammonium** (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>)

**B** metal cation = **Lead** (Pb<sup>+</sup>)

**X** anion = **Iodine** (I<sup>-</sup>) and/or **Bromine** (Br<sup>-</sup>) and/or **Chlorine** (Cl<sup>-</sup>)

Synthesis DOES NOT REQUIRE energy-intensive high temperature crystal growth!

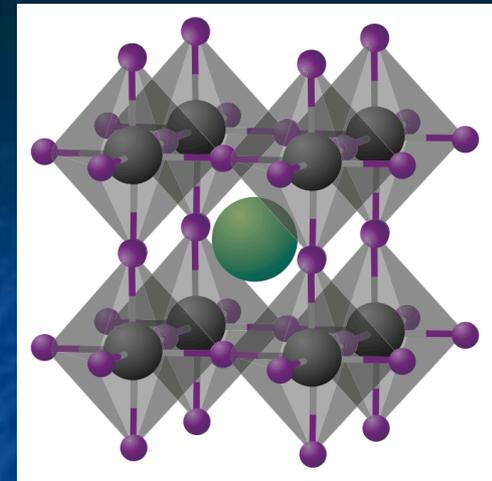
Perovskites can instead be evaporated onto surfaces OR

**Deposited from liquid** using PbX<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>X dissolved in solvents

Offering: 1) Simple (almost trivial!) fabrication technology

2) Excellent performance due to long free electron / hole diffusion lengths

3) Combined or separated absorption + hole & electron transport by layer



## *Which makes Perovskites sound like the PV silver bullet*

But the "fly in the ointment" is:

- The most common Perovskites are built around toxic lead
- And, because Perovskites go together so easily, they also fall back apart!

Specifically: In contact with **water**, lead iodide Perovskite releases PbI

Which is a known carcinogen

That is banned in many countries <sup>1</sup>

This has fueled intensive research on **alternate Perovskites**

Including those which replace Pb with Sn

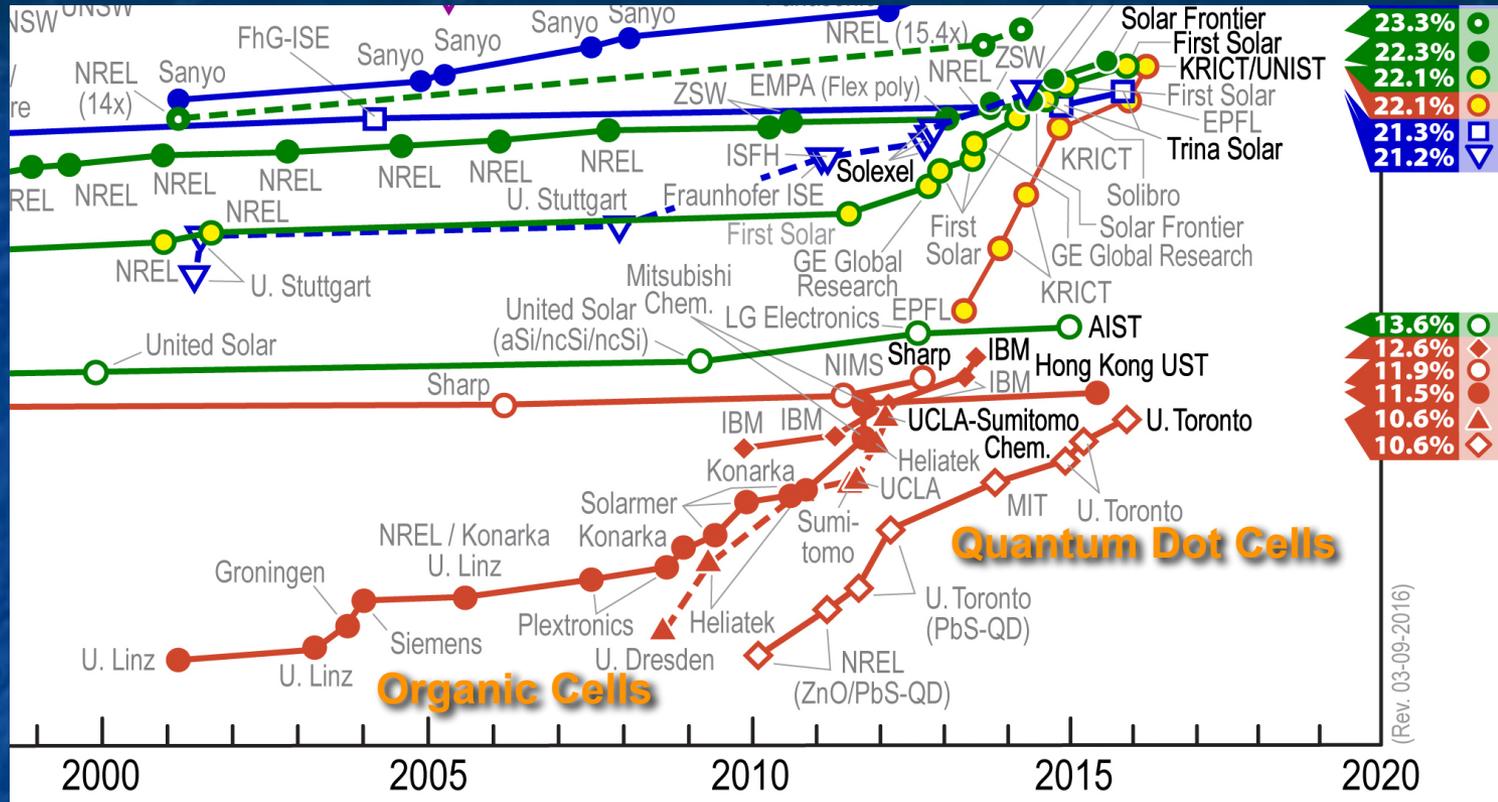
But these have **not** yet produced comparable solar cell performance

Nor do they achieve comparable cell stability/lifetimes

So Perovskite PV is a "Stay tuned for further developments" sort of story

<sup>1</sup>The Light and Shade of Perovskite Solar Cells, Michael Grätzel, Nature Materials 13, pp. 838-842 (November 2014)

# Completing the emerging group are Organic PV and Quantum Dot Cells:



Efficiency of light to electric power conversion

- Emerging PV**
- Dye-sensitized cells
  - Perovskite cells (not stabilized)
  - Organic cells (various types)
  - ▲ Organic tandem cells
  - ◆ Inorganic cells (CZTSSe)
  - ◇ Quantum dot cells

## "Organic" PV cells share the chemistry of earth-borne life:

Using complex molecules & polymers consisting of mostly C, H, O & N

Organic cells work, they can be very cheap to build, they can literally be flexible

But you **know** what happens if organics are left in sunlight (e.g., rubbers & plastics)

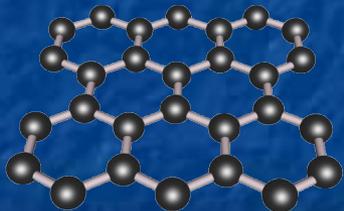
They fade, crack, and eventually crumble - Why?      Answer:

UV not only liberates electrons from organic bonds, it often **breaks** those bonds

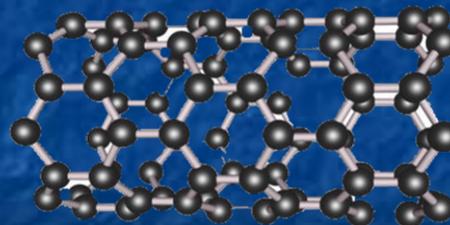
=> A major reason Organic PV cells end up at the very bottom of NREL's chart

But one group of **TOUGH ORGANICS** has been getting a lot of **press attention**:

Graphene:



Carbon Nanotubes - CNTs (Rolls of Graphene)

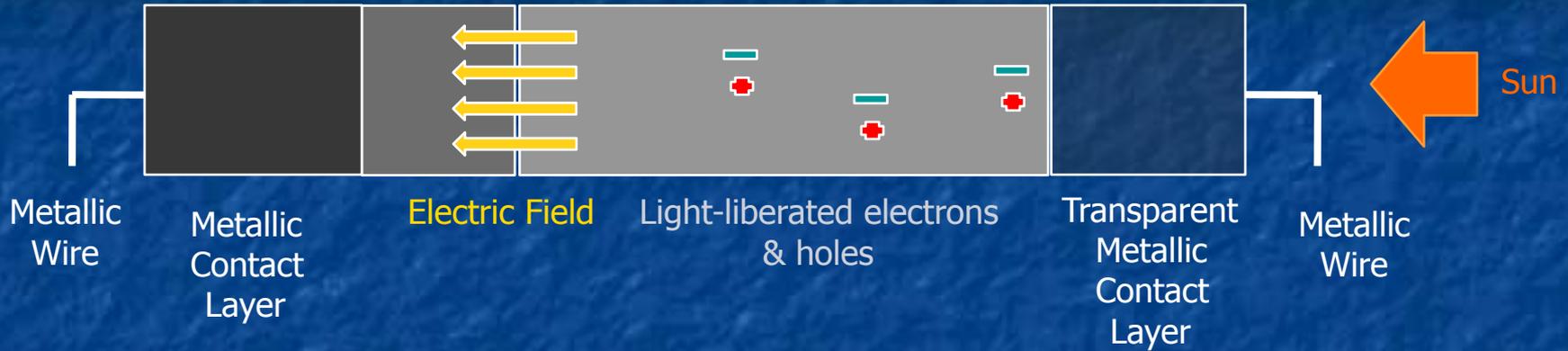


But these "tough organics" appear **NOWHERE** on NREL's Best PV Cell chart!

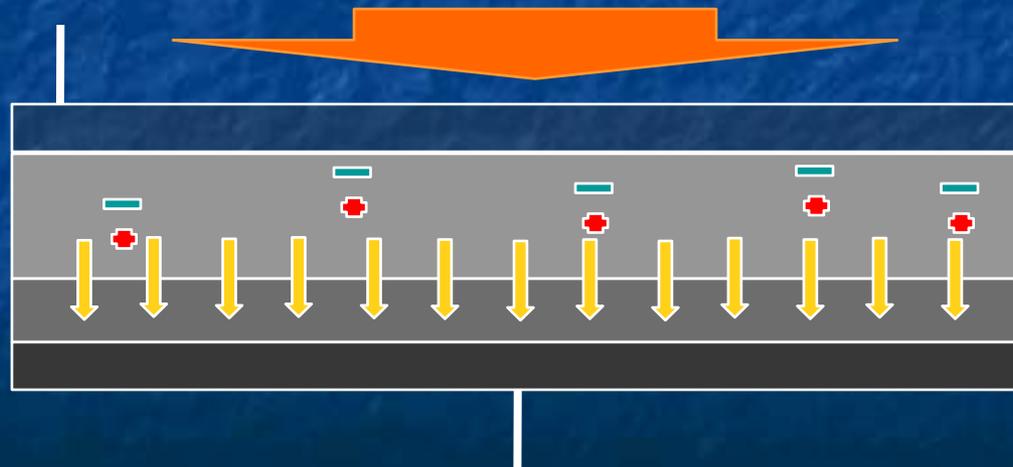
So why all of the hype? What is really going on?

To explain, I need to discuss the **complete** structure of a solar cell:

Which would have to include at least these parts:



But likely with these final proportions / arrangement:



*In that full structure, where might Graphene/Nanotubes be used ?*

**Well, what are they really good at / good for?**

- 1) They are really, really **strong** – but that's largely irrelevant to solar cells
- 2) Electrons can move through them really, really easily and quickly

Which is to say that they are **superb conductors**

So they COULD be used in: **Top wire, bottom metallic contact, bottom wire**

And this IS (frequently) suggested in the press and by researchers

But in those places standard metals already work pretty well

And substitution of graphene/CNTs => Minimal impact on efficiency

The **top contact** offers a somewhat bigger opportunity for improvement:

IT must be both a **good conductor** and **largely transparent**

THAT is a rare and scientifically challenging combination:

A "**good conductor**" must pass a lot of electrical current easily

Electrical current = (#number of free electrons) x (average electron speed)

Graphene/CNT electrons can travel at **exceptionally** high speeds

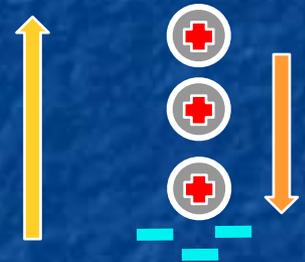
So graphene is a good conductor **despite** having fewer electrons than metals

A "**transparent material**" has to allow light (here sunlight) to pass through

Light = Oscillating **electric (and magnetic) fields**

When light's electric field strikes conductor, field shifts electrons:

Electron shift => polarization => **counter electric field**



If there are enough electrons, counter electric field cancels light field

And such free-electron rich materials (metals) end up acting as **mirrors**

But graphene has fewer electrons => Poor mirror (i.e., it's more transparent!)

*So graphene/CNT's could help out in transparent front conductor*

This could trim the cost a little

Because alternatives such as Indium Tin Oxide (ITO) are costly

And/or it might slightly goose up efficiencies (say, a few percent)

Which would certainly be nice, but which would not yet be a huge deal

To be a huge deal, graphene/CNT's would have **get out of the boonies** of the cell!

AND instead enable big improvement in the function of the:

Semiconductor/dye, electron or hole transport layers

But graphene is NOT a natural semiconductor, it's effectively a metal meaning that:

Electron liberation energy  $\sim 0$   $\Rightarrow$  No pushing force (Voltage) from layer(s)

However, SOME forms of CNT are semiconductors so there is a possibility here

*But the ONLY possibility justifying the current level of excitement is:*

If, in the **heart** of the cell, CNT's (or some modified form of graphene)

could use **excess photon energy** to **liberate additional electrons**

Instead, now, one photon gives **all** of its energy to only one electron

And if that photon's energy is MORE than enough to liberate that electron

excess energy goes into electron's **kinetic** energy and it just ricochets around,

causing atoms to vibrate, sucking up that energy as waste heat

= Fundamental reason ALL solar cell efficiencies are  $\ll$  100%

But in graphene, it's **believed** that energetic photon **might** liberate 2 electrons

HOWEVER, reports have been rare and that result has been very hard to replicate

*Leading to my personal conclusion that:*

*Current bubbly press about graphene/CNT solar PV is premature and/or naive*

## Bringing us to *Quantum Dots* and the weird world of *Quantum Mechanics*

Which invokes the famous (or infamous) "**Wave / Particle Duality**"

Specifically, in about 1900, it was recognized that electrons (thought to be particles) exhibited behavior then **only** recognized in waves (of sound / water / light . . . )

Compelling the invention of a whole new set of rules, called quantum mechanics

For which the saving grace was that **all waves exhibit very similar behavior**

So electron waves **should** act like sound / water / light . . . waves

**UNCONSTRAINED** sound / water / light . . . waves can have all sorts of energies

The greater their energy, the greater their frequency (the lower their wavelength)

But **TRAPPED** in boxes (e.g., "dots"), waves bounce back & forth and back & forth . . .

With the generated left & right moving waves tending to cancel one another out

*But in such boxes, cancellation does NOT occur for certain wavelengths*

A ricocheting wave CAN survive IF its wavelength "fits" in the box, for instance when:

Wavelength ( $\lambda$ ) = Box-width, Box-width/2, Box-width/3, Box-width/4 . . .

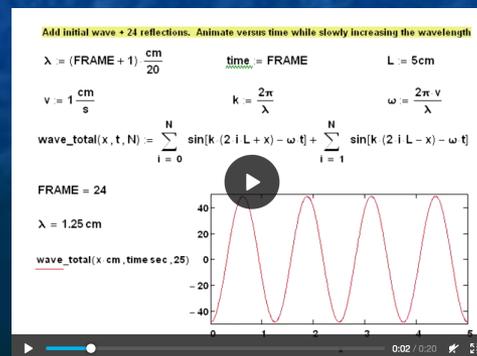
In my Nanoscience class lab, we observed this for waves trapped in springs and water

I also created a mathematical simulation of waves bouncing within a box

My Nanoscience class notes on: "**Waves (electron)**" ([pptx](#) / [pdf](#) / [key](#))

That note set's Resource Webpage ([Link](#)) with embedded movies of:

- The lab's trapped water waves
- My animated mathematical simulation of trapped waves
- YouTube's **Mythbuster** & other demonstrations of trapped waves



## *Summarizing Quantum Dot (Q-dot) factoids to this point:*

### **Electrons act like waves**

Unconstrained waves can have all sorts of frequencies & wavelengths

Implying different energies, because higher frequency => higher energy

### **But when trapped, and forced to ricochet back and forth within a BOX:**

Most waves end up canceling themselves out

### **AN EXCEPTION = Trapped waves whose wavelength's = (width of box) / (an integer)**

Surviving waves thus have QUANTIZED ENERGIES (these waves = **"standing waves"**)

Which is HOW Quantum mechanics got its name!

As it struggled to explain known energy levels of electrons bound within atoms

**CONSEQUENCE:** As size of box changes, so should surviving electrons' wavelengths

Different size "atomic boxes" => Different allowed electron wave energies

**THUS: Different size quantum-dots have different electron energy levels =**

**The "QUANTUM SIZE EFFECT"**

*Quantum-dots can be made of ALL SORTS of different materials  
But the exact choice of their material becomes largely irrelevant!*

Because sunlight's absorbance is no longer due to electron liberation from bonds

It's instead due to light kicking electrons from one quantum-energy-level to another

With energy levels (and hence their differences) determined by the Q-dot SIZE

**Thus, to make a solar cell with peak Shockley-Quiesser efficiency:**

You no longer need to find a material with electron liberation energy of  $\sim 1.3$  eV

Instead, just embed Q-dots with two trapped wave energies differing by  $\sim 1.3$  eV

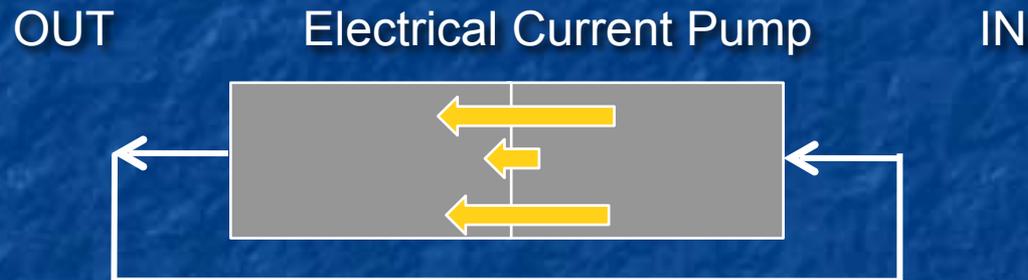
Which is no longer determined by material, but (mostly) by the Q-dot's SIZE

**Which YOU CAN CONTROL (vs. Mother Nature's control of material's bandgap)**

## *What would such an embedded Q-dot solar cell look like?*

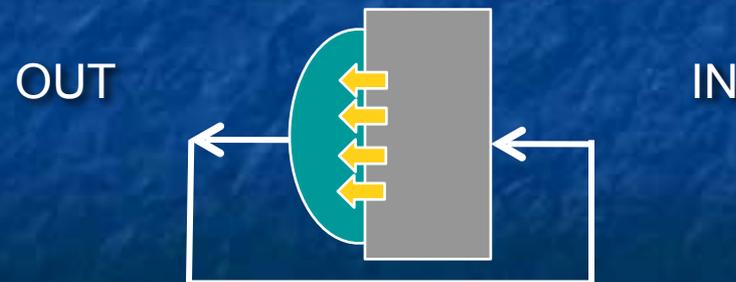
Building from the example of conventional semiconductor photovoltaic cells:

Swap of charge across junction => ELECTRIC FIELD => Sorting of electrons/holes



An analogous one **Quantum Dot** photovoltaic cell:

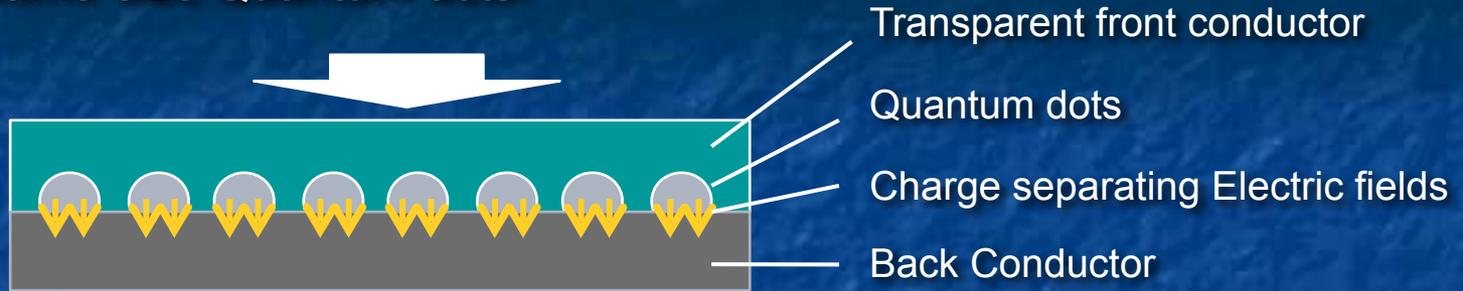
For instance, when semiconductor or polymer quantum dot meets metal:



**Nano sized Q-dots => Nano power so we need LOTS of them working together:**

## A better Quantum dot solar cell:

With lots of same-size Quantum dots:



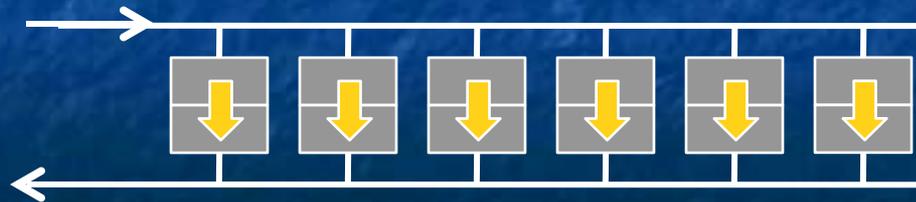
What's going on here? You choose special quantum dot & back conductor materials

So that interface between them swaps charge, setting up electric field

Which propels **ONLY** photo-generated **holes** into **back conductor**

Leaving photo-generated **electrons** to be collected by **front conductor**

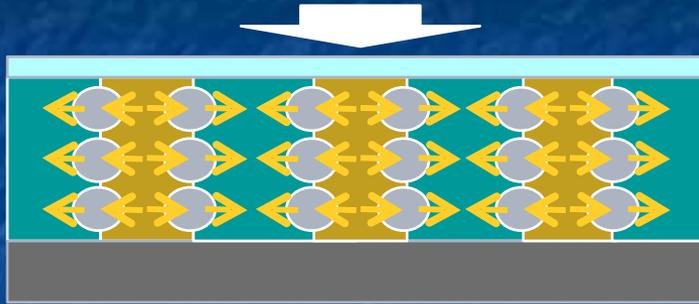
Result is **MANY** nano electron pumps working together ("in parallel"):



**But this STILL uses only 1 thin light-absorbing QD layer => Very little current**

# An improved FOLDED quantum dot layer solar cell:

THIS would be much better = MORE DOTS! With materials chosen so that:



- Blue metal collects only charge from green
- Green sucks positive charge from dots
- Yellow sucks negative charge from dots
- Gray metal collects only current from yellow

- Green and yellow self-segregate into such a pillared structure in which Q-dots go to interface

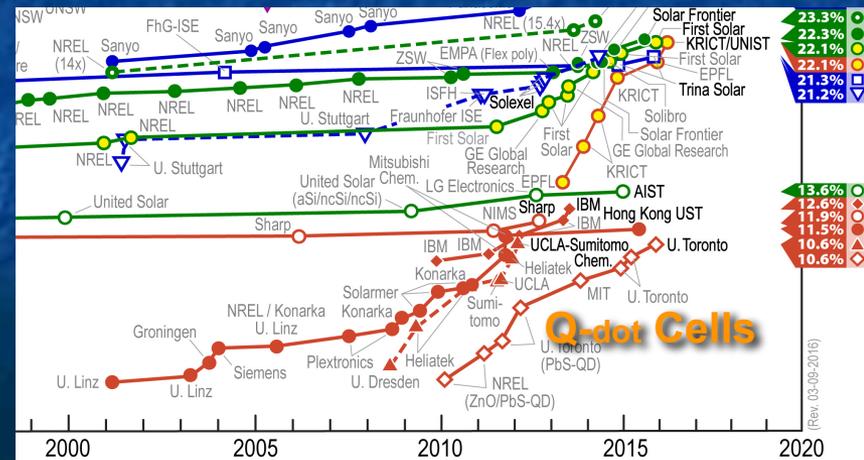
Sounds incredibly complex, doesn't it? But such designs ARE being researched

E.G., Green and Yellow = Immiscible conducting polymers (e.g. "Block co-polymers")

But single size Q-dots cells STILL convert only ~ 10.6% of sunlight energy to electrical energy

Putting them near bottom in the NREL chart:

Could Q-dots be used more effectively?



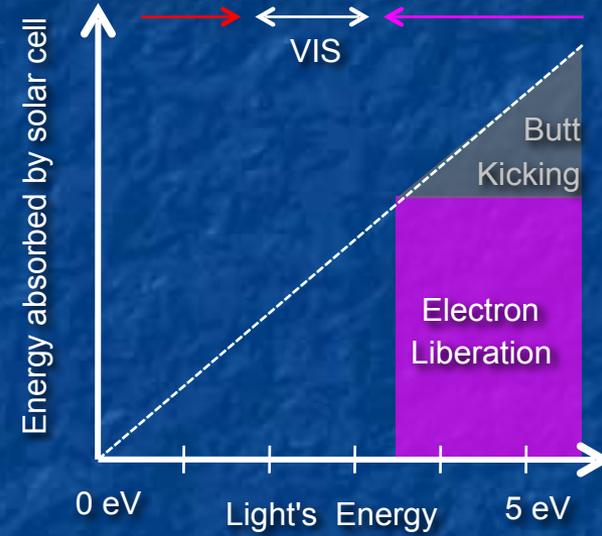
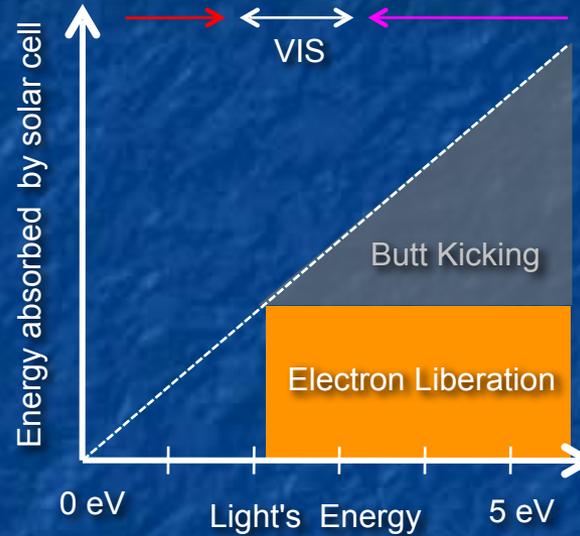
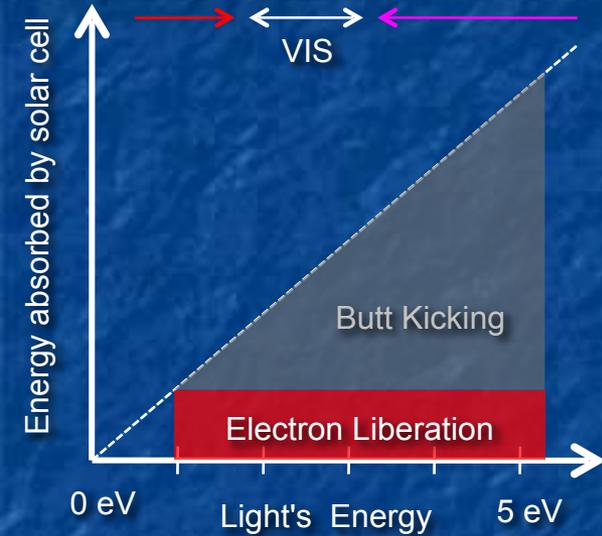
# *Emerging "Multi-junction" / "Tandem" Photovoltaic Solar Cells*

# The Shockley-Quieser Limit = Choice of one "best" solar cell material:

Cell with small "bandgap"

Cell with medium "bandgap"

Cell with large "bandgap"



But in even BEST ~1.3 eV material, a good chunk of sunlight's energy (**two-thirds!**) is wasted on non-electricity-producing electron "Butt-Kicking"

= Excessive kinetic energy of liberated electrons (ultimately lost as heat)

**What if cells of EACH different material were stacked atop one another?**

**Top / first PV cell: Material with large bandgap:**

Absorbs UV light with only weak butt-kicking

Absorbs purple-ish light with ~ zero butt-kicking

But lets almost all lower energy light pass right through

**Middle / second PV cell: Material with medium bandgap:**

Absorbs green-ish light with only weak butt-kicking

Absorbs orange-ish light with ~ zero butt-kicking

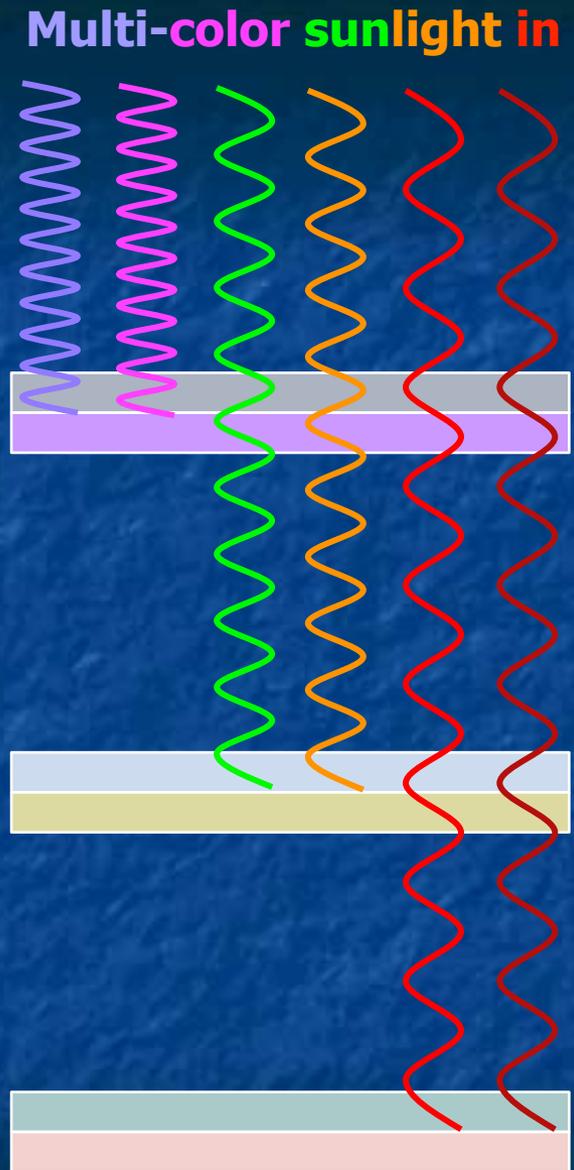
But lets almost all lower energy light pass right through

**Bottom / third PV cell: Material with small bandgap:**

Absorbs red-ish light with only weak butt-kicking

Absorbs near-infrared light with ~ zero butt-kicking

Allowing only-deep infrared to pass through unmolested



**This is called a "Multi-junction" or "Tandem" PV solar cell**

*By hugely reducing electron "Butt-kicking" waste, efficiency might soar!*

Indeed, overall light to electrical power conversion might approach 100%,  
shattering single-cell PV's Shockley-Quiesser limit of ~ 35%

But use of three cells might also triple overall cost of Multi-junction / Tandem PV

Or more than triple it, given challenges of electrically & optically merging cells

**PV cell cost per electrical power out might then actually INCREASE!**

Relegating Tandem / Multi-junction PV to sites requiring **high power per array SIZE**

Such as in prime urban environments:

Or when minimizing satellite weight/size:



Where Tandem PV might supercharge this NYC complex:  
<https://www.stuytown.com/sustainability/solar>

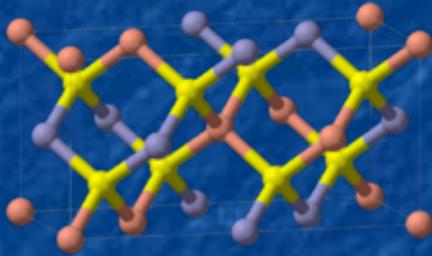


Where NASA is promoting Tandem PV research:  
[https://spinoff.nasa.gov/Spinoff2016/ee\\_5.html](https://spinoff.nasa.gov/Spinoff2016/ee_5.html)

*To cut cost, you must create all necessary layers in a single manufacturing step*

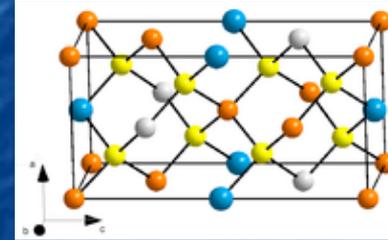
For instance, by depositing a **full set** of CIGS or CZTSSe thin-film layers:

### CIGS:



Alloys of **CuInSe** and **CuGaSe**

### CZTSSe:



Alloys of **CuZnSnS** and **CuZnSnSe**

### Full Multi-junction / Tandem structure:

High-energy-light absorbing **CuGaSe**

Atop:

Mid-energy-light absorbing **CuIn<sub>x</sub>Ga<sub>1-x</sub>Se**

Atop:

Low-energy-light-absorbing **CuInSe**

### Full Multi-junction / Tandem structure:

High-energy-light absorbing **CuZnSnS**

Atop:

Mid-energy-light absorbing **CuZnSnS<sub>4x</sub>Se<sub>4(1-x)</sub>**

Atop:

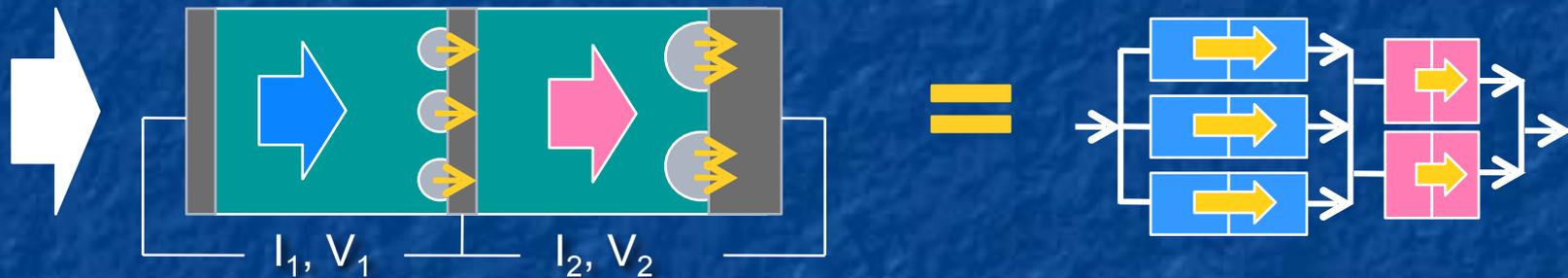
Low-energy-light-absorbing **CuZnSnSe**

***OR** you could stack layers containing differently-sized Q-dots:*

Smaller Q-dots => Shorter wavelength trapped electron waves => Higher electron energies

First capture **Blue Light** with small quantum dots

Then capture **Red Light** with deeper large quantum dots



Done right (probably with more layer/sizes), you might efficiently capture light of ALL colors

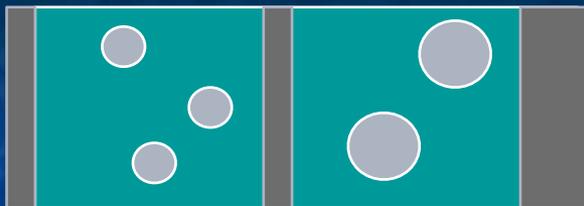
But this would require incredible control of Q-dot arrangement and electrical current paths

Making the creation of quantum dots the **almost trivial** part of task

**REAL CHALLENGE here is the required complex 3D SELF-ASSEMBLY**

*It would be easier if quantum dots could be randomly distributed in layers:*

More like this:



You'd still need electric fields to separate light-liberated electrons from holes

But HERE you would NOT want fields between the dots and their surrounding layer:

For instance, field below would drive positive holes out of dot, trapping electrons

Until dot got so negative that it started pulling holes back

Then NOTHING (electrons nor holes) would escape to deliver power!



You'd instead want electric fields at **layer** (rather than dot) boundaries

Which MIGHT be accomplished by:

1) Choosing dot and surrounding layer material to have **similar** energy levels

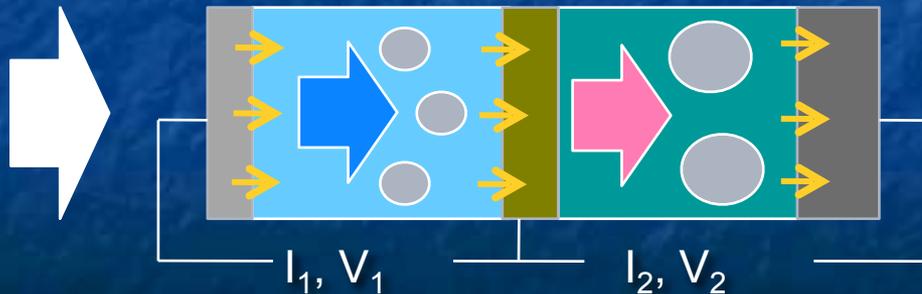
So they **don't** naturally swap charge, thereby building interfacial electric fields

2) But choosing layer materials with **differing** energy levels

So that they **do** transfer charge across **their** interfaces

Thereby adding properly directed charge-pumping electric fields

Producing this Quantum dot multi-junction / tandem solar cell:

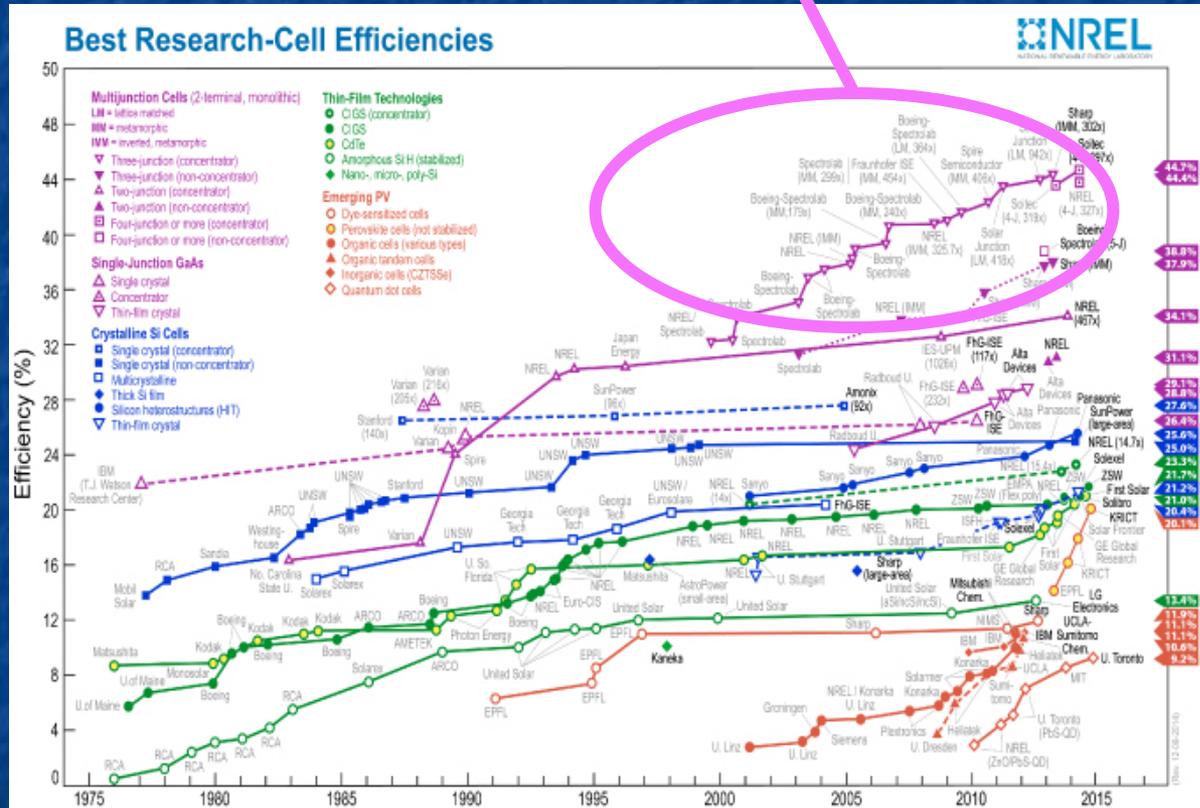


3D self-assembly => A LOT easier

Layer material selection => More difficult

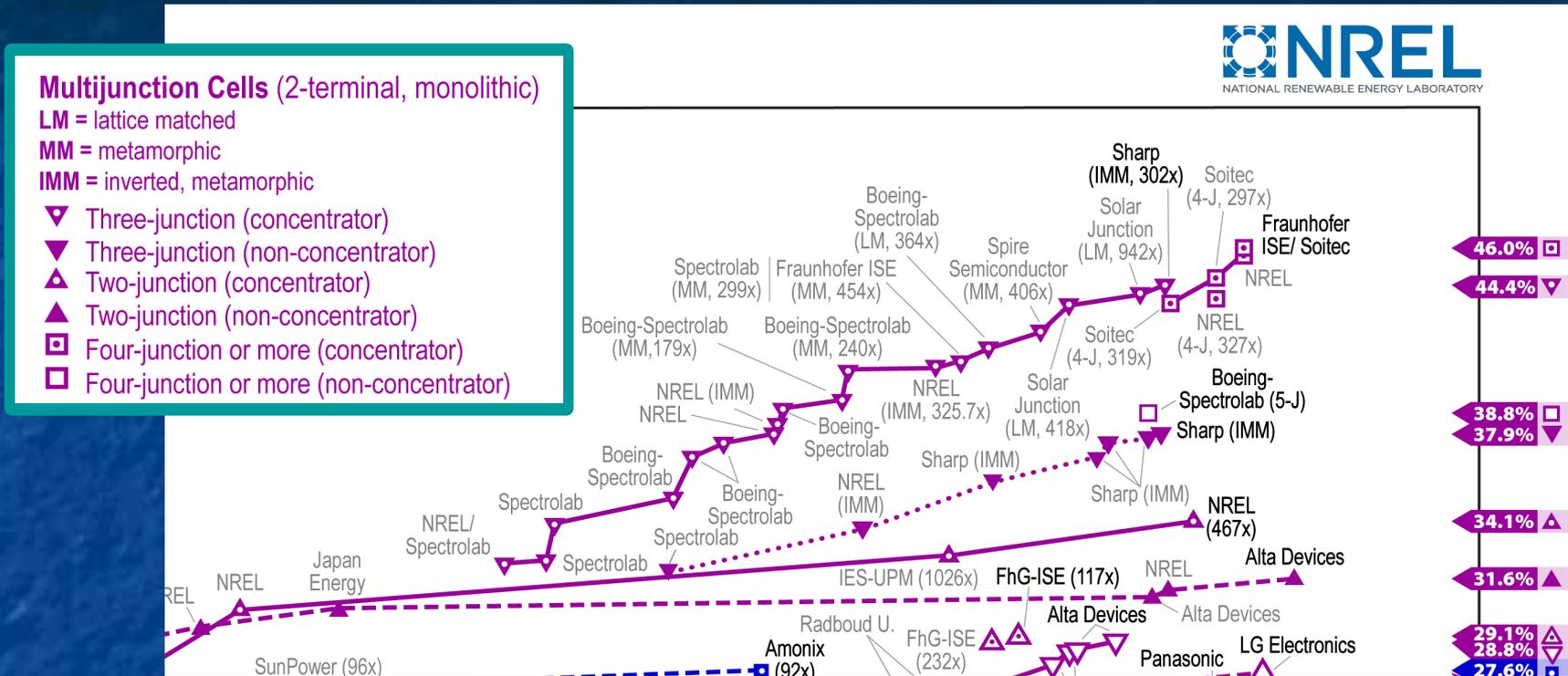
# How well are Multi-junction / Tandem PV Cells actually doing?

## Emerging Multi-junction / Tandem PV



Enlarging that part of the NREL chart (and its relevant key):

# NREL data on Multi-junction / Tandem PV cells (~ 1992 - 2016):



Reading off values called out on the chart's right margin:

Multi-junction / Tandem PV's are approaching 50% efficiency

But NOT the near 100% efficiencies one might expect

if "butt-kicking" wastage of light energy were TOTALLY eliminated!

But what's NREL referring to here?

Or here (for CIGS thin films)?

**Multijunction Cells** (2-terminal, monolithic)

LM = lattice matched  
 MM = metamorphic  
 IMM = inverted, metamorphic

- ▽ Three-junction (concentrator)
- ▽ Three-junction (non-concentrator)
- △ Two-junction (concentrator)
- △ Two-junction (non-concentrator)
- ◻ Four-junction or more (concentrator)
- ◻ Four-junction or more (non-concentrator)

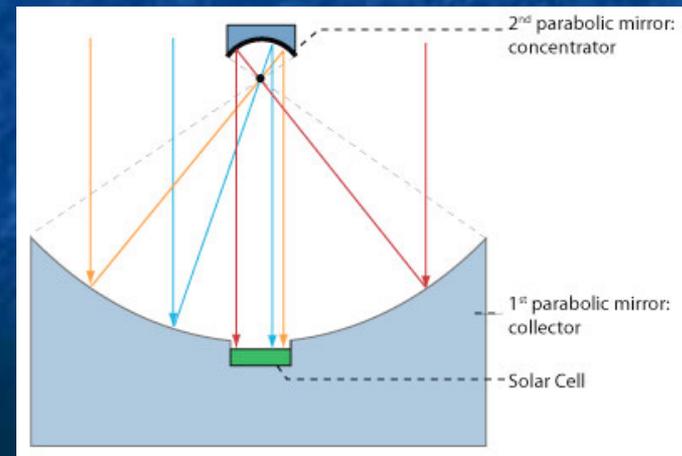
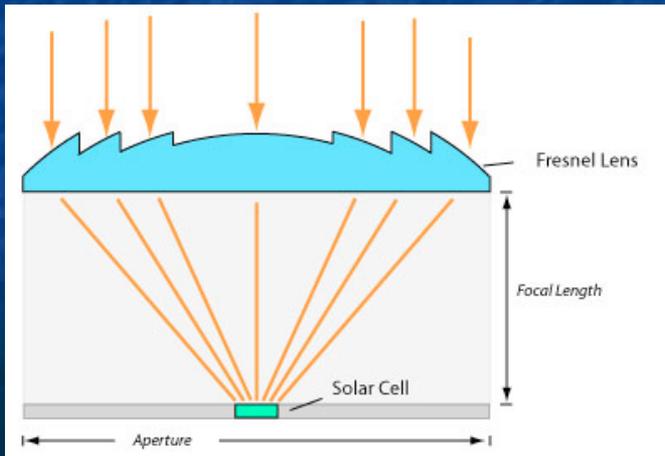
**Thin-Film Technologies**

- CIGS (concentrator)
- CIGS
- CdTe
- Amorphous Si:H (stabilized)

What are **Concentrator** Multi-junction PV cells?

What are **Concentrator** Thin-Film PV cells?

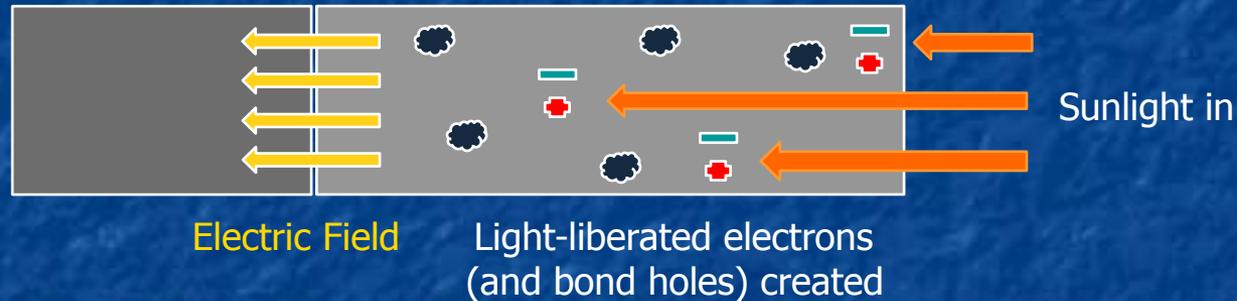
It refers to concentrating sunlight on **SMALL** cells via **LARGE** lenses or mirrors:



# Why would concentrating sunlight be desirable?

**Reason #1)** Photovoltaic cells get more efficient as light gets more intense

Revising earlier figure to explicitly depict "traps" created by impurities/flaws:



Even the **most** crystalline / **highest** purity PV materials have some "traps" ( ☁ )

These reduce the "diffusion length" of wandering holes and electrons

Reducing number reaching to, and then sorted/pumped by, the electric field

**But there are a limited number of "traps" interfering with wandering electrons/holes**

So overwhelm traps by sending in more intense light => More electrons + holes

These **saturate** (fill up) the traps allowing other electrons/holes to pass by!

*Reason #2 is easier to understand:*

If the cost per square meter of PV cell  $\gg$  Cost per square meter of lens or mirror

(which is VERY likely for complex Multi-junction / Tandem PV cells)

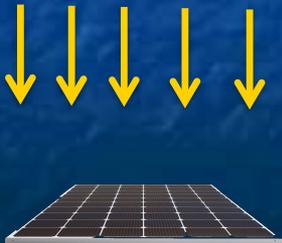
**It's cheaper to buy large lenses / mirrors and combine them with small PV cells**

You still use all of the light captured by the large lens or mirror

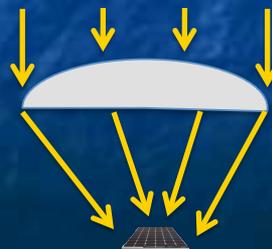
AND

You still get benefit of Reason #1 improvement in small cell's efficiency

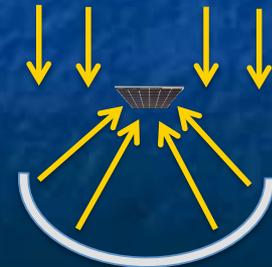
COMPARABLE POWER: Large/expensive array vs. tiny PV cells + cheap lens / mirror



VS.

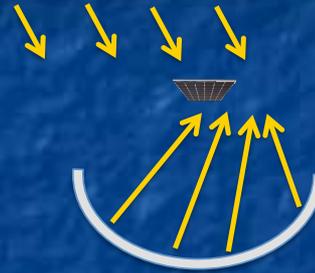
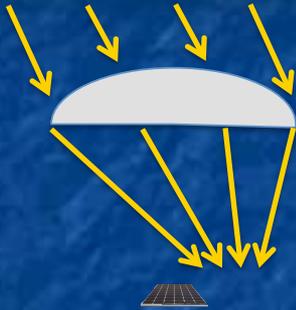


OR



# *The big problem with concentrators? The sun won't sit still!*

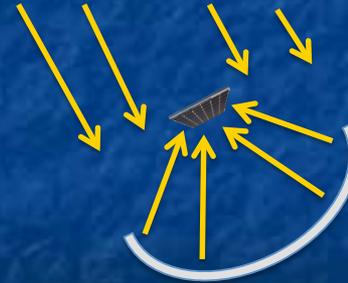
And when it moves off lens / mirror axis, light no longer concentrates on the PV cell



RESULT: The whole **ASSEMBLY** of PV cell PLUS lens / mirror must track the sun:

Tilting East to West (minute by minute) EVERY DAY

AND tilting more SOUTHWARD during (northern hemisphere) winter



***Likely demolishing the cost advantage of Concentration + Tandem PV cells!***

***(at least until a tilt-proof concentrator is invented)***

# *Luminescent Solar Concentrators*

## How to build a concentrator that is at least **tilt-resistant**:

Imagine a shiny ball-bearing inside a sheet of transparent plastic (seen here edge on)

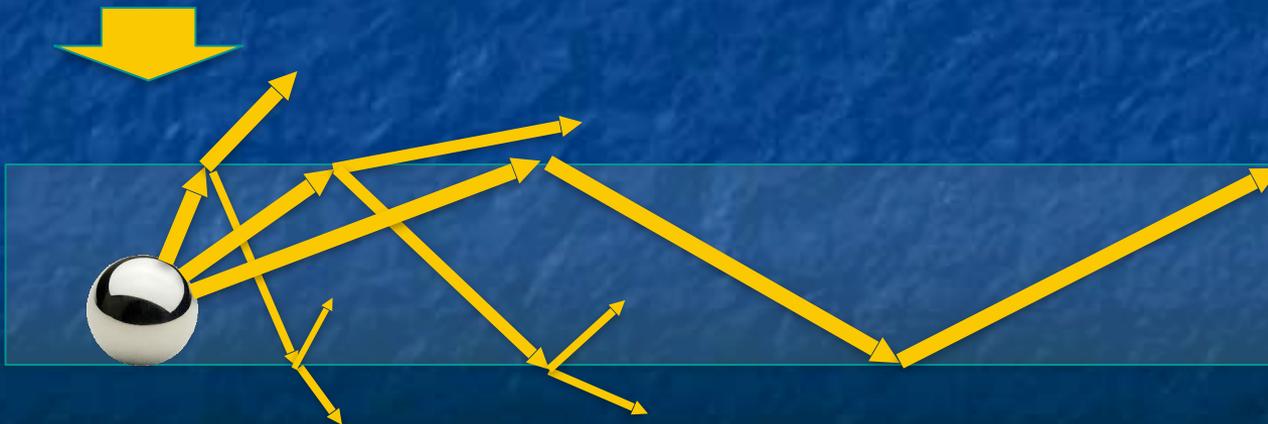
Think about how different rays of light will bounce off that ball-bearing (**click now**):

A ray of light from the center will bounce back downward (even (more to the side) side)

**BUT NONE** of it will escape the (front) edge of **total internal reflection** ("Law")

**ALL** of it will bounce, heading toward the back of the sheet's end!

(And so on and so on. . . getting weaker with each bounce) **click**



## *Remember lurking on the bottom of a swimming pool?*

From its depths you could see the sky far above

But looking to the side, the sky's image mixed with a reflection of the pool's bottom

And far to the side, you could see **ONLY** a reflection of the pool's bottom

***THAT was total internal reflection:***

*Where light moving at a glancing angle to an interface*

*gets trapped inside the material in which light moves more slowly*

*(i.e., inside the material that has the higher "index of refraction")*

**The critical angle for total internal reflection =  $\text{Sin}^{-1} (n_{\text{surrounding}} / n_{\text{sheet}})$**

Where  $n_{\text{sheet}}$  = the transparent sheet or fiber's index of refraction

And  $n_{\text{surrounding}}$  = the surrounding material's index of refraction

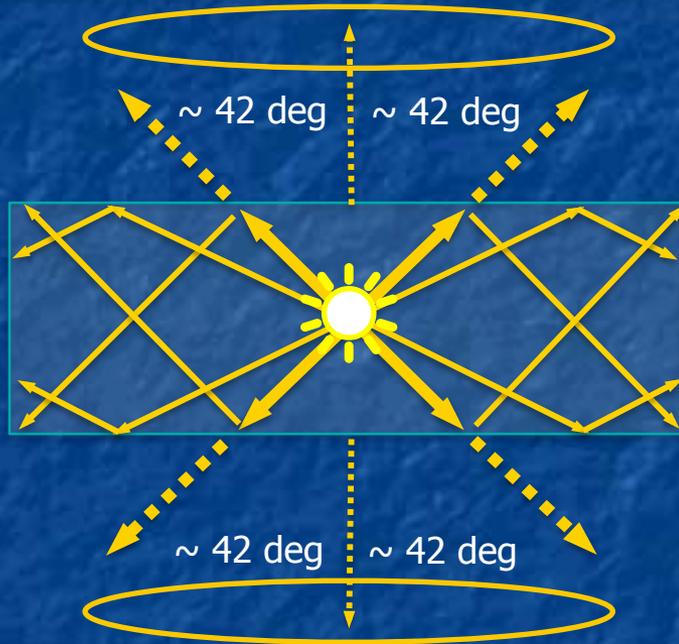
If the sheet / fiber is made of **typical transparent glass or plastic**, then  $n_{\text{material}}$  is  $\sim 1.5$

And if the surrounding material is air,  $n_{\text{surrounding}} = 1$

**In which case, the critical angle for trapping light is about 42 degrees**

*Much/most of light emitted within such a layer **stays within that layer***

Only light directed toward front & back (into ~ 84 degree wide cones) can escape



Light is similarly trapped within glass fibers enabling the fiberoptic telecommunication underlying CELL PHONES & THE INTERNET



*For more info, including a derivation of the critical angle formula, see Wikipedia's relevant webpage:*

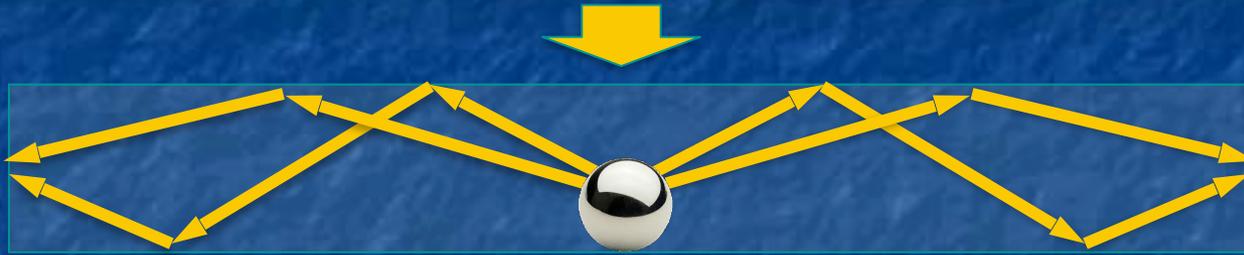
[https://en.wikipedia.org/wiki/Total\\_internal\\_reflection](https://en.wikipedia.org/wiki/Total_internal_reflection)

*Image at is from a tutorial on Fiber Optic Telecommunications:*

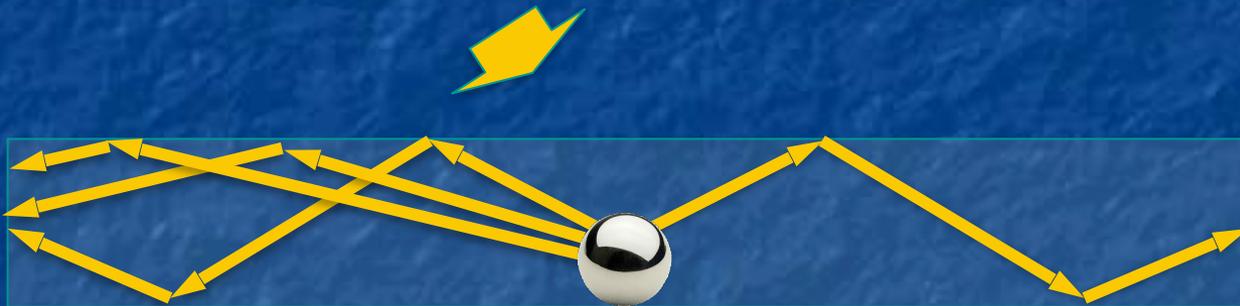
<https://www.elprocus.com/basic-elements-of-fiber-optic-communication-system-and-its-working/>

*Returning to our embedded-ball-bearing would-be concentrator:*

Lots of **light from above** travels to sheet's ends - where it's **concentrated**



Lots of **light from the side** ALSO travels to sheet's ends - where it's **also concentrated**

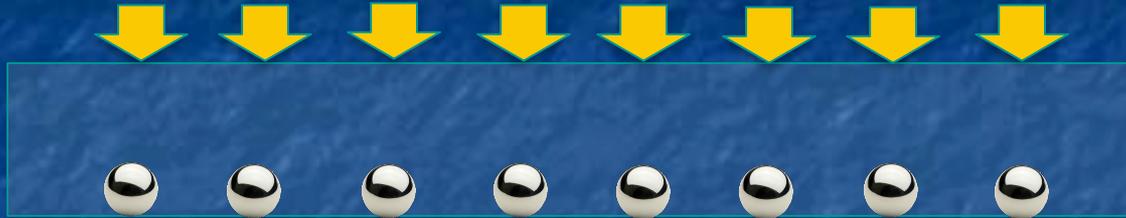


Suggesting that we've might have found our **cheap tilt-resistant concentrator**

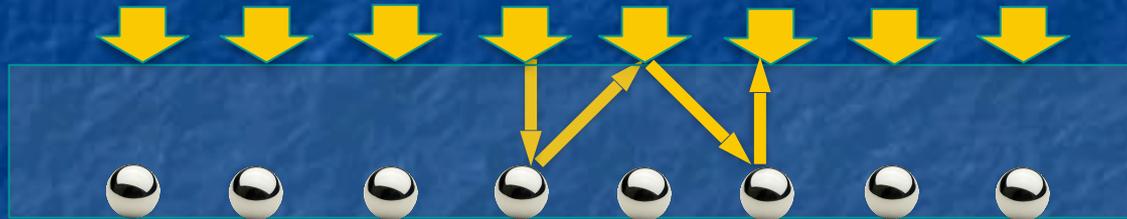
**To which we could just connect tiny PV cells at its ends!**

*But a solar concentrator should capture light from its **entire** front:*

Suggesting a concentrator more like this:



But then, what one ball-bearing **helped trap**, another might just go and **untrap!**



For such a scheme to work over the entire area, we'd really need:

**Magical ball-bearings that ONLY REFLECT NEWLY ARRIVED light,  
ignoring light that's already bounced off another magical bearing**

# Bringing us to the "luminescent" in Luminescent Solar Concentrators

Forget the ball-bearings, and substitute Quantum-dots or organic "dye" molecules

Quantum-dots & Dyes are extremely small and subject to **The Quantum-Size Effect**

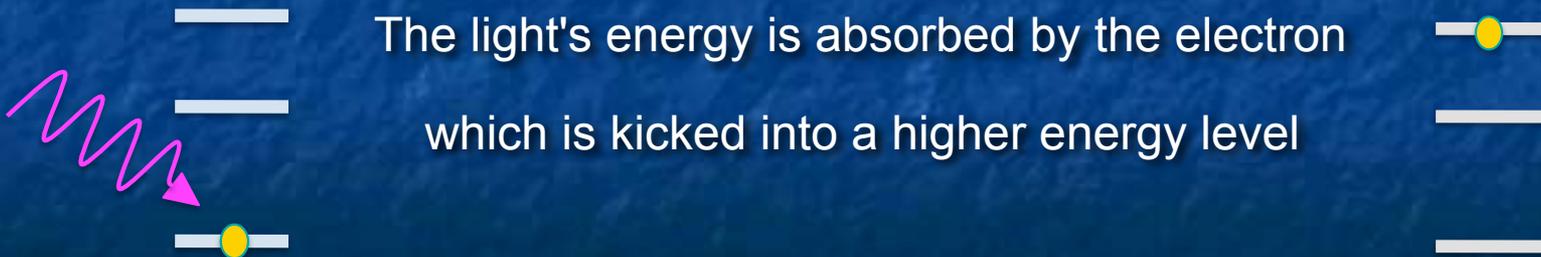
Their trapped electron waves thus have only a few short wavelengths

Which correspond to only a few widely spaced energy levels

Here showing the top electron-filled level, plus two higher unfilled levels:



**Shine high-energy sunlight (violet or bluish) on that Dot / Dye:**

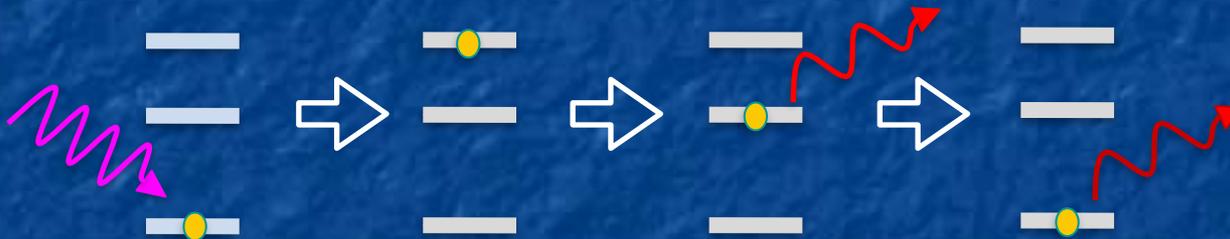


*The electron can then trickle back down, losing energy by emitting light*

In some dyes, the falling electron may "rest" at intermediate energy levels

Losing energy stepwise, via the emission of multiple photons of lower energy

(this would produce "**down-conversion**" of the light):



**Luminescence** = This process of induced light emission:

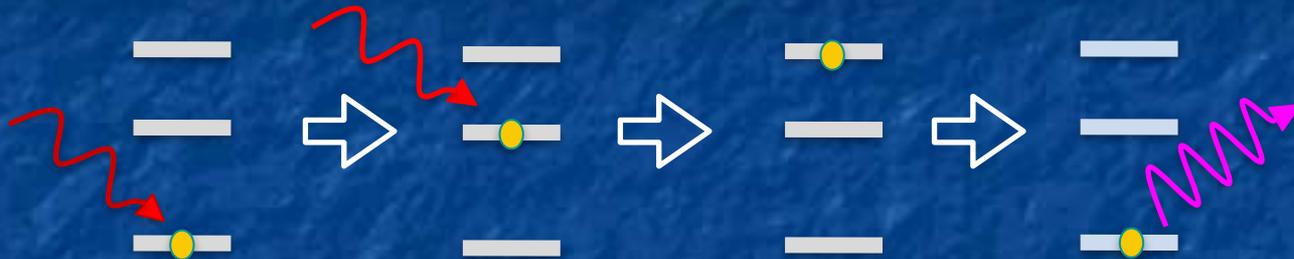
If the incoming energy was electronic, it's called **electroluminescence**

If the incoming energy was light, it's called **photoluminescence**

Alternate term for light in => lower energy light out = **fluorescence**

*One would expect photoluminescence to be reversible:*

Allowing multiple red photons to (ultimately) generate a violet photon:



But in many dots & dyes the reverse is **possible but highly improbable**

As governed by weirdness such as "Selection Rules" & "Fermi's Golden Rule"

Bringing to mind the classic quote from the father of Quantum Mechanics, Neils Bohr:

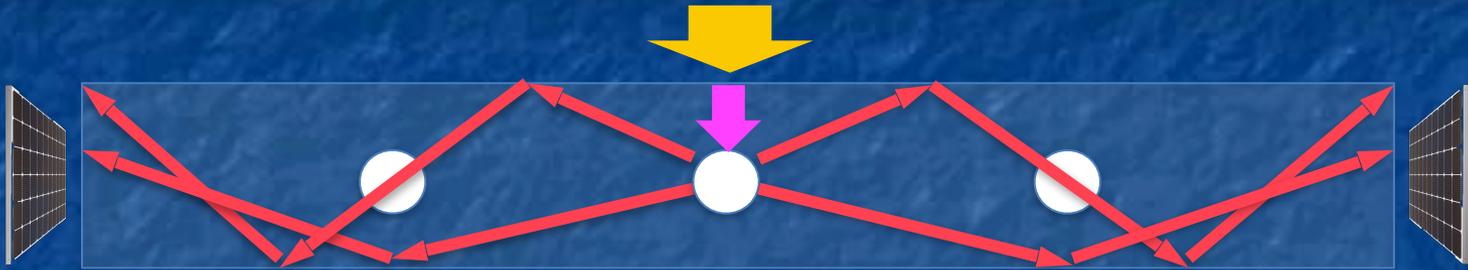
*"If quantum mechanics hasn't profoundly shocked you,  
you haven't understood it yet"*

**THOSE** are the dots & dyes chosen for luminescent solar concentrators:



## *Non-reversible down-conversion => Luminescent Solar Concentrators:*

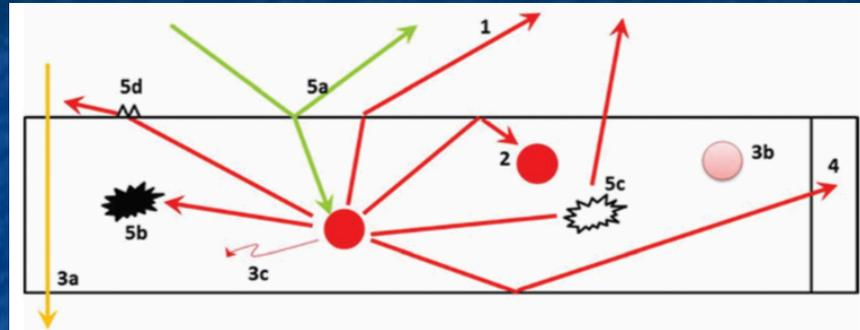
Which replace reflecting ball-bearings with those specially chosen Quantum-dots or Dyes:



- Full spectrum sunlight shines on **LSC** from above
- Only high-energy **violet** / **blue** light is absorbed by Quantum-dots / Dyes
- Absorbing Quantum-dot / Dye then re-emits that light as **redish** photons
- **Redish** photons **pass unaffected by (or through) other Quantum-dots / Dyes**
- **Redish** photons trapped by total internal reflection bounce to ends of sheet
- Encountering narrow bandgap PV cells optimized for conversion of **redish** photons

## Why is such an apparently good idea a no-show on NREL's chart?

Because of its many inefficiencies, as identified in a recent comprehensive review: <sup>1</sup>



- 1) Emitted **redish** light from some Q-dots / Dyes is directed into angles escaping total internal reflection
- 2) Some emitted **redish** light is re-absorbed by other Q-dot / Dye's (the process IS reversed!)
- 3a) Some entering light misses all of the Q-dots / Dyes, passing straight through
- 3b) Some Q-dots / Dyes fail to absorb incoming light (e.g., due to chemical aging or "light bleaching")
- 3c) Some Q-dots / Dyes absorb incoming light but fail to re-emit **redish** light
- 4) Solar cells at ends of layer fail to convert all of incoming **redish** light energy into electrical power
- 5a) Some sunlight bounces right off the concentrator's top surface
- 5b & 5c) Some light is absorbed or scattered outward by impurities (same symbol used for such traps!)
- 5d) Some light fails to internally reflect due to roughness or flaws on surfaces of concentrator layer

*Result? LSC power conversion efficiencies of ~ 5% or less <sup>1</sup>*

Then why bother with such an apparently complex but inefficient scheme?

Think a bit more about these thin flat stationary sheets

They might ultimately be quite cheap as they consist of only:

- Thin transparent plastic sheets or films

- Having small added quantities of easy-to-make Q-dots or Dyes

- With tiny (e.g., 1 millimeter wide slivers) of PV cells facing their edges

But even as flat stationary sheets they can capture light from lots of angles

- Directly from the shining sun AND/OR from the whole sky on overcast days

Filtering out (often harmful) UV light, but passing through a lot of visible light

*Figured out their potentially "golden" application?*

## *As windows in big urban office buildings and apartments:*

Where they could provide at least **some** of the building's power

While blocking **some** sunlight of all colors

as is now commonly done via semi-mirror coatings

Reducing the heat load to the building

thereby reducing air-conditioning power expenditure

But especially blocking the UV end of the solar spectrum and its

damage to plastics, rubbers, paints & pigments

And, by using liquid-crystal Dyes (re-orientable by voltage),

light blocking in different parts of spectrum (IR / Vis / UV)

might be controlled electronically and tailored

to prevailing temperature & sunlight conditions <sup>1,2</sup>



LSC window from U.S.  
Los Alamos National Lab <sup>2</sup>

1) M.G.Debije & P.P.C. Verbunt, *Advanced Energy Materials* 2, pp. 12-35 (2012)

2) Li et al., *Nature Energy* 157, pp. 1-9 (2016)

## How efficient are these LSC's?

The 2016 Los Alamos National Lab paper claims <sup>1</sup>

**10% internal quantum conversion efficiency**

But a 10% quantum efficiency means only that within the device

1 electron is liberated per 10 incoming solar photons

**That is NOT the same as a 10% power conversion efficiency**

= Electrical Power Out / Solar Power In

For an LSC window, I'd think the figure-of-merit might be

= Electrical Power Out / Blocked Solar Power In

"Blocked" because windows **NEED** to pass a lot of light

**I found no reports about this (or a comparable figure)**

**and thus cannot yet assess the power potential of LSC's**



Los Alamos  
National Lab <sup>1</sup>

1) Li et al., *Nature Energy* 157, pp. 1-9 (2016)

# *Thermophotovoltaics*

## *Thermophotovoltaics*

Thermophotovoltaics echo LSCs in that they seem to have come out of nowhere,  
they embody unusually obscure and exotic science,  
and they offer whole new sources of photovoltaic power

Thermophotovoltaics are all about **heat** - more often than not about **waste heat**

**Which our factories & engines produce in truly prodigious quantities:**

Fossil fuel power plants waste 60-70% of fuel energy as heat

(for details, see my **Fossil Fuels** note set ([pptx](#), [pdf](#), [key](#)))

Internal combustion engines waste almost 80% of fuel energy as heat

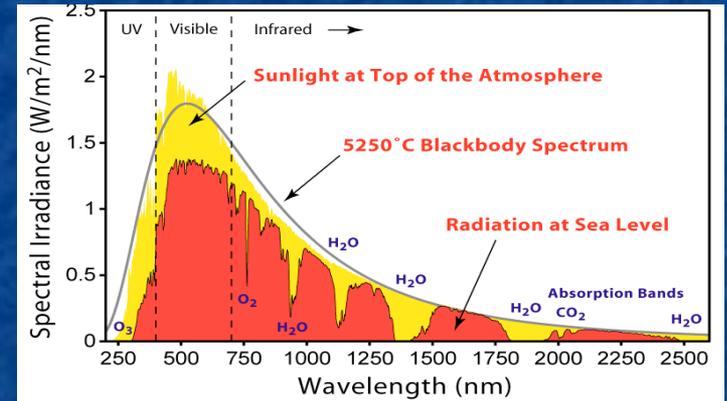
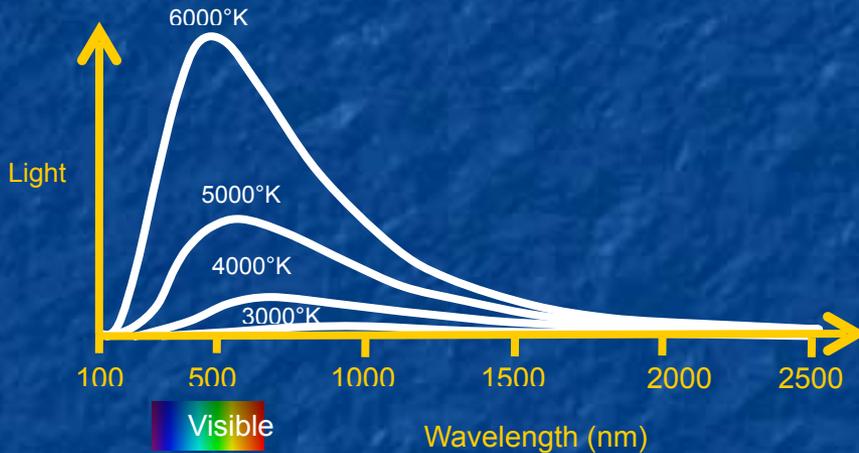
(for details, see my **Transportation** note set ([pptx](#), [pdf](#), [key](#)))

**Capturing even a small fraction of that waste heat  
and converting it into electrical power could be a HUGE deal!**

# Heat is all about vibrating atoms

But vibrating atoms radiate away electromagnetic energy (a.k.a. "light")

Physicists characterize this radiation from heated objects by "Black Body" curves, which plot light intensity vs. wavelength (vs. the object's temperature):



Comparison with our sun's spectrum (at the right) shows that our sun emits energy like a 6000°K black body (which is indeed the temperature of the sun's surface)

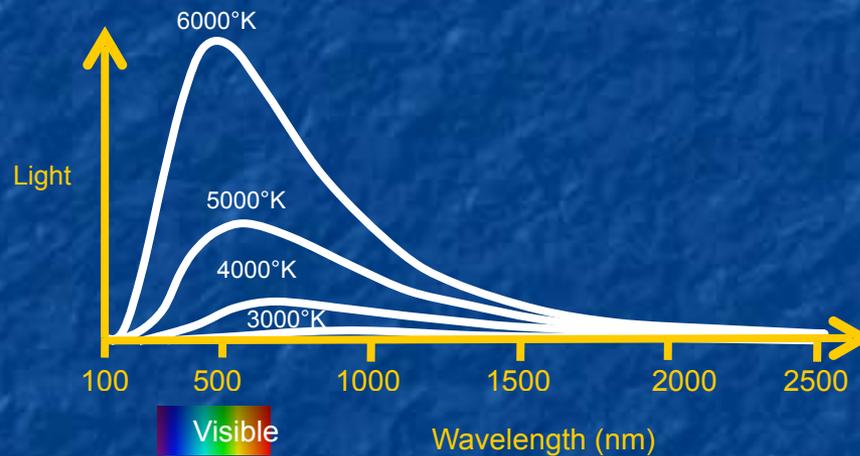
(In a sense, this makes ALL photovoltaic devices **thermophotovoltaic** devices)

*But these **new** thermophotovoltaics target cooler temperatures*

Temperatures produced by our factories, by our motors, by our . . .

At their hottest, these objects tend to glow from dark red to pale yellow,  
indicating temperatures of roughly 500 to 1000°C (~ 750 to 1250°K)

**That's COLD by black body standards, producing very little light emission:**



Indeed, the integrated power radiated from a black body (over all wavelengths)

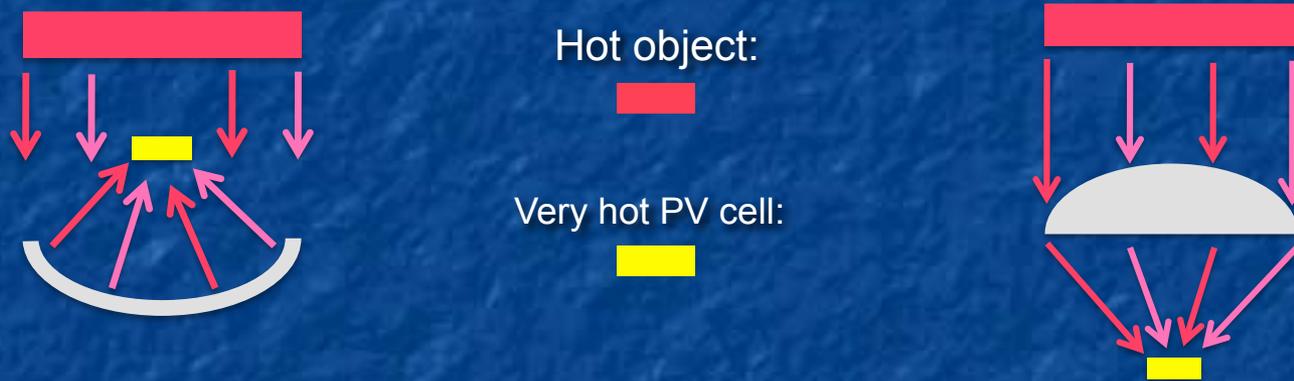
**scales as that black body's temperature to the FOURTH POWER**

(Which is known as the "Stefan-Boltzman Law")

*In response, thermophotovoltaic schemes first try to jack up temperatures:*

This can be done by concentrating the hot object's weak infrared emission

using the same sort of mirrors or lenses we saw used with conventional PV:



But neither scheme is entirely satisfactory - for at least two reasons:

- PV cells like intense light but need to stay cool themselves - **cooling** is thus required
- The PV cells still receive black body light which has a range of colors

limiting them to **low Shockley-Quisser power conversion efficiencies**

*Here's where thermophotovoltaics pull out all of the (scientific) stops:*

The thermophotovoltaic converter is built in flat layers

If flexible and thin, it might even be wrapped around the **heat-wasting hot object**

The hot object's mixed infrared radiation strikes a **two-layer absorber / emitter**

The top **absorber layer** captures essentially ALL of that incoming energy

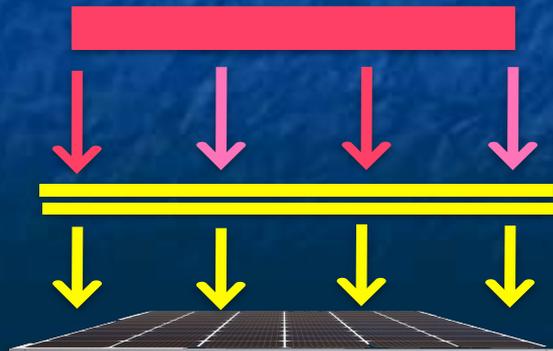
But, **magically**, it does NOT then radiate energy back outward - as black bodies should!

Which means that the absorber soon becomes **VERY HOT**

Indeed, **hotter** than the **hot object** from which it gathered its energy

It transfers energy **ONLY** to the attached **emitter layer** which **magically** radiates

**one pure PV pleasing (Shockley-Quiesser subverting) color** to the PV cell below



## *The source of that magic? **Metamaterials***

A **material's** properties are determined by the atomic structure nature built into it

**But metamaterials incorporate very un-natural manmade structures**

**Which, if built cleverly, have properties NOT found in nature <sup>1</sup>**

Metamaterials can take many, many forms

Ranging from 2D SiGe strained-layer "superlattices" I pioneered at Bell Labs <sup>2</sup>

To 3D Photonic Crystals <sup>3</sup> assembled by microfabrication <sup>4</sup>

To dense arrays of carbon nanotubes created via nanoscale self-assembly <sup>5</sup>

1) Review Article: *Metamaterials in Electromagnetics*, Ari Sihvola, *Metamaterials* 1, pp.2-11 (2007)

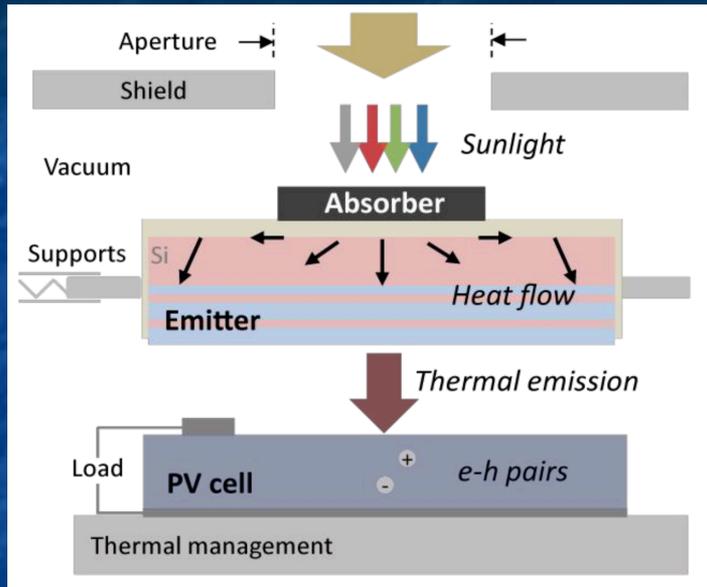
2) Review Article: *Silicon Based Semiconductor Heterostructures: Column IV Bandgap Engineering*, John C. Bean, *Proceedings of the IEEE* 80 (4), pp. 571-587 (1992)

3) *Photonic Band-Gap Crystals*, Eli Yablonovitch, *J. Physics of Condensed Matter* 5, pp. 2243-60 (1993)

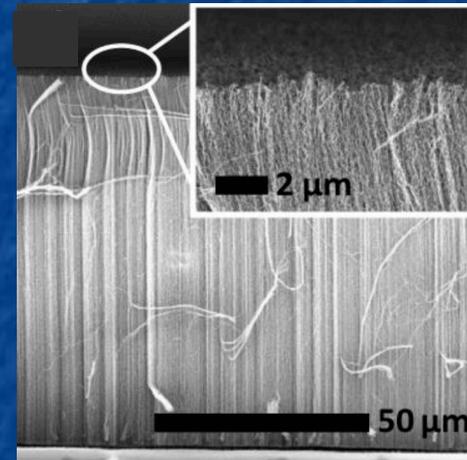
4) See my Nanoscience class note set on *Microfabrication / Micromachining* ([pptx](#) / [pdf](#) / [key](#))

5) See my Nanoscience class note set on *The Need for Self-Assembly* ([pptx](#) / [pdf](#) / [key](#))

# One way of applying metamaterial magic to thermophotovoltaics: 1



The absorber traps the **heated object's** light in an array of nanometer thick **carbon nanotubes**:



The carbon nanotube array resembles a brush with very widely spaced bristles

The wide nanotube spacing slashes light reflection from the array's surface

Simultaneously, the carbon nanotube's exceptionally conductivity boosts light absorption

Together these yield a **near perfect, angle-independent, light absorber** 2, 3

1) *A Nanophotonic Solar Thermophotovoltaic Device*, Lenert et al., *Nature Nanotechnology* 9 (2), pp. 126-30 (2014)

2) *Experimental Observation of an Extremely Dark Material made by a Low-density Nanotube Array*, Yang et al., *Nano Letters* 8 (2), pp. 446-51 (2008)

4) *Effective Medium Theory of the Optical Properties of Aligned Carbon Nanotubes*, Garcia-Vidal et al., *Phys Rev Lett* 78(22), pp. 4289-92 (1997)

## *The absorber thus heats up dramatically*

As a black body, that absorber should then increasingly radiate away power

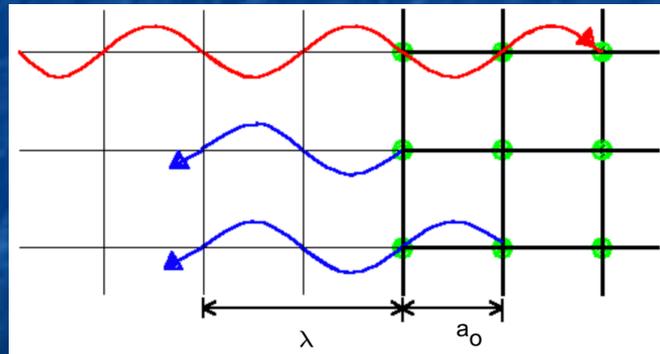
Further, that radiation should include a black body's typical span of colors

But in this device, radiation is blocked (& filtered) by **Photonic Crystal** metamaterials

In **natural crystals**, waves can slightly reflect off consecutive atomic planes

When those reflections are "in phase" they interfere constructively

And net reflection increases until the wave can no longer propagate forward:

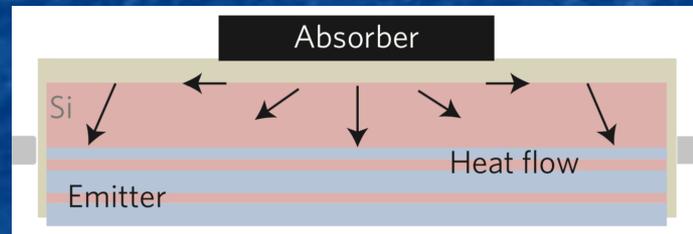


This occurs when wavelength =  $2 a_0 / n$  where  $n = 1, 2, 3 \dots$

(where  $a_0$  denotes the spacing between the atomic planes)

**Photonic Crystals** do the same thing at larger scales <sup>1, 2</sup>

By simply exchanging atoms for layers or arrays of larger manmade objects,  
which are defined by the same microfabrication techniques  
originally developed for the integrated circuit industry



<= Photonic Crystal

THIS crystal is designed to reflect back (and thus trap) **MOST** wavelengths of light

Its wavelength-blocking span might be enhanced, for instance,

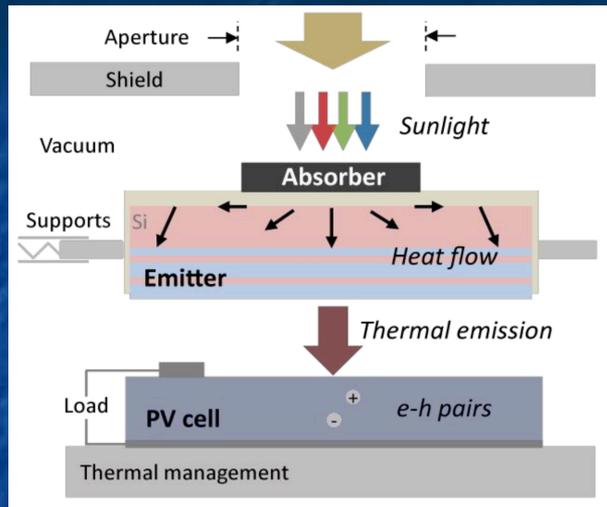
by stacking Photonic Crystals with different layer / array spacings

But it **ALLOWS** a narrow range of wavelengths (= colors) to continue downward

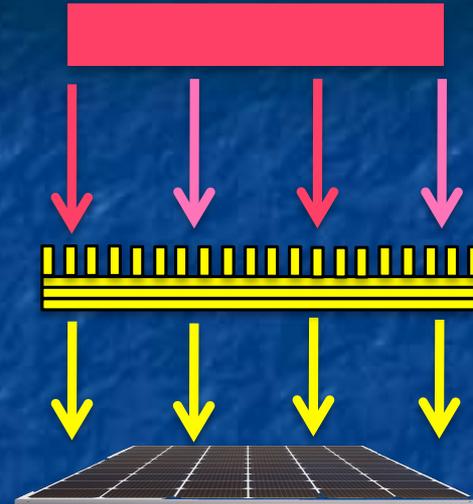
1) *Photonic Band-Gap Crystals*, Eli Yablonovitch, *J. Physics of Condensed Matter* 5, pp. 2243-60 (1993)

2) *Photonic Crystals in the Optical Regime - Past, Present and Future*, Kraus & de la Rue, *Progress in Quantum Electronics* 23, pp. 51-96 (1999)

*Only that almost-single-color light reaches the PV cell below:*



**Equals:**



But - **importantly!** - that now **almost single color of light** ends up carrying forward **essentially all of the energy** that left the bottom face of the **hot object**

The PV cell's bandgap can thus be tailored to that almost single color, which virtually eliminates liberated electron "butt-kicking,"

allowing that PV cell to shatter the Shockley-Quiesser efficiency limit

*At least that's the plan*

## *How well are **actual** thermophotovoltaic devices doing?*

For the 2014 MIT device, above, **power conversion efficiency of 3.2%** was reported <sup>1</sup>

Claimed to be a notably improvement upon then prevailing efficiencies of ~ 1%

But far short of cited theoretical limits of of ~ 40% <sup>2-4</sup>

What has happened since that 2014 publication?

An early review reported prototypes with efficiencies reaching 11% <sup>5</sup>

But in 2018 a team including Sandia National and MIT Lincoln Lab members  
claimed a **power conversion efficiency of 24.1%** <sup>6</sup>

**= Very respectable / rapidly improving TPV power conversion efficiencies**

1) *A Nanophotonic Solar Thermophotovoltaic Device*, Lenert et al., *Nature Nanotechnology* 9 (2), pp. 126-30 (2014)

2) *Absorber and Emitter for Solar Thermo-photovoltaic Systems to Achieve Efficiency Exceeding the Shockley-Queisser Limit*, Rephaeli et al., *Optics Express* 17(7), 15145 (2009)

3) *Design and Global Optimization of High-efficiency Thermophotovoltaic Systems*, Bermel et al., *Optics Express* 18(S3), A314 (2010)

4) *Metamaterial-based Integrated Plasmonic Absorber/Emitter for Solar Thermo-Photovoltaic Systems*, Wu et al., *J. Optics* 14, pp. 1-7 (2012)

5) **Overview and Status of Thermophotovoltaic Systems**, Ferrari et al., *Energy Procedia* 45, pp. 160-9 (2014)

6) *High-efficiency Thermophotovoltaic Energy Conversion Enabled by a Metamaterial Selective Emitter*, Woolf et al., *Optica* 5(2), pp.213 (2018)

## *A postscript concerning Metamaterials:*

The preceding discussion of metamaterials may puzzle some readers,  
as it corresponds only weakly with results you might get from a Google search

**Why? Because there are TWO commonly accepted definitions of metamaterials**

**The broad definition (which I employed):**

Manmade artificially structured materials with properties not found in nature

**The narrow definition (popular within one particular research community):**

Manmade artificially structured materials that subvert Maxwell's Equations

Explanation: **Electricity & Magnetism** were explored throughout the 1700's and 1800's

With observations spawning literally dozens of different "Laws"

But in the mid-1800's, **James Clerk Maxwell** managed to unify all of those laws

into just four (decidedly not simple) coupled equations which ~ completely

describe the behavior of Electric (E) and Magnetic (B) fields <sup>1, 2</sup>

1) For details see my note set: **Electric and Magnetic Fields** ([pptx](#) / [pdf](#) / [key](#)) and its Resources webpage ([link](#))

2) For details see my note set: **Magnetic Induction** ([pptx](#) / [pdf](#) / [key](#)) and its Resources webpage ([link](#))

## Maxwell's Equations (as applied within a material):

$$\nabla \cdot \mathbf{D} = \rho$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}$$

$$\mathbf{E} = \text{Electric Field} \quad \mathbf{D} = \epsilon \mathbf{E}$$

$$\mathbf{B} = \text{Magnetic Field} \quad \mathbf{H} = \mu \mathbf{B}$$

$\epsilon$  = Material's "Permittivity"

$\mu$  = Material's "Permeability"

$\rho$  = Electrical charge / volume

$\mathbf{J}$  = The flow of that charge

$\epsilon$  and  $\mu$  capture how the material reacts to applied electric or magnetic fields

In sensibly acting natural materials, both are positive numbers

**But what if artificial alteration of material structure made one or both negative?**

The weirdness this would produce, and how to drive  $\epsilon$  and/or  $\mu$  negative,

are the focus of the other (narrower) definition of metamaterials <sup>1</sup>

**But negative values have only yet been achieved at "microwave" sublight frequencies**

**Making those "metamaterials" irrelevant (so far) to photovoltaic power conversion**

<sup>1</sup> See: *Introduction to Metamaterials*, Wartak et al., *Physics in Canada* 67 (1), pp. 30-34 (2011)

# *Credits / Acknowledgements*

Some materials used in this class were developed under a National Science Foundation "Research Initiation Grant in Engineering Education" (RIGEE).

Other materials, including the "Virtual Lab" science education website, were developed under even earlier NSF "Course, Curriculum and Laboratory Improvement" (CCLI) and "Nanoscience Undergraduate Education" (NUE) awards.

This set of notes was authored by John C. Bean who also created all figures not explicitly credited above.

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