

The Bleeding Edge – Part II:

Nano Energy Technologies

Today we'll discuss the possible use of nano in power production and storage:

Starting with a short visit to James Clerk Maxwell, then proceeding to . . .

A careful look at Photovoltaics (a.k.a. "solar cells"), including:

- The critical difference between photovoltaics and photoconductors
- The impact (present and future) of nano-quantum structures

Then on to ways of storing electrical energy:

- Nano Capacitors
- Nano Batteries
- Nano Fuel Cells

*For even **more** information on today's topics see:*

From the Sustainable Energy Systems part of WeCanFigureThisOut.org:

[Solar Power](#)

[Next Generation Solar Power](#)

[Batteries and Fuel Cells](#)

[Power Cycles & Energy Storage](#)

MUCH attention is now focused on use of nano for power

For PRODUCTION of power via "Quantum Dot" **solar cells**

Using light to move electrons

Or STORAGE of power via nano **capacitors** and **batteries**

Into which excess electrons can be driven and temporarily stored

That is as far as most news reports (and much research) goes

But if this is all you consider (and engineer):

Weak photo-current will **briefly** flow from quantum dot cell, and then **stop**

Or nano capacitors will only **ever** store nano electrical power

What then are the problems?

A short visit with James Clerk Maxwell:

Maxwell's 1st Equation: Electric Field builds in proportion to net charge

"Net charge" = Positive charge density – Negative charge density

Electric force is then proportional to the strength of that electric field

So just a TINY ACCUMULATION of net charge => HUGE FORCES

For a second or two:



Then there is a loud snap
as charge build-up dissipates

On scales much greater than molecular dimensions

Nature will not LET you remove or add significant net charge!

So "electricity" is almost all about **pumping** charge

PUMP charge in one end of something and out the other end:



"Something" = Battery, solar cell, generator, . . .

That's WHY it's called electrical **current**: An analogy to incompressible water:

Can pump water **THROUGH** pipes, but if try to increase water **IN** pipe => Explosion!

Battery, solar cell, generator . . . are all **CHARGE PUMPS**

And pumps are judged on basis of the **flow** and **pressure** they can generate:

Water Power = Flow x Pressure which is analogous to:

Electrical Power = "Current" x "Voltage"

Photovoltaics: What happens when light strikes a material?

Case 1) Photon energy < Material's bond energy:

Photons can't shake anything loose, most just proceed on through

That is, material is ~ transparent to these too low energy photons

Case 2) Photon Energy ~ Material's bond energy

Photon IS now absorbed and its energy used to kick an electron out of a bond

Case 3) Photon Energy > Material's bond energy

Photon is absorbed: Part of its energy kicks an electron out of a bond

Rest of its energy also goes to that electron in the form of **kinetic energy**

That is, photon kicks electron out of the bond, then **kicks it in the butt!**

So when we shine light having bond energy onto a material:

(Remembering that I want is power = current x voltage out of a solar cell)

This light is (at least eventually) going to be absorbed by a bond in our material:

Before: *Atom cores* (positive nuclei + inner electrons) + *bonding electrons*



After: One negative electron is liberated, leaving behind a positive region:



Electron is drawn BACK to positive region => falling back into bond

(or a FEW might wander out the left or right end)

But this only gives me a photoconductor:

Most electrons just wander until pulled back into bonds

Or ones that DO exit are equally likely to exit right or left

Nothing is pumping (pushing) electrons to flow in one direction!

Application? ADD external battery/power supply and use as a light detector:

No light: All electrons in bonds, no current through sample (despite battery)

Light: Freed electrons.

Battery can now suck them out one end and push back into other

But where did the light's energy go? Into the atoms

Freed electrons fell back into atoms' clutches

Giving the atoms a kick => atomic vibrations (a.k.a. **heat**)

To produce power we've *ALSO* got to drive (*PUMP*) electrons somewhere!

Classic Technique:

START with fully-bonded electrically neutral material, most commonly **silicon**

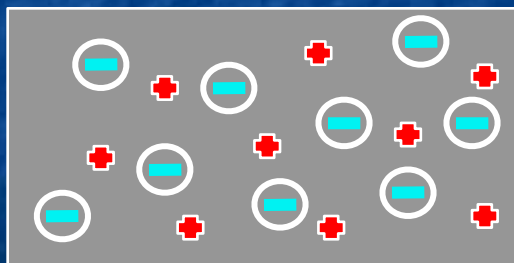
It sets the bonding rules with its crystal structure: Rule with Si = **four bonds**

ADD atom of almost same size but with one less bonding electron (e.g. **boron**)

Fits into crystal, steals electron from elsewhere, making it an **Acceptor** ion (thief?) 

Bond where electron stolen **from** now becomes a positive **Hole** 

Add **neutral** Acceptor atoms to Si => Negative ions + Liberated holes:



← Silicon atoms = Grey (fixed neutral atoms)

← Acceptor ions also **FIXED** in position

← Holes = **MOBILE** Why?

ANSWER: Hole grabs electron from neighbor, leaving hole in a **NEW** place . . .

And holes don't fill with electrons from outside because that would add net charge

Can also add things that will shed electrons

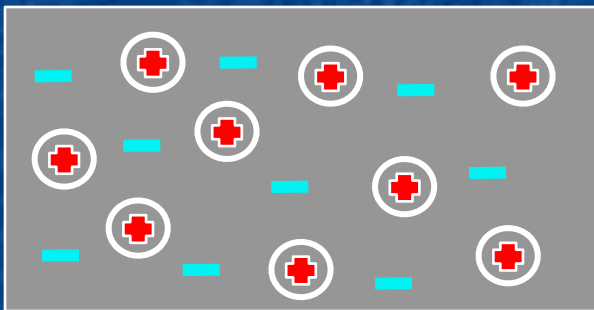
Donor = Similar to Si in size, but with one additional bonding electron (e.g. P, As)

Fits into crystal but final electron has nothing to pair with and bond

Add room temperature heat, and this atom ionizes => **Donor** ion: 

By liberating its last, weakly attached, electron: 

Silicon with added Donor impurity atoms => Positive ions + Liberated electrons:



Here only liberated electrons are **MOBILE**

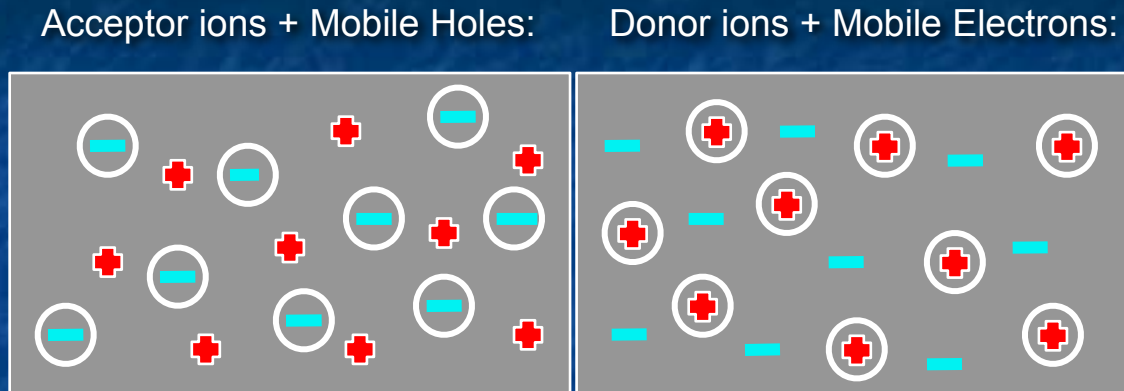
And, as in other material, net charge is still zero!

So James Clerk Maxwell is still happy

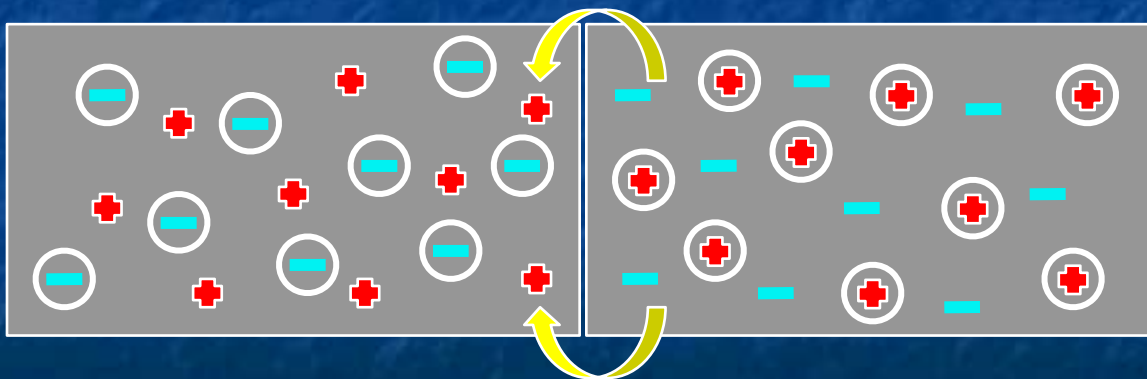
And if mobile electrons return home, heat will eventually kick them back out!

NOTE: Acceptor and Donor impurities are called "DOPANTS"

Payoff comes when you put two such "doped" regions side by side:

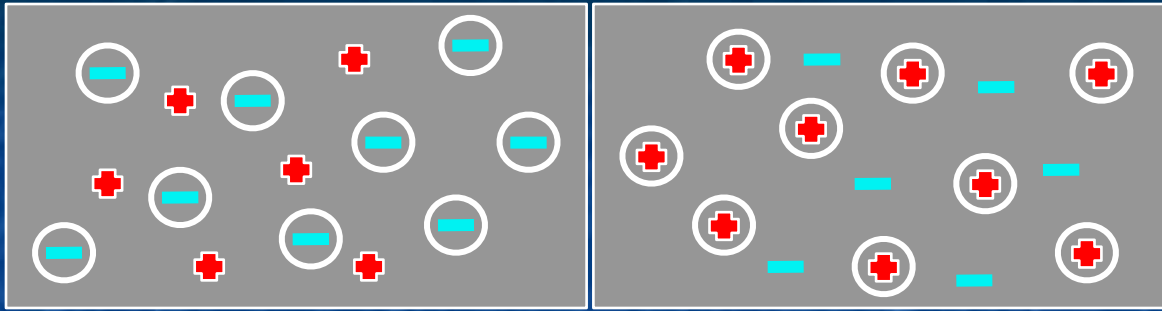


At intersection ("**junction**") mobile electrons are going to rush across to FILL mobile holes!!
(Because holes ARE just bonds that have lost one of the normal paired electrons!)



Mobile electrons filling the holes (in the bonds) is called "**recombination**"

Central junction thus becomes **depleted** of ALL mobile charges (liberated electrons or holes):

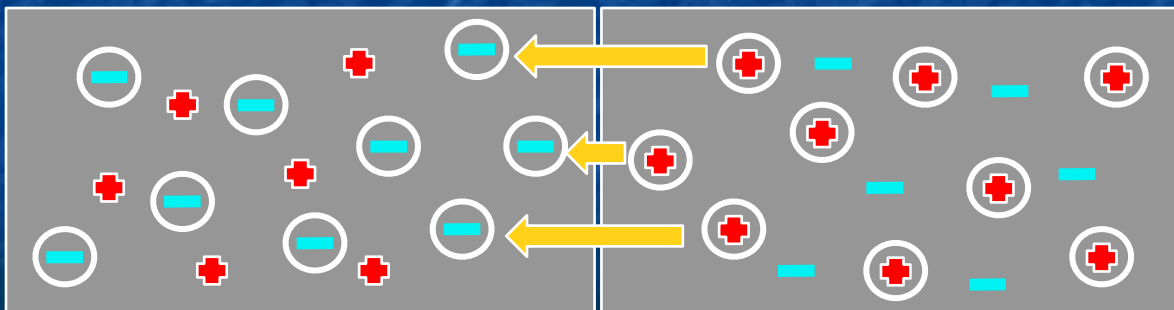


But this leaves uncompensated FIXED acceptor ions (-) / donor ions (+) at the junction

Which produces a growing **Electric field** at that junction

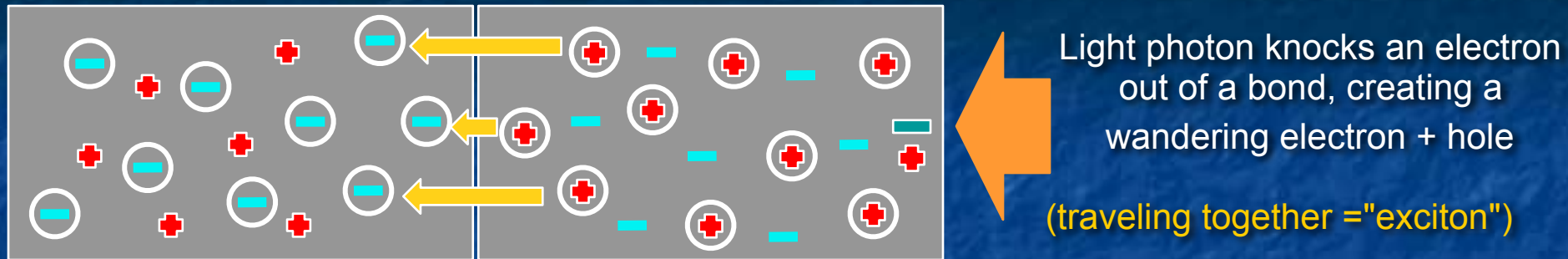
Migration / recombination continues UNTIL field is strong enough to block further migration

Because **Electric field** pushes positive charges left and negative charges right

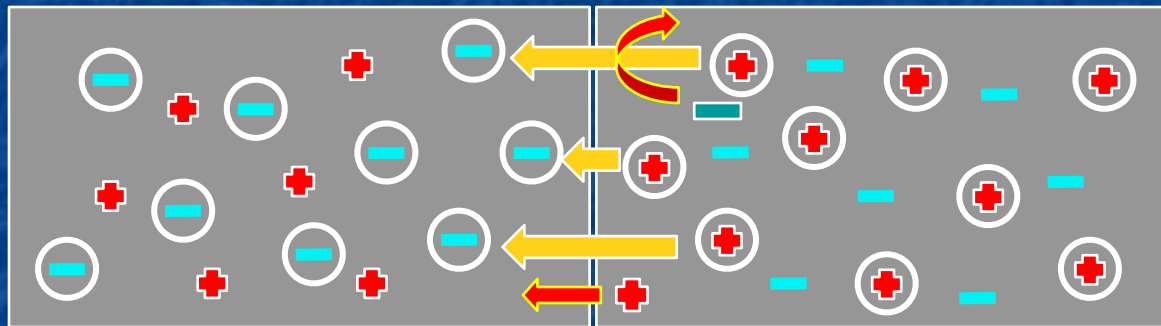


Electric field thus locks **remaining** mobile holes and electrons on their respective sides

NOW add light to knock electrons out of background silicon:



New electron and hole can both wander, but if reach "junction:"



"Built-in" electric field traps new electron on right, but propels hole to left

If instead created on left, hole trapped on left, but electron swept to right

= A CHARGE PUMP

(BTW this is also a **DIODE**: Can only force current through it in **ONE** direction)

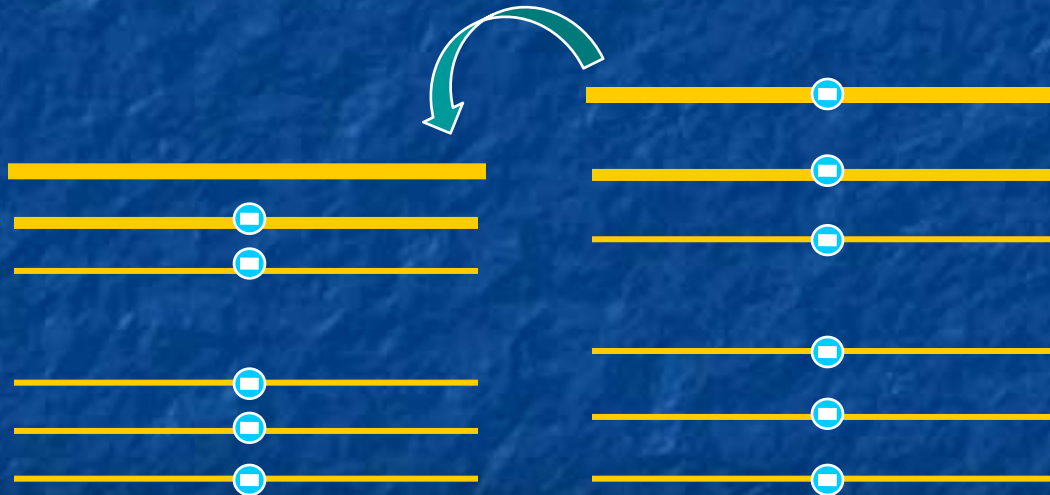
More general way of creating boundary charge-separating electric field:

ABOVE: ONE MATERIAL but divided it in TWO DIFFERENTLY BEHAVING REGIONS

Made two regions different by adding acceptor OR donor impurity atoms

ALTERNATIVE: Just put two DIFFERENT MATERIALS side by side

Electrons at higher energies on one side will try to cross over to other side



NET RESULT (again) = Build up of electric field at boundary

Leading to common rules for almost all photovoltaics (solar cells):

Must have at least one set of paired materials:

Be it two distinctly different materials OR

One basic material (e.g., silicon) modified into two differently acting layers

In that pair, one layer/material must cling onto electrons more tightly

So that electrons will flow into it from second material

Until shift of charge across boundary builds up ELECTRIC FIELD at interface

Which will tend to counter further shifting of charge

That "interfacial" electric field will then provide the critical push

Light energy => breaking electron bonds

But ELECTRIC FIELD then pushes freed electrons all in one direction

But solar energy is all about "efficiency"

Solar cell efficiency = Power produced / Power received

Power received = Solar power:

Above the earth's atmosphere, peaks at about 1350 Watts / square meter

This value is referred to as "AM0" (air mass zero)

Atmosphere will absorb ~ 25% of this power => ~ **1000 Watts / square meter**

Referred to as "AM1.5" (air mass 1.5) But this = MAX surface intensity

Because this is value for sun DIRECTLY overhead

Which happens only in certain locations, in certain seasons, once a day

AND clouds / haze / fog will further reduce intensities!

But what is the amount of POWER (= current x voltage) PRODUCED?

Current comes from the number of electrons liberated by light / second

- Function of how strongly **that** material absorbs photons of **that** color
- AND of **how much** material is doing the absorbing (e.g. its layer thickness)

Voltage comes from charge driving/separating junction ELECTRIC FIELD

Which was created by process of bond filling/liberating. Leading to fact that:

Photo-electrons/holes are driven out of cell by ~ 60-70% of liberation energy =>

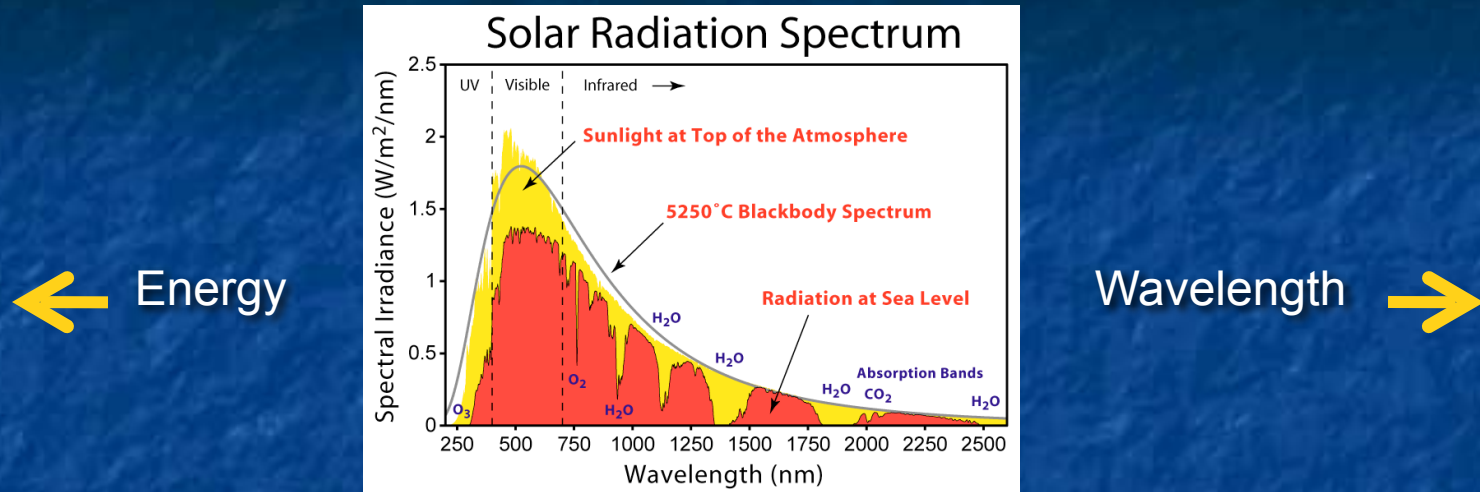
Solar cell voltage ~ (0.65) (liberation energy) / (electron charge = "e")

For Si solar cell, " V_{oc} " ~ (0.65) (Si electron liberation energy = 1.1 eV) / e ~ 0.7 Volt

Larger liberation-energy ("bandgap") solar cell materials => More VOLTAGE

But Less current: Why? (Answer => motivation for using quantum dots)

For answer, we must go back to solar spectrum



If this strikes a solar cell made of a material having **Small liberation energy** =>

MOST colors liberate electrons, but are driven out of cell by small voltages

If this strikes a solar cell made of a material having **Large liberation energy** =>

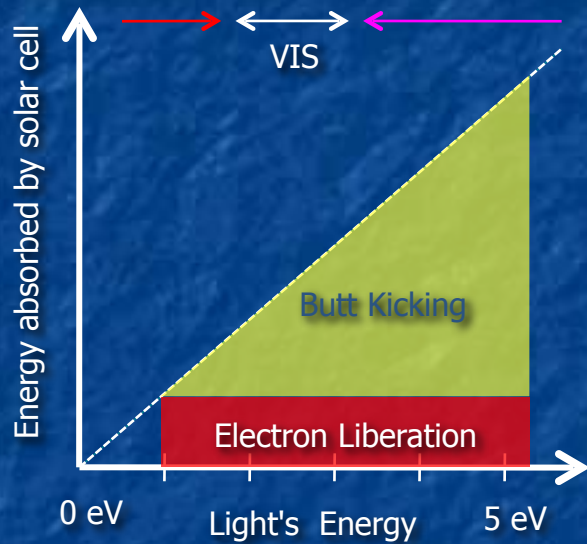
Only HIGH ENERGY light liberates electrons

But fewer electrons that ARE liberated will be driven by higher voltages!

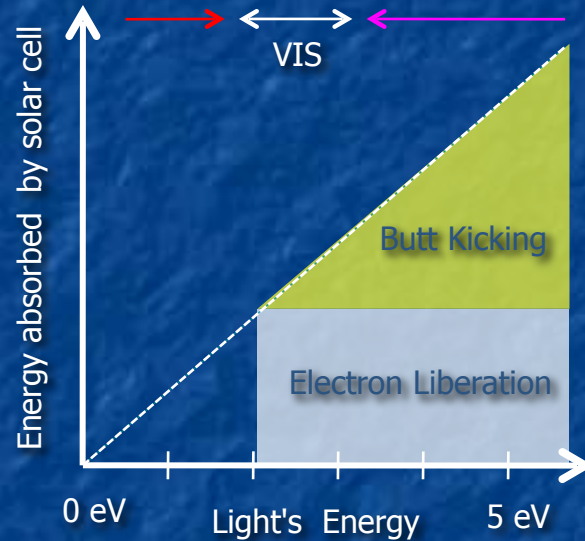
So now try to find optimum combination (based on choice of optimum material):

Energy absorbed by cells made of different materials:

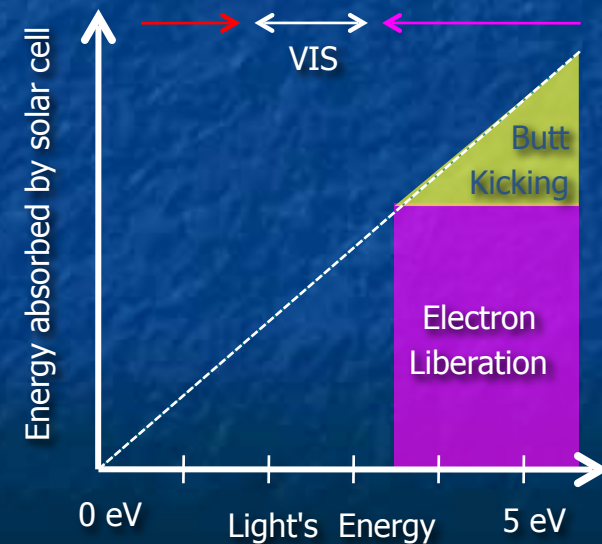
Cell with small "bandgap"



Cell with medium "bandgap"



Cell with large "bandgap"



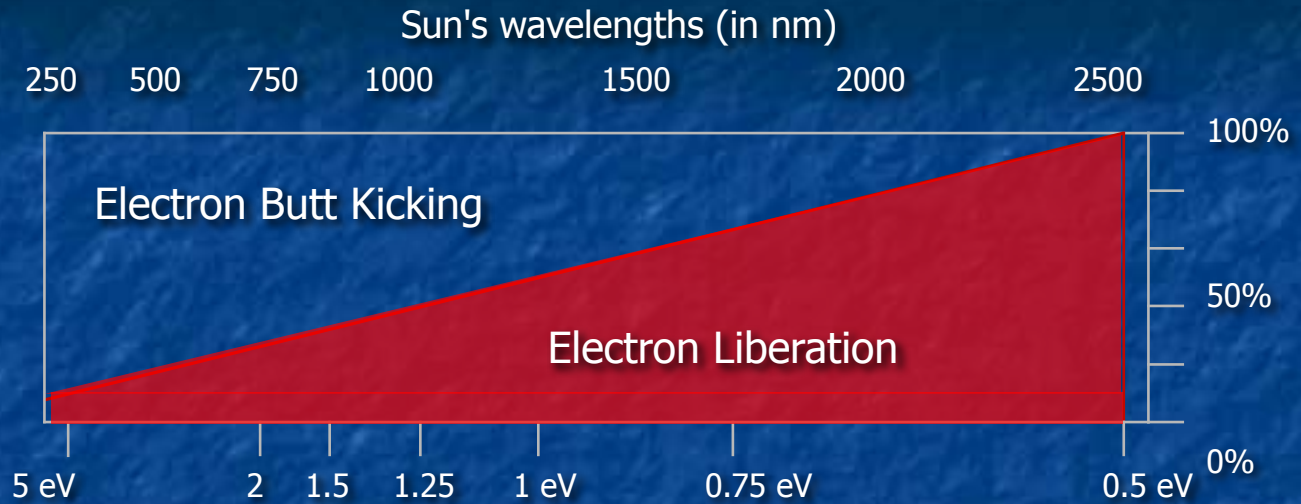
Blue Triangles => Energy passing right thru the cell!

Yellow Triangles => Energy lost to heating of the cell

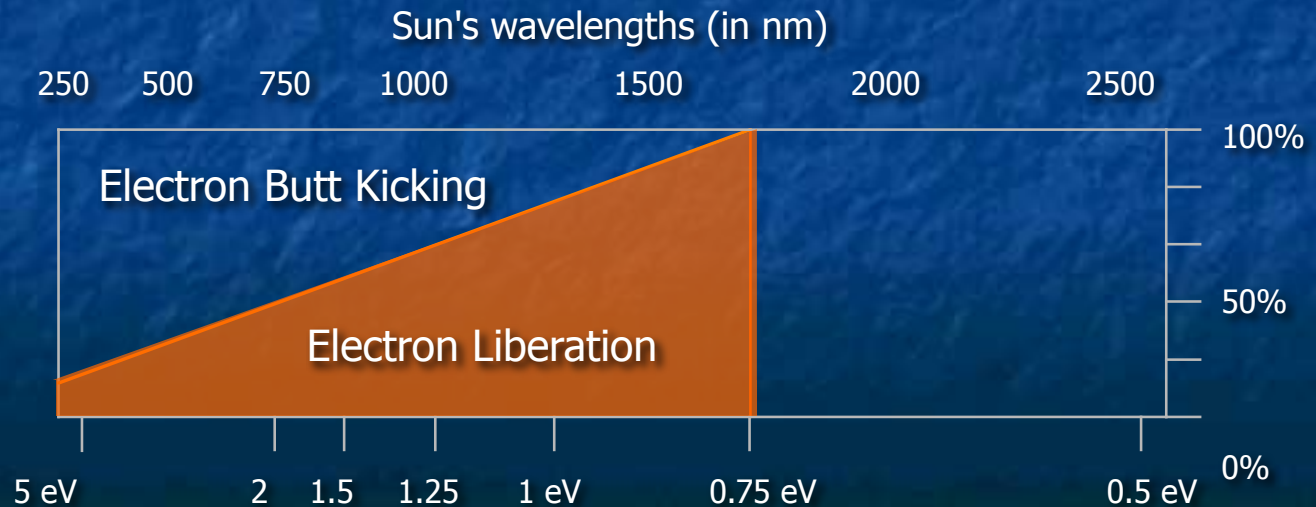
Rectangles (**only!**) => Electricity out of the cell

Plotting backward, as percentages (preparing to blend in solar intensities):

For solar cell using material with 0.5 eV electron liberation energy (bandgap):

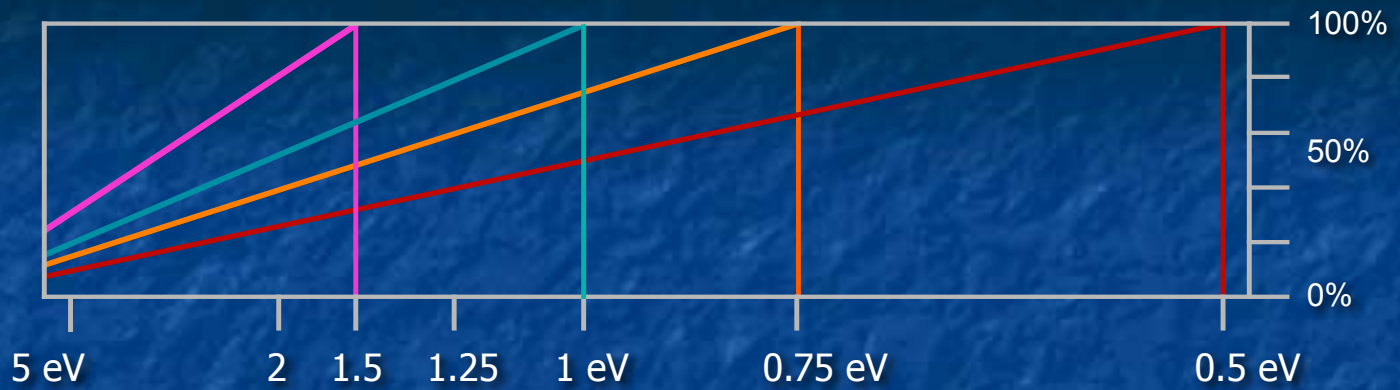


For solar cell using material with 0.75 eV electron liberation energy (bandgap):

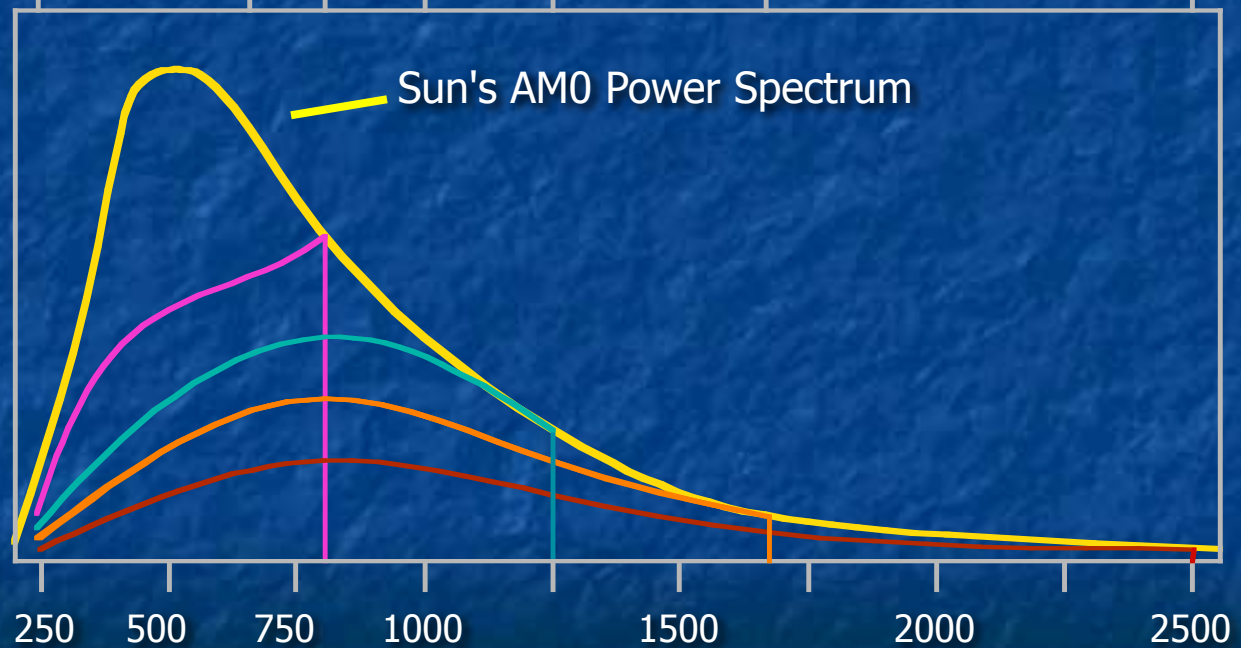


Now for solar cells with a LOT of different bandgaps:

PERCENTAGE of light's energy captured as electricity by different bandgap materials:



Sun's Energy Spectrum:



Energy captured by different bandgap cells:

(I really should've used Sun's AM1.5 spectrum)

Wavelength in nm (or above, equivalent energy in eV)

Larger the area under a bottom curve => More solar energy captured

BIGGEST area comes between 1 eV and 1.5 eV curves, for ~ 1.3 eV material

Material of this bandgap could capture & convert ~ 35% of Sun's energy

It's called the **Shockley-Queisser Limit** after William Shockley & Hans Queisser

So fact that single-material solar cells efficiencies top out at 35% is

NOT because we are doing a poor job of engineering!

It is instead because:

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

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

All because photons refuse to divide their energy between multiple electrons!

(Sure would be nice if we could weasel our way around that!)

Si has ALMOST perfect bandgap to reach S-Q Limit!

So can approach ~ 30% efficiency. But silicon is also fragile and expensive

"TIME OUT! Elsewhere in class you say Si is tough and cheap!"

Fragility: It's tougher than OTHER semiconductors, but it is still brittle/breakable

Expense: In solar cell want light-liberated electrons/holes to wander a long time

So have good chance of wandering into electric field at junction (**essential!**)

But wandering electrons/holes tend to STOP at impurities

If both stop there, likely that electrons will fill holes (effectively vanishing)

So solar cell grade Si must be about 1000X more pure than electronic grade

About 1 part in 10^{12} pure! => Much more expensive than normal Si

So would really like some sort of breakthrough!

To beat the Shockley-Quiesser Limit, minimize the electron butt kicking:

How? By stacking solar cells of DIFFERENT materials atop one another

Materials with different bond energies/"bandgaps"

Top: Material with large bond energies ~ purple/blue light:

High energy photons use ALMOST ALL of their energy liberating electrons

While less energetic photons pass right through!

Middle: Material with medium bond energies ~ green light:

Medium energy photons use ALMOST ALL of their energy liberating electrons

While less energetic photons pass right through!

Bottom: Material with low bond energies ~ red light:

Low energy photons use ALMOST ALL of their energy liberating electrons



~ ALL photon energy => electron liberation => ~ 100% energy capture!!

Called "Multi-Junction" or "Tandem" Solar Cells"

BIG REMAINING PROBLEM:

Shockley-Quiesser Limit was ~ 33% energy capture efficiency

Multi-junction cell could approach ~ 3X (= 100%) energy capture efficiency

but requires the combination of ~ 3 different cells to get there

So it likely costs (at least) 3X times as much!!!! (!\$#!\$@\$%)

To beat this must produce ~ three layers of cells for cost of about one layer

Very difficult with semiconductors which don't like to grow on one another:

Different crystal structures OR different atom spacings OR dope one another

Here is where quantum dots (or other tunable nanostructures) might come in!

Remember the "Quantum Size Effect" of Lecture 3 and Labs?

Happened when trapped waves in box

Only waves that survived had to "fit the box"

Quantum Dots act as such electron wave containing boxes

Smaller dots =>

Smaller electron standing waves =>

Higher electron energies

Can **TUNE** quantum dot size to **TUNE** electron energy

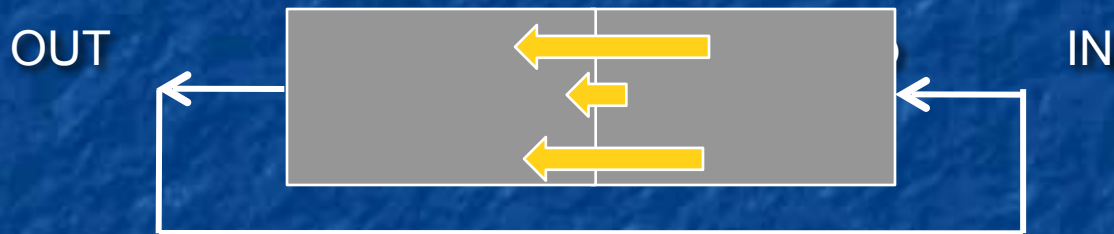
And, at least in principle, grow layers of different size dots atop one another

Yielding a "multi-junction" Shockley-Queisser beating Quantum Dot solar cell

Let's explore that possibility in smaller steps:

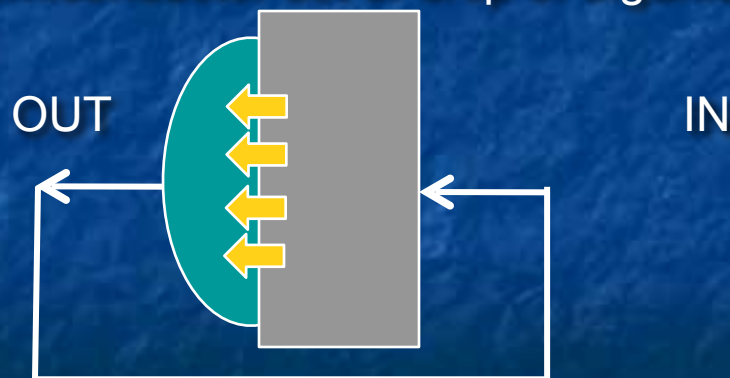
Building from earlier example of conventional semiconductor photovoltaic cell:

ELECTRIC FIELD from acceptor / donor ions provides sorting & direction of flow



An analagous one Quantum Dot photovoltaic cell:

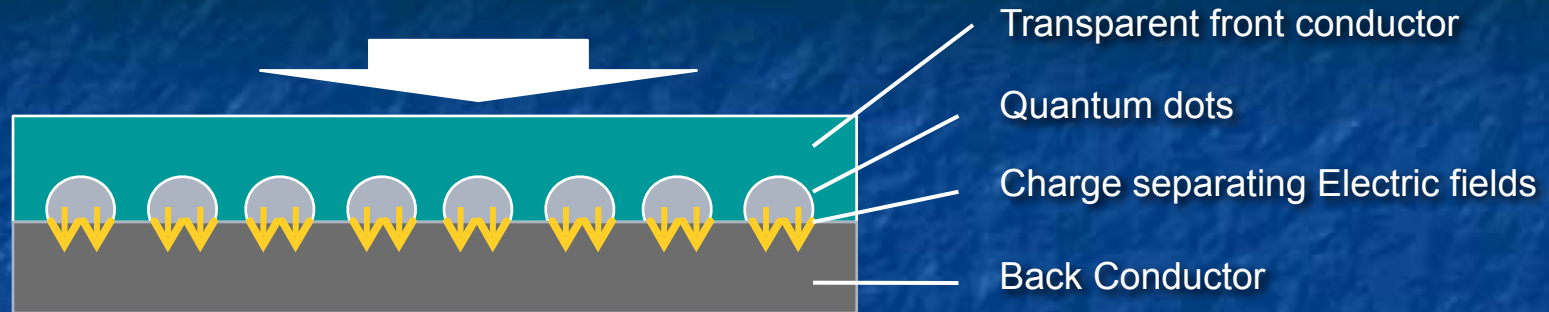
For instance, when semiconductor dot or drop of organic polymer meets metal:



But nano dots put out nano power, so want LOTS of them to work together:

A multi quantum dot (but not yet "multi-junction") solar cell:

Sticking, for the moment, with dots still of the same size:



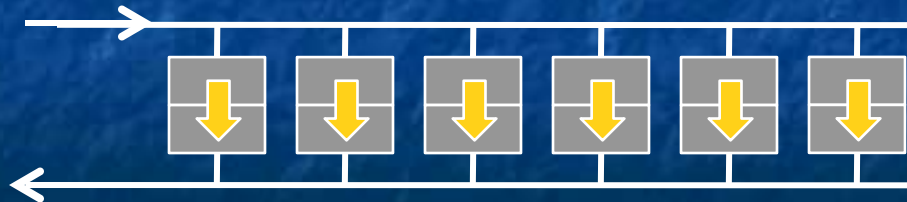
What is going on here? Have specially selected quantum dot and back conductor materials

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"):



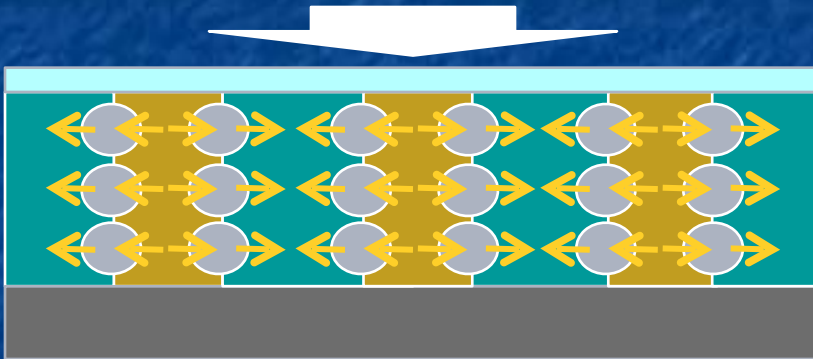
But this still allows for only ONE very thin light-absorbing QD layer => Very little current

An improved multi quantum dot 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
- Dots go to interface

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

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

But additional quantum dots STILL achieve light to electrical energy conversion of only ~ 9%

Compared to polycrystalline Si solar cell efficiencies of ~ 20%

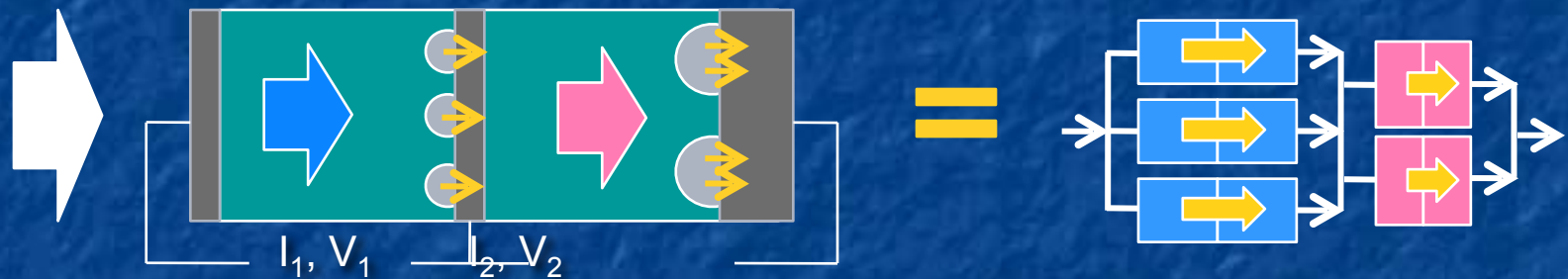
Or to single crystal Si or GaAs efficiencies of 25 - 35% !!

A REALLY improved quantum dot solar cell:

Using Quantum Size Effect + flexibility of quantum dots to give **multi-junction** design:

First capture **Blue Light** with small quantum dots => few higher voltage electrons

Then capture **Red Light** with deeper large quantum dots => many lower voltage electrons



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

But would require incredible control of internal arrangement and electrical current paths

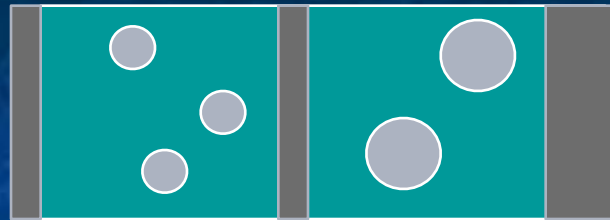
Making the creation of quantum dots the **almost trivial** part of task

REAL CHALLENGE here is required complex 3D SELF-ASSEMBLY

(Why I discussed possibility of QD's tethered to DNA scaffolds in last lecture!!)

It'd be LOT easier if quantum dots could be randomly distributed in layers!

More like this:



Yes, but we still need electric fields to separate light-liberated electrons from holes!

Here we would NOT want fields between the dots and their surrounding layer:

For instance, this field 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** boundaries*

Which COULD be accomplished by:

1) Choosing dot and layer materials with **similar** energy levels

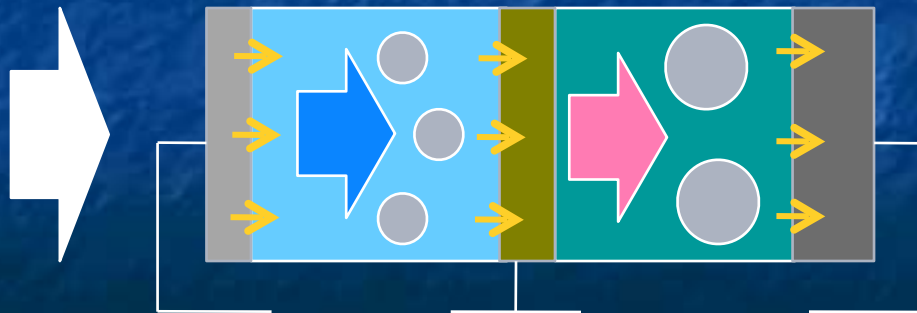
So they don't naturally transfer charge / build up interface electric fields

2) Choosing layer materials with **differing** energy levels

To promote charge transfer across their interfaces

Thereby engineering properly directed charge-pumping electric fields

To produce this alternate QD tandem solar cell:



3D self-assembly => A LOT easier

Layer material selection =>
A LOT more difficult

HAVE "multi-junction" and/or Quantum Dot solar cells broken through?

Following figure:

Compilation by U.S. National Renewable Energy Lab (NREL) of

latest,

greatest,

one of a kind,

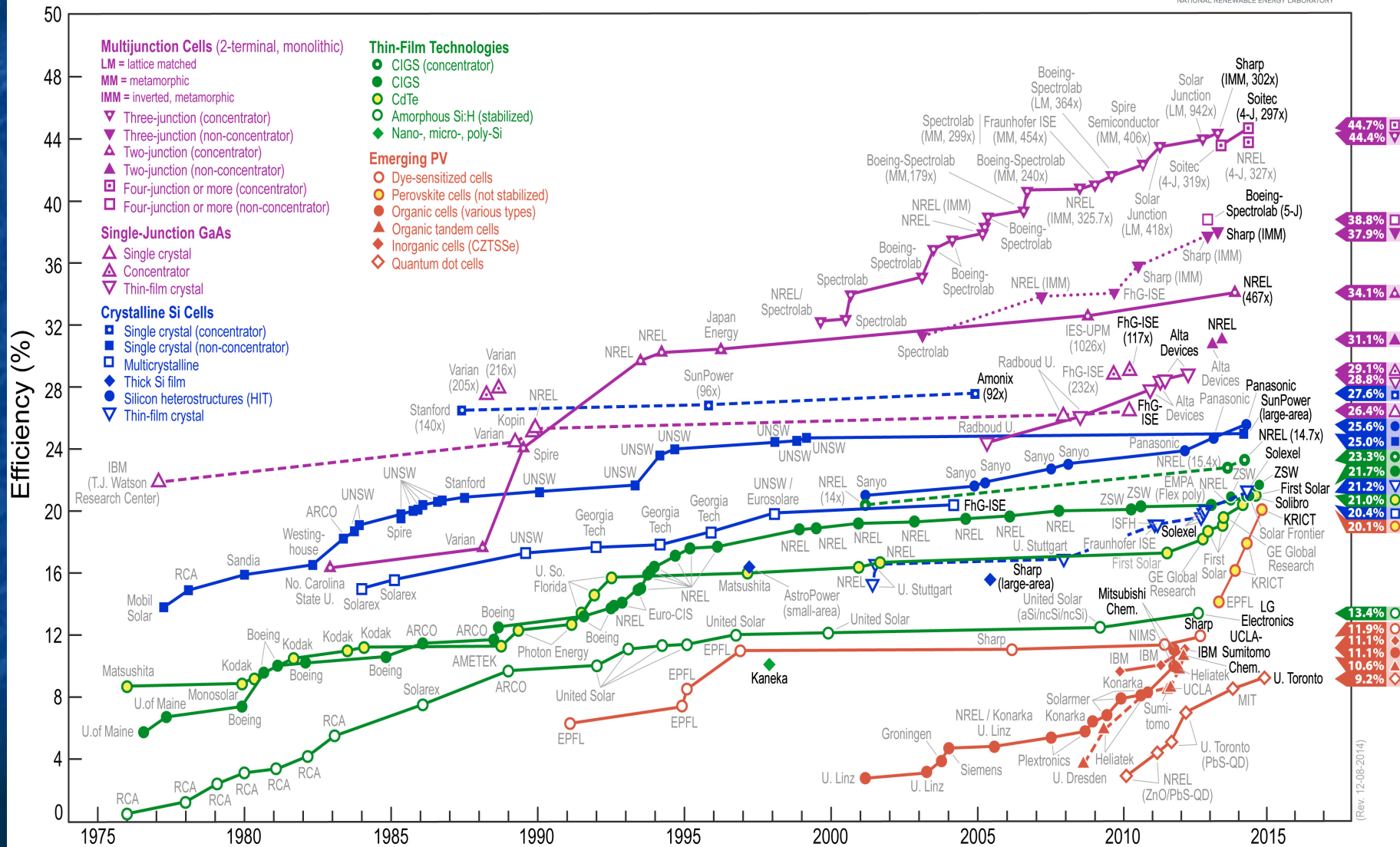
possibly never reproduced

(or horrendously expensive),

solar cell efficiency records:

Best RESEARCH solar cells (1976 – 2015):

Best Research-Cell Efficiencies



(Rev. 12-08-2014)

At lower resolution but with some guidance as to cell types:

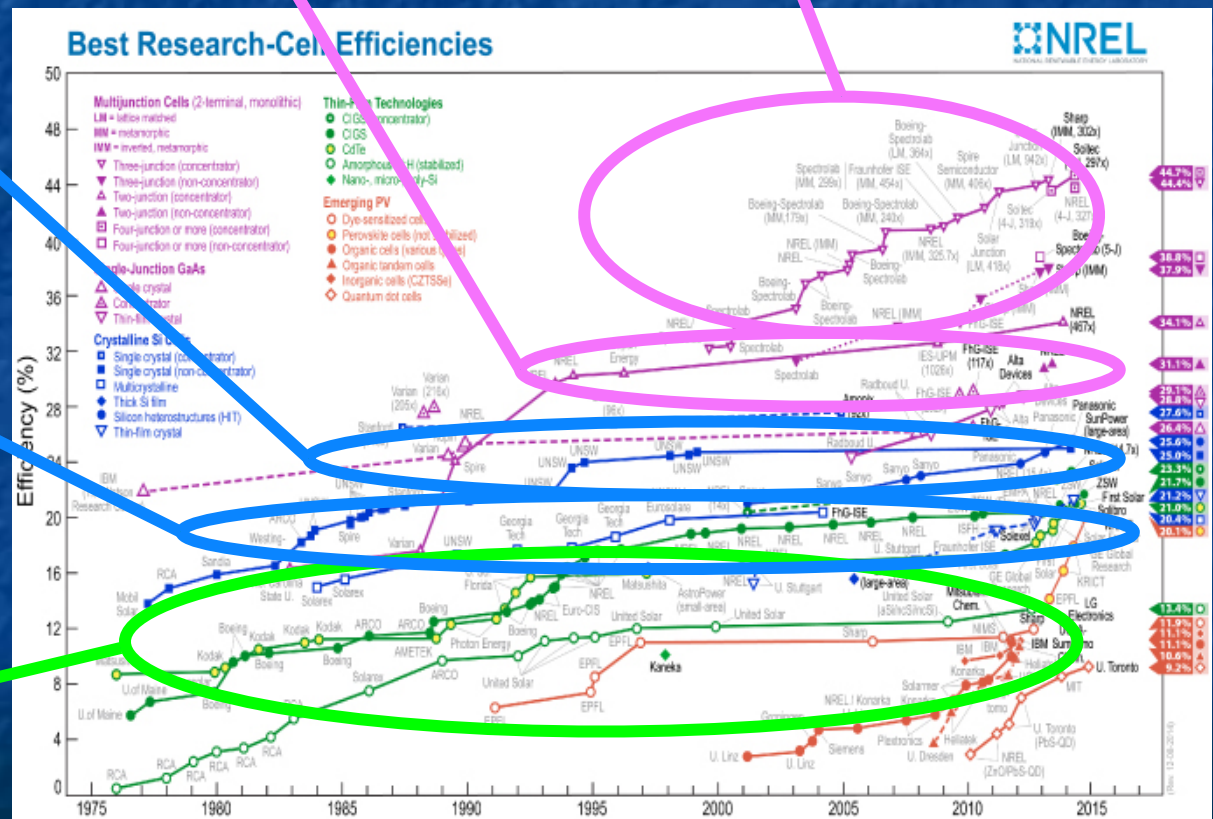
Multi-junction / Tandem

Single crystal GaAs

Single crystal Si

Polycrystal thin film Si

Other thin films



"Hero" (best in lab / single shot) efficiencies, top to bottom:

Multi-junction solar cells: Highest at almost 45%

So have beat, but not shattered, Shockley-Queisser Limit

Crystalline GaAs solar cells (more exotic/\$ crystal than Si): **Hair over 34%**

Crystalline silicon solar cells: Highest at 27.6%

Thin-film cells (e.g. polycrystalline/amorphous Si and CdTe): **Highest at 23%**

Perovskite cells: **Highest just over 20%**

Dye-sensitized, organic . . . cells: **Highest at 12%**

Quantum Dot solar cells: **Highest at 9.2%**

NOTE: In minority of cases where affordable commercial versions even exist, they have efficiencies $\frac{1}{2}$ or less than above hero numbers!

What happened to Nano's would-be impact upon photovoltaics?

Quantum Dot cells - As illustrated by my earlier figures:

Difficult to get multiple dots in **single layer** wired together and working together

EXTREMELY difficult to get **different layers** of different dots to work together

So the real (still in the future) breakthrough must be in SELF-ASSEMBLY

GRAPHENE – Where did this "wonder material" disappear to? (!@!%!%!#%)

*As a career specialist in photon capture I see four themes in graphene research
(**very often confused and hugely over sold**):*

- 1) Graphene's exceptional conductivity could be used for input/output wiring
- 2) Graphene's exceptional conductivity could be used for transparent top contact
- 3) Graphene could substitute for top contact AND top semiconductor layer
(changing semiconductor "P-N" diode to "Schottky Barrier" diode)
- 4) Might get single photon to liberate MORE than one graphene bonding electron
(Some reports of this, including by former Bell Labs colleague Art Hebard)

What exactly **MAKES** something a good "conductor" or "top contact?"

"**Good conductor**" must pass a lot of electrical current easily

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

Graphene's electrons travel at **exceptionally** high speeds

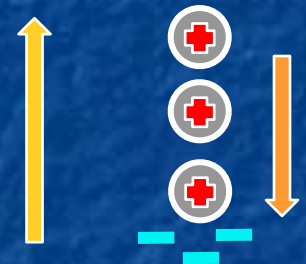
So graphene is a good conductor **despite** having fewer electrons than metals

"**Good top contact**" has to be good conductor AND let most light pass through

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

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

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

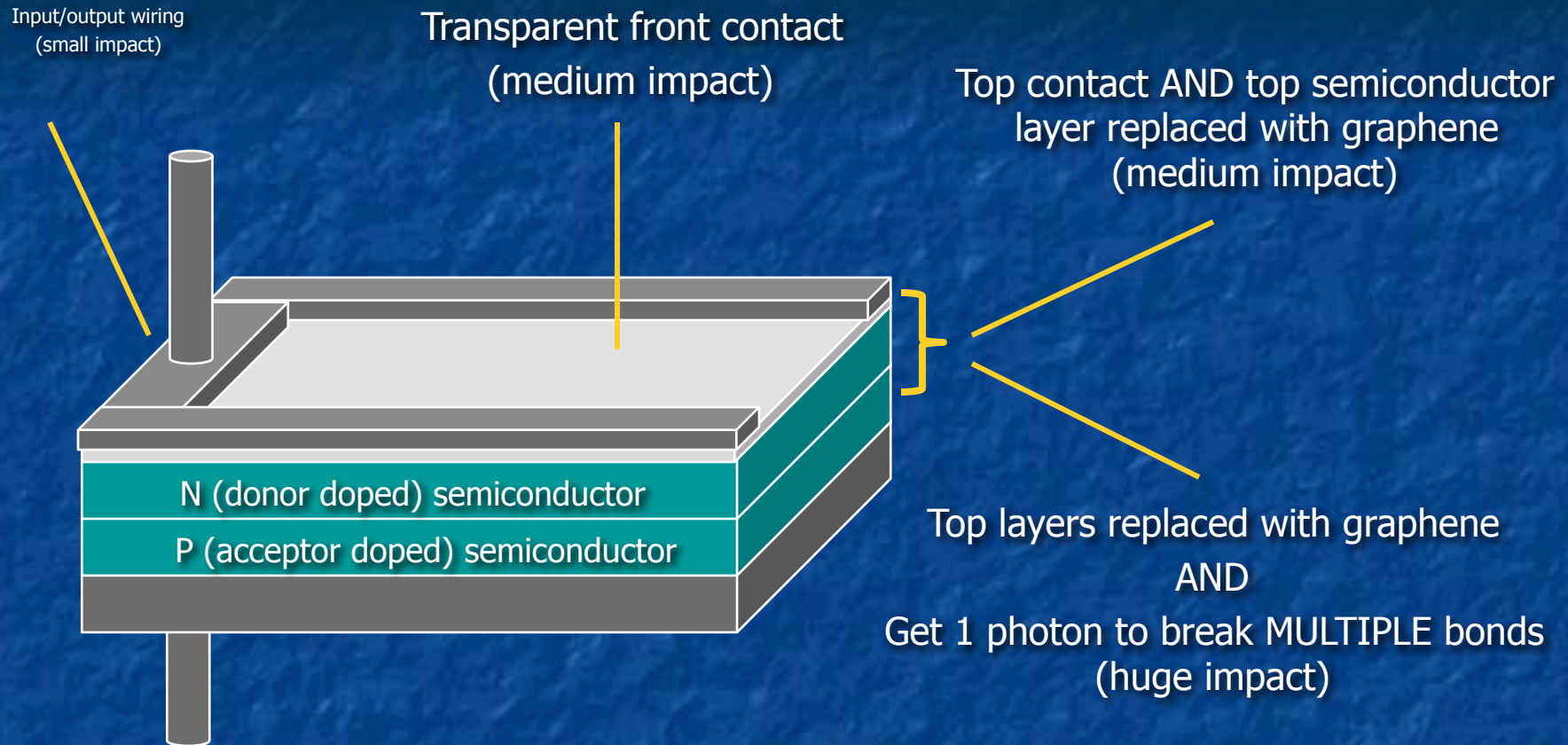


If there are enough electrons, counter electric field cancels light field

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

But graphene has fewer electrons => poor mirror (i.e. is more transparent!)

Combining this with pictorial depiction => Graphene's potential impact:



The final alternative (only) would completely sidestep Shockley-Quiesser limit:

~ ALL photon energy would go into freeing electrons (= recoverable energy)

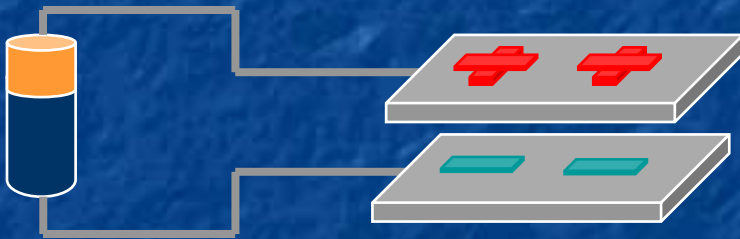
~ No photon energy would go into electron kinetic energy (=unrecoverable energy)

2) Nano Capacitors: *Key to tomorrow's energy storage?*

What IS a capacitor? A clever way of side-stepping Maxwell's 1st equation:

Trying to push more charge into an object doesn't really work

So instead build two closely spaced parallel conducting plates:



Overcomes need for local charge balance

Excess +'s on top plate don't like one another

But repulsion balanced by attraction to -'s below

Becomes more effective the closer the plates are:

$$\text{Capacitance} = \text{Area} \times (\text{dielectric constant in gap}) / (\text{gap thickness}) = A \epsilon / d$$

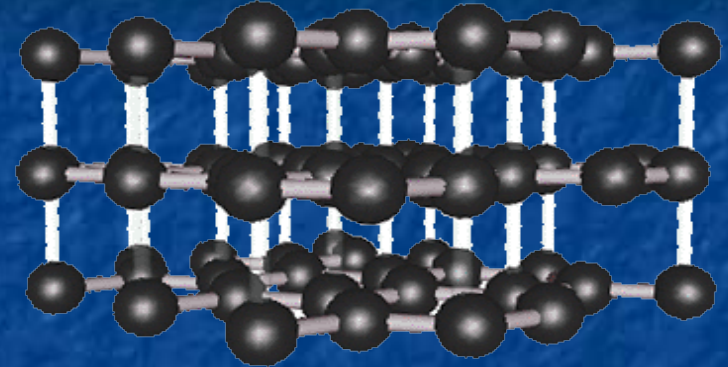
So where might we come up with some **really small** gaps?

Possible nano capacitor materials?

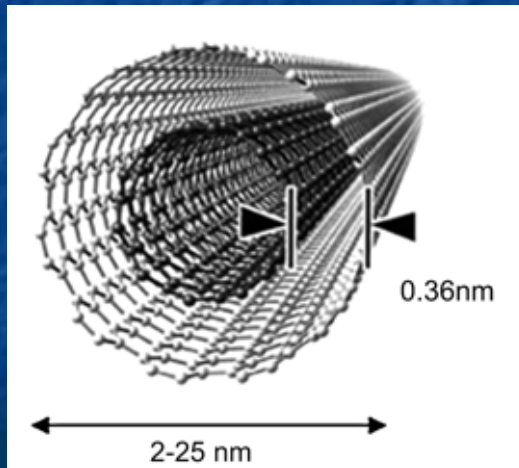
What about graphite?

No, in normal graphite electrons are able to jump between layers

But MIGHT prevent by alternating graphene layers with insulating spacer layers



What about nested carbon nanotubes?



Would again need non-electron conducting spacer layer to hold conducting tubes apart

With some success, such nano capacitors ARE being built

Much of the effort is going into creating those thin insulating spacer layers

Rather than trying to **slide** insulating layers into place

Better strategy is to form them IN PLACE. For instance, by oxidizing surfaces

Quantum mechanical tunneling sets limit on minimum spacer thickness:

Because (lecture 3): If insulator is too thin, electrons just "tunnel" right through it

How thin is "too thin?" Spacer must be $> 0.5 - 1$ nanometer

But capacitance = $A \epsilon / d$ So nano capacitors could still have d 's ~ 1 nm

While conventional macro capacitors use d 's of microns or even millimeters

So, per unit area, nano capacitors might store 10^3 to 10^6 more charge !

Important ramifications:

When (in previous section) we reduced solar cells to nano size (i.e. to single Q-dots)

We only got nano-power out (i.e. power out shrunk with **cell area**)

Forcing us to try to wire huge numbers (1 / nano) of Q-dot solar cells together!

But situation is better for nano capacitors:

Stored charge shrinks with **capacitor area / layer separation**

Smaller numerator hurts. But smaller denominator helps

So, done right, a single nano capacitor could store a LOT of charge per volume !

Making them great candidates for powering nano things

But to power **MACRO** things, would **STILL** have to wire huge numbers together

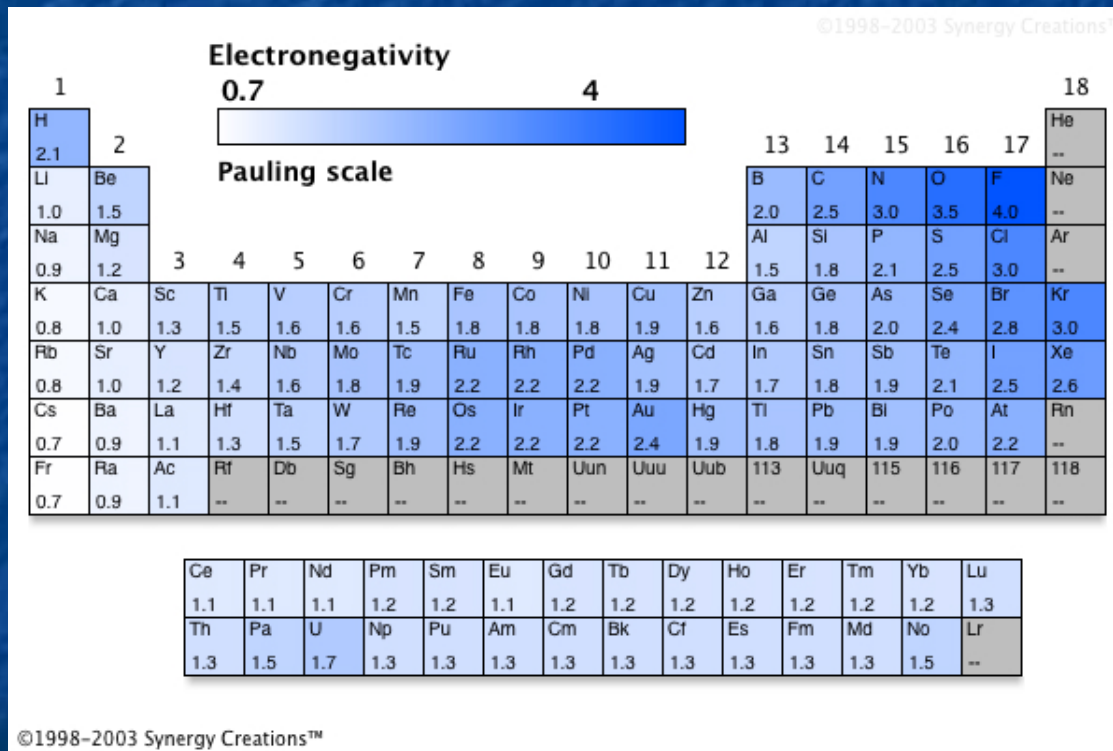
Bringing us right back to 3D SELF-ASSEMBLY challenge of last section

3) Nano Batteries: Chemistry class meets reality

The most important nano-engineered battery is the **lithium ion battery**

Batteries maximize power by using Group I alkali metals: Li, Na, K, Rb, Cs, Fr

Alkali metals hold onto their electrons VERY loosely (= **least electronegative**)



<http://www.chemistry-reference.com/pditable/>

Highest voltage batteries then **pair** alkali metals

with highly electronegative atoms or compounds

But that is a double edged sword:

At right of the periodic table, **oxygen** is one of the **most** electronegative elements

Alkali metal reacting with oxygen (or water) maximizes energy of electron transfer

RESULT: Alkali metals can burn spontaneously in contact with air

Some even explode violently if dropped in water

Thus Li in **lithium batteries** is generally provided as a compound, e.g.: **LiCoO₂**

Which is used as the battery's cathode:

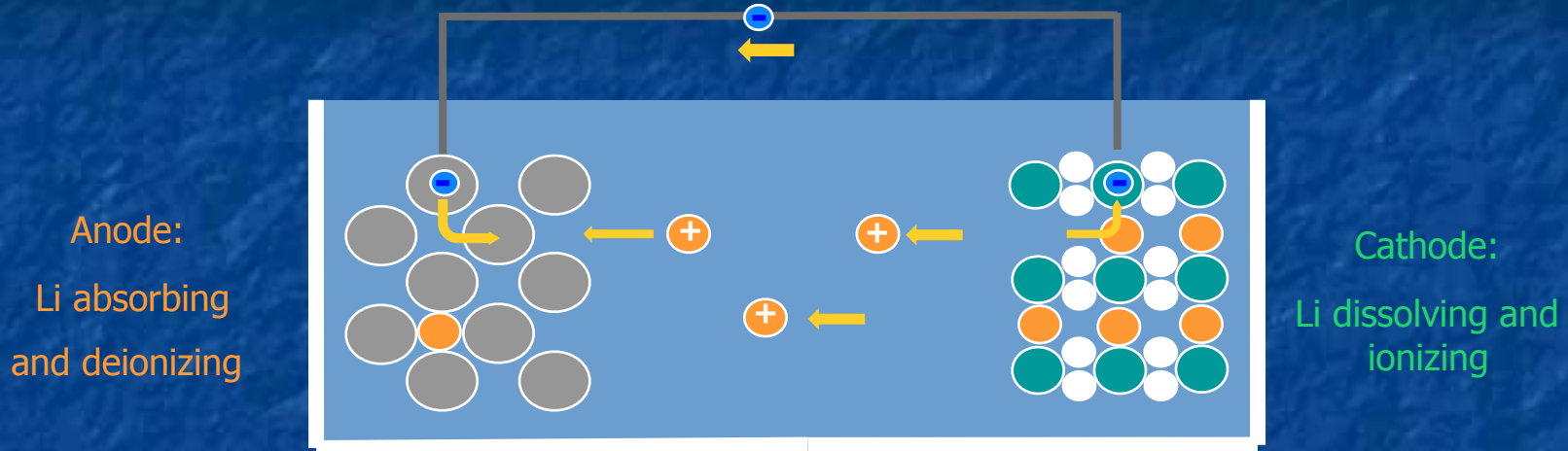


For the anode, carbon or silicon are the first choices (for reasons I'll soon explain):

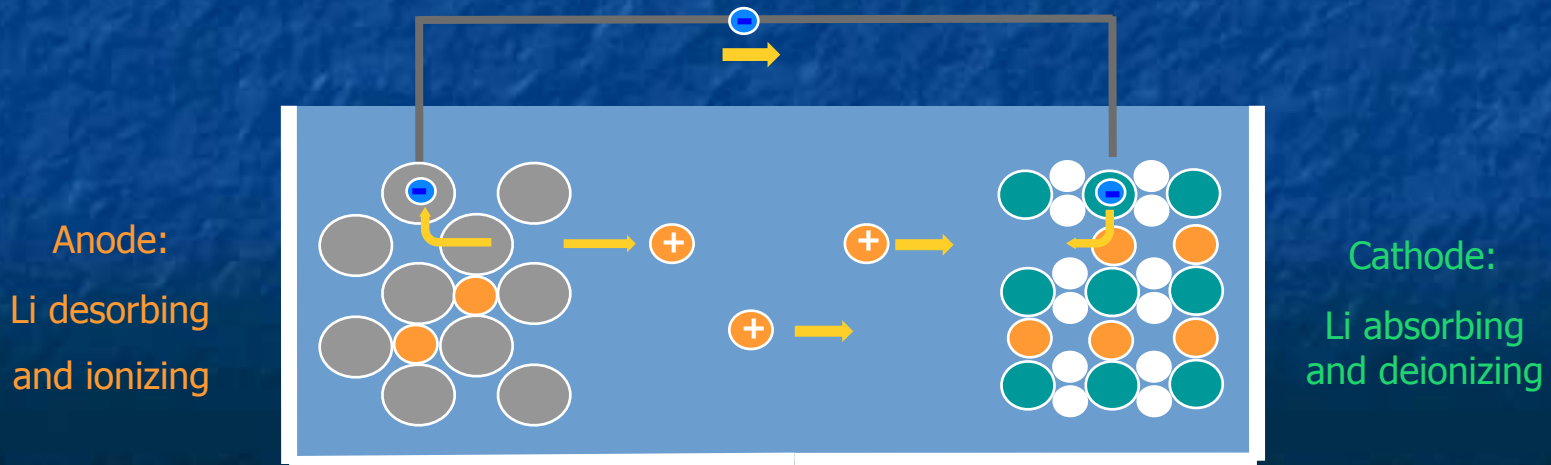


Yielding Li ion battery structure and behavior:

During CHARGING, Li is actually transferred from **inside** cathode to **inside** anode

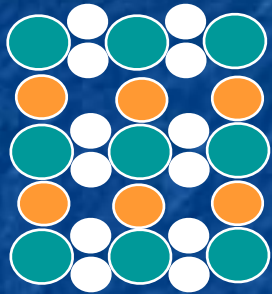


DISCHARGE reverses this: Li transferred from **inside** the anode to **inside** cathode:

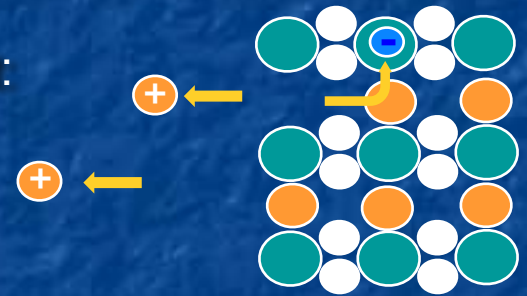


Look more closely at action during charging of the Li ion battery:

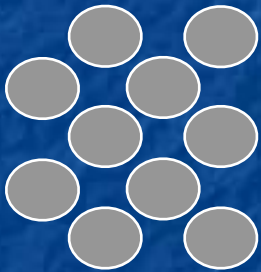
Cathode starts out as a naturally layered chemical compound LiCoO_2 :



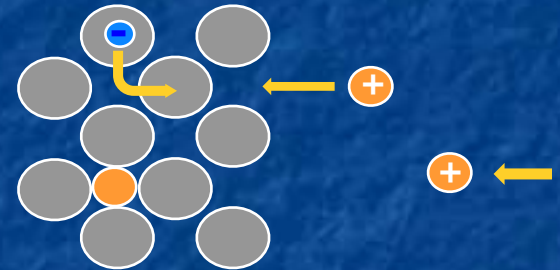
During charging Li **must** diffuse out:



Anode instead starts out as **pure solid carbon or silicon**:



But then, during charging,
how the heck does Li get **inside!**

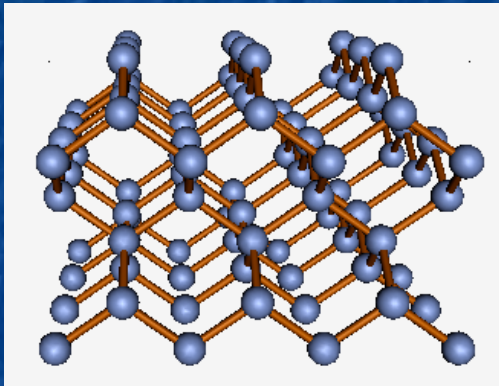


It's made possible by uniquely accommodating crystal structures of C / Si

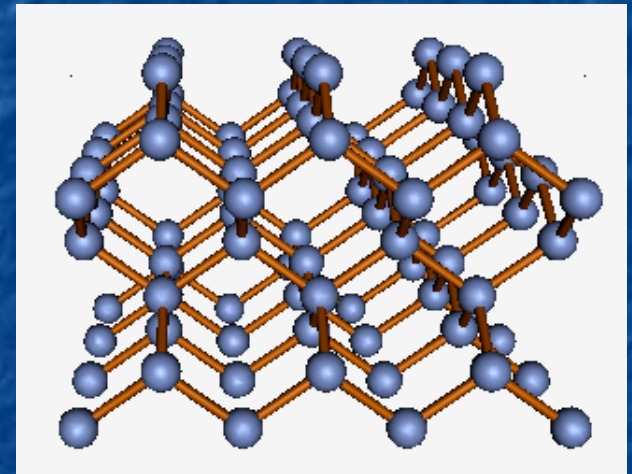
Carbon and silicon are column IV neighbors in the periodic table:

They thus share the tetrahedrally bonded "**diamond**" crystal structure:

Diamond Carbon (bond length = 0.154 nm)



Silicon (bond length = 0.235 nm)



"Diamond" type of crystal structure has a lot of open space

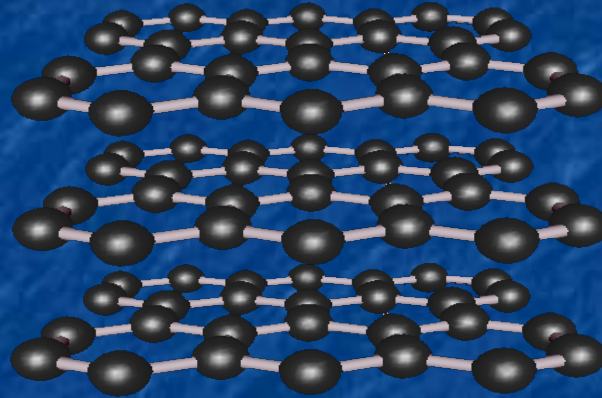
Li is small enough to squeeze into spaces between Si atoms

But Li is less likely to squeeze into spaces between closely spaced C atoms

And such true diamond electrodes would be hopelessly expensive anyway!

But we know that carbon has a second possible crystal structure:

Carbon in its alternate (also cheaper) "**graphite**" structure, with stacked planes:



Li CAN slide between these "graphitic" carbon planes

But in some ways, Si anodes are still more attractive

Because silicon crystal growth was **perfected** by the microelectronics industry

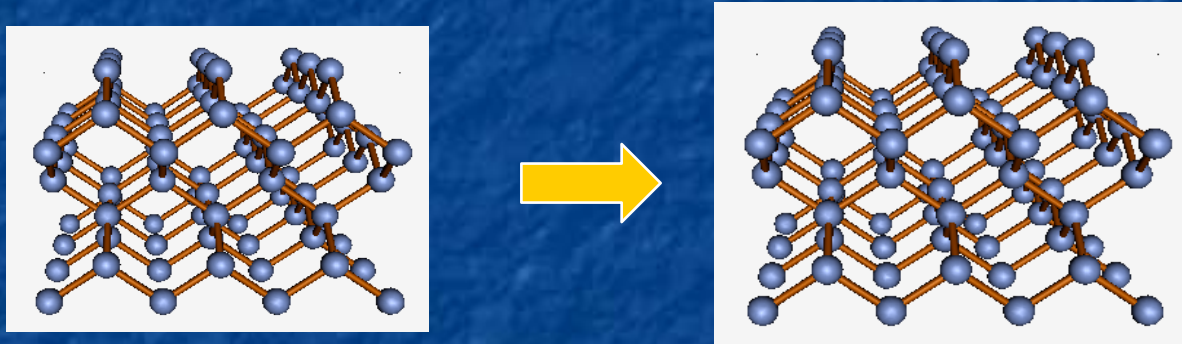
And crystals are now available in huge sizes (30 cm dia. x meters long)

With precut and fully polished wafers costing only ten's of dollars

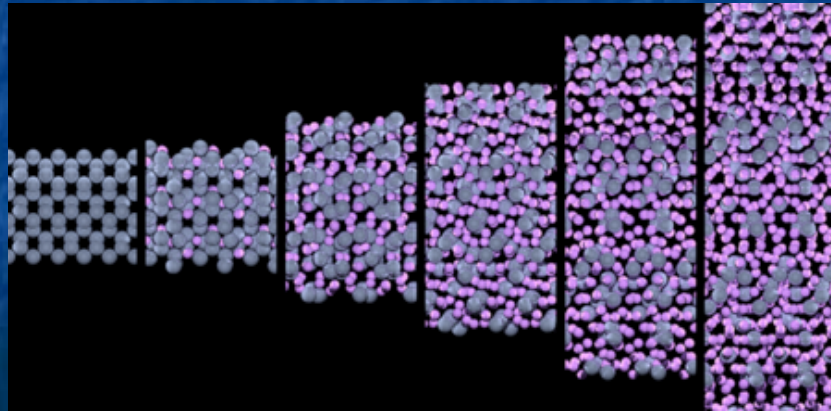
But there is still a problem (or challenge) for Si anodes:

To increase Li battery capacity we cram as much Li into the anode as possible

But when a LOT of Li slithers into the spaces, the **Si crystal actually expands**



With enough added Li, silicon expands by 2-3 times, actually changing its structure:



Top from my "UVA Virtual Lab" website: https://WeCanFigureThisOut.org/VL/Semiconductor_crystals.htm

Bottom: <http://www.greencarcongress.com/2014/02/20140204-nmr.html>

When Li ion battery discharges, silicon anode shrinks and reorders:

Or at least it may do that the first few (or few hundred) times

But during **charging** it's likely that Li is not added **uniformly** to the Si

And during **discharging** it's likely that Li is not removed **uniformly**

Resulting in non-uniform expansion and contraction of the silicon =>

Huge non-uniform stress across the crystal =>

Eventual development of cracks and fractures

With these cracks/fractures, as silicon shrinks upon battery discharge:

Si pieces separate =>

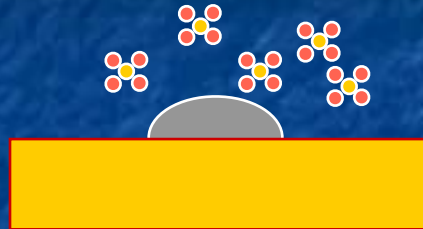
Electrical contact between pieces is lost =>



Shrinking effective anode size & capacity

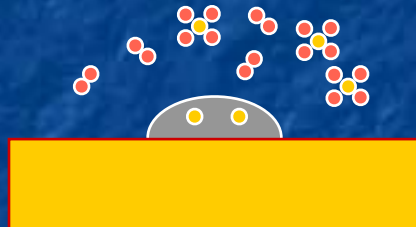
*A solution is provided by **nanoscale self-assembly**:*

On Si wafer, lay down nanopattern of metal, heat to melt, then expose to SiH_4 vapor:

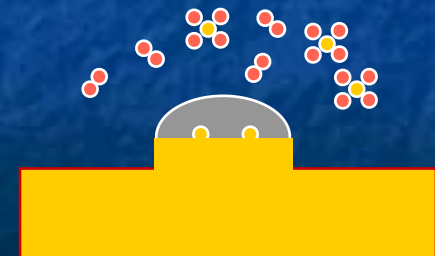


$\leftarrow \text{SiH}_4$ approaching one of a vast array
of now molten metal dots

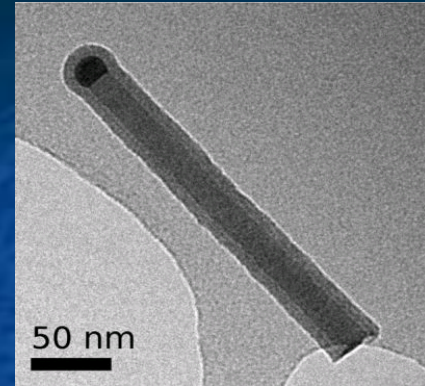
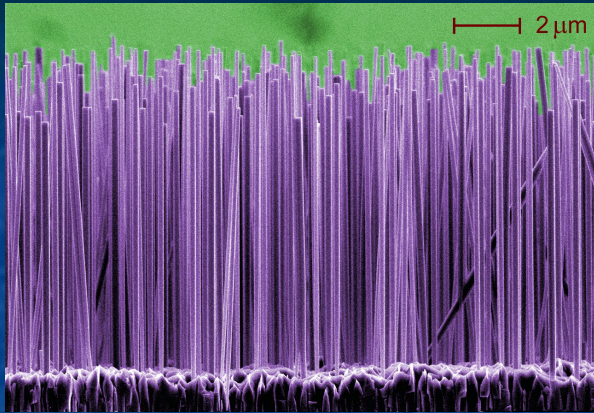
SiH_4 decomposes, releasing Si to dissolve into the molten metal dot



Si diffuses down to wafer where it solidifies creating a growing column of new Si:



With results such as these:

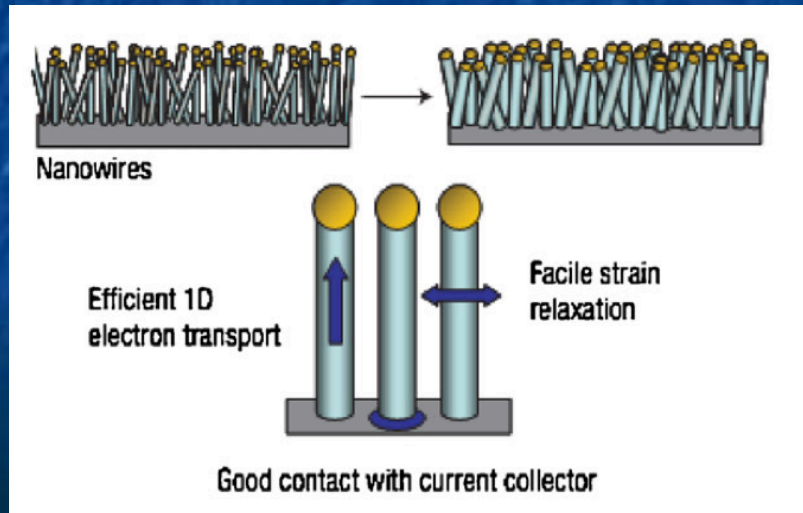


Lorelle Mansfield -NIST:

http://www.nist.gov/public_affairs/techbeat/tb2006_0525.htm

U. Helsinki: www.micronova.fi/units/ntq/research/nanowires.php

Small size + accessibility => Uniform Li absorption, even stress, minimal Si cracking:



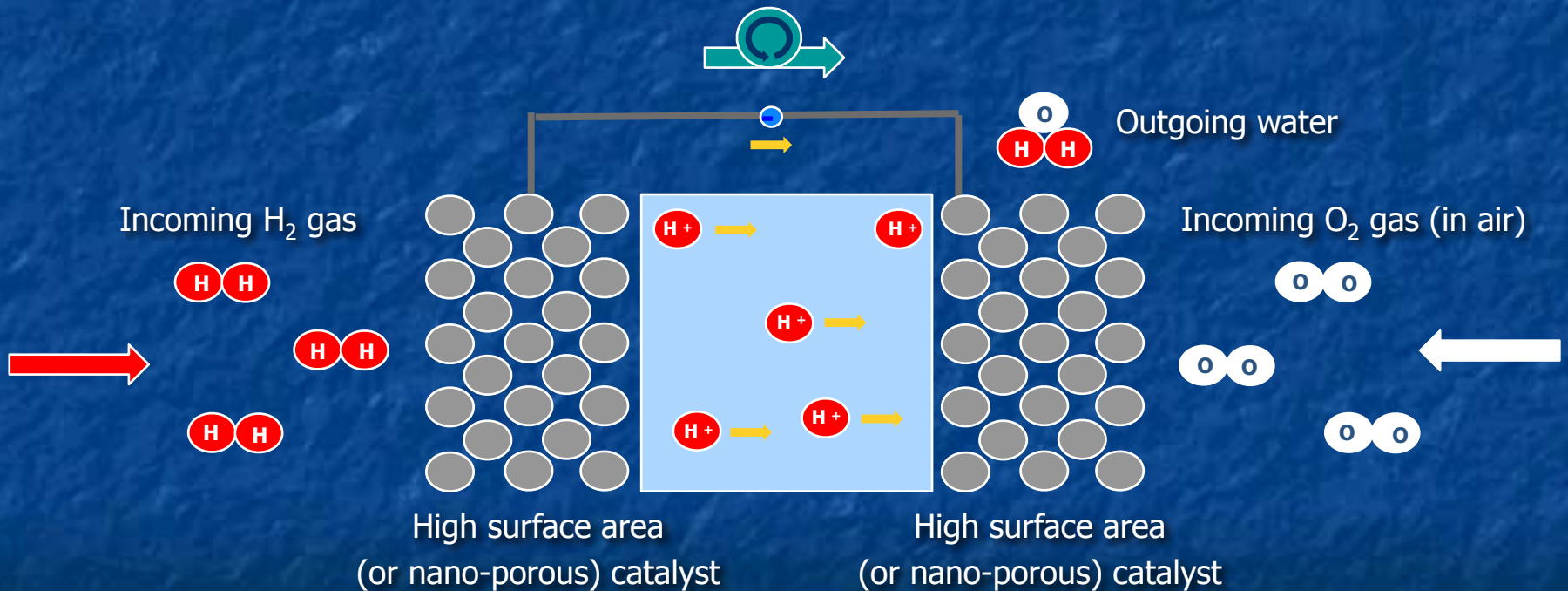
New nano-structured
Li ion battery anodes

Nanostructures are also being investigated for **Fuel Cells**:

For example, ones such as this to power automobiles

Fueled by hydrogen gas + oxygen gas

Producing only water vapor as exhaust:



Electrolyte capable of passing H⁺ ions:
Aqueous OR Solid Solution OR Proton permeable membrane

Batteries and Fuel Cells are "kissing cousins"

Battery: Pair of "redox" materials comes from the electrodes themselves

Fuel Cell: Redox materials come from external fuels

And electrodes themselves are not consumed . . . however:

They often act as catalysts => Need for exotic / \$\$\$ materials

E.G. Platinum = **36,667 \$/kg (27 March 2015)**

Good News:

Quantity of catalyst can be vastly reduced w/ high surface area nanostructures

Bad News:

Fuel cell energy return ~ 40% vs. batteries energy return ~ 80%

For more on fuel cells / nanostructured fuel cells see my Energy note set:

[Batteries and Fuel Cells](#)

But BOTH batteries and fuel cells have BIG weight + size problems

With critical ramification that for transportation (especially air transportation!):

Fossil fuels are going to be REALLY HARD to replace:

Comparison of various energy storage technologies (energy / mass vs. gasoline):

Conventional Battery	=	0.001 x Gasoline's energy density
PC Battery	=	0.01 x Gasoline's energy density
TNT (0.65 Cal/gm)	=	1/15 x Gasoline's energy density
Butyl alcohol	=	0.9 x Gasoline's energy density
Kerosene / JP-A / Jet Fuel	=	0.93 x Gasoline's energy density
Gasoline (9.75 Cal /gm)	=	1 x Gasoline's energy density
Natural Gas (liquid)	=	1.3 x Gasoline's energy density
Hydrogen (liquid)	=	2.6 x Gasoline's energy density

(data mostly from Richard A. Muller's book "Physics for Future Presidents")

Conclusions

Discussed: Nanostructured Photovoltaics
 Nano Capacitors
 Nano batteries (and very similar nano electrochemical cells)

These represent only a small sample of the “bleeding edge” of nano energy

But, as in Bleeding Edge: Part I, range of potential applications is already stunning

Nevertheless, this lecture also highlighted a recurring nanotech issue:

Making the nano things was once again often the "easy" part

But getting them **organized** often ends up limiting technological application

Credits / Acknowledgements

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

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