Theoretical and Practical limits on solar energy conversion : Why use nanostructured materials?

Phil Duxbury
Physics, Michigan State University

A group of us are starting an MSU effort on polymer/nanoparticle cells : Michael Mackay, Jon Kiel, Erika Tseng, Shannon Nicely, Dan Olds, Erin McGarrity, Alison Walker (UK), Jos Thijssen (TUDelft).

Solar conversion strategies : Photovoltaic, Solar thermal, Photo-electrochemical

- Photovoltaic ~ 25-50c/kWh

Tuscon electric power - Springerville - 6.4MW

Record efficiency - **42.8%** (**1.7GW world total**)

- Solar thermal (mirrors focus the sun)

Current plants ~ 13-17c/kWh (Mojave -SEGS 354MW)

Sandia Labs. Dish 25kW system is **40.7%**.

But only 0.5GW world installed capacity

Many plants are being built – e.g. dish with Stirling Engine

In the US southeast, deserts could provide over 7TW (World Tot. 4TW)

- Photo-electrochemical (light to fuel).

Natural photosynthesis 3–4% (biofuels, biogas are ~0.3%)

10% efficiencies for photoassisted electrolysis of water into hydrogen and oxygen

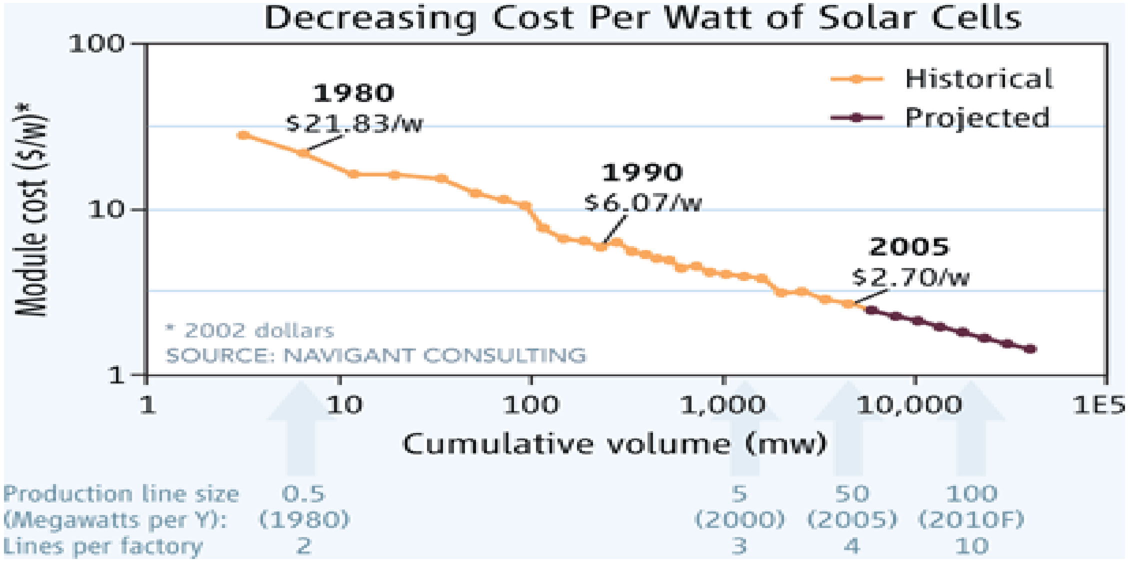
5–7% efficiencies for the production of Br_2 and H_2 from HBr

1–3% efficiencies for the unassisted production of H_2 and O_2 from water.

Other design objectives

- Distributed generation – e.g. Rooftops
- Portable power, flexible coatings – Windows, clothing, tents. E.g. Canvas cover for your car that protects it and generates power.
- Note : At 10% efficiency there is plenty of close to zero cost surface area to power the USA.

Practical goals of solar research : (1) Reduce cost ; (2) Flexible devices



- Cost is dollars per Peak Watt.

- The cost of installation is currently about 55% of total cost.

- Retail prices for all types of commodity photovoltaic cells are currently about the same in units of cost per watt. Thin film solar devices e.g. CdTe, CIGS are expected to further reduce in cost. Incentives e.g. Germany, California (20% by 2017)

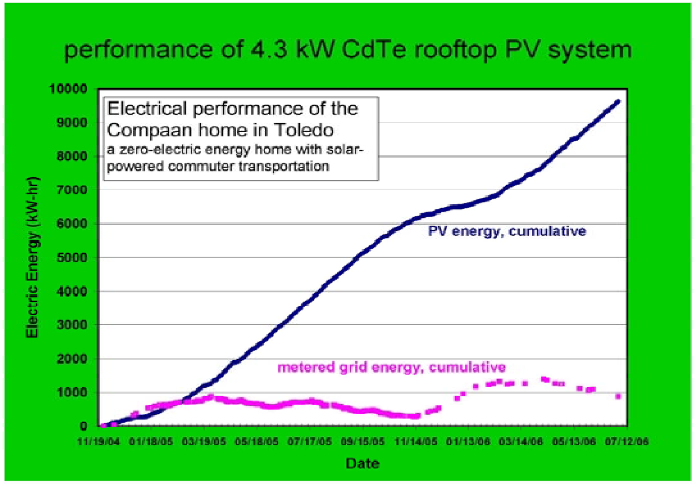
Another key factor :
Net energy gain (NEG).

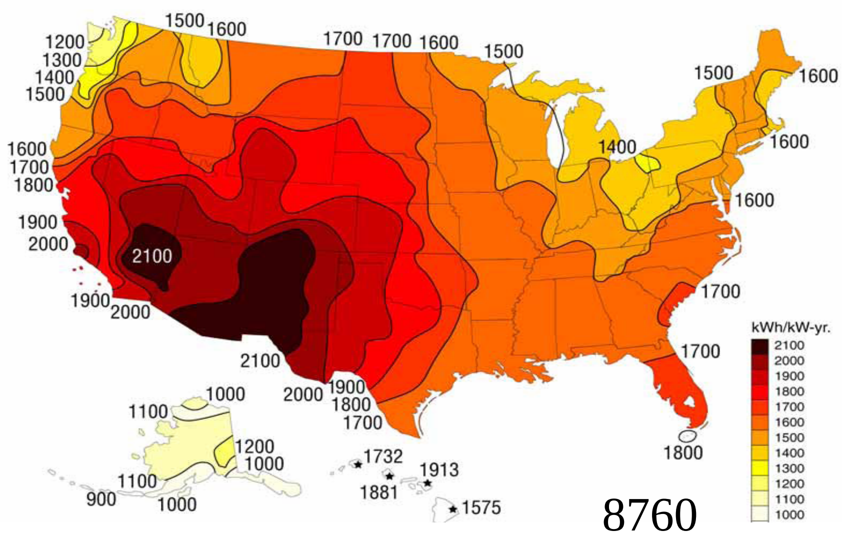
- One complaint about Si solar cells used to be that their manufacture requires more energy than can be recovered during their useful device lifetime. i.e. NEG < 0

$$NEG = Energy\ Consumable - Energy\ Expended$$

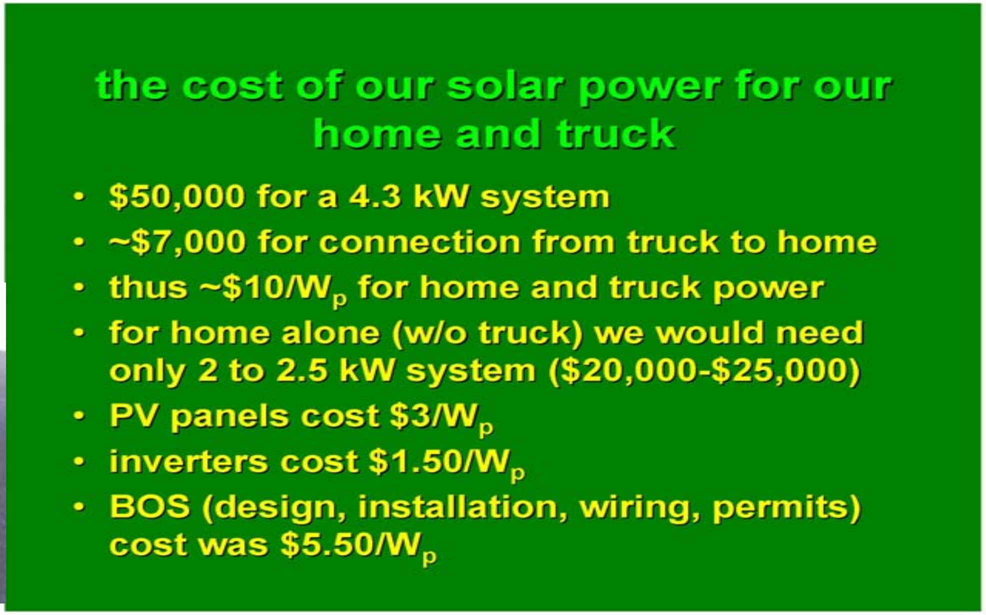
This is no longer true with payback times now five years or less. For thin film materials payback time is shorter and in most cases less than 3 years.

Rooftops – e.g. Toledo, Ohio - Truck + 2800 sq. ft. home





8760



the cost of our solar power for our home and truck

- $50,000 for a 4.3 kW system
- ~$7,000 for connection from truck to home
- thus ~$10/$W_p$ for home and truck power
- for home alone (w/o truck) we would need only 2 to 2.5 kW system ($20,000-$25,000)
- PV panels cost $3/$W_p$
- inverters cost $1.50/$W_p$
- BOS (design, installation, wiring, permits) cost was $5.50/$W_p$

Al. Compaan

The current price of rooftop photovoltaics – using Compaan data

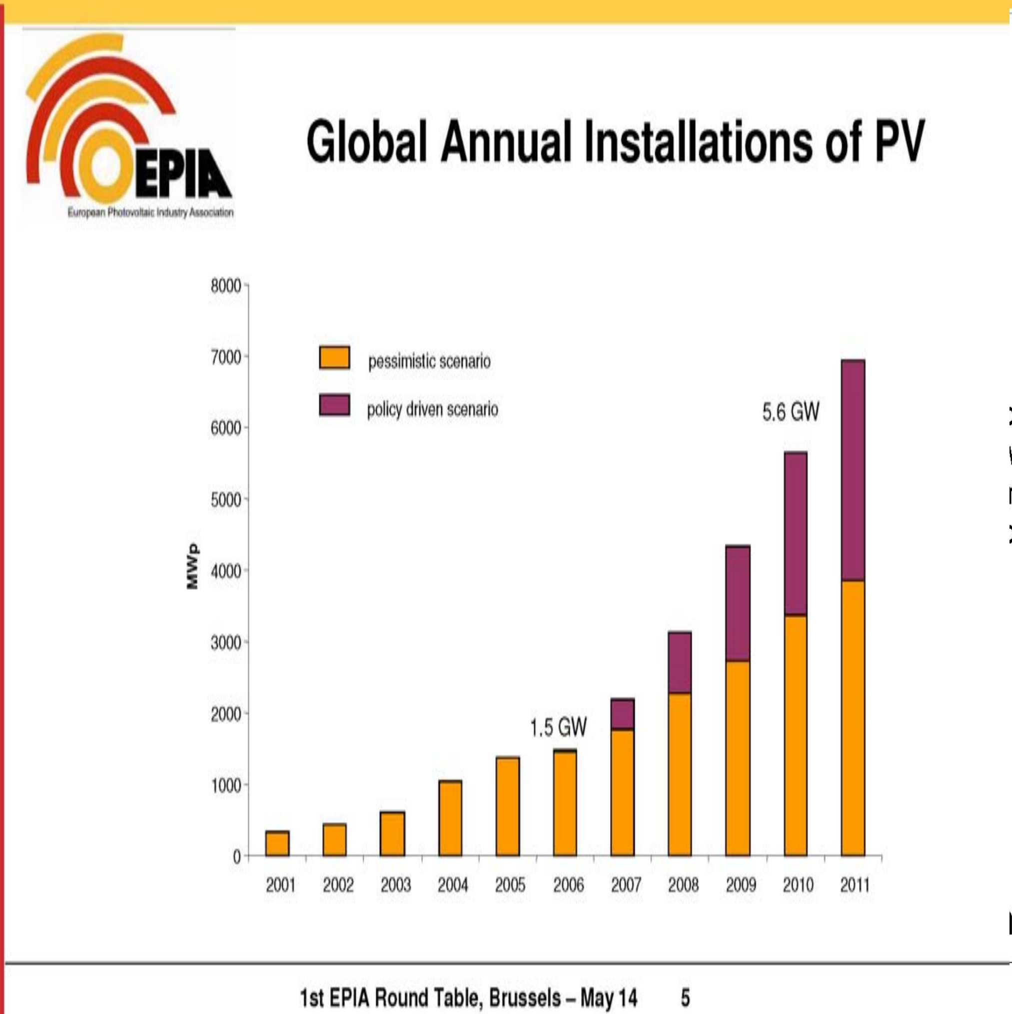
Total installed cost ~ $10/W (Larger installations may be cheaper)

- Installed cost $50,000 for 4.3 kWh peak system
- Power recovered over 2 year period 10,000kWh
- Cost of grid power in MI : 10c/kWh
- Value of electricity generated by Compaan ~ $500/yr
- Therefore 100 years to break even. Lifetime of cells ~ 25yr

Based on these numbers, for Michigan the price of solar is currently 4-5 times higher than grid electricity

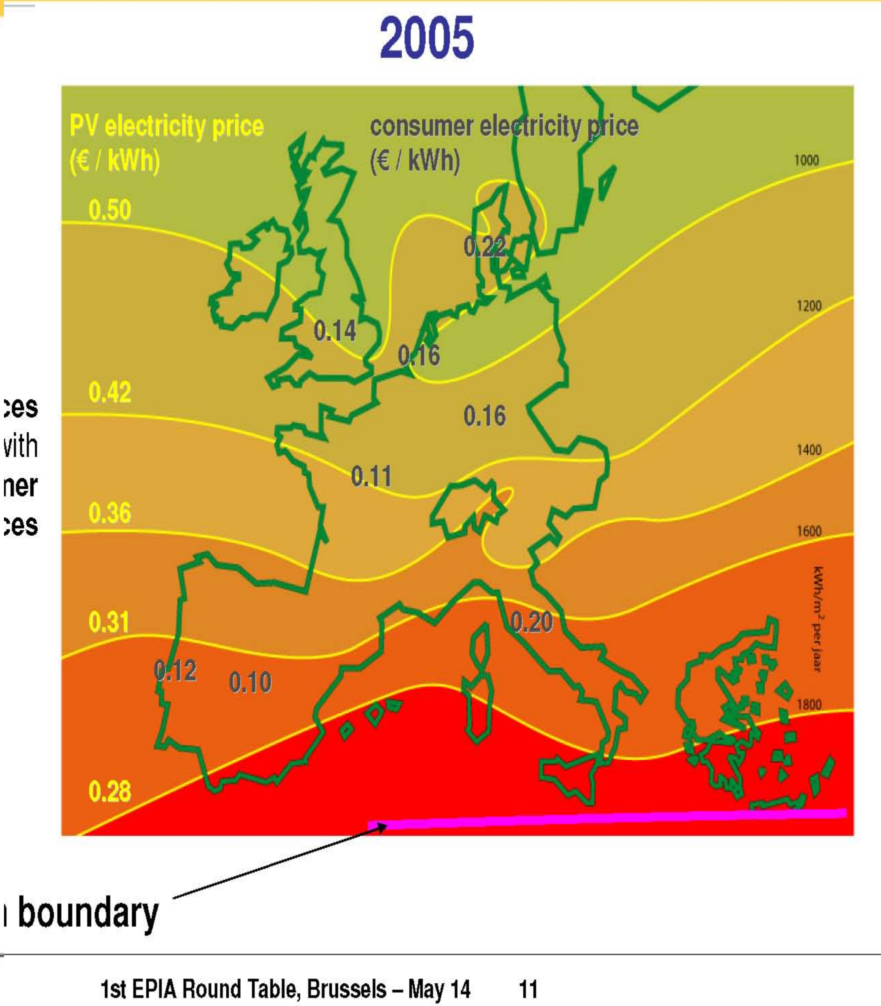
Mitigating factors – Price of electricity is likely to keep going up and may be twice as high in 10 years. Price of solar is likely to reduce by a factor of two due to large scale fabrication plants that are being built. Also in some states peak electricity is higher priced making solar use, for e.g. air-conditioning, more viable.

PV sales in Europe are growing rapidly – German subsidies (1/2 the world solar market!)



Global Annual Installations of PV

1st EPIA Round Table, Brussels – May 14 5



2005

ces
vith
ner
ces

boundary

1st EPIA Round Table, Brussels – May 14 11

Table 5.6.A. Average Retail Price of Electricity to Ultimate Customers by End-Use Sector, by State, November 2007 and 2006

(Cents per Kilowatthour)

Census Division and State	Residential		Industrial[1]		Transportation[1]		All Sectors	
	Nov-07	Nov-06	Nov-07	Nov-06	Nov-07	Nov-06	Nov-07	Nov-06
New England	**16.18**	**15.58**	**12.75**	**11.44**	**8.28**	**11.71**	**14.62**	**13.97**
Middle Atlantic	**13.94**	**12.89**	**7.86**	**7.87**	**10.25**	**10.14**	**12.11**	**11.58**
New Jersey	13.79	12.17	11.6	10.42	12.73	9.9	12.84	11.25
New York	17.03	16.33	8.96	9.05	11.23	10.98	14.9	14.65
East North Central	**9.99**	**8.86**	**5.55**	**5.31**	**7.11**	**6.11**	**8.07**	**7.26**
Illinois	10.96	7.78	5.09	4.59	6.65	5.38	9.18	6.63
Michigan	10.04	9.63	6.17	6.05	13.11	12.31	8.36	7.99
Ohio	9.55	9.05	5.73	5.6	10.88	11.35	7.77	7.6
West North Central	**7.98**	**7.69**	**4.75**	**4.68**	**6.62**	**6.06**	**6.34**	**6.2**
Iowa	9.14	9.13	4.45	4.5	NM	7.05	6.26	6.44
Kansas	7.74	7.53	5.02	4.77	–	–	6.44	6.15
Tennessee	8.31	7.85	5.43	5.1	–	–	7.27	6.93
Pacific Contiguous	**11.6**	**11.53**	**7.89**	**7.96**	**7.77**	**7.26**	**10.36**	**10.42**
California	14.26	14.47	9.75	9.66	7.8	7.27	12.23	12.38
Oregon	8.52	7.63	5.4	5.3	6.77	6.58	7.31	6.78
Pacific Noncontiguous	**21.76**	**19.46**	**18.46**	**15.81**	**--**	**--**	**19.62**	**17.31**
Alaska	15	15.02	12.66	11.84	–	–	13.12	12.92
Hawaii	26.6	22.66	20.61	17.1	–	–	23.67	20.01
U.S. Total	**10.69**	**10.18**	**6.22**	**6.04**	**9.46**	**9.4**	**8.98**	**8.63**

Photovoltaic technologies

Established technologies

- Single crystal silicon, polysilicon
- Thin films : Amorphous silicon (Unisolar), CdTe (First Solar)
- Semiconductor multilayers (high end - SpectraLab)

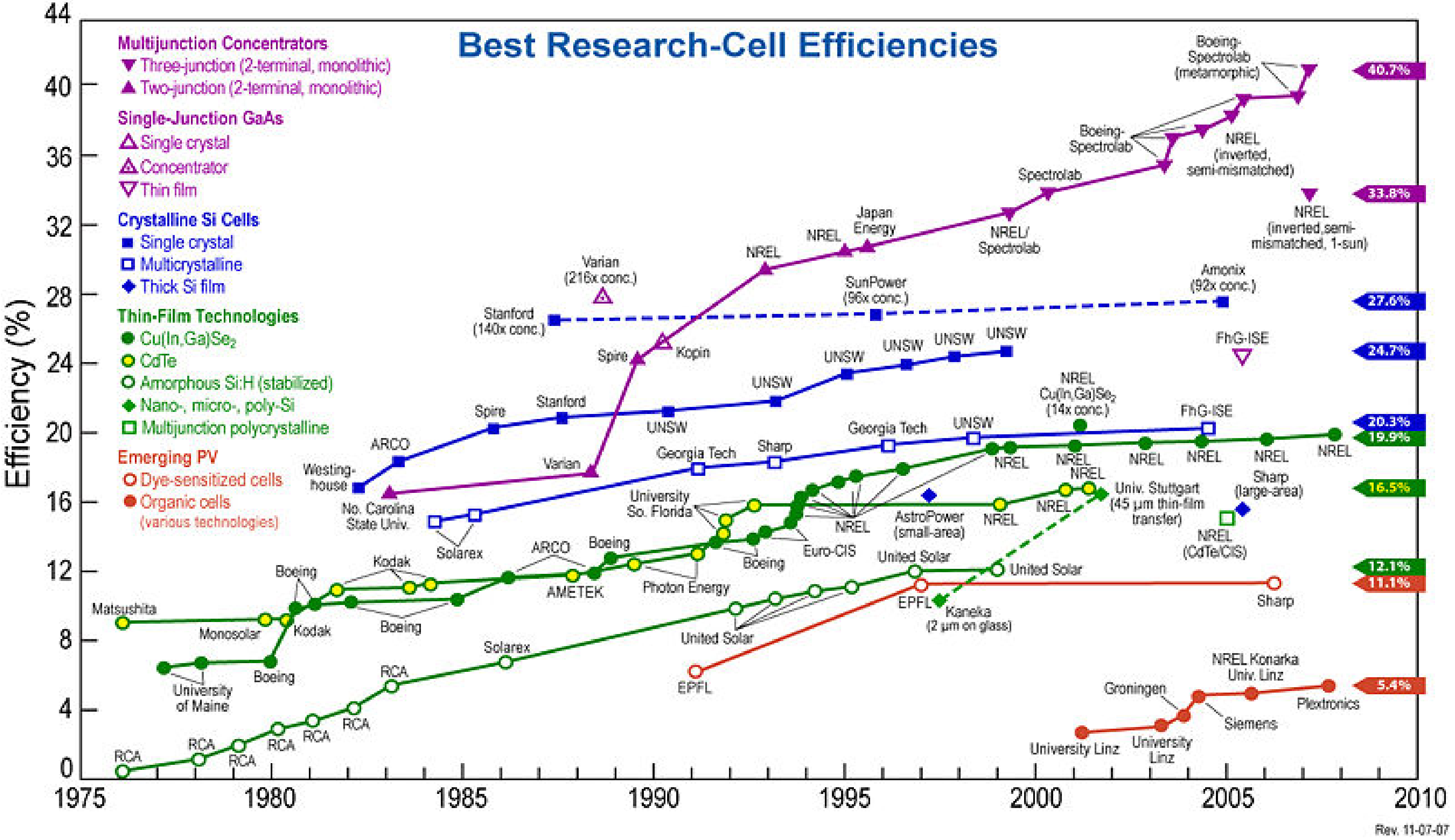
Emerging technologies

- CuInGaSe (CIGS) thin films (NanoSolar, Miosole…)
- Cheaper Si, poly Si

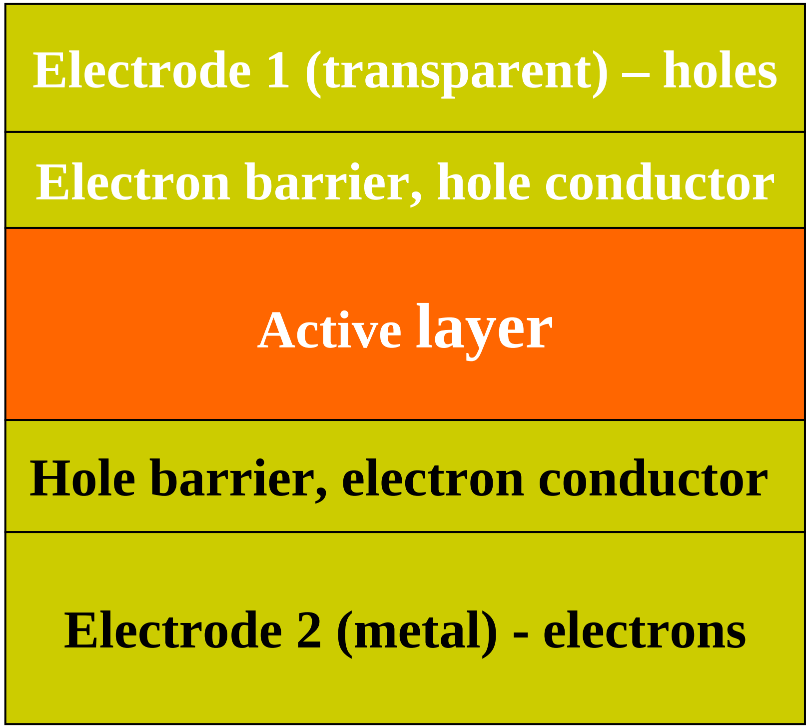
Still confined to research labs.

- Dye Cells (First delivery 2008?)
- Organics / nanoparticles

The mandatory solar efficiency slide



The “universal” photovoltaic and LED device geometry



Electrode 1 (transparent) – holes

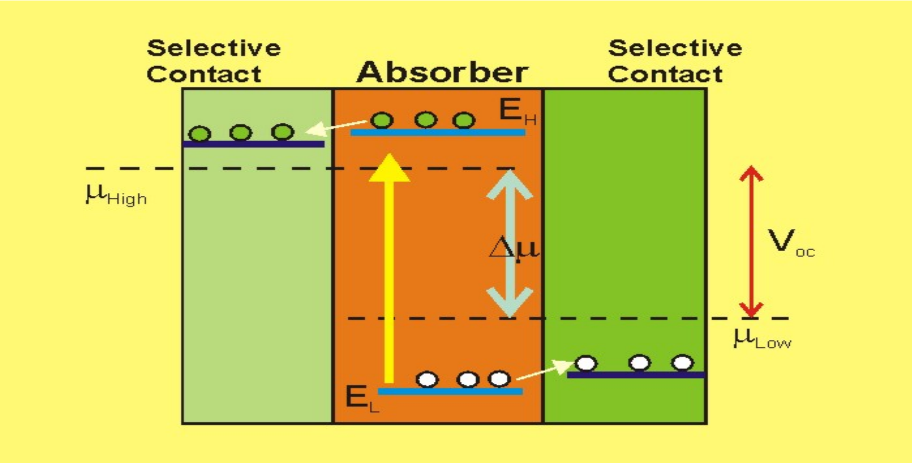
Electron barrier, hole conductor

Active layer

Hole barrier, electron conductor

Electrode 2 (metal) - electrons

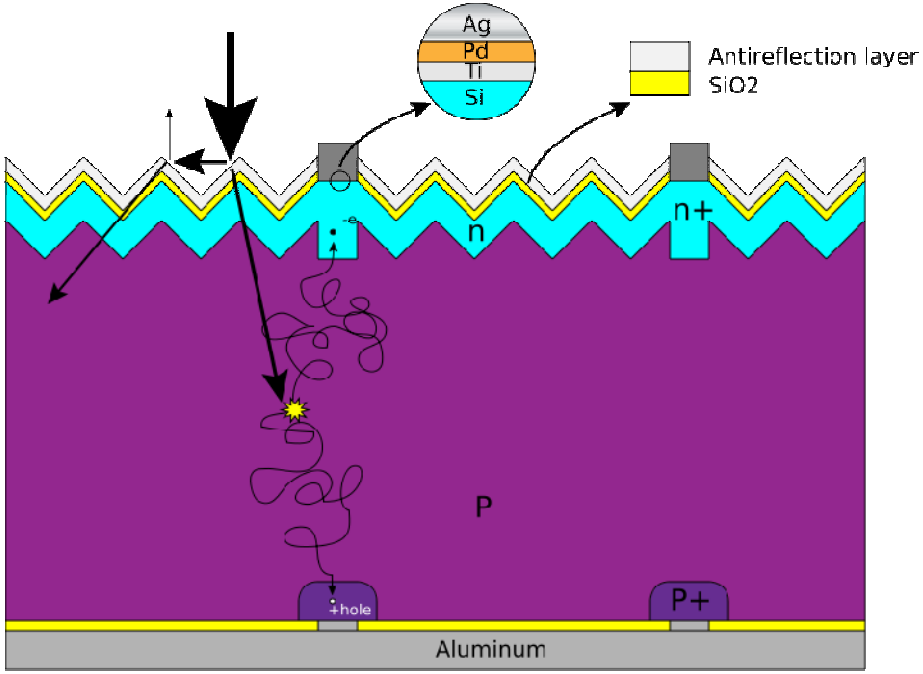
Photovoltaics – Light is absorbed in the active layer, generating either free carriers (silicon and thin film devices) or excitons (dye sensitized, organics, nanoparticles) which must then disassociate to generate carriers. Carriers drift or diffuse to electrodes.



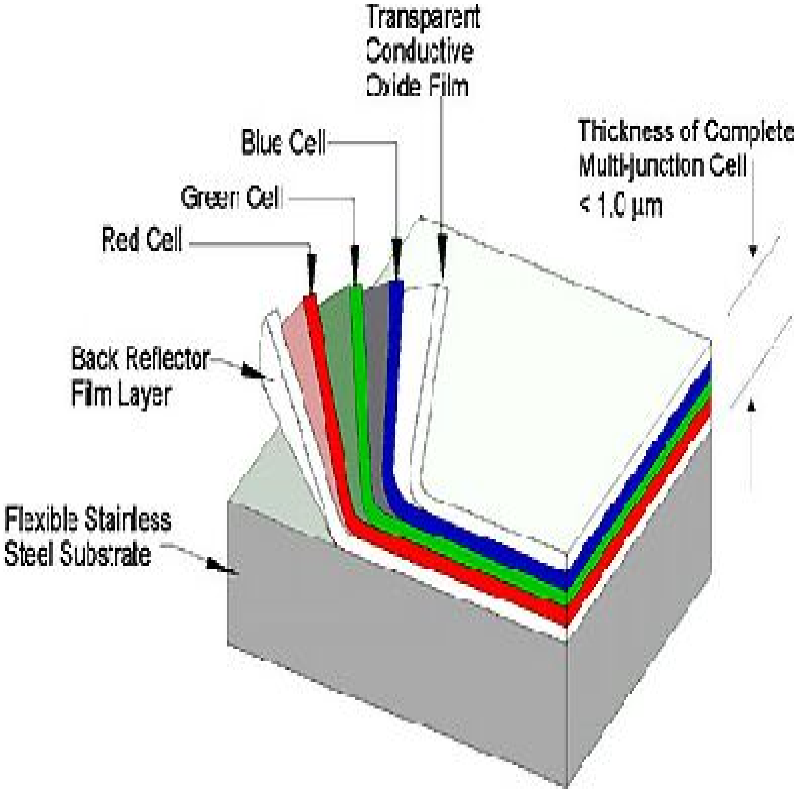
The device physics of LED’s and photovoltaics are similar

What has this got to do with diodes?

Silicon p-n photovoltaic

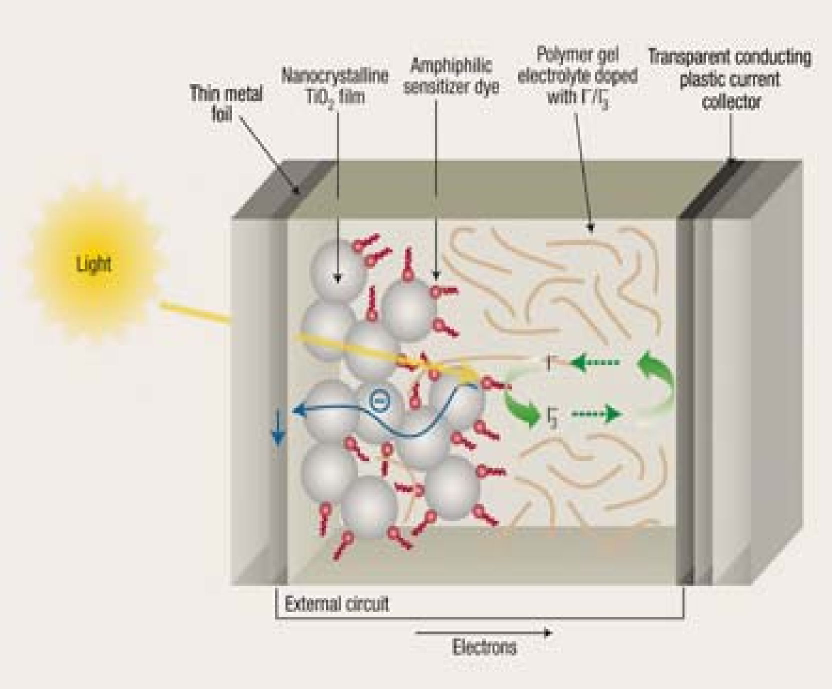


Amorphous Si



Both n and p type layers are active. The n-layer is less than one micron, while the p-layer is a hundred micron or more

Cell geometries/materials



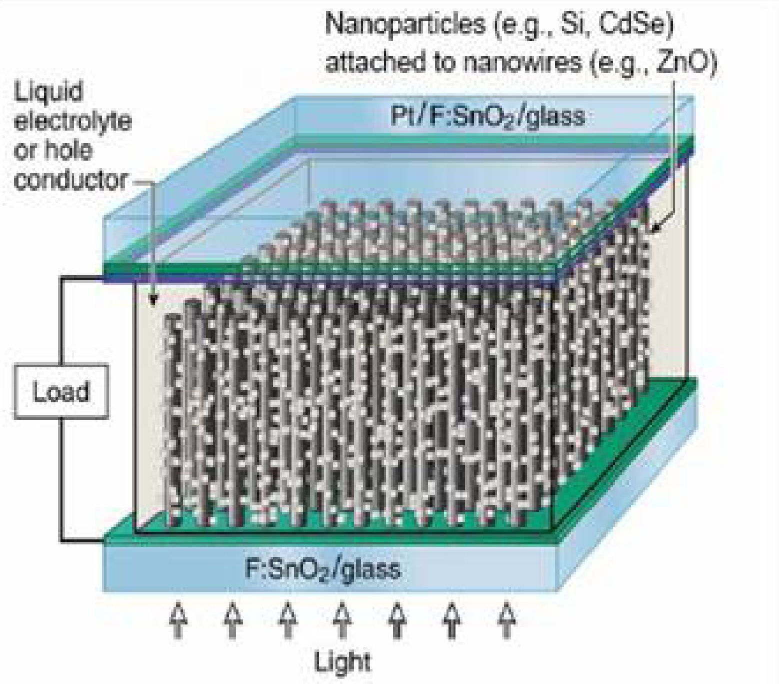


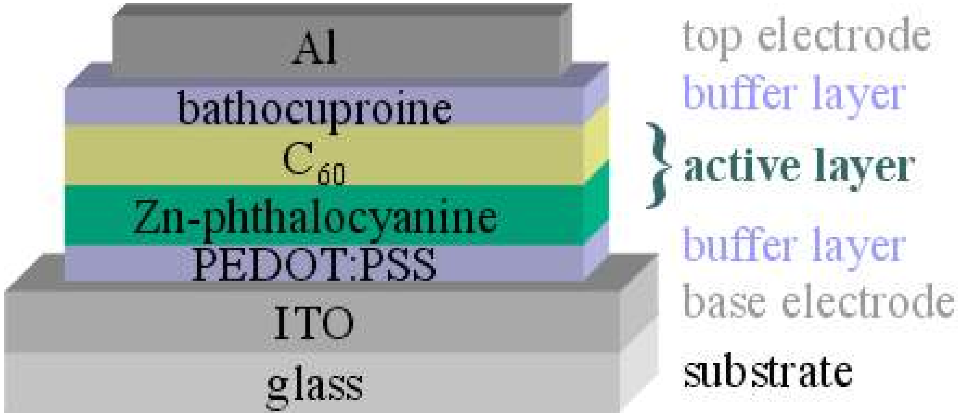
FIGURE 1. Schematic of a solar cell based on an ensemble of nanometer scale heterojunctions between semiconductor nanoparticles (e.g., CdS, CdSe, or Si) and wide band gap semiconductor nanowires (e.g., ZnO).

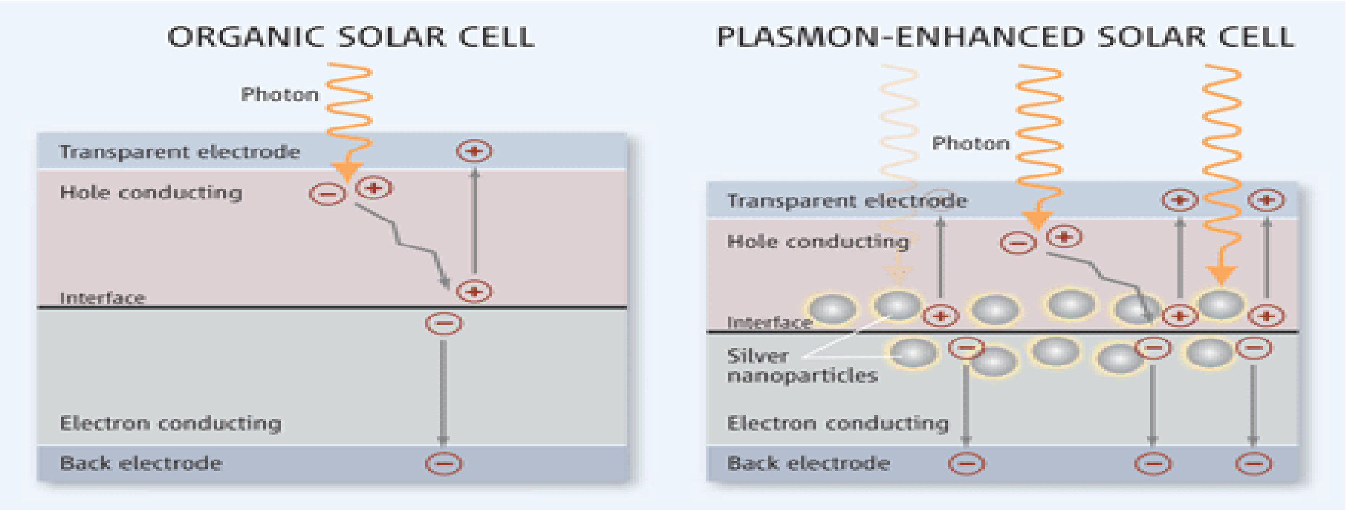
Dye sensitized cell

Light absorption occurs at interfaces. Nanoparticles maximize interface area

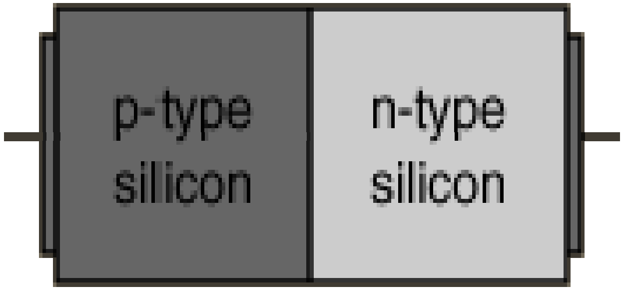
Cell geometries/Materials

Nanoparticles
-Transport electrons
-Enhance absorption
-Multiexciton processes

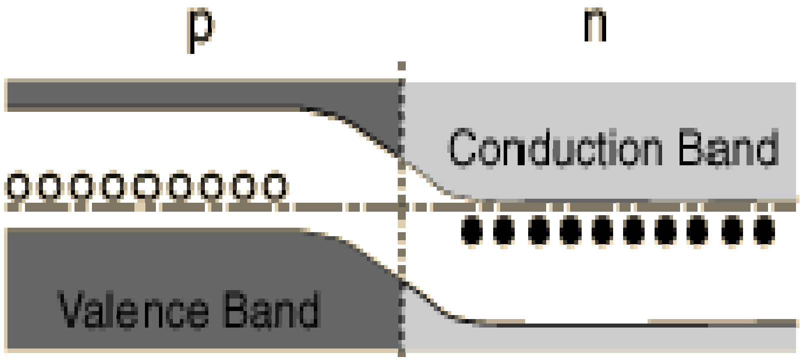




Solar cell based on p-n junction (e.g. Silicon solar cell…)



p-n junction

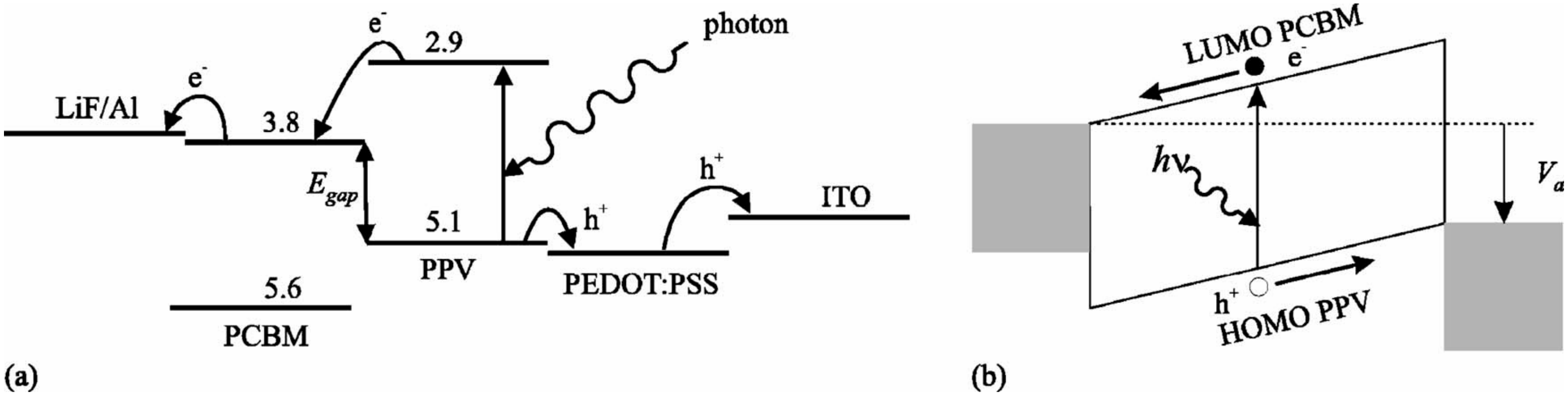


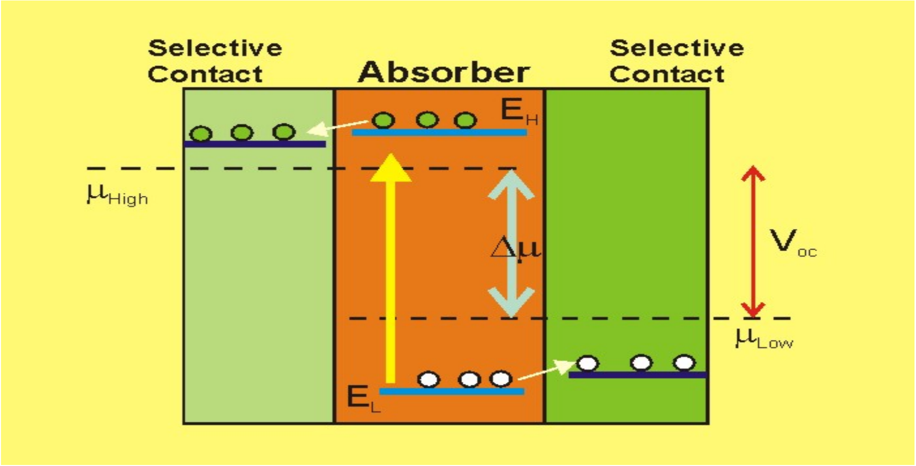
Energy bands at equilibrium

Under illumination, e-h hole pairs are generated. **Electrons** move to the **right**. Holes move to the left. Useful current is generated at applied potentials $V_a < E_g$. Note that electrons and holes are separated by interface potential.

Dark Current : Electrons move **left**

Energy level diagram for conducting polymer/PCBM (fullerene) cell.





1-D device model
Koster et al. 2005
PRB 72, 85205

Making efficient cells : T_s ~ 6000K ~ 0.5eV - Simple upper bounds

P = VI, ie maximize the product of voltage and current

Ideal efficiency of a solar cell, without dark current and with a single gap.

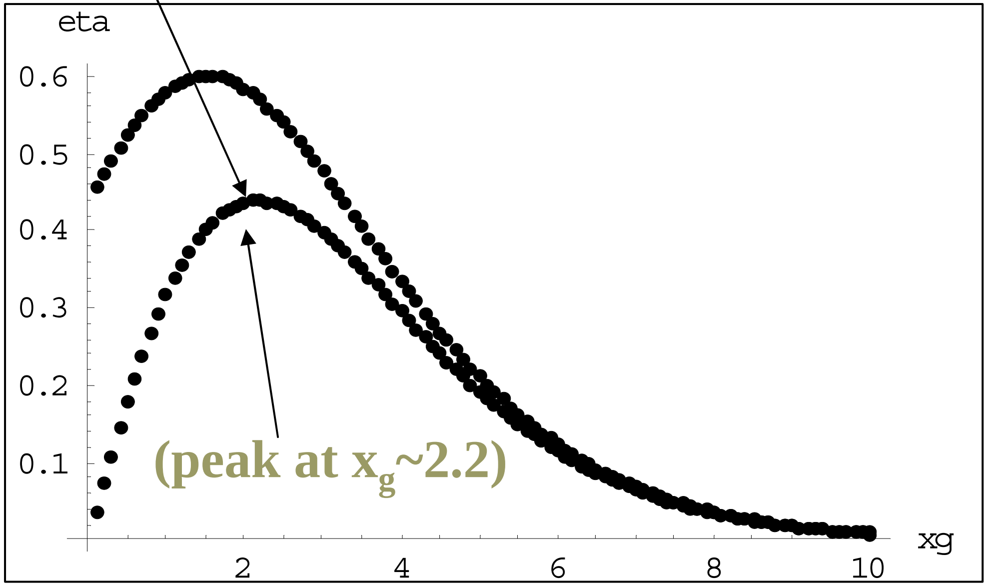
Define : $x_g = E_g/kT_s$

Efficiency: $\eta = P_{out}/P_{in}$

Let $N(\nu)$ = # photons at frequency ν

$$P_{in} = \int_0^\infty h\nu\, N(\nu)\, d\nu$$

$$P_{out} < V_{oc} I_{sc} \sim E_g \int_{Eg}^\infty N(\nu)\, d\nu$$



(peak at x_g~2.2)

Peak efficiency 44% at 2.2kT_s = 1.1 eV (Single gap)
60% at (0.7eV, 1.6eV) (Tandem)

Realistic maximum efficiencies of mono-junction devices (Shockley-Queisser limit)

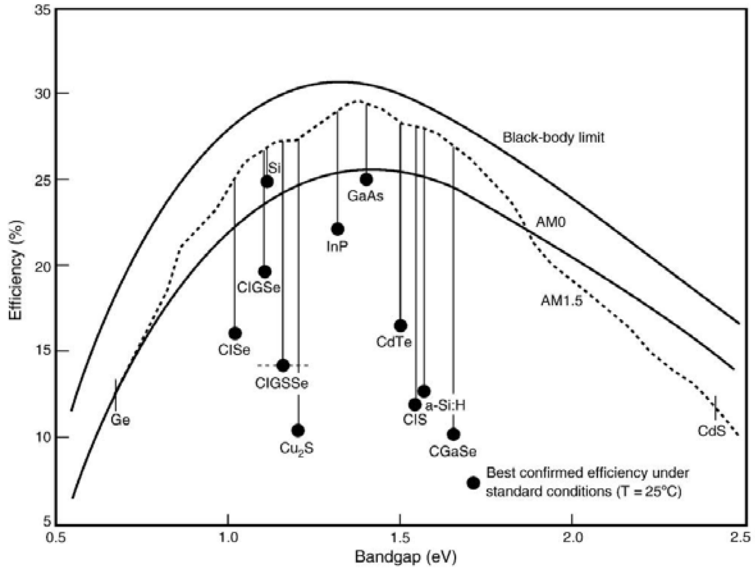
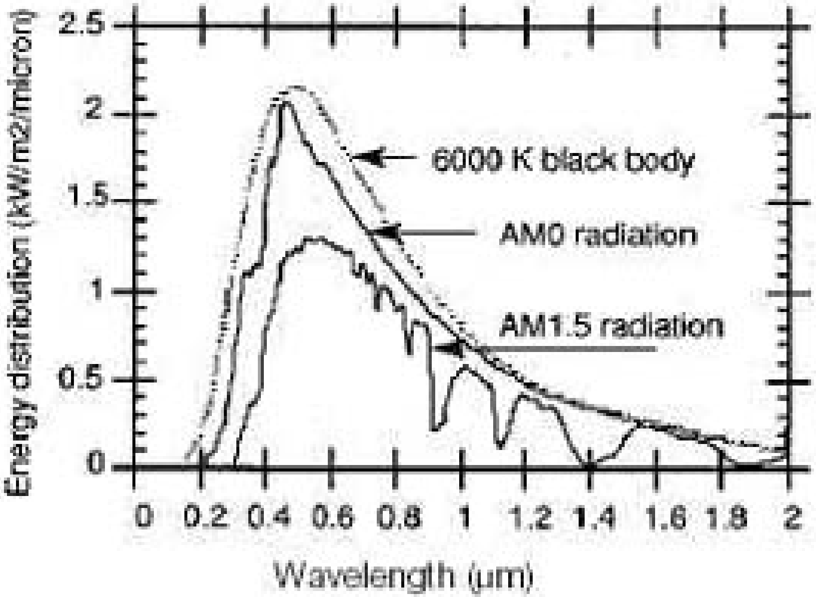


Fig. 3. Performance gaps between best device efficiencies in the laboratory and attainable efficiencies for several solar cell technologies.

Single Junction, Lawrence L. Kazmerski
Journal of Electron Spectroscopy
and Related Phenomena 150 (2006) 105–135



Multi-junction devices

Antonio Marti *, Gerardo L. Arafijo
Solar Energy Materials and Solar Cells
43 (1996) 203-222

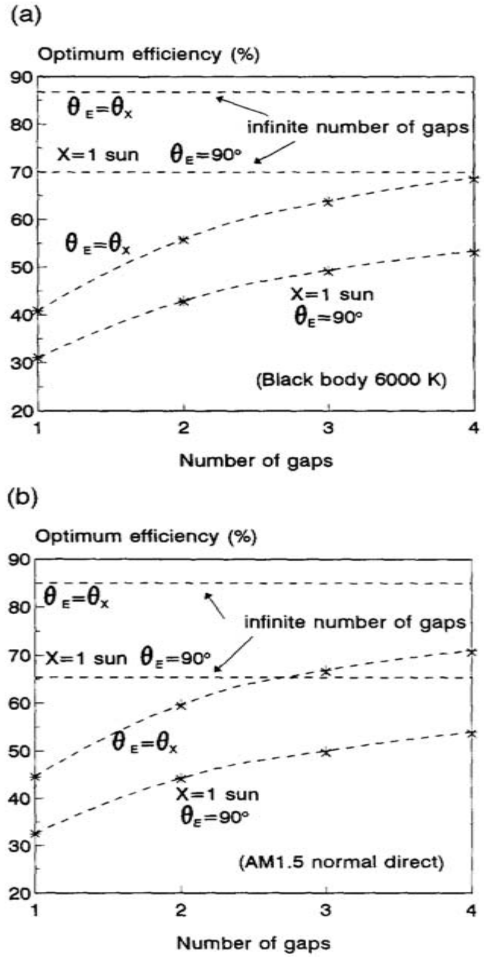
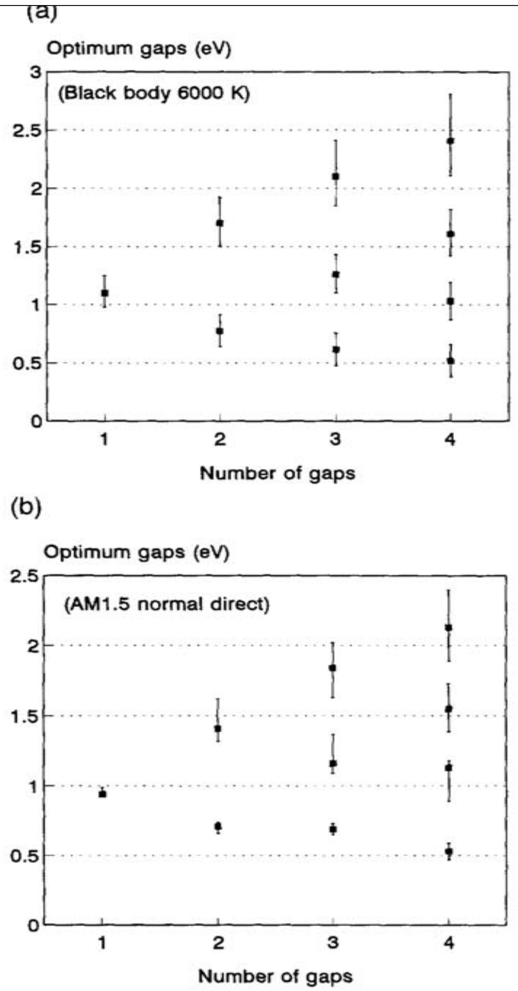


Fig. 6. Maximum efficiency as a function of the number of cells: (a) for the sun assumed as a black body at 6000K, (b) for AM1.5 direct normal irradiance [23]. In both cases, dots marked as "+" corresponds to the case with reflectors (illustrated in Fig. 5a) and dots marked as "X" to the case without reflectors (Fig. 5b). Both values are very close but the one corresponding to the case with reflectors is slightly higher.



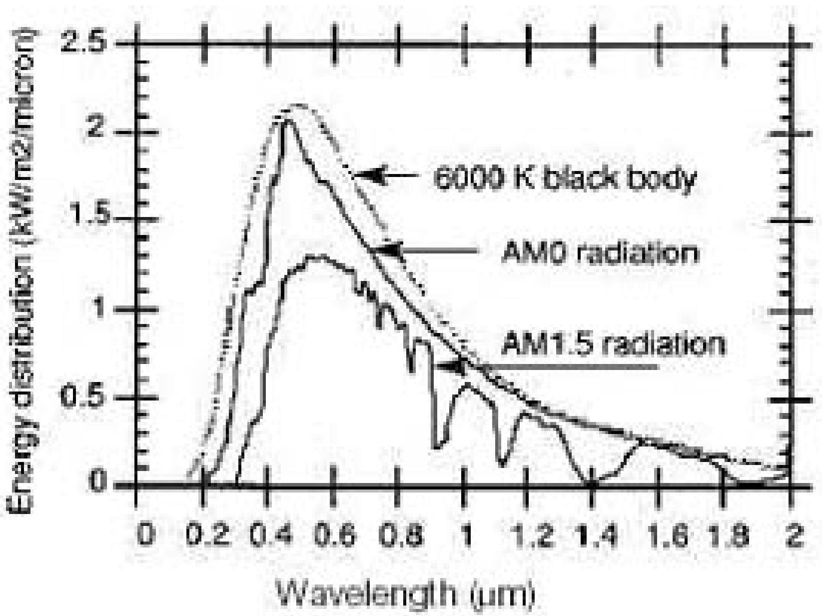
Materials viewpoint – atomistic processes/materials choices.

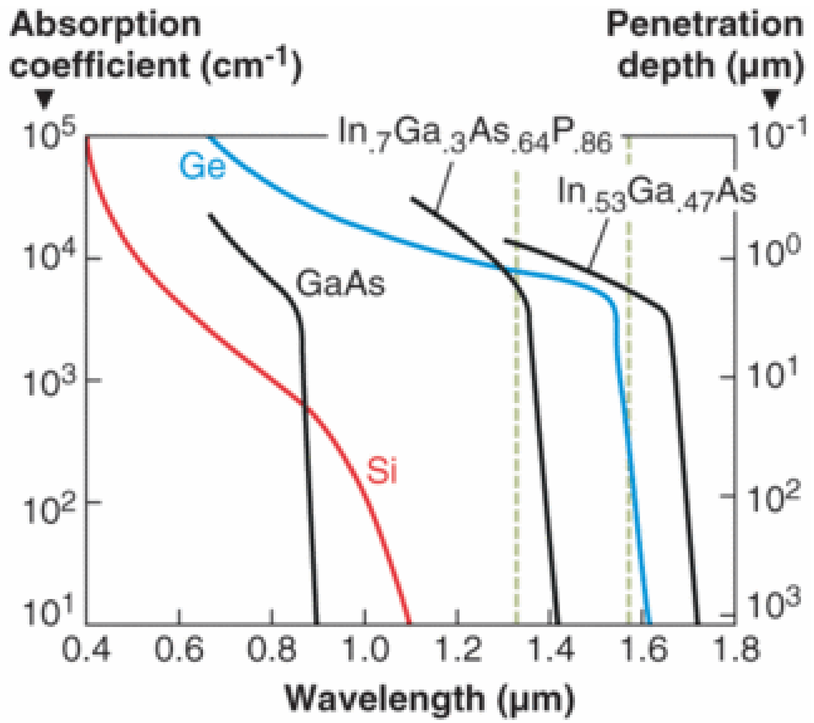
1. **Design materials to efficiently absorb photons and generate electron-hole pairs – light management (avoid losses due to incomplete spectral coverage)**

2. **Disassociate e-h pairs. Excitons are strongly bound in polymers. Electrons and holes need to be extracted from dyes and other supramolecular complexes. Voltage needed is of order 0.2-0.4V.**

3. **Transport e-h pairs to electrodes with minimal loss**
   Minimize current loss due to recombination/traps
   Minimize current loss due to dark current
   Minimize voltage loss due to dissipation (low mobility)

1. Materials to absorb photons





Indirect bandgap semiconductors (e.g. Si) – Penetration depth > 10µm
Direct bandgap semiconductors (e.g. GaAs, InP, Ge) – Penetration depth ~ 1µm
Polymers and nanoparticles – Penetration depth ~ 100nm

Materials to absorb photons

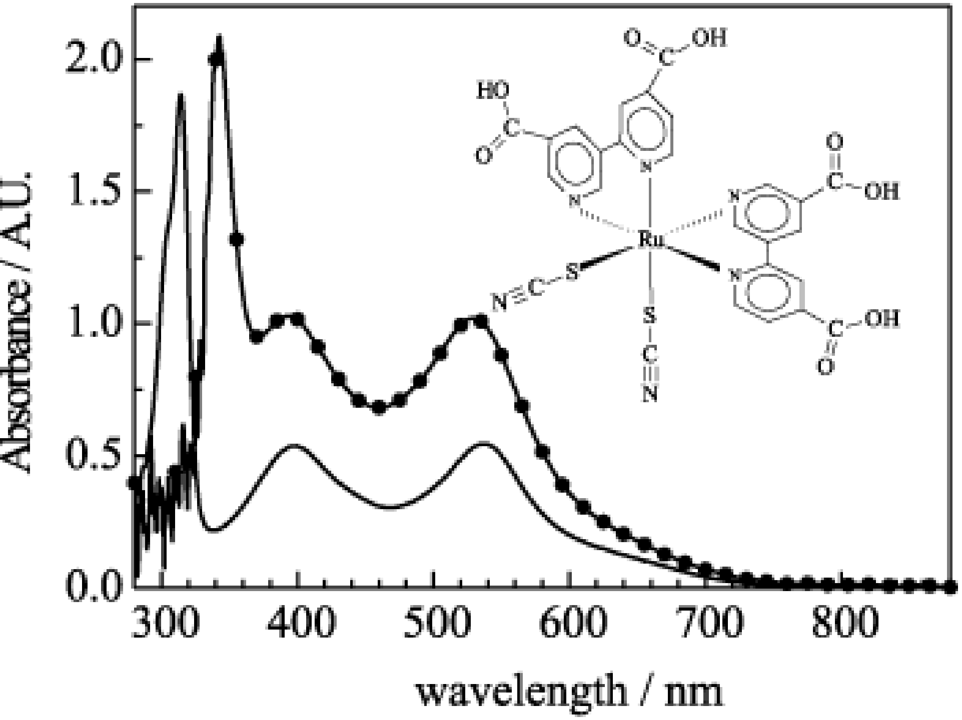
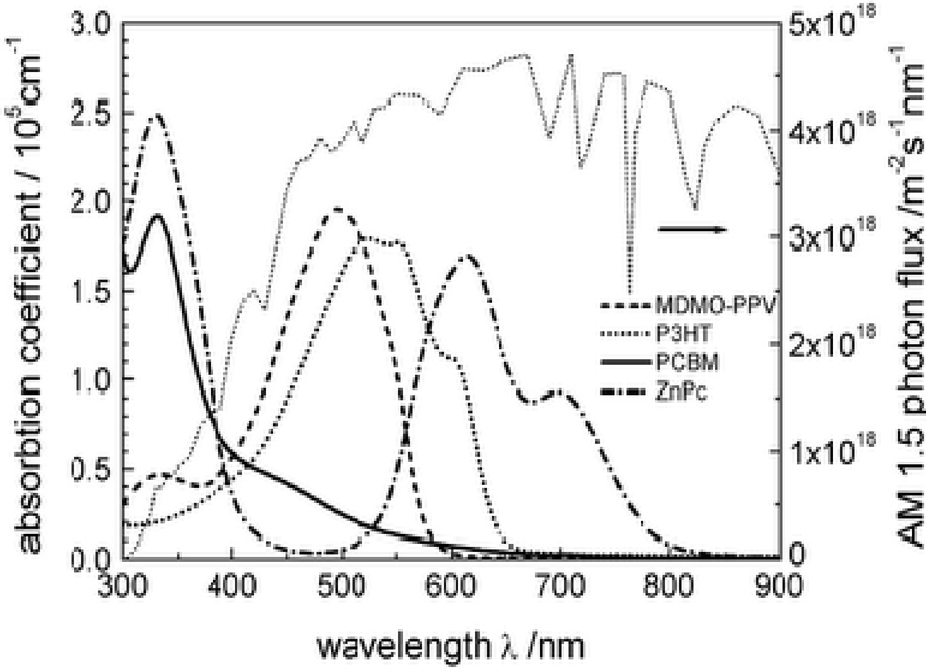
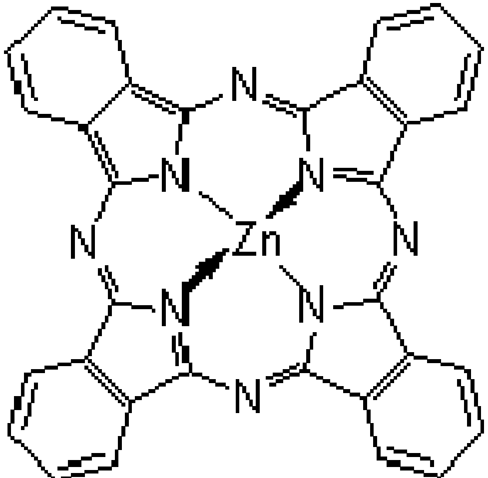


Figure 4. Absorption spectrum of the N3 dye in ethanol solution (—) and of a N3 dye-sensitized nanocrystalline TiO_2 electrode (-•-).



Zinc phthalocyanine = ZnPc



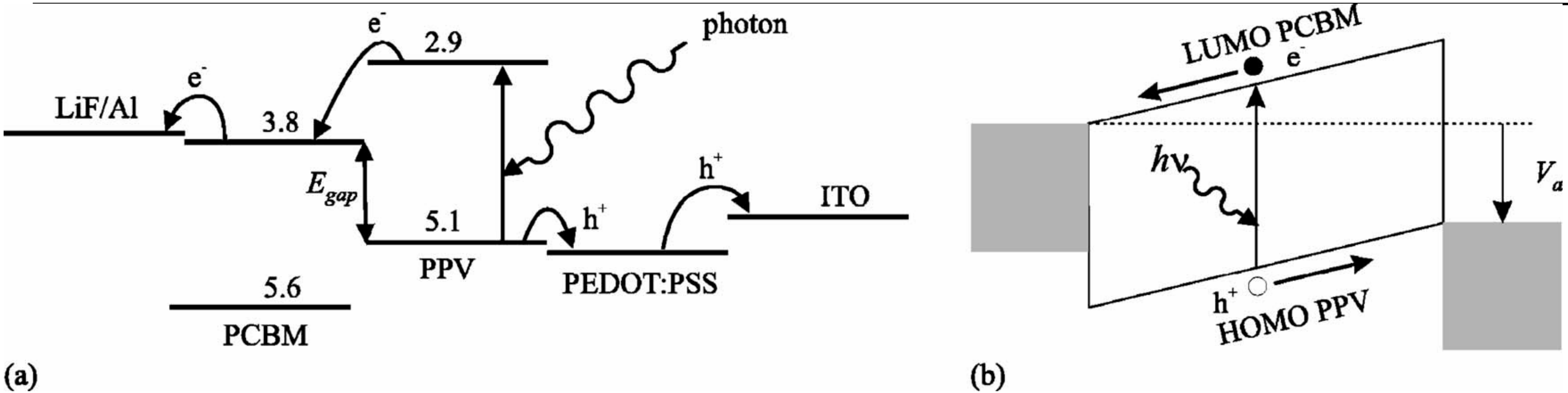
Materials choices to achieve absorption at lower cost

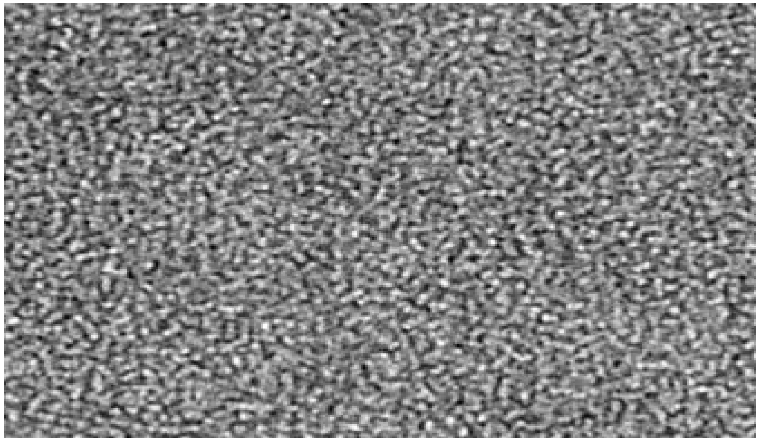
- First choice would be polymer / nanoparticle/ supramolecular structures as they achieve absorption with less material. Next best are thin films of direct gap materials. Silicon is poorest.
- Problems to overcome : 1. Broaden absorption bands of polymer/nanoparticle/supra-molecular structures 2. Improve durability. 3. Control nanostructure.
- Other light management issues : minimize reflection, maximize internal reflection, use plasmonics to concentrate light at heterojunction interfaces.

2. Disassociate and separate e-h pairs

- Separation of electrons and holes is essential to prevent recombination.
- In Si and thin film solar materials (CdTe, Amorphous Si, CIGS) e-h pairs disassociate thermally and drift to the appropriate electrodes.
- In organics and dyes, e-h pairs need to be torn apart. This requires an electric field and it needs to be carried out relatively quickly. In dye sensitized cells this leads to reduction of junction voltage, while in polymers it requires use of bulk heterostructures.

Organics example : Exciton is generated in polymer, disassociates at polymer C_{60} interface





Exciton diffusion length in PPV is about 10nm before recombination, requiring a fine grained "bulk heterostructure"

TEM of Bulk heterostructure of Polymer – Fullerene solar cell
Ma et al Advanced Materials 2007

3. Transport to electrodes

- Recombination and traps need to be avoided (reduce impurities). In Si the thickness is large so the impurity level needs to be very low. In bulk heterostructures recombination is a problem.
- Reduce dark current – a problem in polycrystals where grain boundary dark current leads to significant losses. Grain boundary resistance of the photocurrent is also a problem.
- Low mobility of carriers in many polymers is a severe problem as is low mobility of carriers in nanoparticle aggregates.

Device models

Lumped circuit, device physics

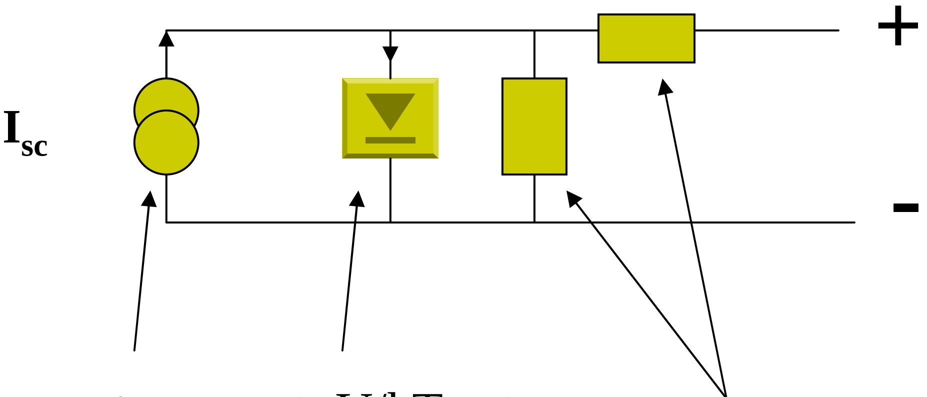
In the absence of light, a solar cell is like a diode. The voltage is applied in a forward bias mode, so the “dark” I-V behavior is approximately

$$I(V) = a(e^{V/kT}-1).$$

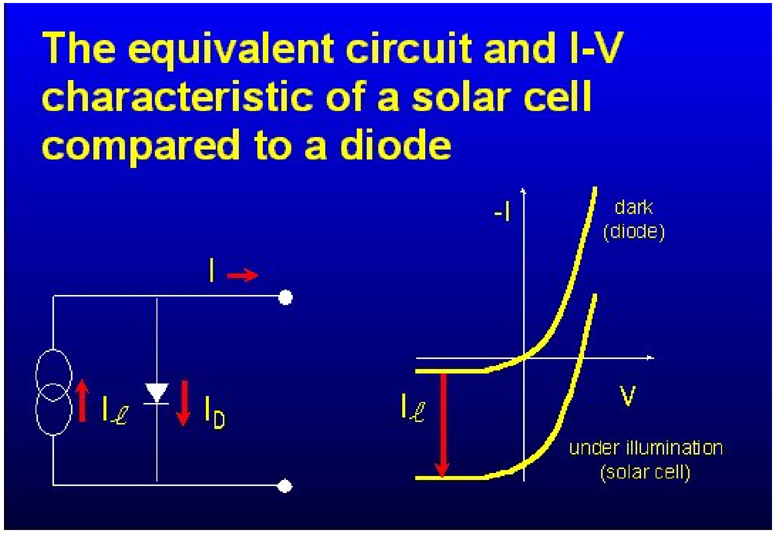
This “**dark**” current flows in the **forward** direction.

Light generates carriers which generate current in the **reverse** direction.

Lumped circuit – A solar cell charging a battery



$j(V) = -\mathbf{j}_{sc} + A(e^{V/kT}-1) + J$Resistive losses


The equivalent circuit and I-V characteristic of a solar cell compared to a diode

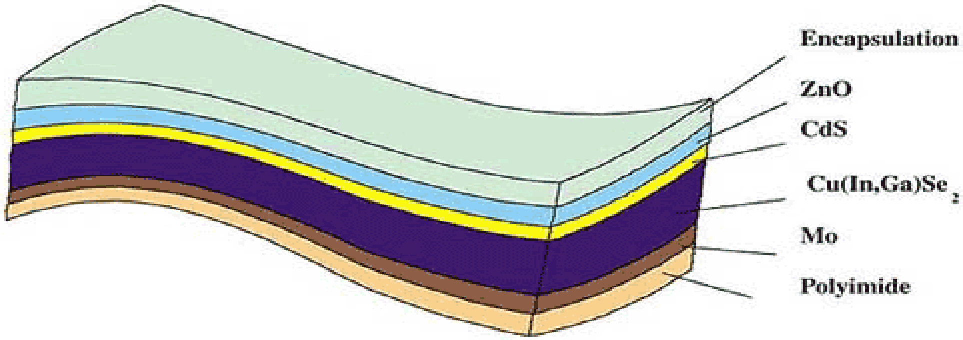
j_{sc} is the photocurrent density and is proportional to the intensity of the incident light, I_{light}

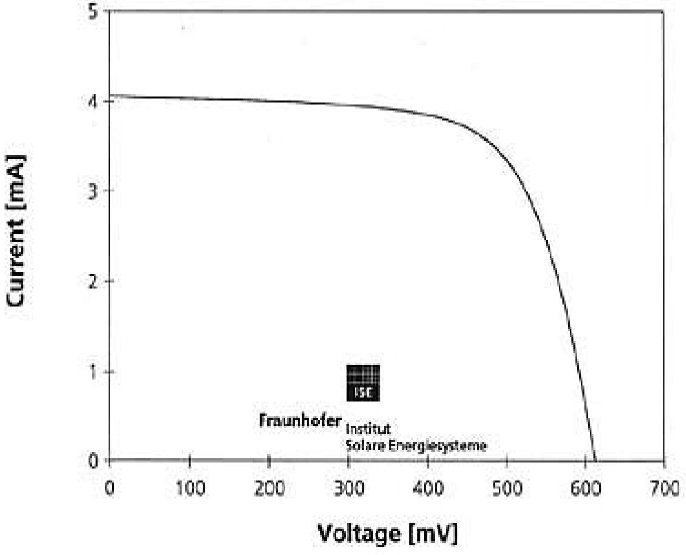
The dark current is $a(e^{V/kT}-1)$

IV curves

Kim et al (2006) Nature Materials effect of regioregularity of P3HT on absorption and efficiency of P3HT/fullerene cells

CIGS cell – ETH Zurich





V_{oc} = 612.7 mV

I_{sc} = 4.072 mA

J_{sc} = 30.62 mA/cm²

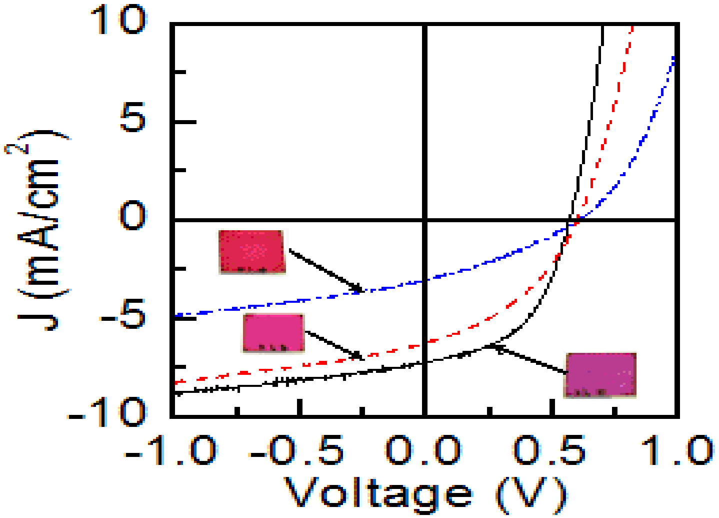
V_{max} = 479.2 mV

I_{max} = 3.550 mA

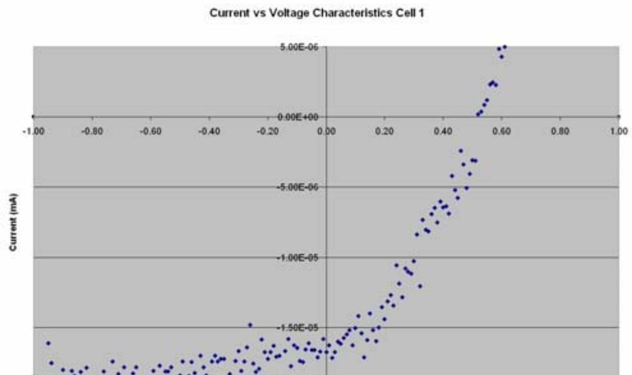
P_{max} = 1.702 mW

FF = 68.2 %

ETA = 12.8 %



An MSU Solar Cell
Jon Kiel/Mackay



Device physics of excitonic cells

Poisson Equation

Drift diffusion equation for holes and electrons (n,p)

Exciton diffusion equation (x)

D is disassociation rate of excitons

R is recombination rate. G is exciton generation rate

$$\nabla \cdot (\epsilon \nabla \psi) = -q\,(p - n), \tag{1}$$

$$\frac{\partial n}{\partial t} = \boldsymbol{D}(\boldsymbol{E}, x) - \boldsymbol{R}(n, p) - \frac{1}{q} \nabla \left[q n \mu_n \nabla \psi - k_\beta \boldsymbol{T} \mu_n \nabla n \right], \tag{2}$$

$$\frac{\partial p}{\partial t} = \boldsymbol{D}(\boldsymbol{E}, x) - \boldsymbol{R}(n, p) - \frac{1}{q} \nabla \left[-q p \mu_{\mathrm{p}} \nabla \psi - k_\beta \boldsymbol{T} \mu_{\mathrm{p}} \nabla p \right], \tag{3}$$

$$\frac{\partial x}{\partial t} = \boldsymbol{G}(\boldsymbol{r}) + \frac{1}{4} R(n, p) - \boldsymbol{R}(x) - \boldsymbol{D}(\boldsymbol{E}, x) - \frac{1}{q} \nabla \left[-k_\beta \boldsymbol{T} \mu_x \nabla x \right], \tag{4}$$

Solution of 1-D model (Koster 2005)

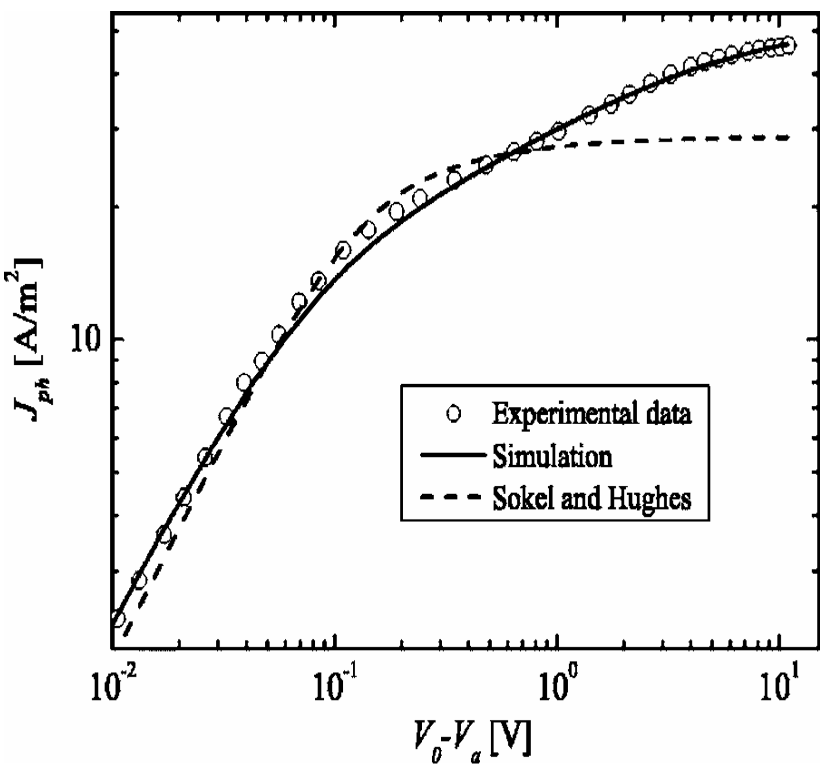


TABLE I. Overview of the parameters used in the fit to the data shown in Figs. 4 and 5.

Parameter	Symbol	Numerical value
Band gap	E_{gap}	1.34 eV
Electron mobility	μ_n	2.5×10^{-7} m^2/V s
Hole mobility	μ_p	3.0×10^{-8} m^2/V s
Eff. density of states	N_c	2.5×10^{25} m^{-3}
Generation rate	G	2.7×10^{27} m^{-3}
Dielectric constant	$\langle\varepsilon\rangle$	3.0×10^{-11} F/m
e/h Pair distance	a	1.3 nm
Decay rate	k_f	1.5×10^{6} s^{-1}

TABLE II. An overview of voltage, current density, average dissociation probability, and relative number of free carriers lost due to recombination at short-circuit (SC), maximum power (MP), and open-circuit (OC) conditions.

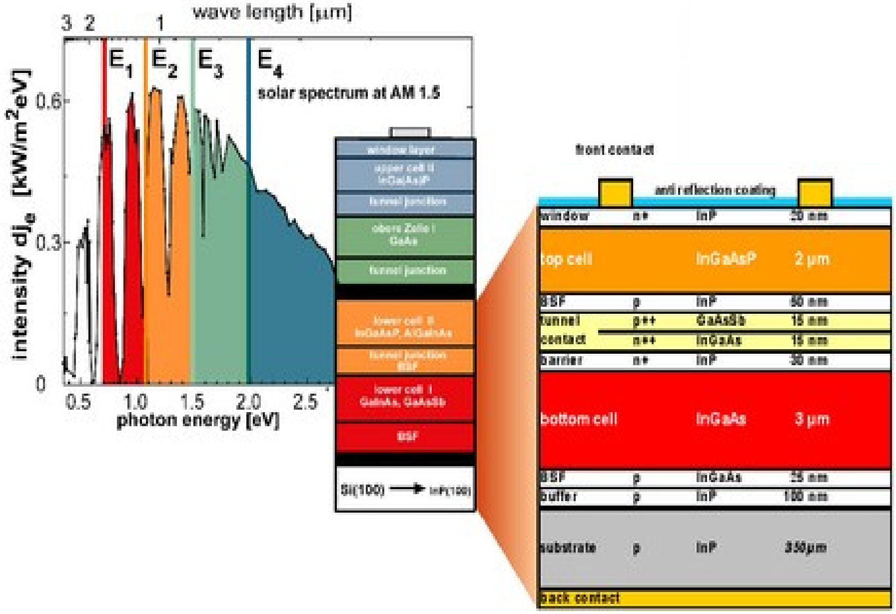
	V_a (V)	J (A/m^2)	$\langle P\rangle$ %	rec. loss %
SC	0	29.0	61.0	7.0
MP	0.653	19.5	51.5	24.9
OC	0.846	0	47.4	97.8

Two strategies for higher efficiency

1. Multi-exciton generation (quantum dots) ; Nozik, Inorg. Chem. **2005**, 44, 6893-6899

2. Multi- junction

-Record is 42.8%



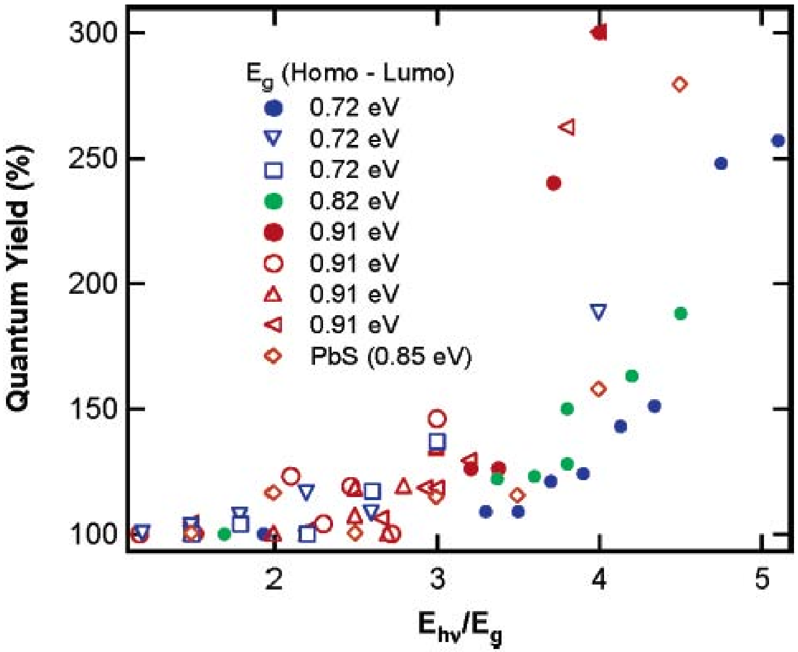


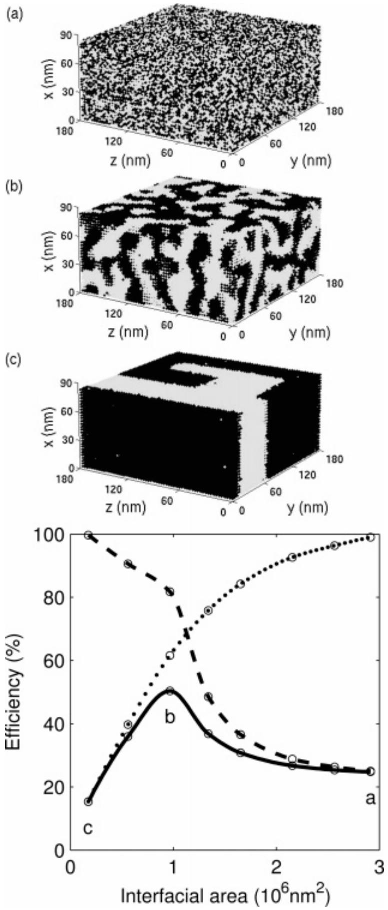
Figure 4. QY for exciton formation from a single photon vs photon energy expressed as the ratio of the photon energy to the QD band gap (HOMO—LUMO energy) for three PbSe QD sizes and one PbS (diameter = 3.9, 4.7, 5.4, and 5.5 nm, respectively, and E_g = 0.91, 0.82, 0.73, and 0.85 eV, respectively). Solid symbols indicate data acquired using a mid-IR probe; open symbols indicate band-edge probe energy. QY results were independent of the probe energy utilized (from ref 38).

Nanomaterials and nanostructures issues for excitonic/dye sensitized cells

1. Semiconductor nanoparticles to absorb light
2. Semiconductor nanoparticles for multi-exciton generation
3. Metal nanoparticles – plasmonics to control light?
4. Wide bandgap NP for electron transport (C_{60},TiO_2)
5. Nanostructured electrodes to maximize interfacial area
   -dyes/charge transfer complexes
5. Nanostructured electrodes to provide interfaces
   - to ensure exciton disassociation – bulk heterostructures
6. Polymers for ease of processing
   – hole conducting/electron conducting, tandems

Recent review "Nanoparticle-polymer photovoltaic cells", Advances in Colloid and Interface Science, in press (2007) – available on line.

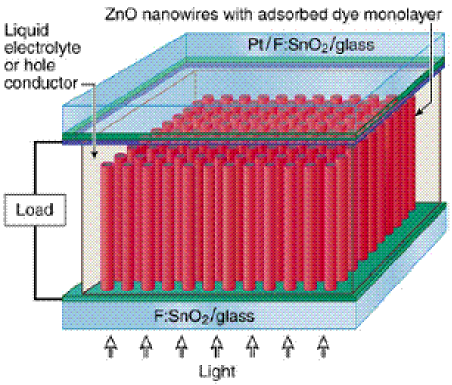
Nanostructures – bulk heterostructures



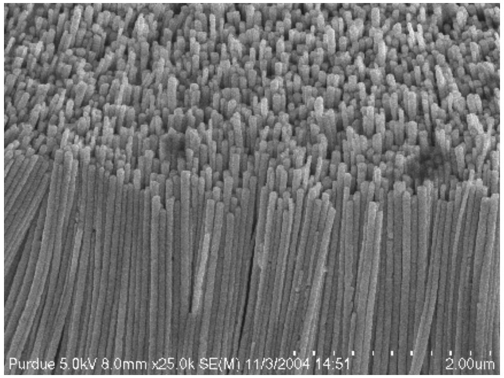
Competing factors (Watkins, Walker Nanoletters 2005)

1. Interfaces promote exciton disassociation
2. Interfaces also promote e-h recombination

Ideal structure?



Experimental progress



Closing remarks – industry status

1. Silicon, a-Si (UniSolar), CdTe (First Solar)

-Steady decrease in cost expected, new UniSolar facility in MI (50MW)

-Cost still a factor of 4-5 too high to compete in Michigan grid market.

2. CIGS : Nanosolar (roll to roll inkjet), Miosole

- Several startups are building 100MW plants, first delivery 2008.

3. Dye sensitized (Dyesol, G24 Innovations – 30MW plant)

- Expected to be cheaper, first delivery 2008

4. Excitonic/Organic cells are still in research stage (see Konarka)

- Note P-OLEDS are in production (e.g. Cambridge Display)

Need better understanding of (i) Exciton generation, recombination and disassociation in polymers and quantum dots. (ii) Nanoscale control of electrode structure, nanoparticle/organic assembly and interfaces.