MATERIALS RESEARCH SOCIETY
SYMPOSIUM TUTORIAL PROGRAM
April 5, 2010

2010 MRS SPRING MEETING

Symposium HH:
Organic Photovoltaic
Science and Technology

Foundations of Organic Photovoltaics

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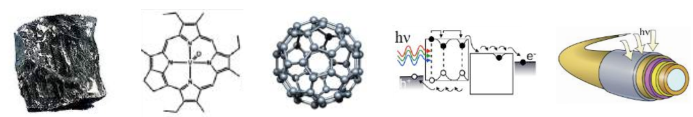
Foundations of Organic Photovoltaics II: **Small Molecule-based OPV**



Tutorial HH
MRS – April 5, 2010
San Francisco

MAX SHTEIN
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University of Michigan

Selected Reports & Articles

- DOE Report: Basic Research Needs for Solar Energy Utilization *http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf*
- Weisz, Physics Today, 57 (July 2004) p. 47
- Shaheen et al., MRS Bulletin 30 (2005) p.10
- Würfel, Physica E 14 (2002) p.18
- Henry, J. Appl. Phys. 51 (1980) p.4494
- Goetzberger et al., Mater. Sci. and Engin. R 40 (2003) p.1
- Shah et al., Science 285 (1999) p.692
- Green et al., Prog. Photovolt.: Res. Appl. 12 (2004) p.365
- Grätzel, Nature 414 (2001) p.338
- Brabec & Sariciftci, Monatshefte fur Chemie, 132 (2001) 421
- Tang, Appl. Phys. Lett. 48 (1986) p.183
- Forrest, Chem. Rev. 97 (1997) p.1793
- Peumans et al., J. Appl. Phys. 93 (2003) p.3693
- Rand et al., Prog. in Photovolt. 15 (2007) p.659
- Hains et al., Chem. Rev. DOI: 10.1021/cr9002984

Acknowledgements

- Peter Peumans (Stanford)
- Marc Baldo (MIT)
- Vladimir Bulovic (MIT)
- Barry Rand (IMEC)
- Russell Holmes (Minnesota)
- Jiangeng Xue (Florida)
- Richard "Johnny" Lunt (Michigan, OCM)
- Abhishek Yadav (Michigan, LNECD)
- Shaurjo Biswas (Michigan, LNECD)
- Kyle Luck (Michigan, LNECD)

Laboratory for Nanostructured Energy Conversion Devices
http://www.umich.edu/~lnecd/

Outline

1. Energy & solar cells
- A. Why we need energy in the first place
- B. Where does our energy come from and how do we use it?
- C. Why bother with solar electricity?
- D. Scalability & cost challenges of conventional solar cells

2. Small molecular organic PV cells – Part 1
- A. Material system
- B. Physics of organic PV materials & devices

3. Improving efficiency of OPV cells – Part 2
- A. Thin-film optics & plasmonics for improved absorption
- B. Exciton diffusion to and dissociation at D/A interface
- C. Increasing open circuit voltage and fill factor

4. Enabling low-cost modules & installation
- A. Eliminating costly materials from device structure
- B. Novel architectures
- C. Device processing

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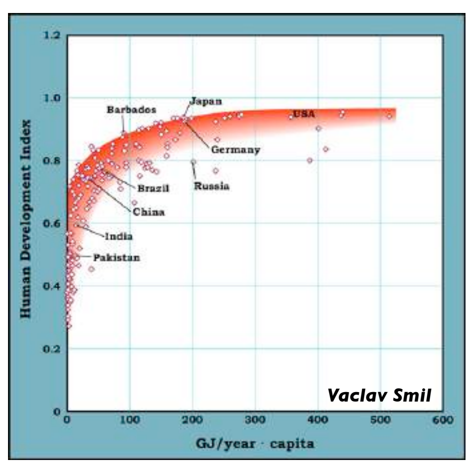
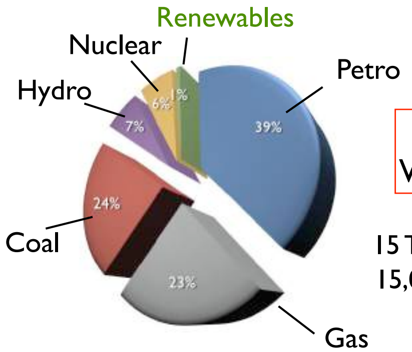
Quantifying the need for energy



Current Energy Mix in U.S.



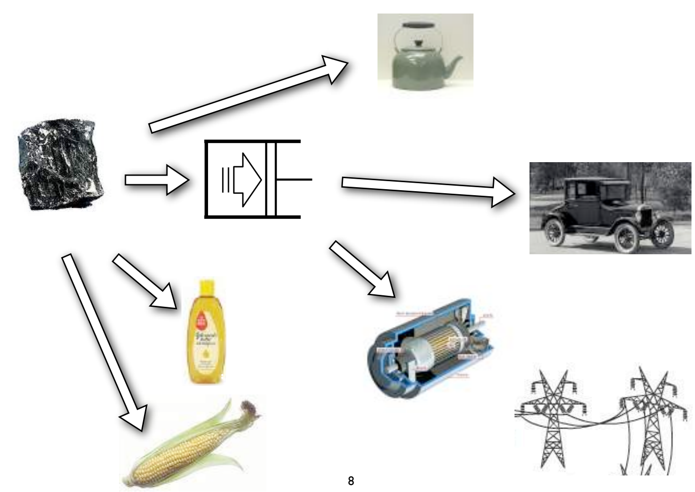
US: 3.3 TW
World: 15 TW

$15\ TW = 15 \cdot 10^{12}\ W =$
15,000,000,000,000W

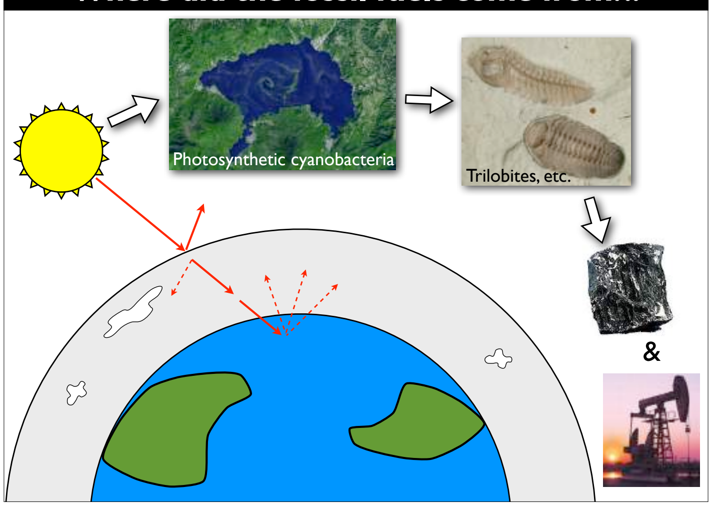
Data: DOE Energy Statistics;

A huge amount of energy is needed to power human activity
87% of our energy sources are from fossil fuels

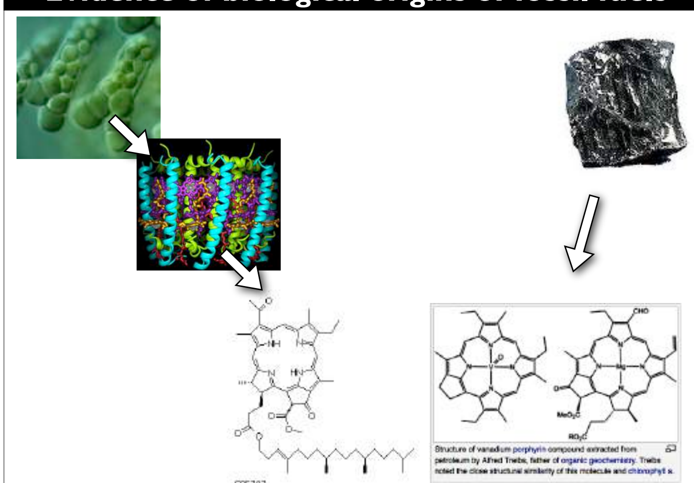
What do we associate with a high standard of living?



Where did the fossil fuels come from?..

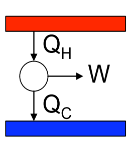


Evidence of biological origins of fossil fuels



The largest source of electricity in US: *coal*

~ 15,000,000 J / lb



~30% efficient

5,000,000 J of electricity per 1 lb coal

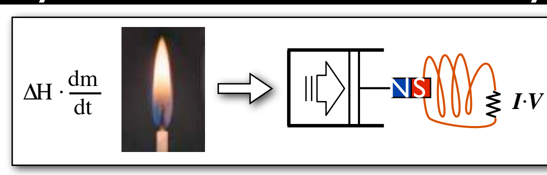
60 W bulb

1 day
2 lbs CO_2

Problem 1: Pollution

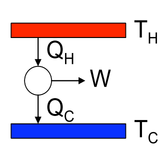
Thermodynamic limit of conversion efficiency

Example: Convert hydrocarbon into electricity



Sadi Carnot

Carnot Efficiency
→ thermodynamic limit of efficiency!

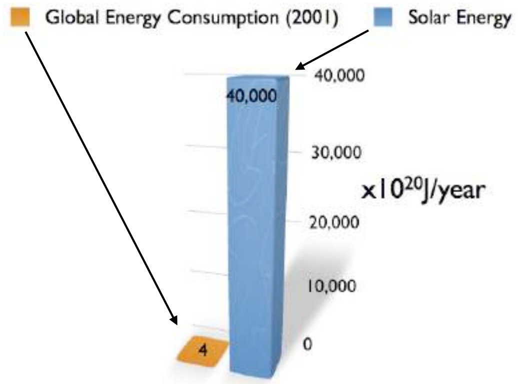


$\eta = (T_H - T_C) / T_H$

$I \cdot V \leq \eta \cdot \Delta H \cdot \frac{dm}{dt}$

Typical combustion of coal for <u>electricity</u> ➔ 33% efficient
Typical combustion of gas for <u>electricity</u> ➔ 70% efficient
Direct sunlight to <u>electricity</u> (T_H=5800K, T_C=300K)➔ 86% efficient

Abundance of Solar Energy is Staggering



10,000 times more solar energy than consumption

...Converting even a small fraction into electricity has tremendous potential

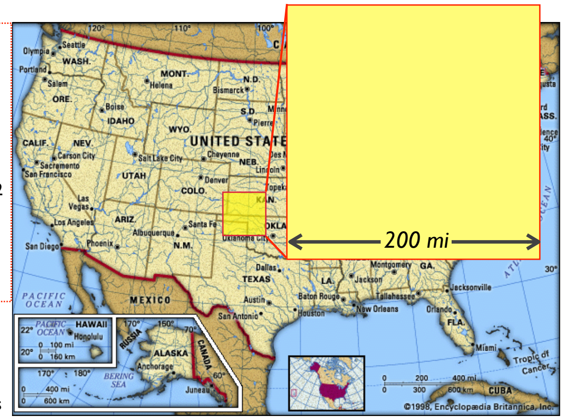
Why bother with solar electricity?

Assume:
1 kW / m^2 for
5.5 hrs / day
10% Efficient

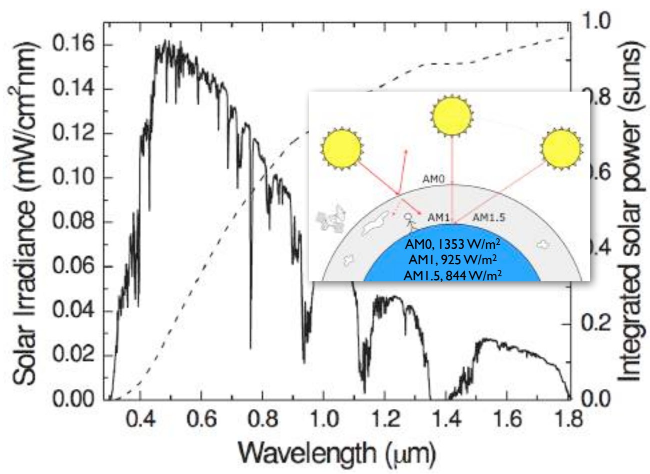
Need:
200x200 mi^2

Get:
>3 TW

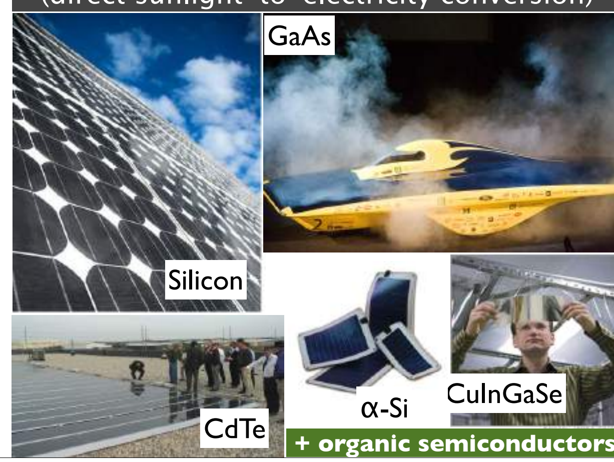
~ 2% of the dry land mass
~ surf. area of national highways



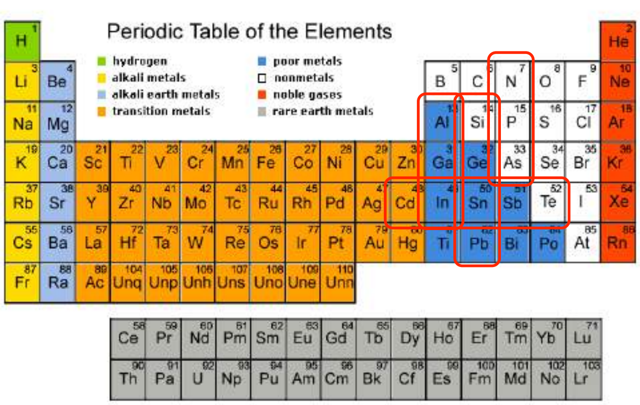
Obtaining energy from the sun



Solar Cells
(direct sunlight-to-electricity conversion)

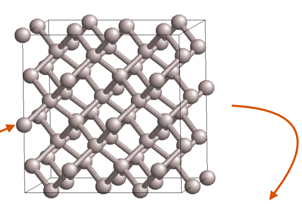


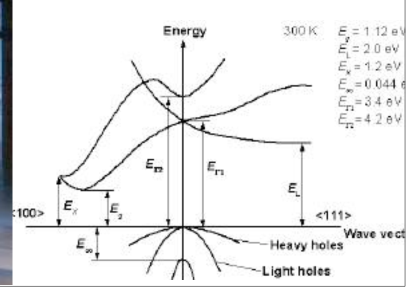
Semiconductors



http://www.elementsdatabase.com/

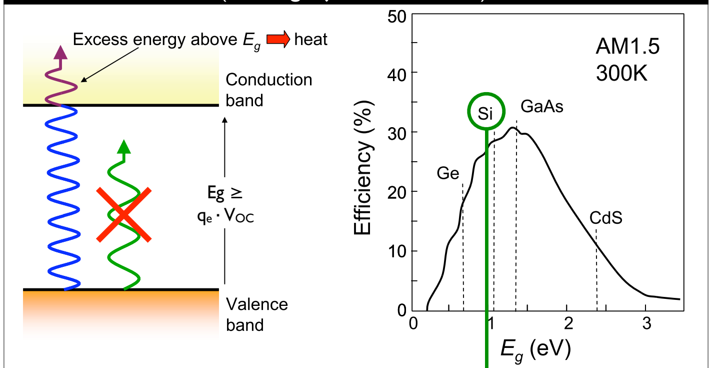
Ex.: Silicon:





Shockley-Queisser Limit of Efficiency

(for single junction PV cell)



When E_g ↑, V_{OC} ↑ but P_{abs} ↓

adapted from M. Baldo (MIT)

Silicon is a really good PV material!

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PV business booming: 40% annual growth

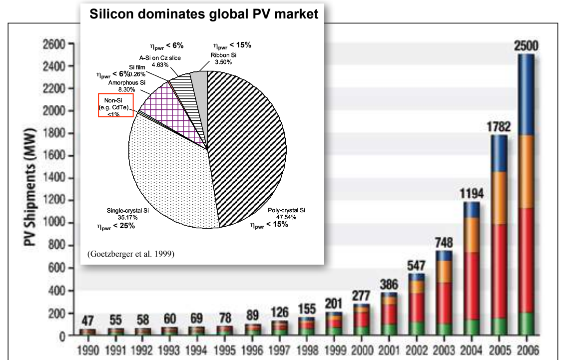

Figure 1. World photovoltaic module production (in megawatts), total consumer, and commercial per country (from *PV News*, Paul Maycock, Editor; February 2004). Most of this production is from crystalline or multicrystalline Si solar cells at present.

Si > 90% of the market

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But total area of PV modules installed to date is negligible

Total area of installed PV modules to date:

10x10 mi^2
\$400/m^2

10^3x less than needed
50-100x too expensive

PV HAS A SCALABILITY PROBLEM

1. National Council of Textile Organizations, 2005
2. The American Textile Manufacturers Institute, 2006
3. Green, M. 3rd Generation Photovoltaics, 2003

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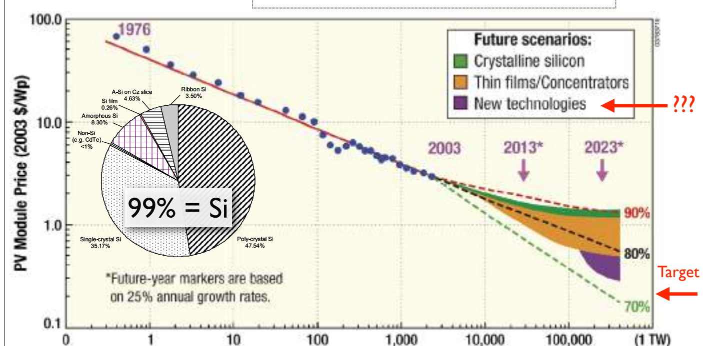
Bridging the scalability gap

Si & 80% learning curve
PRODUCTION x 2 ⇒ COST x 0.80



Need: new materials & reel-to-reel processing

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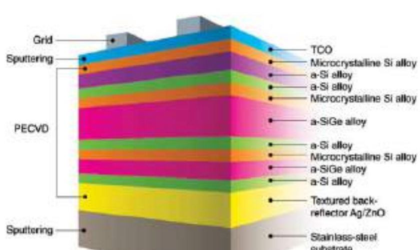
Ex. of Thin-film + Reel-to-reel: Silicon (+ multi-junction)

UniSolar Ovonic



Ginley, Green, Collins
MRS BULLETIN **33** *(2008) p.355*

Advantages: Flexible, Cheap

Disadvantages: Low efficiency, Need large area

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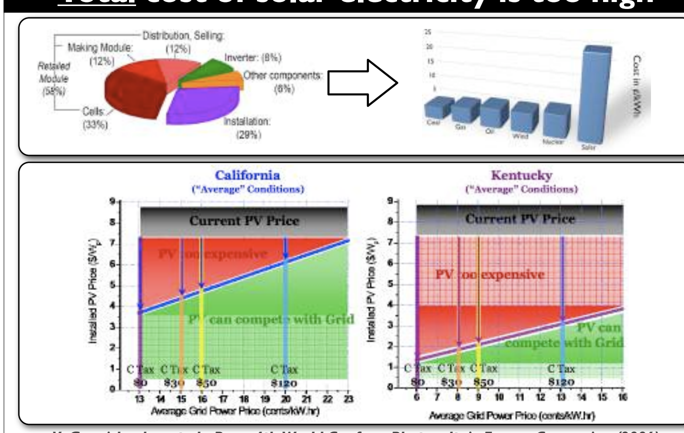
Total cost of solar electricity is too high



V. Gowrishankar et al.; Proc. 4th World Conf. on Photovoltaic Energy Conversion (2006)

To attain \$1/Wp installed price-point, need to manufacture cells at \$0.30 / Wp

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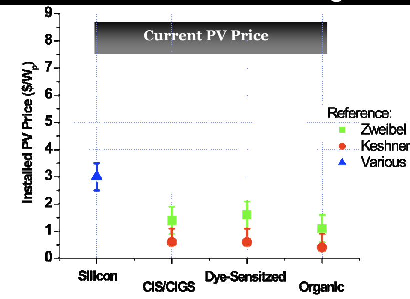
Semiconductor costs are **~5%** of a thin-film module

Table 3
Summary of the First Solar CdTe manufacturing model at 20 MW/yr

Component	Direct manufacturing cost ($/m^2)	Comments
Materials (all)	$48	Semiconductors only about $5; mostly encapsulation, substrate, and modularization
Capital (all)	$10	Semiconductors only about $5
Heat, electricity, water	$3	Energy payback < 3 months for energy added during manufacturing
Labor	$12	Plant labor and operations management
Maintenance of Equipment	$3	4% of initial capital cost
R&D	$4	Must maintain technical lead
Warranty	$5	3% of sales (very high for early high prices)
Rent and factory overhead	$5	Factory overhead at 1.5% sales
Total direct manufacturing	$90/m^2	Projected from existing technology, not yet optimized

Zweibel – Solar Energy Materials & Solar Cells **59** (1999) pp.1-18

...and installation costs make the situation worse. (need more than low cost; need high efficiency)



K. Zweibel, *"The terawatt challenge for thin-film PV"* NREL/TP-520-38350 (2005)
Keshner et al., *"Potential cost reductions super-large-scale manuf. of PV modules"* NREL (2005)

So… Challenge for (O)PV is 3-fold:
1. Increase Efficiency (need >15% to compete)
2. Reduce cost of module (reel-to-reel a must)
3. Reduce cost of installation (novel form factors)

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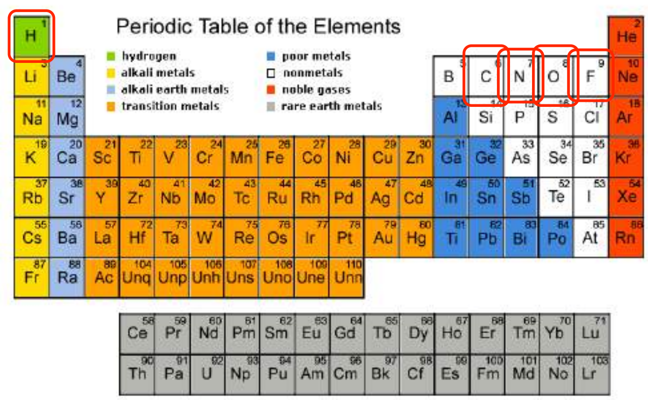
Organic Materials



http://www.elementsdatabase.com/

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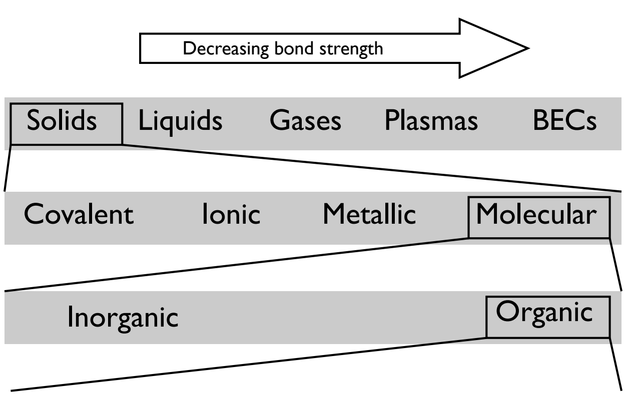
Classification of matter



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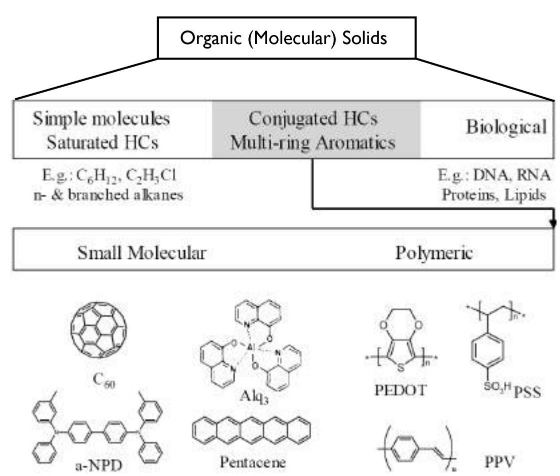

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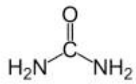
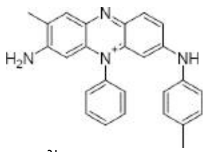
Earliest synthesized organic compounds

➢ In 1828, Wohler synthesizes Urea without the assistance of a living organism.



➢ In 1856, Sir William Henry Perkin,*** synthesizes the first artificial dye – aniline purple.



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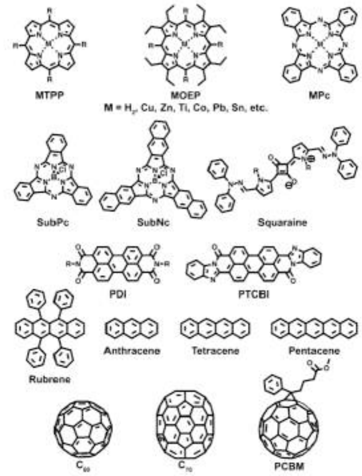
Archetypal materials common in OPV devices:



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Photovoltaic Effect and Photoconductivity in Laminated Organic Systems*

David Kearns and Melvin Calvin

Department of Chemistry and Radiation Laboratory, University of California, Berkeley, California

(Received July 28, 1958)

J. Chem. Phys. 29 (1958) p.950

a suggestion has been made[8–13] that the primary quantum conversion process in photosynthetic tissues involves the creation and separation of charge to opposite sides of an asymetrically constructed lamina followed by the trapping of both the electrons and the holes which then lead to their respective chemical processes; namely, reduction of carbon dioxide and oxidation of the water to oxygen.

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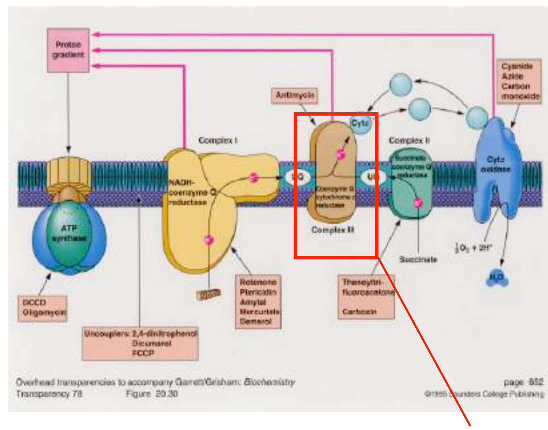
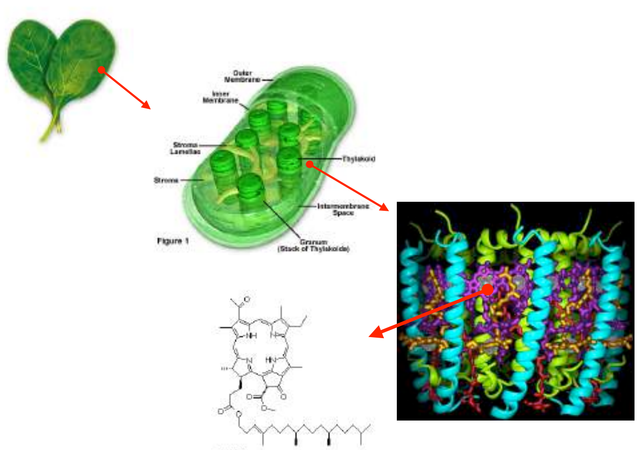
Solar Energy Conversion in Plants

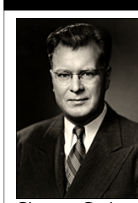


ATP Synthase needs a proton gradient → Use a **Solar Cell**!

Light harvesting complex

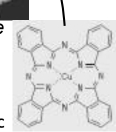


Organic dyes are used everywhere around us: In 1970s, Xerography was developed

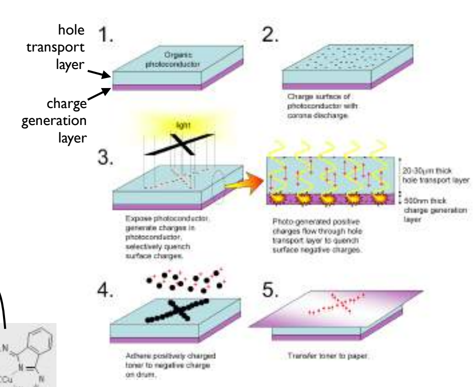


Chester Carlson

dye particle



CuPc

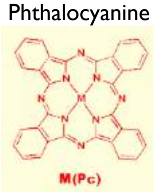


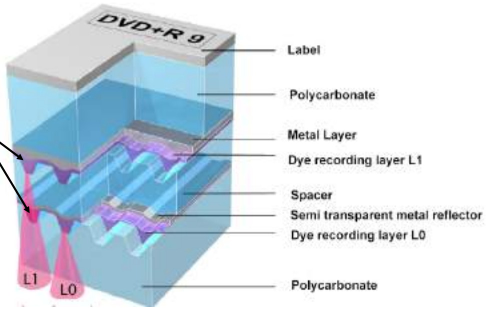
http://www.xerox.com/innovation/Storyofxerography.pdf
http://members.tripod.com/~earthdude1/xerox/index.html

Recordable CDs / DVDs use organic dyes:

"The beam heats and melts the recording layer of organic dye on the polycarbonate substrate, forming a series of pits. This pits are physically extremely stable, and are ideal for long-term data storage with the highest degree of reliability."

Phthalocyanine



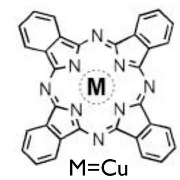


Read more: http://www.ngfdigital.com/pages/FAQs/CD-R_Dye.htm

37 http://www.research.phillips.com/

Pigment Molecules

- Pigments = Stable, small molecular weight absorbers in the visible wavelength range
- Mature industry/market
- Advantages:
  - Abundant: > 70,000 tons/year
  - Non-toxic
  - Low-cost: ~1$/g → 17¢/m2
  - Stable

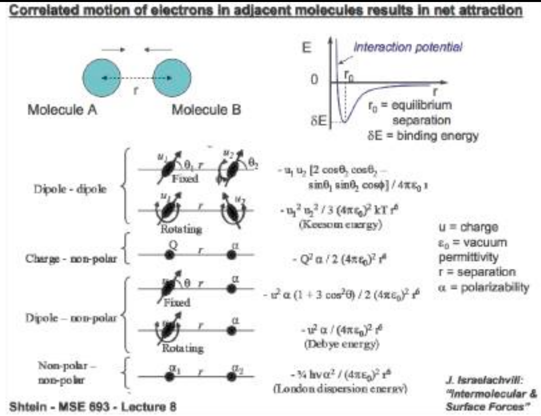


Low cost, abundant, safe, stable... The future of PV!

slide courtesy of P. Peumans, Stanford

Molecular organic solids are Van Der Waals bonded

Correlated motion of electrons in adjacent molecules results in net attraction

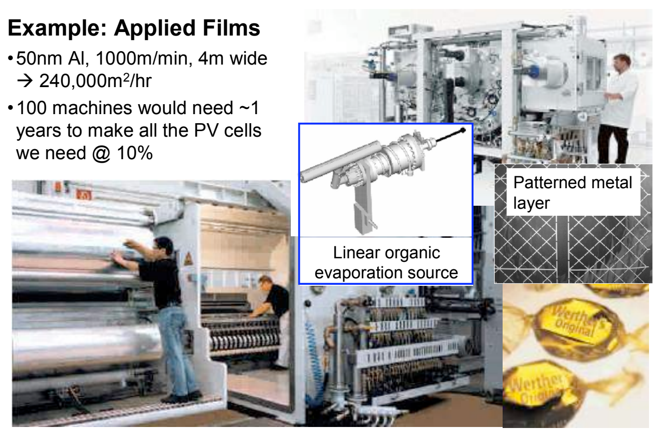


Can deposit these materials on virtually any substrate without regard for lattice matching!

Lower Cost: Roll-to-Roll Processing

Example: Applied Films

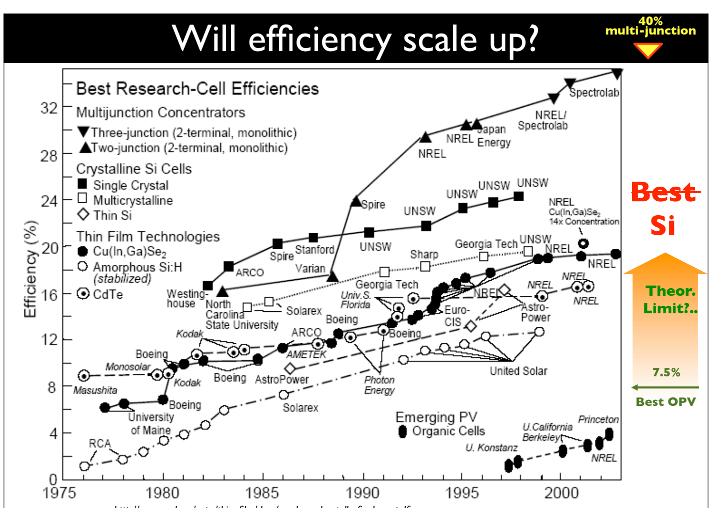
- 50nm Al, 1000m/min, 4m wide → 240,000m²/hr
- 100 machines would need ~1 years to make all the PV cells we need @ 10%



R. Ludwig, R. Kukla, and E. Josephson, *Proceedings of the IEEE* **93**, 1483 (2005).

Slide courtesy of P. Peumans

Will efficiency scale up?



http://www.nrel.gov/ncpv/thin_film/docs/surek_osaka_talk_final_vgs.pdf

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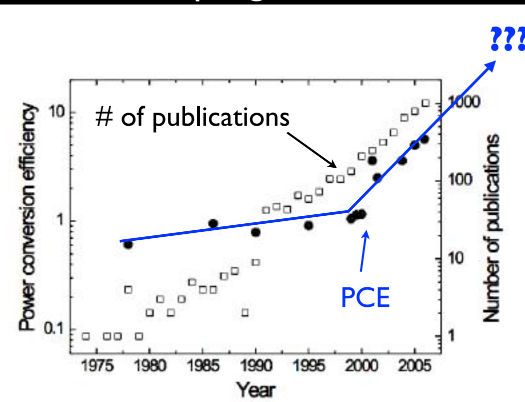
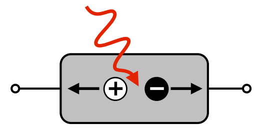
A closer look at progress in OPV efficiency



"Solar cells utilizing small molecular weight organic semiconductors"

Barry P. Rand,* Jan Genoe, Paul Heremans, and Jef Poortmans

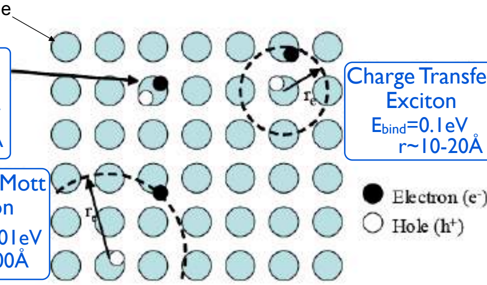
Molecular Organic PV cells:
Materials, Device physics, Efficiency



1. Capture photons
2. Convert energy into charge
3. Extract the charge to electrodes

How?

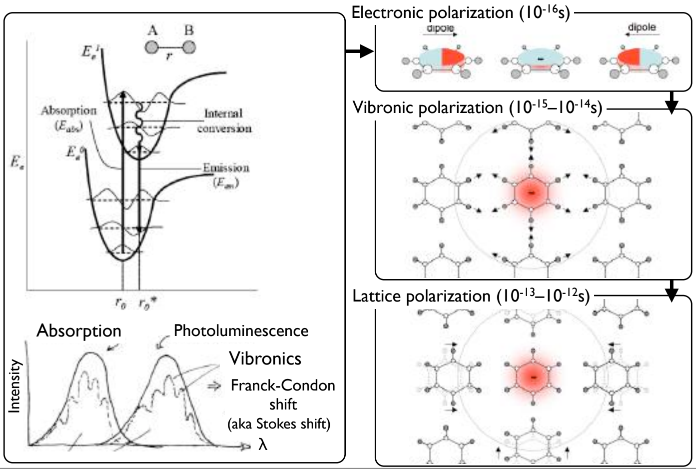
Types of excitons, spatial & energetic aspects



- *Weak intermolecular overlap*
  ➥localized electronic states
- *Localization*
  ➥electronic excitations with polarization of e^- clouds and molecular configurations
- *Excitation + polarization cloud*
  ➥***"Polaron"***

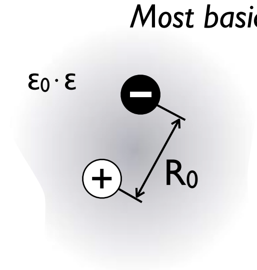
After Pope & Swenberg

Weak intermolecular binding ➜ Molecular properties dominate... ... but are subject to aggregate effects



Absorption ➜ Excitons
(Excitons = Bound e^-/h^+ pairs)

Most basic situation (continuum):



$$E_{Coul} = \frac{e^2}{4 \cdot (\varepsilon_0 \cdot \varepsilon) \cdot R_0}$$

$\varepsilon_{GaAs} = 13 \cdot \varepsilon_0$

$\varepsilon_{organic} = 3 \cdot \varepsilon_0$

- $\varepsilon_{organic} = 3 \cdot \varepsilon_0$ ➜ strong Coulomb attraction
- Narrow electronic bandwidth ➜ localization due to lattice polarization
- Instead of free e^- & h^+, have ***Excitons***
- Tightly bound exciton on a single molecule = Frenkel exciton

Exciton binding energy in organics is indeed large:

Hill, Kahn, Soos, and Pascal, Chem. Phys. Lett. 327, 181 (2000)

At surface: $$E_t^S - E_{opt} = c(P_+ + P_-) + \frac{e^2}{4\pi\varepsilon_0 \varepsilon R_0}$$

In the bulk: $$E_t - E_{opt} = \frac{e^2}{4\pi\varepsilon_0 \varepsilon R_0}$$

Table 1

$E^{UPS/IPES}$ is the measured HOMO–LUMO peak-to-peak gap; the 'surface' transport gap, E_t^S, is obtained from the first column by subtracting the vibrational contribution, 0.2 eV; the bulk transport gap, E_t, is obtained from E_t^S by subtracting the difference between bulk and surface polarization, $c(P_+ + P_-) = 0.6$ eV; E_{opt} is the absorption peak; the charge separation energy is $E_t - E_{opt}$

Organic material	$E^{UPS/IPES}$ ±0.2 (eV)	E_t^S ±0.2 (eV)	E_t ±0.4 (eV)	E_{opt} (eV)	$E_t - E_{opt}$ ±0.4 (eV)
CuPc	3.1	2.9	2.3	1.7	0.6
PTCDA	4.0	3.8	3.2	2.6	0.6
α-6T	4.2	4.0	3.4	3.0	0.4
α-NPD	5.3	5.1	4.5	3.5	1.0
Alq_3	5.4	5.2	4.6	3.2	1.4

Exciton binding energy also depends on the molecular size and shape...

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Trends in E_{bind} with molecular size

M Knupfer

Exciton binding energies in organic semiconductors

Appl. Phys. A 77, 623–626 (2003)
DOI: 10.1007/s00339-003-2182-9

Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, 01171 Dresden, Germany

Molecule	Binding energy E_B (eV)
Alq_3	1.4
α-NPD	1.0
Anthracene	1.0
PTCDA	0.8
CuPc	0.6
α-6T	0.4
MEH-PPV	0 – 0.6
PPV	0.05 – 1.1
Alkoxy-PPV	0.36
PFO	0.3
PPPV	0.4
DO-PPP	≤ 0.2
PT	0.6
PA	0.5
PDA	0.5
C_{60}	1.4 – 1.6 (U)
C_{70}	1.0 (U)

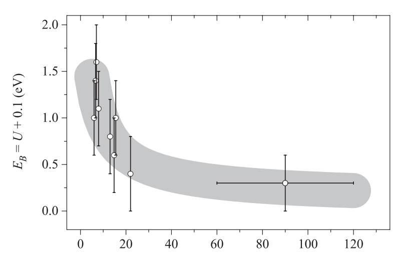
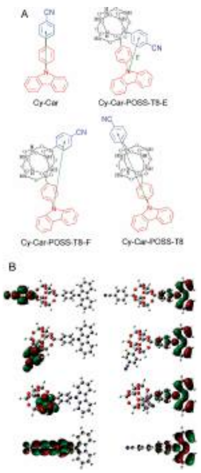


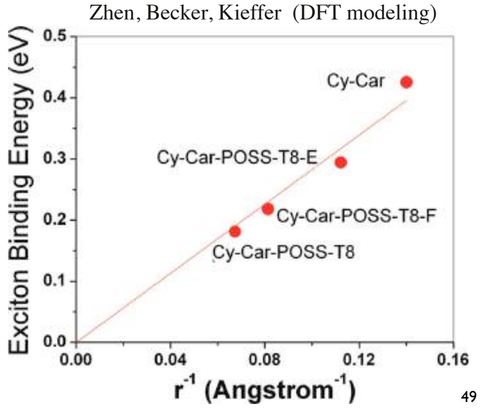
FIGURE 2 Exciton binding energies of various organic semiconductors as a function of the length of the corresponding molecules (see also Table 1). The *grey ribbon* depicts the prediction on the basis of the charging energy of the molecules

Binding energy ranges from 0.25 to 1.6 eV!

Tuning exciton binding energy via molecular shape:

J. Phys. Chem. A (2009), ***113***, 9707–9714
Zhen, Becker, Kieffer (DFT modeling)





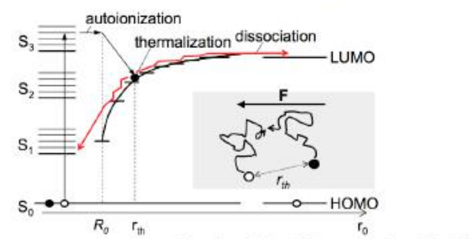
Dissociating excitons in organic materials:

Even the lowest E_{bind} (0.2 eV) > kT (0.026 eV)

Must introduce considerable driving force to dissociate the excitons

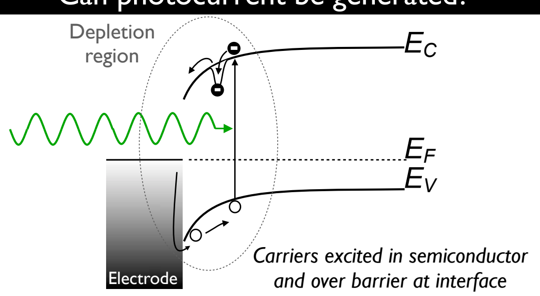
Apply Onsager theory of recombination to dissociating molecular excitons

Onsager theory of geminate recombination
1. Photon absorption
2. Excess energy is partially used to drive high energy electron (~hot electron) into neighboring molecules
3. After thermalization, electron hops in molecular lattice under the influence of the Coulomb attraction and externally applied field



Pope and Swenberg, *Electronic Processes in Organic Crystals*

Can excitons be dissociated using Schottky junctions? Can photocurrent be generated?



Carriers excited in semiconductor and over barrier at interface

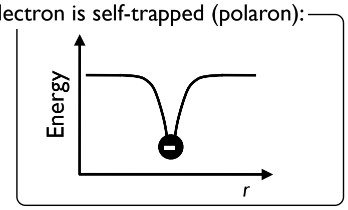
Potential advantages of this approach:
- Simplicity
- Low temperature processing
- Could be used with materials difficult to dope (i.e. no *p-n* junctions)

After M.A. Baldo

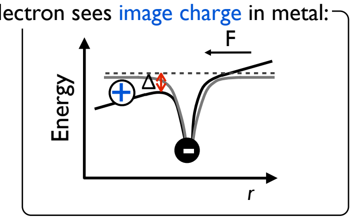
See also: Ghosh & Feng, *J. Appl. Phys.* **49**, 5982 (1978)

EXCITON DISSOCIATION PHYSICS

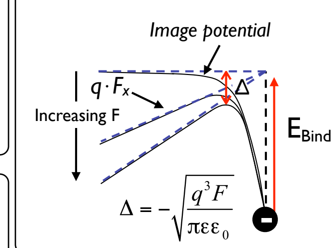
Electron is self-trapped (polaron):



Electron sees image charge in metal:



Apply field to pull e- out of trap
(Poole-Frenkel – high field, 1-D limit)



$$\Delta = -\sqrt{\frac{q^3 F}{\pi\varepsilon\varepsilon_0}}$$

Escape probability, *f*

$$f \propto \exp\left[\frac{q}{kT}\sqrt{\frac{qF}{\pi\varepsilon\varepsilon_0}}\right]$$

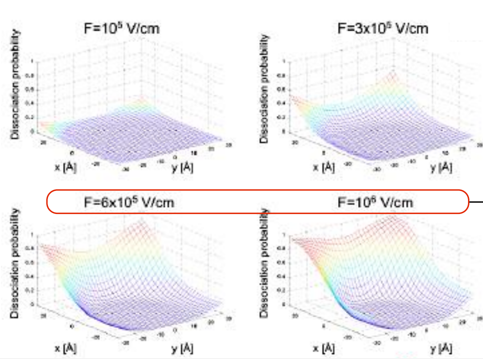
Also see:
Hains, Liang, Woodhouse, Gregg, Chemical Reviews (2010, DOI: 10.1021/cr9002984)

After M.A. Baldo

Charge separation in organic semiconductors – Onsager Model

Q1: What is the probability that the geminate e$^-$/h$^+$ will recombine?
Q2: What should the built-in E-field be to permanently separate the e$^-$/h$^+$?

$$f(r,\theta) = \exp\left[-\frac{q^2}{4\pi\varepsilon\varepsilon_0 kTr}\right]\exp\left[-\frac{qFr(1+\cos\theta)}{2kT}\right]\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{\left(\frac{q^2}{4\pi\varepsilon\varepsilon_0 r kT}\right)^m}{m!}\frac{\left(\frac{qFr(1+\cos\theta)}{2kT}\right)^{m+n}}{(m+n)!}$$

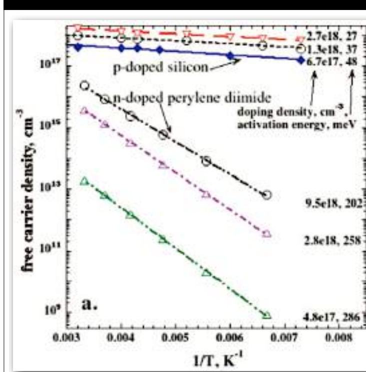


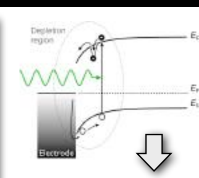
Rather large field

M.A. Baldo (MIT)

Organic semiconductors:

Free carrier concentration is typically low;
Doping usually not very effective (e.g. relative to Si).
➥ Depletion region not as pronounced





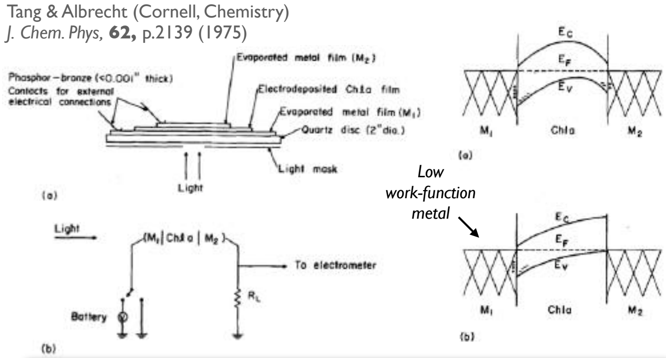
This won't work well in organics:
- Dielectric constant is much lower than in covalent semiconductors (such as Si, GaAs, InP, CdTe, CIGS, etc.), so that E_{bind} >0.2 eV
- Insufficient charge screening & therefore...
- Built-in field (< 10^5 V/cm) is too weak to alone dissociate charge pairs
- **Cannot overcome exciton binding energy using Schottky**

Hains, Liang, Woodhouse, Gregg, *Chem. Rev.* (2010)

Early evidence of Schottky barriers not working very well with organics

"Photovoltaic effects of metal-chrolorphyll-a–metal sandwich cells"

Tang & Albrecht (Cornell, Chemistry)
J. Chem. Phys, **62,** p.2139 (1975)



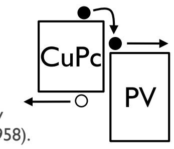
Power conversion efficiency ~ 10^{-3} % (among highest OPVs at the time)

Open circuit voltage 0.2 – 0.5 V, but very low fill factor

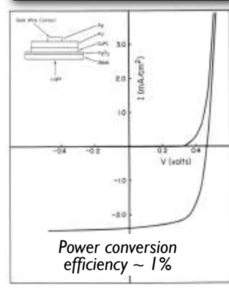
See also: Ghosh & Feng, *J. Appl. Phys.* **49**, 5982 (1978)

Solution: Heterojunction organic PV cell

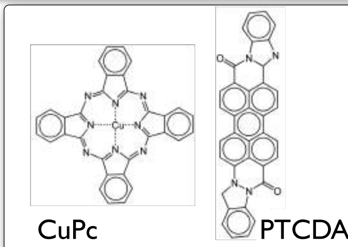
Use Donor/Acceptor interface to maximize exciton dissociation:



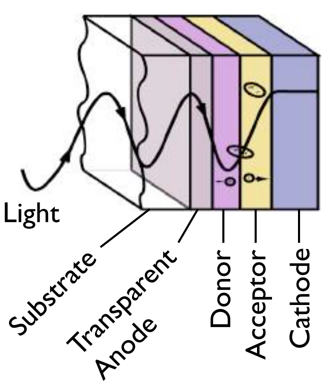
Note: First bi-layer OPV device reported by Kearns & Calvin in J. Chem. Phys. 29, p.950 (1958).

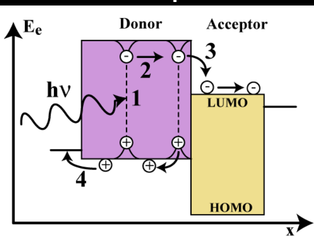


*Tang, APL, **48** 183 (1985)*



So.... Heterojunction OPV device & its operation:





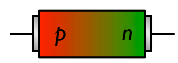
(1) Absorb - η_A
(2) Diffuse - η_{ED}
(3) Charge-Transfer - η_{CT}
(4) Charge-Collect - η_{CC}

$\eta_{EQE} = \eta_A \cdot \eta_{ED} \cdot \eta_{CT} \cdot \eta_{CC}$

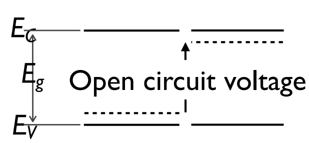
Physics: Peumans et al. J. Appl. Phys. ***93*** *3693 (2003)*
slide courtesy B. O'Connor

Simple p-n solar cell

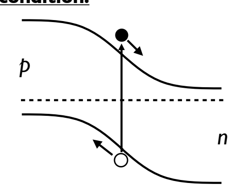
Si *pn* diode:



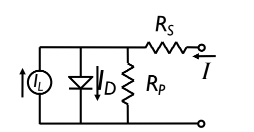
Open circuit condition:



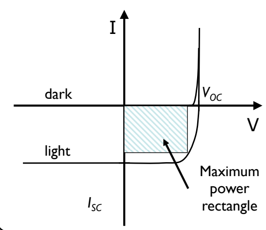
Short circuit condition:



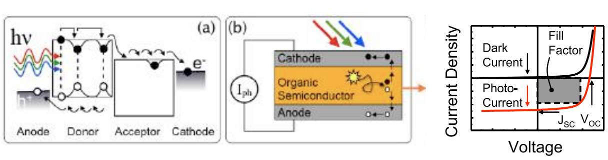
Circuit model:



$$I = I_S\left(e^{qV/kT} - 1\right) - I_L$$



Organic solar cell: Defining and predicting efficiency



$$\eta = \frac{J_{SC} V_{OC} FF}{P_{inc}}$$

Want to:
Increase Jsc
Increase Voc
Increase FF

Q: HOW?

Outline

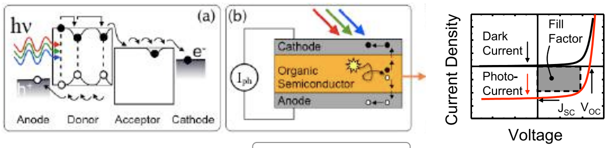
✓ **1. Energy & solar cells**
   A. Why we need energy in the first place
   B. Where does our energy come from and how do we use it?
   C. Why bother with solar electricity?
   D. Scalability & cost challenges of conventional solar cells

✓ **2. Small molecular organic PV cells – Part I**
   A. Material system
   B. Physics of organic PV materials & devices

3. Improving efficiency of OPV cells – Part 2
   A. Thin-film optics & plasmonics for improved absorption
   B. Exciton diffusion to and dissociation at D/A interface
   C. Increasing open circuit voltage and fill factor

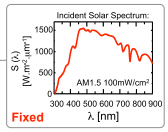
4. Enabling low-cost modules & installation
   A. Eliminating costly materials from device structure
   B. Novel architectures
   C. Device processing

OPV Efficiency – Focus on J_{SC}



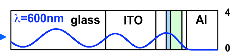
$$\eta = \frac{J_{SC} V_{OC} FF}{P_{inc}}$$

$$J_{SC} = \int \eta_{EQE} S(\lambda) d\lambda$$



$$\eta_{EQE}(\lambda) = \eta_A(\lambda)\eta_{IQE}(\lambda)$$

$$G(x) = \frac{1}{2} c\varepsilon_0 n\alpha \frac{|(E_I+E_R)^2|}{|E_0^2|}$$



Increase absorption (& exciton gen. rate) via constructive interference

$$\frac{\partial^2 n}{\partial x^2} = -\frac{1}{L_D^2} n - \frac{\tau}{L_D^2} G(x)$$

Exciton generation rate dictates exciton flux at D/A junction

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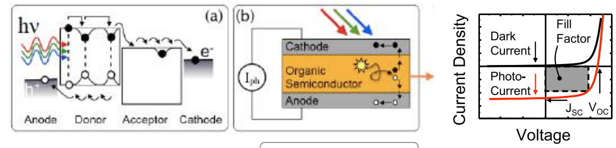
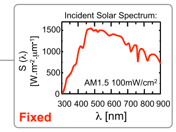
OPV Efficiency – Focus on J_{SC}



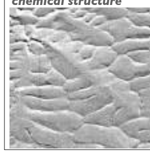
$$\eta = \frac{J_{SC} V_{OC} FF}{P_{inc}}$$

$$J_{SC} = \int \eta_{EQE} S(\lambda) d\lambda$$

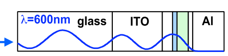


$$\eta_{EQE}(\lambda) = \eta_A(\lambda)\eta_{IQE}(\lambda)$$

Improve exciton diffusion via ordering, chemical structure



$$G(x) = \frac{1}{2} c\varepsilon_0 n\alpha \frac{|(E_I+E_R)^2|}{|E_0^2|}$$



$$\frac{\partial^2 n}{\partial x^2} = -\frac{1}{L_D^2} n - \frac{\tau}{L_D^2} G(x)$$

Rapid exciton diffusion favors internal quantum efficiency

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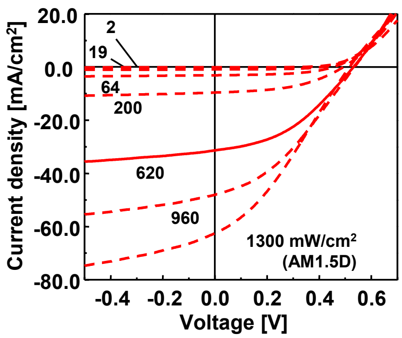
Typical I-V response of a small molecular OPV

J_{SC} scales with illumination intensity
(Notice: FF suffers...)

ITO / 90Å CuPc / 90Å PTCBI / 150Å BCP / Ag



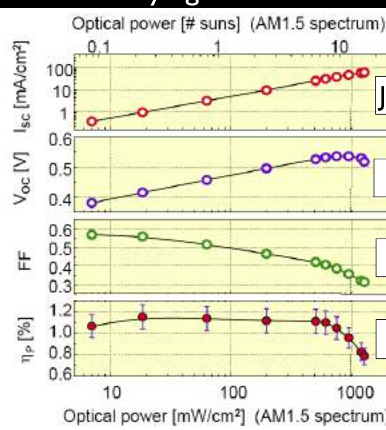
@ 100mW/cm²
V_{OC}=0.45
FF=0.52
η_P=1.1%

- Operate at high optical intensities
- Same efficiency but less absorptive

P. Peumans (Stanford)

63

Typical I-V response of a small molecular OPV at varying illumination intensity



J_{SC} increases linearly

V_{OC} increases

FF decreases

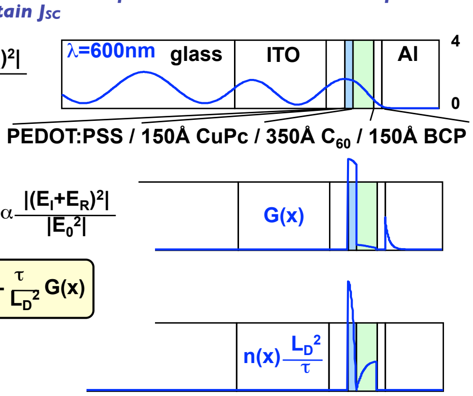
η_{pwr} ~invariant

Peumans et al., Appl. Phys. Lett. **76**, 2650 (2000).

J_{SC} can be predicted via thin-film optics + transport equations

- ***Calculate optical field distribution***
- ***Calculate rate of absorption (exciton generation)***
- ***Calculate rate of exciton arrival at D/A interface***
- ***Obtain J_{SC}***

$$\frac{|(E_I+E_R)^2|}{|E_0^2|}$$



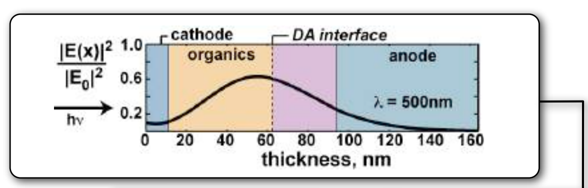
$$G(x) = \frac{1}{2} c\varepsilon_0 n\alpha \frac{|(E_I+E_R)^2|}{|E_0^2|}$$

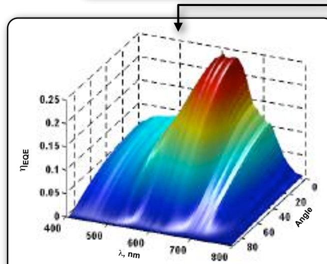
$$\frac{\partial^2 n}{\partial x^2} = -\frac{1}{L_D^2} n - \frac{\tau}{L_D^2} G(x)$$

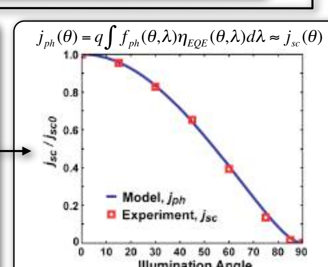
$n(x)$

Petterson et.al. J. Appl. Phys. 86(1) 487-496 (1999) *Peumans et al. J. Appl. Phys.* ***93*** *3693 (2003)*

Use optical modeling to predict J_{SC} vs. λ & $\theta_{incident}$







$$j_{ph}(\theta) = q\int f_{ph}(\theta,\lambda)\eta_{EQE}(\theta,\lambda)d\lambda \approx j_{sc}(\theta)$$

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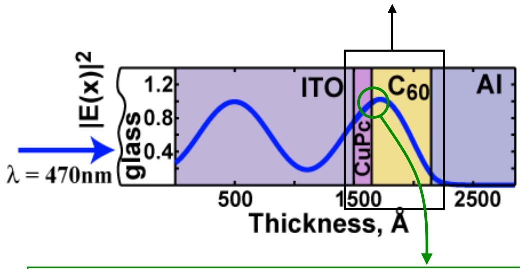
O'Connor et al., *(in preparation)*

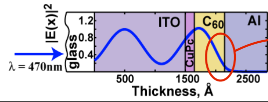
Strongest influence on J_{SC} is via $|E|^2$ at the D/A interface:

1. $G(x) \sim |E(x)|^2$
2. Active layer thickness < λ



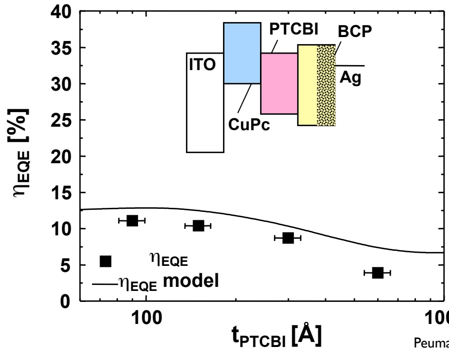
Need to maximize $|E|^2$ near D/A junction

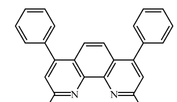
Can be achieved by using ARC coatings



Field intensity close to "back" electrode is low...
(+exciton quenching @ cathode)

Use an optical spacer to move active layer closer to high intensity region





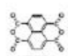
BCP
(2, 9-dimethyl, 4, 7-diphenyl, 1, 10-phenanthroline)
(aka bathocuproine)

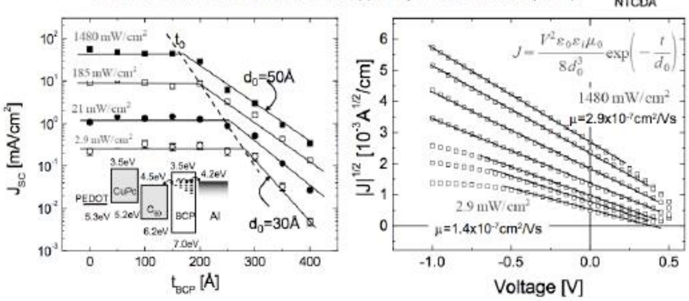
- Transparent
- Electron conducting
- Wide bandgap

Peumans et al., *Appl. Phys. Lett.* **76**, 2650 (2000).

Conduction mechanism of the optical spacer / EBL

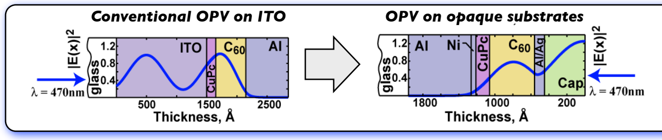
- Energy barrier for electrons at PTSBI/BCP interface ~1eV
- Rely on metal contact-induced sub-energy-gap states for conduction
- State density = exponentially decaying into organic thin film
- Space-charge limited conduction through defect states
- Solution:
  - 600nm-thick NTCDA: Suemori, et al., *Appl. Phys. Lett.* **85**, 6269 (2004).

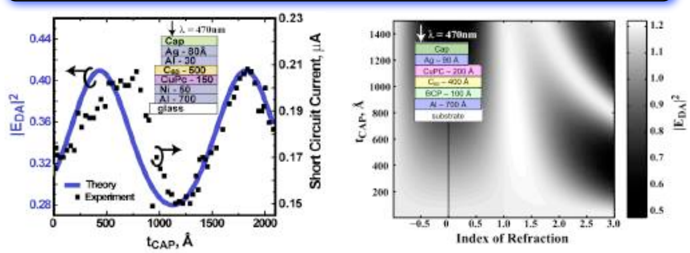




Peumans, *et al., J. Appl. Phys.* **93**, 3693 (2003).

Evidence of phase-matching (monochromatic illumination)





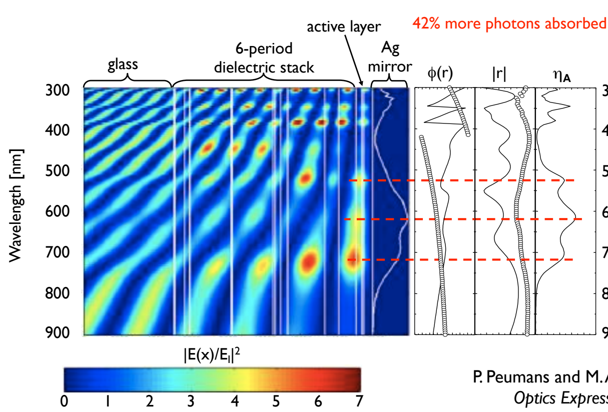
~ 30% increase in Short Circuit Current for an optimized single-layer cap

Can be extended to broad-band illumination

O'Connor et al., Appl. Phys. Lett. ***89*** *233502 (2006)*

Design for Broadband resonant cavity

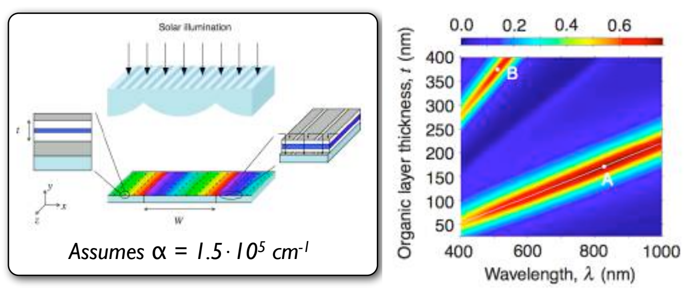
glass/[SiNx/SiO$_2$]$_6$/15nm ITO/32nm PEDOT:PSS/
10 nm CuPc:PTCBI (1:1)/50nm BCP/200nm Ag



P. Peumans and M. Agrawal,
Optics Express (2008)

Another example of microcavity-tuned OPV design

"Organic photovoltaic cell in **lateral-tandem configuration** employing continuously-tuned microcavity sub-cells"
Changsoon Kim & Jung-Sang Kim, Optics Express, **Vol. 16**, p.19987



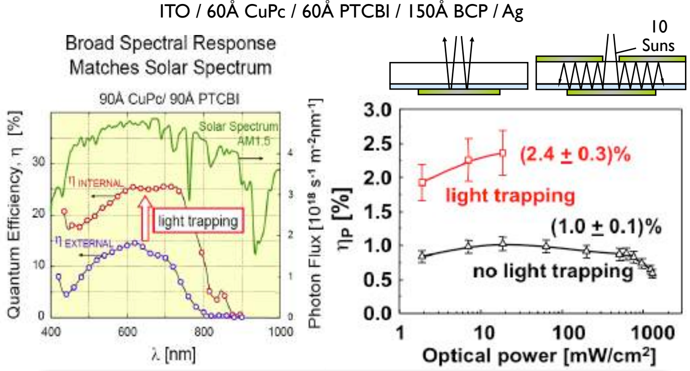
Assumes $\alpha = 1.5 \cdot 10^5$ *cm*$^{-1}$

If all light is ideally directed to a tuned OPV sub-cell, η_{pwr} *→ 18%*

Requires dispersion element & tracking

Another way to increase J_{SC}: light trapping (+ thin active layers)

ITO / 60Å CuPc / 60Å PTCBI / 150Å BCP / Ag

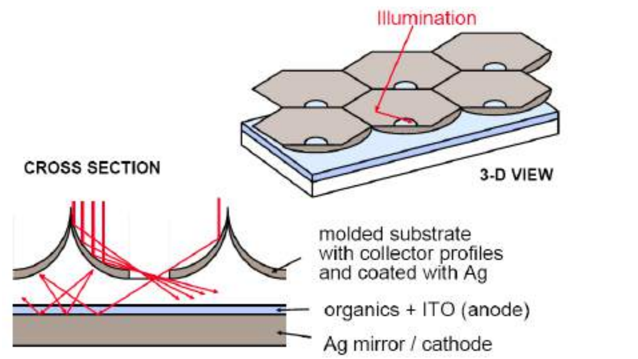


Factor of 2.5 improvement in power conversion efficiency

Peumans et al., APL **76**, p. 2650 (2000).

Practical realization of light trapping:

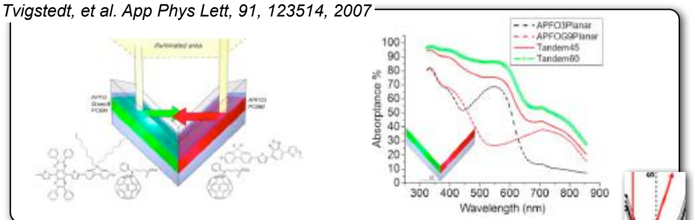
E.g.: Micro-molded Winston Collectors



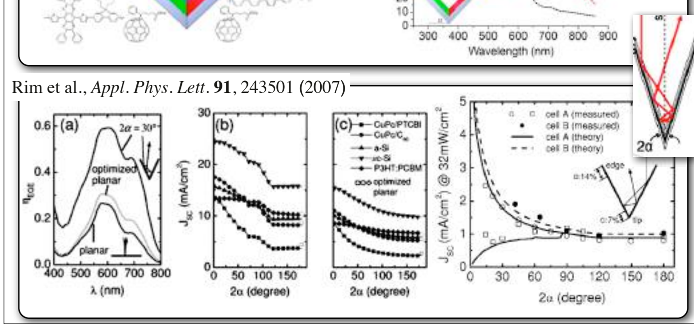
Peumans et al, US Patents #6440, 769, Aug 27, 2002

More concentration: "V-cells" & Reflective tandems

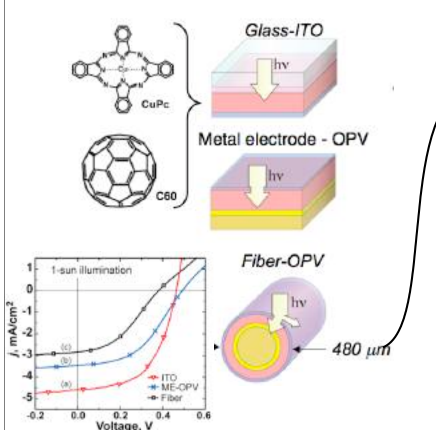
Tvigstedt, et al. App Phys Lett, 91, 123514, 2007

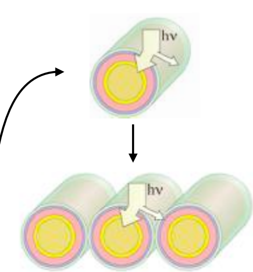


Rim et al., *Appl. Phys. Lett*. **91**, 243501 (2007)



Light trapping can also be enhanced in other non-planar structures:

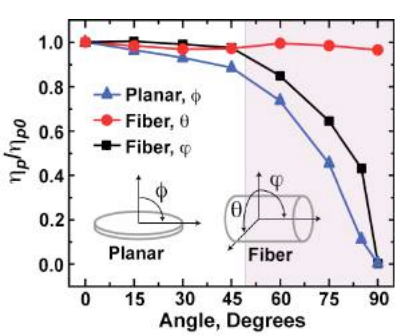


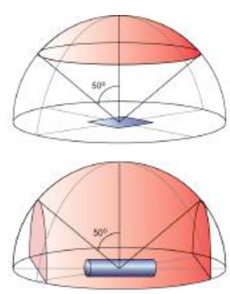


Significant efficiency gains are possible via enhanced light trapping & better transport in thinner layers (predicted η_{pwr} > 10% in some fiber-based configurations using archetypal absorbers)

O'Connor et al. *App Phys Lett*, **92**, 193306 (2008)

"Round" = better for mobile & no-tracking systems





Region of high performance

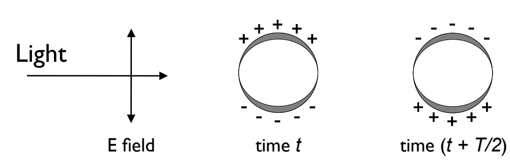
Power:

$$P = \int \eta(\theta)\cdot \text{Intensity}(\theta)\cdot d\theta$$

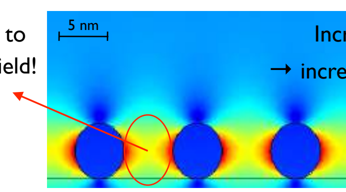
	Normal incidence	Hemispherical Ave.
Planar	0.76 mW/cm²	0.3 mW/cm²
Fiber	0.50 mW/cm²	**0.4 mW/cm²**

O'Connor et al., *App Phys Lett*, **92**, 193306 (2008)

Using Plasmons for absorption enhancement



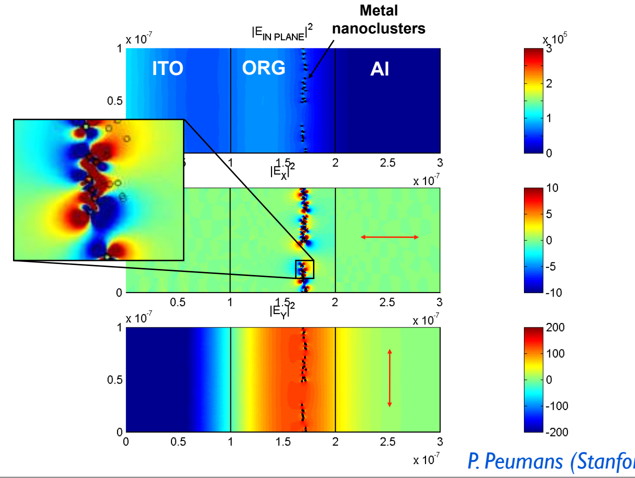
Local field up to 15 x incident field!



Increased field → increased absorption!

P. Peumans (Stanford)

E.g.: Model a Randomized Layer of 10Å Clusters of Ag



P. Peumans (Stanford)

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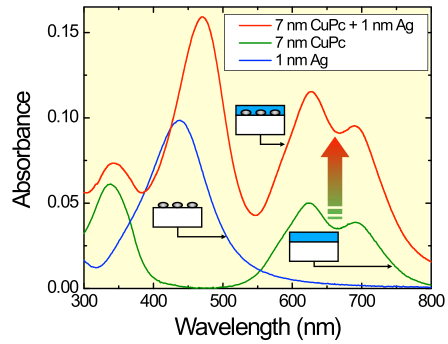
Ag clusters displace absorber molecules... Will the system "break even?"

➥ **Experimental evidence of non-Linear Enhancement of Absorption in CuPc:**



➥ **Have some resonant absorption (potentially very lossy?..)**

➥ **Have some non-resonant absorption (coupled oscillator? incr. path length?)**

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What shape & size of Ag particles are best?

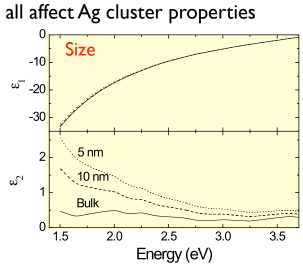
Shape, size, and embedding media all affect Ag cluster properties

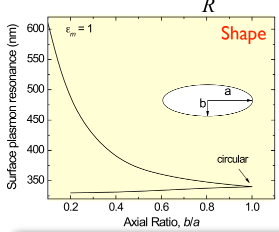
- $\varepsilon(\omega,R)$ for diameter $2R$ less than mean free path, l = 52 nm

$$l(R) = (4/3)R$$

- Relaxation frequency Γ,

$$\Gamma(R) = \Gamma_\infty + \frac{Av_F}{R}$$





Embedding medium

$$\varepsilon_1(\omega) = -2\varepsilon_m(\omega)$$

Rand et al., J. Appl. Phys., 96, 7519 (2004)

Should be possible to red-shift the absorption enhancement region with oblong Ag particles

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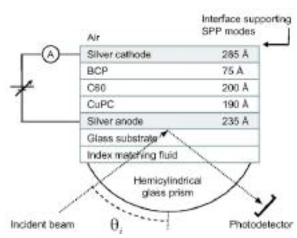
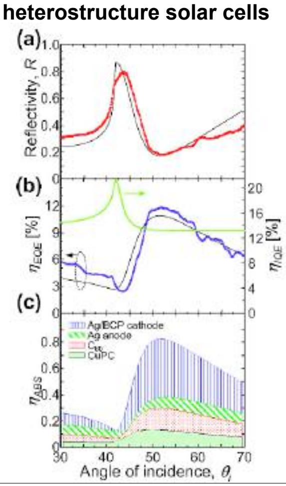
Appl. Phys. Lett. **90**, 121102 (2007); doi:10.1063/1.2714193 (*3 pages*)

Plasmonic excitation of organic double heterostructure solar cells

J. K. Mapel[1], M. Singh[1], M. A. Baldo[1], and K. Celebi





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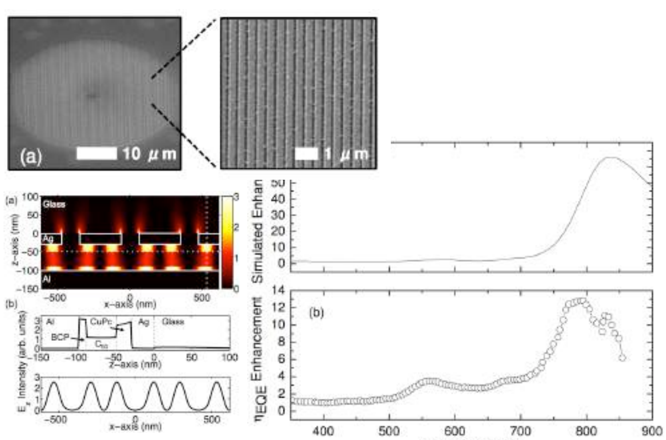
Plasmonic nanocavity arrays for enhanced efficiency in organic photovoltaic cells

Lindquist et al., *Appl. Phys. Lett.* **93**, 123308 (2008)



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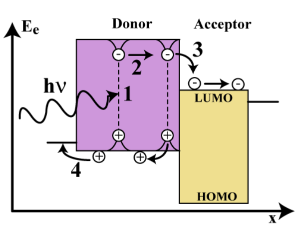
OPV Efficiency – Role of exciton diffusion & dissociation



1. Absorb - η_A
2. Diffuse - η_{ED}
3. Charge-Transfer - η_{CT}
4. Charge-Collect - η_{CC}

$$\eta_{EQE} = \eta_A \cdot \eta_{ED} \cdot \eta_{CT} \cdot \eta_{CC}$$

Until now, we assumed perfect exciton dissociation (η_{ED}~1)
We also didn't discuss the exciton diffusion process...

Next:
Exciton diffusion
Exciton dissociation

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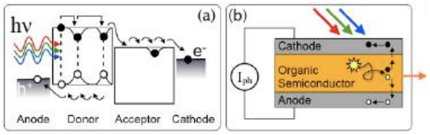
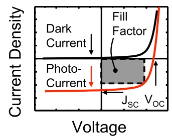
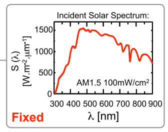
OPV Efficiency – Role of exciton diffusion & dissociation



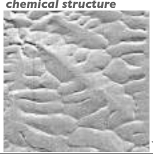


$$\eta = \frac{J_{SC} V_{OC} FF}{P_{inc}}$$

$$J_{SC} = \int \eta_{EQE} S(\lambda) d\lambda$$

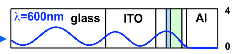


Improve exciton diffusion via ordering, chemical structure



$$\eta_{EQE}(\lambda) = \eta_A(\lambda)\eta_{IQE}(\lambda)$$

$$G(x) = \frac{1}{2} c\varepsilon_0 n\alpha \frac{|(E_I+E_R)^2|}{|E_0^2|}$$



$$\frac{\partial^2 n}{\partial x^2} = \frac{1}{L_D^2} n - \frac{\tau}{L_D^2} G(x)$$

Origins and magnitude of L_D?..

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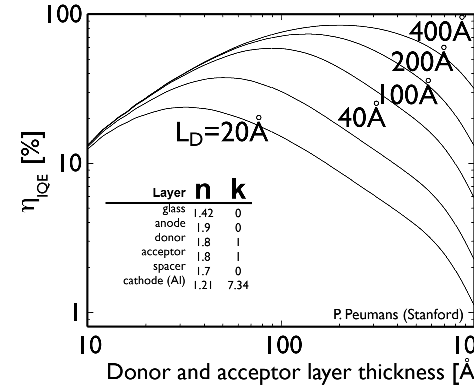
How much influence does L_D have on efficincy?



Data courtesy P. Peumans

For typical nano-xtalline or amorphous thin films, L_D = small;
L_D is very important for device performance ($L_D \sim L_{abs}$ is good)

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Exciton diffusion ("Excitation energy transfer = EET")

Exciton diffusion length $L = \sqrt{D\tau}$

Diffusivity [cm²/s] : $D = a^2 k_{ET}$

$$k = \frac{2\pi}{h} \times V^2 \times \int dE \times J(E)$$

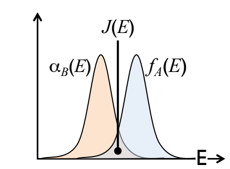
Electronic coupling
Energy independent
Distance dependent

V^2 has a more complicated form...

Franck Condon weighted density of states
Energy independent
Distance dependent

$$J(E) = f_A(E)\alpha_B(E)$$

(spectral overlap factor)



- $J(E)$ implies conservation of energy
- $\alpha_B(E)$ and $f_A(E)$ are normalized absorption & emission spectra on energy scale

Scholes, et al. *Annu. Rev. Phys. Chem.* **54**, 57–87 (2003)

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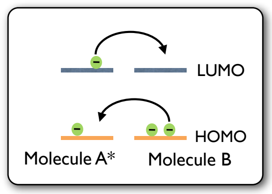
Electronic coupling, V_{DA}



Many electron wavefunction

$$\psi_i = \frac{1}{\sqrt{2}}\left(\psi_A^*(r_1)\psi_B(r_2) - \psi_A^*(r_2)\psi_B(r_1)\right)$$

$$\psi_f = \frac{1}{\sqrt{2}}\left(\psi_A(r_1)\psi_B^*(r_2) - \psi_A(r_2)\psi_B^*(r_1)\right)$$

$$V_{DA} = \langle\psi_i|H_{AB}|\psi_f\rangle$$
$$= \langle\psi_A^*(r_1)\psi_B(r_2)|H_{AB}|\psi_A(r_1)\psi_B^*(r_2)\rangle - \langle\psi_A^*(r_1)\psi_B(r_2)|H_{AB}|\psi_A(r_2)\psi_B^*(r_1)\rangle$$

Coulomb integral

Forster transfer $\propto \frac{1}{r_{AB}^6}$

Exchange integral

Dexter transfer $\propto \exp(-\beta r_{AB})$

Scholes et. al *Annu. Rev. Phys. Chem.* **54**, 57–87 (2003)

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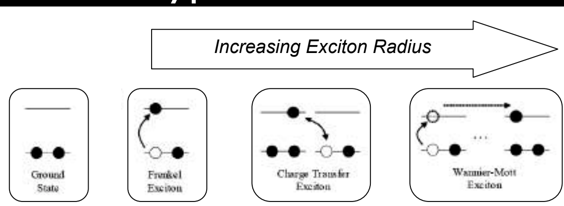
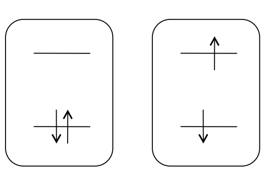
Types of excitons:



Qauntum Mechanics | Spin States of Excitons:



$\Psi = |\uparrow\uparrow\rangle$
$\Psi = |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$ S=1, Triplet
$\Psi = |\downarrow\downarrow\rangle$

$\Psi = |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$ S=0, Triplet

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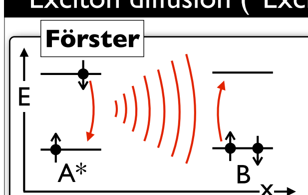
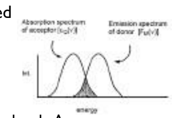
Exciton diffusion ("Excitation energy transfer = EET")

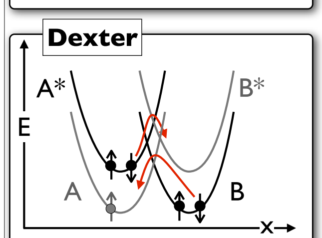


Singlets:
Forster transfer is dominant
Electrons are not exchanged

$$k_{EET} = \frac{1}{\tau_D}\left(\frac{R_0}{r_{AB}}\right)^6$$



R_0: Forster critical radius
τ_D: Fluorescence lifetime of molecule A
Long-range (>100Å), incr. with η_{PL} & oscil. str. & spectral overlap



Triplets:
Dexter transfer is dominant
Electrons are exchanged

$$k_{EET} = \frac{2\pi}{h} K J_{ex} \exp\left(-\frac{2r_{AB}}{L}\right)$$

K: Exchange integral strength
J_{ex}: Spectral overlap
L: Average van der Waals radius
Poor for R > 10 Å
Favors conserved spin
Indep. of oscillator strength of A or η_{PL} of B

Pope & Swenberg
Electronic Processes in Organic Crystals, p.102

Speiser et al., *Chem. Rev.* **96**, 1953 (1996)

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Measuring Exciton Diffusion

From:
"Molecular Semiconductors in Organic Photovoltaic Cells" by Hains, Liang, Woodhouse, and Gregg, *Chemical Reviews* (2010)

- Measurement of exciton diffusion length is tricky...
- Most prior measurements seem to be limited by exciton quenching, rather than diffusion:

Kenkre, V. M.; Wong, Y. M. *Phys. Rev. B: Condens. Matter* **22**, p5716., (1980)

Kenkre, V. M.; Parris, P. E.; Schmidt, D. *Phys. Rev. B: Condens. Matter.*, **32**, p.4946, (1985)

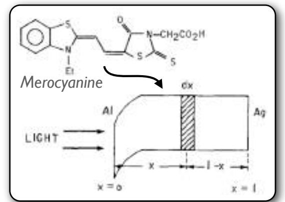
Lunt et al., *J. Appl. Phys.* **105**, p.053711 (2009)

Rim & Peumans, *J. Appl. Phys.* 103, 124515 (2008)

Measuring Exciton Diffusion

Example 1: Photocurrent spectroscopy

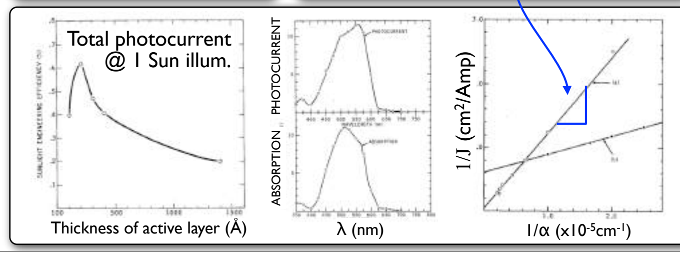
Ghosh & Feng, *J. Appl. Phys.* **49**, 5982 (1978)



$$J_1 = -q\phi J_{A1} = qN\phi\,[\alpha/(\beta+\alpha)]$$

$$1/J_1 = (1+\beta/\alpha)(N\phi q)^{-1}$$

$$\beta = 1/L \qquad \alpha(\lambda)$$

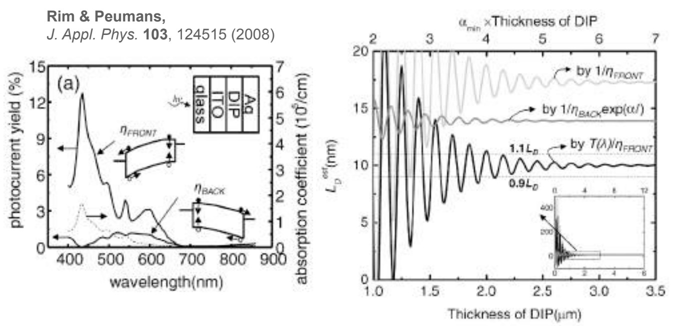


Measuring Exciton Diffusion

Example 1: Photocurrent spectroscopy (e.g. device modeling)

Beware of optical interference effects...

Rim & Peumans, *J. Appl. Phys.* **103**, 124515 (2008)



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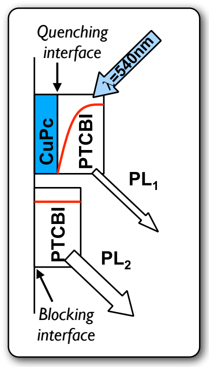
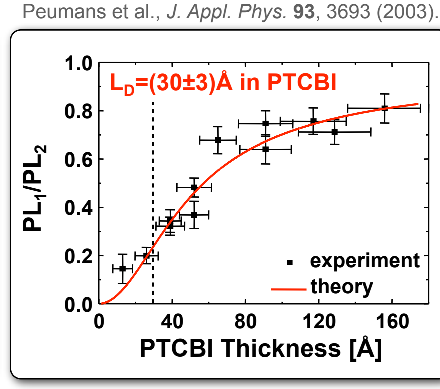
Measuring Exciton Diffusion

Example 2: Photoluminescence quenching (Assume continuum, isotropic diffusion)

Peumans et al., *J. Appl. Phys.* **93**, 3693 (2003).

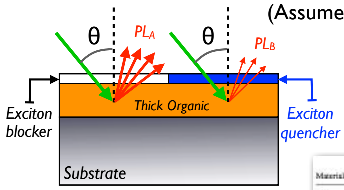




Measuring Exciton Diffusion

Method 3: Spectrally resolved PL quenching (Assume continuum, isotropic diffusion)

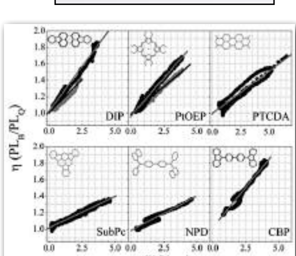
Lunt et al., *J. Appl. Phys.* **105**, 053711 (2009)



$$\eta(\alpha) = \frac{PL_B(\alpha)}{PL_Q(\alpha)} = \frac{\alpha(\lambda)L_D}{\cos(\theta_\lambda)} + 1$$

Material	Exciton	Crystallinity (Orientation)	Quenching/Blocking Layers	R_0 with C_{60} (nm)	L_D (nm)
NPD	S	Amorph.	C_{60}/BCP	2.4	5.1 (±1.0)ᵃ
CBP	S	Amorph.	C_{60} (or NTCDA)/Bare	2.7	16.8 (±0.8)ᵃ
SubPc	S	Amorph.	C_{60}/Bare	1.1	8.0 (±0.3)
PTCDA	S	C.-55 nm (flat)	C_{60} (or NPD)/NTCDA	0.9	10.4 (±1.0)
DIP	S	C.->150 nm (upright)	C_{60}/Bare	1.2	16.5 (±0.4)
DIP	S	C.-30 nm (flat)	C_{60}/Bare	1.2	21.8 (±0.6)
PtOEP	T-Mon.	C.->150 nm (upright)	C_{60}/BCP	0.6	18.0 (±0.6)
PtOEP	T-Dim.	C.->150 nm (upright)	C_{60}/BCP	0.6	13.1 (±0.5)

Material	Exciton	(ns)	$(10^{-4}\ cm^2/s)$
NPD	S	3.5ᵃ	0.7(±0.2)
CBP	S	0.7ᵃ	40 (±12)
SubPc	S	≤1	≥6.4
PTCDA	S	3.2 (±0.7)	3.4 (±0.9)
DIP (upright)	S	1.8 (±0.5)	15 (±4)
DIP (flat)	S	1.8 (±0.5)	26 (±7)
PtOEP	T-Mon.	800 (±50)	0.041 (±0.003)
PtOEP	T-Dimer	2800 (±300)	0.00061 (±0.0001)



Designing devices around L_D

Strategy 1:
* Accept short L_D
➡Design device around short L_D

Strategy 2:
* Do not accept low L_D
➡Find materials with large L_D
➡Increase L_D through ordering

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Designing devices around L_D

Strategy I:
* Accept short L_D
➥ Design device around short L_D

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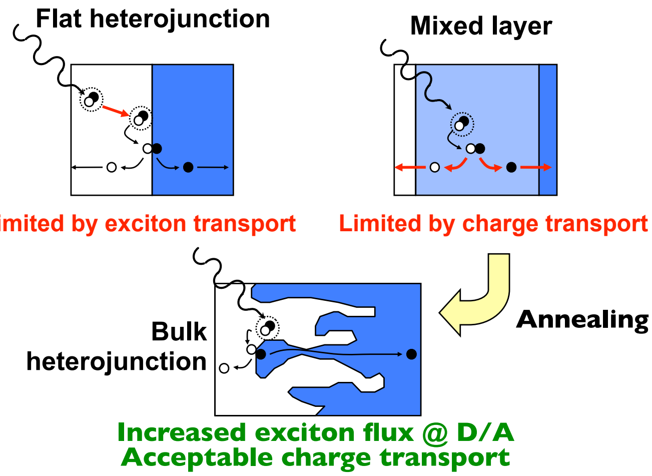
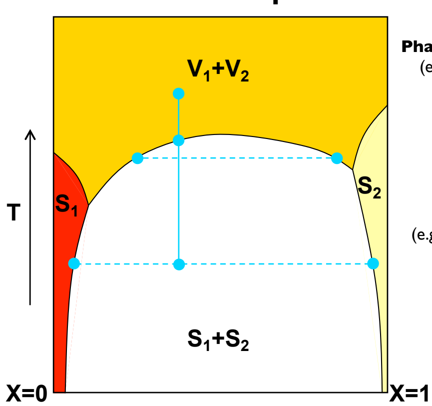
Bulk Heterojunction (BHJ)



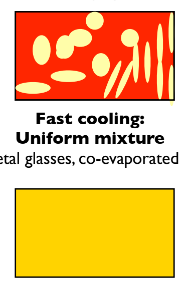
Non-Equilibrium Mixture of Immiscible Phases

➥ **Model: spinodal decomposition**



Slow cooling:
Phase-separated microstructure
(e.g. stainless steel, polymer blends)

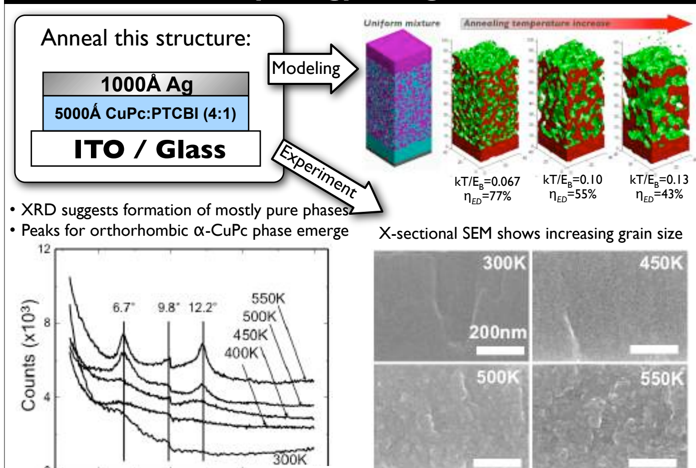
Fast cooling:
Uniform mixture
(e.g. metal glasses, co-evaporated mat'ls)



Courtesy P. Peumans

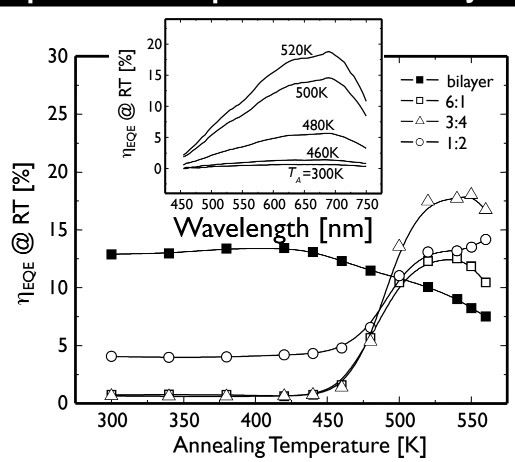
Note: Spinodal decomposition ➔ phases aren't pure D / pure A! (see D. Ginger's work, UWash)
But... some evidence exists that the phase-segregated regions could be "pure" D or A...

Evidence for morphology change in annealed films



From Peumans, *et al.* Nature (2003)

Device performance improves as result of BHJ formation:



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From Peumans, *et al.* Nature (2003)

Outline

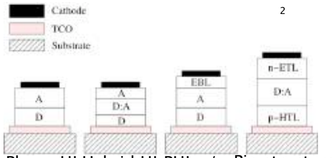
✔ **1. Energy & solar cells**
- A. Why we need energy in the first place
- B. Where does our energy come from and how do we use it?
- C. Why bother with solar electricity?
- D. Scalability & cost challenges of conventional solar cells

✔ **2. Small molecular organic PV cells – Part 1**
- A. Material system
- B. Physics of organic PV materials & devices

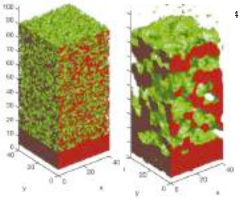
✔ **3. Improving efficiency of OPV cells – Part 2**
- A. Thin-film optics & plasmonics for improved absorption
- B. Exciton diffusion to and dissociation at D/A interface
- C. Increasing open circuit voltage and fill factor

4. Enabling low-cost modules & installation
- A. Eliminating costly materials from device structure
- B. Novel architectures
- C. Device processing

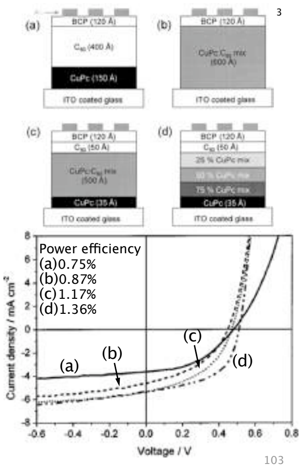
VTE deposited OPV – structure and morphology



Not annealed Annealed – 550K



BHJ from mixed layer 1:1 D:A deposited by VTE via phase segregation on annealing



[2] Riede M. et al., Nanotechnology, **19** 424001 (2008)
[3] Sullivan P. et al., APL **84** 1210 (2004)
[4] Peumans P. D et al., Nature **425** 158 (2003)

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How much interface is needed?..

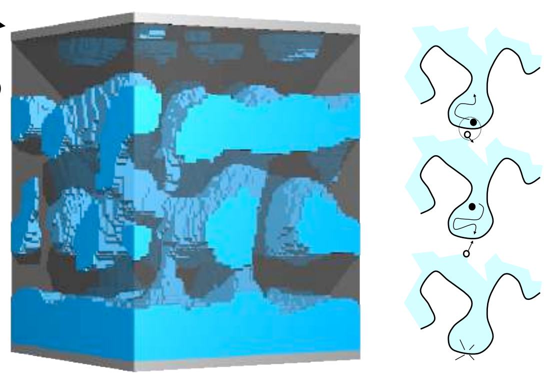
Balance between: Exciton dissociation
Charge collection

TABLE 2. Average Domain Size, Specific Interface Area, and Cell Efficiencies of Mixed Films before and after Annealing at Different Numbers of MC Steps for a 100 × 100 × 60 nm³ Lattice

MC steps	0	1	10	50	100
Morphology					
Domain size (a)	0.98± 0.02	2.02± 0.04	4.9± 0.1	7.9± 0.2	10.3± 0.7
Specific interface area (a^2)	61.22±0.03	29.70±0.06	12.2±0.1	7.6±0.3	6±1
Charge collection	0.31±0.01	0.34±0.01	0.40±0.01	0.44±0.02	0.43±0.01
Exciton diffusion	1.00±0.01	1.0±0.01	0.97±0.01	0.93±0.01	0.87±0.02
Int. Quant. Eff.	0.31±0.01	0.34±0.01	0.39±0.01	0.41±0.02	0.37±0.02

Fan Yang, S.R. Forrest, *ACS Nano*, **2**, 1022 (2008)

Modeling charge separation & extraction in molecular BHJ solar cells



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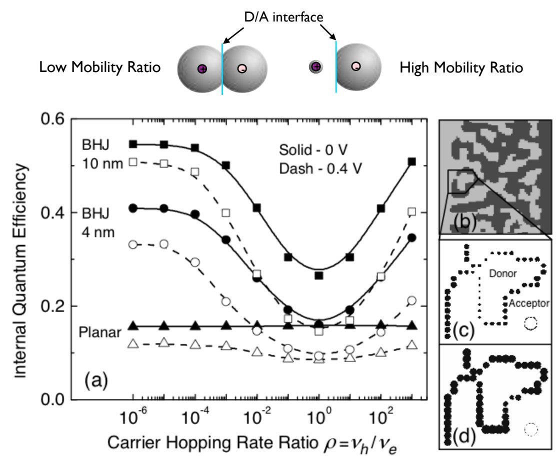
Courtesy of P. Peumans (Stanford)

Role of the Ratio of Charge Carrier Mobilities



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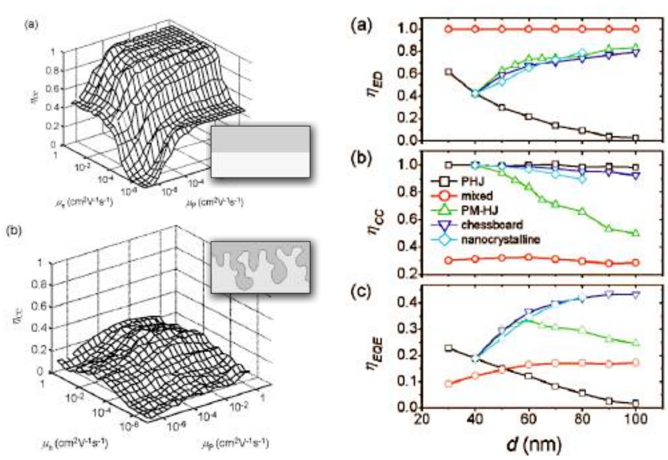
S. Zhao and P. Peumans, submitted

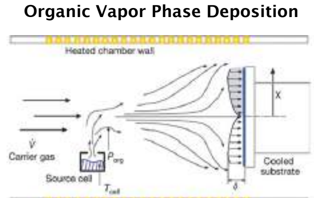
Role of BHJ morphology, charge mobility in η_{PWR}



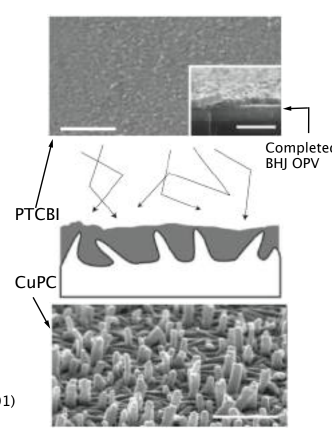
Fan Yang, S.R. Forrest, *ACS Nano*, **2**, 1022 (2008)

OVPD (organic vapor phase deposition) growth of high quality films (incl. controlled BHJ OPV)

Organic Vapor Phase Deposition



- ✓ Compact
- ✓ Ultra-clean chamber
- ✓ Parameter control (T_{source}, T_{sub}, Flow Rate, carrier gas)
- ✓ High morphology control



[5] Shtein M. et al, J. Applied Physics, **89** 1470 (2001)
[6] Yang F. et al, Nature Mater., **4** 37 (2005)

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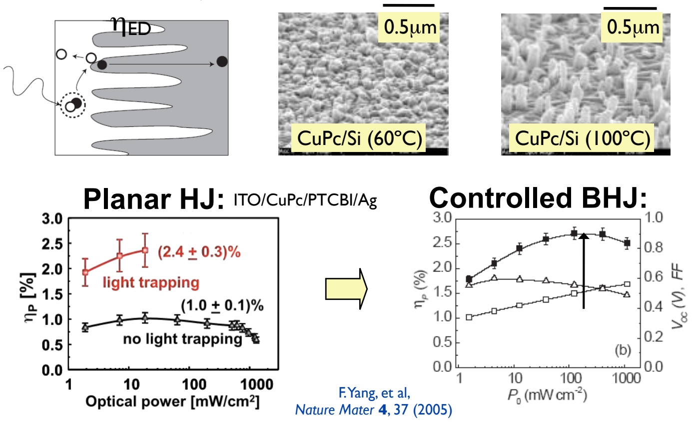
Ordered Bulk Heterojunction works better

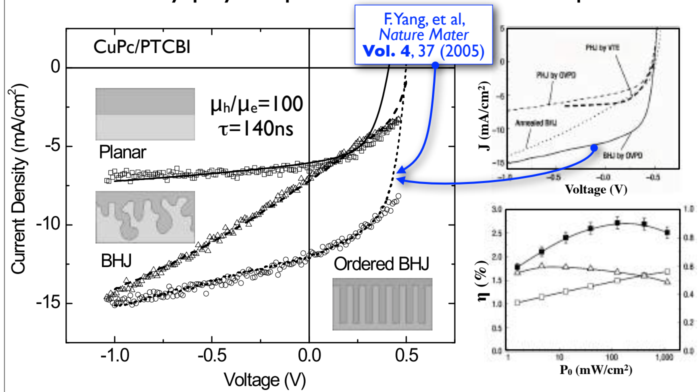
Lots of Interface, incr

Line-of-sight pathway: reduces chance of parasitic recombination
improves rate of charge extraction



BHJ geometry comparison: Tortuosity kills

- Compare: same parameters, but different geometries
- Geometry plays important role for device optimization



Model: P. Peumans (Stanford) *Expt: Yang, Shtein, Forrest (Nature Mater. **4**, p.37, 2005)*

Designing devices around L_D

Strategy 2:

* Do not accept low L_D

➥Find materials with large L_D

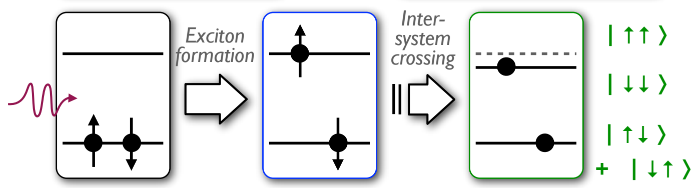
➥Increase L_D through ordering

Increasing L_D via exciton lifetime

$$L_D \sim \sqrt{D \cdot \tau}$$

D = diffusivity
[=] cm²/s
∝ electronic coupling

τ = lifetime
[=] s
∝ *f(structure, quenching)*

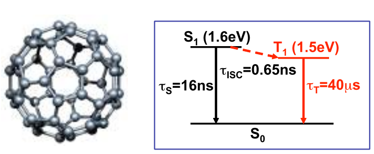


Absorption

Singlet exciton
| ↑↓ 〉 – | ↓↑ 〉 τ~10⁻⁹s
Can undergo Förster Xfer

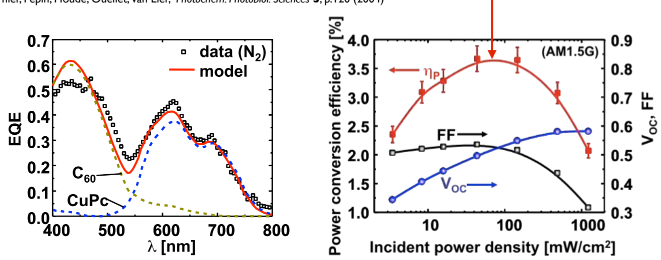
Triplet exciton
τ~10⁻⁶–10⁻³s
Dexter Xfer dominates

Example: C_{60} has large L_D, improves device



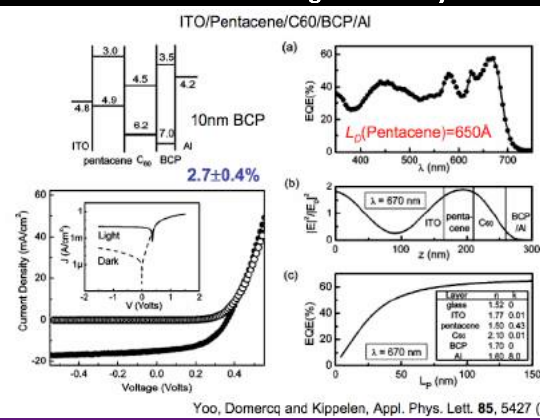
Fast ISC $S_1 \rightarrow T_1$
Long-lived T_1 (triplet)
→ $L_{D\ C60}$ ~ 400A
→ η_{pwr} = 3.6%

Fournier, Pepin, Houde, Ouellet, van Lier, *Photochem. Photobiol. Sciences* **3**, p.120 (2004)



Peumans & Forrest, *Appl. Phys. Lett.*, **79** (2001) p.126

OK, we found C_{60}, now need exciton blocking layers (EBL) to maintain high efficiency



Yoo, Domercq and Kippelen, Appl. Phys. Lett. **85**, 5427 (2004).

Knowing L_D is important for efficiency, device design
1) Can we measure it? 2) What can we do about it?..

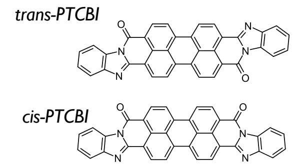
Designing devices around L_D

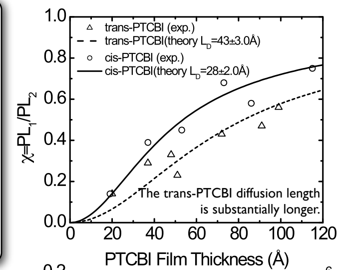
Strategy 2:
* Do not accept low L_D
➥Find materials with large L_D
➥Increase L_D through ordering

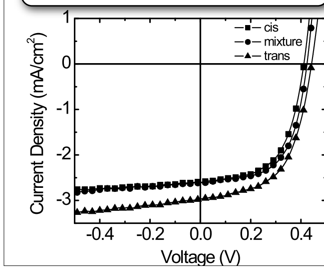
Increase L_D via molecular ordering

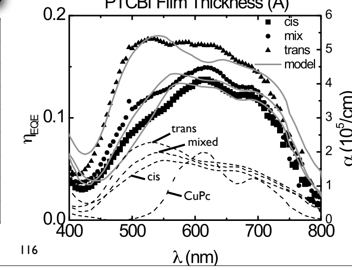
trans-PTCBI

cis-PTCBI









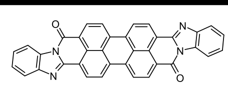
Increase L_D via molecular ordering ➡ Keep molecule same

Relationship between Crystalline Order and Exciton Diffusion Length in Molecular Organic Semiconductors

By Richard R. Lunt, Jay B. Benziger, and Stephen R. Forrest*

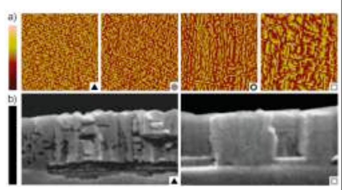
Adv. Mater. (2009)
DOI: 10.1002/adma.200902827

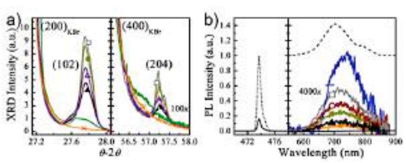
PTCBI
KBr

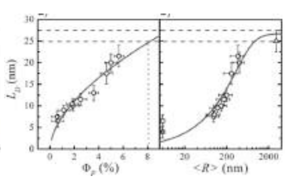


$$L_D = \sqrt{\frac{\kappa^2\Phi_F}{8\pi n^4}\frac{\sigma}{a^4}} = \sqrt{\frac{\Phi_F}{6}\frac{R_{00}^3}{a^2}}$$

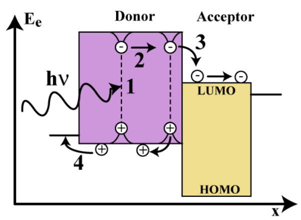
σ = Förster overlap integral
Φ_F = Fluoresc. quantum yield
a = Average hopping distance







OPV Efficiency – Role of exciton diffusion & dissociation



1. Absorb - η_A
2. Diffuse - η_{ED}
3. Charge-Transfer - η_{CT}
4. Charge-Collect - η_{CC}

$\eta_{EQE} = \eta_A \cdot \eta_{ED} \cdot \eta_{CT} \cdot \eta_{CC}$

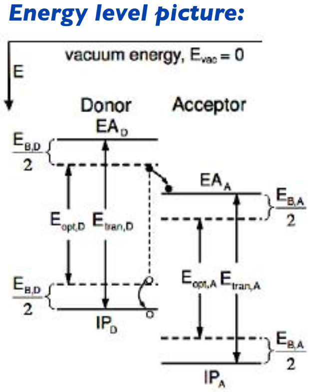
Until now, we assumed perfect exciton dissociation (η_{ED}~1)
We also didn't discuss the exciton diffusion process...

Next:
managing excitons:
☑ 1. Exciton diffusion
2. Exciton dissociation

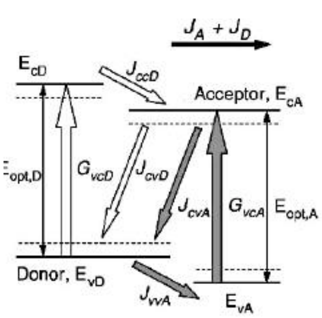
Is exciton dissociation @ D/A interface perfect?

Exciton dissociation at D/A junctions

Energy level picture:



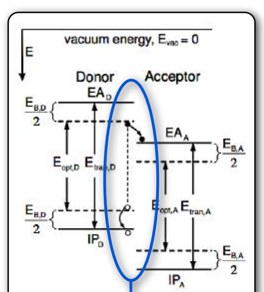
Important fluxes:

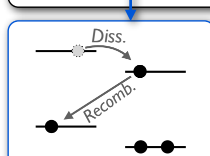


$$k_{if} = \left(\frac{4\pi^3}{h^2\lambda_{if}k_BT}\right)^{1/2} V_{if}^2 \exp\left(-\frac{(E_{if}+\lambda_{if})^2}{4\lambda_{if}k_BT}\right)$$

Rand et al. *Phys. Rev. B* **75**, 115327 (2007)
Rand et al., Prog. in Photovoltaics, **15**, 659 (2007)

Look at the Charge-Transfer exciton forming @ D/A interface





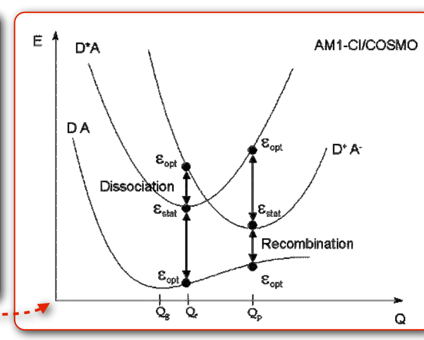
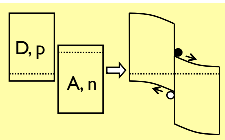


Figure 5. Potential energy curves of the donor/acceptor pair in the ground state (DA), the lowest intramolecular excited state (D*A), and the lowest charge-transfer state (D⁺A⁻). We illustrate the nature of the transitions calculated at the AM1-CI/COSMO level and the dielectric constants chosen to do so in order to calibrate the location of the CT state in the INDO/SCI calculations for the two processes.

Lemaur, et al., *JACS* **127**, 6077 (2005)

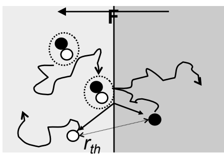
Why do bilayer D/A organic solar cells work so well?

1. Doping→V_{bi} is localized

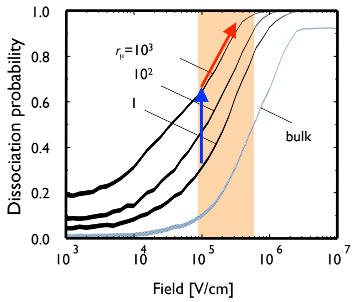


Peumans, *et al.*, *J. Appl. Phys.* **93**, 3693 (2003).

2. Entropic Driving Force



Peumans and Forrest, Chem. Phys. Lett. (2004).



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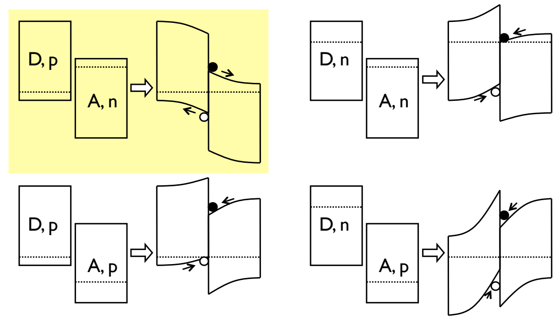
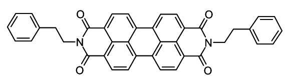
Doping is important

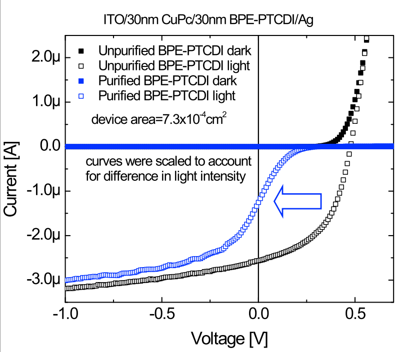


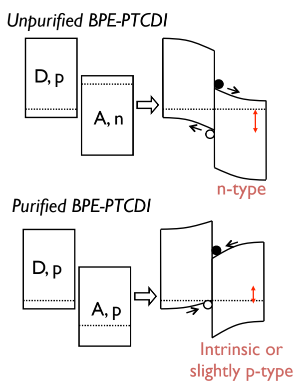
- Doping determines the location of the Fermi-level
- Only combination that works: p-type doped donor and n-type doped acceptor
- If there is unintentional doping: make sure it's the right type or correct it

Example of doping @D/A: CuPc/BPE-PTCDI

- Purification of BPE-PTCDI results in an almost rigid shift of the photocurrent-voltage curve







A. Liu, et al., Adv. Mater. **2008**, 1065-1070 (2008).

Next:

Origins of V_{OC} & ways to increase it

a. Eg & tandem devices
b. Doping
c. HOMO-HOMO offset @ D/A
d. Work function
e. Structural characteristics (J_{SO})

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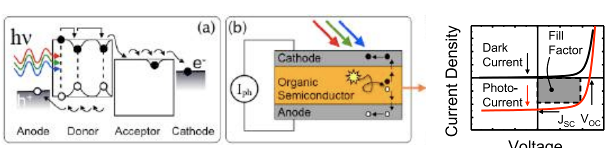
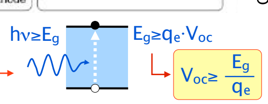
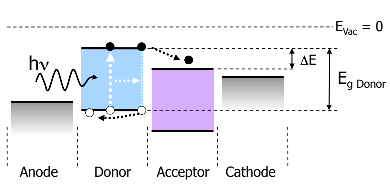
OPV Efficiency: Role & origins of V_{OC}



$$\eta=\frac{J_{SC}V_{OC}FF}{P_{inc}}$$

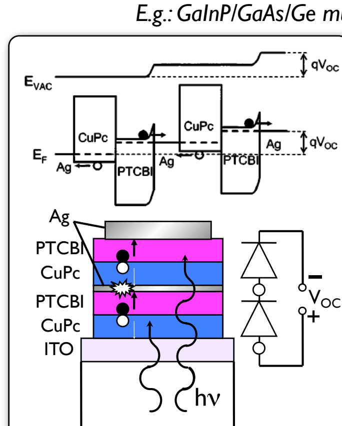


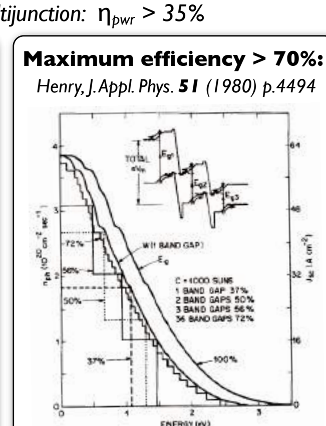


$V_{OC\ max}$ is limited firstly by the absorption gap (energy of e/h pair cannot exceed E_g)

Increasing V_{OC}: Use multiple cells (E_{g1}, E_{g2},..)

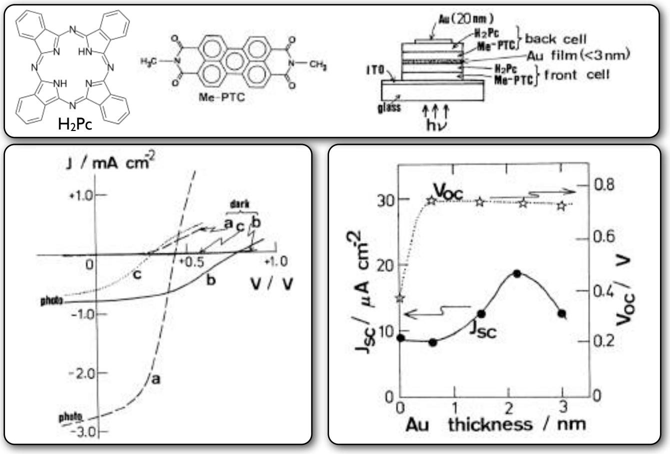
Multiple band-gap cells in series can better match the solar specturm
E.g.: GaInP/GaAs/Ge multijunction: η_{pwr} > 35%





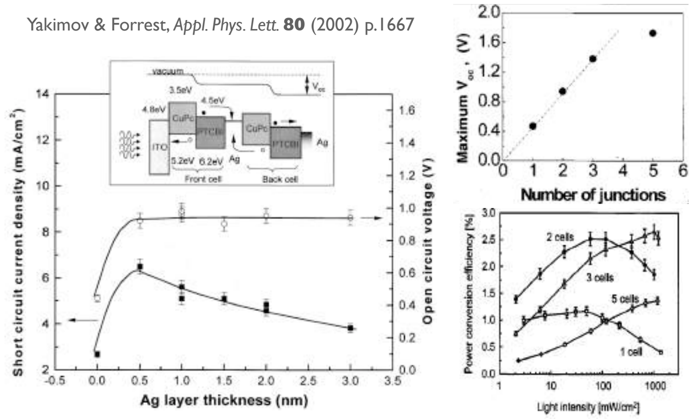
Early small-molecular tandem OPV cell

Hiramoto et al., Chemistry Letters, ***19*** *(1990) p.327*



Multiple stacked small-molecular OPV cells:

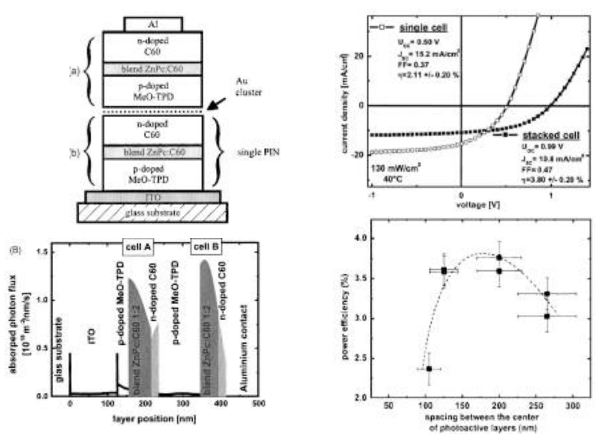
Yakimov & Forrest, *Appl. Phys. Lett.* **80** (2002) p.1667



V_{OC} increases with # of sub-cells
Diminishing returns for η_{pwr} due to R_S

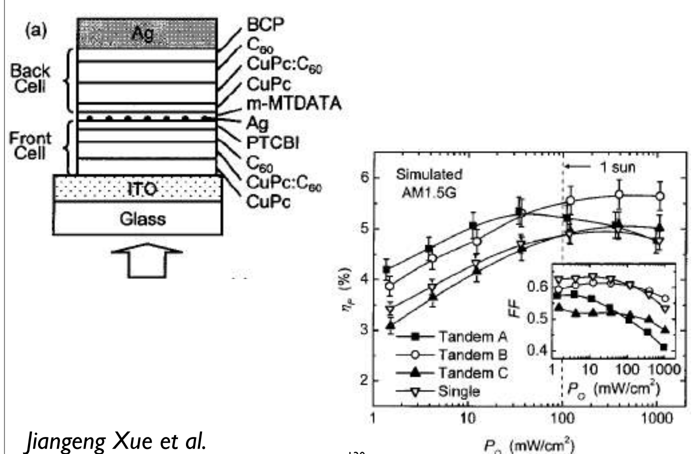
Reducing R_S via *p-i-n* architecture (doped wide-gap transport layers)

Drechsel et al. *Applied Physics Letters,* **Vol. 86**, p. 244102 (2005)



Some improvement, but better to find complementary E_g

Tandem + BHJ combination in small molecular OPV cells



Jiangeng Xue et al.

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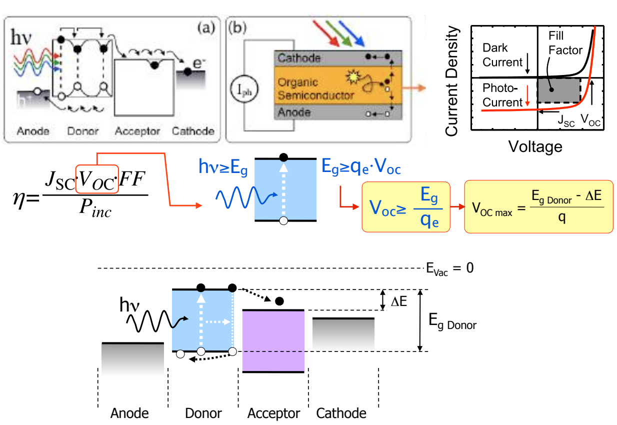
OPV Efficiency: Role & origins of V_{OC}



But $V_{OC\,max}$ in a heterojunction cell is lower than E_g/q_e,
because need to overcome E_{bind} & drive e/h separation &

Linear dependence of JSC on light intensity is evidence for *geminate charge-pair recombination*:

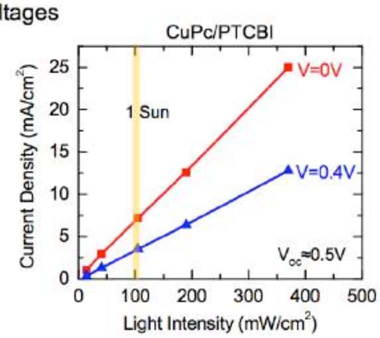
Current density vs. light intensity
- is linear
- for all voltages

$$J = R_{Generation} - R_{Recombination}$$

$$J = \alpha \cdot L - (\beta \cdot n + \gamma \cdot n^2)$$

Non-geminate

Geminate Recombination



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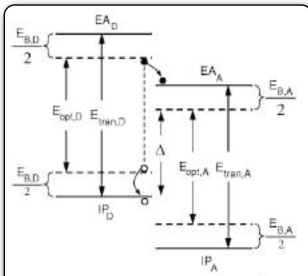
P. Peumans (Stanford)

Voc vs. Absorption gap, Exciton binding energy, Offsets

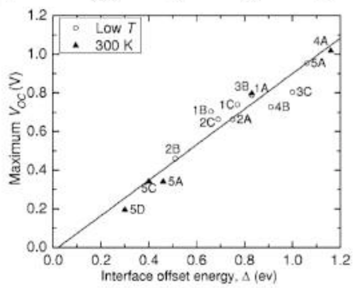
Rand et al., Phys. Rev. B, **75**, p.115327 (2007)



$$qV_{OC}^{max} = IP_D - EA_A - \frac{q^2}{4\pi\varepsilon_0\varepsilon_r r}$$

Δ E_Bind

Label[a]	Material[b]	IP[c] (eV)	EA (eV)[d]	E_{opt} (eV)
1	CuPc	5.2(7)	3.2(7)	1.7
2	Pentacene	5.1(9)	3	1.8(8)
3	NPD	5.5	1.7	3.1
4	SubPc	5.6		2.0
5	Ru(acac)$_3$	4.9		2.1
A	C_{60}	6.2(4)	3.6	1.8
B	C_{70}	6.4(1)	4.3	1.7(3)
C	PTCBI	6.2	3.6	1.7
D	PTCDA	6.8	4.6	2.2



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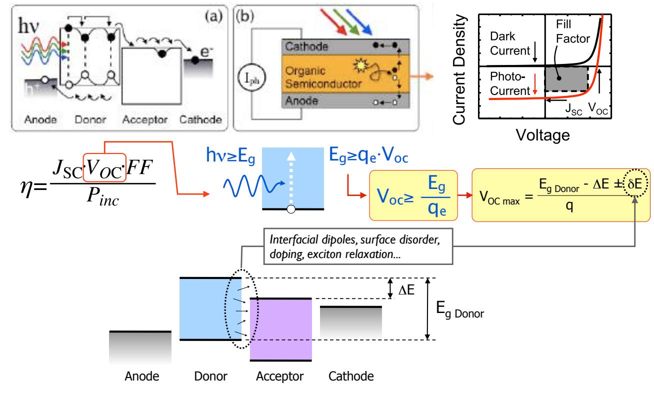
Role of doping in Voc



... but can have additional polarization due to doping, interfacial disorder / dipoles, carrier and exciton polarization effects

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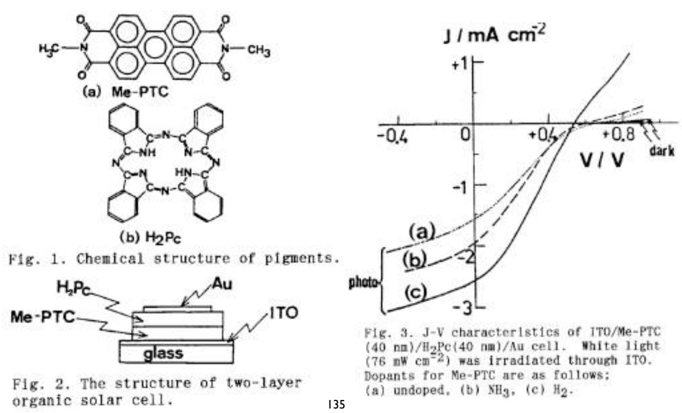
Early example of doping in bi-layer OPV cell

Hiramoto et al., *Chemistry Letters* **19** (1990) p.119: use NH_3 & H_2 to dope

➥ *Minimal effect on Voc, large effect on Jsc*



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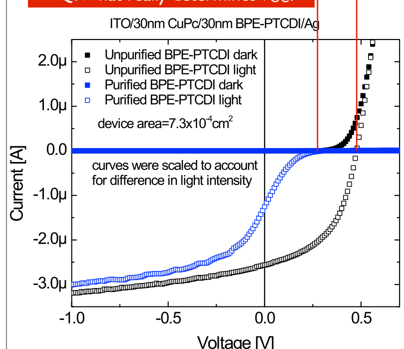
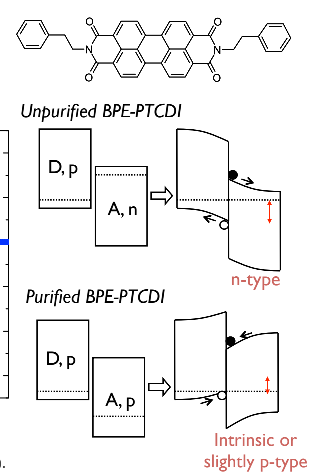
Recent example of doping in organic OPV cell

- Purification of BPE-PTCDI results in an almost rigid shift of the photocurrent-voltage curve
- Note also the shift in Voc
- Q: What really determines Voc?





A. Liu, et al., Adv. Mater. **2008**, 1065-1070 (2008).

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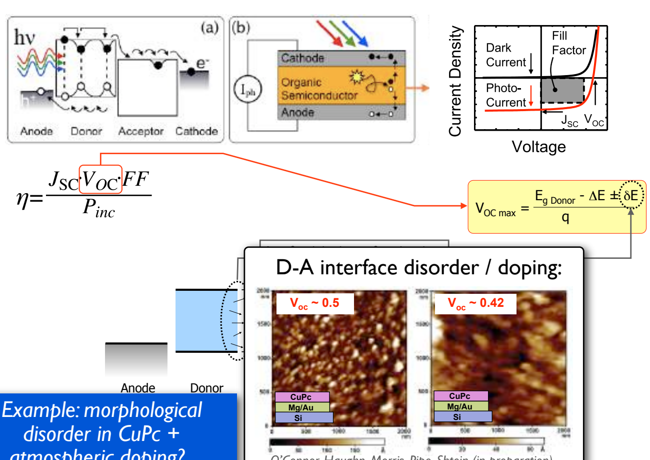
Unintentional doping via grain boundary diffusion?



Example: morphological disorder in CuPc + atmospheric doping?..

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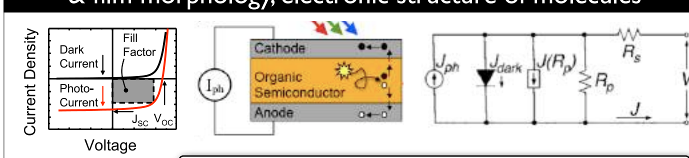
Further insights into Voc based on *equivalent circuit* analysis & film morphology, electronic structure of molecules



Current density in photodiode:

$$J = \frac{R_p}{R_s + R_p}\left\{J_s\left[\exp\left(\frac{q(V-JR_s)}{nk_BT}\right)-1\right]+\frac{V}{R_p}\right\} - J_{ph}(V)$$

If minimal leakage, $R_P \gg R_S$

$$J = J_s\left[\exp\left(\frac{q(V-JR_s)}{nkT}\right)-1\right] - J_{ph}(V)$$

Saturation current density

Diode Ideality factor

Thermally generated current

Photo-generated current

Bube & Fahrenbruch, Advances in Electronics and Electron Physics, Vol. 56, Academic Press, New York, 1981
Fahrenbruch & Aranovich, Solar Energy Conversion, Springer-Verlag, New York, 1979
Rand et al., Phys. Rev. B **75**, 115327 (2007)

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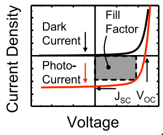
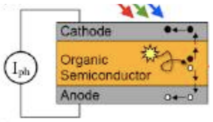
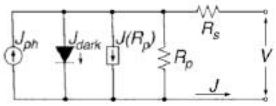
Further insights into V_{OC} based on *equivalent circuit* analysis & film morphology, electronic structure of molecules







$$J = \frac{R_p}{R_s + R_p}\left\{J_S\left[\exp\left(\frac{q(V - JR_s)}{nk_BT}\right) - 1\right] + \frac{V}{R_p}\right\} - J_{ph}(V)$$

$$J = J_S\left[\exp\left(\frac{q(V - JR_s)}{nkT}\right) - 1\right] - J_{ph}(V)$$

Assume:
$J = 0$ → $V = V_{OC}$,
$J_{SC} = J_{ph}(0)$
R_S = small
→
$$V_{oc} \approx \frac{nkT}{q}\ln\left(\frac{J_{SC}}{J_S}\right)$$
→ ***Need to minimize dark current, J_S***

Q: What are the origins of J_S?

Perez et al.,
JACS **131** (2009) 9281

Further insights into V_{OC} based on *equivalent circuit* analysis & film morphology, electronic structure of molecules

$$J = J_S\left[\exp\left(\frac{q(V - JR_s)}{nkT}\right) - 1\right] - J_{ph}(V) \quad \& \quad V_{oc} \approx \frac{nkT}{q}\ln\left(\frac{J_{SC}}{J_S}\right)$$

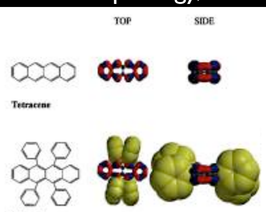
$$J_S = J_{SO}\exp\left(\frac{-\Delta E_{DA}}{2nkT}\right) \rightarrow V_{oc} = \frac{nkT}{q}\ln\left(\frac{J_{SC}}{J_{SO}}\right) + \frac{\Delta E_{DA}}{2q}$$

So…

- Know ΔE_{DA} (from Rand *et al.*)
- Know J_{SC} from measurements
- Can find V_{OC} from measurements
- ➥ Compile **J_{SO}** for various materials, look for trends

Perez et al.,
JACS **131** (2009) 9281

Further insights into V_{OC} based on *equivalent circuit* analysis & film morphology, electronic structure of molecules



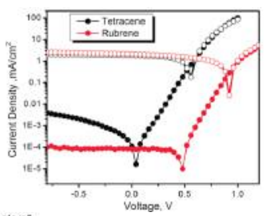


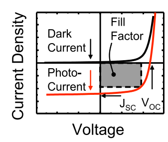
Table 2. Comparison of Measured and Calculated Performance Parameters[a]

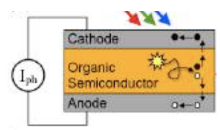
donor	J_{SO}	film	$(nkT)/(q)\ln((J_{sc})/(J_{so}))$	$(\Delta E_{DA})/(2q)$	V_{oc} calcd	V_{oc} exptl
SubPc	5.5	Am	−0.02	1.0	0.98	0.97
rubrene	0.43	Am	0.09	0.9	0.99	0.92
NPD	11	Am	−0.10	0.95	0.85	0.85
PtTPBP	12	Am	−0.05	0.7	0.65	0.69
tetracene	150	PC	−0.24	0.80	0.56	0.55
PtOEP	5.1×10^{3}	PC	−0.40	0.9	0.50	0.52
PdTPBP[b]	9.1	–	−0.082	0.65	0.57	0.61
CuPc	1.5×10^{4}	PC	−0.41	0.85	0.44	0.48
PtTPNP	62	–	−0.15	0.45	0.30	0.31

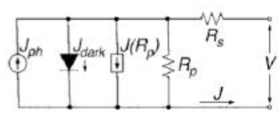
[a] J_{SO} are in mA/cm², and the remaining data are in V. "Film" refers to the morphology of the donor thin film, as determined by X-ray diffraction, Am = amorphous, PC = polycrystalline.[17,30−36] [b] Illumination intensity = 0.5 suns.

Perez et al., *JACS* **131** (2009) 9281

Fill Factor







$$FF \equiv \frac{J \cdot V}{J_{SC} \cdot V_{OC}}$$ & ideally, $R_P \rightarrow \infty$ and $R_S \rightarrow 0$

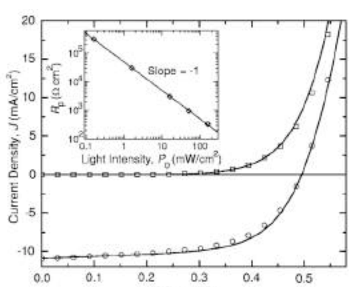
Realistically: $$\mathrm{FF}(R_s, R_p) \approx \mathrm{FF}(0, \infty)\left(1 - \frac{J_{SC}R_s}{V_{OC}} - \frac{V_{OC}}{J_{SC}R_p}\right)$$

For given V_{OC}, want to **minimize R_S**, **maximize R_P**

(i.e. conductive layers, low leakage & dark currents = good)

Rand et al., Phys. Rev. B **75**, 115327 (2007)

Effects of photoconductivity on R_P:



Rand et al.,
Phys. Rev. B **75**, 115327 (2007)

Molecular structure & R_P, R_S:

Donor-Acceptor interface[a]	J_S (A/cm²)	n	R_s (Ω cm²)	R_p (Ω cm²)
Pentacene/C_{70}	3.3×10^{-5}	2.1	3.4	3.5×10^{4}
CuPc/C_{70}	1.0×10^{-5}	2.0	0.7	7.9×10^{4}
Pentacene/C_{60}	2.7×10^{-6}	2.0	0.1	8.1×10^{4}
Pentacene/PTCBI	2.5×10^{-7}	1.6	0.7	5.0×10^{5}
CuPc/C_{60}	1.0×10^{-6}	2.0	0.1	1.1×10^{6}
CuPc/PTCBI	5.5×10^{-7}	1.7	0.2	9.1×10^{5}
NPD/C_{60}	7.1×10^{-10}	2.6	28.4	2.2×10^{6}
SubPc/C_{60}	5.8×10^{-9}	1.6	0.9	1.2×10^{5}

Perez et al.
JACS 131, (2009) 9281

Outline

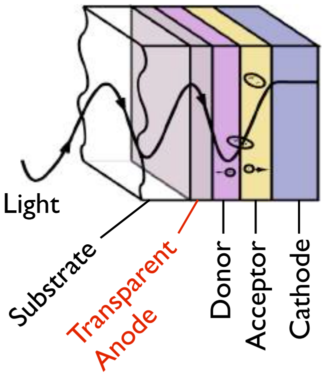
✓ **1. Energy & solar cells**
  A. Why we need energy in the first place
  B. Where does our energy come from and how do we use it?
  C. Why bother with solar electricity?
  D. Scalability & cost challenges of conventional solar cells

✓ **2. Small molecular organic PV cells – Part 1**
  A. Material system
  B. Physics of organic PV materials & devices

✓ **3. Improving efficiency of OPV cells – Part 2**
  A. Thin-film optics & plasmonics for improved absorption
  B. Exciton diffusion to and dissociation at D/A interface
  C. Increasing open circuit voltage and fill factor

4. Enabling low-cost modules & installation
  A. Eliminating costly materials from device structure
  B. Novel architectures
  C. Device processing

OPV structure: ITO is a typical electrode



ITO: Indium Tin Oxide

Also:
- FTO, AZO, etc.

"TCO" Transparent Conducting Oxide

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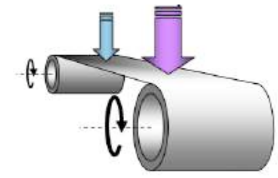
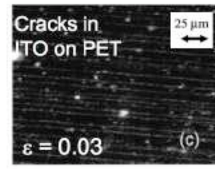
Challenges with Roll-to-Roll processing & TCOs

Want:



Get:



@ ε = 0.04
ΔR/R = 150

Cairns D., APL Vol.76 No. 11 Mar, 2000

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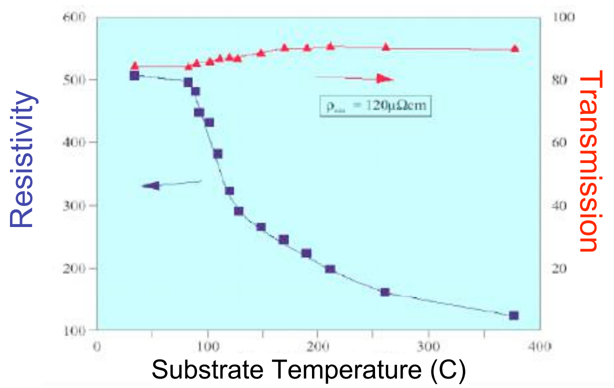
Good TCO usually requires high substrate temperature



Applied Films, 2002 in "Roadmap toward flexible displays," J.N. Bardsley, USDC 2003

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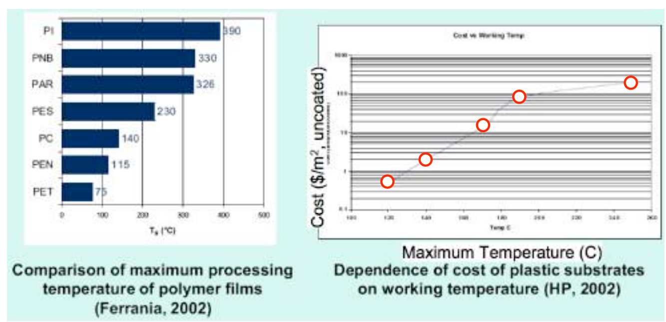
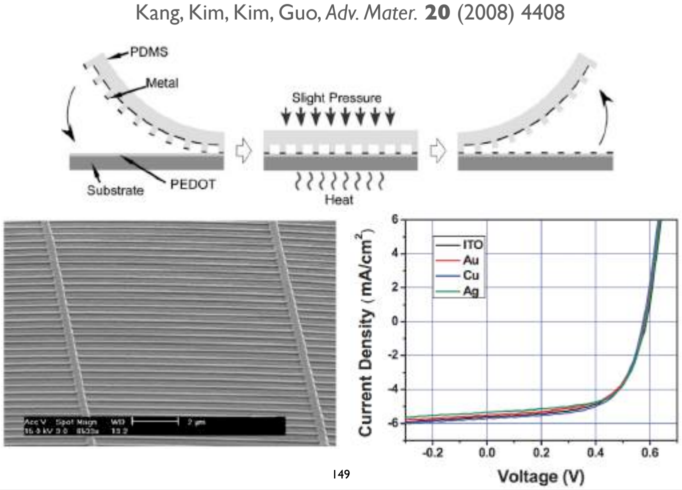
But... High-temp. plastic substrates can be expensive



"Roadmap toward flexible displays," J.N. Bardsley, USDC 2003

Organic solar cells using nanoimprinted transparent metal electrodes

Kang, Kim, Kim, Guo, *Adv. Mater.* **20** (2008) 4408



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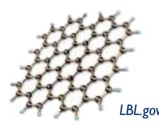
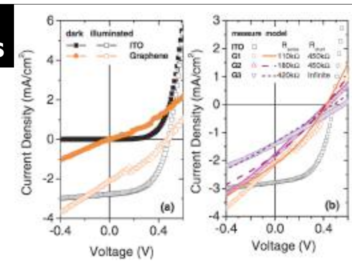
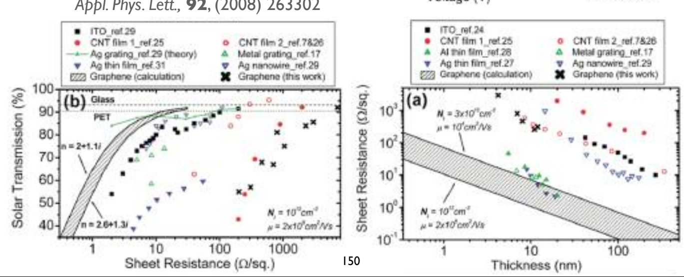
Graphene-based transparent electrodes





Wu et al.,
ACS Nano, **4** (2010) 43
Appl. Phys. Lett., **92**, (2008) 263302



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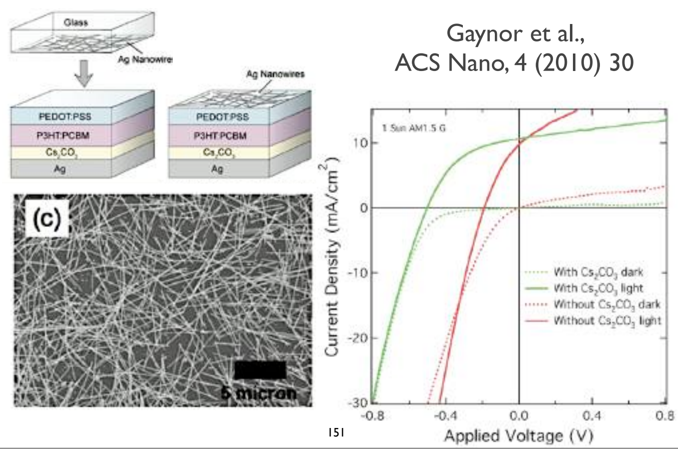
Fully Solution-Processed Inverted Polymer Solar Cells with Laminated Nanowire Electrodes

Gaynor et al., ACS Nano, 4 (2010) 30



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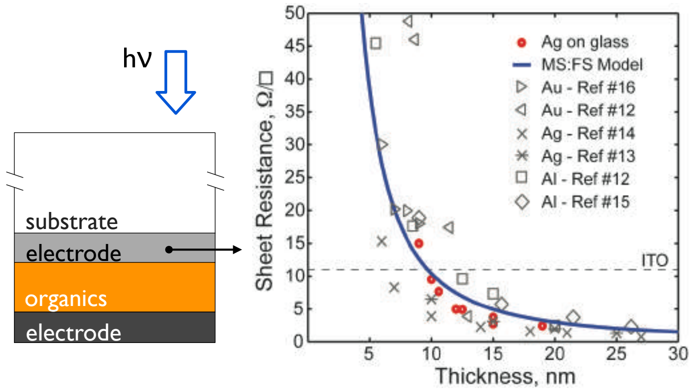
Thin Metal Films Are Quite Conductive
(widely used in low-E windows, food packaging)



O'Connor et al., Appl. Phys. Lett. **93**, *223304 (2009)*

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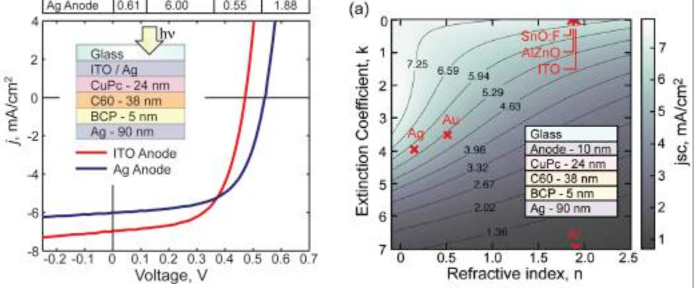
Experimental metal-organic-metal PV cells work well if the stack is designed appropriately, &...

Materials can be selected / developed based on model of light in-coupling

PV cell type	FF	j_{SC}, mA/cm^2	Voc, V	η, %
ITO Anode	0.60	6.97	0.48	1.86
Ag Anode	0.61	6.00	0.55	1.88



O'Connor et al., Appl. Phys. Lett. **93**, *223304 (2009)*

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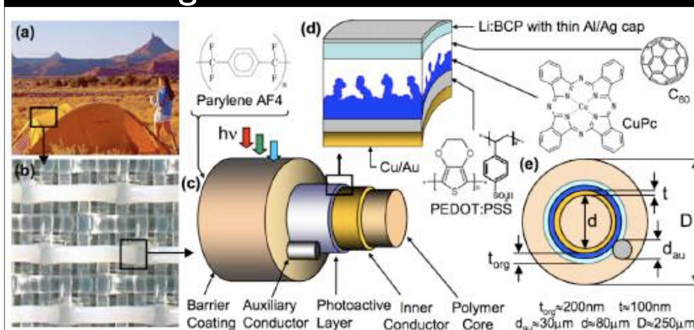
Apply the metal-organic-metal structure to organic solar cells on **fibers**



Can potentially get away with moderate efficiency, provided the BOS + installation costs are reduced

Why fibers?..
Area of Textiles Imported *Annually*:

Annual textile imports into US:

140x140 mi^2
\$3.40 / m^2

Textiles are scalable!

1. National Council of Textile Organizations, 2005
2. The American Textile Manufacturers Institute, 2006
3. Green, M. 3rd Generation Photovoltaics, 2003

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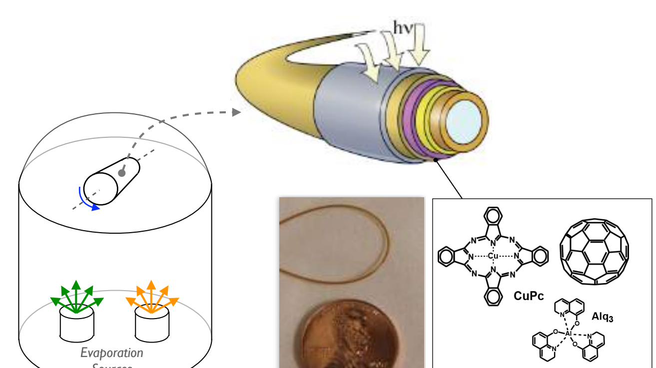
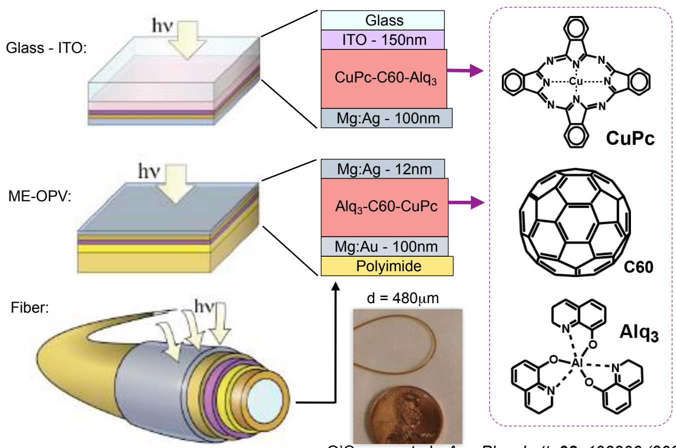
Method for Prototype Fiber PV Fabrication?



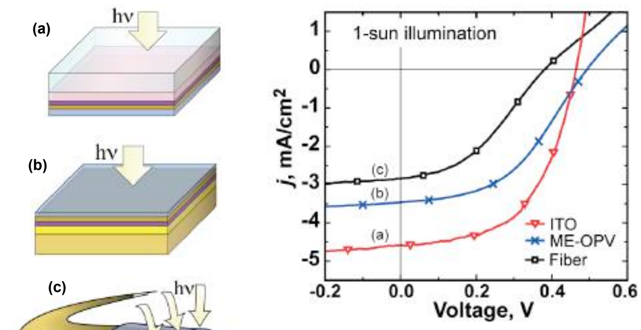
Can this be done?.. What are the challenges?

Fiber & control device structure details



O'Connor et al., *App Phys Lett*, ***92***, *193306 (2008)*

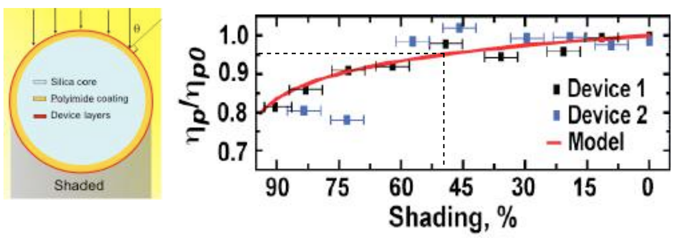
Comparing Organic PV Performance: Fiber vs. Planar



- η_{ITO} = 1.07%
- $\eta_{ME\text{-}OPV}$ = 0.76%
- η_{Fiber} = 0.50%

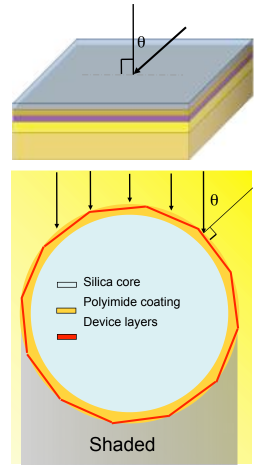
O'Connor et al., *App Phys Lett*, ***92***, *193306 (2008)*

Shading doesn't contribute much loss

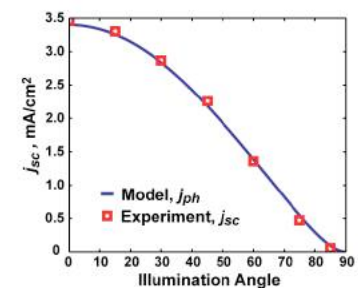


O'Connor et al., *App Phys Lett*, ***92***, *193306 (2008)*

Losses due to glancing incidence reflections



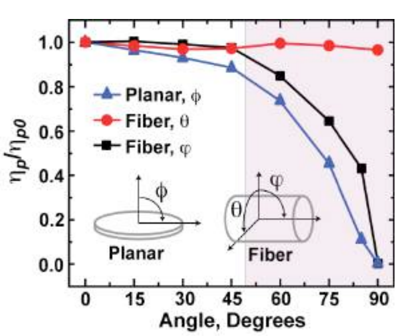
$$j_{ph}(\theta) = q\int f_{ph}(\theta,\lambda)\eta_{EQE}(\theta,\lambda)d\lambda \approx j_{sc}(\theta)$$

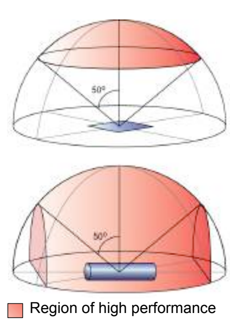


Fiber Performance	j_{sc}, mA/cm^2
Model	2.96
Experiment	2.85

O'Connor et al., *App Phys Lett*, **92**, 193306 (2008)

"Round" = better for mobile & no-tracking systems





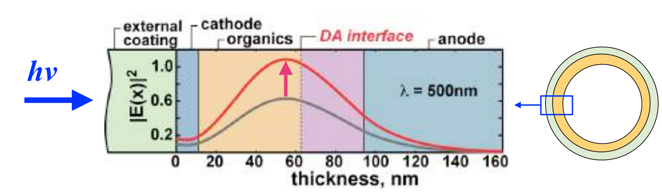
Power:

P = $\int \eta(\theta)\cdot\text{Intensity}(\theta)\cdot d\theta$

	Normal incidence	Hemispherical Ave.
Planar	0.76 mW/cm^2	0.3 mW/cm^2
Fiber	0.50 mW/cm^2	**0.4 mW/cm^2**

O'Connor et al., *App Phys Lett*, **92**, 193306 (2008)

Reducing reflection losses by external coatings



- Coatings enhance the optical intensity within the organic layers
- Design: multi-layer coating, different (n,k)

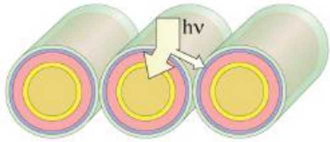
Device type:	j_{ph}, mA/cm^2
Planar (Glass ITO)	4.70
Fiber	2.96
Fiber w/ external coating	3.87

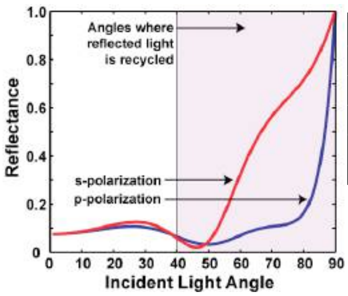
29% improvement over basic fiber

O'Connor et al. APL, ***89*** *233502 (2006), O'Connor et al. (in preparation)*

...or do both!

coatings
+
fiber bundles



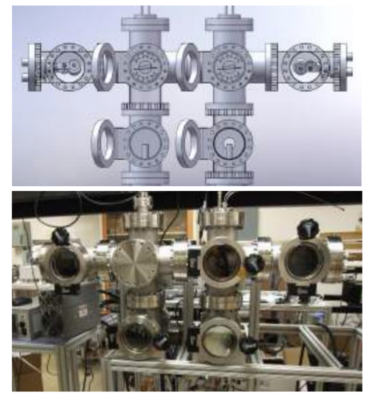


Device type:	j_{ph}, mA/cm²
Planar (Glass ITO)	4.70
Single Fiber	2.96
Single Fiber with Coating	3.87
Adjacent Fibers with external coating	4.70

57% Improvement over basic fiber
Performs as well as glass-ITO cell

O'Connor et al. (in preparation)

We're so enthusiastic about this approach, we are building a Reel-to-Reel fiber device coating system

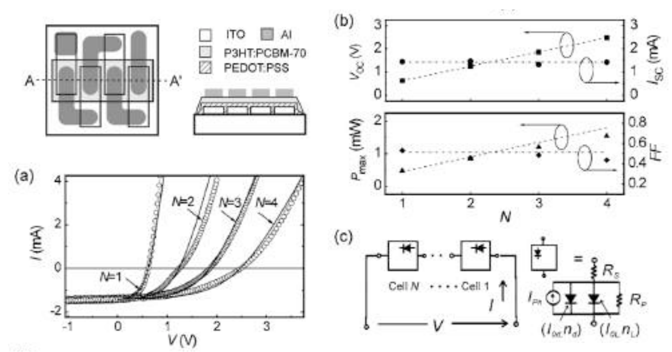


Morris et al., (in preparation)
LNECD – University of Michigan

...and are starting to collaborate with weavers (C. Amidei, EMU)

Modularization: stepping up voltage, mitigating series resistance

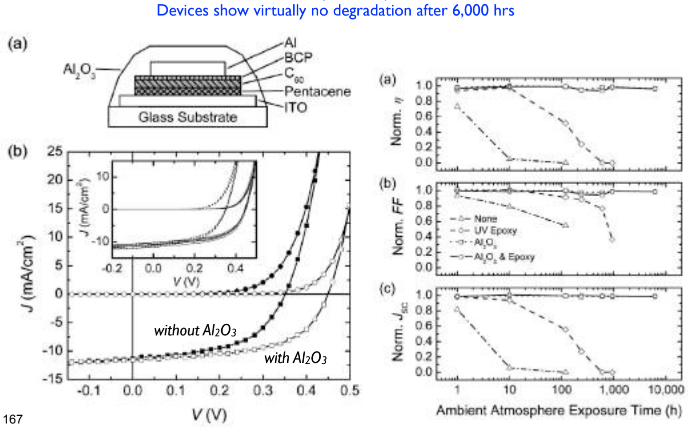
Yoo et al., Appl. Phys. Lett. **89**, 233516 (2006)



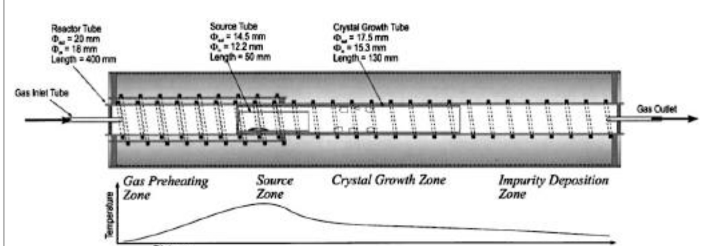
Properly encapsulated devices exhibit very long lifetimes

Potscavage et al., Appl. Phys. Lett. **90**, 253511 (2007)

200nm thick Al_2O_3 deposited by ALD @ 100°C
Devices show virtually no degradation after 6,000 hrs



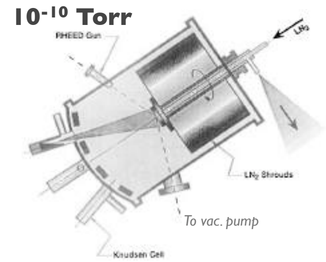
Purification of organic semiconductors & growth of crystals



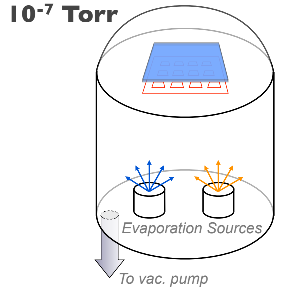
R.A. Laudise *et al.*, *J. Crystal Growth* **187** (1998) 449

Deposition in vacuum

Organic molecular beam deposition — **Vacuum thermal evaporation**



S. R. Forrest, *Chemical Reviews*, **97** 1793 (1997)



✓ Thickness control
✓ Very clean process
✓ Monolayer control
✓ Analogous to MBE

$r_{dep} = \eta \cdot A_{evap} \cdot \bar{u}_0 \cdot P_0 \exp(-\Delta H / RT_{cell})$

x Rate control
x Dusty chamber
x Morphology control

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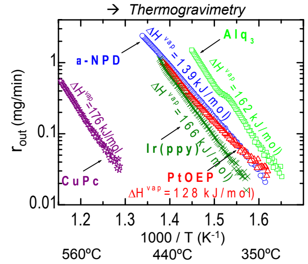
Evaporation rate is governed by vaporization enthalpy and limited by thermal stability of source materials

$$r_{out_i} = \frac{P_0 \exp\left(-\Delta H_i^{vap} / RT_{cell}\right)}{\frac{\sqrt{2\pi \cdot mw_i \cdot RT_{cell}}}{\alpha \cdot A_e} + \frac{RT_{std}}{\dot{V}_{sccm}} \cdot \frac{P_{cell}}{P_{std}}}$$

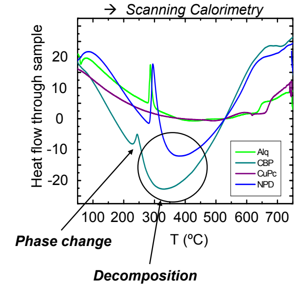
→ Evaporation faster with Temperature

→ Decomposition faster w/ Temperature

Evaporation vs. Temperature
→ *Thermogravimetry*

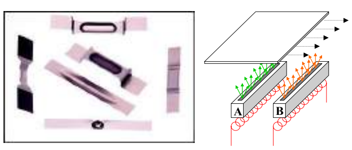


Decomposition vs. Temperature
→ *Scanning Calorimetry*

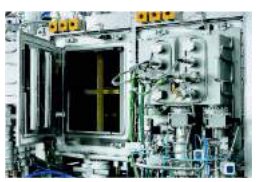


Shtein et al., J. Appl. Phys., ***89***, *2001*

Linear sources can be used to coat large substrates / webs

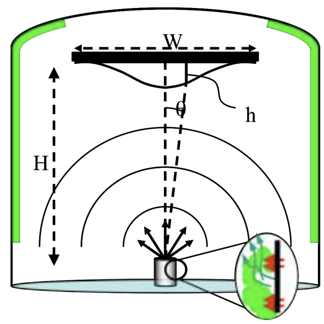


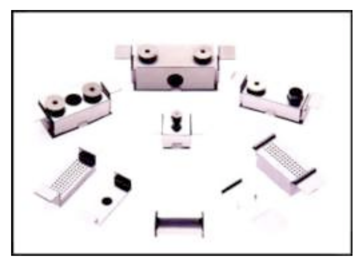
→ Use "left-right" deposition instead of "bottom-up"



A fully integrated, vertical evaporation system utilizing linear sources to achieve up to 50% materials use efficiency and uniform coating of substrates up to 400x500mm² in size. (b) A close-up photograph of one of the evaporation chambers. (**Applied Films, GMBH, Germany**)

Another problematic aspect of VTE: Poor heat distribution within source





Uneven heating can lead to fluctuations in evaporation rate

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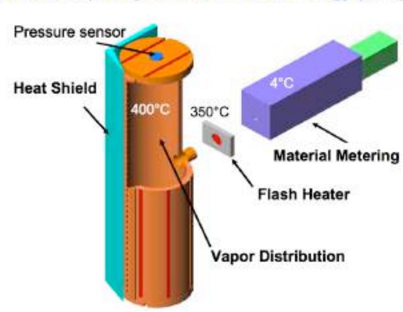
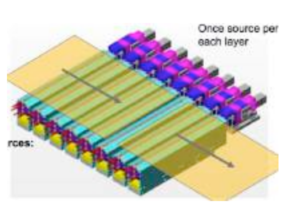
Kodak's vapor injection sources appear very promising

Kodak's Vapor Injection Source Technology (VIST):





So far Kodak published **OLED** deposition by VIST,
20 sec TAC Time, 70% Material Utilization

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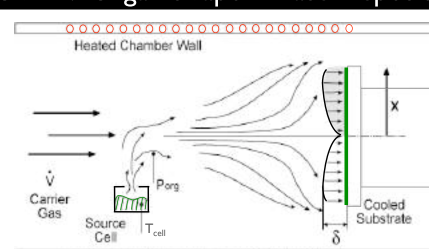
Potentially better approach: OVPD: Organic Vapor Phase Deposition

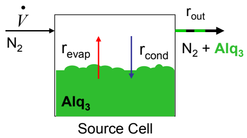


- 0.1 – 10 Torr → *Convective + Diffusive Transport*
- Decoupled evaporation & deposition → *Control*
- Dopant control by Temperature & Flow
- Heated chamber walls → *cleaner, more efficient*
- Flow engineering → *Uniformity*

- *Burrows et al., J. Cryst. Growth 156 (1995); Vaeth and Jensen, Apl. Phys. Lett. 71 (1997)*
- *Baldo et al., Appl. Phys. Lett. 71 3033 (1997); Shtein et al., J. Appl. Phys. 89 1470 (2001)*

OVPD: Scaling Analysis & Material Transport Regimes

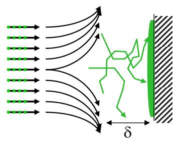
Evaporation: *mass balance on* organic species



$$r_{out_i} = \frac{P_0 \exp\left(-\Delta H_i^{vap}/RT_{cell}\right)}{\frac{\sqrt{2\pi \cdot mw_i \cdot RT_{cell}}}{\alpha \cdot A_e} + \frac{RT_{std}}{\dot{V}_{sccm}} \cdot \frac{P_{cell}}{P_{std}}}$$

200°C < T_{cell} < 400°C
5 sccm < $\dot{V}$ < 1000 sccm

Deposition: *diffusion across* boundary layer



$$r_{dep} = D \cdot \frac{\Delta C}{\delta} = D \cdot \frac{r_{out} / (\dot{V}_{src} + \dot{V}_{dil})}{\delta}$$

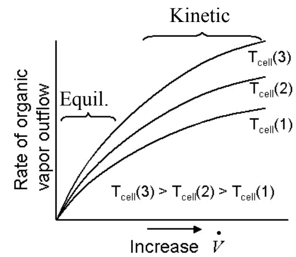
$$D = \frac{\bar{c}}{3\lambda} = \frac{\bar{c} \cdot kT}{3\sqrt{2}\sigma P}$$

1 μm < λ < 100 μm
1 mm < δ < 10 mm

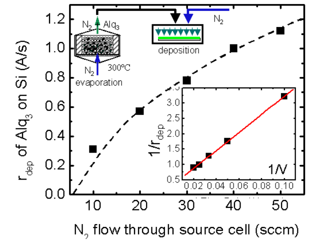
Shtein et al., J. Appl. Phys., **89**, 2001

OVPD: Scaling Analysis & Material Transport Regimes

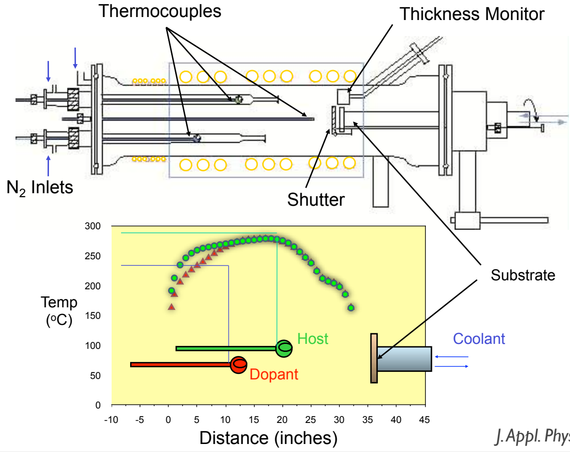
Source Cell Regimes:



Experiment:
(Flow-control of deposition)



Lab-scale OVPD deposition system (inexpensive, modular)

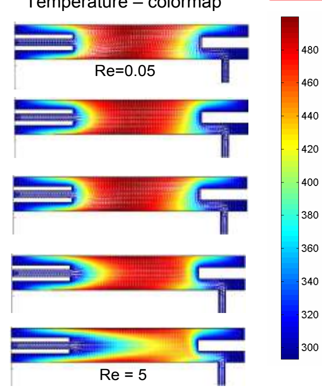


Shtein et al., J. Appl. Phys., **89**, *2001*

Simulation of hydrodynamic flows & mass transfer in OVPD

Flow field – white arrows
Temperature – colormap

1 μm < λ < 100 μm   10 cm < L< 10 m



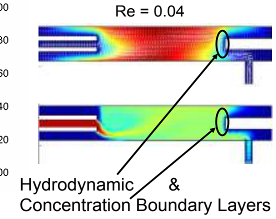
$$\rho\frac{\partial \vec{u}}{\partial t} + \rho(\vec{u}\cdot\nabla)\vec{u} = -\nabla p + \eta\nabla^2\vec{u} + \rho\vec{g}$$

$$\nabla \cdot \vec{u} = 0$$

$$\rho c_P \frac{\partial T}{\partial t} + \nabla(-k\nabla T + \rho c_P T\vec{u}) = Q$$

$$\frac{\partial c}{\partial t} + \nabla(-D\nabla c + c\vec{u}) = Q_D$$

Re = 0.04



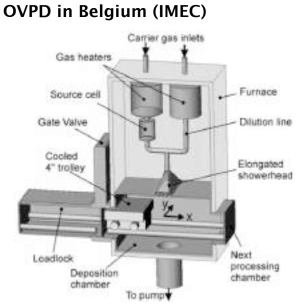
*M. Shtein et al. J. Appl. Phys., **93**, 4005, (2003)

OVPD systems

OVPD-I in Princeton

OVPD-II in Michigan

OVPD in Belgium (IMEC)



Rolin C. *et al*, *Org. Elec.*, **11** (2010) 100

Solvent processing of small molecule films

Xi H. *et al.*, *J. Phys. Chem. C* **112**, 19934 (2008)