# Week 2-7

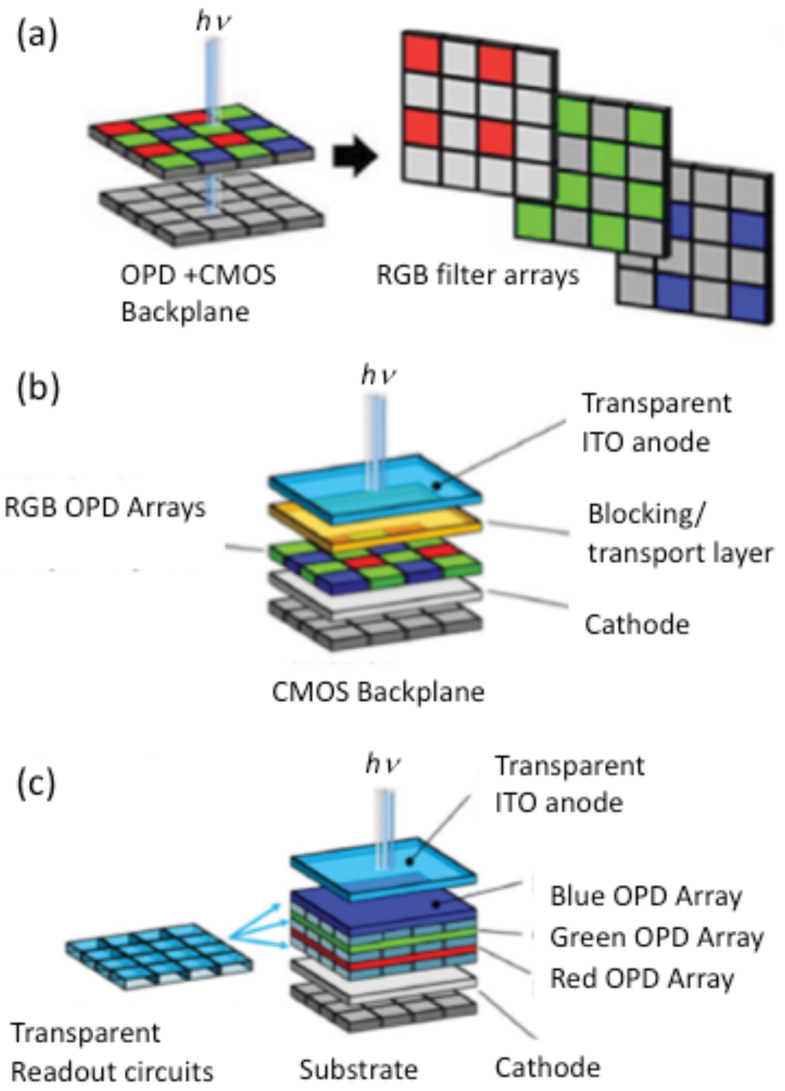
## Optical Detectors 2

Photodetector applications (cont'd)
Solar cell basics
Measuring OPV efficiency
Device Architectures: Exciton Blocking Layers

Chapter 7.2.2.4-7.4.1

# Photodetectors for Imaging

## How your camera works

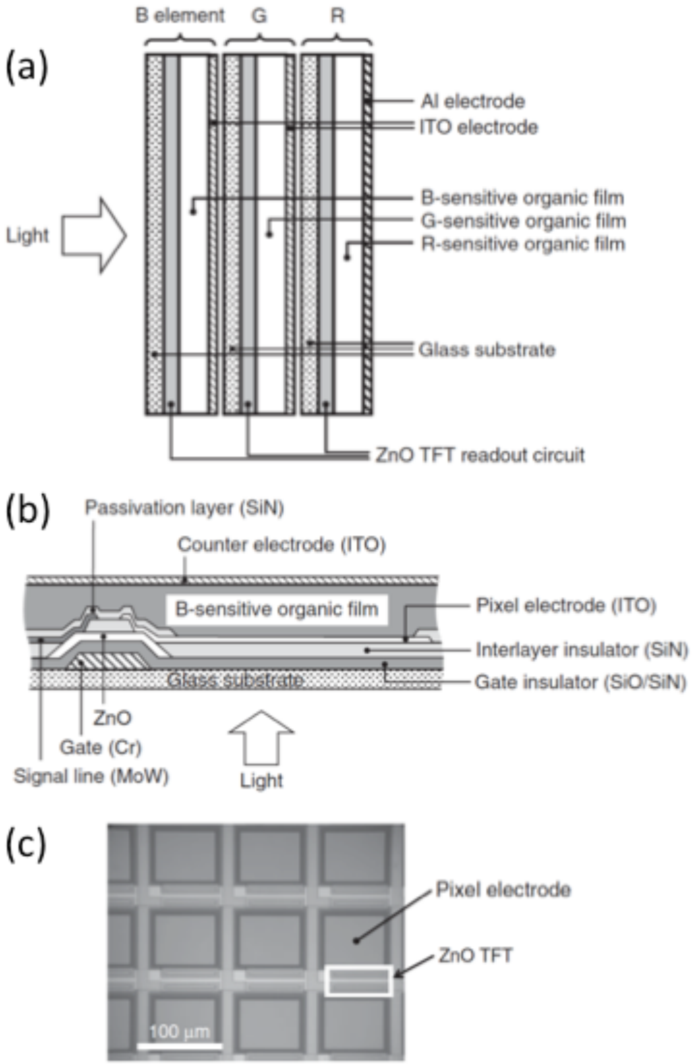


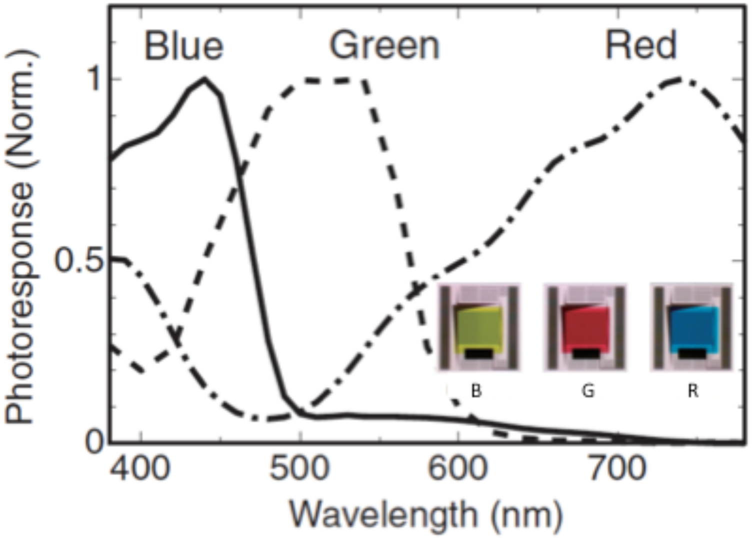
Color filters

Integrated RGB Sensitive OPDs

Stacking R, G, B layers

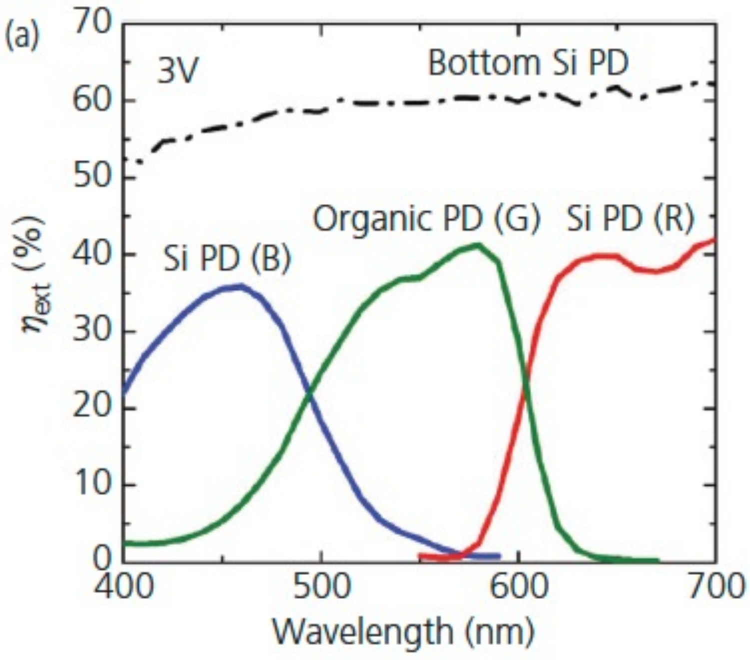
# Stacked sensors



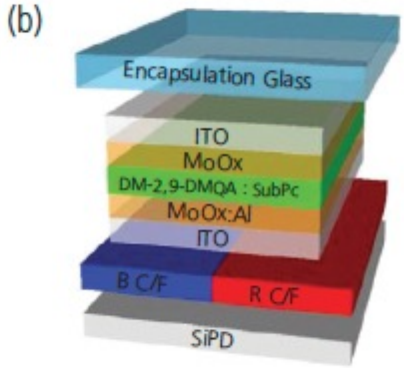


S. Hokuto, et al., *Japan. J. Appl. Phys.*, **50**, 024103, 2011.

# Hybrid Organic/Si CMOS Imager

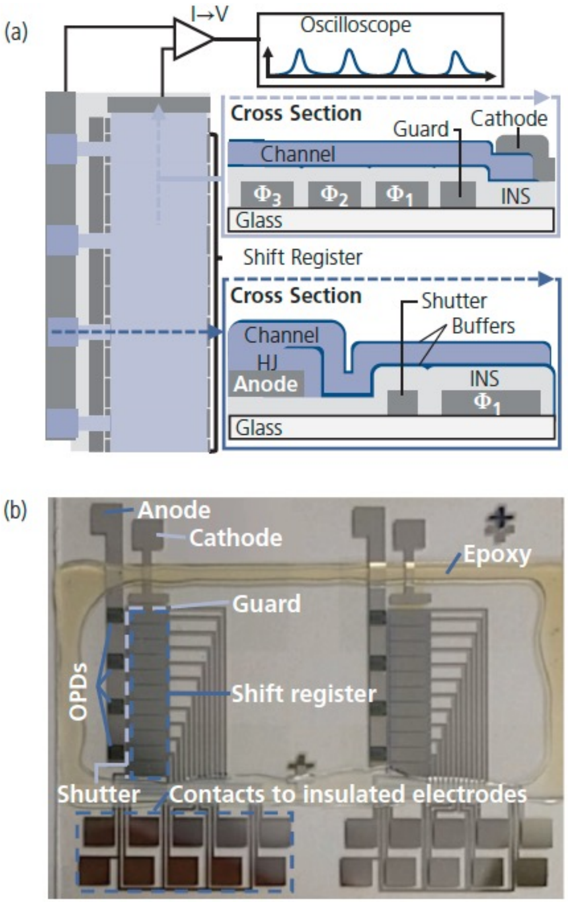


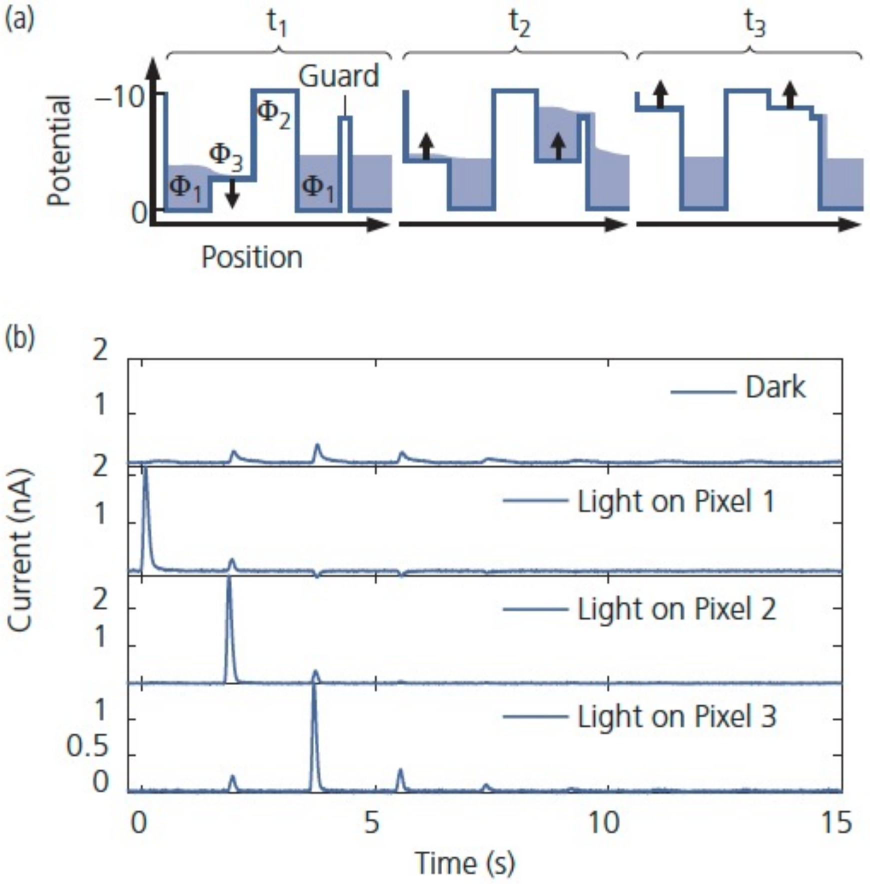
Combination of CMOS focal plane array, B & R color filters, and a G OPD



Lim et al. Sci. Rep. 5, 7708 (2015)

# Organic Charge Coupled Device

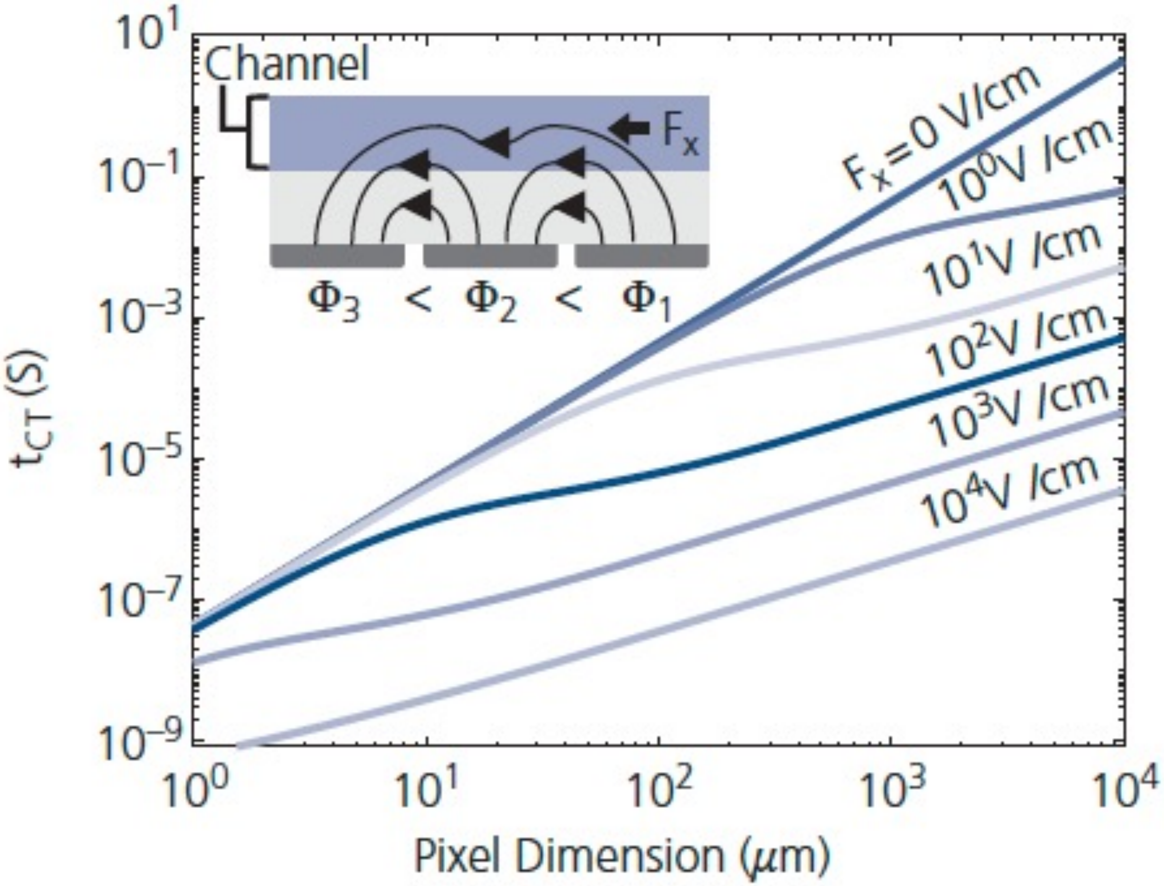




- 4 Heterojunction detectors connected to a 3 phase (f) shift register to advance the charge collected during each clock cycle
- Exploits long range (cm scale) electron diffusion in fullerene channel
- Diffusion is slow and omnidirectional

Coburn, et al. ACS Photonics 6, 2090 (2019)

# OCCD: How Fast Can It Respond?



Fringe fields between shift register contacts can greatly increase charge transfer rate

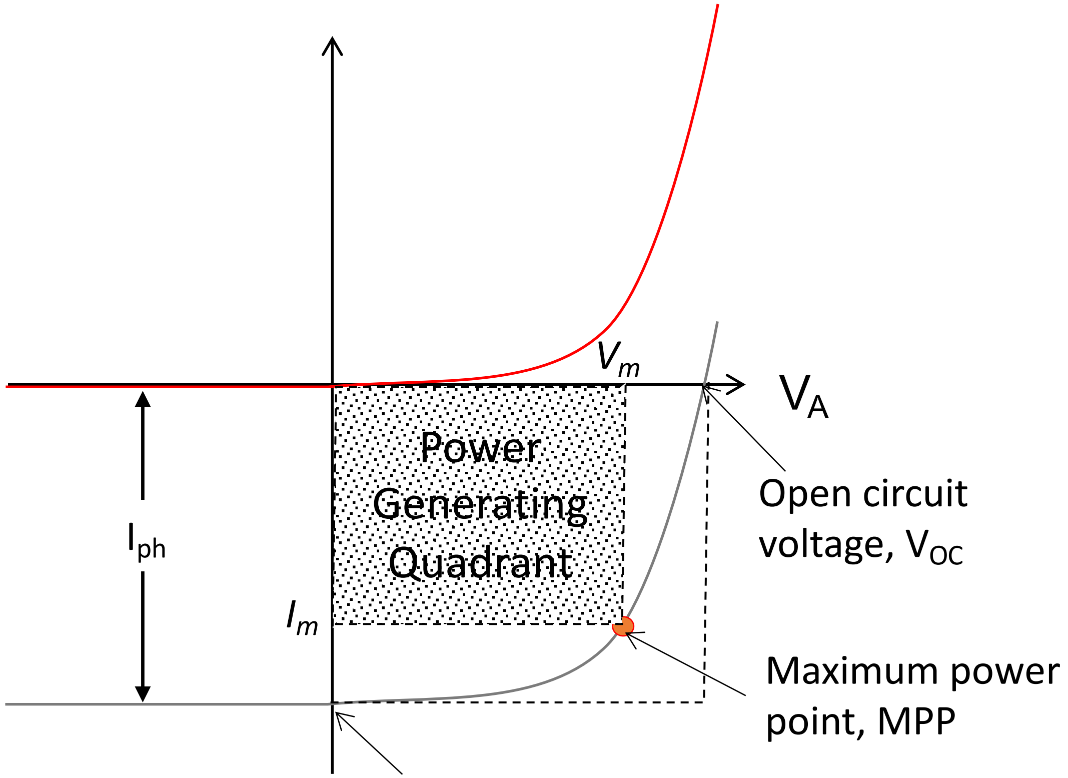
Transfer times ~10 ns possible, similar to Si sensors

Coburn, et al. ACS Photonics 6, 2090 (2019)

# Solar Cell Basics

**Power Conversion Efficiency, $\eta_P$:**

- $I_{SC} \propto$ number of photons absorbed
- $V_{OC}$ determined by material
- Fill factor (FF) related to device resistance



$$\boxed{Power = IV}$$

Maximum power generated: $P_m = I_m V_m = FF I_{SC} V_{OC}$

Fill Factor: $FF = \dfrac{V_m I_m}{V_{OC} I_{SC}}$

$$\boxed{\eta_P = \frac{FF \cdot I_{SC} \cdot V_{OC}}{P_{inc}}}$$

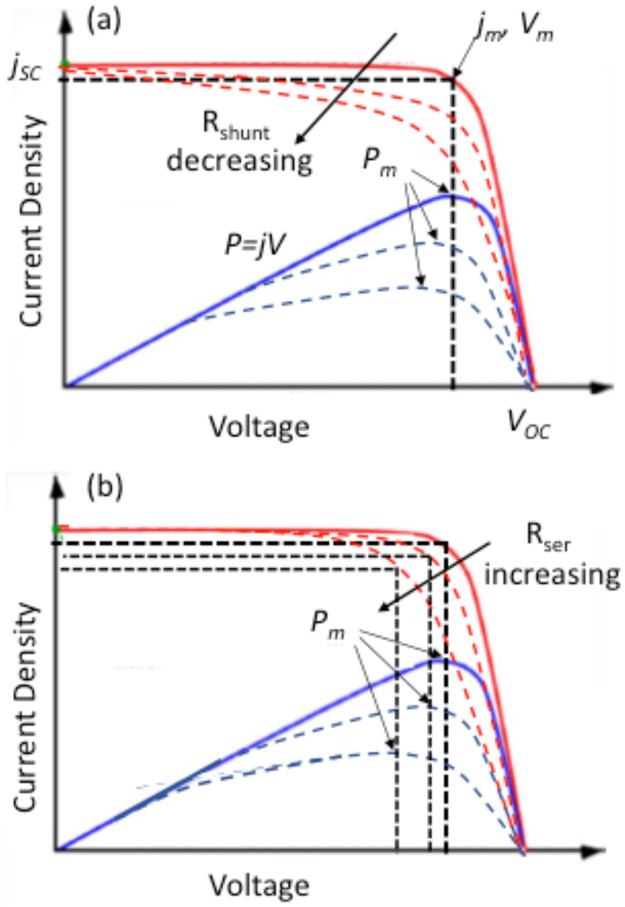
# No Cell is Ideal

(see Ch. 4.7)

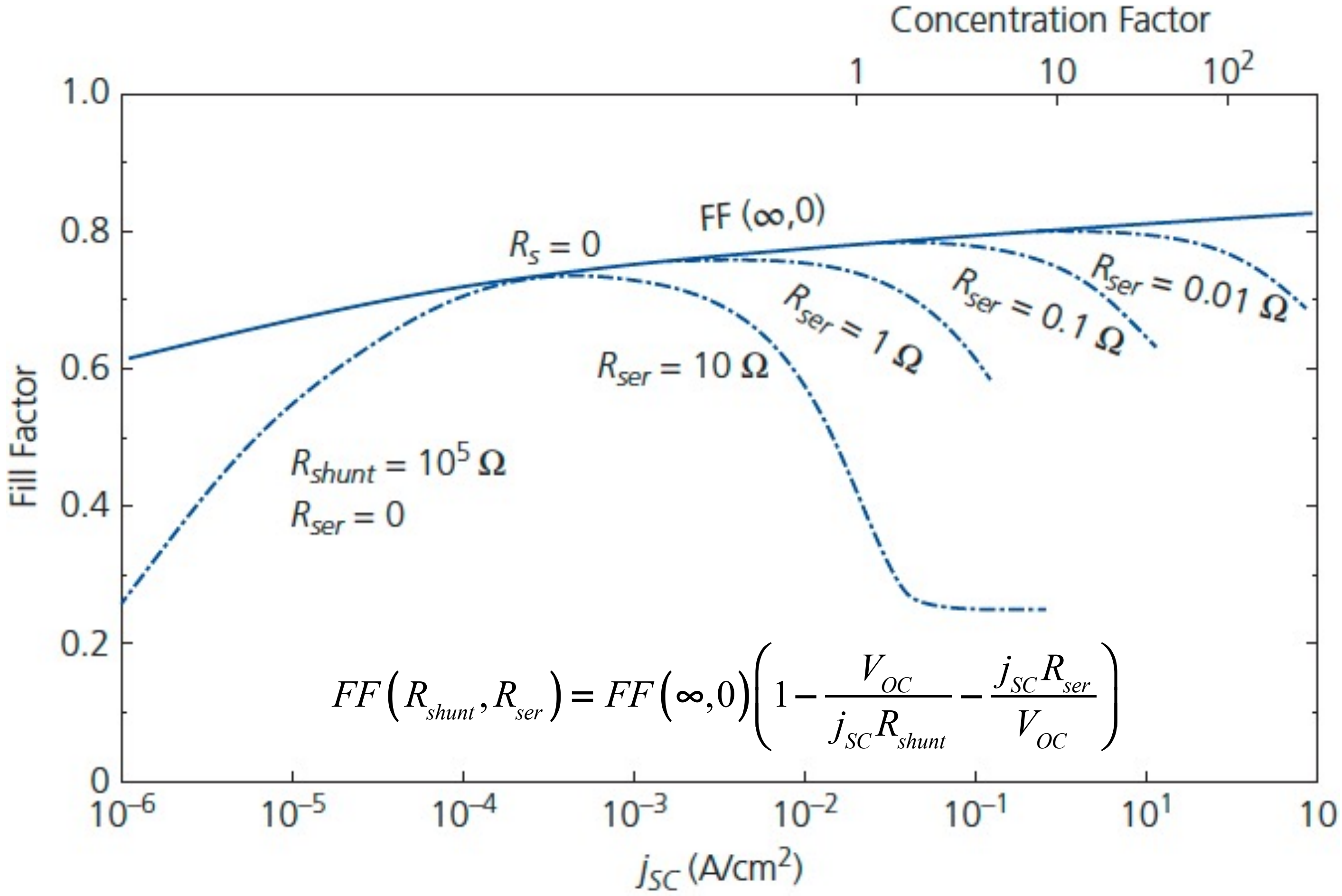
$$j = j_0\left[\exp\left(q\left(V_a - jAR_{ser}\right)/n_S k_B T\right) - \frac{k_{PPd}}{k_{PPd,eq}}\right] + \frac{V_a - jAR_{ser}}{R_{shunt}} - j_{ph}$$

$$V_{OC} = \frac{n_S k_B T}{q}\log\left(\frac{j_{ph}}{j_0} + \frac{k_{PPd}}{k_{PPd,eq}}\right) \approx \frac{n_S k_B T}{q}\log\left(\frac{j_{SC}}{j_0} + 1\right)$$

- It is customary to plot power generating *j-V* of 4th quadrant in the 1st
- P = (+j)(+V) > 0



# Fill Factor Depends on Series & Shunt Resistance



$$FF\left(R_{shunt}, R_{ser}\right) = FF\left(\infty, 0\right)\left(1 - \frac{V_{OC}}{j_{SC}R_{shunt}} - \frac{j_{SC}R_{ser}}{V_{OC}}\right)$$

Solar concentration factor: $CF = \dfrac{P_{inc}}{P_{inc-1sun}(1\ \mathrm{kW\text{-}m^{-2}})}$

- Series resistance depends on morphology, contacts
- Shunt resistance depends on D-A junction quality

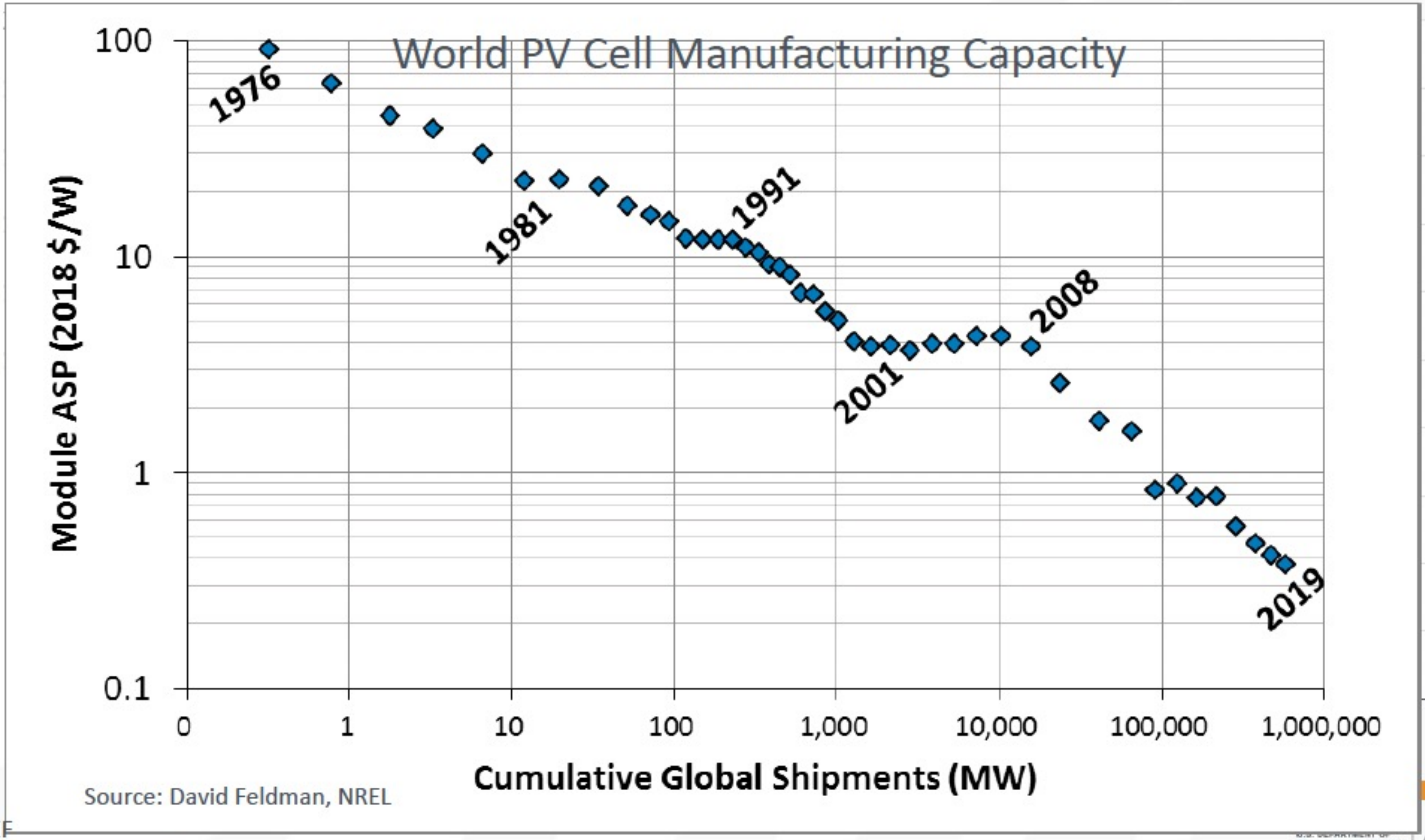
Bube & Fahrenbruch, Adv. Electron. Electron Phys., 56 163 (1981)

# Solar Cell Facts

- Solar power at Earth's surface on sunny day: 1 kW/m$^2$
- Power conversion efficiency of a solar cell: electrical power generated per Watt of sunlight in units of W/W or %

| Technology | Max. PCE | Pros & Cons |
|---|---|---|
| Single junction solar cell thermodynamic limit | 31% | - |
| Multijunction solar cell record under concentrated sunlight | 46% | Very efficient & expensive (100X Si) |
| Silicon solar cell | 24% | - |
| Silicon cell when installed | 18-20% | Competitive w. fossil fuel wide deployment |
| GaAs single junction cell | 29% | Very expensive, useful for space applications |
| Perovskite cells | 24+% | Unstable, toxic materials, potentially low cost, flexible |
| Organic cells | 18% | Potentially low cost, flexible, transparent |

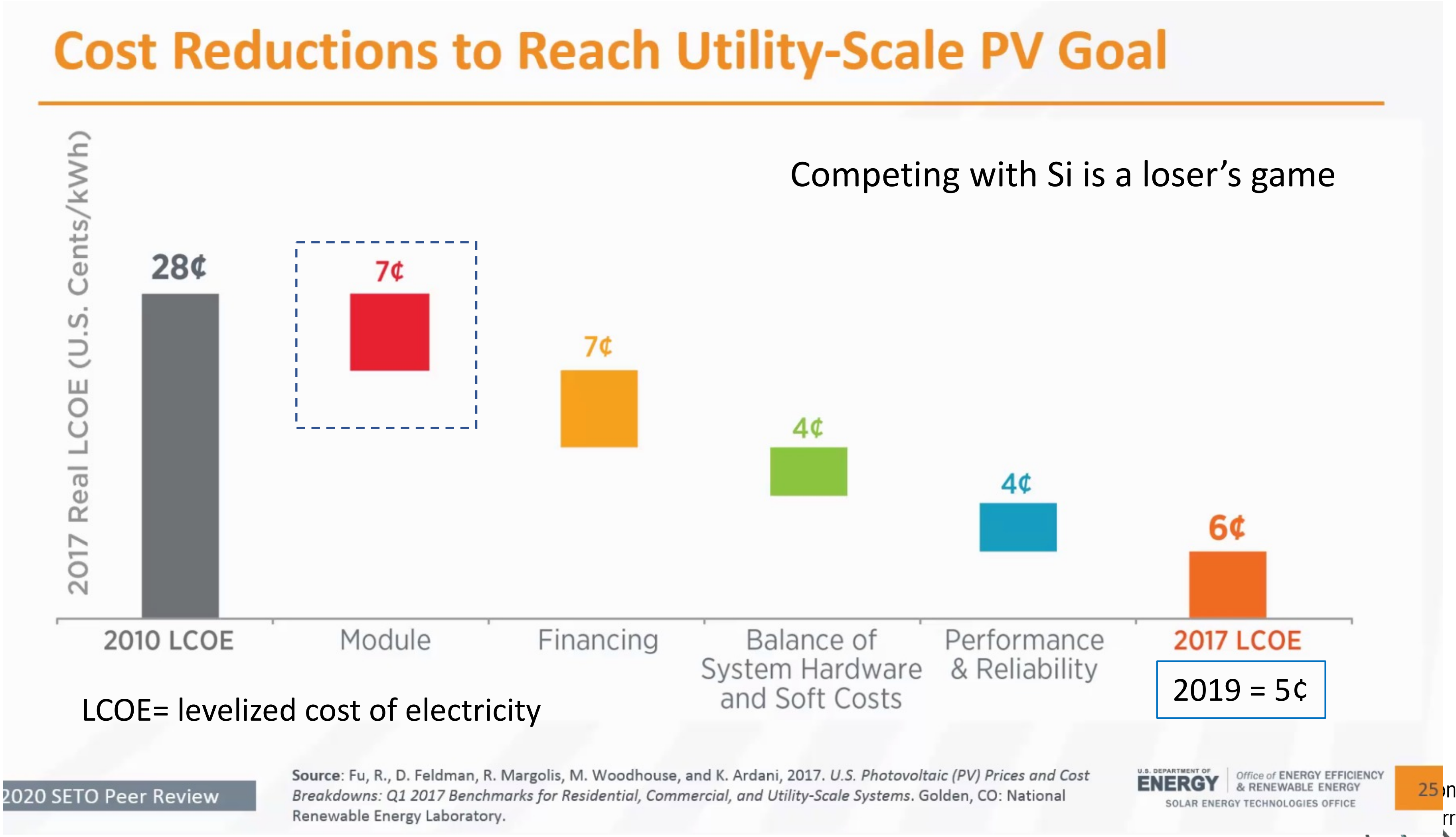
# Economies of Scale: A Powerful Engine of Solar Cost Reduction



Source: David Feldman, NREL

ASP = Average sale price

# Cost Reduction of Silicon Solar



## Cost Reductions to Reach Utility-Scale PV Goal

Competing with Si is a loser's game

2019 = 5¢

LCOE= levelized cost of electricity

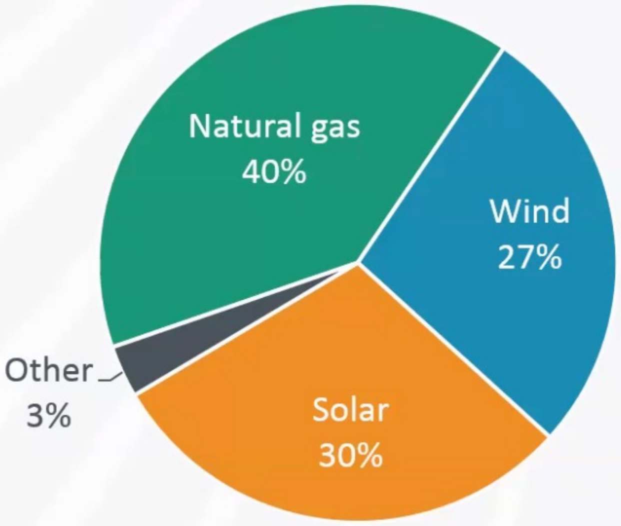
2020 SETO Peer Review

**Source**: Fu, R., D. Feldman, R. Margolis, M. Woodhouse, and K. Ardani, 2017. *U.S. Photovoltaic (PV) Prices and Cost Breakdowns: Q1 2017 Benchmarks for Residential, Commercial, and Utility-Scale Systems*. Golden, CO: National Renewable Energy Laboratory.

# Solar is growing fast!

and continuing well into the future

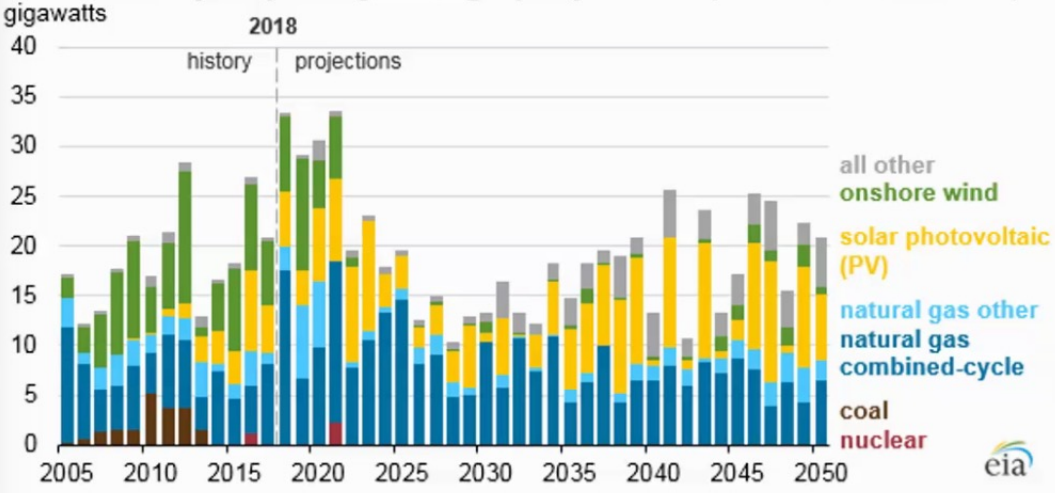
New Capacity from 2015 - 2019



Solar energy represented **30%** of new capacity additions **over the past 5 years** and now supplies over 2.5% of the nation's annual U.S. electricity.

U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
SOLAR ENERGY TECHNOLOGIES OFFICE

**Annual electricity utility-scale generating capacity additions (AEO2019 Reference case)**

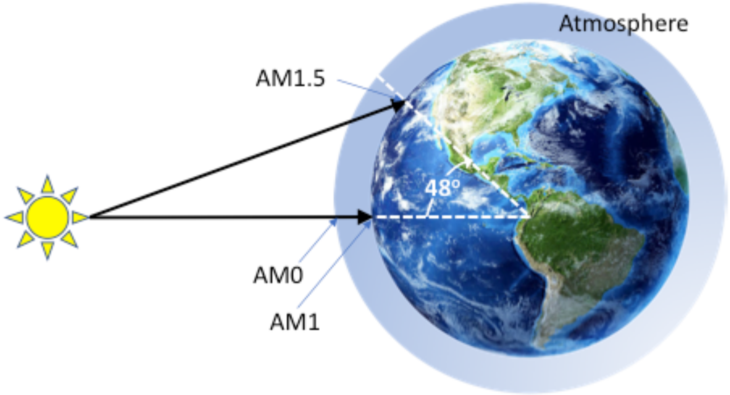


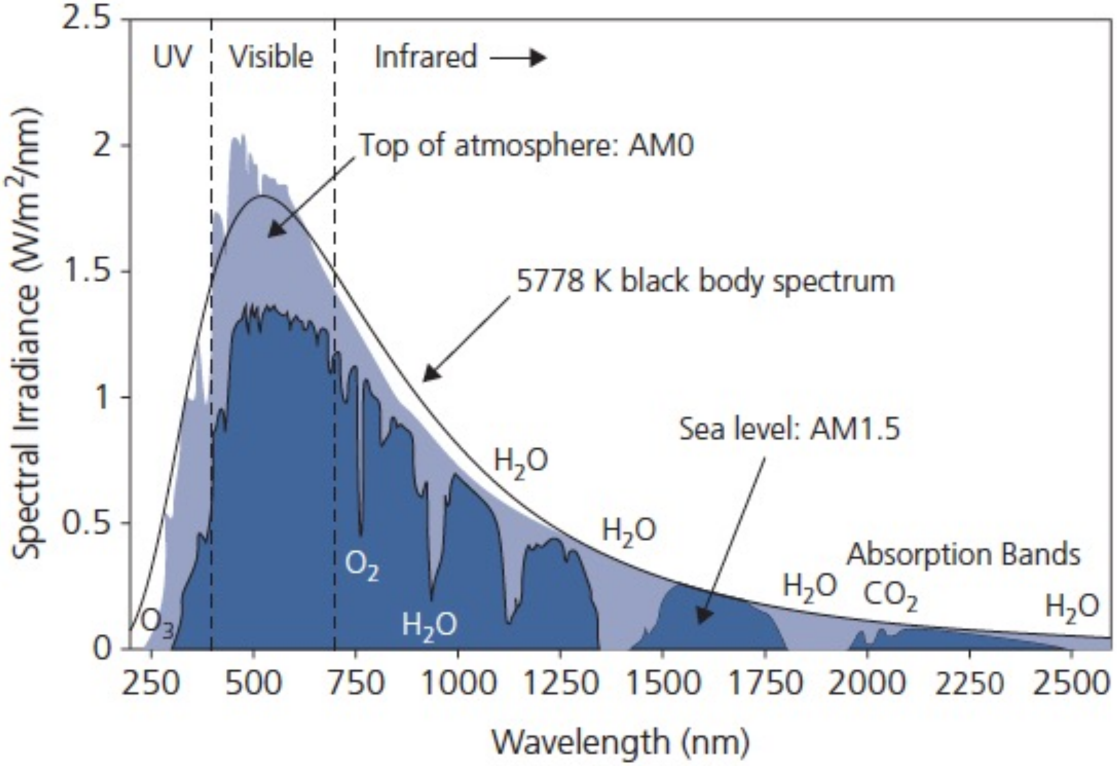
Source: Energy Information Administration, 2019 Annual Energy Outlook

Sources: BNEF, "New Energy Outlook 2019;" EIA, "2020 Annual Energy Outlook;" reference case; EIA, "2020 Annual Energy Outlook;" NREL, "2019 Standard Scenarios," mid case.

2020 SETO Peer Review

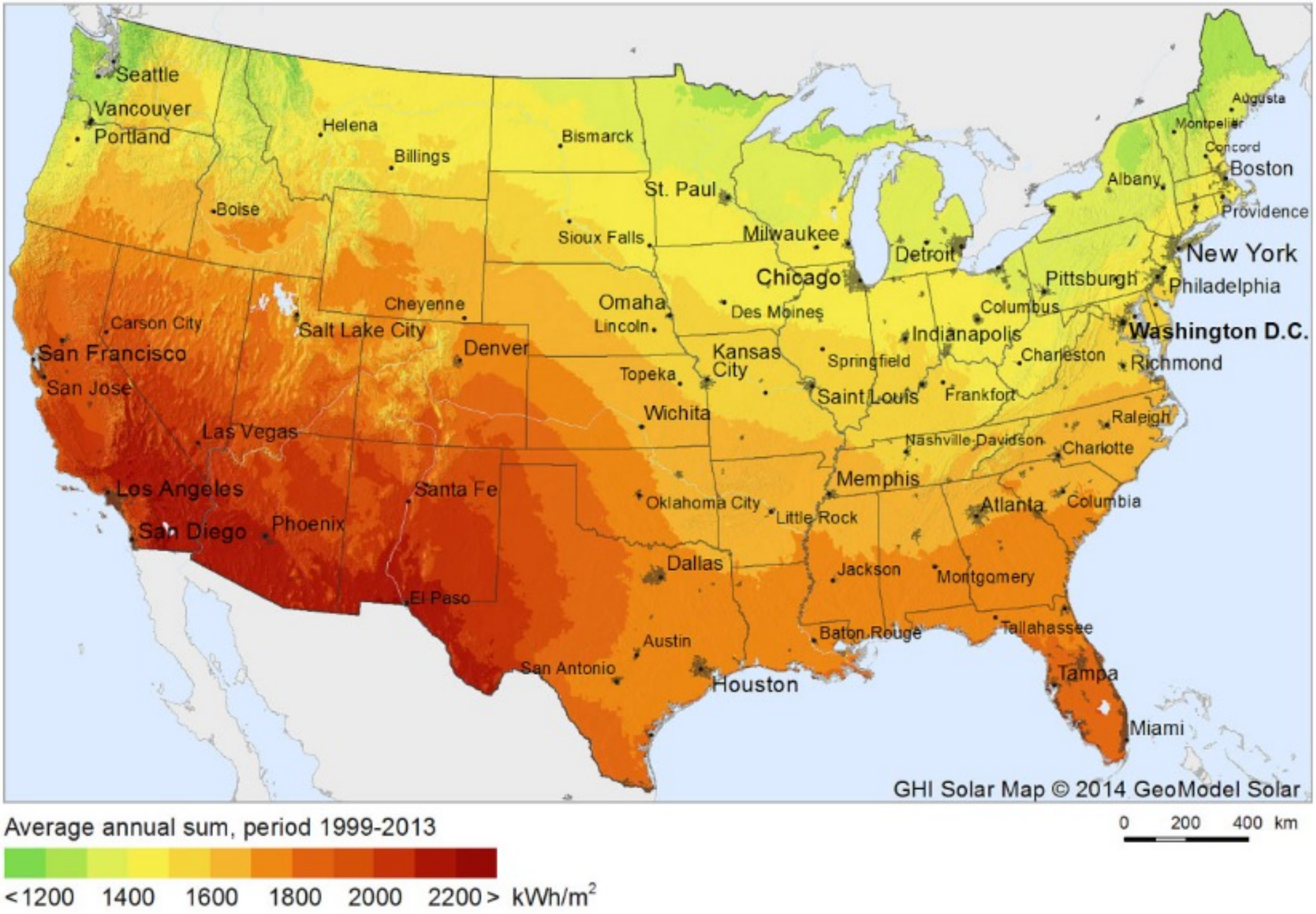
# Consider the Source



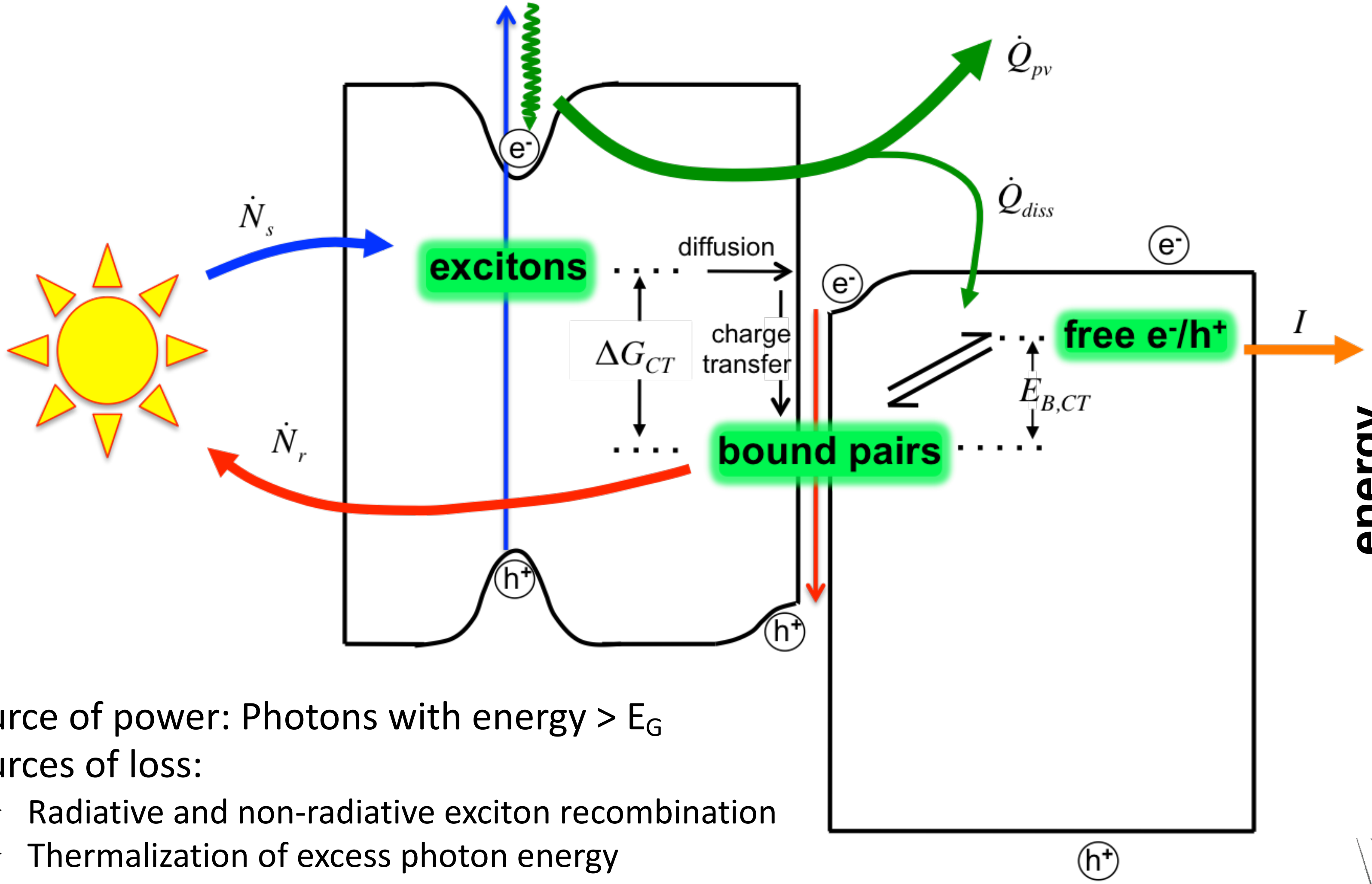


Organic Electronics
Stephen R. Forrest

# Annual Solar Insolation: US



# Thermodynamic Limits to OPV cell Efficiency



- Source of power: Photons with energy > $E_G$
- Sources of loss:
  - Radiative and non-radiative exciton recombination
  - Thermalization of excess photon energy
  - Recombination of CT states

Loss in *EXCITONIC* Solar Cells

Giebink, et al., Phys. Rev. B **83**, 195326 (2011)

# Calculating the Thermodynamic Efficiency Limit

In OPVs (vs. inorganics), absorption by the CT state, intermediate between the exciton and charge generation, must be considered

Exciton energy

Free energy loss due to relaxation of Ex → CT

Polaron pair energy: $E_{PP} = E_X + \Delta G_{CT}$

Then: $j_{SC} = q\int_{E_{PP}}^{\infty} \alpha(E)\left(\phi_s(E) - \phi_r(E)\right)dE$

BB rad. from sun

BB rad. from cell

dark current

$$j_0 = \frac{q}{\eta_{EL}}\int_0^{\infty} \eta_{ext}(E)\phi_{BB}(E,T_a)\,dE$$

$$\alpha(E) = \begin{cases} 0 & for \quad E < E_{PP} \\ \alpha_{PP} & for \quad E_{PP} < E < E_X \\ 1 & for \quad E > E_X \end{cases}$$

: CT absorption

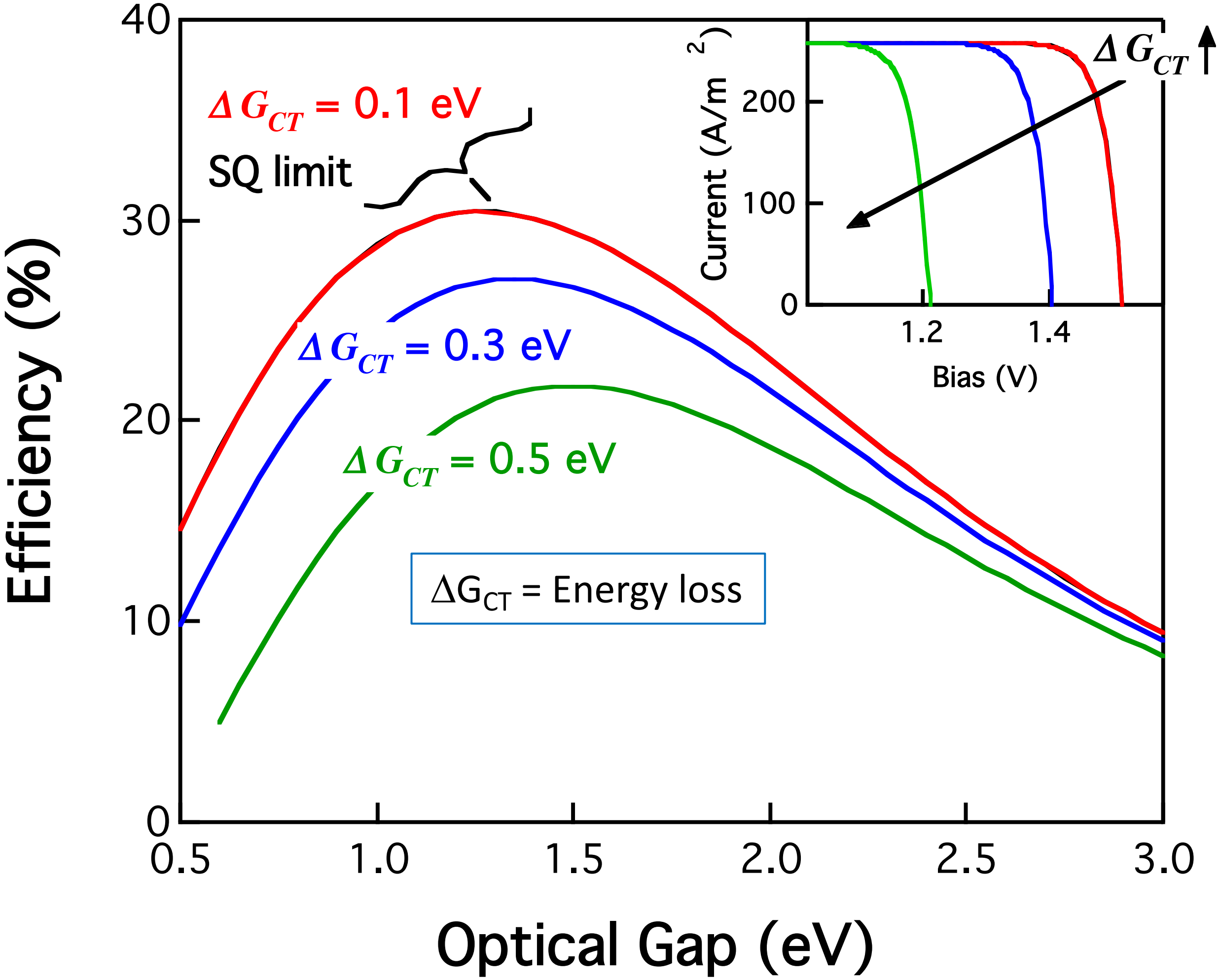
There are losses in $V_{OC}$ due to CT cell recombination (measured by the EL eff. in forward bias)

$$\Delta V_{OC}^{nr} = V_{OC}^{rad} - V_{OC} = -\frac{mk_BT}{q}\log(\eta_{EL})$$

m ≥ 1 due to cell non-idealities

Reduced non-radiative recombination
⇒The best detectors (i.e. smallest $\Delta V_{OC}$ and largest $j_{SC}$) are the most radiative

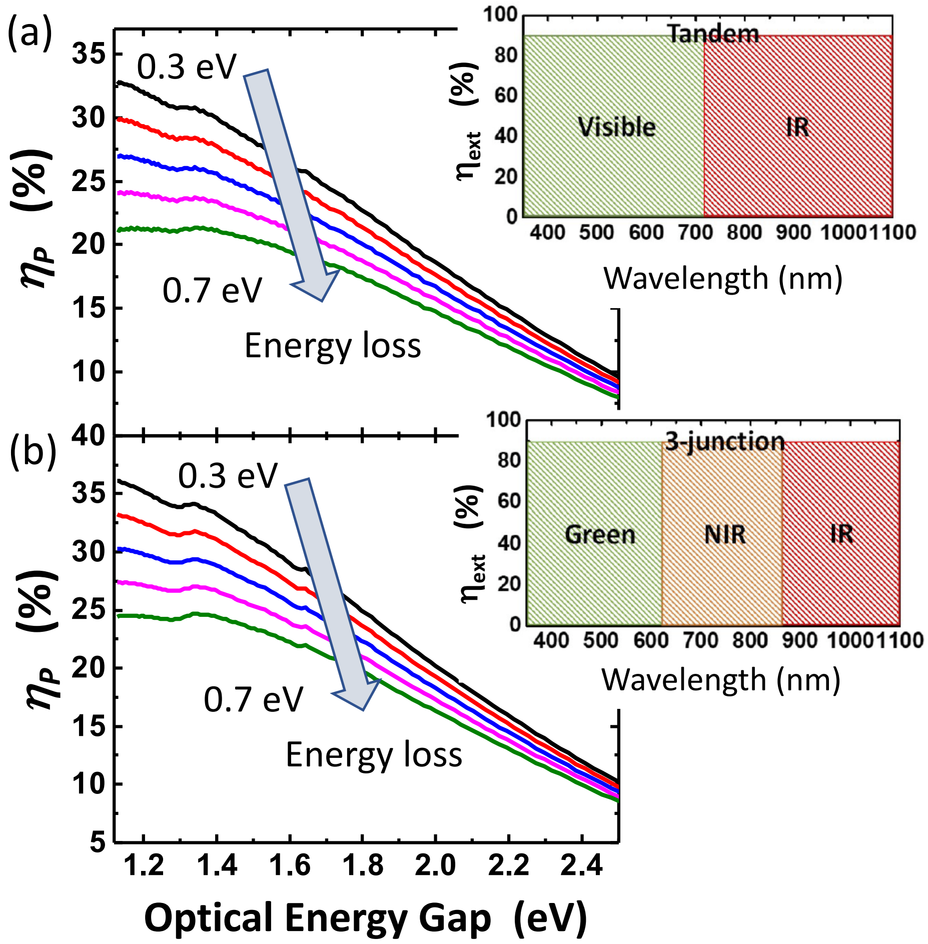
# Single-Junction OPV Efficiency Limit



Assumptions:
- Based on 2nd Law of Thermodynamics
- Sun=Black Body Source at 5770K
- Polaron pairs mediate photogeneration

Observations:
- OPV efficiency limit: 21.7-27.1%
- Polaron pair energy ⇒$V_{oc}$ redux
- Theory gives SQ limit (⇒general!)

# Single Junction Efficiency Can Be Exceeded in Multijunction Cells



These are not ideal (thermodynamically limited) cells

Assumptions:
$\eta_{ext}$ = 90%
FF = 0.75

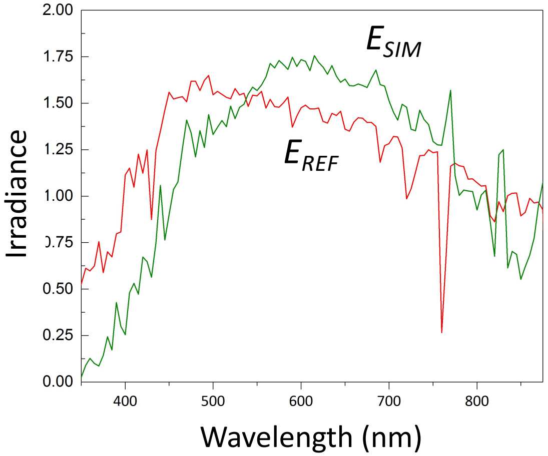
Che, PhD Thesis, U. Michigan (2018)

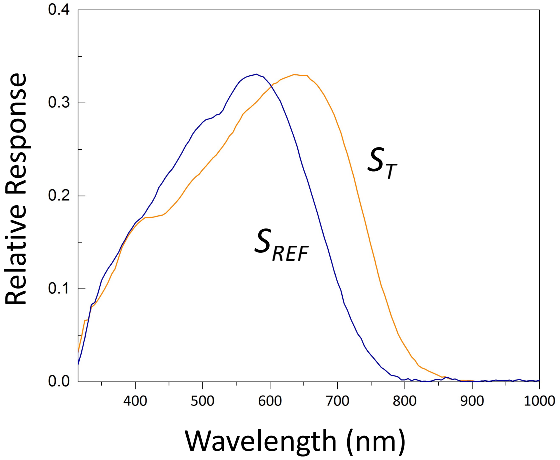
# Measuring *Single Junction* Solar Cell Efficiency

Challenges:

- The laboratory spectrum ($E_{REF}$) is not identically equal to the reference solar spectrum (AM1.5G):
  It is only simulated ($E_{SIM}$)
- Reference detector spectral response ($S_{REF}$) not identical to the test solar cell ($S_T$)

Example spectra:





To correct for these differences we calculate the *spectral mismatch factor*

$$M = \frac{j^T_{SIM}}{j^T_{REF}}\frac{j^{REF}_{REF}}{j^{REF}_{SIM}} = \frac{\int_{\lambda_1}^{\lambda_2} E_{SIM}(\lambda)S_T(\lambda)d\lambda \int_{\lambda_1}^{\lambda_2} E_{REF}(\lambda)S_{REF}(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{REF}(\lambda)S_T(\lambda)d\lambda \int_{\lambda_1}^{\lambda_2} E_{SIM}(\lambda)S_{REF}(\lambda)d\lambda}$$

$j^T_{SIM} = j_{SC}$ of test device using the simulated spectrum at 1 sun

$j^T_{REF} = j_{SC}$ of test device using the reference AM1.5G spectrum at 1 sun

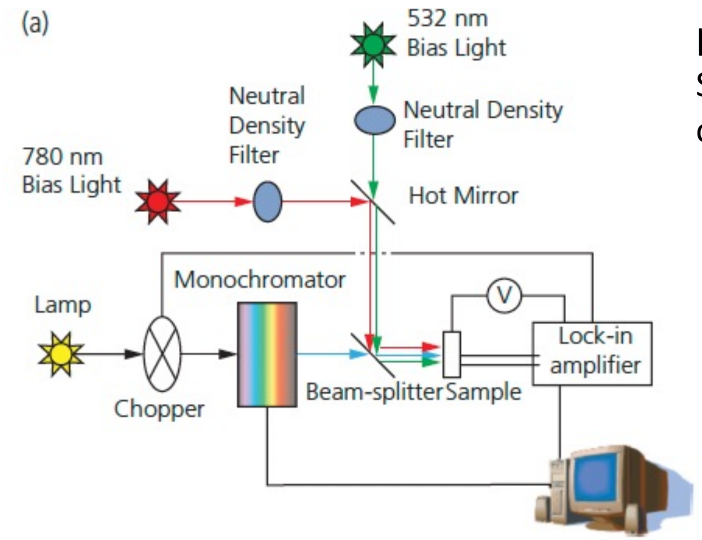
... etc.

$M = 1$ if $S_{REF} = S_T$ or $E_{REF} = E_T$

Solar cell calibration is then: $j^T_{REF} = \frac{j^{REF}_{REF} \bullet j^T_{SIM}}{M \bullet j^{REF}_{SIM}}$

For most accurate calibration: $M \cong 1$

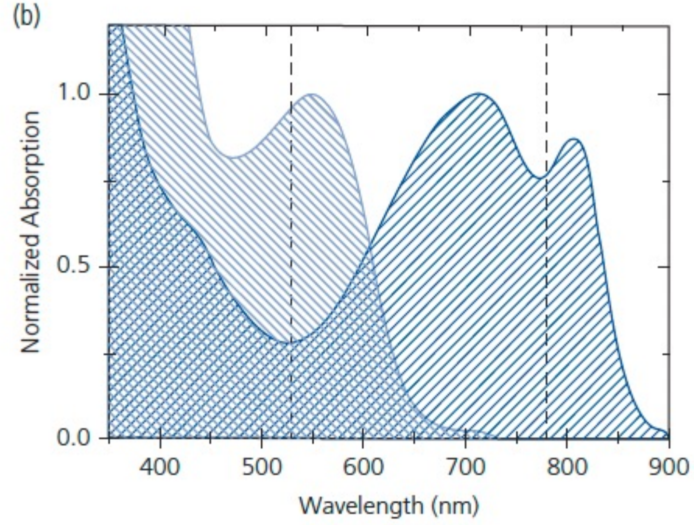
# Measuring Multijunction Cell Efficiency Is Tricky

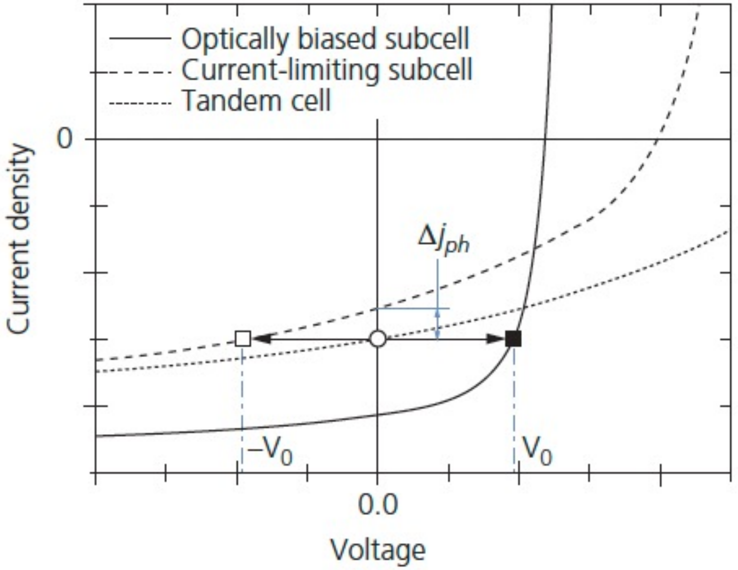


Cannot calculate spectral correction factor since relative excitation of subcells in stack finds a different current balance point than the reference spectrum

Solution: Directly measure the quantum efficiency of each subcell and calculate efficiency assuming the ref. spectrum

- Light bias the “other subcell” to create an optical short circuit
- Measure the desired cell $\eta_{ext}(\lambda)$ by usual means
- Light bias the desired subcell and measure $\eta_{ext}(\lambda)$ of the other cell by usual means
- Correct the efficiencies to their operating voltage points in the multijunction cell to compensate for slope in efficiency under reverse bias (due to $k_{PPd}$(V)) – see below
- Sum the two efficiencies to obtain $j_{SC}$ assuming the ref. spectrum

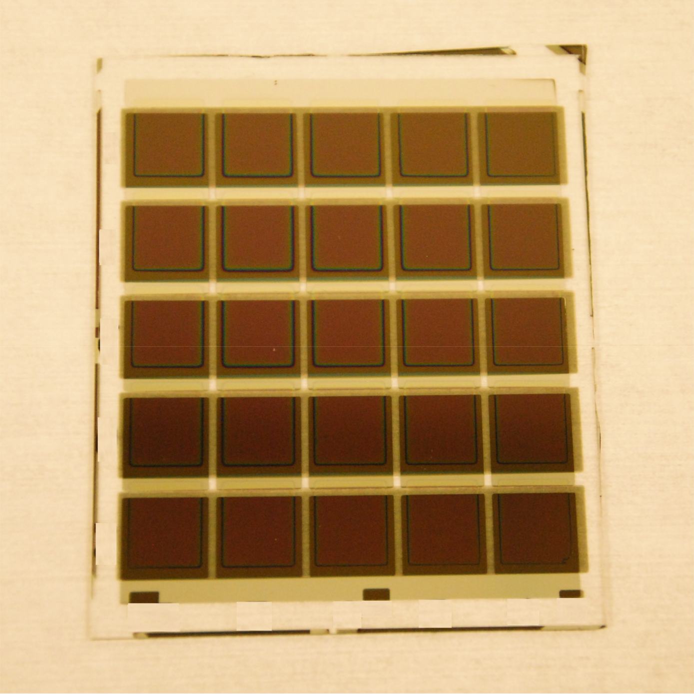


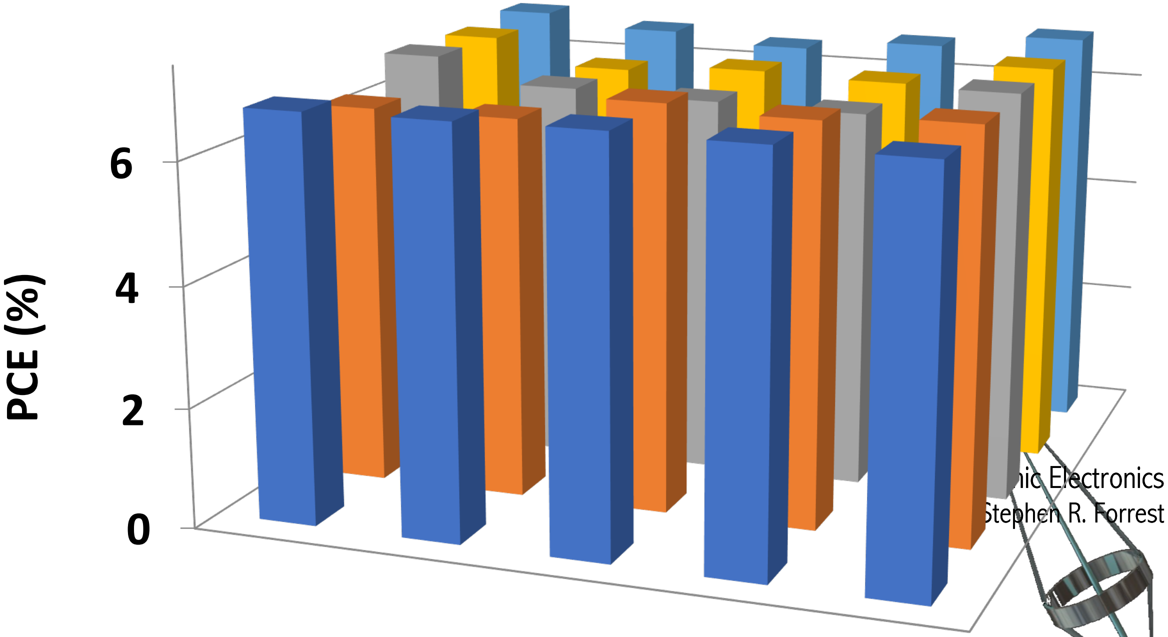


Gilot, et al. Adv. Funct. Mater., 20, 3904 (2010)

# Organic Solar Cell Challenges

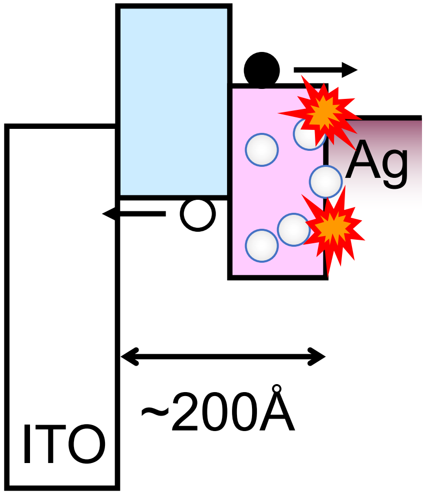
- High efficiency (>17%)
- Large Module Size
- High Reliability (>20 years)
- Low Production Cost (<$0.50/Watt)





# Getting to High Efficiency: The Double Heterojunction

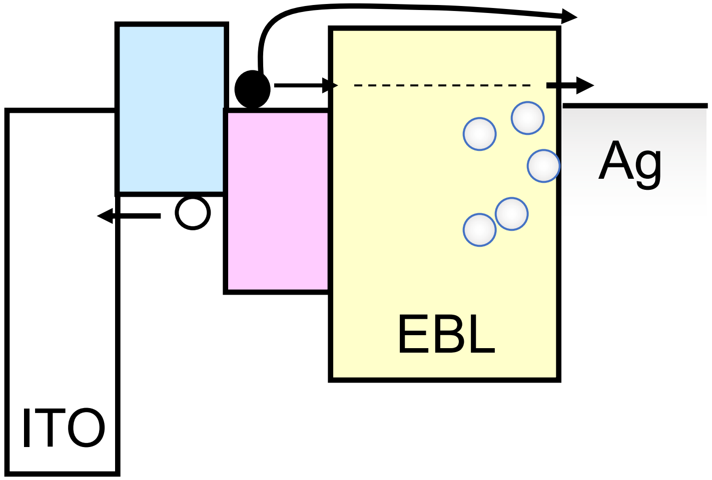
## Problem



(Tang cell: 1%)

- •cathode metal diffusion
- •deposition damage
- •exciton quenching
- •vanishing optical field
- •electrical shorts

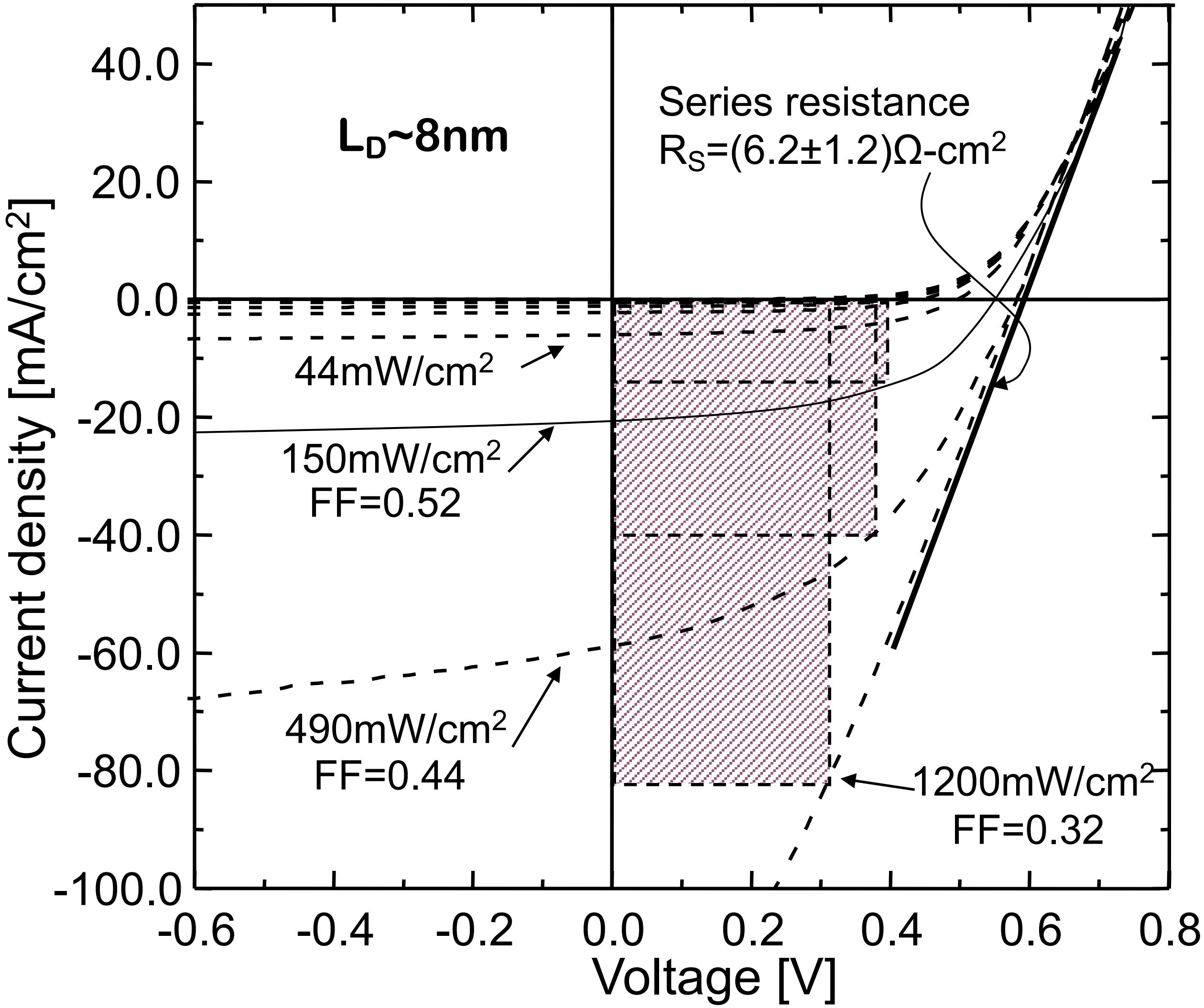
## Solution

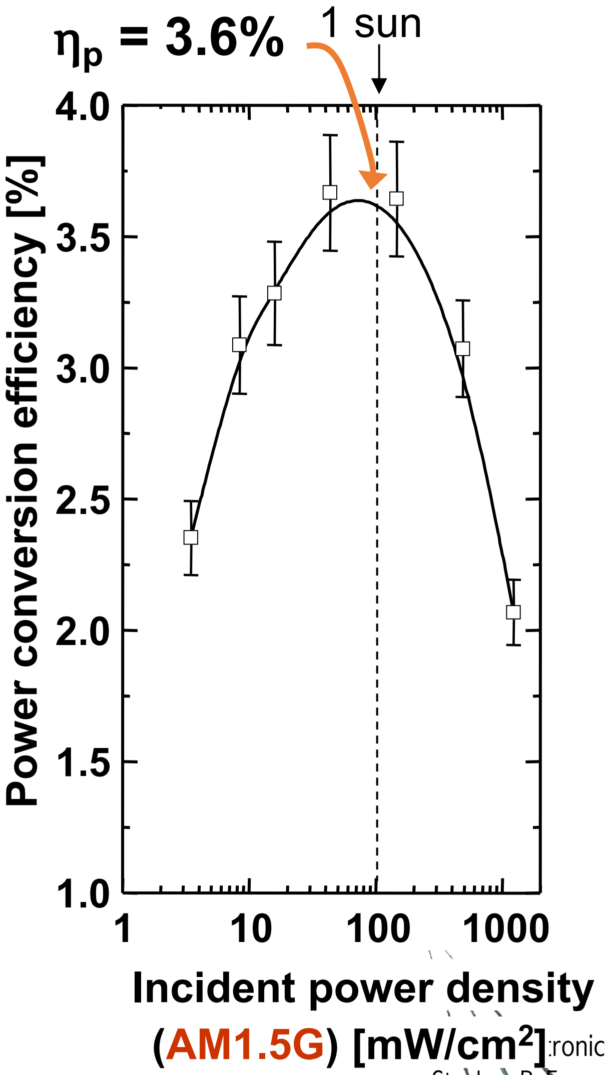


Introduce ‘Exciton Blocking Layer’ (EBL) to:

- confine excitons to active region
- separates active layer from metal
- act as a buffer to damage
- EBL thickness determined by depth of damage (if too thick, EBL is insulating)

# High efficiency via increased exciton diffusion length: Fullerene acceptors & double HJs



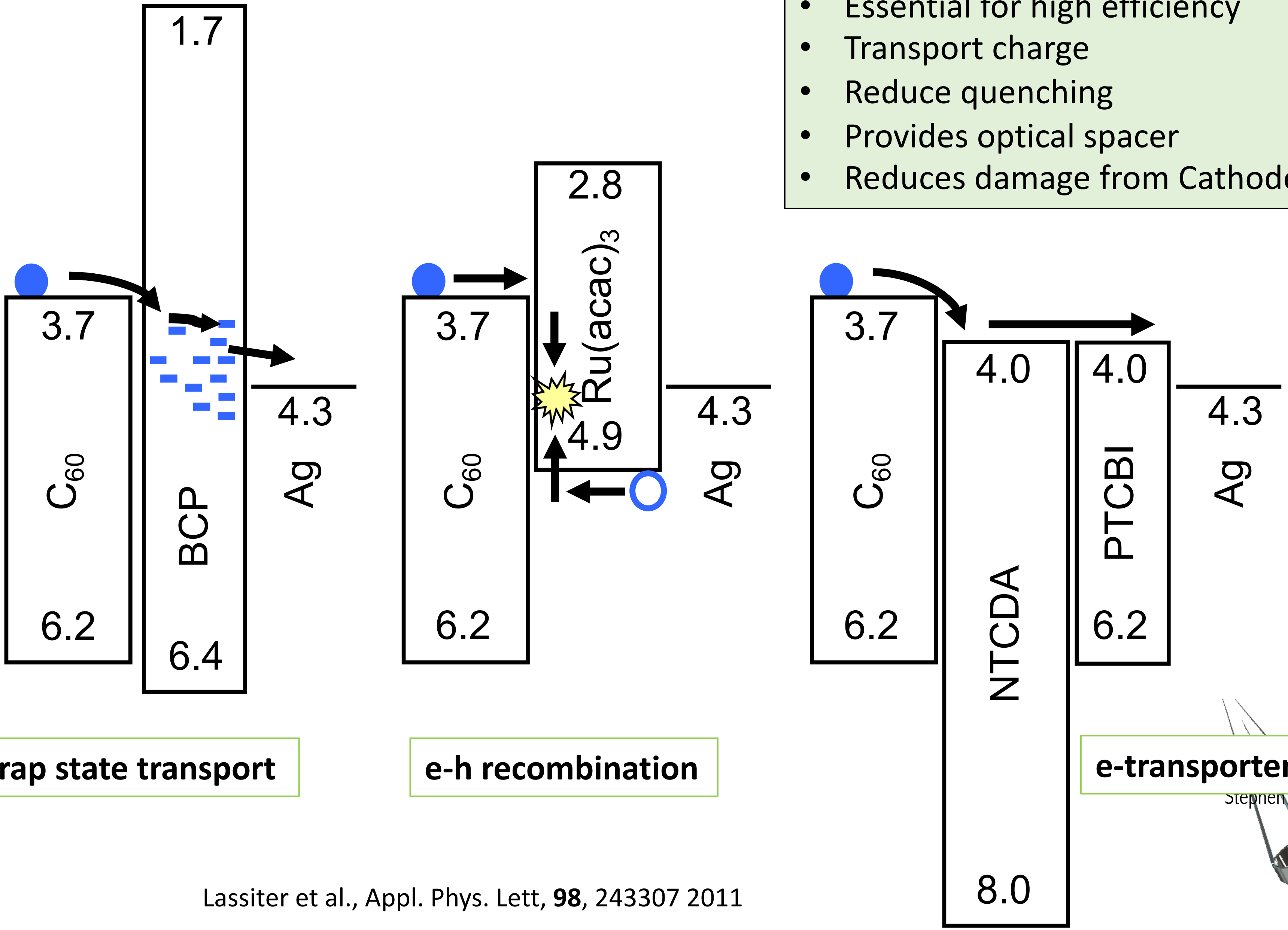


ITO/PEDOT/200Å CuPc/400Å $C_{60}$/**150Å BCP**/800Å Al

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

# Species of Exciton Blockers

- Essential for high efficiency
- Transport charge
- Reduce quenching
- Provides optical spacer
- Reduces damage from Cathode



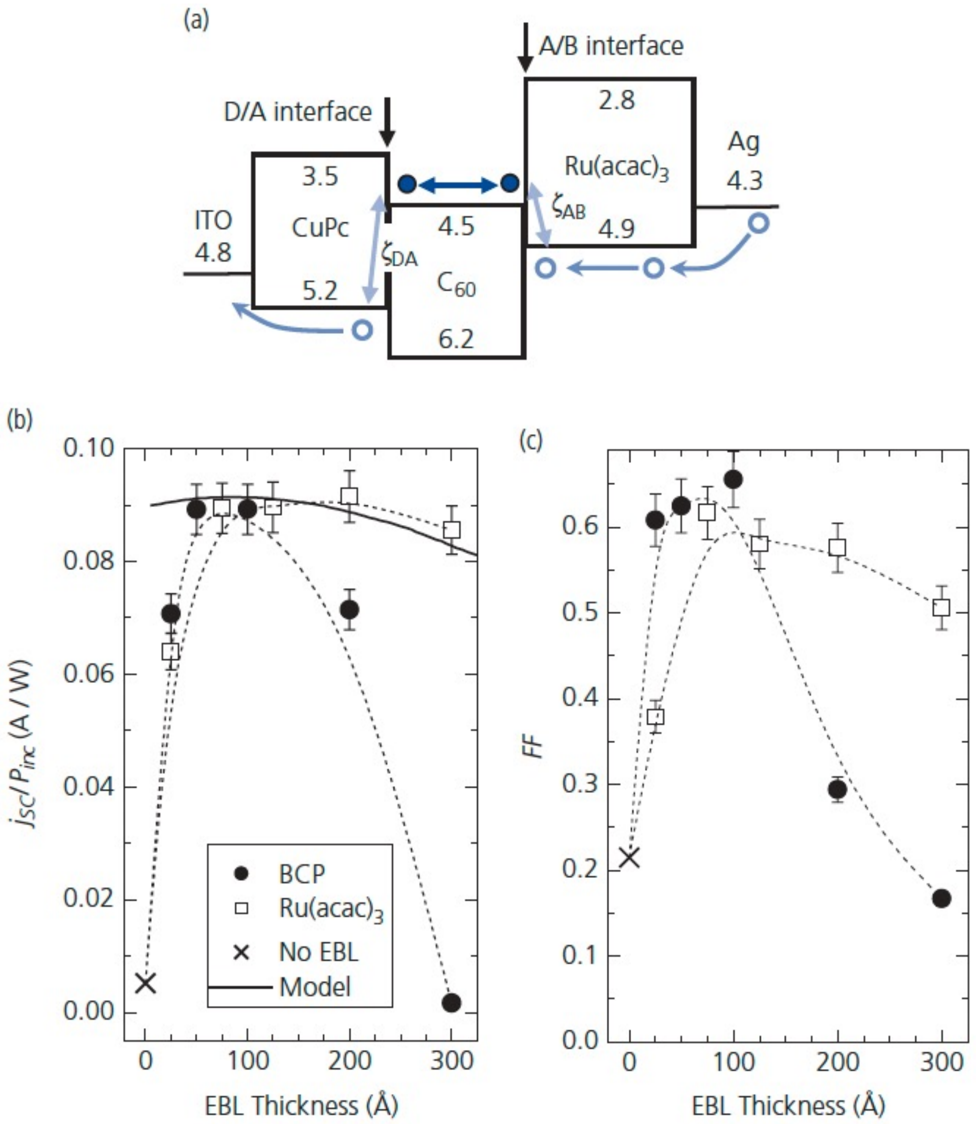
**Trap state transport**

**e-h recombination**

**e-transporter**

Lassiter et al., Appl. Phys. Lett, **98**, 243307 2011

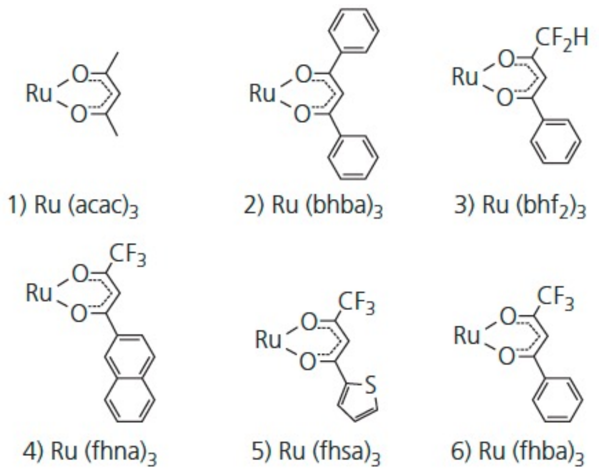
# e-h Recombination Buffers



Does not depend on defect formation
⇒ layer thickness can be optimized
for optical coupling to active region

Rand, et al. Adv. Mater. 17, 2714 (2005)

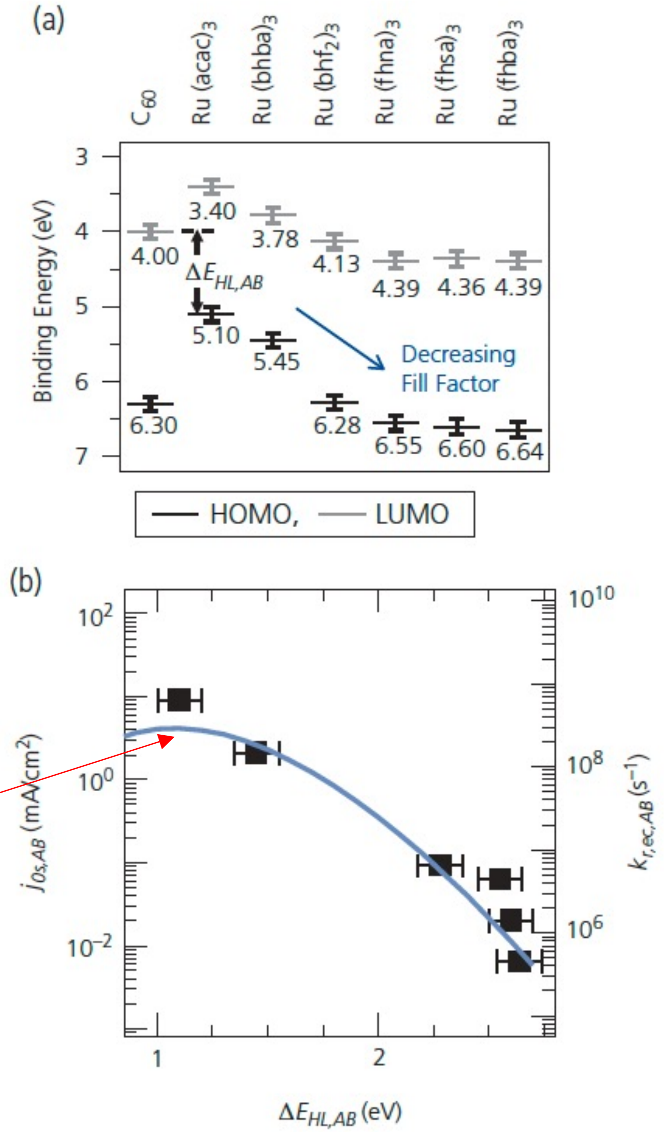
# Recombination Rate Determined by HOMO-LUMO Offset at Acc.-Buffer Junction



1) Ru (acac)$_3$ 2) Ru (bhba)$_3$ 3) Ru (bhf$_2$)$_3$

4) Ru (fhna)$_3$ 5) Ru (fhsa)$_3$ 6) Ru (fhba)$_3$

Family of Ru-compounds with varying Acc.-Buffer Energy Offsets

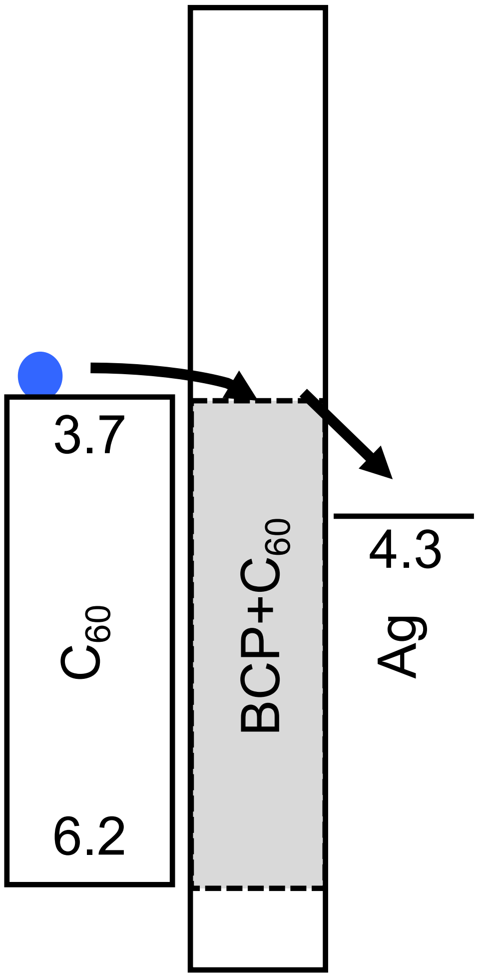


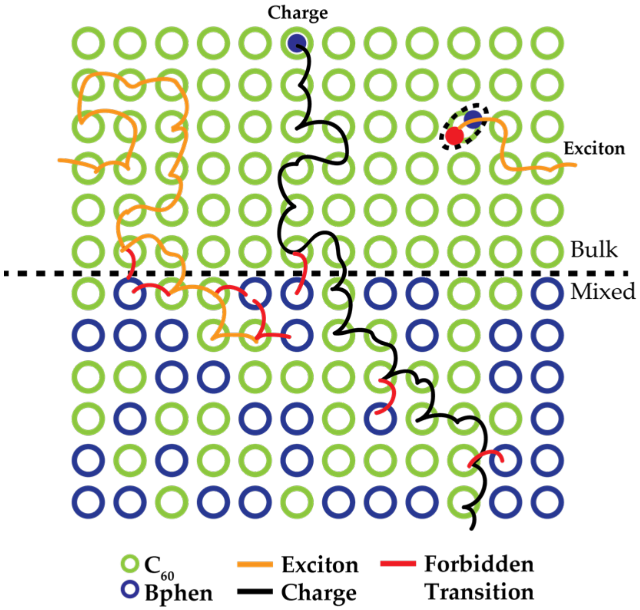
Marcus inversion

Renshaw et al. Phys. Rev. B, 84, 045315 (2011)

Organic Electronics
Stephen R. Forrest

# Electron Filtering Buffer Layer

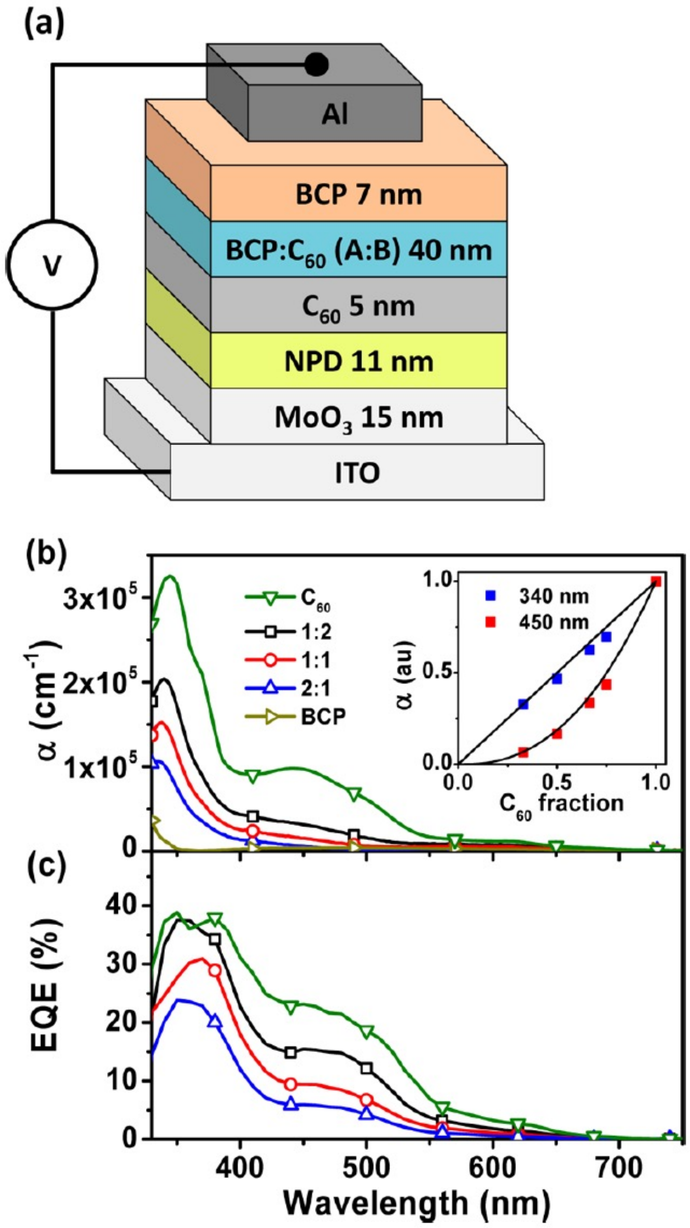


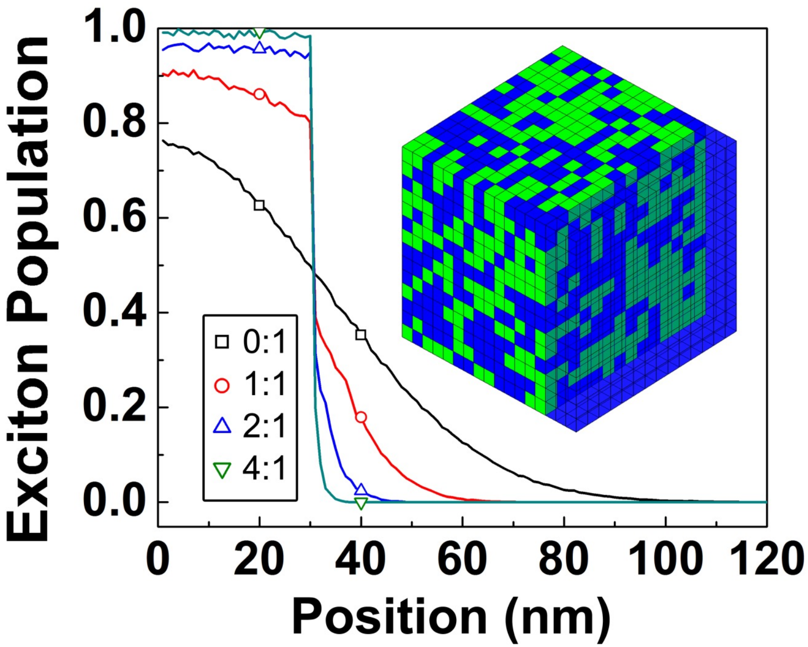


- Highly transparent
- Electron conductivity independent of $C_{60}$ conc. to ~30%
- Compound buffer: $C_{60}$:Bphen/BPhen
- Active region: DBP:$C_{70}$

Bartynski, et al., 13, 3315 Nano Lett (2013)

# $C_{60}$:Bphen Electron Filtering Blockers





| Doping ($C_{60}$:BCP) | Blocking Efficiency (%) |
|---|---|
| 1:0 | 49.9 ± 0.8 |
| 1:1 | 81.0 ± 0.6 |
| 1:2 | 94.9 ± 0.6 |
| 1:4 | 98.4 ± 0.6 |

Bartynski, et al., 13, 3315 Nano Lett (2013)