Week 11

Light Detectors 1

Photodetection basics
Photoconductors and Photodetectors
Solar Cell basics

Chapter 7.1-7.3.2

Objectives

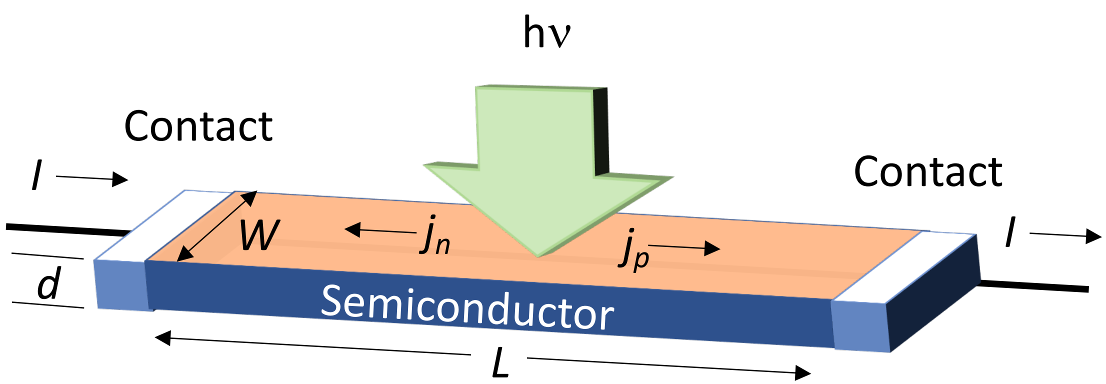
- Understand the physics of photodetection in organic photoconductors and photodiodes
- Understand OPD performance characteristics
  - Dark current
  - Efficiency and responsivity
  - Bandwidth
  - Noise
- Learn about OPD applications
- Solar cells: what makes OPVs a compelling story?
- Learn how to characterize solar cell performance
- Solar cell architectures
  - Thermodynamic efficiency limits to single junction cells
  - Multijunction cells and other architectures
  - The role of morphology
  - Some materials
- What lies beyond the horizon?

Photodetectors

- Transducers that convert light to another energy form (in our case, electricity)
- Types
  - Photoconductors
  - Photodiodes
    - These are operated in the reverse-biased (photodetection) or photovoltaic mode
- Properties
  - Sensitivity & Efficiency
  - Spectral range
  - Bandwidth
  - Dynamic range

Photoconductors

- Earliest organic electronic devices
- Simplest (no HJs needed)



When illuminated, conductivity changes

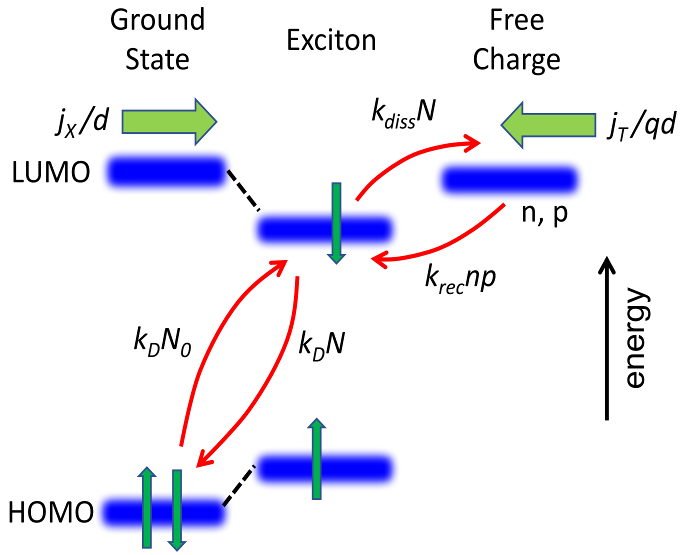
$$\sigma = q\left(\mu_n n + \mu_p p\right) \quad \begin{cases} p = p_{ph} + p_0 \\ n = n_{ph} + n_0 \end{cases}$$

$n_{ph} = p_{ph}$

Without background doping: $n_0 = p_0 = n_i$

Photocharge generation

- Generation does not occur through an intermediate CT state as it does at OPD heterojunctions:



Generation rate: $G_{ph} = k_D n_{ph} = \dfrac{\eta_{ext}\left(P_{inc}\lambda/hc\right)}{dWL}$

$\tau_D = 1/k_D$ = lifetime of charge

η_{ext} = external quantum efficiency (electrons out/photons in)

⇒ Photocurrent:

$$j_{ph} = \sigma F = qn_{ph}\left(\mu_n + \mu_p\right)\frac{V_a}{L} = q\frac{\eta_{ext}\left(P_{inc}\lambda/hc\right)}{k_D}\left(\mu_n + \mu_p\right)\frac{V_a}{dWL^2}$$

Gain and bandwidth

Photoconductors operate in the Ohmic (near equilibrium) regime

$$j_{ph} = \sigma F = q n_{ph} \left(\mu_n + \mu_p\right) \frac{V_a}{L} = q \frac{\eta_{ext} \left(P_{inc} \lambda / hc\right)}{k_D} \left(\mu_n + \mu_p\right) \frac{V_a}{dWL^2}$$

$\Rightarrow$ A photoconductor has gain: $g = \dfrac{j_{ph}}{j_0} = \tau_D \left(\mu_n + \mu_p\right) \dfrac{V_a}{L^2}$

Where: $j_0 = q\eta_{ext} \left(P_{inc} \lambda / hc\right) / dW$

That is: gain = τ_D / t_{tr}, where the carrier transit time is $t_{tr} = L/v = L/\mu F = L^2/\mu V$

$$g\eta_{ext} = \frac{j_{ph} A}{q\left(P_{inc} \lambda / hc\right)}$$

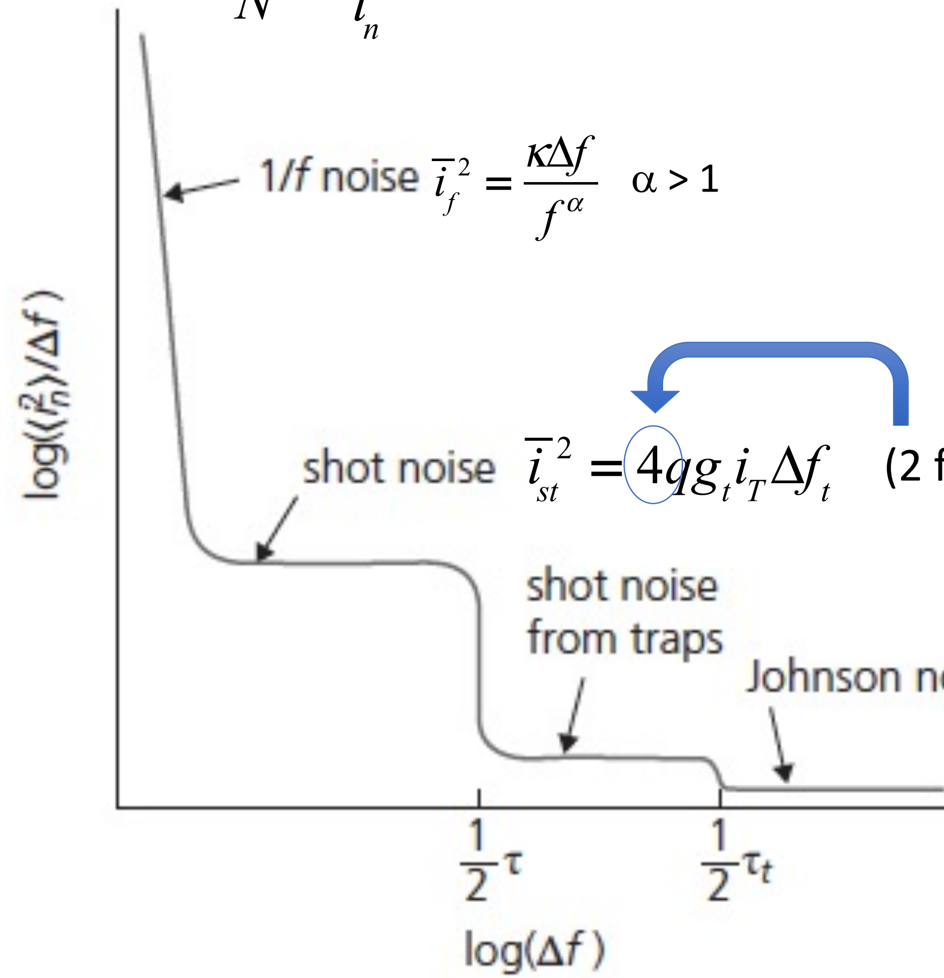
Quantum efficiency cannot be separated from gain

- Bandwidth: $\Delta f = 1/2\pi \tau_D$
- Leading to a gain-bandwidth product: $g\Delta f = 1/2\pi t_{tr}$

Noise

- Determines the sensitivity of a photodetector to low intensity signals

- Signal-to-noise ratio: $\frac{S}{N} = \frac{\overline{i}_{ph}^{2}}{\overline{i}_{n}^{2}} > 1$



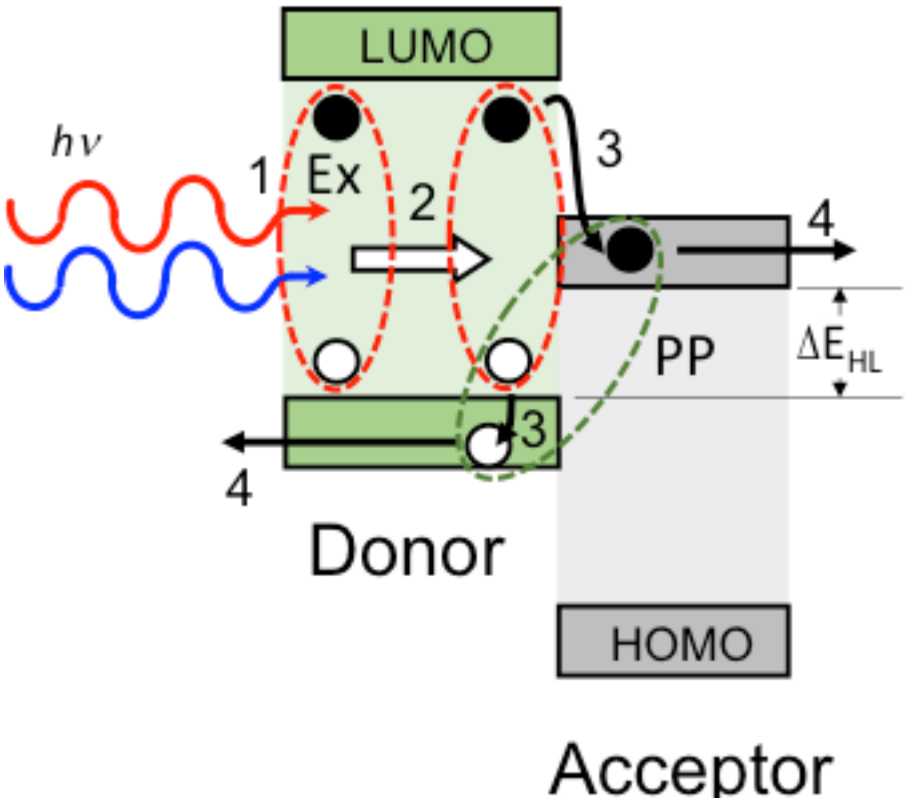
1/f noise $\overline{i}_{f}^{2} = \frac{\kappa \Delta f}{f^{\alpha}}$ $\alpha > 1$

shot noise $\overline{i}_{st}^{2} = 4 q g_t i_T \Delta f_t$ (2 for OPD)

Johnson noise $\overline{i}_{th}^{2} = \frac{4 k_B T \Delta f}{R_{PC}}$

Photodiodes and solar cells

- Many of the same considerations as photoconductors except there is a junction for efficient charge separation.

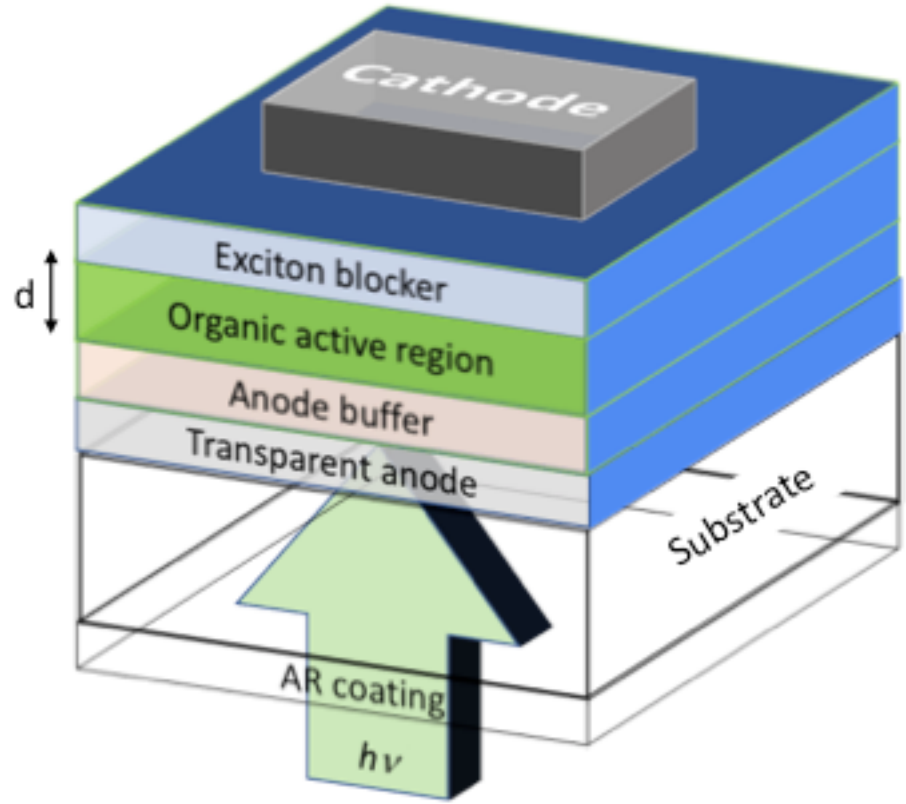


1. Exciton generation by absorption of light (abs length~1/α)
2. Exciton diffusion over ~L_D
3. Exciton dissociation by rapid and efficient charge transfer
4. Charge extraction by the internal electric field

Typically: $L_D \ll 1/\alpha$

$$\eta_{ext} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC}$$

Basic OPD/OPV structure

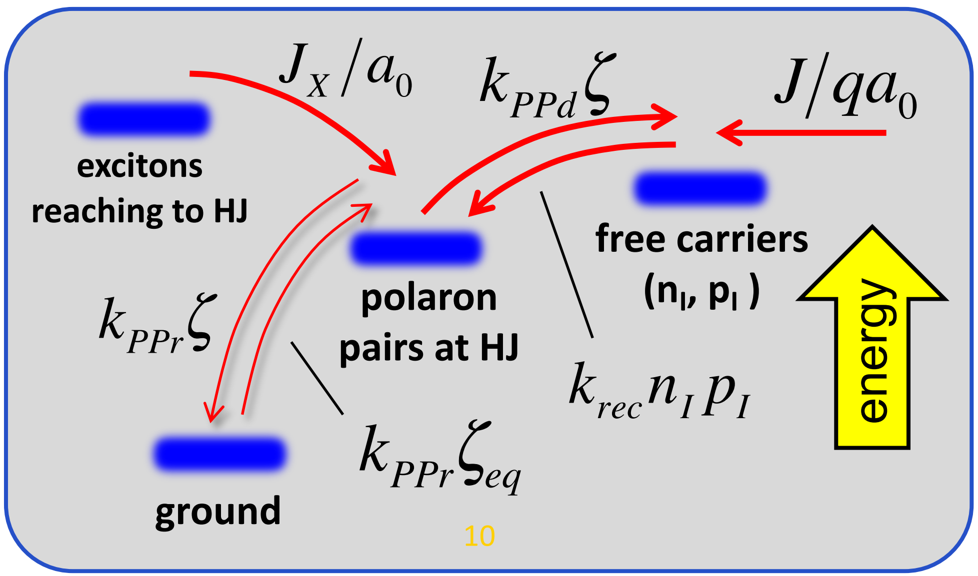


Current generation

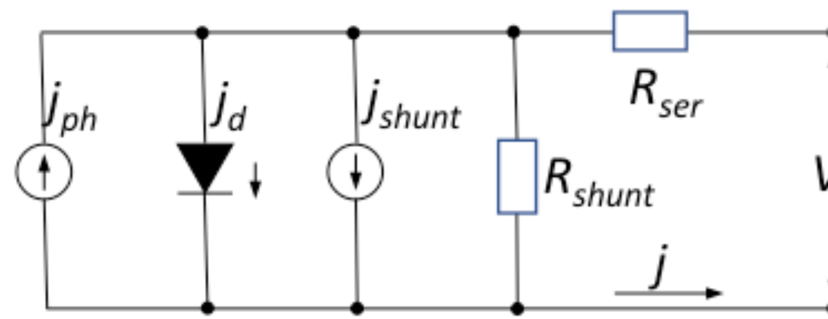
- Recall (Ch. 4) that the *j-V* characteristics are given by:

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

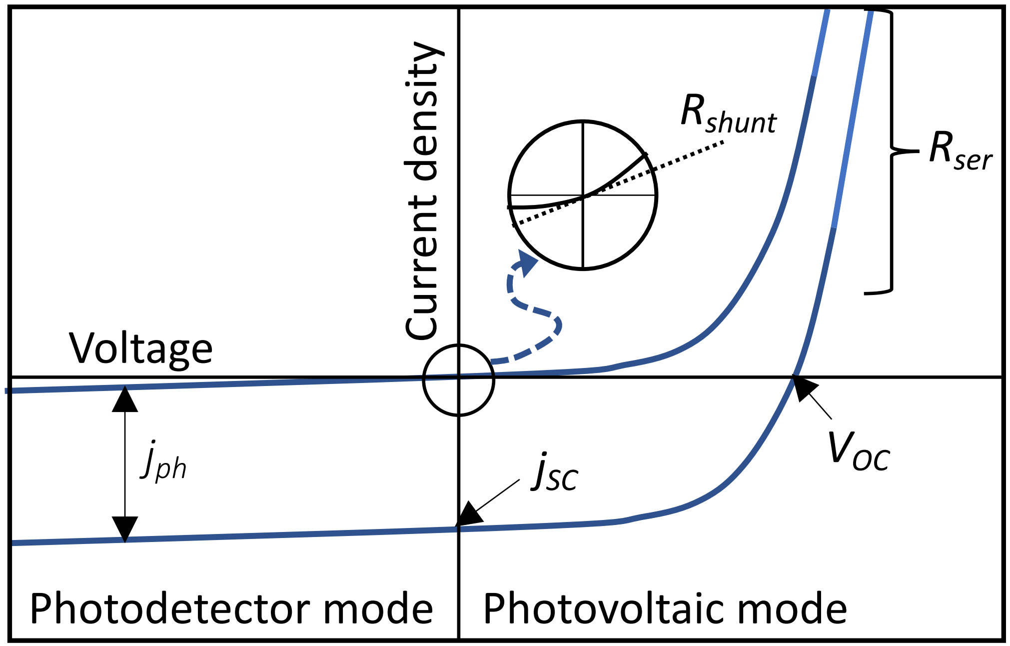
Saturation current $j_0 = q a_0 k_{rec} N_S^2 \left(1 - \eta_{PPd}\right)\exp\left(-\Delta E_{HL}/k_B T\right)$



Equivalent circuit



Current-Voltage Characteristics

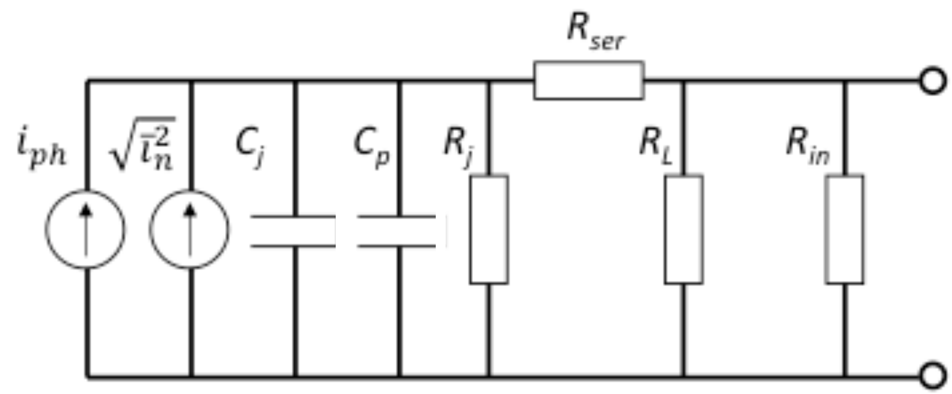


$$R_{shunt} = \frac{1}{A}\frac{dV_a}{dj}\bigg|_{V_a=0}$$

- In the photovoltaic mode, the power is $P = jV < 0$; i.e. the device delivers power to the external circuit.
- In the photodetector mode, $P > 0$ and the detector dissipates power.

Photodiode bandwidth

PD Equivalent Circuit



$$\Delta f = \frac{1}{2\pi}\left(\frac{1}{t_{tr}} + \frac{1}{\tau_{ED}} + \frac{1}{\tau_{RC}}\right)$$

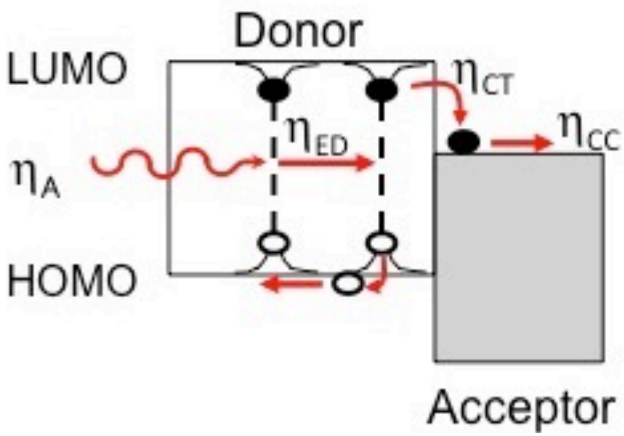
$$\tau_{RC} = (R_{ser} + R_L || R_{in})(C_j + C_P)$$

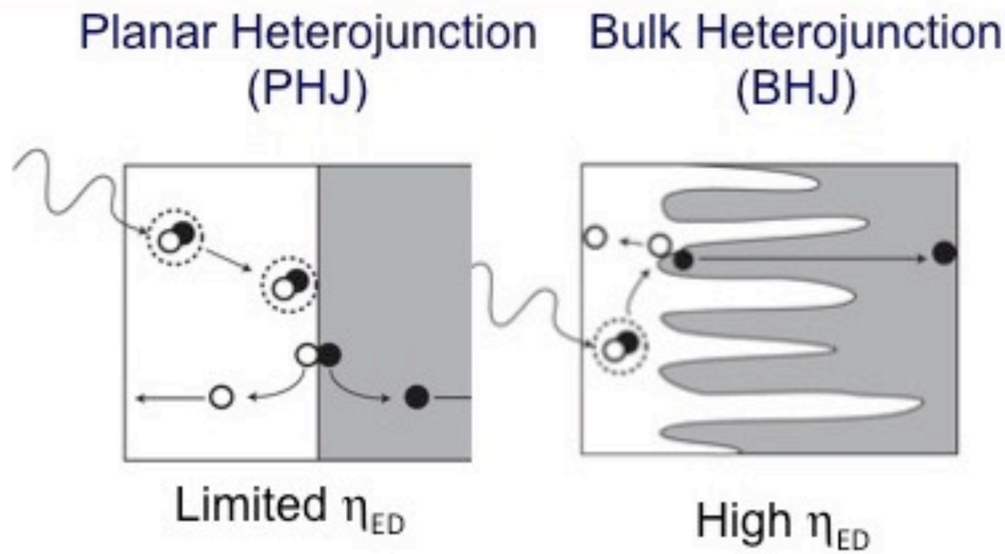
$$R_j \to \infty$$

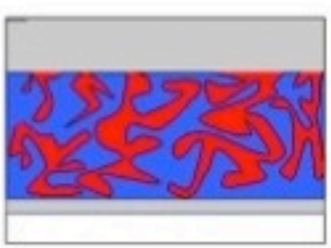
In an OPD *g* = 1, such that $g\Delta f = \Delta f$

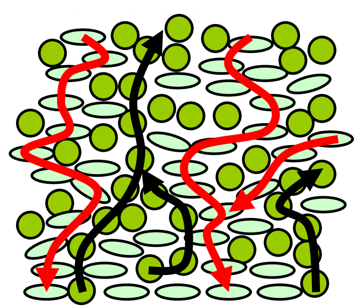
Heterojunction Morphologies

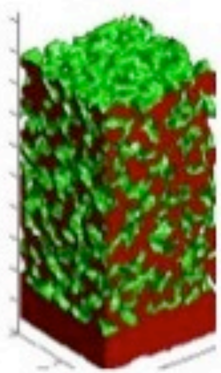
Breaking the tradeoff between L_D and α with BHJs

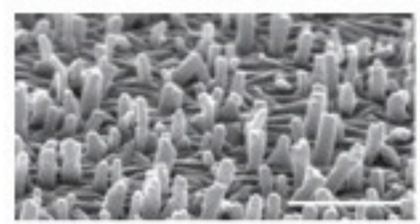




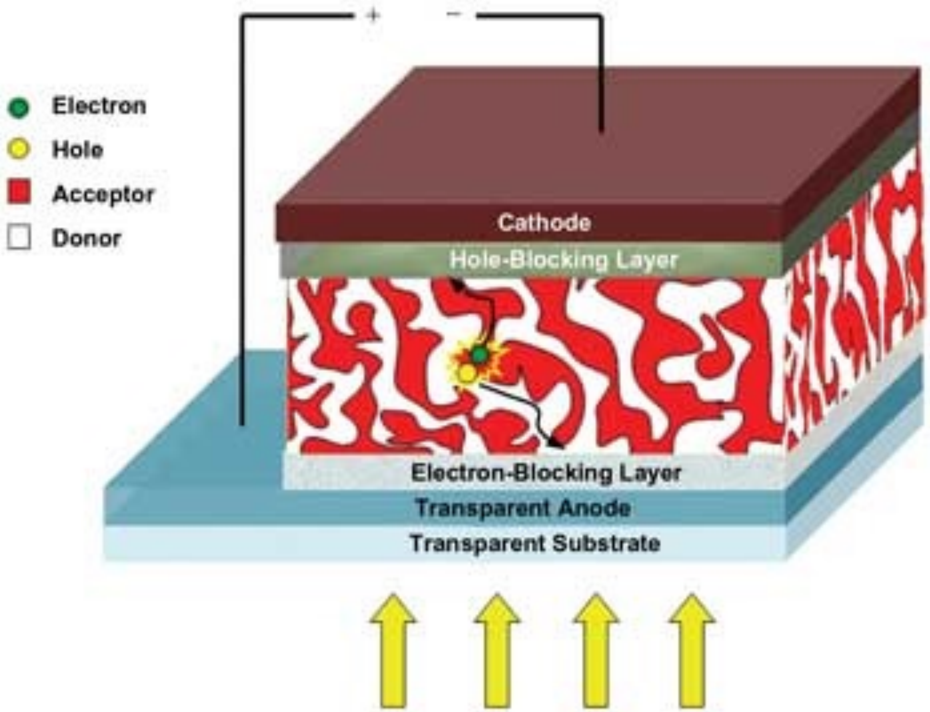

Bulk HJ

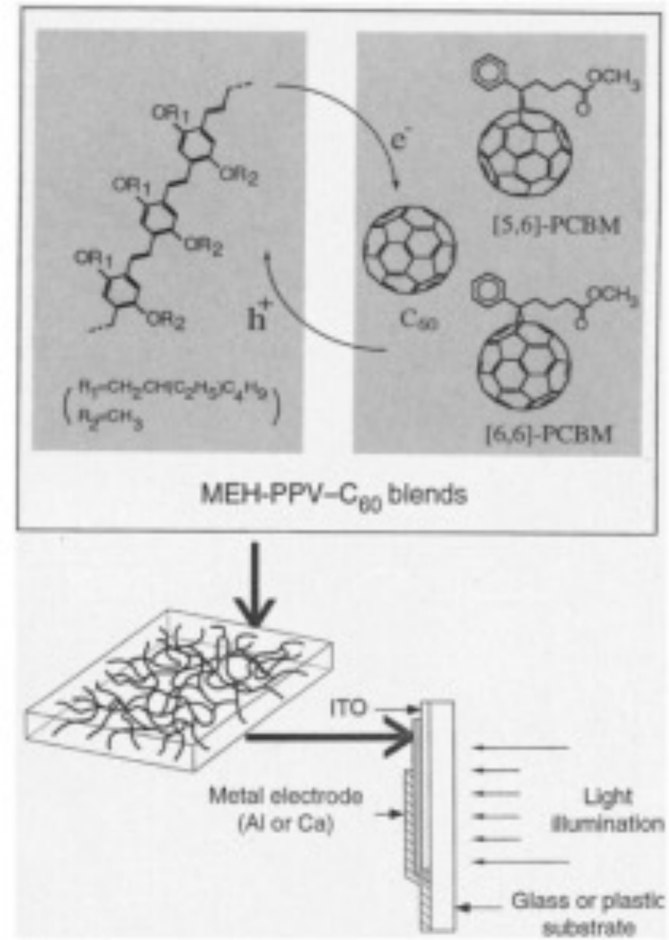

Mixed HJ


Annealed BHJ


Controlled BHJ

Polymer Bulk HJ



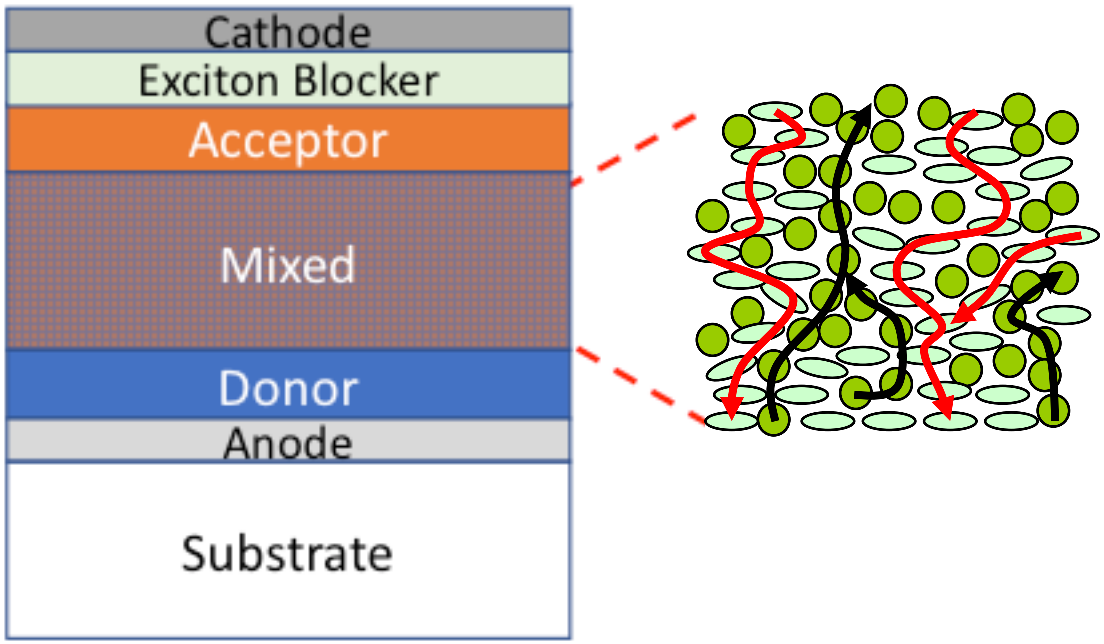


Yu et al. Science, **270**, (1995), 1789

Halls et al., (1995) Nature, 376, 498.

Small Molecule Planar-Mixed HJ

Small molecule blends: $\eta_{ED} = 1$



$$\eta_{CC} = \frac{L_C}{x_M}\left(1-\exp\left(-x_M/L_C\right)\right)$$

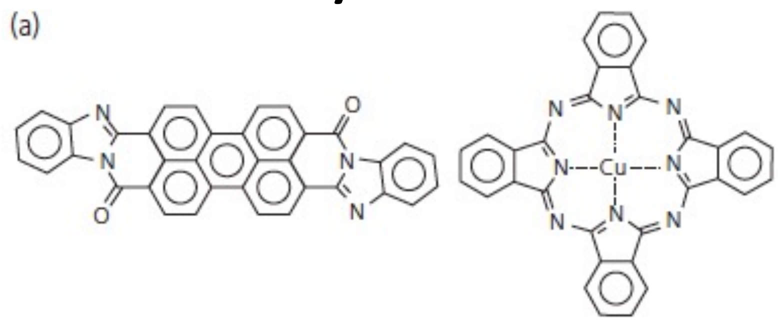
Charge carrier collection length, L_C, replaces diffusion length since excitons dissociate at point of generation without diffusion to HJ

J. Xue, *Adv. Mater.*, vol. 17, p. 66, 2005.

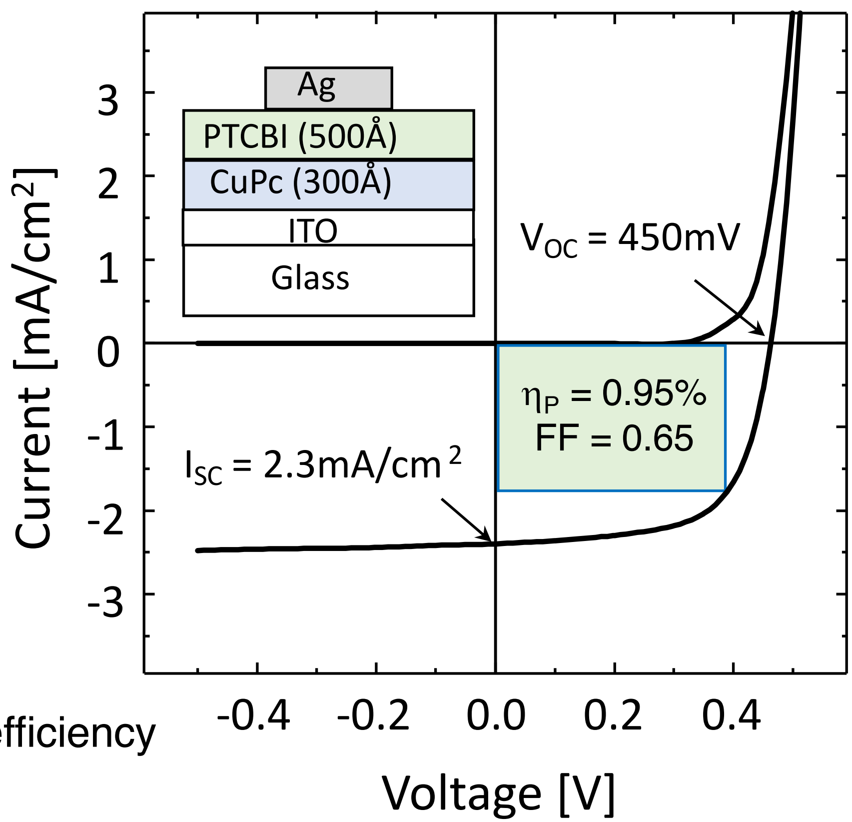
Comparison of OPCs and OPDs

Parameter	Photoconductor	Photodiode
Operating voltage	Near equilibrium ($V_a \to 0$)	Reverse bias
Photocurrent gain (g)	τ/t_{tr} (1-10^6)	1
η_{int}	$k_{diss}/(k_{diss}+k_D)$	$k_{ppd}/(k_{PPd}+k_{PPr})$
η_{ext}	$\dfrac{j_{ph}A}{qg(P_{inc}\lambda/hc)}$	$\dfrac{j_{ph}A}{q(P_{inc}\lambda/hc)}$
Responsivity	$qg\eta_{ext}(\lambda/hc)$	$q\eta_{ext}(\lambda/hc)$
Bandwidth (Δf)	$1/2\pi\tau_D$	$1/2\pi t_{tr}$
Gain-bandwidth product ($g\Delta f$)	$1/2\pi t_{tr}$	$1/2\pi t_{tr}$
$\overline{i}_n^2/\Delta f$	$(4k_BT)/R_{PC}+\kappa/f^{\alpha}$	$2qi_T+4k_BT/R_L \parallel R_{in}$
Specific detectivity ($D*$)	$q\eta_{ext}(\lambda/hc)\sqrt{\dfrac{A}{(4k_BT)/R_{PC}+\kappa/f^{\alpha}}}$	$q\eta_{ext}(\lambda/hc)\sqrt{\dfrac{A}{2qi_T+4k_BT/R_L \parallel R_{in}}}$

The first bilayer OPD/OPV



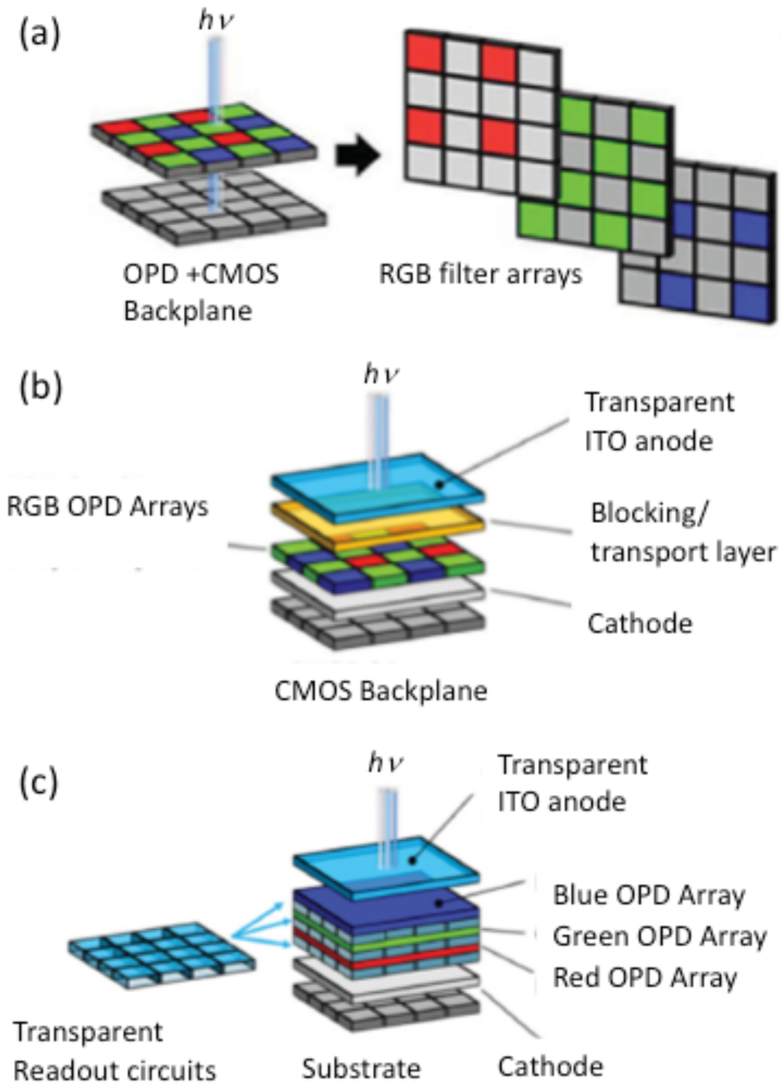
acceptor donor



η_P = power conversion efficiency
FF = fill factor

Tang, Applied Phys. Lett., (1986) **48**, 183.

How your camera works

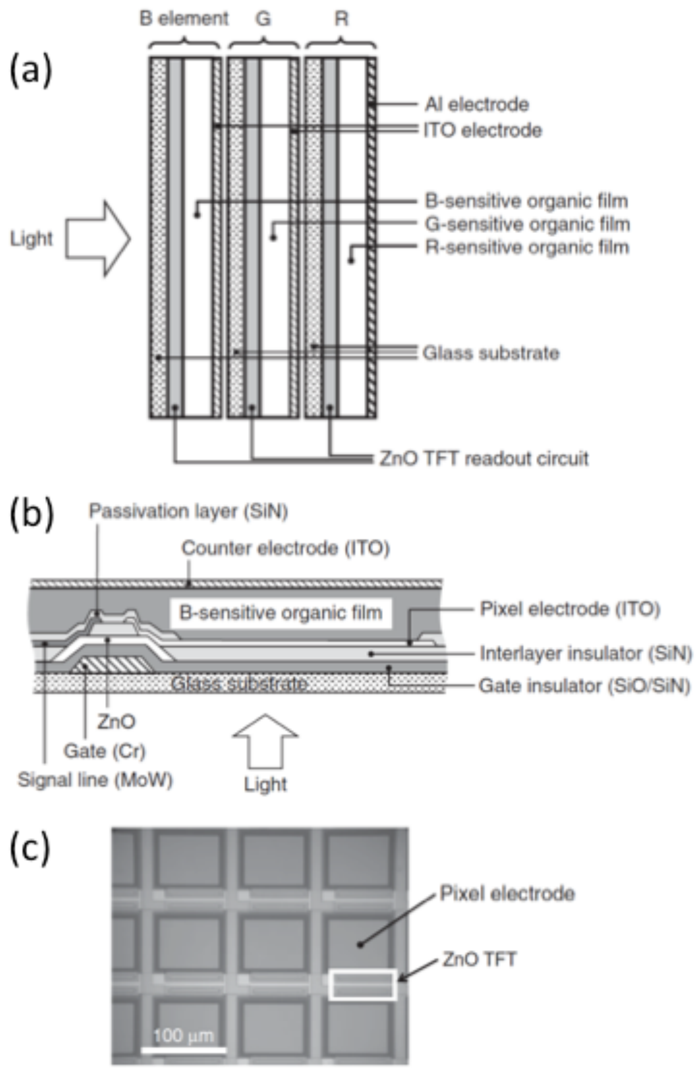


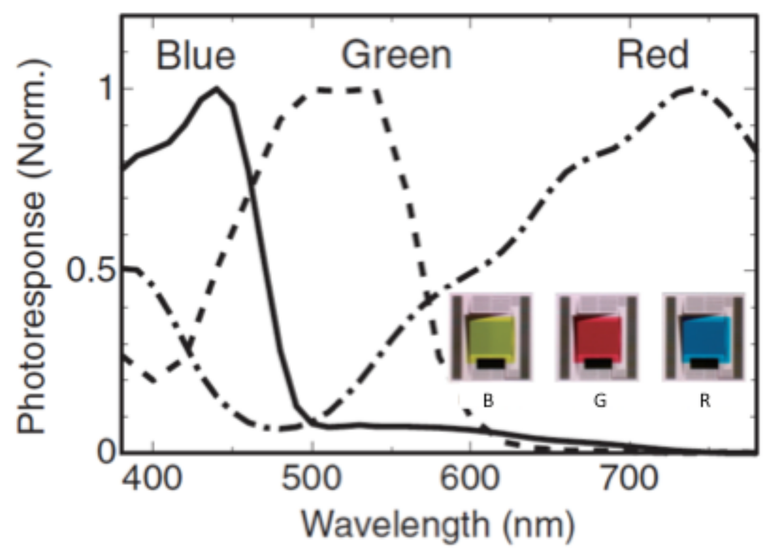
Color filters

Integrated RGB Sensitive OPDs

Stacking R, G, B layers

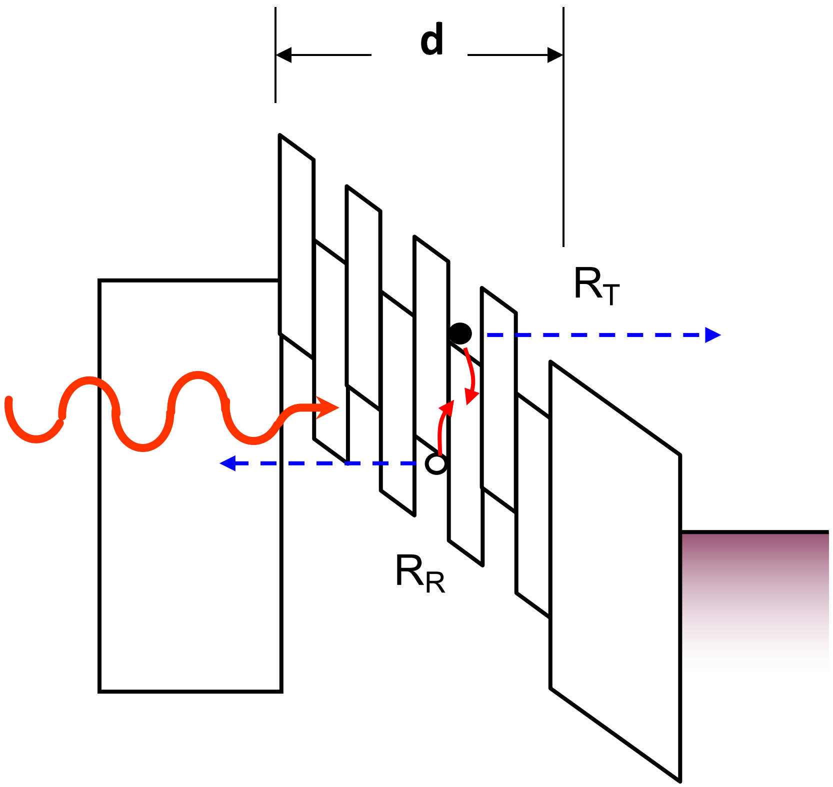
Stacked sensors





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

High Bandwidth Multilayer Photodetectors



Place all D/A junctions within L_D of absorption site

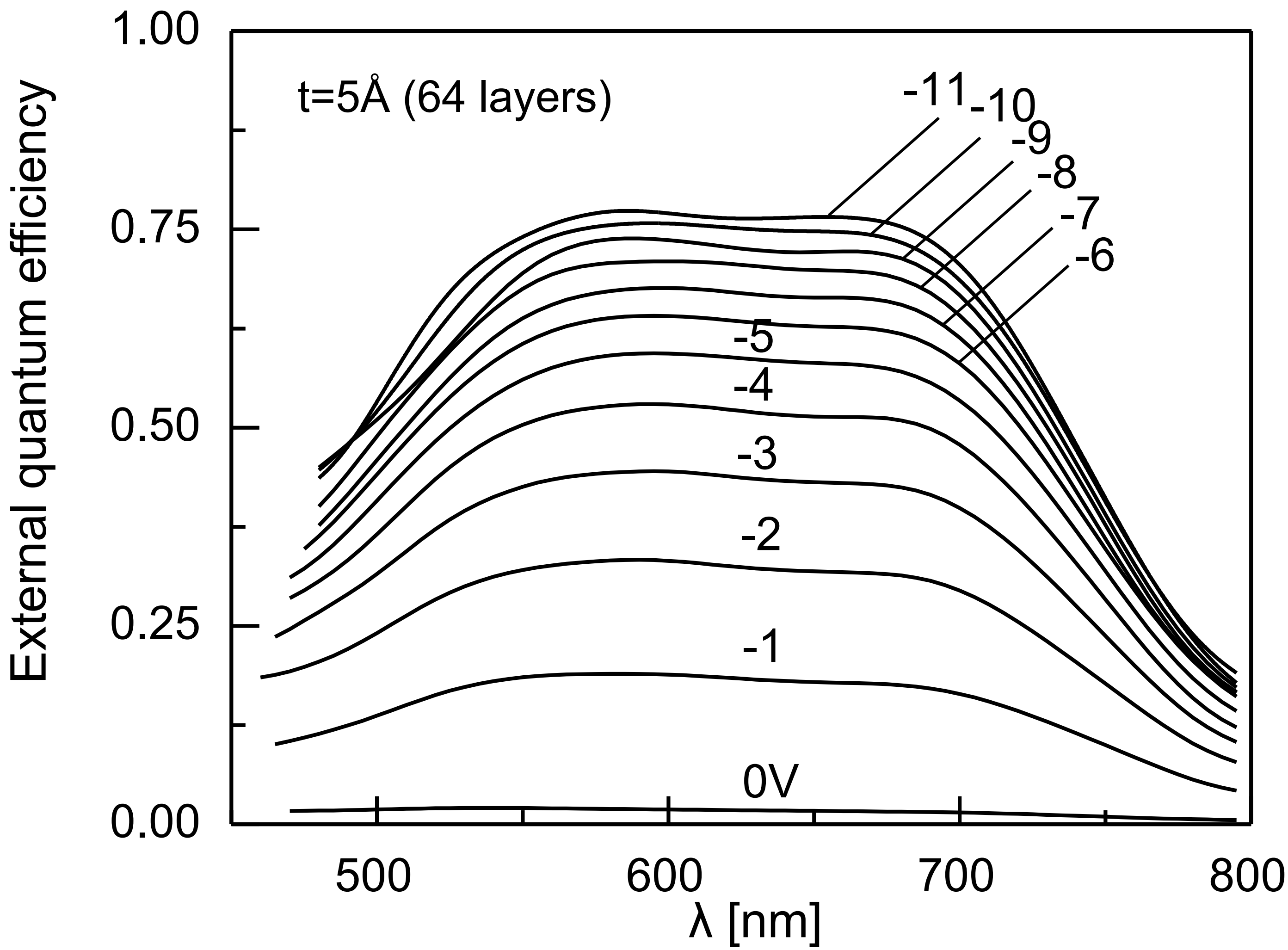
Stack layers until total thickness d ~ $1/\alpha$

Apply voltage to sweep charge out of potential wells

Bandwidth due to transit time across d.

Spectral + Voltage Dependence of the EQE

- Sensitive to visible + NIR wavelengths
- Strong dependence on bias: EQE~75% @ -10V



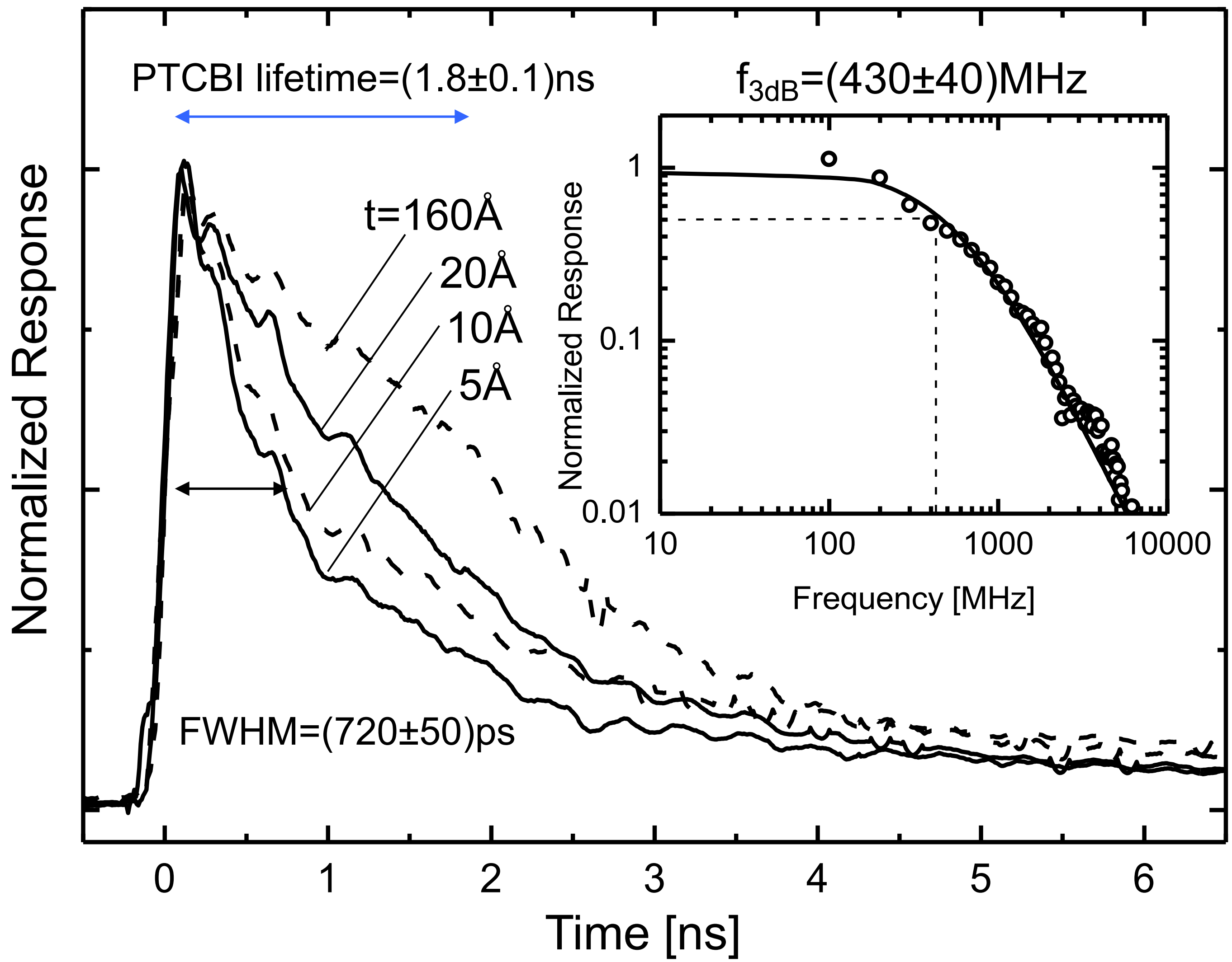
P. Peumans, et al. *Appl. Phys. Lett.*, **76,** 3855 (2000).

Response Time

Thinner individual layers makes faster devices due to a reduced exciton lifetime

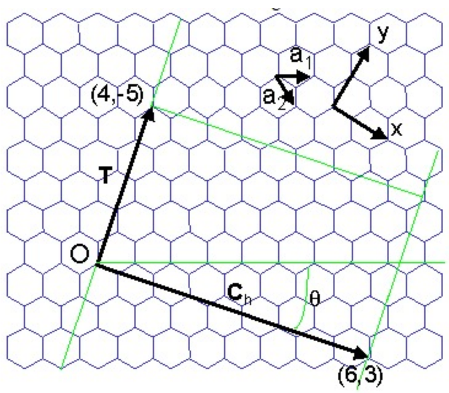
100 μm diameter, -9V, 1.4ps excitation @ 670nm at (1.0±0.3)W/cm².

Estimated carrier velocities: $v = d/\tau = (1.1 \pm 0.1) \times 10^4\ cm/s$

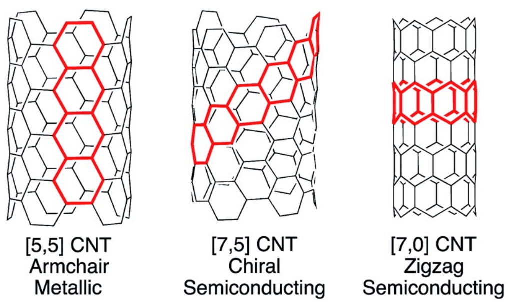


Long wavelength Detectors

Carbon Nanotubes Can Stretch Detection to NIR



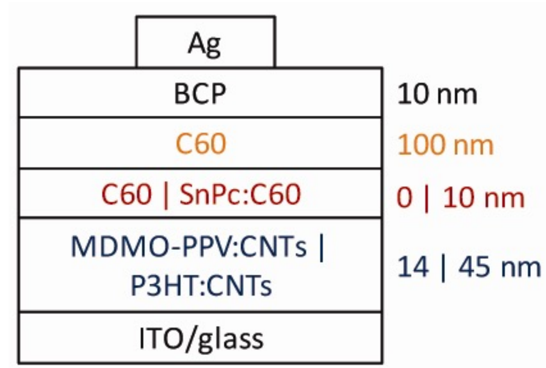
$$C_h = n\mathbf{a}_1 + m\mathbf{a}_2$$

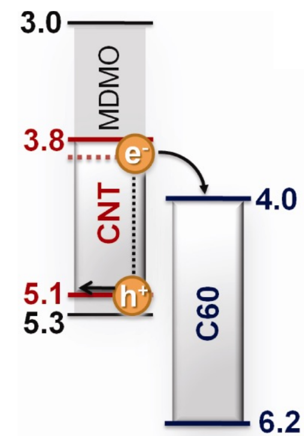


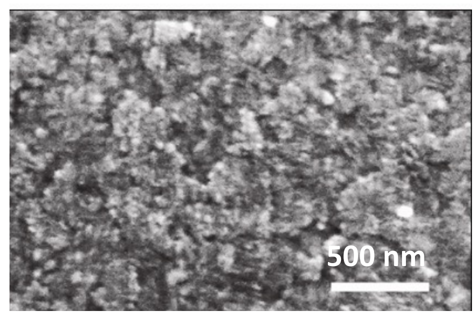
Chirality determines if CNT
is metallic, semiconducting or insulating

$n = m$: Metallic
$n\text{-}m = 3i$ (i integer), $n \neq m$, $nm \neq 0$: semimetal
otherwise: semiconductor

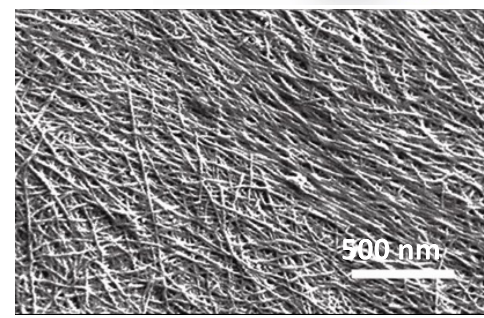
Organic/CNT Detector







CNT:MDMO-PPV composite

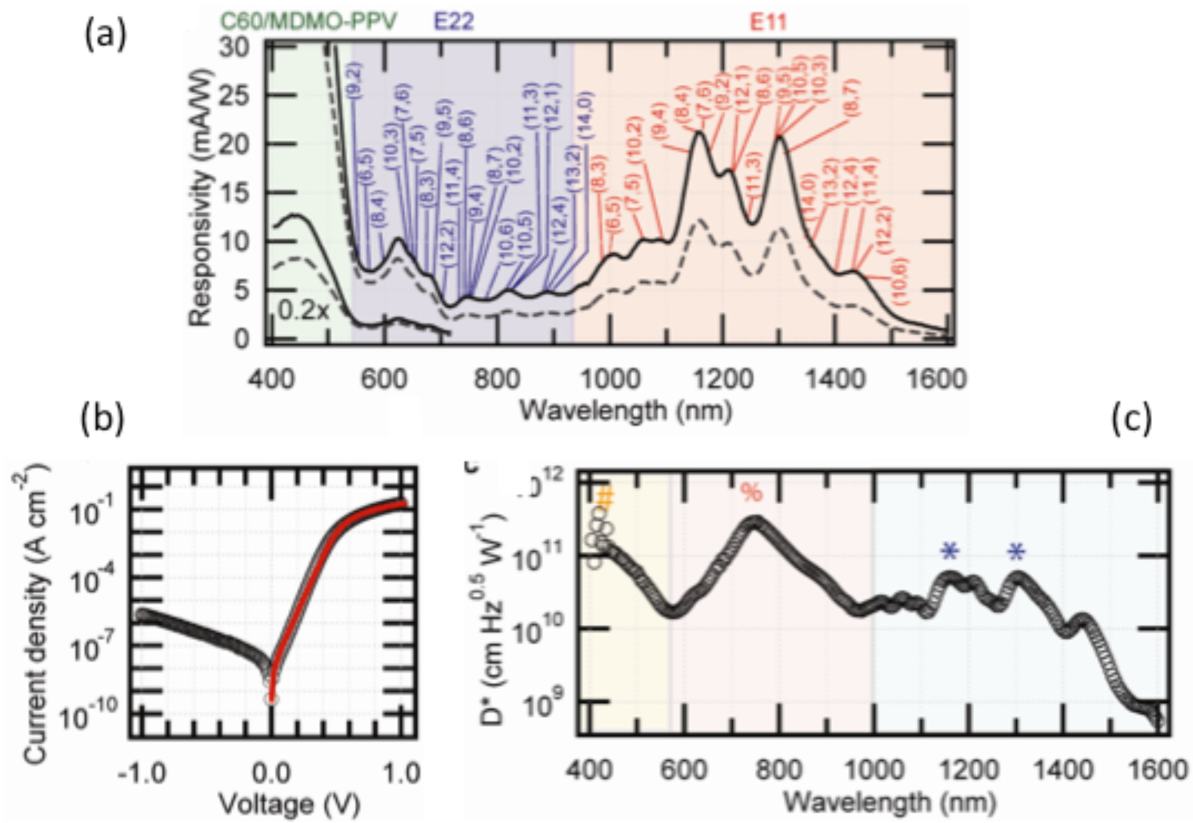


Mat of bare CNT

M. S. Arnold, et al., *Nano Letters,* **9**, 3354, 2009.

Long wavelength Detectors

Single Walled Nanotubes Wrapped in Polymer



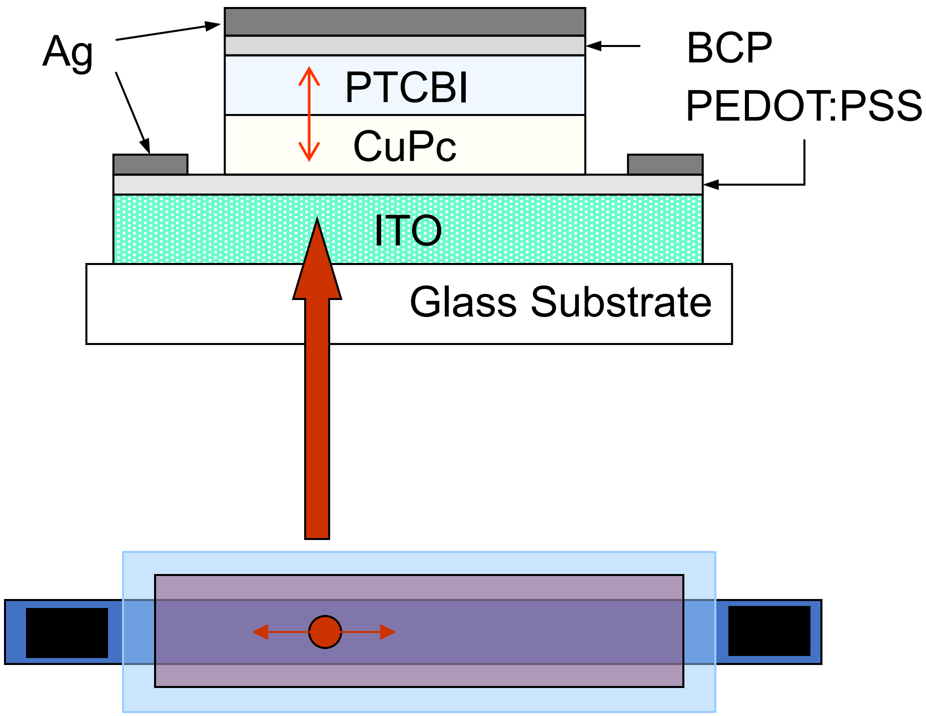
Responsivity and Specific Detectivity:

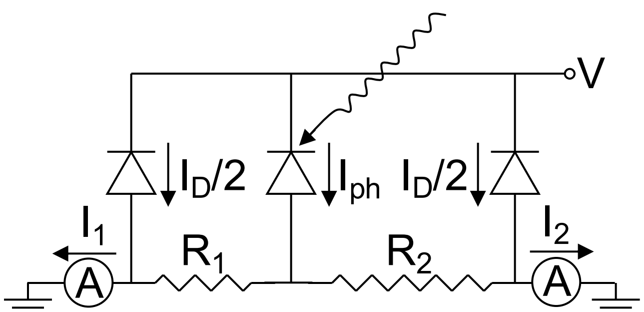
$$\mathcal{R} = \frac{j_{ph}A}{P_{inc}} = qg\eta_{ext}\left(\frac{\lambda}{hc}\right) \text{ [A/W]} \qquad D^* = \frac{\sqrt{A\Delta f}}{NEP} = \mathcal{R}\sqrt{\frac{A\Delta f}{\overline{i_n^2}}} \text{ [cm-Hz}^{1/2}\text{/W]}$$

M. S. Arnold, et al., *Nano Letters,* **9**, 3354, 2009.

Position Sensitive Detectors

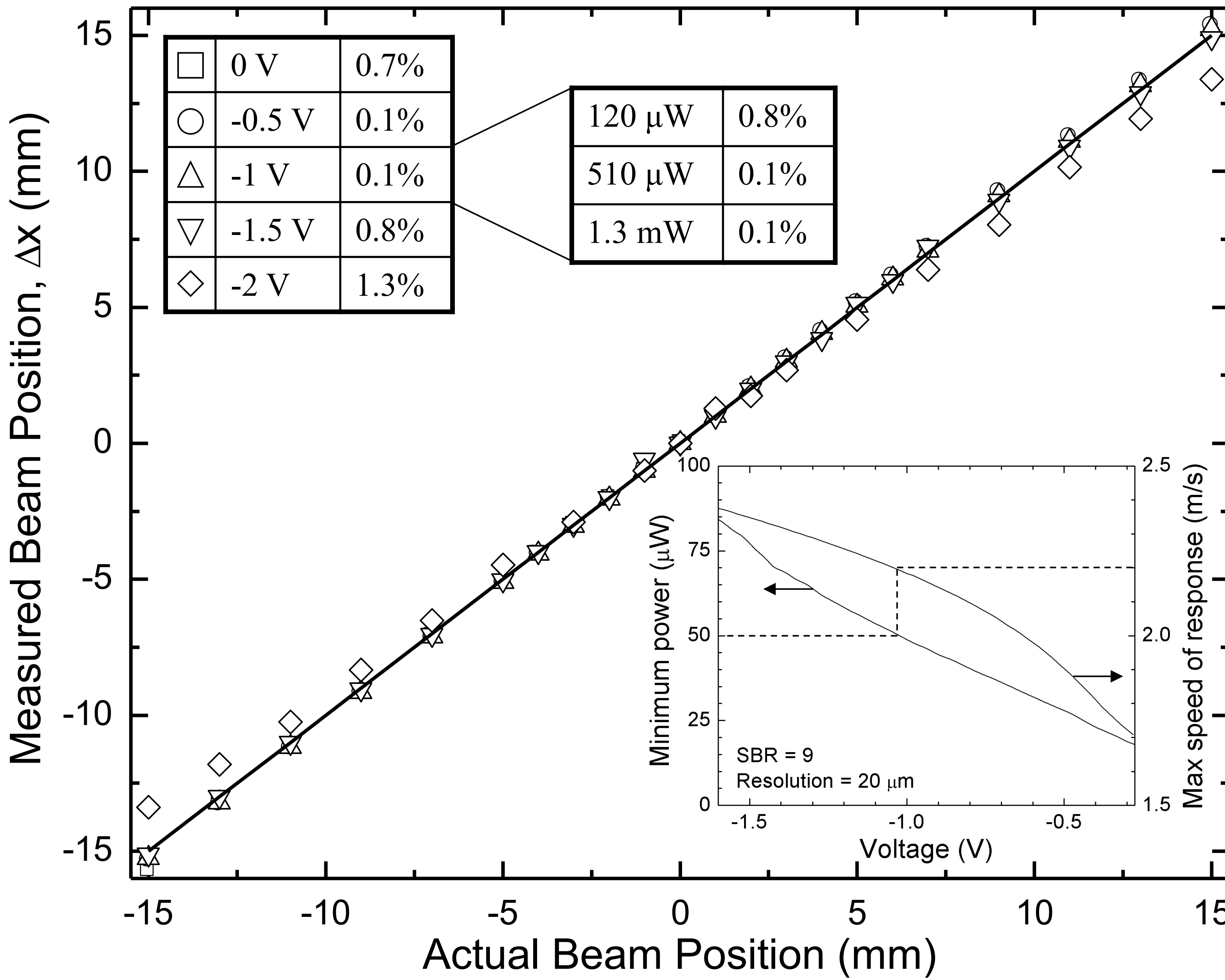
- Mechanism of operation
  - Extended junction transports charge vertically (no current spreading)
  - Current divided by *linear* resistance of ITO strip





Rand, et al. *IEEE Photon. Technol. Lett.*, **15,** 1279 (2003).

Position Detection Characteristics



Applications of PSDs

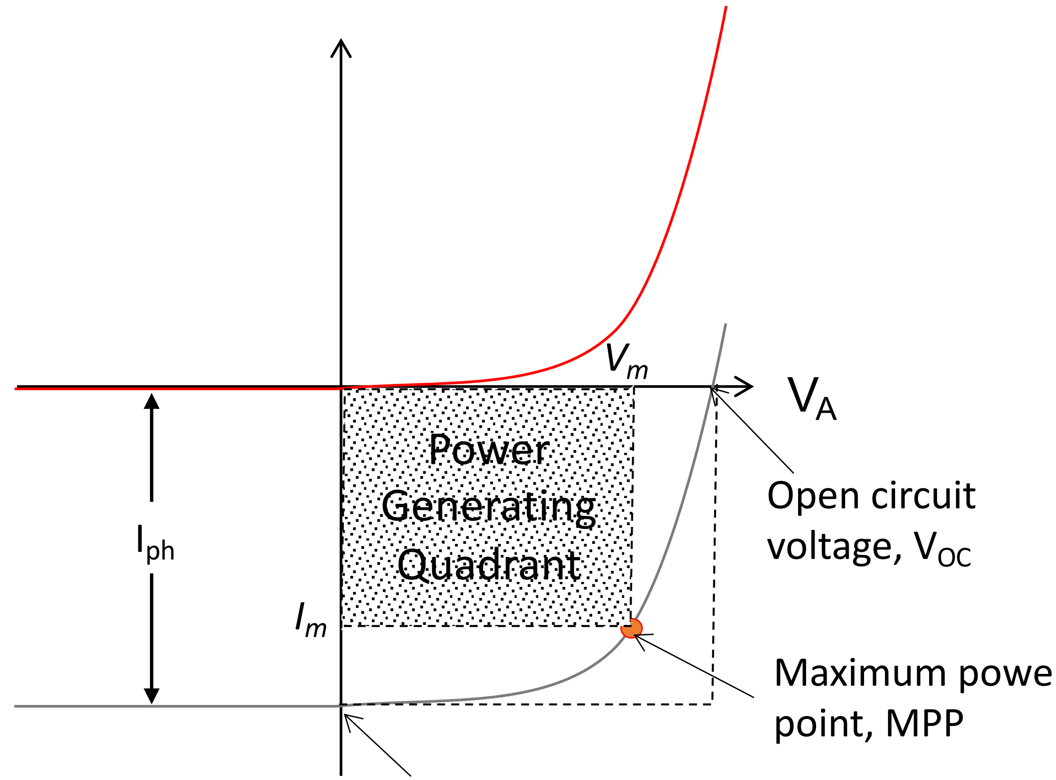
- Machine vision
  - Part location and positioning
  - Robot servo feedback
  - 2D possible
- Lab bench positioning
- Free space communication

(1 to 1 correlation between
object location and position of image)

Solar Cell Basics

Power Conversion Efficiency, η_P:

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



$$Power = IV$$

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

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

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

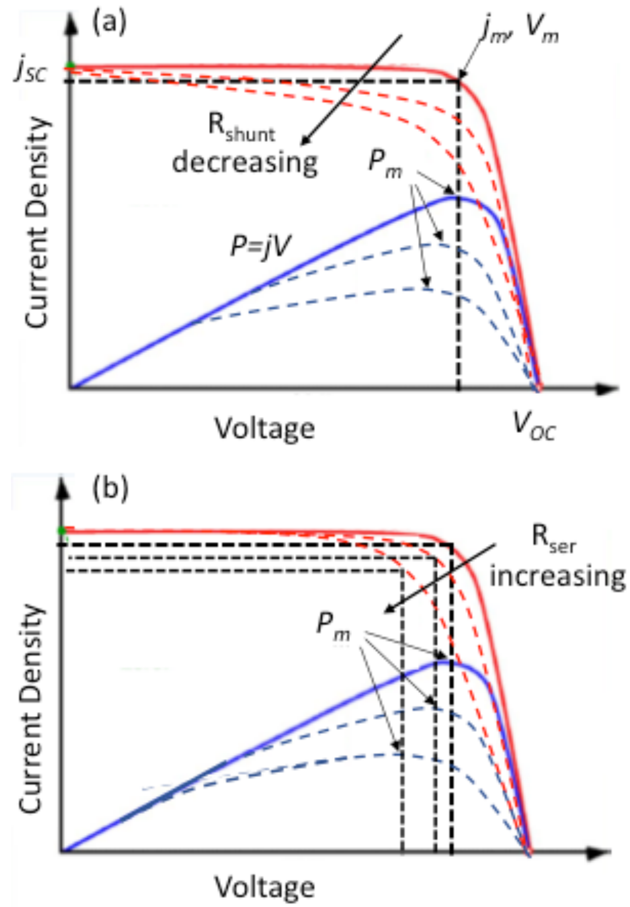
No Cell is Ideal

(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



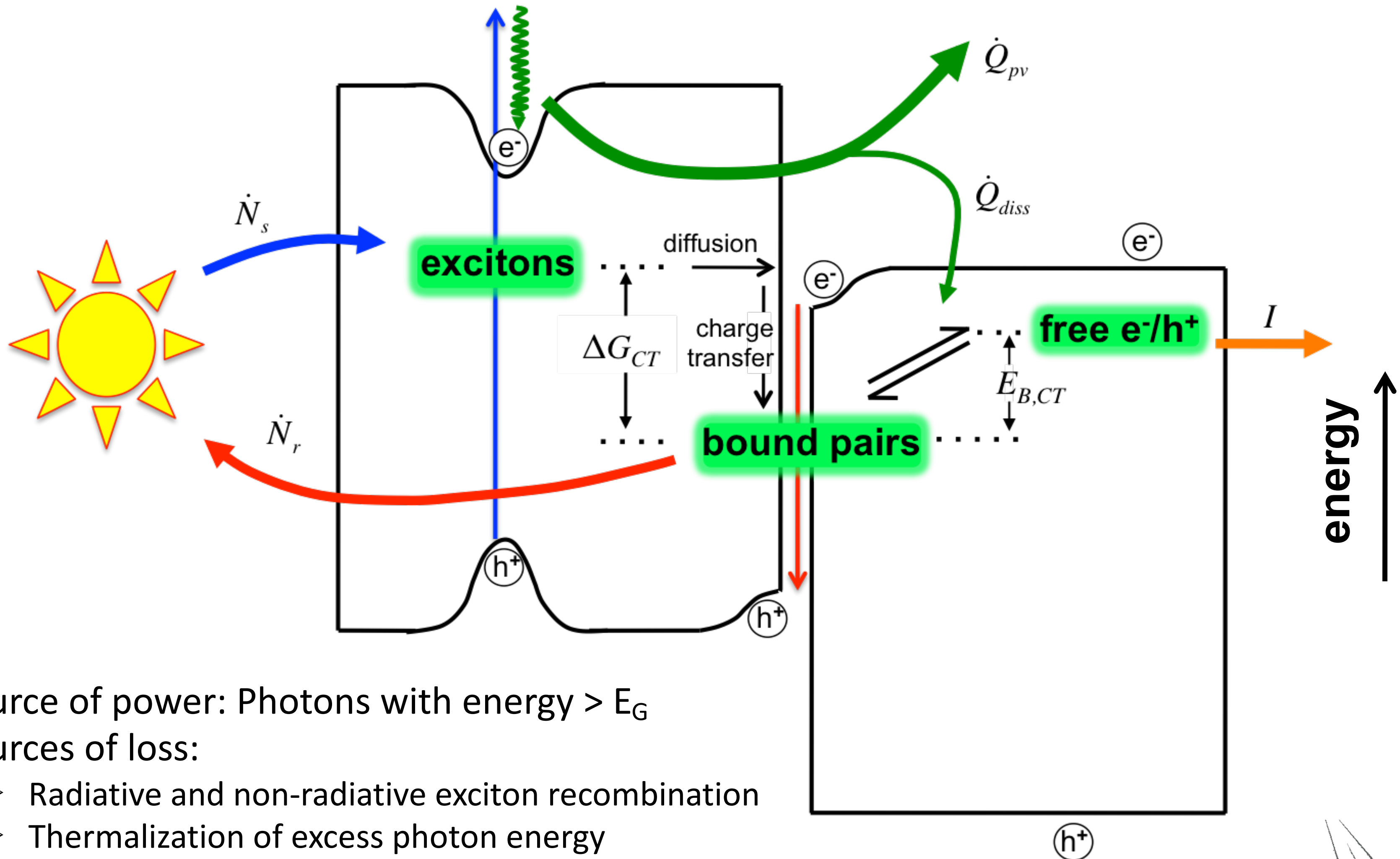
Solar Cell Facts

- 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

tronics
Forrest

Thermodynamic Limits to OPV cell Efficiency

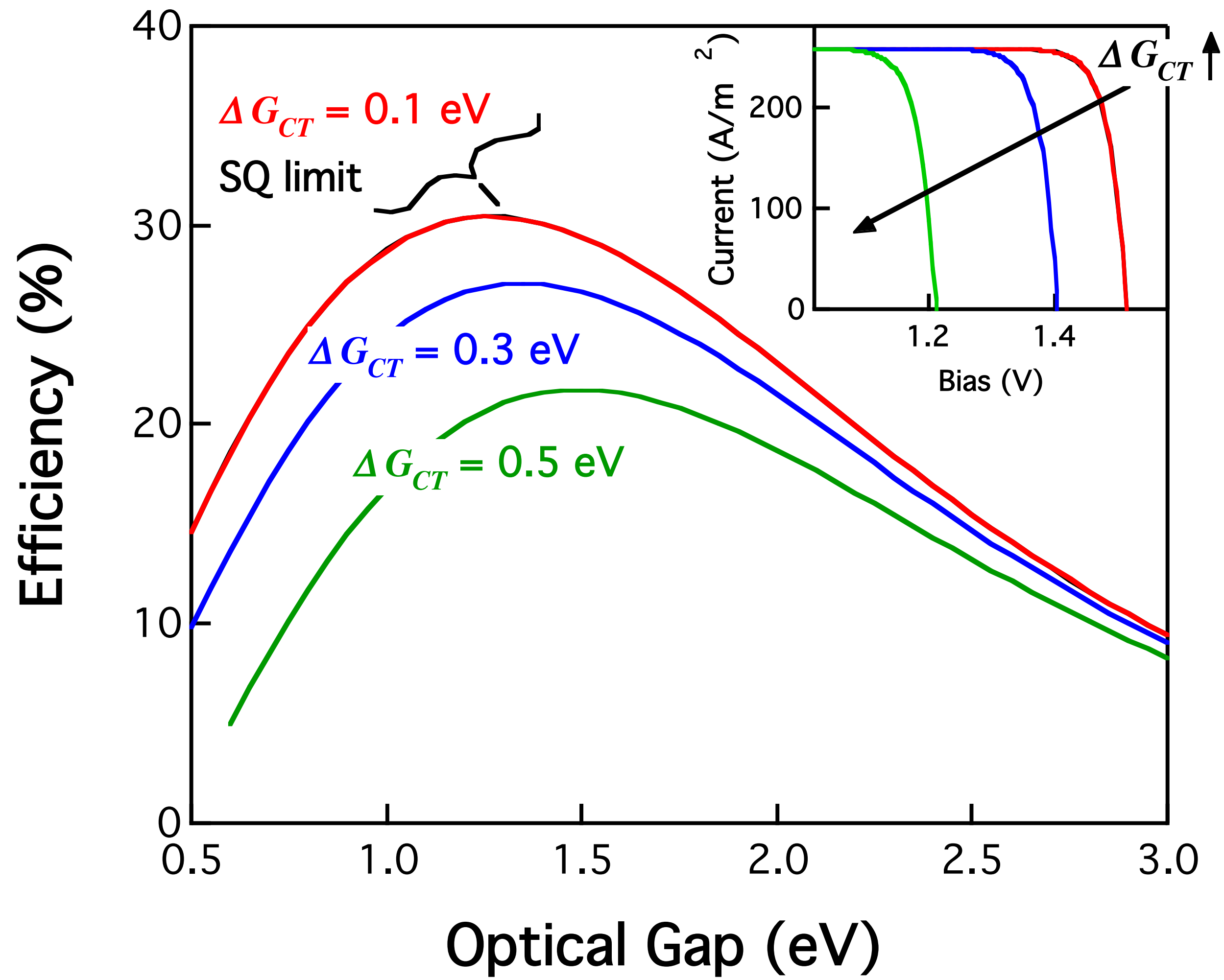


- Source of power: Photons with energy > E_G
- Sources of loss:
  - Radiative and non-radiative exciton recombination
  - Thermalization of excess photon energy
  - Recombination of CT states

Loss in *EXCITONIC* Solar Cells

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

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!)