Week 2-6

Optical Detectors 1

Photodetection Basics
Organic photoconductors and photodiodes

Chapter 7.1-7.2

Organic Electronics
Stephen R. Forrest

Objectives

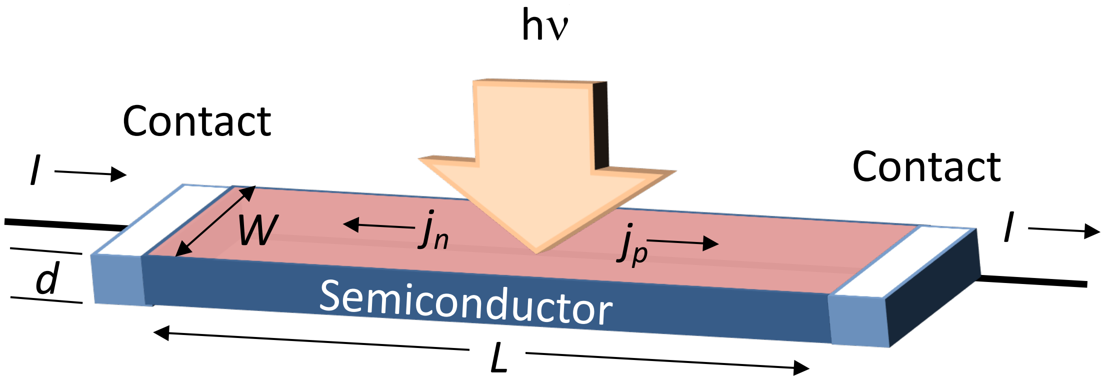
- Understand the physics of photodetection in organic photoconductors and photodiodes
- Understand OPD performance characteristics
  - Dark current
  - Efficiency and responsivity
  - Bandwidth
  - Noise
- Learn about OPD applications
- Solar cells: what makes OPVs a compelling story?
- Learn how to 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

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

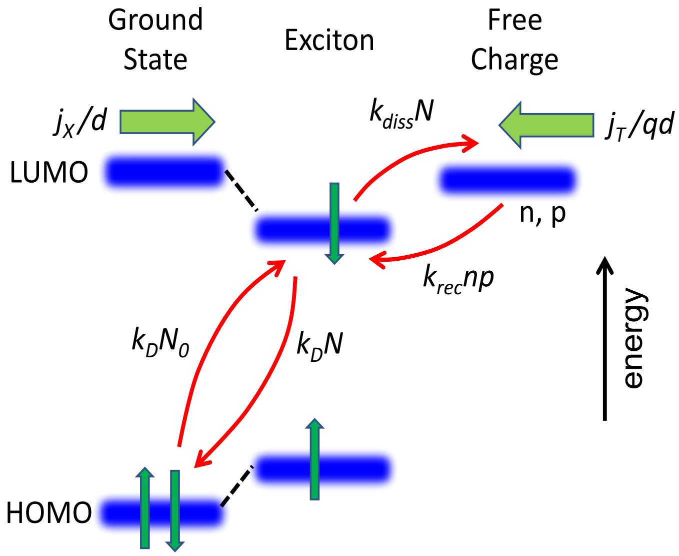
$$\boxed{n_{ph} = p_{ph}}$$

Without background doping: $n_0 = p_0 = n_i$

Organic Electronics
Stephen R. Forrest

Photocharge generation

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



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

τ_D = $1/k_D$ = lifetime of charge

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

⇒ Photocurrent:

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

Quantum Efficiency and Responsivity

$$\text{External quantum efficiency} = \frac{\text{No. electrons generated}}{\text{No. of photons incident}} = \eta_{ext} = \frac{hcj_{ph}}{q\lambda P_{inc}}$$

$$\text{Internal quantum efficiency} = \frac{\text{No. electrons generated}}{\text{No. of photons absorbed}} = \eta_{int} = \frac{hcj_{ph}}{q\lambda n_{ph} P_{inc}}$$

where: $n_{ph} = \frac{(1-R)}{d}\int_0^d exp(-\alpha(\lambda)x)dx$

for a total reflection coeff’t, *R*, from the surface, and an absorption coeff’t of α in an active region of thickness, *d*.
Note: the total thickness must account for internal reflections and other cavity effects

$$\text{Responsivity} = \frac{\text{Current generated}}{\text{Power incident}} = \mathcal{R} = \frac{j_{ph}}{P_{inc}} = \frac{q\lambda}{hc}\eta_{ext} \quad \text{[A/W]}$$

Gain and bandwidth

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

⇒ 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**: $g\Delta f = 1/2\pi t_{tr}$

Calculating the Noise Current

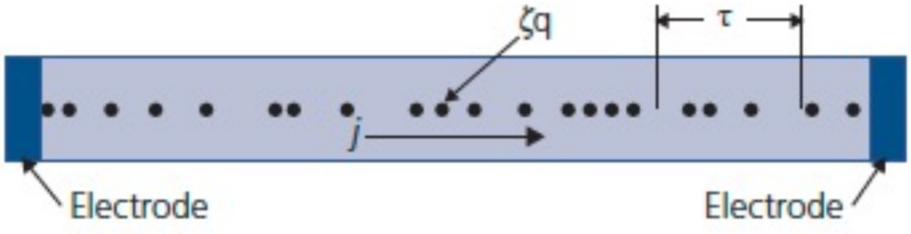
(after Rose, 1963. *Concepts in Photoconductivity and Allied Problems*)

- Determines the sensitivity of a photodetector to low intensity signals
- Signal-to-noise ratio: $\frac{S}{N}=\frac{\langle i_{ph}^2\rangle}{\langle i_n^2\rangle}>1$

$\langle i_{ph}^2\rangle=$ mean square photocurrent
$\langle i_n^2\rangle=$ mean square noise current

minimum level of detectability

Consider a "general" photodetector. It has randomly generated particles, each carrying charge ζq in time interval, τ, between electrodes, resulting in current, *j*.



Then, the noise current is: $\langle i_n^2\rangle^{1/2}=\frac{\langle n\rangle^{1/2}}{\tau}\zeta q$

where $\langle n\rangle^{1/2}$ is the rms number of particles collected in τ.

Calculating Noise Current, con't

Thus, in terms of the total mean current, i_T, the mean square noise current is:

$$\langle i_n^2 \rangle = \frac{\langle n \rangle}{\tau^2}(\zeta q)^2 = \frac{q i_T \zeta}{\tau}$$

Since the bandwidth is $\Delta f=1/2\tau$, and accounting for both generation and recombination, we get a **shot noise current** of:

$$\boxed{\langle i_s^2 \rangle = 4qgi_T\Delta f}$$

If diffusion is dominant, then the charge delivered per particle is reduced by the fraction of charge diffusing to the contacts for a slab of length, L: $\zeta = L_D/L$.

Using $L_D = \sqrt{D\tau}$ and the Einstein relation for mobility, we obtain the **thermal**, or **Johnson noise**:

$$\boxed{\langle i_{th}^2 \rangle = \frac{4k_B T\Delta f}{R_{PC}}}$$

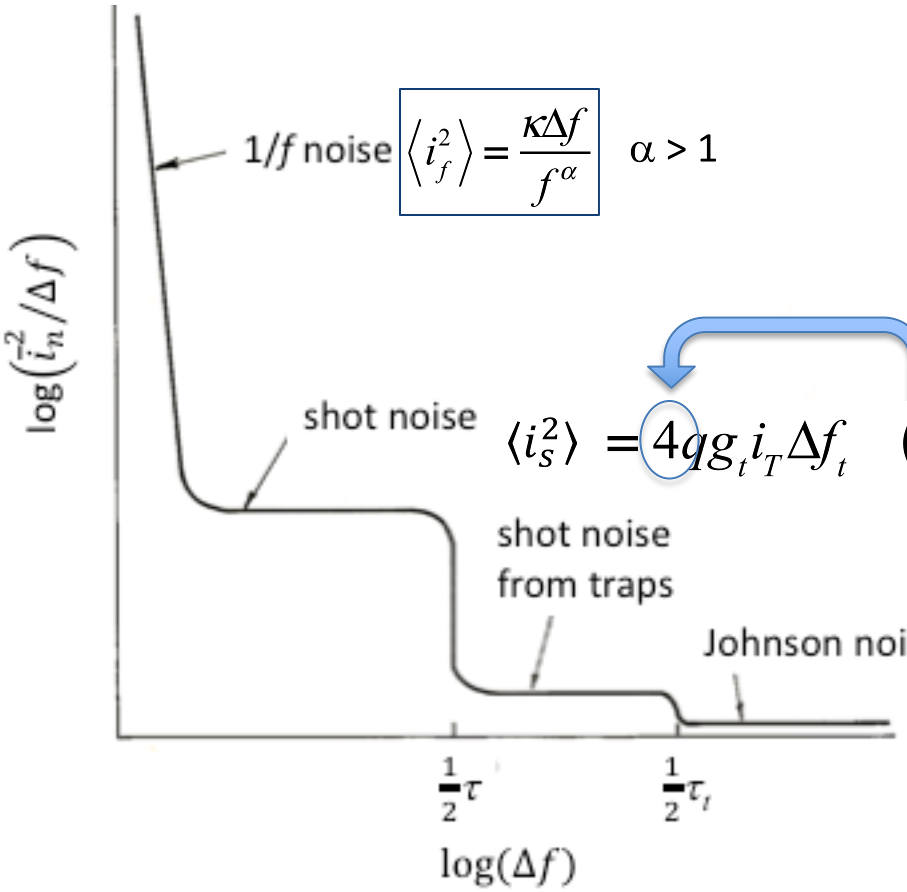
R_{PC} is the resistance of the conductor

Finally, there is **flicker**, or **1/f noise**: $\boxed{\langle i_f^2 \rangle = \frac{\kappa\Delta f}{f^\alpha}}$

κ, α are empirical constants

The total noise current is then the sum of the squares of the various contributions (they are uncorrelated): $\langle i_n^2\rangle = \langle i_s^2\rangle + \langle i_{th}^2\rangle + \langle i_f^2\rangle + \ldots$

Graphically, Noise Spectra Look Like...



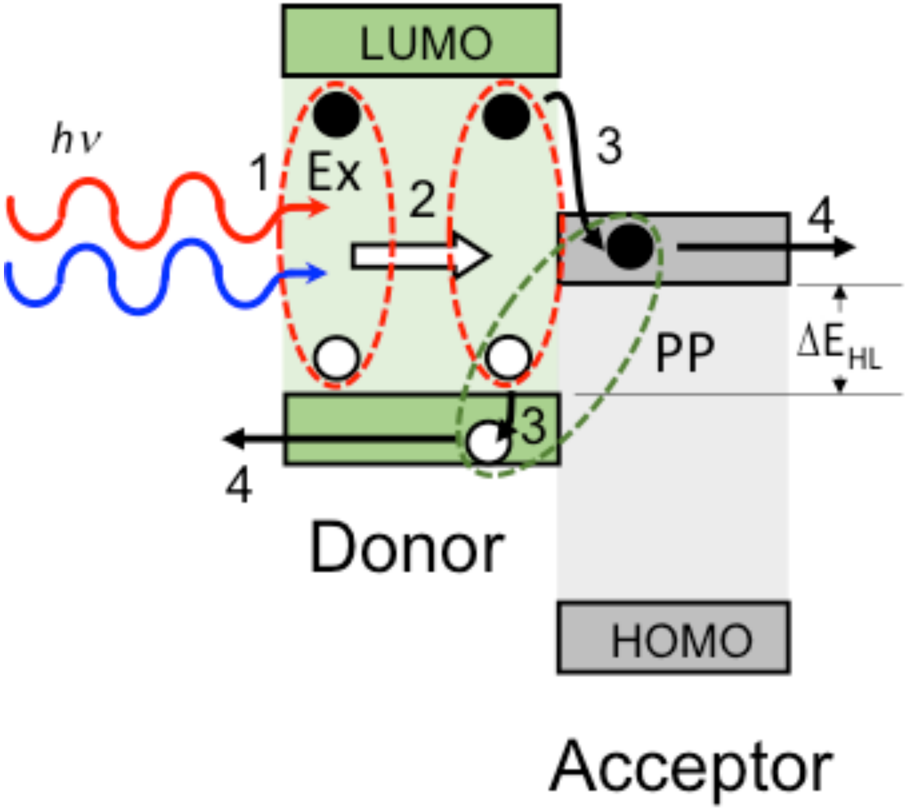
$$\boxed{\left\langle i_f^2 \right\rangle = \frac{\kappa \Delta f}{f^{\alpha}}}$$ $\alpha > 1$

$$\langle i_s^2 \rangle = \boxed{4} q g_t i_T \Delta f_t$$ (2 for OPD)

$$\left\langle i_{th}^2 \right\rangle = \frac{4 k_B T \Delta f}{R_{PC}}$$

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

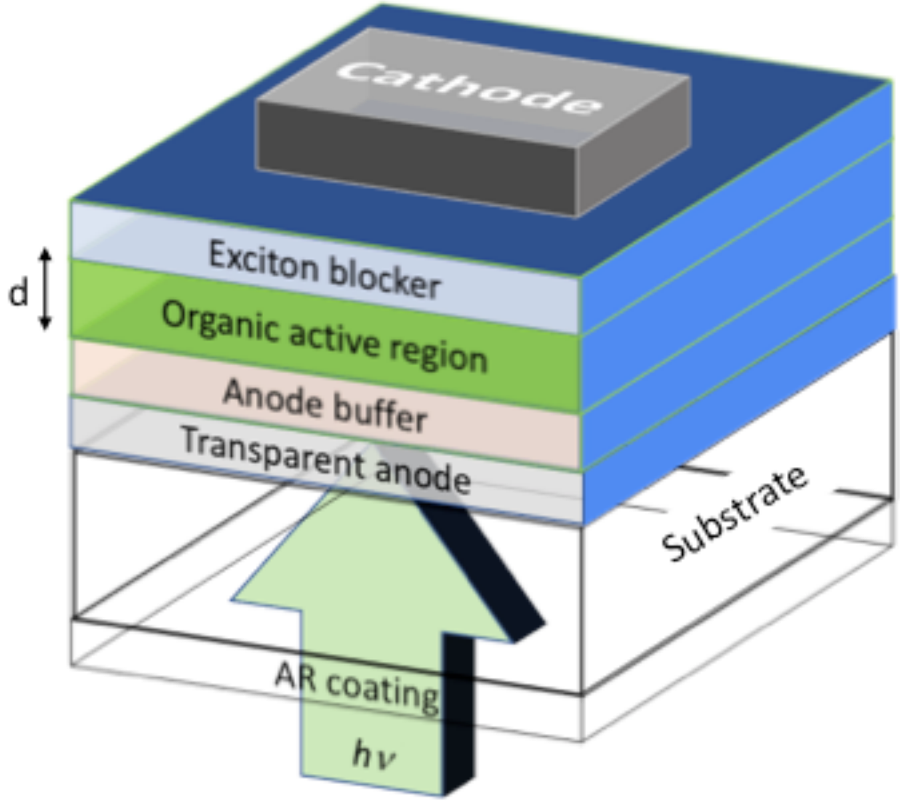
③ Exciton dissociation by rapid and efficient charge transfer

④ Charge extraction by the internal electric field

Typically: L_D<<1/α

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

Basic OPD/OPV structure

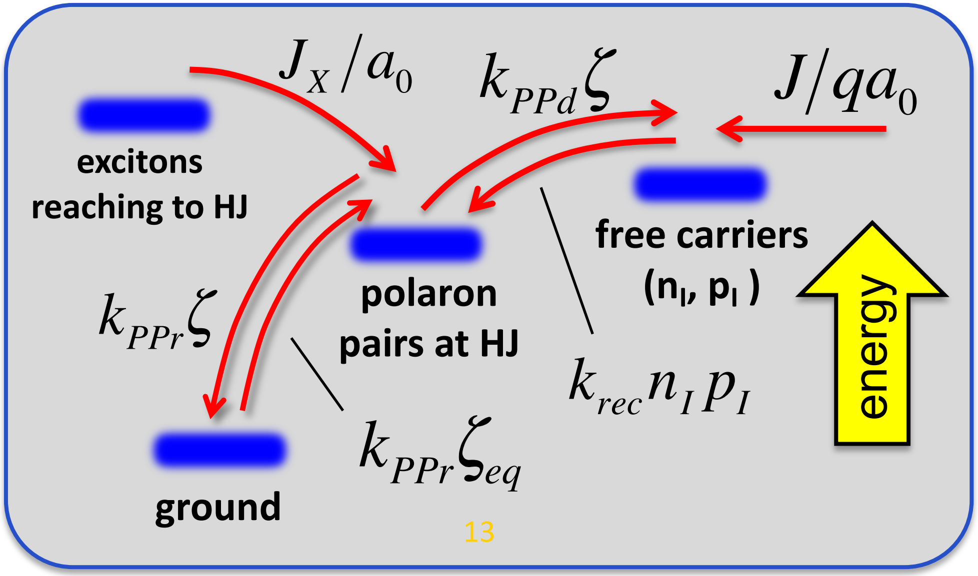


Current generation

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



J_X/a_0

$k_{PPd}\zeta$

J/qa_0

excitons reaching to HJ

polaron pairs at HJ

free carriers (n_I, p_I)

energy

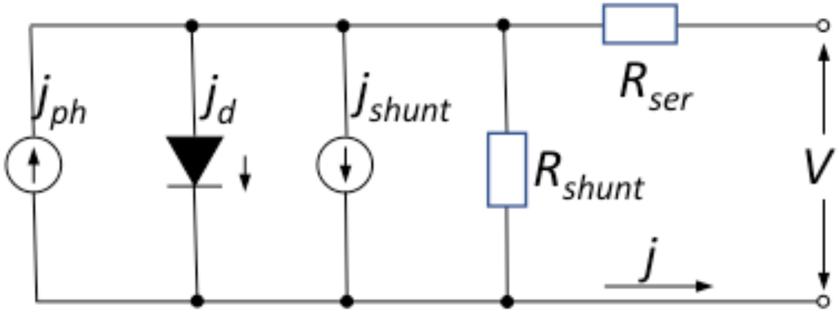
$k_{PPr}\zeta$

$k_{PPr}\zeta_{eq}$

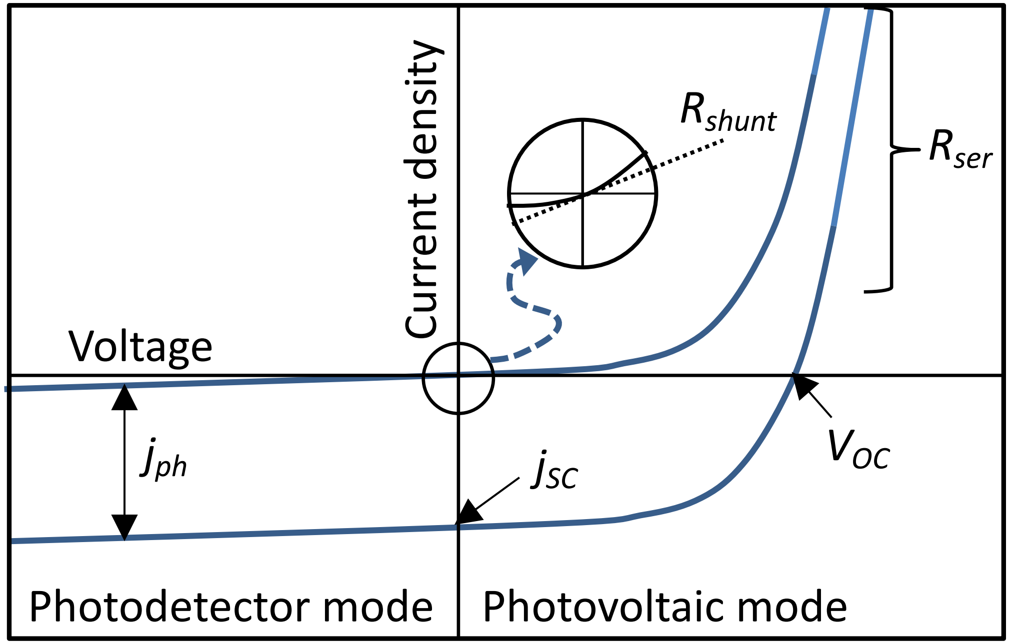
$k_{rec}n_I p_I$

ground

Equivalent circuit



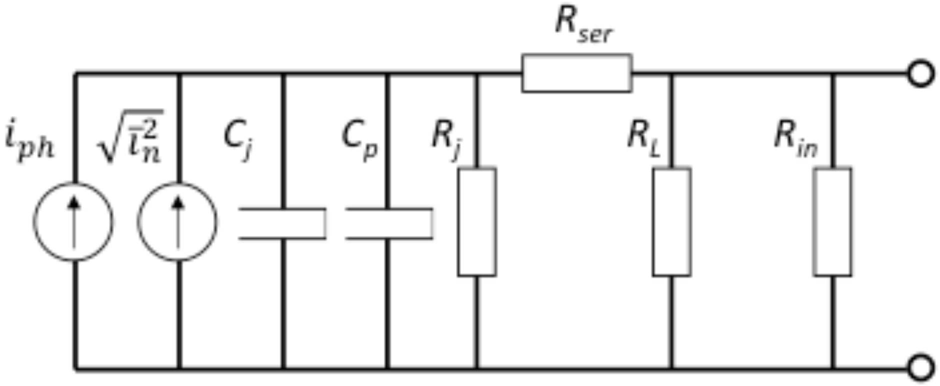
Current-Voltage Characteristics



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

- 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.

Photodetector Equivalent Circuit & Frequency Response



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

$\tau_{RC} = (R_{ser} + R_L || R_{in})(C_j + C_P)$ $(R_j \rightarrow \infty)$: RC time constant

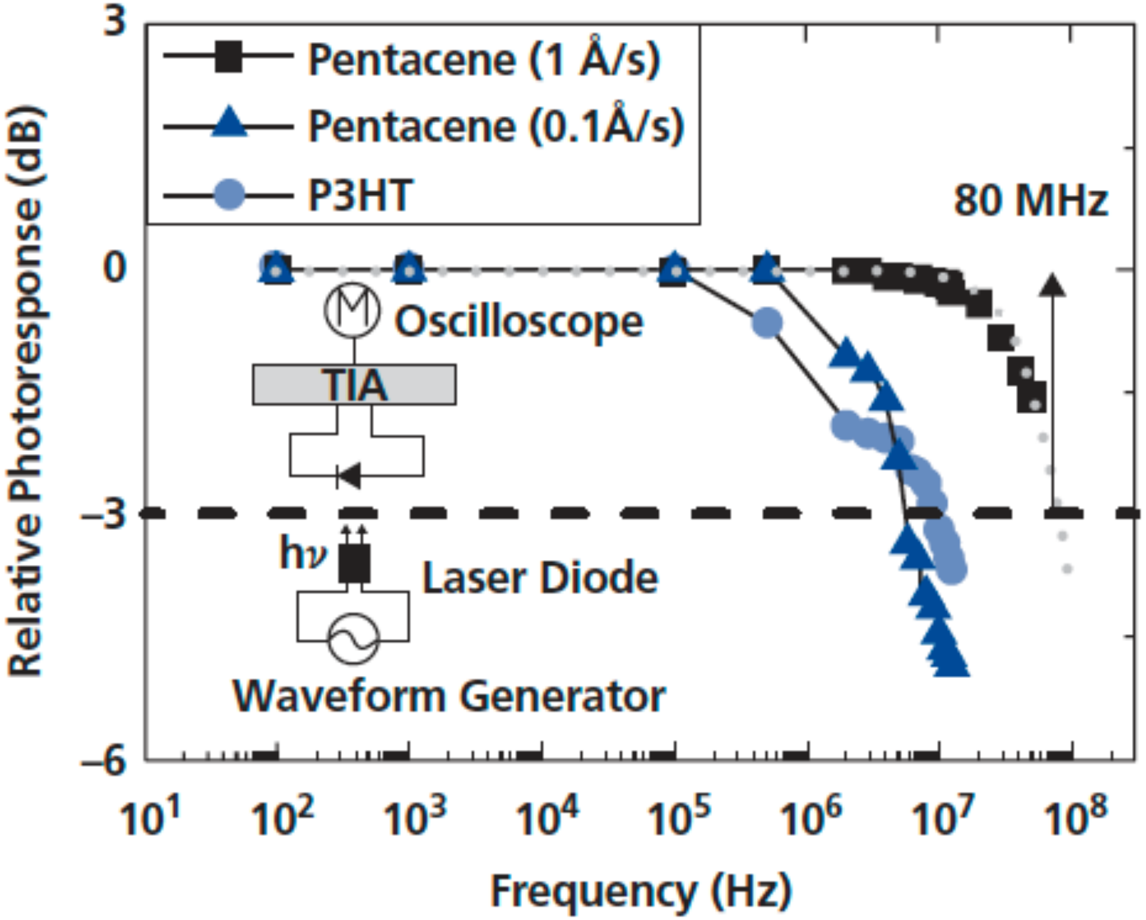
τ_{ED} : exciton diffusion time

$t_{tr} = w^2/\mu V$: transit time through depleted regions of the device (w)

Gain-Bandwidth product $= g\Delta f = \Delta f$ since in a PD, $g = 1$.

Pentacene/C_{60} OPD Frequency Response

High frequency response due to high pentacene mobility

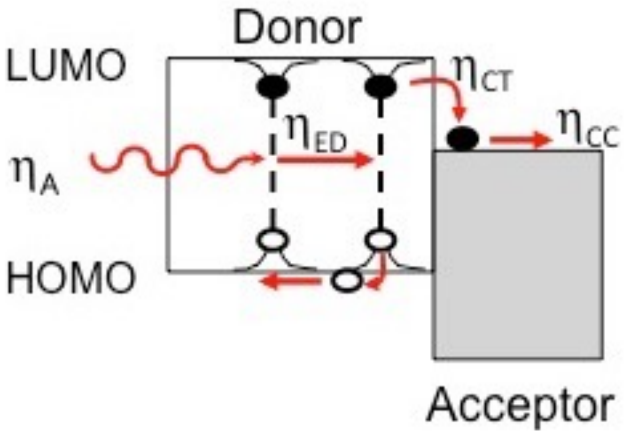


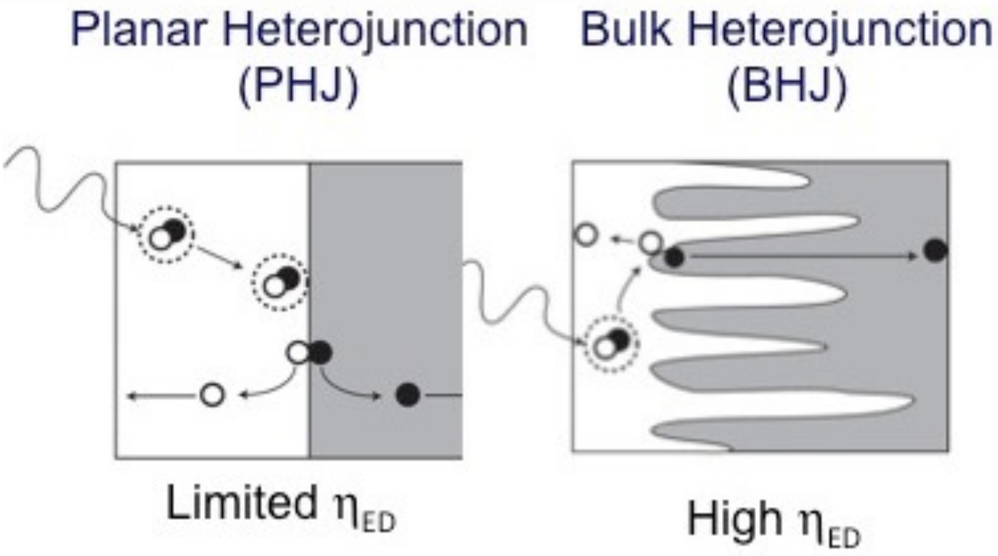
TIA: Transimpedance amplifier through which the diode is biased

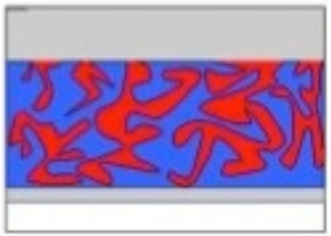
Tsai et al. Appl. Phys. Lett., 95, 213308 (2009)

Heterojunction Morphologies

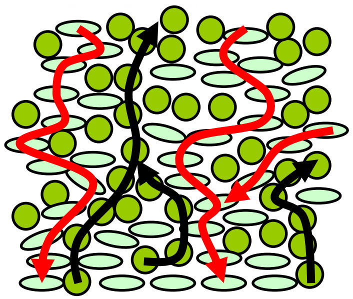
Breaking the tradeoff between L_D and α with BHJs



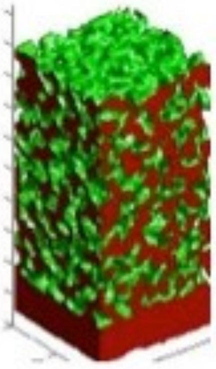




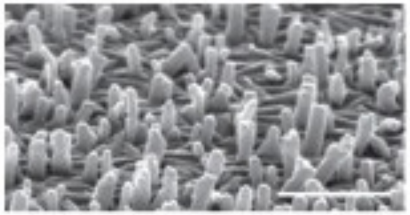
Bulk HJ



Mixed HJ

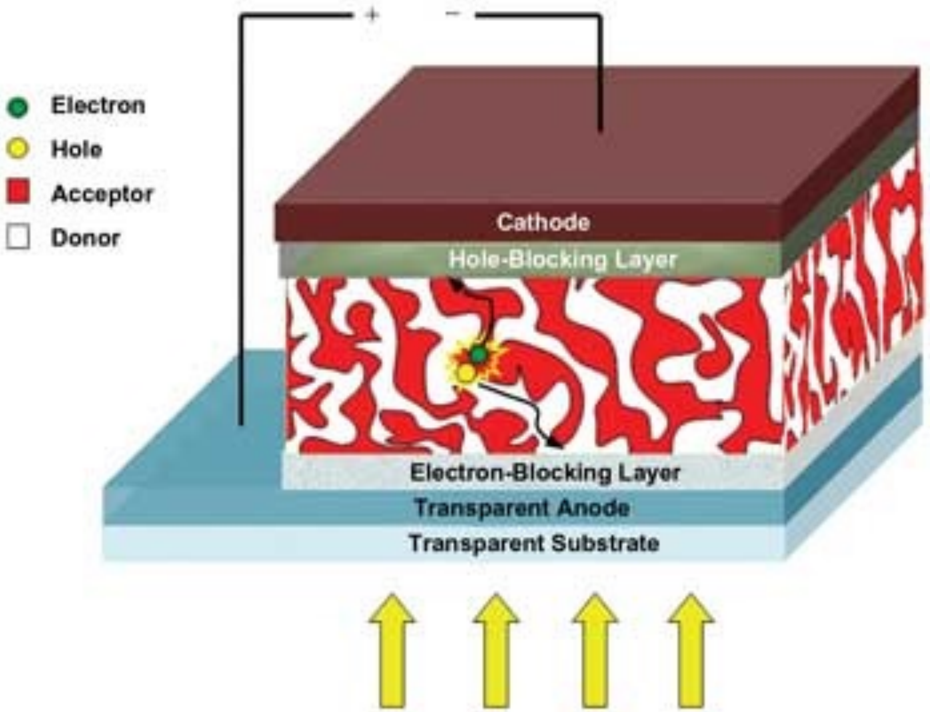


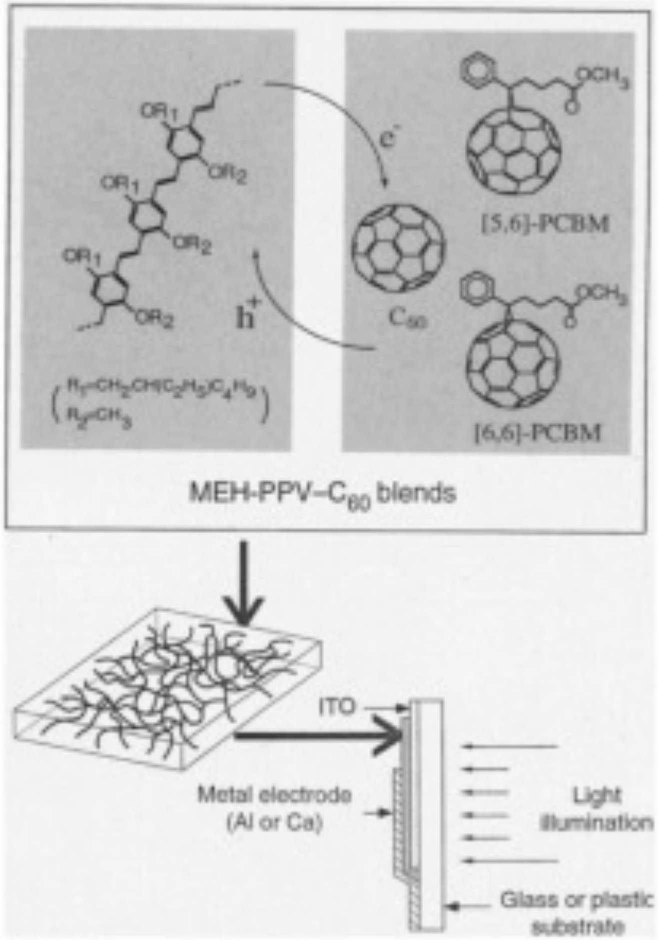
Annealed BHJ



Controlled BHJ

Polymer Bulk HJ



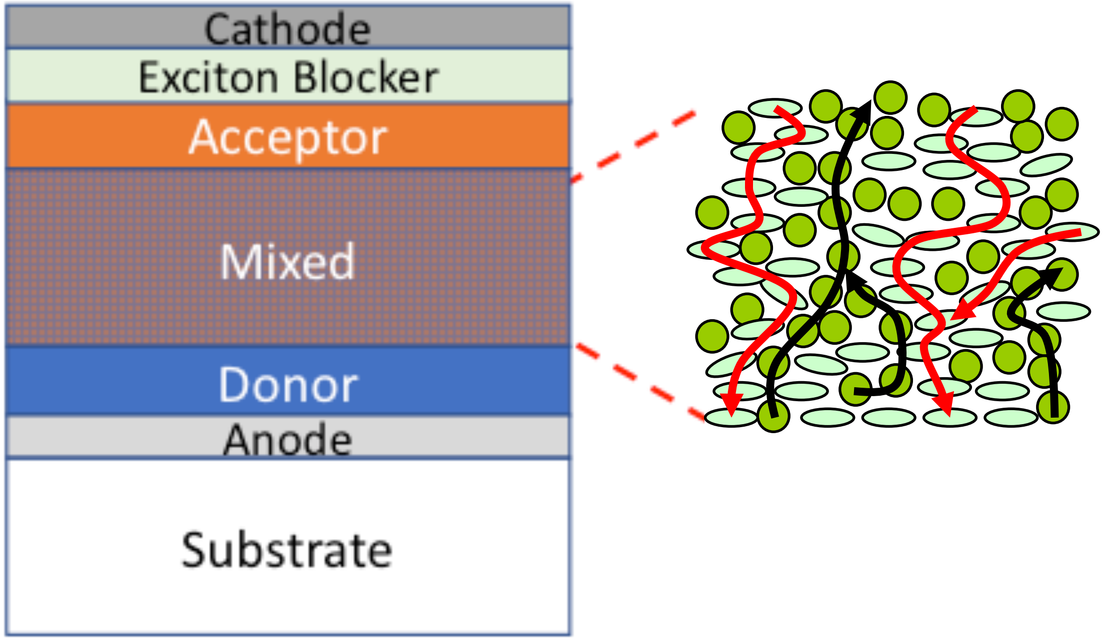


Yu et al. Science, **270**, (1995), 1789

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

Small Molecule Planar-Mixed HJ

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



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

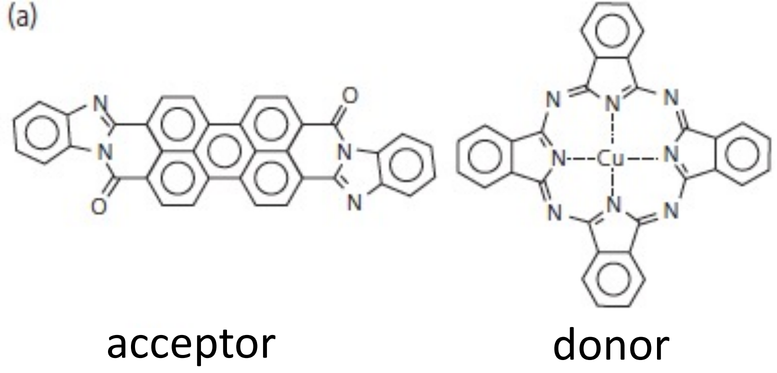
Charge carrier collection length, L_C, replaces diffusion length since excitons dissociate at point of generation without diffusion to HJ

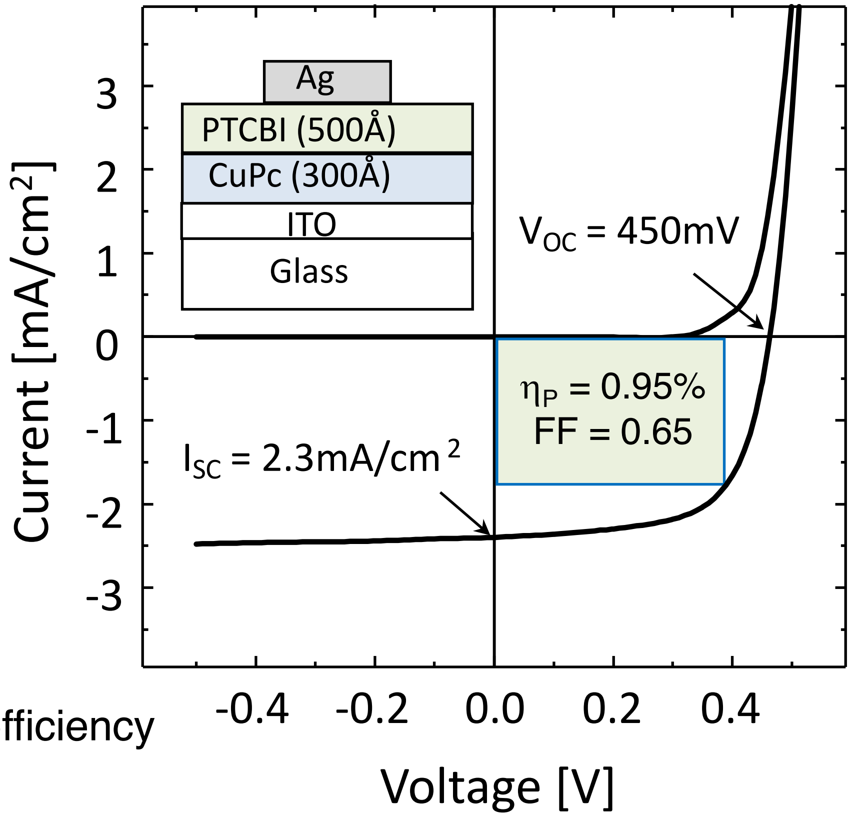
J. Xue, *Adv. Mater.*, vol. 17, p. 66, 2005.

Comparison of OPDs and OPCs

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}	$k_{diss}/\left(k_{diss}+k_D\right)$	$k_{ppd}/\left(k_{PPd}+k_{PPr}\right)$
η_{ext}	$\dfrac{j_{ph}A}{qg\left(P_{inc}\lambda/hc\right)}$	$\dfrac{j_{ph}A}{q\left(P_{inc}\lambda/hc\right)}$
Responsivity	$qg\eta_{ext}\left(\lambda/hc\right)$	$q\eta_{ext}\left(\lambda/hc\right)$
Bandwidth (Δf)	$1/2\pi\tau_D$	$1/2\pi t_{tr}$
Gain-bandwidth product ($g\Delta f$)	$1/2\pi t_{tr}$	$1/2\pi t_{tr}$
$\overline{i}_n^{\,2}/\Delta f$	$\left(4k_BT\right)/R_{PC}+\kappa/f^{\alpha}$	$2qi_T+4k_BT/R_L \parallel R_{in}$
Specific detectivity ($D*$)	$q\eta_{ext}\left(\lambda/hc\right)\sqrt{\dfrac{A}{\left(4k_BT\right)/R_{PC}+\kappa/f^{\alpha}}}$	$q\eta_{ext}\left(\lambda/hc\right)\sqrt{\dfrac{A}{2qi_T+4k_BT/R_L \parallel R_{in}}}$

The first bilayer OPD/OPV





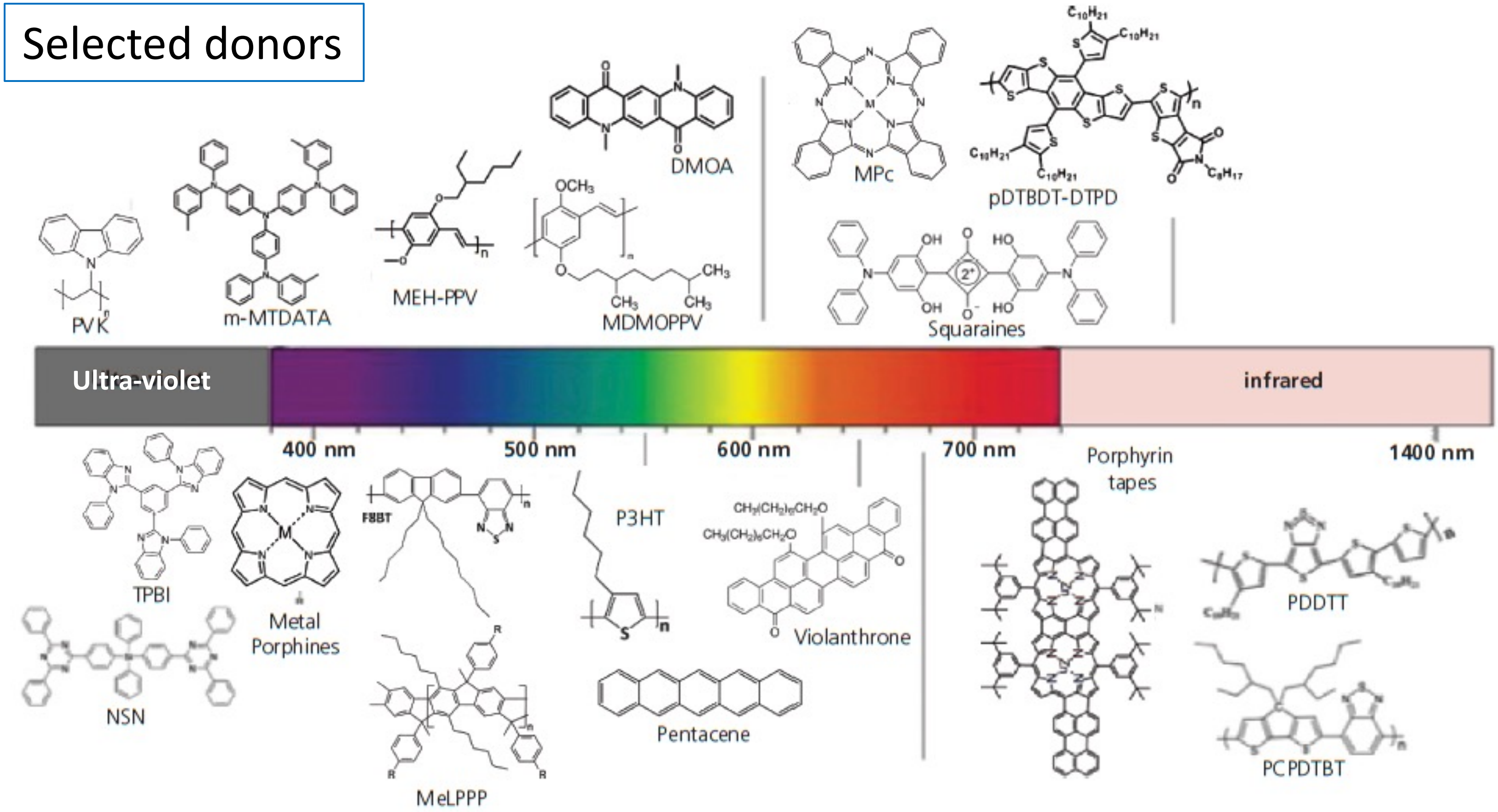
η_P = power conversion efficiency
FF = fill factor

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

Photodetector Materials

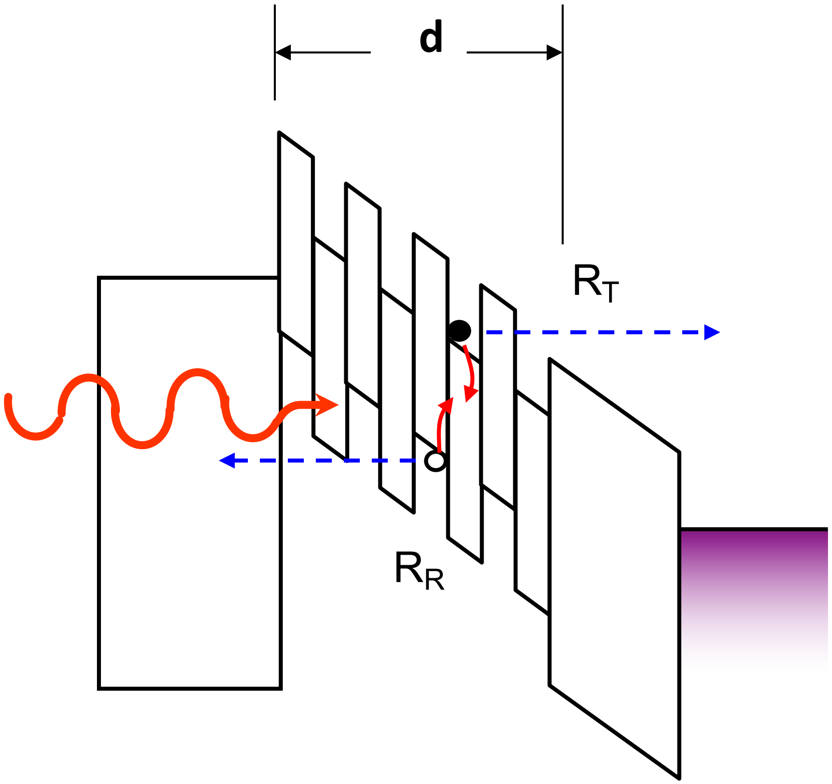
- Good materials absorb in the region of interest
- Morphology promotes exciton diffusion and charge conduction (high mobility)

Selected donors



Generally, donors employ fullerene acceptors in OPDs

High Bandwidth Multilayer Photodetectors



Place all D/A junctions within L_D of absorption site

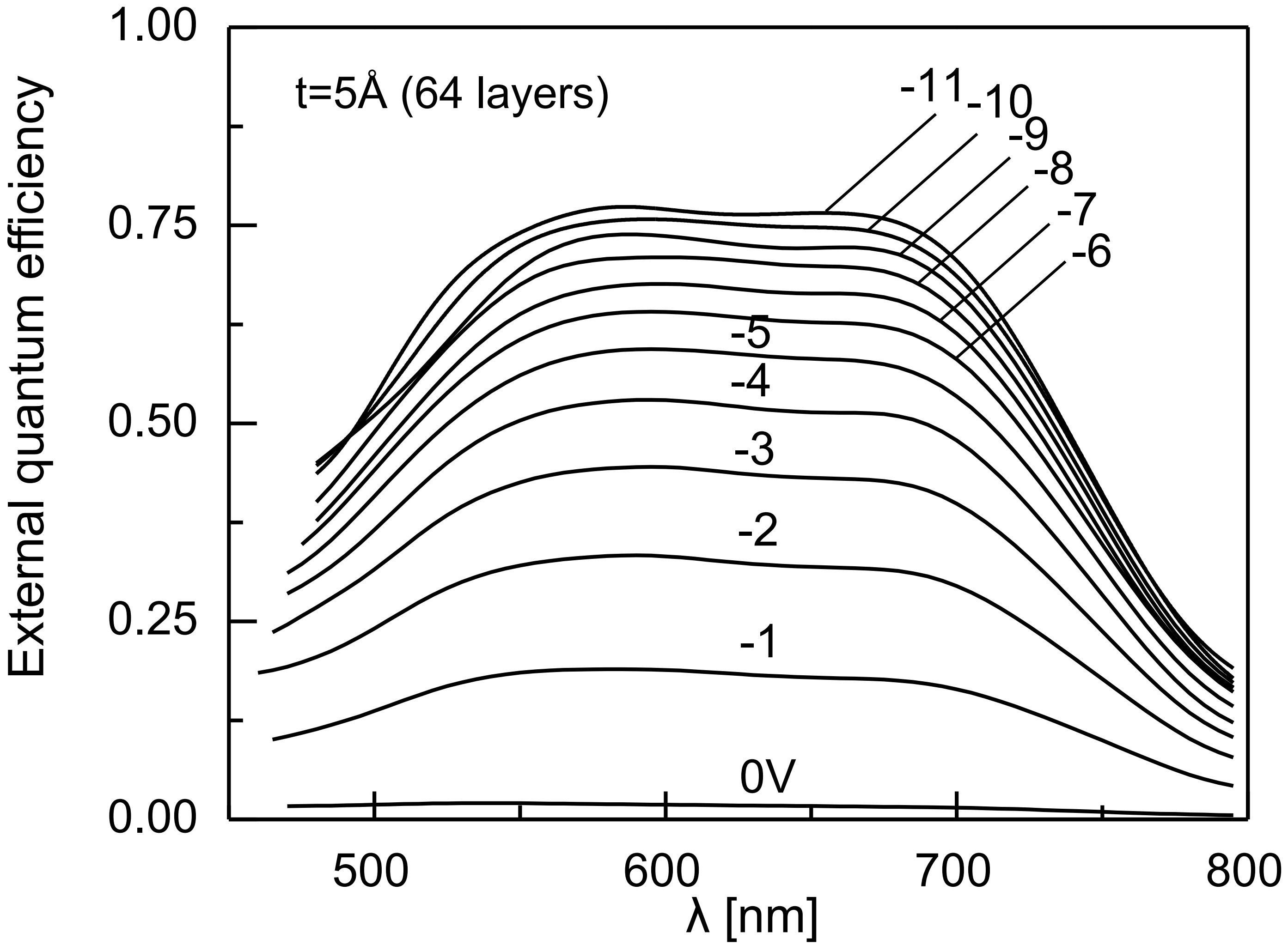
Stack layers until total thickness d ~ $1/\alpha$

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



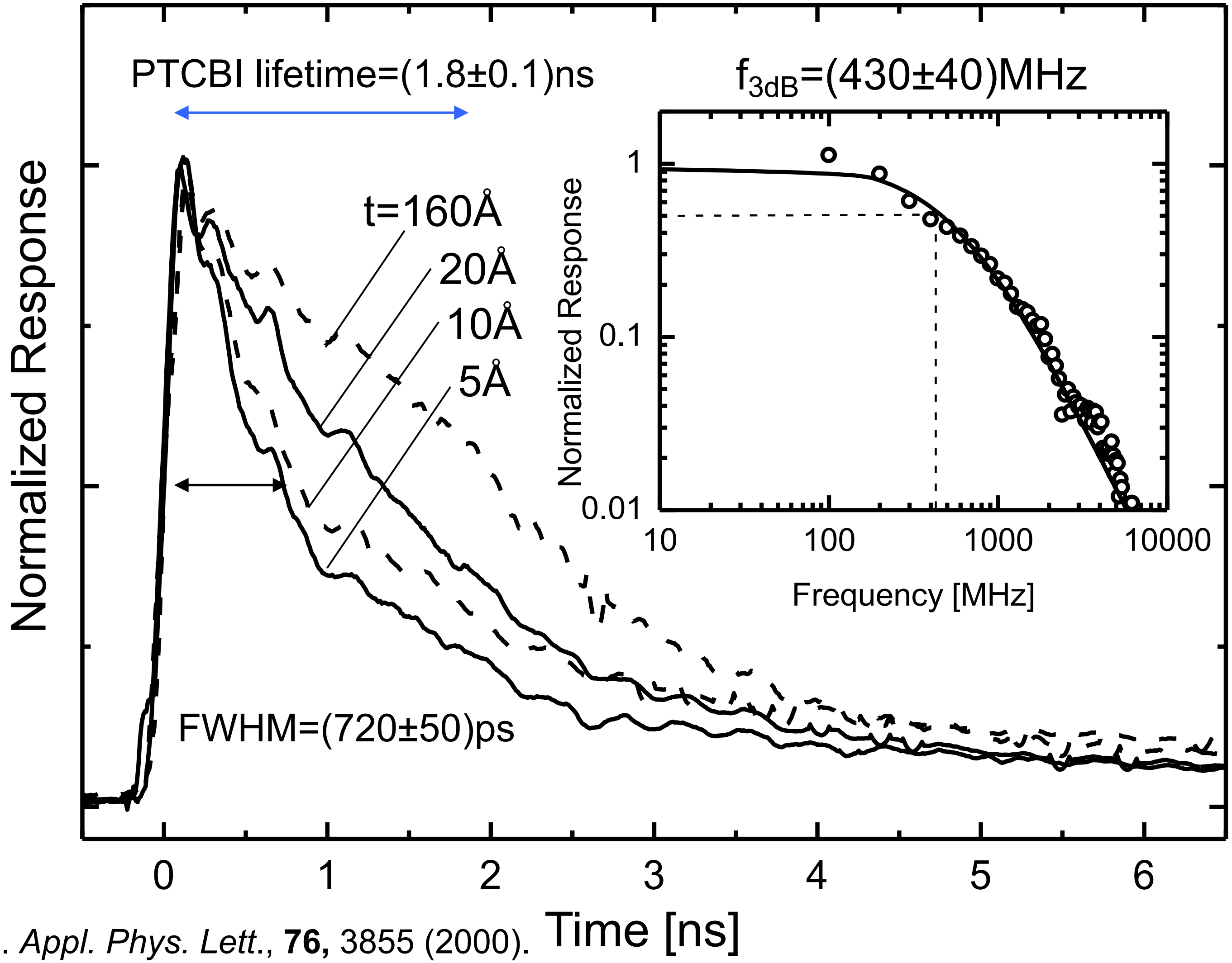
Peumans, et al. *Appl. Phys. Lett.*, **76,** 3855 (2000).

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/cm^2.

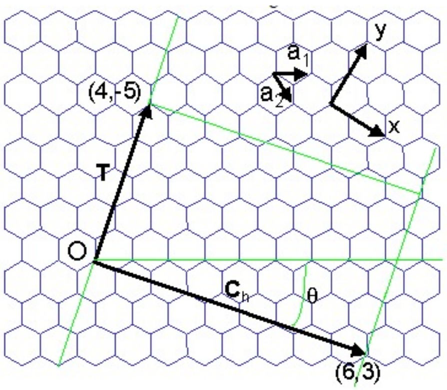
Estimated carrier velocities: $v = d/\tau = (1.1 \pm 0.1) \times 10^4\ cm/s$



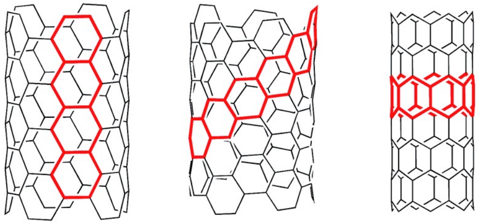
Peumans, et al. *Appl. Phys. Lett.*, **76,** 3855 (2000).

Long wavelength Detectors

Carbon Nanotubes Can Stretch Detection to NIR



$$C_h = na_1 + ma_2$$


[5,5] CNT
Armchair
Metallic

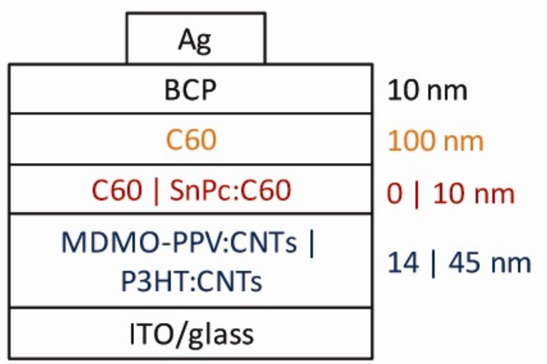
[7,5] CNT
Chiral
Semiconducting

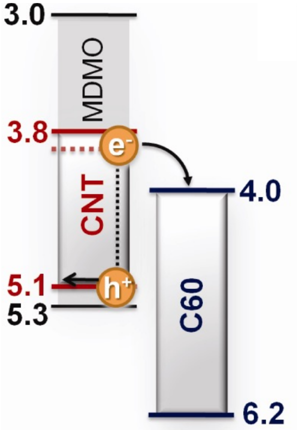
[7,0] CNT
Zigzag
Semiconducting

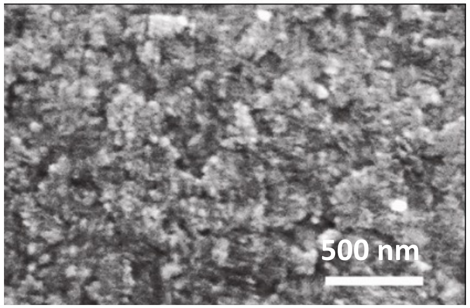
Chirality determines if CNT is metallic, semiconducting or insulating

n = *m*: Metallic
n-*m* = 3*i* (i integer), *n*≠*m*, *nm*≠0: semimetal
otherwise: semiconductor

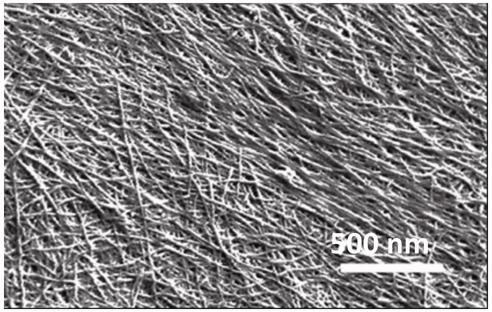
Organic/CNT Detector


Ag
BCP — 10 nm
C60 — 100 nm
C60 | SnPc:C60 — 0 | 10 nm
MDMO-PPV:CNTs | P3HT:CNTs — 14 | 45 nm
ITO/glass





CNT:MDMO-PPV composite

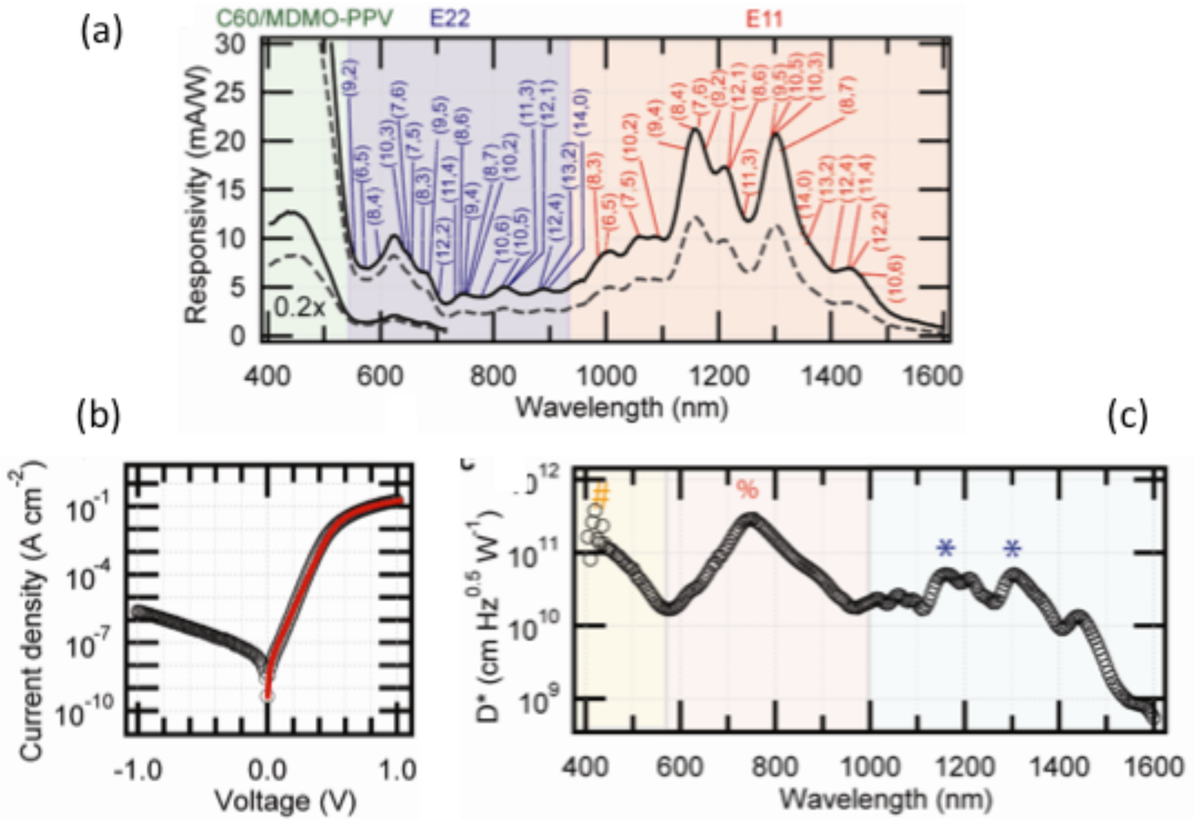


Mat of bare CNT

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

Long wavelength Detectors

Single Walled Nanotubes Wrapped in Polymer



Responsivity and Specific Detectivity:

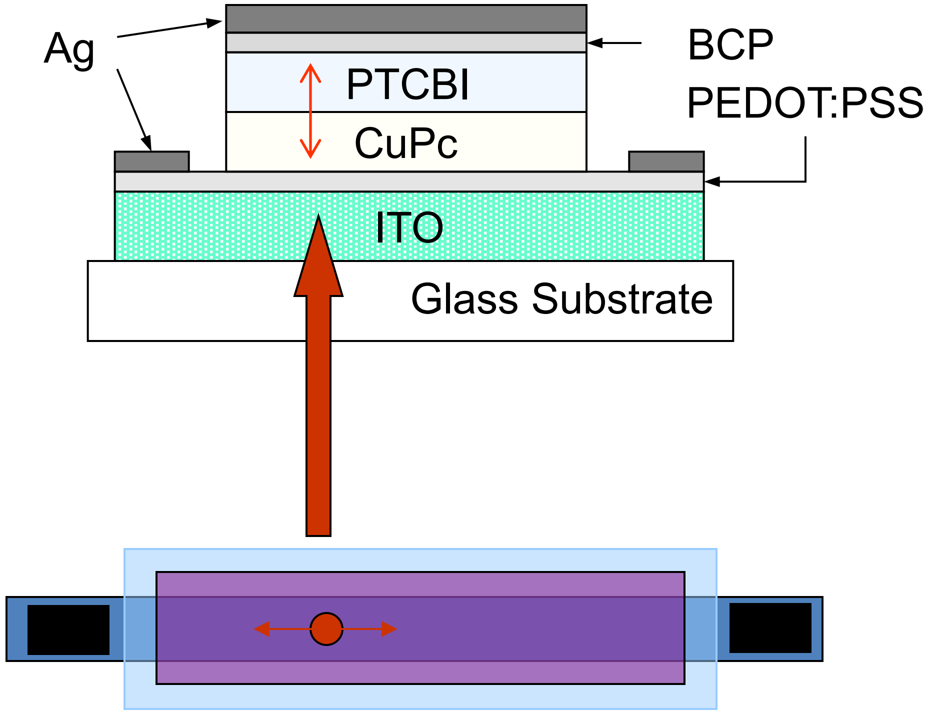
$$\mathcal{R} = \frac{j_{ph}A}{P_{inc}} = qg\eta_{ext}\left(\frac{\lambda}{hc}\right) \quad \text{[A/W]}$$

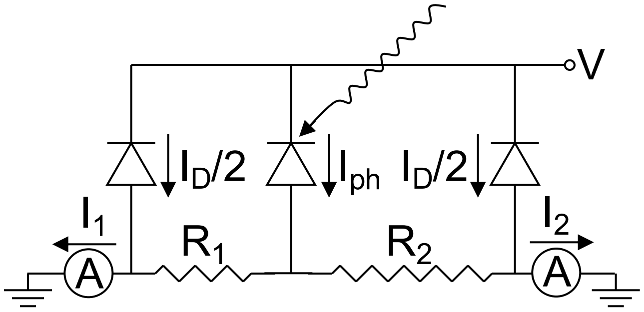
$$D^* = \frac{\sqrt{A\Delta f}}{NEP} = \mathcal{R}\sqrt{\frac{A\Delta f}{\overline{i_n^2}}} \quad [\text{cm-Hz}^{1/2}/\text{W}]$$

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

Position Sensitive Detectors

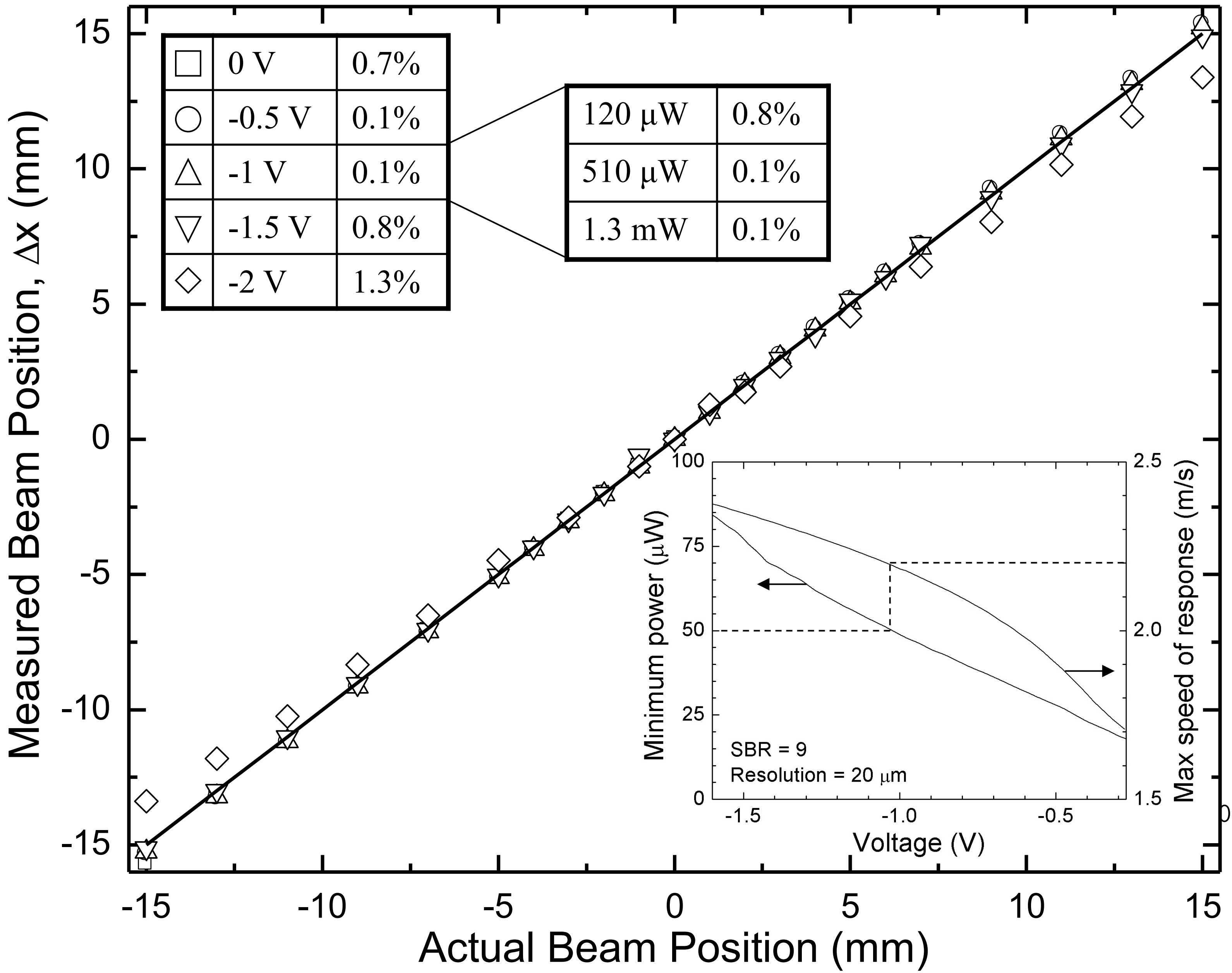
- Mechanism of operation
  - Extended junction transports charge vertically (no current spreading)
  - Current divided by *linear* resistance of ITO strip





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)