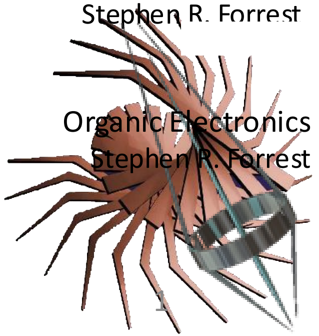
Week 11

Photodetectors

Chapter 7



Objectives

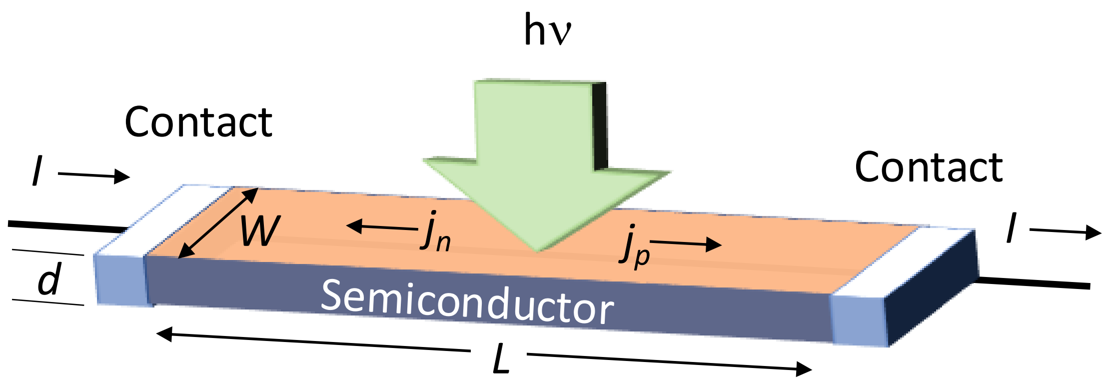
- Understand the physics of photodetection in organic photoconductors and photodiodes
- What materials and device structures useful in detectors?
- Understand OPD performance characteristics
  - Noise
  - Dark current
  - Efficiency and responsivity
  - Bandwidth
  - Noise
- Learn about OPD applications: Imagers and imaging

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)

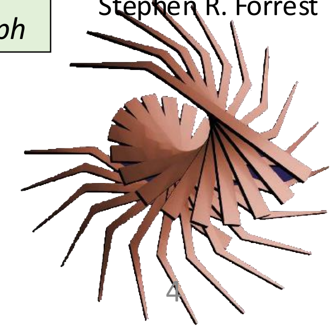


When illuminated, conductivity changes

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

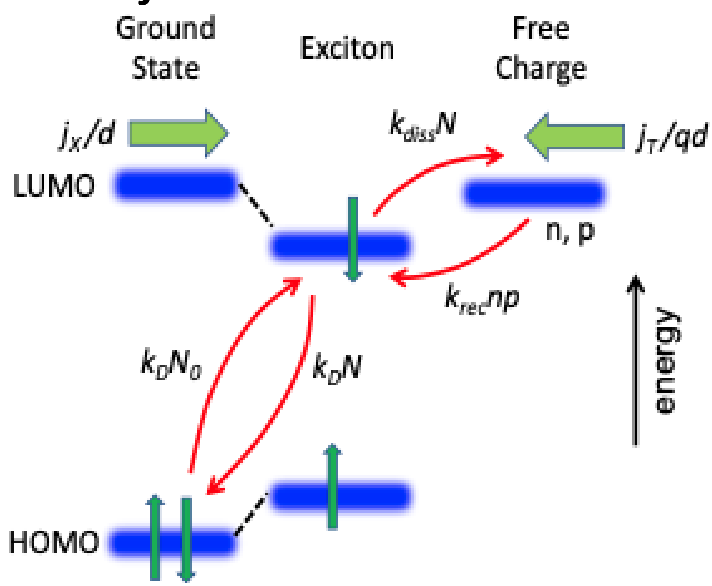
$n_{ph} = p_{ph}$

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

τ_D = 1/k_D = lifetime of charge

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

⇒ Photocurrent:

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

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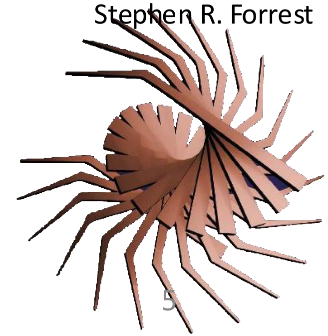


Gain and bandwidth

Photoconductors operate in the Ohmic (near equilibrium) regime

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

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

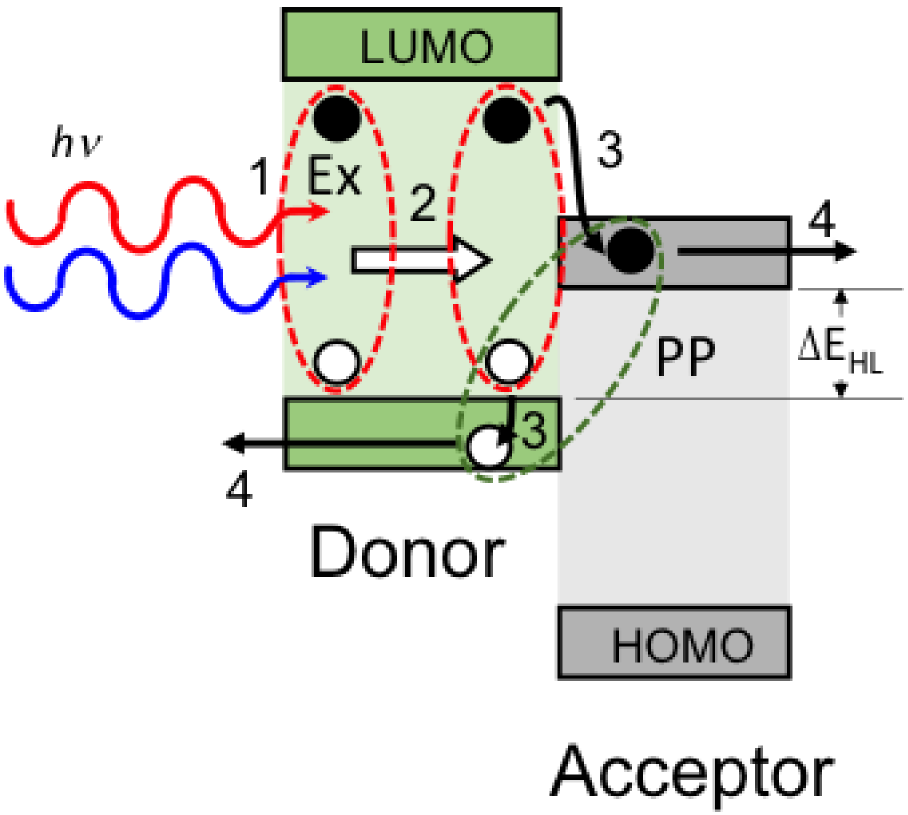
$$g\eta_{ext} = \frac{j_{ph}A}{q\left(P_{inc}\lambda/hc\right)}$$

Quantum efficiency cannot be separated from gain

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

Photodiodes and solar cells

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



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

Typically: $L_D \ll 1/\alpha$

Efficiency and responsivity

- Internal quantum efficiency

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

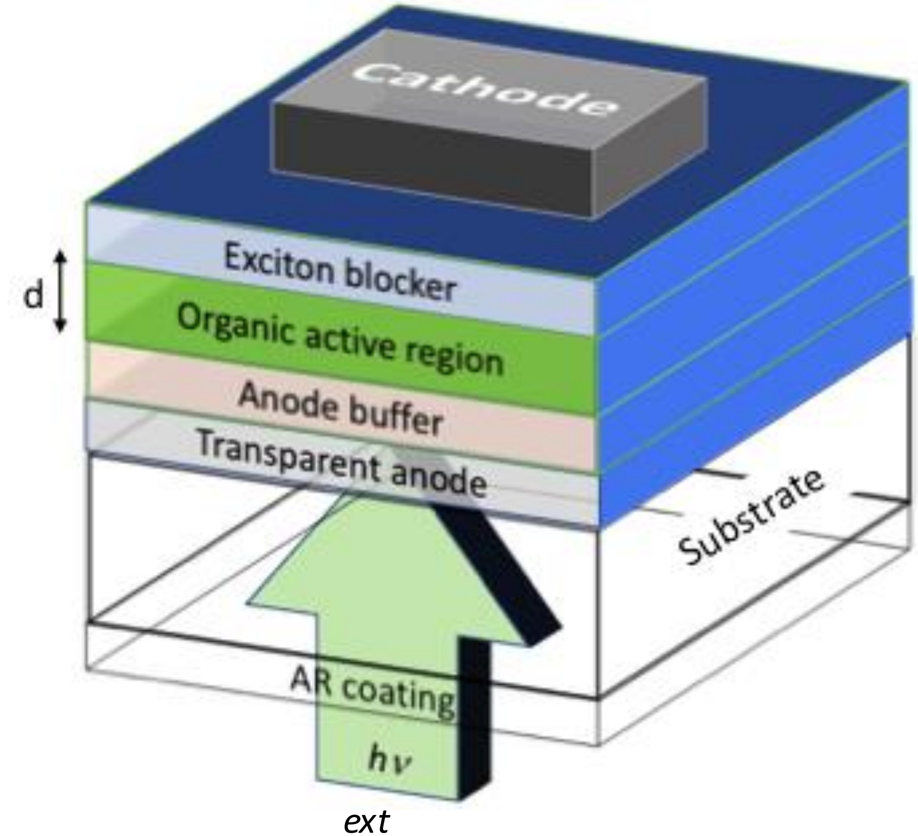
- External quantum efficiency

$$\eta_{ext} = (1 - R)\eta_{int}$$:R = reflectance at det. surface

- Responsivity

$$\mathcal{R}(\lambda) = \frac{j_{ph}(\lambda)}{P_{inc}} = g\,\frac{q\lambda}{hc}\eta_{EQE}(\lambda) \quad [\mathrm{A/W}].$$

Basic OPD/OPV structure



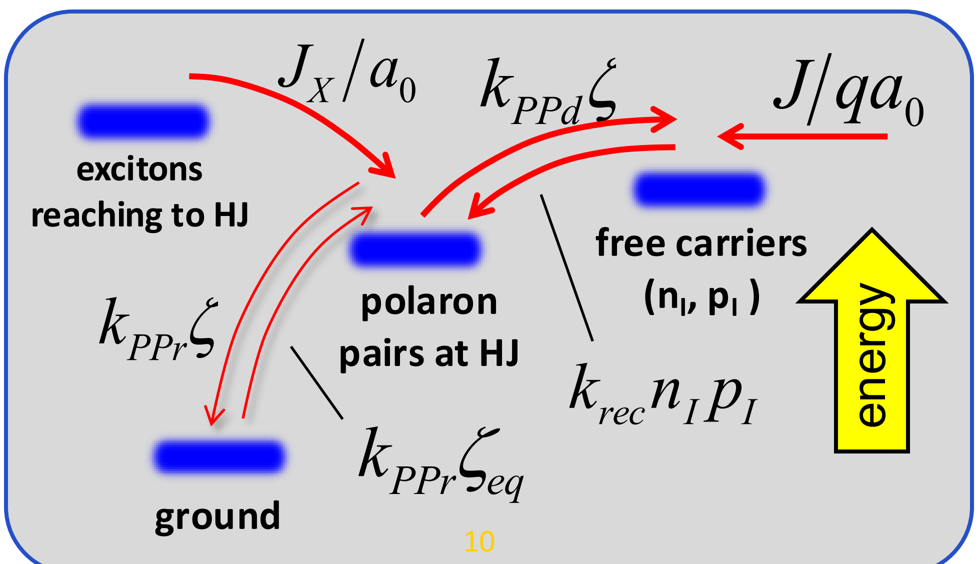
$$\boxed{\eta_{int} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC}}$$

Current generation

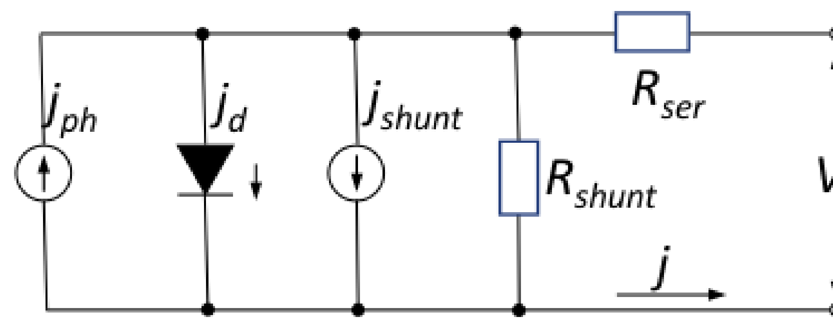
- Recall (Ch. 4) that the *j-V* characteristics are given by:

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

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



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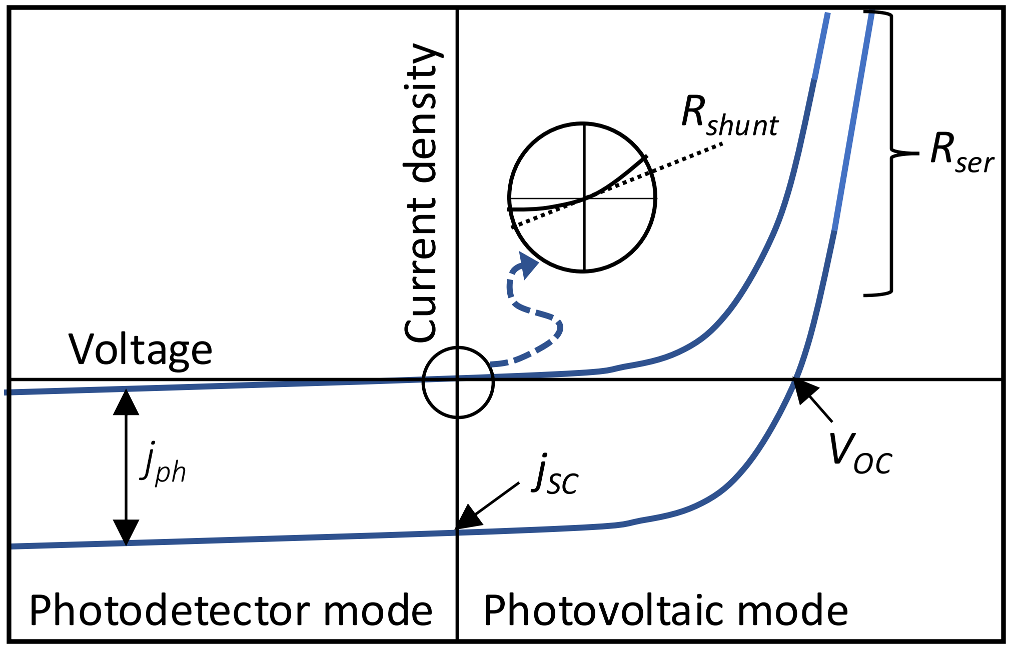
Current-Voltage Characteristics



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

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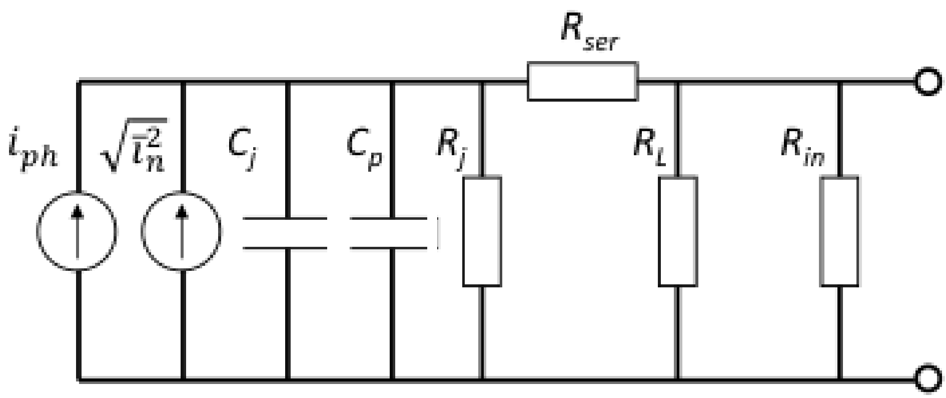
- In the photovoltaic mode, the power is $P = jV < 0$; i.e. the device **delivers power** to the external circuit.
- In the photodetector mode, $P > 0$ and the detector **dissipates power**.

Photodiode bandwidth

PD Equivalent Circuit



$$\Delta f = \frac{1}{2\pi}\left(\frac{1}{t_{tr} + \tau_{ED} + \tau_{RC}}\right) \qquad \tau_{RC} = (R_{ser} + R_L || R_{in})(C_j + C_P)$$

$$R_j \to \infty$$

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

Calculating the Noise Current

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

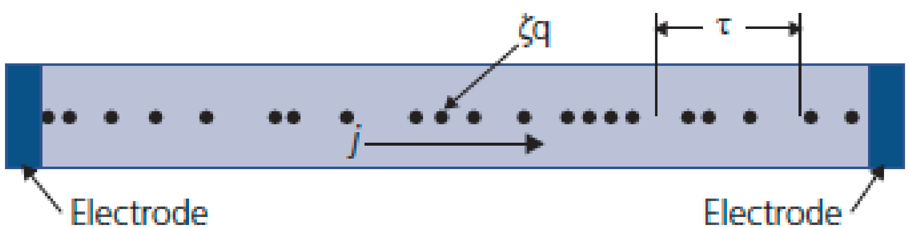
- Determines the sensitivity of a photodetector to low intensity signals

- Signal-to-noise ratio: $\frac{S}{N} = \frac{\left\langle i_{ph}^2 \right\rangle}{\left\langle i_n^2 \right\rangle} > 1$

$\left\langle i_{ph}^2 \right\rangle$ = mean square photocurrent
$\left\langle i_n^2 \right\rangle$ = 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*.



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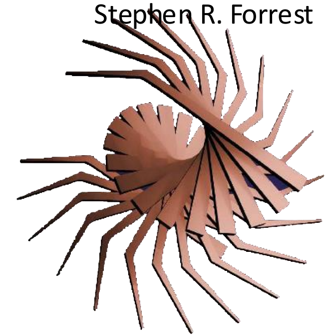


Then, the noise current is: $\left\langle i_n^2 \right\rangle^{1/2} = \frac{\left\langle n \right\rangle^{1/2}}{\tau} \zeta q$

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:

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

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

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

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**:

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

R_{PC} is the resistance of the conductor

Finally, there is **flicker**, or **1/f noise**:

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

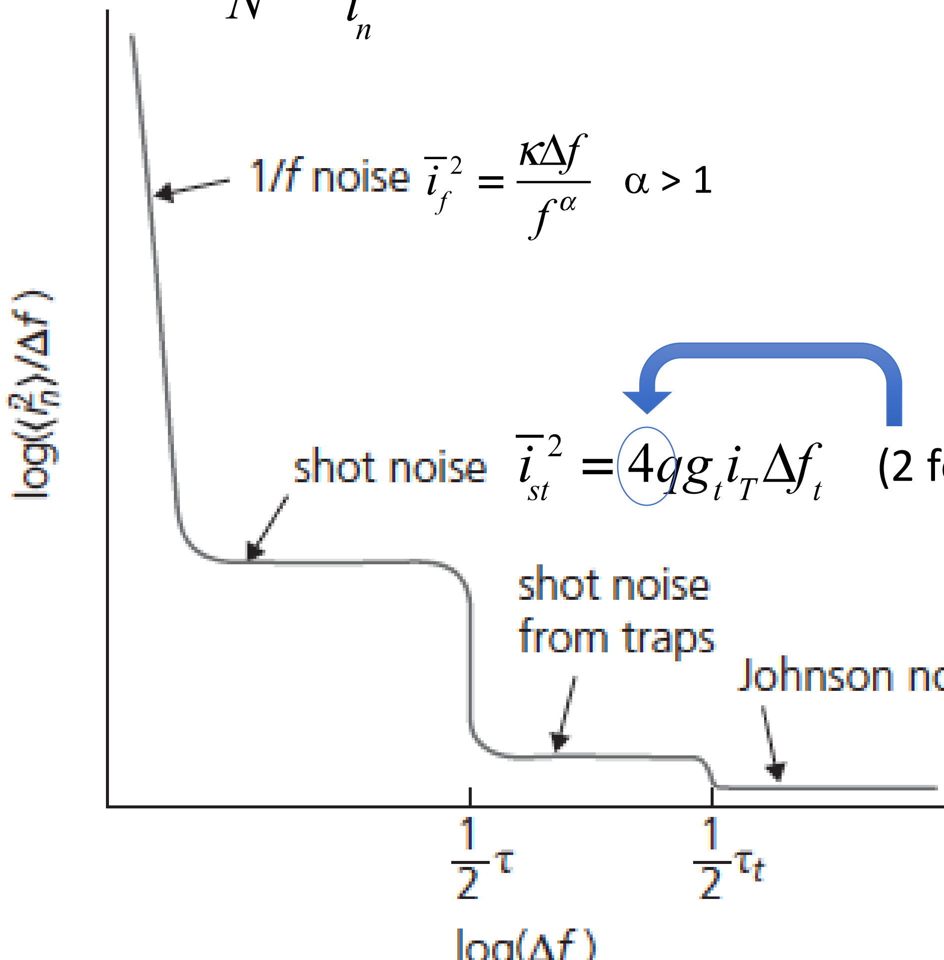
κ, α are empirical constants

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

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

Detectivity and dynamic range

- Noise equivalent power

$$NEP = \sqrt{\langle i_n^2 \rangle / \Delta f} / \mathrm{R} = 1/D, \qquad [\mathrm{W}/\sqrt{\mathrm{Hz}}]$$

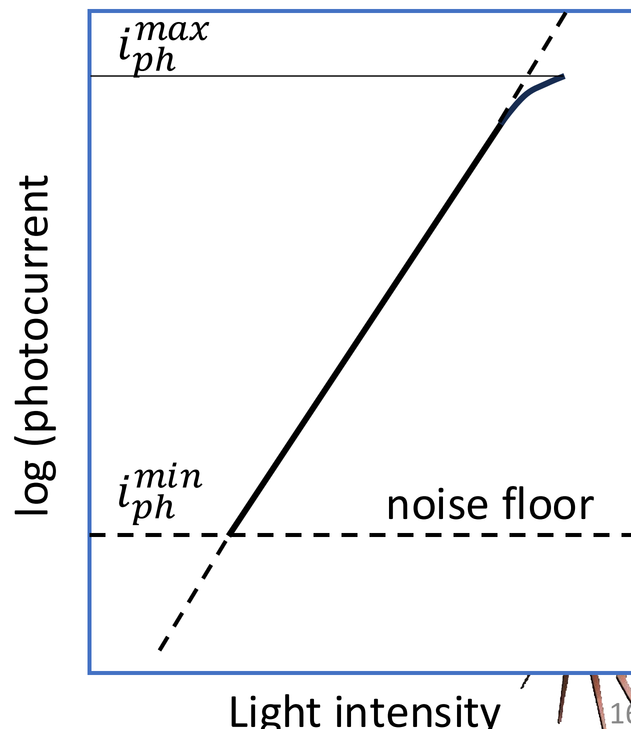
D = Detectivity

- Specific detectivity ("D-star" normalizes D to area)

$$D^* = \sqrt{A}/NEP = \mathrm{R}\sqrt{A\Delta f / \langle i_n^2 \rangle}. \quad \text{[Jones]}$$

- Dynamic range

$$DR = 20log_{10}\left(i_{ph}^{max} / i_{ph}^{min}\right).$$



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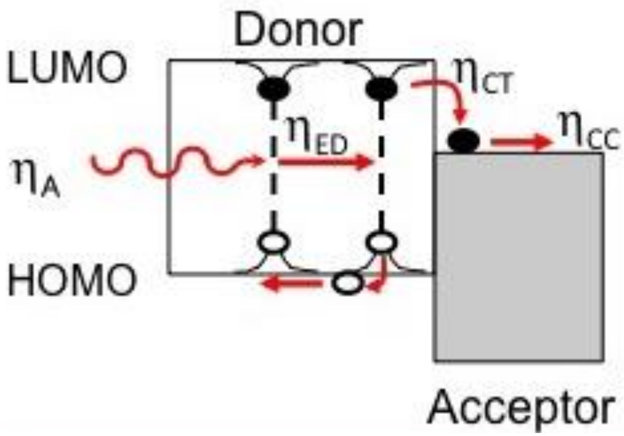
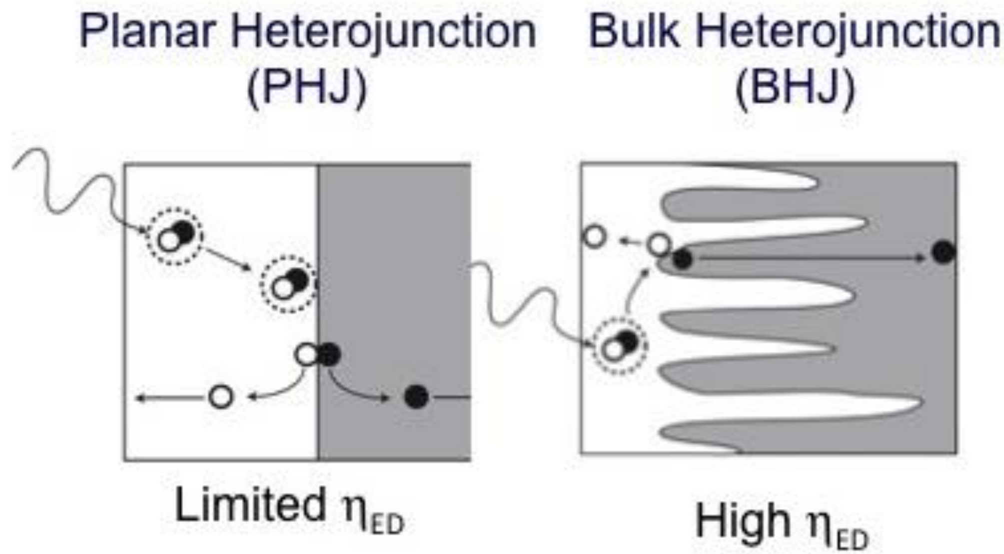
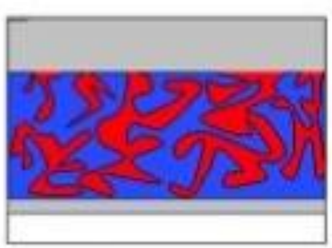
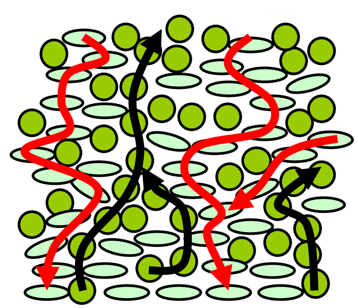
Heterojunction Morphologies

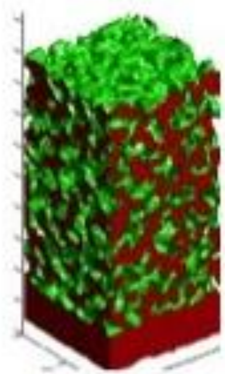
Breaking the tradeoff between L_D and α with BHJs

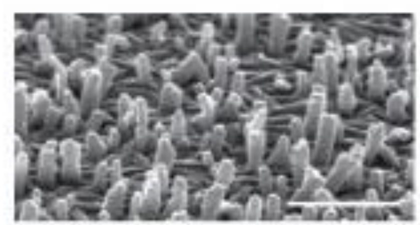






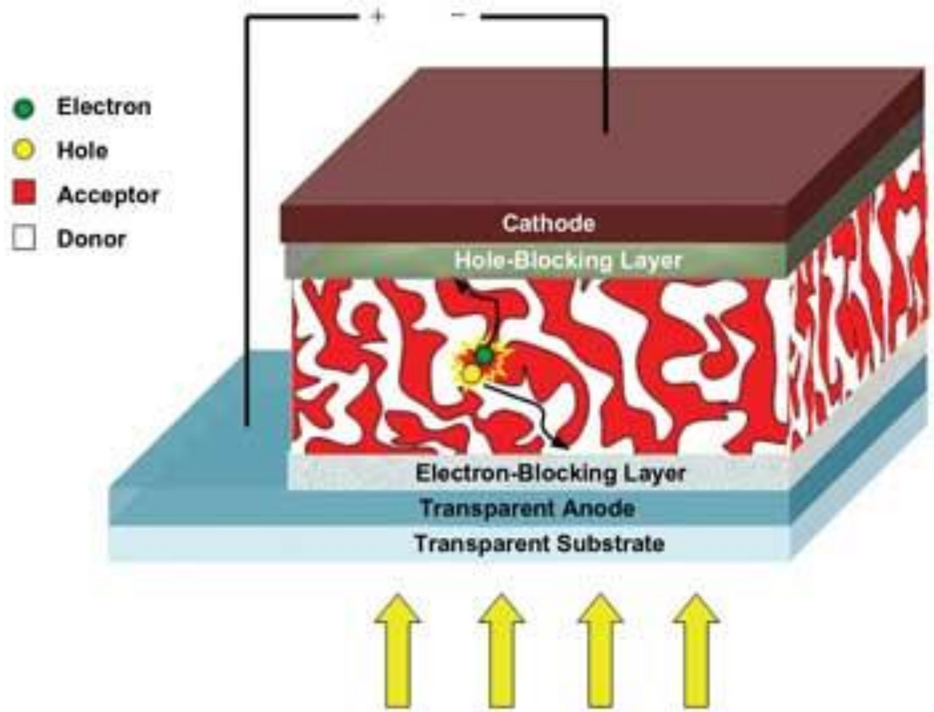


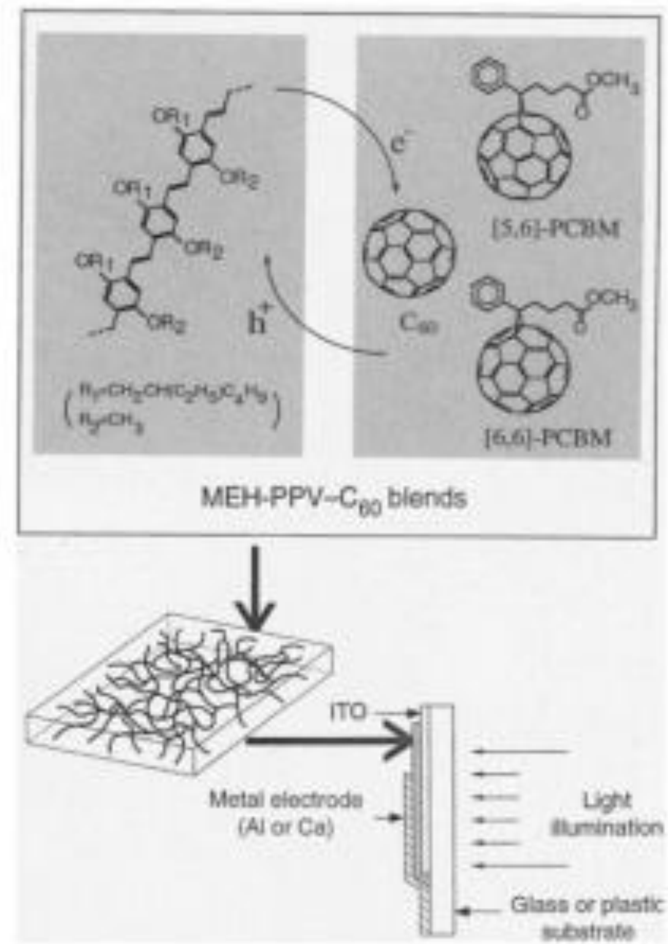




Bulk HJ | Mixed HJ | Annealed BHJ | Controlled BHJ

Polymer Bulk HJ



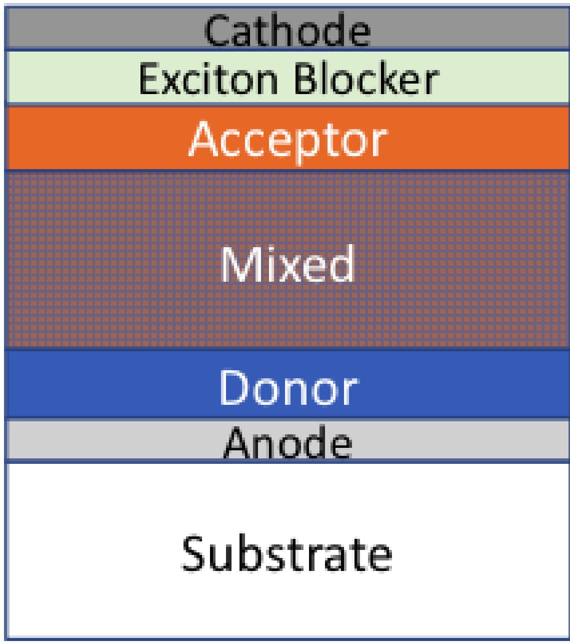


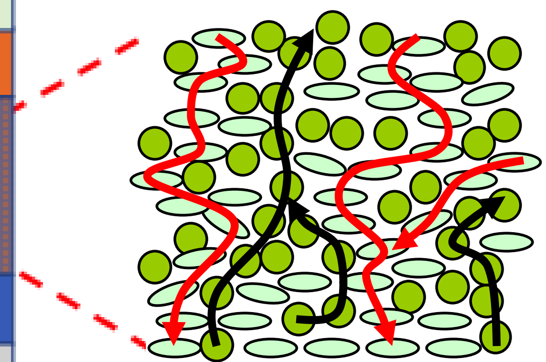
Yu et al. Science, **270**, 1789 (1995)

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

Small Molecule Planar-Mixed HJ

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





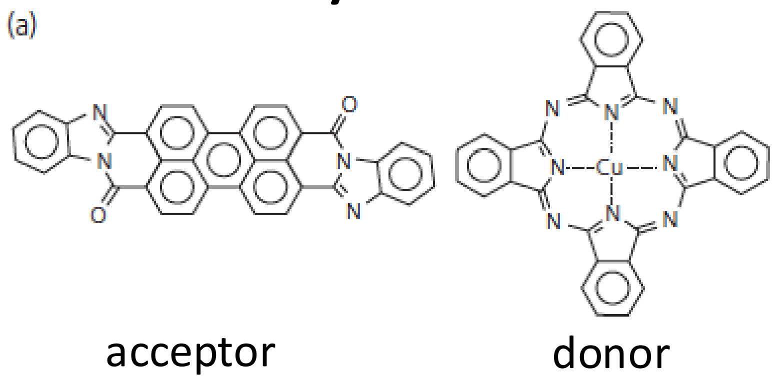
$$\eta_{CC} = \frac{L_C}{x_M}\left(1-\exp\left(-x_M/L_C\right)\right)$$

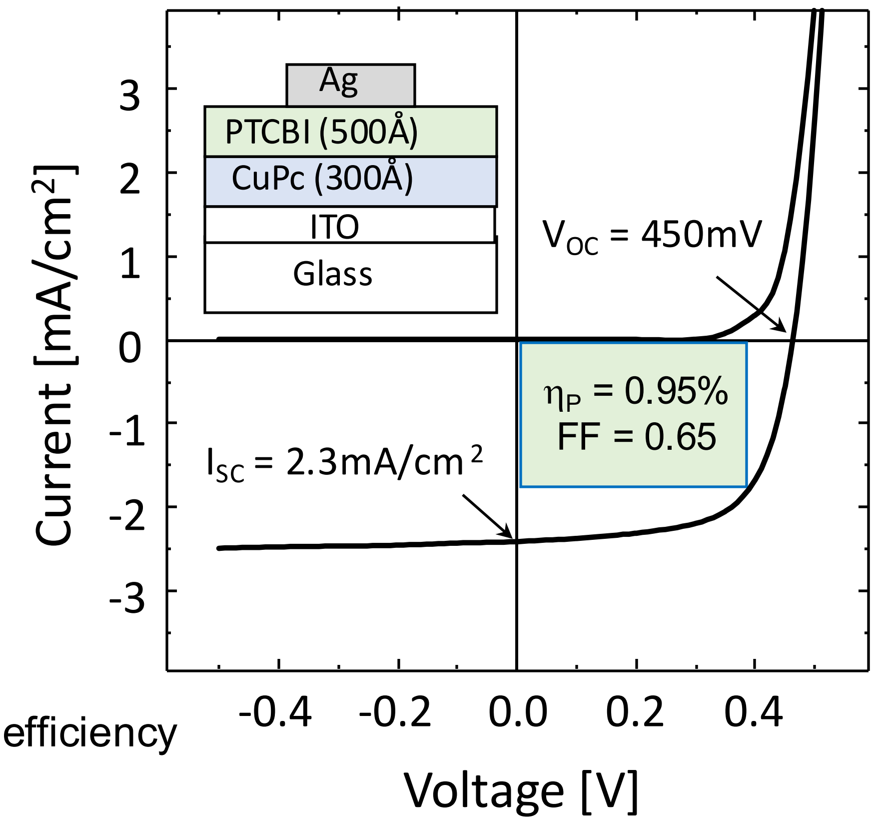
Charge carrier collection length, L_C, replaces diffusion length since excitons dissociate at point of generation without diffusion to HJ

J. Xue, *Adv. Mater.*, **17**, 66, (2005).

The first bilayer OPD/OPV

(a)





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

η_P = power conversion efficiency
FF = fill factor

Comparison of OPCs and OPDs

Parameter	Photoconductor	Photodiode
Operating voltage	Near equilibrium ($_{a} \to 0$)	Reverse bias
Photocurrent gain (g)	$/ \ _{tr}$ (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)	$1/2 \quad _{D}$	$1/2 \quad _{tr}$
Gain-bandwidth product ($g\Delta f$)	$1/2 \quad _{tr}$	$1/2 \quad _{tr}$
$\overline{i_n}^2/\Delta f$	$(4k_BT)/R_{PC}+\kappa/f^{\alpha}$	$2qi_T+4k_BT/R_L \parallel R_{in}$
Specific detectivity (D^*)	$q\eta_{ext}(\lambda/hc)\sqrt{\dfrac{A}{(4k_BT)/R_{PC}+\kappa/f^{\alpha}}}$	$q\eta_{ext}(\lambda/hc)\sqrt{\dfrac{A}{2qi_T+4k_BT/R_L \parallel R_{in}}}$

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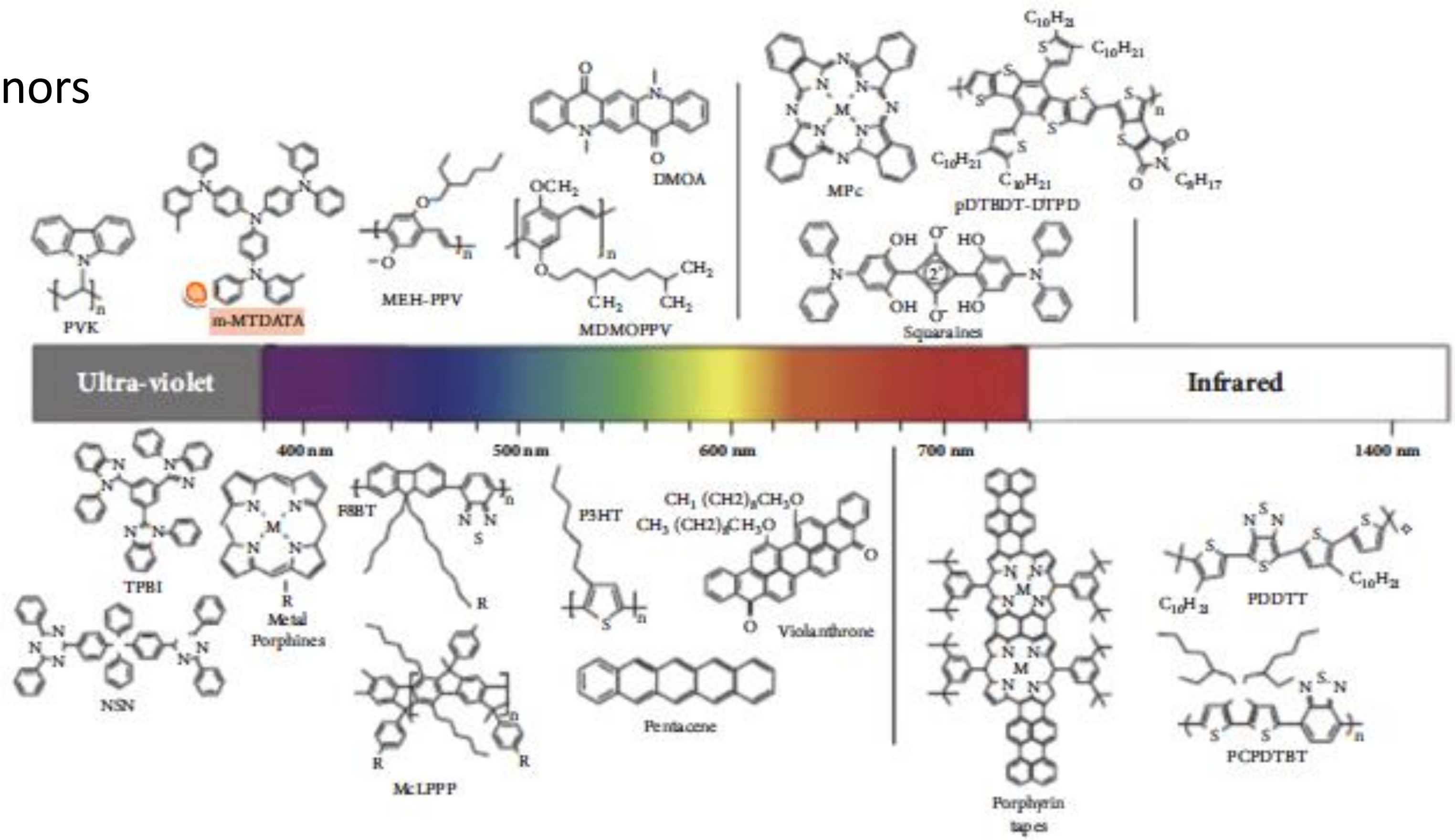
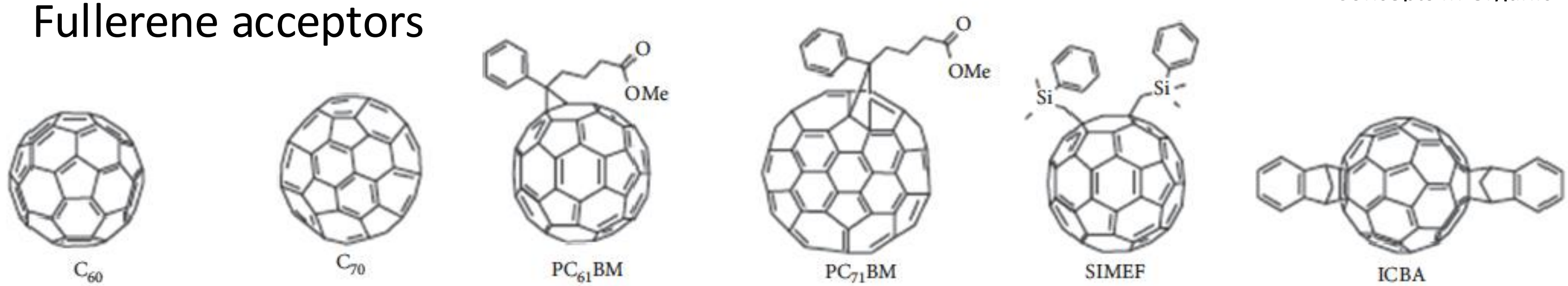
rest

Common photodetector materials

Donors



Fullerene acceptors



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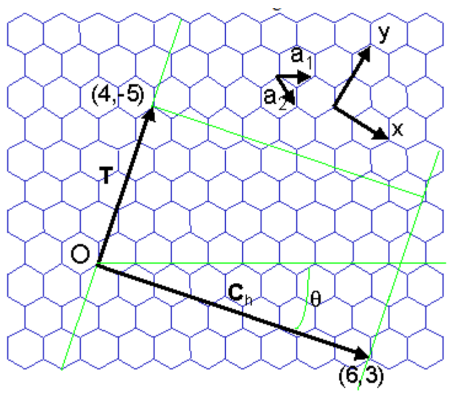
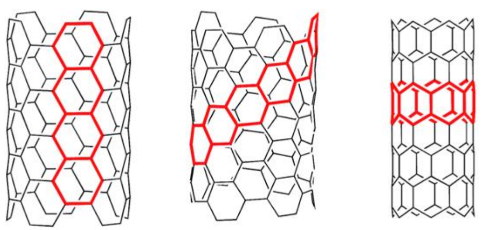
Long wavelength Detectors

Carbon Nanotubes Can Stretch Detection to NIR: Avoiding the Energy Gap Law



$$C_h = na_1 + ma_2$$



[5,5] CNT
Armchair
Metallic

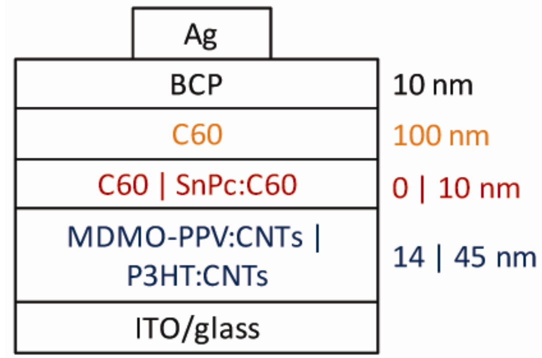
[7,5] CNT
Chiral
Semiconducting

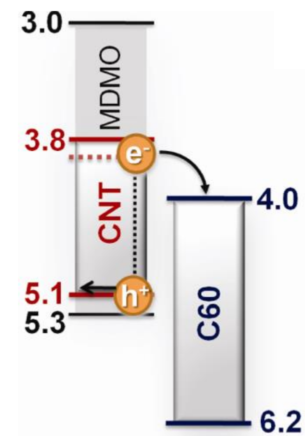
[7,0] CNT
Zigzag
Semiconducting

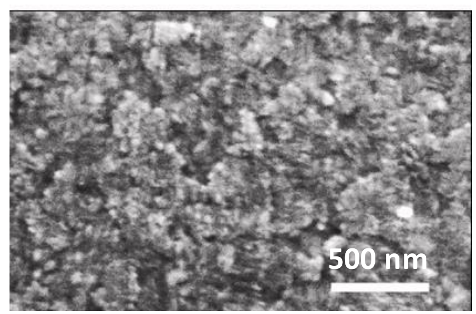
Chirality determines if CNT
is metallic, semiconducting or insulating

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

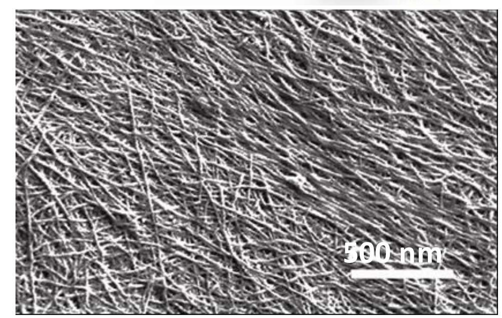
Organic/CNT Detector







CNT:MDMO-PPV composite

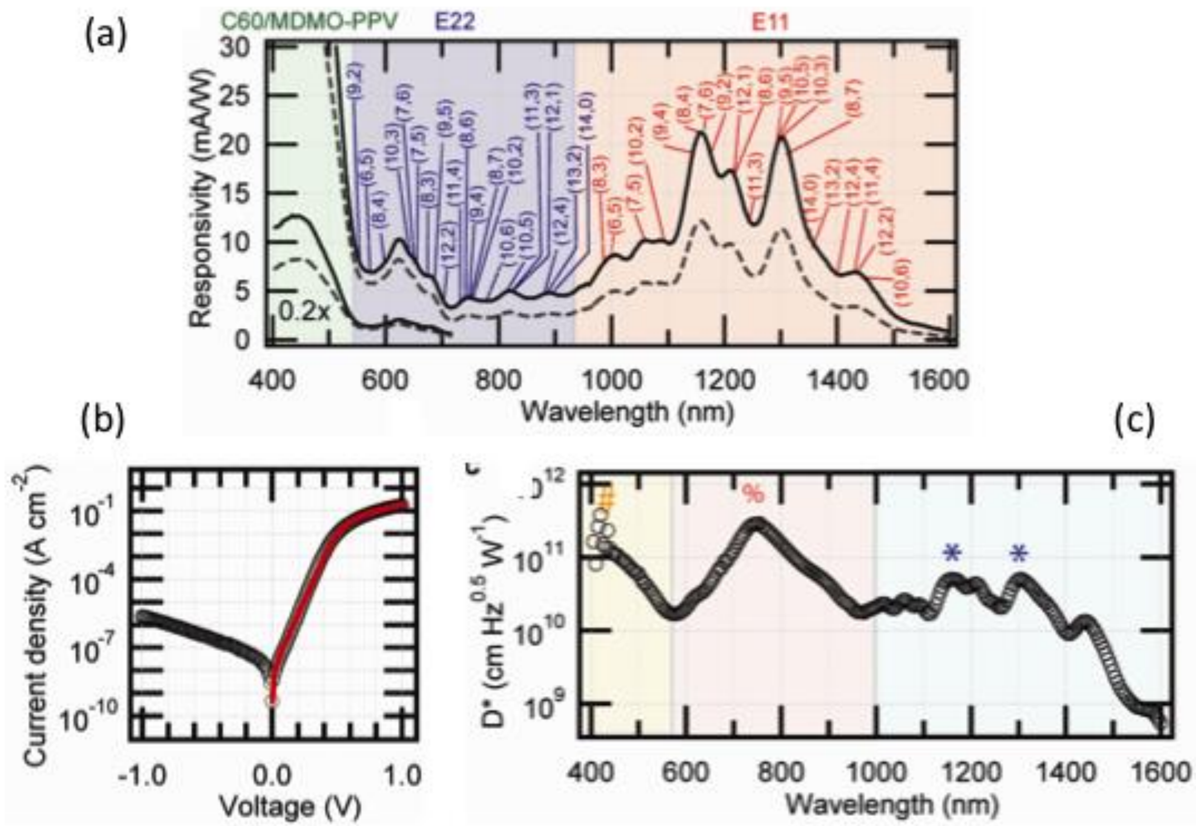


Mat of bare CNT

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

Long wavelength Detectors

Single Walled Nanotubes Wrapped in Polymer



Responsivity and Specific Detectivity:

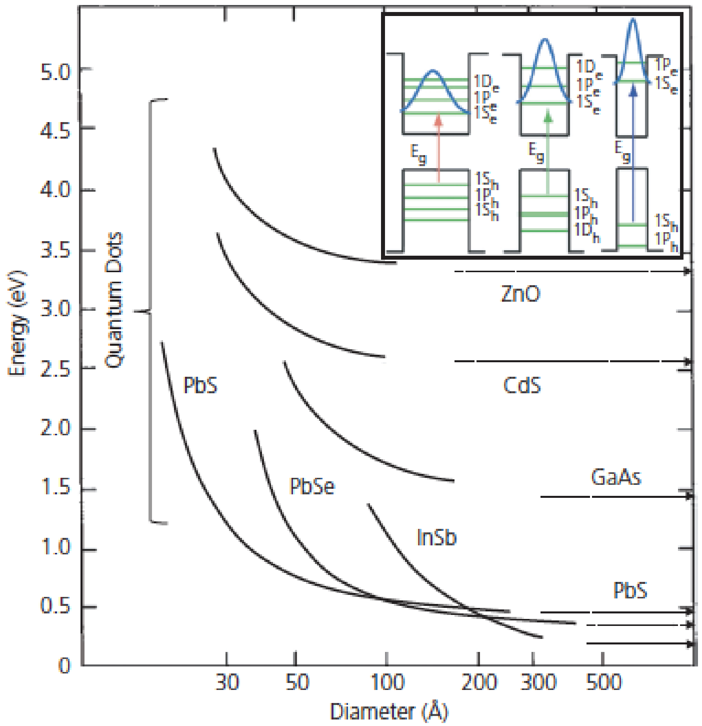
$$\mathcal{R} = \frac{j_{ph}A}{P_{inc}} = qg\eta_{ext}\left(\frac{\lambda}{hc}\right) \quad \text{[A/W]}$$

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

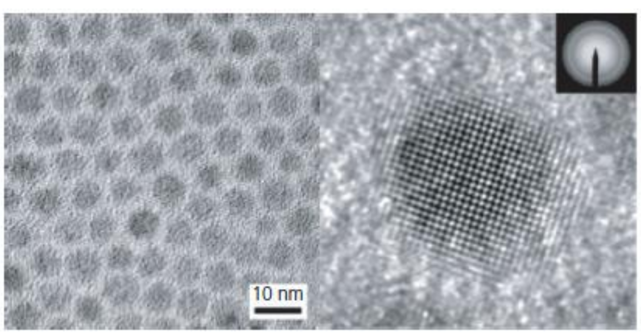
M. S. Arnold, et al., *Nano Letters,* **9**, 3354, 2009.

Quantum Dots: Another Path to Long Wavelength

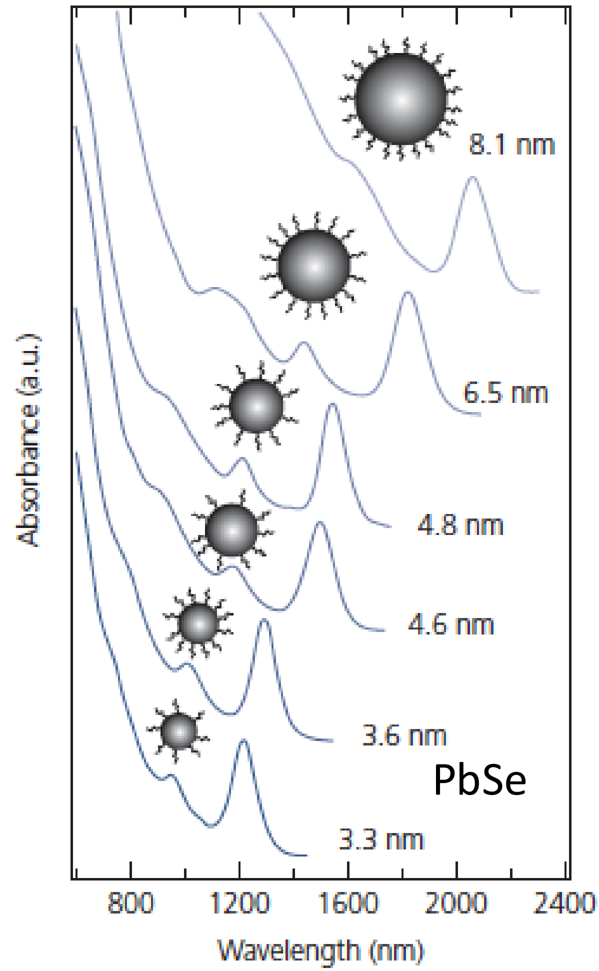
Larger diameter = Longer Wavelength



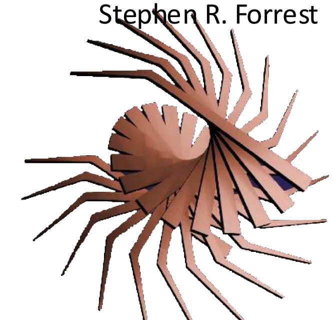
PbS Dots and Colloids



M. A. Hines & G. D. Scholes, *Adv. Mater.,* **15**, (2003)

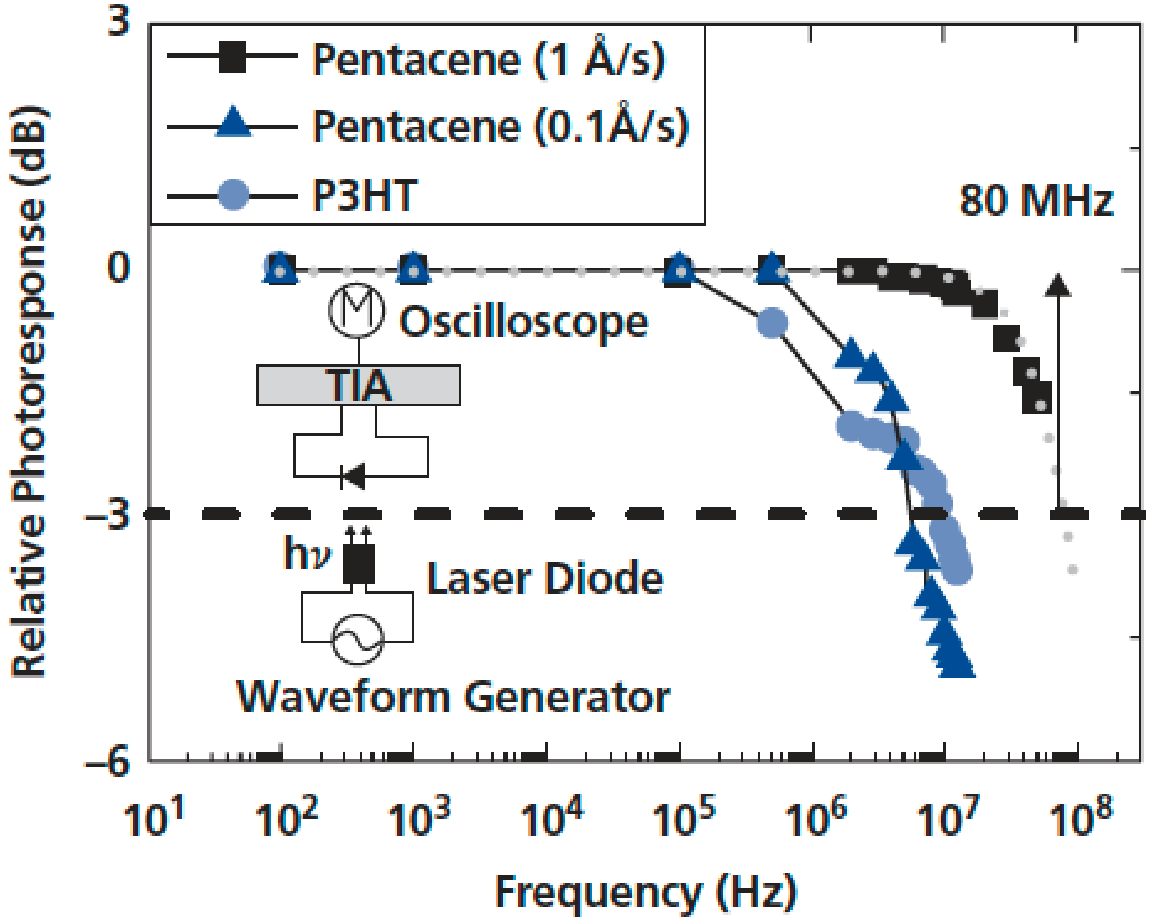


O. E. Semonin, et al. *Mater. Today,* **15**, 508, (2012).



Pentacene/C_{60} OPD Frequency Response

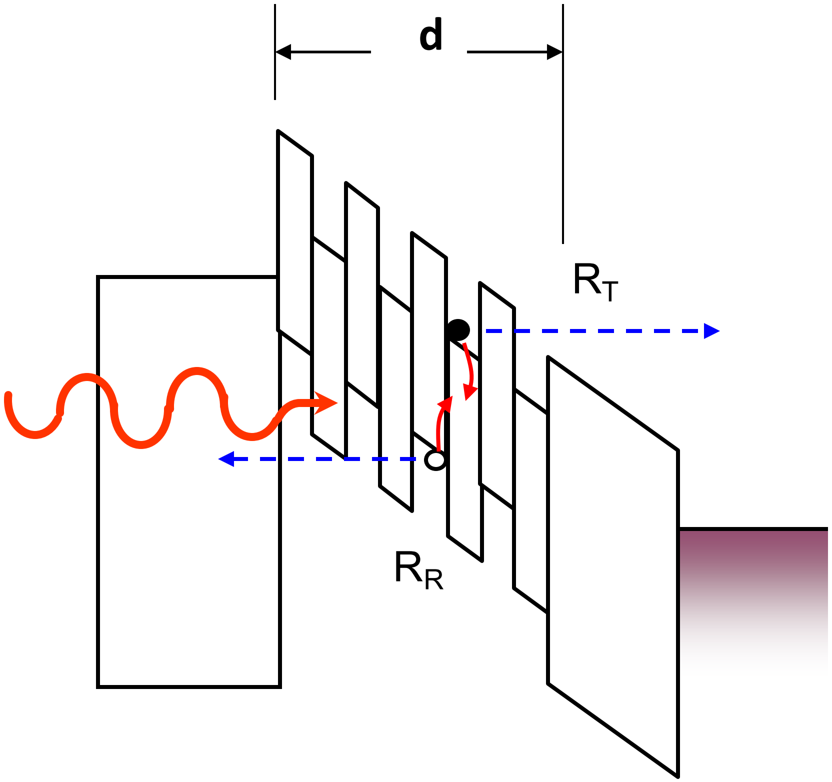
High frequency response due to high pentacene mobility



TIA: Transimpedance amplifier through which the diode is biased

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

High Bandwidth Multilayer Photodetector

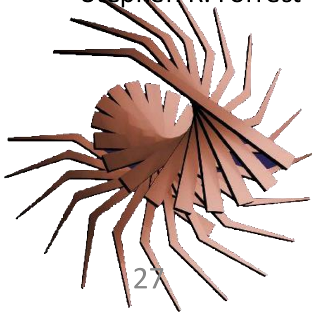


Place all D/A junctions within L_D of absorption site

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

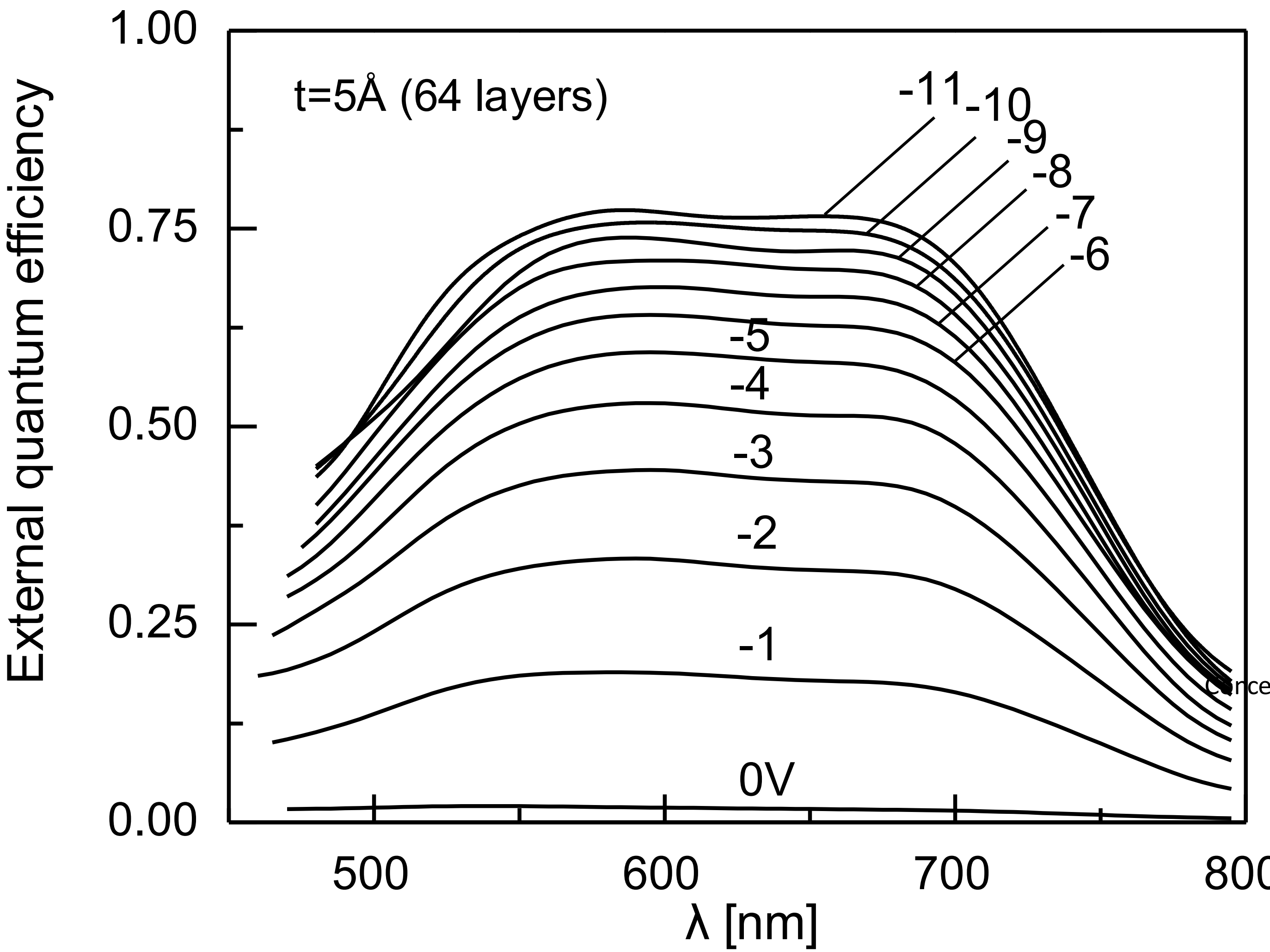
Apply voltage to sweep charge out of potential wells

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



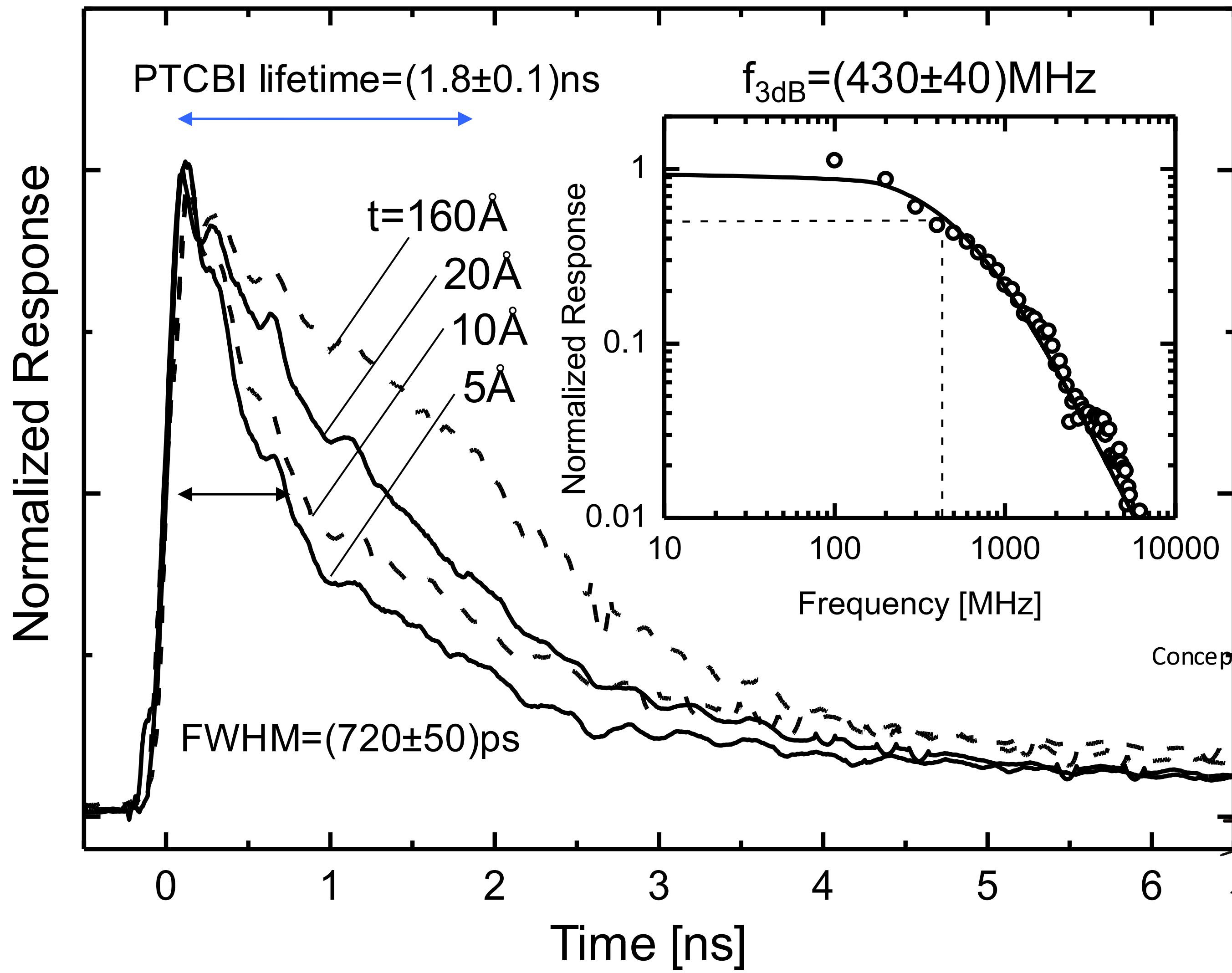
P. Peumans, et al. *Appl. Phys. Lett*., **76,** 3855 (2000).

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 W/cm^2.

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



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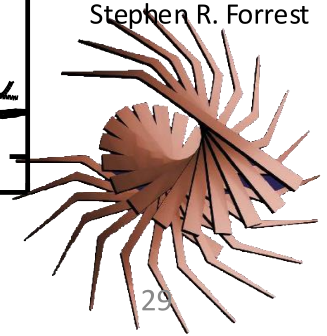
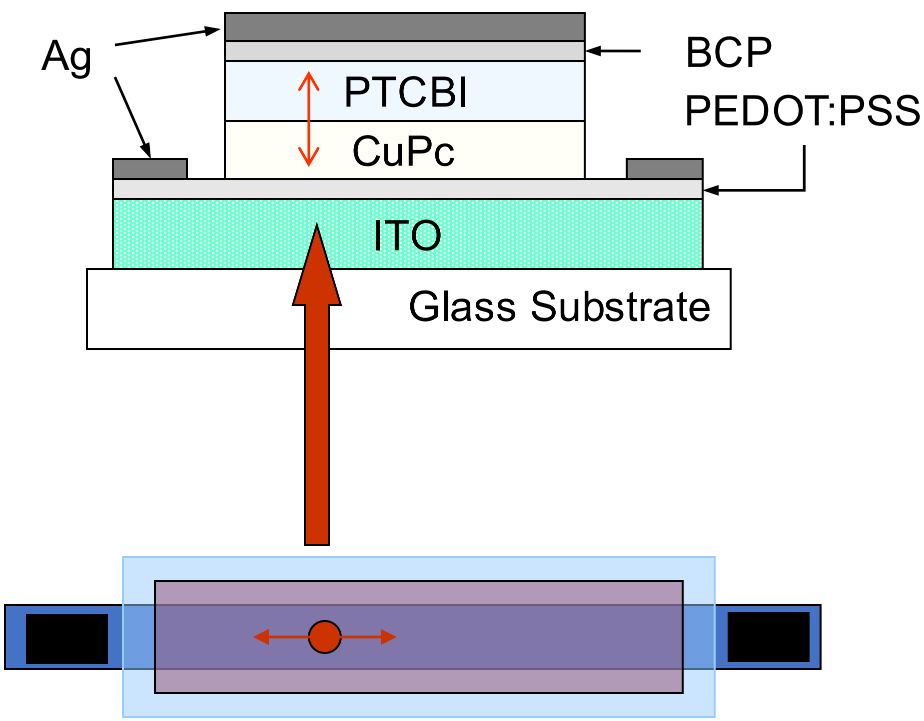
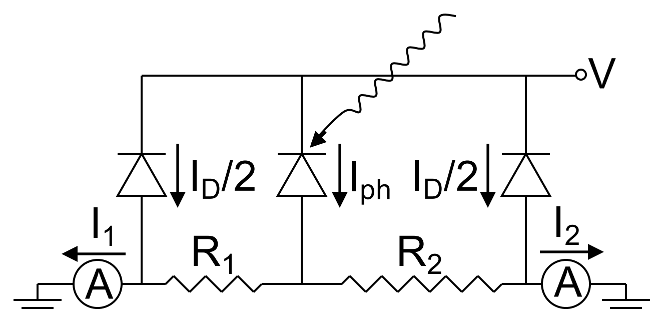


Position Sensitive Detector

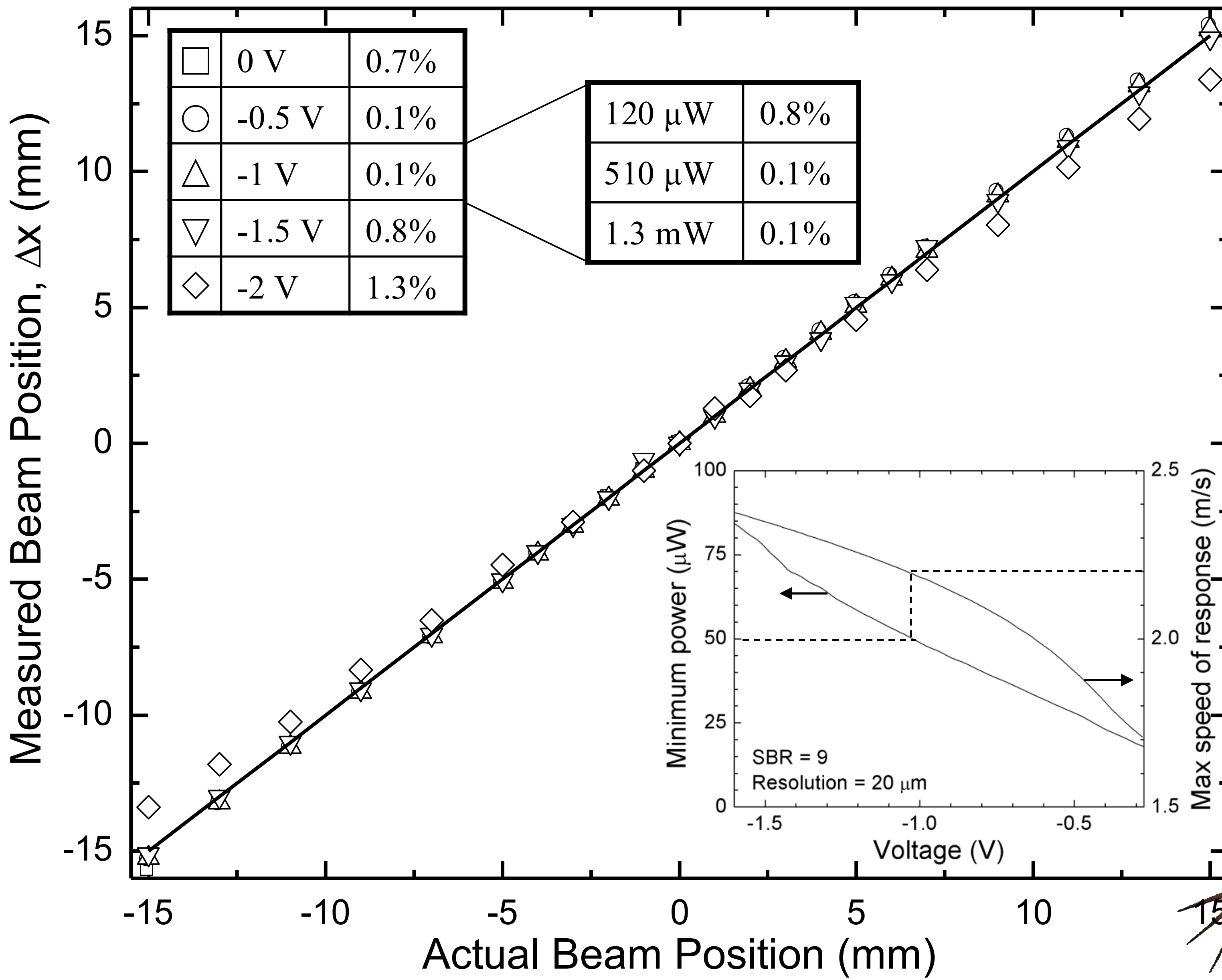
- Mechanism of operation
  - Extended junction transports charge vertically (no current spreading)
  - Current divided by *linear* resistance of ITO strip





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

Position Detection Characteristics



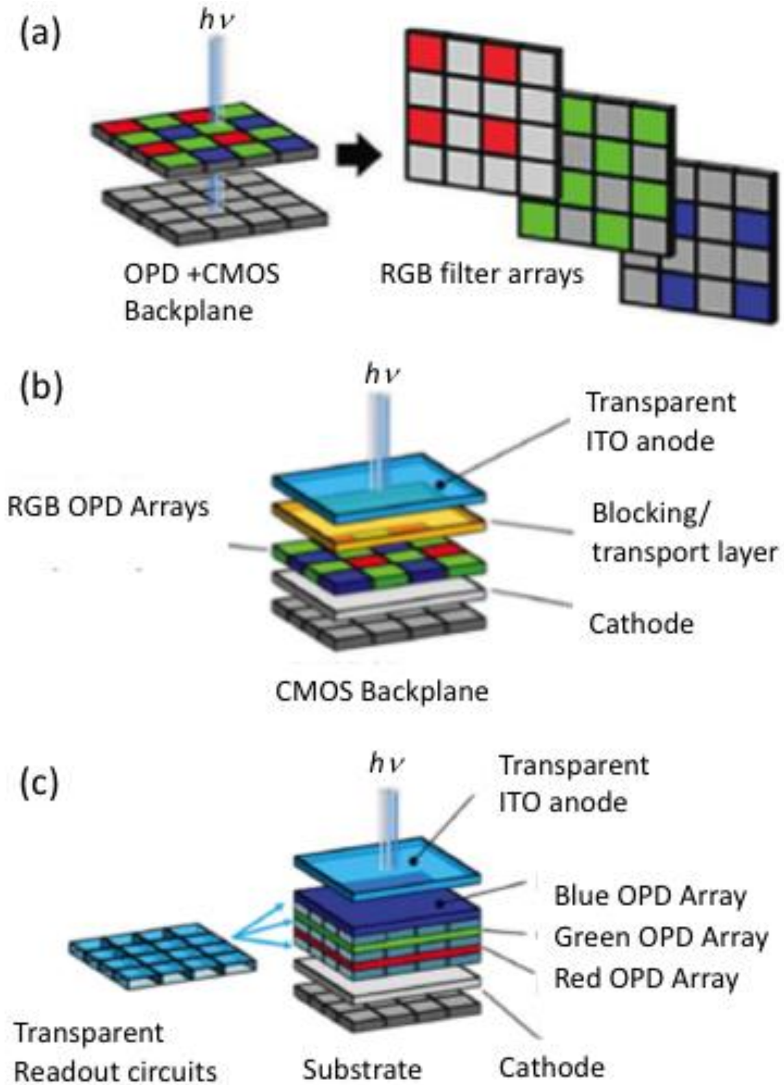
Rand, et al. *IEEE Photon. Technol. Lett.*, **15,** 1279 (2003).

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)

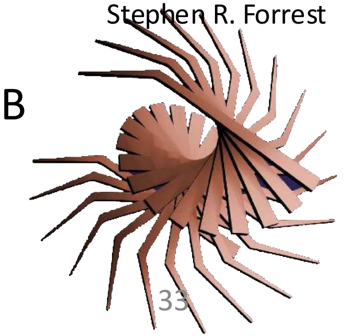
How a camera works



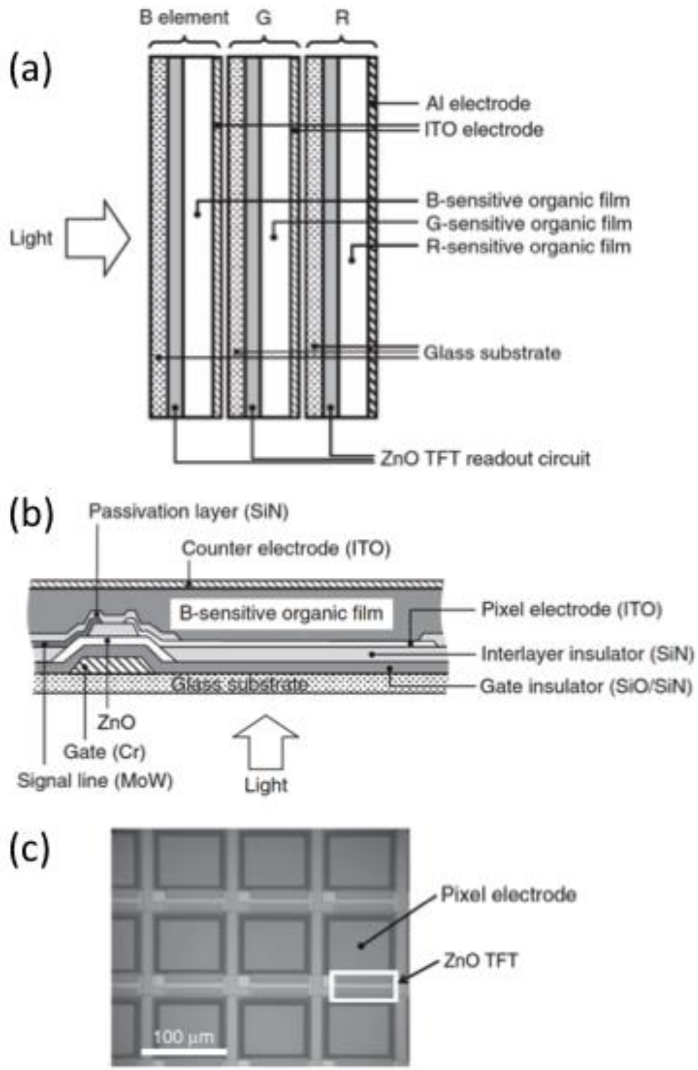
Color filters

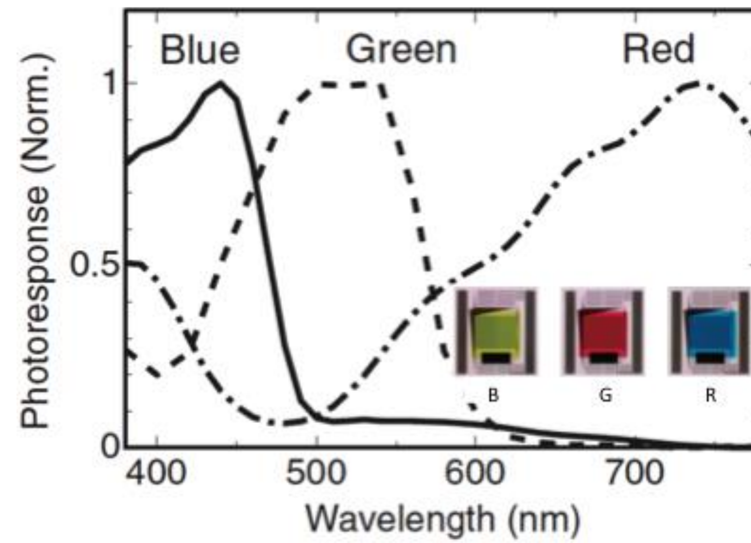
Integrated RGB Sensitive OPDs

Stacking R, G, B layers



Stacked sensors





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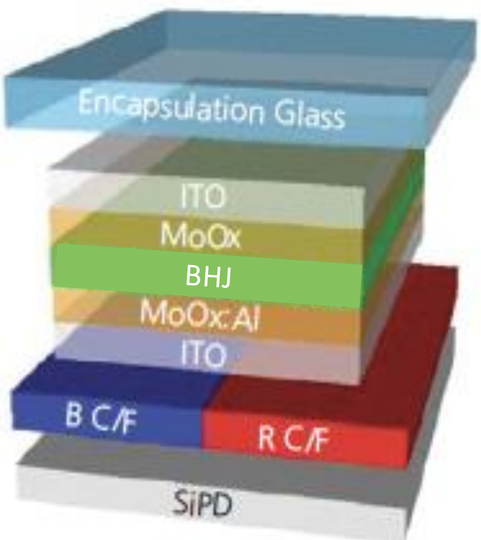
S. Hokuto, et al., *Japan. J. Appl. Phys.,* **50**, 024103, 2011.

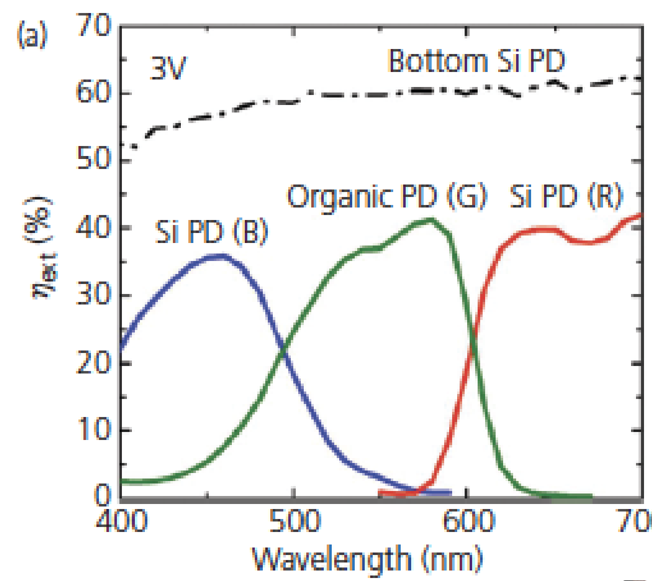
Hybrid Si CMOS/organic imaging array



Schematic of the detector stack

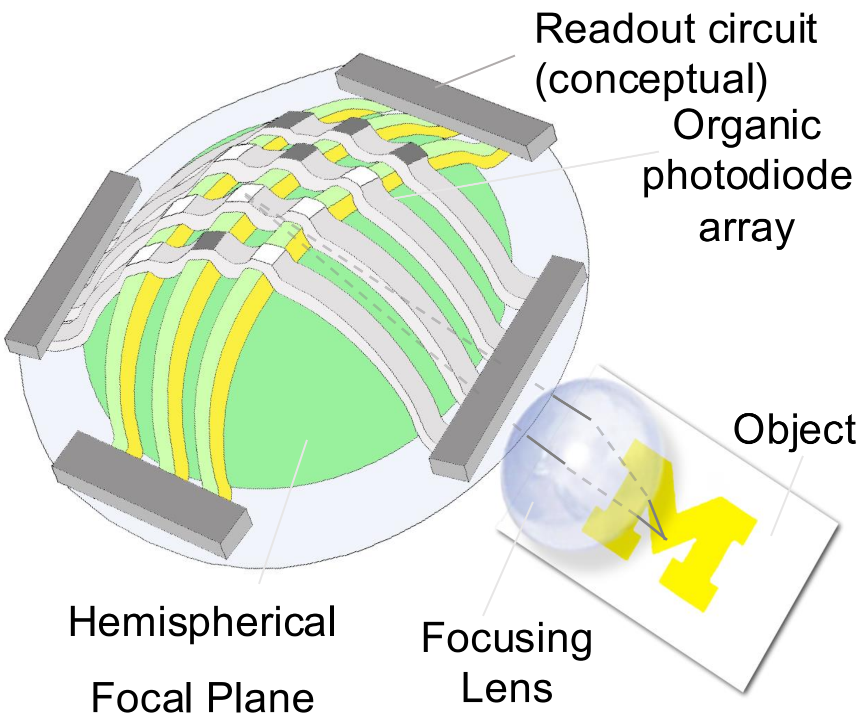
Image reproduction as detected

Spectral response of the 3 color pixels:
B and R use Si PDs with color filters
G uses an organic PD

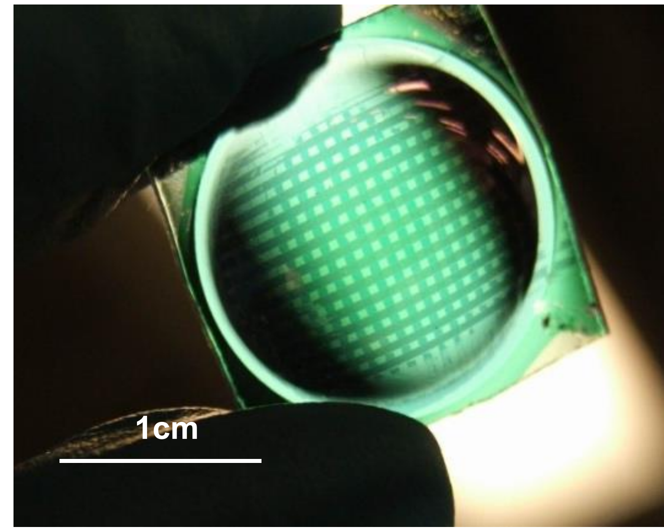


S.-J. Lim, et al. (2015) Sci. Reports, 5, 7708

Hemispherical Focal Plane Array: Making electronics on non-developable surfaces via printing

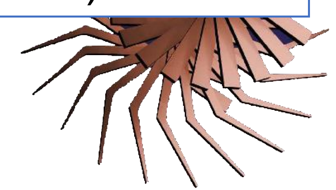


Au anode
organics
Ag cathode



Eye-sized imager

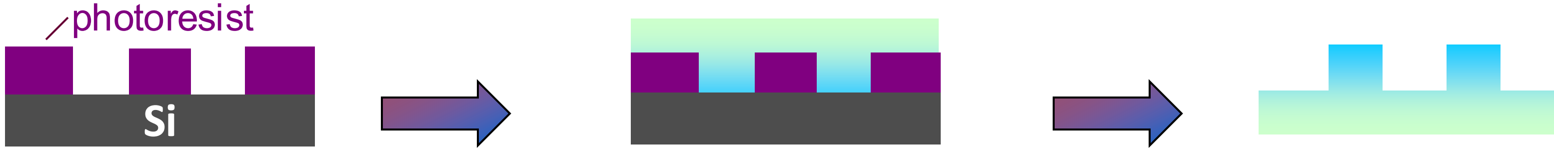
Materials: Metals and organics
(flexible, inexpensive)
Patterning at the micro-scale: Direct transfer of materials
(printing, minimal strain)



X. Xu, et al. (2008) Org. Electron. **9**, 1122.

3D Patterning by Stamping

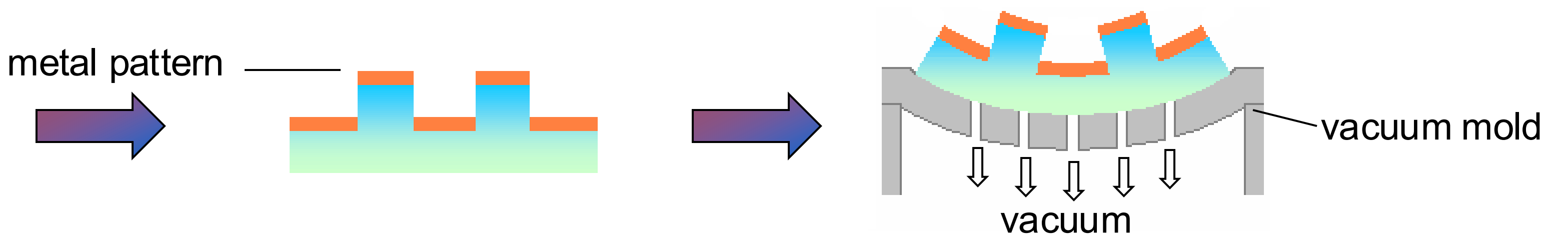
Step 1) Formation of 3D stamps



Si master with photo-resist patterned on it

Pour PDMS prepolymer & cure

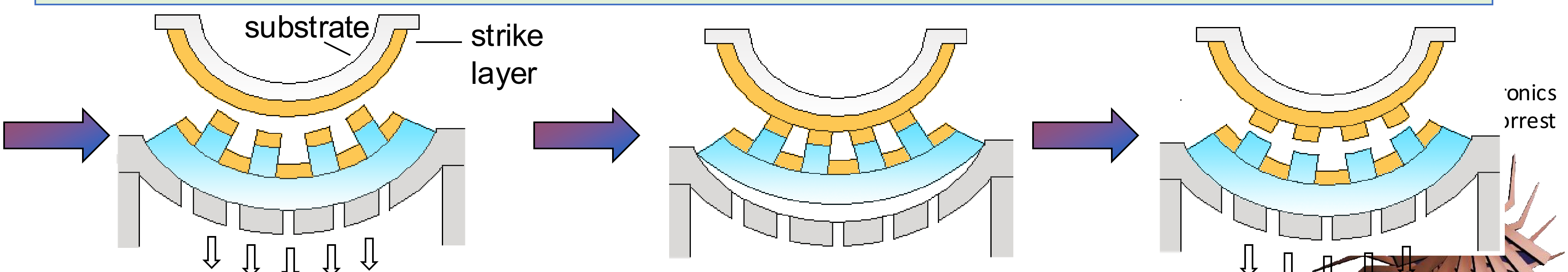
Remove PDMS elastomer from master



Evaporate metal on PDMS stamp

Deform PDMS + metal using hemispherical mold

Step 2) Transfer materials by stamping



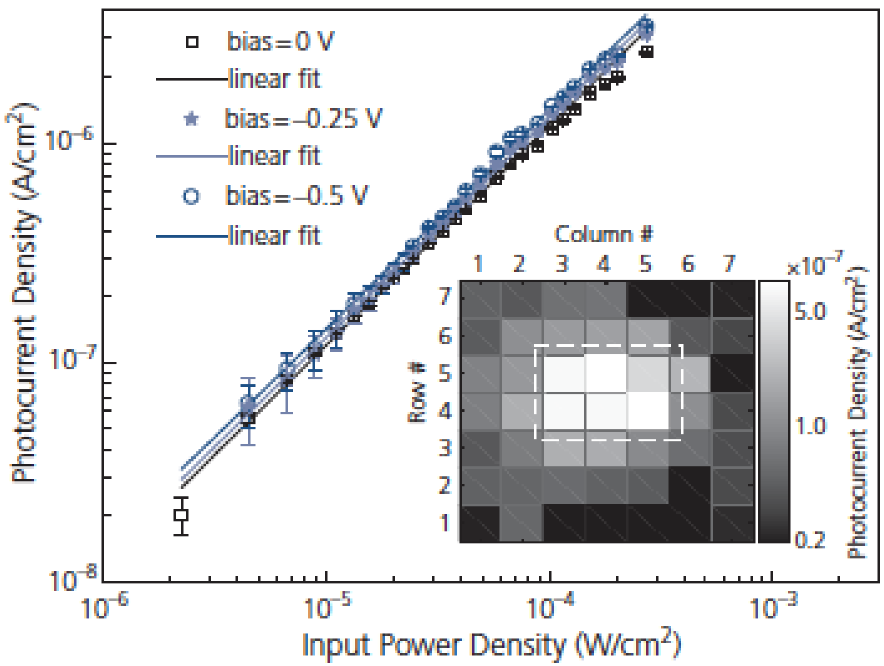
Bring hemisphere to stamp

Release vacuum "snap the suspenders"

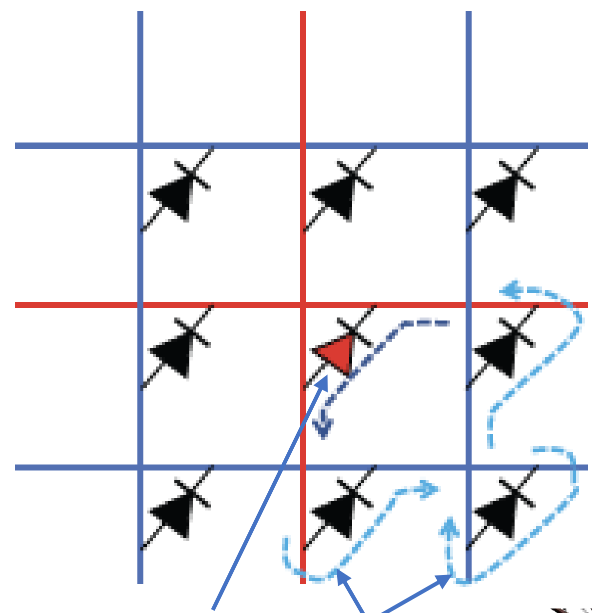
Withdraw stamp and substrate

Performance of the hemispherical focal plane array

Dynamic range



Pixel addressing and sneak currents in a passive matrix imager



What we learned

- The operating principles of organic photoconductors and photodetectors
- Performance characteristics
  - Gain and gain-bandwidth product
  - Efficiency and Responsivity
  - Noise
  - Detectivity and dynamic range
- Materials and device structures
- Achieving long wavelength and high bandwidth detection
- Imagers