The Abdus Salam International Centre for Theoretical Physics

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Winter College on Optics and Energy

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Lateral PV Effects, Near Field Probes, Current Status and Strategies in BHJ-PSCs

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- Measure of mobility in ambipolar systems

(regimes: $\mu_e\tau_e/\mu_h\tau_h$ >> 1 or << 1 and $\mu_e\tau_e/\mu_h\tau_h \approx 1$)

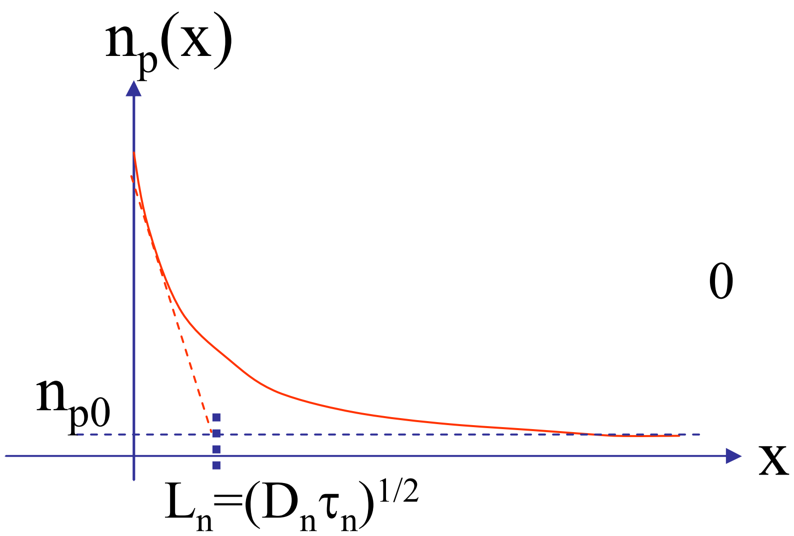
- Bulk versus lateral mobility

(transverse-lateral correlation)

- Mobility in 2D systems, anisotropic linear systems…
- Solar cell dimensions and optimized efficiencies.

$$\frac{\partial n_p}{\partial t} = G_n - \frac{n_p - n_{p0}}{\tau_n} + n_p \mu_n \frac{\partial E}{\partial x} + \mu_n E \frac{\partial n_p}{\partial x} + D_n \frac{\partial^2 n_p}{\partial x^2}$$

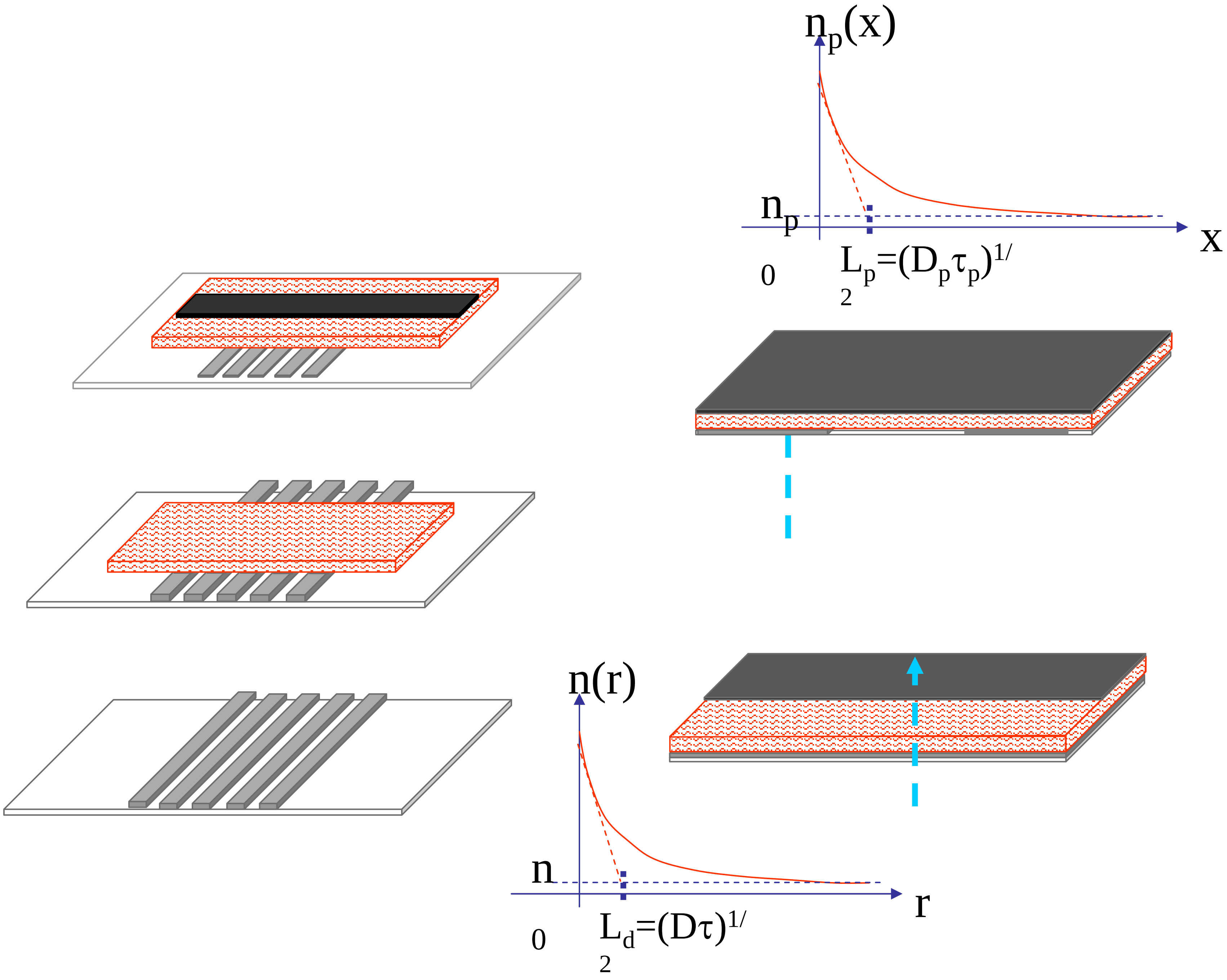
$$n_p(x) = n_{p0} + \left\lfloor n_p(0) - n_{p0} \right\rfloor \exp(-x/L_n)$$



$$\langle L \rangle = (D_n.\tau)^{1/2} = \left(\frac{k_B T \mu_n.\tau}{e} \right)^{1/2}$$

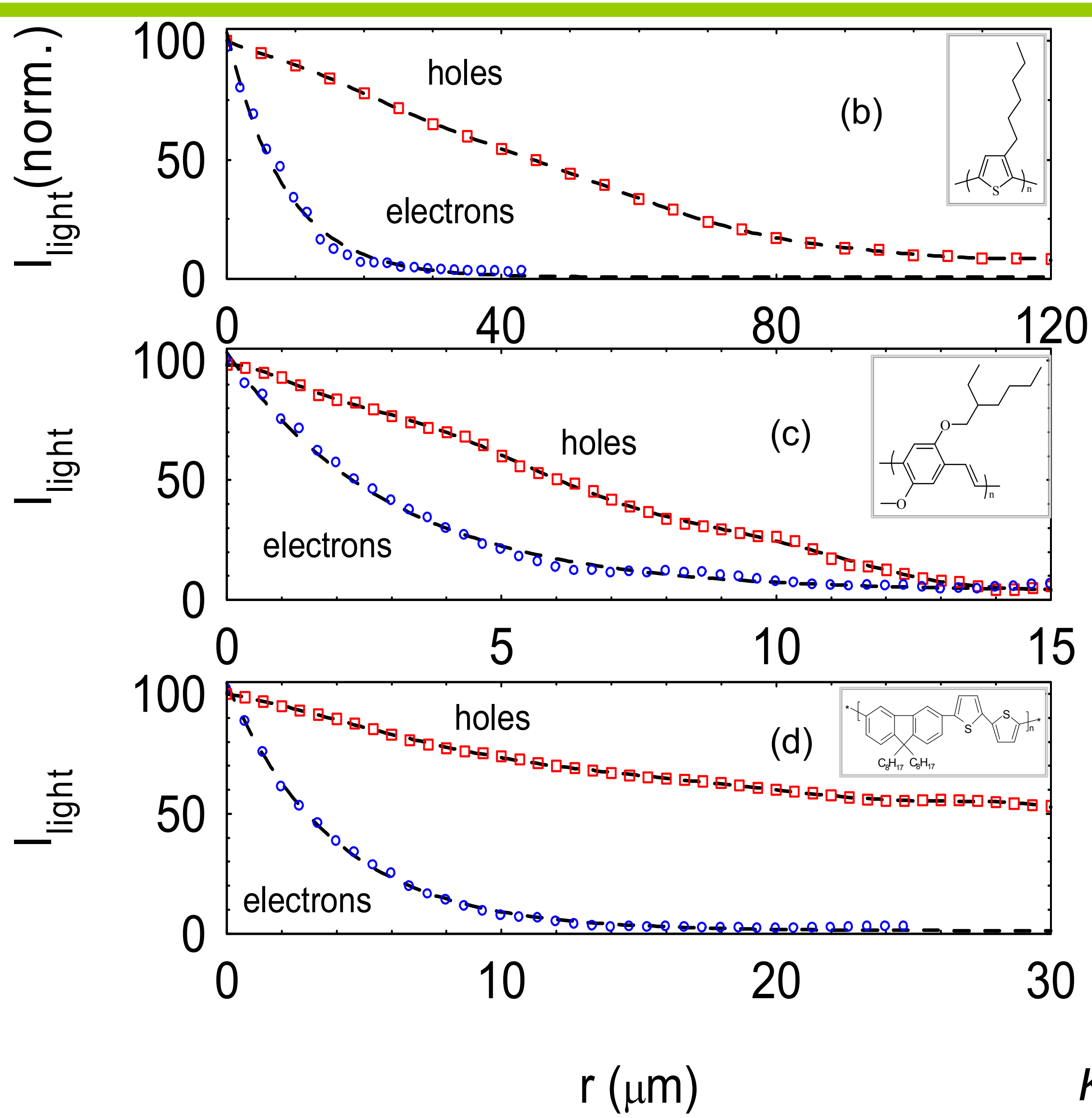
Einstein Relation: $D_n = \mu_n k_B T/e$?

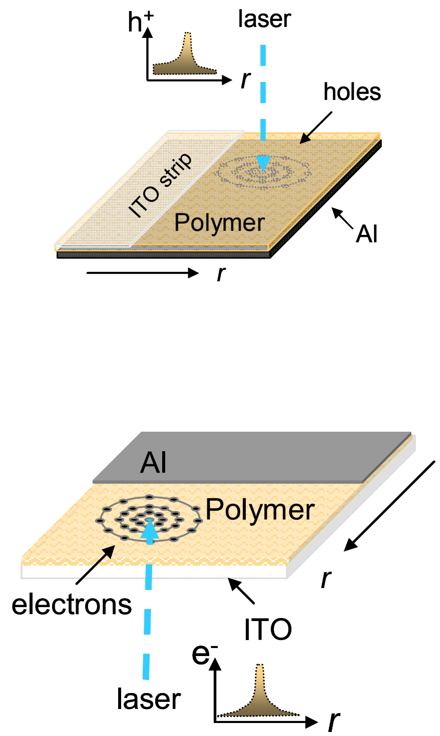
For Polymer Semiconductors
Lateral Diffusion coefficient D_l = ??



movie

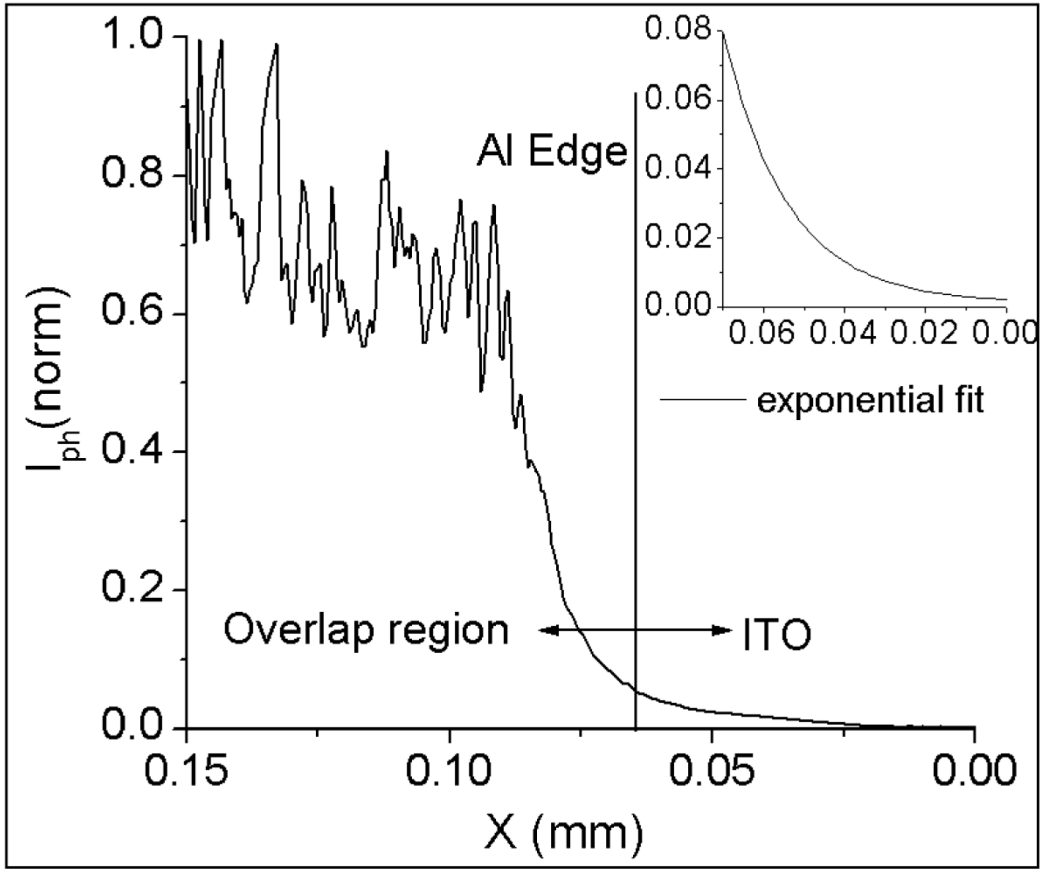
Experiments.........(Spatial Dependence)

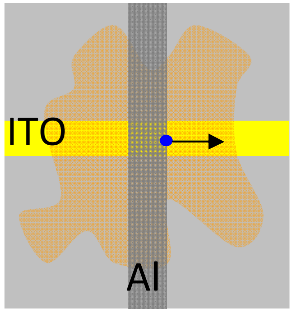




Kabra & Narayan Adv. Mat. 2007

Photocurrent decay profile near the Al edge.

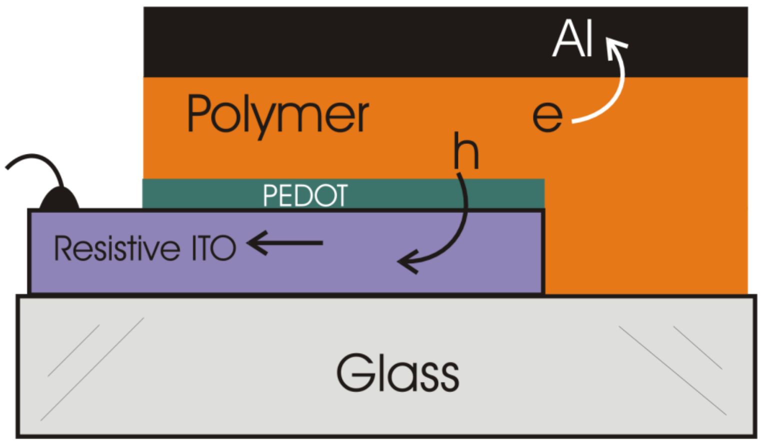




$(L_d)^{electrons} \sim 16\ \mu m$

Narayan, Gupta, Vidhyadhiraja Proc. Of IEEE 2009

Optimum Size of Solar "Cell" ……… ?



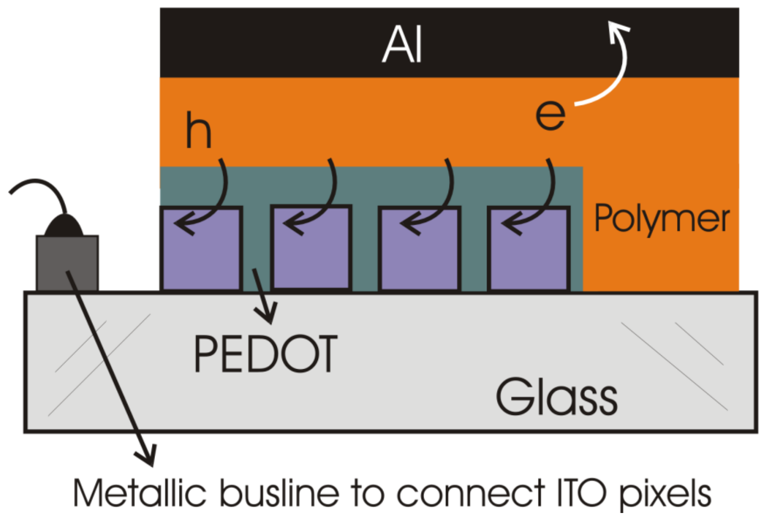
Large area means, ITO layer has to drain larger current so more I^2R drop

$$P_{loss} = J^2 R^{Sheet} a \int_0^L x^2 dx = J^2 R^{Sheet} a \frac{L^3}{3}$$

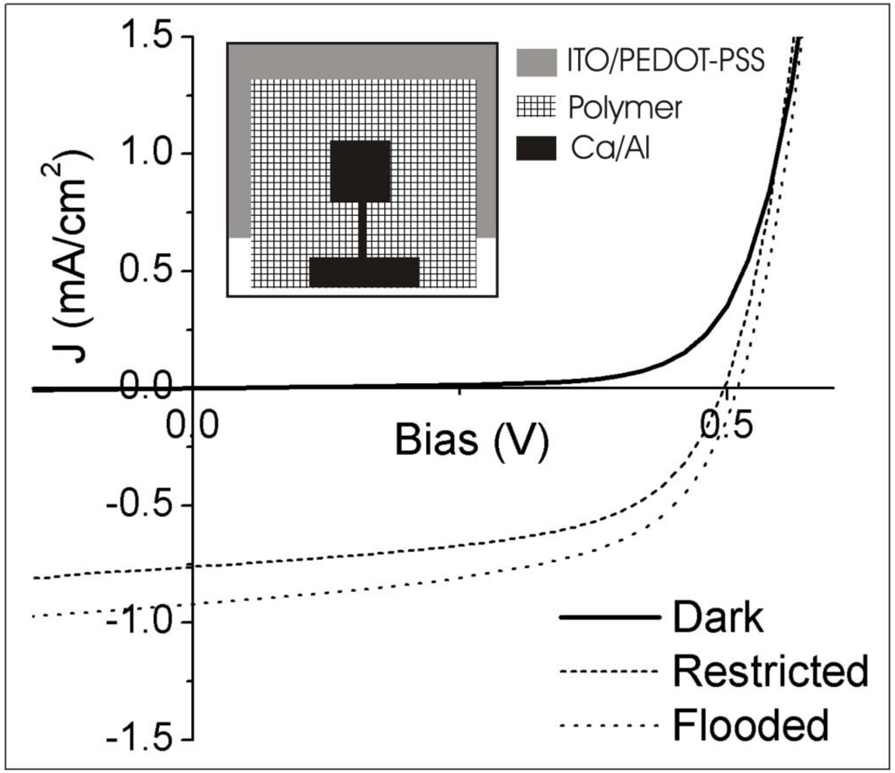
Alternative is Pixilation

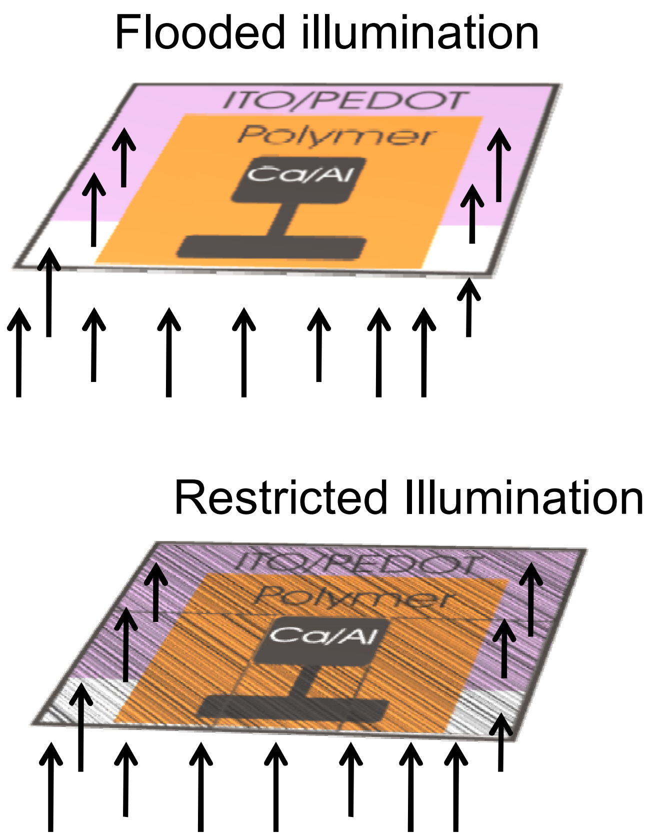
Underlying unpatterned PEDOT works as an anode and efficiency measurement becomes erratic

Patterning PEDOT is difficult



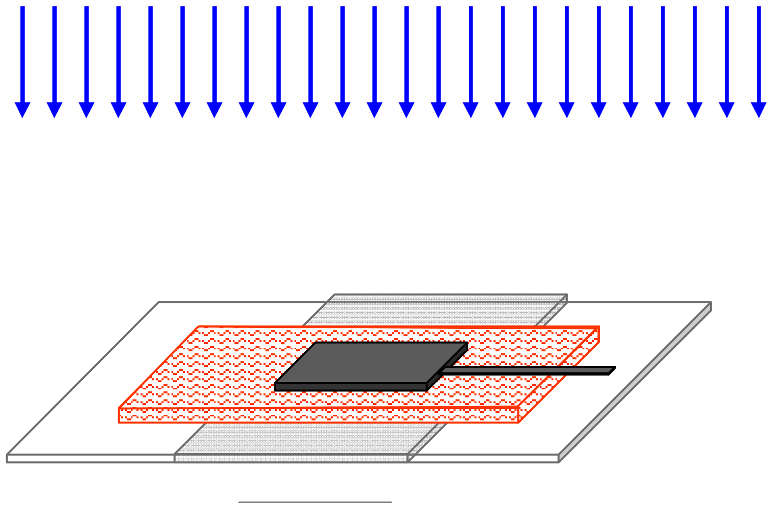
Complete and restricted illumination





J_{SC} increases by 15% for 0.25 cm^2 device

The increase in current from the peripheral regions can not solely be attributed to the optical effects.



movie

Possible sources for the current from the periphery

1. Optical effects
   i) Scattering from rough surface
   ii) Waveguiding of emitted PL from the polymer region

2. Finite extent of electric field outside the overlap region.

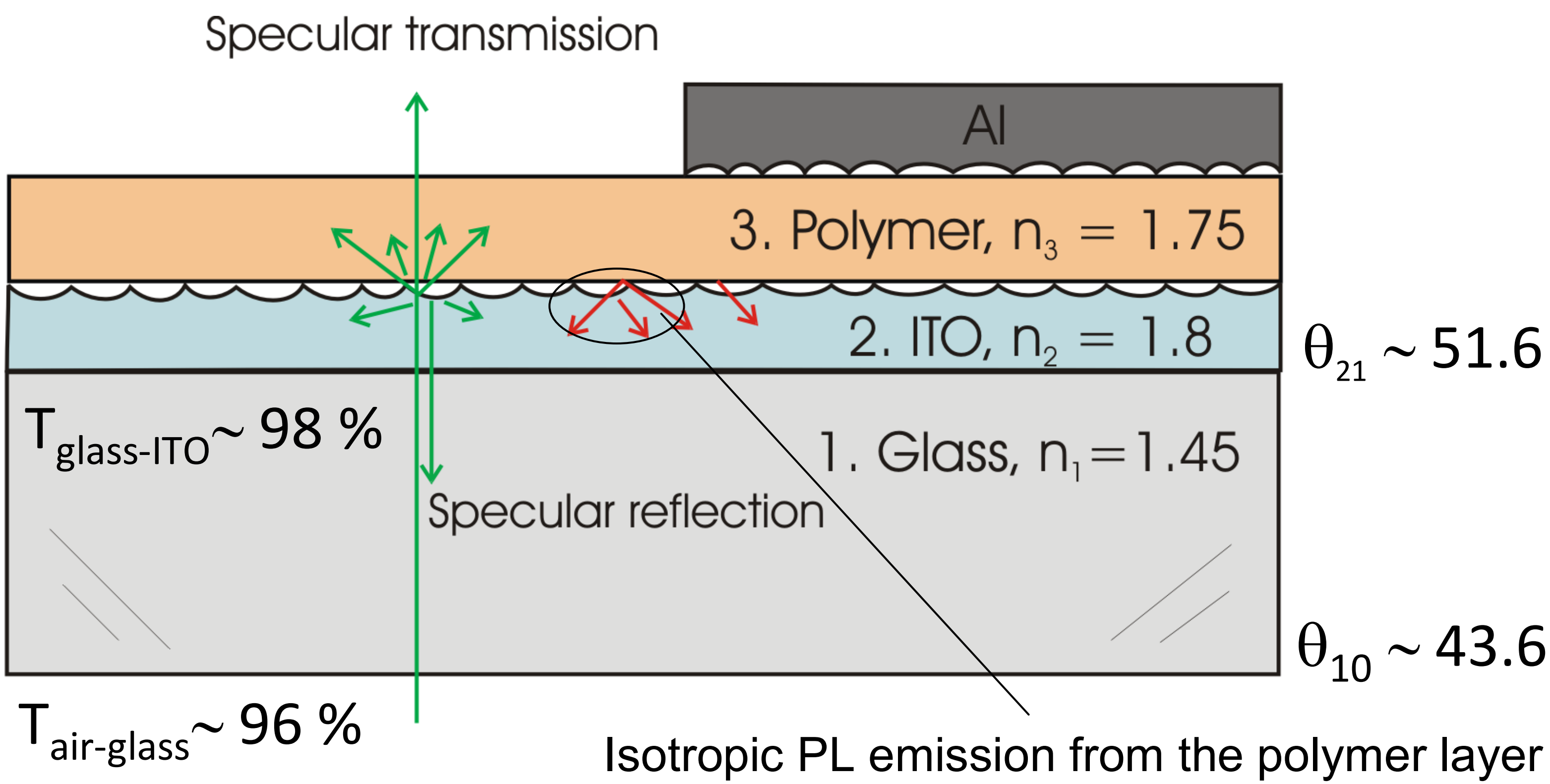
3. Lateral diffusion of charge carriers.

Optical scattering and waveguiding

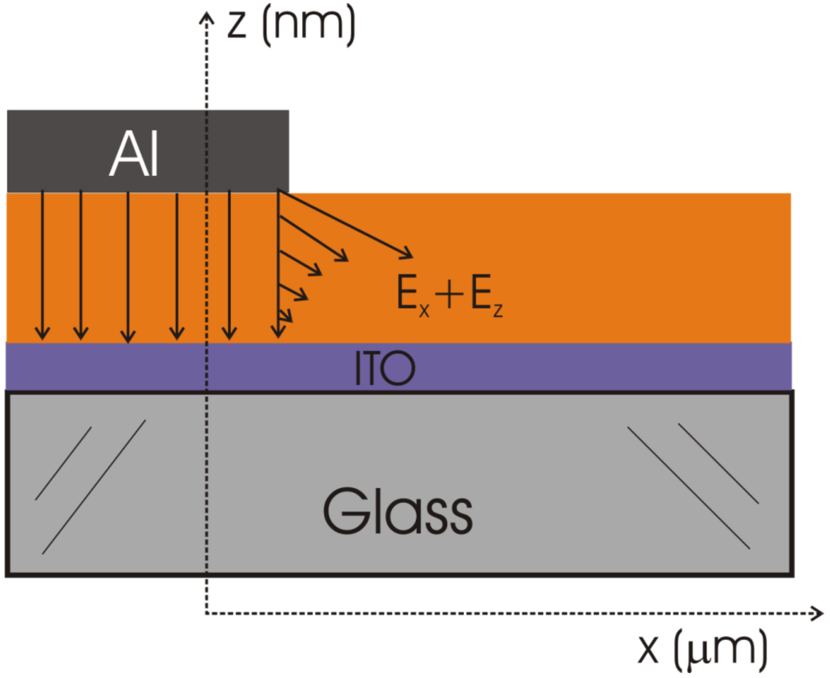
Since $n_2 \approx n_3$ reflectivity is very low, $R_{ITO\text{-}polymer} \sim 10^{-4}$ for near normal incidence.

Haze parameter = diffused/(diffused+specular) $\propto$ (surface RMS roughness σ, λ)

For λ (400 nm) >> σ (1 nm), H_T << 10%

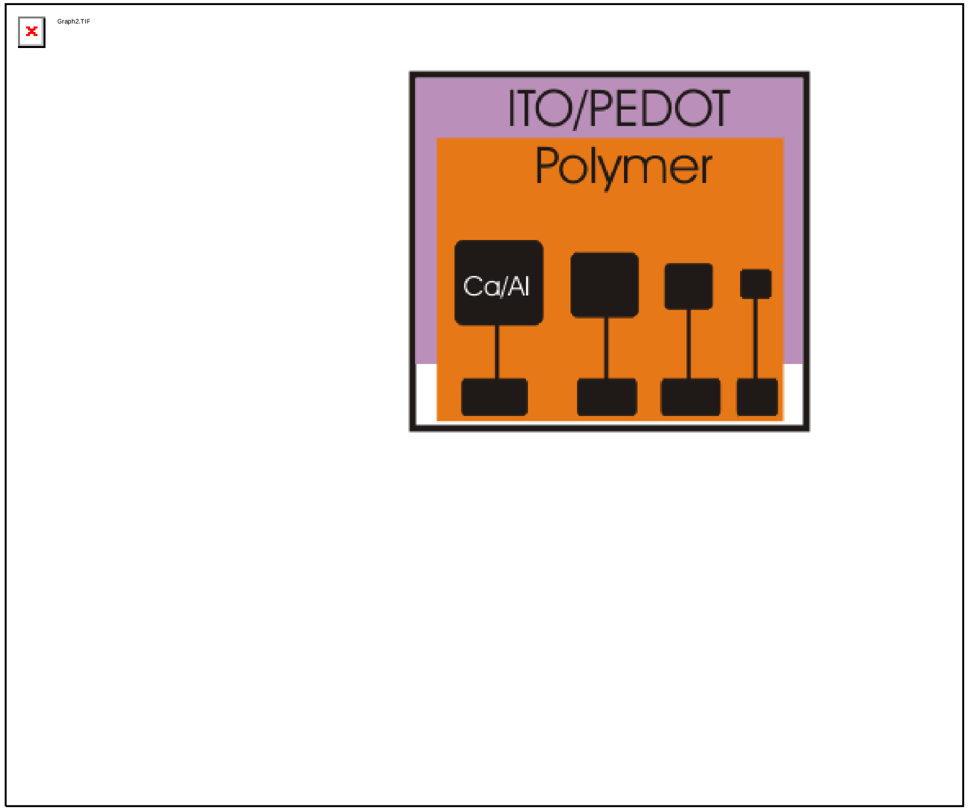


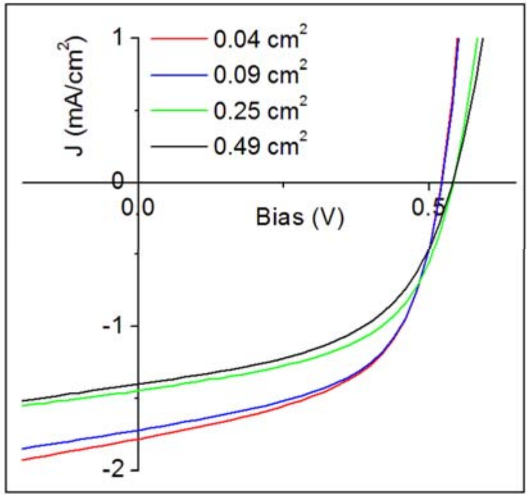
Finite fringing field outside the electrode



The estimated decay lengths for the electric field to decay to strength of $\sim$ 10 - 100 V/cm are quite small (< 50 nm)

Different Active area devices under complete illumination





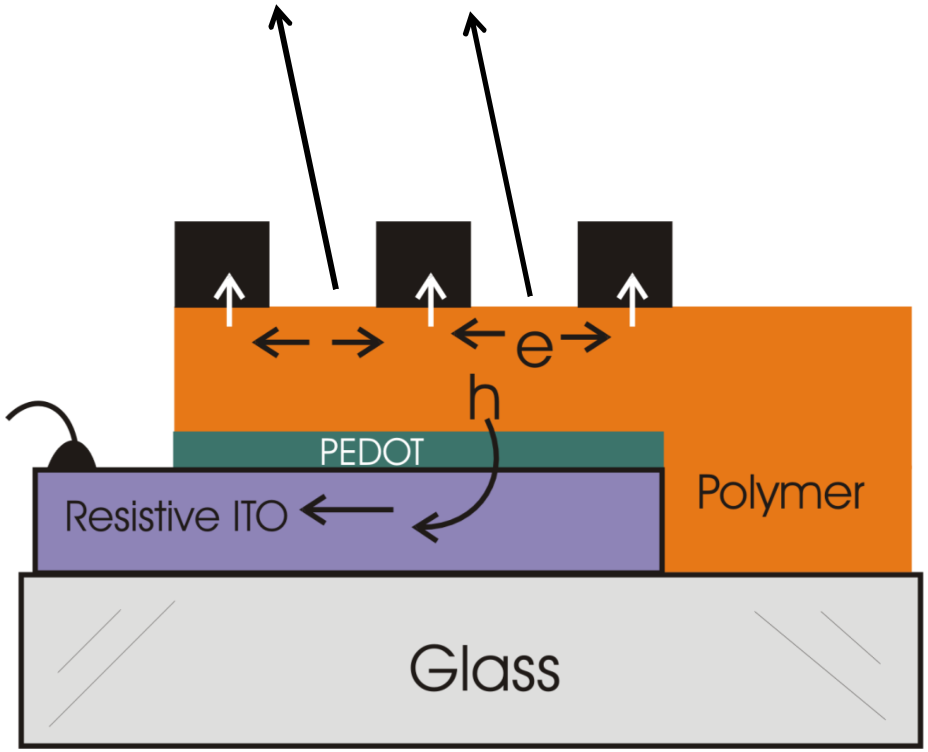
Appl. Phys. Lett. 2008
SPIE News 2009

Current density number shoots up as the cathode-area becomes smaller
Perimeter/Area varies as 1/x : The effect is pronounced for small area devices
Efficiency estimates can increase drastically for small area devices (< 0.01 cm^2)

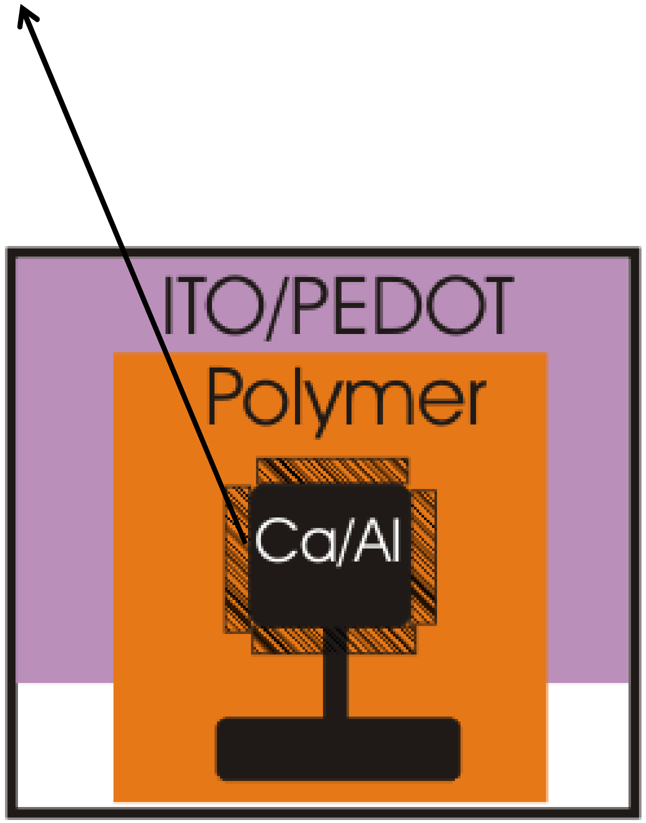
To keep device area small top Al can be pixilated

Since it is just a single masking step

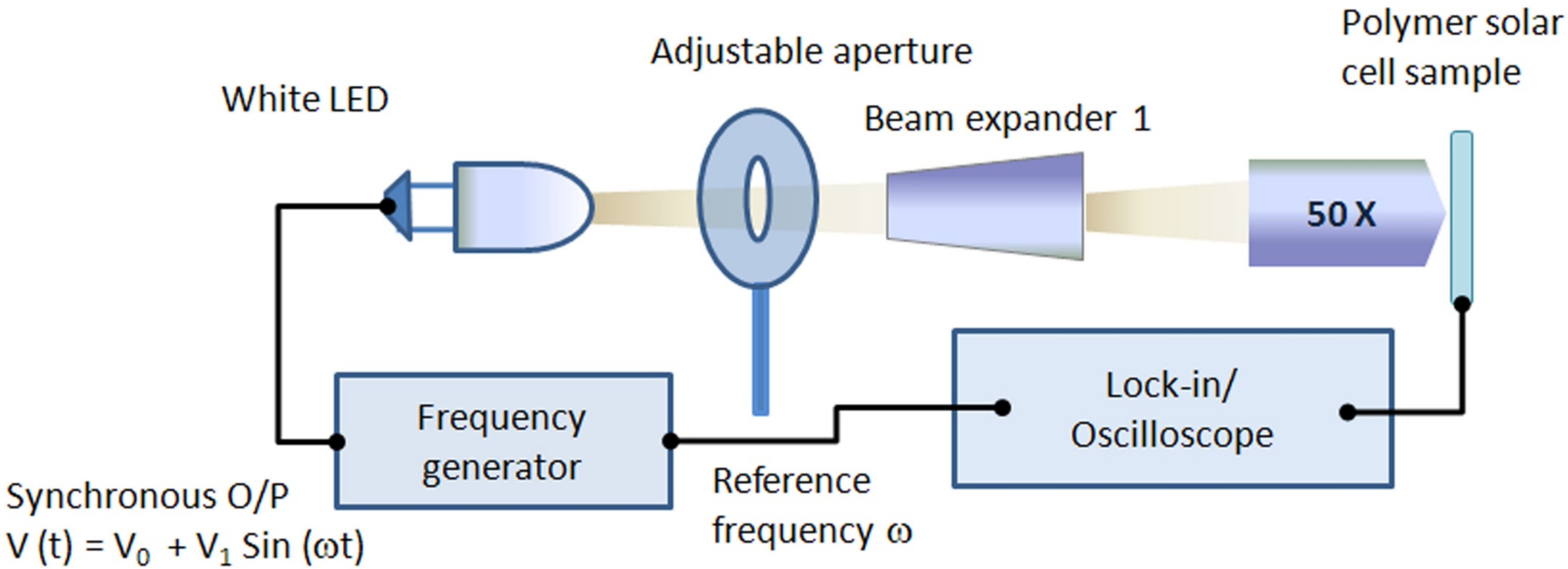
Lateral current contribution from the uncovered regions

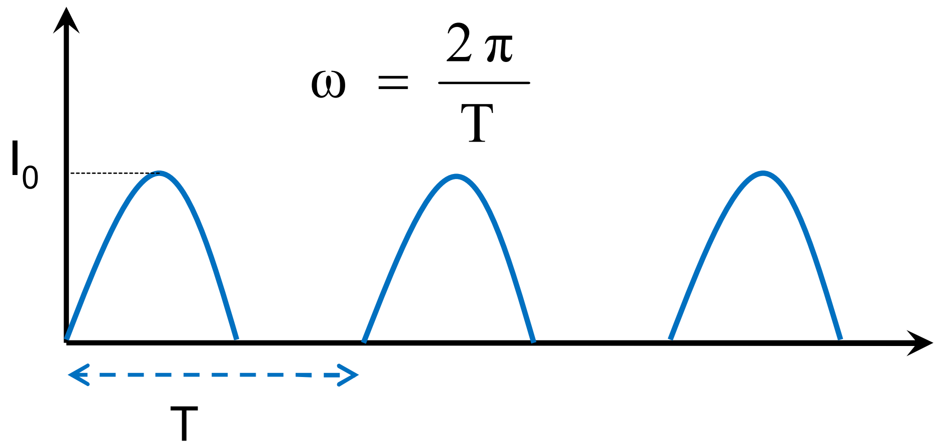


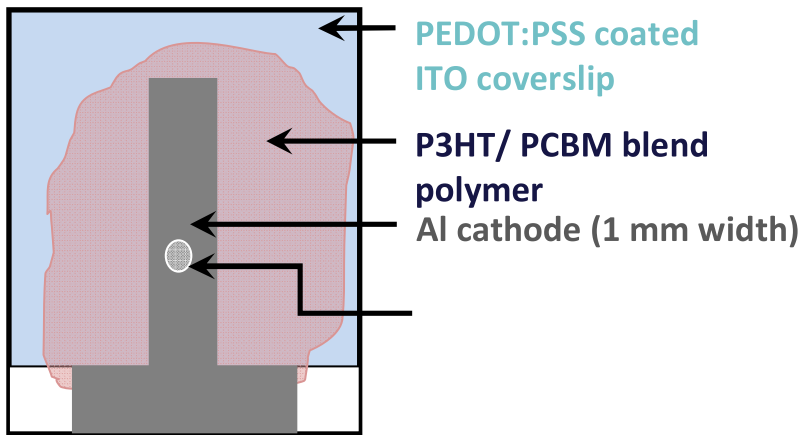
Photoactive region around the periphery



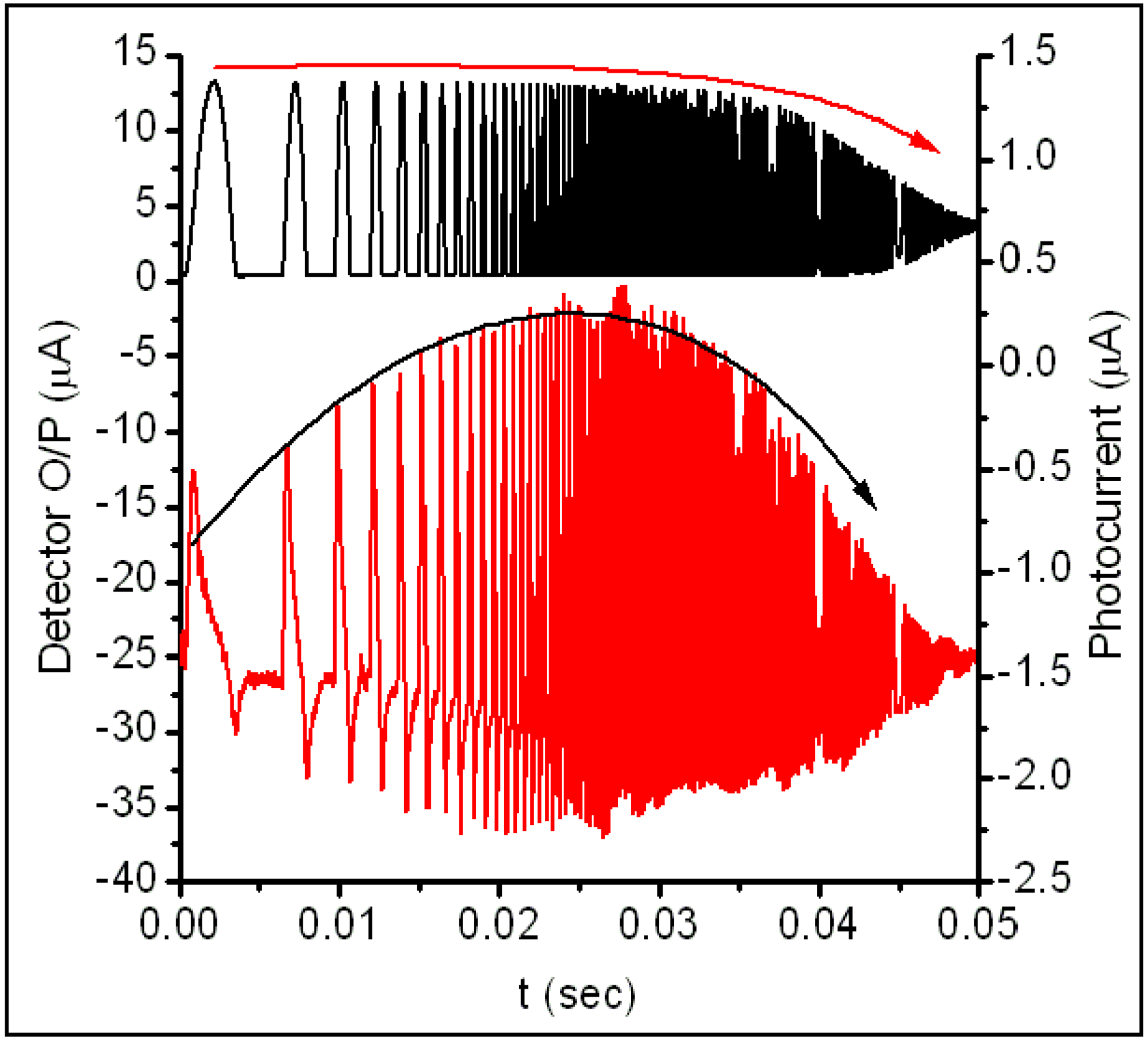
INTENSITY MODULATED PHOTOCURRENT MEASUREMENT







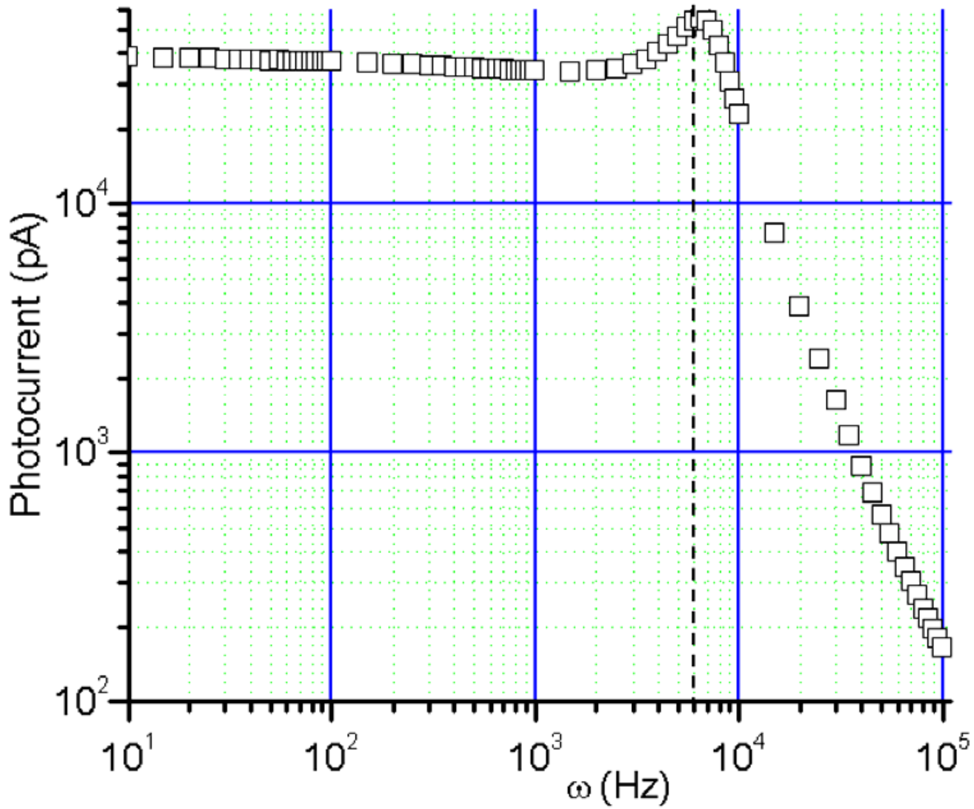
REAL TIME PHOTOCURRENT DATA FOR A FREQUENCY SWEEP FROM 100 HZ TO 100 KHZ



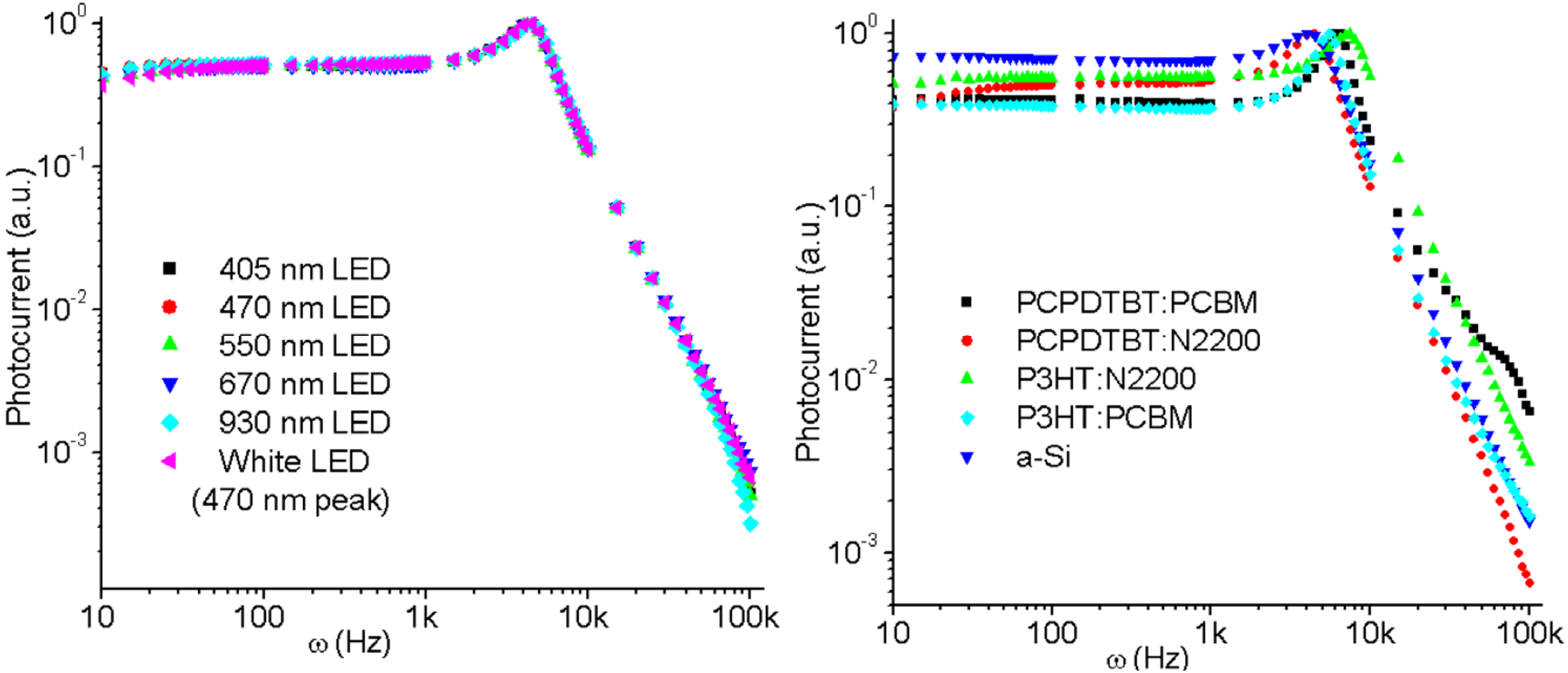
Device photocurrent is not purely sine wave (half wave) as the detector photocurrent is and there is always a phase lag between incident light and generated photocurrent.

PHOTOCURRENT FEATURES IN POLYMER BLEND SOLAR CELLS

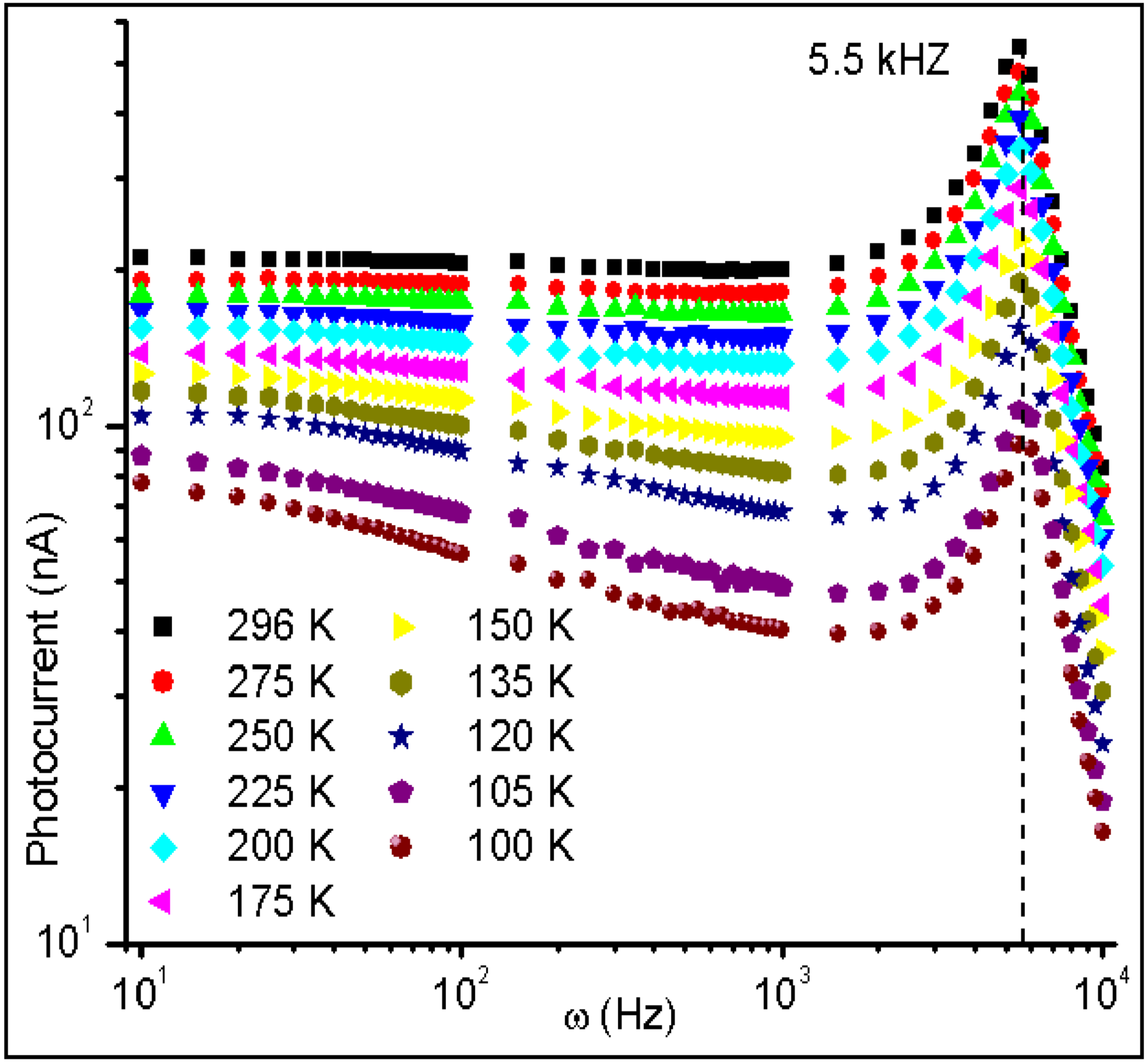
- Low frequency regime (photocurrent independent of frequency)
- Photocurrent peak at ω_{max} between from 5 kHz -9 kHz.
- High frequency regime – photocurrent drops very sharply



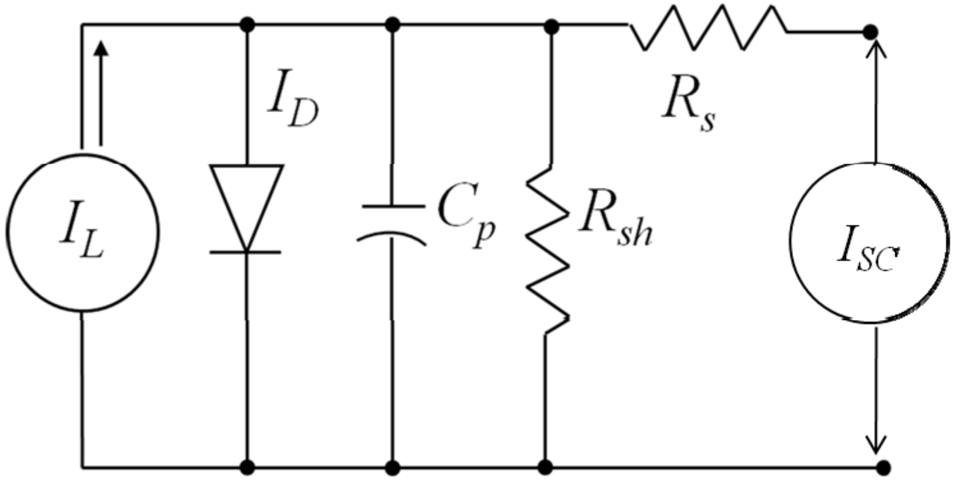
PHOTOCURRENT PEAK: A UNIVERSAL FEATURE IN POLYMER BLEND SOLAR CELL??



The origin of photocurrent peak is microscopic nature of the polymer blend solar cells. However macroscopic parameters modify it depending on the experimental condition.


5.5 kHZ
Photocurrent (nA)
ω (Hz)
10^1
10^2
10^3
10^4
296 K
275 K
250 K
225 K
200 K
175 K
150 K
135 K
120 K
105 K
100 K

Step 1: Macroscopic model



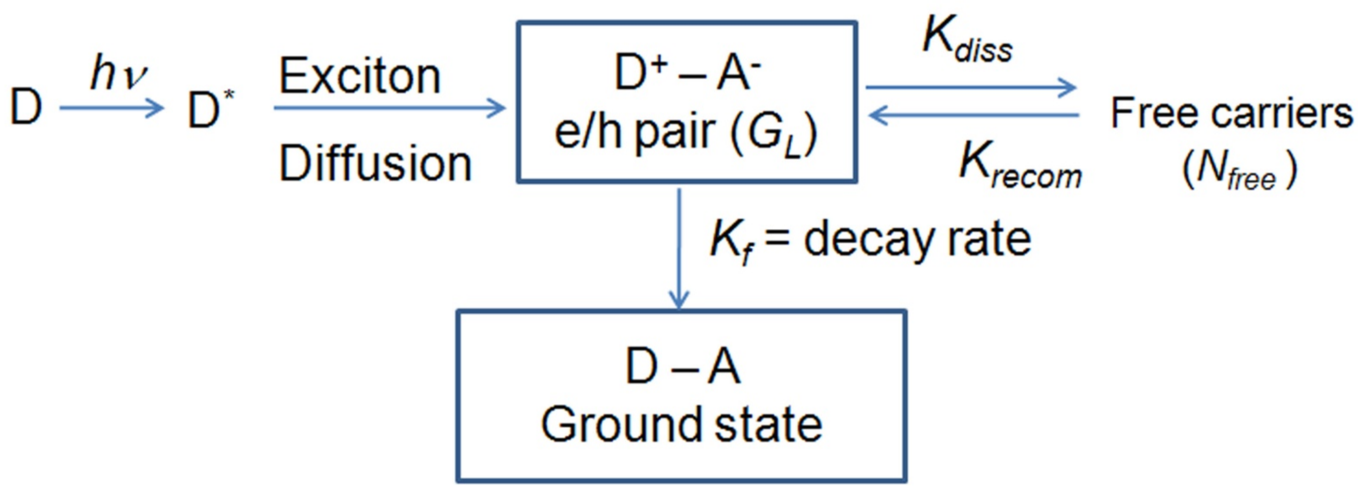
$$I_{SC} = CTF \times I_L$$

$$I_L = TF_{microscopic} G_L$$

$$I_{SC} = TF \times G_L$$

$$TF = CTF \times TF_{microscopic}$$

Step 2: Microscopic model



B. Mazhari, Solar Energy Mater. & Solar Cells, **90** (2006)
L. J. A. Koster *et. al*. Phys. Rev. B, **72** (2005)

MACROSCOPIC MODEL

$$I_{sc}(\omega) = \frac{R_{sh}}{\left[R_{sh} R_s C_p i\omega + (R_{sh} + R_s)\right]} I_L(\omega) \text{.........................(1)}$$

$$CTF = \frac{I_{sc}(\omega)}{I_L(\omega)} = \frac{R_{sh}}{\left[R_{sh} R_s C_p i\omega + (R_{sh} + R_s)\right]} \text{....................(2)}$$

$$CTF = \frac{R_{sh}}{R_{sh} + R_s} \times \frac{(ai\omega + 1)}{(bi\omega + 1)} \text{...................................(3)}$$

$$C_p(\omega) = \frac{C}{(ai\omega + 1)}$$

$$b = a + \frac{R_{sh} R_s C}{R_{sh} + R_s}$$

MICROSCOPIC PROCESSES

$$\frac{dg_L(t)}{dt} = -\frac{g_L(t)}{\tau_1} + K_{recom} n_{free}(t) \qquad \text{..................................}(4)$$

$$\frac{dn_{free}(t)}{dt} = -\frac{n_{free}}{\tau_2} + K_{diss} g_L(t) - Q_{trp} \qquad \text{..................................}(5)$$

$$\frac{dn_{free}(t)}{dt} = -\frac{n_{free}}{\tau_2} + K_{diss} g_L(t) - \int \kappa_{eff} n_{free}(t) dt \qquad \text{............}(6)$$

Where $\quad Q_{trp}\Big|_{t=t_0} = \int_{t_0-\Delta t}^{t_0+\Delta t} \kappa_{eff} n_{free}(t) dt$

MODEL CONTINUED………

Solving coupled equation 4 and 6

$$K_1 \frac{d^2 n_{free}(t)}{dt^2} + K_2 \frac{dn_{free}(t)}{dt} + n_{free}(t) = -Qg_L(t) \ldots\ldots\ldots\ldots\ldots(7)$$

$$K_1 = \frac{1}{\left(\kappa_{eff} - K_{recom} K_{diss}\right)} \qquad K_2 = \frac{1}{\tau_2\left(\kappa_{eff} - K_{recom} K_{diss}\right)}$$

$$Q = \frac{K_{diss}}{\tau_1\left(\kappa_{eff} - K_{recom} K_{diss}\right)}$$

$$g(t) = g_0 + g_1 \exp(-i\omega t) \qquad n(t) = n_0 + n_1 \exp(-i\omega t)$$

CONTINUED………

$$N_{free}(\omega) = \frac{-Q}{\left[-K_1\omega^2 + K_2 i\omega + 1\right]} G_L(\omega)$$

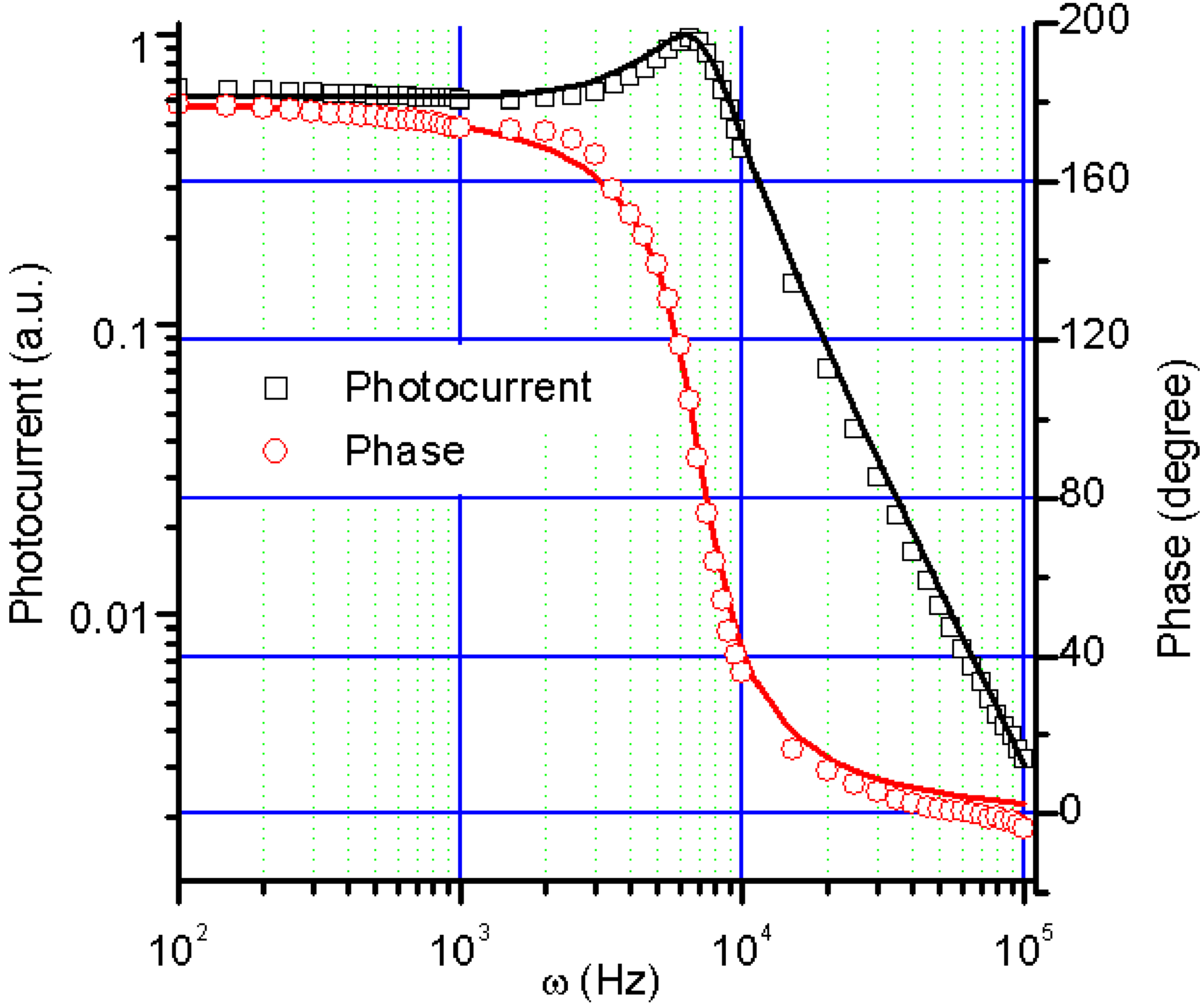
$$I_L(\omega) \propto N_{free}(\omega)$$

$$I_{sc}(\omega) = CTF \times I_L(\omega) = CTF \times TF_{microscopic} G_L(\omega)$$

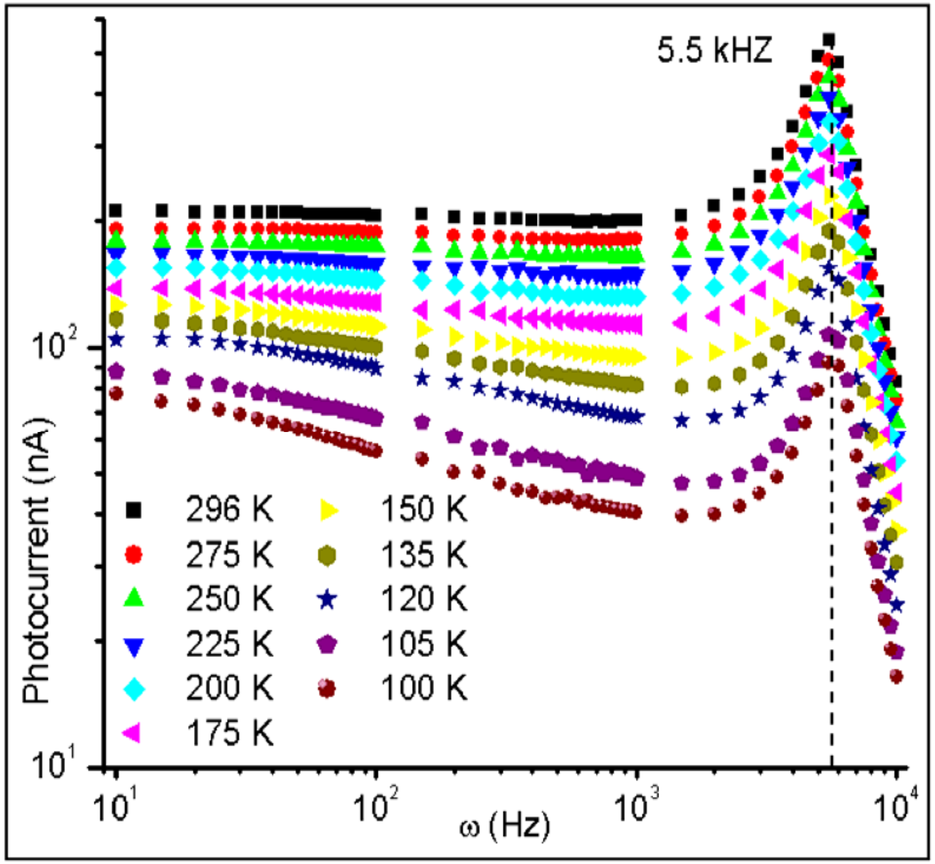
$$TF = K \frac{(as+1)}{(bs+1)\left(K_1 s^2 + K_2 s + 1\right)}$$

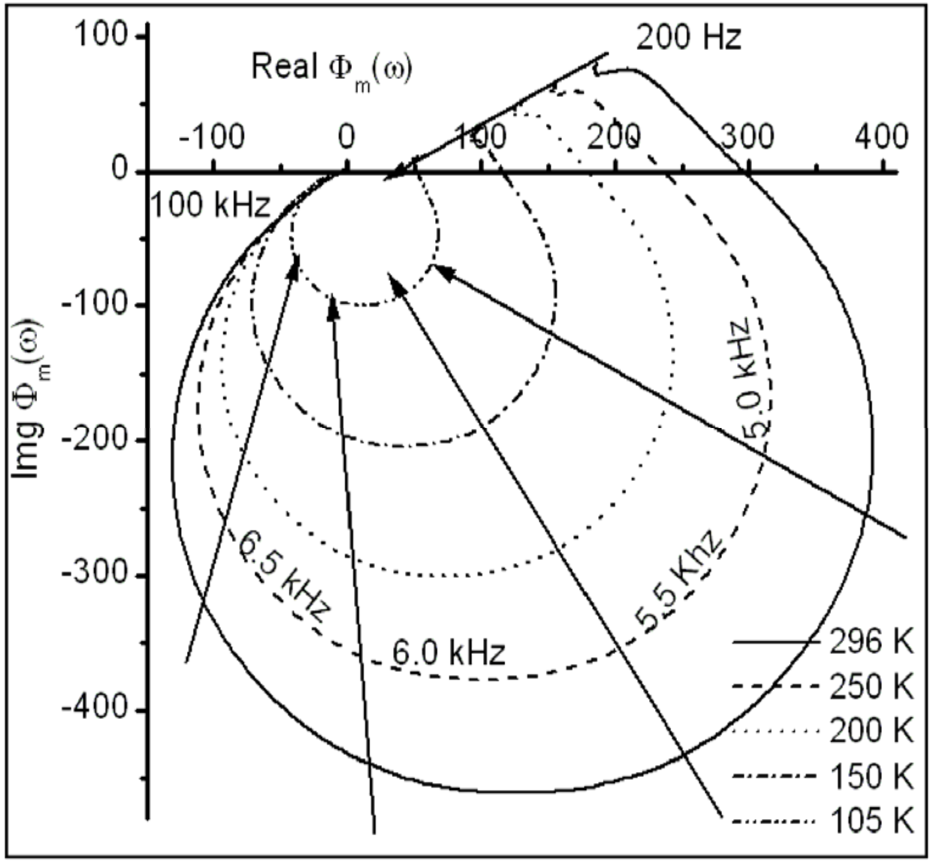
Where ‘*s*’ is a complex frequency ‘$i\omega$’

EXPERIMENTAL AND MODEL $I_{PH}(\omega)$ AND $\phi(\omega)$

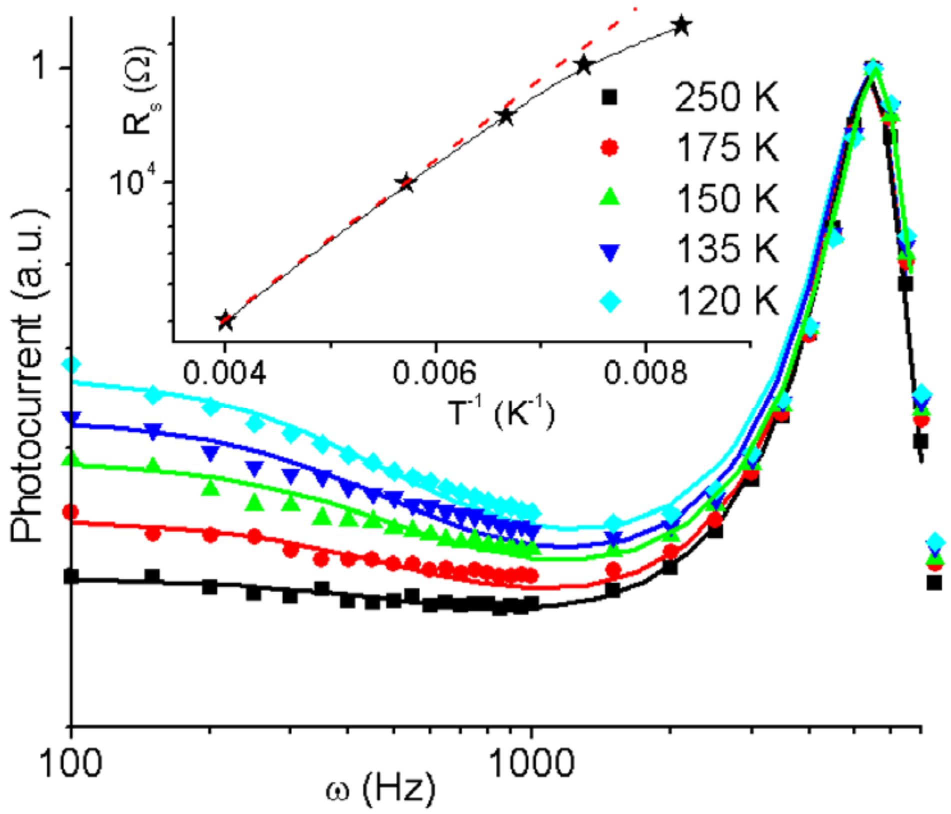


TEMPERATURE DEPENDENT STUDY FOR P3HT:PCBM SOLAR CELLS





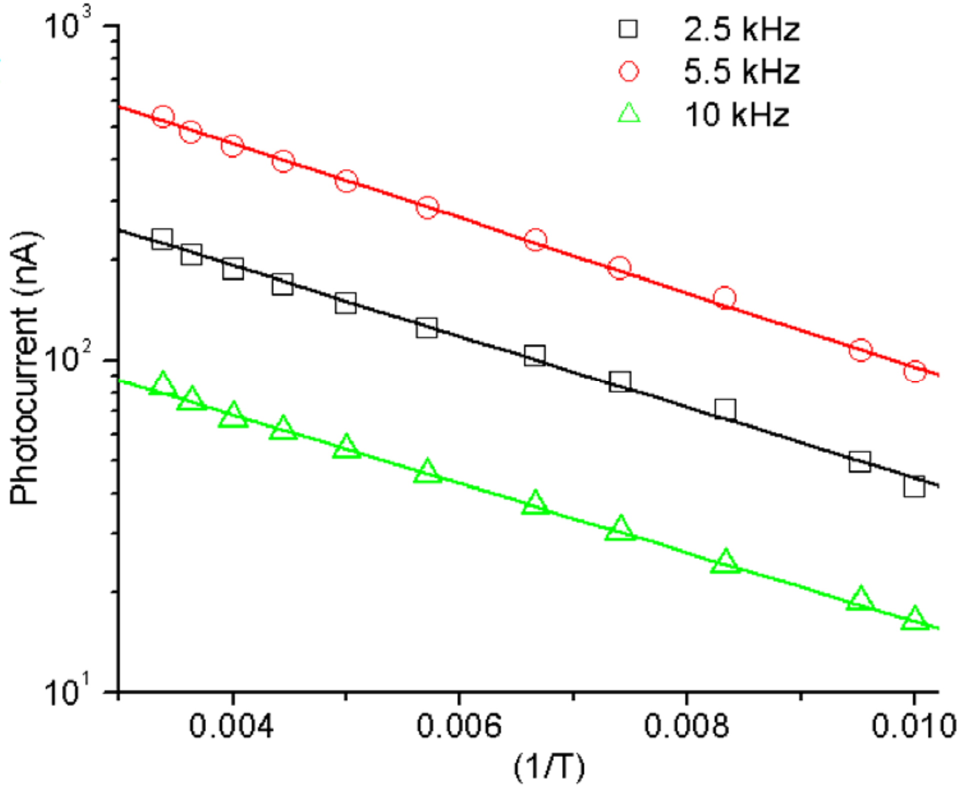
TEMPERATURE DEPENDENT MODULATE PHOTOCURRENT MODEL



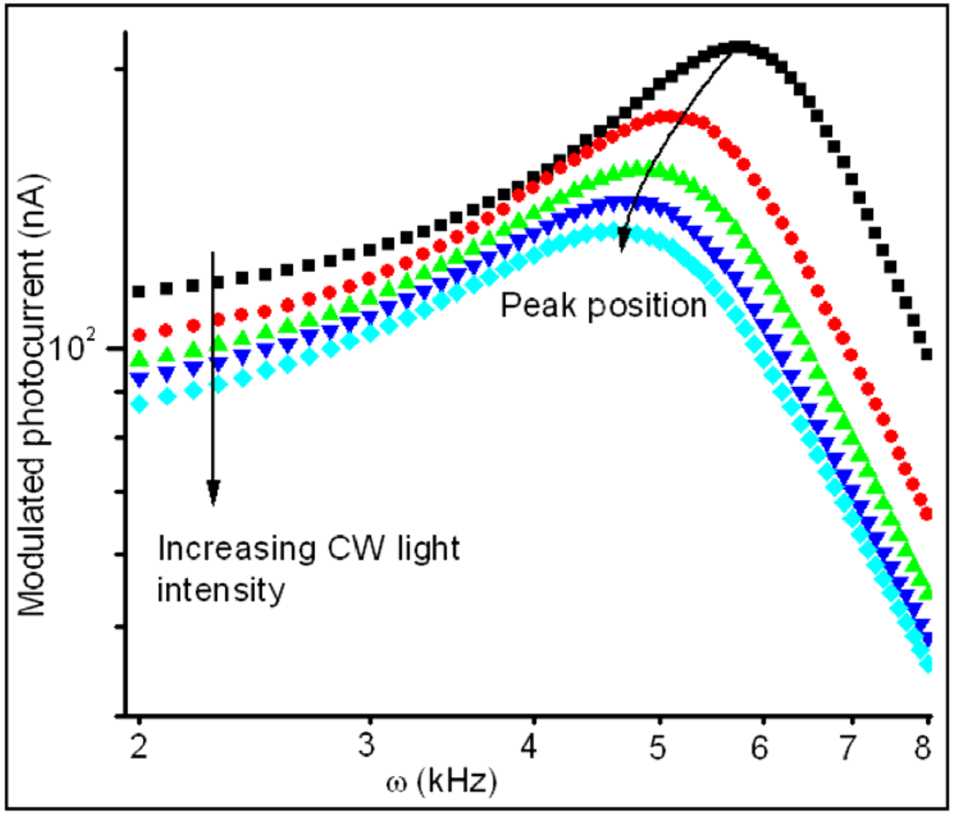
In our model we vary R_s as charge extraction is an activated process follows exponential dependence

$$R_s = R_0 \exp\left(E_a / k_B T\right)$$

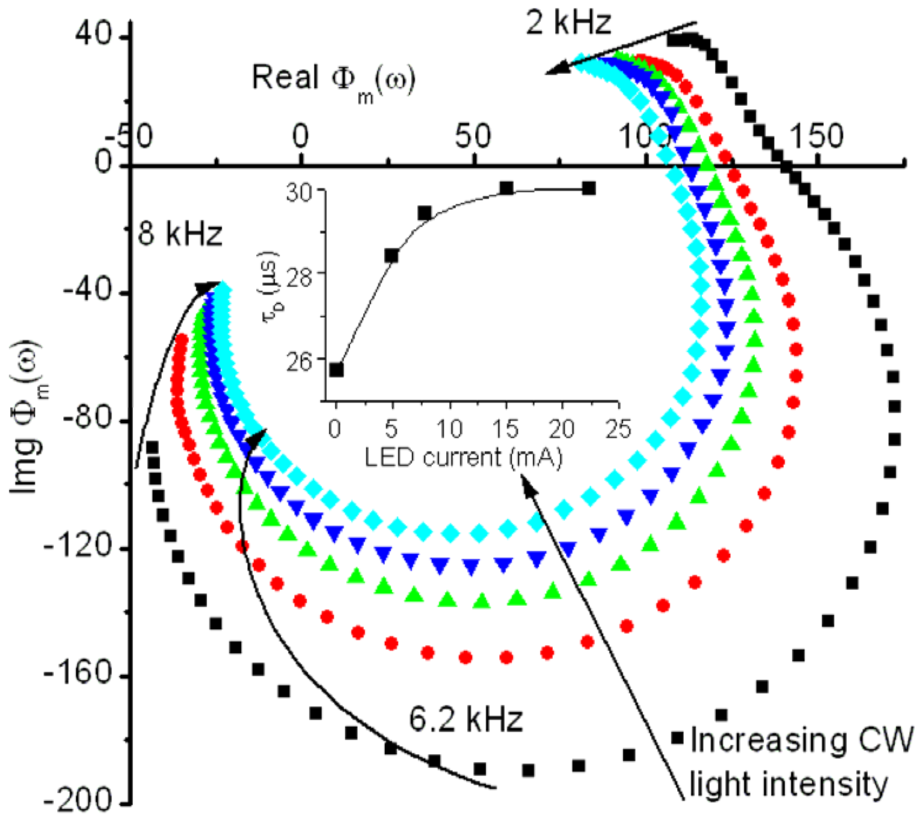
From log (I_{sc}) Vs T^{-1} activation energy E_a = 21 meV which is of same order as simulated value 30 meV at room temperature



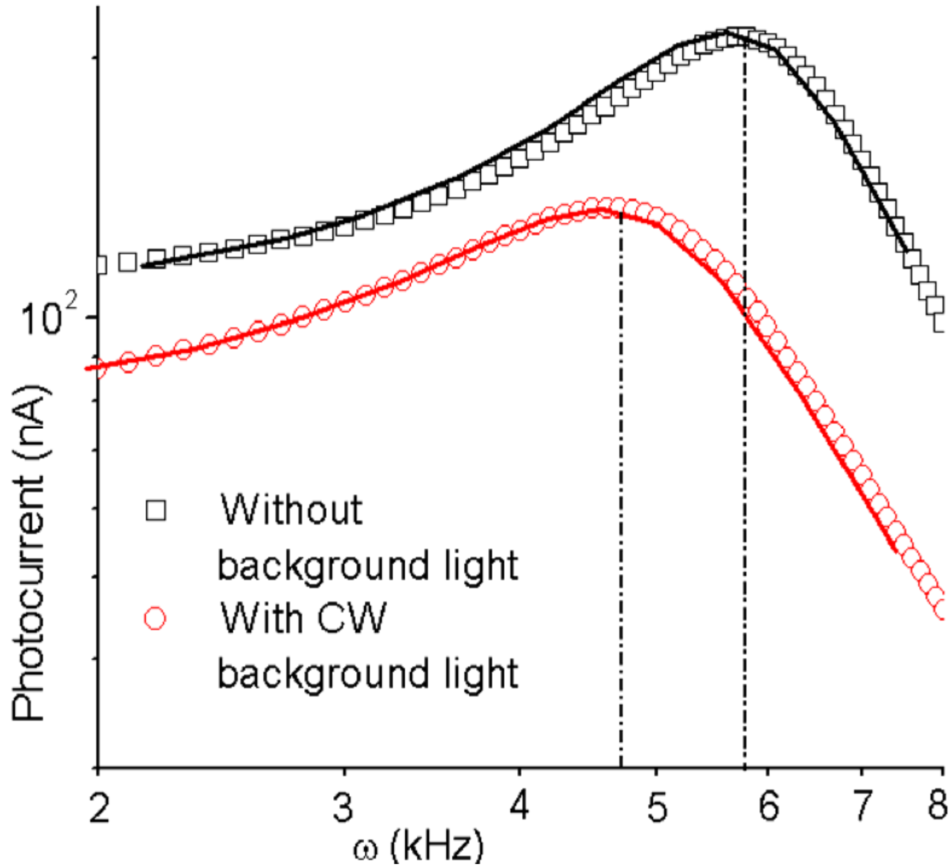
INTENSITY MODULATED PHOTOCURRENT WITH CW WHITE BACKGROUND LIGHT



With background CW light charge carrier concentration increases and hence recombination rate increases which leads to decrease in modulated photocurrent



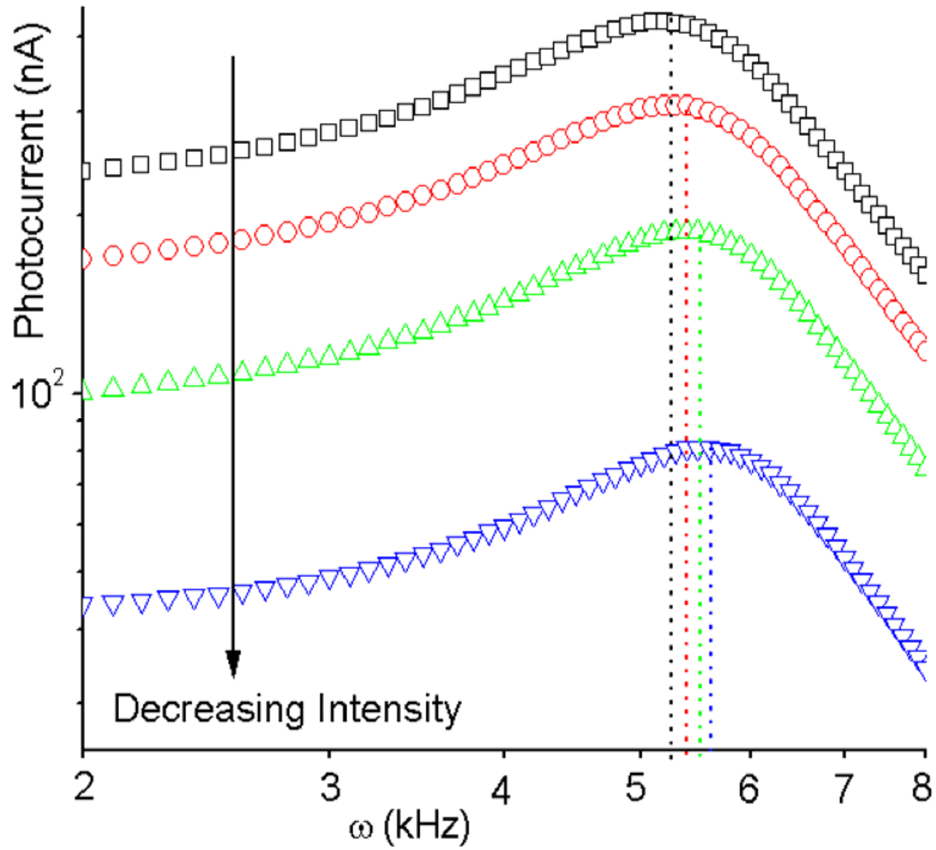
INCREASE IN INTENSITY OF MODULATED LIGHT SOURCE



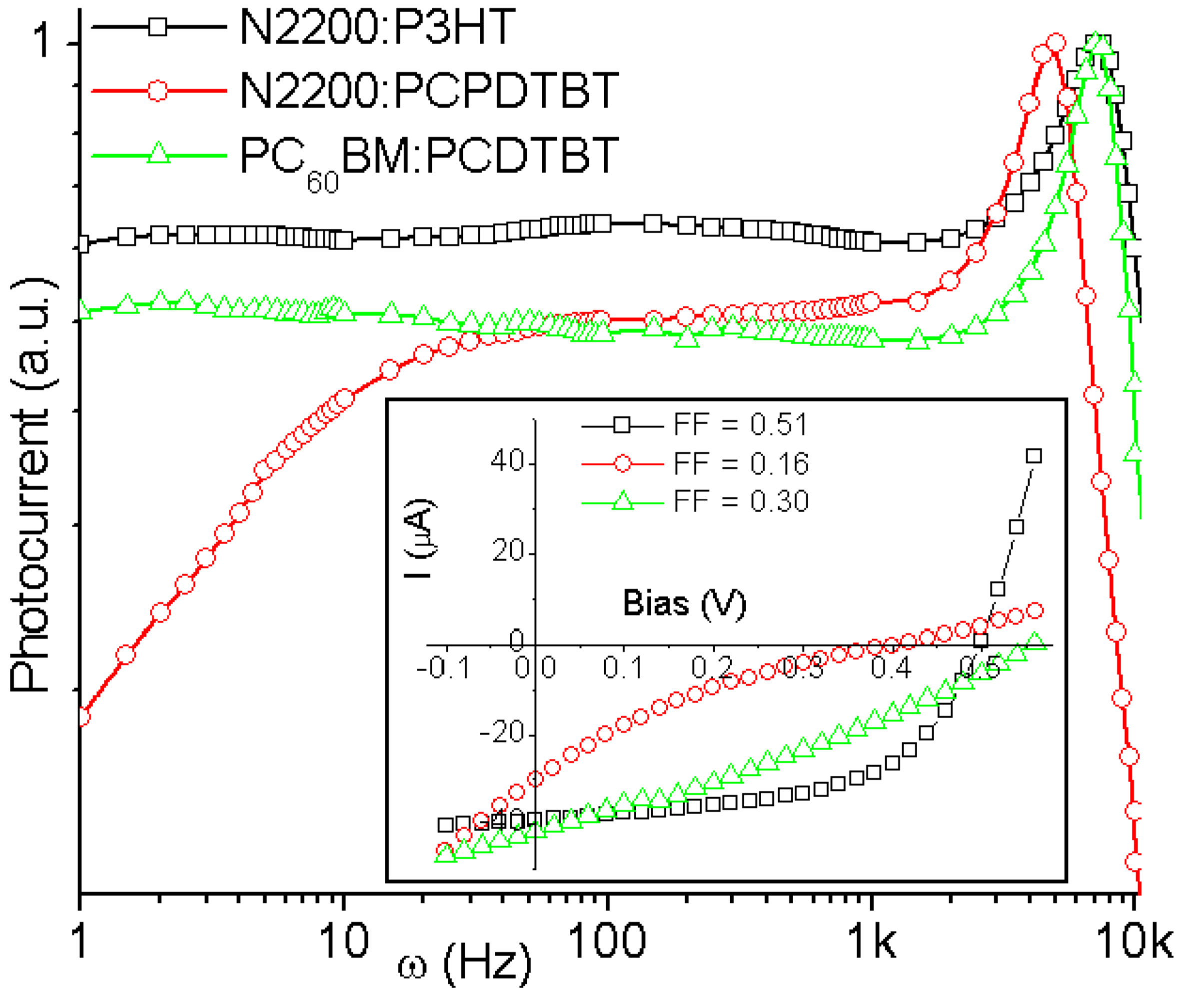
Symbols are for experimental

Lines are fit to the model

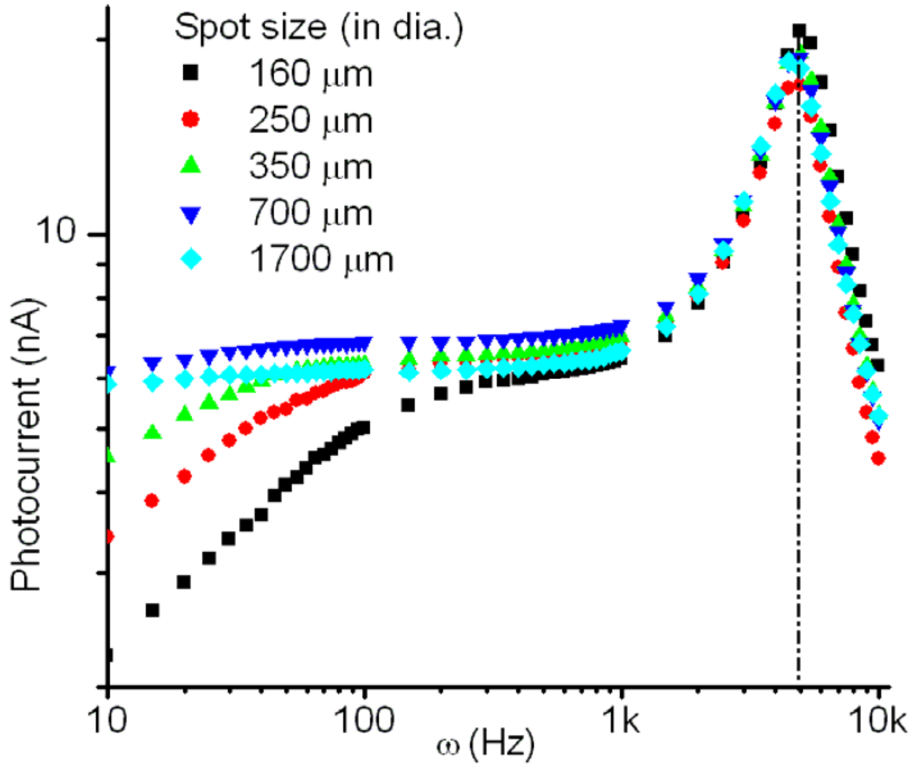
However increase in modulated intensity does not show significant peak shift except increase in modulated photocurrent



EFFECT OF MORPHOLOGY-FF DEPENDENCE

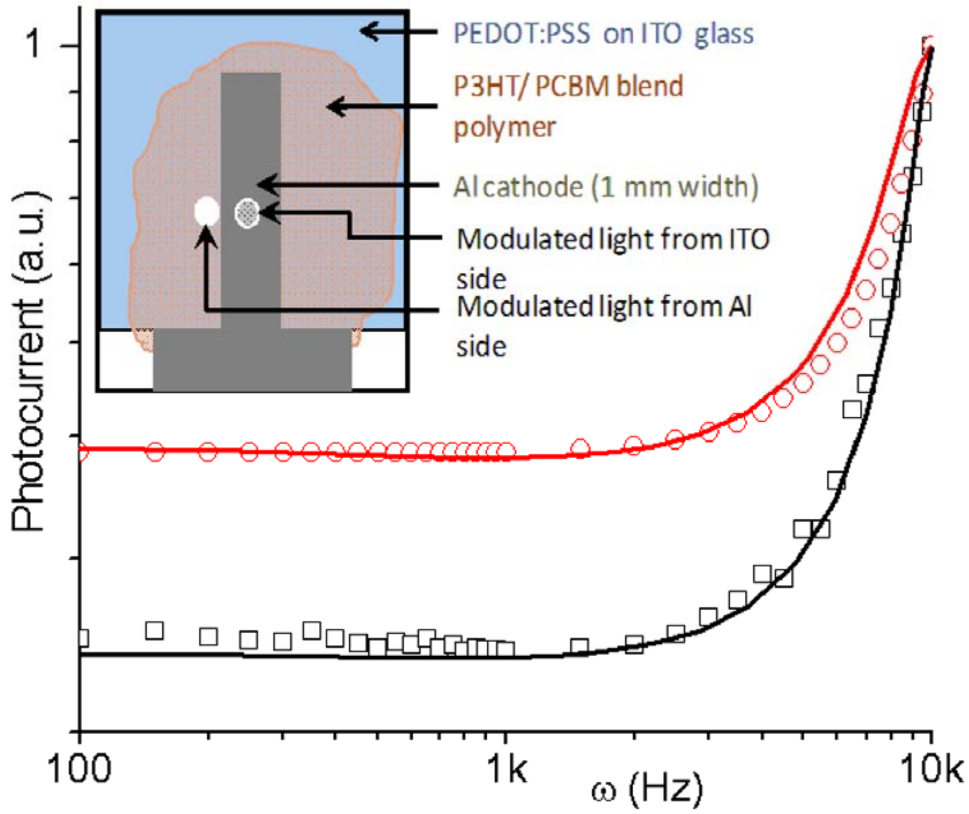


Recombination losses at low frequency is more dominating when morphology/ interface is not perfect; leading to reduced fill factor



Photocurrent peak has been observed in relatively less efficient solar cells. However these devices show intensity dependent at low frequency regime.

Photocurrent from the peripheral region also shows photocurrent peak at same position when illumination is on overlap region, but absolute photocurrent drops at low frequency regime.



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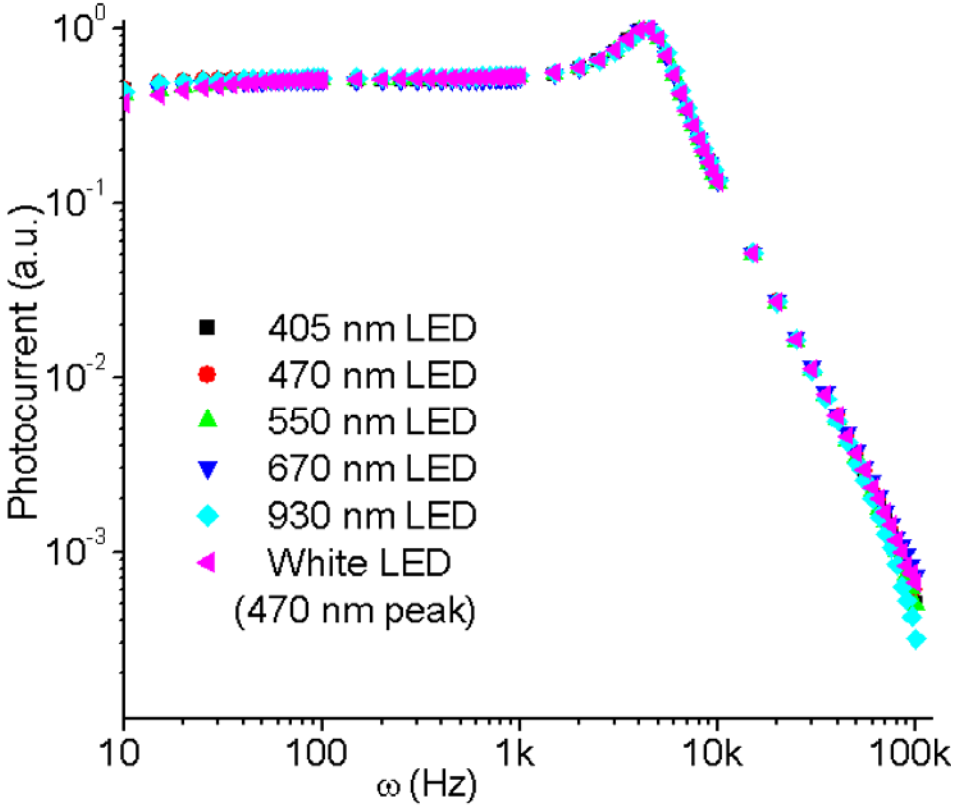

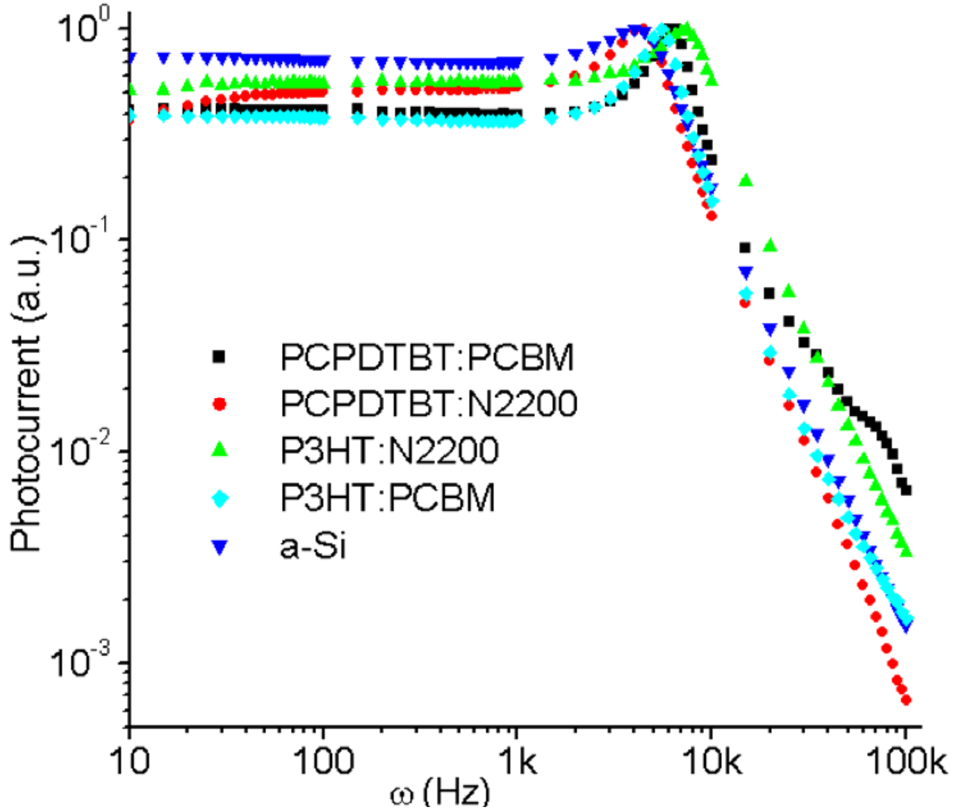

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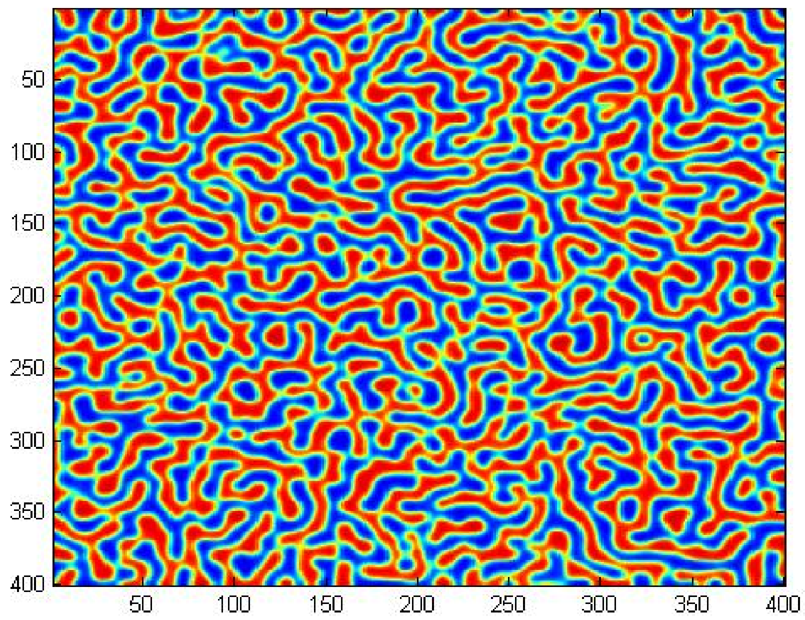
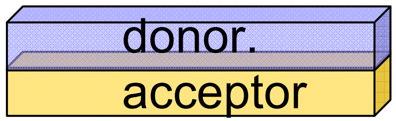


- Universal response in BHJ-PSCs

- Low frequency response is related to the morphology and fill factor

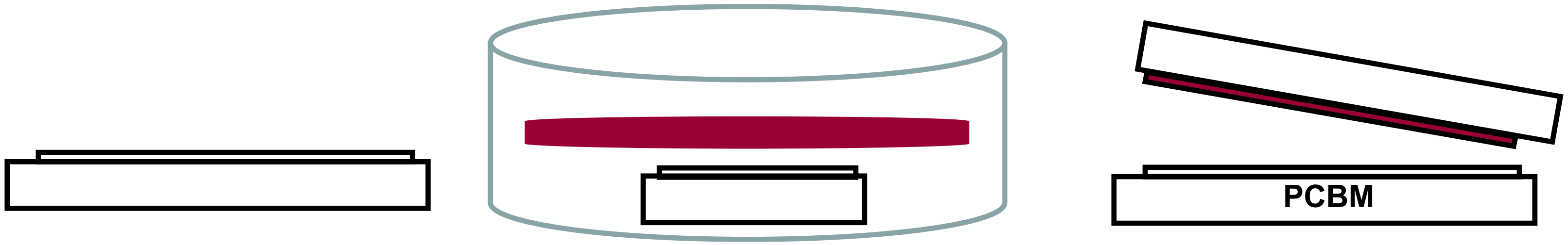


To probe D-A interface, in a non-invasive manner

Effect of Electrostatic field on the interfacial processes

FETs of stable Acceptor systems can be fabricated

Transfer Printing Method



PDMS coated
glass substrate

P3HT dropped
on water solution.

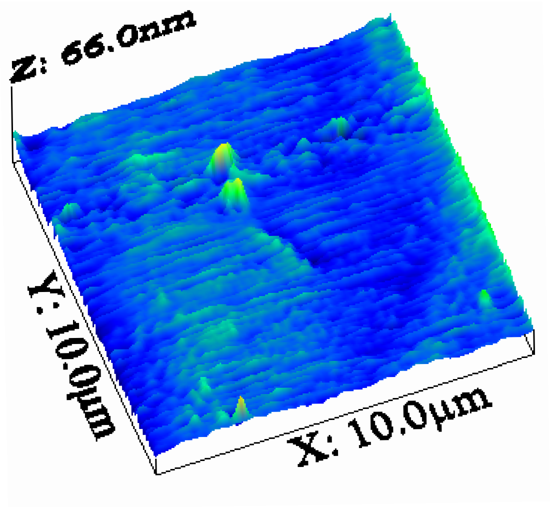
Dry film transfer
On PCBM surface.

Depositing P3HT film on spin coated PCBM film is not solution processible.

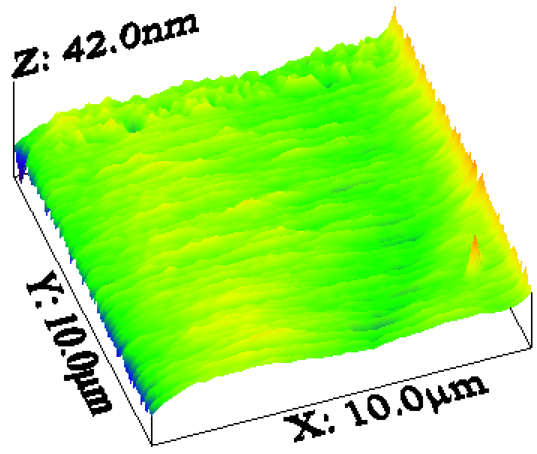
P3HT films were suspended on water and transferred onto PDMS substrate and then laminated onto PCBM film.

P3HT on PCBM laminates giving rise to good structural film.

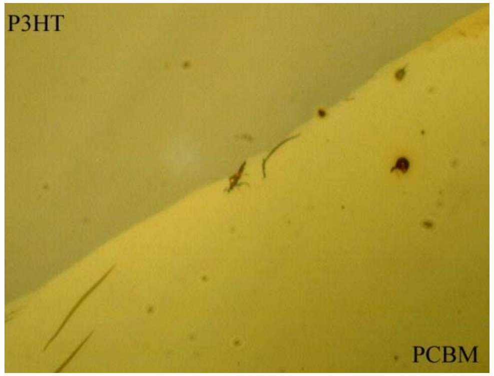
Bilayer configuration has well defined D-A interface as opposed to D-A interface formed in blend morphology.

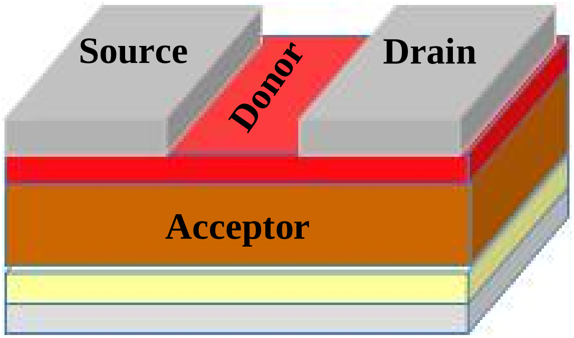


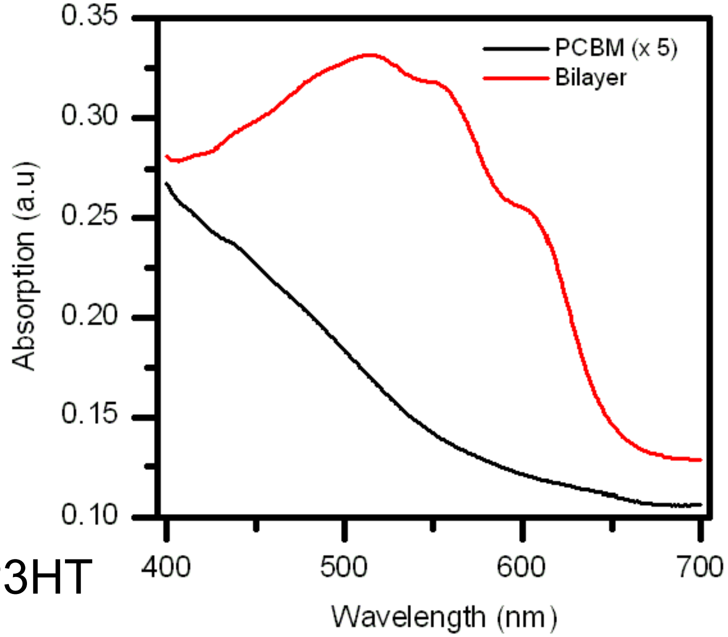
PCBM rms roughness: 1.9 nm



P3HT rms roughness 2.9 nm

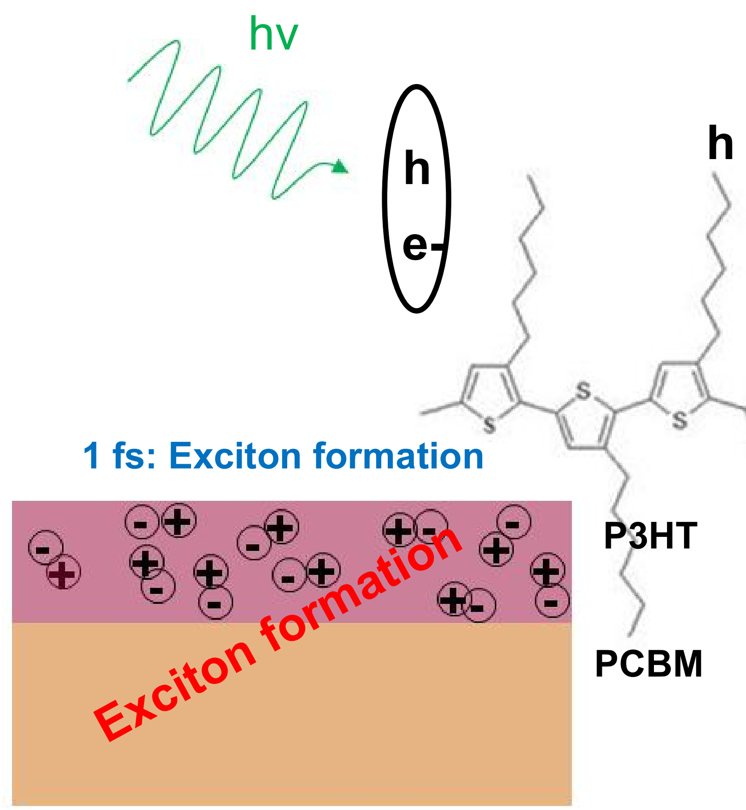






PCBM absorption is not optically active, whereas P3HT is optically active.

Based on energy symmetry level HOMO-LUMO optical transition are not allowed allowing weak absorption above 500 nm for PCBM.

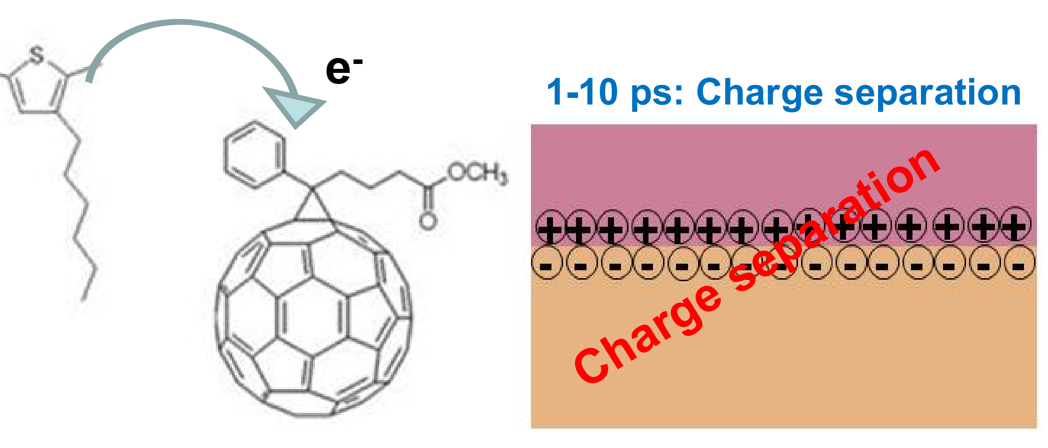


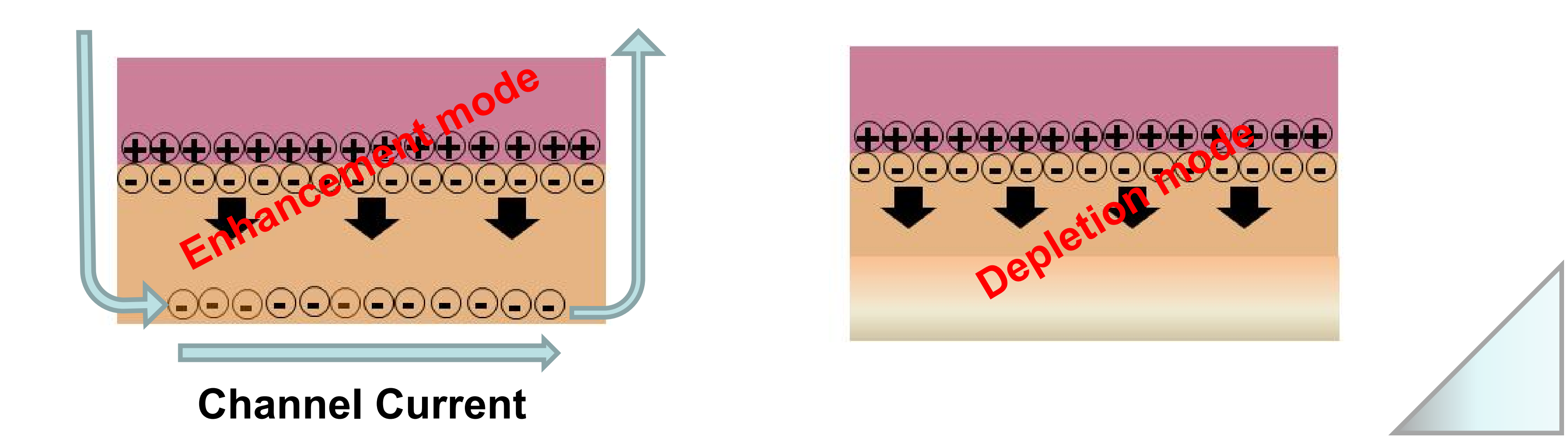
Time Scales

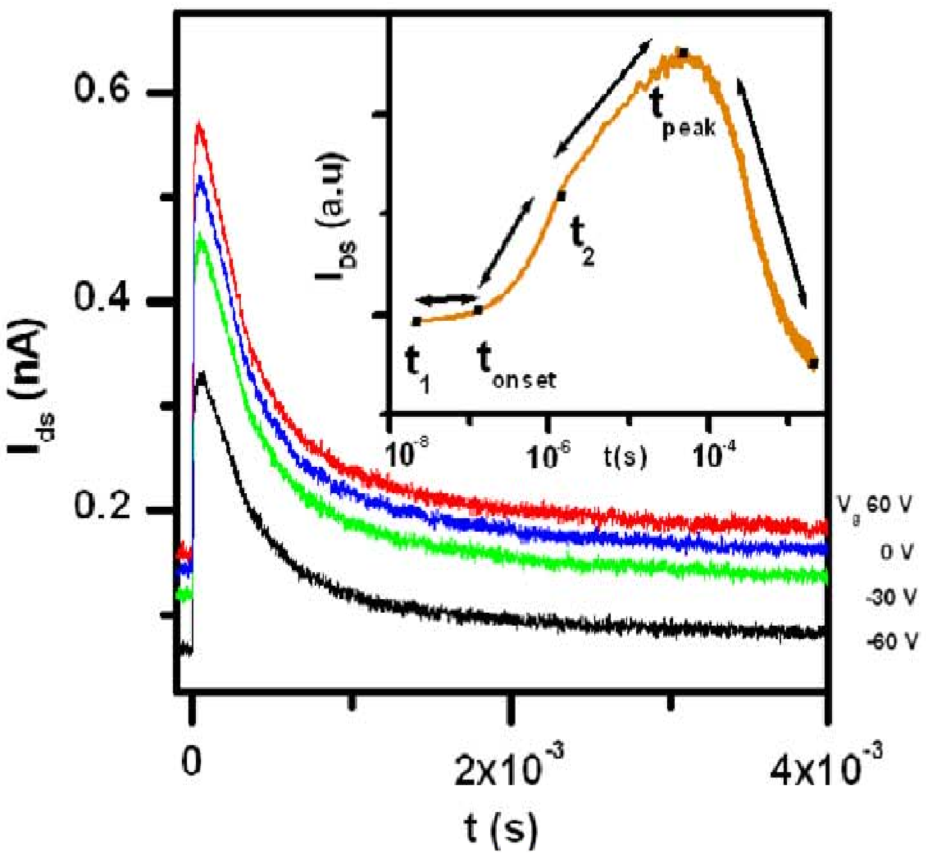
1-10 ns: Exciton diffusion towards interface

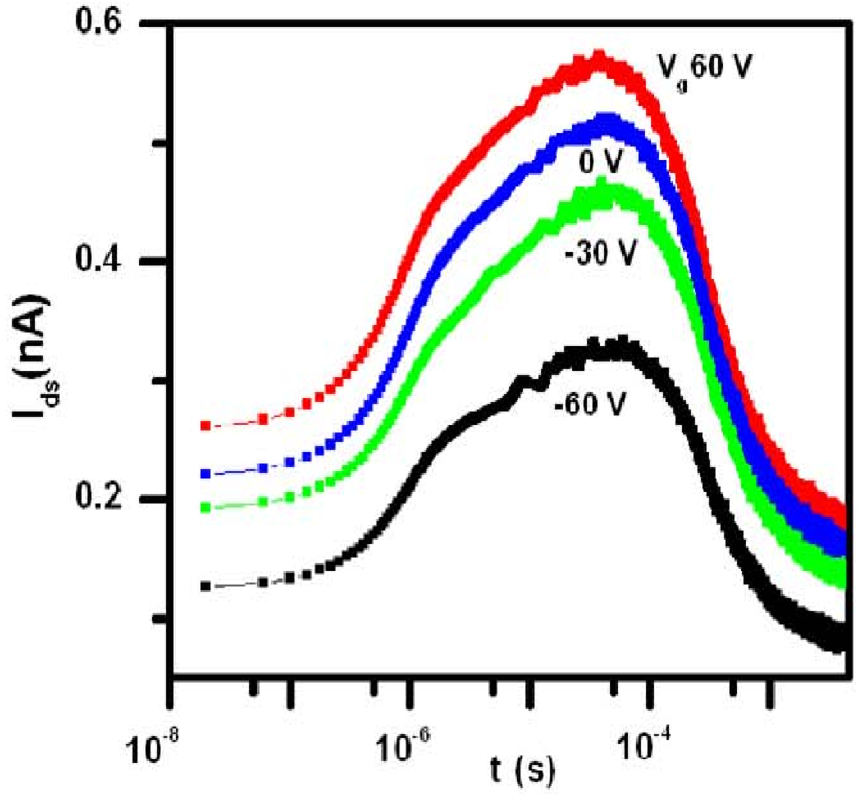
1-10 ps: Charge separation at Donor–Acceptor interface

1-100 μs: free charge carrier transport towards electrode









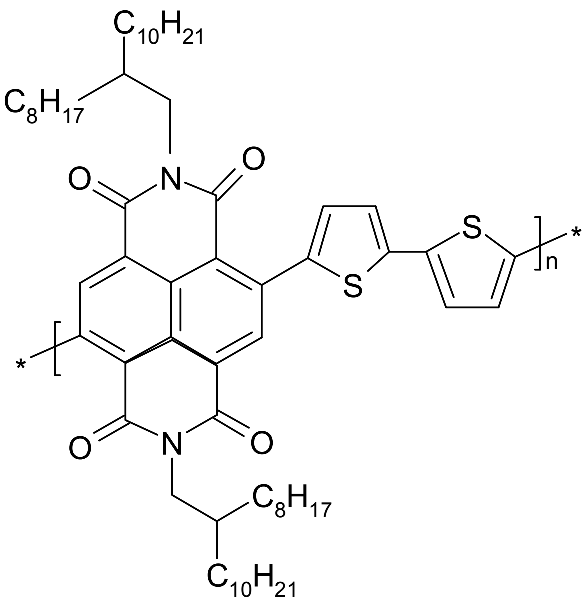
APPLIED PHYSICS LETTERS **95**, 183306 (2009)

Studies of charge transfer processes across donor-acceptor interface using a field effect transistor geometry

Manohar Rao and K. S. Narayan[a)]
Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P. O., Bangalore 560 064, India

High mobility electron transporting polymer

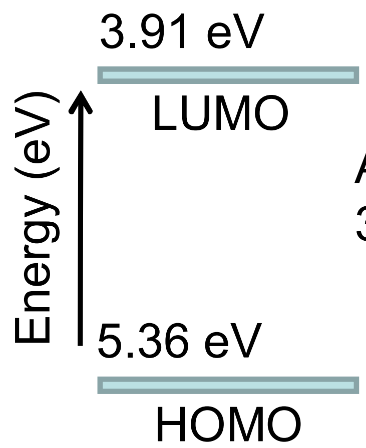
Electron depleted core has been used for n-channel polymer building block.
Electron poor NDIR core has been used because of large electron affinity and T2(dithiophene) because of stability resulting in highly conjugated, planar and rod like polymers.



P(NDI20D-T2)

poly{[N,N'-bis(2-octyldodecyl)-napthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl—alt-5,5'-(2,2'-bithiophene)}, (P(NDI20D-T2)

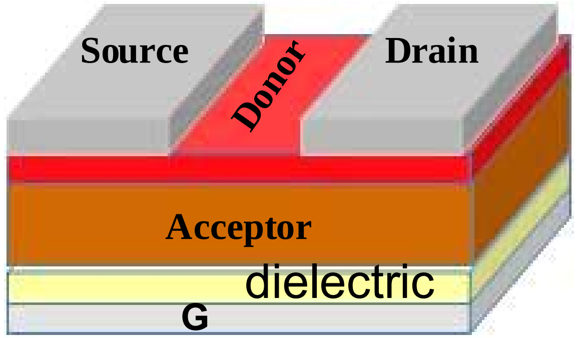
Air stable electron transporting Polymer FET can be fabricated

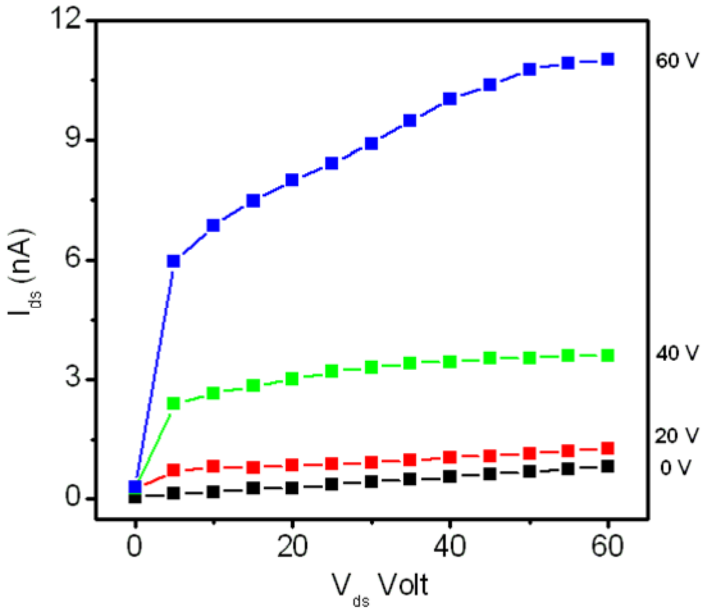


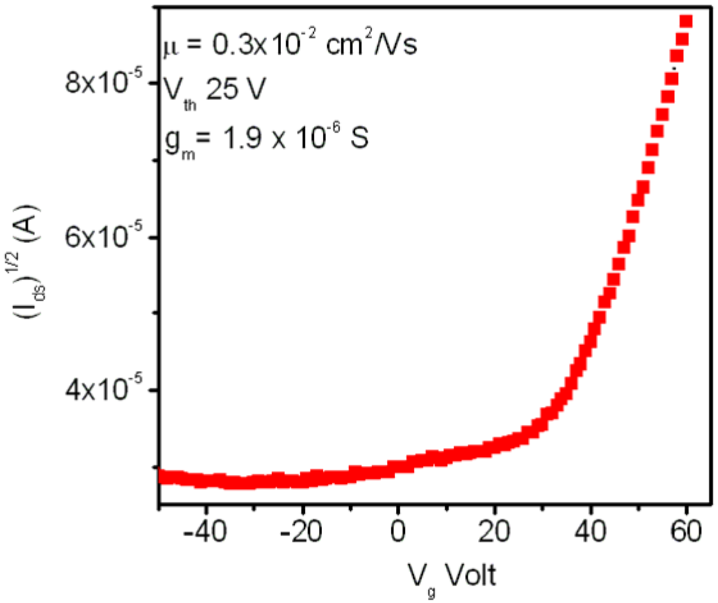
Absorption max:
391 nm & 697 nm

Fachetti et. al. JACS, 131, (2009)
Nature, 457, 679, (2009)

N2200 & P3HT based bilayer FET on Al gate electrode with BCB as dielectric and AL as source drain injecting electrode.



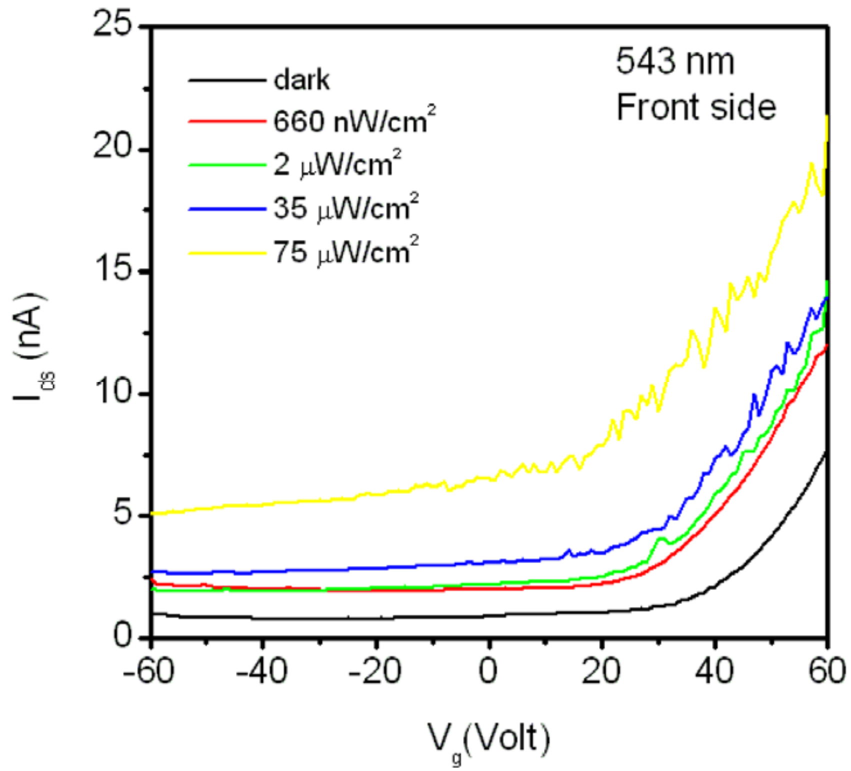




On-Off ratio: 20-100

Mobility ~ 10^{-3} cm^2 /Vs

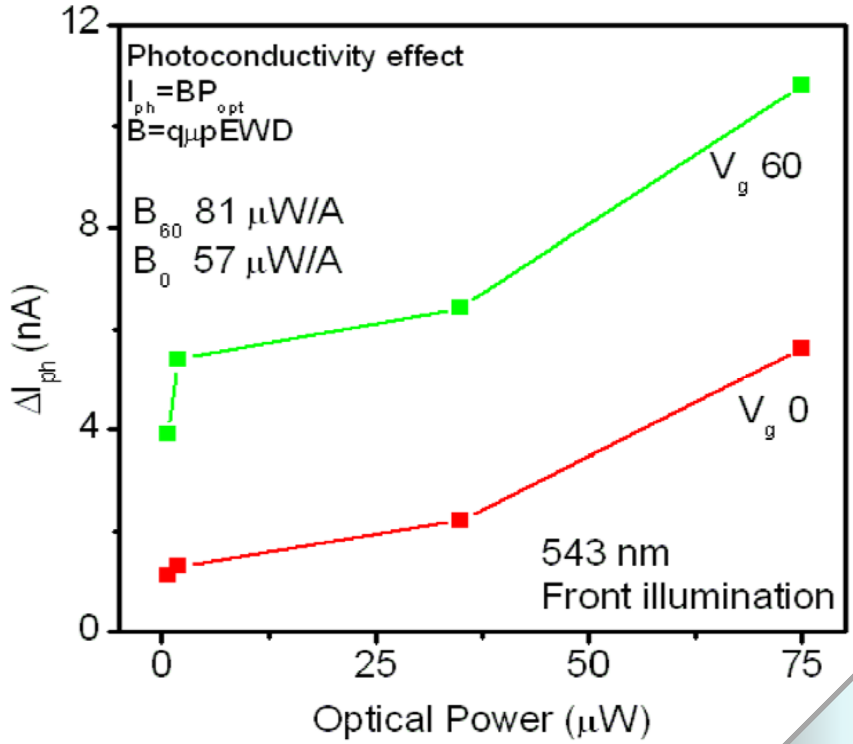
Threshold voltage: ~20 volt



DA-FET with 543 nm excitation from D side

Its shows linear change in I_{ds} in both depletion and enhancement mode of operation.

ΔV_{th} shift with increasing light intensity is in negative V_g



For DA-FET upon channel illumination from D-side
PC effects were observed.

Photocurrent Spectrum

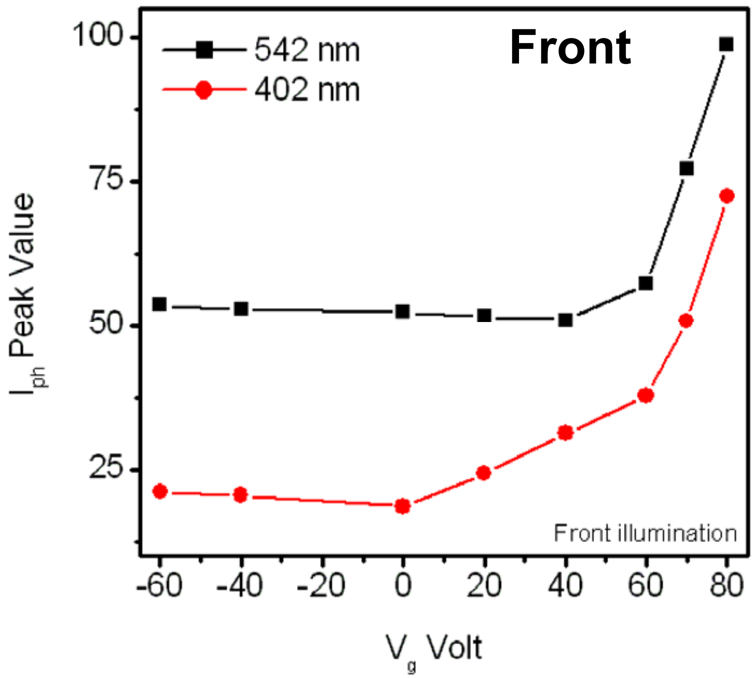
Spex-front.TIF

V_g dependent spectral features for DA-FET, illuminated from Front.

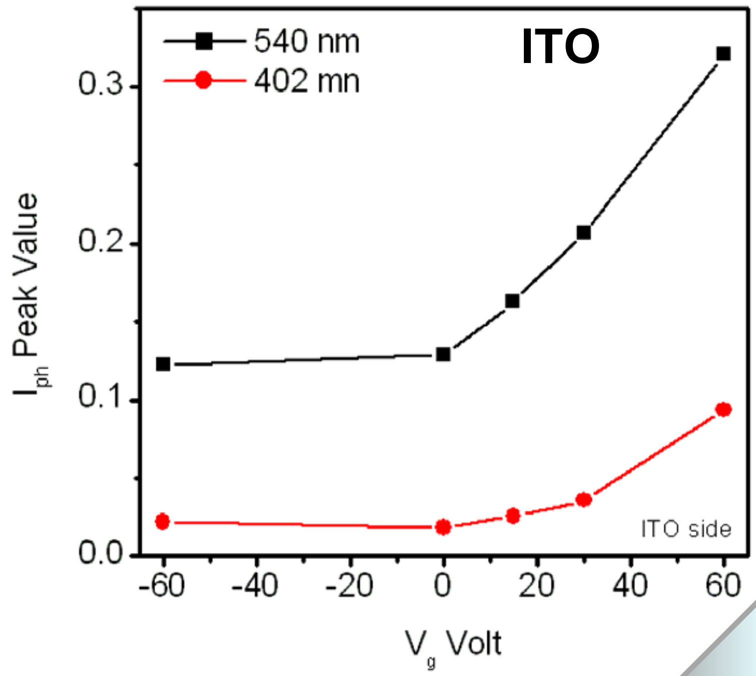
400 nm features exclusively originates from N2200, while spectral features from 540 nm contribution is from P3HT.

For 400 nm I_{ph} scales uniformly with V_g.

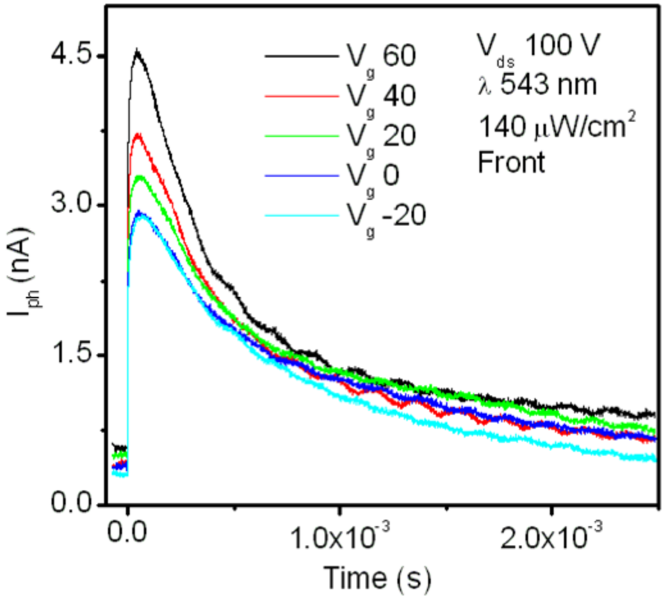
Negligible changes for 542 nm with V_g, since photoactivity is restricted to Donor interface, while transport occurs through acceptor channel region.



For 540 nm, the change is large since bulk of N2200 also absorbs 540 nm, thus large contribution to I_{ph}.

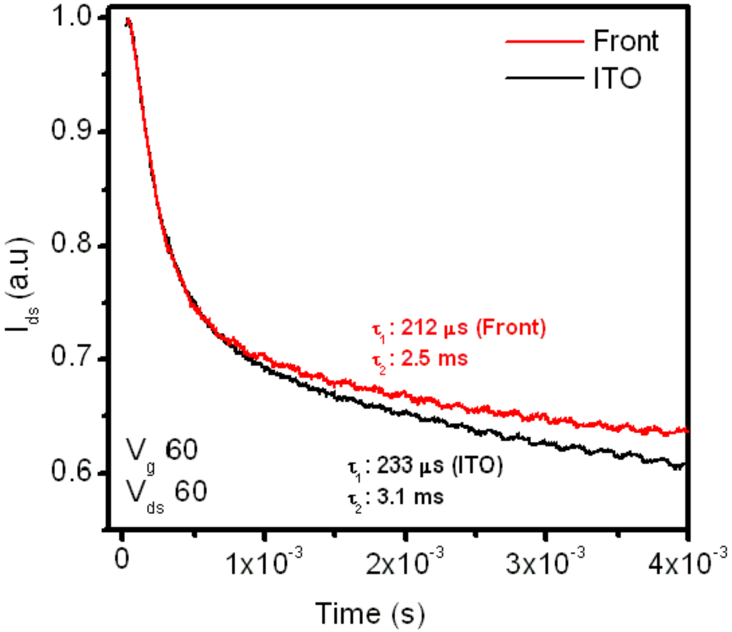


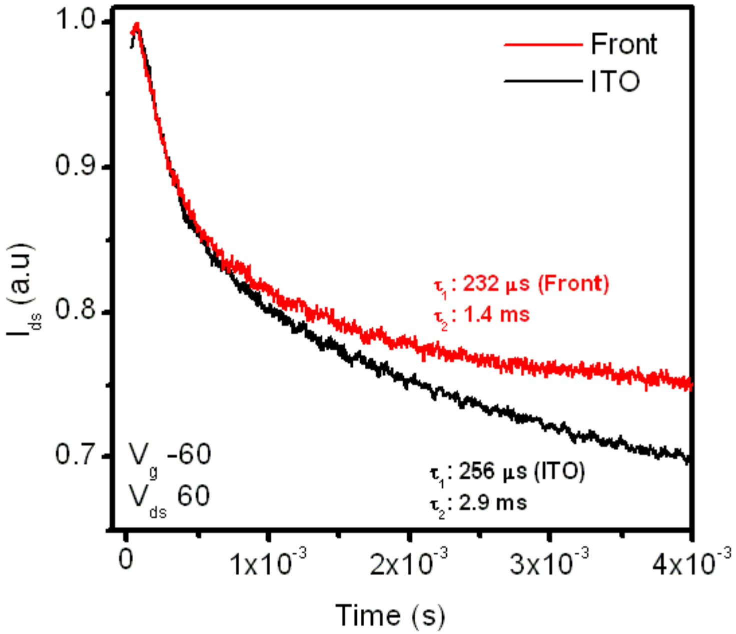
Illumination from ITO allows for charge carrier generation close to dielectric interface, which can be modulated through V_g.



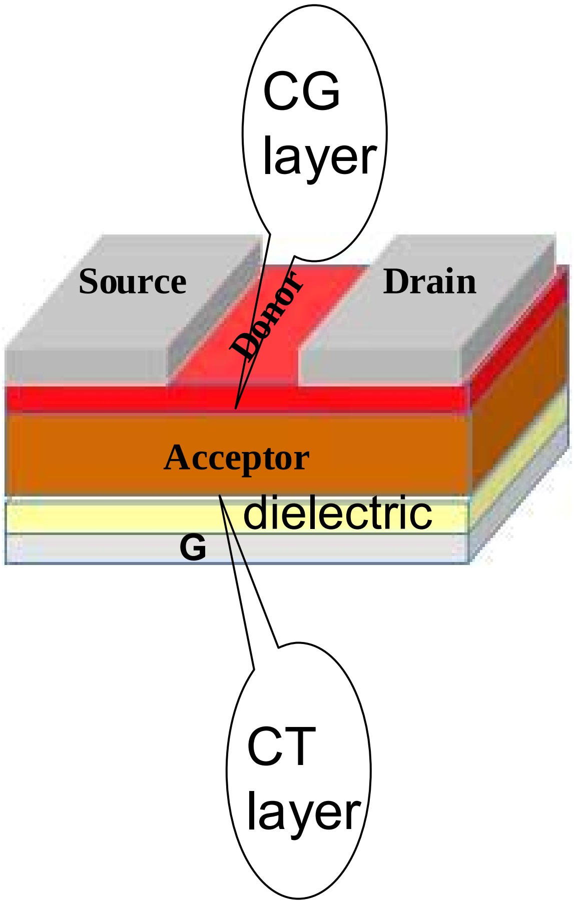
Transient-TOF measurement N2200-P3HT DA-FET, for Front & ITO side illumination.

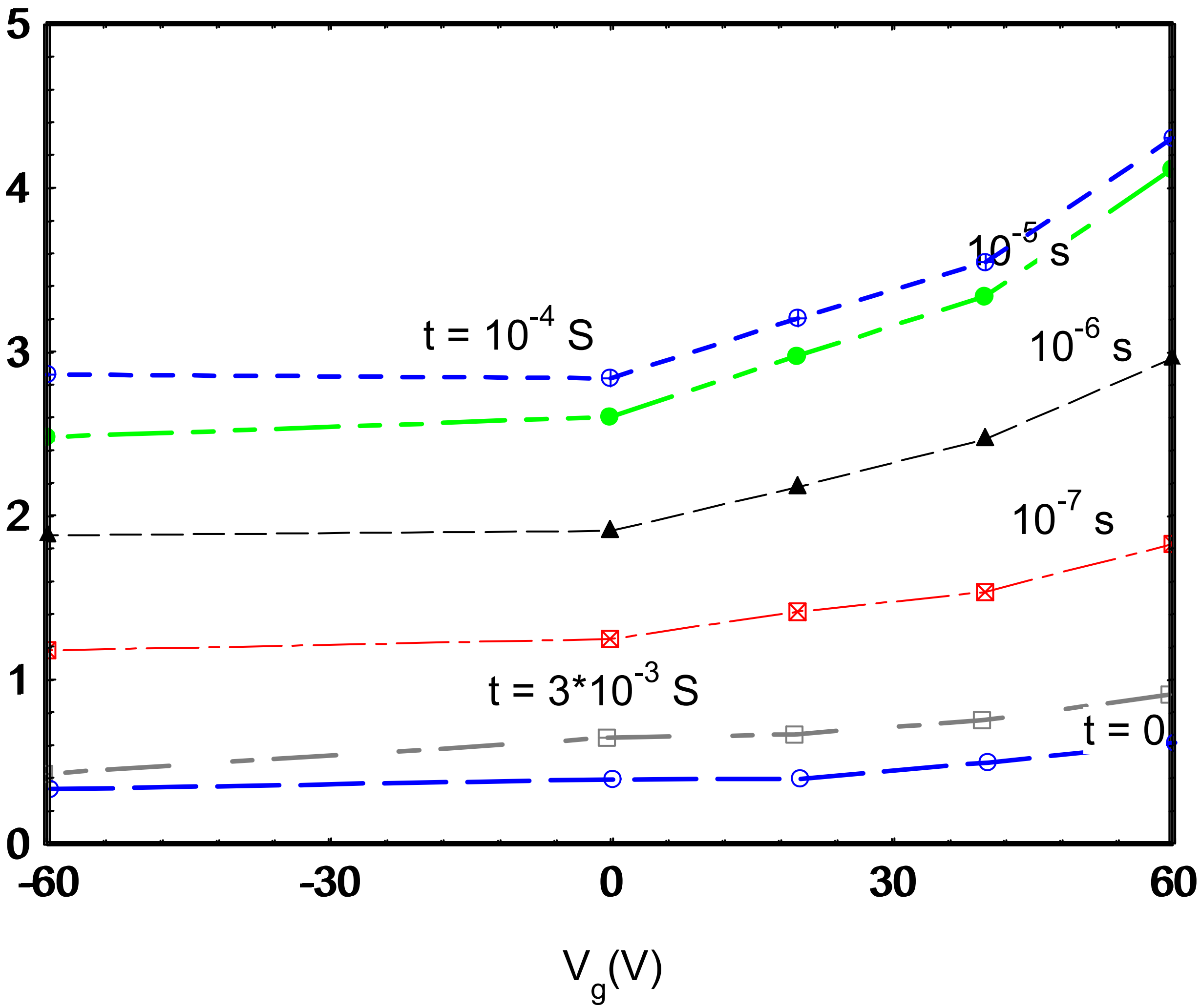
Decay constant increases, when illuminated from ITO side, for both mode of operation.





Bilayer FET Response after a light pulse



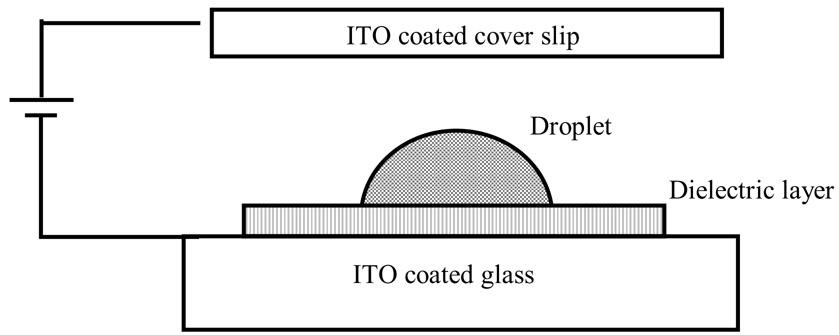


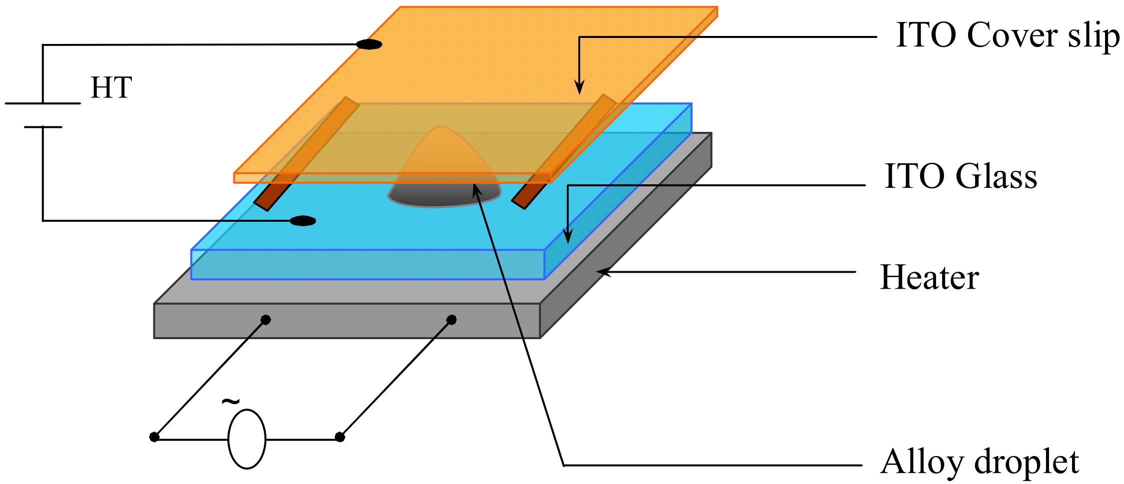
Simultaneous measurement of Field Effect mobility
and bulk mobility (TOF) !!

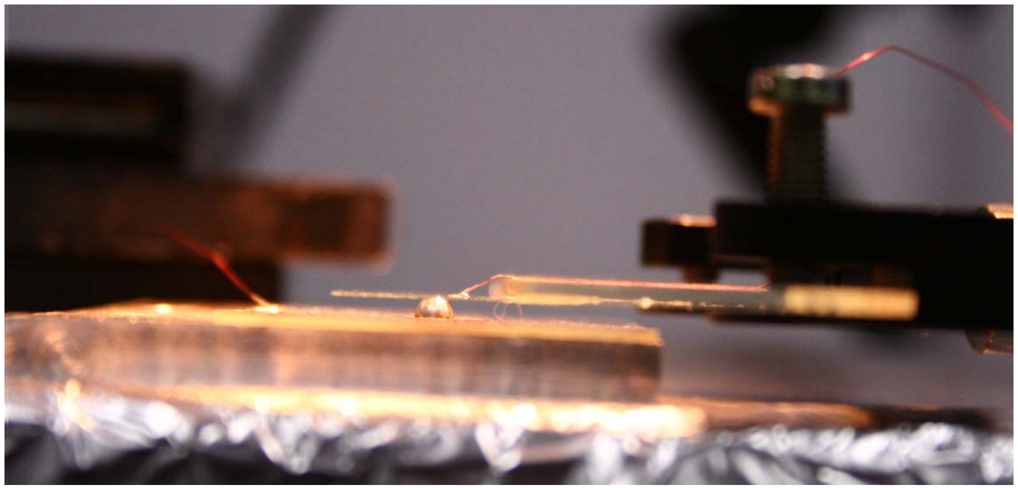
Deformation of a metal-drop induced by electric-field for organic-electronics and molecular electronics

Origin:

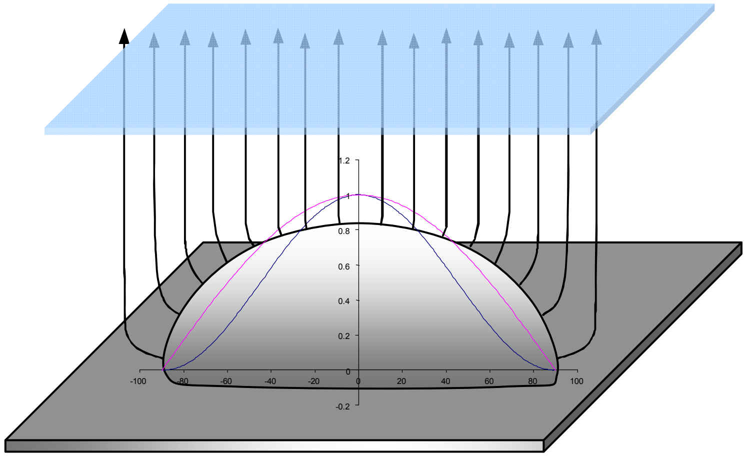
•Metallic Drop on conducting substrate or on dielectric substrate
(Landau Lifshitz – Electrodynamics Home Assignment)


ITO coated cover slip
Droplet
Dielectric layer
ITO coated glass


ITO Cover slip
HT
ITO Glass
Heater
~
Alloy droplet

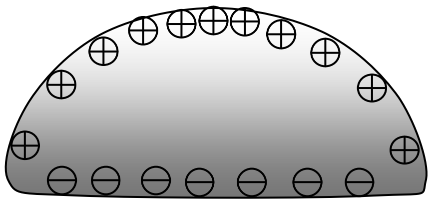


Charged deformable conducting-drop

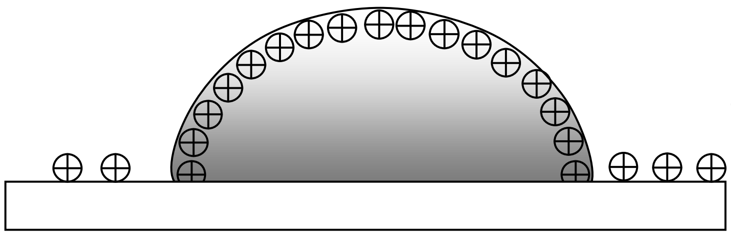


$$\vec{E} = -\frac{\partial \phi}{\partial r}\hat{r}\bigg|_{r=R} = \left(3E\cos\theta\right)\hat{r}$$

$$\vec{F}_s = \frac{E^2}{8\pi}\hat{r} = \frac{9E^2\cos^2\theta}{8\pi}\hat{r}$$



Uncharged droplet under constant electric field



Charged conductor

$$\left(\vec{E}^2 / 8\pi\right)\hat{r} + \rho_0 = \left(2\gamma / r\right)\hat{r}$$

- For low Bond number and assuming spheroid

$$\vec{F}_{el} = \left(\vec{E}^2 / 8\pi\right)\hat{r} = \frac{9E^2 \cos^2\theta}{8\pi}\hat{r}$$

$$\vec{F}_s = \left(2\gamma / r\right)\hat{r}$$

$$E \geq \frac{4}{3\cos\theta}\sqrt{\frac{\gamma\pi}{r}}$$

For charged conductor

- Electrostatic pressure

$$F_{el} = e\phi / 6V$$

Where V is the volume of the droplet

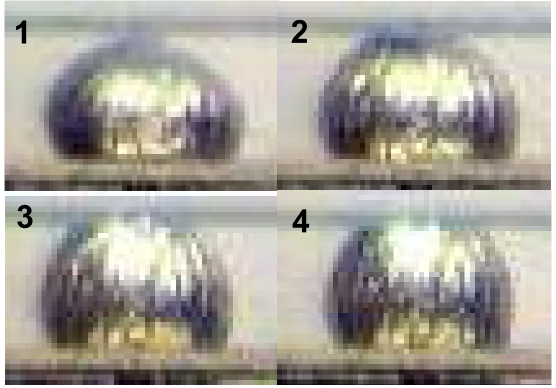
$$\phi \geq \sqrt{\frac{12\gamma V}{Cr}}$$

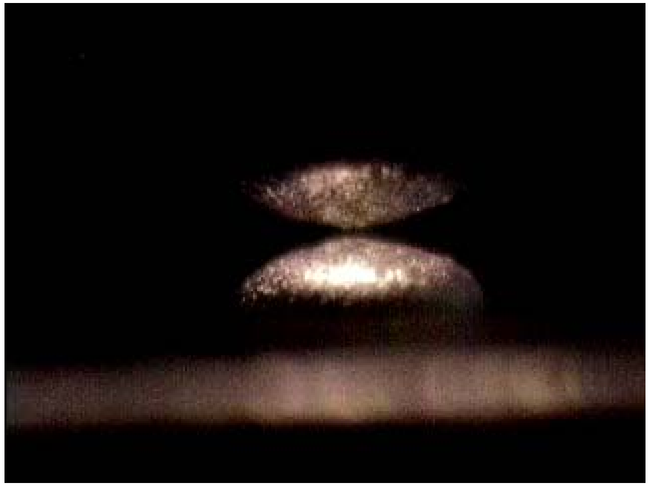
C is the capacitance of the droplet

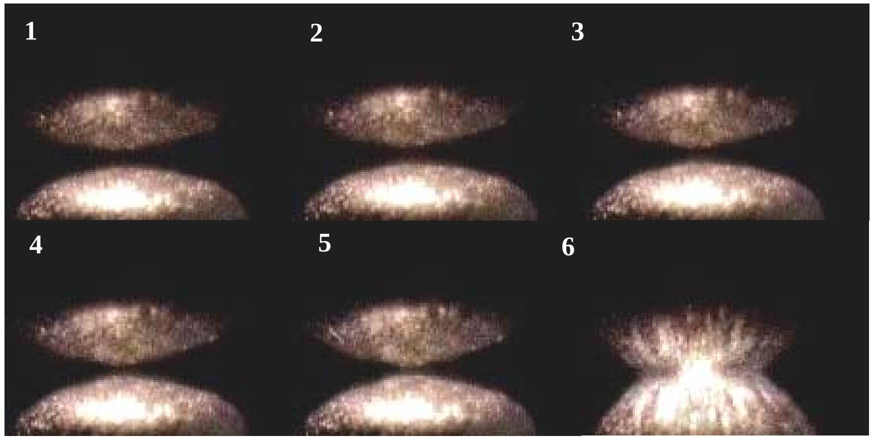
In the linear regime, experimental results ~ analytical soln. with foll. assumptions:

- Materials - perfect conductor.
- Unperturbed electric field is constant and along *z* direction only.
- Droplet is hemispherical hemispheroid and it is deformable.
- Temperature gradient is zero and elastic property is uniform through out the materials
- Gravity effect is neglected compare to surface energy and electrostatic energy term.
- Electrowetting neglected (substrate-droplet interaction)

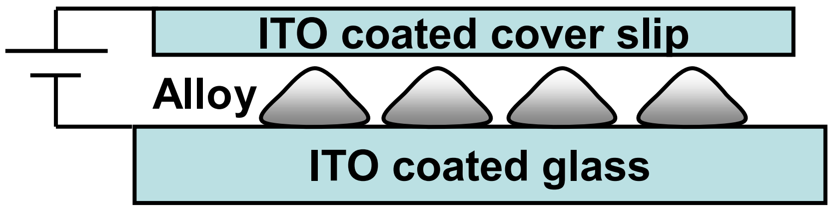
Monojit and Narayan Proc. Of Royal Soc. 2008

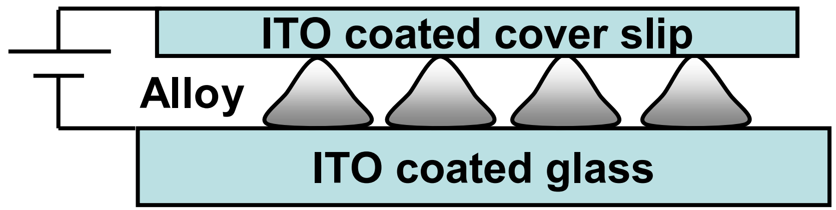


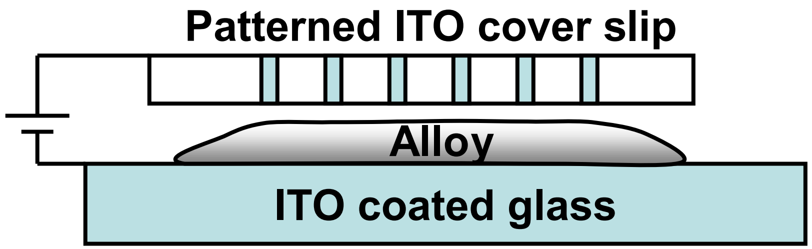


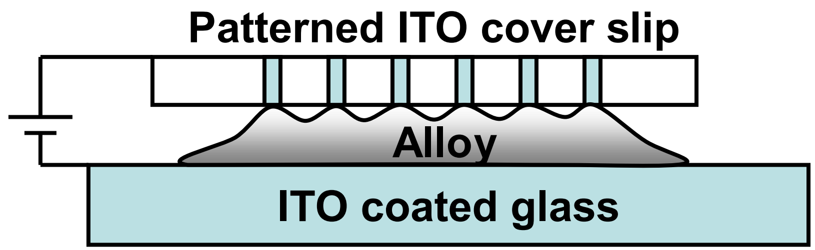


Monojit and Narayan Proc. Of Royal Soc. 2008


ITO coated cover slip
Alloy
ITO coated glass


ITO coated cover slip
Alloy
ITO coated glass


Patterned ITO cover slip
Alloy
ITO coated glass


Patterned ITO cover slip
Alloy
ITO coated glass

“Organic Solar Cells”

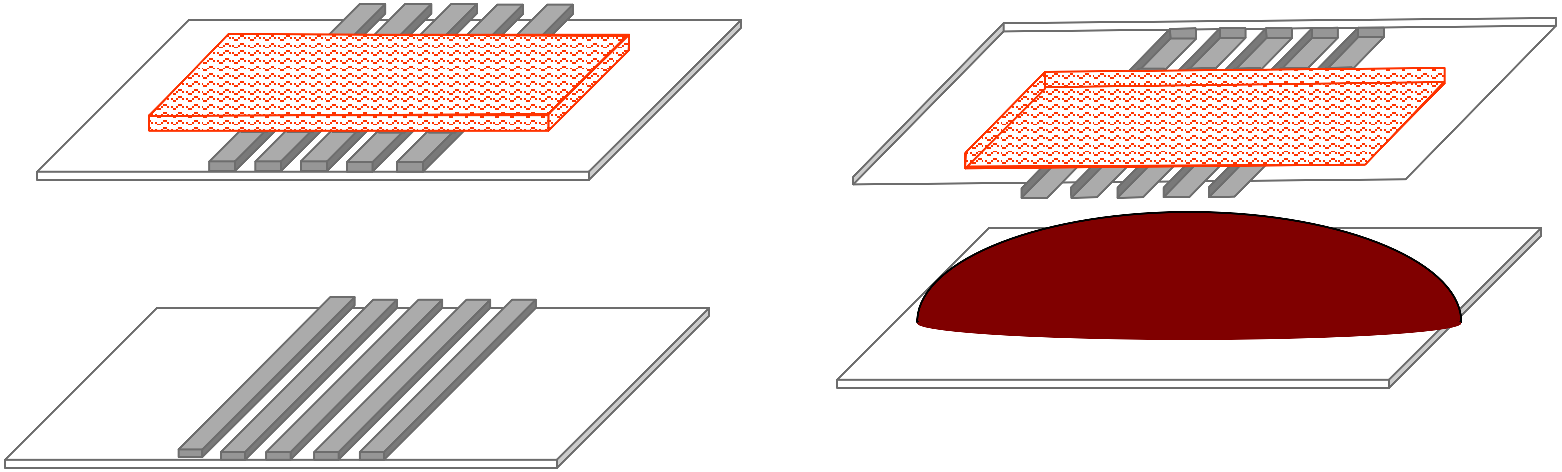
Energy input from the sun in a single day could supply the needs for all of the earth's inhabitants for a period of about 3 decades.

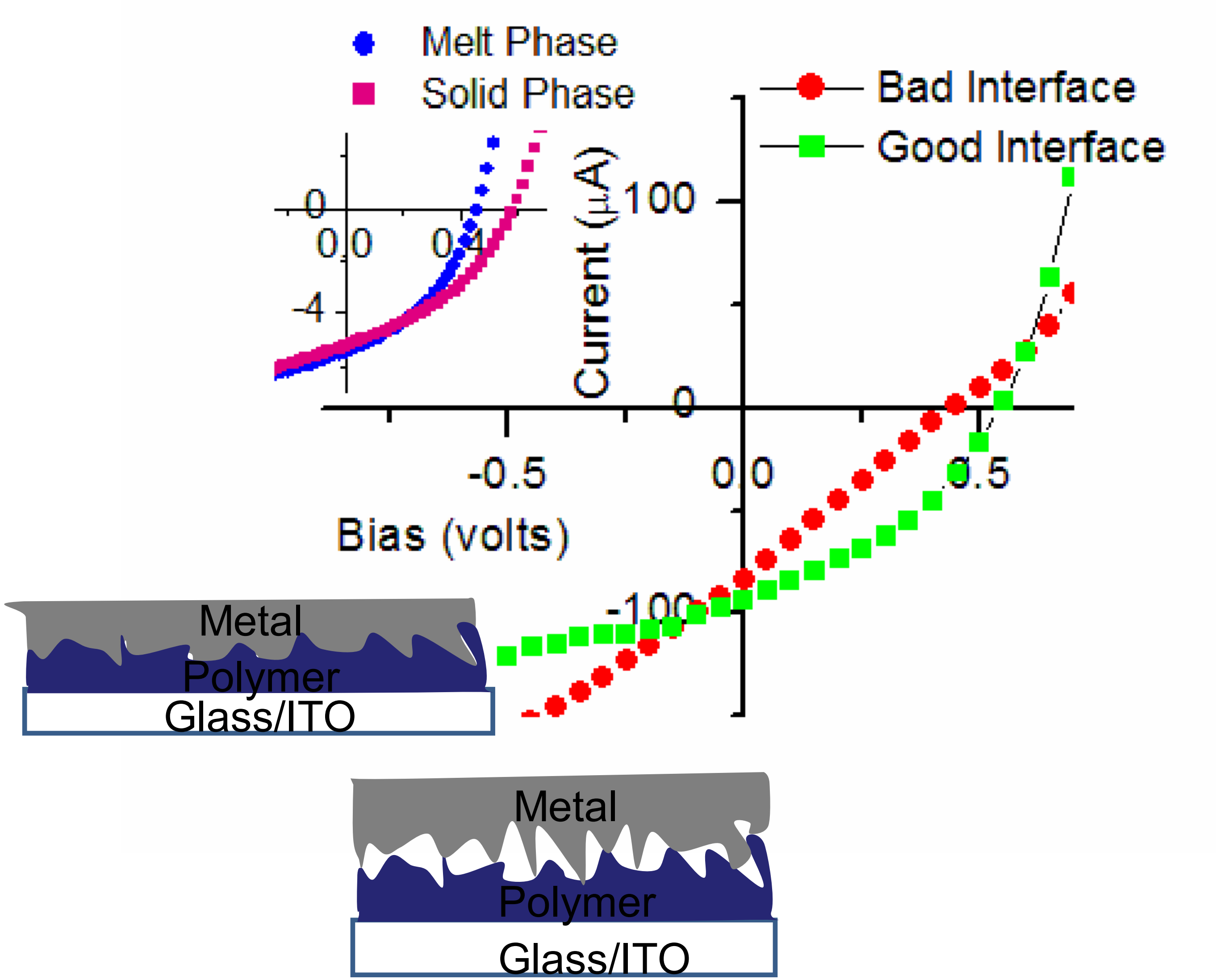
Needs to be affordable: money wise + CO_2 emission wise + …

Energy Payback Time

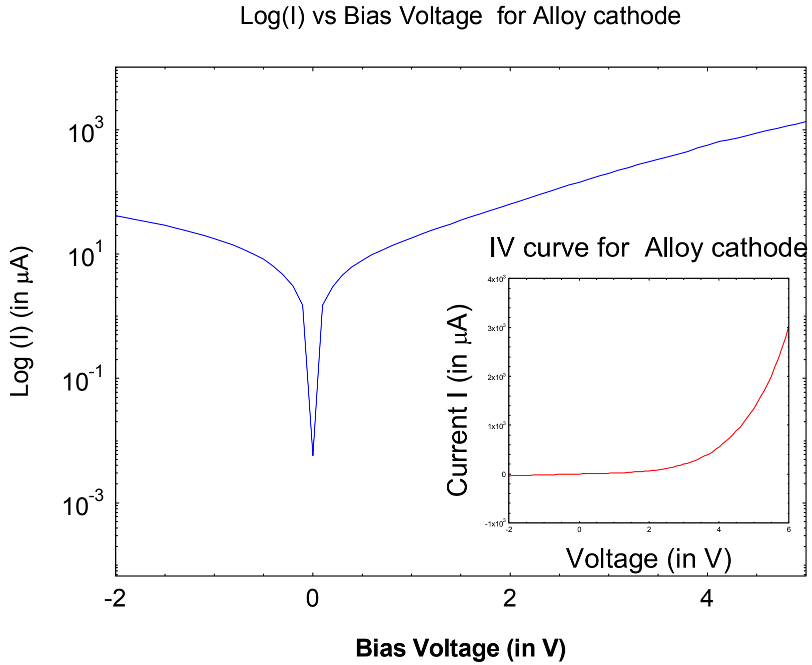
Renewable-energy technologies promise to liberate us from fossil fuels. But this implies that their energy payback periods—the time it takes for a system to recover the energy used to produce it—is just as important as financial payback

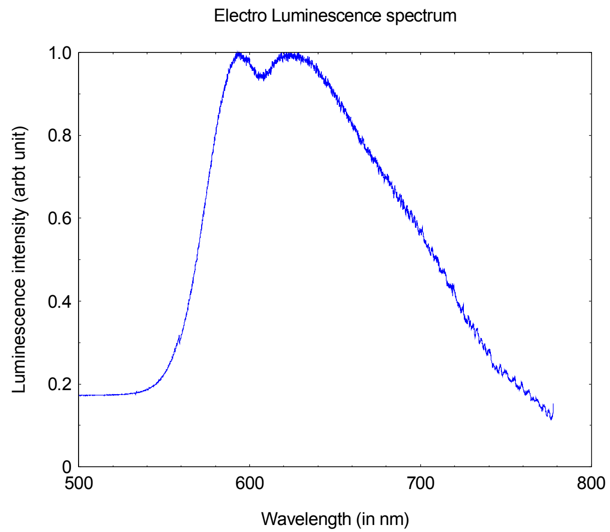
Polymer Solar Cells with Low Melting Alloys

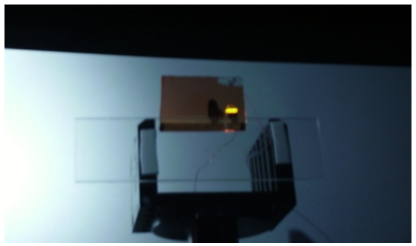




Gupta and Narayan – Appl. Phys. Lett. 2008







PV/OLED fabrication technology without vacuum requirement

सर्वदेवात्मको ह्येष तेजस्वी रश्मिभावनः ।

एष देवासुरगणाँल्लोकान् पाति गभस्तिभिः ॥ ७ ॥

He indeed represent the totality of all celestial beings. He is self-luminous and sustains all with his rays. He nourishes and energizes the inhabitants of all the worlds.