Effect of 2D delocalization on charge transport and recombination in bulk-heterojunction solar cells

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The people!

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- G. Juška, G. Sliauzys, K. Arlauskas, N. Nekrasas, K. Genevicius/Vilnius Univ

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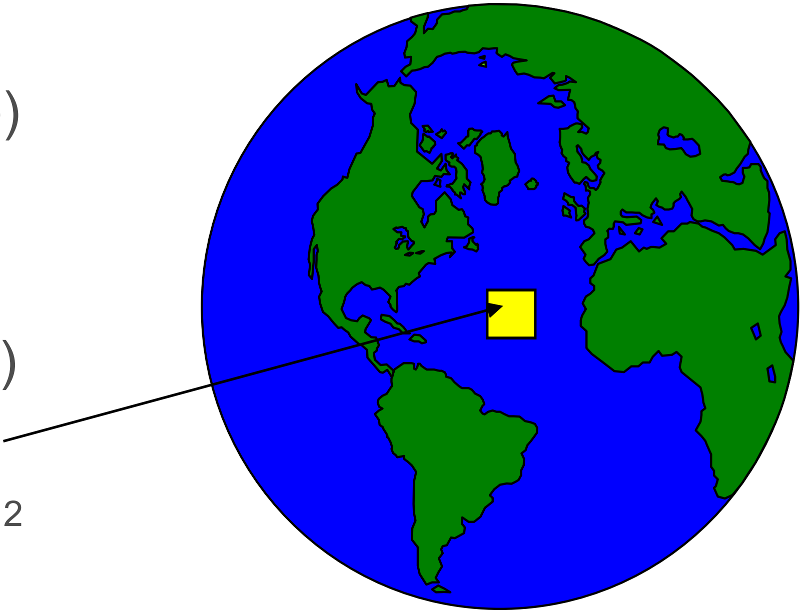
- G. Dennler and M. Scharber, Konarka Austria
- D. Vanderzande, Universiteit Hasselt, Belgium

Outline

1. Motivation for plastic solar cells
    - Langevin recombination
2. Effect of morphology on transport
    - Treated/untreated bulk-heterojunction solar cells
3. 3D vs 2D Langevin recombination
    - Drift model
    - Full drift-diffusion model
4. Importance of the interface
    - Cw-PIA on treated and untreated solar cell blends
    - 2D polarons generated
    - Hybrid interfaces

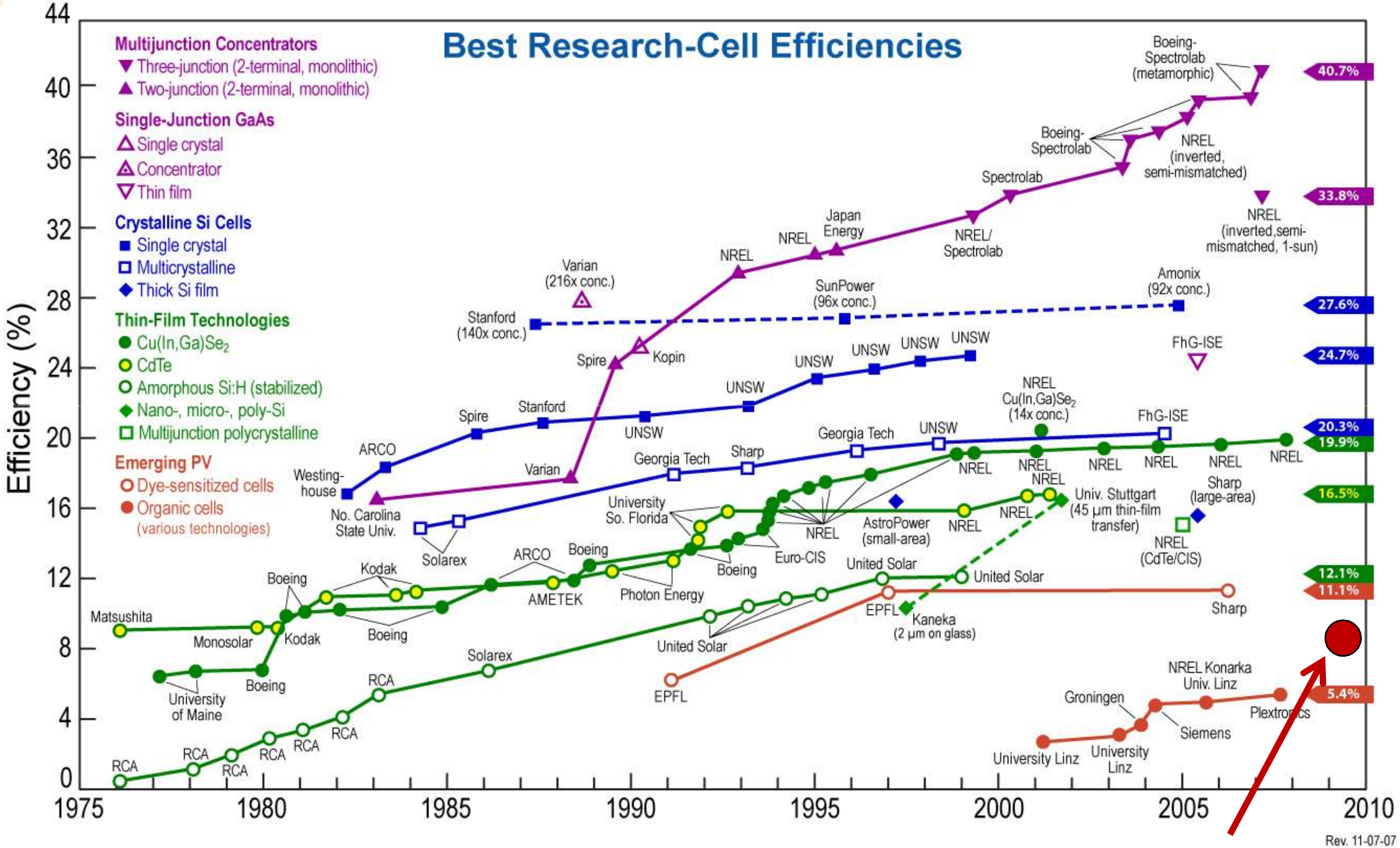
Why Solar Energy?

- Available solar power:
  - 20 MW p.p. (total earth surface)
- Human energy consumption:
  - range 100 W - 10 kW p.p.
  - average 2.5 kW p.p. (NL: 6 kW)
- at 10% overall efficiency:
  - surface needed 1400x1400 km^2 to cover energy needs in 2050 (~1500 EJ)
- How to store and distribute?



Source: ECN, Slide courtesy of P.W.M. Blom

The challenge for plastics



7.87%, Solarmer Energy Inc, November 2009

Source: NREL/Wikipedia

Motivation

- High power conversion efficiencies in solar cells of low-mobility materials require high carrier densities.

- Higher carrier densities leads to shorter lifetimes

$$\boxed{\tau = \left[n(0)\beta\right]^{-1}}$$

where β is the bimolecular recombination coefficient

- To understand charge transport and recombination is crucial for making more efficient solar cells!

Langevin Recombination

Expected in all low-mobility (μ<1 cm^2/Vs) materials

Necessary condition: The carrier mean free path is much smaller than the Coulomb capture radius r_c, i.e. $a << r_{C.}$

$$r_c = \frac{e^2}{4\pi\varepsilon\varepsilon_0 kT} \approx 19\mathrm{nm}$$

Langevin recombination is determined by the probability for the charge carriers to meet in space, independent of the subsequent fate of the carriers

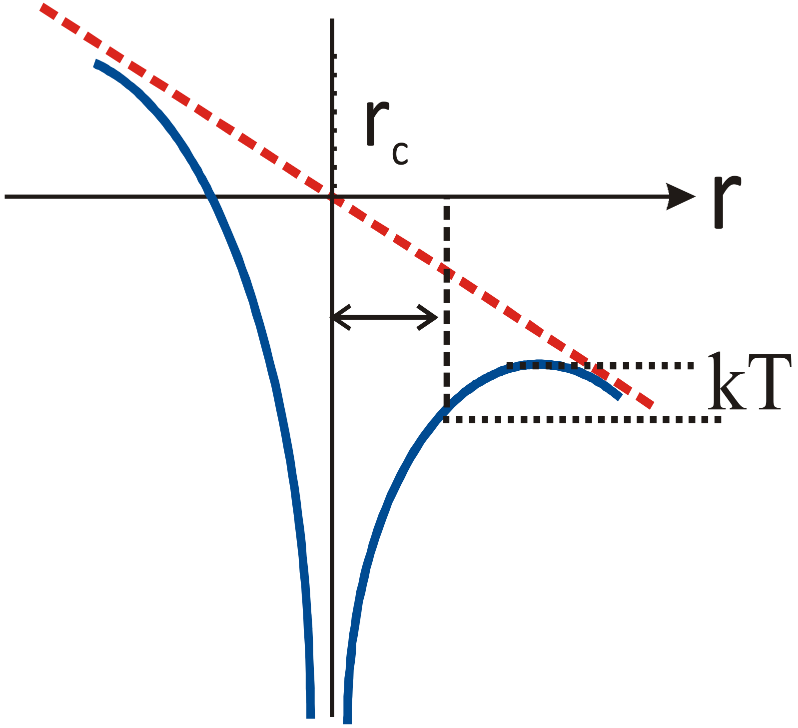
$$\frac{dp}{dt} = \frac{dn}{dt} = -\beta_L np = -\beta_L n^2$$

$$\beta_L = \frac{e(\mu_n + \mu_p)}{\varepsilon\varepsilon_0} \propto \mu_f(F,T)$$

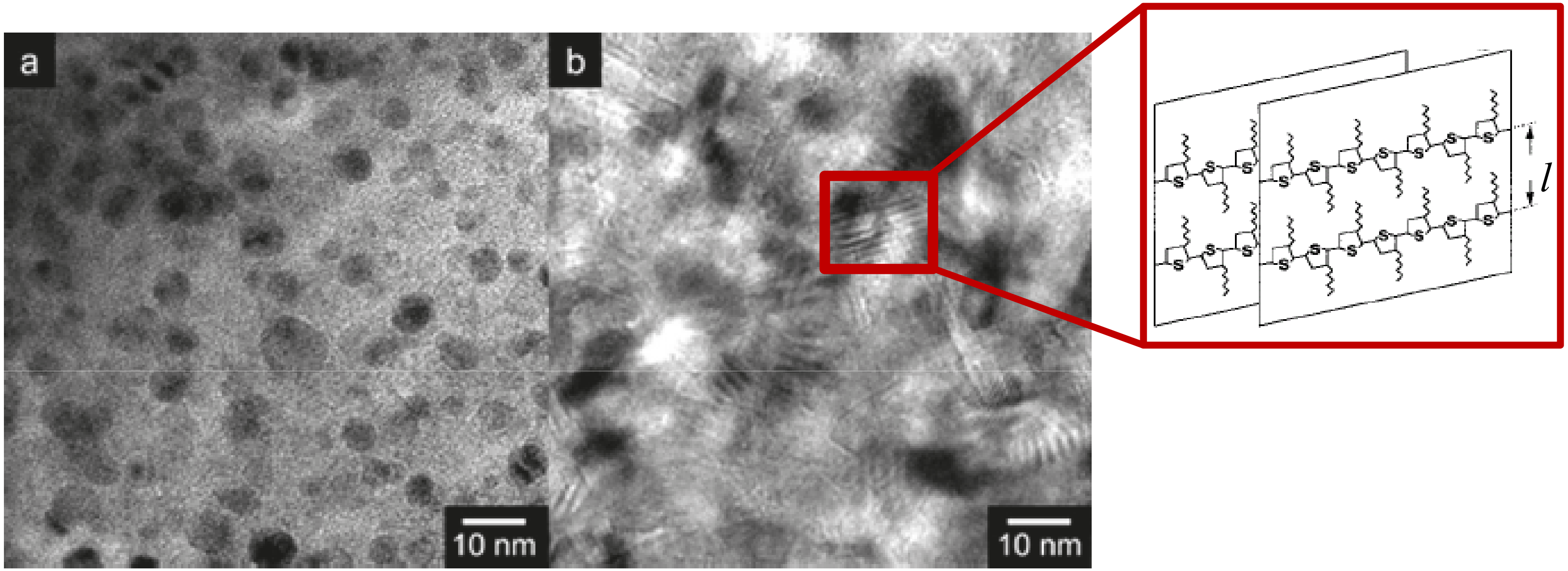
P. Langevin, Ann. Chim. Phys. **28**, 433 (1903).

Consequences of Langevin recombination

- Langevin recombination is the *time reversed process* to Onsager-type generation
- Photogenerated charges will be bound within the Coulomb radius, r_c
- Field dependent generation of free carriers due to lowering of barrier
- Clarifying the recombination mechanism yields also information about generation!



Effect of morphology



Untreated

Treated

Beal et al., Macromolecules **43**, 2343–2348 (2010)

3D vs 2D Langevin recombination

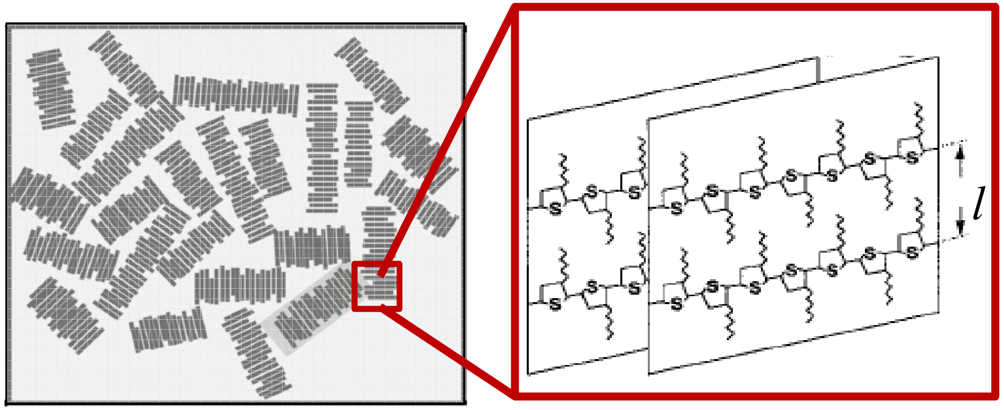
Homogeneous (3D)

$$f_{3D} = \frac{e(\mu_n + \mu_p)}{\varepsilon\varepsilon_0} n$$

$$\frac{dn}{dt} = -\beta_L n^2$$

$$\beta_L = \frac{e(\mu_n + \mu_p)}{\varepsilon\varepsilon_0}$$

Lamellar structure (2D)



$$f_{2D} = \frac{3\sqrt{\pi}}{4}\frac{e(\mu_n + \mu_n)}{\varepsilon\varepsilon_0}(ln)^{3/2} = \gamma_{2D} n^{3/2}$$

$$\frac{dn}{dt} = -\gamma_{2D} n^{5/2}$$ (*)

$$\frac{\gamma_{2D}}{\beta_L} = \frac{3\sqrt{\pi}}{4} l^{3/2} n^{1/2} = 6\times 10^{-3}$$

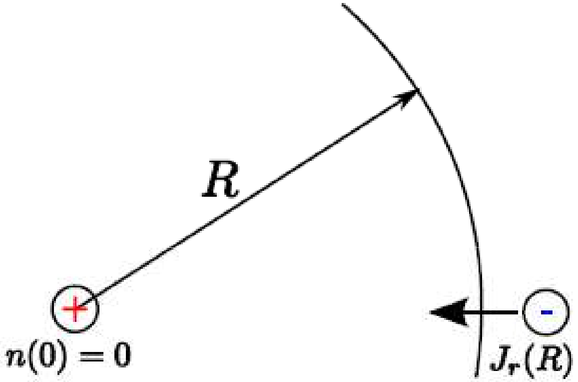
for l = 1.6 nm
n=10^{16}cm^{-3}

Juska et al., APL **95** 013303 (2009)

(*)Shuttle et al., APL **92**, 093311 (2008)

Including diffusion in 2D

Following Greenham & Bobbert
consider a fixed hole at the origin



$$\mathbf{J}(\mathbf{r}) = -\mu\, n(\mathbf{r})\,\mathbf{E}(\mathbf{r}) - D\,\nabla n(\mathbf{r}),$$

$$\nabla \cdot \mathbf{J}(\mathbf{r}) = 0, \qquad 0 < r < R$$

Generation at the periphery

$$J_r(R) = -f\,R/2$$

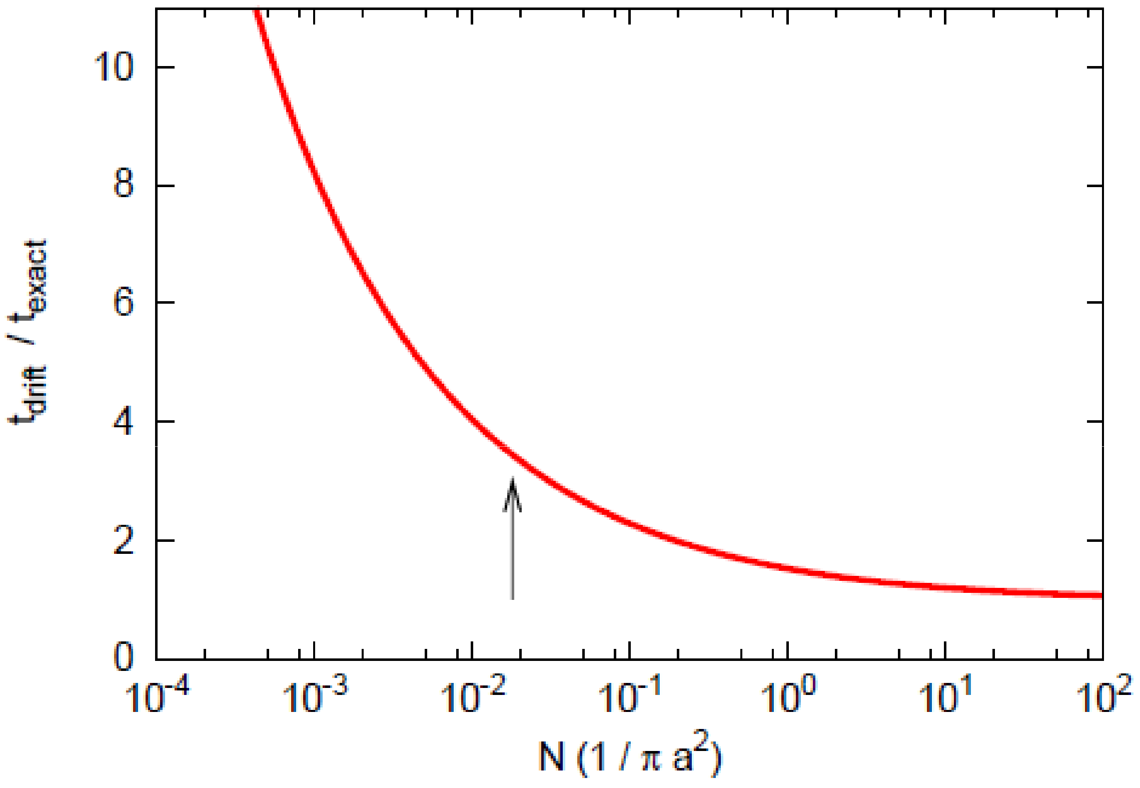
Einstein relation: $eD = \mu kT$

Solution:
solve J(r) then n(r)...

$$t = \frac{n_e}{f} = \int_0^R 2\pi r\, n(r)\, dr \quad \Big/ \; (f\pi R^2)$$

Greenham and Bobbert, PRB **68**, 245301 (2003)

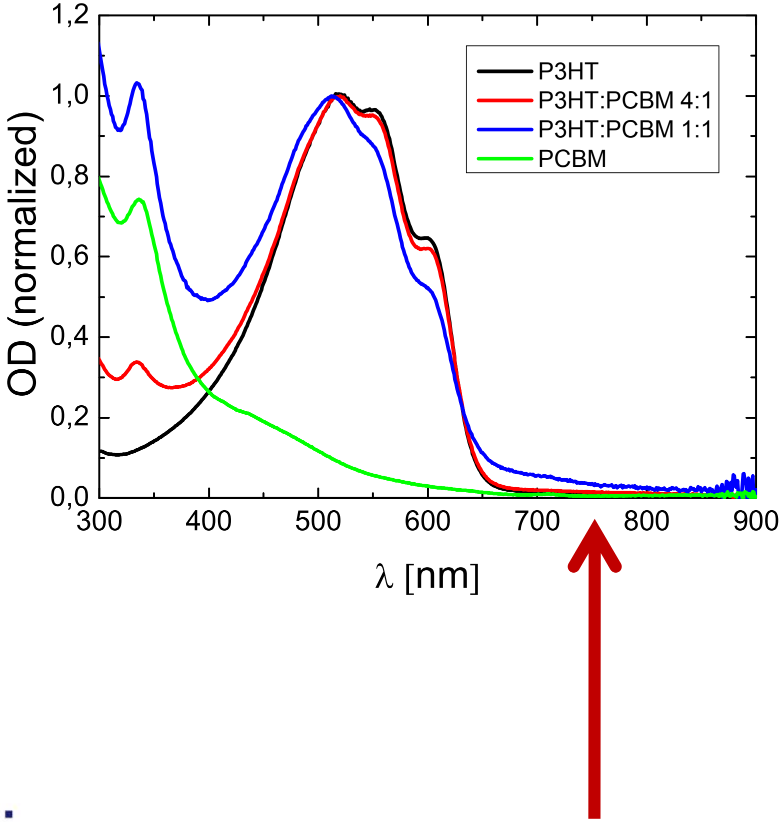
Inclusion of diffusion important in 2D!



Neglecting diffusion underestimates the recombination time!

V.I. Nenashev, F. Jansson et al., APL in press.

Importance of the interface



754 nm

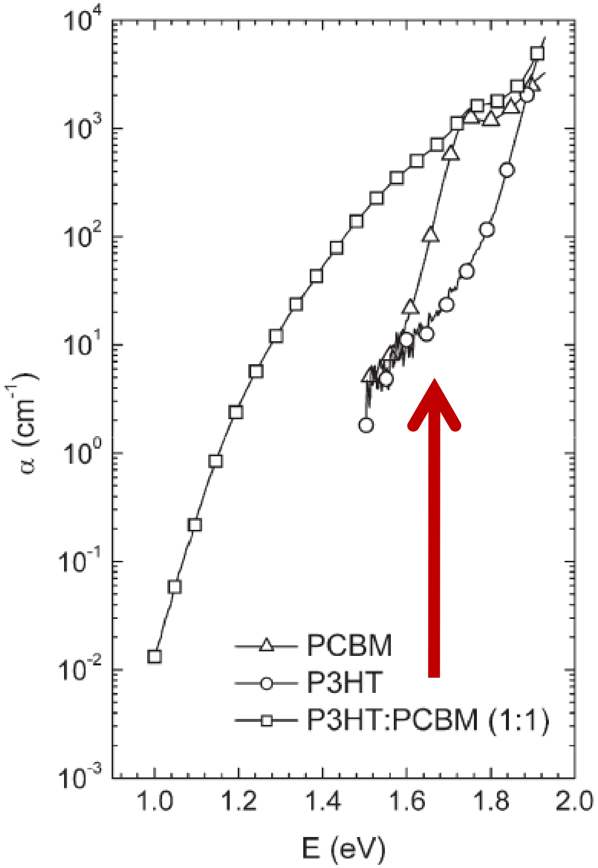
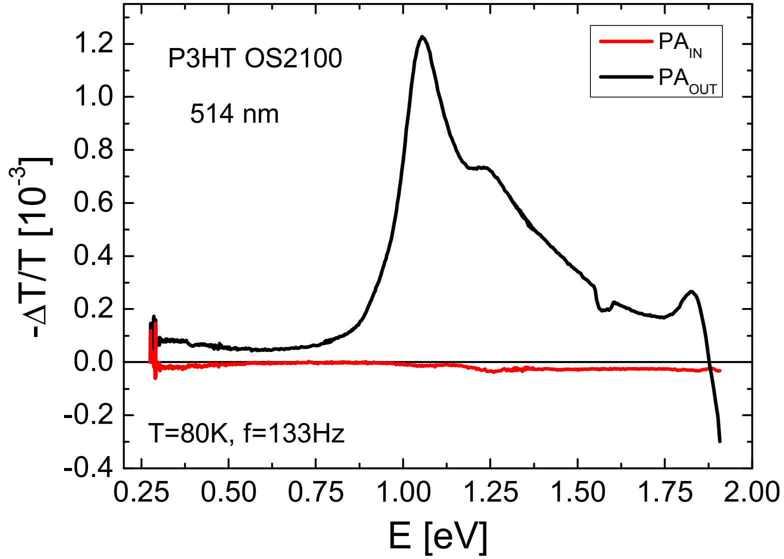


Fig. 3. Absorption coefficient below the bandgap of P3HT, PCBM and P3HT: PCBM as measured by FTPS.

K. Vandewal et al. / Thin Solid Films 516 (2008) 7135–7138

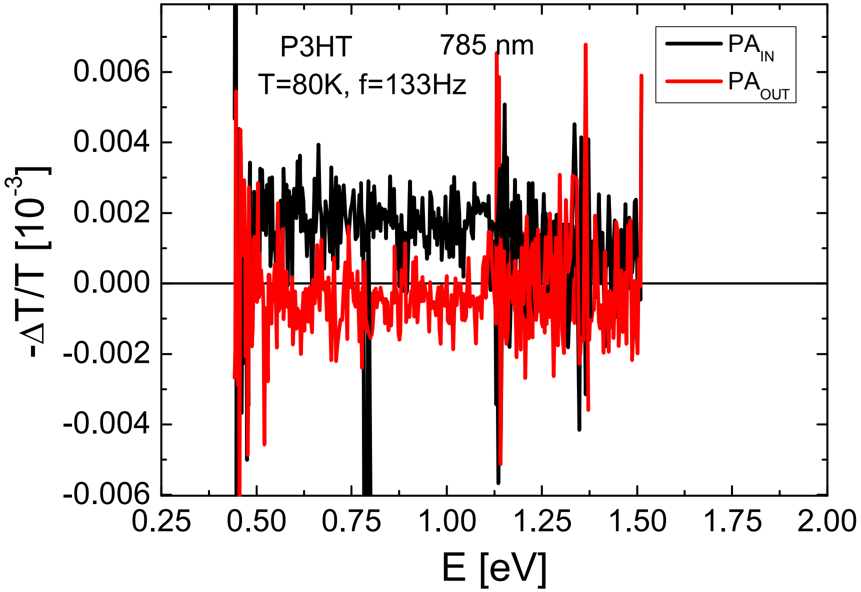
Cw-PIA in RR-P3HT

514 nm



Above gap excitation

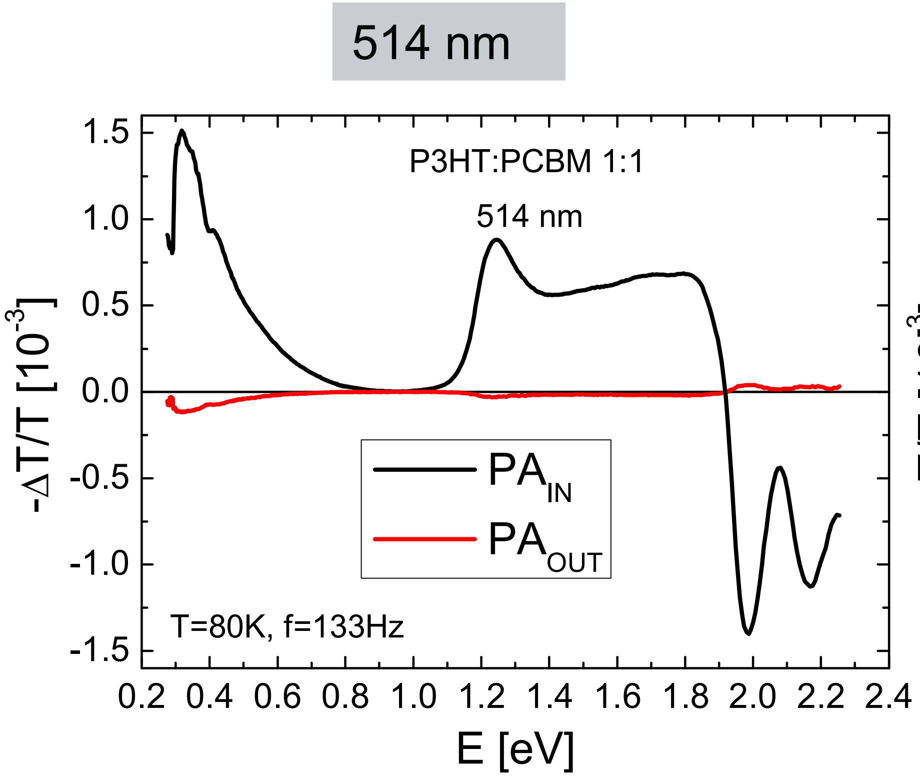
754 nm

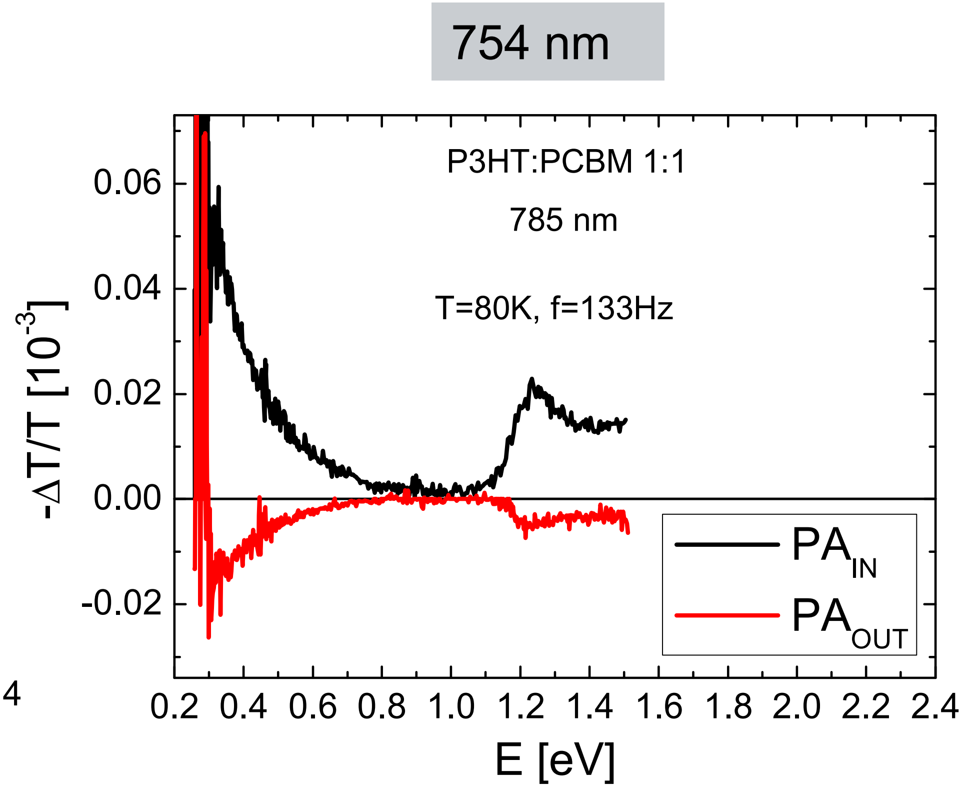


Below gap excitation

H. Aarnio et al., manuscript in preparation

Cw-PIA in P3HT:PCBM

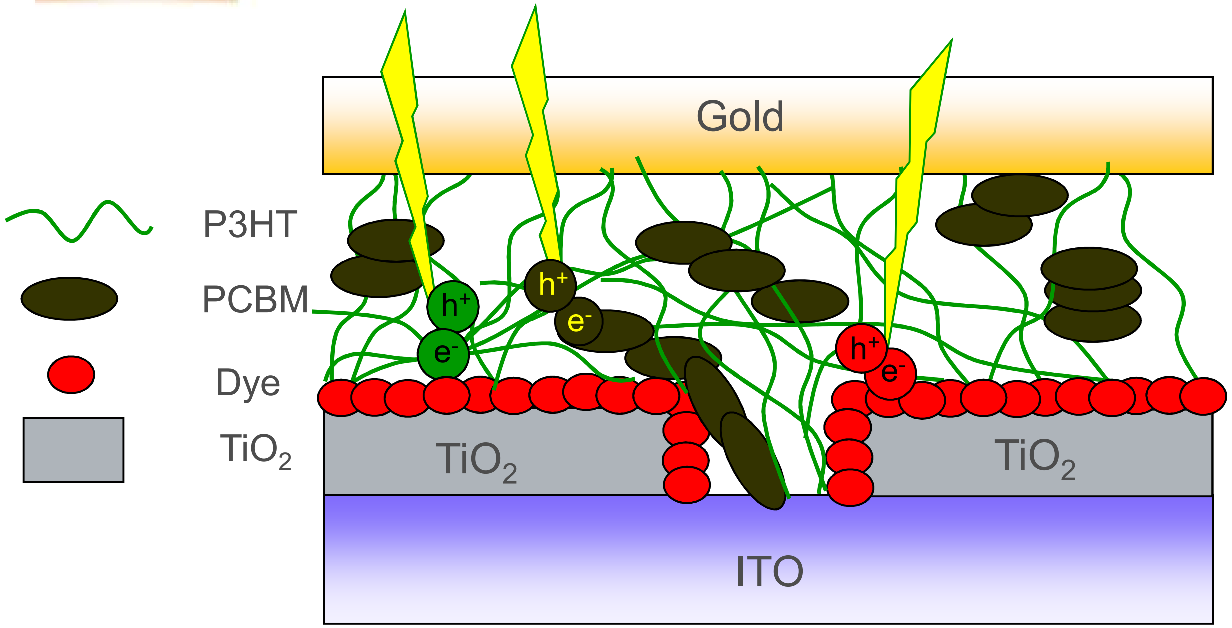


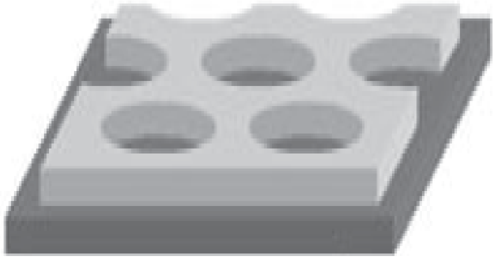


- Signs of 2D-delocalized polarons
- Also with sub-gap excitation!

H. Aarnio et al., manuscript in preparation

Use of nanostructured TiO_2 for hybrid solar cells



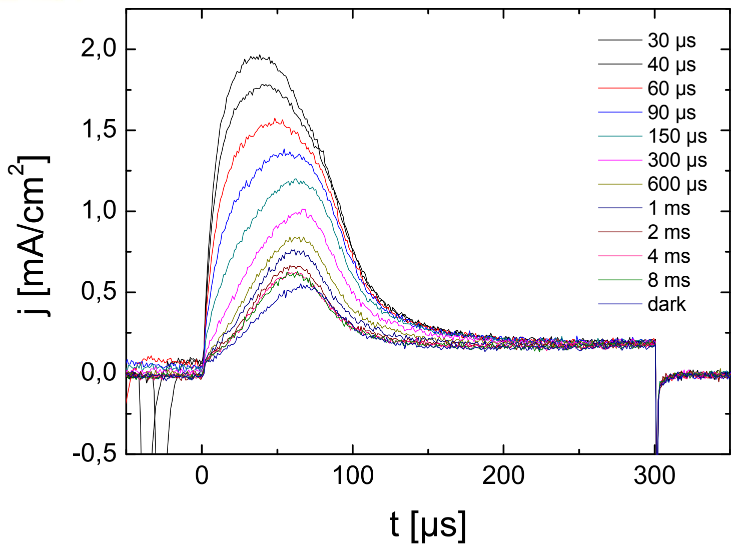


Nanocrater monolayer

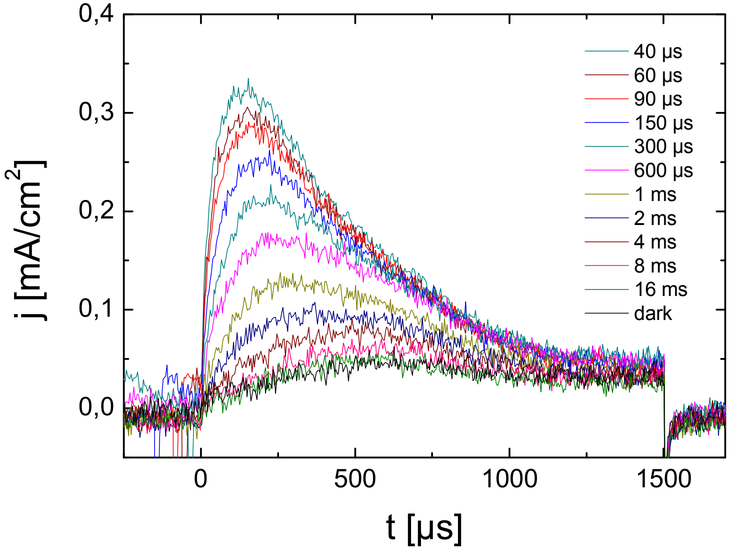
- Access to substrate through TiO_2 pores
- Charges can dissociate at:
  - — P3HT:TiO_2
  - — P3HT/PCBM
  - — Dye:TiO_2 interface
- Extraction can take place directly to ITO or through TiO_2
- Effective charge screening?
- Possibility to expand the absorption by using an IR-dye

S. Sanden, Q. Xu, J.-H. Smått, et al.,

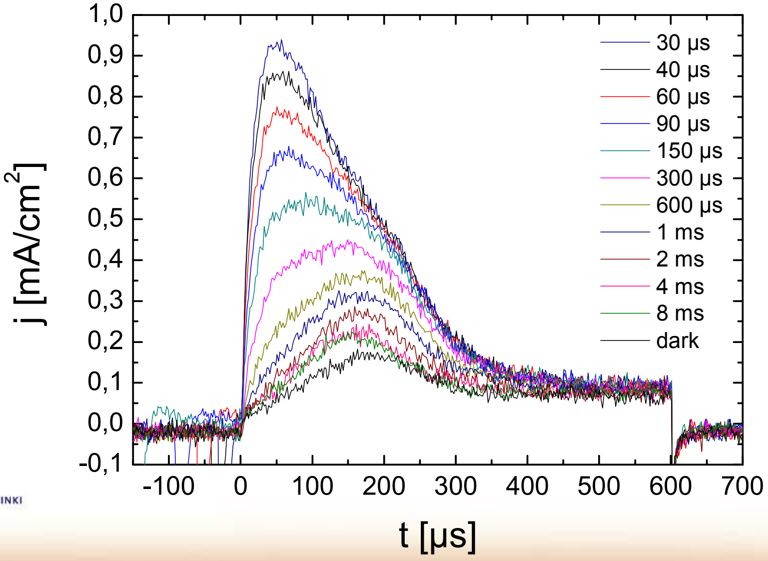
300 K, V_{off} = 0,05 V



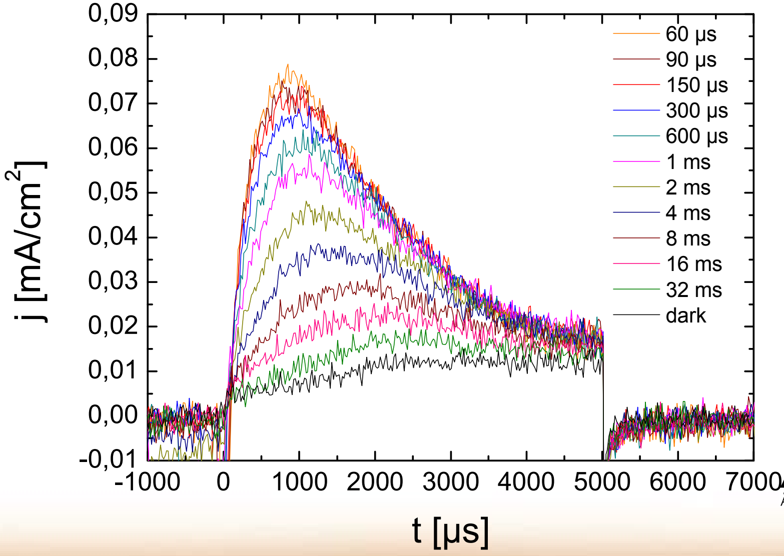
180 K, V_{off} = 0,14 V



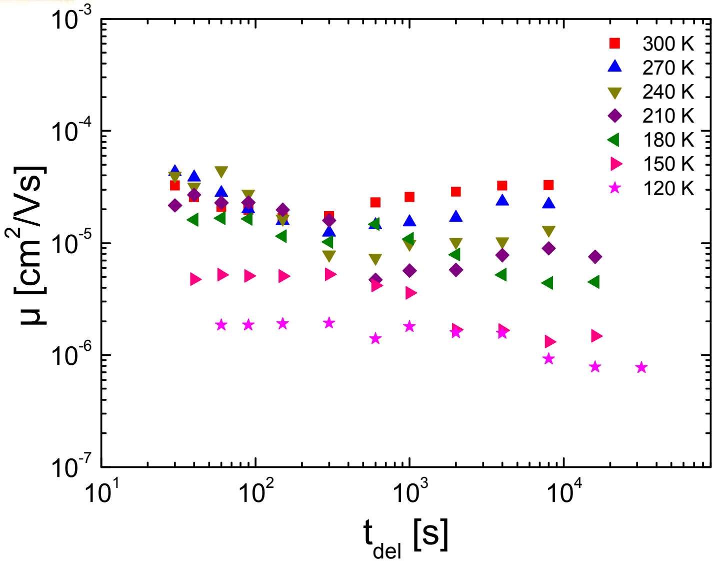
240 K, V_{off} = 0,07 V

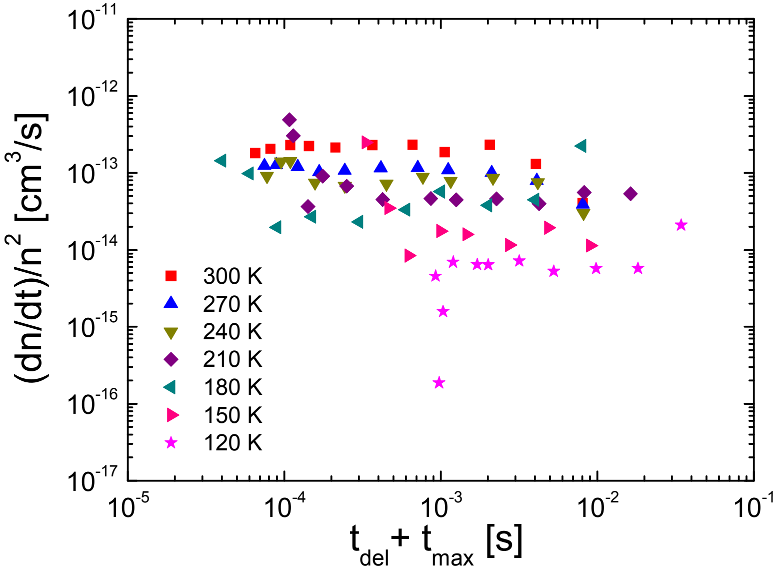


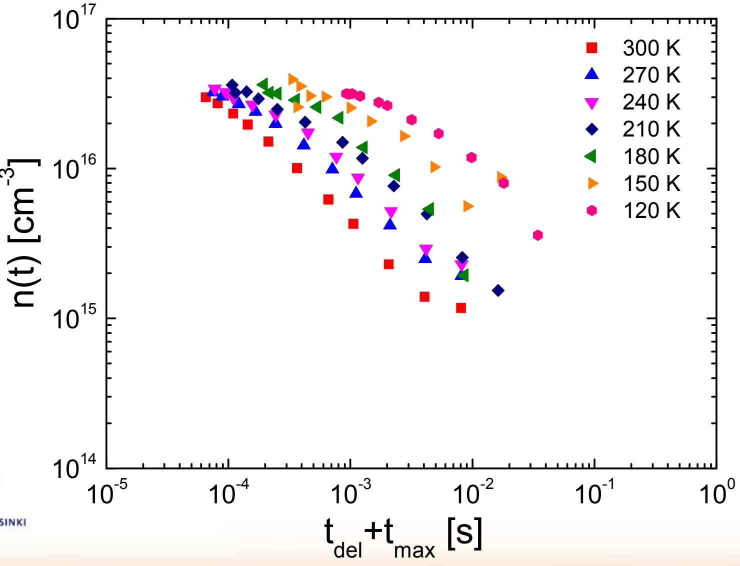
120 K, V_{off} = 0,15 V

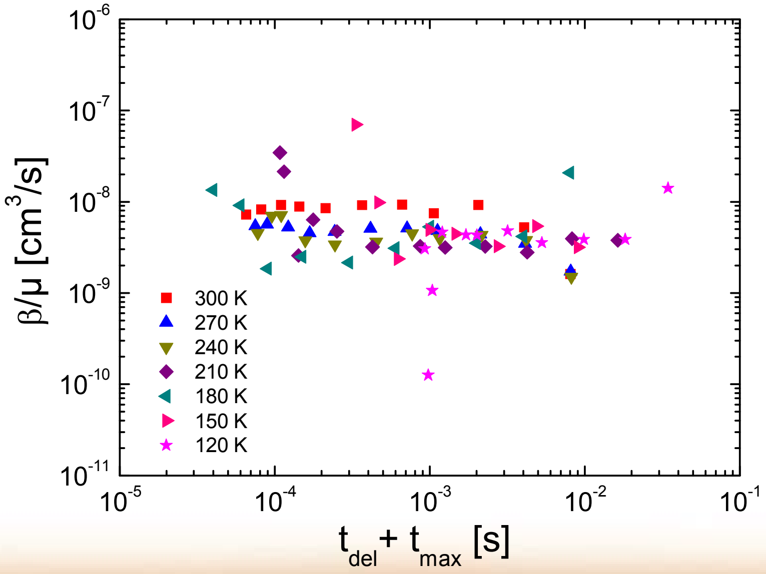


FUN MAT
FUNCTIONAL MATERIALS









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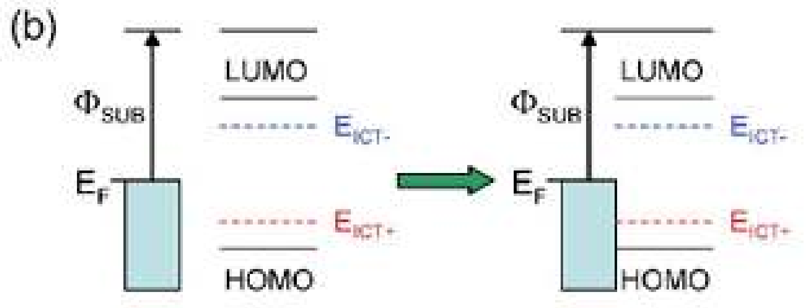
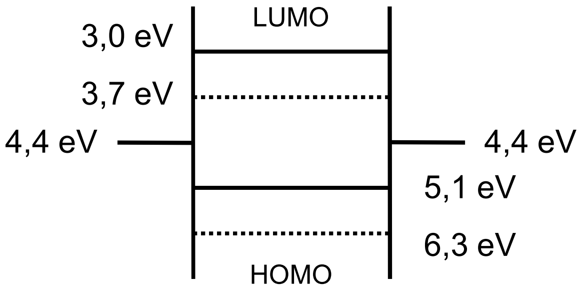
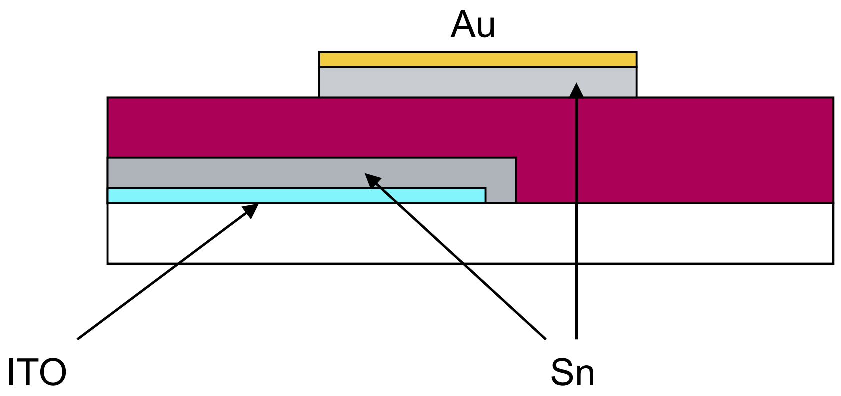
Measurements on Sn:Sn Devices

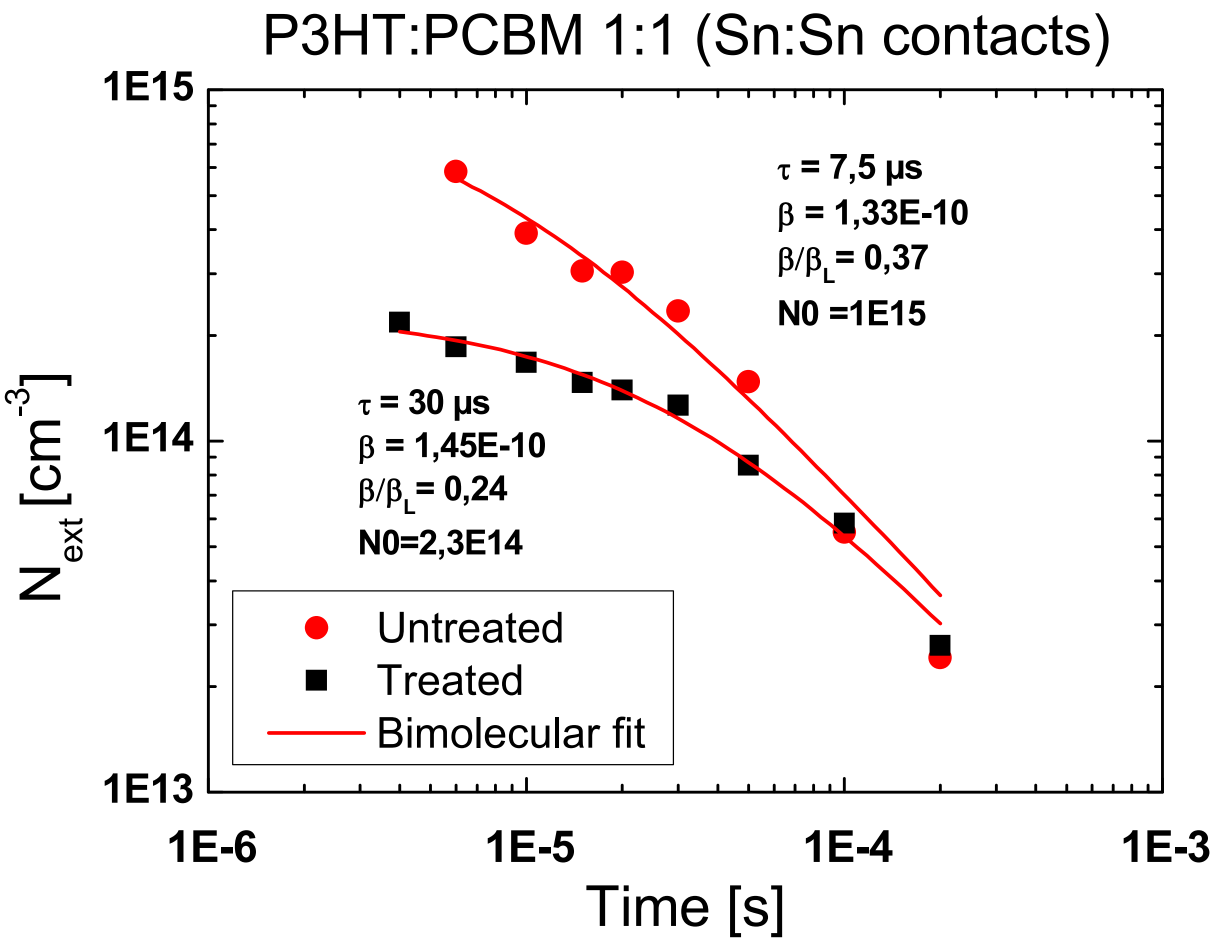






- The work function of Sn lies between the LUMO of PCBM and the HOMO of P3HT
- The low conductivity of Sn is problematic

Measurements on Sn:Sn Devices



Mathias Nyman

In collaboration with Fraunhofer ISE and Linköping niversity

Summary

- We have measured charge tranport and recombination in bulk heterojunction solar cells
  - We found greatly reduced recombination in annealed RR-P3HT/PCBM
- Demixing and formation of lamellar structures in P3HT seems to be very important
  - 2D Langevin model suggested
  - Neglecting diffusion underestimates the recombination time in 2D
- Photoinduced absorption shows that 2D delocalized polarons are generated even with sub-gap excitation
- Hybrid interfaces offer new challenges

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Thank You!

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