筑波大学
University of Tsukuba

TIMS

ESRによる高効率有機太陽電池の評価と素子特性向上

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数理物質融合科学センター（CiRfSE）第１回ワークショップ、筑波大学、
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Outline

1. Electron spin resonance (ESR)

New analytical method of organic solar cells

2. ESR study of organic solar cells

Direct observation of charge accumulation during device operation

1) P3HT:$PC_{61}BM$ blend films

Power conversion efficiency 3.5%

2) PTB7:$PC_{71}BM$ blend films

High power conversion efficiency 8.5%

Light-induced ESR and performance of devices

⇒ analyze the internal states of solar cells

Intrinsic deterioration mechanism

3. Summary

Why ESR is useful for organic devices?

Traditional research methods for organic devices

- Electrical measurements (current, voltage,…)
- Scanning microscopes (AFM, STM,…), etc.

cannot directly observe **internal states** in organic devices.

⇨ Understanding of device operation
Improvement of device performance

Advantages of ESR for organic devices:

- In situ direct observation of internal states in organic devices
- High sensitive and high precision analysis at molecular level
  $\sim 10^{10}$ spins are enough for ESR measurement
- Quantitative measurements of charges with spins in devices

First ESR application to organic devices was reported in 2004

J. Phys. Soc. Jpn. **73** (2004) 1673.

Principal of ESR and system

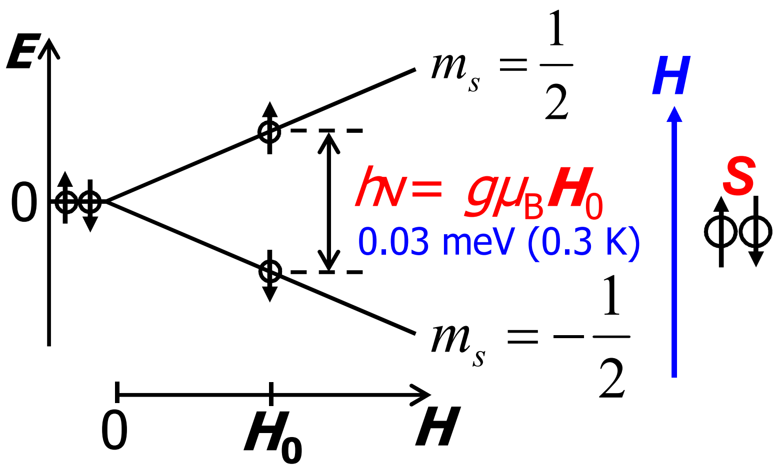
High sensitive and precision analytical method
Evaluation of organic devices at the molecular level

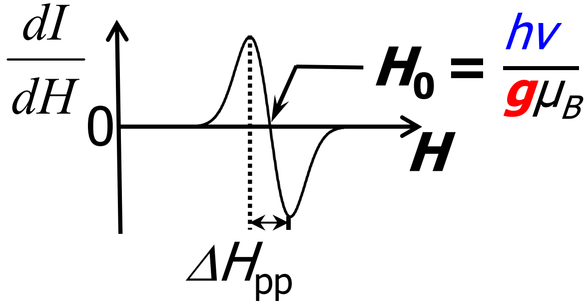
Principle of ESR

Electron energy in magnetic field H

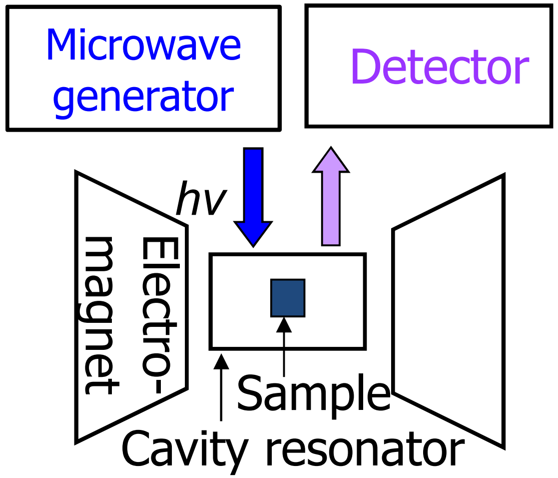
Spin Hamiltonian:

$\mathcal{H} = \mu_B \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} = g\mu_B H m_s \quad (m_s = \pm 1/2)$





ESR system



Microwave resonant absorption in magnetic field for charges with **magnetic moment, spin *S***

Resonant magnetic field: ***g* value**
A unique value for material

Organic solar cells

Features

- Advantages: low cost, flexible, light weight
- Disadvantages: low efficiency and durability

  Recently, ~12% efficiency has been reported

Sumitomo Chemical

Problems for practical application

- Further improvement of performance: more than 15%
- Elucidation of degradation mechanisms

Deterioration mechanism due to an intrinsic problem,

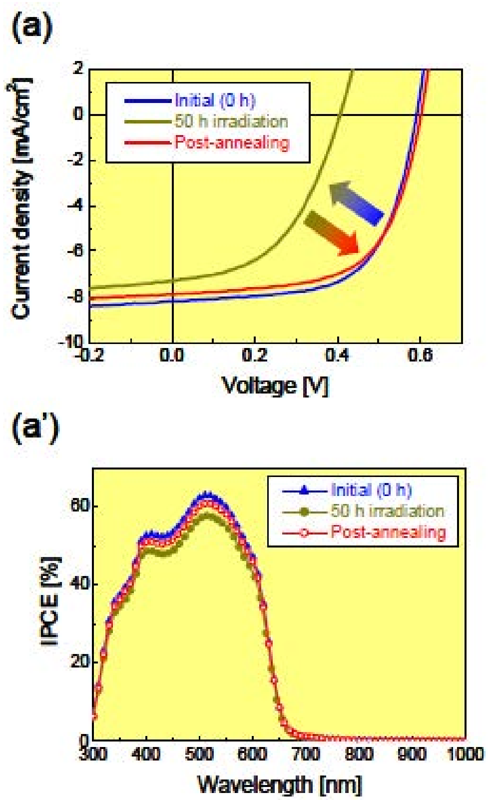
not due to extrinsic problems such as O_2 and H_2O

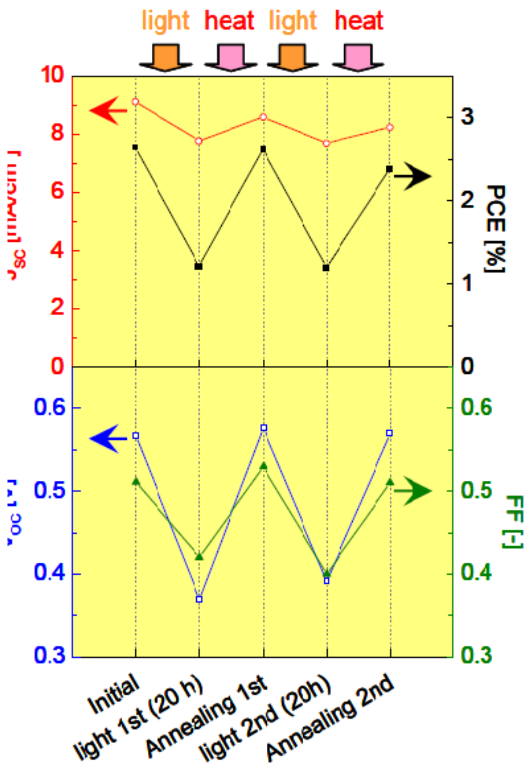
- Charge accumulation in devices is reported for polymer solar cells

Charge accumulation deteriorate device performance

Deterioration and recovery of performance

P3HT:PCBM solar-cell performance is deteriorated by irradiation and recovered by thermal annealing under N_2 condition





T. Yamanari et al., *2010 35th PVSC IEEE*, (2010) 001628.

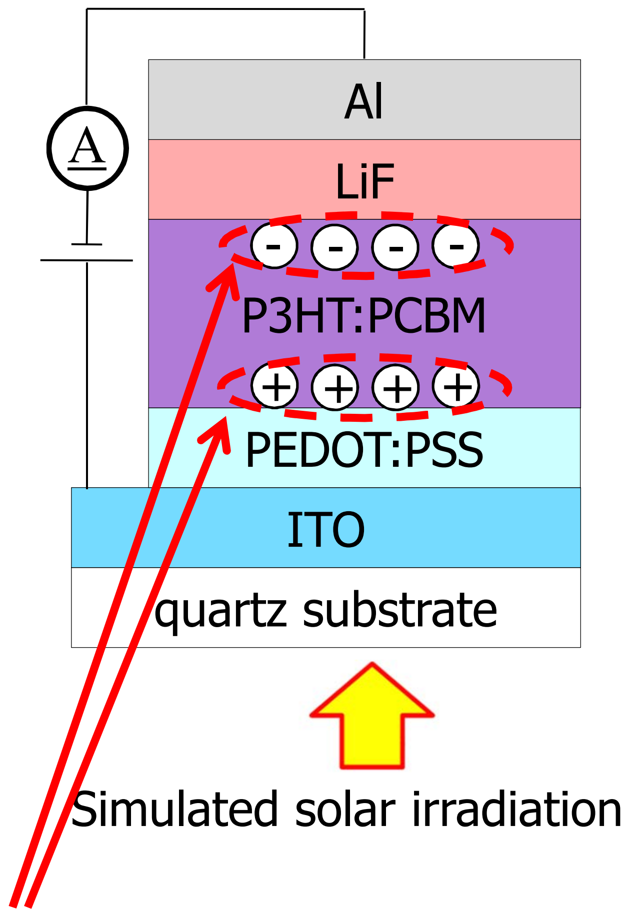
- Reversible
- No IPCE change
  No molecular degradation
- Intrinsic problem,
  not extrinsic problems

Deterioration due to charge accumulation

- Extrinsic problems can be solved by device sealing.
- However, the sealing cannot solve intrinsic problem.

Which molecules charges accumulate? Where?

Charge accumulation in organic solar cells



For ideal solar cell, no charge accumulation occurs

One photon creates hole and electron, which are collected by electrodes.

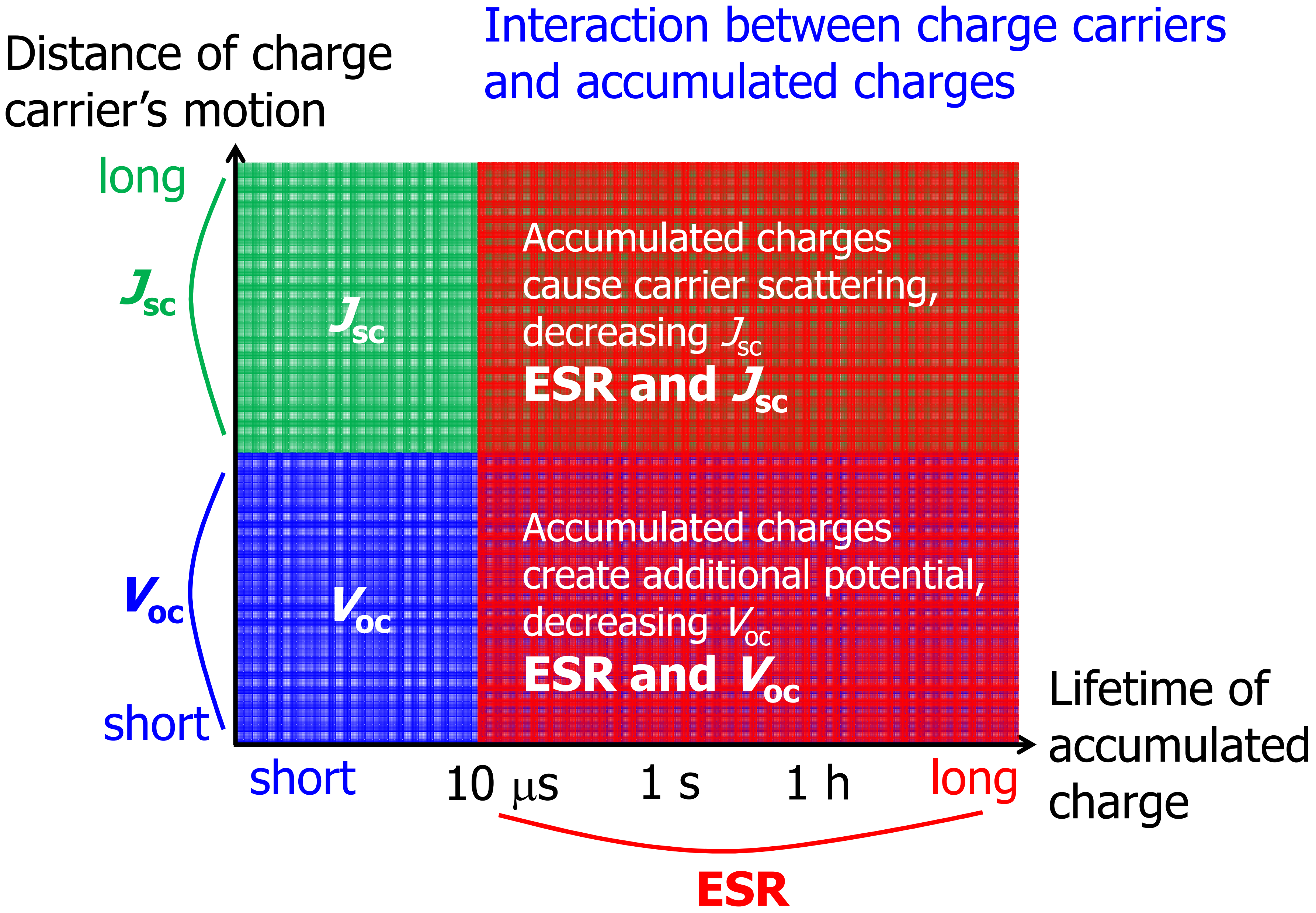
However, in actual solar cells, what happens?
...Charges accumulate.

Microscopic analysis of organic solar cells

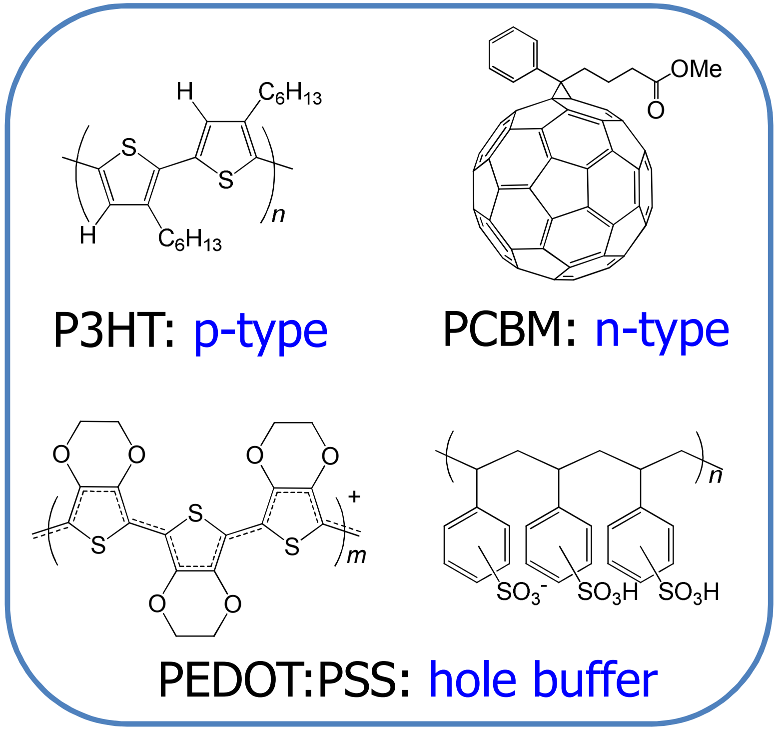
by detecting charge accumulation during device operation

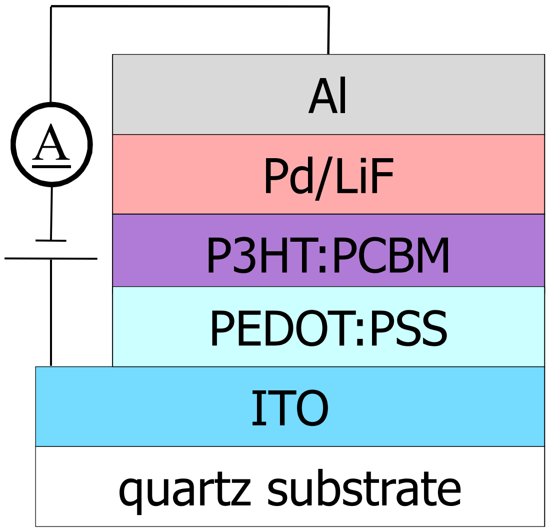
The sites can be clarified by unique *g* values for materials

What happens from charge accumulation?

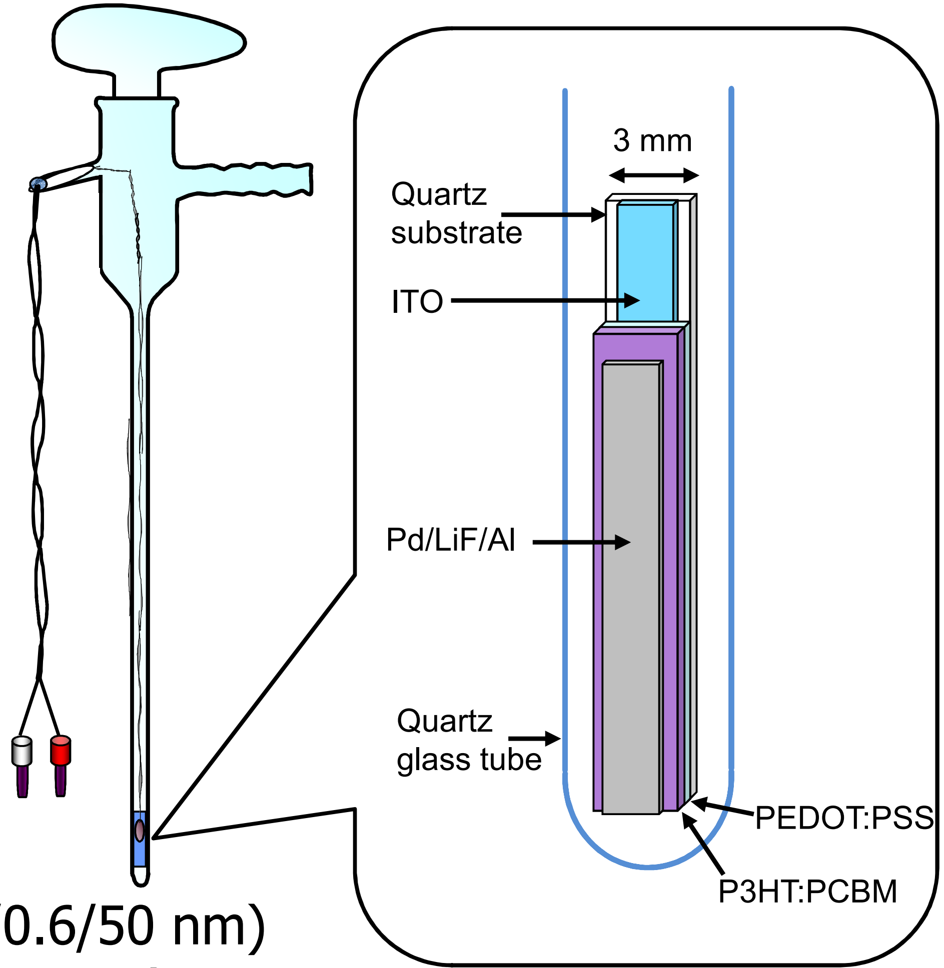


Device structure of P3HT:PCBM cells for ESR



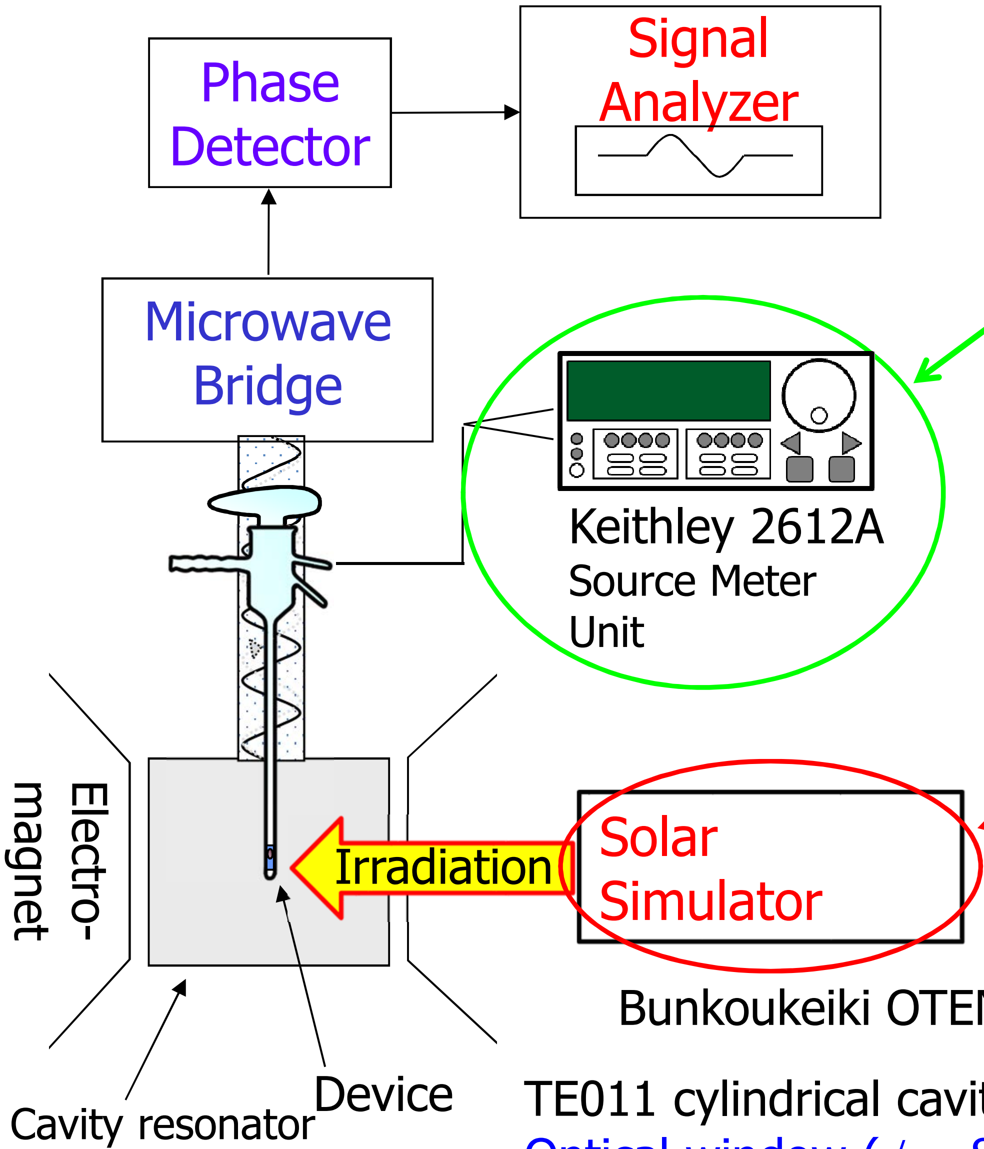


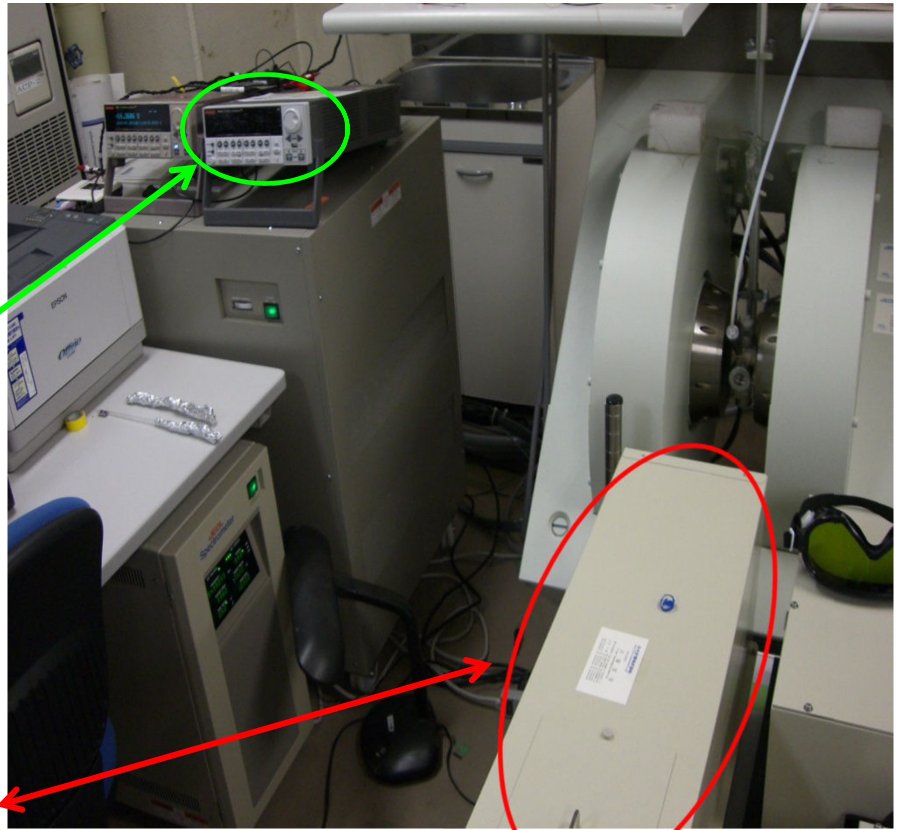
- Pd/LiF/Al (1.2/0.6/50 nm)
- P3HT:PCBM (165 nm)
  Bulk heterojunction
  active layer
- PEDOT:PSS (40 nm)
- ITO: transparent electrode



Device was sealed in an ESR sample tube under vacuum condition to avoid extrinsic problems

Light-induced ESR system





JEOL FA200 X-band ESR spectrometer

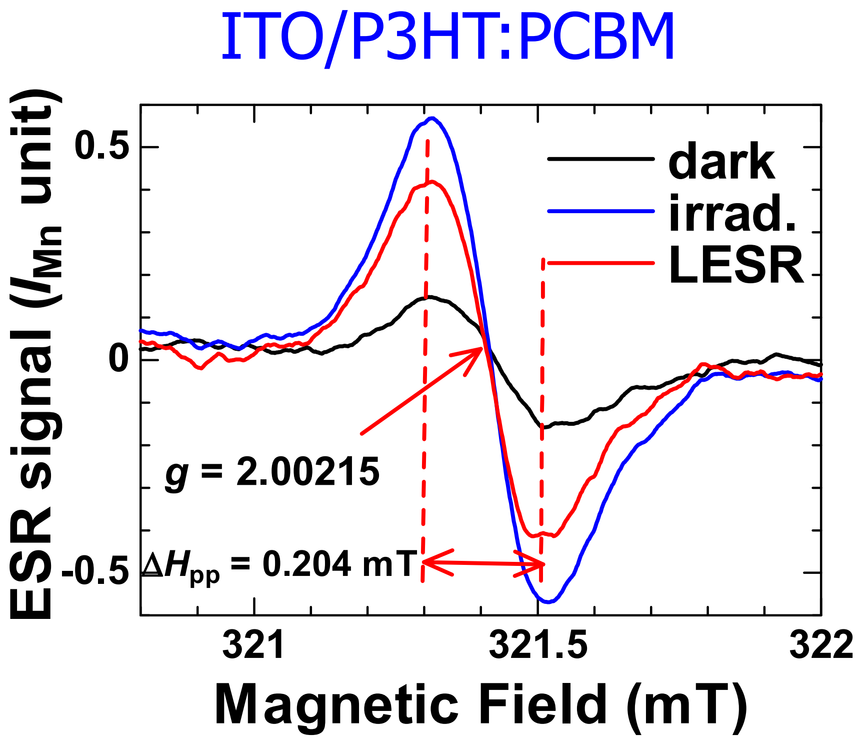
Bunkoukeiki OTENTOSUN-150BMX

TE011 cylindrical cavity
Optical window (ϕ = 8 mm)

Optical system: large irradiation area more than ϕ = 10 mm

Simultaneous measurements of ESR and device performance at RT

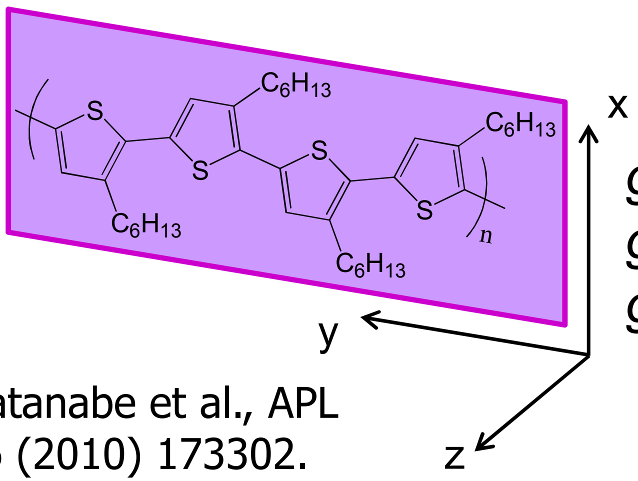
ESR signals of ITO/P3HT:PCBM



Light-induced ESR (LESR): difference between signals under irradiation and dark condition

	P3HT radical cation	PCBM radical anion
g-value	2.00152–2.00310	1.99845-2.00058

O. G. Poluektov et al., *J. Phys. Chem B* **114** (2010) 14426.



$g_x = 2.00310$
$g_y = 2.00152$
$g_z = 2.00203$

Watanabe et al., APL **96** (2010) 173302.

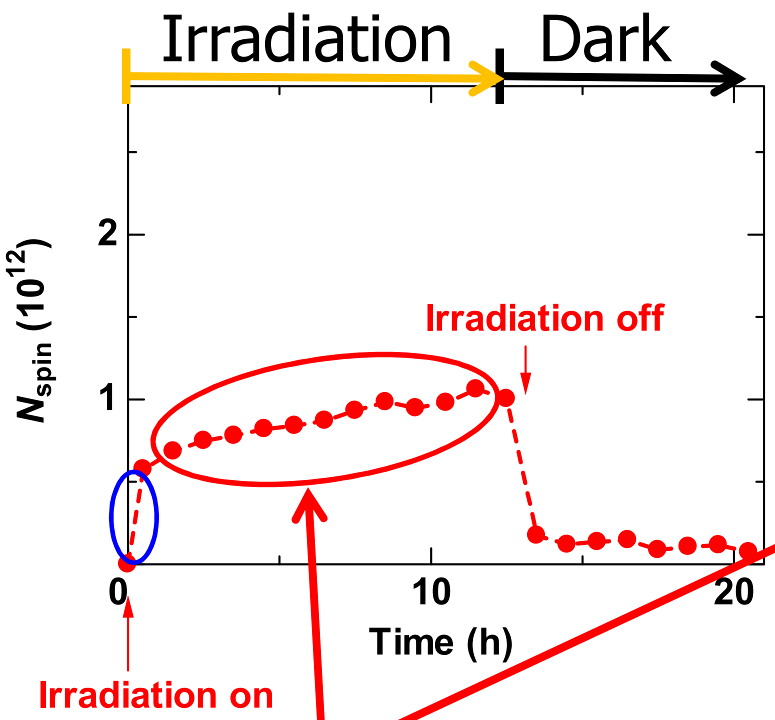
Hole accumulation in P3HT in the film by irradiation

Hole = Radical cation
= Positive polaron

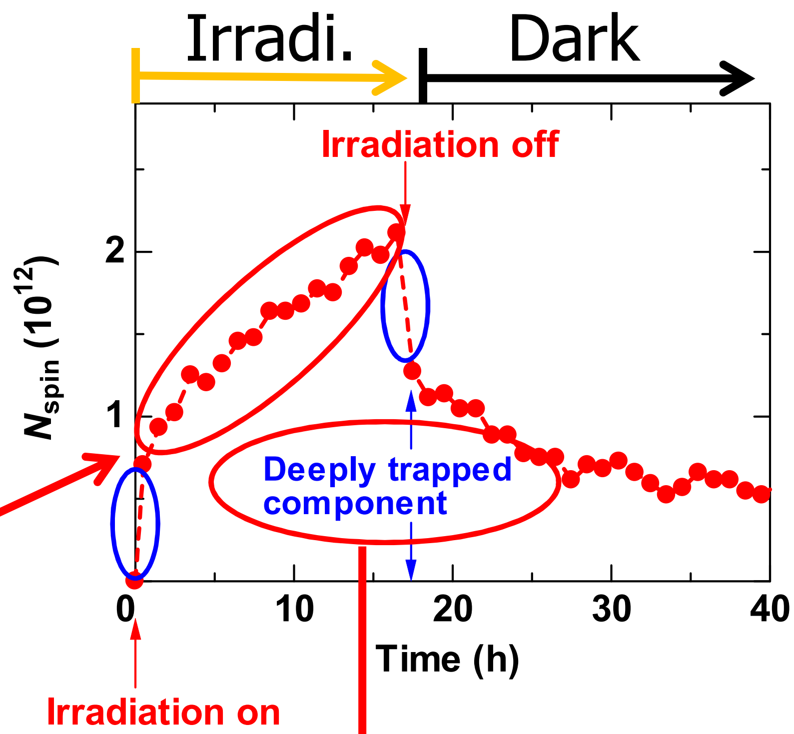
Absence of PCBM signal is due to the signal broadening from fast spin-relaxation time at RT

Transient response of hole accumulation

ITO/P3HT:PCBM



ITO/PEDOT:PSS/P3HT:PCBM



PEDOT:PSS insertion

⇩

Hole accumulation with slow rate is enhanced

Slow hole accumulation:

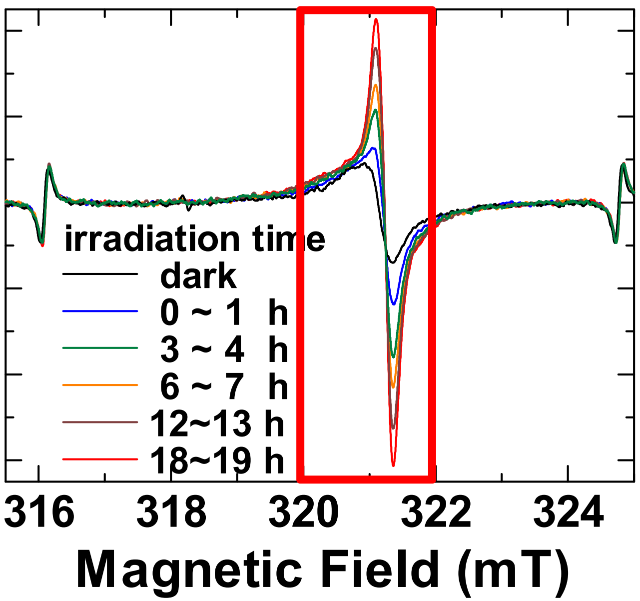
deep trappings in P3HT at PEDOT:PSS/P3HT:PCBM interface

Fast component:

bulk P3HT:PCBM materials

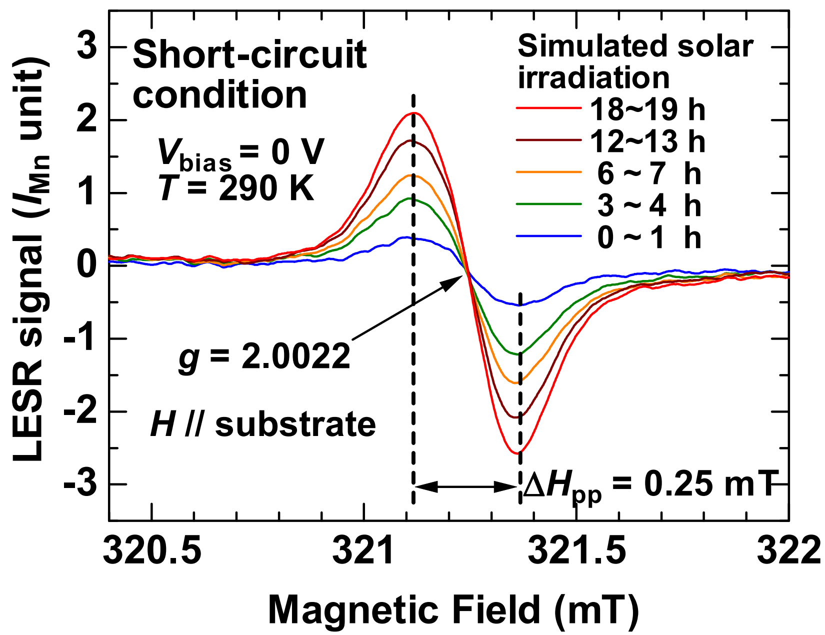
LESR signals under short-circuit conditions

ESR signals under solar irradi.



LESR

Increase in LESR signals



ESR parameters:
g = 2.0022, ΔH_{pp} = 0.25 mT

Consistent with those of holes in neat P3HT films

Hole accumulation in P3HT in the device by irradiation

Hole = Radical cation
= Positive polaron

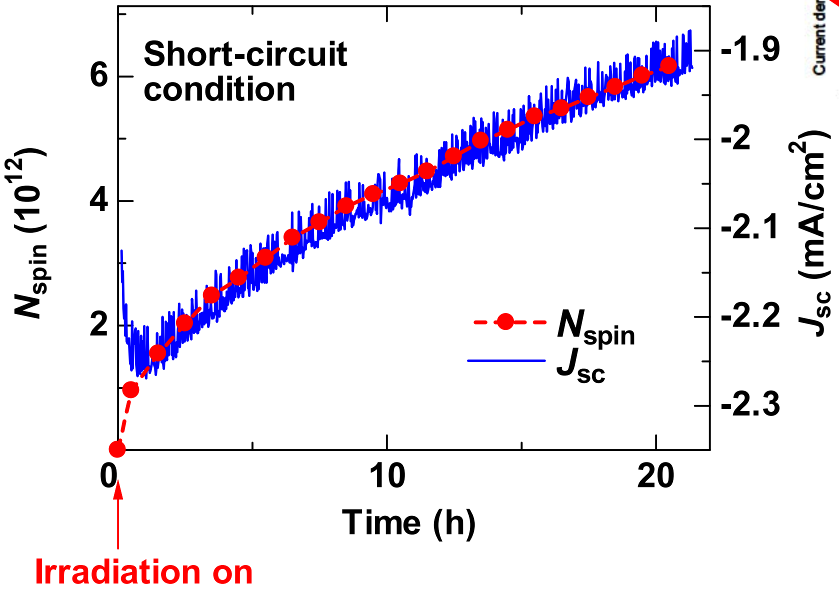
Adv. Mater. **25** (2013) 2362.

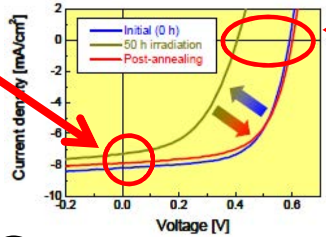
No electron accumulation in PCBM was confirmed from low temperature ESR measurements

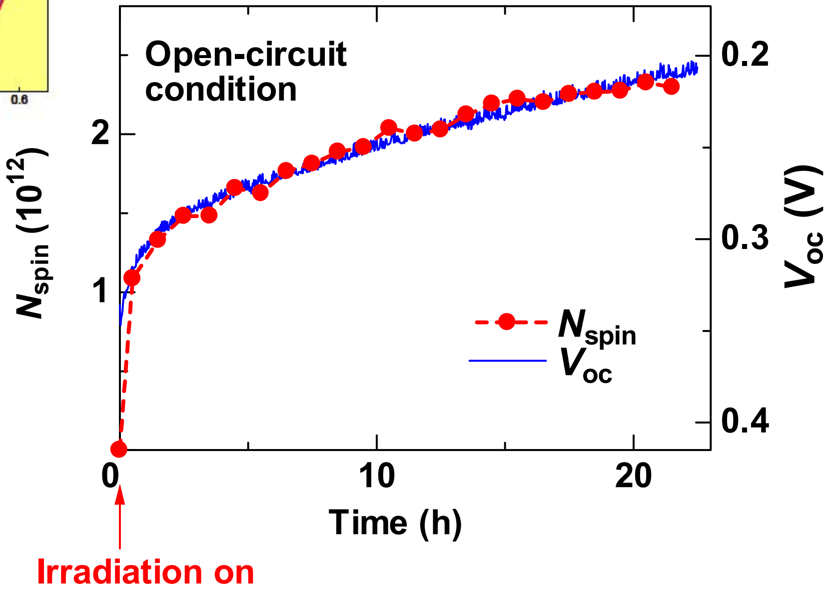
Hole accumulation and device performance

Short-circuit condition

Open-circuit condition







N_{spin}: number of accumulated holes in P3HT

Increase in N_{spin} ⟺ Decrease in J_{sc}, V_{oc}

Clear correlation

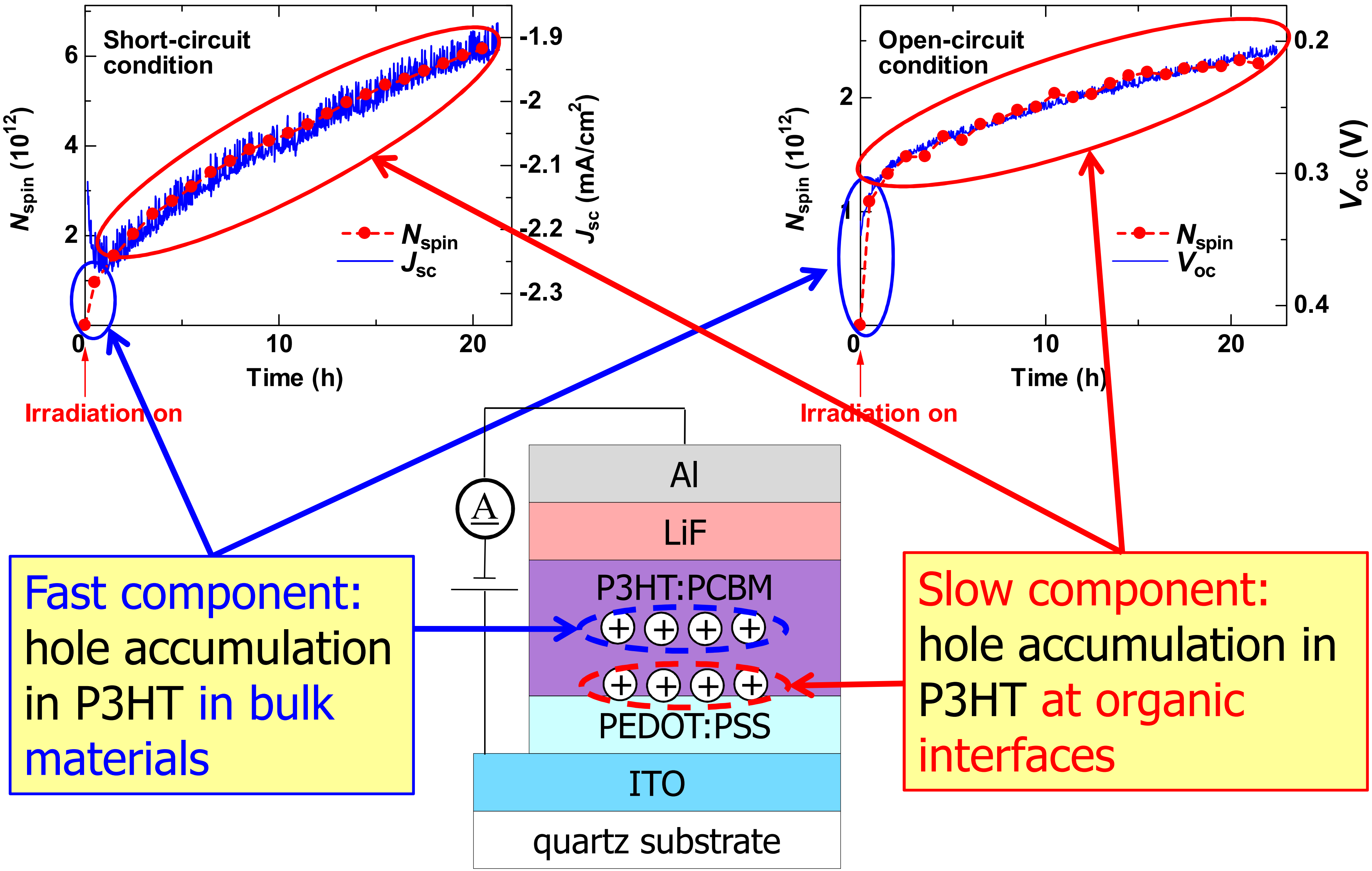
Hole accumulation in P3HT

Deterioration of device performance

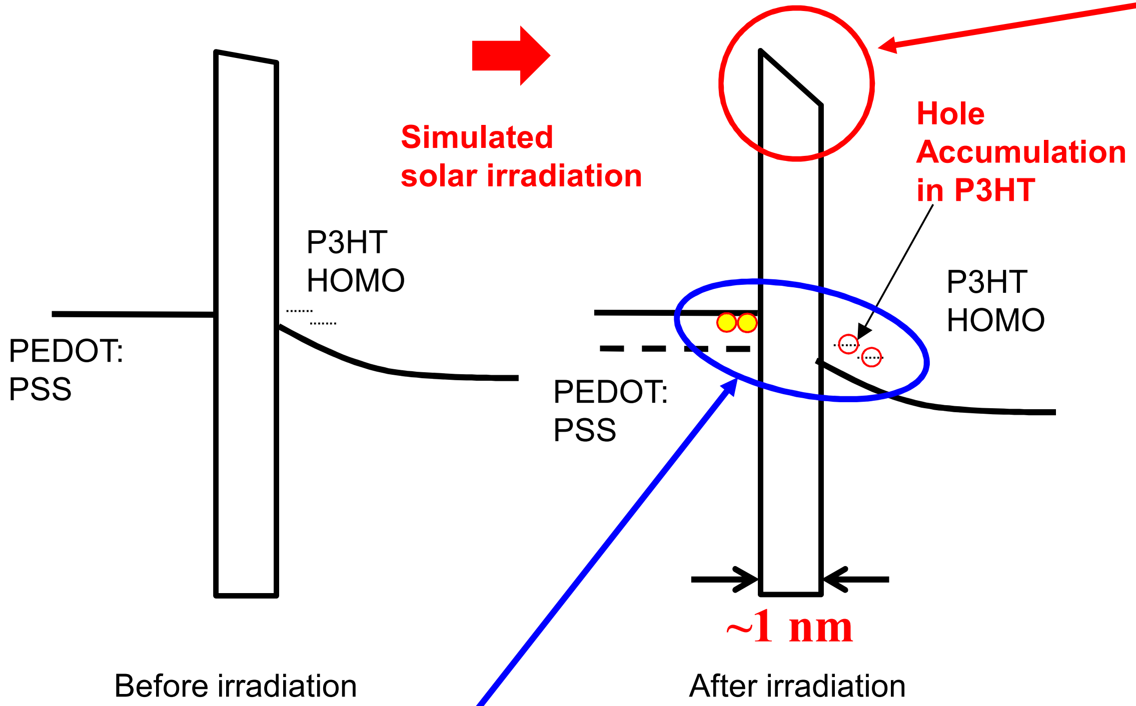
Adv. Mater. **25** (2013) 2362.

Intrinsic deterioration mechanism

Accumulation sites for fast and slow components

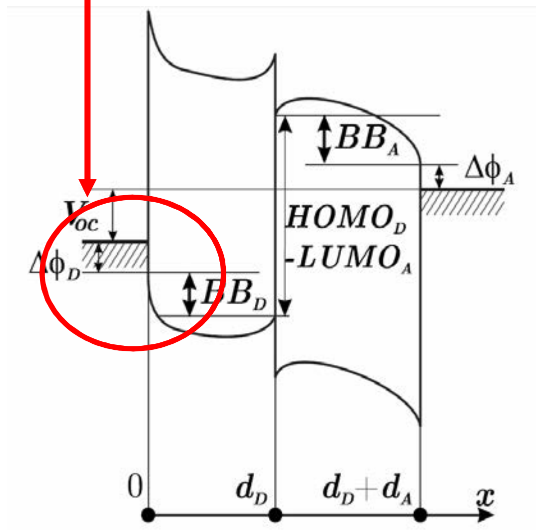


Mechanism of the decrease in V_{oc}



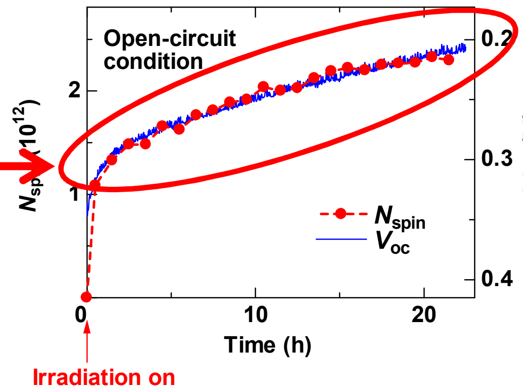
Interfacial electric dipole layer

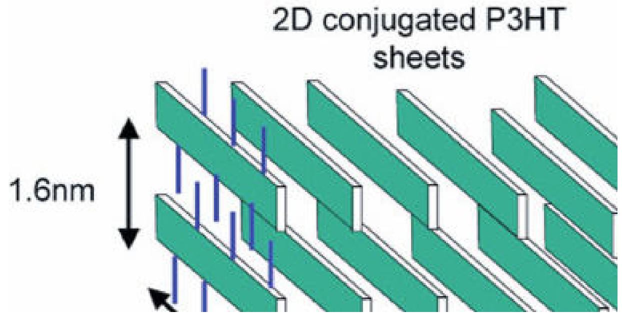
Vacuum-level shift



$$V_{OC} = |HOMO_D| - |LUMO_A| + BB_D + BB_A - \Delta\phi_D - \Delta\phi_A$$

$$\Delta V_{oc} = \frac{ed}{\varepsilon_0 \varepsilon_r S} \Delta N_{spin}$$



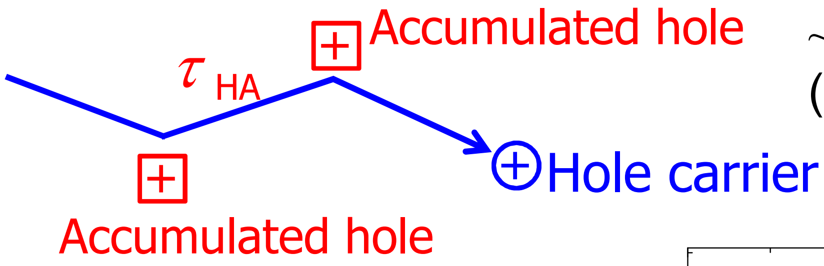


M. Brinkmann et al.,
Adv. Mater. **18** (2006) 860.

Mechanism of the decrease in J_{sc}

Matthiessen's rule

$$\frac{1}{\tau} = \frac{1}{\tau_{SC}} + \frac{1}{\tau_{HA}}$$

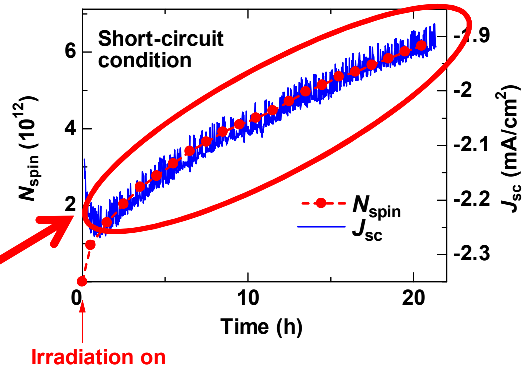


Surface con.:
~2×2 nm^2
(~4% per unit)

τ : collision time of carrier scattering

τ_{SC} : w/o hole accumulation

τ_{HA} : w/ hole accumulation



$$\Rightarrow \quad \frac{1}{\mu} = \frac{1}{\mu_{SC}} + \frac{N_{spin}}{c\mu_{HA}}$$

$$\therefore J_{sc} = ne\mu E = ne\frac{\mu_{SC}\mu_{HA}}{\mu_{HA} + (\mu_{SC}/c)N_{spin}}E$$

μ : mobility of device

μ_{SC} : w/o hole accumulation

μ_{HA} : w/ hole accumulation

N_{spin} : number of holes

J_{sc} decreases as N_{spin} increases because of carrier scattering by accumulated holes

K. Harada et al., *APL* **91** (2007) 092118.

Summary

ESR studies of internal states in organic thin-film solar cells

Charge accumulation during device operation

- $P3HT:PC_{61}BM$ polymer solar cells
- High efficiency $PTB7:PC_{71}BM$ cells

Intrinsic deterioration mechanism

ESR analysis:

useful knowledge for

understanding of device operation and improvement of device performance

at the microscopic level

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