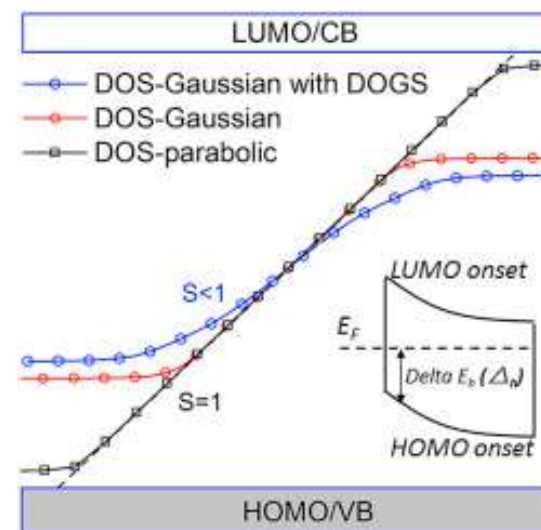
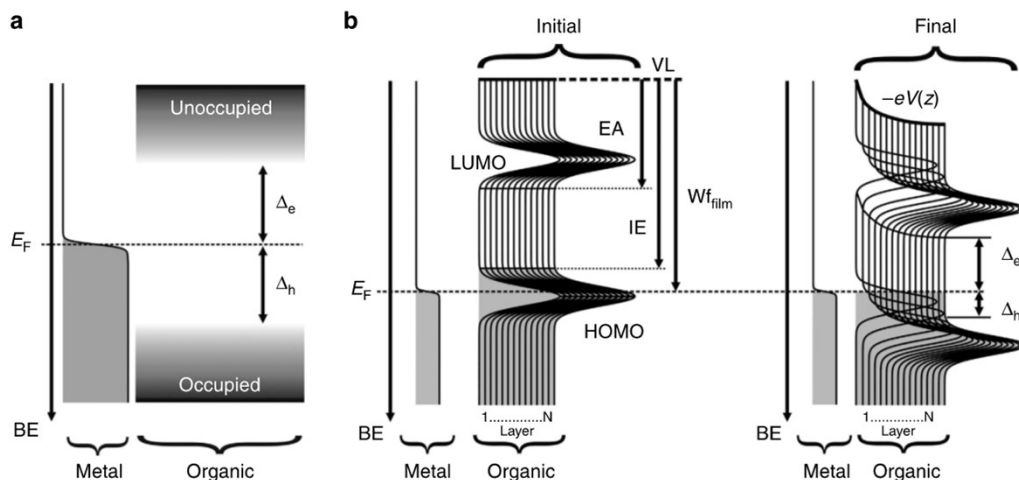
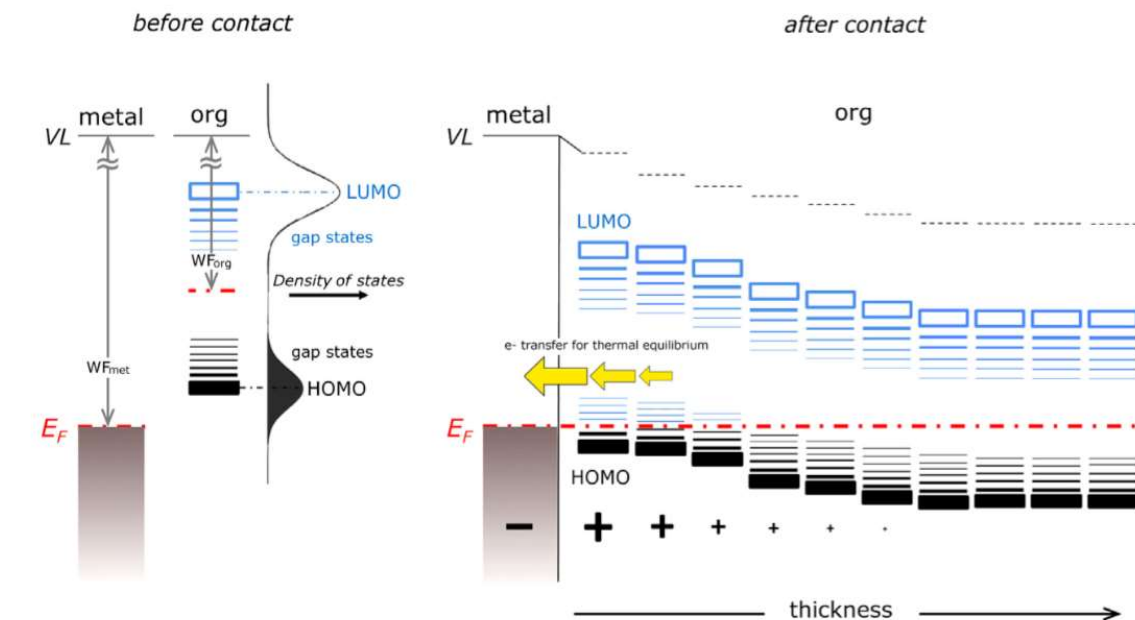


# How weak DOS is important: Energy level alignment

F. Bussolotti / *Journal of Electron Spectroscopy and Related Phenomena* 204 (2015) 29–38



Yang et al  
*Org. Elect.* 48, 172(2017)



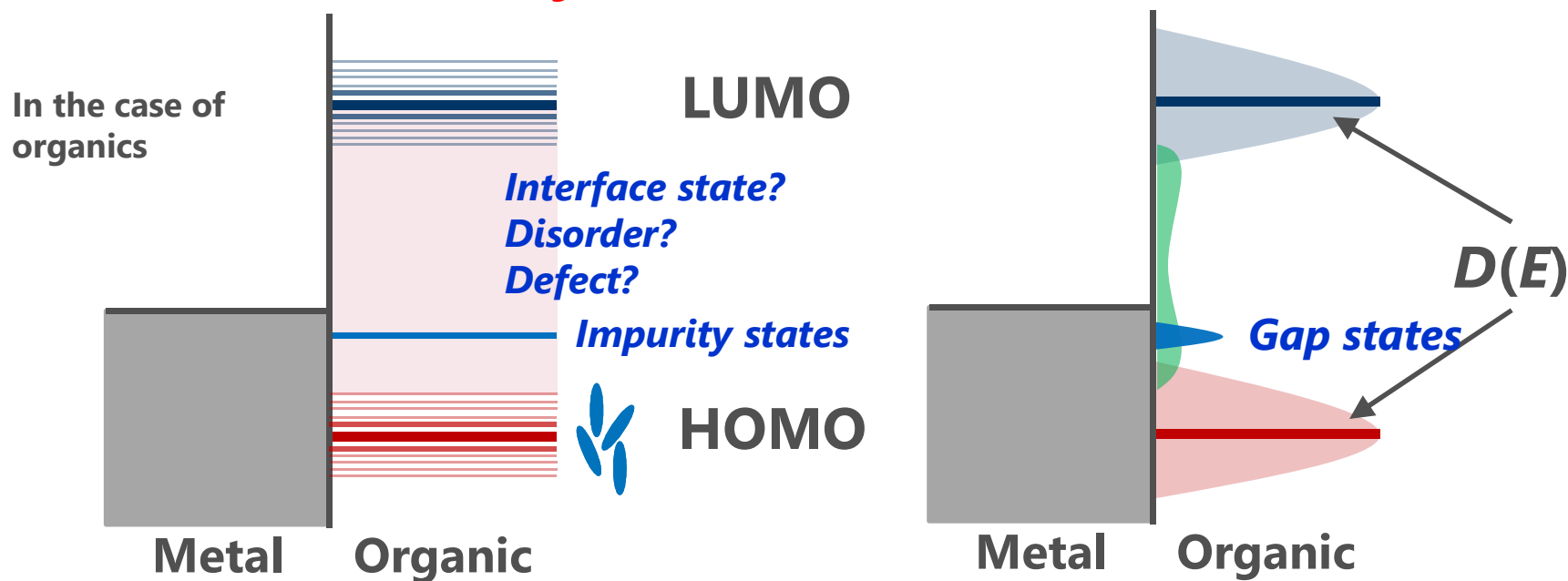
Importance of low density states in energy gap

1) Impurity (doping)

2) Defect • Disorder

# Gap States of Materials

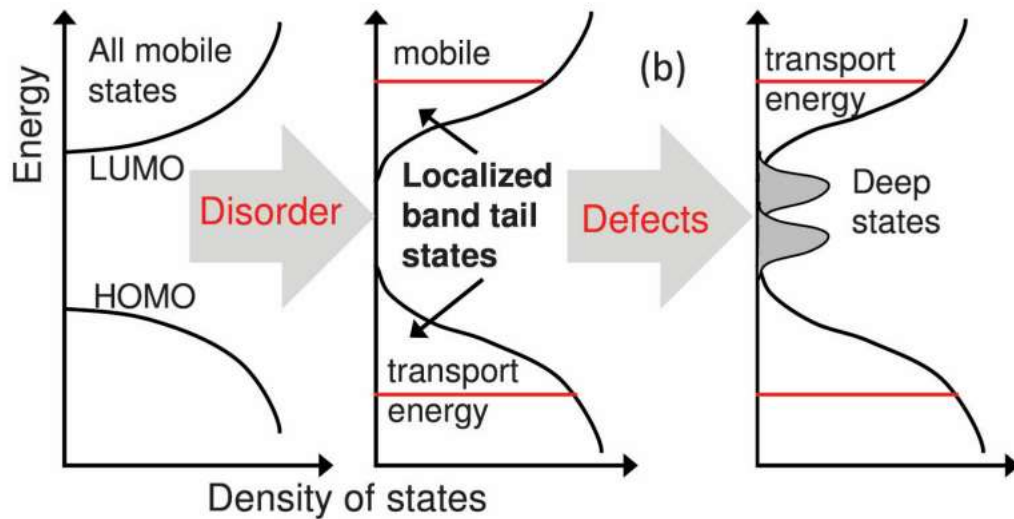
The electric properties of materials are governed by not only **HOMO (Valence band)** and **LUMO (Conduction band)** but also **weak density of states** in HOMO-LUMO gap.



**"Gap states"** are important for...

- ✓ Energy level alignment and carrier injection
- ✓ Control of Fermi level position → p-type, n-type
- ✓ Carrier trap → Electric transporting nature

# DOS in energy gap has been evaluated by using indirect methods such as electric measurements and optical



Band Tail

$$D(E) \propto \exp\left(-\frac{E}{E_0}\right)$$

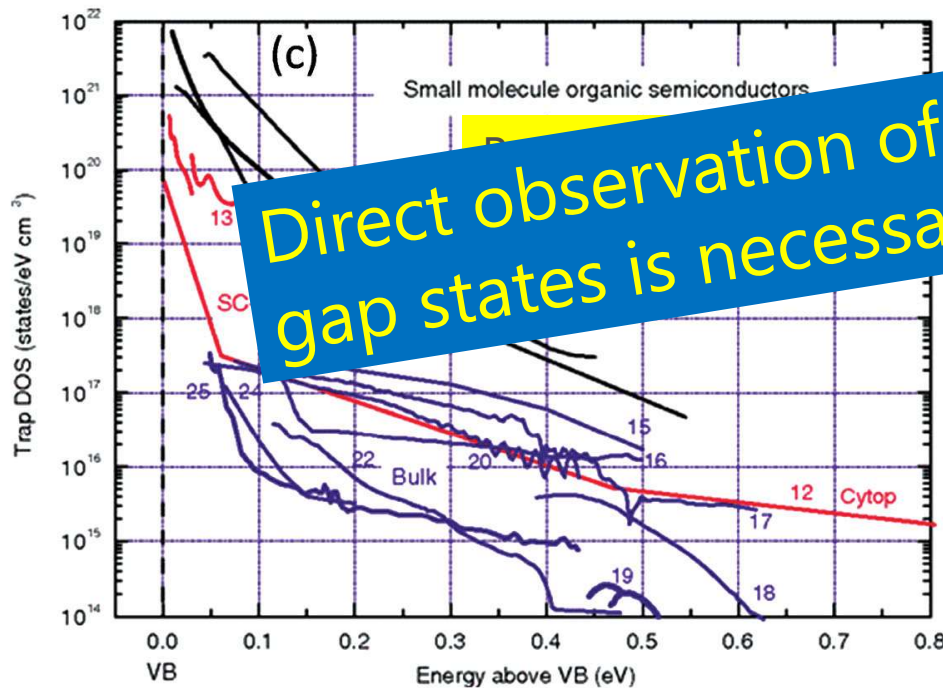
$E_0$ : decay parameter

Urbach tail

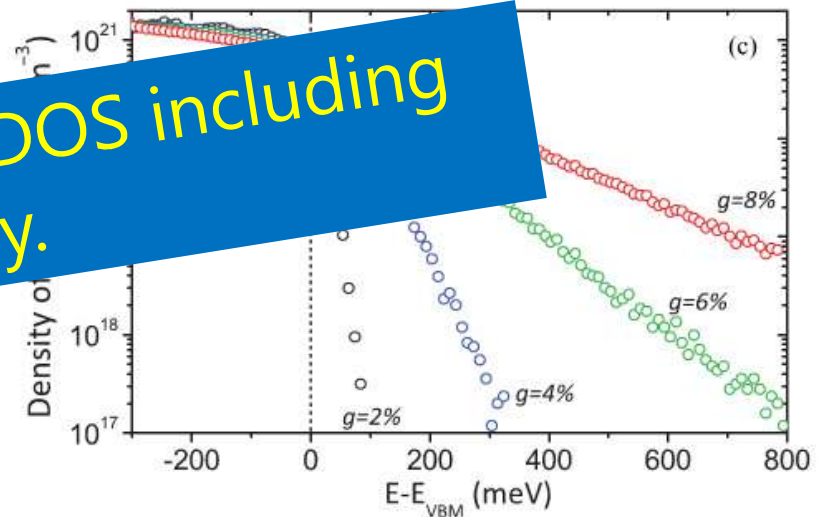
Joint-density-of-state

$$I \propto \int D(E)D(h\nu - E)dE$$

R. A. Street, *Adv. Mater.* **2016**, *28*, 3814



Direct observation of DOS including gap states is necessary.



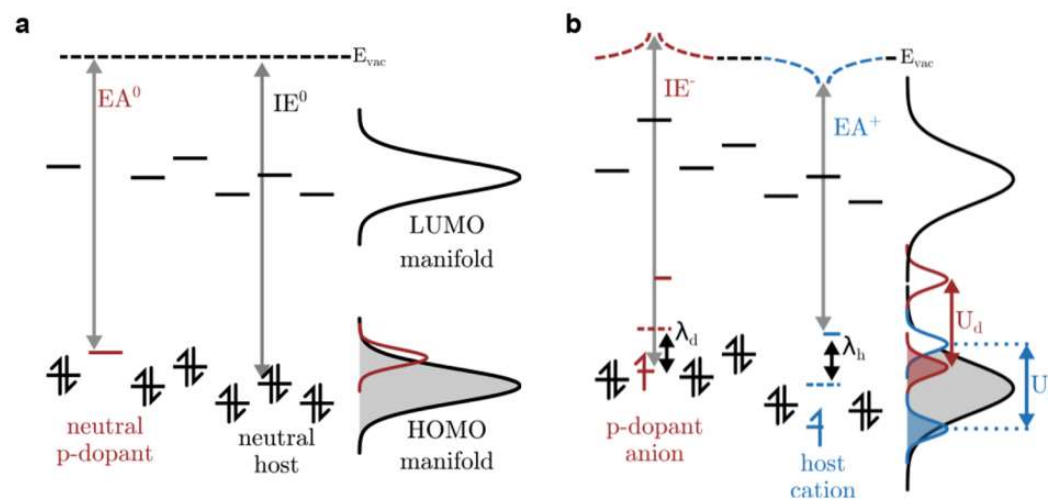
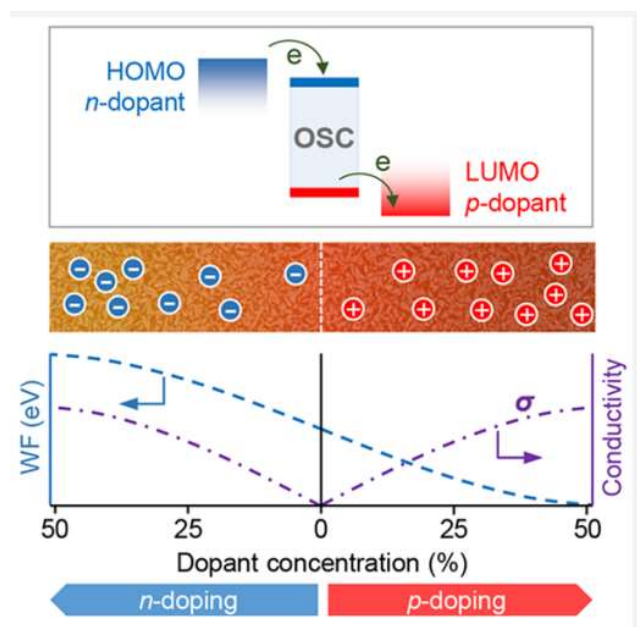
Rivnay et al., *PRB* **83**, 121306(R)(2011)

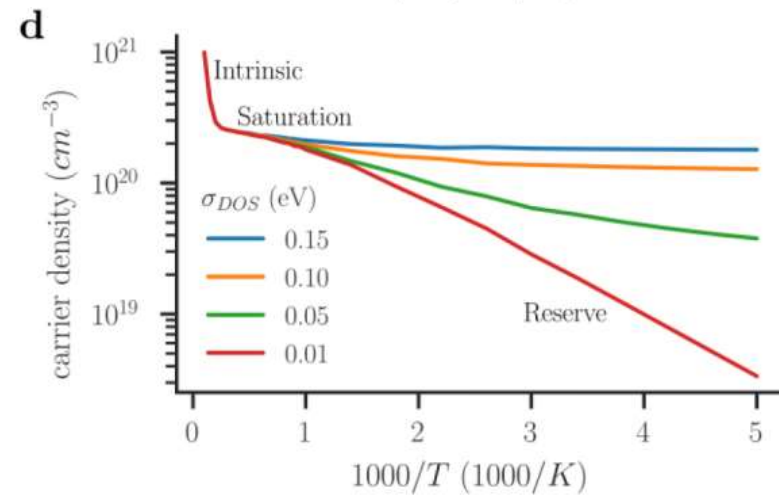
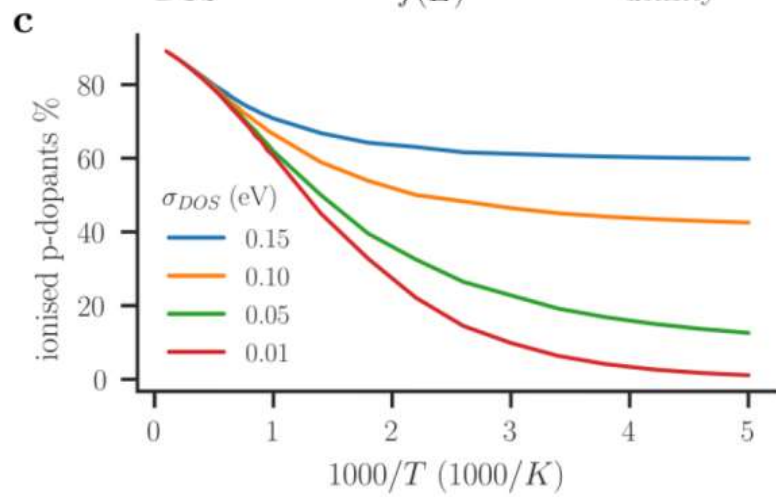
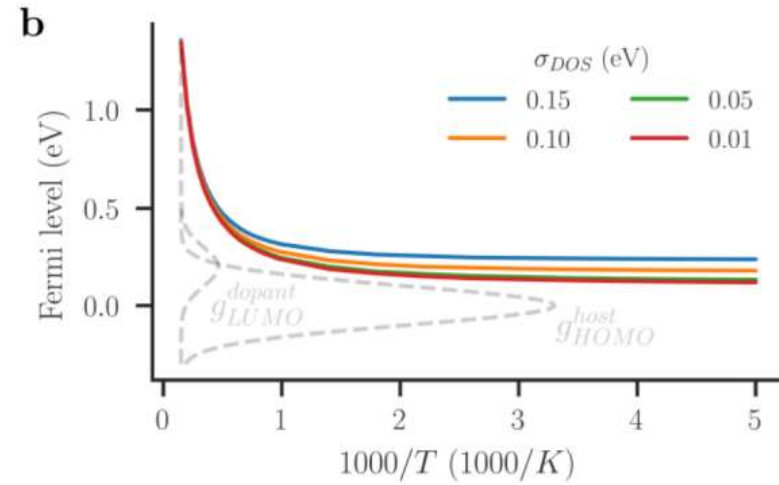
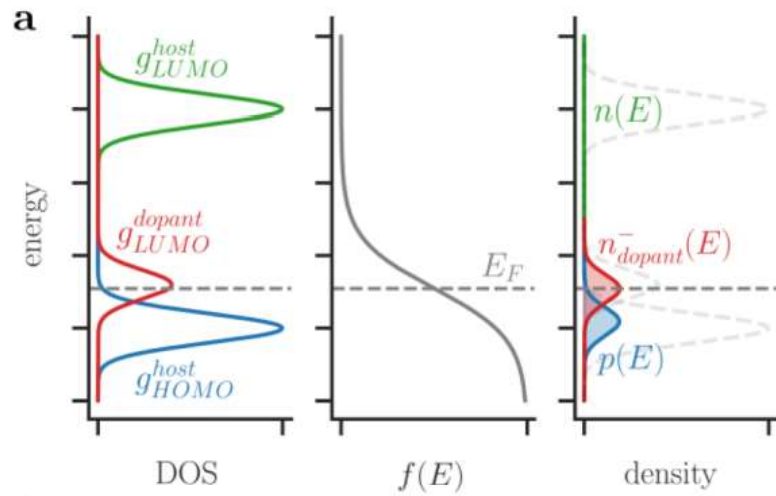
Paracrystallinity parameter  $g^2 = \langle d'^2 \rangle / d_0^2 - 1$

# 有機半導体のドーピング

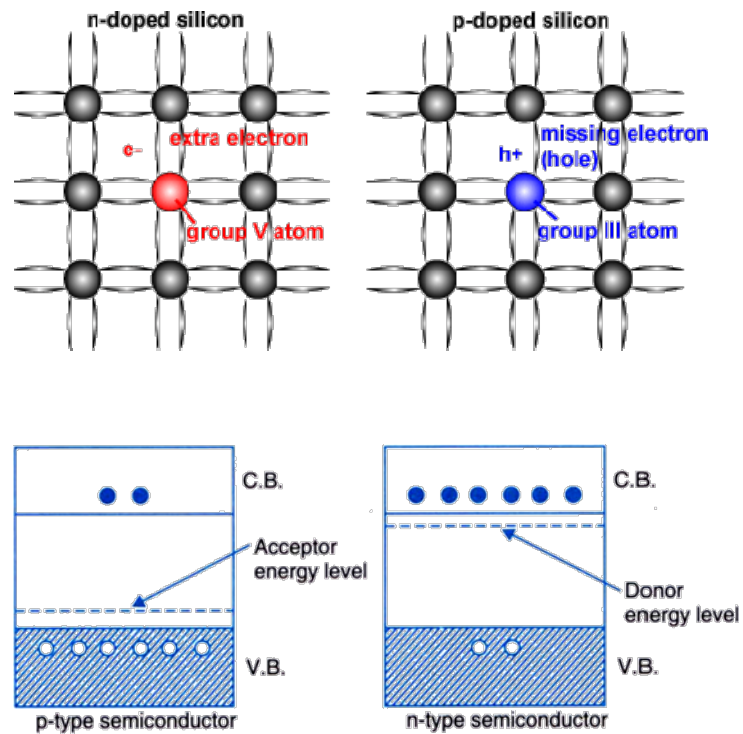
## Doping Approaches for Organic Semiconductors

Alberto D. Scaccabarozzi,<sup>\*,\*</sup> Aniruddha Basu,<sup>\*</sup> Filip Aniés, Jian Liu, Osnat Zapata-Arteaga, Ross Warren, Yuliar Firdaus, Mohamad Insan Nugraha, Yuanbao Lin, Mariano Campoy-Quiles, Norbert Koch, Christian Müller, Leonidas Tsetseris, Martin Heeney, and Thomas D. Anthopoulos<sup>\*</sup>









Impurity state is shallow for inorganic case

本質的に浅い不純物準位

Organic case

Hiramoto

<https://www.ims.ac.jp/news/2014/11/141118.html>

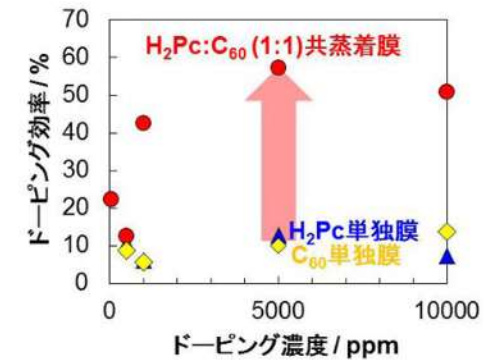


図1 ドーピング効率とドナードーピング濃度との関係。

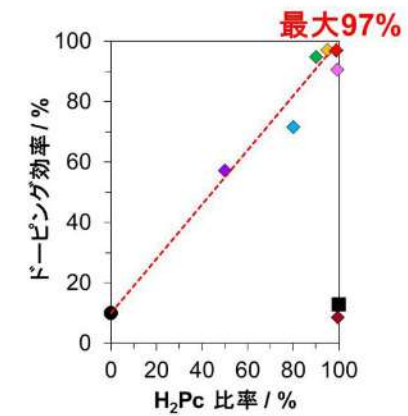
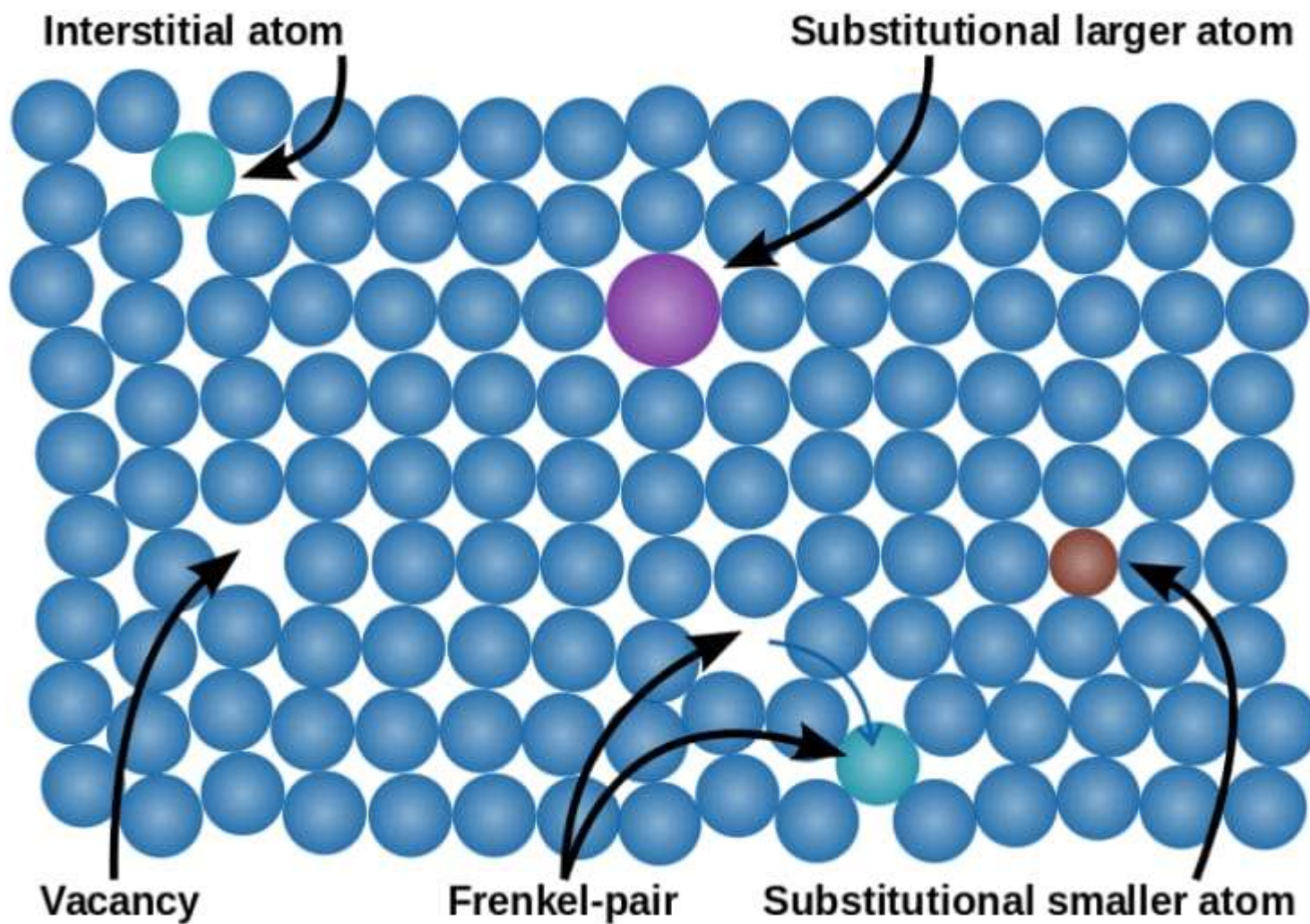


図2 ドーピング効率とC<sub>60</sub>:H<sub>2</sub>Pc共蒸着膜のH<sub>2</sub>Pc比率との関係。

欠陥

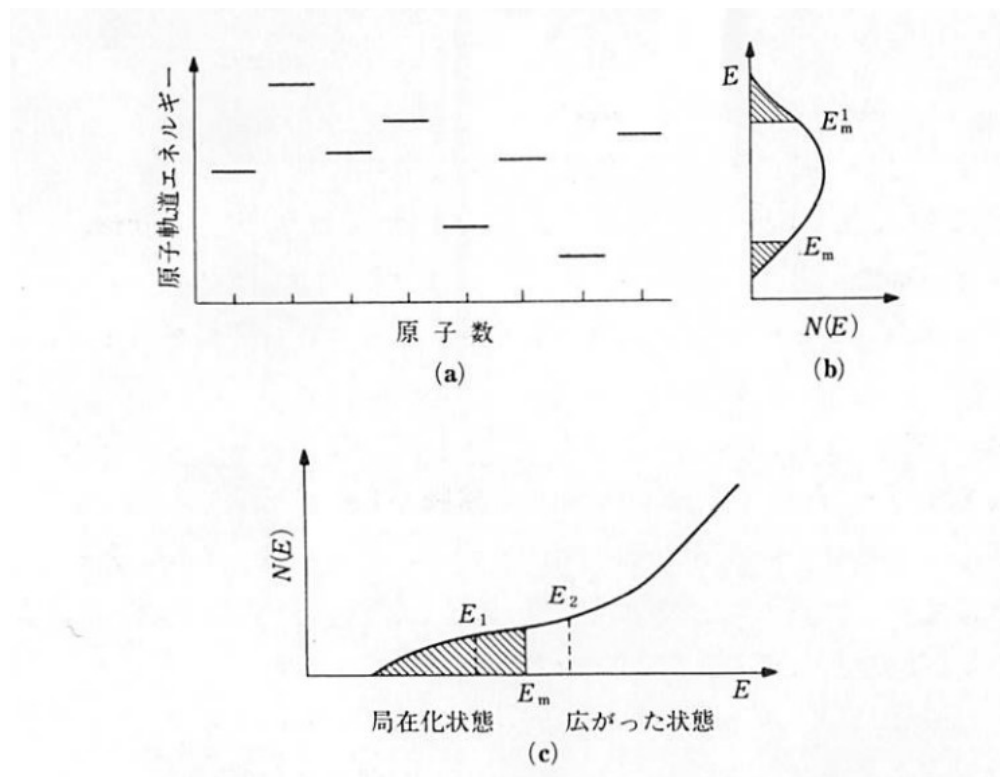


<https://sirs4quality.org/ja/difference-between-point-defect-and-line-defect>



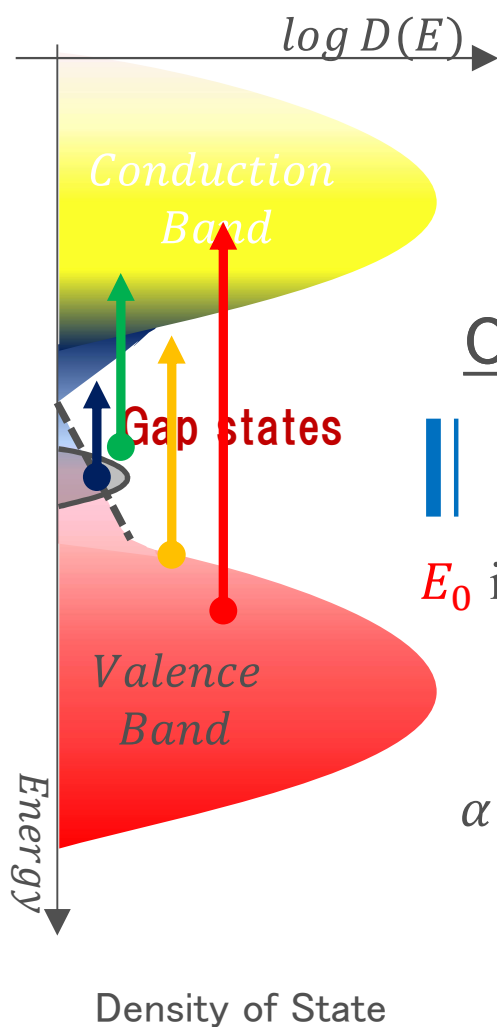


# Anderson localization



Mobility edge

# Gap states



Due to disorder and defects?

Energetically localized states

Tail states

Exponential decay  
 $\exp(-E/E_0)$

$E_0$  not directly measurable

## Optical Absorption



Urbach tail

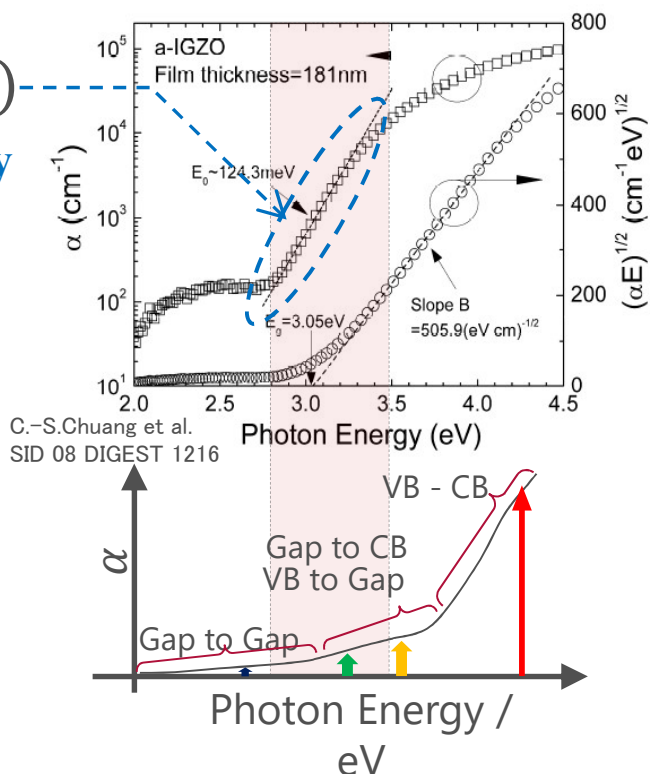
$\exp(-E/E_u)$   
Urbach energy

$E_0$  is estimated from  $E_u$

Joint density of states

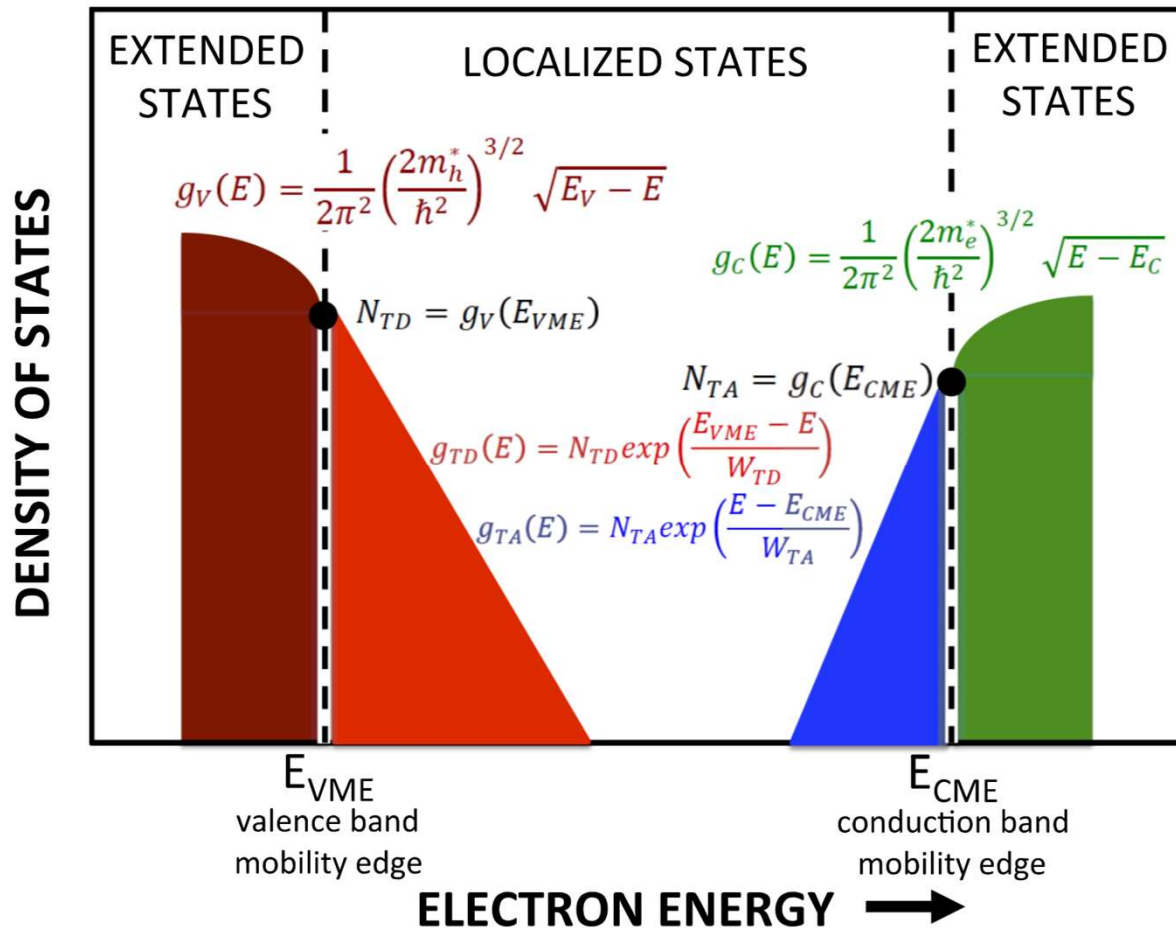
$$\alpha \propto \int |M_{fi}|^2 \frac{D(h\nu - \varepsilon) \cdot D(\varepsilon)}{d\varepsilon}$$

$E_u \neq E_0$



# Band Tail State

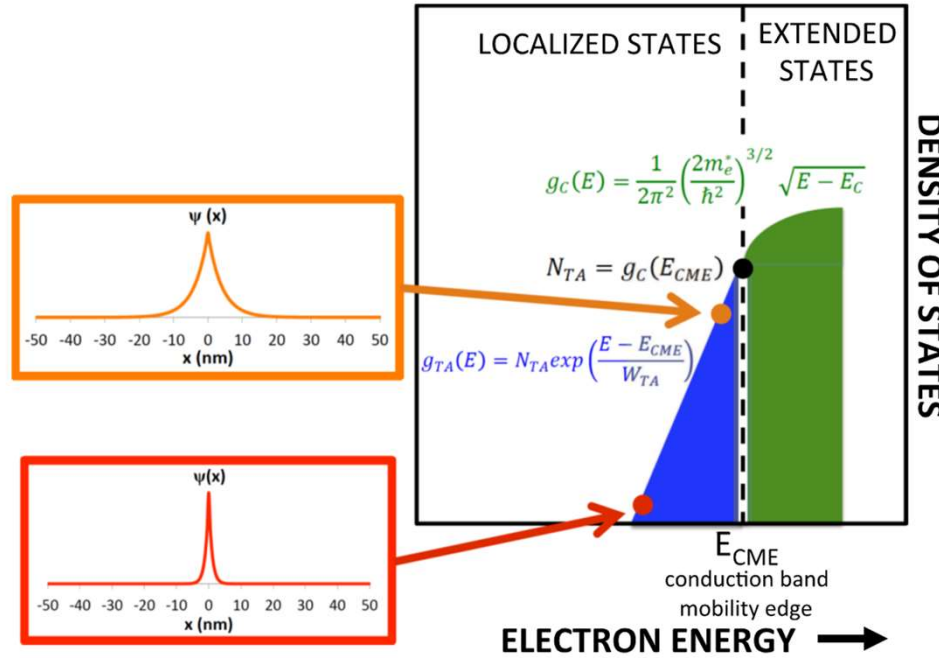
J. F. Wager, AIP ADVANCES 7, 125321 (2017)



Thermal, structural, impurity, and/or compositional disorder can all lead to the formation of band tail states.

Although it is evident that band tail states are exponentially distributed in energy as a result of disorder, their precise atomistic nature and a clear explanation for why they give rise to an exponential distribution are questions that seem to have not yet been answered to everyone's satisfaction.

J. F. Wager, AIP ADVANCES 7, 125321 (2017)



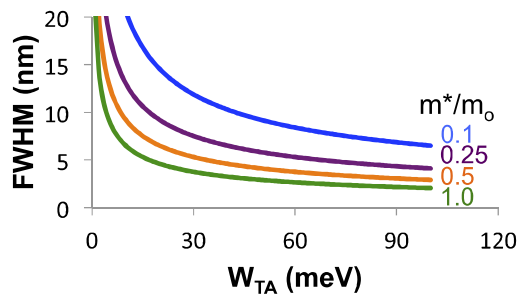
$$n_{TOTAL} = 4.9 \times 10^{21} \left(W_{TA} \frac{m_e^*}{m_o}\right)^{3/2} \quad (cm^{-3})$$

$$\langle x_{TA} \rangle = 2 \left(\frac{3}{4\pi n_{TOTAL}}\right)^{1/3} \quad (cm)$$

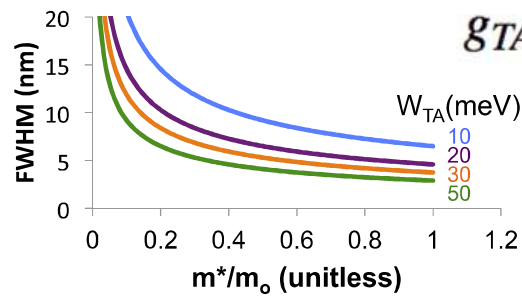
$$E - E_{CME} = \frac{-\hbar^2 k^2}{2m_e^*}$$

$$g_{TA}(k) = e^{\frac{-\hbar^2 k^2}{2m_e^* W_{TA}}} \quad (\text{unitless})$$

$$g_{TA}(x) = \frac{1}{\hbar} \sqrt{\frac{m_e^* W_{TA}}{2\pi}} e^{\frac{-m_e^* W_{TA} x^2}{2\hbar^2}} \quad (cm^{-1})$$



(a)

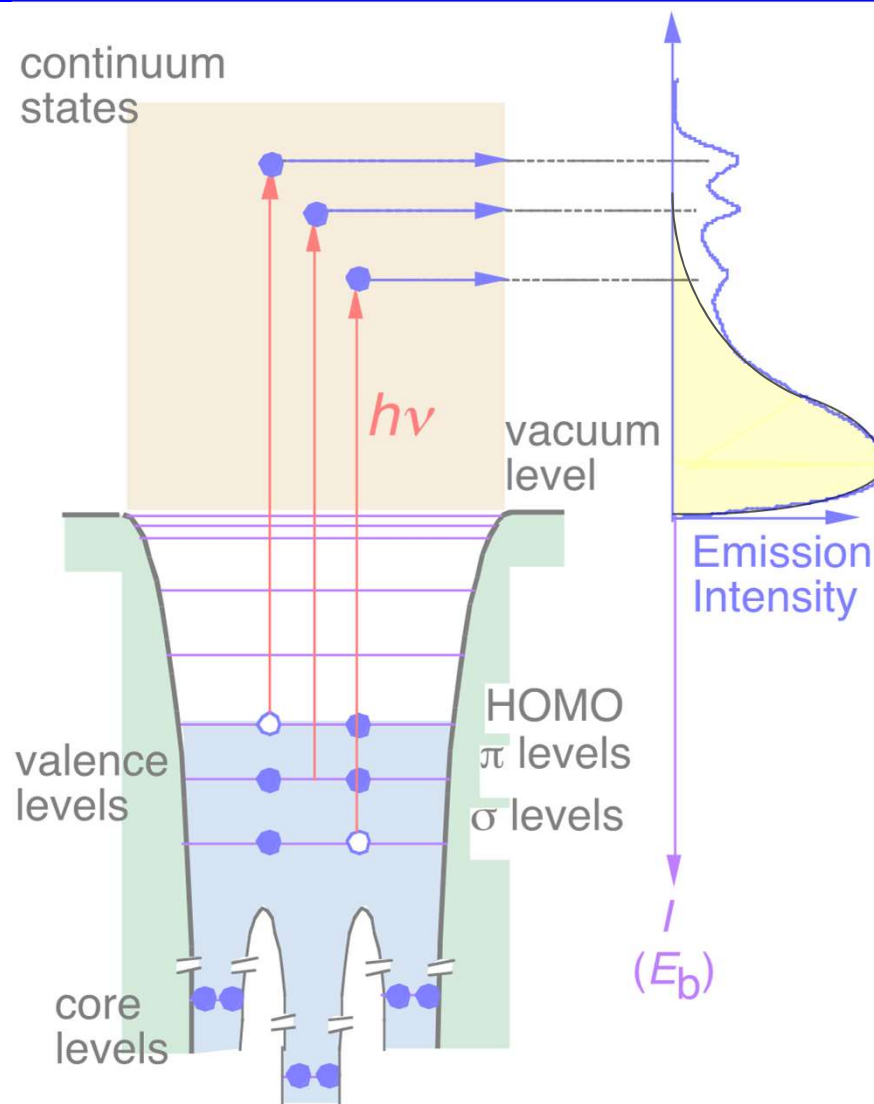
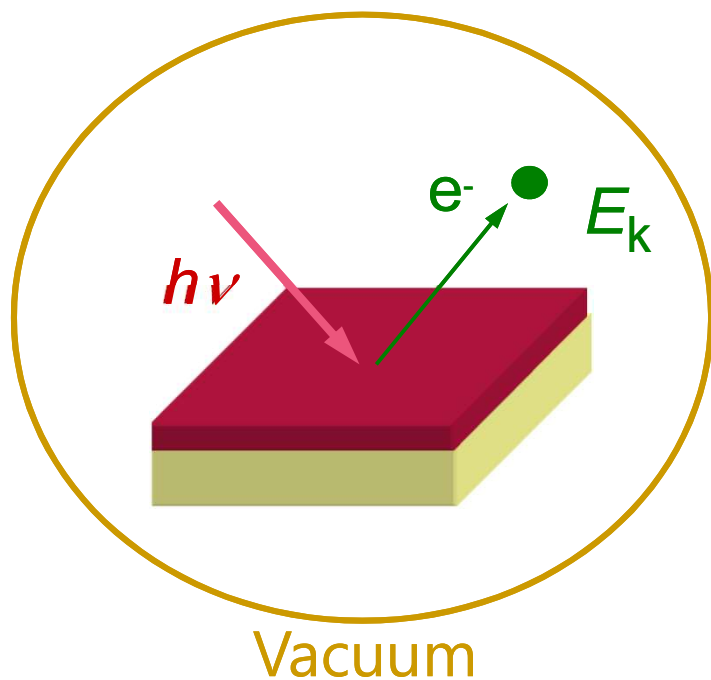


(b)



# Photoemission spectroscopy

$$E_k = h\nu - E_B$$

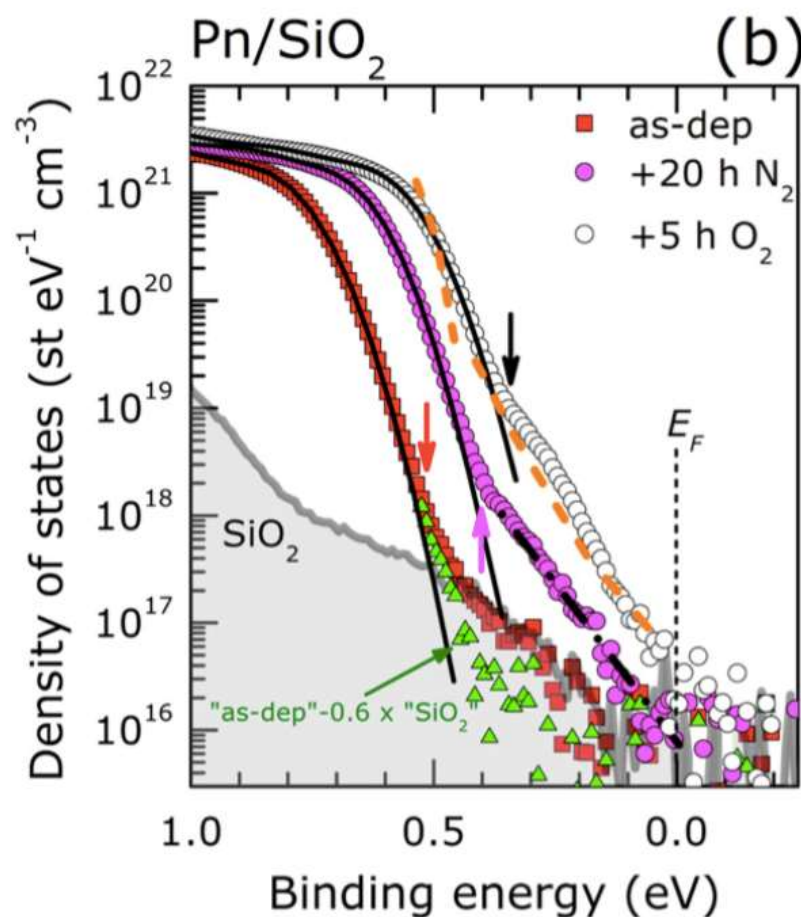


Available information : ionization energy, density of states (DOS), band dispersion, molecular orientation etc.

# High-Sensitivity Photoemission

Photoemission is a good tool to probe DOS

Extremely low background level by pure monochromatic light



(b)

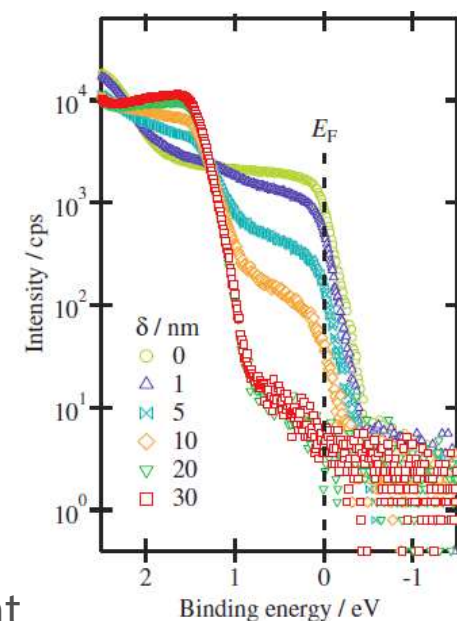
By using monochromatized Discharge lamp

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

F. Bussolotti, *et al.*, Phys. Rev. Lett. **110**, 267602 (2013)

F. Bussolotti *et al.*, J. Electron Spectrosc. Relat. Phenom.

**204**, 29 (2015).

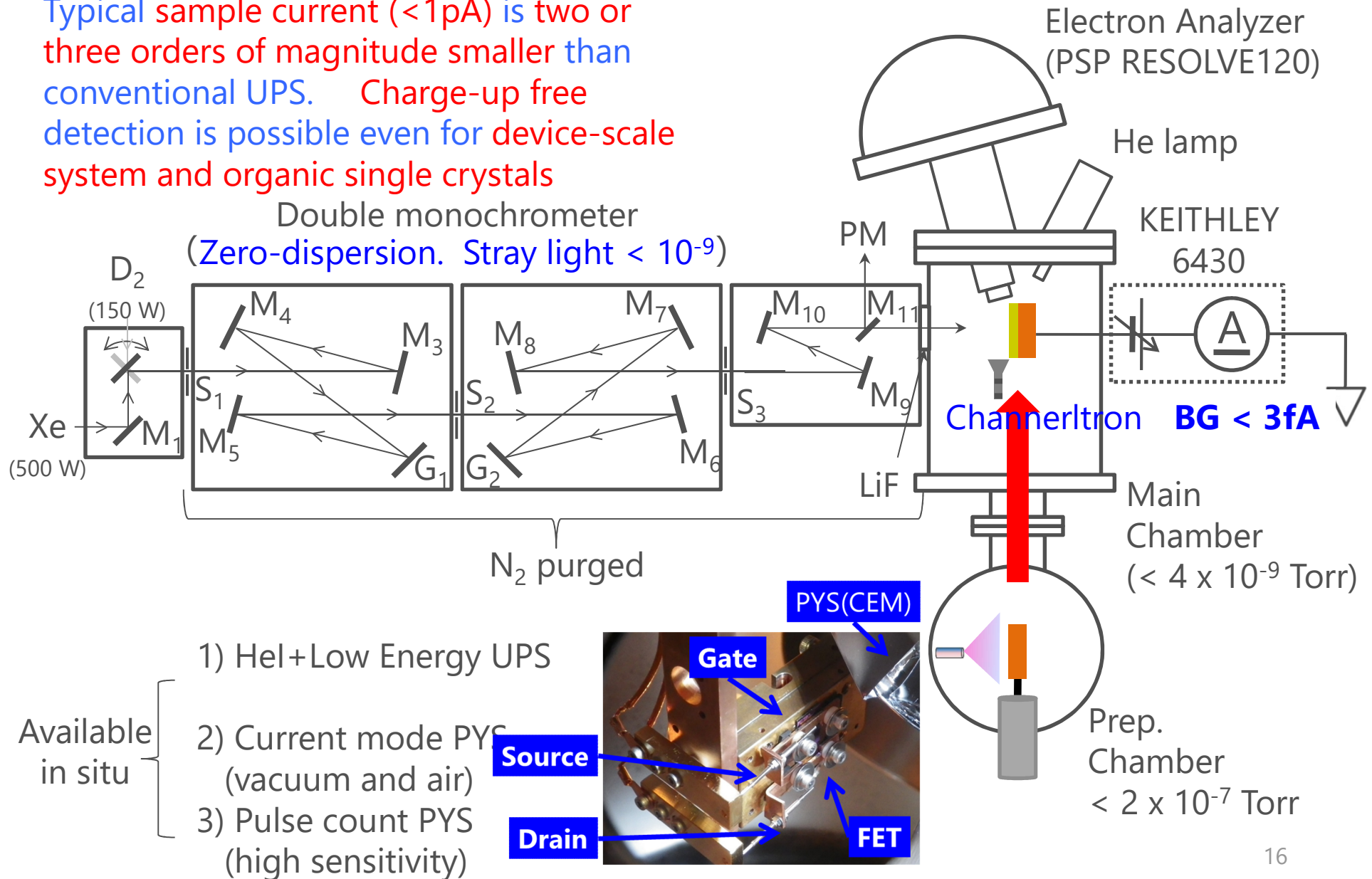


By using low energy light

S. Machida *et al.*, Appl. Phys. Express, **6** (2013)

# Our Apparatus for UPS and PYS

Typical sample current (<1pA) is two or three orders of magnitude smaller than conventional UPS. Charge-up free detection is possible even for device-scale system and organic single crystals



# Photo of Our Apparatus





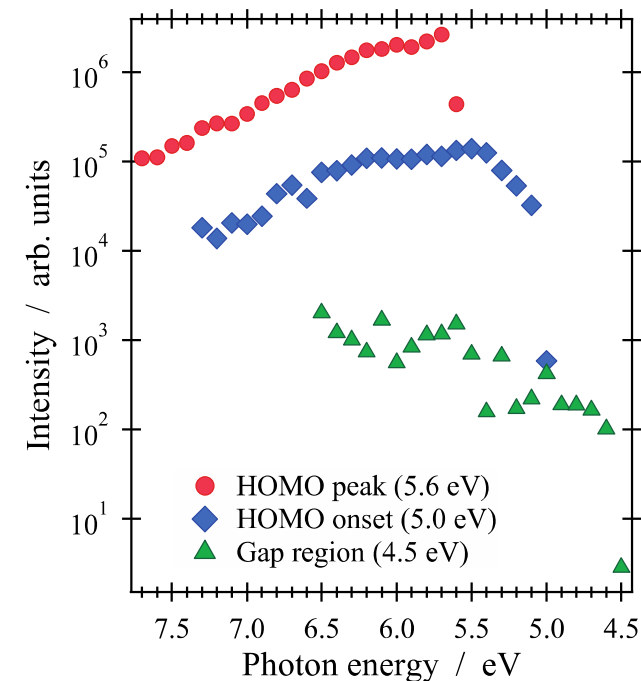
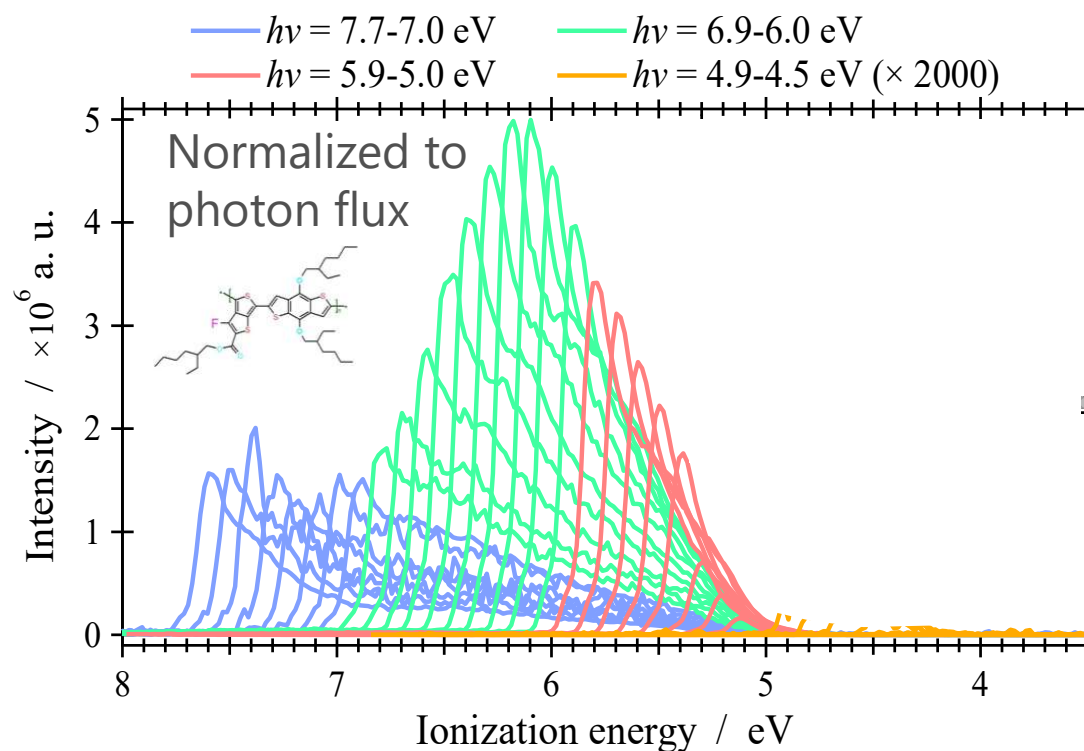
# $h\nu$ -dependent HS-UPS of PTB7 film



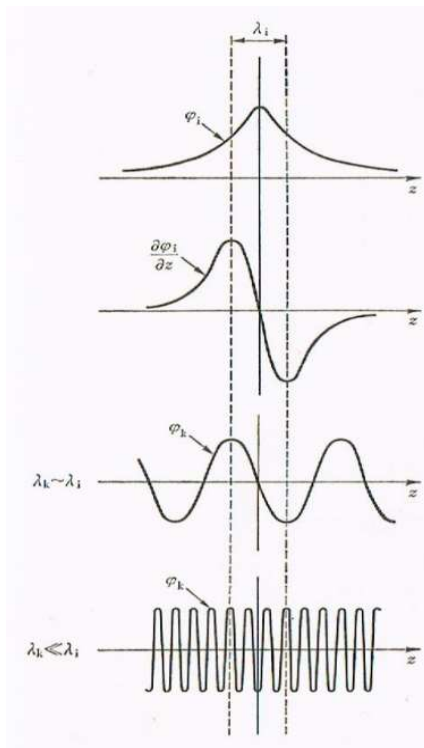
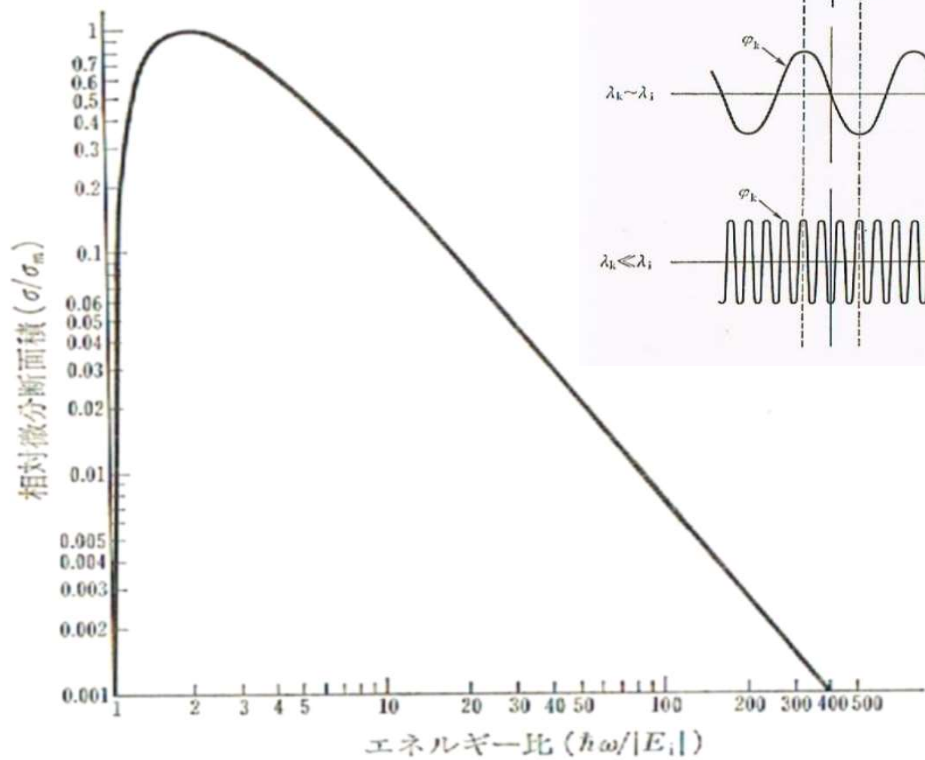
T. Sato

$$\sigma(h\nu) * D(E)$$

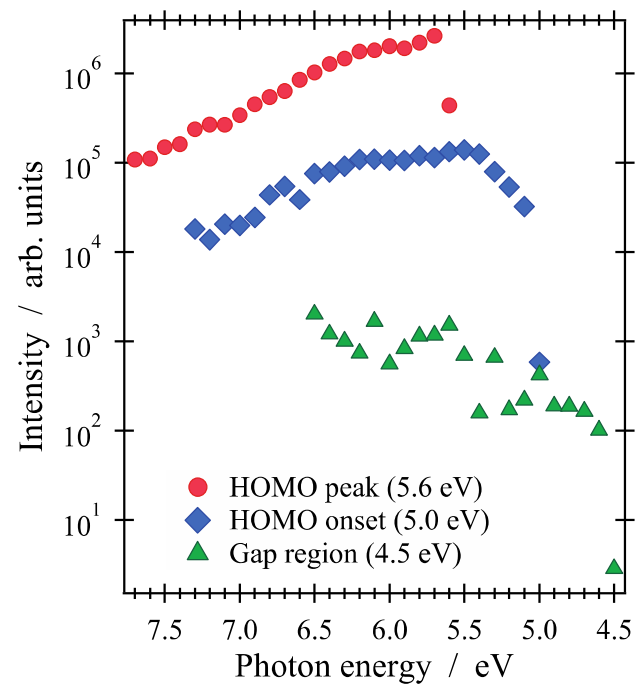
$\sigma$ : Photoionization crosssection







$$\langle e^{ikr} | er | \phi_i \rangle$$

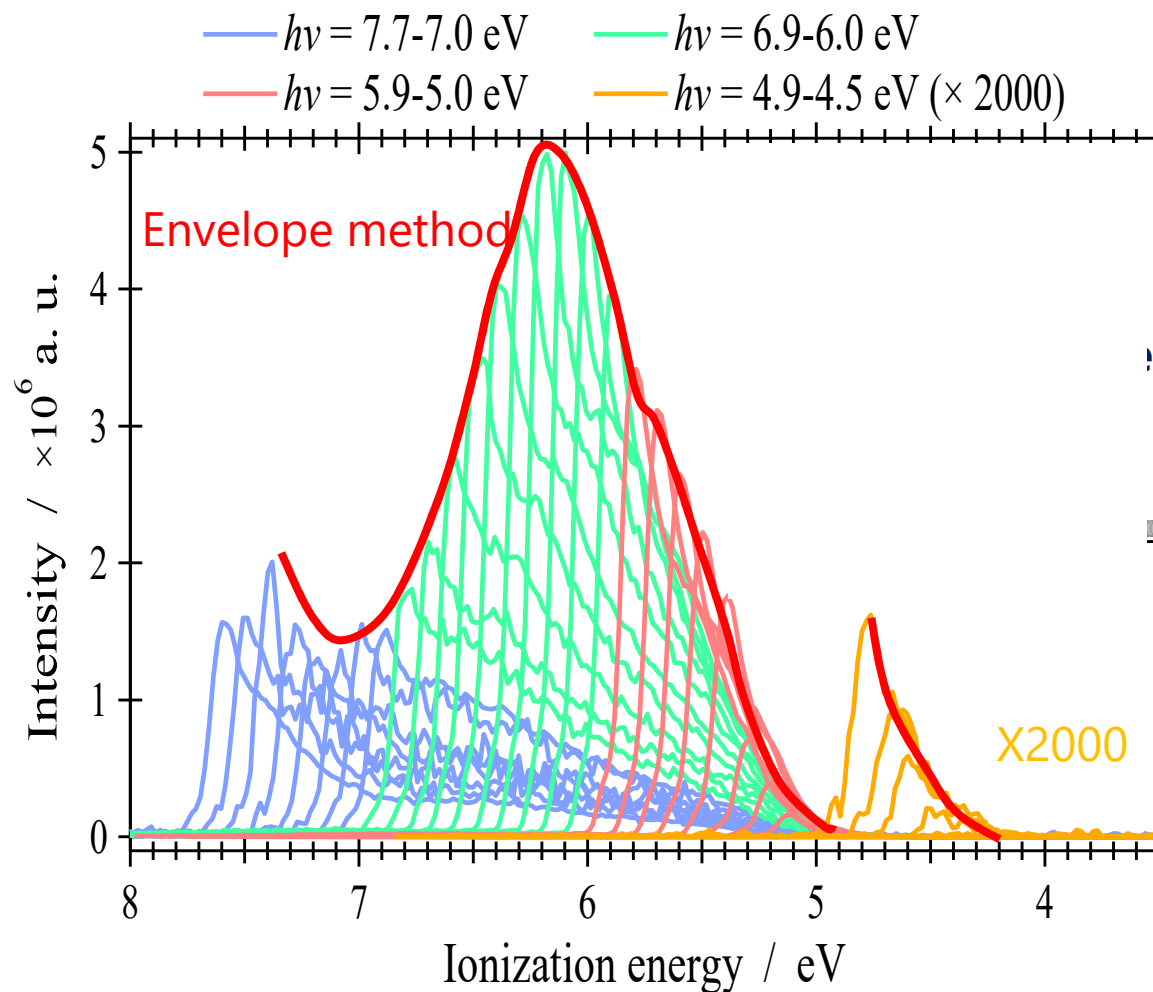


# $h\nu$ -dependent HS-UPS of PTB7 film



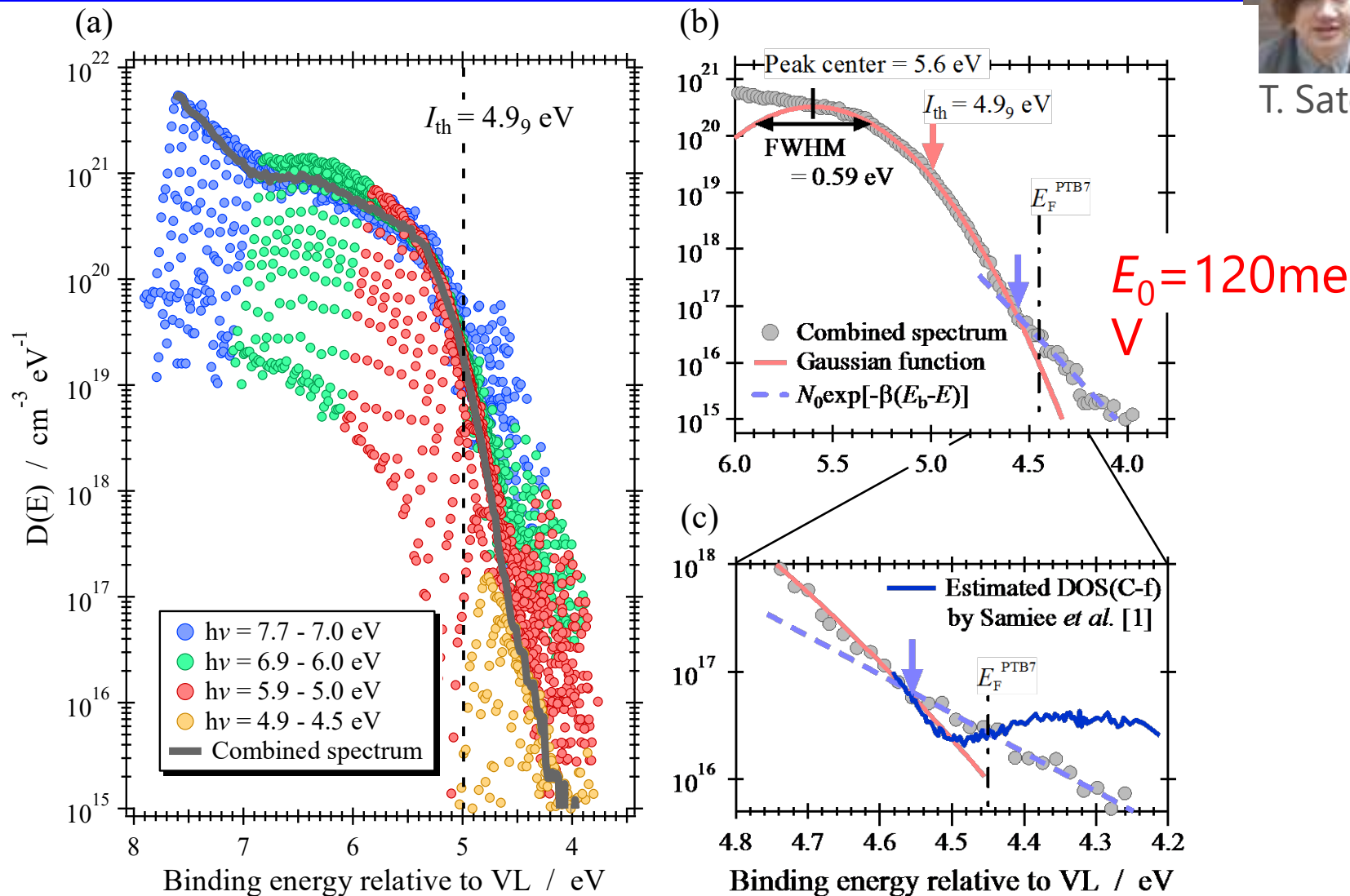
T. Sato

T. Sato et al., Applied Physics Express 10, 011602 (2017)



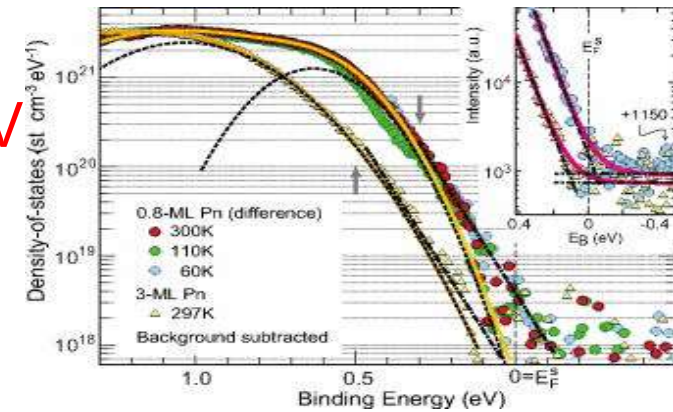
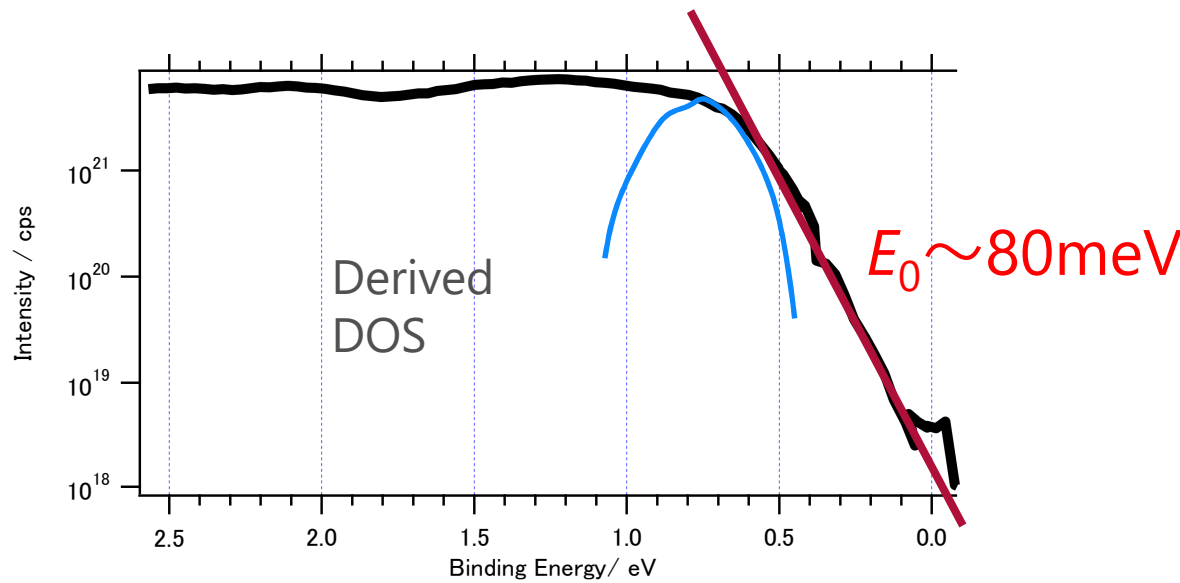
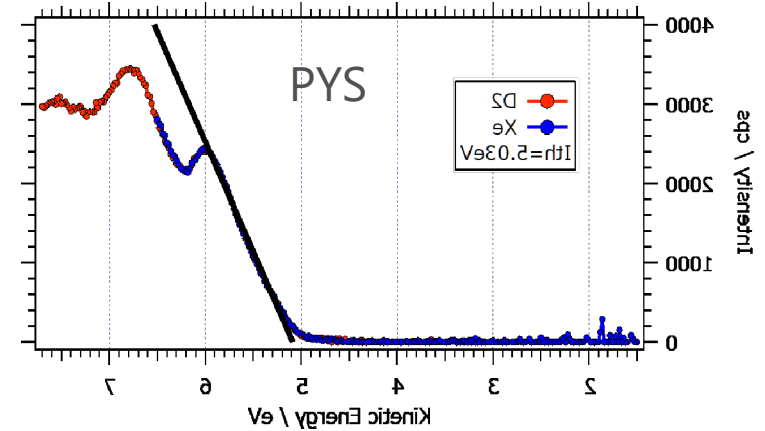
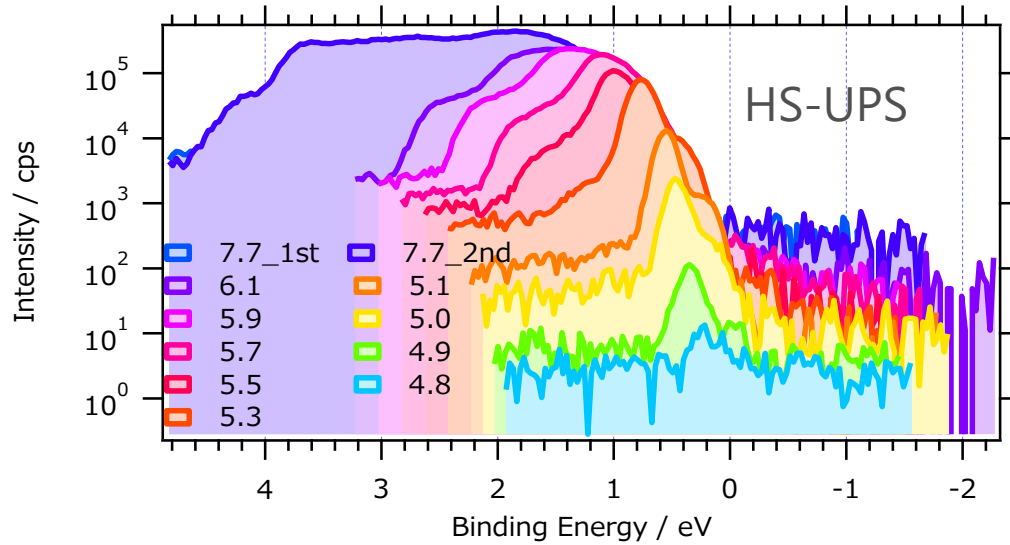


T. Sato



Combined DOS was obtained by overlapping the spectral part with a similar line shape between adjacent photon energy spectra

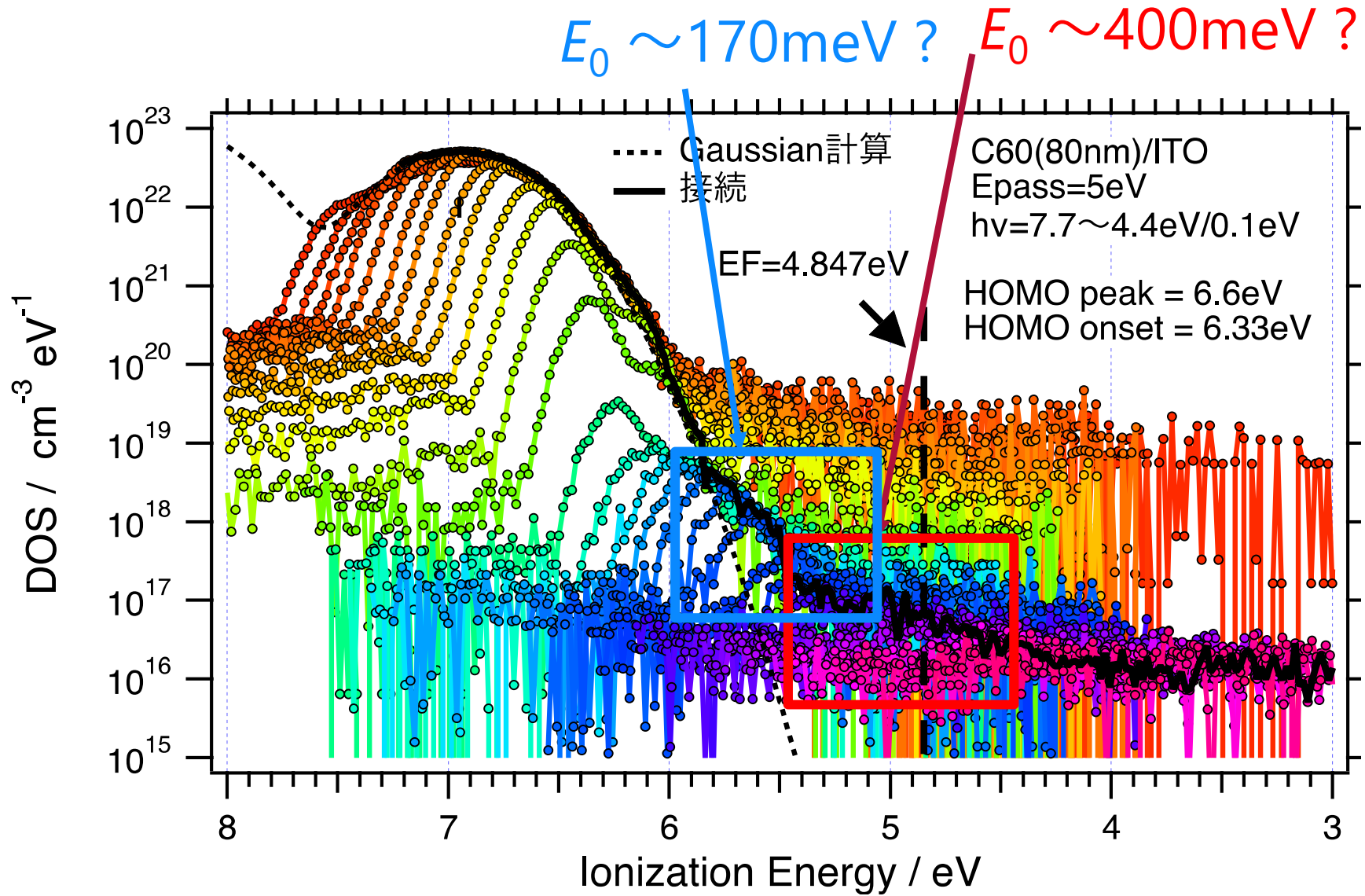
# HS-UPS of Pentacene film



Maruyama et al in preparation

Tomoki Sueyoshi et al.  
Appl. Phys. Lett. 95, 183303 (2009)

# HS-UPS of C60



The relation between the observed DOS and electric characteristic is unde

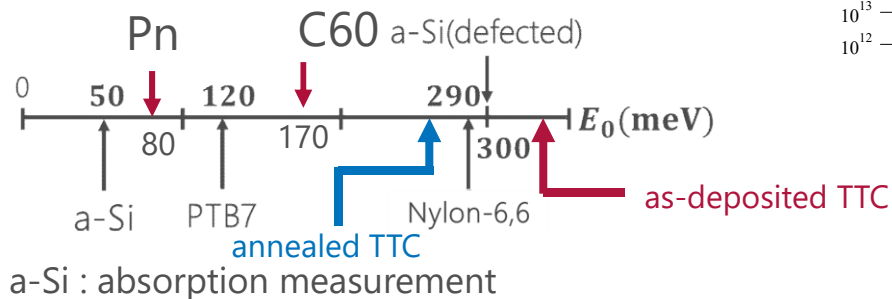


# Exponential Decay

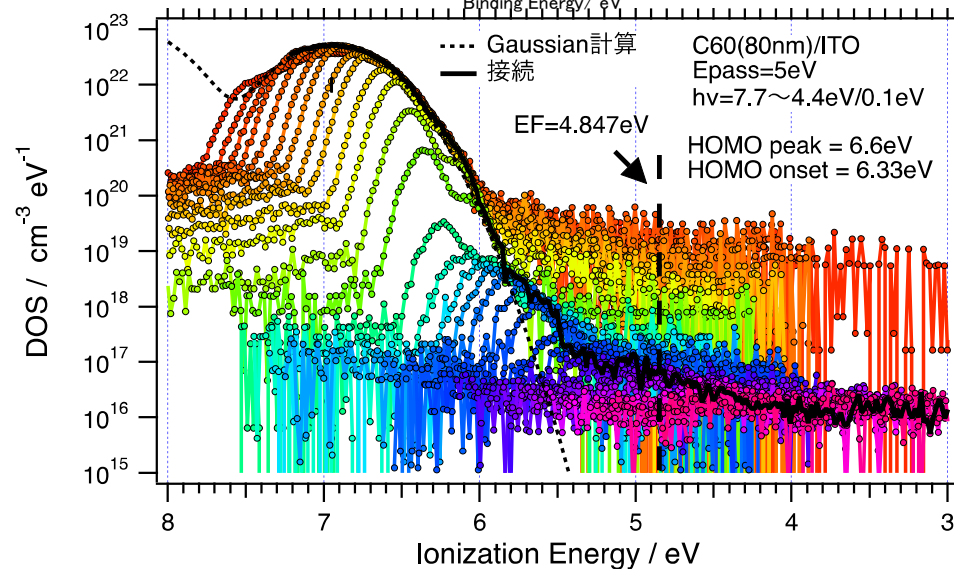
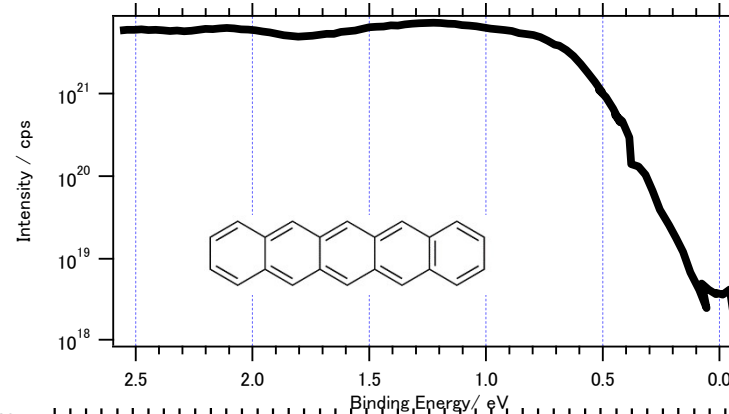
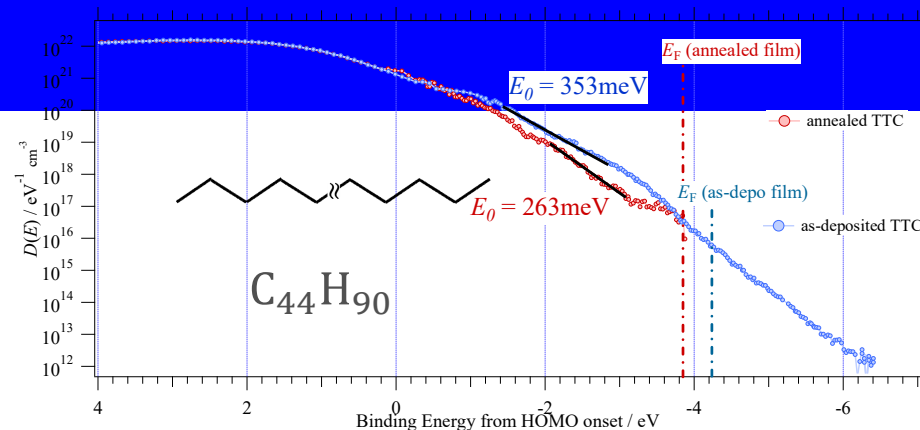
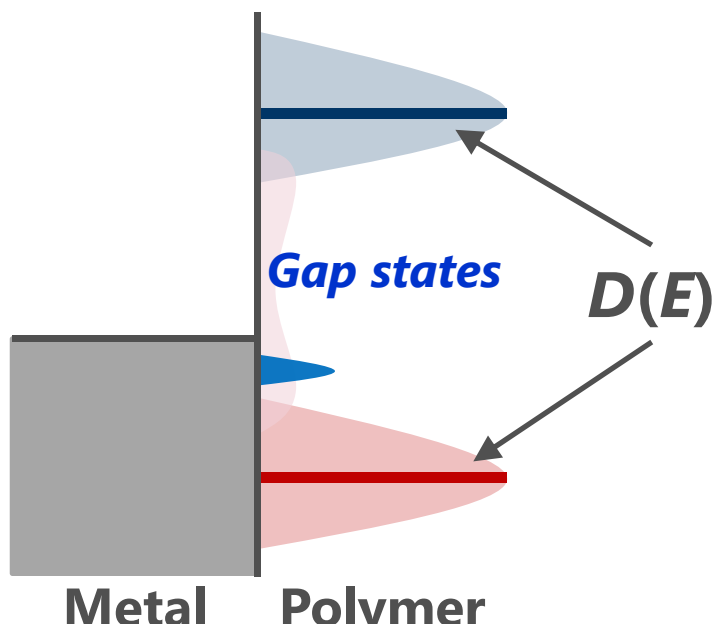
$$f(E) = A \exp\left(\frac{E}{E_0}\right)$$

$E_0$  : decay parameter

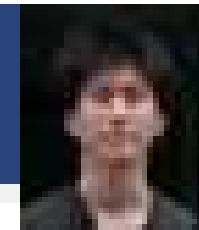
## Example of decay parameter



Appl. Phys. Lett. **110**, 111102 (2017)  
 Applied Physics Express **10**, 011602 (2017)

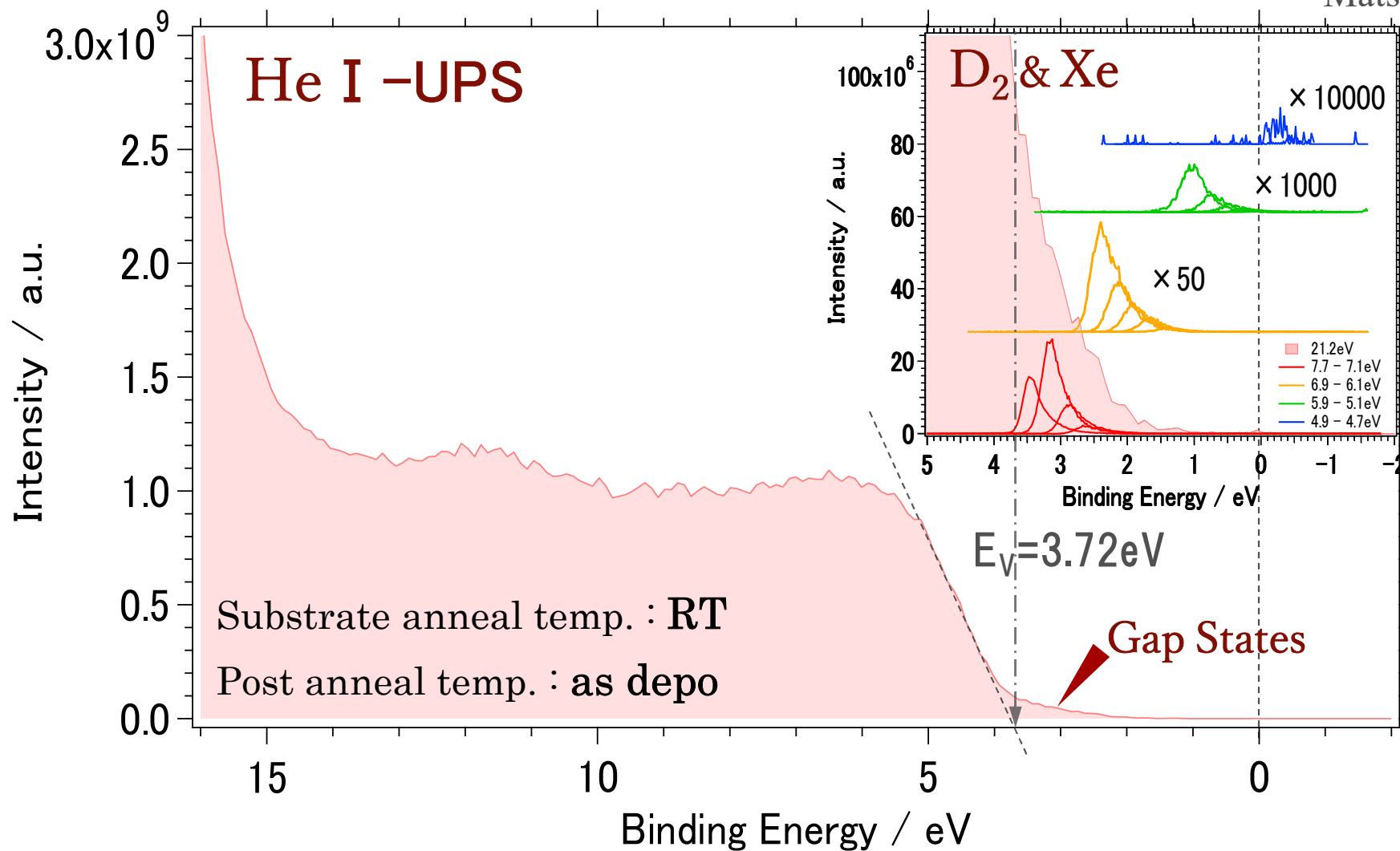


# Gap States of a-IGZO



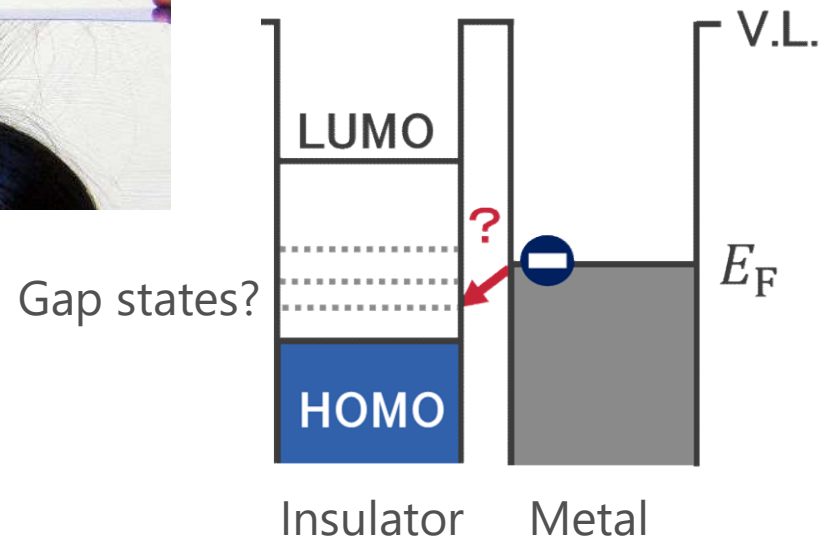
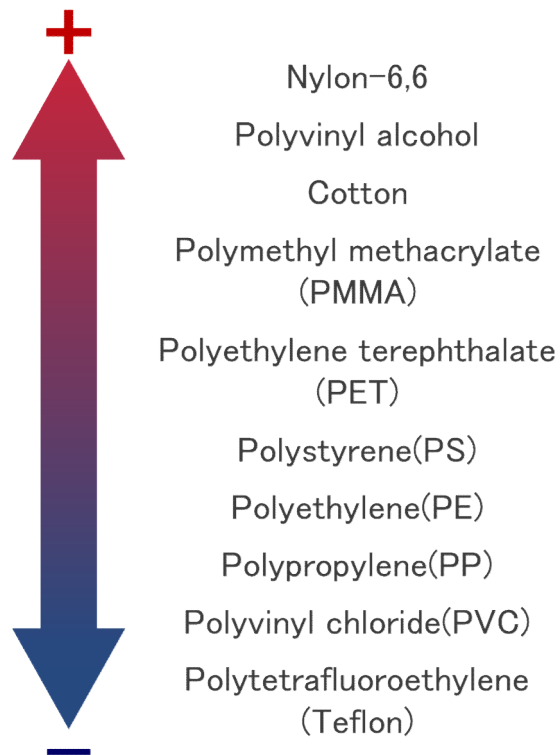
Matsuzaki

Indium gallium zinc oxide (IGZO)



# Application to Insulating Polymer: Triboelectricity

## Triboelectric series



Long-standing discussion  
on the tribo-charging mechanism:  
Electron transfer or Ion transfer?

We have tried to examine whether the gap state density is enough to explain charging properties.

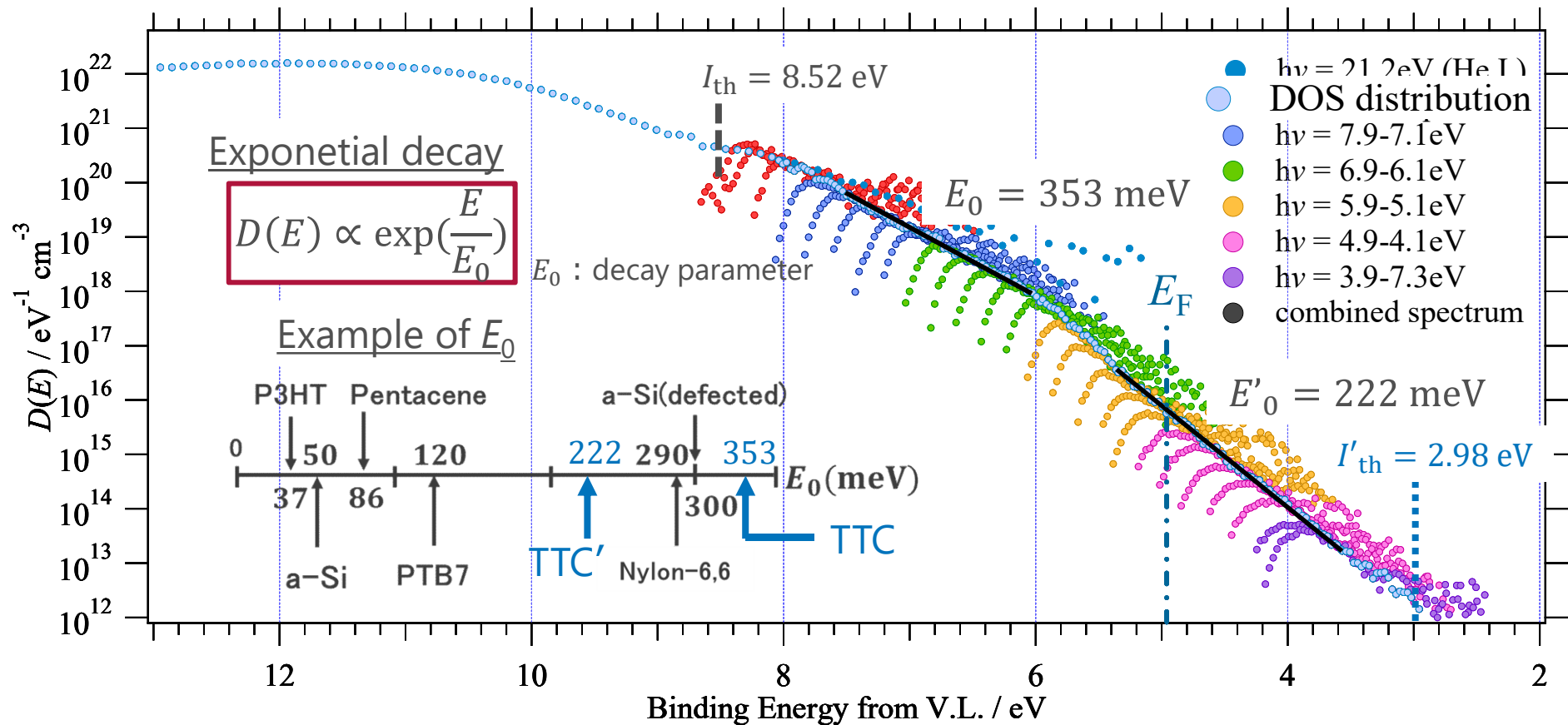
Y. Yamaguchi et al., IEICE Trans. Electron., E102-C, 168 (2019).

T. Sato et al., Appl. Phys. Lett. 110, 111102-1~4 (2017)

# Density of states



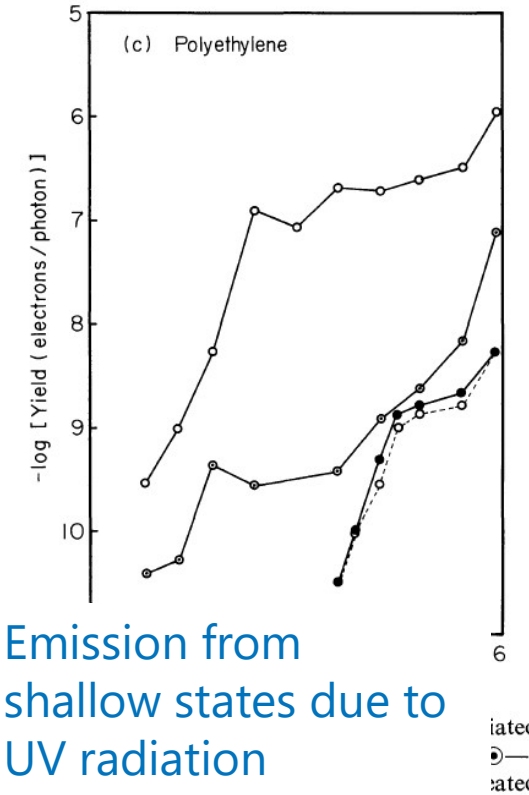
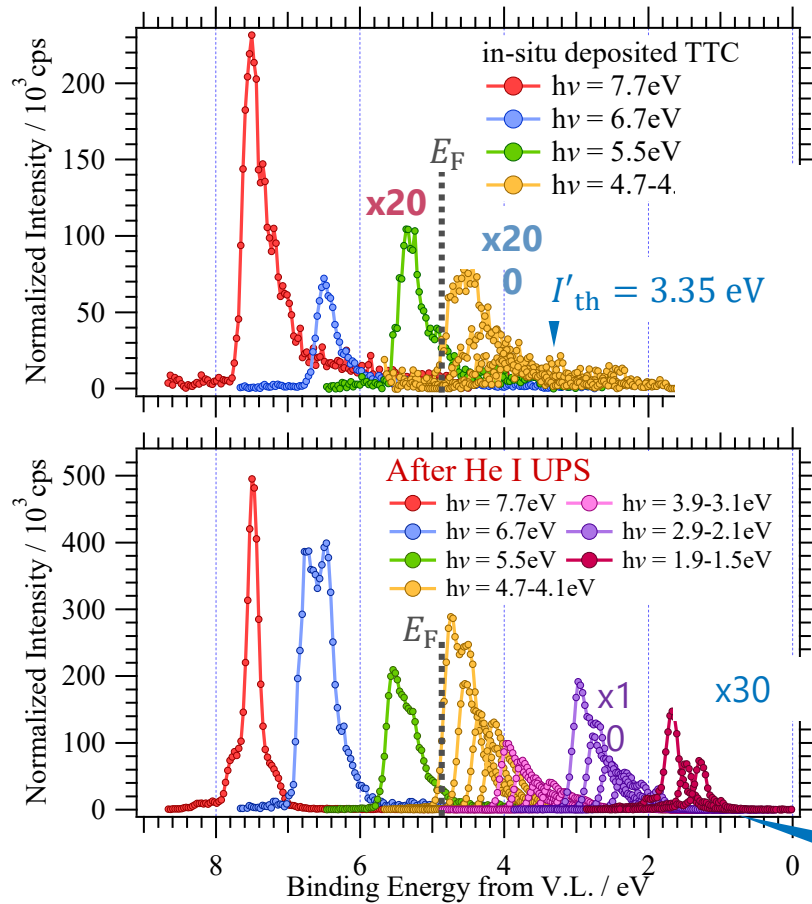
Yamaguchi



# Too much trapped electrons?



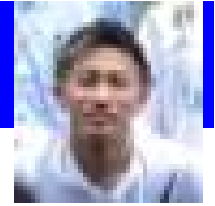
Yamaguchi



Shigeyoshi Kittaka and Yuji Murata  
 J. J. Appl. Phys. 18, 3 (1979)

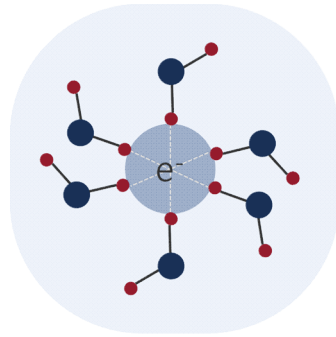


# Analogy with solvated electron?



Yamaguchi

## VBE & cavity radius



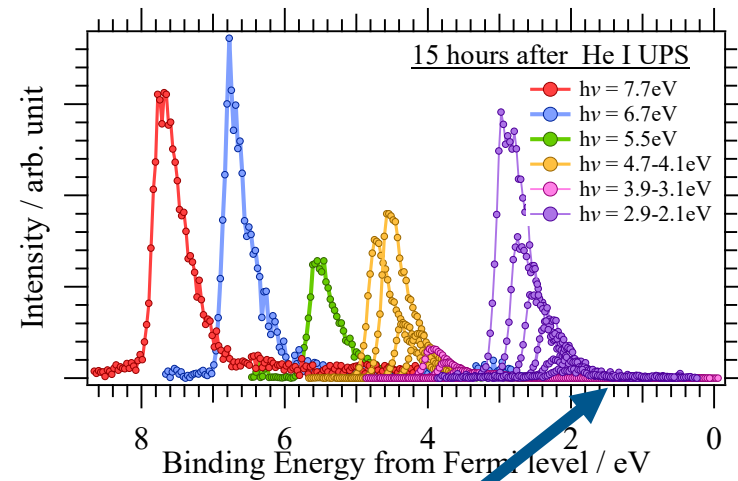
$$VBE = \frac{1}{4\pi\epsilon_0} \left( 1 + \frac{1}{\epsilon_{op}} - \frac{2}{\epsilon_s} \right) \frac{e}{2a} [\text{eV}]$$

$\epsilon_{op}$  : the optical dielectric constant

$\epsilon_s$  : the static dielectric constants

$a$  : the cavity radius for an excess electron

Shen Huan *et al.* Chem. Lett. Vol. 39, Issue 7



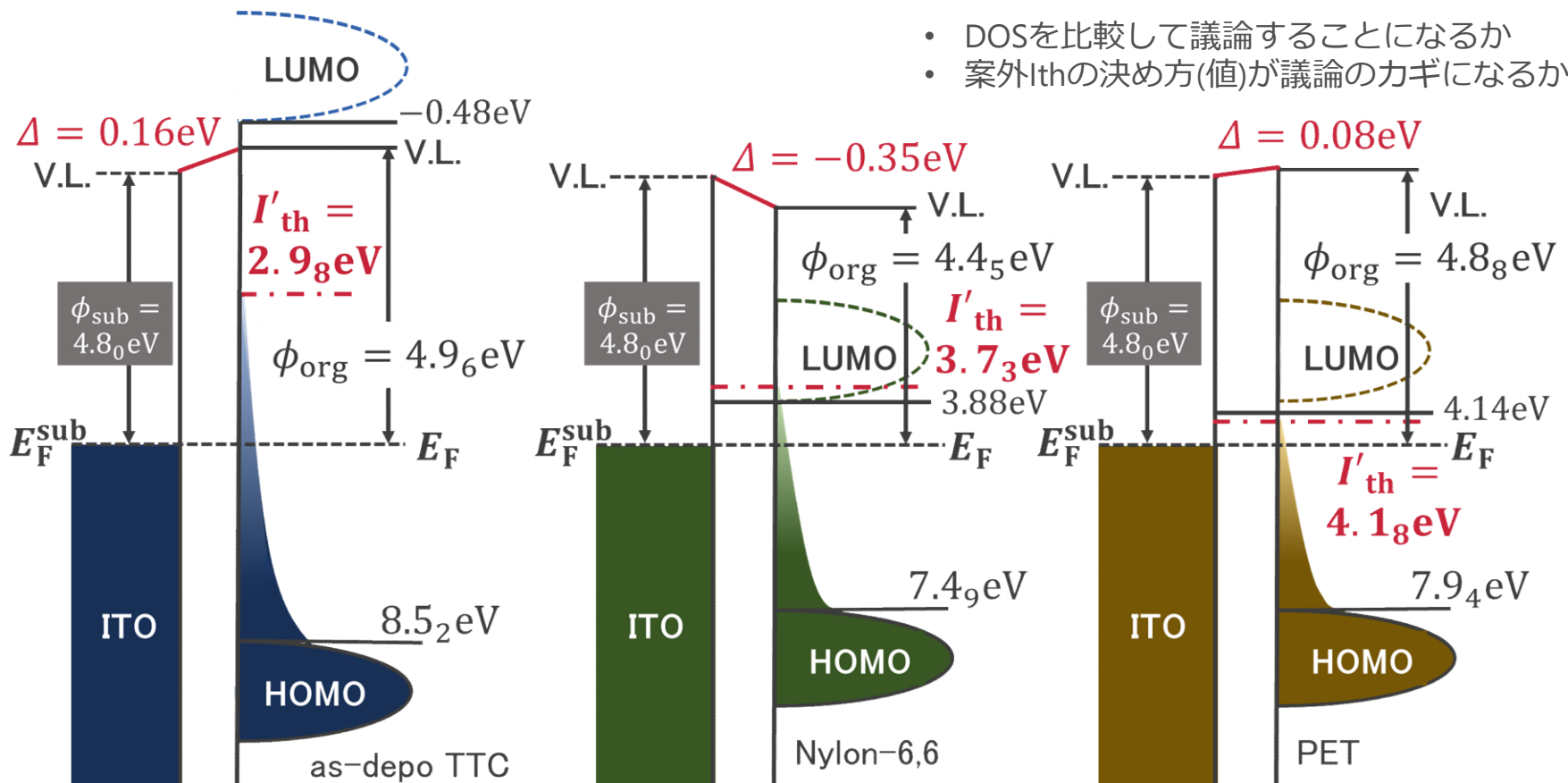
$$I'_{th}(VBE) = 1.45 \text{ eV}$$



$$a = 0.48 \text{ nm}$$

Interchain electron states in polyethylene によれば  
鎖から5 Å離れたところがconduction states の安定点なの  
測定から求めたVBEは妥当なのか。

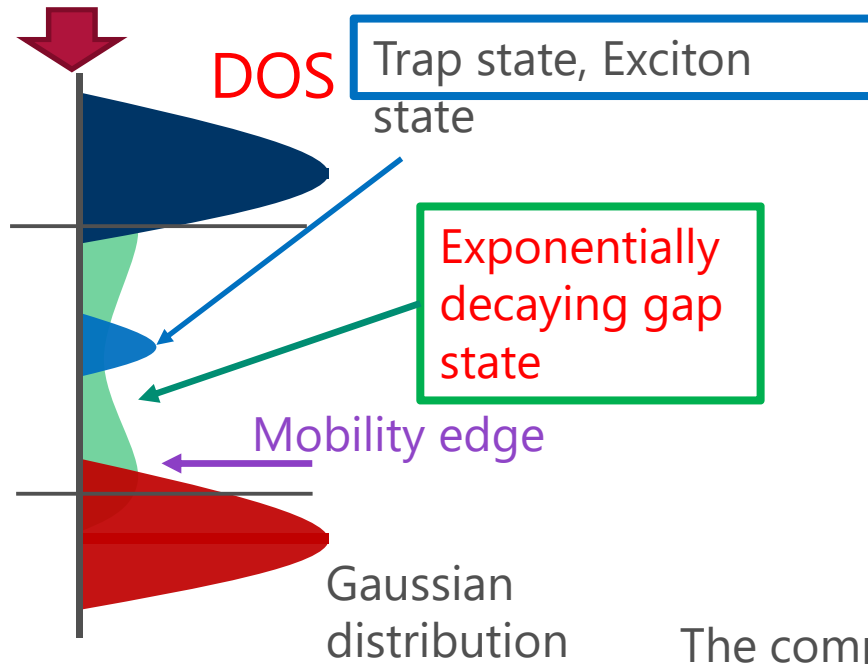
# Energy Diagram



- DOSを比較して議論することになるか
- 案外 $I_{\text{th}}$ の決め方(値)が議論のカギになるか

# Summary

Energy level alignment



High-Sensitivity UV  
Photoemission Spectroscopy  
(HS-UPS)

We have succeeded to directly measure tail states of organic and inorganic materials with exponential decay.

The gap states of tetratetracontane (TTC), a model oligomer of polyethylene was observed.

TTC has a high-density trap states.

Electron emission from the trap states above the vacuum level was observed.

The comparison with theoretical work is underway.

