

Band bending at Org/Metal

Band bending model

$$\frac{d^2 \Phi}{dx^2} = -\frac{\rho(x)}{\epsilon}$$

$$\rho(x) = e(N_D - N_A + p - n).$$

Schottky depletion space-charge layer model

Vacuum level,
VL

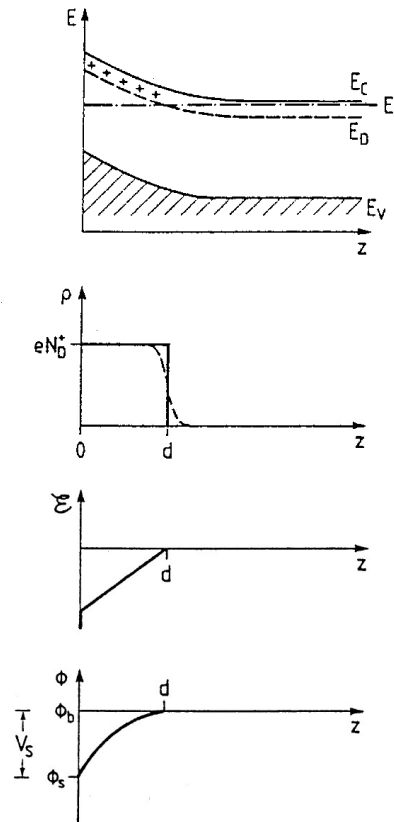
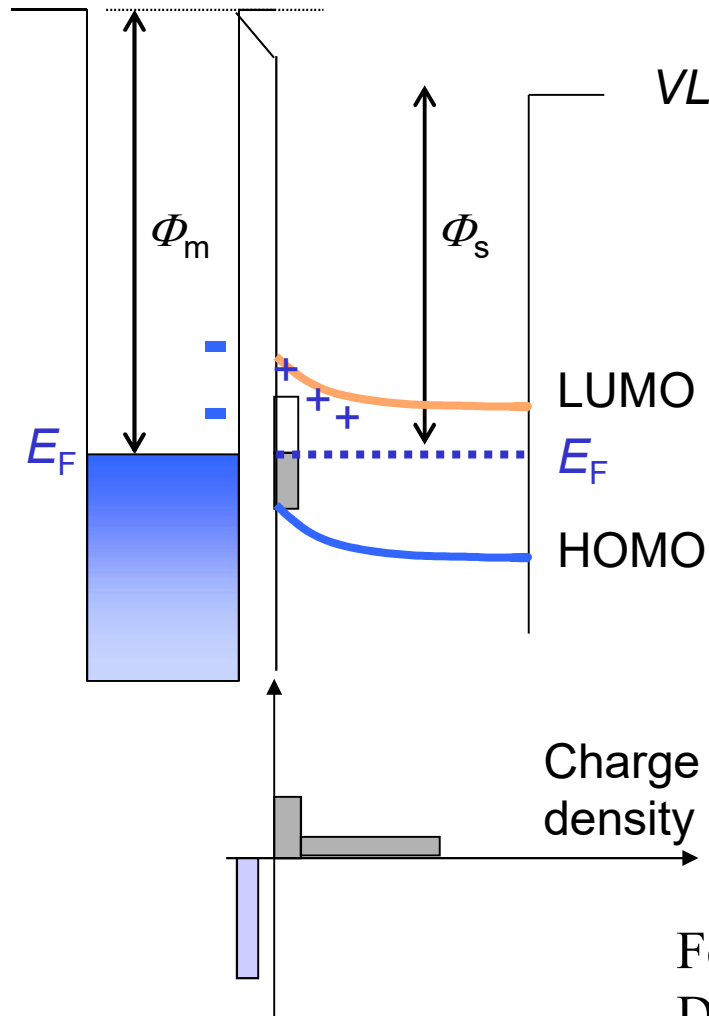


Fig. 7.4a-d. A depletion layer on an n-type semiconductor in the Schottky approximation: (a) Band scheme with symbols as in Figs.7.1-3. (b) Volume density ρ of the space charge, realistic density (broken line) and Schottky approximation (full line). d is the thickness of the space-charge layer and N_D^+ the density of the ionized bulk donors. (c) Electric field $\mathcal{E}(z)$ in the space charge layer. (d) Electric potential $\phi(z)$ with values ϕ_b and ϕ_s in the bulk and at the surface, respectively

$$J_n = en\mu_n\mathcal{E} - eD_n\frac{dn}{dx} = 0$$

Fermi level is constant everywhere.

Drift current is compensated by diffusion current.

Weak space-charge layer

Weak band bending model in inorganic

$$p(z) = -en_b \left(e^{v(z)} - e^{-v(z)} \right).$$

For small band bending $|v| \ll 1$ the following approximation follows

$$\rho(z) \simeq -2en_b v(z),$$

and Poisson's equation is obtained as

$$\frac{d^2 v}{dz^2} = \frac{v}{L_D^2},$$

with the Debye length L_D given by

$$L_D = \sqrt{\frac{kT\epsilon\epsilon_0}{2e^2 n_b}}.$$

The solution is an exponentially decaying band bending

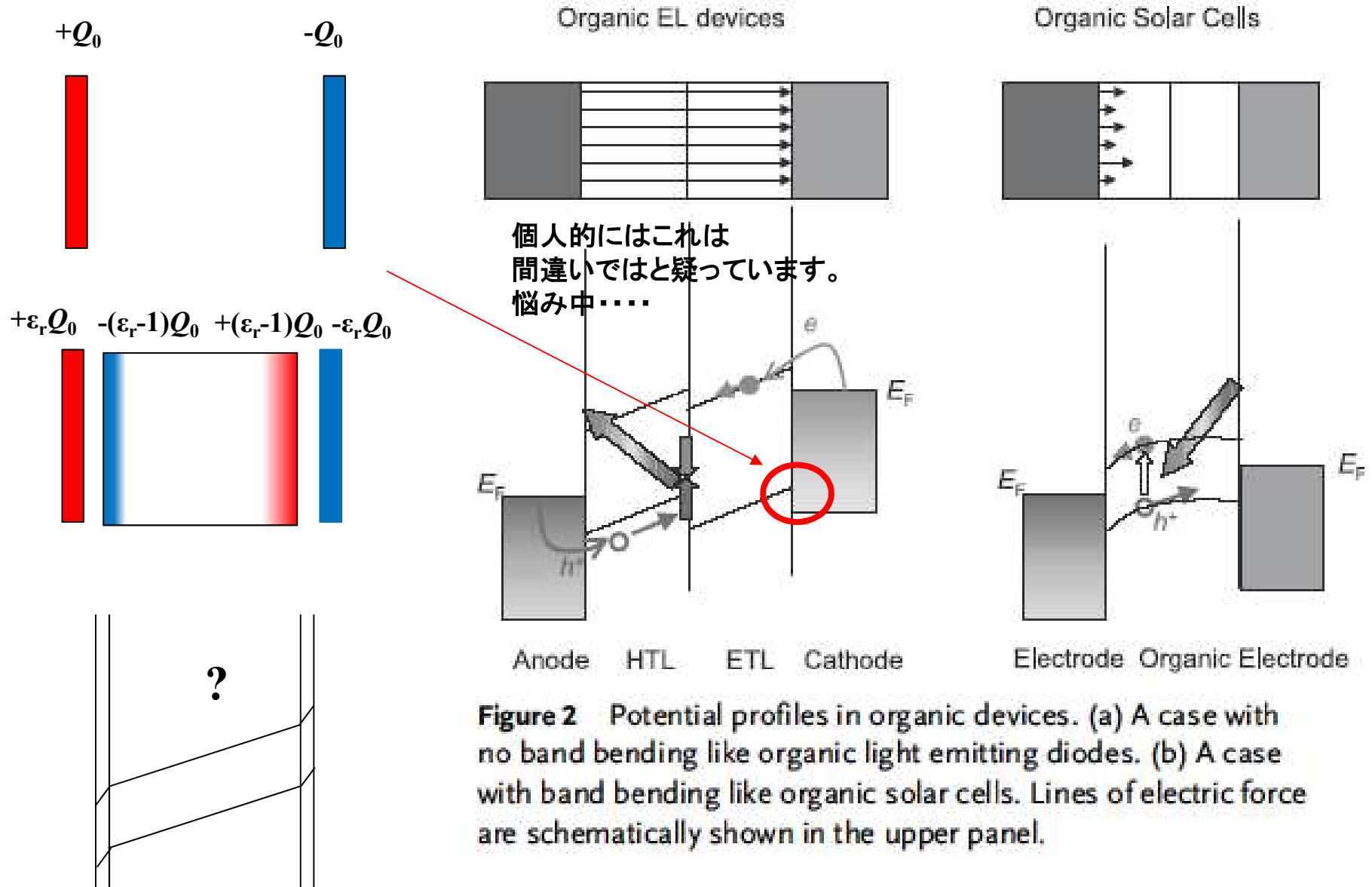
$$v(z) = \frac{eV(z)}{kT} = v_s e^{-z/L_D},$$

For general case

$$\frac{d^2 v}{dz^2} = -\frac{e^2}{kT\epsilon\epsilon_0} (n_b - p_b + p_b e^{-v} - n_b e^v)$$

$$L = \sqrt{\frac{\epsilon\epsilon_0 kT}{e^2 (n_b + p_b)}}$$

Band bending in organic interface



Band bending at Org/Metal Interface

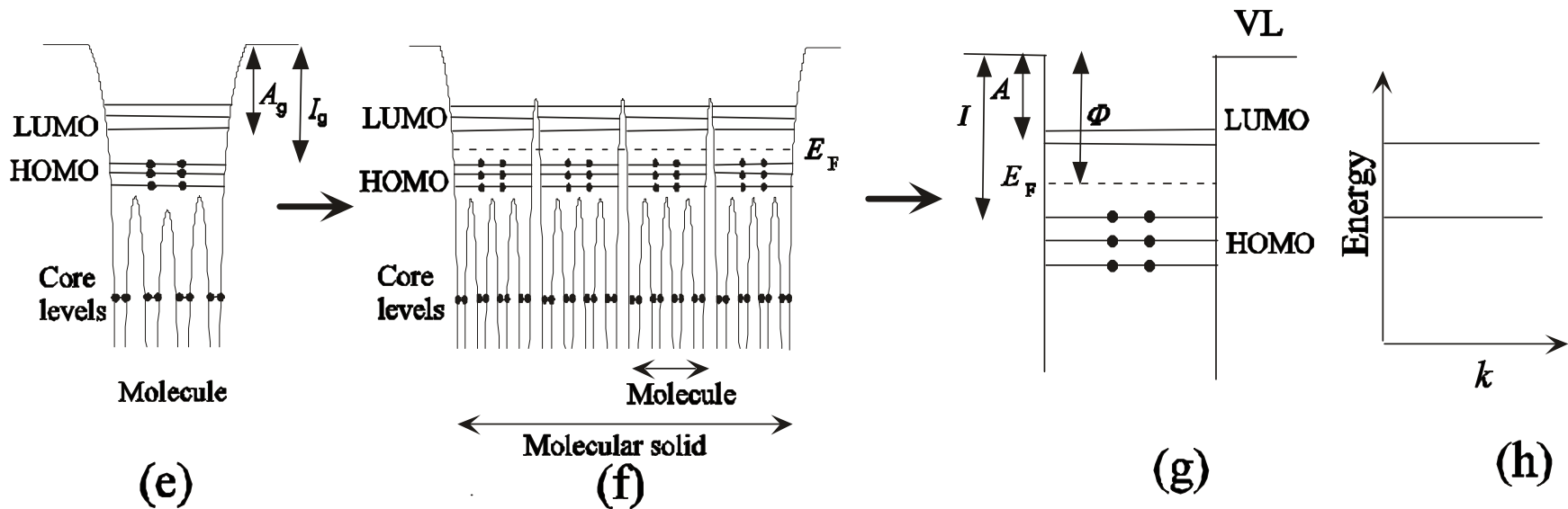
- The observed energy level position often shows thickness dependence.
 - These shifts are intrinsic or extrinsic phenomenon at interface
- ✧ In my definition,
 - ✧ Intrinsic Band bending in Schottky model is called as *narrowly defined band bending*.
 - ✧ Other extrinsic band bending is called as *widely defined band bending*.
 - ✧ “Energy level bending”?

Inorganic SC v.s. Organic SC

分子間力はファンデルワールスカ → 分子性個体

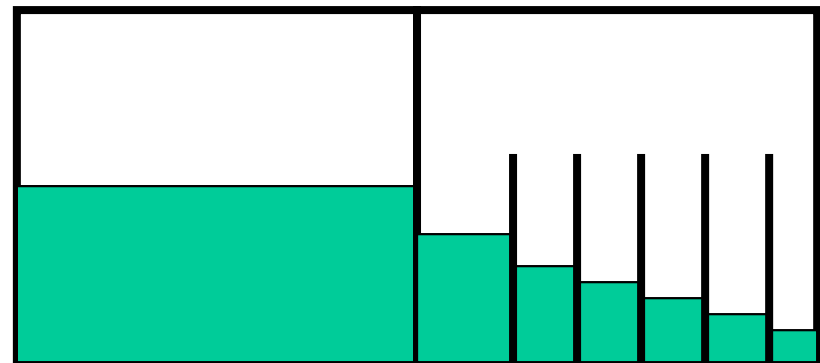
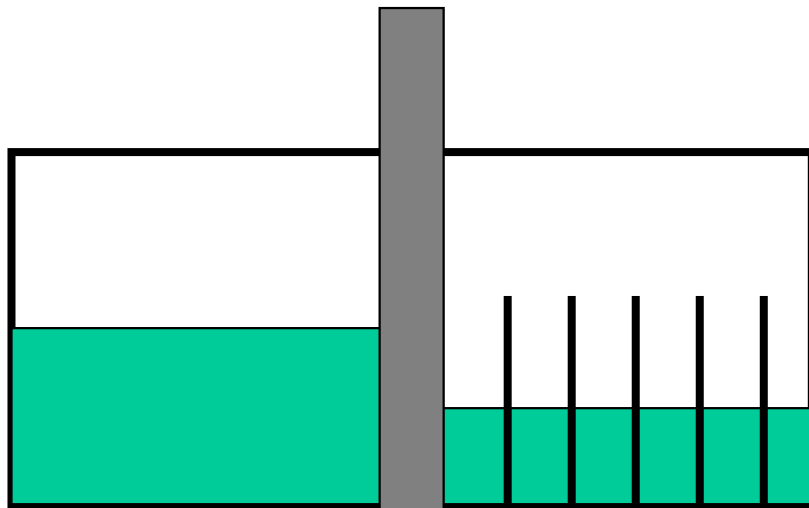
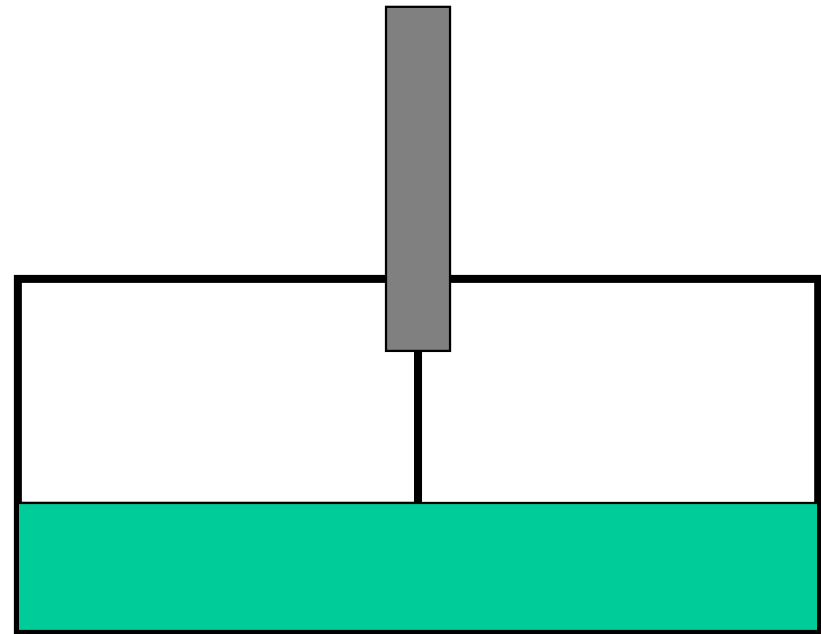
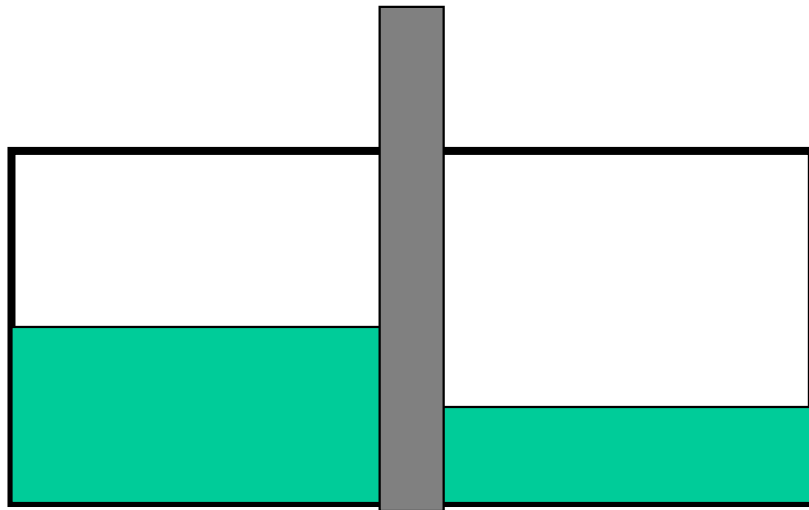
電子は分子内に局在

広いバンドギャップ → 熱励起のキャリア小



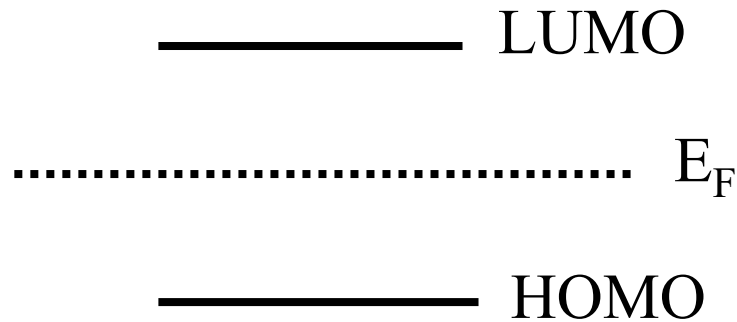
バルクのフェルミ準位の一致といった熱平衡状態を達成することは必ずしも容易ではない。

Water levels in tank with separator



Estimation of thermal carrier density in organic semiconductor

$$n = N_{\text{LUMO}} \exp(-(E_{\text{LUMO}} - E_{\text{F}})/kT)$$



室温では、

$$kT = 25 \text{ meV}$$

$E_{\text{LUMO}} - E_{\text{F}} = 1 \text{ eV}$ とすると、

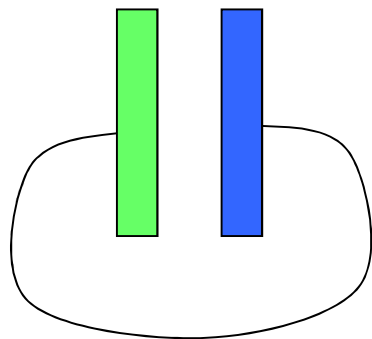
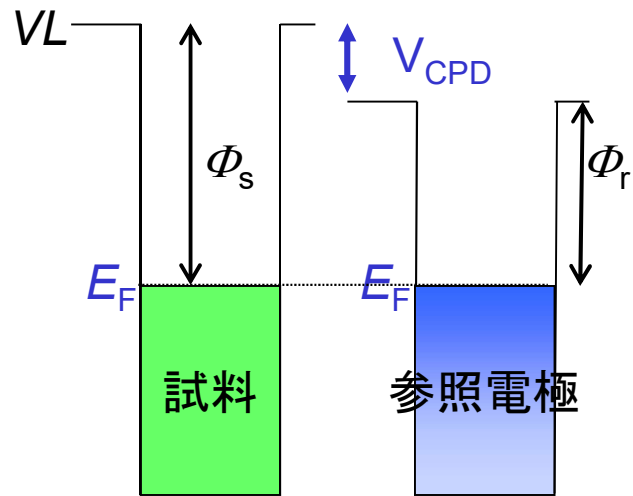
$$\exp(-(E_{\text{LUMO}} - E_{\text{F}})/kT) \sim 4 \cdot 10^{-18}$$

$n = 100 \sim 1000$ 個程度

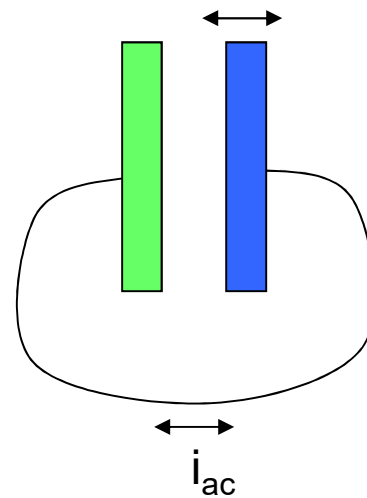
Experimental technique to examine
band bending

Kelvin probe

$V_{CPD} = \phi_s - \phi_r$
:接触電位差



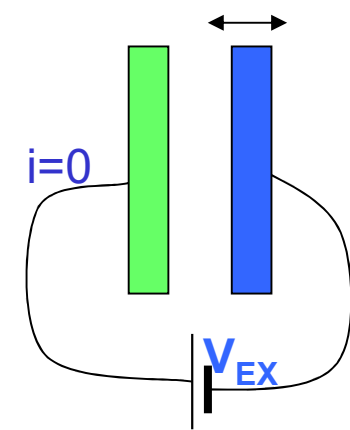
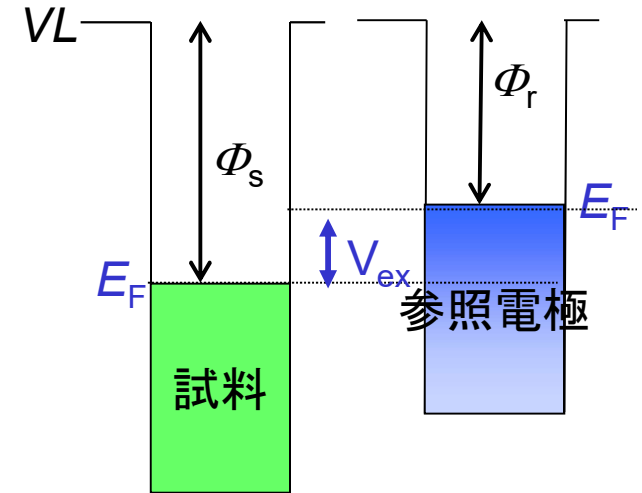
電極を振動



$i_{ac} \propto V_{CPD} dC/dt$

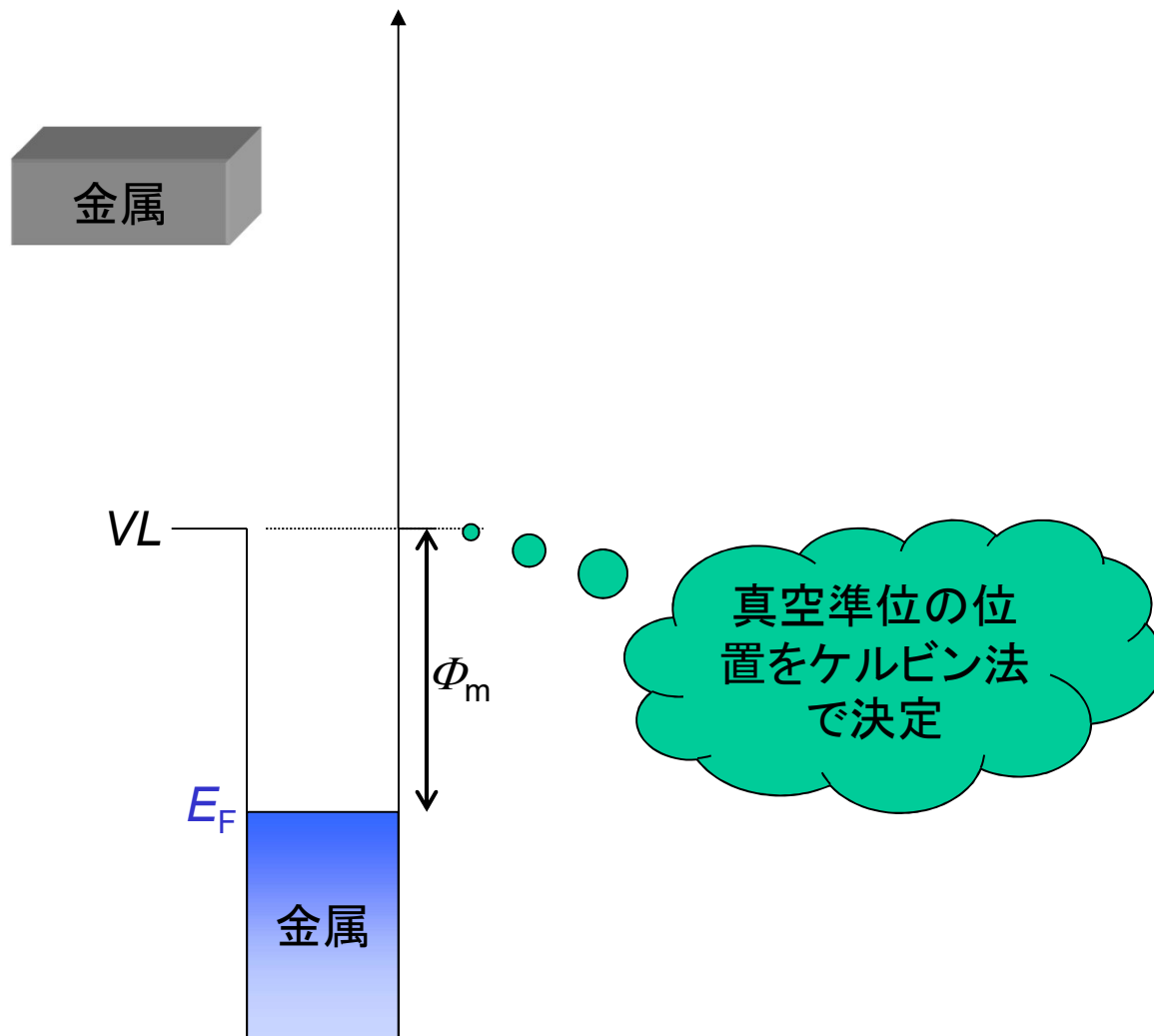
試料帯電の影響が無く、
厚い膜にも適用可能

When $i_{ac} = 0$
 $V_{ex} = V_{cpd}$

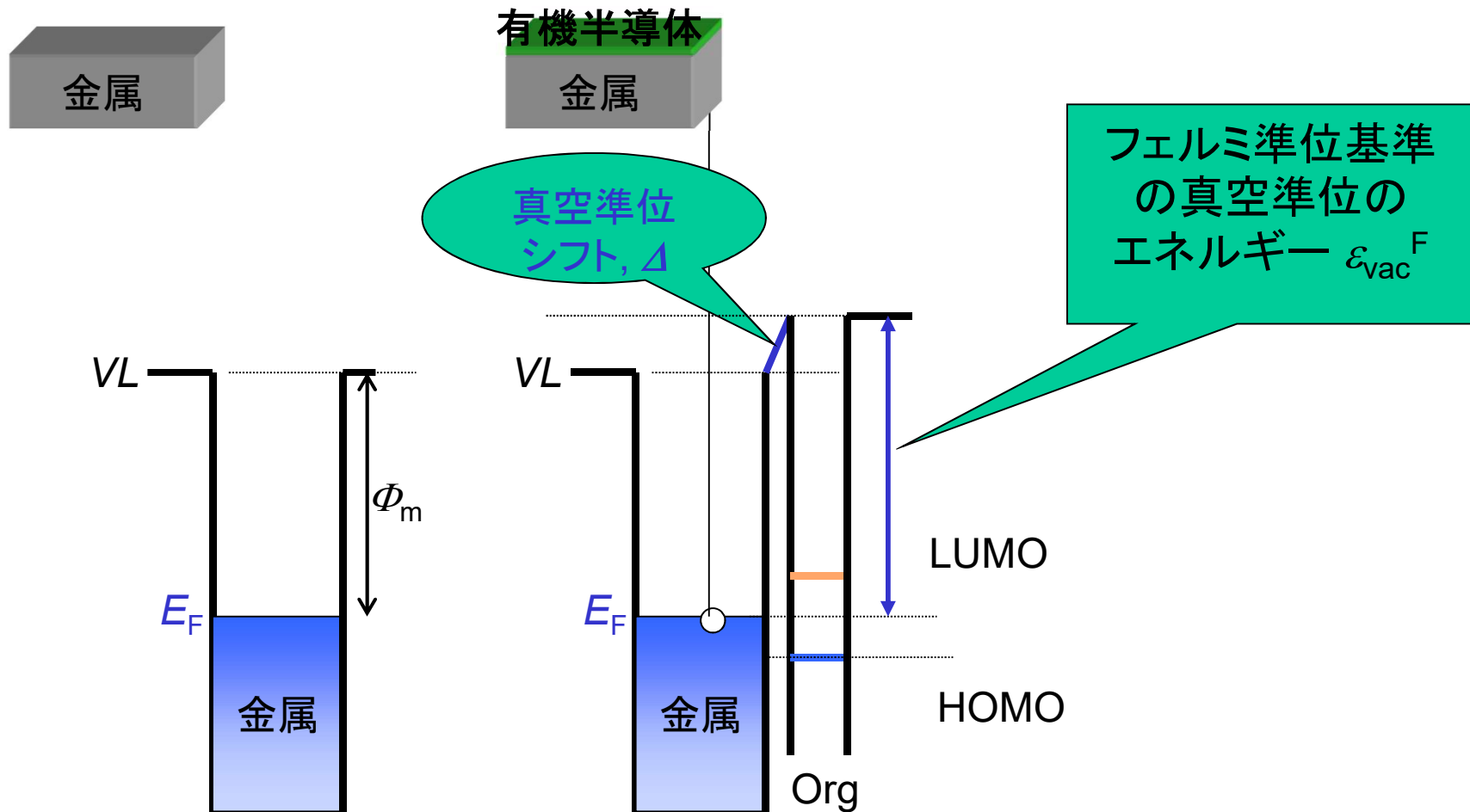


How to investigate interface :

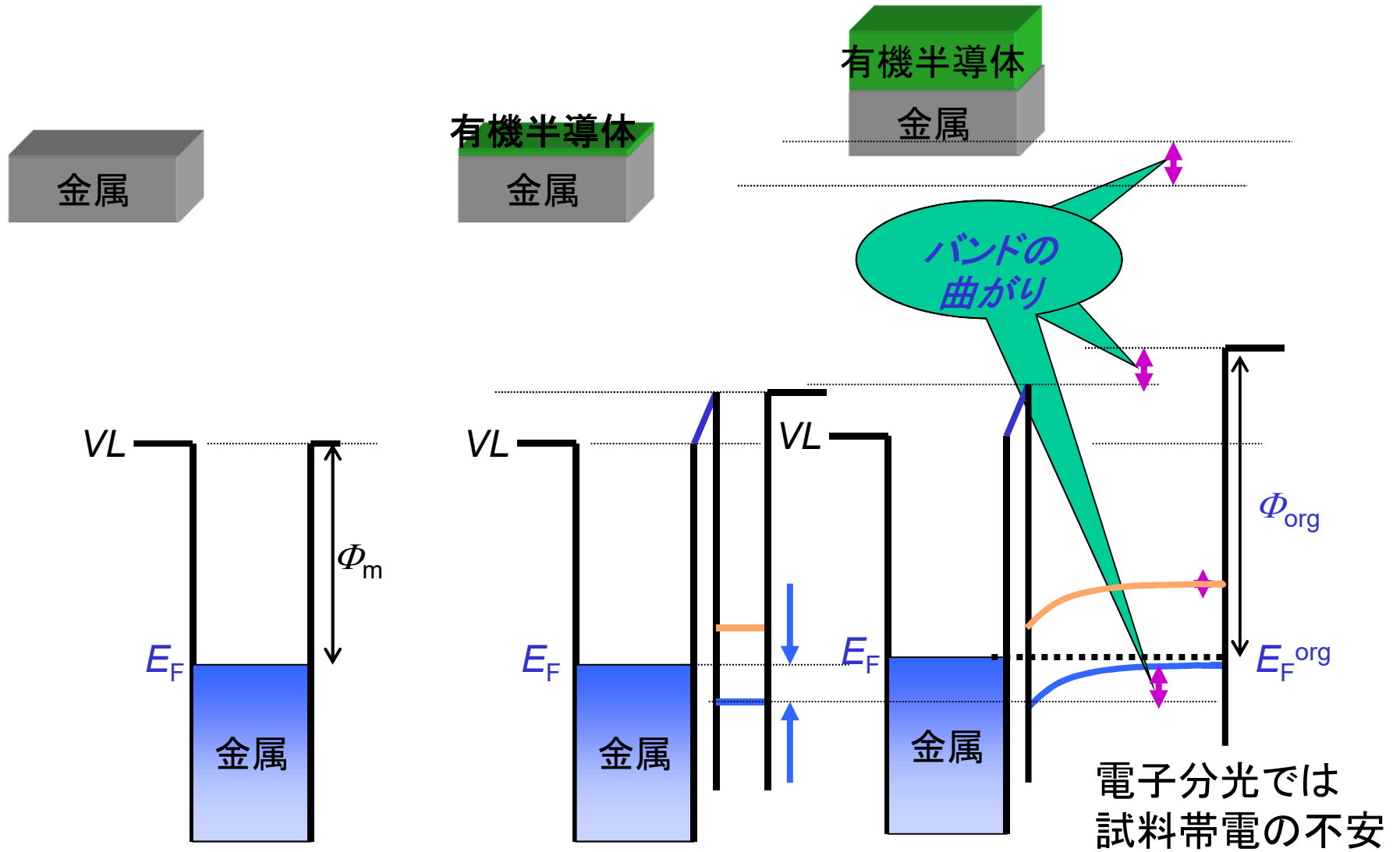
① Measurement of metal substrate



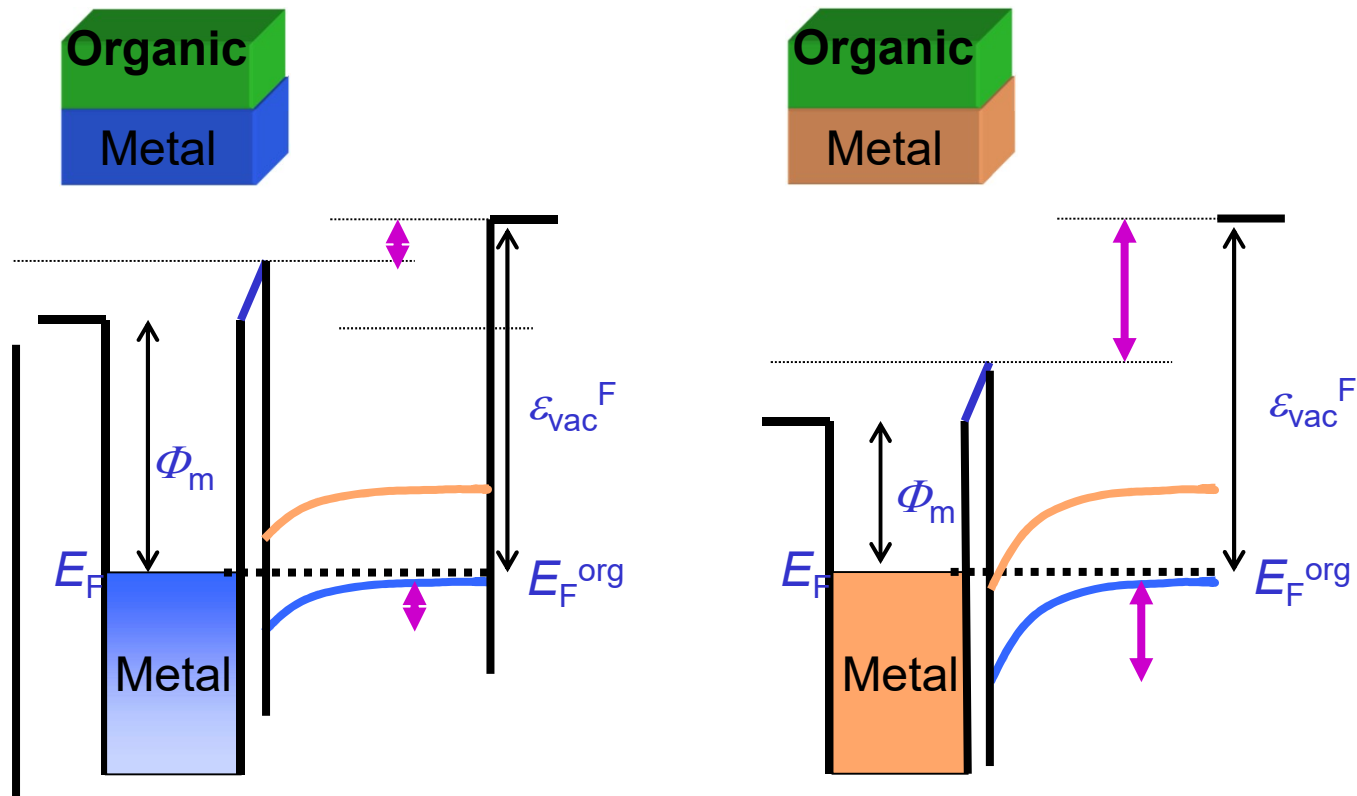
② Monolayer deposition



③ band bending during deposition

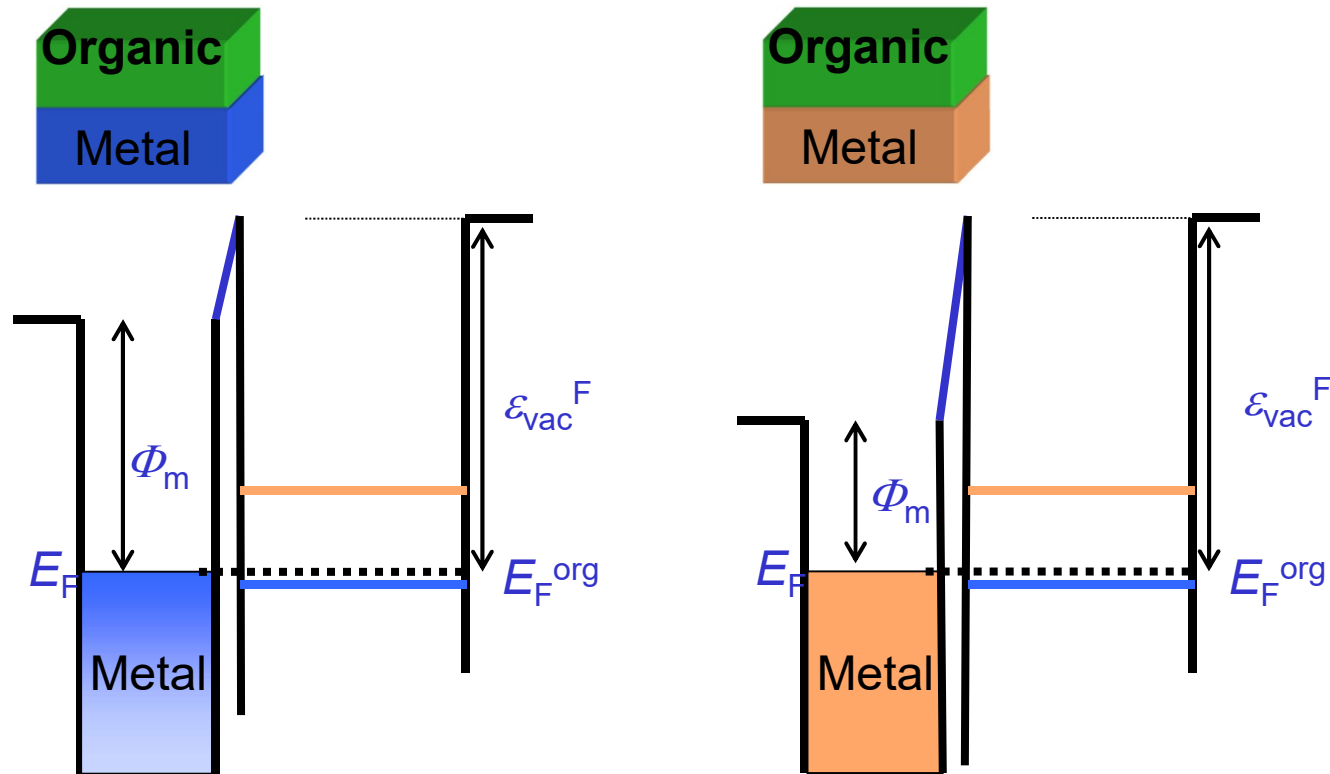


How to judge the establishment of Fermi level alignment



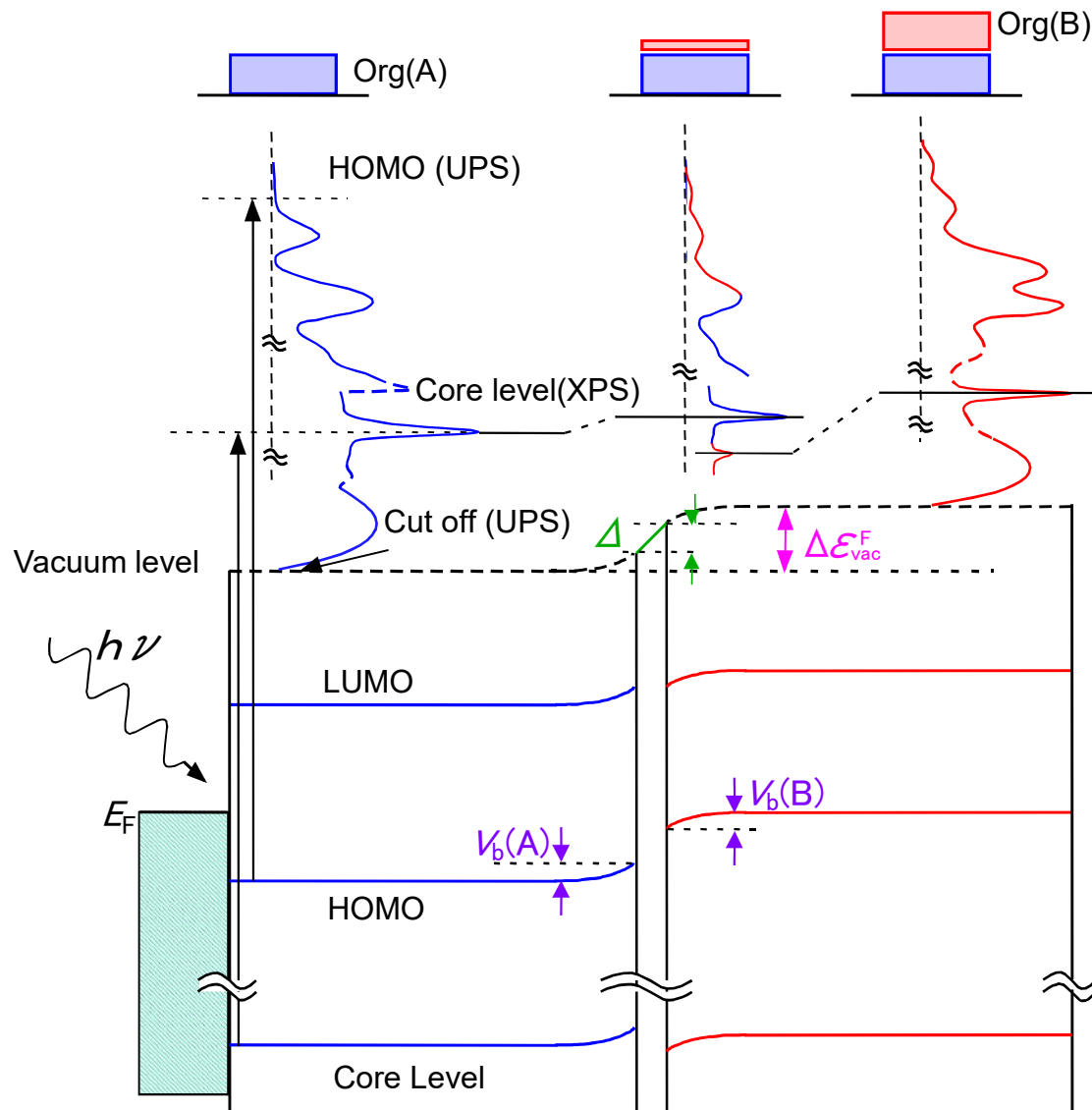
- 真空準位のエネルギー ($\epsilon_{\text{vac}}^{\text{F}}$) が基板の金属の仕事関数 (Φ_{m}) によらないことを、少なくとも異なる3種以上の金属基板に対して検証することが必要

Distinction from Fermi level pinning



- ϵ_{vac}^F は界面ピン止めの際も、基板の仕事関数 (Φ_m) に依存しない。
- 単分子層で真空準位が一定値になる。膜厚依存性を測れば、フェルミ準位一致と区別できる。
- フェルミ準位の一致を十分吟味して初めて有機物の仕事関数 (Φ_{org}) が求まる。

How to determine the energy level alignment by UPS and XPS

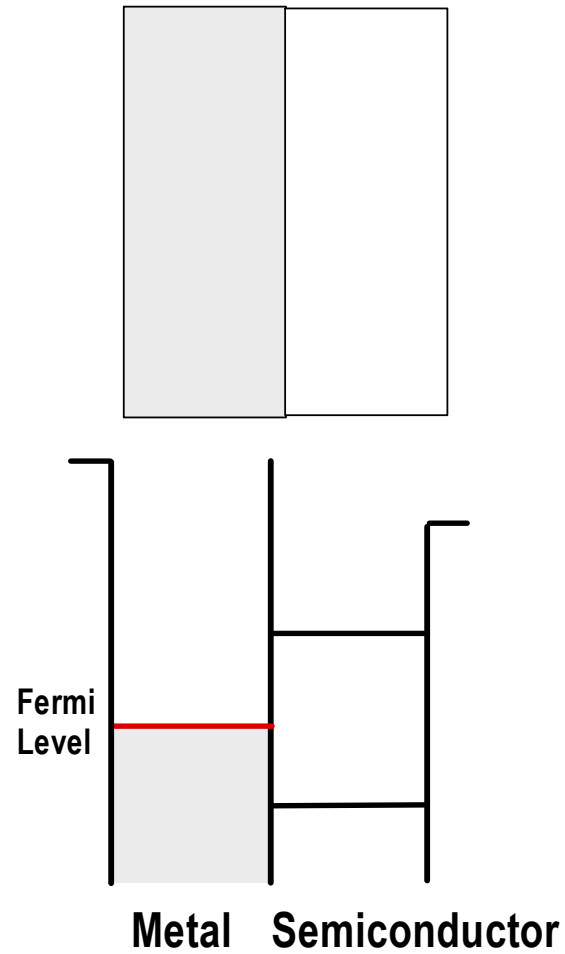


$$\Delta = \Delta \epsilon_{vac}^F - V_b(A) + V_b(B)$$

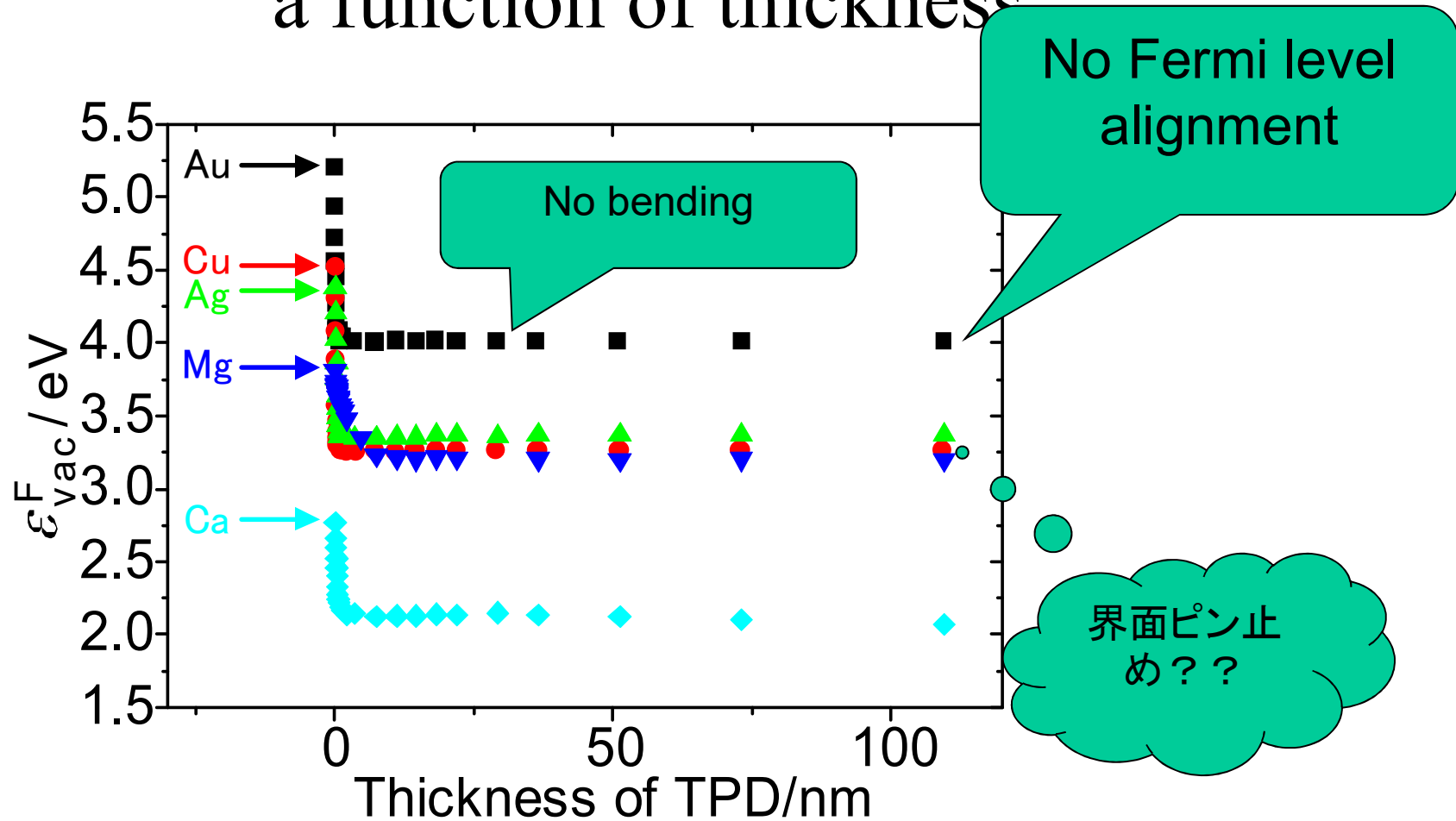
Narrowly defined band bending:

①intrinsic bending (flat band)

(B) フラットバンド

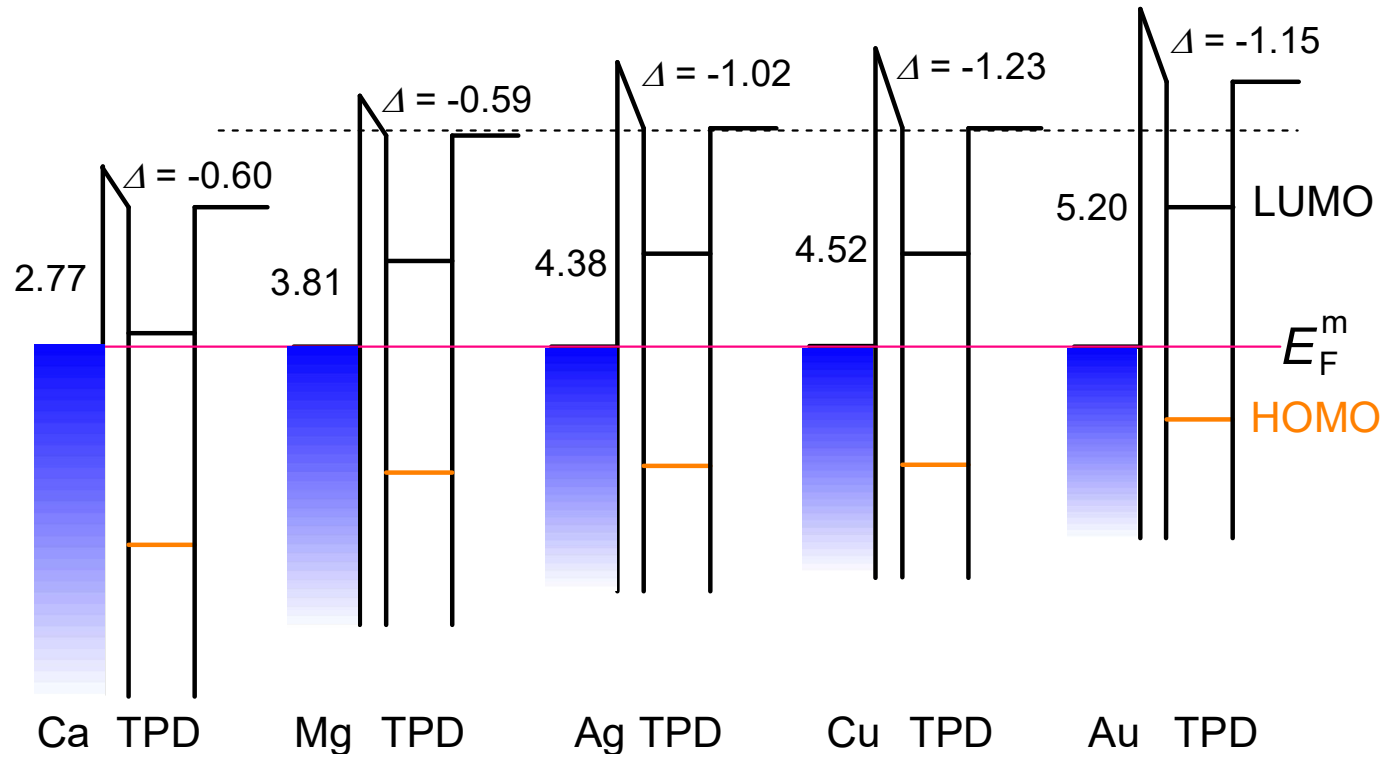


Surface potential of TPD film in UHV as a function of thickness



Well-purified organic semiconductor
→ Intrinsic SC **no band bending**

Energy diagrams of TPD/metal interfaces

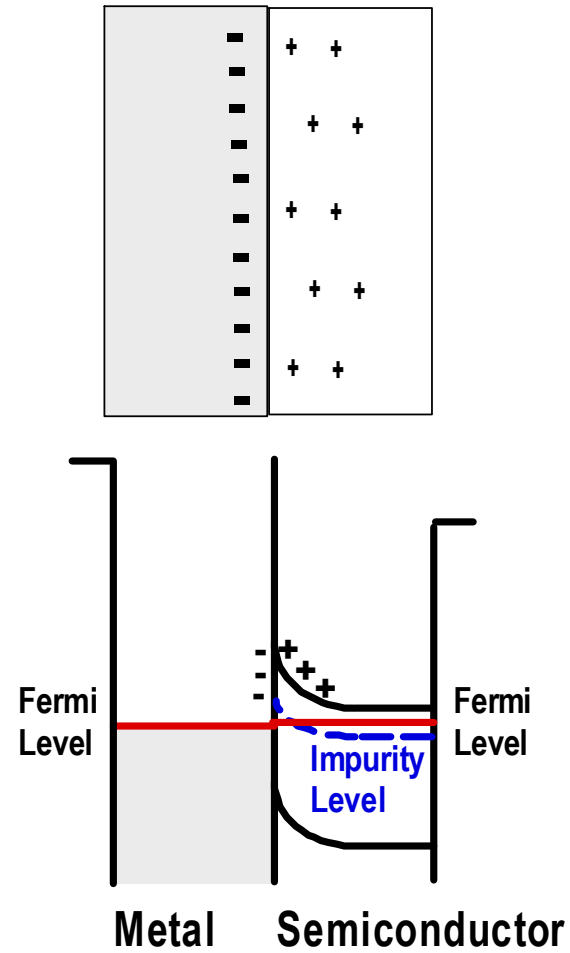


- No Fermi level alignment

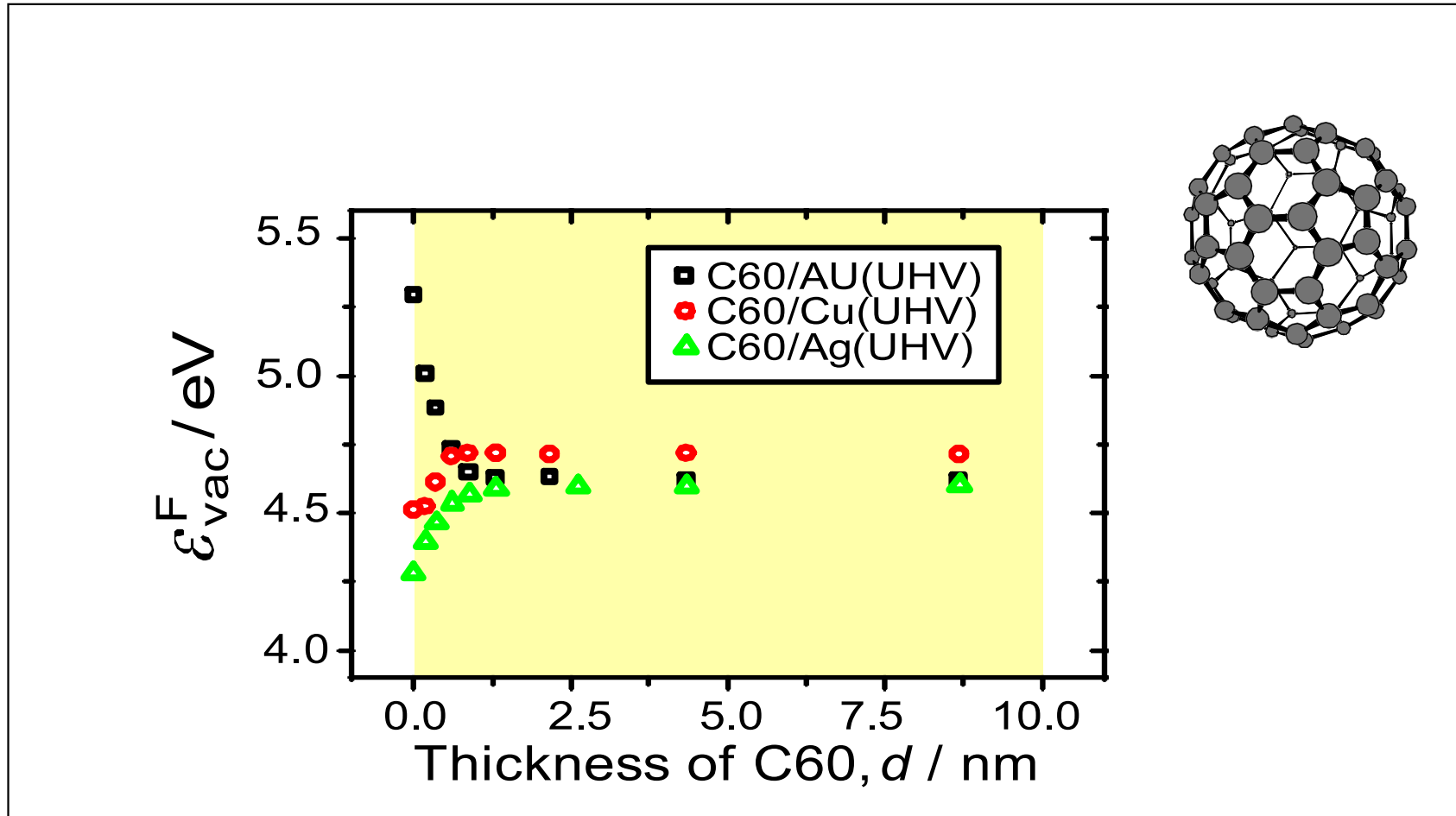
Intrinsic band bending

② band bending due to ionization of impurity

(A) フェルミ準位の一致

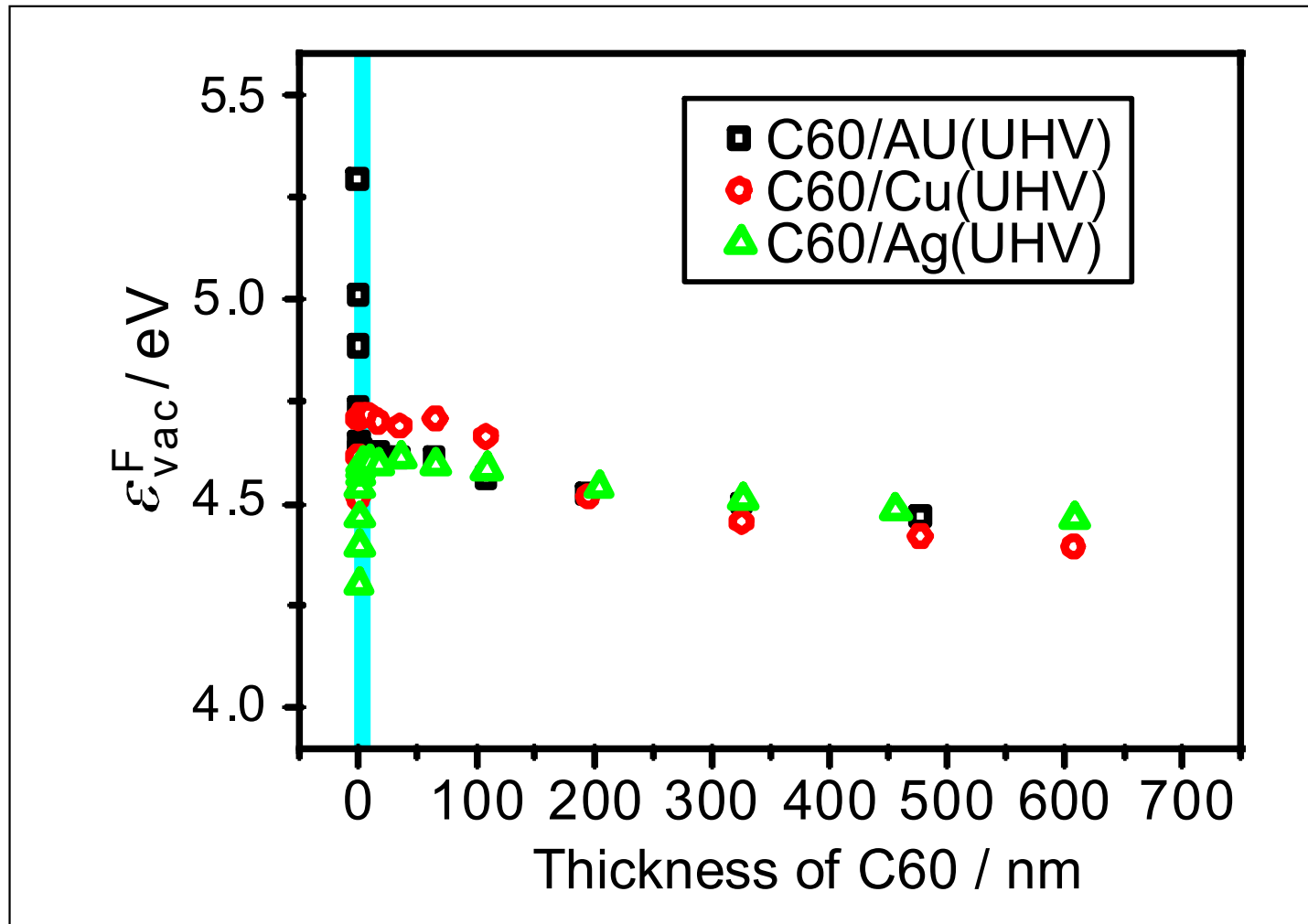


KP result: C60 thin region



- 4.65eV付近に収束→
- Weaverら: C60の電子準位は金属のフェルミ準位に対して並ぶ
- フェルミ準位の一致???

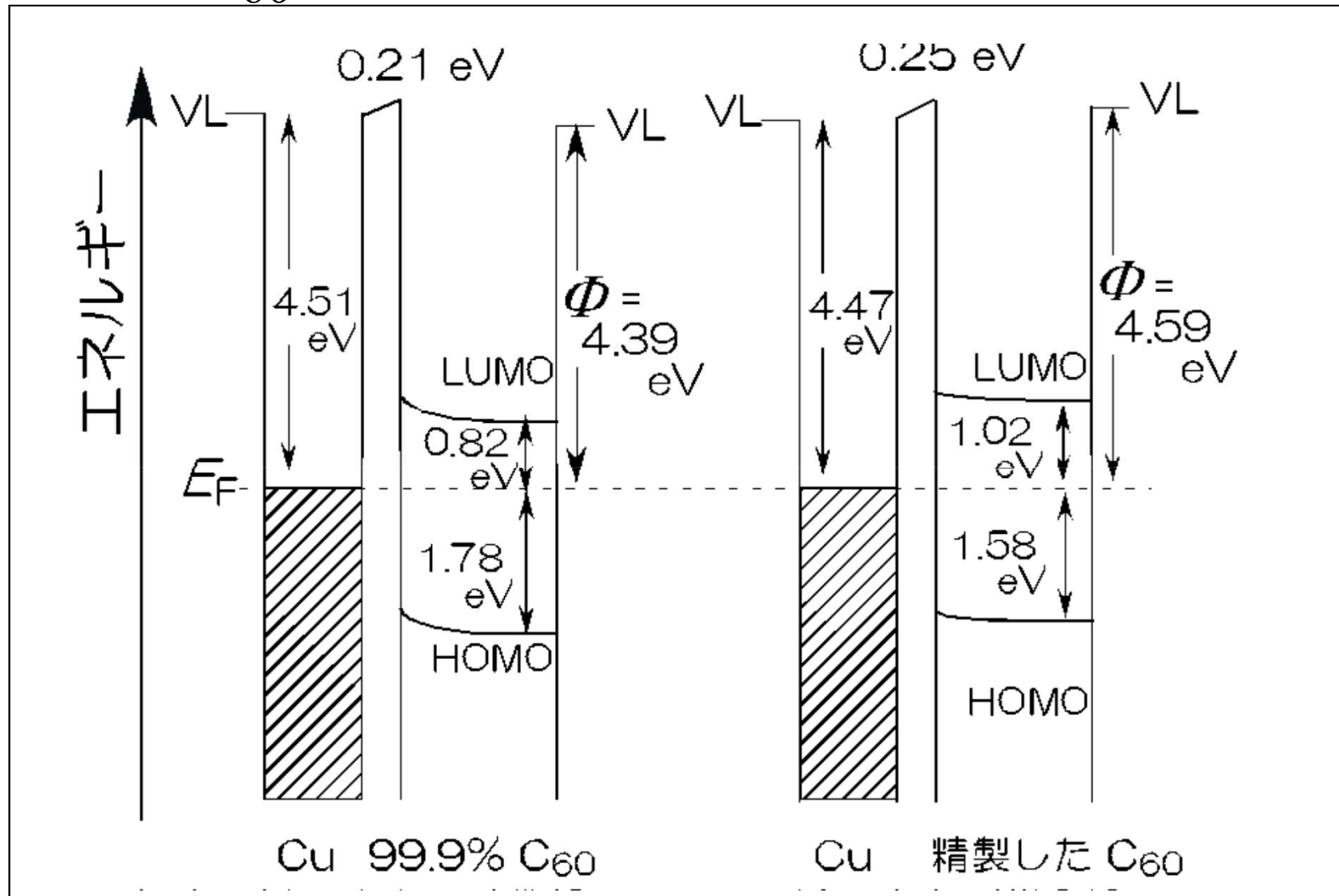
KP result: thick region



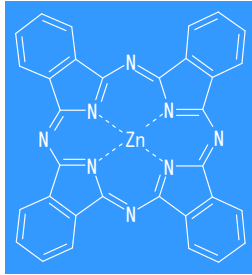
- 4.4eVへの収束→フェルミ準位の一致 Fermi level alignment
- $W=495\text{nm}$, $V_{BB}=0.21\text{eV}$ --> $N_D=4\times 10^{14}/\text{cm}^3$ (ppmレベル)

Purification effect, C₆₀

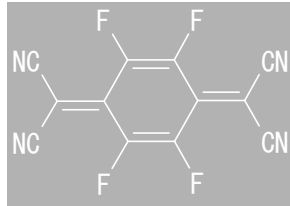
- E_F はギャップの中心より上方 (n 型)
- 精製により E_F はギャップの中心よりにシフト → donorの減少!



Band bending due to intentional doping

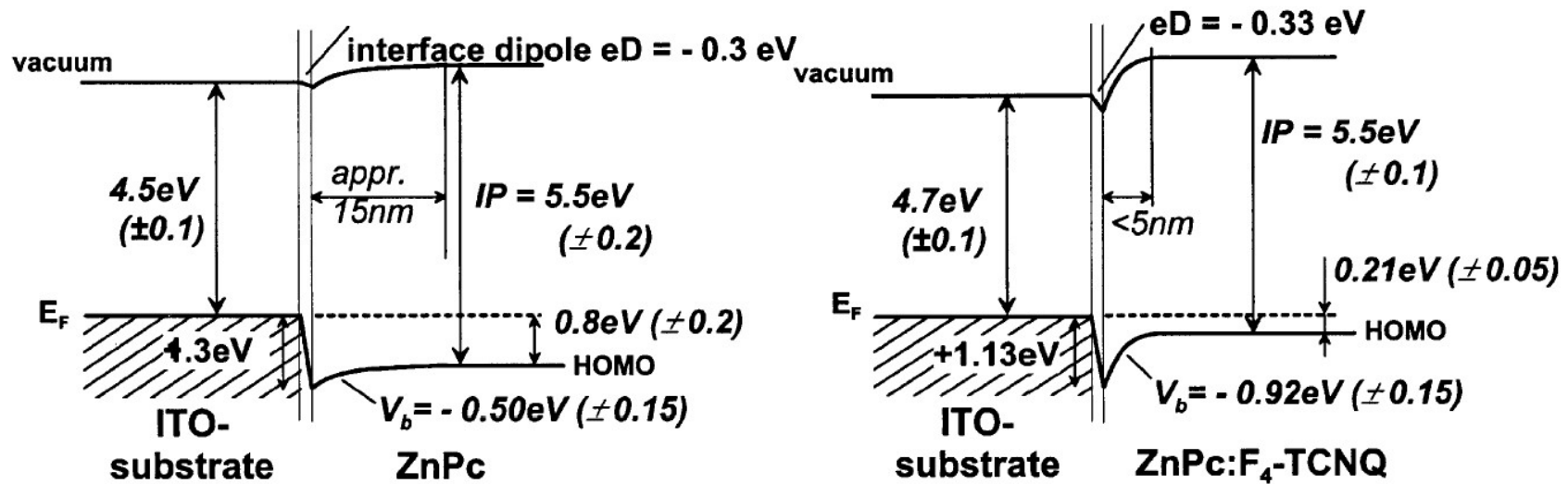


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= 30:1

J. Blochwitz et al. / Organic Electronics 2 (2001) 97–104



Spatial distribution of charges in ultrathin polyimide Langmuir-Blodgett films

Mitsumasa Iwamoto, Atsushi Fukuda, and Eiji Itoh
 Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku,
 Tokyo 152, Japan

J. Appl. Phys. 75 (3), 1 February 1994

大気中のポリイミド膜 Fermi準位の一致

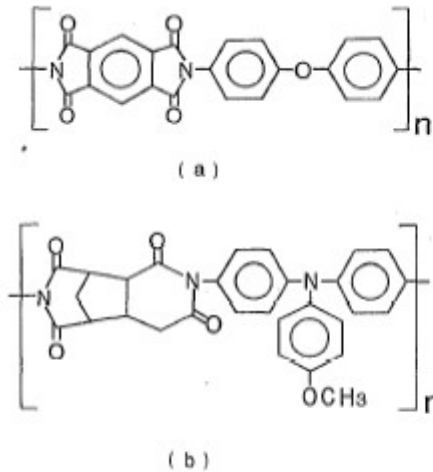


FIG. 1. Chemical structure of molecules used in this study. (a) PI, and (b) TRIPI.

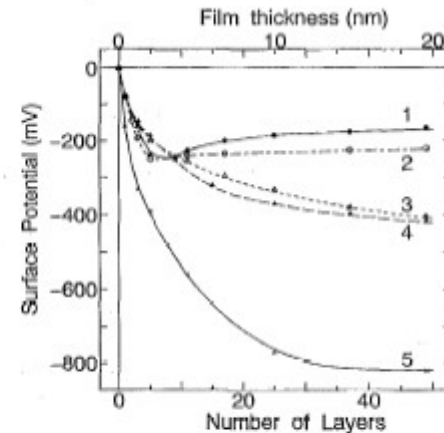


FIG. 2. The relationship between the potential difference across heat-treated PI LB films and the number of deposited layers. The monolayer thickness is 0.4 nm. Curves 1, 2, 3, 4, and 5 represent the surface potential built-up across PI LB films deposited on Au, Ag, Sn, Cr, and Al electrodes, respectively.

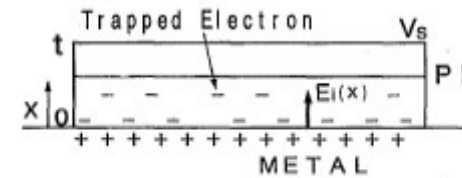


FIG. 3. Excess charges displaced from base electrodes. Potential difference vs the established between metals and the surface of the film is measured in the surface potential measurement.

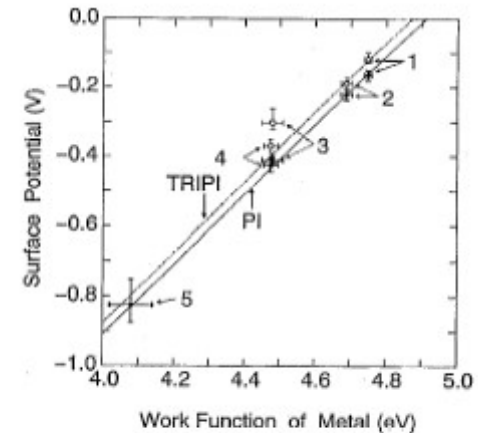


FIG. 5. The relationship between the saturated surface potential and the work function of metals. Open circles are for TRIPI LB films and closed circles are for PI LB films.

Fermi level alignment due to exposure to air

金井 要、他、有機分子・バイオエレクトロニクス分科会誌15(1) (2004)17-22

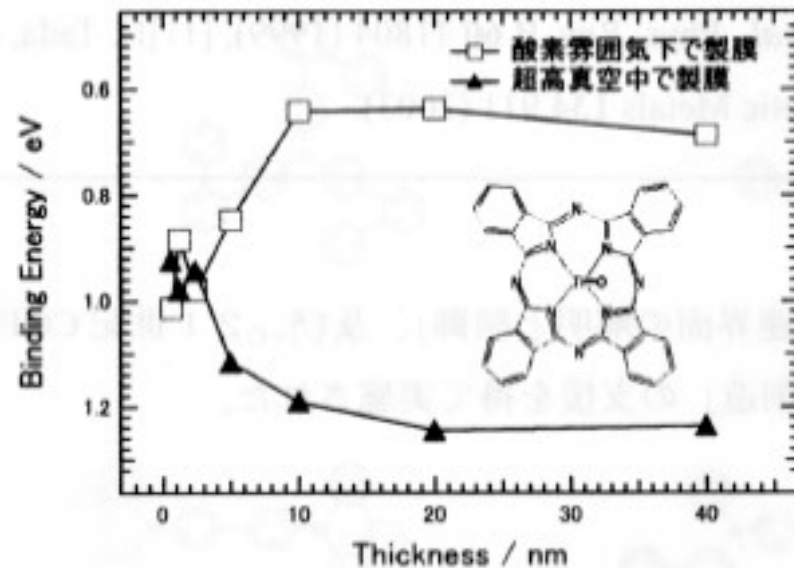


図 5. 超高真空中と、酸素雰囲気下で HOPG 上に製膜した TiOPc 薄膜の HOMO エネルギー位置の膜厚依存性

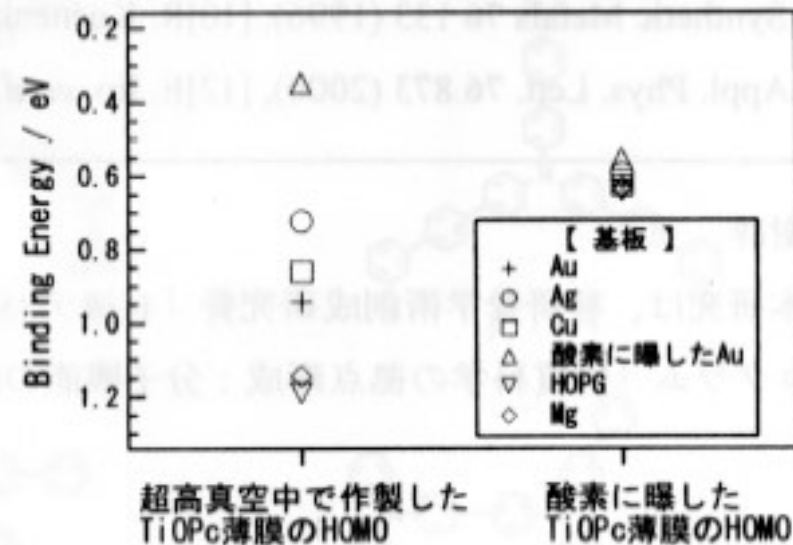
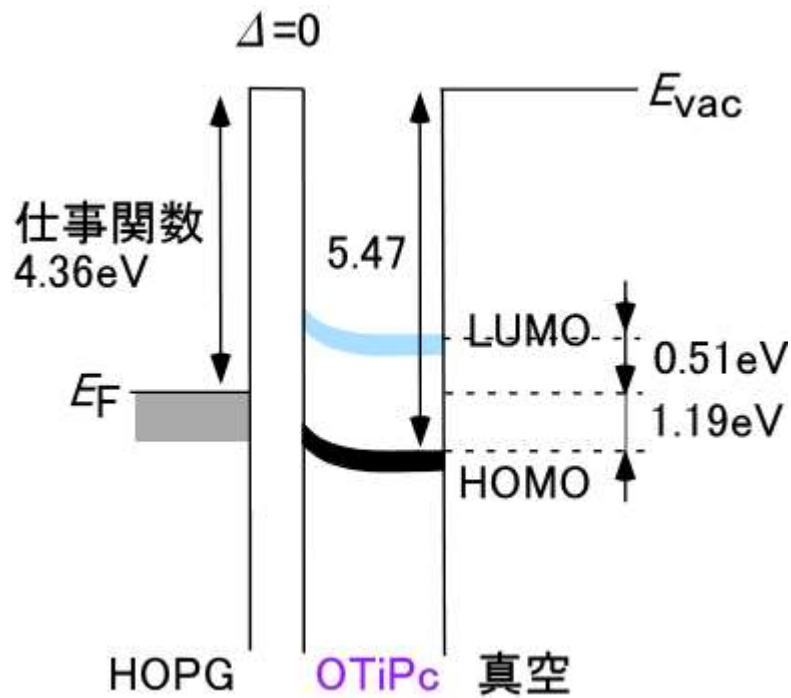


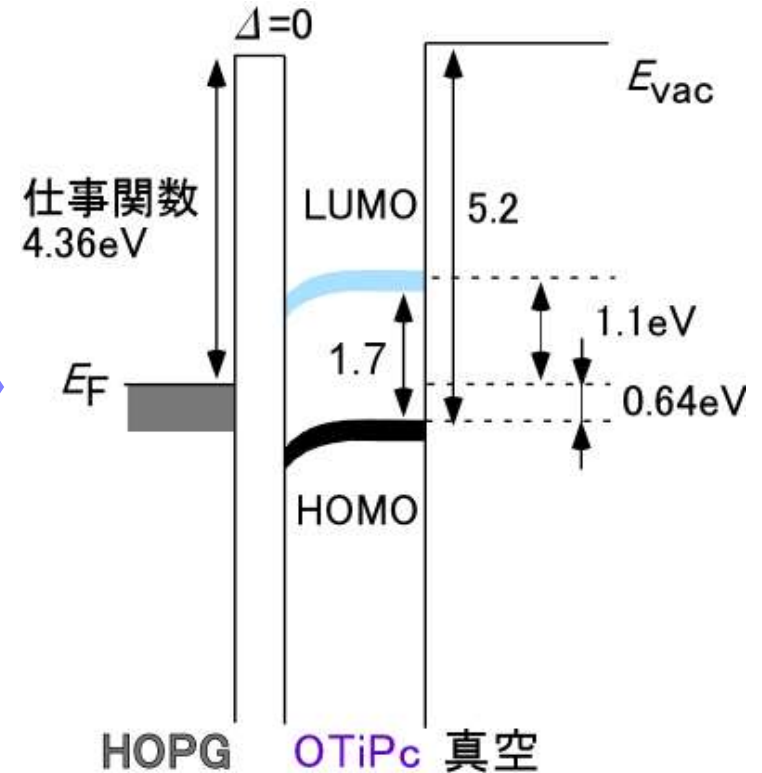
図 6. 様々な基板上的の TiOPc 薄膜の酸素暴露による HOMO エネルギー位置の変化

OTiPc / HOPGのエネルギーダイアグラム

n型(UHV)



p型(O₂曝露)



超高真空中で作製したOTiPc (10nm) 薄膜

T. Nishi, et al., CPL, (2005).

酸素雰囲気下で作製したOTiPc薄膜

O₂: 1.3 × 10⁻²Pa

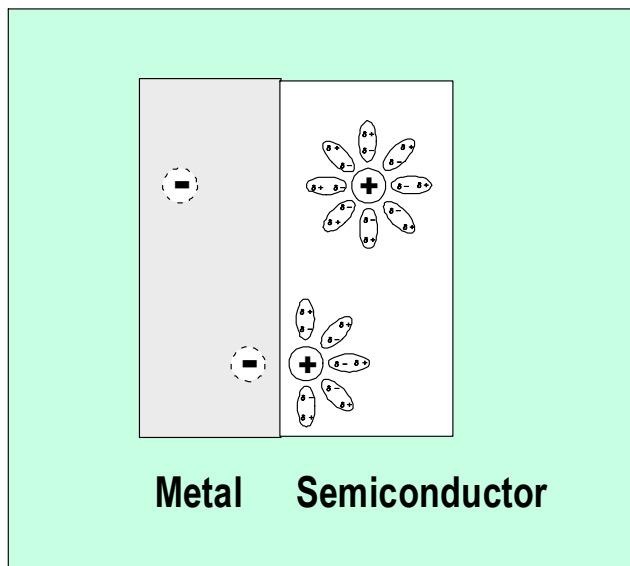
Energy gap data: H. Yanagi et al., *J. Phys. Chem.* 100 (1996) 5447

Narrowly defined band bending

- Band bending due to impurity ionization seems common even in organic system.
- Intentional heavy doping actually bend the band.
- Realistic material has more or less impurity which changes band bending feature.
- We cannot always assume Fermi level alignment.

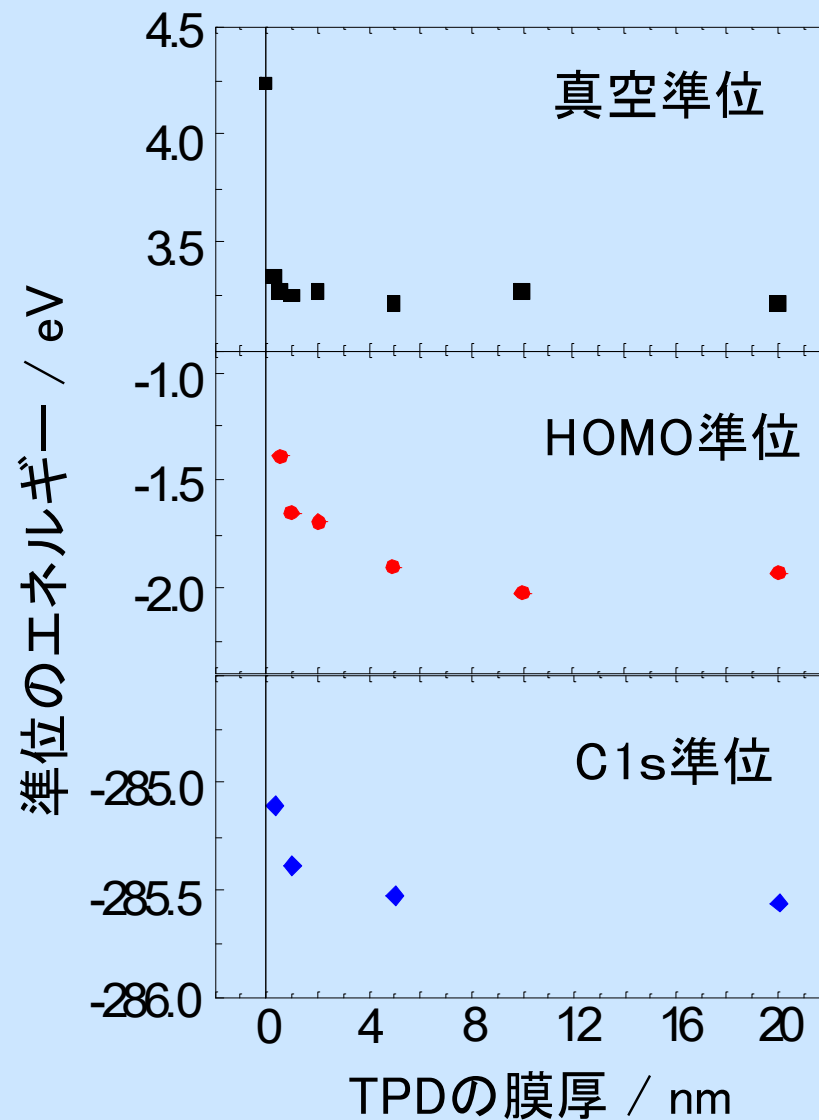
Widely defined band bending

① Screening effect

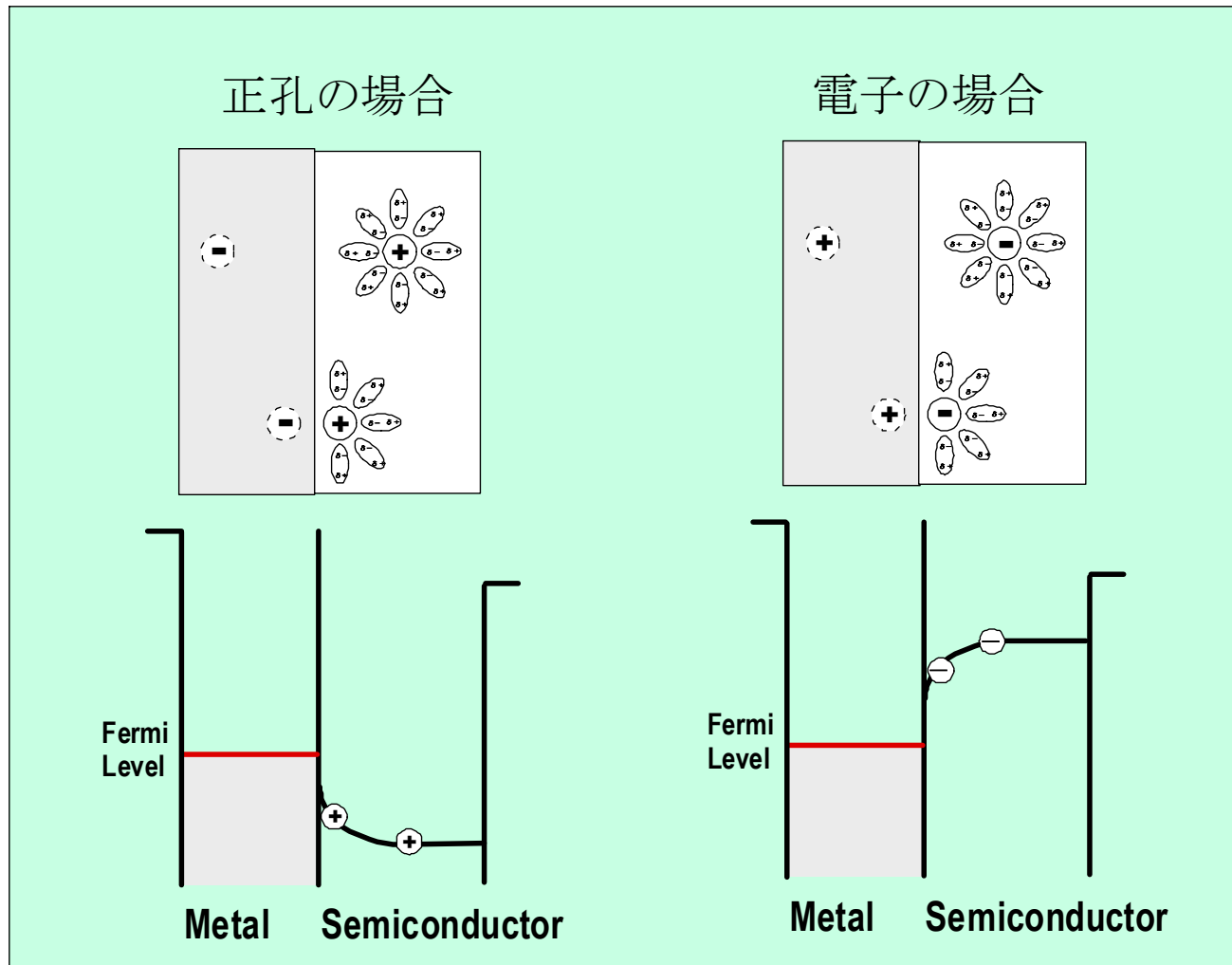


TPD/Au界面

$$I = E(M^+) - E(M)$$



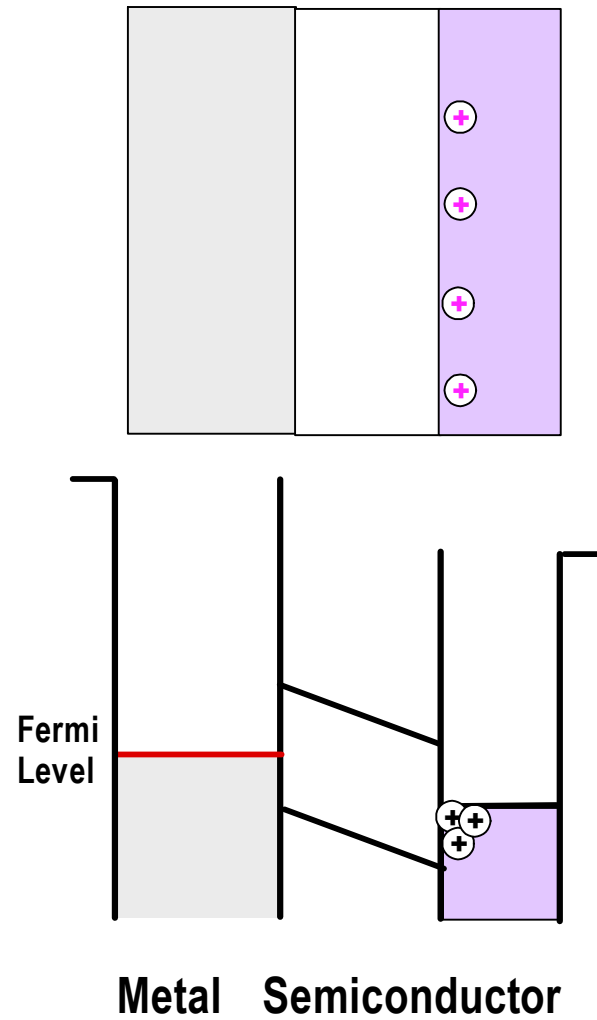
Screening effect for hole and electron

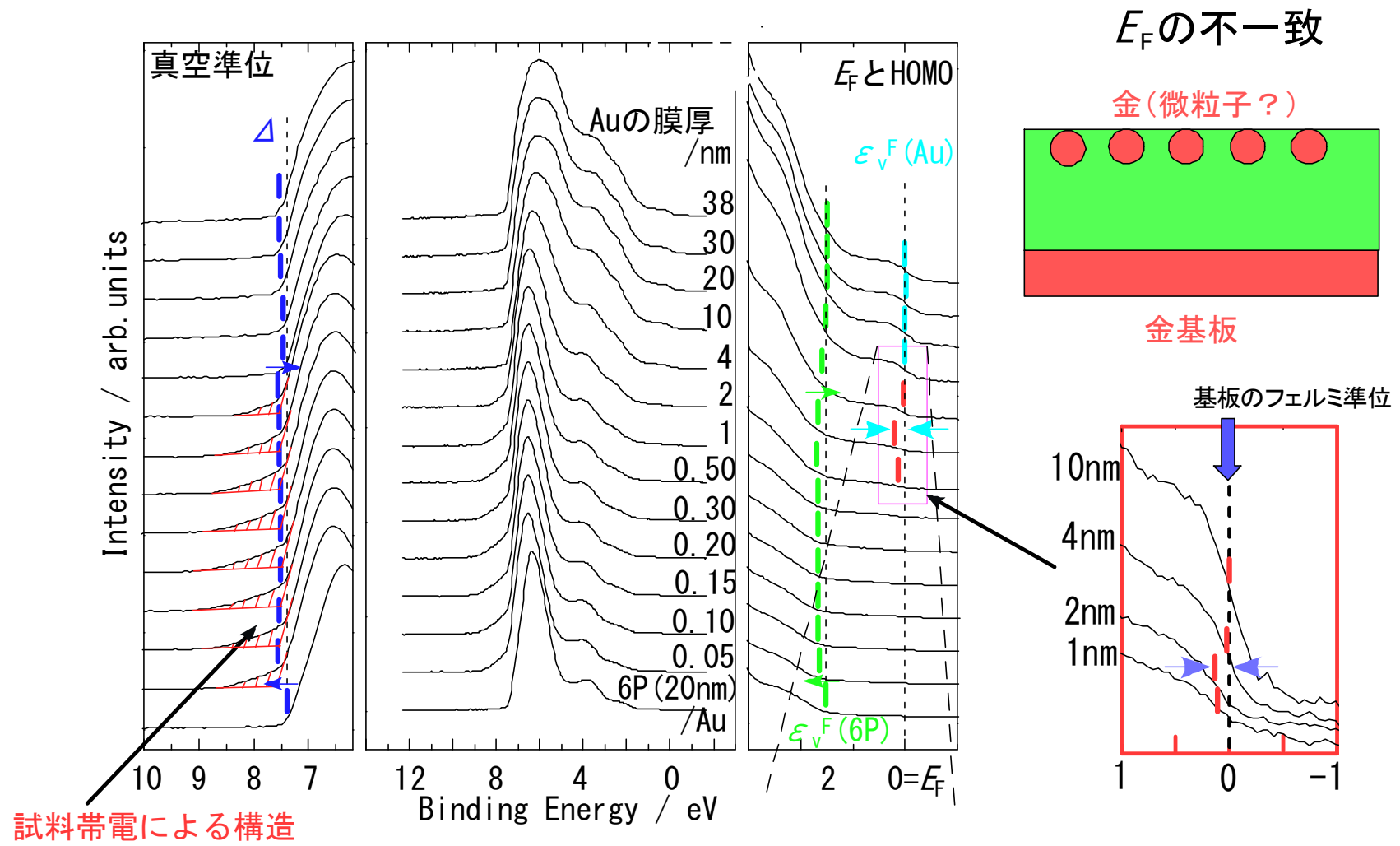


実デバイスにおける注入キャリアにも同様の効果

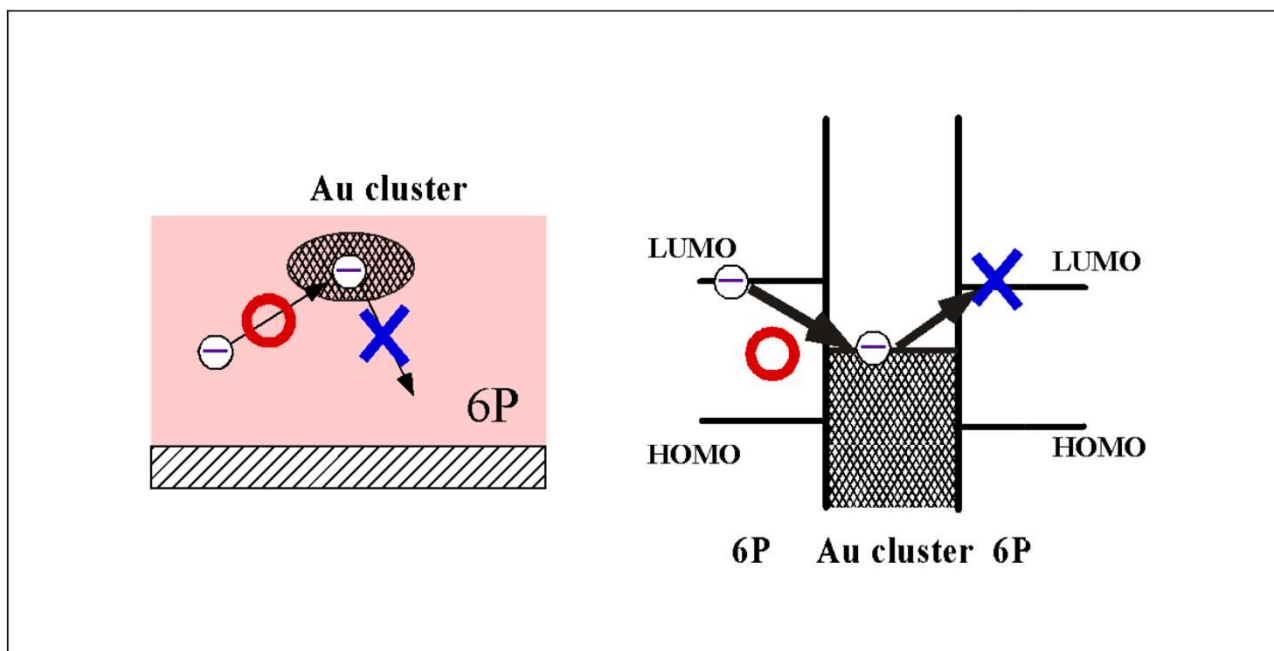
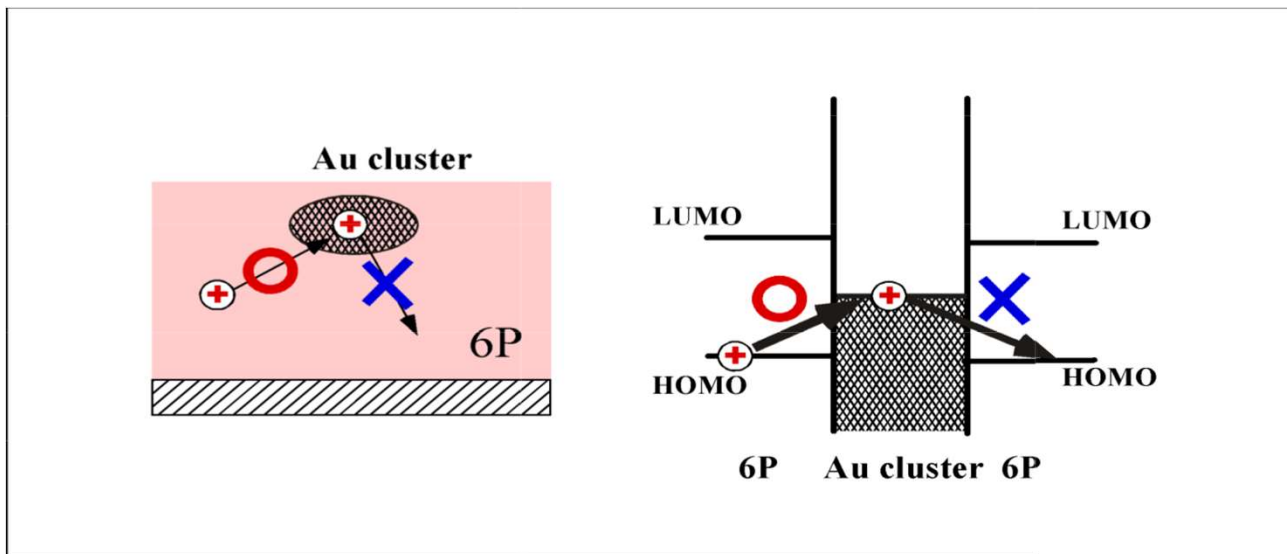
②Charging due to nano particles and blocking interface

(d) キャリアのブロック



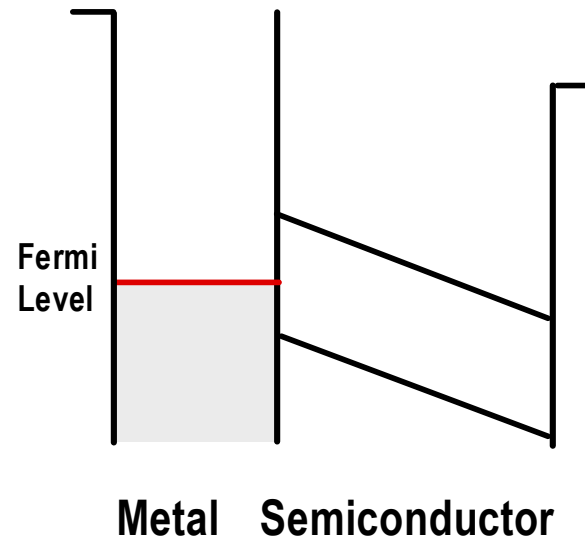
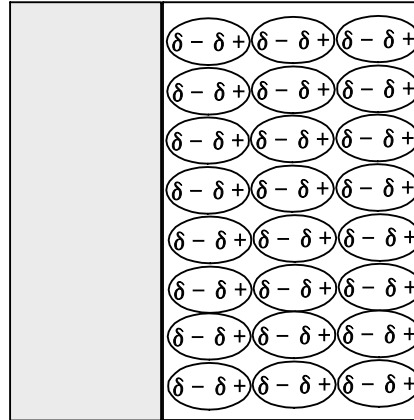


Buried metal cluster works as trap

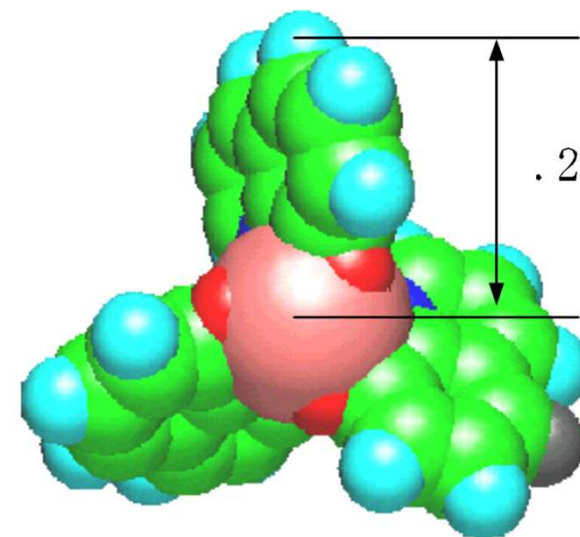


③永久双極子の配列効果

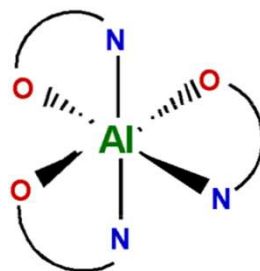
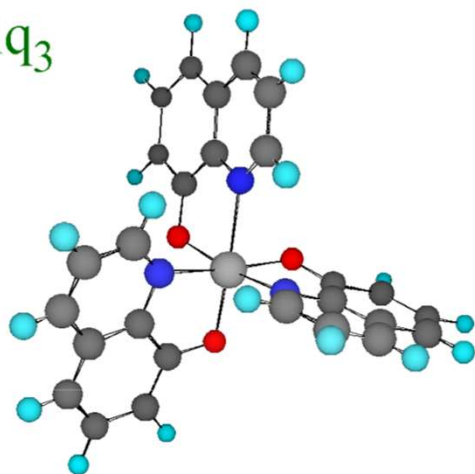
(e) 永久双極子の配列



Alq₃の分子構造

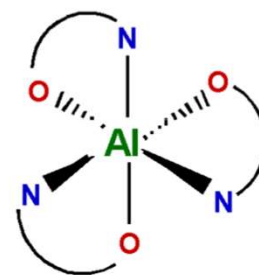


Alq₃



Meridional

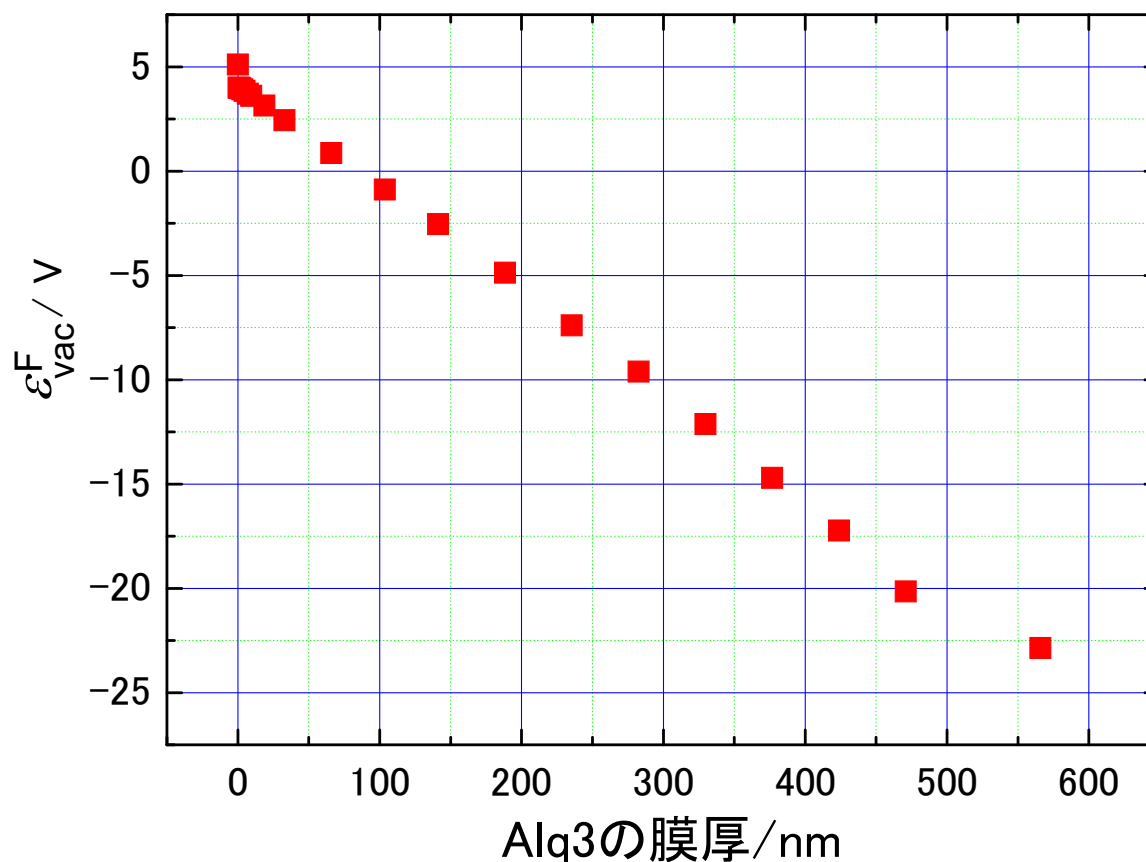
$m = 4.1 \text{ D}$



Facial

$m = 7.1 \text{ D}$

遮光環境下で成膜・測定した Alq₃膜の表面電位の膜厚依存性

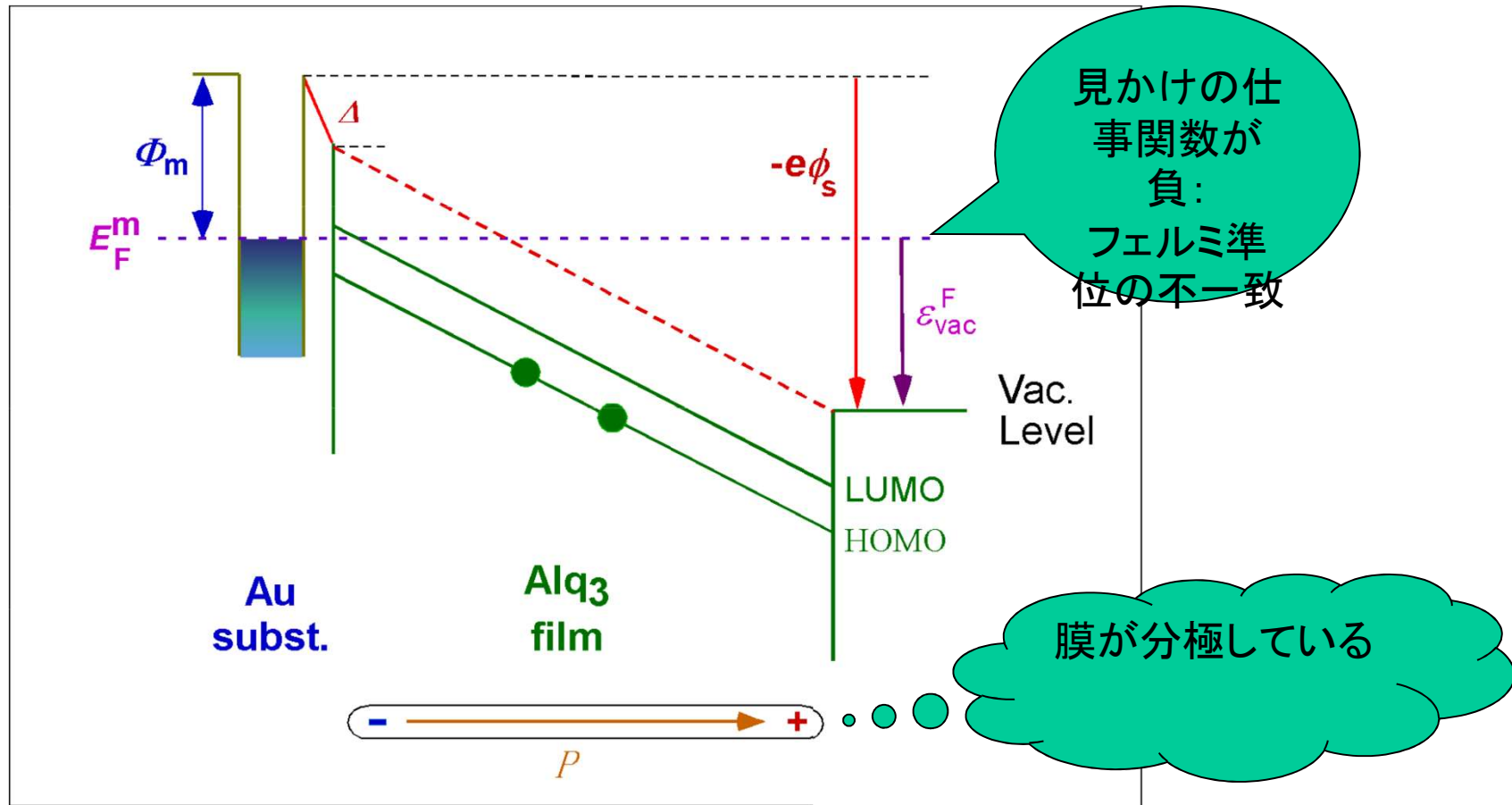


基板はAu

膜厚に比例した表面電位.

30V@600nmもの巨大な表面電位

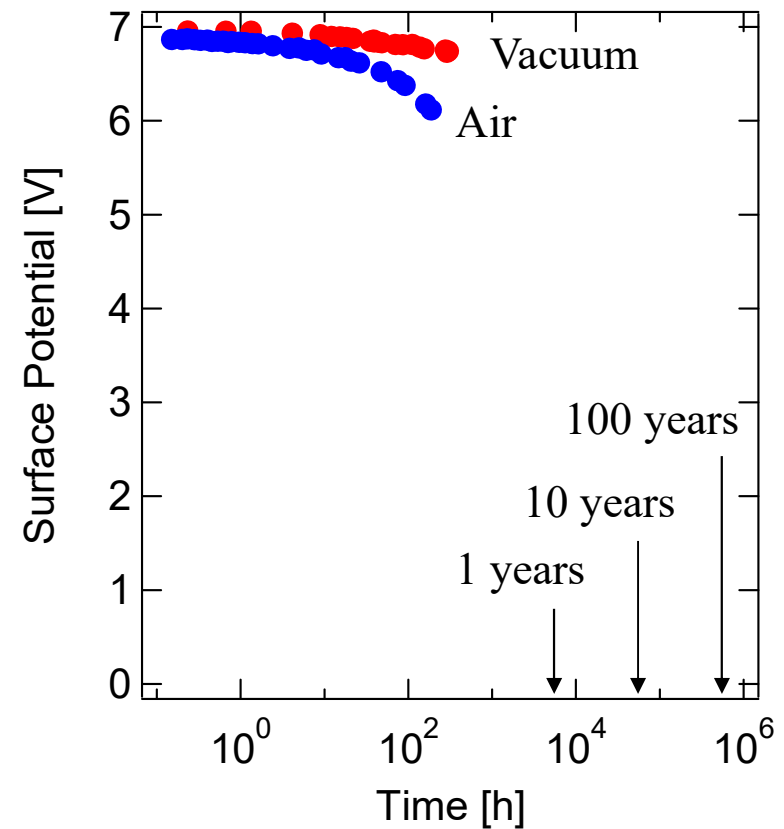
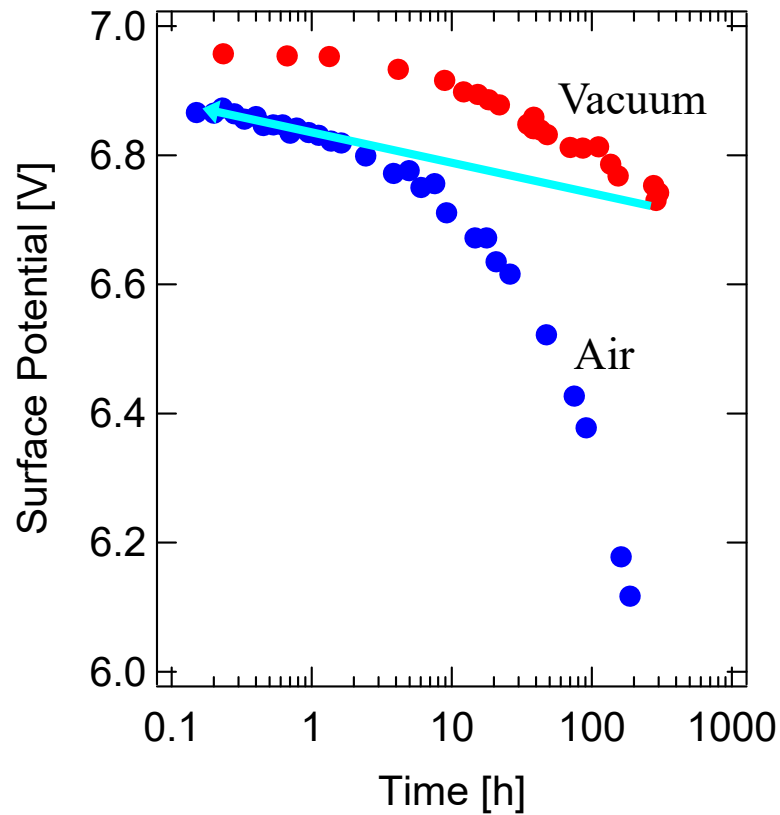
Alq₃膜のエネルギー図



熱平衡状態からかけはなれた状態。

電位の保持時間

After the measurement of the retention time in vacuum,
we exposed the sample to air and then measured the retention time in air.



The retention time in air is shorter than that in vacuum.

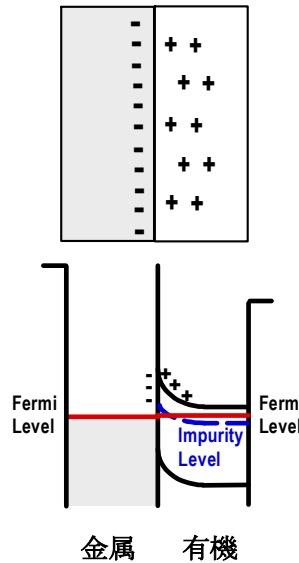
Band bending

有機半導体において、
界面からの関数として
エネルギー準位が変化
する現象はしばしば観
測されている。

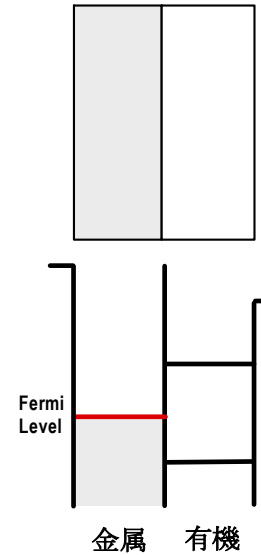
曲がるのか？
なぜ曲がるのか？
コントロールできるか？

狭義のバンドの曲がり
V.S.
広い意味での曲がり

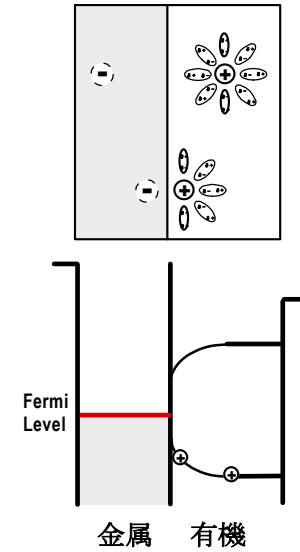
(A) フェルミ準位の一致



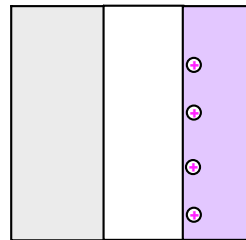
(B) フラットバンド



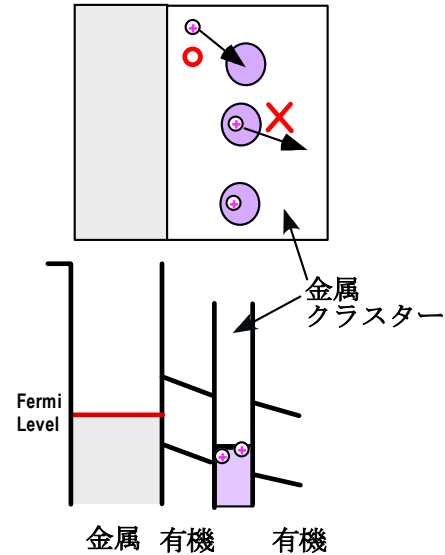
(c) 遮蔽効果



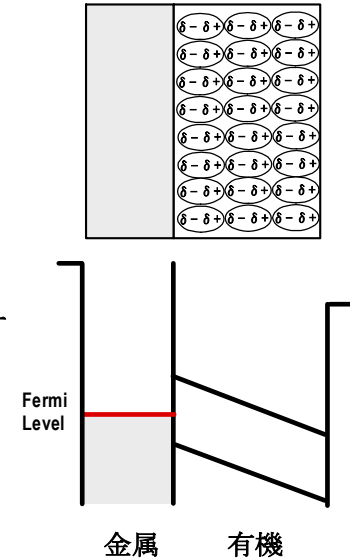
(d) キャリアのブロック



(d) キャリアのトラップ



(e) 永久双極子の配列



金属 有機1 有機2

金属 有機 有機

金属 有機