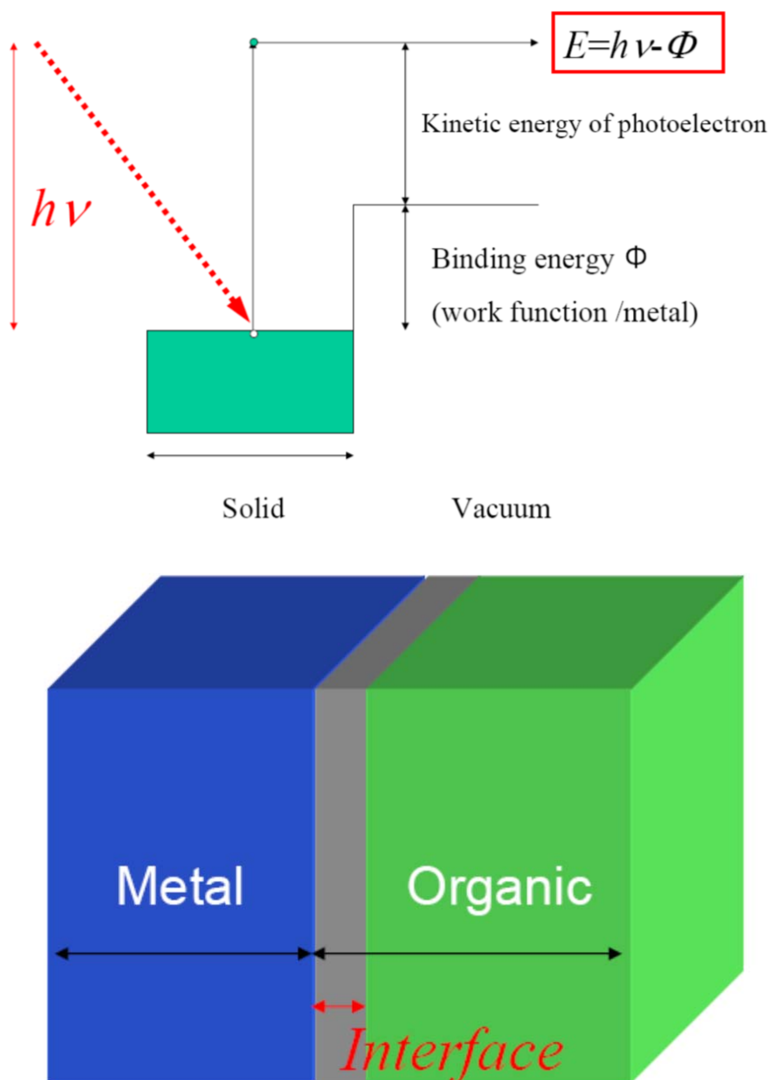
Metal/Organic Semiconductor Contacts

2014. 4. 15.

Changhee Lee
School of Electrical and Computer Engineering
Seoul National Univ.
chlee7@snu.ac.kr

Workfunction & IP Measurement: Photoelectric effect



Excited / vacuum level

Work function (ϕ)

e^-

E_F

hν

Secondary electrons

E_F ←Fermi level

Ionization potential —IP

e^-

E_F

E_K = hν -IP

e^-

hν

Secondary electrons

E_{vac}

E_F

Ionization potential

UPS for metal

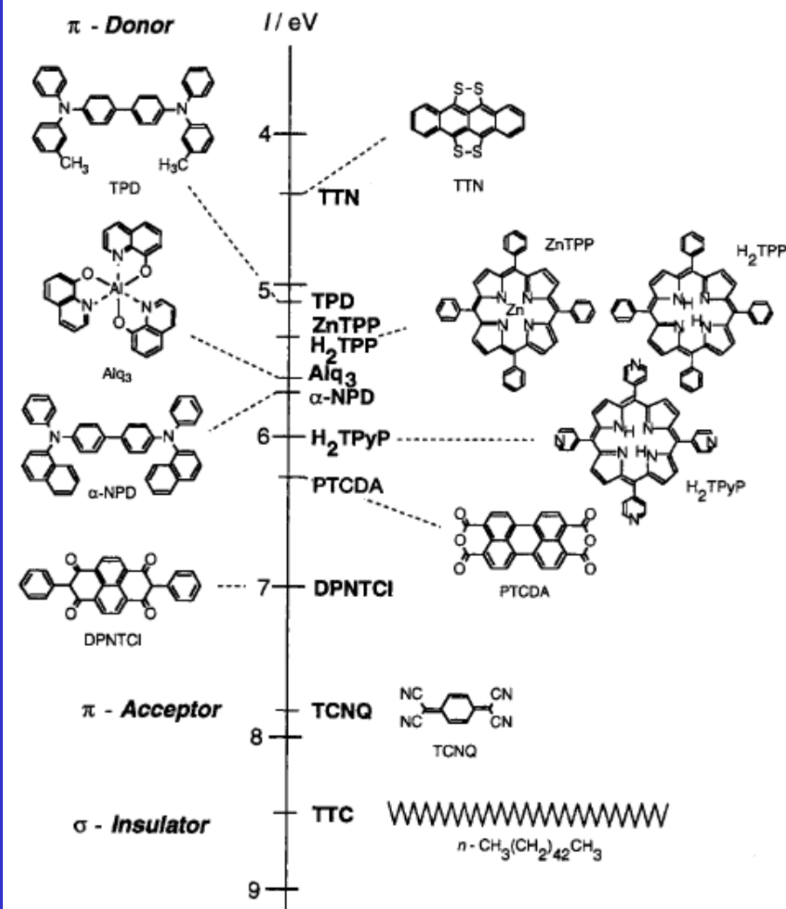
UPS for organic film

Energy level alignment at interface: Molecular orientation, reaction with metal, distortion of electronic distribution, existence of electric dipoles, etc.

Energy levels of Organic Materials

Metal work function
E (eV)
2
3
4
5
6
7
8
Mg
Al, In
Ag
Sn
PEDOT :PSS
Au
F4-TCNQ
NTCDA
TCNQ
PTCDA
BCP
CBP
F16-CuPc
PTCBI
Alq3
α-NPD
CuPc
ZnPc
Pentacene
6T
Transport levels
LUMO
HOMO
Transport gap

Ionization Potential (eV)



Weiying Gao and Antoine Kahn (Princeton Univ.), NSF workshop, "Technological Challenges for Flexible, Light-weight, Low-cost and Scalable Organic Electronics and Photonics," January 16-17, 2003

H. Ishii, K. Sugiyama, E. Ito, and K. Seki, Adv. Mater. **11**, 605 (1999).

Neutral contact, Schottky contact

neutral contacts : (1) we assumed that the semiconductor is not doped and thus contains no charge carriers of its own, and (2) we assumed that the contact interfaces consist only of the pure materials, i.e. that they are ideally clean and the states at the surface are the same as those in the bulk.

Schottky contacts: the depletion zones are formed near the contacts, for example, in doped semiconductors, and for one of the two polarities of the applied voltage they are inhibiting contacts (**Schottky barriers**) that prevent the flow of current.

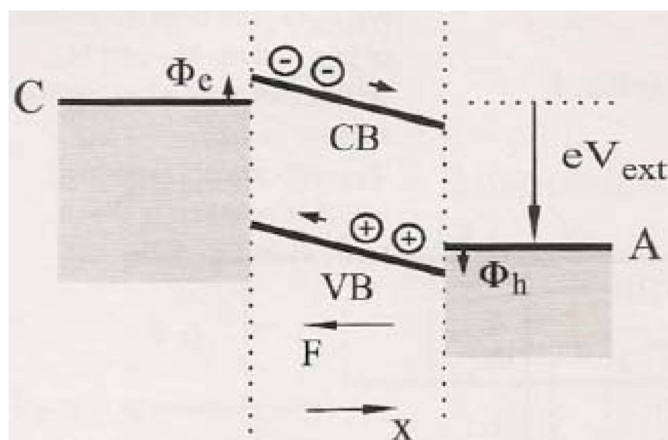


Fig. 8.22 The term diagram of an ideal intrinsic semiconductor with neutral contacts (see Fig. 8.21) and an applied voltage V_{ext}. Here, only the transport levels are shown. F is the electric field strength; the remaining notation is as in Figs. 8.19–8.21. The transport levels in semiconductors are flat and not curved only when the semiconductor is not p- or n-doped and V_{ext} is so low that the density of injected charge carriers cannot measurably influence the field F. This case is also termed the "flat band case". When the applied voltage is higher, so many charge carriers are injected that the space charge determines the field within the semiconductor and thereby dominates the charge transport (see Sect. 8.4.4).

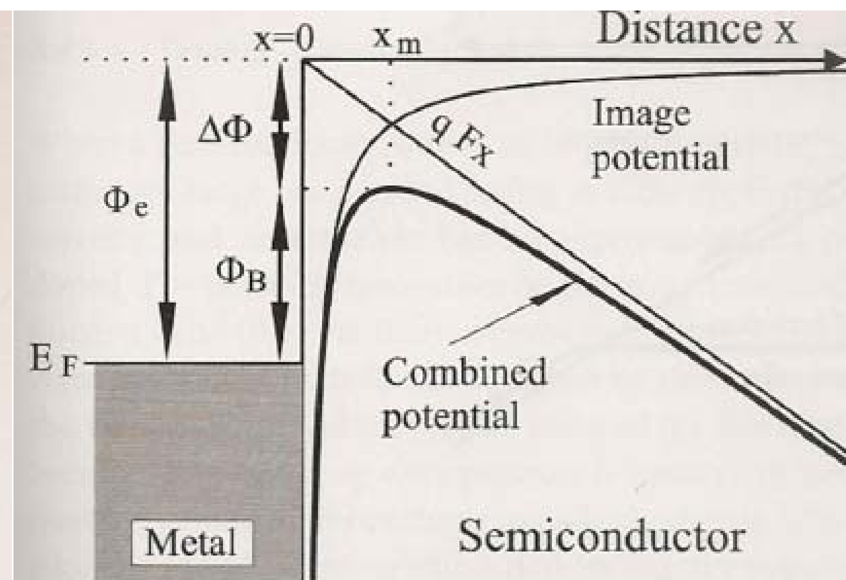


Fig. 8.23 The barrier for the injection of an electron from a metal into a semiconductor with an applied electric field F. Φ_e and $\Phi_B = \Phi_e - \Delta\Phi$ are the barrier heights without and with the image charges taken into account. x_m is a measure of the width of the barrier (see text).

Contacts

$\Phi_e = \Phi_m - A_c, \quad \Phi_m =$ workfunction of metal, $A_c =$ electron affinity of the semiconductor

$\Phi_h = \Phi_m - A_c, \quad I_c =$ Ionization potential of the semiconductor

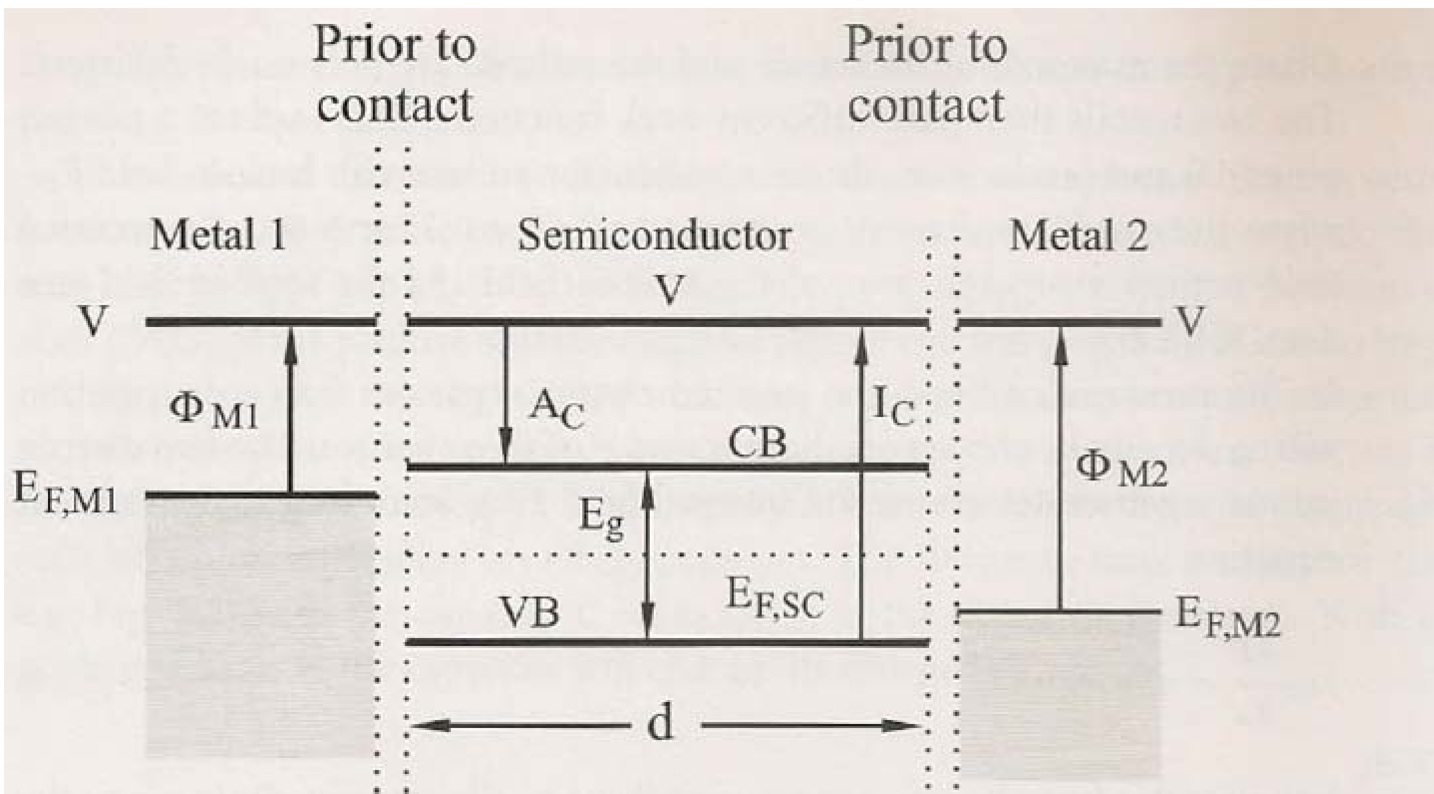


Fig. 8.19 The term diagrams of an (organic) semiconductor SC and two metals M_1 and M_2, which are not in contact. V is the vacuum energy level, E_F the Fermi energy, Φ the work function, CB the lower edge of the conduction band at the energy E_e, VB the upper edge of the valence band at the energy E_h, E_g the band-gap energy, A_C the electron affinity, I_C the ionisation energy, and d the thickness of the semiconductor sample (cf. also Fig. 8.6).

Changhee Lee, SNU, Kor

Contact potential and built-in electric field

$$V_{BI} = \frac{\Phi_{BI}}{e} = \frac{1}{e}(\Phi_{m2} - \Phi_{m1}), \quad \text{Contact potential}$$

$$F_{BI} = \frac{V_{BI}}{d} =, \quad \text{built-in electric field}$$

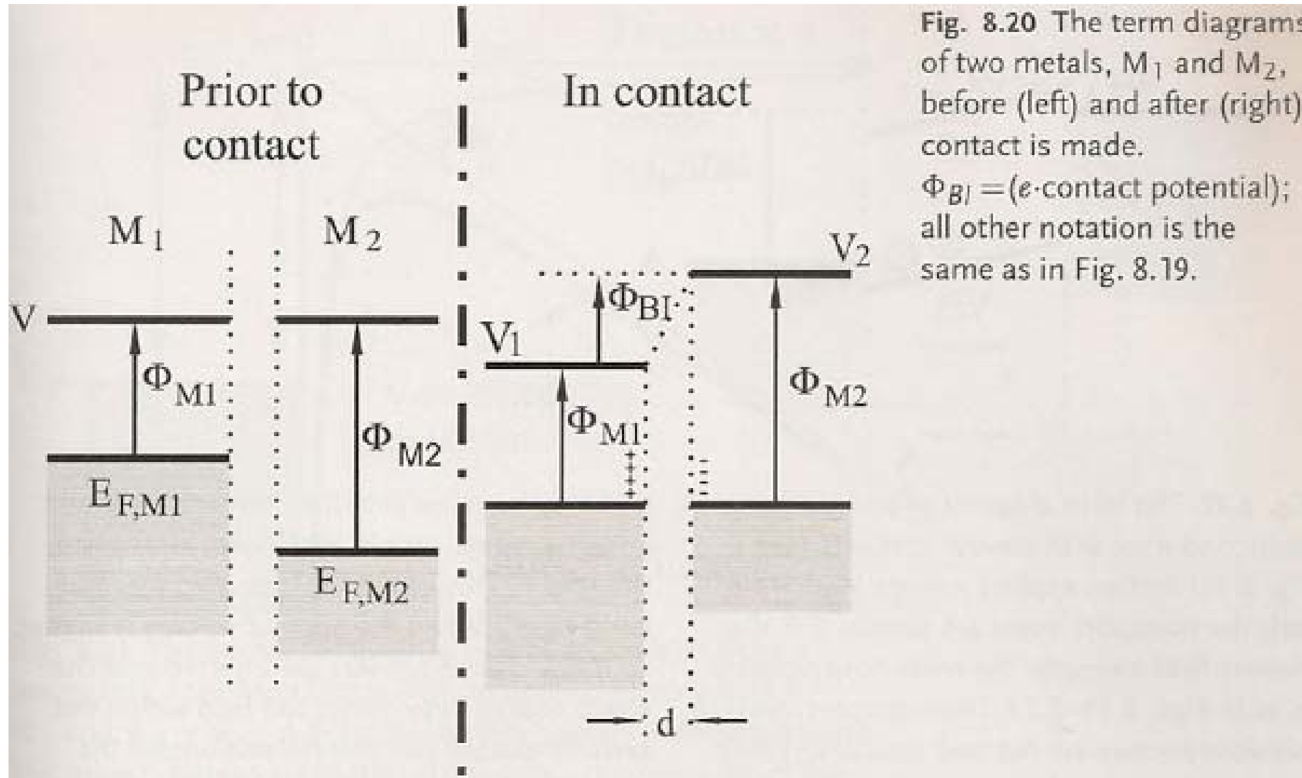
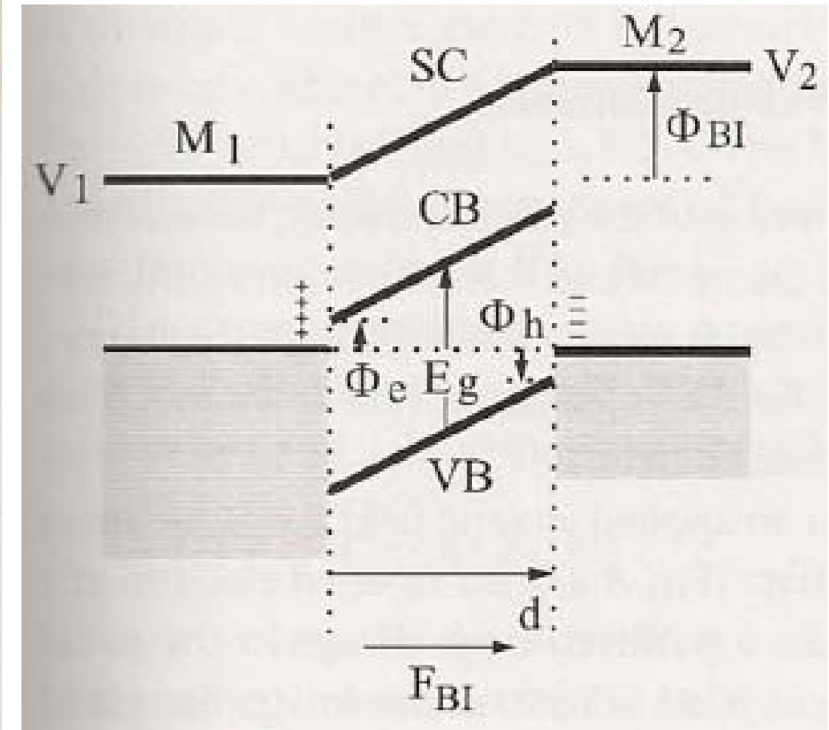


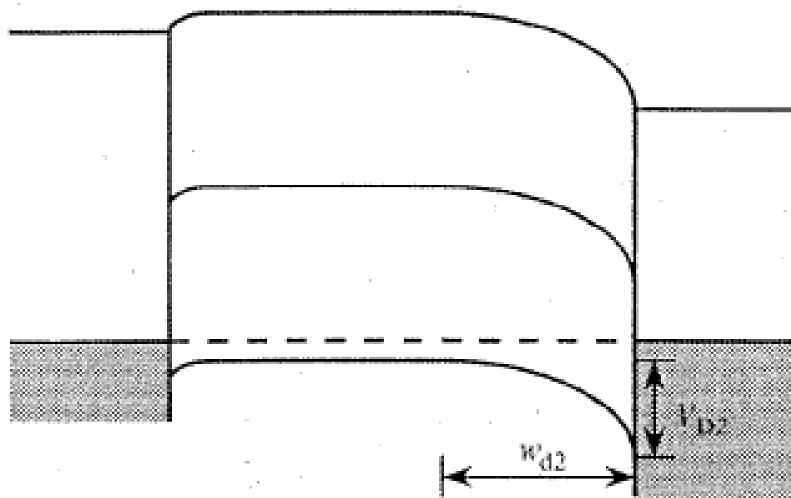
Fig. 8.20 The term diagrams of two metals, M_1 and M_2, before (left) and after (right) contact is made. Φ_{BI} = (e·contact potential); all other notation is the same as in Fig. 8.19.



Schottky barrier

Schottky barrier

Fermi level is equalized throughout the M/S/M structure by the diffusion of the carriers: Diffusion of holes from the molecular material into the metals leaves the negative ionized acceptor dopants at the interface **(band bending)**: This diffusion will continue until the internal energy barrier (eV_D: diffusion potential) is large enough to stop it.



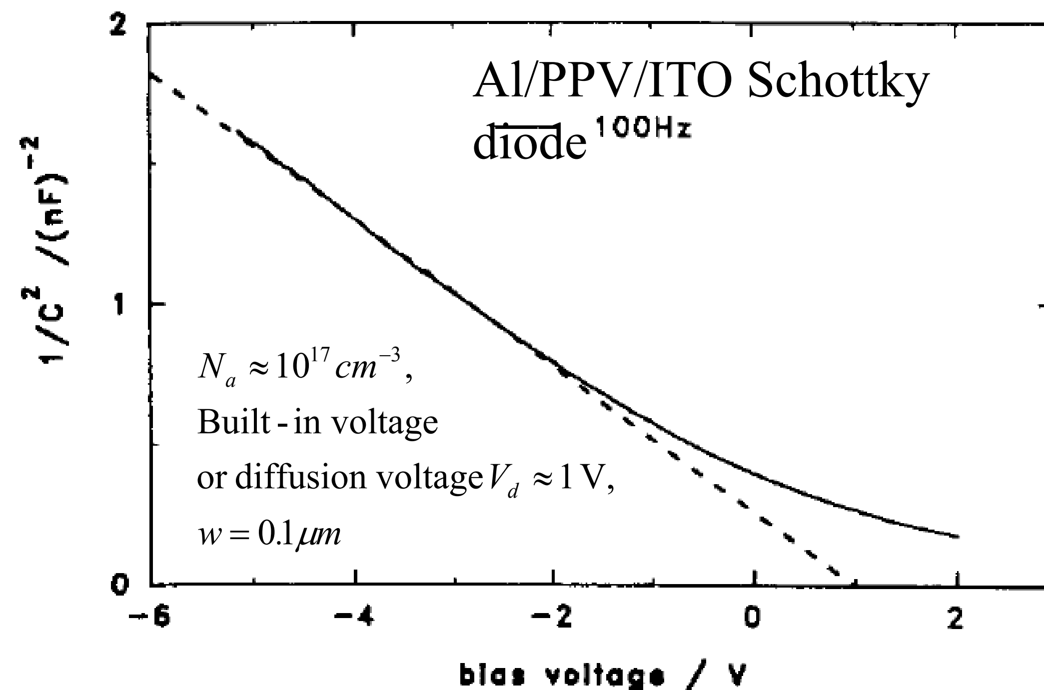
Depletion region

$$w_d = [\frac{2\varepsilon_o \varepsilon_r (V_D - kT/q)}{qN_a}]^{1/2}$$

Under reverse bias the measured capacitance corresponds to the junction capacitance

$$\frac{C}{A} = (\frac{e\varepsilon_o \varepsilon_r N_a}{2} \times \frac{1}{V_d + V})^{1/2}$$

$$w = [\frac{2\varepsilon_o \varepsilon_r (V_d + V)}{eN_a}]^{1/2}$$

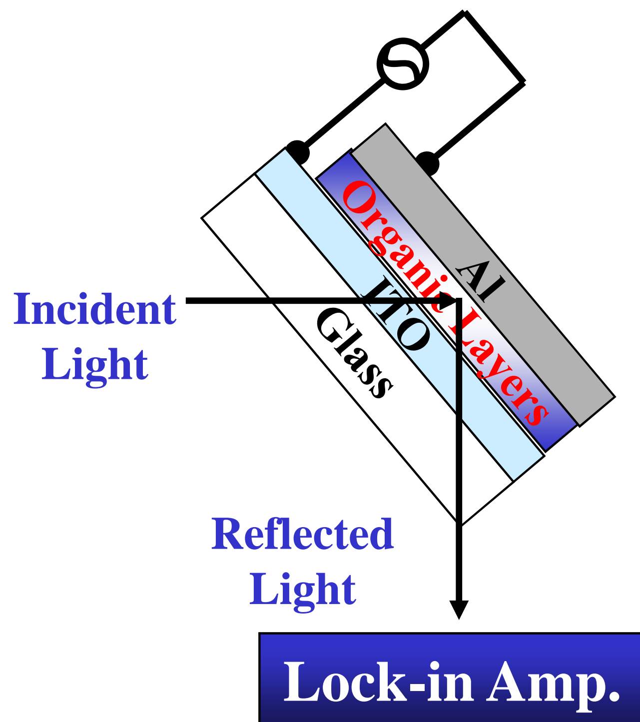


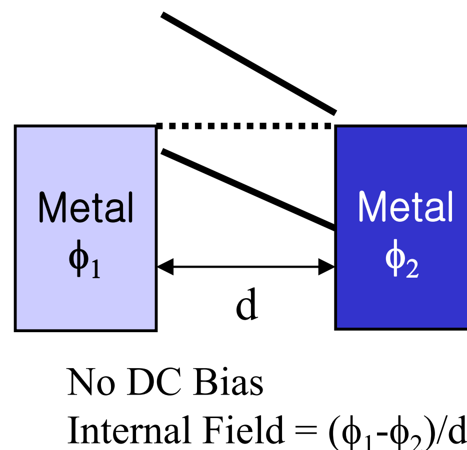
S. Karg, W. Riess, V. Dyakonov, M. Schwoerer, *Synth. Met.*, **54**, 427 (1993).

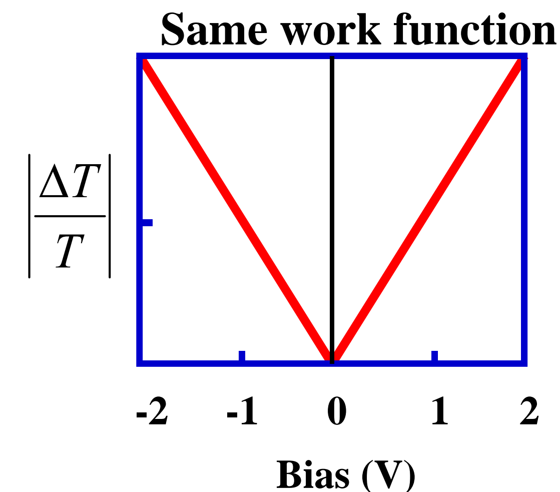
Measurement of an internal electric field

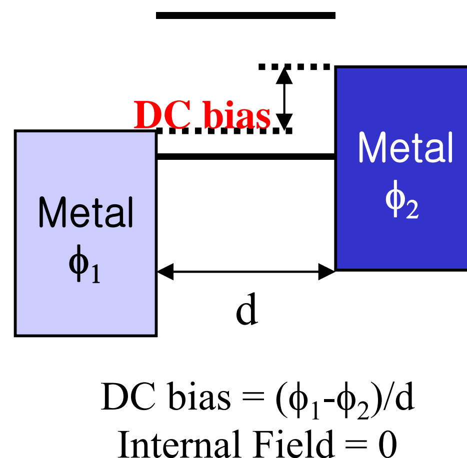
Electroabsorption Measurement

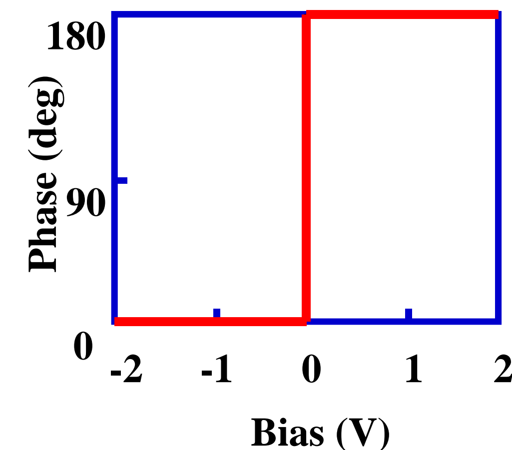
a.c. Field $E = E_{dc} + E_{ac}\cos(\Omega t)$











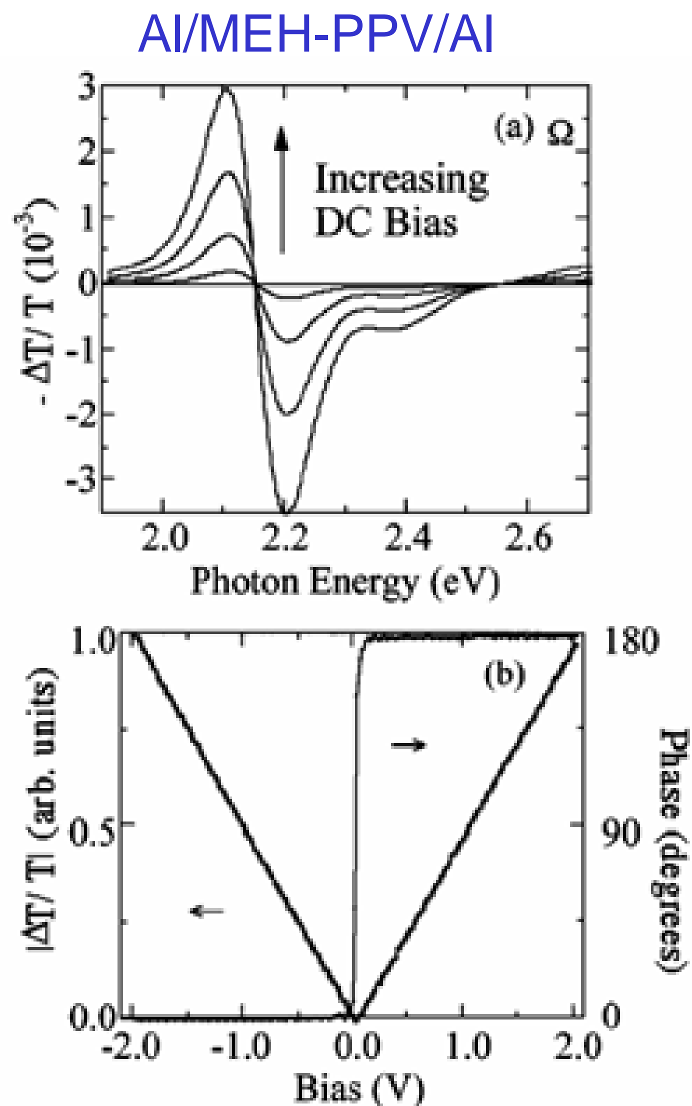
Electroabsorption response to an E field

$$\Delta\alpha(h\nu) \propto -\frac{\Delta T}{T}(h\nu) \propto \mathrm{Im}\,\chi^{(3)}(h\nu)E^2$$

Changhee Lee, SNU, Kor

Measurement of an internal electric field

Al/MEH-PPV/Al



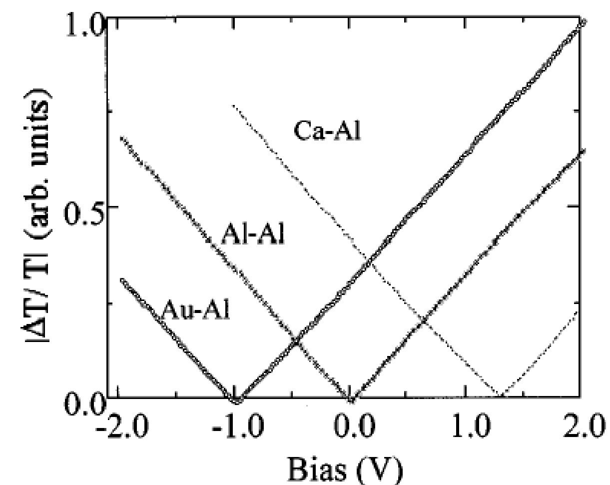


FIGURE 5. Magnitude of the electroabsorption response at 2.1 eV as a function of bias for three metal/MEH–PPV/Al structures.

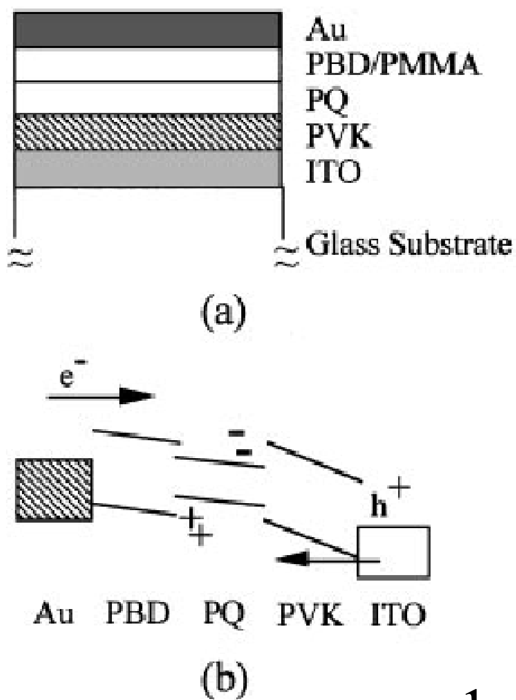
TABLE 1. Work Function Difference, $\Delta\phi$, and Electroabsorption Zero Field Bias, V_0, for a Series of Metal Contact Pairs to MEH–PPV

Contact metals	$\Delta\phi$	V_0
Au–Al	−0.8	−1.0
Al–Al	0.0	0.0
Ca–Al	1.4	1.3
Sm-Al	1.6	1.3
Ag-Ca	1.4	1.4
Cu–Ca	1.7	1.7
Au–Ca	2.2	2.0
Pt–Ca	2.7	2.1

Ian H. Campbell, John P. Ferraris, Thomas W. Hagler, Michael D. Joswick, Ian D. Parker, Darryl L. Smith
Polymers for Advanced Technologies, **8** (7), pp. 417 – 423

Internal electric field and accumulated charges

MULTILAYER ORGANIC LED



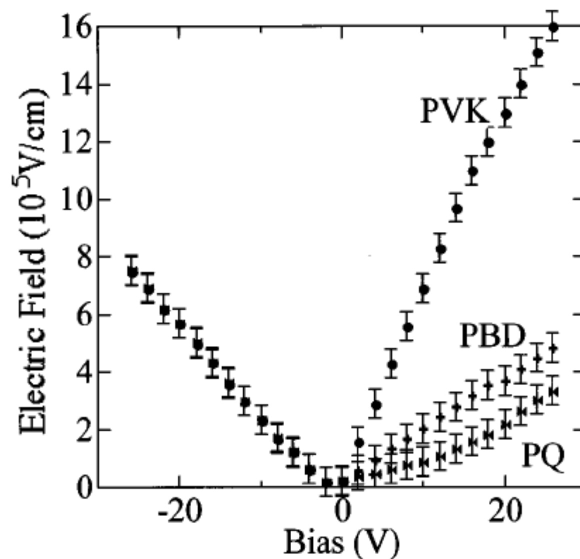


FIGURE 9. Electric field as a function of d.c. bias voltage in each layer of the LED. The a.c. bias amplitude was 3 V.

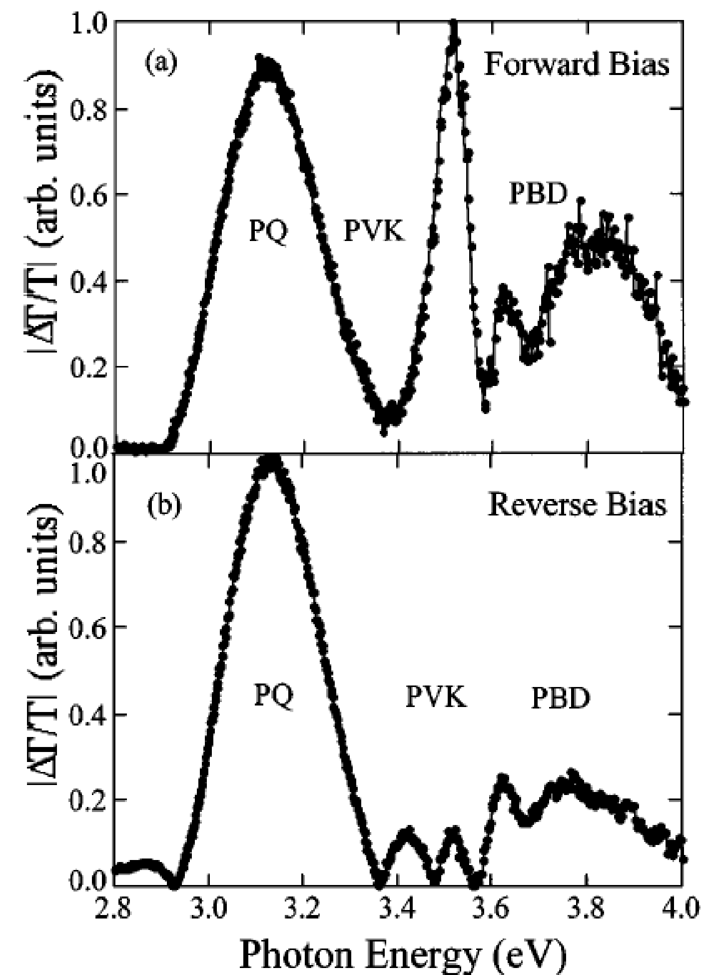


FIGURE 8. Electroabsorption spectra of the three layer LED under (a) 20 V forward bias and (b) − 20 V reverse bias at the fundamental frequency of the applied a.c. bias. The relative changes in the amplitudes of the signal from each layer are evident. The a.c. bias amplitude was 3 V.

$$\sigma = \frac{1}{4\pi}\Delta(\varepsilon E_{dc})$$

At the largest forward bias voltage measured,
electron density at the PQ/PVK interface: 2×10^{12} electrons/cm^2

hole density at the PBD/PQ interface: 3×10^{11} holes/cm^2.

I.H. Campbell, M.D. Joswick, I.D. Parker, Appl. Phys. Lett. 67 (1995) 3171.

Fermi level alignment at the metal/semiconductor contact

VL VL
Φ_m I χ
CB
E_F E_F
Impurity level
E_g
VB
Metal Semiconductor

Before contact a)

VL
Φ_m I χ Φ_s
E_F Φ_B^n eV_{bi} CB E_F
Φ_B^p E_g VB
Metal Semiconductor

After contact: Mott-Schottky model b)

VL Δ VL
Φ_m I χ Φ_s
Φ_B^n eV_{bi} CB
E_F E_F
Φ_B^p E_g VB
Metal Semiconductor

After contact: vacuum level shift c)

ϕ_m: 금속의 work function

ϕ_s : 반도체의 work function

χ:electron affinity

Barrier height for e injection

$\Phi_{Bn} = \Phi_m - \chi$

built-in potential

$eV_{bi} = |\Phi_m - \Phi_s|$

Formation of interface dipole inducing vacuum level shift (Δ)

→Barrier height is modified:

$\Phi_{Bn} = \Phi_m + \Delta - \chi$

→V_{bi} is also modified:

$eV_{bi} = |\Phi_m + \Delta - \Phi_s|$

. H. Ishii, N. Hayashi, E. Ito, Y. Washizu, K. Sugi, Y. Kimura, M. Niwano, Y. Ouchi, and K. Seki, phys. stat. sol. (a) 201, 1075 (2004)

Metal/Organic interface

Schottky-Mott model

Common vacuum level assumption

Interface Dipole Model

$$\Delta = N\frac{p}{\varepsilon_i}$$

No interface dipole

(a)

Interface dipole $\vec{p}$

(b)

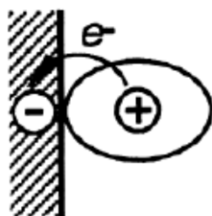
Interface dipole $\vec{p}$

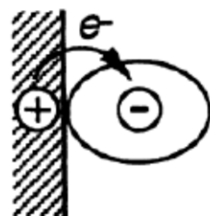
(c)

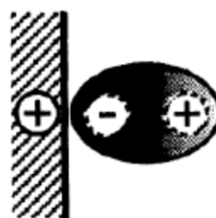
I. H. Campbell, S. Rubin, T. A. Zawodzinski, J. D. Kress, R. L. Martin, D. L. Smith, N. N. Barashkov, and J. P. Ferraris, Phys. Rev. B 54, R14321 (1996).

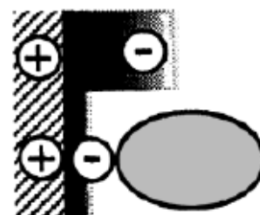
Origin of interface dipole

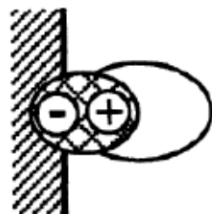
Charge Transfer

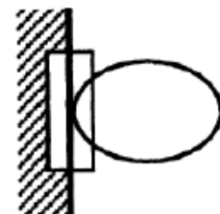


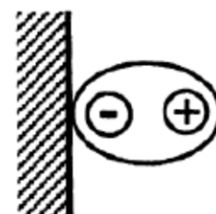












Possible factors forming and affecting the interfacial dipole layer.
a1) and a2): Charge transfer across the interface,
b) Concentration of electrons in the adsorbate leading to positive charging of the vacuum side,
c) Rearrangement of electron cloud at the metal surface, with the reduction of tailing into vacuum,
d) Strong chemical interaction between the surface and the adsorbate leading to the rearrangement of the electronic cloud and also the molecular and surface geometries (both directions of dipoles possible),
e) Existence of interface state serving as a buffer of charge carriers,
f) Orientation of polar molecules or functional groups.

H. Ishii, K. Sugiyama, E. Ito, and K. Seki, Adv. Mater. **11**, 605 (1999).

Effect of interface dipole on the hole injection barrier

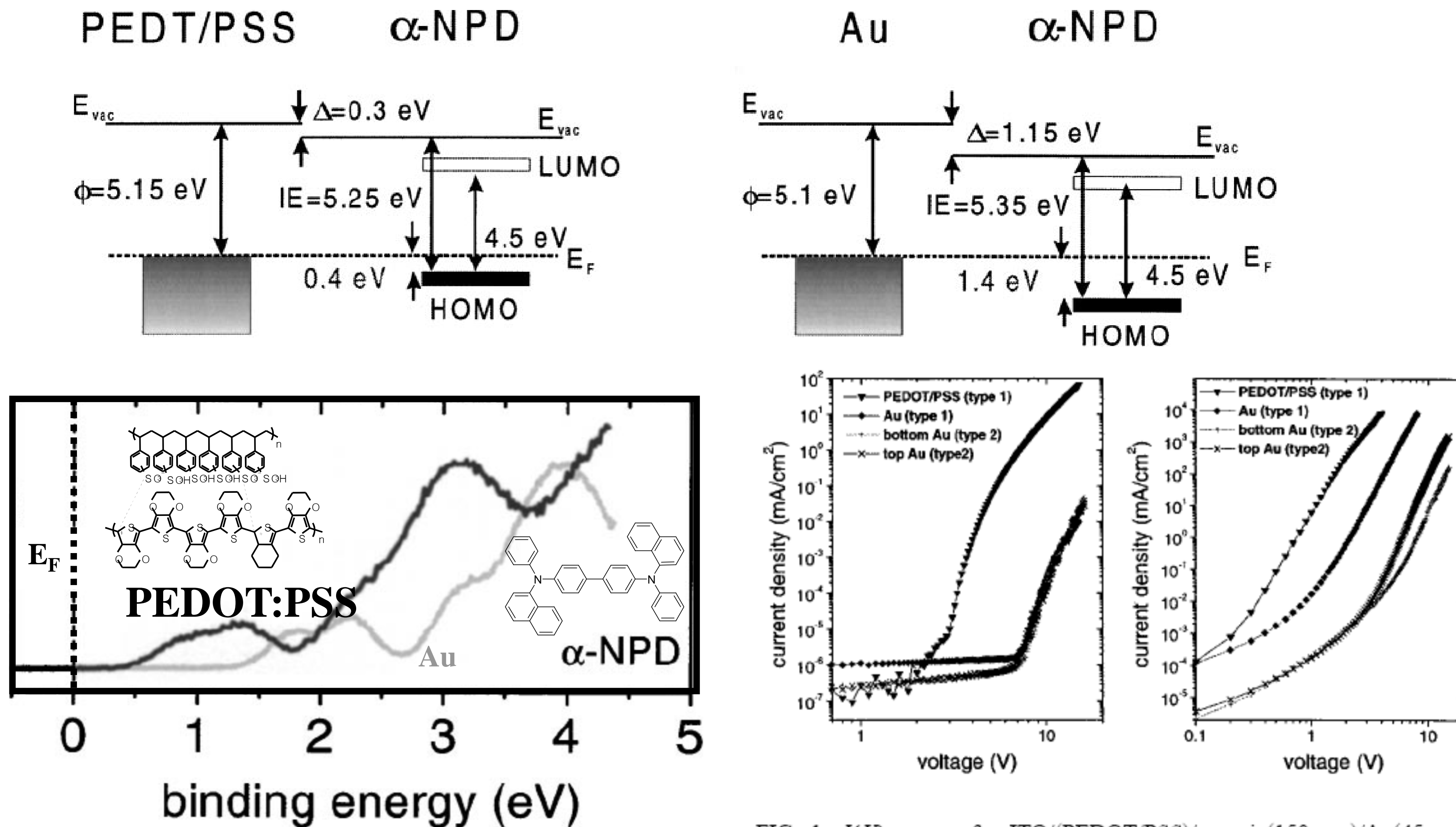


FIG. 1. $I(V)$ curves for ITO/(PEDOT/PSS)/organic(150 nm)/Au(45 nm) (type 1) devices, and ITO/(PEDOT/PSS)/Au(80 nm)/organic(150 nm)/Au(45 nm) (type 2) devices: (a) α-NPD; (b) pentacene.

N. Koch, A. Kahn, J. Ghijsen and J.-J. Pireaux, J. Schwartz, R. L. Johnson, A. Elschner, Appl. Phys. Lett. **82**, 70 (2003)