7th edition

ORGANIC ELECTRONICS

Principles, devices and applications

Metal Organic interfaces

D. Natali

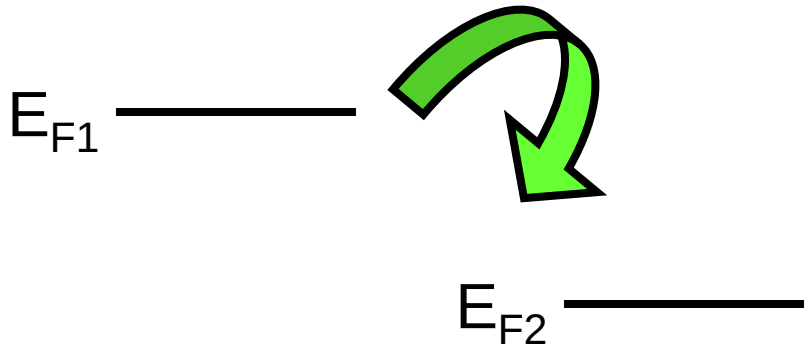
Milano, 23-27 Novembre 2015

Outline

- general concepts
- energetics
- Interfaces: tailoring
- injection mechanisms

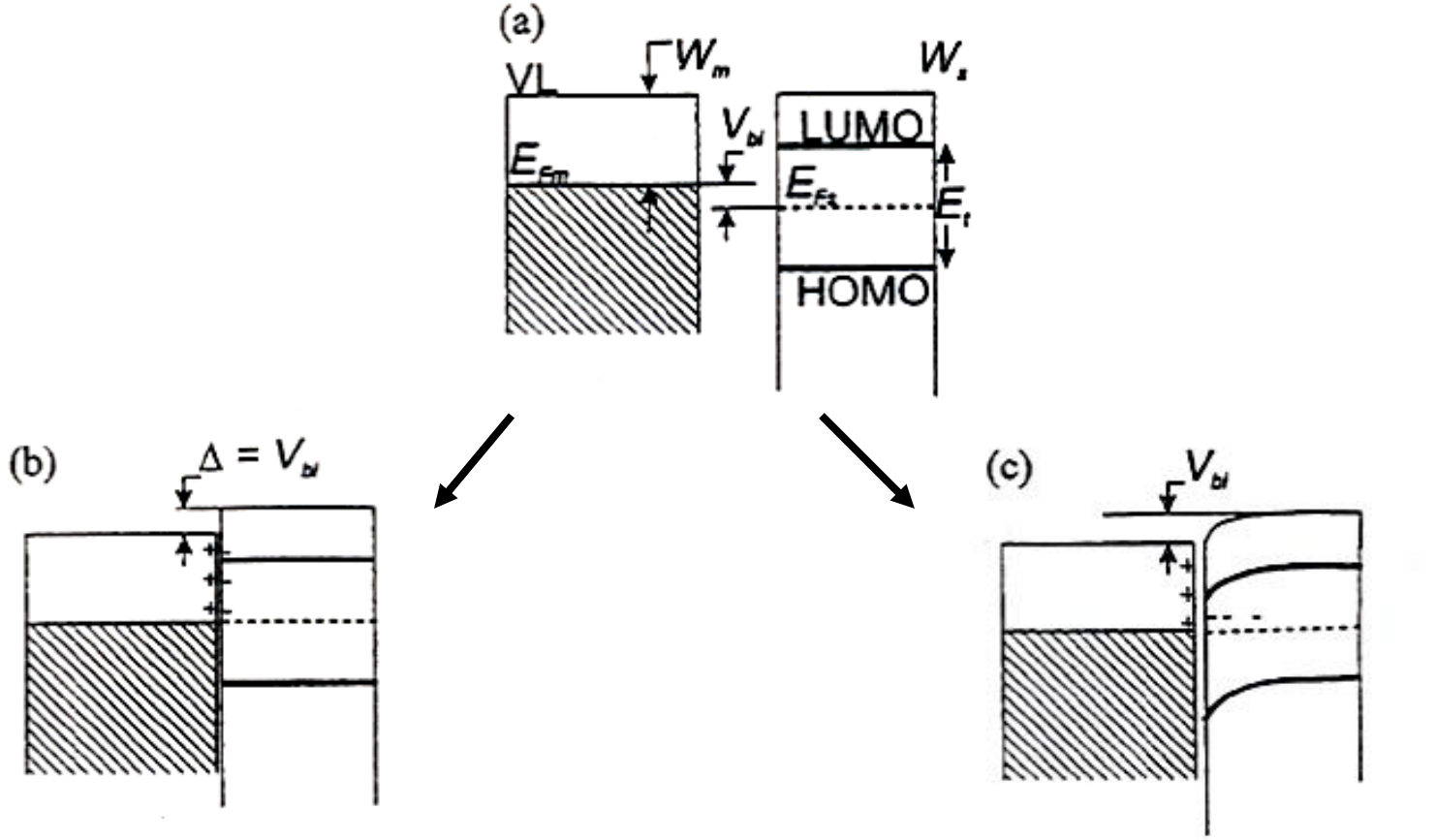
Thermal Equilibrium (1)

@Thermal Equilibrium a common Fermi level is established by means of *charge transfer…*



..from higher lying to lower lying Fermi level

Thermal Equilibrium (2)

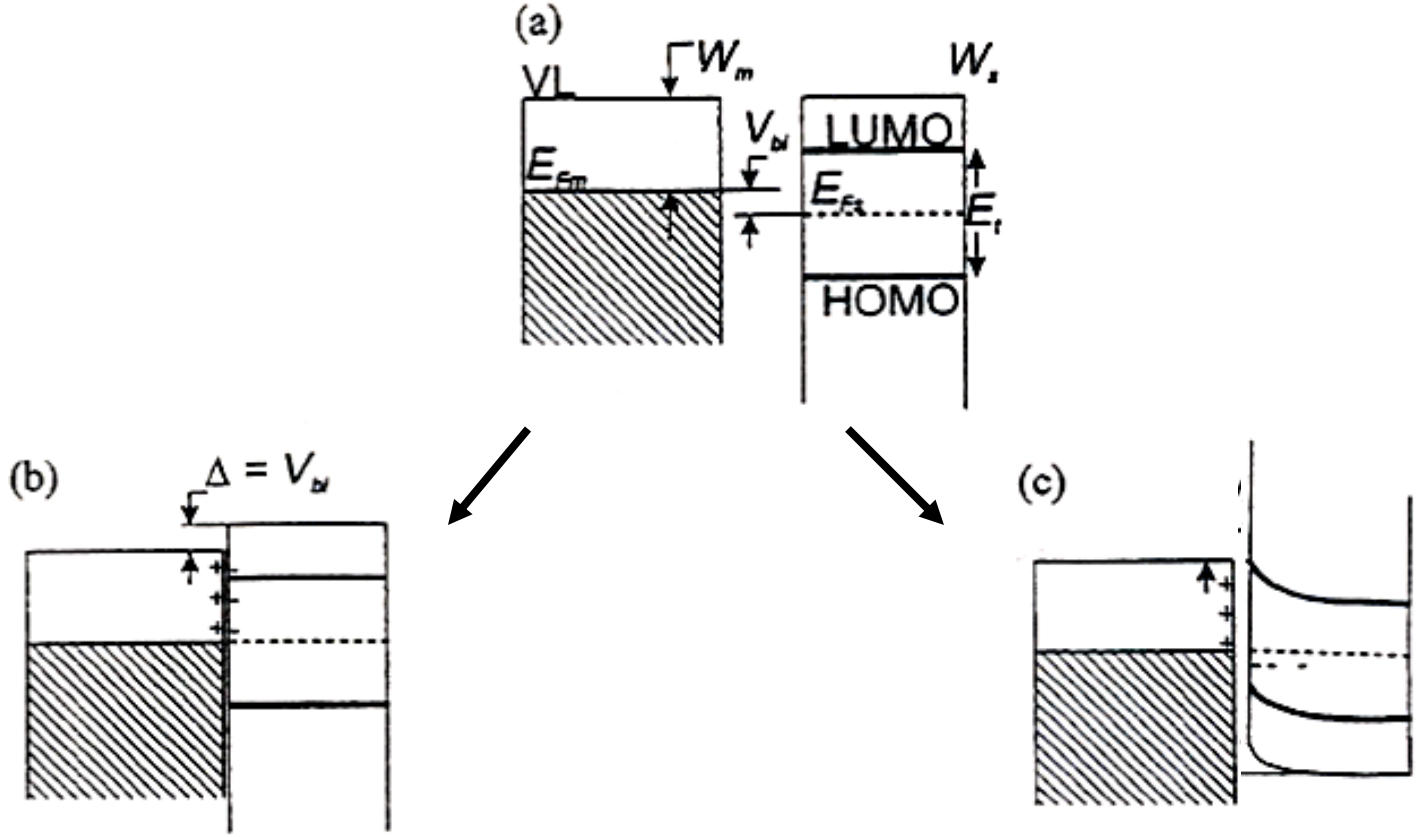


Interface dipole layer

Space charge region

Scott, J.Vac.Sci.Tech. A 21(3) 2003 521 Tung Mat.Sci.Eng R 35 2001 1

Thermal Equilibrium (2)

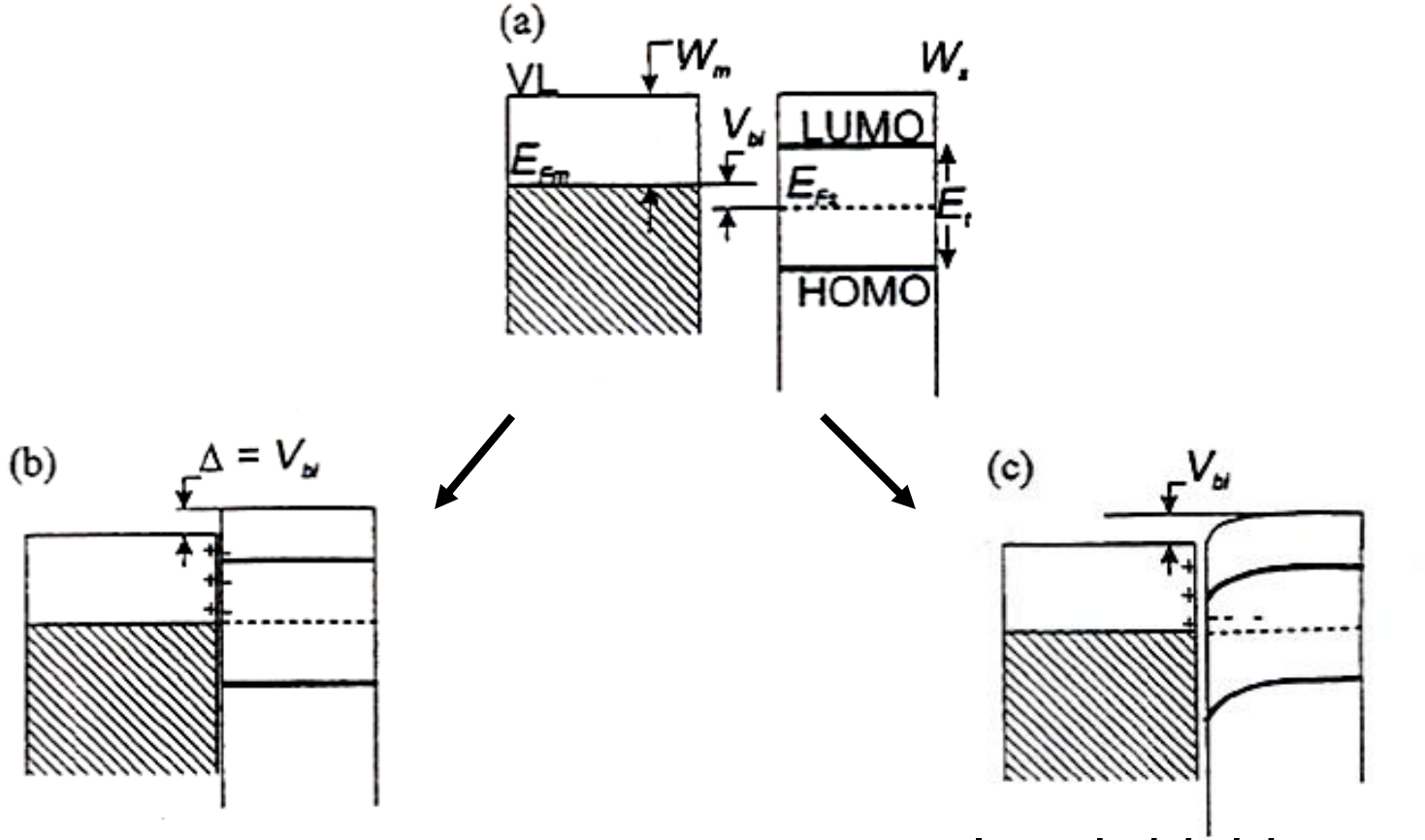


Interface dipole layer

Depleted, *poorly conductive (poorer than bulk)* space charge region

Scott, J.Vac.Sci.Tech. A 21(3) 2003 521 Tung Mat.Sci.Eng R 35 2001 1

Thermal Equilibrium (2)

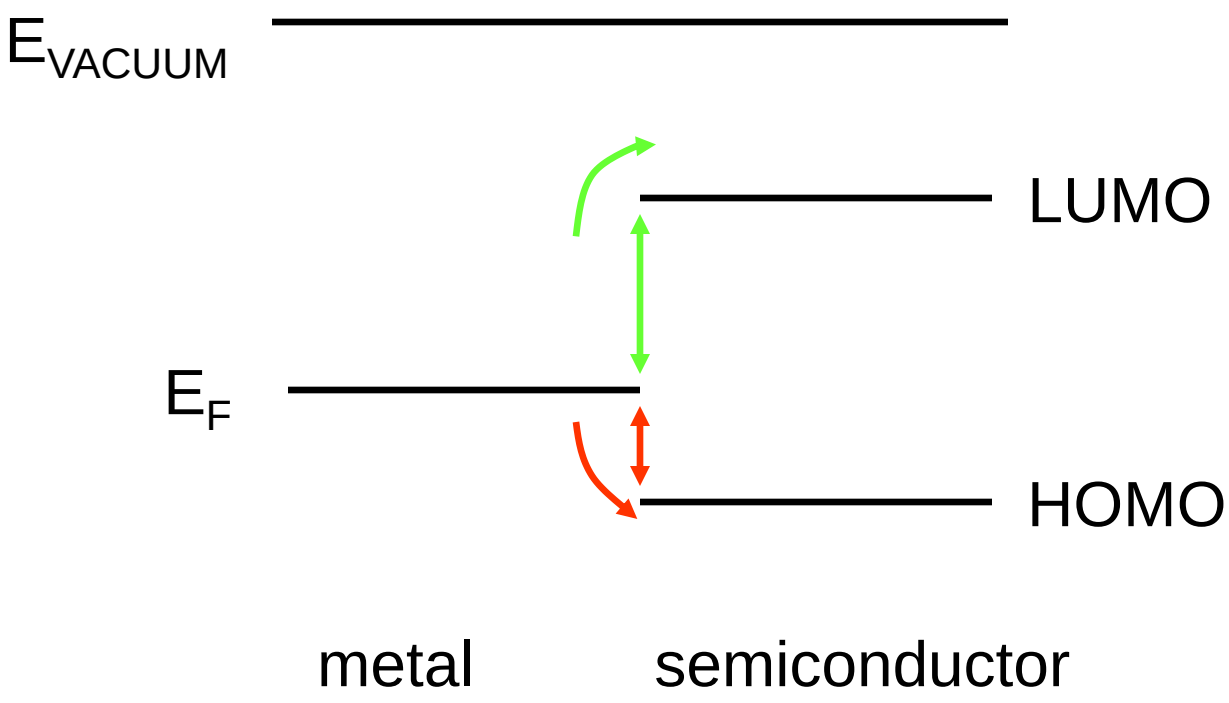


Interface dipole layer

Accumulated, *highly conductive (higher than bulk)* space charge region

Scott, J.Vac.Sci.Tech. A 21(3) 2003 521 Tung Mat.Sci.Eng R 35 2001 1

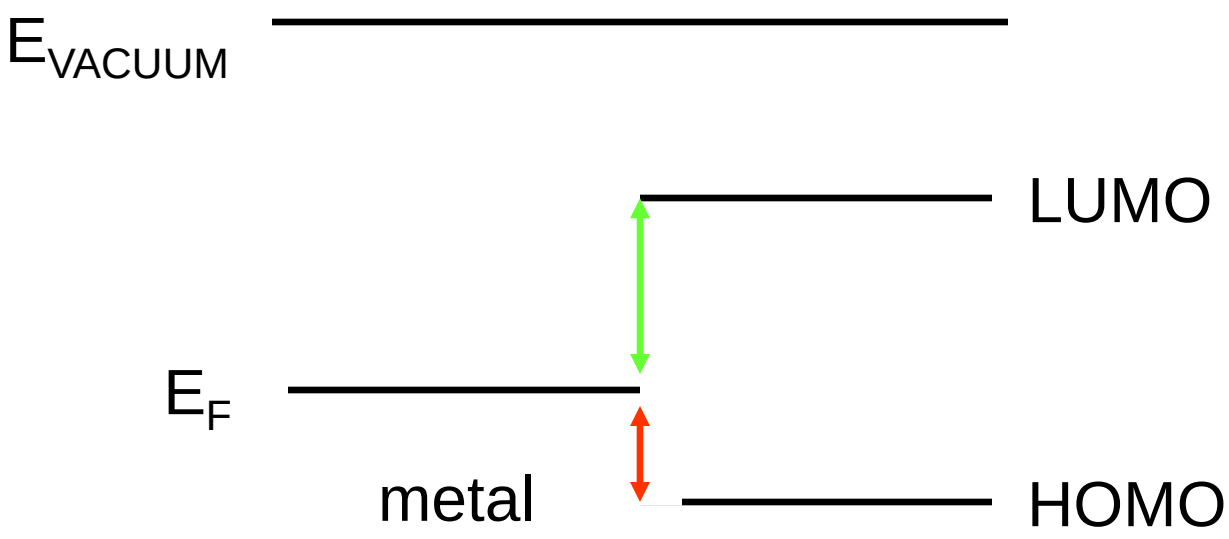
Metal-semiconductor contacts



Φ_{Be} barrier to electron injection

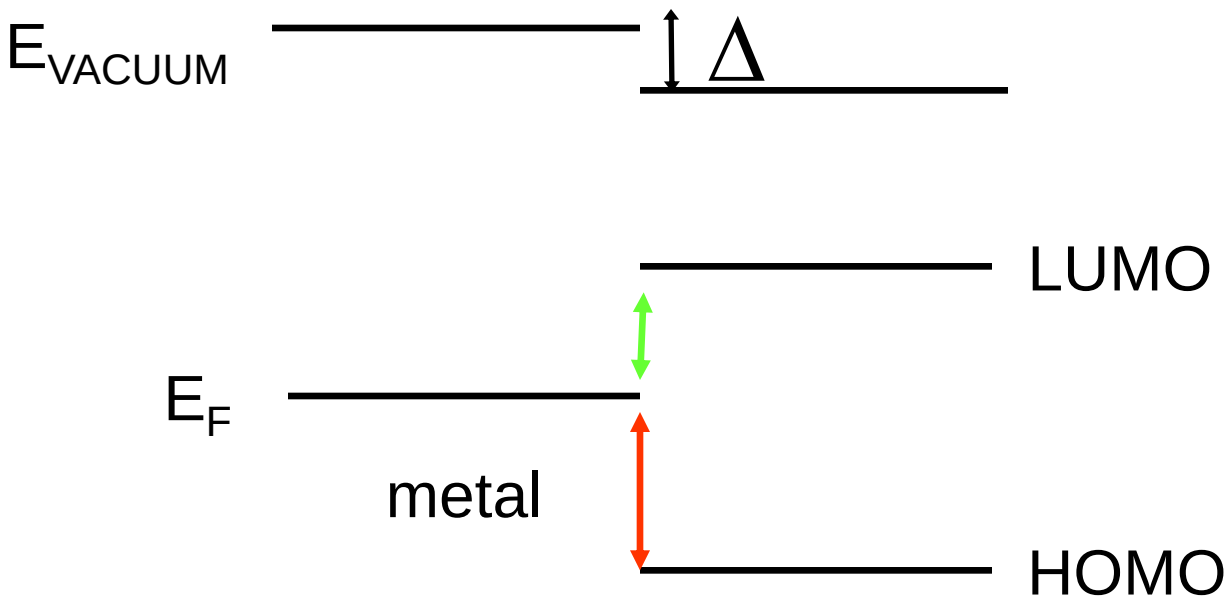
Φ_{Bh} barrier to hole injection

Interface dipoles (1)



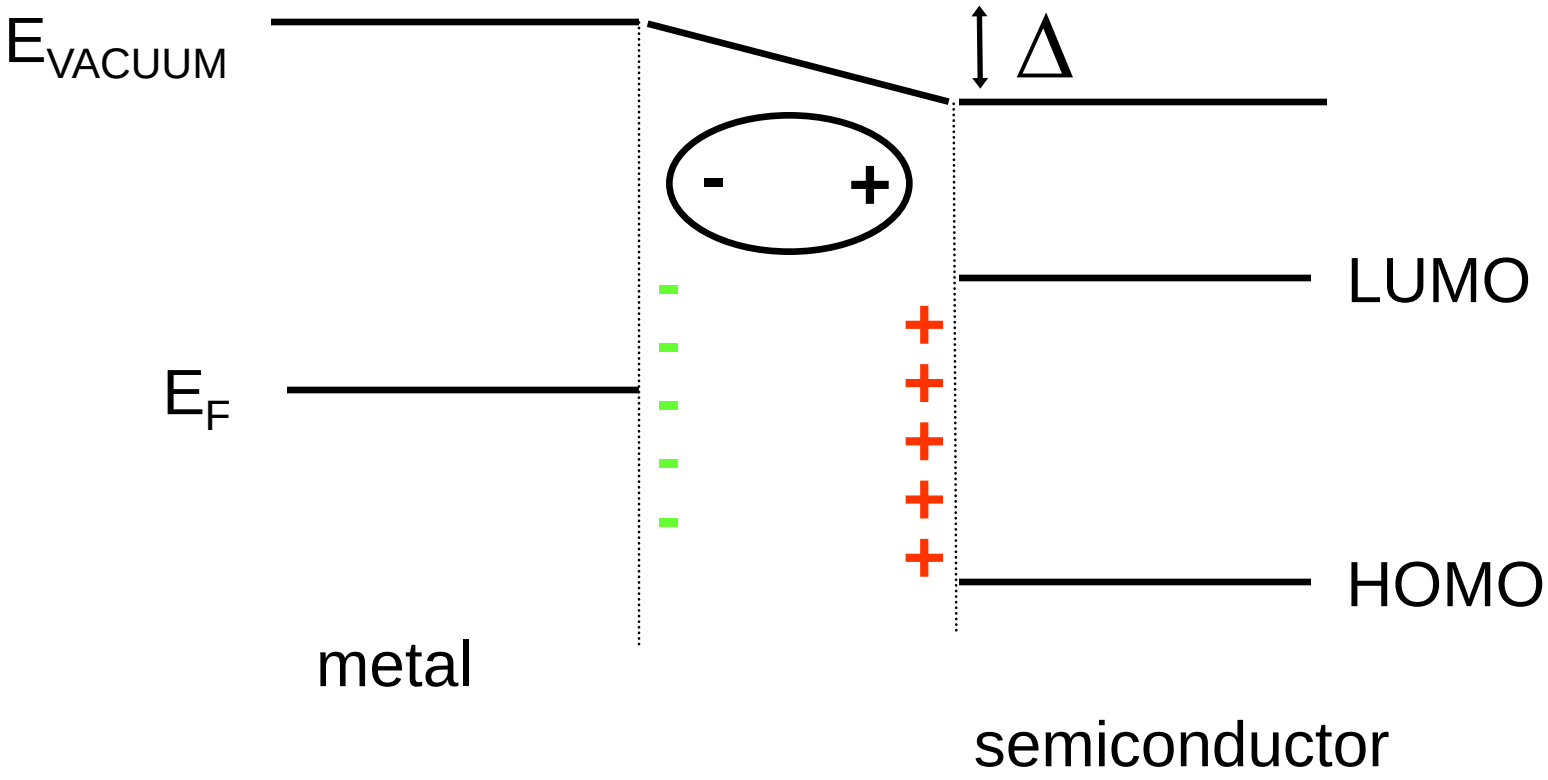
Barriers Φ_{Be} and Φ_{Bh} do change***!!***

Interface dipoles (1)

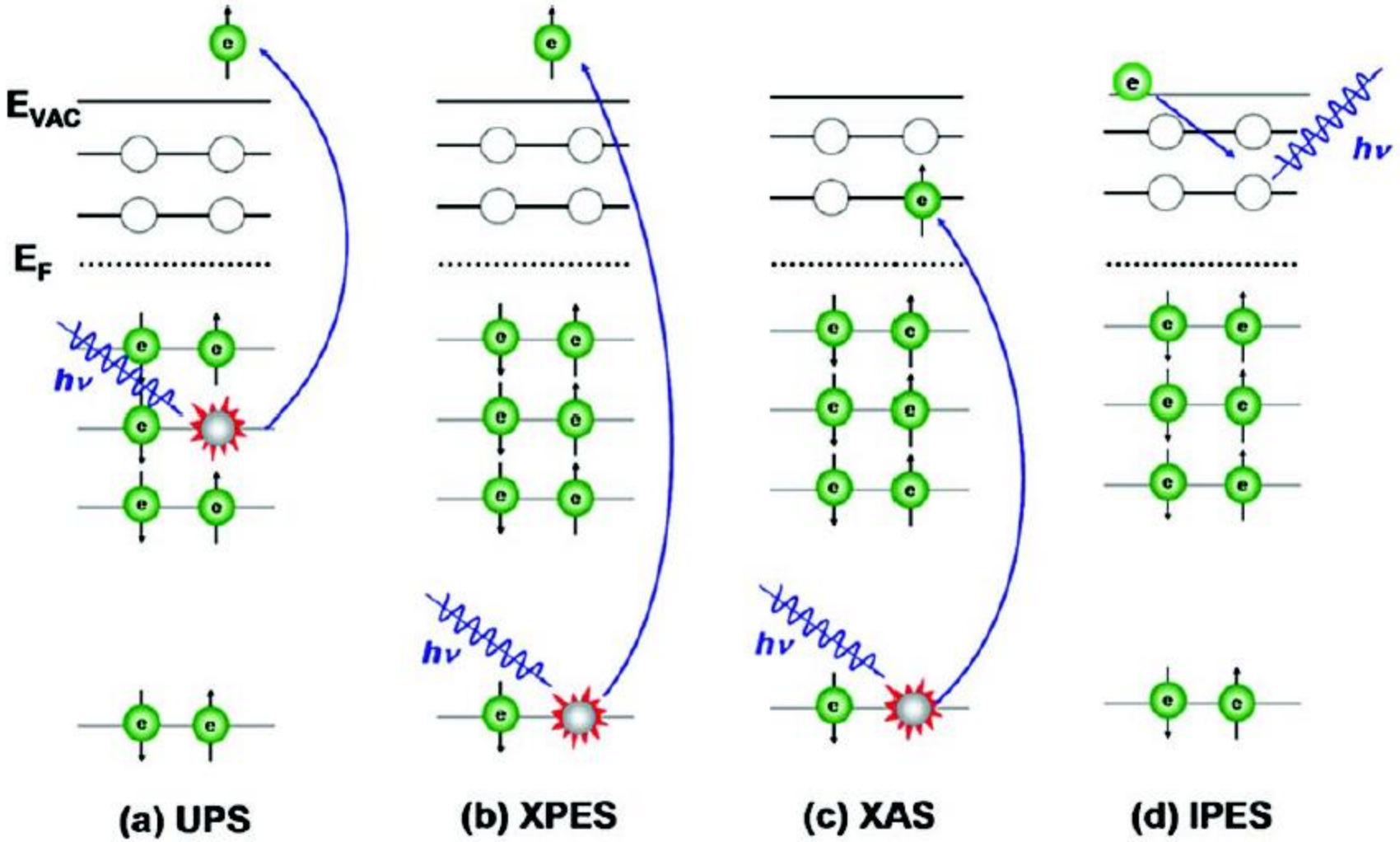


Barriers Φ_{Be} e Φ_{Bh} do change***!!***

Interface dipoles (2)



Spectroscopical techniques



Kahn Adv.Mat. 2003 15 271

Zahn, Chemical Reviews, 2007, Vol. 107, No. 4 1181

Interface interaction strength

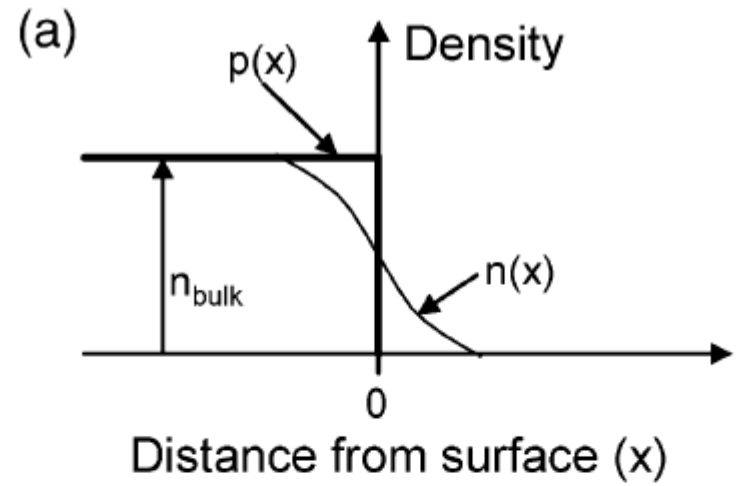
Example of interface	Interaction type	Refs.
Noble gas atoms or saturated hydrocarbons on clean metal surfaces	Physisorption, absence of charge transfer	59, 61-63
π-conjugated molecules and polymers on organic or passivated metal surfaces	Physisorption, possible integer electron charge transfer through tunneling	22, 68
π-conjugated molecules on non-reactive clean metal surfaces	Weak chemisorption, possible partial charge transfer	21, 80
(π-conjugated) molecules on reactive clean metal surfaces	Strong chemisorption, covalent bonding between molecule and metal, (partial) charge transfer	20
(π-conjugated) molecules with intrinsic dipole and anchoring groups on clean metal surfaces	Strong chemisorption, covalent bond at *specific* sites of the molecule and metal, (partial) charge transfer, surface dipole	24, 97

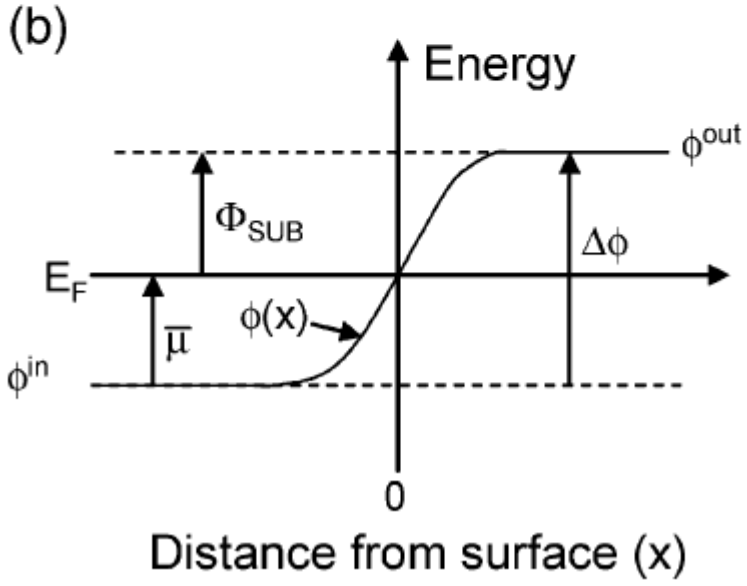
Salaneck Adv.Mater. 2009 21 1-23

Metal/organic interfaces:

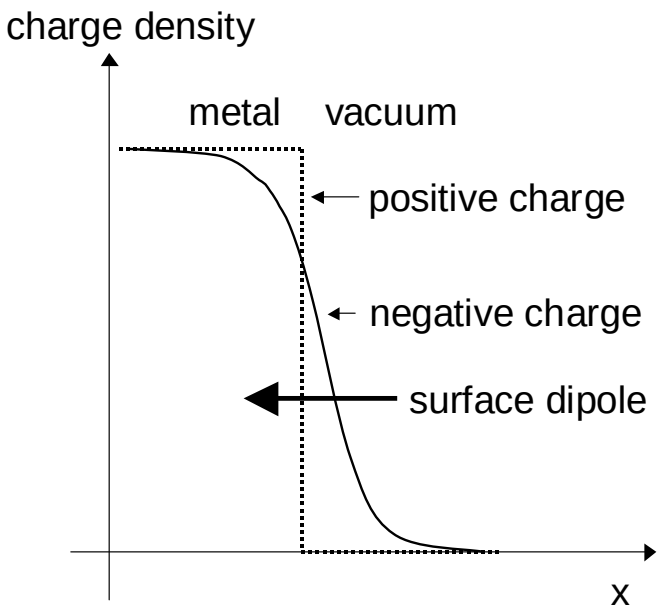
Metal/organic interfaces:

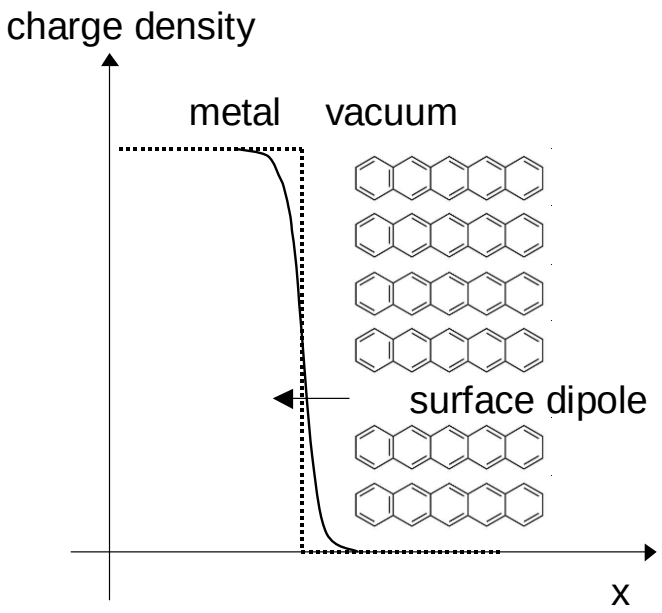
Real Metal surfaces: pushback effect





Real Metal surfaces: pushback effect





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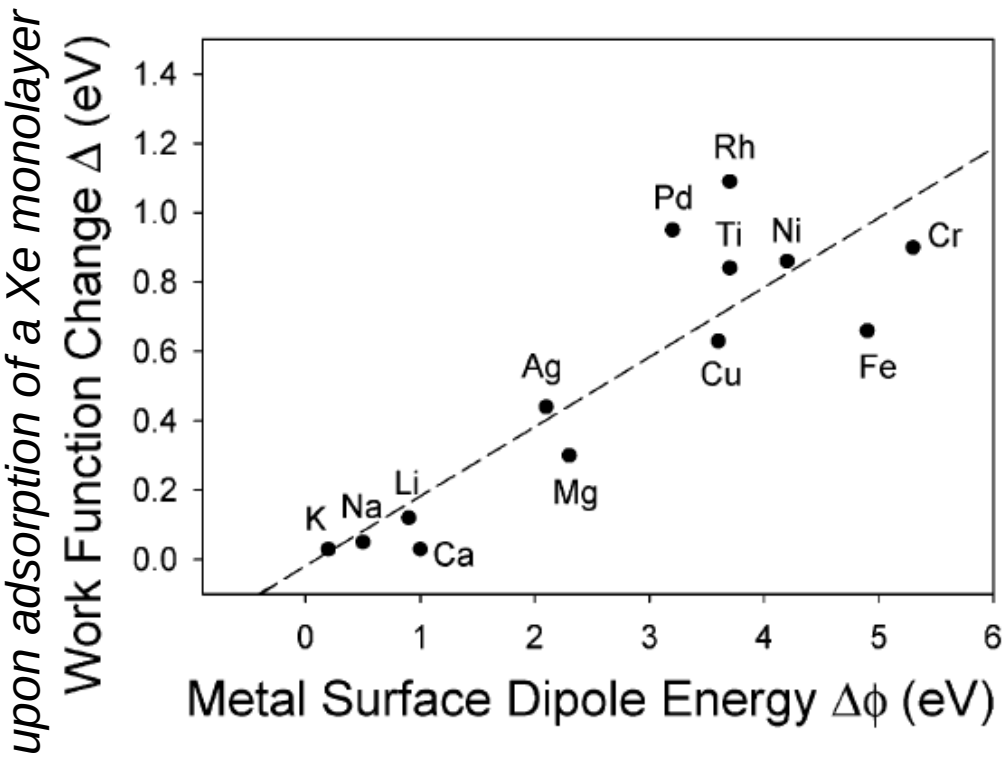

	1	2	3	4	5	6	7
Polymer-on-Au	4.4	4.5	4.6	4.5	4.4	4.4	4.5
Au-on-Polymer	4.4	4.5	4.4	4.5	4.4	4.5	4.4

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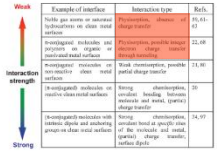
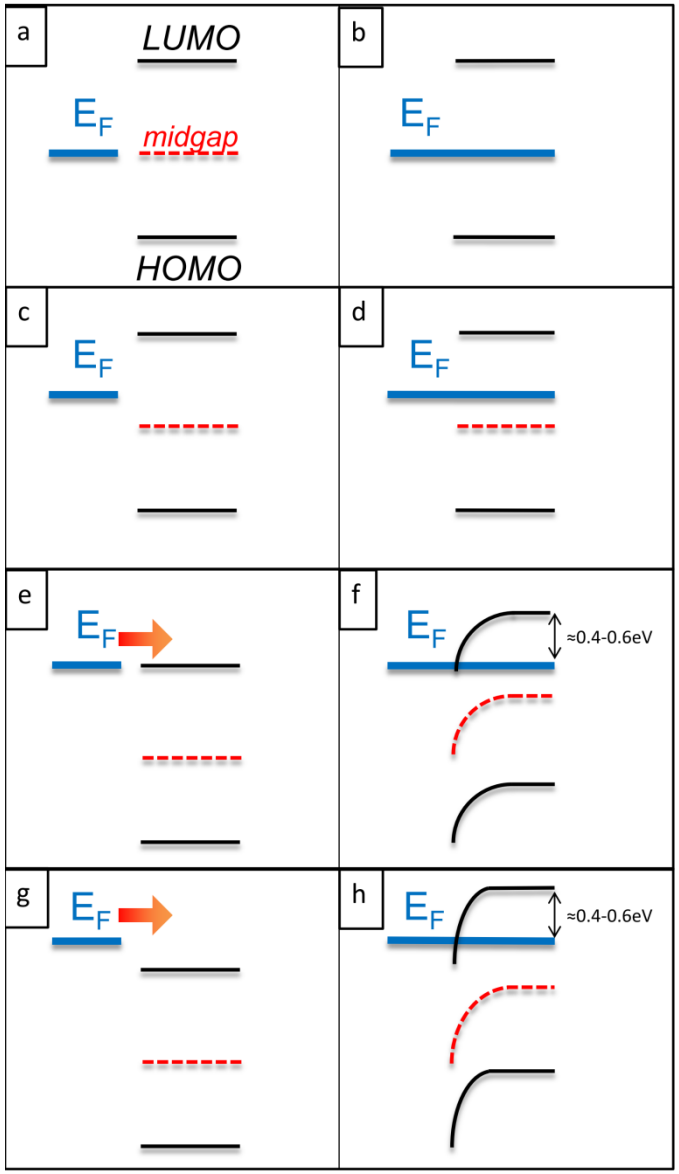
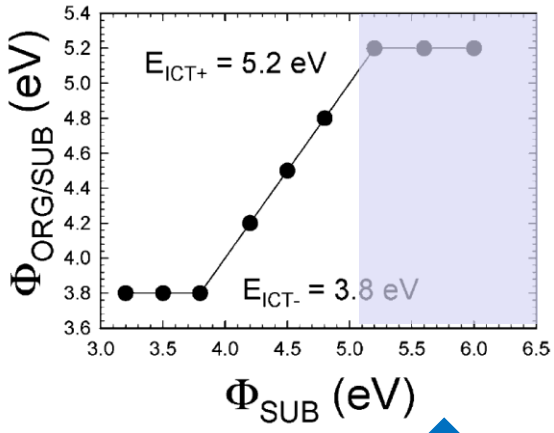
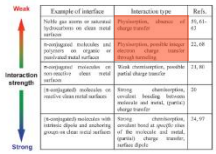
Physisorptive regime

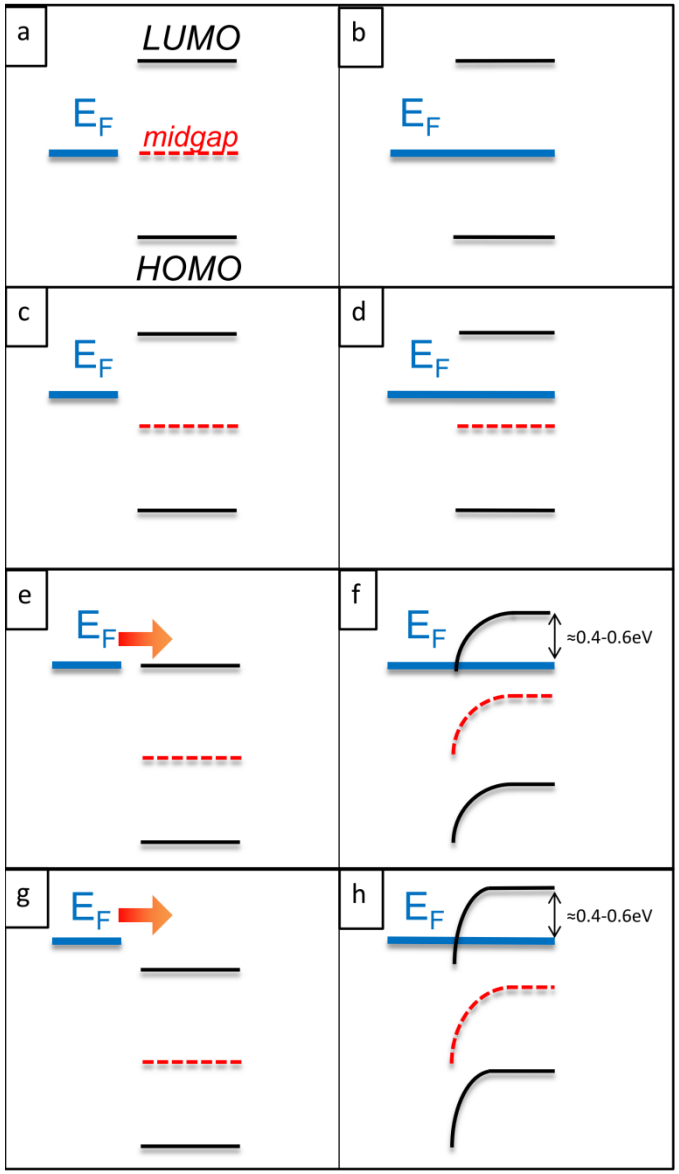


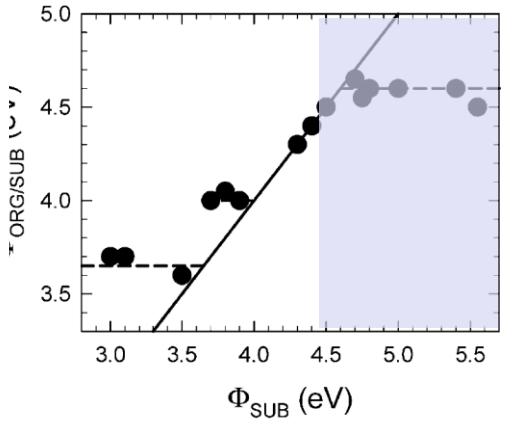




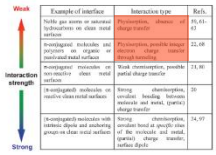
Physisorptive regime







Physisorptive regime: who cares Φ_B?



$$n_1 \propto N_{eff} \exp^{-\Phi_B/kT}$$

$$\rho = \frac{e n_1}{\left(\frac{x}{L_1} + 1\right)^2}$$

$$L_1 \propto \sqrt{\frac{\phi_{th}}{n_1}}$$

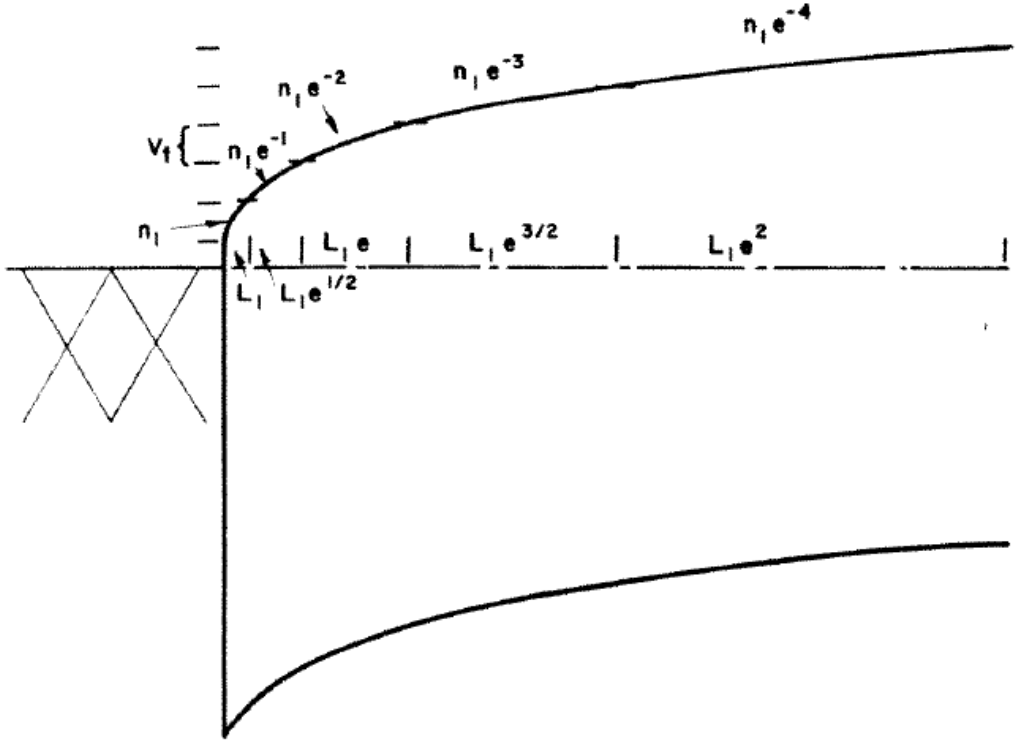
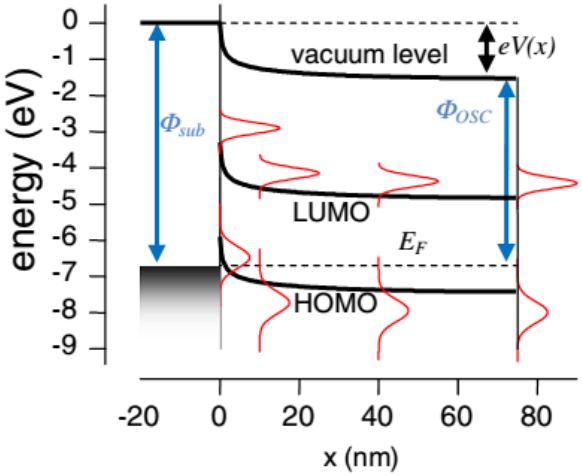
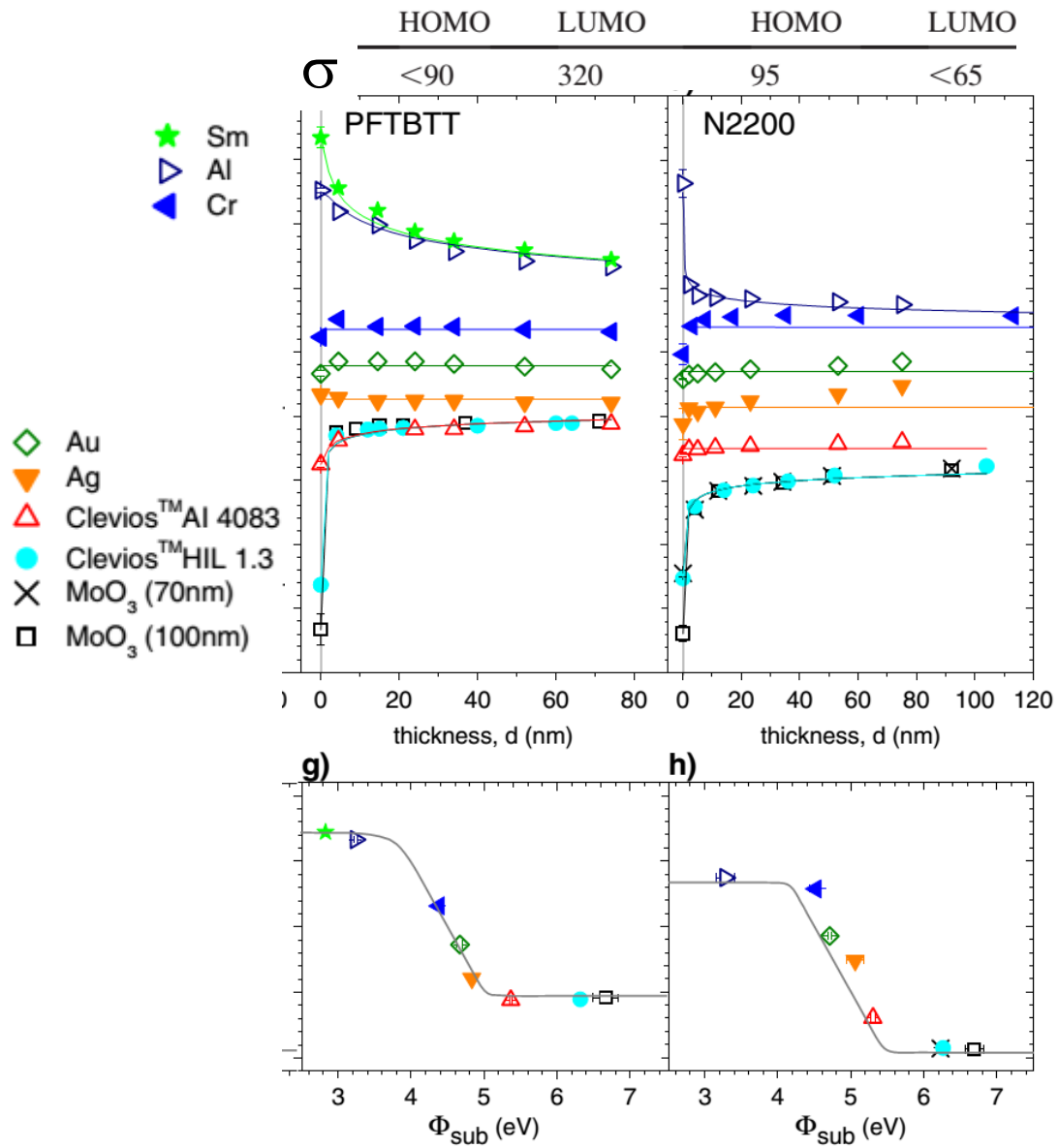


Fig. 8.3. Density of electrons and rise in potential near an Ohmic contact. L_1 is the Debye length for the density n_1.

Rose Photoconducitivty and allied problems 1963

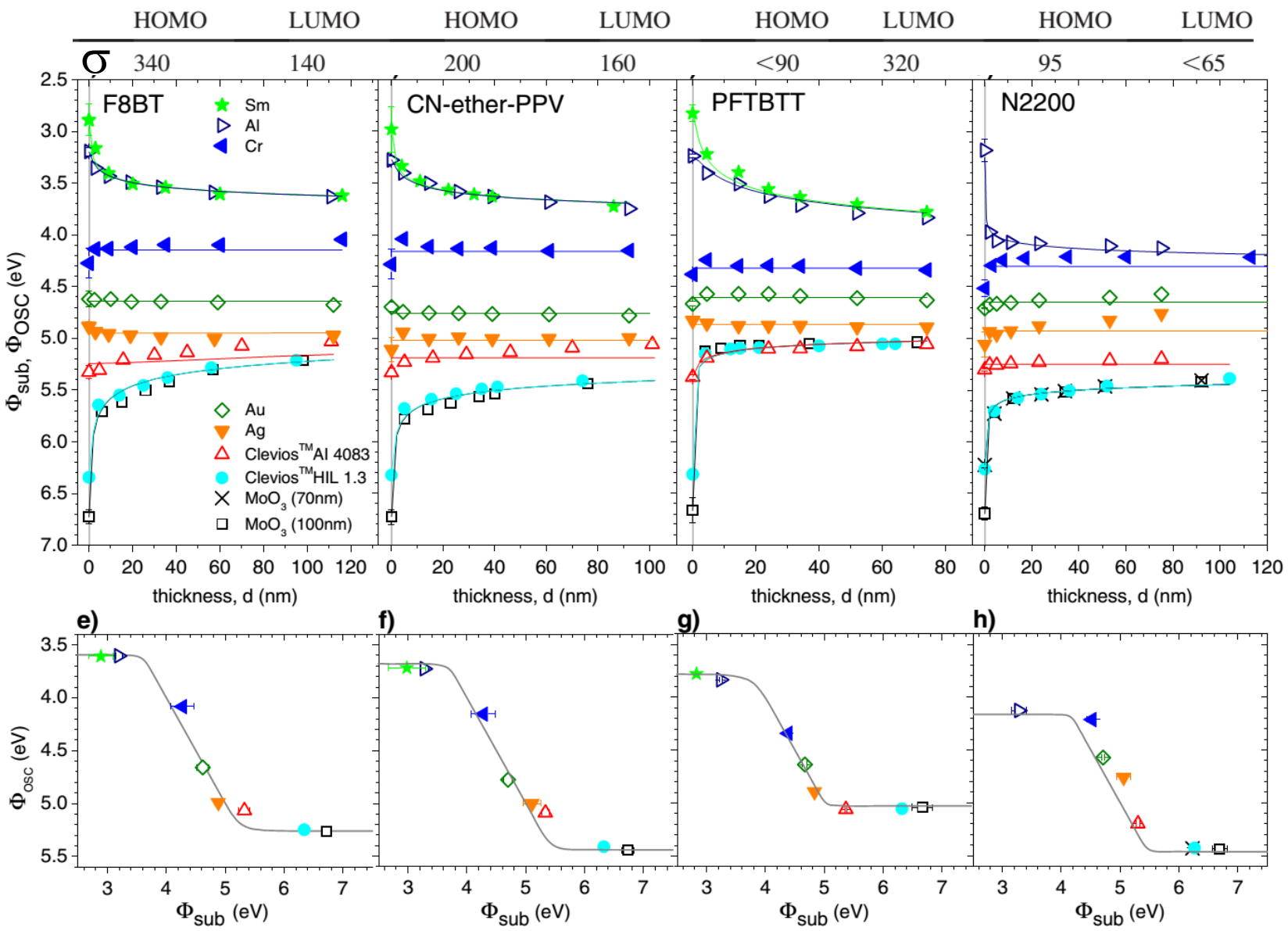
Physisorptive regime:





Lange at al. PRL106,216402 (2011)

Physisorptive regime: effect of disorder



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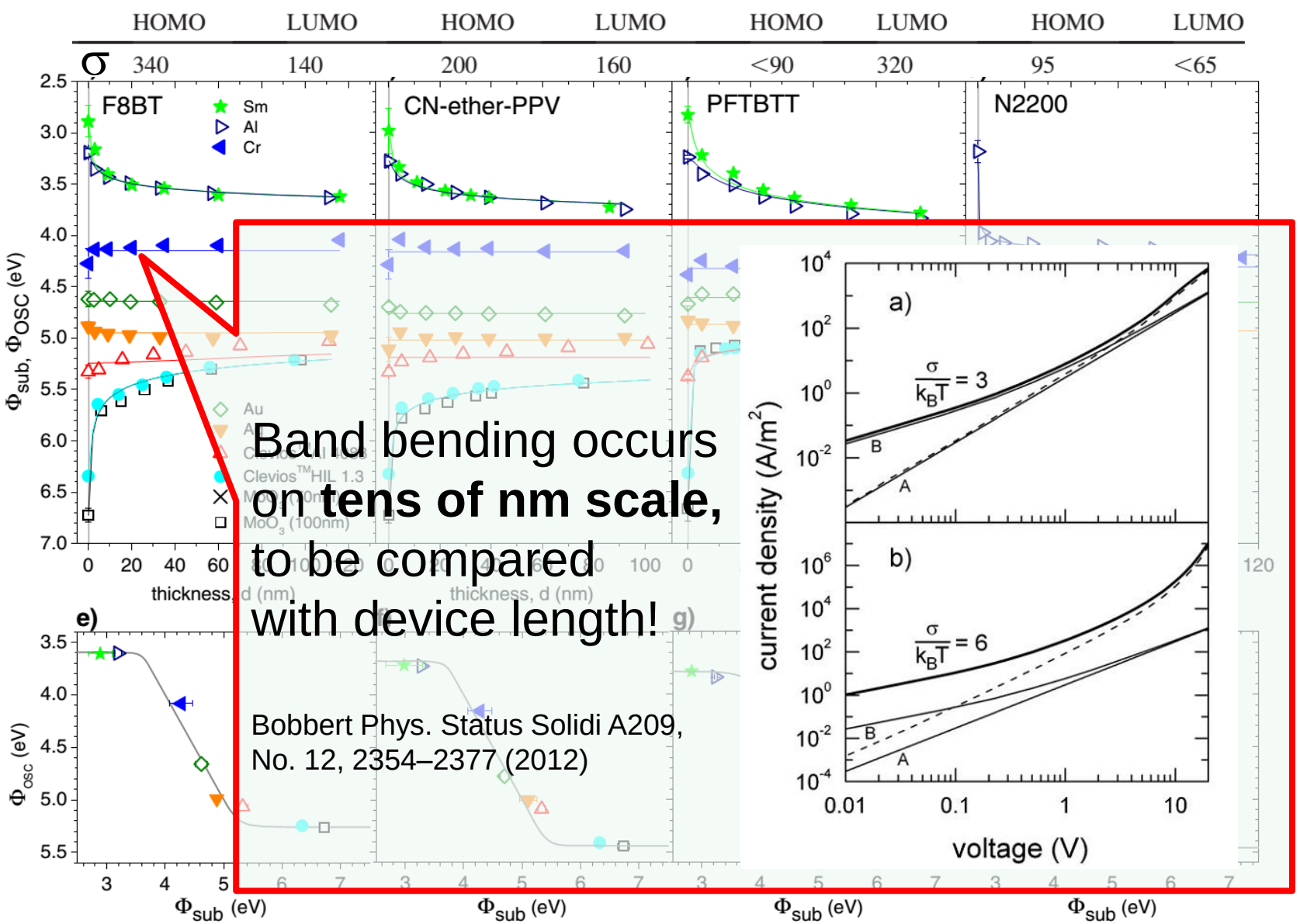
Physisorptive regime: effect of disorder

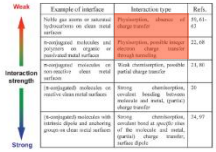


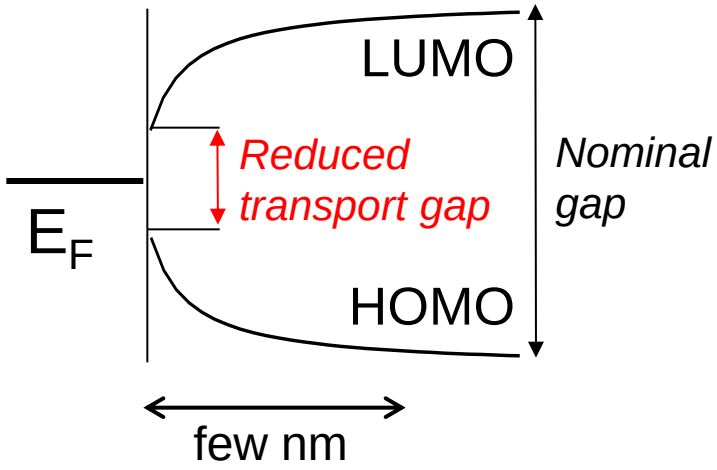
Band bending occurs on **tens of nm scale,** to be compared with device length!

Bobbert Phys. Status Solidi A209, No. 12, 2354–2377 (2012)

Oehzelt et al. *Nat. Commun.*, vol. 5, no. May, p. 4174, Jan. 2014.
Lange at al. PRL106,216402 (2011)

Physisorptive regime: image charge





Clean Metal/molecule interfaces: weak chemisorption

Example of interface	Interaction type	Refs.
Noble gas atoms or saturated hydrocarbons on clean metal surfaces	Physisorption, absence of charge transfer	59, 61-63
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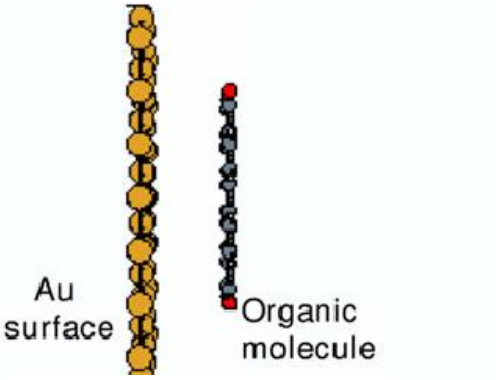
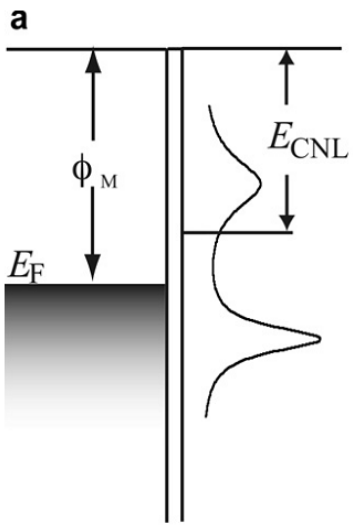
Induced Density of states model



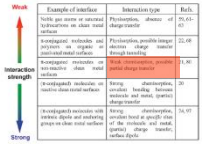


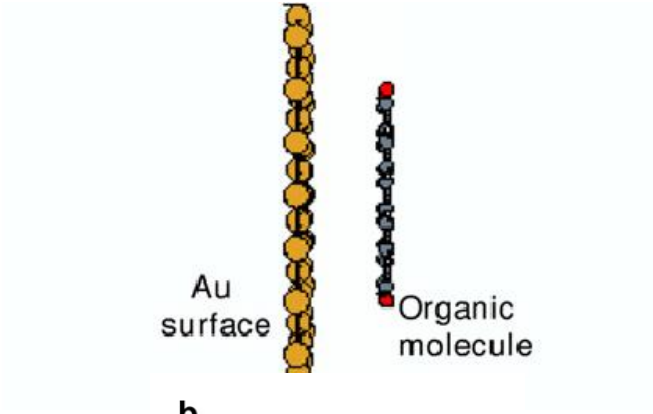
Charge Neutrality Level

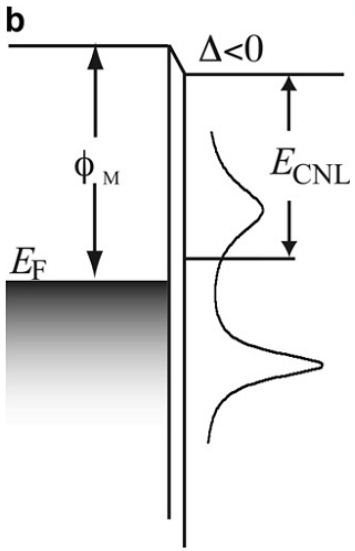
In organic molecule CNL accounts for:

- all Molecular Orbitals
- Metal induced orbitals broadening-> midgap states

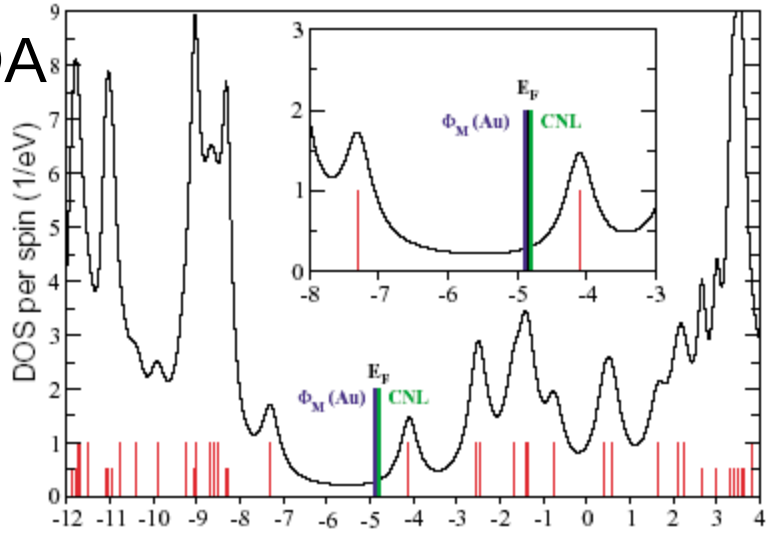
Charge Neutrality Level



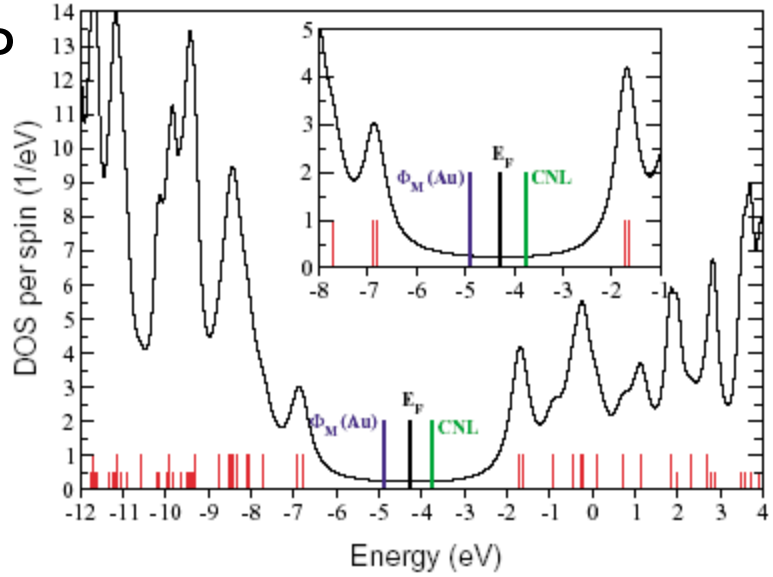




PTCDA



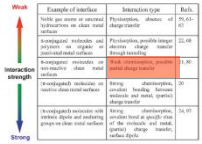
CBP

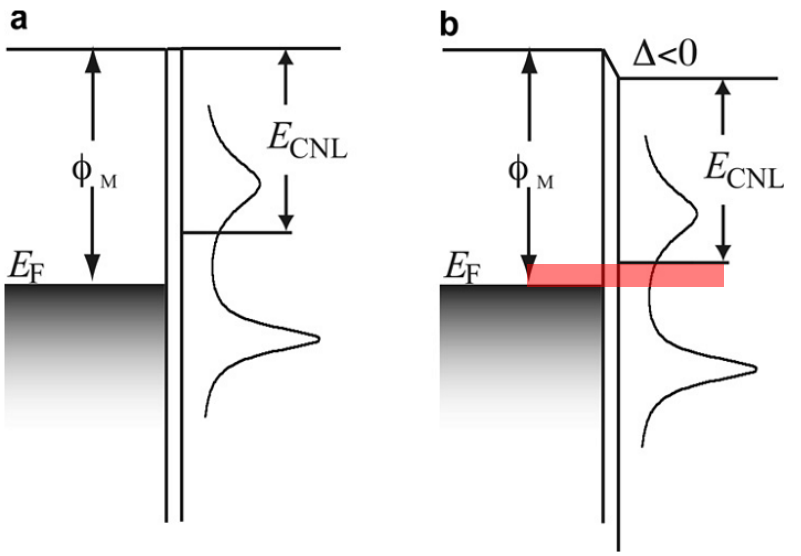


Y. Morikawa et al. / Current Applied Physics 12 (2012) S2-S9

Kahn, Org. El. 8 2007 241

Charge Neutrality Level



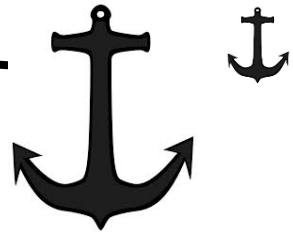


$$E_F - CNL = S(\phi_M - CNL)$$

$$\Delta^{IDIS} = (1-S)(\phi_M - CNL)$$

$$S = dE_F/d\phi_M = \frac{1}{1 + (4\pi e^2 D(E_F) d/A)}$$

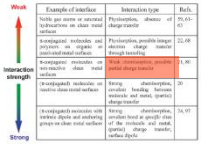
0<S<1, screening parameter



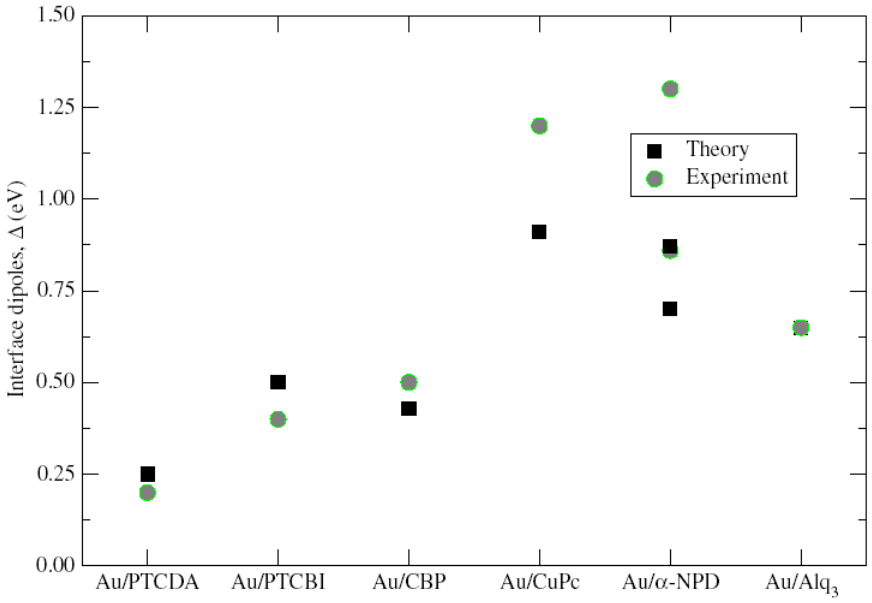
S describes the degree of pinning of the Fermi level at the interface

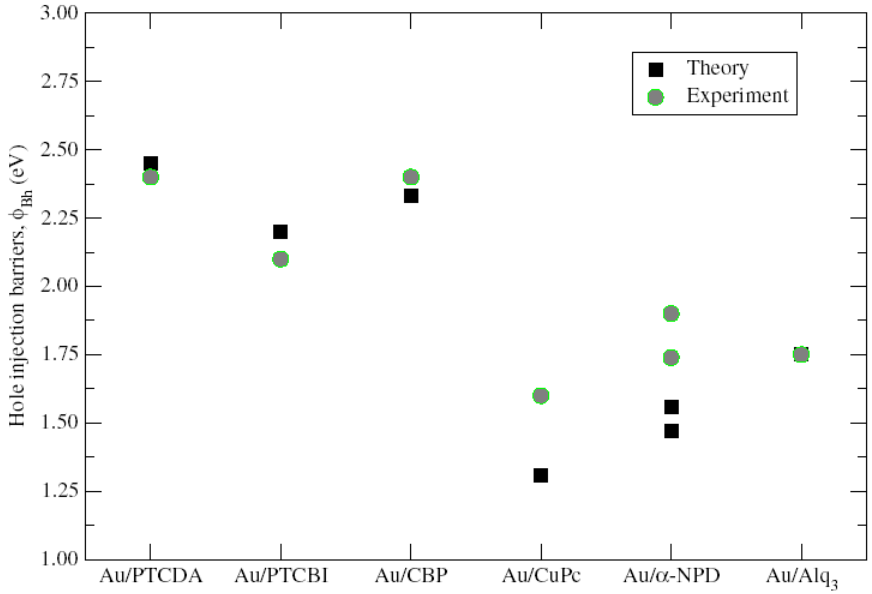
Applied Surface Science Volume 254, Issue 1, 31 October 2007, Pages 378–382

CNL: Theory vs Experiment

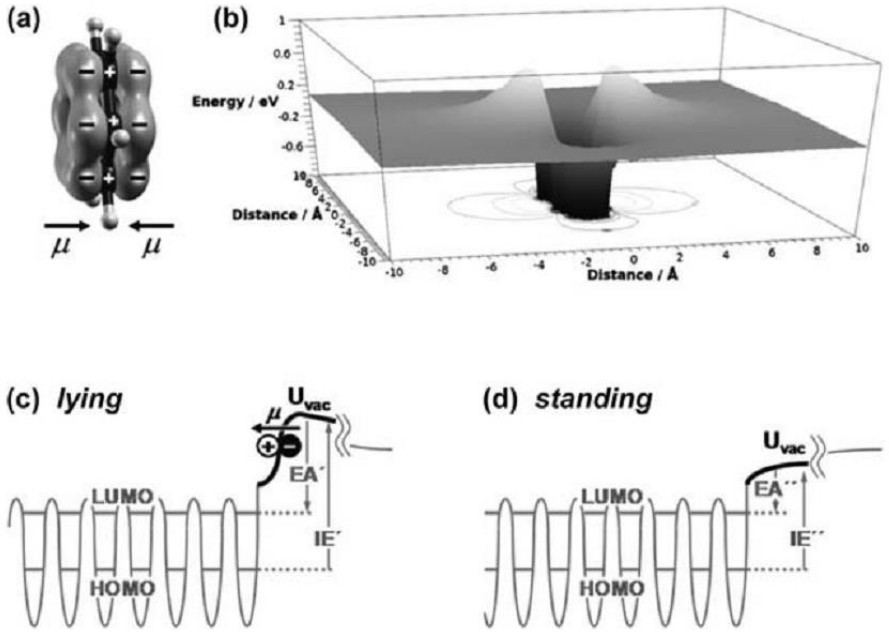


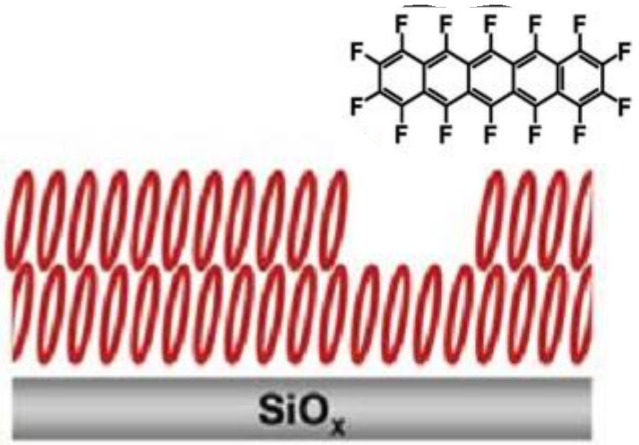
	−CNL	−IE	$-\phi_M$	S (theortical)	Δ (theortical)	Δ (experimental)	ϕ_{Bh} (theortical)	ϕ_{Bh} (experimental)
PTCDA	4.8	7.3 (6.8)	5.1 [6]	0.16	0.25	0.2 [6]	2.45	2.40 [6]
PTCBI	4.4	6.7 (6.2)	5.0 [7]	0.16	0.50	0.4 [7]	2.20	2.10 [7]
CBP	4.05	6.8 (6.3)	4.9 [10]	0.50	0.43	0.5 [10]	2.33	2.40 [10]
CuPc	4.0	5.7 (5.2)	5.3 [31]	0.30	0.91	1.2 [31]	1.31	1.60 [31]
α-NPD	4.1	6.0 (5.5)	5.14 [32]	0.33	0.70	0.86 [32]	1.56	1.74 [32]
			5.4 [33]		0.87	1.3 [33]	1.47	1.9 [33]
Alq_3	3.65	6.3 (5.8)	5.2 [6]	0.58	0.65	0.65 [6]	1.75	1.75 [6]
BCP	3.65	6.9(6.4)	–	0.42	–	–	–	–

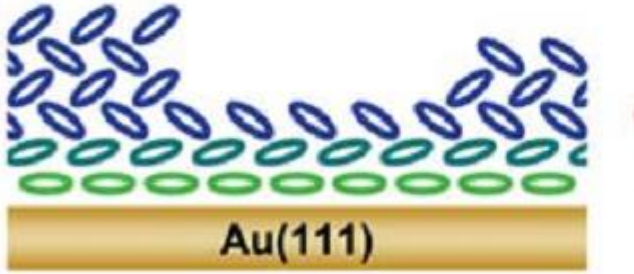


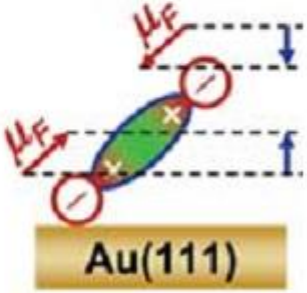


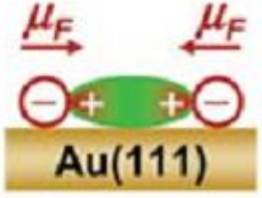
Metal/**ordered** molecule interfaces: n-poles











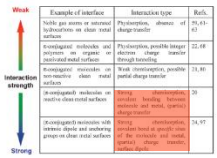
Quadrupoles
and intrinsic dipoles

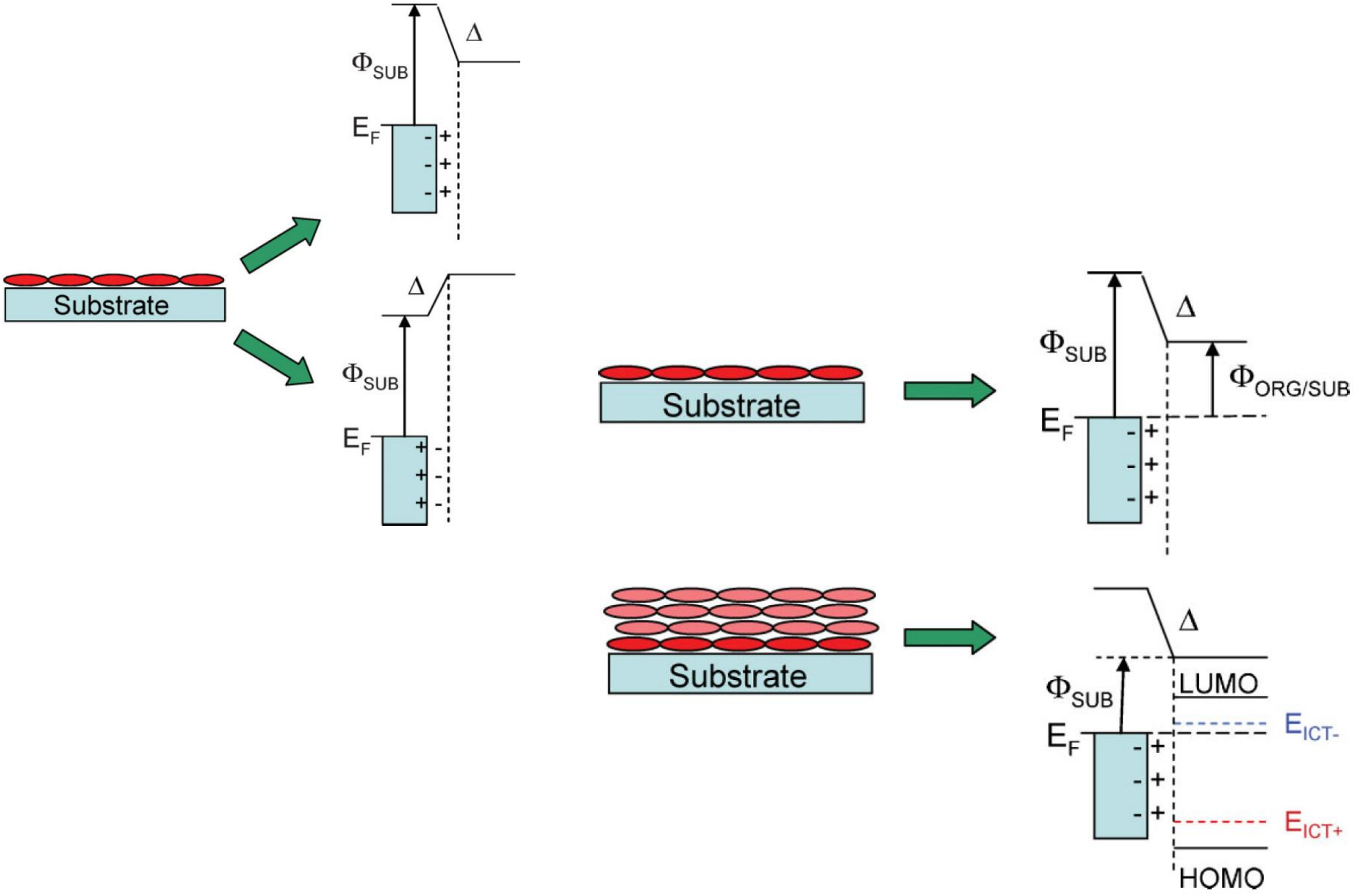
Phys. Status Solidi RRL 6, No. 7, 277– 293 (2012

Strong chemical interaction @ Interface

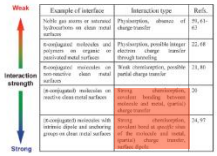
Example of interface	Interaction type	Refs.
Noble gas atoms or saturated hydrocarbons on clean metal surfaces	Physisorption, absence of charge transfer	59, 61-63
π-conjugated molecules and polymers on organic or passivated metal surfaces	Physisorption, possible integer electron charge transfer through tunneling	22, 68
π-conjugated molecules on non-reactive clean metal surfaces	Weak chemisorption, possible partial charge transfer	21, 80
(π-conjugated) molecules on reactive clean metal surfaces	Strong chemisorption, covalent bonding between molecule and metal, (partial) charge transfer	20
(π-conjugated) molecules with intrinsic dipole and anchoring groups on clean metal surfaces	Strong chemisorption, covalent bond at *specific* sites of the molecule and metal, (partial) charge transfer, surface dipole	24, 97

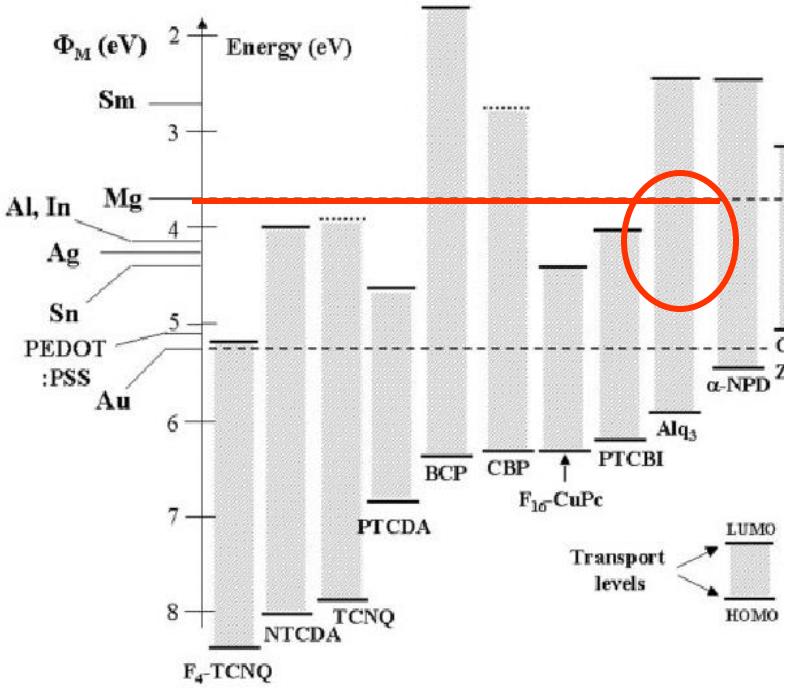
Chemisorption

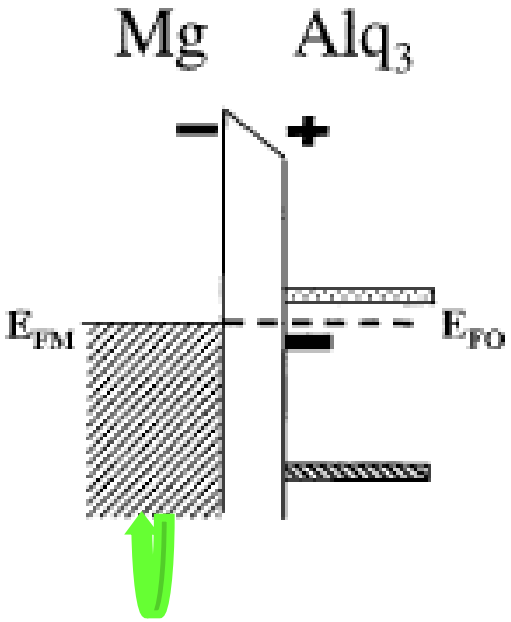




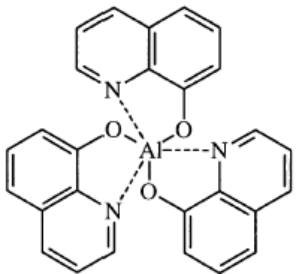
Chemisorption: Alq3/Mg (1)



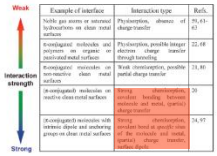


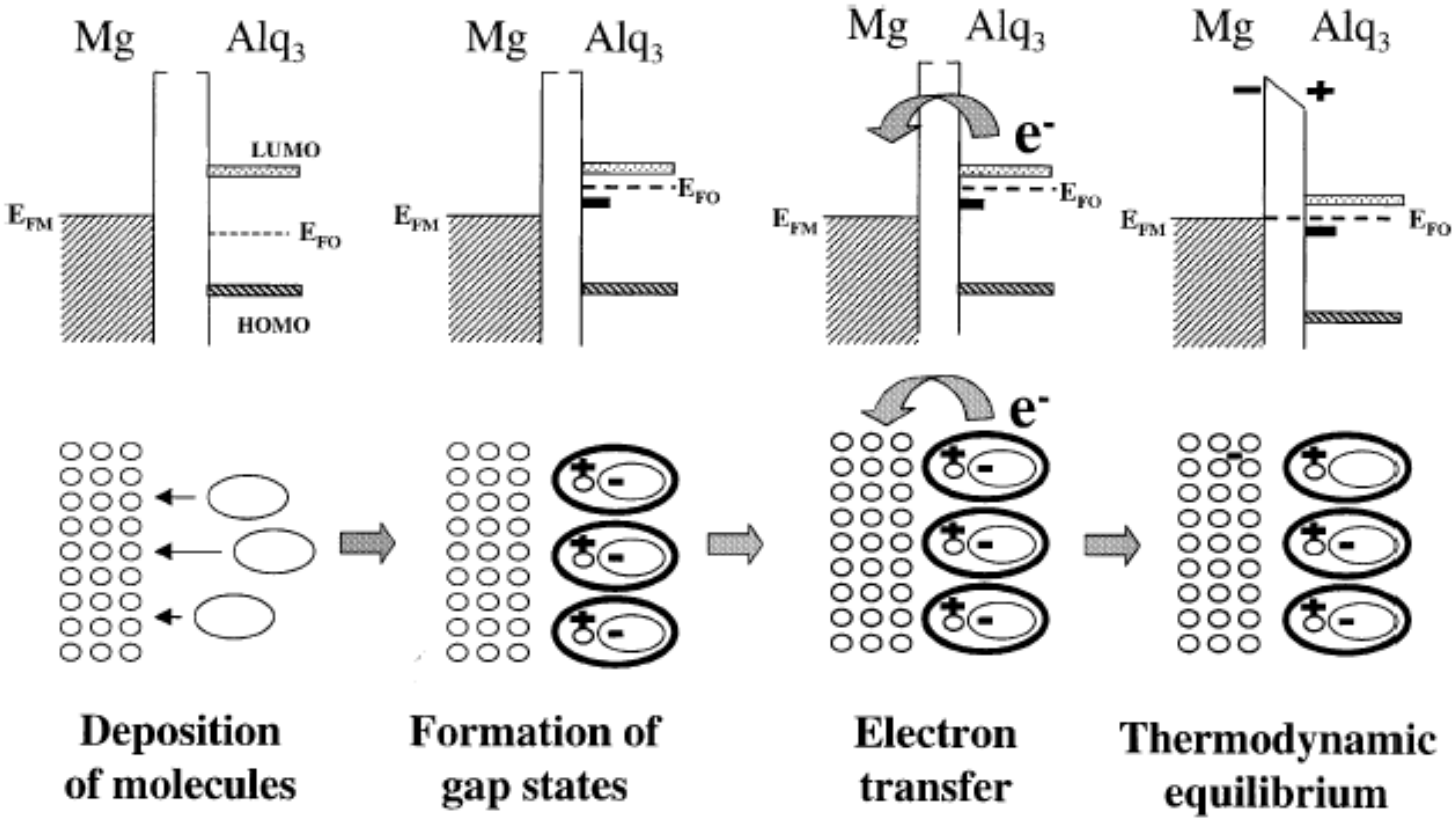


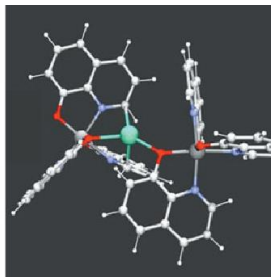
Unexpected electron flow!!



Chemisorption: Alq3/Mg (2)







Chemistry induced electronic states formation:
a new Mg:Alq3 organometallic complex

Interface energetics: summary

Example of interface	Interaction type
Noble gas atoms or saturated hydrocarbons on clean metal surfaces	Physisorption, absence of charge transfer
π-conjugated molecules and polymers on organic or passivated metal surfaces	Physisorption, possible integer electron charge transfer through tunneling
π-conjugated molecules on non-reactive clean metal surfaces	Weak chemisorption, possible partial charge transfer
(π-conjugated) molecules on reactive clean metal surfaces	Strong chemisorption, covalent bonding between molecule and metal, (partial) charge transfer
(π-conjugated) molecules with intrinsic dipole and anchoring groups on clean metal surfaces	Strong chemisorption, covalent bond at *specific* sites of the molecule and metal, (partial) charge transfer, surface dipole

Integer charge transfer

IDIS and partial C.T.

Chemical reactions @ interface

Polymers on metal

Example of interface	Interaction type
Noble gas atoms or saturated hydrocarbons on clean metal surfaces	Physisorption, absence of charge transfer
π-conjugated molecules and polymers on organic or passivated metal surfaces	Physisorption, possible integer electron charge transfer through tunneling
π-conjugated molecules on non-reactive clean metal surfaces	Weak chemisorption, possible partial charge transfer
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(π-conjugated) molecules with intrinsic dipole and anchoring groups on clean metal surfaces	Strong chemisorption, covalent bond at *specific* sites of the molecule and metal, (partial) charge transfer, surface dipole

Integer charge transfer

IDIS and partial C.T.

Chemical reactions @ interface

Solvents "**passivates**" metals-> no *intimate* metal organic contact -> no IDIS nor chemical reaction

Metal on *Polymers*

Example of interface	Interaction type
Noble gas atoms or saturated hydrocarbons on clean metal surfaces	Physisorption, absence of charge transfer
π-conjugated molecules and polymers on organic or passivated metal surfaces	Physisorption, possible integer electron charge transfer through tunneling
π-conjugated molecules on non-reactive clean metal surfaces	Weak chemisorption, possible partial charge transfer
(π-conjugated) molecules on reactive clean metal surfaces	Strong chemisorption, covalent bonding between molecule and metal, (partial) charge transfer
(π-conjugated) molecules with intrinsic dipole and anchoring groups on clean metal surfaces	Strong chemisorption, covalent bond at *specific* sites of the molecule and metal, (partial) charge transfer, surface dipole

Integer charge transfer

IDIS and partial C.T.

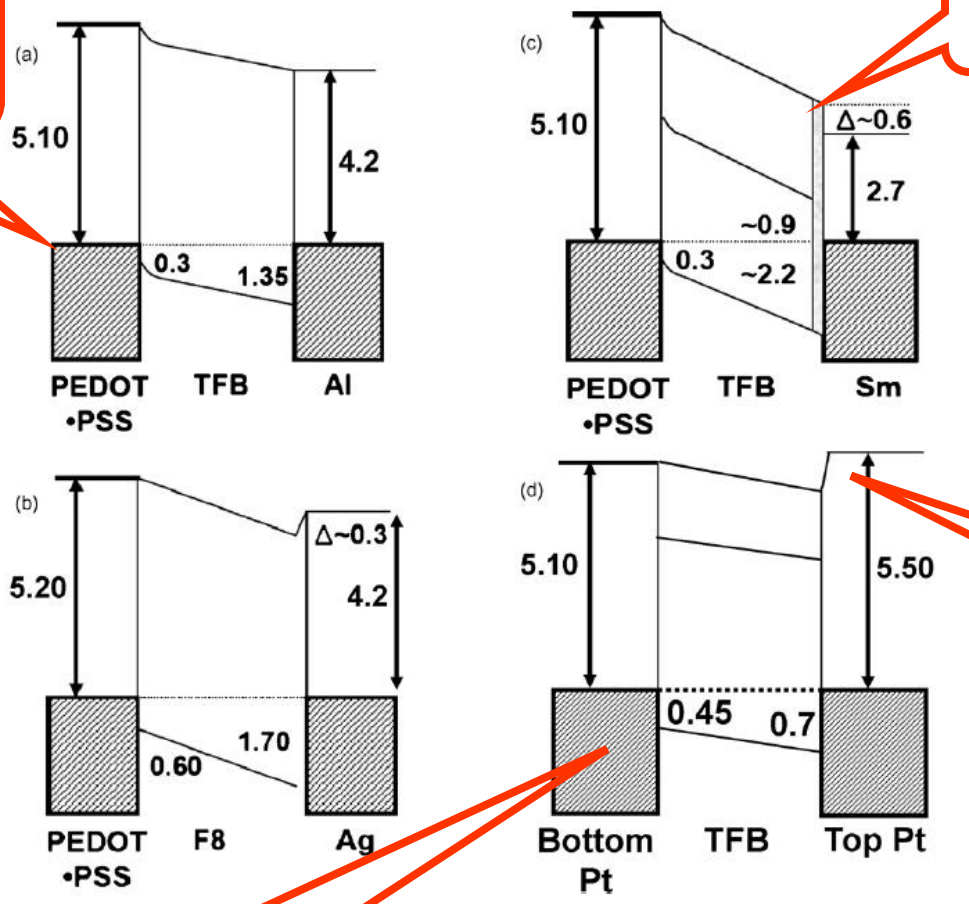
Chemical reactions @ interface

Intimate metal organic contact is *possible*
due to (Ultra) High Vacuum metal evaporation

Metal-Polymers-Metal interfaces

ICT
barriers < 0.3/0.4 eV
Band bending?

Chemical reaction



IDIS dipole

Pushback:
Pt Ef=5.65eV

Hwang Materials Science and Engineering R 64 (2009) 1–31

[Metal/*Small molecule*] – [*Small molecule*/metal] interfaces

Example of interface	Interaction type
Noble gas atoms or saturated hydrocarbons on clean metal surfaces	Physisorption, absence of charge transfer
π-conjugated molecules and polymers on organic or passivated metal surfaces	Physisorption, possible integer electron charge transfer through tunneling
π-conjugated molecules on non-reactive clean metal surfaces	Weak chemisorption, possible partial charge transfer
(π-conjugated) molecules on reactive clean metal surfaces	Strong chemisorption, covalent bonding between molecule and metal, (partial) charge transfer
(π-conjugated) molecules with intrinsic dipole and anchoring groups on clean metal surfaces	Strong chemisorption, covalent bond at *specific* sites of the molecule and metal, (partial) charge transfer, surface dipole

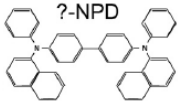
Integer charge transfer

IDIS and partial C.T.

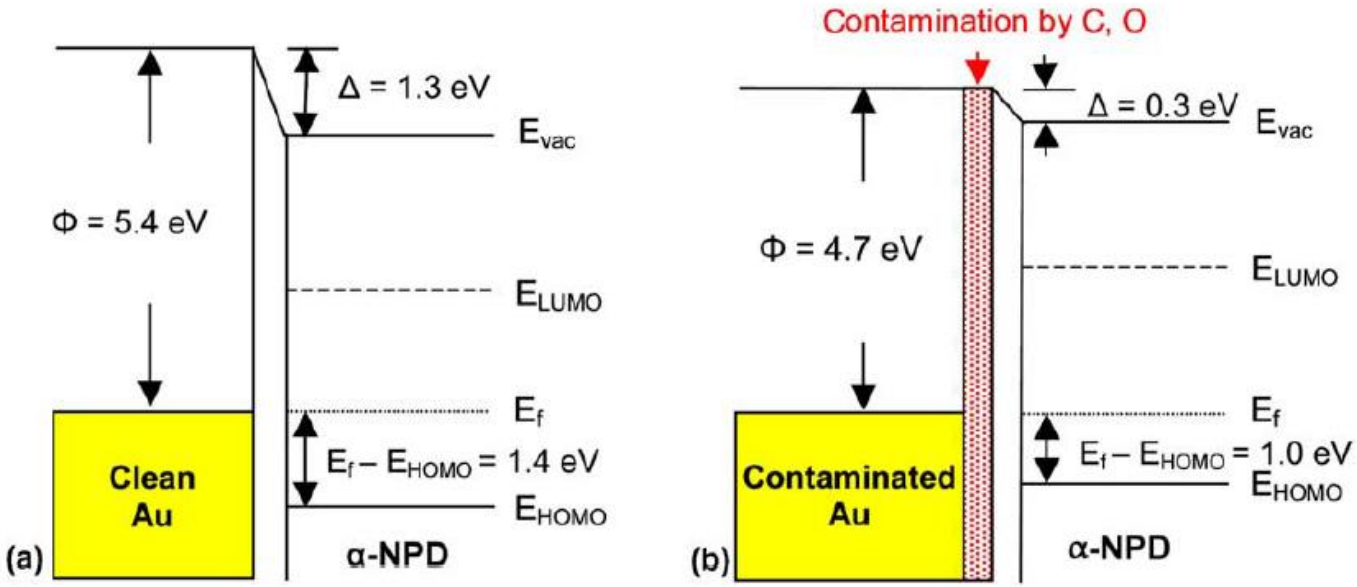
Chemical reactions @ interface

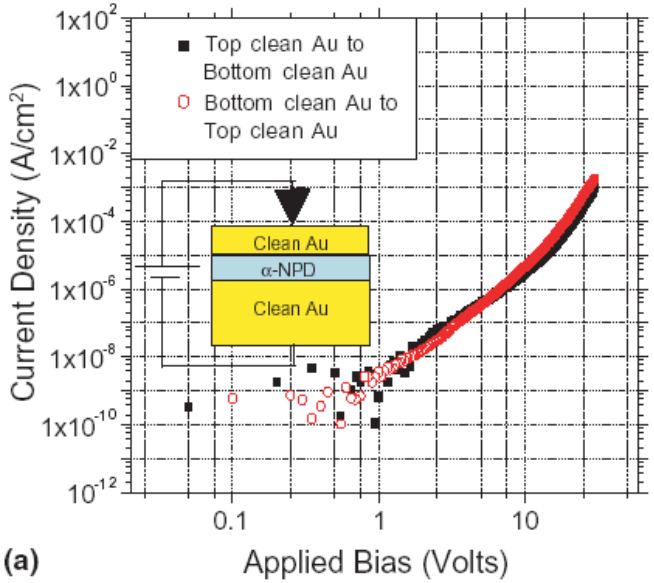
Intimate metal organic contact is *possible*
due to (Ultra) High Vacuum **metal and molecule** evaporation

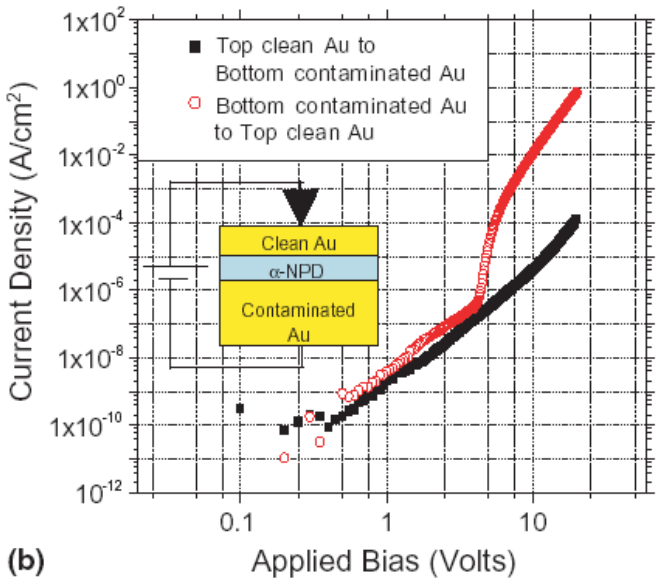
Molecules: Clean Vs. contaminated metal



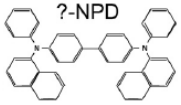
A. Wan et Organic Electronics 6 (2005) 47–54



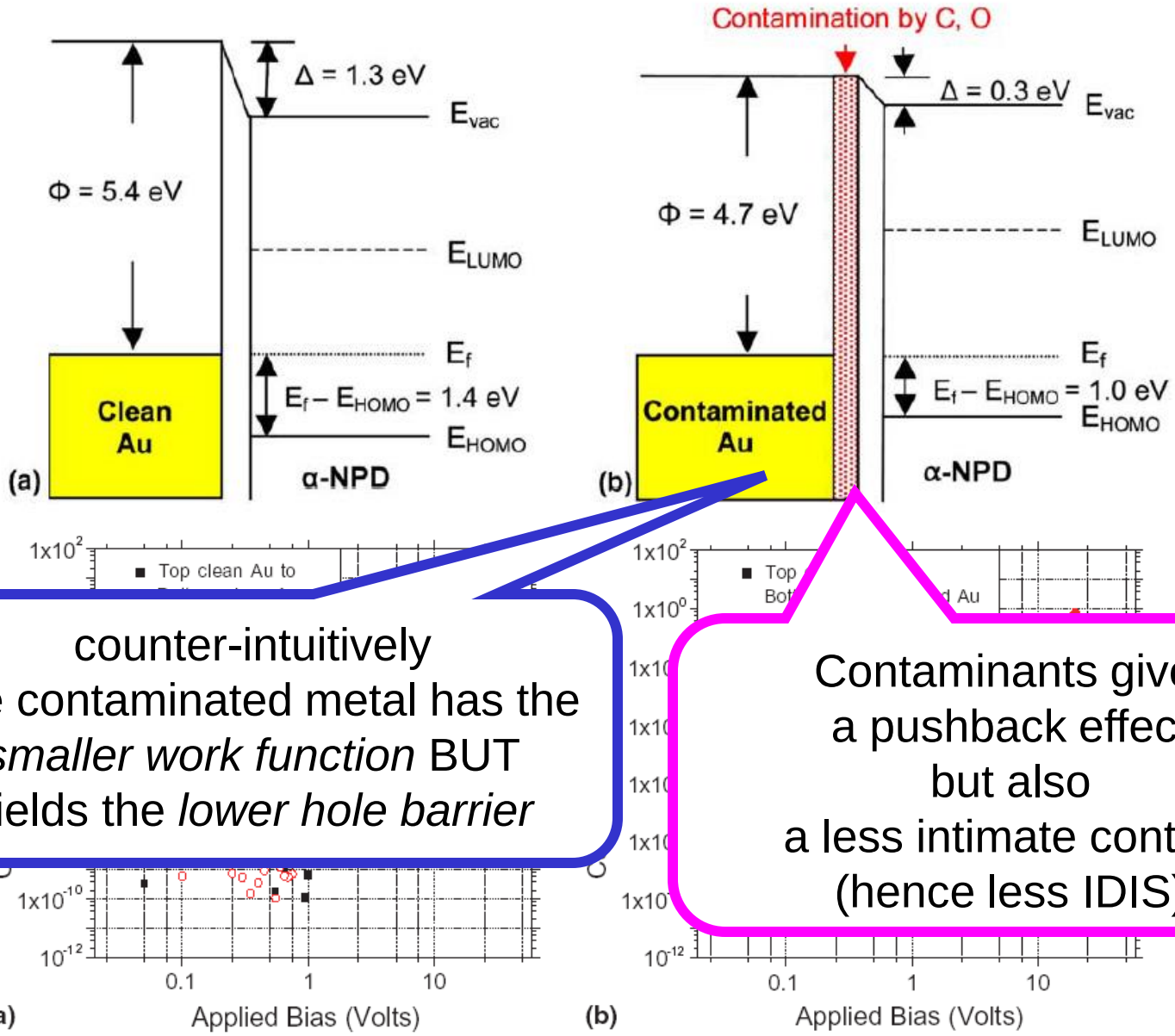




Molecules: Clean Vs. contaminated metal



A. Wan et Organic Electronics 6 (2005) 47–54



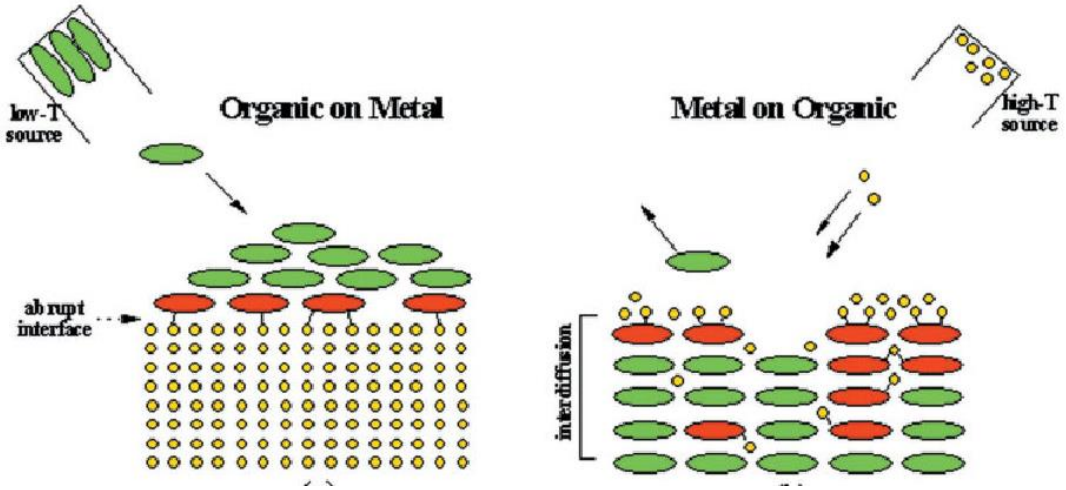
counter-intuitively
The contaminated metal has the *smaller work function* BUT yields the *lower hole barrier*

Contaminants give:
a pushback effect
but also
a less intimate contact
(hence less IDIS)

Effect of deposition technique

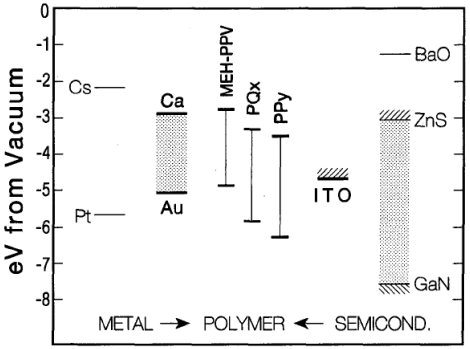
- Vacuum deposited ***vs*** liquid phase deposition: *solvents/air passivates interfaces*
- Metal upon Organics ***vs*** Organics upon Metal

Metal Diffusion



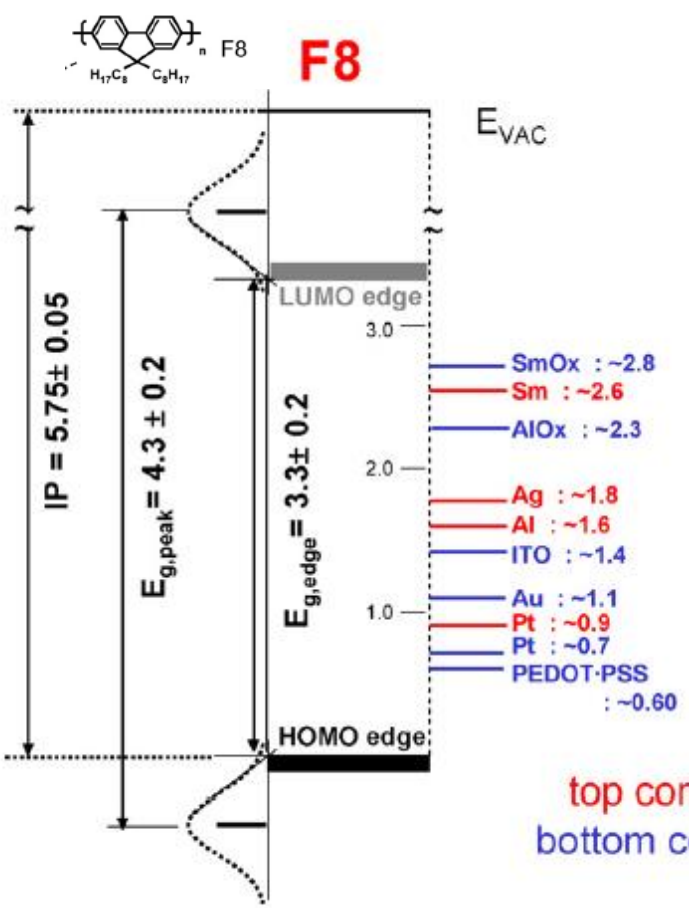
But often this does not give different electrical behavior…

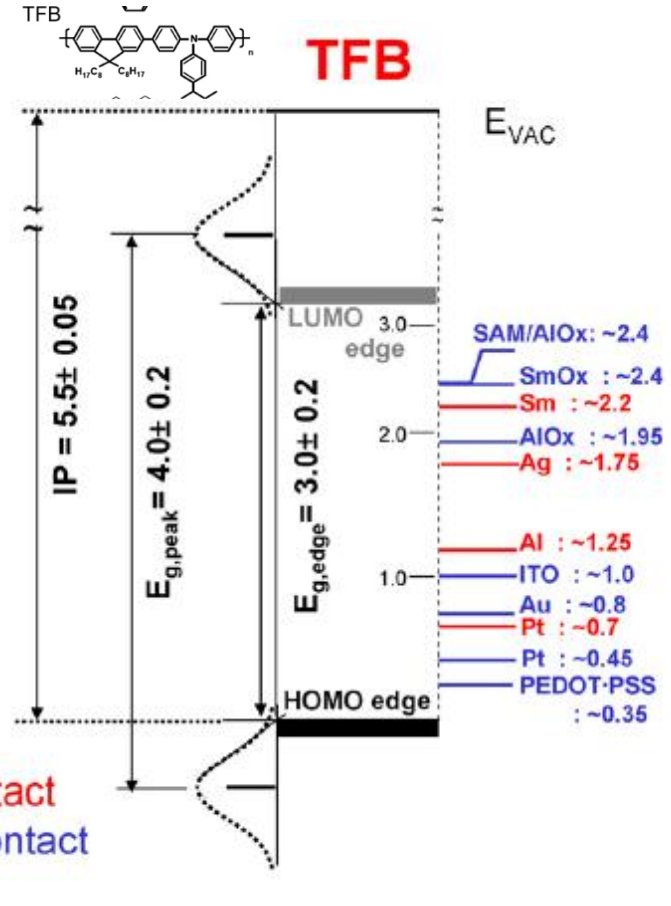
Materials



Theory…

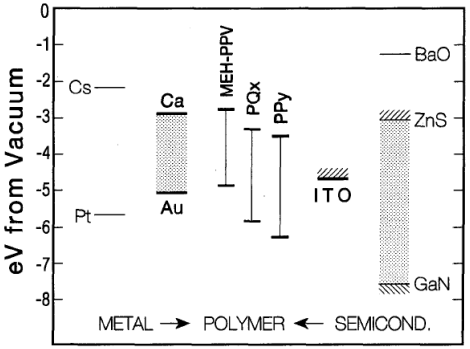
practice…





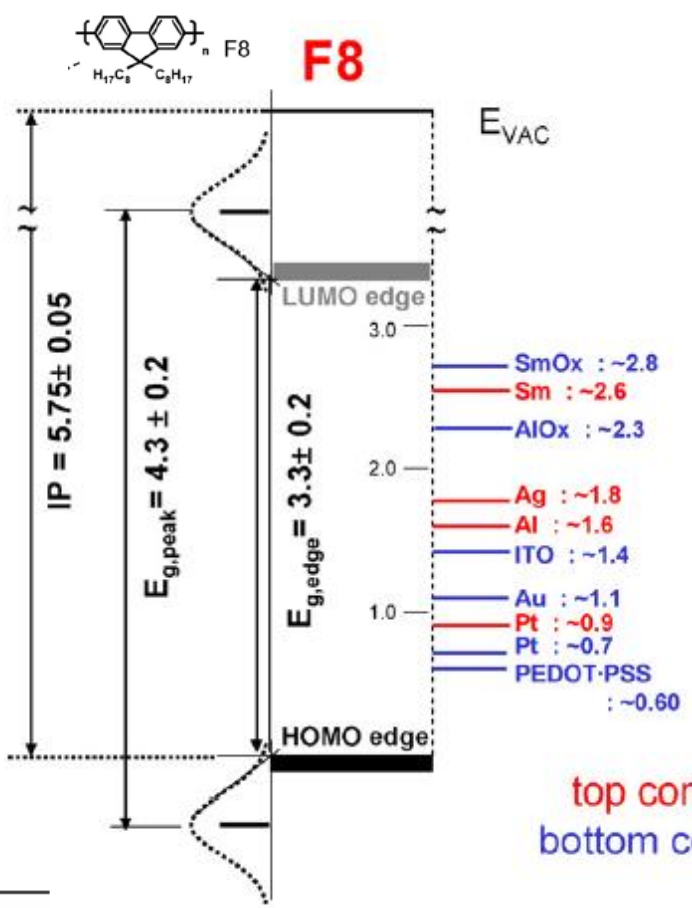
top contact
bottom contact

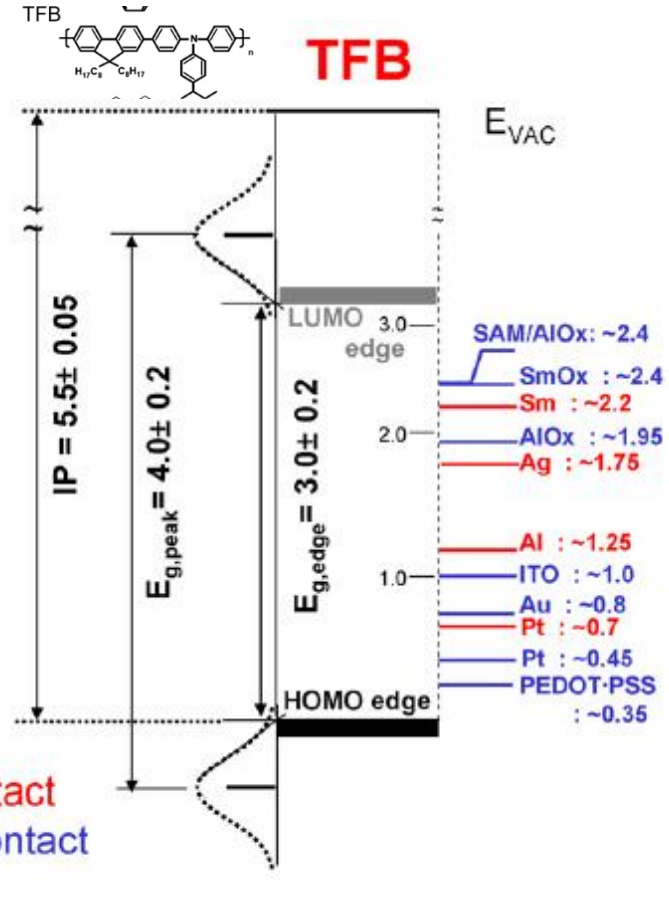
Materials



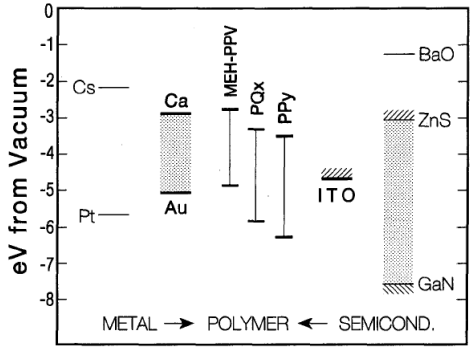
Theory…

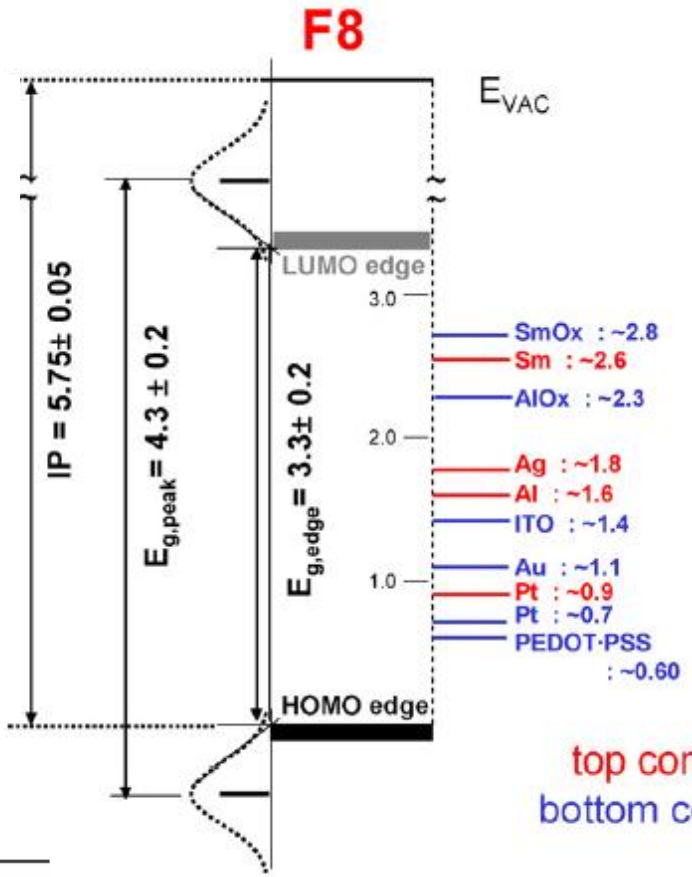
practice…

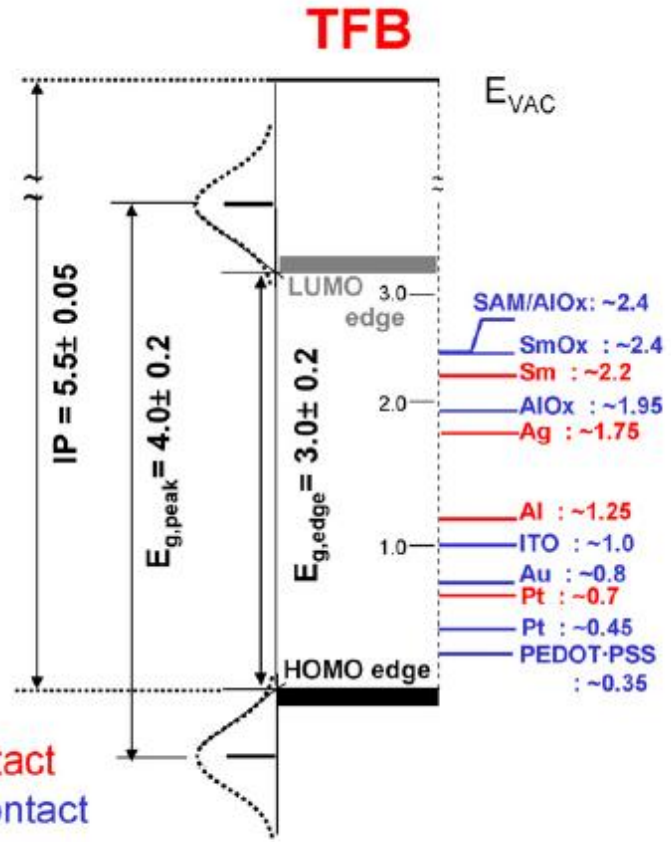




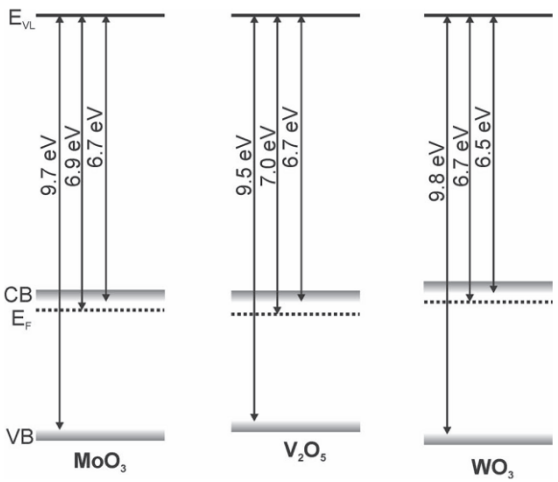
top contact
bottom contact







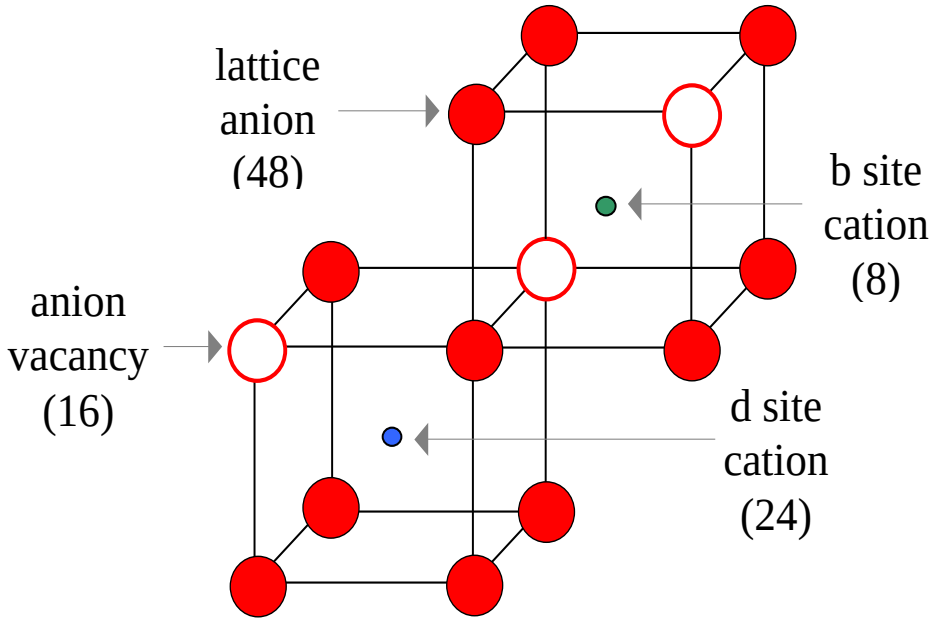
top contact
bottom contact



Transition metal oxides:
n-type semiconductors with low-lying CB, are useful hole inj./extr. layers

J. Mater. Chem. C, 2013, 1,4796
Adv. Mater. 2012, 24, 5408–5427

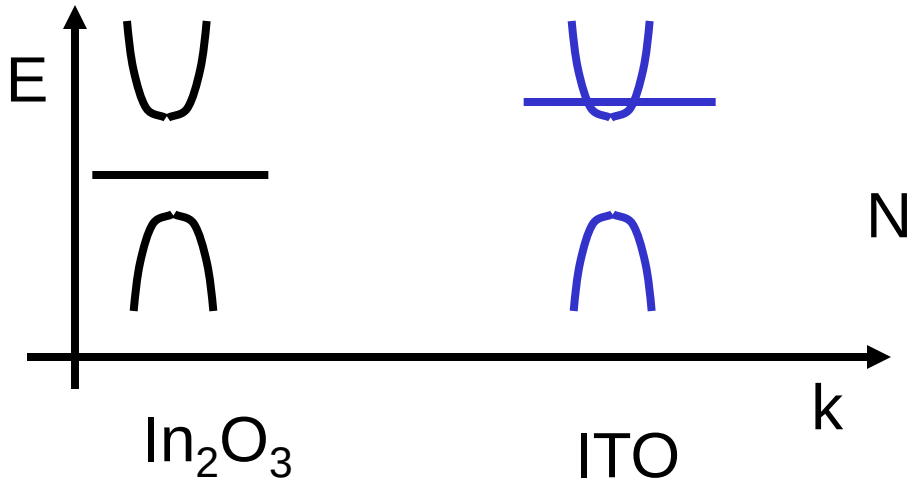
ITO (I)



In_2O_3•

$In_{2(1-x)}Sn_{2x}O_{3+x}$• 1-x

$In_{2(1-x)}Sn_{2x}O_{3+x-y}$• 1-(x-y)



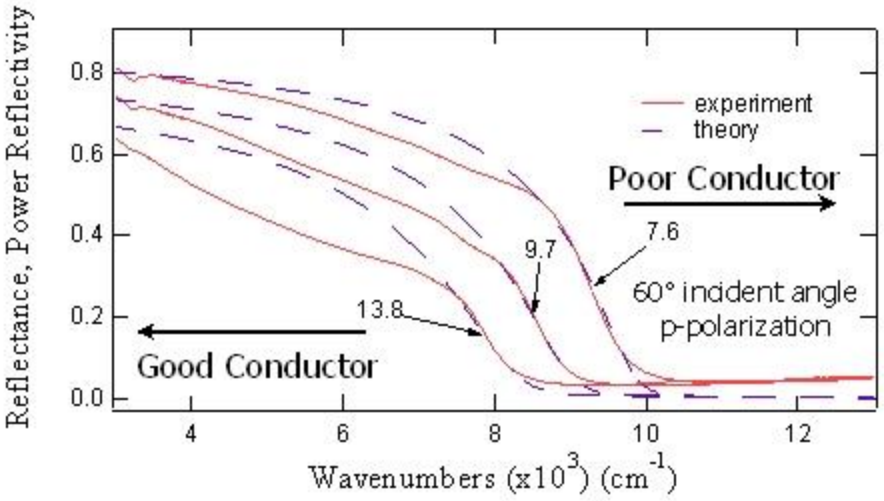
N-type degenerate semiconductor

ITO (II)

$$\varepsilon = 1 - \left(\frac{\omega_p}{\omega}\right)^2 , \omega_p = \left(\frac{n\mathrm{e}^2}{\mathrm{e}_0 m}\right)^{1/2}$$

$\omega > \omega_p$, $\varepsilon > 0$ → transparent insulator

$\omega < \omega_p$, $\varepsilon < 0$ → reflective conductor

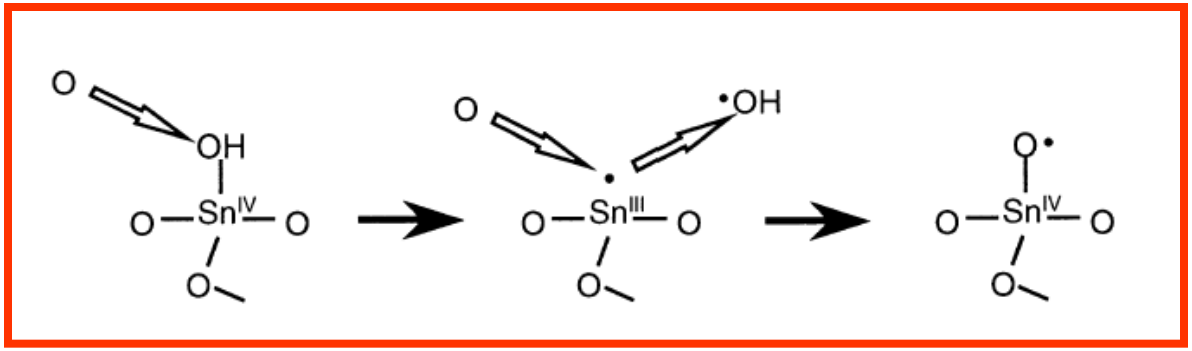


ω_p ITO ≅ 900nm

Interface functionalization

TABLE I. Work function, sheet resistance, and root-mean-square (rms) surface roughness of ITO for the different surface treatments.

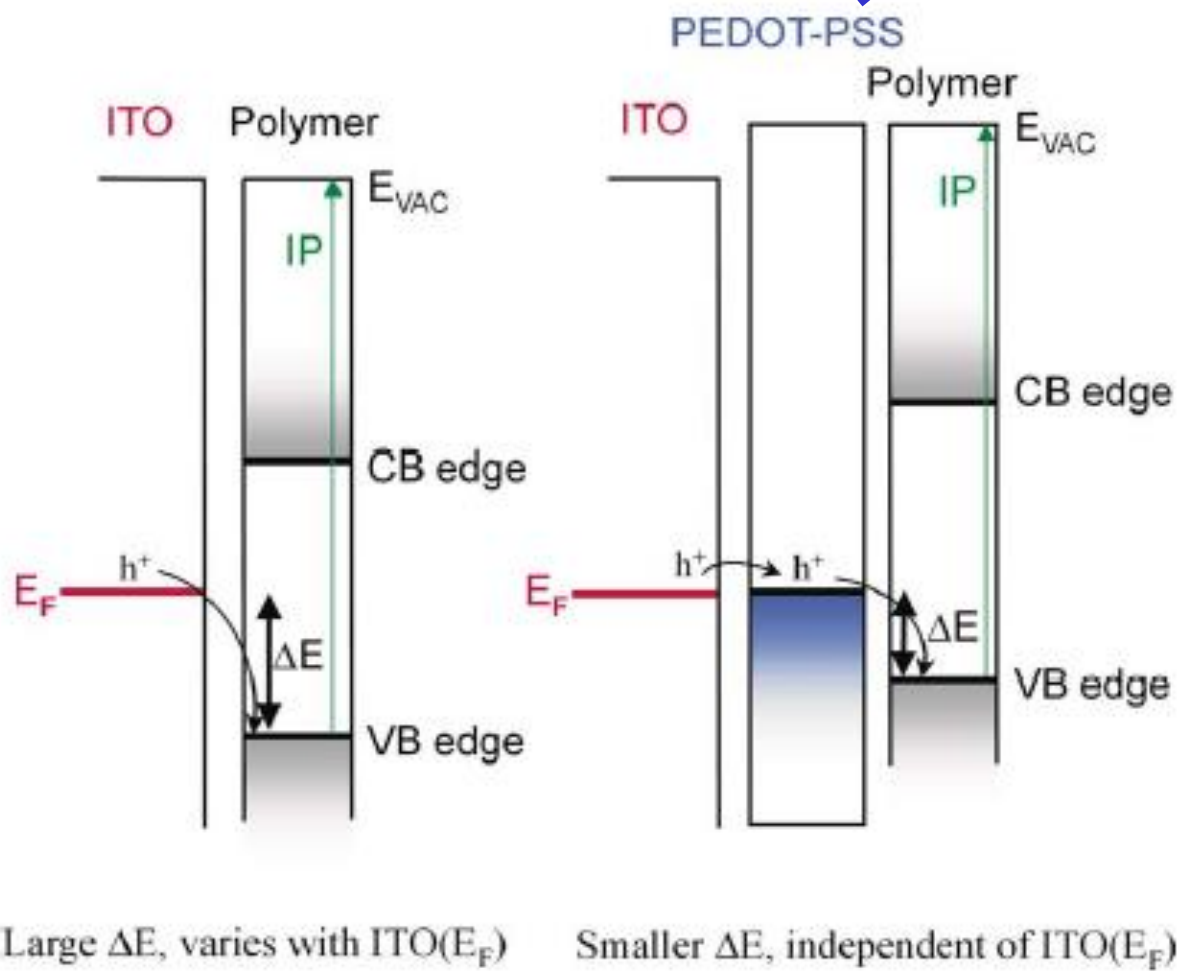
	Surface treatment	Work function (eV)	Sheet resistance (Ω/sq)	Surface roughness (nm)
	As-received	4.5	16.1	2.6
(a) Mechanical	Paper rubbing	4.2	16.3	2.3
	Teflon rubbing	4.2	16.5	2.4
(b) Wet cleaning	Ultrasonic	4.35	15.5	3.4
	RCA (no IPA)	4.35	19.6	2.4
	Aquaregia (10′/20′/30′)	4.6/4.3/4.7	18.5/23.5/28.6	3.8/8.4/8.8
(c) Dry cleaning	O_2 plasma (5′/10′/15′)	4.35/4.75/4.65	16.4/15.0/16.4	1.4/1.4/2.1
	Ar plasma (5′/10′/15′)	4.5/4.5/4.55	16.7/17.3/17.0	10.9/15.4/23.0
(d) Combined*	Aquaregia (20′)/O_2 plasma (10′)	4.6	27.7	6.0
	O_2 plasma (10′)/aquaregia (20′)	4.7	>30.0	1.8

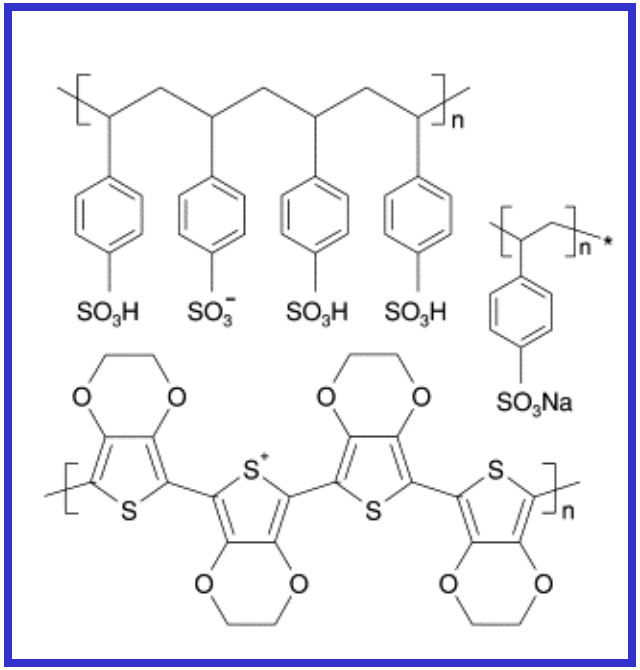


Salaneck J. Appl. Phys., Vol. 84, No. 12, 15 December 1998

Interface functionalization

- PEDOT PSS on ITO:

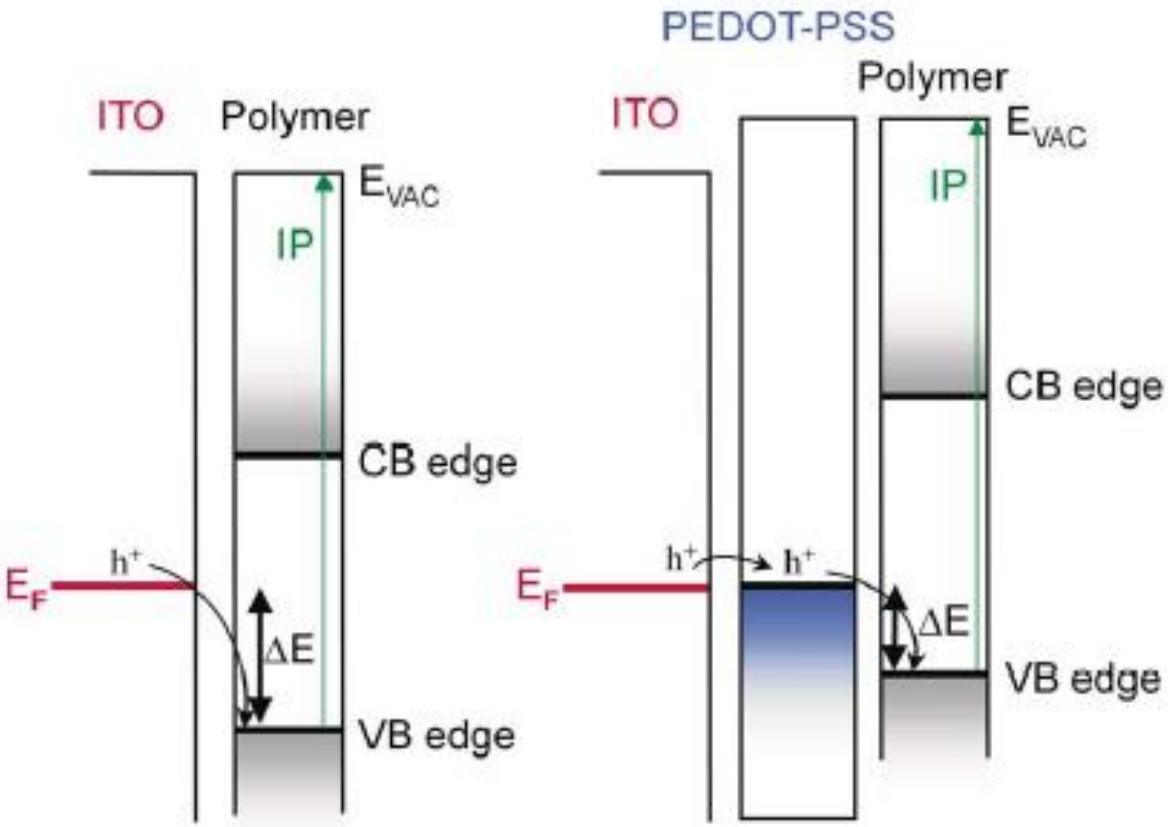




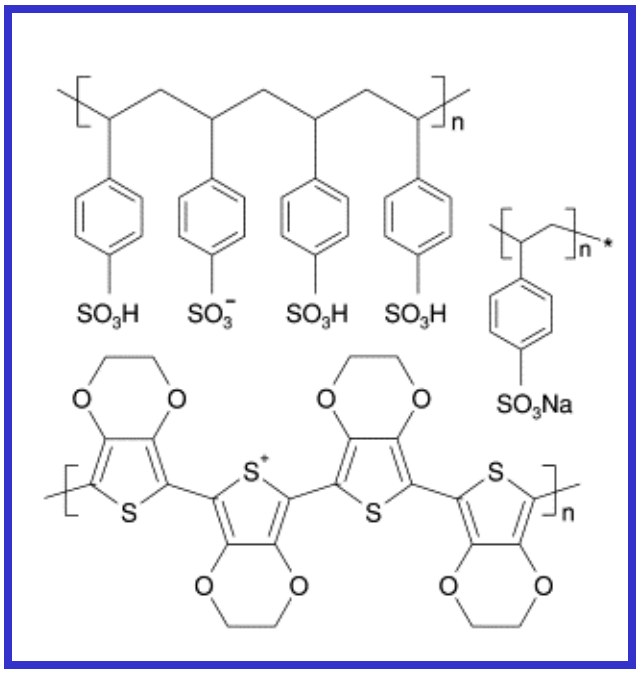
10^{-5} – 100 S/cm depending on processing and composition

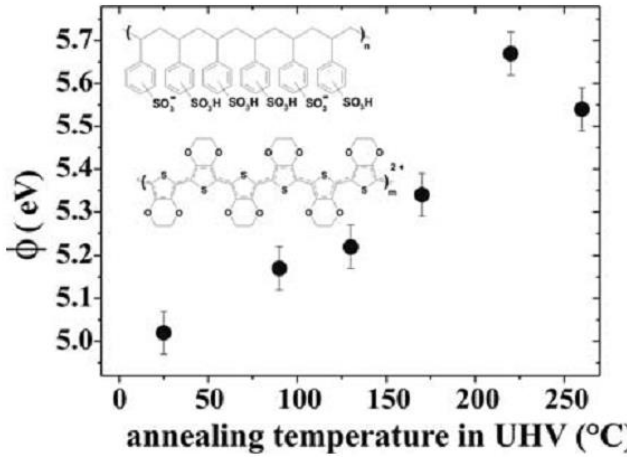
Interface functionalization

- PEDOT PSS on ITO:



Large ΔE, varies with ITO(E_F) Smaller ΔE, independent of ITO(E_F)

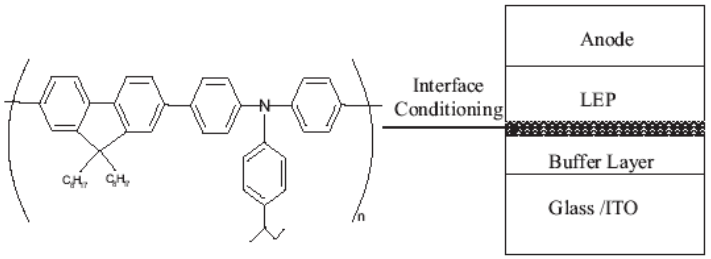


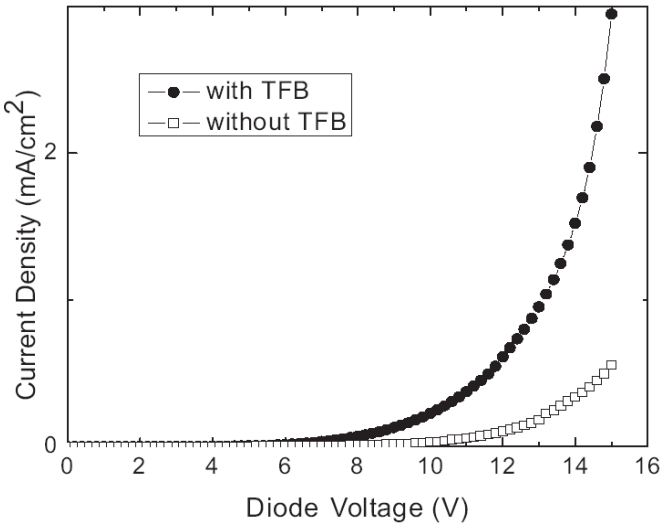


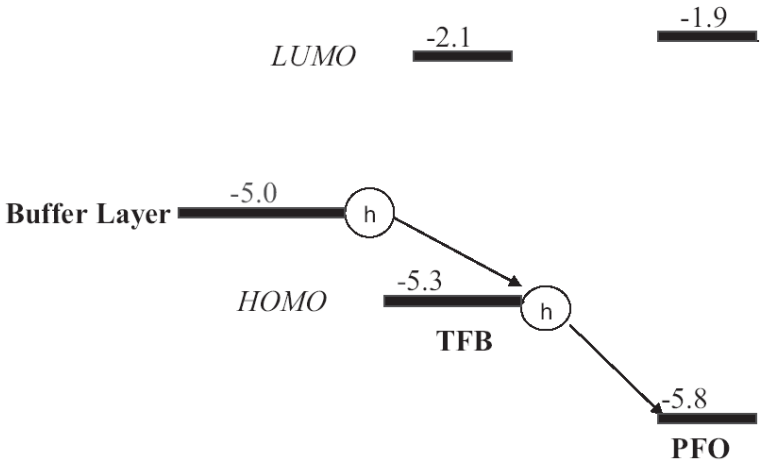
Phys. Status Solidi RRL 6, No. 7 (2012)

Interface functionalization: multilayer

So Adv. Funct. Mater. 2006, 16, 1075–1080



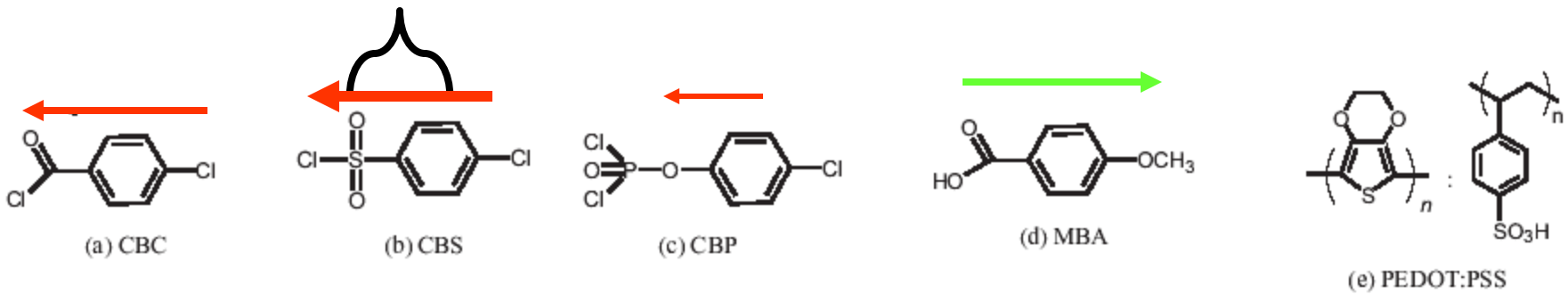


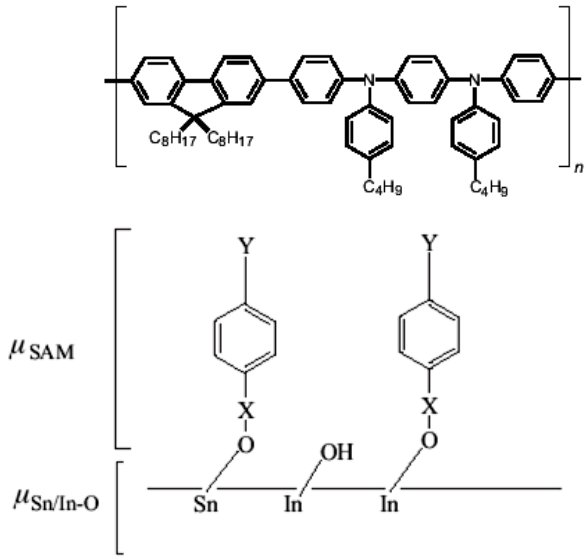


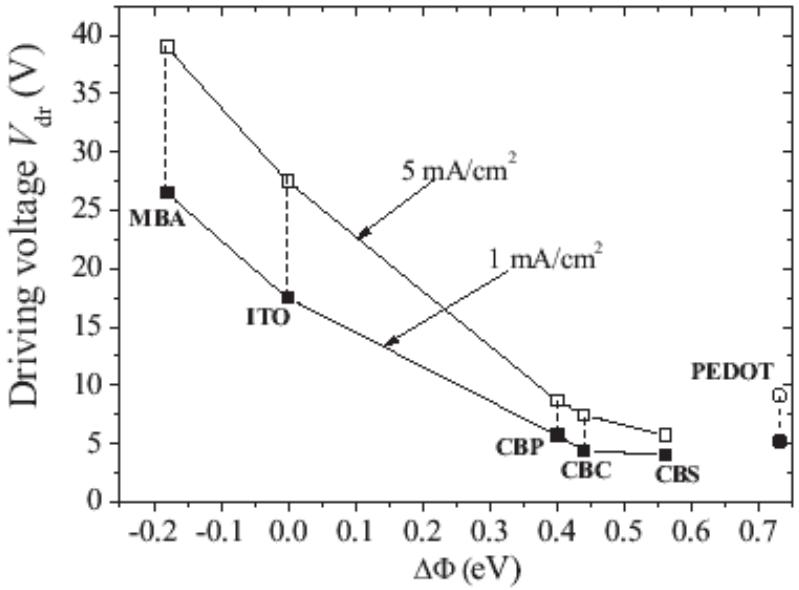
From single large Φ_B to many smaller Φ_{Bi}

Interface functionalization(4)

polar SAM on ITO

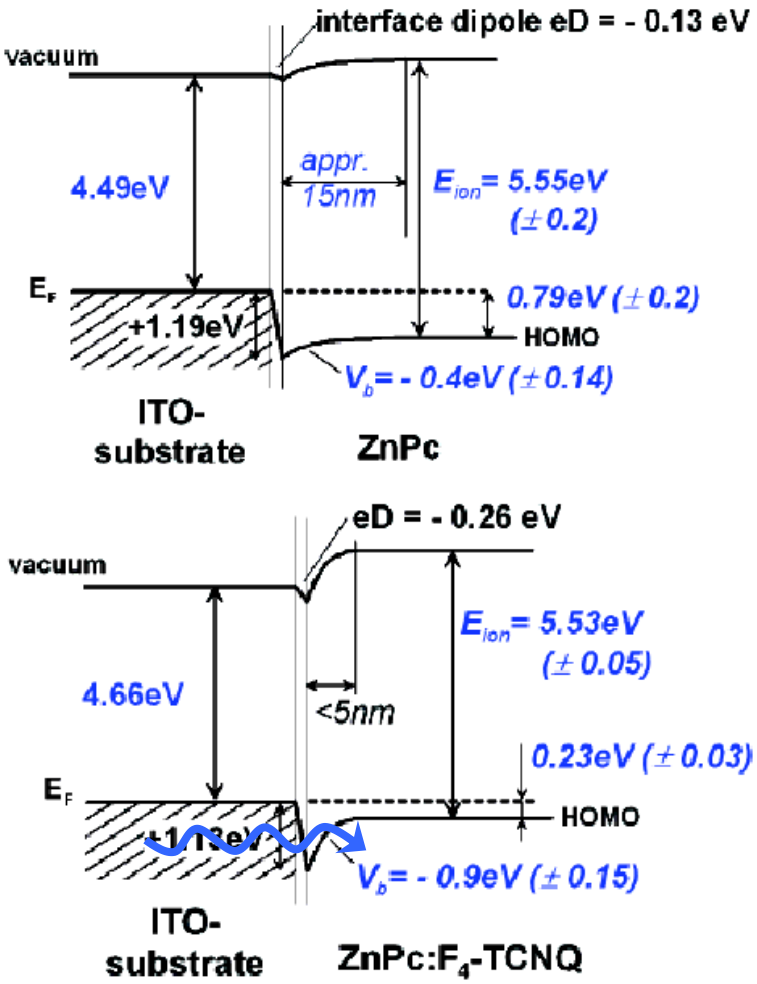


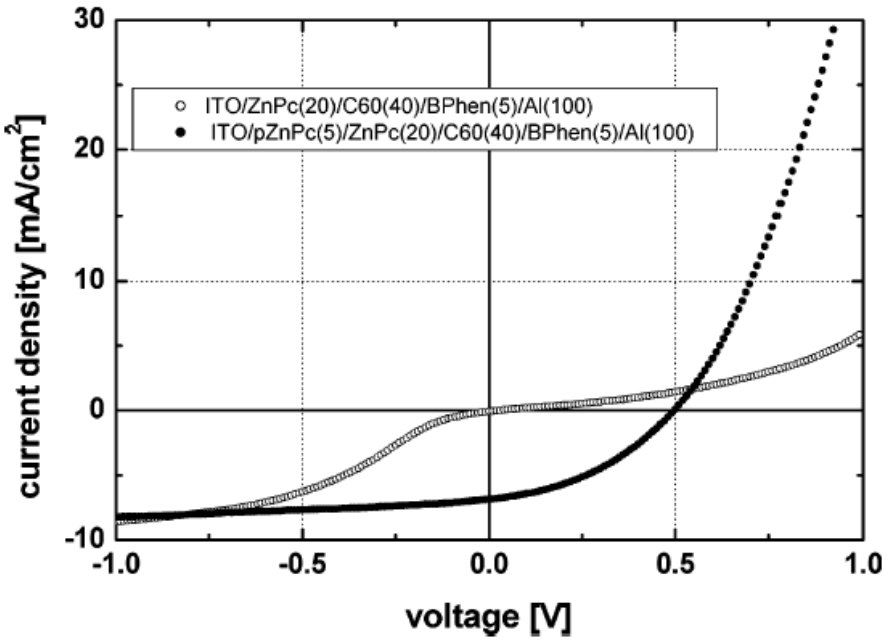




Khodabakhsh Ad.Funct.Mat. 14 2004 1205

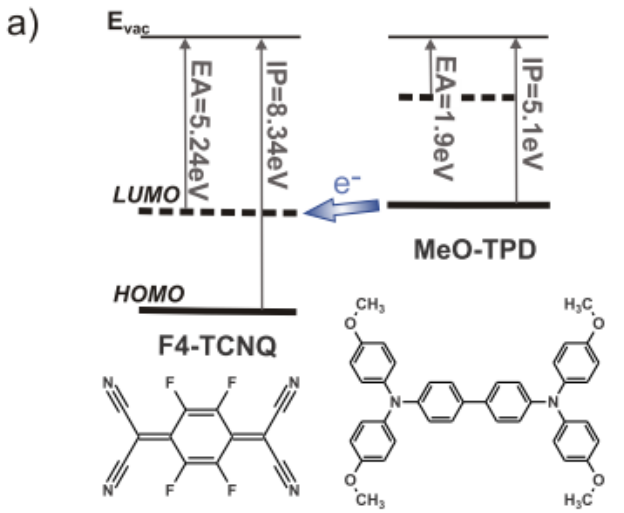
Doping

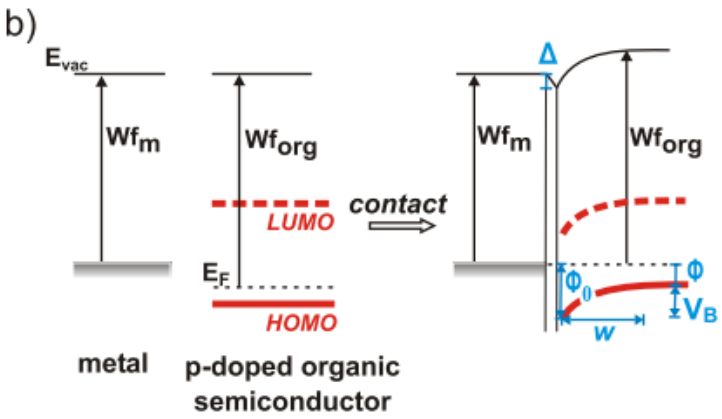


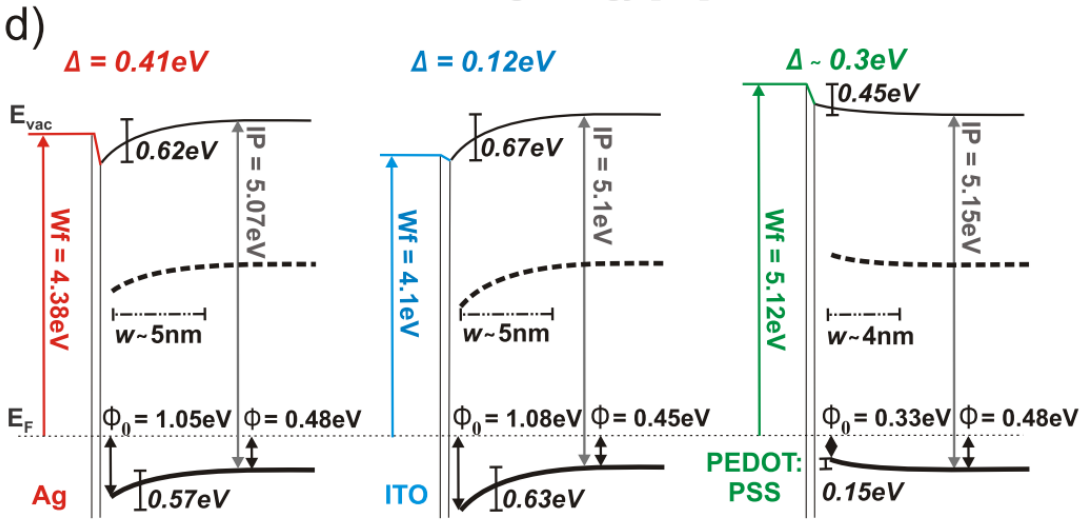


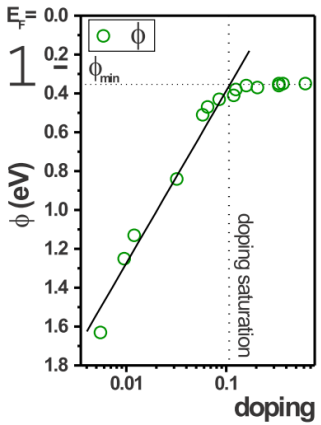
Walzer et al. Chemical Reviews, 2007, Vol. 107, No. 4

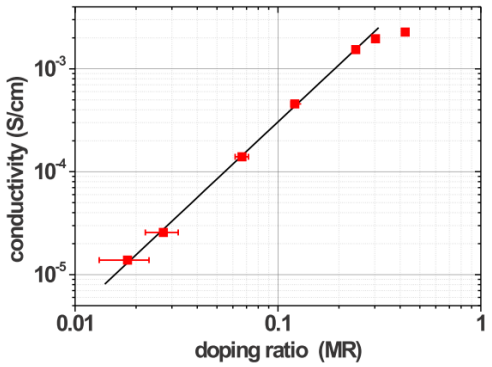
Doping







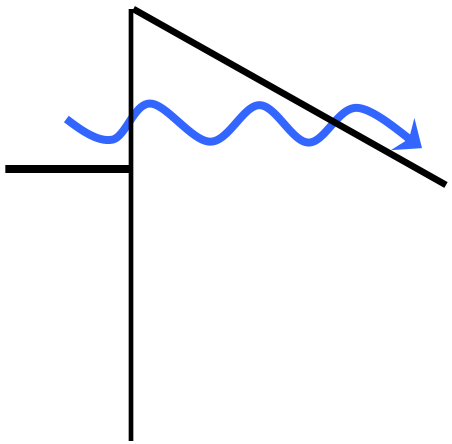




Leo, JOURNAL OF APPLIED PHYSICS 106, 103711 2009

Charge injection

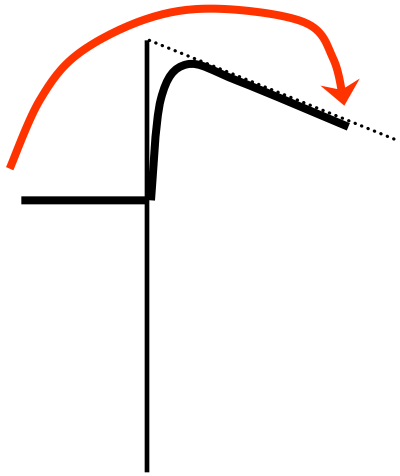
Classic models



Through the barrier:

Fowler-Nordheim $J = BF^2 \exp\left(-\frac{b}{F}\right)$

Needs bands and triangualr barrier

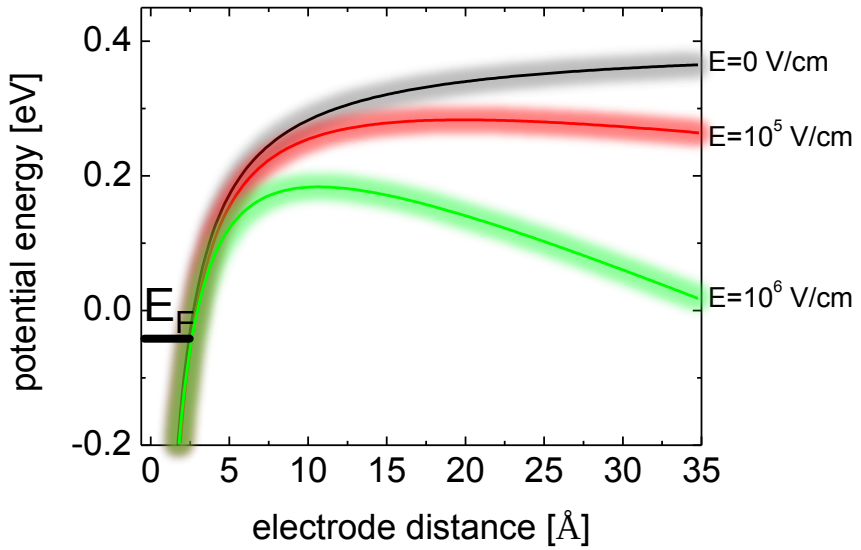


Over the barrier:

Richardson-Schottky $J = A^* T^2 \exp\left(-\frac{\Delta - cF^{1/2}}{kT}\right)$

Does not take hopping into account

Injection in organics



Ingredients:

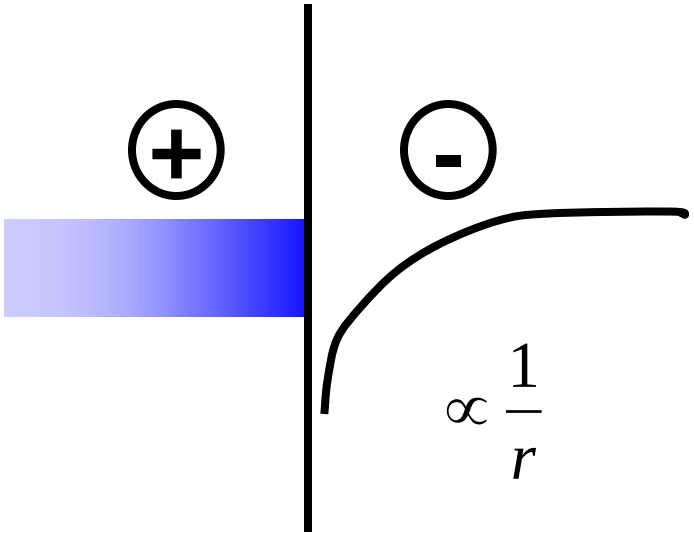
- hopping transport
- Schottky effect
- Energetic disorder

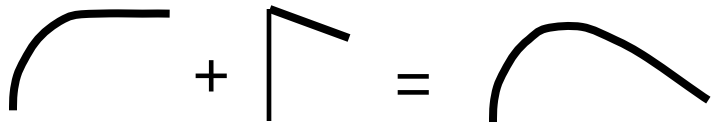
Scott J.Vac.Sci.Technol. A(21)3 2003 521

Wolf et al PhysRevB 59 (1999) 7507

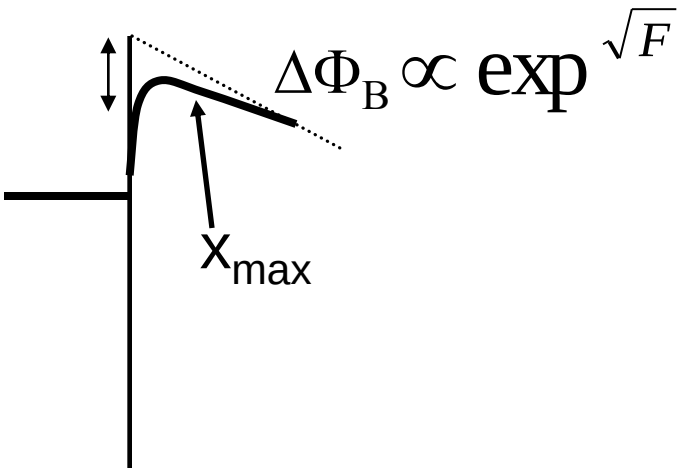
Schottky effect(1)

Ingredients:
- hopping transport
- **Schottky effect**
- Energetic disorder





Schottky ΔV Barrier lowering

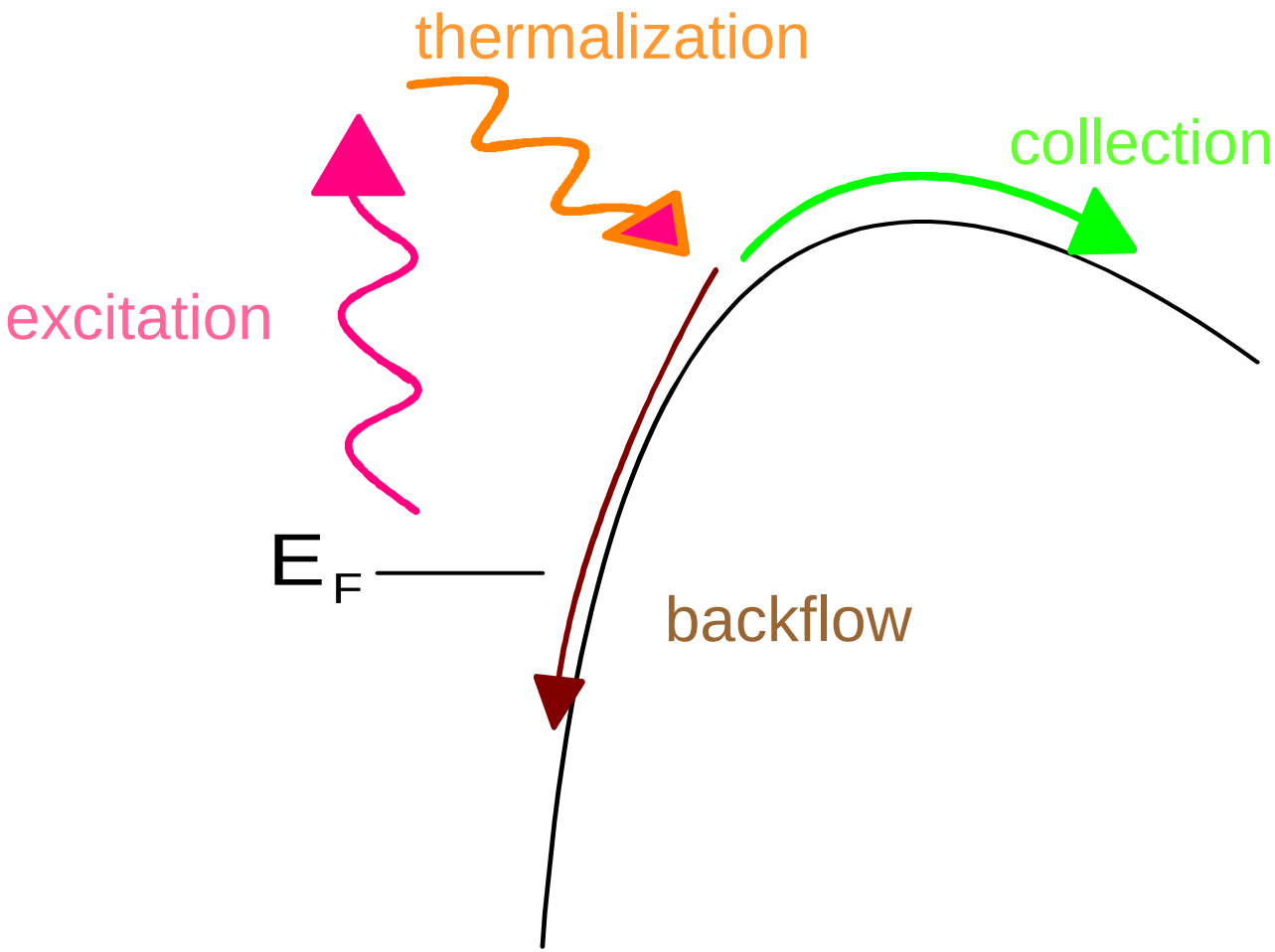


F:	10^5 V/cm	$\rightarrow$ 2x10^6 V/cm
V:	1 V	$\rightarrow$ 20 V su 100nm
$\Delta\Phi_B$:	0.06 V	$\rightarrow$ 0.28 V
X_{max}:	3.2nm	$\rightarrow$ 0.7 nm

Hopping & image potential

Ingredients:

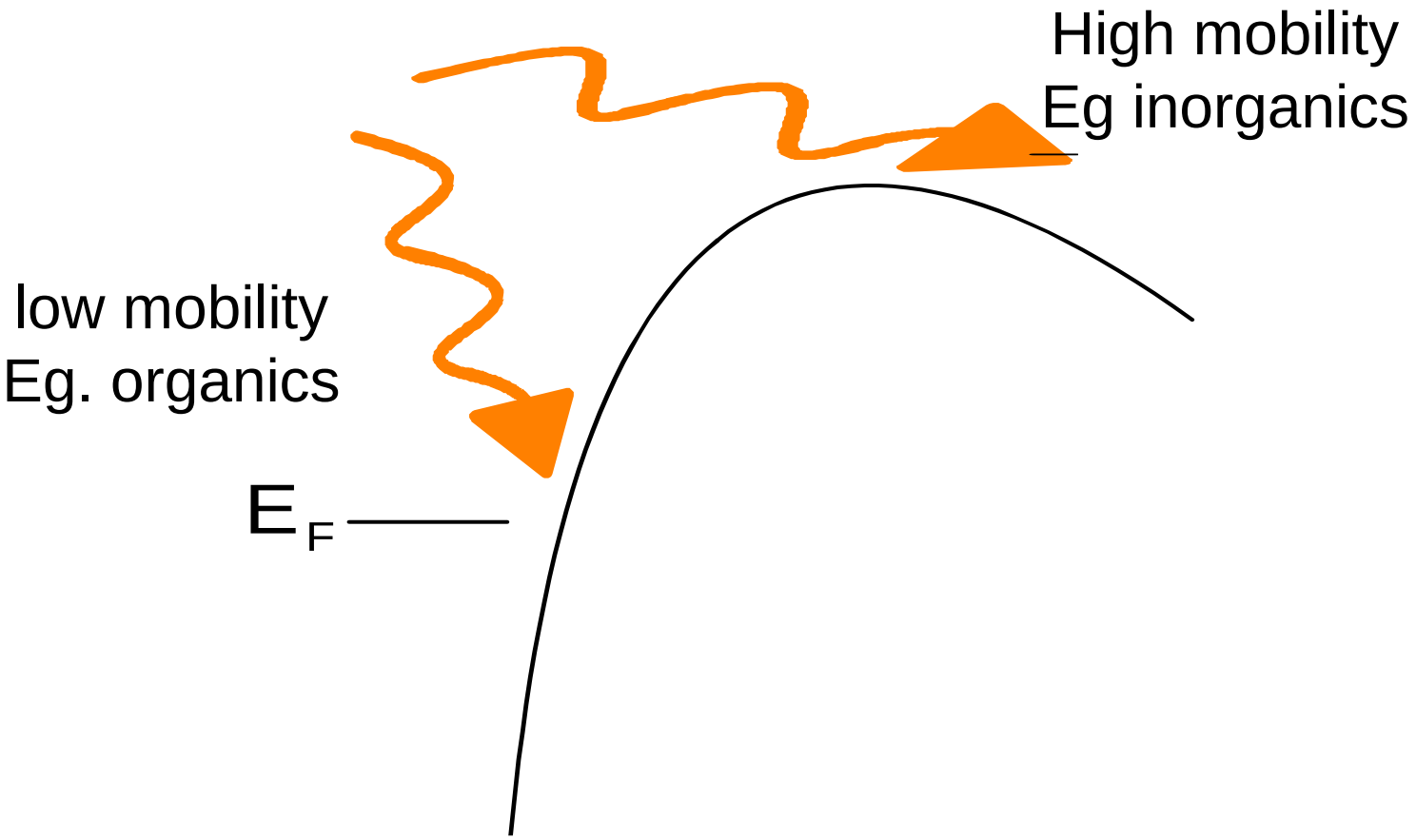
- **hopping transport**
- **Schottky effect**
- Energetic disorder



Thermalization length

Ingredients:

- **hopping transport**
- **Schottky effect**
- Energetic disorder

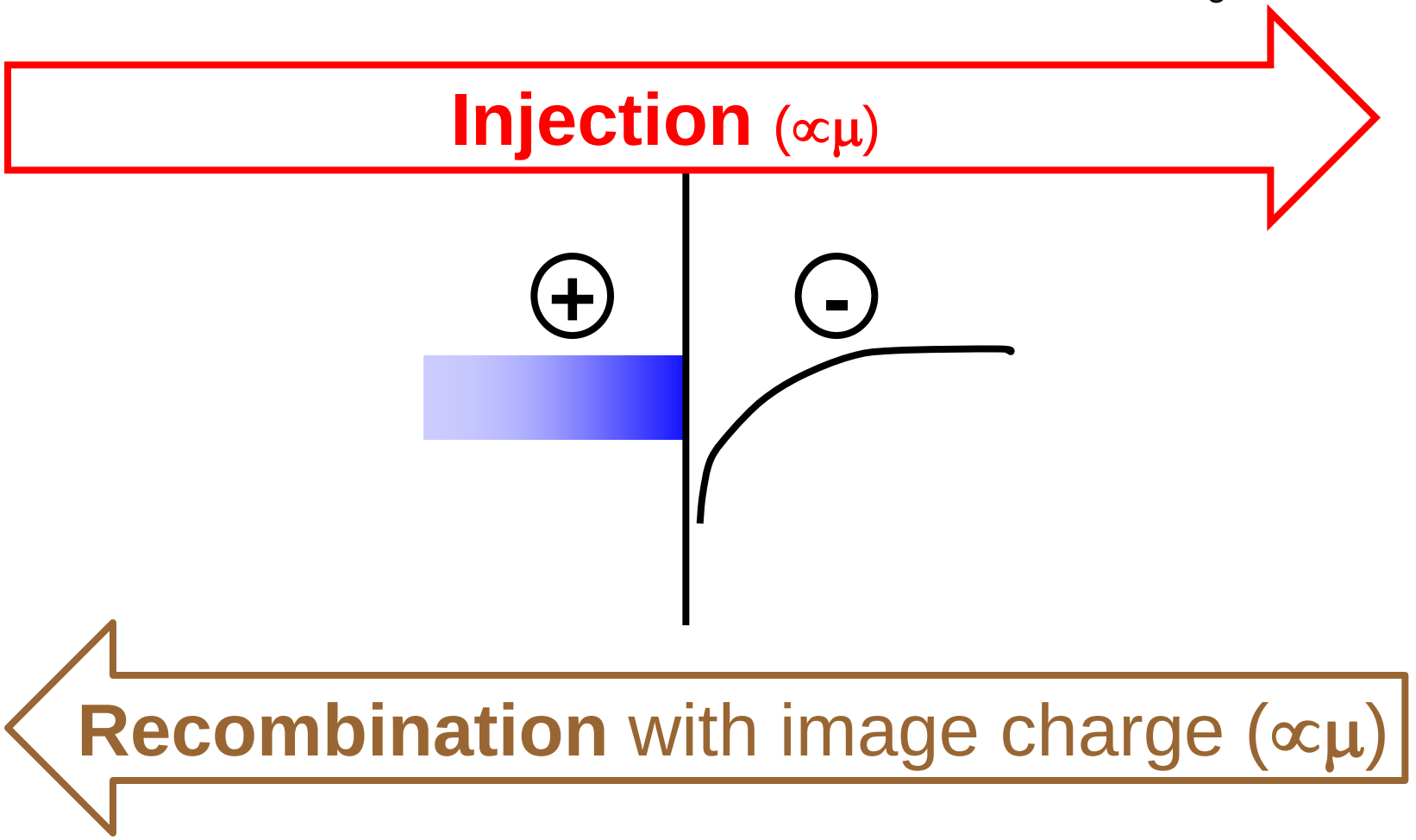


Blossey PhysRevB 9 (1974) 5183

Under thermal equilibrium

Ingredients:

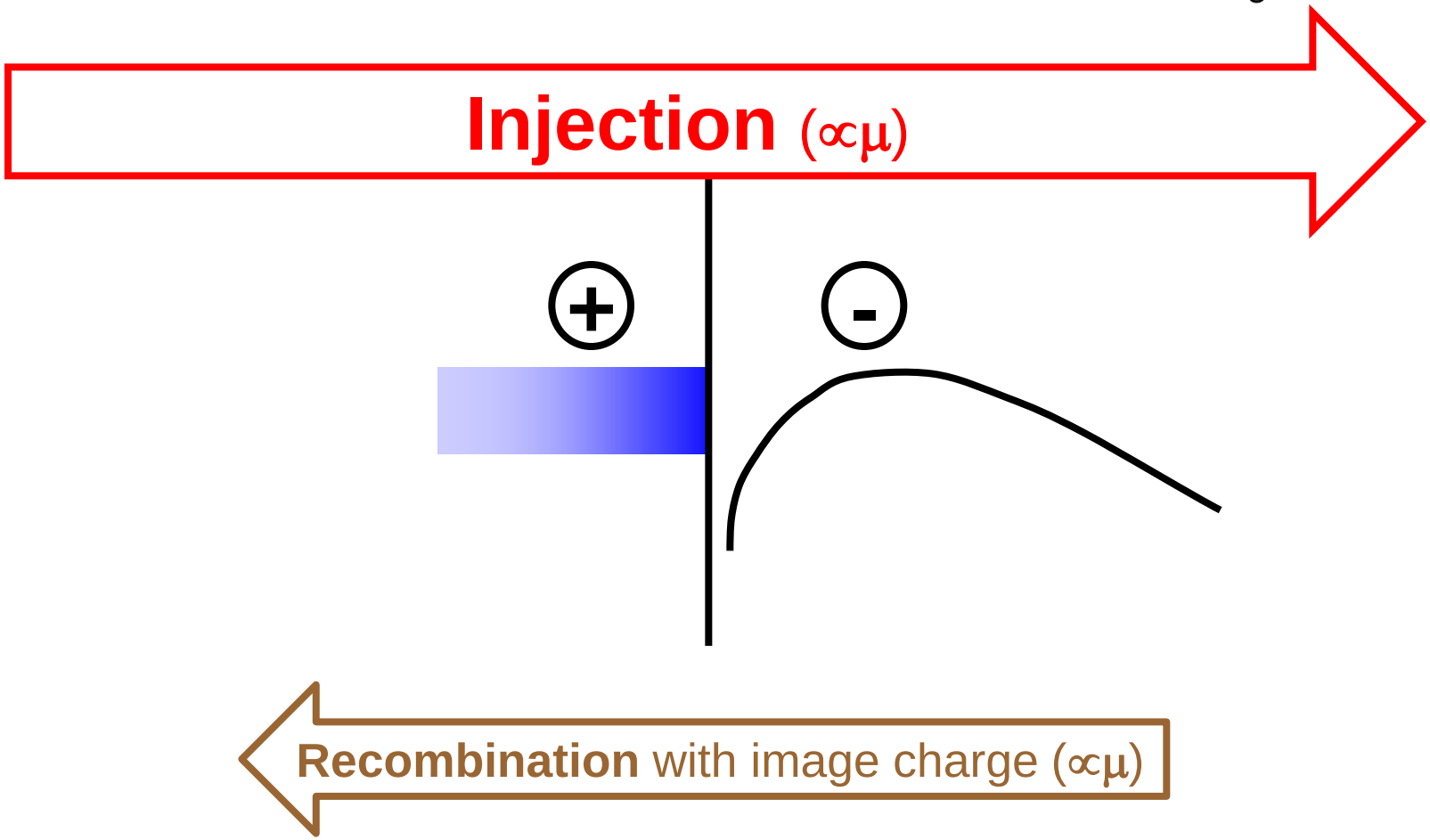
- **hopping transport**
- **Schottky effect**
- Energetic disorder



Under Applied voltage

Ingredients:

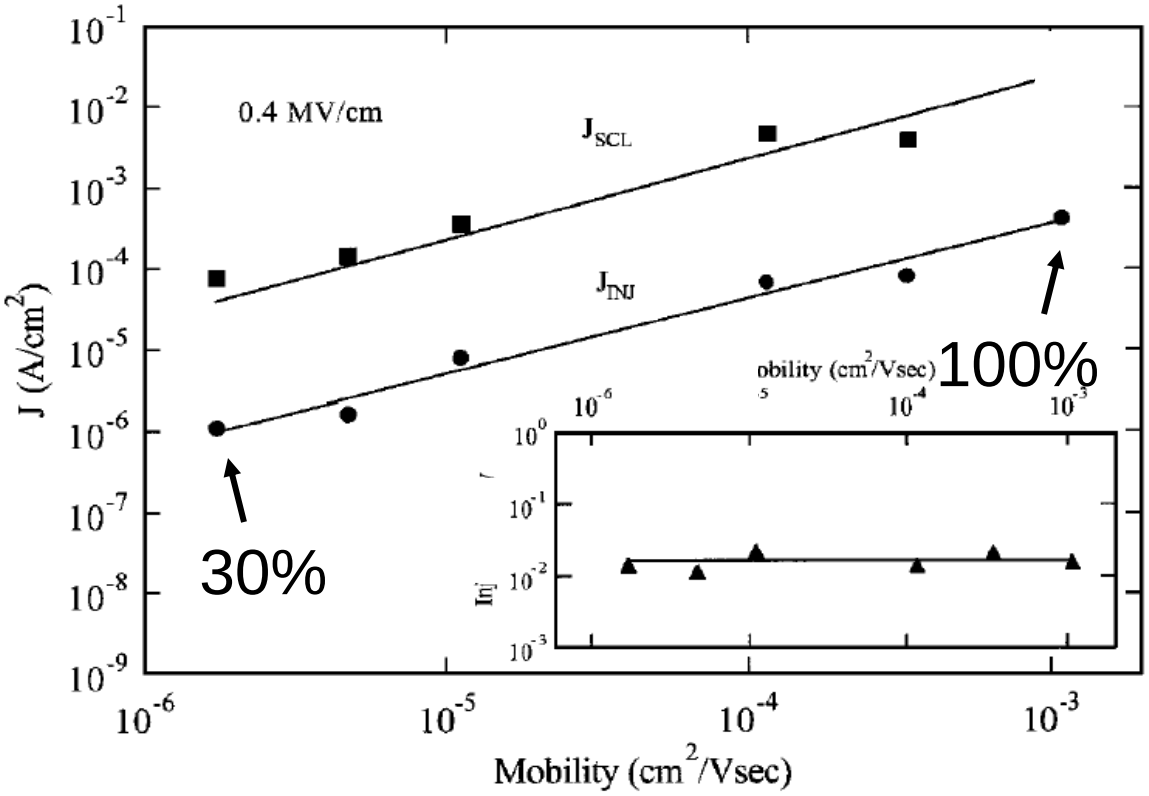
- **hopping transport**
- **Schottky effect**
- Energetic disorder

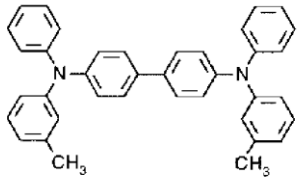


Injection & mobility

Ingredients:

- **hopping transport**
- **Schottky effect**
- Energetic disorder





TPD:PC,
from 30% to 100%

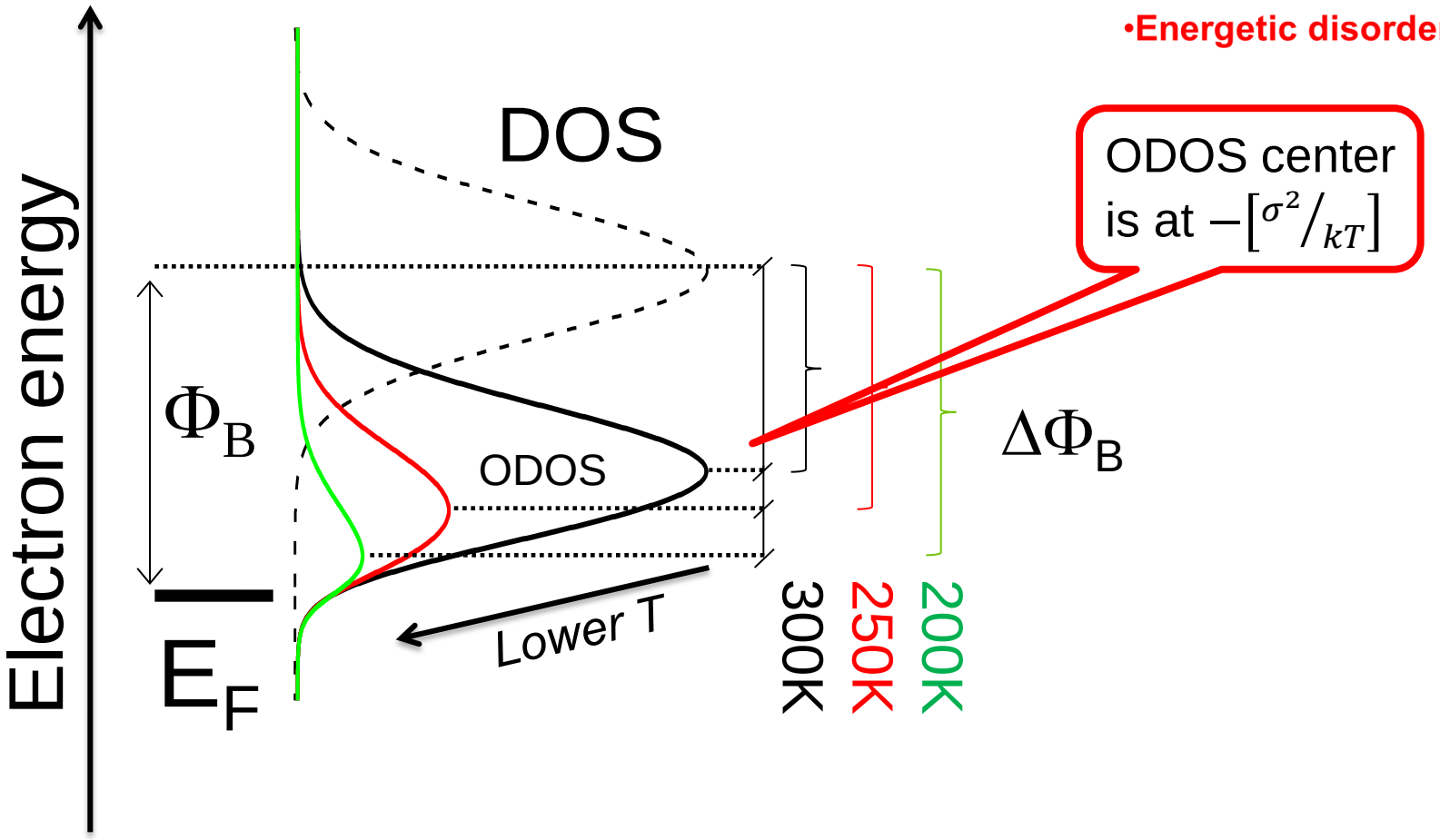
For a given energetics, the larger the mobility,
the higher the injection efficency

Malliaras et al. PhysRevLett 86 (2001) 3867

Disorder & injection

Ingredients:

- **hopping transport**
- **Schottky effect**
- **Energetic disorder**

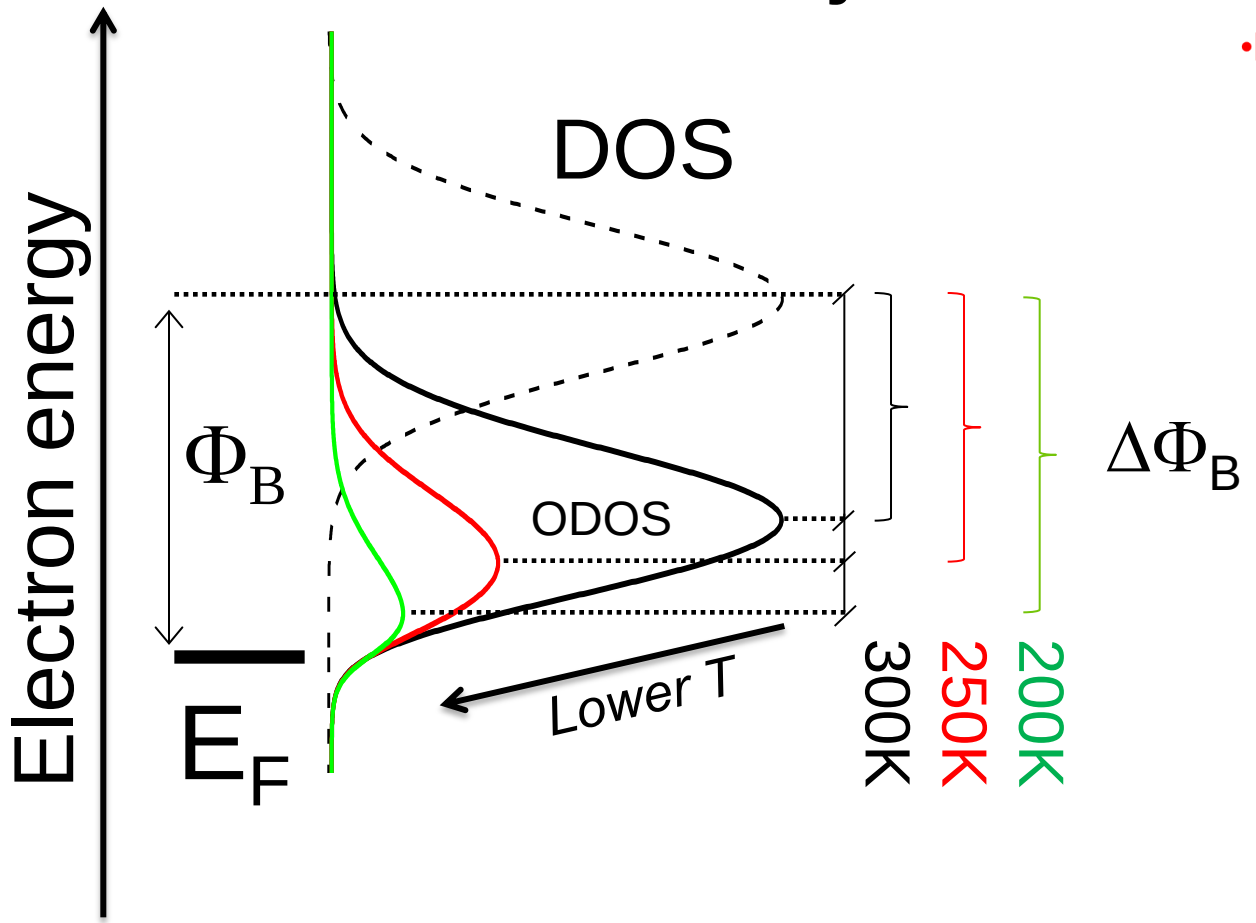


The higher the disorder, the lower Φ_B

Ingredients:

- **hopping transport**
- **Schottky effect**
- **Energetic disorder**

Disorder & injection

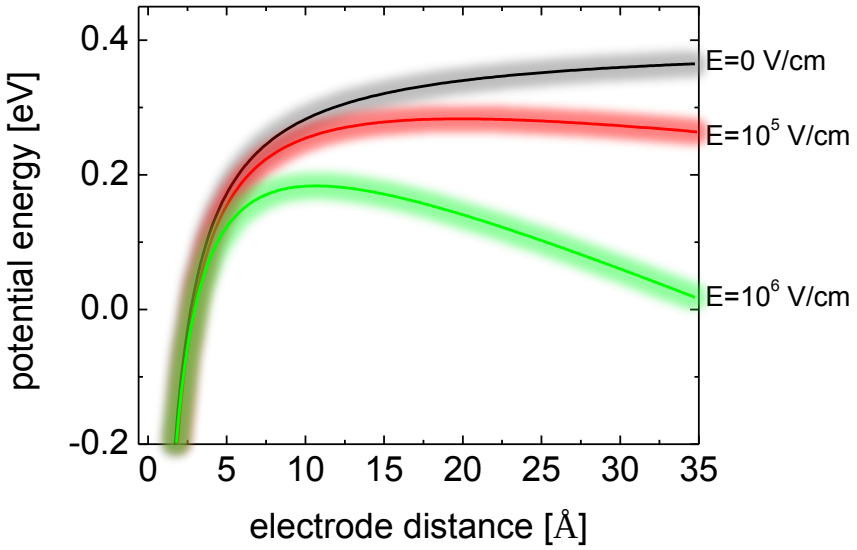


$$J = q\mu N_0 F \exp\left(-\frac{\Phi_B - \frac{1}{2}\frac{\sigma^2}{kT}}{\mathrm{k}T} + \beta_s\sqrt{F}\right)\Psi(F)$$

Disorder & injection

Ingredients:

- **hopping transport**
- **Schottky effect**
- **Energetic disorder**

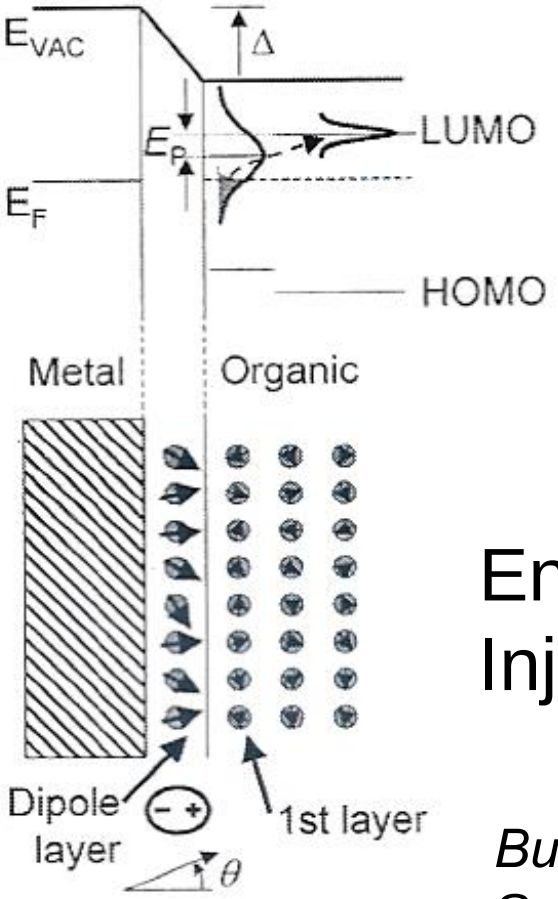


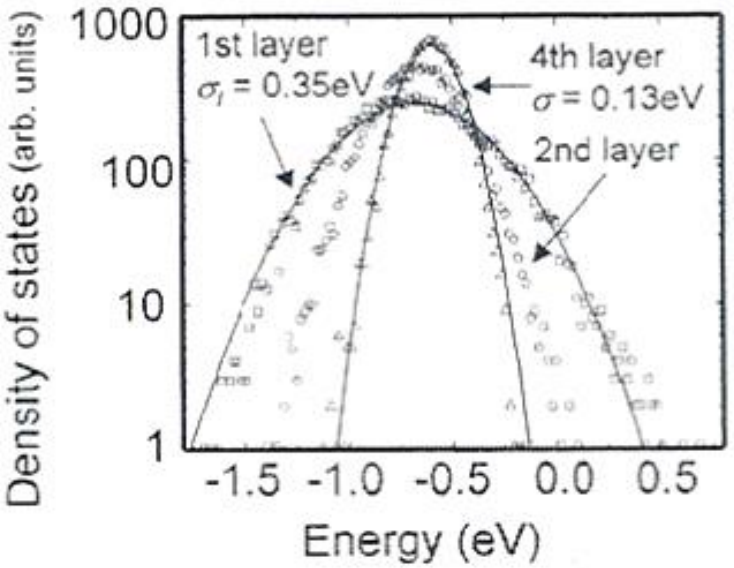
$$J = \mathrm{q}\mu N_0 F \exp\left[-\frac{\Phi_B - \frac{1}{2}\frac{\sigma^2}{kT}}{\mathrm{k}T} + (\beta_s + \beta_\sigma)\sqrt{F}\right]\Psi(F)$$

$$\beta_\sigma = 2^{3/2} / 3[\mathrm{q}a\sigma^2/(\mathrm{k}T)^3]^{0.5}$$

Marohn Phys. Rev. Lett. 2007 66101

Disorder & injection





Enhanced disorder at interface:
Injection **is not** the most diffult step

But! Image charge attenuates interface disorder…..
So what?!

Baldo PhysRevB 64(2001) 85201

S. V. Novikov, *Physica Status Solidi C - Current Topics in Solid State Physics, Vol 5, No 3* **2008**, *5*, 750

Organic Organic interfaces

- Low charge density -> no pillow effect
- Active forces:
  - Van der –waals
  - Electrostatic interfaction
  - Repulsion forces
- Degree of interaction
  - CT@gnd state *(eg. alkyl chains prevent initmate contact)*
  - Orbital mixing @gnd state (short range interaction)
  - Polarizations (long range interaction)

} ***INTERFACE DIPOLE!***

D. Beljonne, J. Cornil, L. Muccioli, C. Zannoni, J. L. Bredas, F. Castet, *Chemistry of Materials* **2011**, *23*, 591

The End