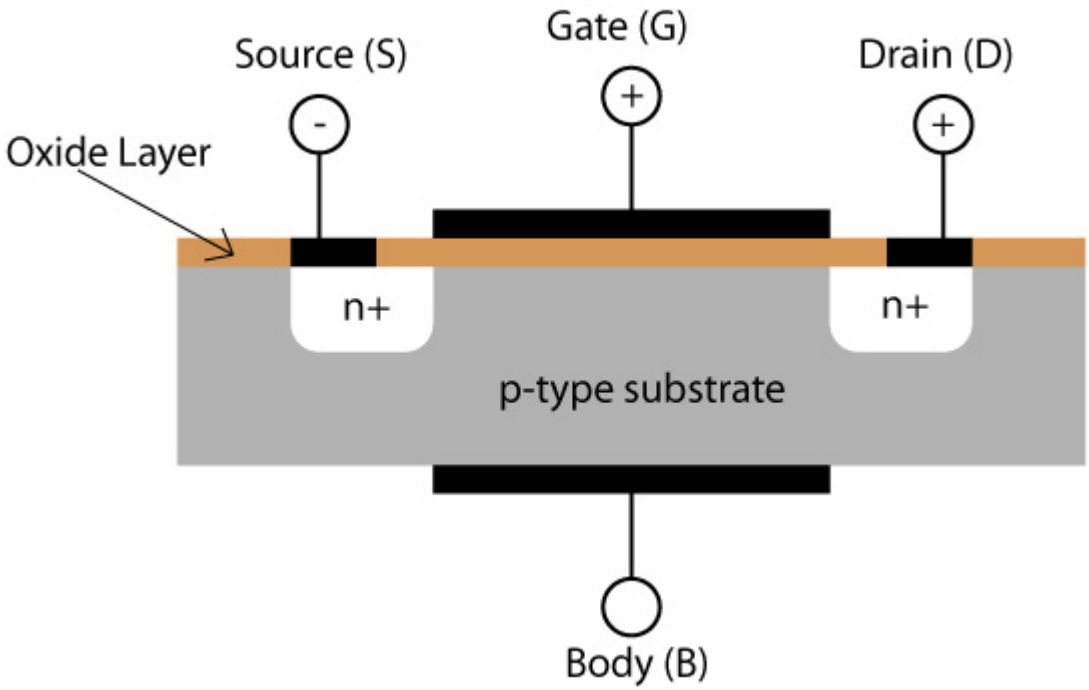
Organic Field Effect Transistors

MOSFET

The MOSFET is a FET in which the conductive channel is obtained by the inversion region of a MOS structure

The gate electrode is the the metal film of the MOS structure. It is insulated with the rest of the device through the gate oxide

In the MOSFET there are two more electrodes, SOURCE e DRAIN, and sometimes also the body eletrode could be employed



Organic Field Effect Transistor

Low mobility semiconductors

Thin Film Transistors **(TFT)**

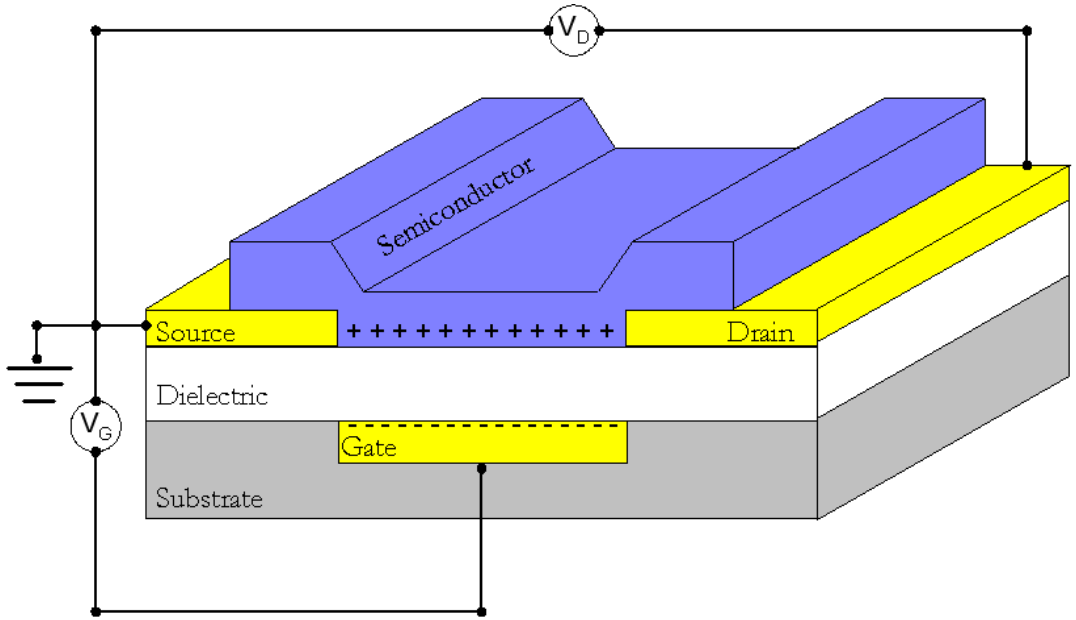
First examples

Substrate highly doped silicon→ Gate

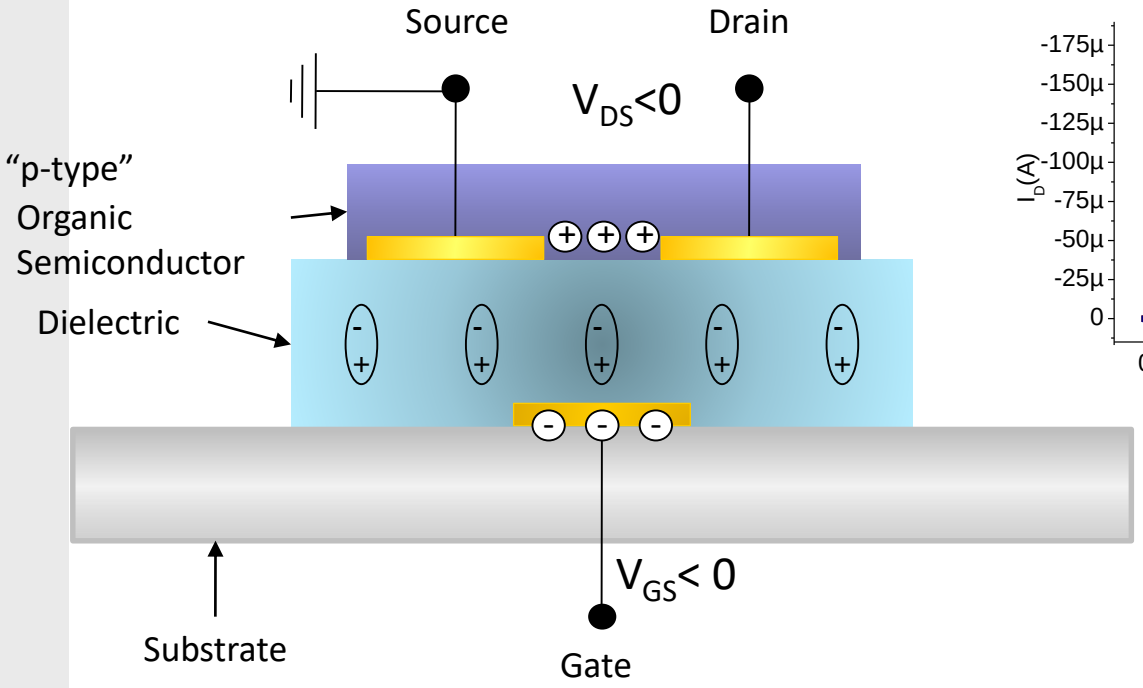
SiO_2 → gate oxide

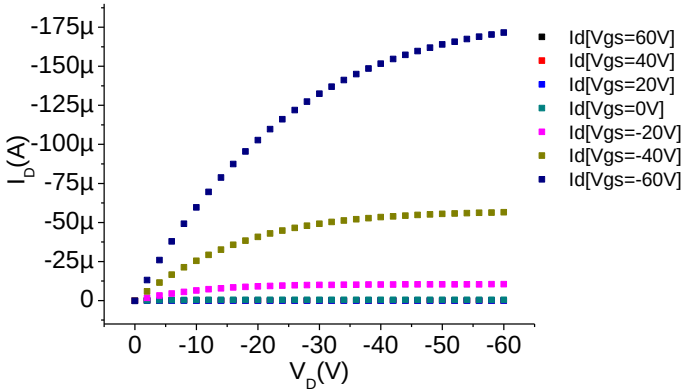
Gold → Source and Drain

Organic semiconductors→ Active layer forming the channel

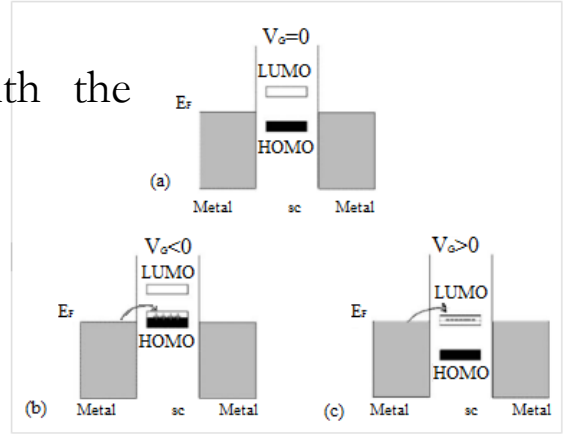


Organic Thin Film Transistor (OTFT)



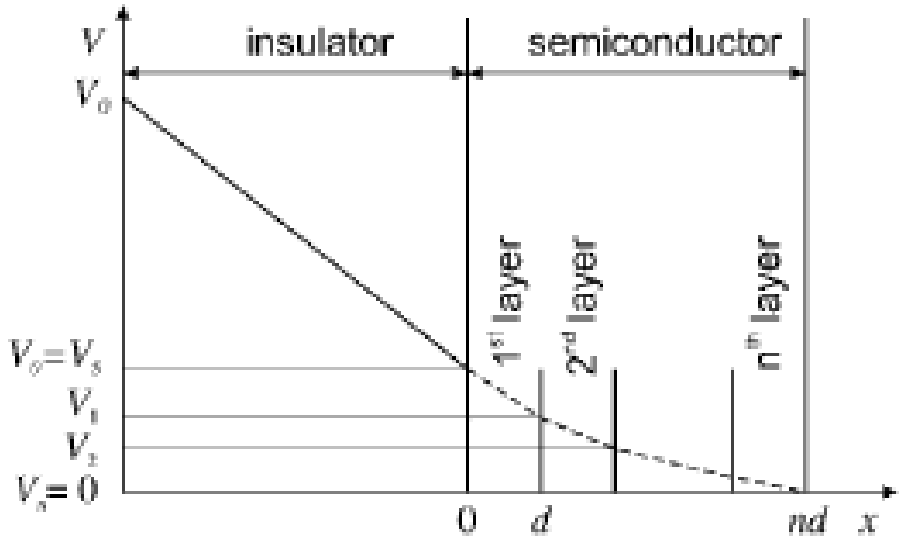


- The channel is already present, but, being the conductivity of the organic semiconductor very small, a low current flows
- P type semiconductor
- VGS < 0: holes accumulation at the interface with the dielectric
- VDS < 0: when channe I formed, current flows

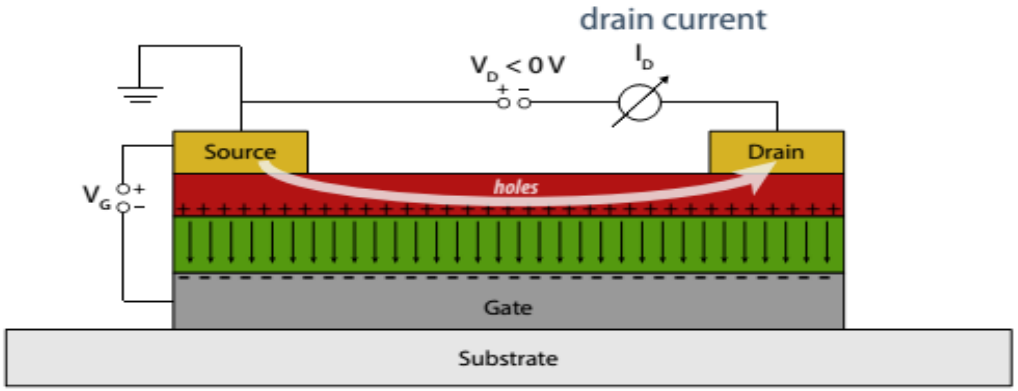


The device works in ACCUMULATION
N.B. MOSFET INVERSION

- The channel is formed at the very interface with the insulating layer, only the first few monolayers are involved in charge conduction!!



Linear Region



Imagine we have a small element of the channel dx. Its resistance dR is given by:

$$dR = \frac{dx}{Z\mu|Q(x)|} \qquad (1)$$

Where Q(x) is the superficial charge along the x axes

Linear Region

In an OFET charge contributions are: the **accumulation layer Qs** and the **charge in the neutral region (bulk) Q_0**
The latter has the following expression

$$Q_0 = \pm q n_0 d_s \qquad (2)$$

Where q is the electron charge, d_s is the organic semiconductor layer thickness and n_0 is the free charges density

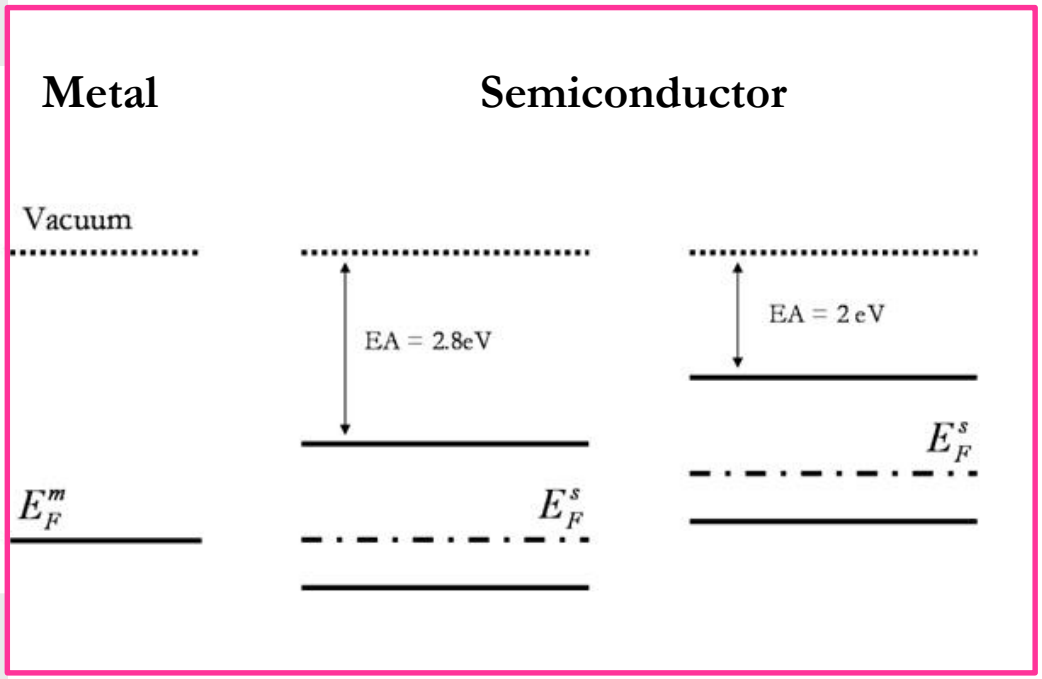
$$Q_s(x) = -C_i\left[V_g - V_{fb} - V_s(x) - V(x)\right] \qquad (3)$$

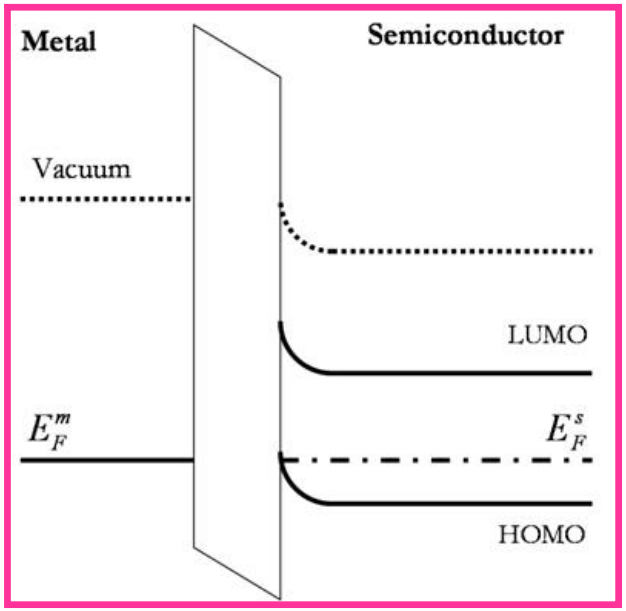
Vs(x) is the ohmic drop in the semiconductor which can be neglected

V(x) voltage in the channel as function of position x

Vfb is the flat band voltage

Different work functions between OS and Gate electrode, charges into the insulating layer





V(x)

Gradual channel approximation $L>>d_s$

When the transversal field (**Ey** perpendicular with respect to current flow) in the channel is much larger than the longitudinal one (**Ex** across the channel, parallel to current)

V(x) only depends on drain voltage and linearly increases from 0 to Vd moving from the source to the drain

$$dR = \frac{dx}{Z\mu|Q(x)|}$$

$$dV = I_d dR = \frac{I_d dx}{Z\mu|Q_s(x)+Q_0|} \qquad (4)$$

Considering the previous expressions and making the integral function across the channel, x=0, V=0 at the source, whereas at the drain x=L, V=V_d we obtain

$$I_d \int_0^L dx = \int_0^{V_d} Z\mu\left[C_i\left(V_g - V_{fb} - V\right) \pm qn_0 d_s\right] dV \qquad (5)$$

Solving, considering the mobility constant

$$I_d = \frac{Z}{L}\mu C_i\left[\left(V_g - V_0\right)V_d - \frac{V_d^2}{2}\right] \qquad (6)$$

where:

$$V_0 = \pm\frac{qn_0 d_s}{C_i} + V_{FB} \qquad (7)$$

A not negligible current could also flow when Vgs=0 V

When a gate **votage larger that the threshold** one is applied, if the voltage applied between source and **drain (V_{DS}) is small** ($V_G < V_{DS} < (V_G - V_T)$), the induced **electrical field is uniformly distributed** in the whole channel where we have an extended accumulation layer.

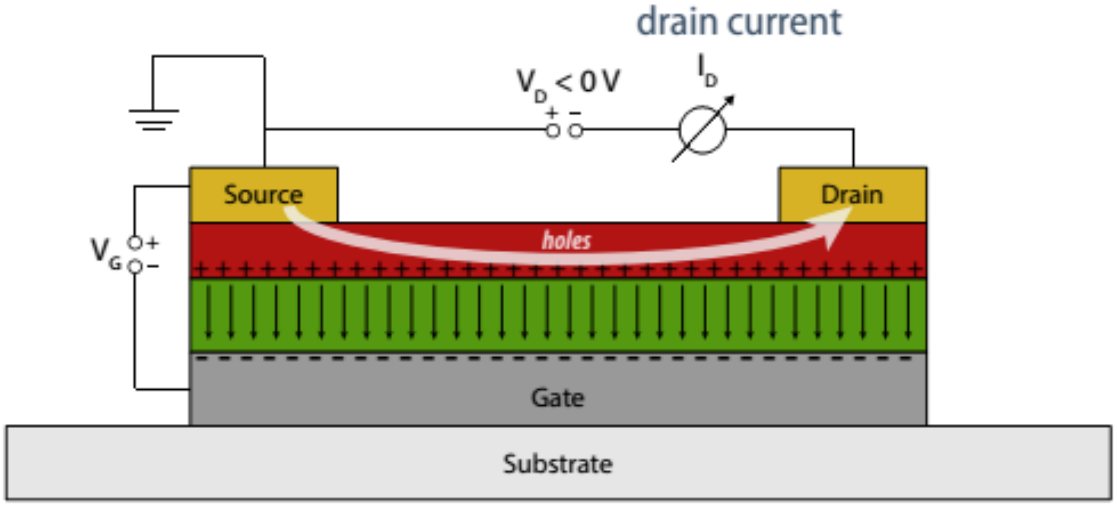
$$I_d = \frac{Z}{L}\mu C_i\left[\left(V_g - V_t\right)V_d - \frac{V_d^2}{2}\right]$$

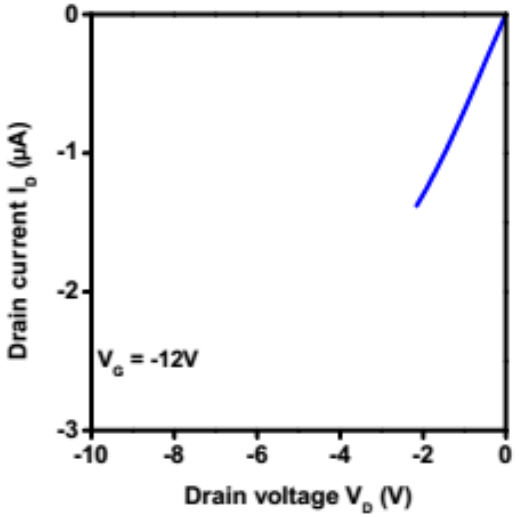
Z channel width, L channel length, C_i insulator capacitance μ is carrier mobility in the channel

For small V_{DS}, ($V_{DS} << V_{GS} - V_T$) charges are uniformly distributed into the channel

The channel behaves as a resistor

Linear Region



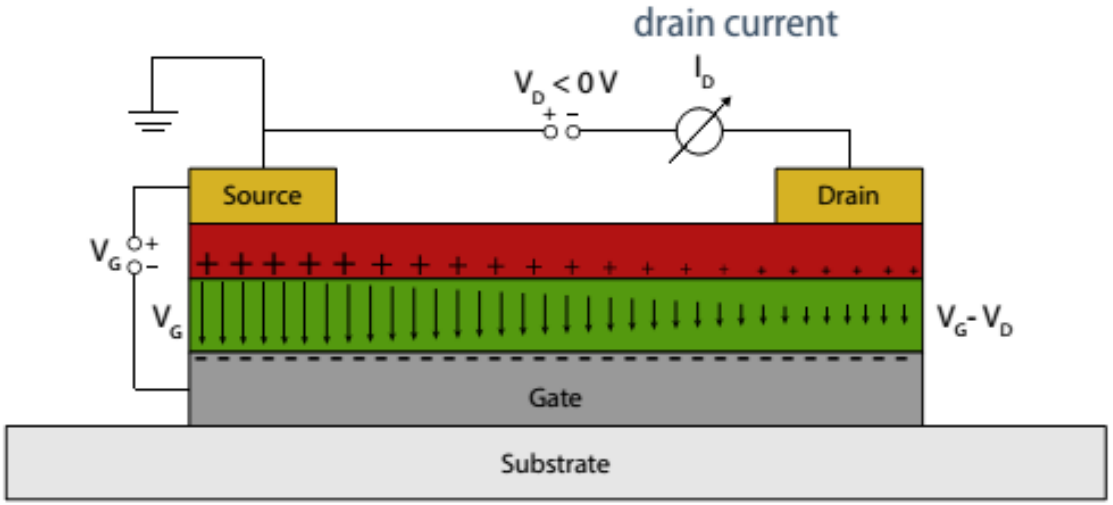


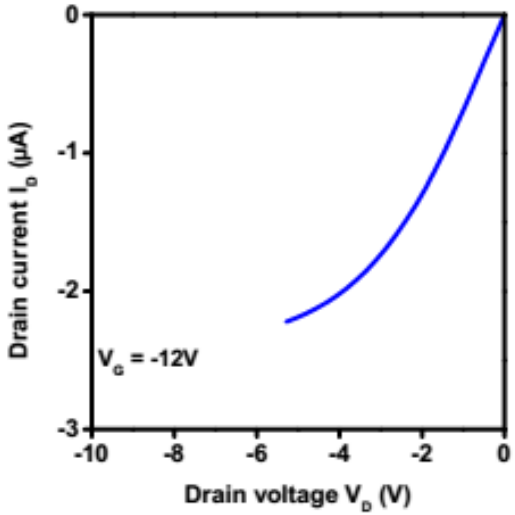
$$I_d = \frac{Z}{L}\mu C_i\left[\left(V_g - V_t\right)V_d - \frac{V_d^2}{2}\right]$$

$$I_d = \frac{Z}{L}\mu C_i \cdot \left(V_g - V_t\right)V_d$$

When V_{DS} increases ($V_{DS} \leq V_{GS} - V_T$) charge distribution is no longer uniform

Current increases as a quadratic function

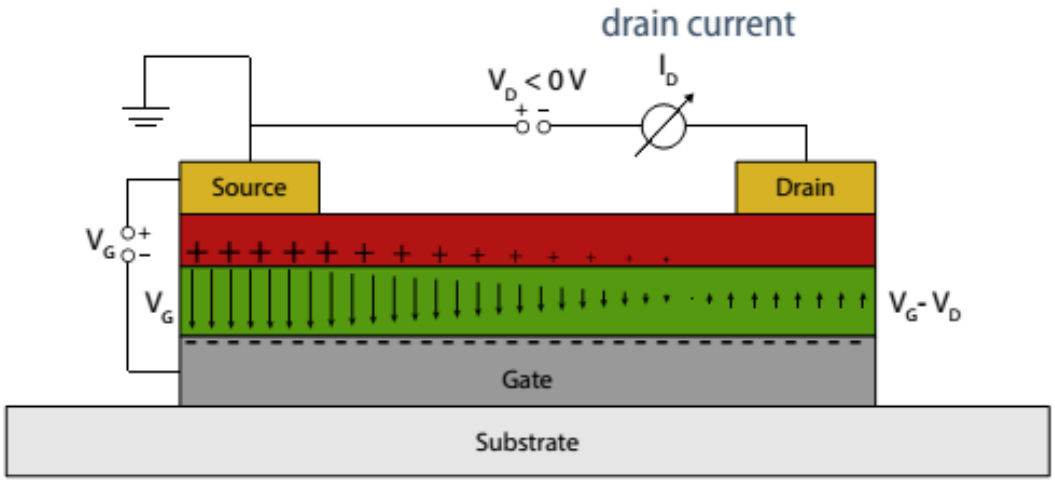




$$I_d = \frac{Z}{L}\mu C_i\left[\left(V_g - V_t\right)V_d - \frac{V_d^2}{2}\right]$$

Saturation Region

If V_{DS} keeps increasing the **channel becomes asymmetric** and thinner in the proximity of the drain



$V_{GD}=V_{GS}-V_{DS}$, when V_{DS} increases, V_{GD} decreases

The vertical potential drops close to the drain ($V_{DS}>0$)

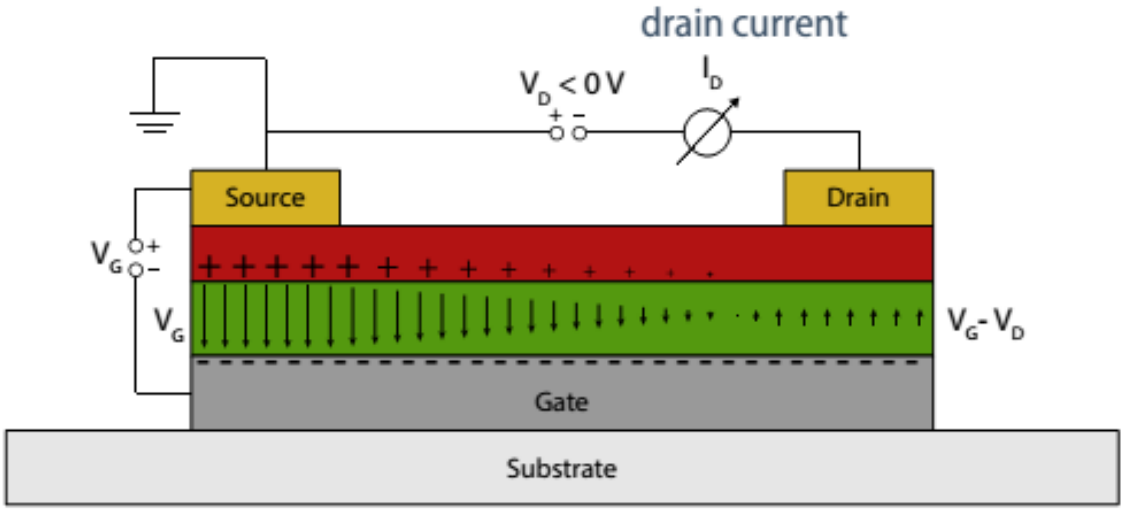
Carrier concentration decreases

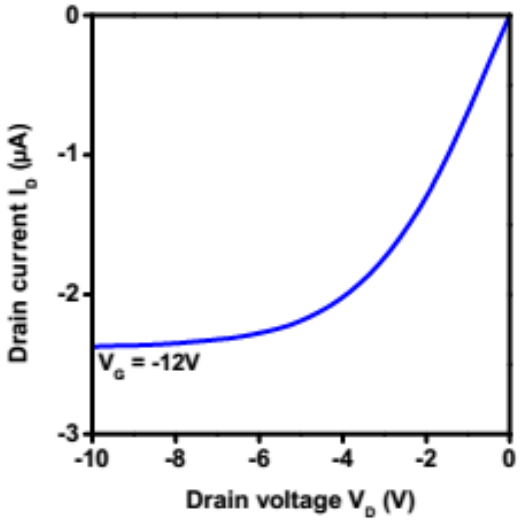
when $V_{GD}=V_T$ pinch-off (V_T limit value below it the channel is fully depleted!)

Saturation Region

Let's call V_{Dsat} the V_{DS} value leading to $V_{GD}=V_T$

$V_{GD}=V_T \rightarrow V_{GS}-V_{DS}=V_T \rightarrow V_{Dsat}=V_{GS}-V_T$

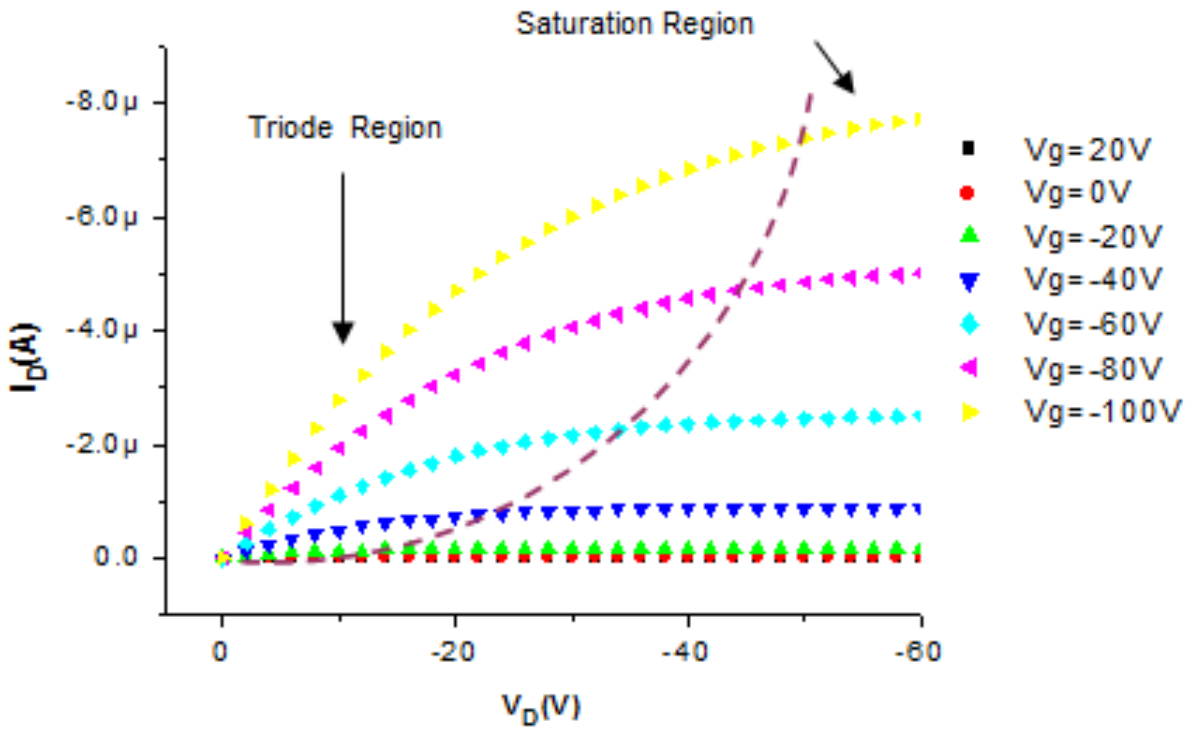




$$I_d = \frac{Z}{L}\mu C_i\left[(V_g - V_t)V_d - \frac{V_d^2}{2}\right]$$

$$Vdsat = (V_g - V_t)$$

$$I_{dsat} = \frac{Z}{2L}\mu C_i (V_g - V_t)^2$$


Saturation Region
Triode Region
-8.0 μ
-6.0 μ
-4.0 μ
-2.0 μ
0.0
I_D(A)
0
-20
-40
-60
V_D(V)
Vg=20V
Vg=0V
Vg=-20V
Vg=-40V
Vg=-60V
Vg=-80V
Vg=-100V

How can we obtain such parameters from the electrical characteristics?

- Output Characteristics [IdVd]
- Transfer Characteristics

  in linear and saturation regions

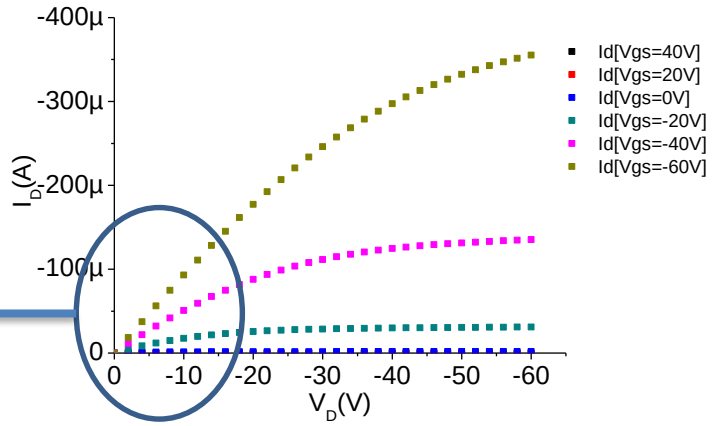
Conductance and transconductance in the linear region

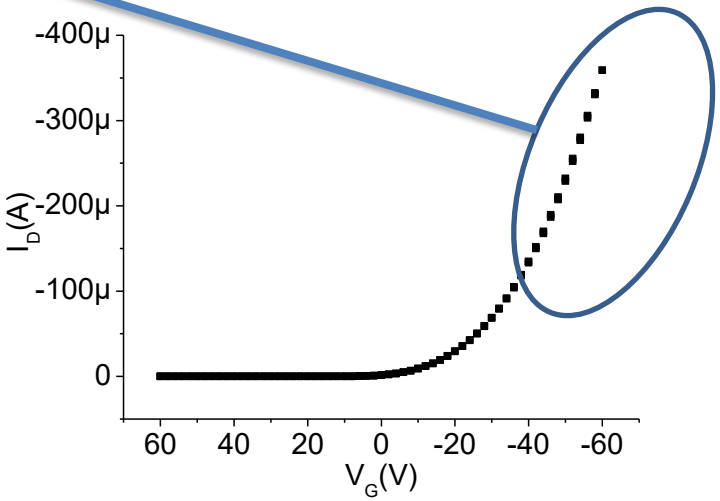
$$I_d = \frac{Z}{L}\mu C_i\left[\left(V_g - V_t\right)V_d\right]$$

$$g_d = \left|\frac{\partial I_D}{\partial V_D}\right|_{V_G=\cos t} = \frac{Z}{L}\mu C_i (V_G - V_T) \qquad (15)$$

$$g_m = \left|\frac{\partial I_D}{\partial V_G}\right|_{V_D=\cos t} = \frac{Z}{L}\mu C_i \, V_D \qquad (16)$$

V_D small enough to be in linear region!





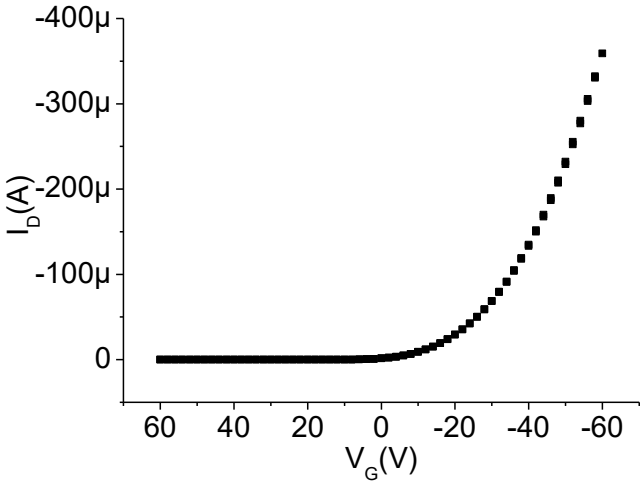
Transconductance in saturation region

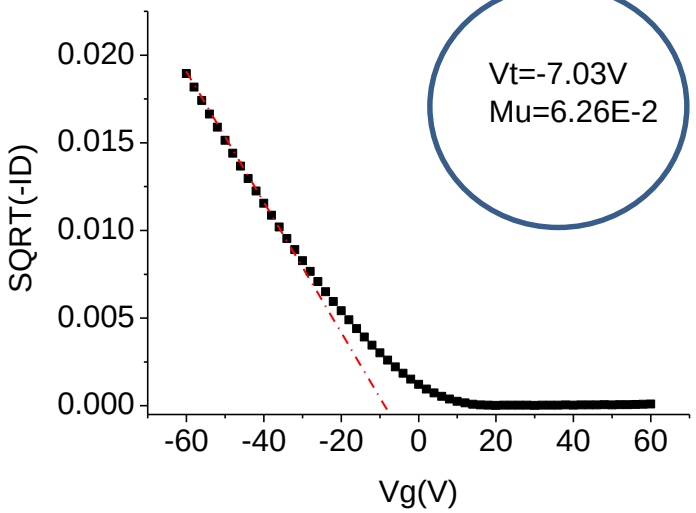
$$I_{dsat} = \frac{Z}{2L}\mu C_i \left(V_g - V_t\right)^2$$

$$g_m = \left|\frac{\partial I_D}{\partial V_G}\right|_{V_D=\cos t} = \frac{Z}{L}\mu C_i \ (V_G - V_T) \qquad (17)$$

How do I measure them?

V_D high enough to be in saturation region!





Tipycal OFETs electricalparametrs

Mobility

Average values $[10^{-1} - 10^{-2}\ cm^2/Vs]$

Off current and Ion/Ioff

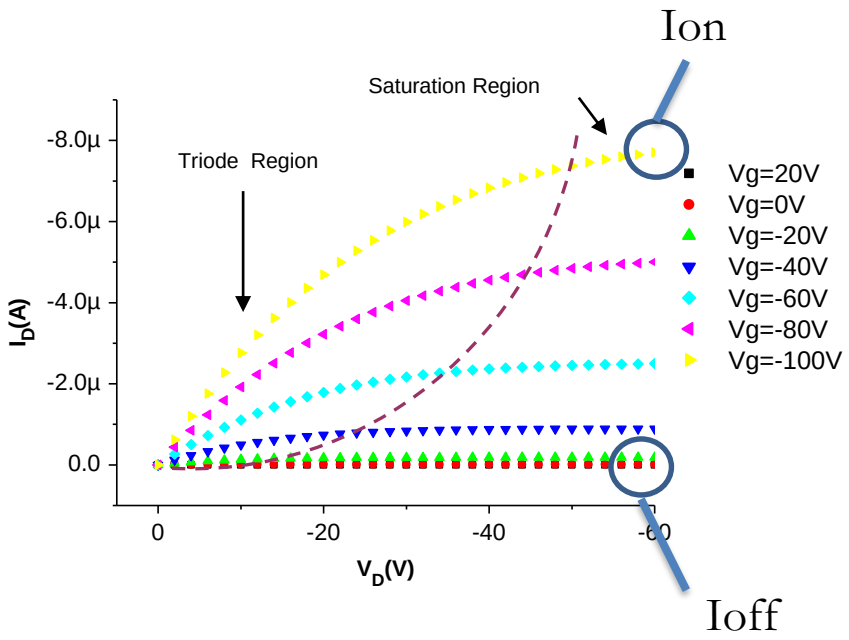
Off current is the current obtained when the devices is off

typical Ion/Ioff values 10^5 - 10^6

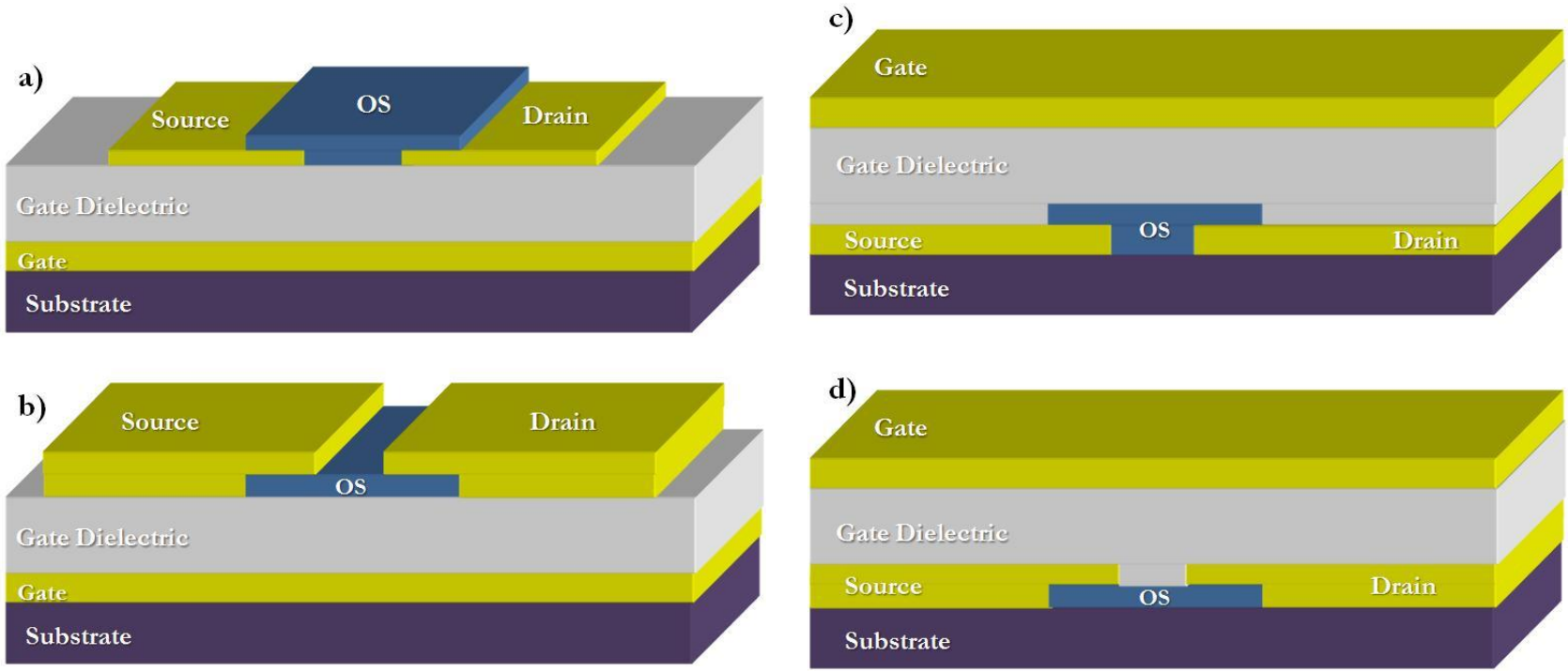
Threshold voltage

Typical values [+10V ; -10V]

N.B. ideally Vt=0V

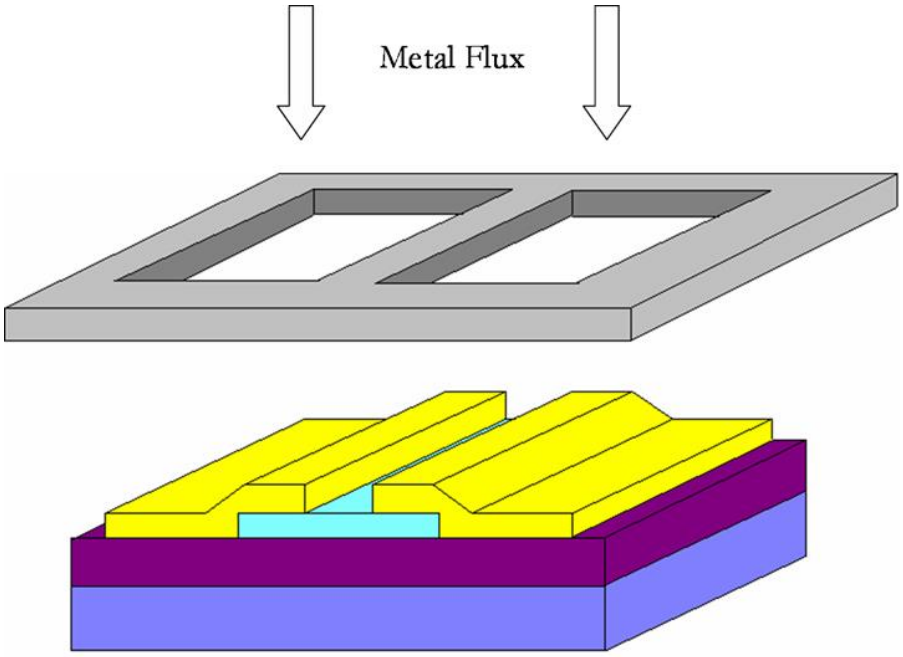


OFETs structures



a) Bottom gate, Bottom Contact
b) Bottom gate, Top Contact
c) Top Gate, Bottom Contact
d) Top Gate, Top Contact

Patterning : Shadow Mask

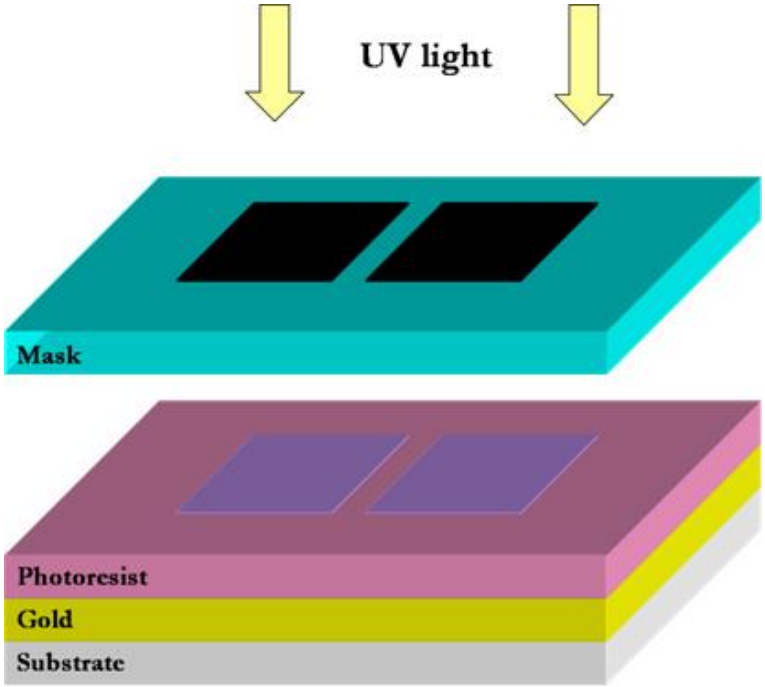


Gate electrode

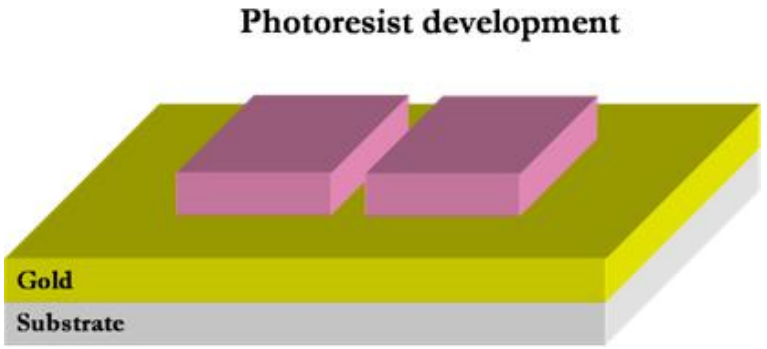
Source e drain electrodes

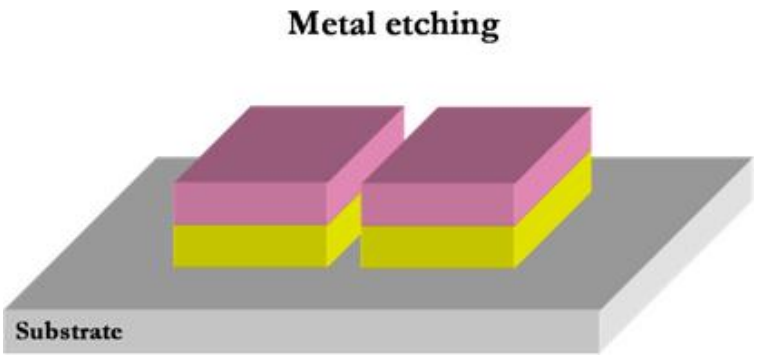
- Low resolution(100 μm)
- not suitable for large area
- Top Contact → possible defects in the channel

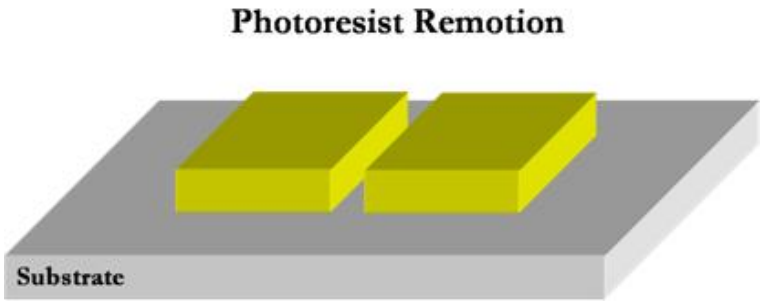
Patterning : Photolitography



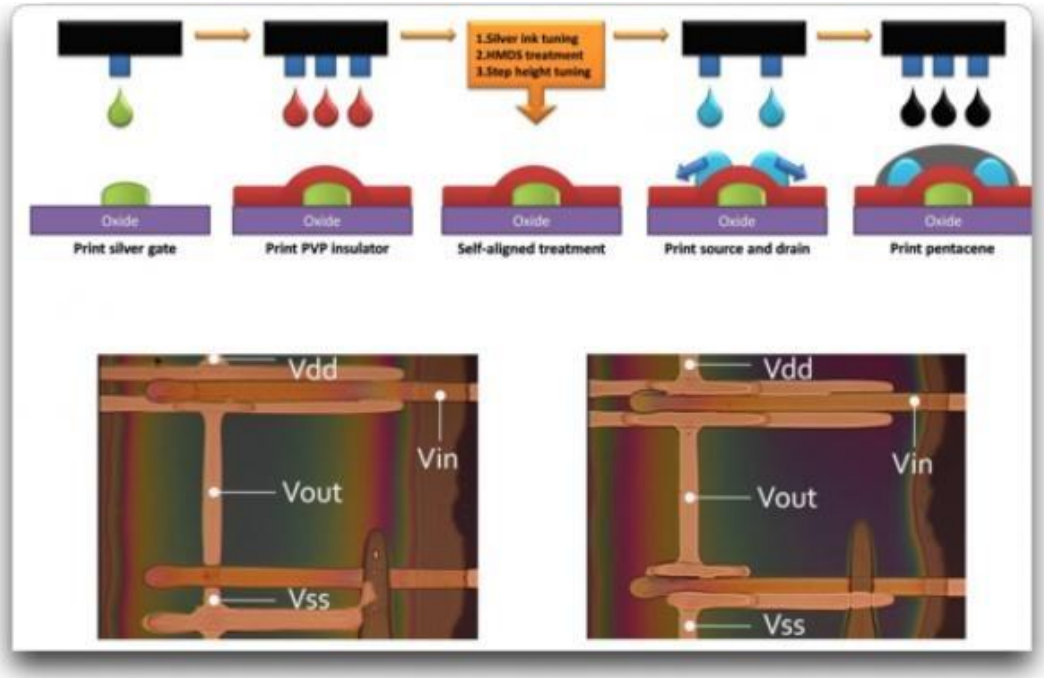
- High resolution
- Only Bottom Contact
- No low cost



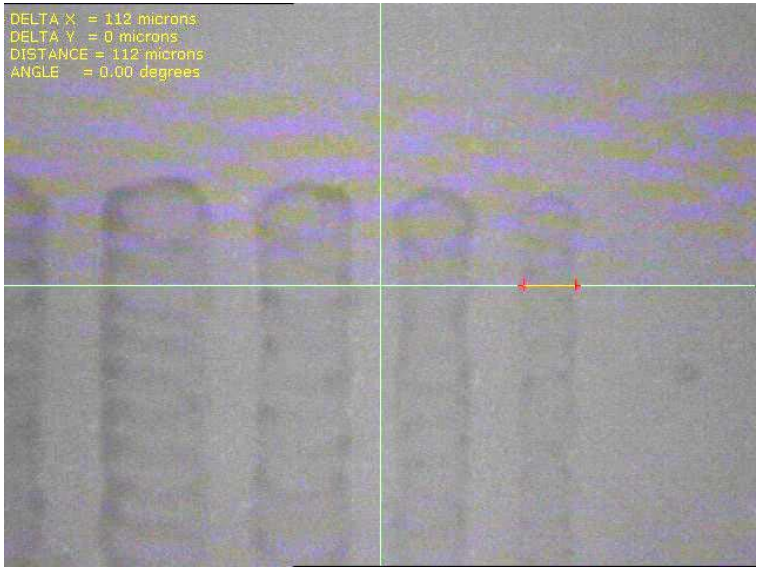




Patterning : inkjet printing



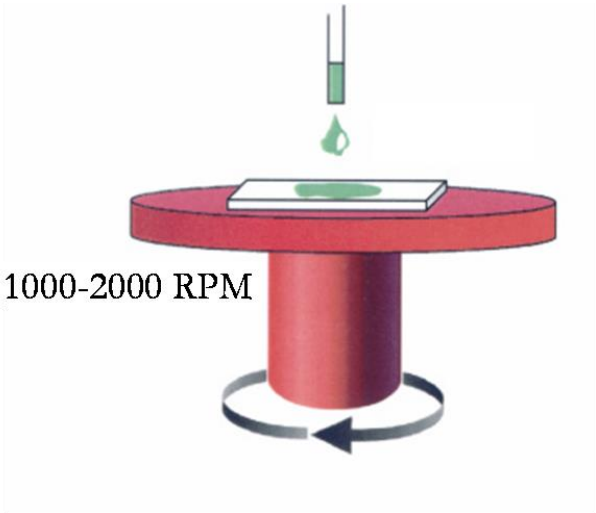
- Low risoluzione (constantly increasing)
- Bottom Contact
- Suitable for larga area
- Low cost



Organic Semiconductor and insulator

Solution processable

Spin coating o drop casting

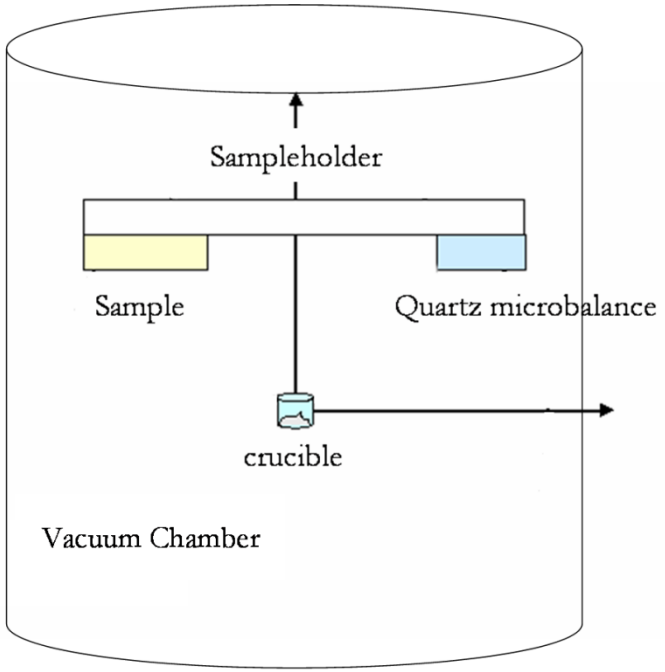


Inkjet printing

Spin coating o drop casting

Small molecule not soluble

Vapor phae



non idealities

- **Metal/Semiconductor interface**

  charge injection → Series resistance

- **insulator/semiconductor interface**

  charge trapping

  Vt shift

  hysteresis

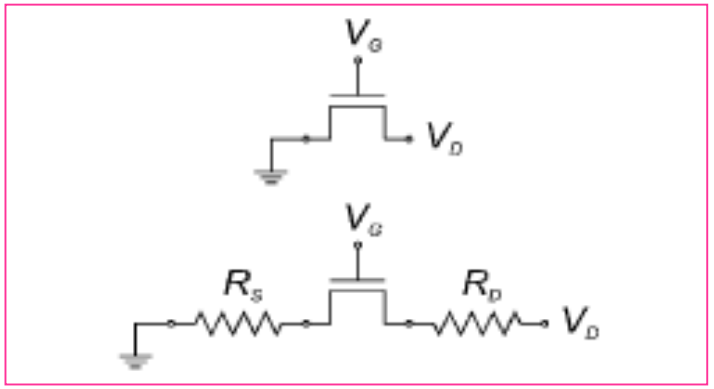
  gate voltage dependance of mobility

- **Metal/Semiconductor interface**

  charge injection → Series Resistance

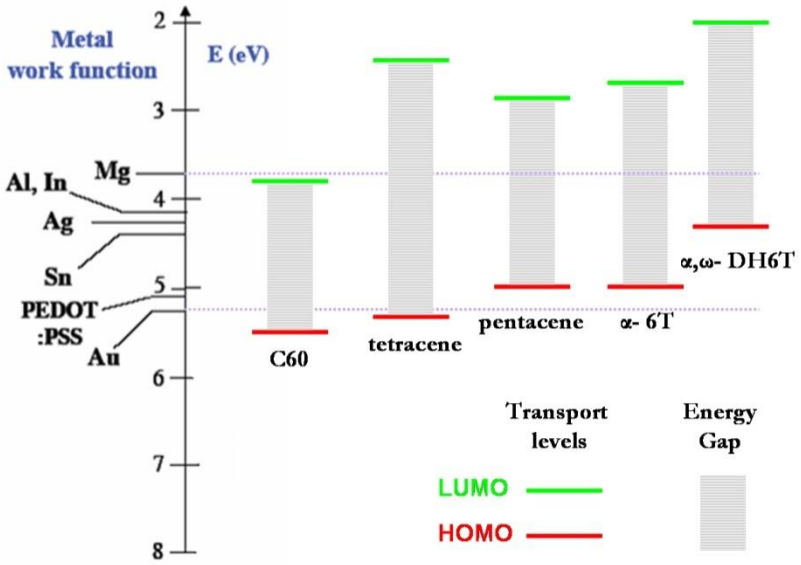
- **Metal/Semiconductor interface**

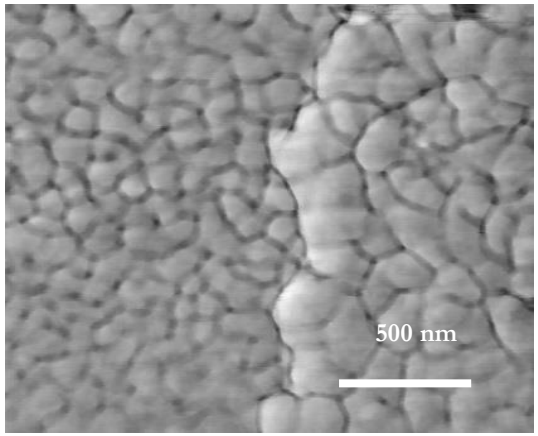
charge injection → *Series Resistance*



Causes:

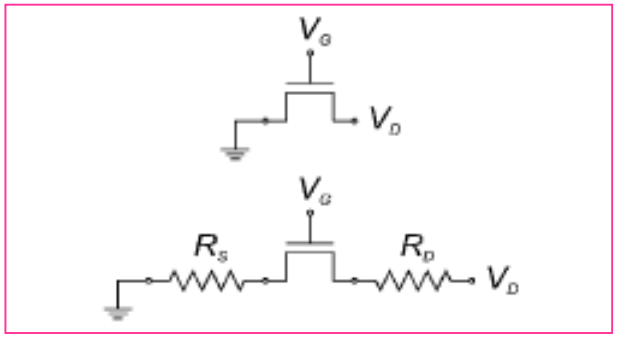
- *structural defects due to processing*
- *energetic levels alignment*





Series resistance

All resistive effects that do not scale down with channel length are call series resistance effects



$$I_D = Z / L \mu C_{ins} (V_G - V_{th}) V_D$$

$$I_D = Z / L \mu C_{ins} (V_G - V_{th})(V_D - R_S I_D) \qquad (18)$$

$$g_D = \left(\frac{1}{\mu (Z / L) C_{ins} (V_{GS} - V_T)} + R_S \right)^{-1} \qquad (19)$$

$$R_S = R_{Total} - \frac{L}{Z \mu C_{ins} \left| (V_{GS} - V_T) \right|} \qquad (20)$$

Using such model it is possible to estimate R_s

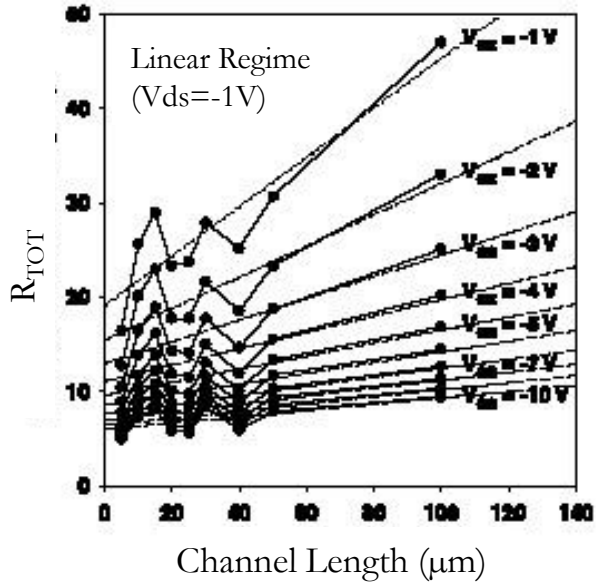
R_{tot} from the output characteristics, the second term is known

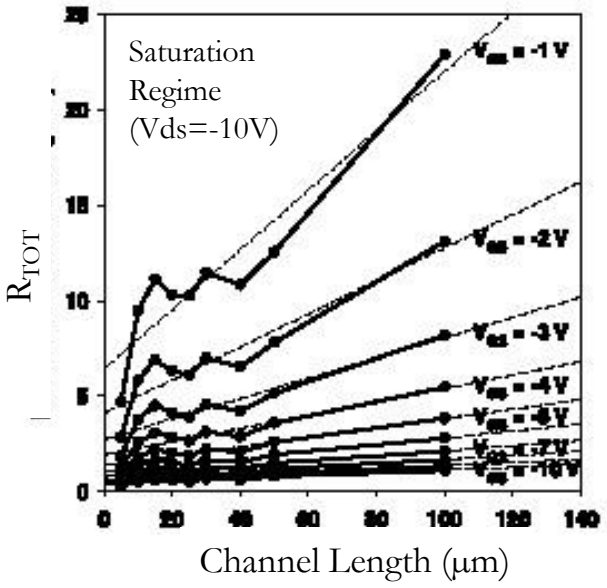
Series resistance– Transfer line method

$R_T = R_S + R_{Ch}$ (24)

R_c can be estimated by plotting the inverse conductance as function of th channel length

Rs → L=0



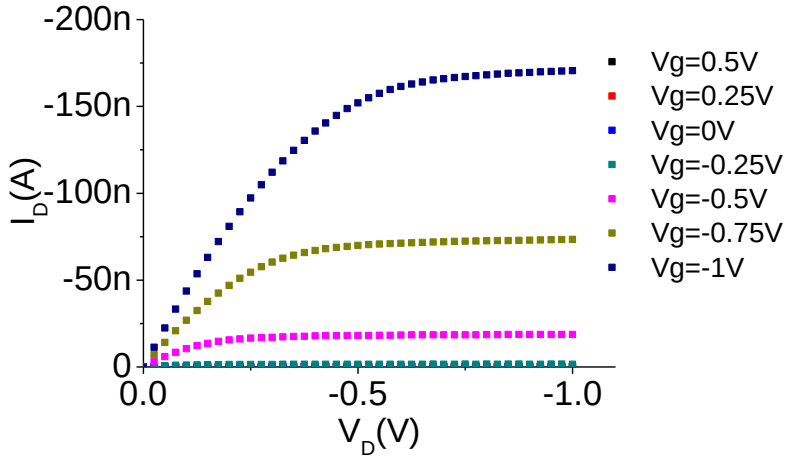


Let's giv it a try

We have three different OTFTs with the following channel lengths, and the following output curves

L= 20 um
L=50 um
L=100 um

Rtot?



Series resistance

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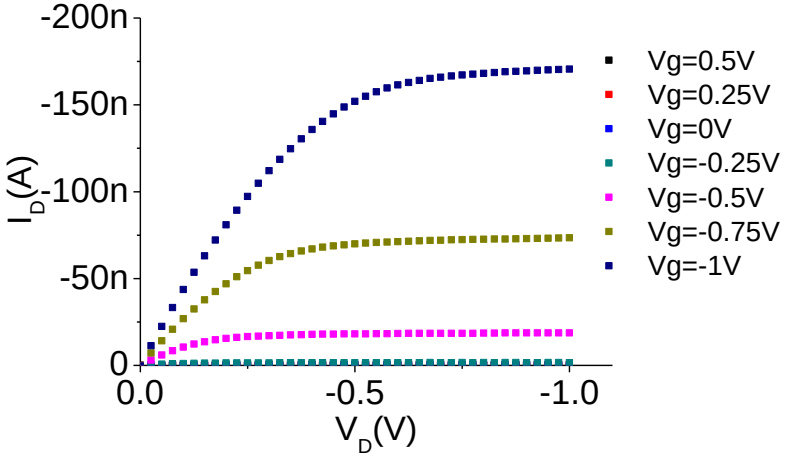
L=100 um

Rtot?



	Vg= -3V	**Vg= -2V**	**Vg= -1V**	**Vg= 0V**
20 um	500 kΩ	700 kΩ	1 MΩ	1,5 MΩ
50 um	1 MΩ	1,3 MΩ	2 MΩ	2,8 MΩ
100 um	1,5 MΩ	1,8 MΩ	2,7 MΩ	4,2 MΩ

Fattori di non idealità

- **Interfaccia Metallo/Semiconduttore**

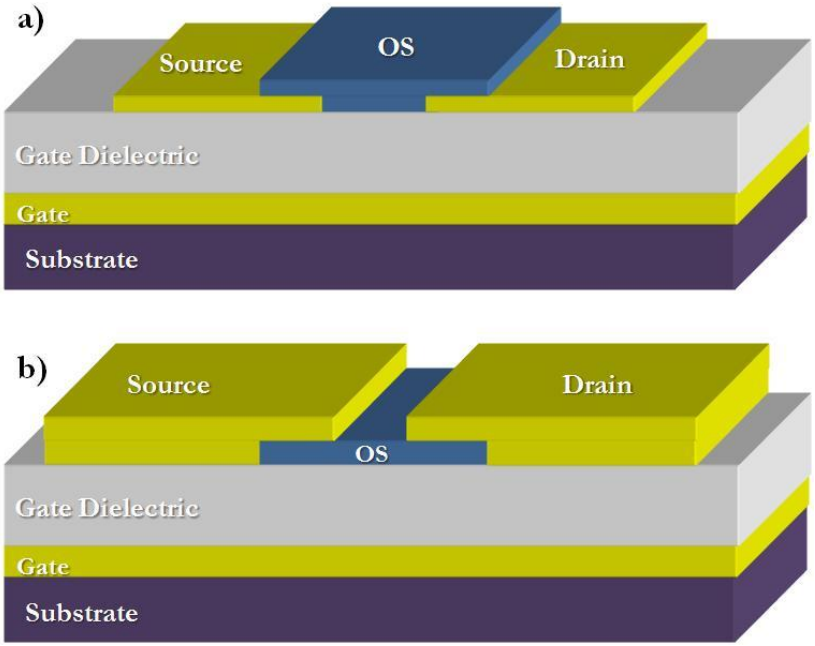
  Iniezione di carica → *Resistenza serie*

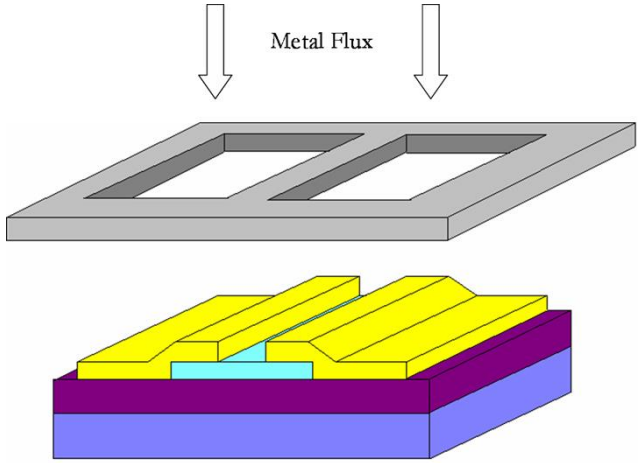
  Cause:

  Difetti strutturali dovuti al processing

  Allineamento dei livelli energetici

Rs – Difetti strutturali





Top Contact

I contatti di Source e Drain vengono realizzati su un film di semiconduttore organico precedentemente depositato → gli atomi del metallo possono diffondere dentro il film organico

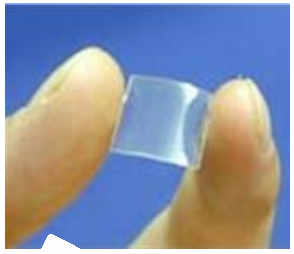
Bottom Contact

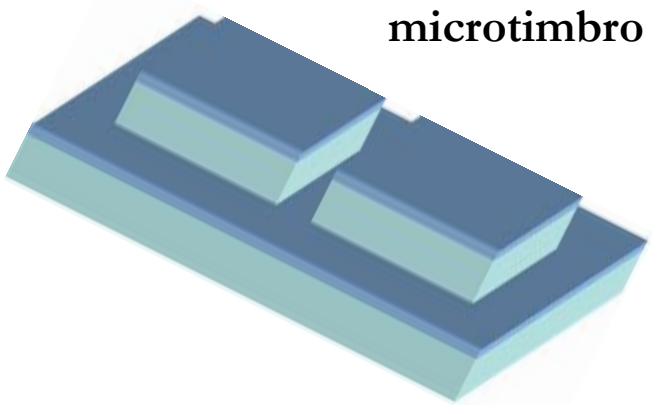
Il semiconduttore organico viene depositato su un substrato già patternato → disomogeneità nella crescita all'interfaccia metallo/semiconduttore

Introduzione

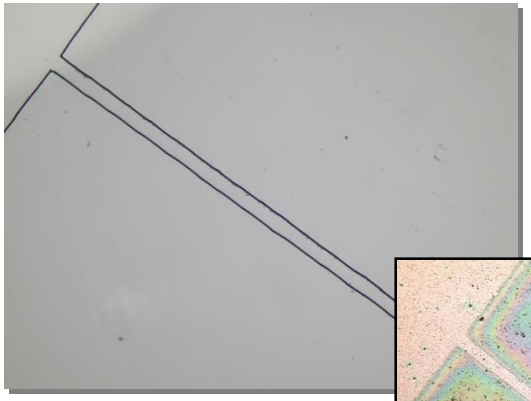
Soft Lithography:

- I microtimbri dovranno riprodurre esattamente il disegno che si intende trasferire su una data superficie
- Inchiostro differente a seconda delle applicazioni

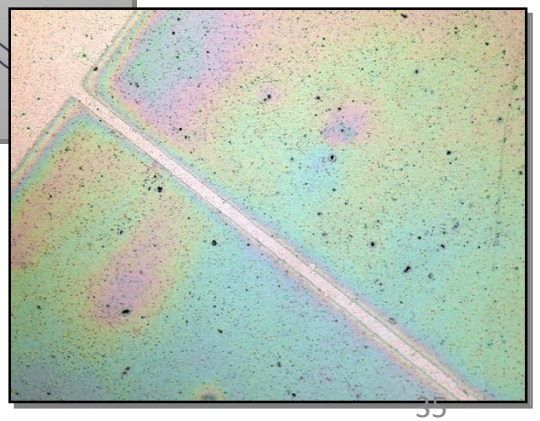




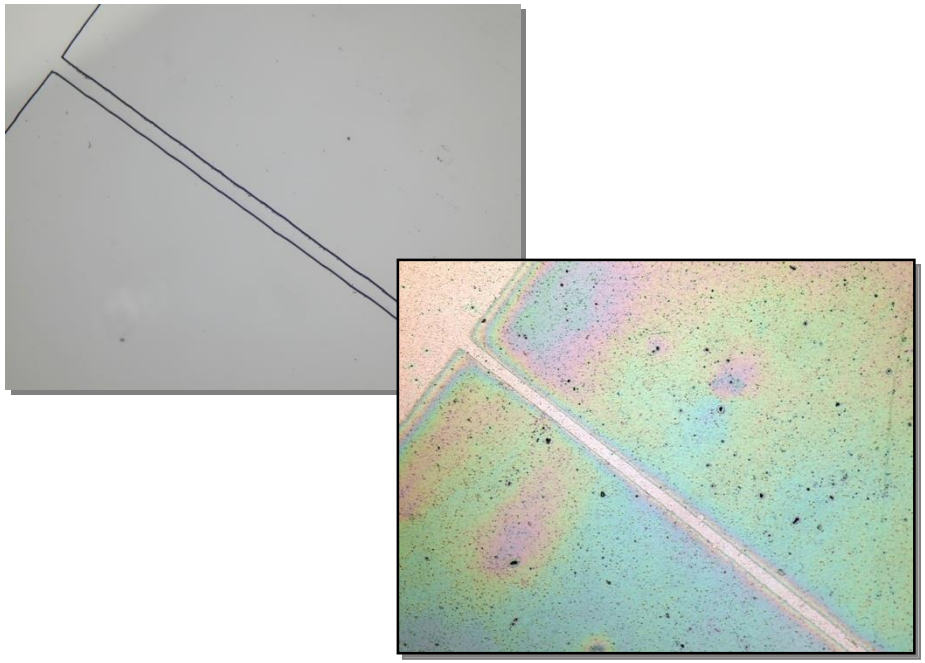
microtimbro

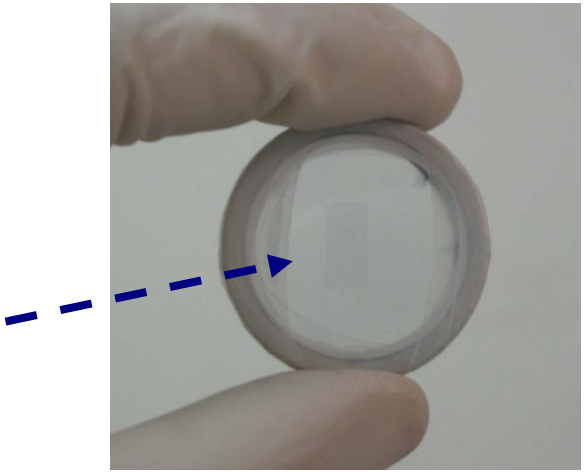


Disegno stampato



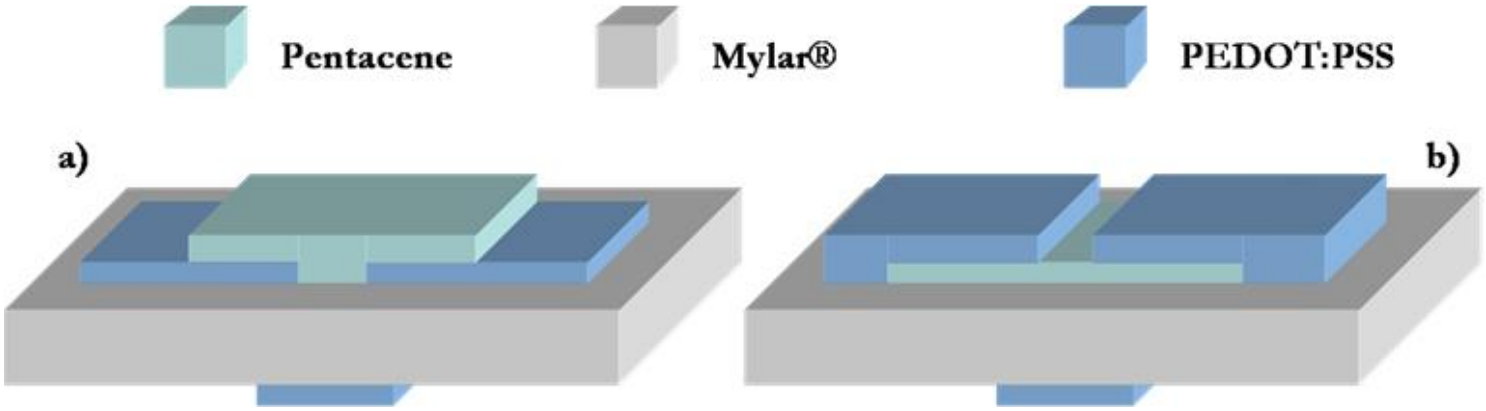
Organic Field Effect Transostors (OFETs)





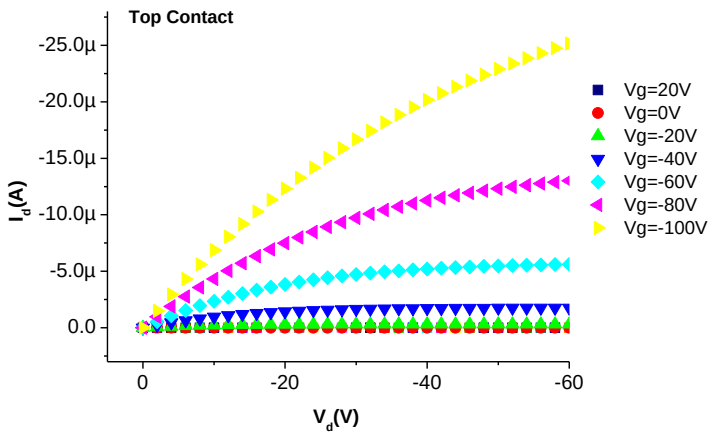
Bottom Contact

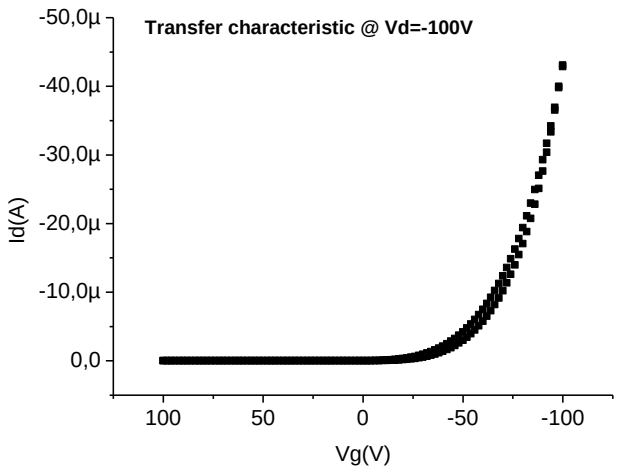
Top Contact



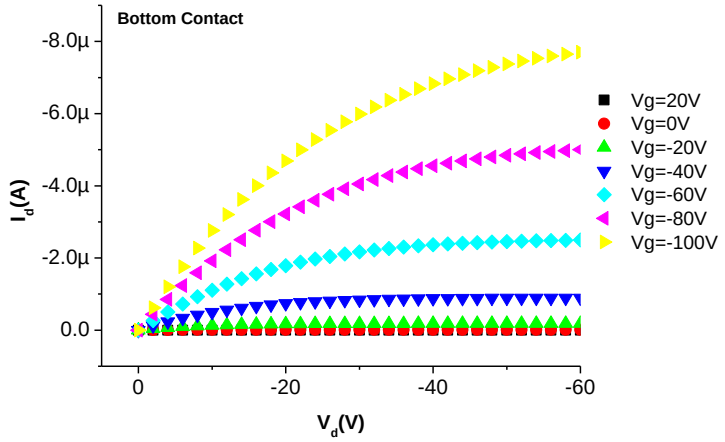
OFETs: T-C vs B-C

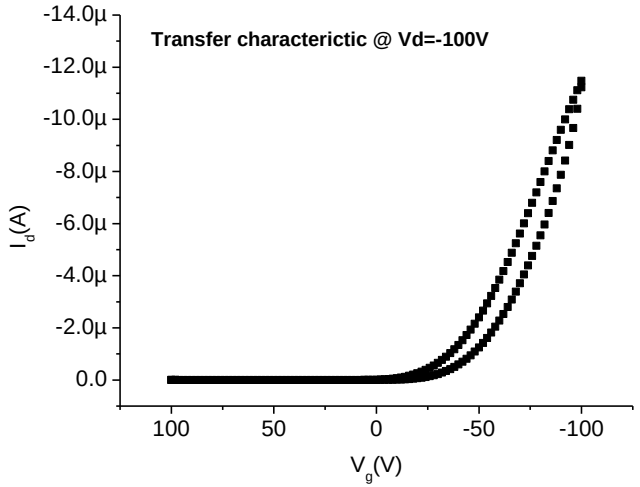
Top Contact





Bottom Contact





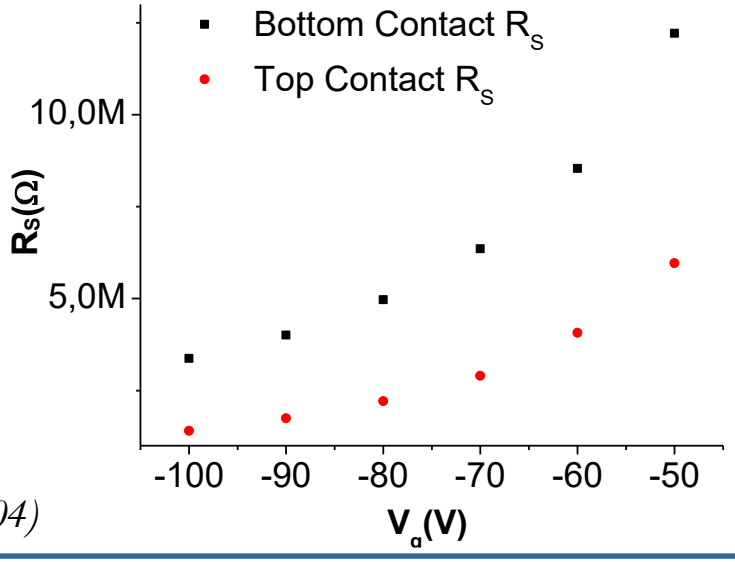
Rs – Difetti strutturali

Contact Resistance

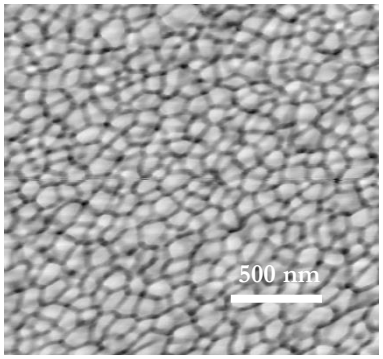
$$I_D = Z / L \mu C_{ins} (V_G - V_{th})(V_D - R_S I_D)$$

$$R_{total} = R_s + \frac{L}{W \mu C_{ins} \left| (V_G - V_{th}) \right|}$$

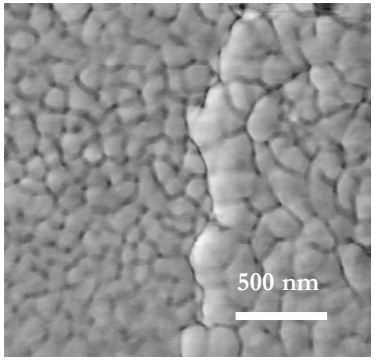
G. Horowitz et al. Adv. Funct. Mater. 14, 1069 (2004)



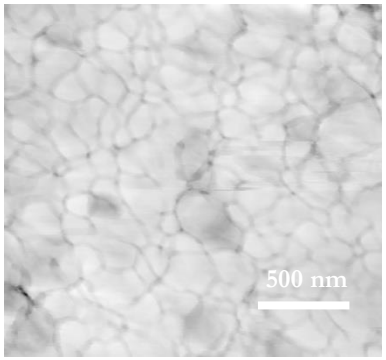
Pentacene in the channel



Pentacene at the channel/electrode interface



Pentacene over the electrodes



P. Cosseddu and A. Bonfiglio, Appl. Phys. Lett. 88 (2006) 023506

- **Metal/Semiconductor Interface**

  Charge injection → Series Resistance

  Causes:

  structural defects due to processing

  Energy levels aligment

R_S – Energy levels alignment

The concentration of intrinsic charge carries in the bulk is very low, therefore, **the most of the charge carries forming the channel are injected by the source electrode**

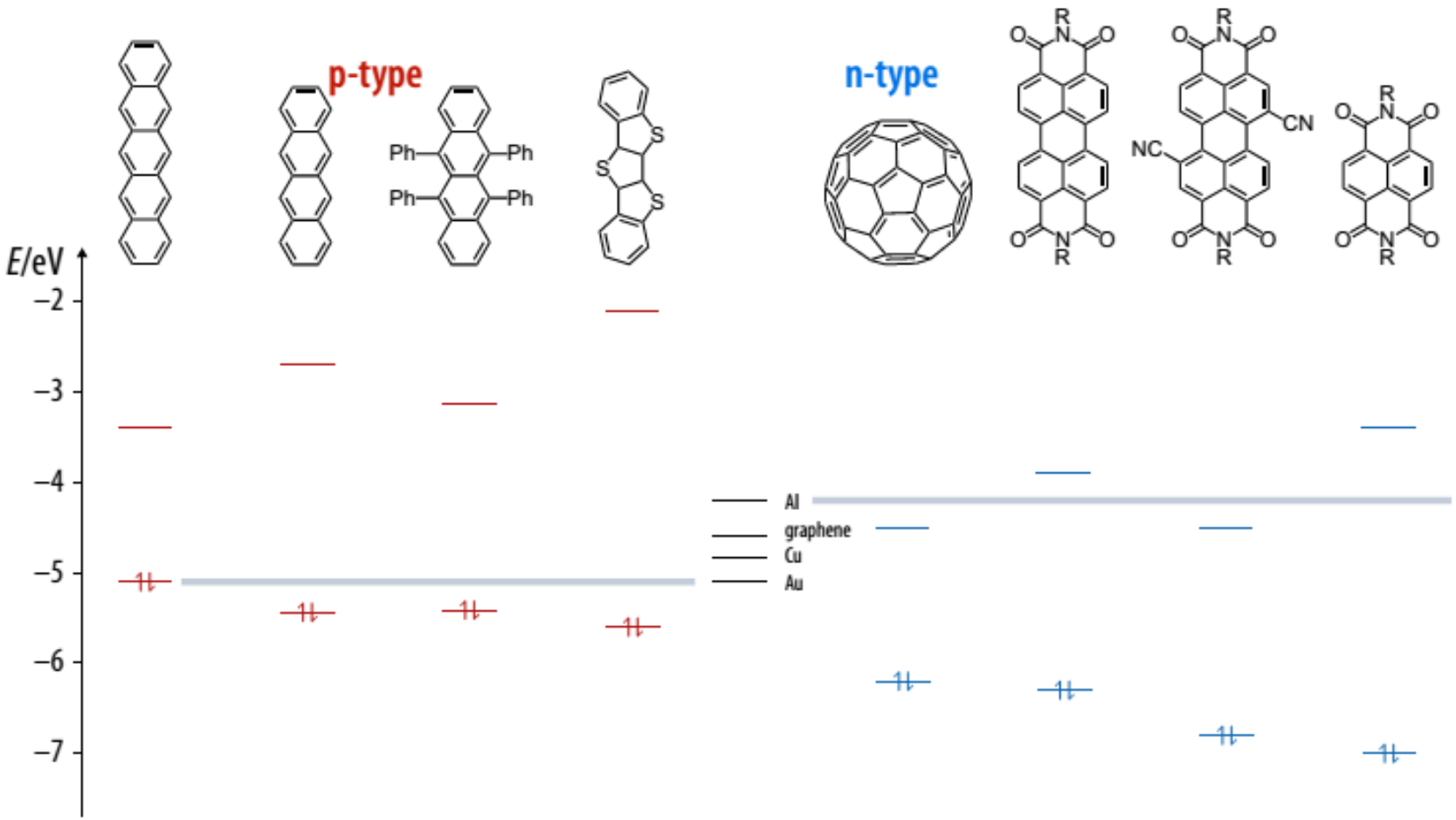
The metal/semiconductor interface plays a fundamental role in determining the final electrical behavior of the organic electronic devices

Also for organic materils, in principle we can use the Schottky-Mott theory to give a first idea of what could happen at the interface, howevr, we will see that such rule is rarely confirmed

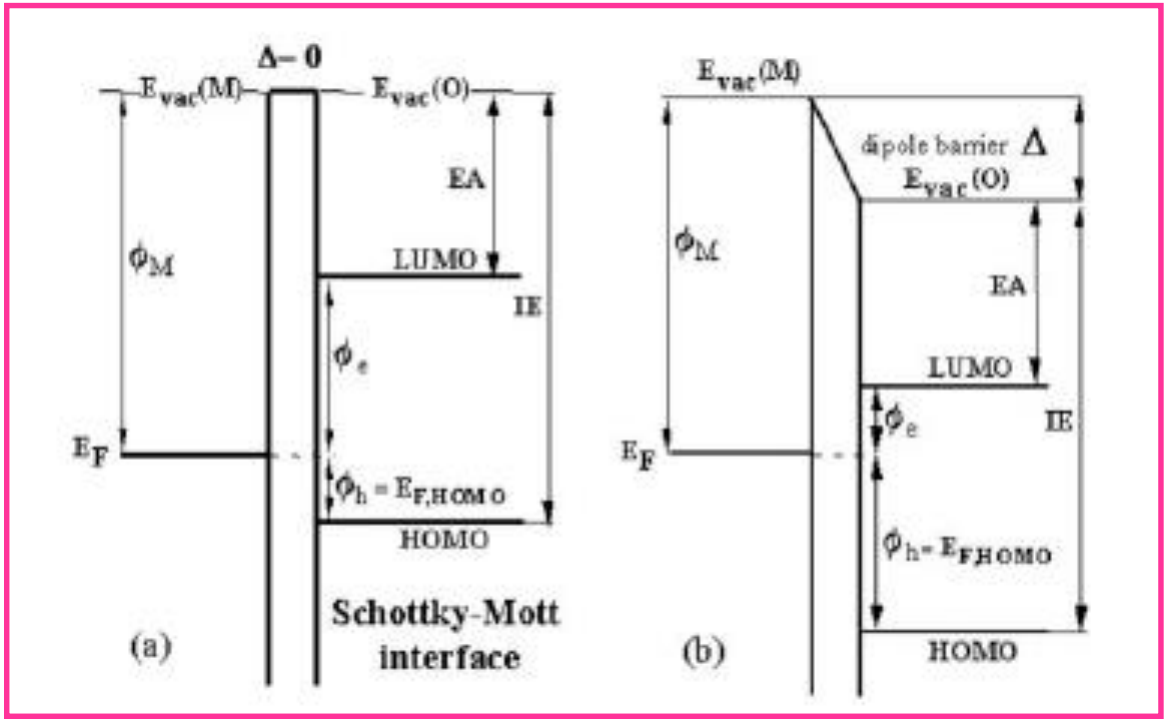
Vacuum level of metal and semiconductor should align, as a aresult, the hole and electron injection barriers, (HIB and EIB respectively) will depend on the HOMO and LUMO energy with respect to the metal Fermi level.

In principle, HIB (Hole Injection Barrier) is defined as the difference between the semiconductor ionization energy and the metal Fermi Energy e MFL (Metal Fermi Level).

Viceversa EIB is the difference between MFL and electron affinity.


p-type
n-type
E/eV
−2
−3
−4
−5
−6
−7
Ph
Ph
Ph
Ph
S
S
S
R
N
O
O
O
N
R
O
NC
CN
Al
graphene
Cu
Au

Schottky-Mott model



In the most of the cases Schottky – Mott model do not apply to organic devices

Injection barriers could differ from theoretical ones by even more than 1 eV!!!

Physical/chemical phenomena taking place at the interface

When the pressure is not sufficiently low, Ultra High Vacuum the metal surface is not perfectly clean, but contaminated by the absorption of water, oxygen and other organic molecules, therefoer its work function could be very different!

The work function is given by the work we have to spend to extract one electron from the metal

Metal work function is generally measured in UHV, 10^{-9} Torr

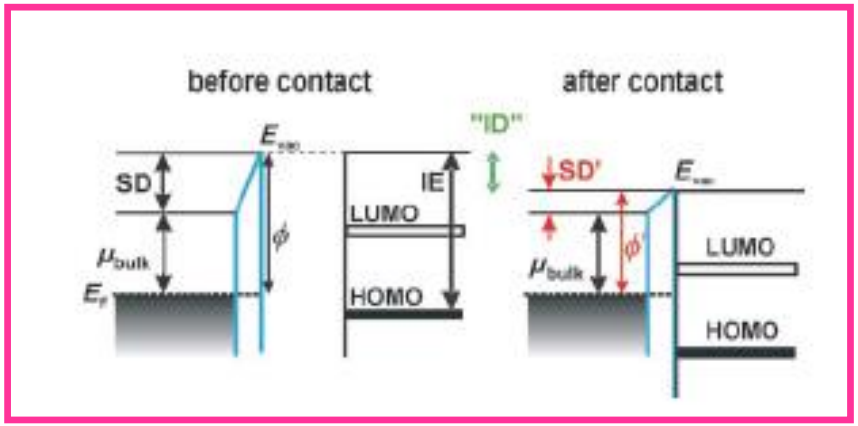
We should consider that in a metal we have the bulk potential, but also surface potential due to superficial electrons spilling out in the vacuum , and letting behind the a positive charge

- Surface dipole

Work function is given by two contribution:

- Bulk potential
- Surface dipole

  (depends on electronic surface density)

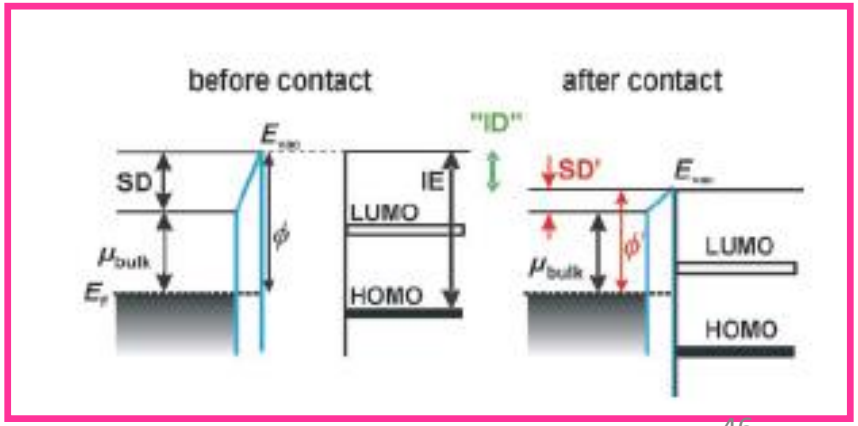


The absorption at the interface of whatever kind of molecule leads to a change in the surface electronic density → change in the metal work function

Such adsorbed molecules push the dipoles back towards the bulk of the metal *(Push Back Effect)* leading to the reduction of the metal work function

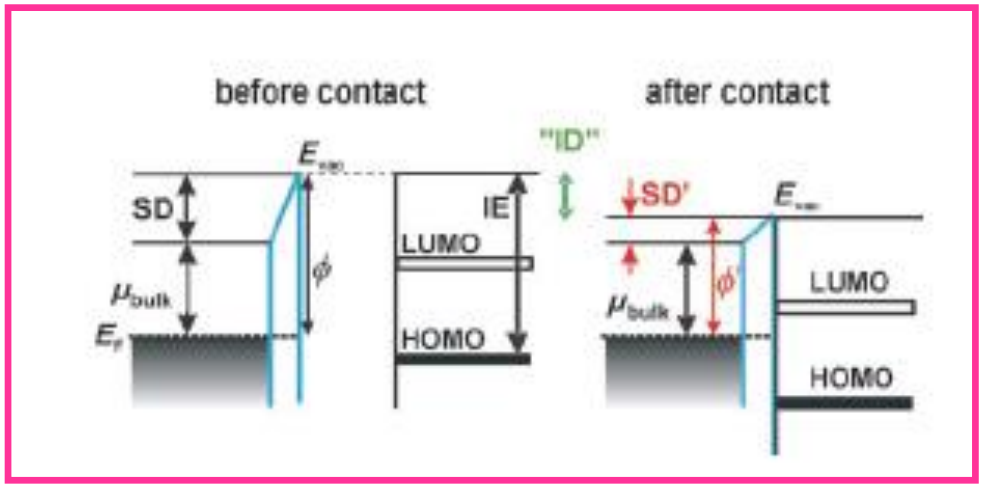
Surface dipole decreases
Re-organization of surface electronic density

$ID=SD-SD^{I}$



How the charge injection is affected by this phenomenon?

HIB increases
EIB decreases



ΔSD value depends on the metal, on the adsorbed molecule and also of the type of interaction, physical, chemical, charge transfer etc.

Consider that simply by moving from 10^{-9} Torr to 10^{-6} Torr a significant ΔSD is induced(Au: from 5.1-5.4 eV to 4.5-4.9 eV)

Moreoevr, there exist some moelcules with an intrinsic dipole moment inducing a further shift of the work function that couls be estimated by:

$$\Delta\phi = \frac{q \cdot N \cdot p}{\varepsilon_0 \cdot \varepsilon_r}$$

Helmholtz Equation

q electron charge, N surface dipole density, p dipole moemntum perpendicular to the surface, ε_0

Such shift can be tuned depending on the employed molecules

Strong electron acceptor

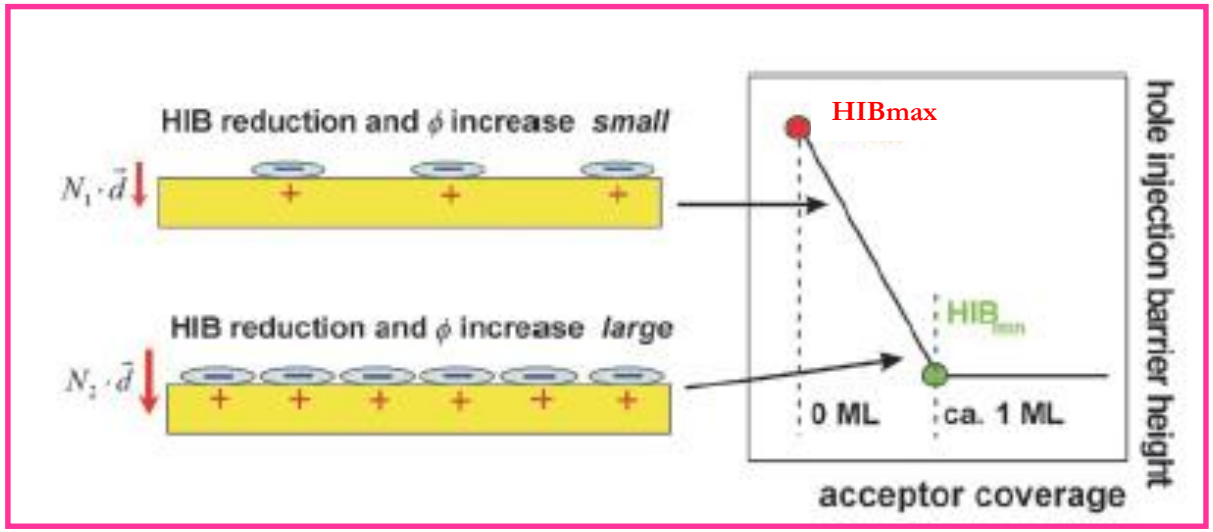
→ electron transfer from the metal to the molecule

→ Surface dipole with the negative side towards the molecule

→ Opposite Shift and increase of the metal work function

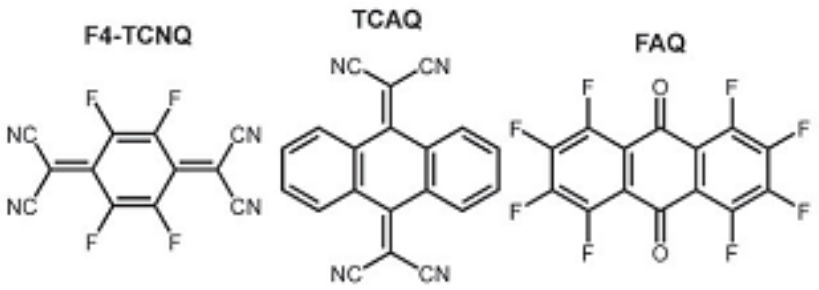
→ Decrease of HIB

The shift can be tuned using different molecules or controlling the density of the molecules on the metal surface



Tuning of the work function by means of molecular layers:

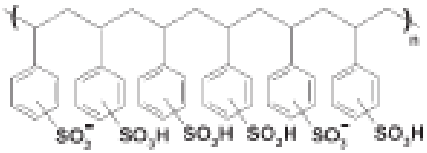
- ✓Small molecules
- ✓Self Assembled Monolayers (SAM)

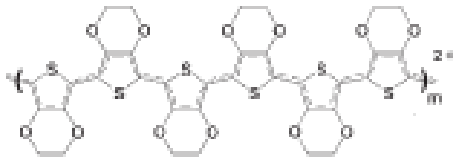


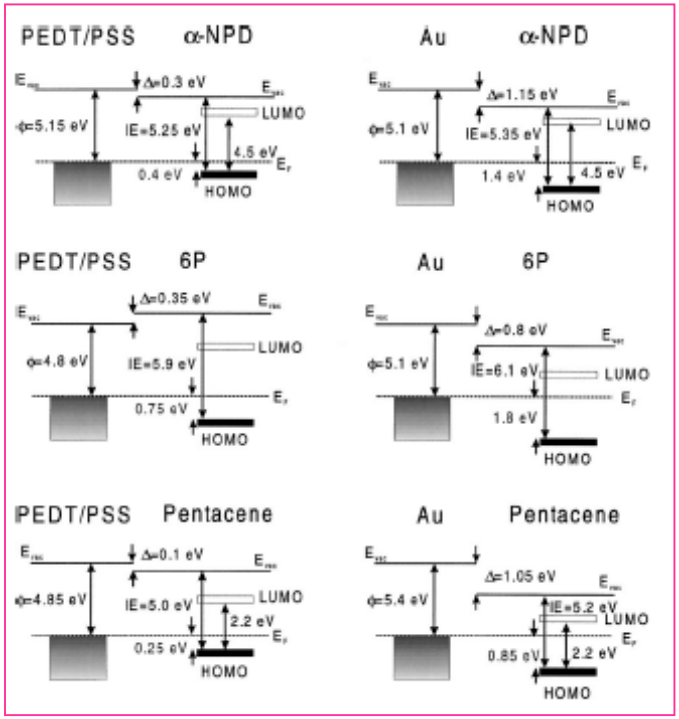
Conductive polymer/organic semiconductor interface

In a conductive polymer the contribution of surface dipoles to the work funtion is poor, due to disorder

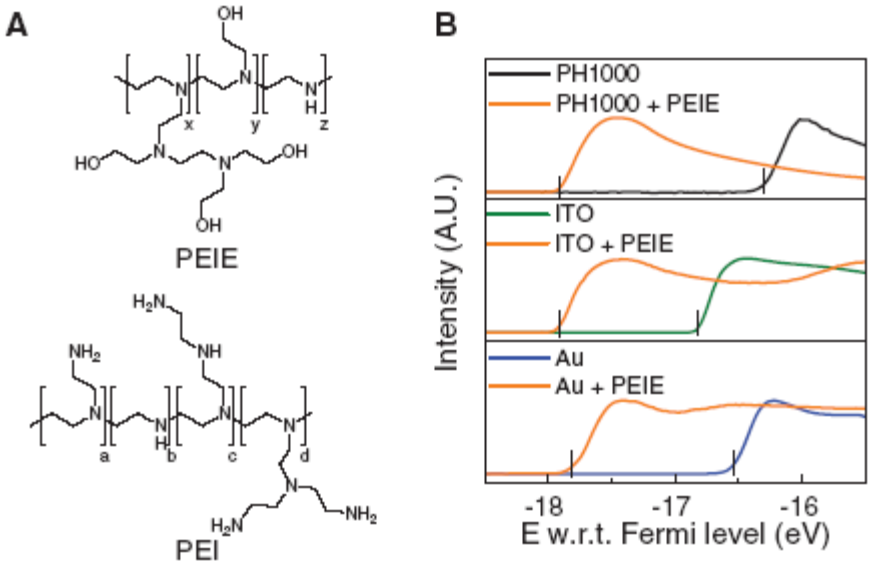
Push back effect not significant, typically Schottky-Mott is valid (S=1)







PEDOT:PSS vs AU
Similar WF but different HIB



Electrodes	Work function (eV)					
	Kelvin probe in air			UPS		
	Pristine	With PEIE	With PEI	Pristine	With PEIE	With PEI
Metal oxides						
ITO	4.62 ± 0.06	3.60 ± 0.06	3.50 ± 0.06	4.40	3.30	3.27
	5.16 ± 0.06*	3.60 ± 0.06*	—	5.00*	3.30*	—
ZnO	4.26 ± 0.06	3.28 ± 0.06	3.10 ± 0.06	3.96	3.55	3.17
FTO	4.68 ± 0.06	3.80 ± 0.06	3.60 ± 0.06	—	—	—
Metals						
Au	5.10 ± 0.10	3.90 ± 0.06	3.94 ± 0.06	4.70	3.40	—
Ag	4.60 ± 0.06	3.70 ± 0.06	3.60 ± 0.06	—	—	—
Al	3.40 ± 0.06	2.75 ± 0.06	—	—	—	—
PEDOT:PSS	4.90 ± 0.06	3.58 ± 0.06	3.88 ± 0.06	4.95	3.32	3.16
Graphene	4.60 ± 0.06	3.80 ± 0.10	—	—	—	—

*Substrate was treated with an O_2 plasma for 2 min prior to measurements or polymer modifier deposition.

Employment of small molecules to intentionally change the metal work funtion

Example PEIE

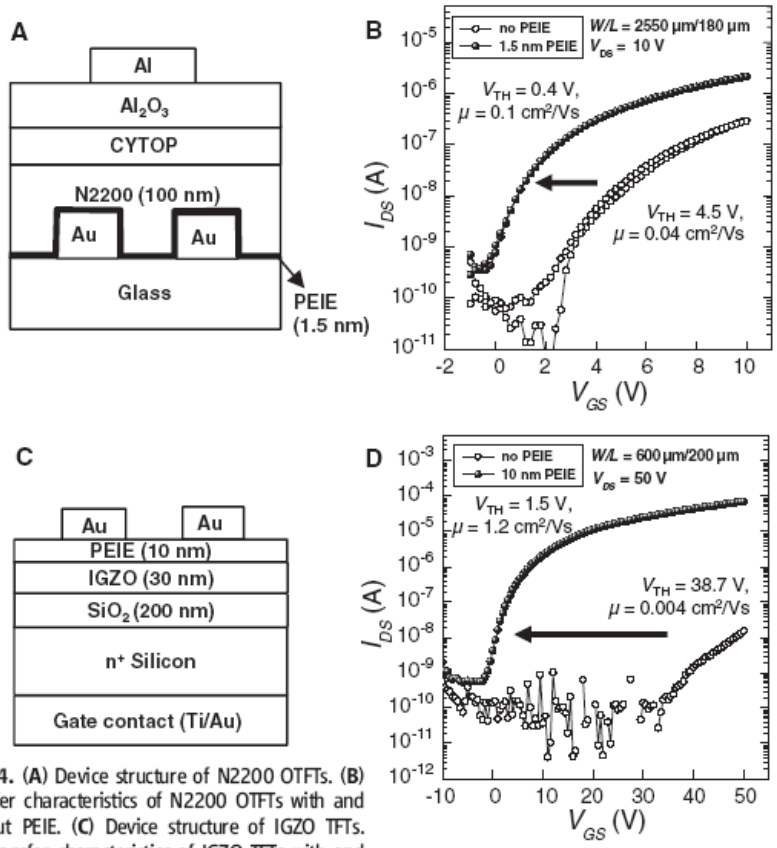
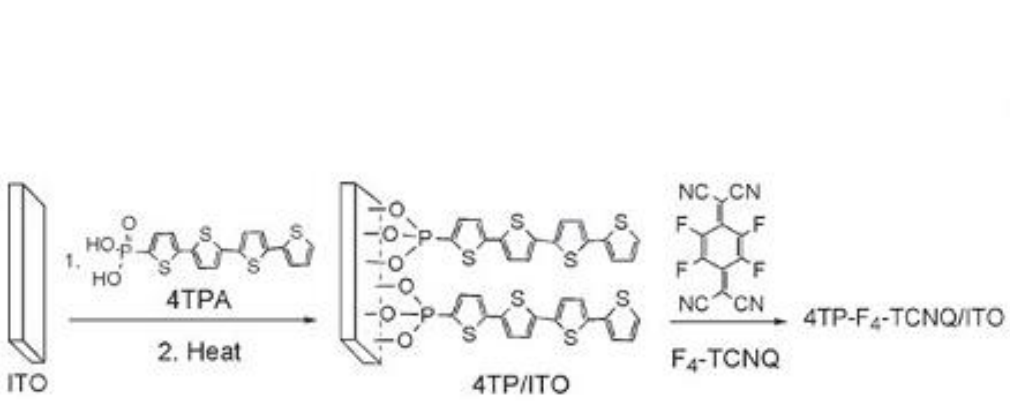
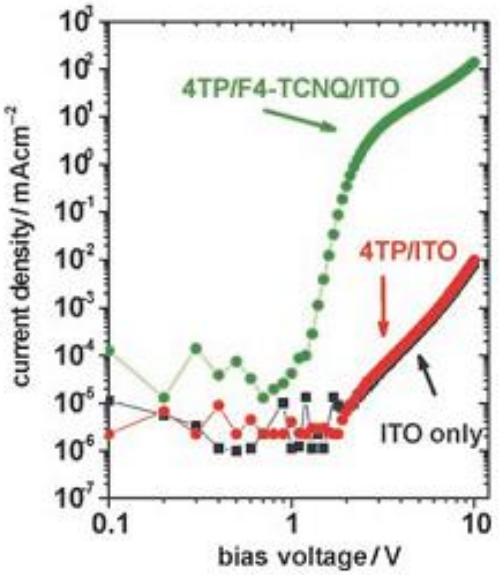


Fig. 4. (A) Device structure of N2200 OTFTs. (B) Transfer characteristics of N2200 OTFTs with and without PEIE. (C) Device structure of IGZO TFTs. (D) Transfer characteristics of IGZO TFTs with and without PEIE. CYTOP (CTL-809M) is a perfluorinated polymer purchased from Asahi Glass.

- Comparison betwee two diodes ITO/4TPA/ITO with and without F4-TCNQ
- In the second case a dramatic increase of the current, due to better charge injection, can be observed





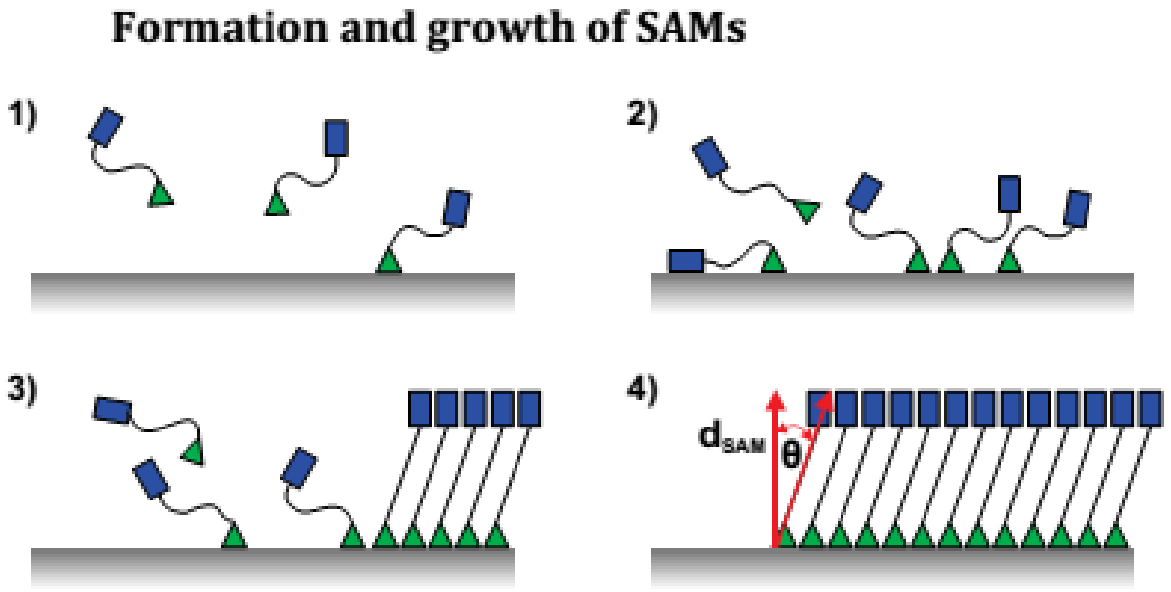
L'argento non viene generalmente considerato come metallo per la fabbricazione di elettrodi source e drain, perché ha una funzione lavoro di circa 4.7 eV

Non si interfaccia bene con la maggior parte dei semiconduttori di tipo p, e neanche con quelli di tipo n

È facile però fare degli inchiostri conduttivi con nanoparticelle d'argento

È possibile modificare la sua funzione lavoro?

Uso di Self Assembled Monolayers (SAMs)



Il gruppo SH del tiolo fa si che si leghi covalentemente al metallo

L'anello aromatico ne modifica la funzione lavoro!

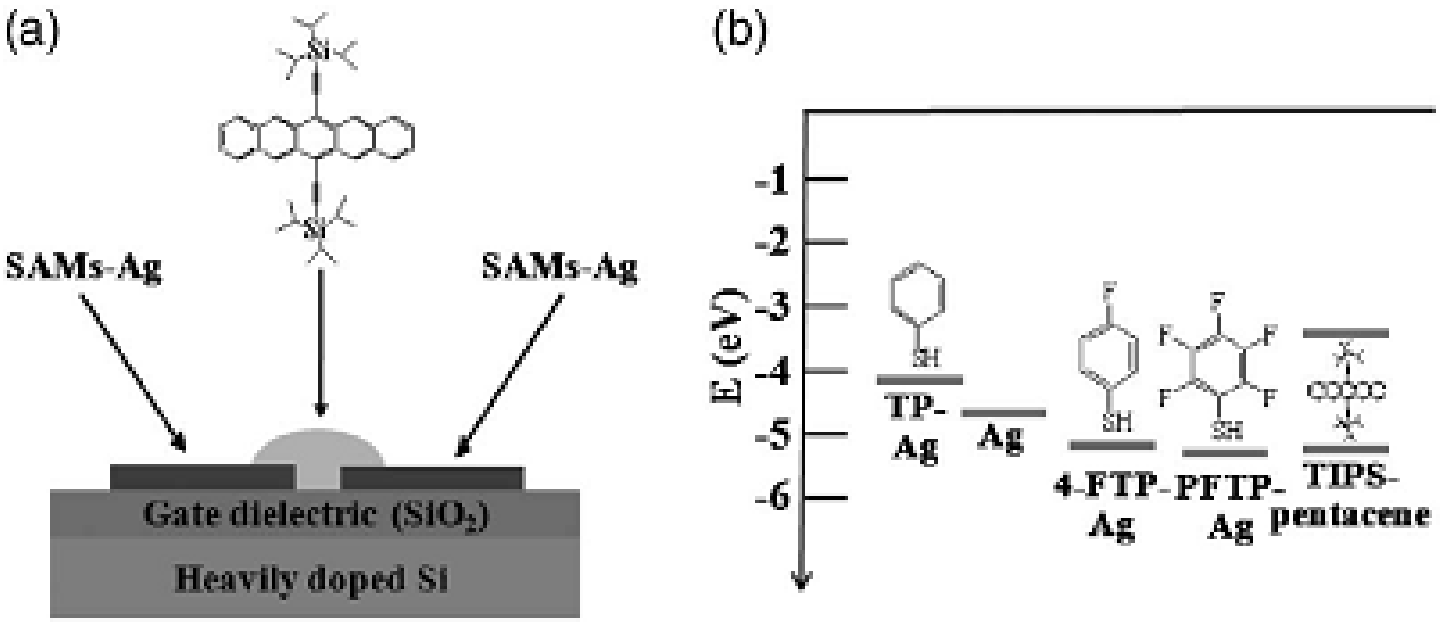
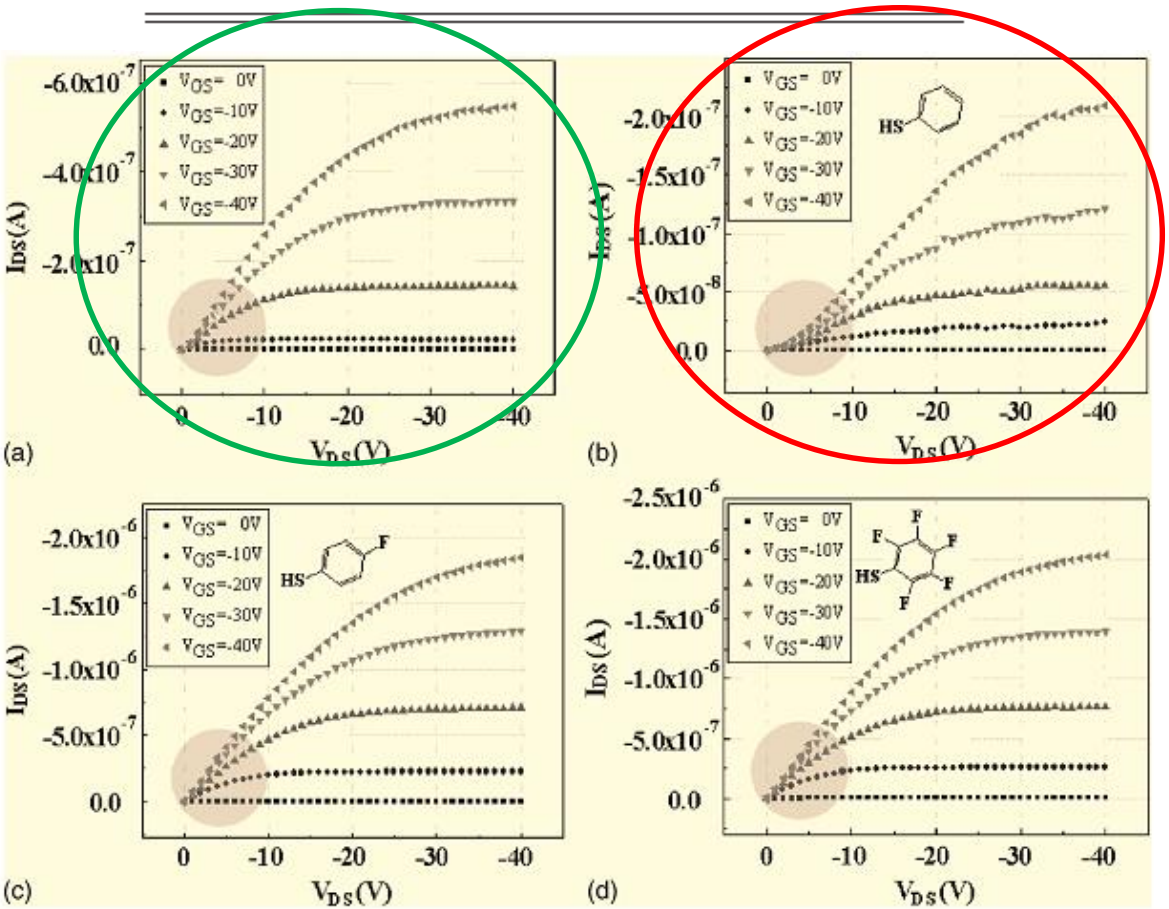


FIG. 1. (a) Bottom contact OTFT with TIPS-pentacene active layer. (b) Energy level diagrams of TP-Ag, pristine Ag, 4-FTP-Ag, PFTP-Ag electrode, and TIPS-pentacene.

TABLE I. Overview of the electrical properties of the bottom contact TIPS-pentacene OTFT devices (L=30 μm, W=60 μm) with various electrodes: TP-Ag, Ag, 4-FTP-Ag, PFTP-Ag electrode.

Sample	Φ_{meas} (eV)	Mobility (cm^2 V s)	on off ratio	V_T (V)	S (V decades)
TP-Ag	4.14	0.02	10^4	1.0	2.4
Ag	4.70	0.045	10^4	1.7	1.3
4-FTP-Ag	5.21	0.15	10^5	3.3	1.1
PFTP-Ag	5.35	0.17	10^5	3.1	1.1



TP
Rs elevata

4-FTP
Iniezione migliore

PFTP
Iniezione migliore

Non idealities

- **Insulator/semiconductor interface**

  charge trapping

  bias stress → Vt shift

  hysteresis

Charge conduction takes place in the first monolayer, therefore the interface with the gate dielectric plays a crucial role in device performances:

- **physical:**

Structural defects→ charge carriers scattering semiconductor morphology→ mobility and charge trapping

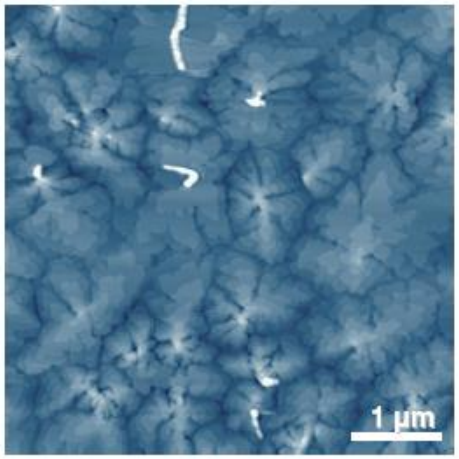
- Chemicals:

Charge trapping

Threshold voltage Shift (surface potential induced by chemical groups at the interface)

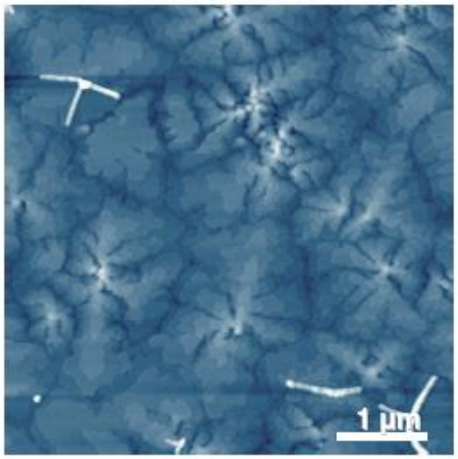
In bottom gate structures the insulator is also the substrate where the organic film is grown → determines the properties of the channel

- Surface energy
- Idrophobic – Idrofilic
- Surface roughness



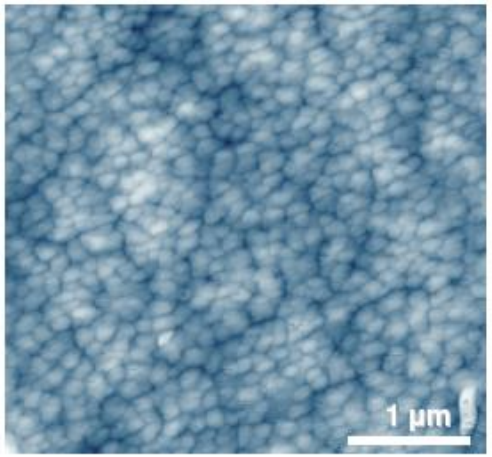
Pentacene su Mica

RMSR=0.2 nm



Pentacene su SiO_2

RMSR=0.2 nm



Pentacene su Mylar

RMSR=2 nm

Surface modifications

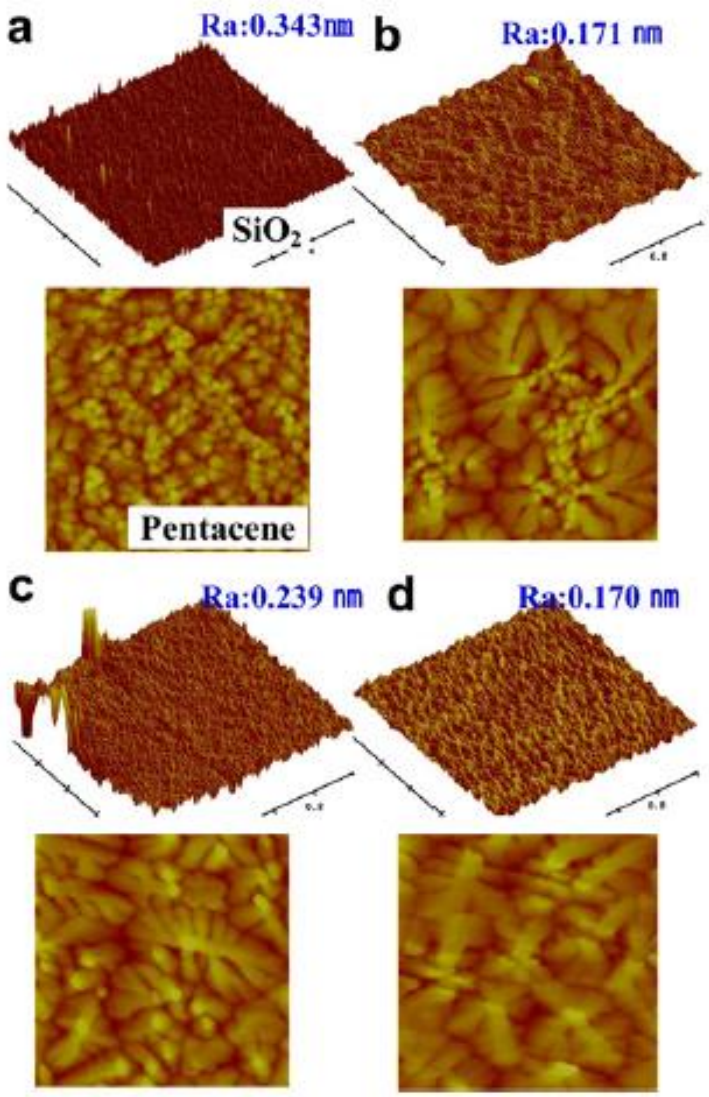


Fig. 4. (a) AFM images of SiO_2 (1 μm × 1 μm) and pentacene (5 μm × 5 μm) of non-treated substrate as reference. (b) After O_2 plasma (RF 100 W, ICP 50 W, 30 s) treatment. (c) After Ar ion beam (25 eV, 60 s) treatment. (d) After Ar ion beam (300 eV, 60 s) treatment.

Surface treatment	Mobility ($cm^2/V\,s$)	I_{on}/I_{off}	I_{off} (A)	Vt (V)	SS (V/dec)
O_2 plasma	0.353	$\sim 10^4$	$\sim 10^{-8}$	4.1	3.1
Ar beam	0.126	$\sim 10^8$	$\sim 10^{-11}$	−7.6	0.6
Reference	0.05	$\sim 10^6$	$\sim 10^{-10}$	−8.1	1.3

- **Argon ion treated**

  increase of mobility and also of Ion/Ioff

- **O2 plasma treatment**

  increase of mobility

  degradation of Ion/Ioff → Ioff increases due to dangling bonds

Charge trapping in the bulk

Charge Trapped Limited Current

Traps need to be filled in order to have free carriers

Mobility is given by the ratio between free charges n_f and the total concentration of charges carries n_{tot}

$$\theta = \frac{n_f}{n_{tot}}$$

Considering the intrinsic mobility of the semiconductor μ_0 the effective mobility in a FET is given by:

$$\mu_{FET} = \mu_0 \cdot \theta$$

Insulator/semiconductor interface

Interfacial states can create charge trapping

They could be given by:

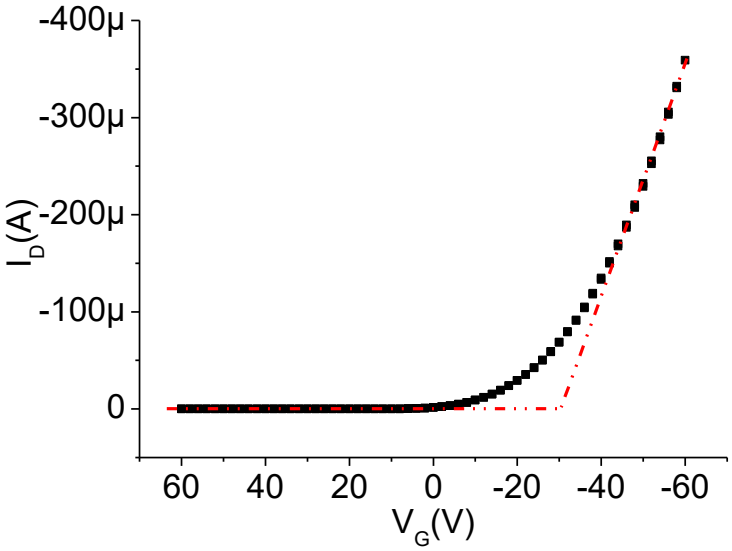
- Organic semiconductor growth
- Chemical interactions

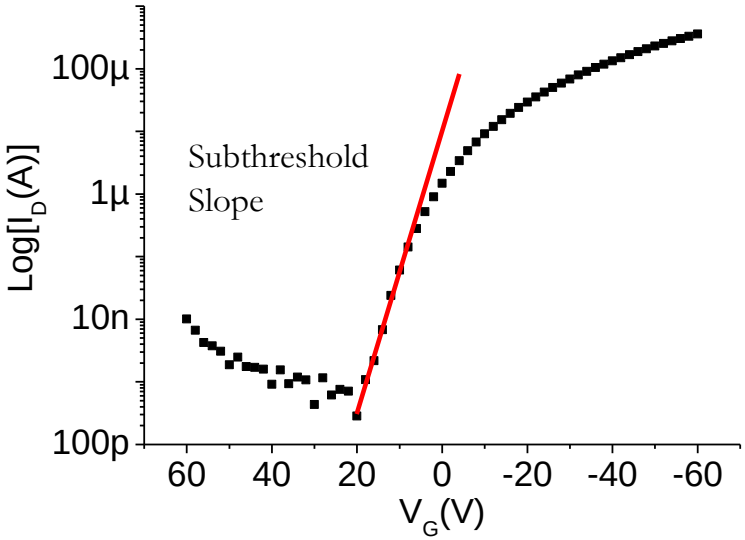
The number of interfacial traps can be estimated using the following expression, considering bulk traps independent on the interfacial ones:

$$N_{SS}^{\max} = \left[\frac{S \cdot \log(e)}{kT/q} - 1 \right] \frac{C_i}{q}$$

$$S = \left[\frac{d \log(I_d)}{dV_g} \right]^{-1}$$

Subthreshold slope





$$N_{SS}^{\max} = \left[\frac{S \cdot \log(e)}{kT/q} - 1 \right] \frac{C_i}{q}$$

Fattori di non idealità

Insulator/semiconductor interface

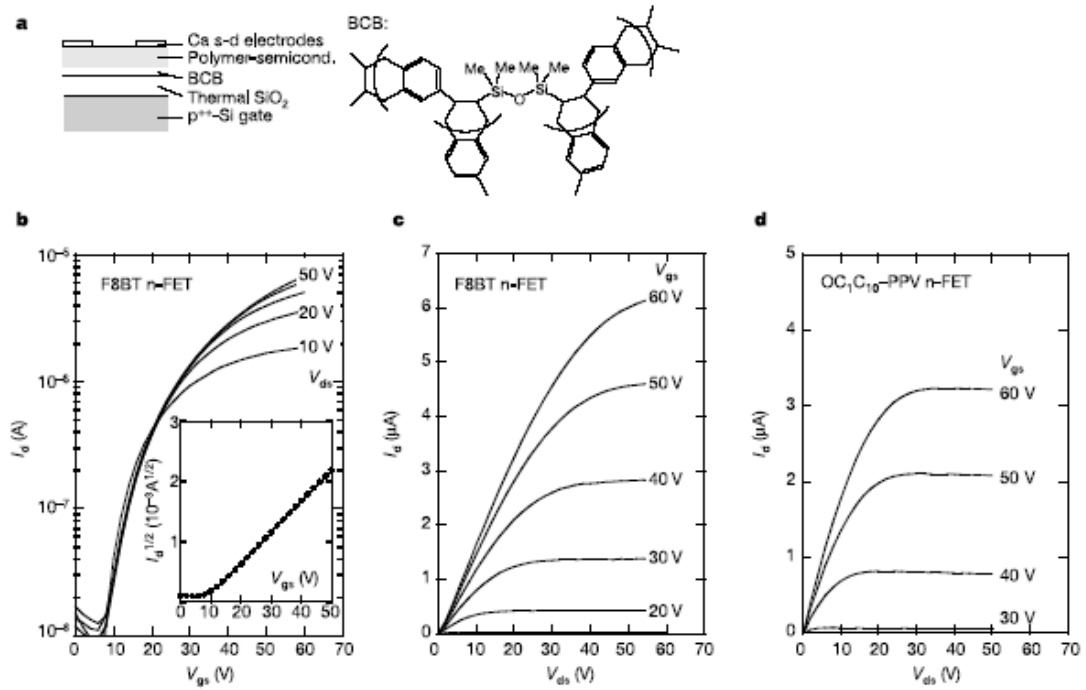
- **Chimicals:**

Charge trapping

Threshold voltage Shift

OH functional groups

OH groups attract elecrons and trap them → Vtn increases, therefore n-type conduction is inhibited



Non polar insulators have no OH groups → n-type conduction

OH functional groups

Solutions:

- Non polar solvents
- Insulator passivation:
  - ✓ SAMs (HDMS) deposition
  - ✓ Thin molecular layers deposition, for instance a p-type material

C60 Single Layer

A) C_{60} 20 nm

At first, all-organic top-contact OFETs were fabricated by employing a single C60 layer as semiconductor. However, no n-type behavior was obtained in such configuration.

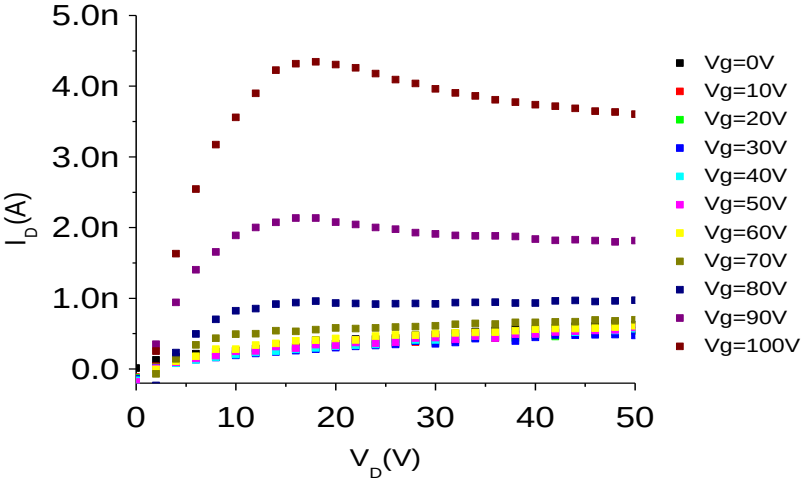
Explanations :

- Rather large electron injection barrier at the PEDOT:PSS/C60 interface, which was estimated to be ca. 1.5 eV under ultrahigh-vacuum conditions
- Poor structural and morphological quality of the C60 layer on bare Mylar®

F. J. Zhang, A. Vollmer, J. Zhang, Z. Xu, J. P. Rabe, N. Koch, Org. Electron. **8** (2007) 606

Pentacene/C60 double layer: n-type

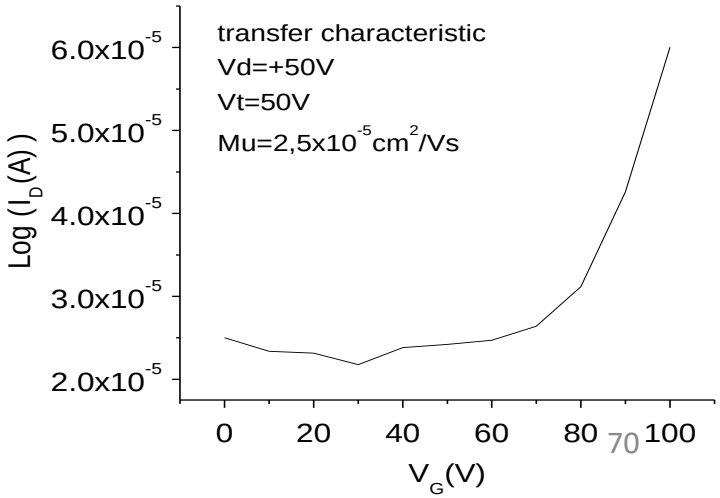
B) C60 20nm on 3 nm pentacene buffer layer



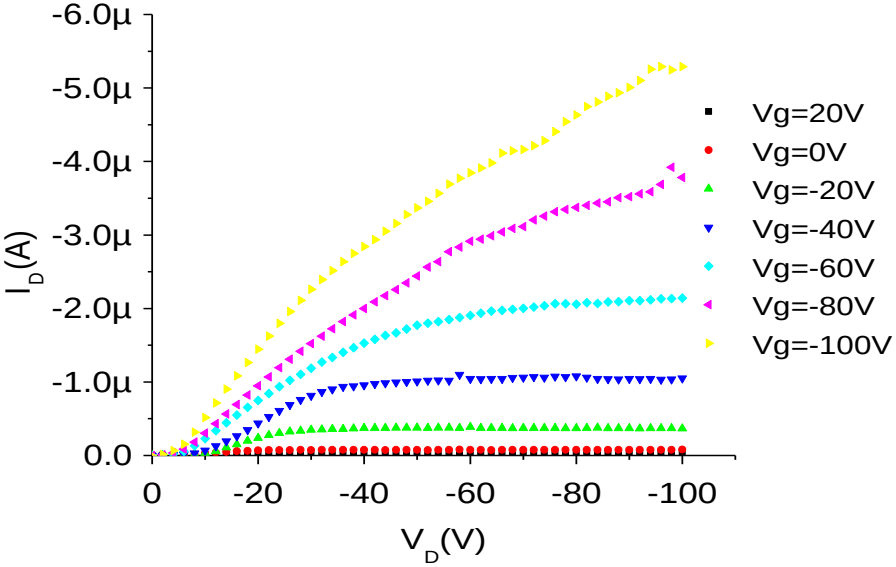
Nevertheless, despite the presence of the 3 nm pentacene layer, **no p-type conduction** was observed.

Island growth on rough substrates such as Mylar® → no closed layer over the entire gate dielectric surface to be formed at this low nominal thickness.

Using a pentacene buffer layer of 3 nm nominal thickness, despite the possibly high electron injection barrier (estimated to be ca. 1.9 eV), we found evidence for a n-type conduction, and the electron mobility was *ca.* $4x10^{-5}$ cm^2/Vs.

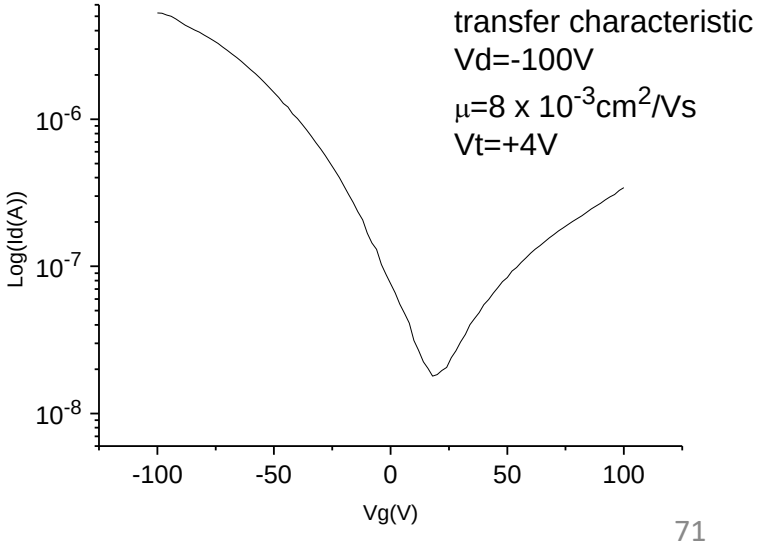


Ambipolar top contact: p-type

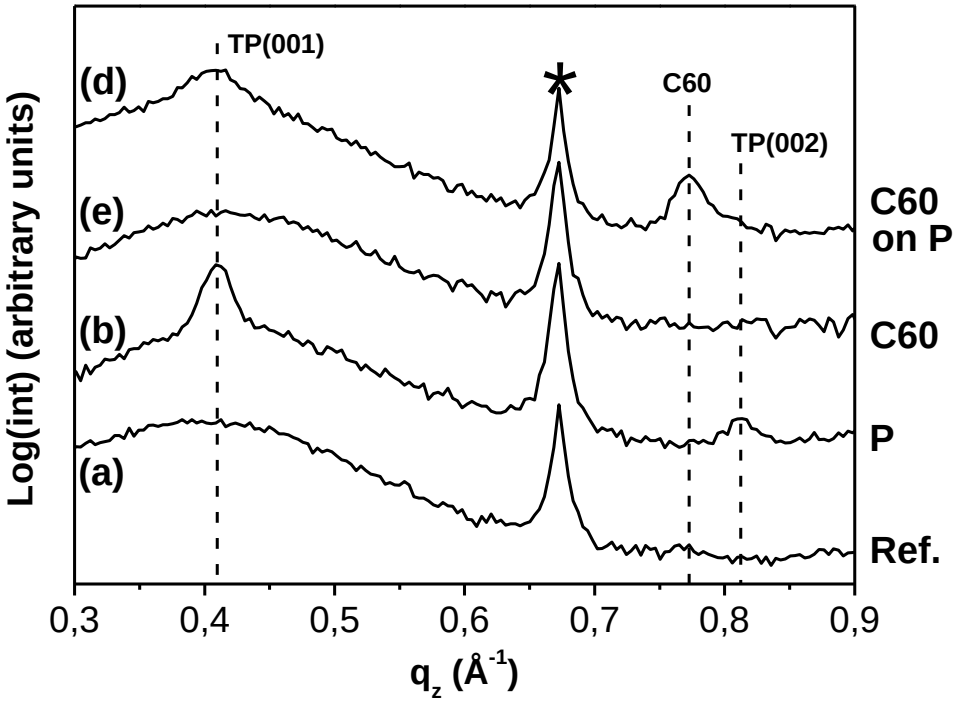


Increasing the **pentacene buffer layer thickness to 10nm** we obtained ambipolar behaviour.

The pentacene layer is thick enough to form a complete monolayer at the interface with the gate dielectric and also p-type conduction can be measured.

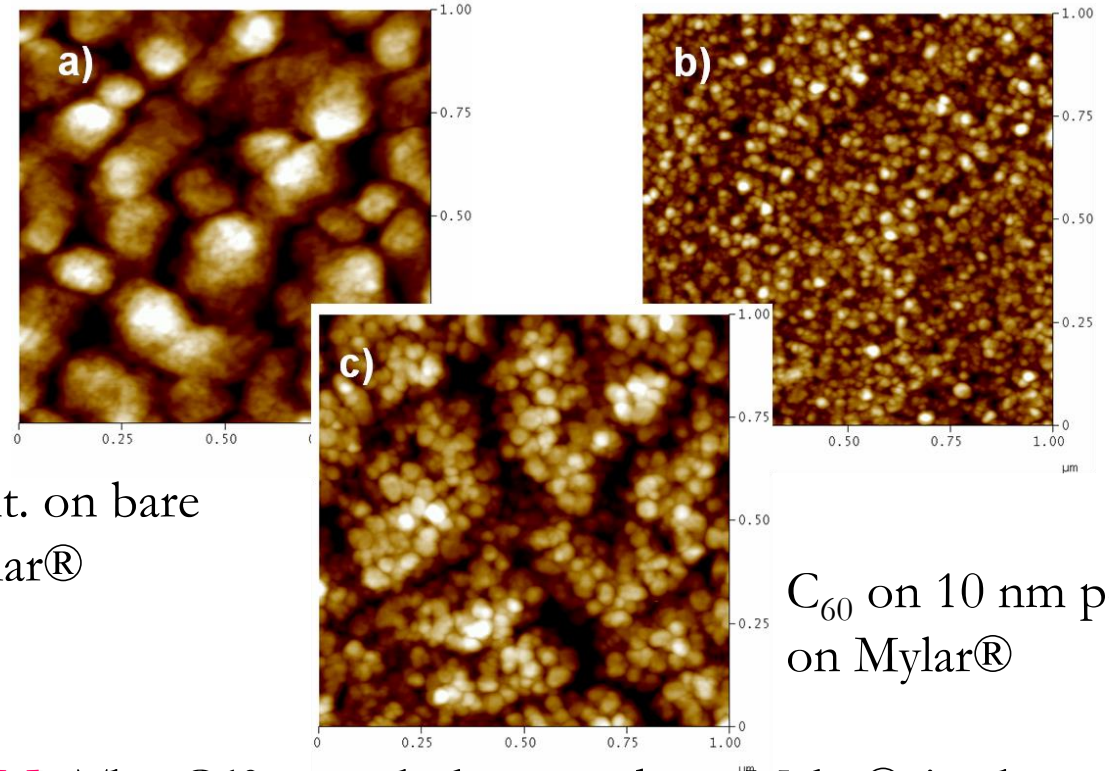


XRD Analysis



XRD: 60 nm thick film of C60 deposited directly on Mylar® does not show any Bragg peaks, in contrast to the film of equal nominal thickness deposited on a 10 nm thick pentacene pre-coating. We find a peak at qz=0.7720 Å-1 (lattice spacing d=0.814nm) that can be assigned to the (111) reflection of cubic C60 polymorphs as well as to the (002) reflection of hexagonally grown C60.

Morphological characterization



C_{60} on bare Mylar®

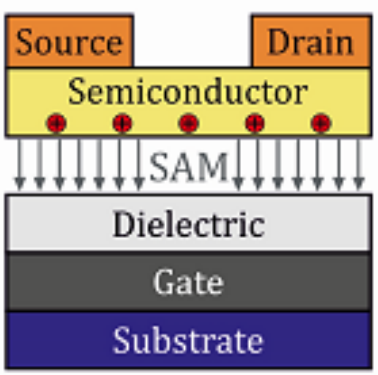
Pent. on bare Mylar®

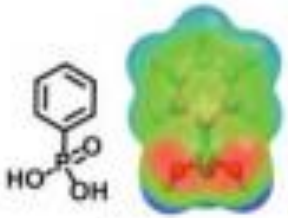
C_{60} on 10 nm pent. buffer layer on Mylar®

AFM: The C60 morphology on bare Mylar® is characterized by a granular structure with grain diameters < 30nm. We can clearly notice that the nucleation of C60 grains on top of the underlying pentacene islands leads to significant increase in the average grain size. Together with our finding of crystalline C60 growth from XRD, this explains the increase of the electron mobility we observed in the OFETs characteristics.

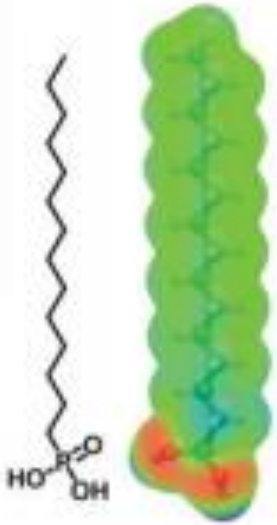
P. Cosseddu, A. Bonfiglio, I. Salzmann, J. P. Rabe and N. Koch, Org. Electron. in press

Dipoles at the insulator/semiconductor interface

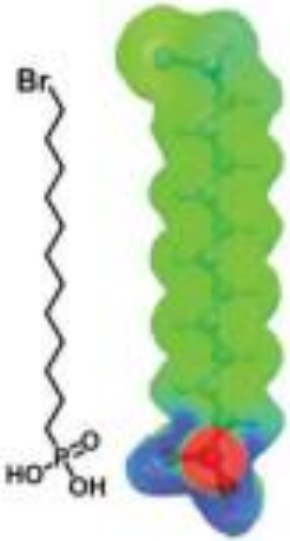




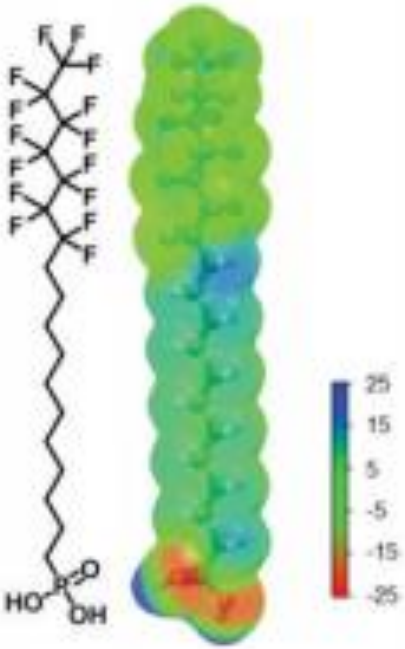
Phenyl



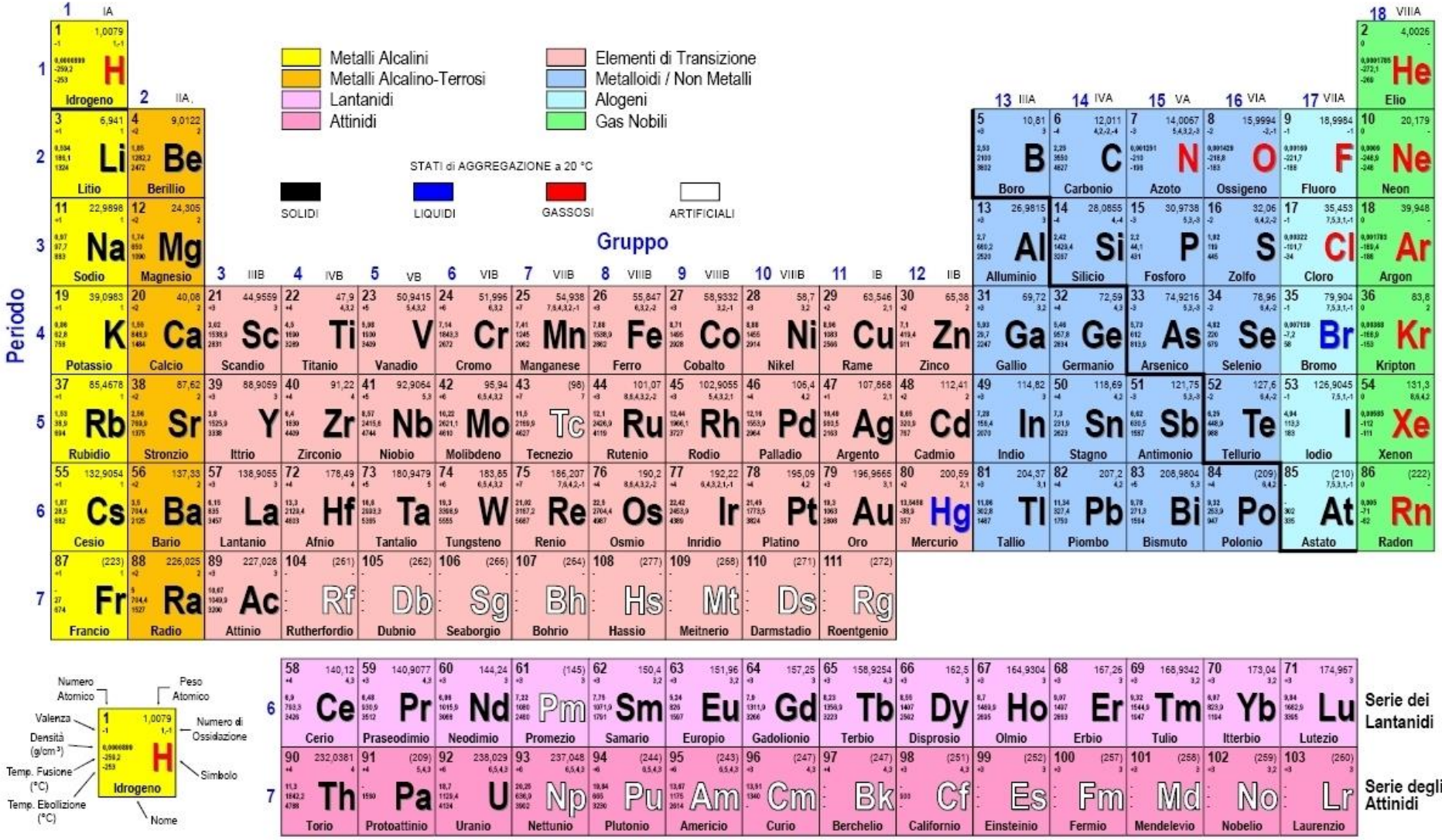
C_{14}



BrC_{12}



$F_{15}C_{18}$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Dipoles at the insulator/semiconductor interface

If the SAM layer is uniform and well ordered, the functional groups can induce a surface potential

Helmholtz

$$V_{SAM} \propto \frac{N\mu_z \cos\theta}{\varepsilon_{SAM}\varepsilon_0}$$

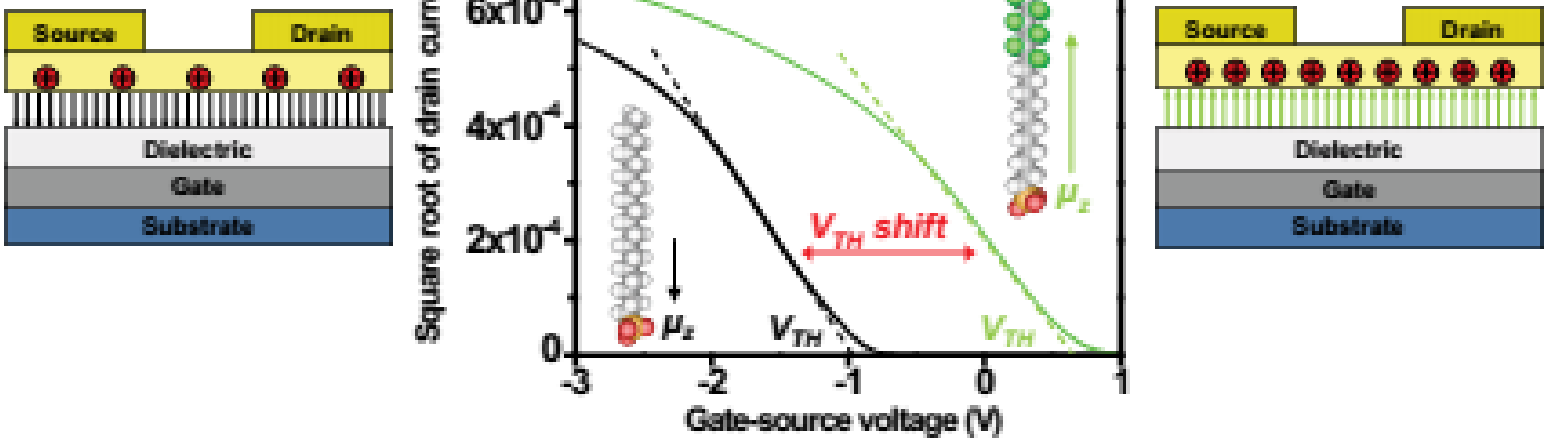

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Table 5: Electrostatic potentials calculated according to Equation (13).

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$V_{SAM,\ 10\ nm}$ (V)	0.67	0.24	-0.82	-2.30
$V_{SAM,\ 20\ nm}$ (V)	0.52	0.22	-0.71	-2.33
$V_{SAM,\ 40\ nm}$ (V)	0.33	0.19	-0.66	-2.44
$V_{SAM,\ 80\ nm}$ (V)	0.44	0.14	-0.47	-2.25

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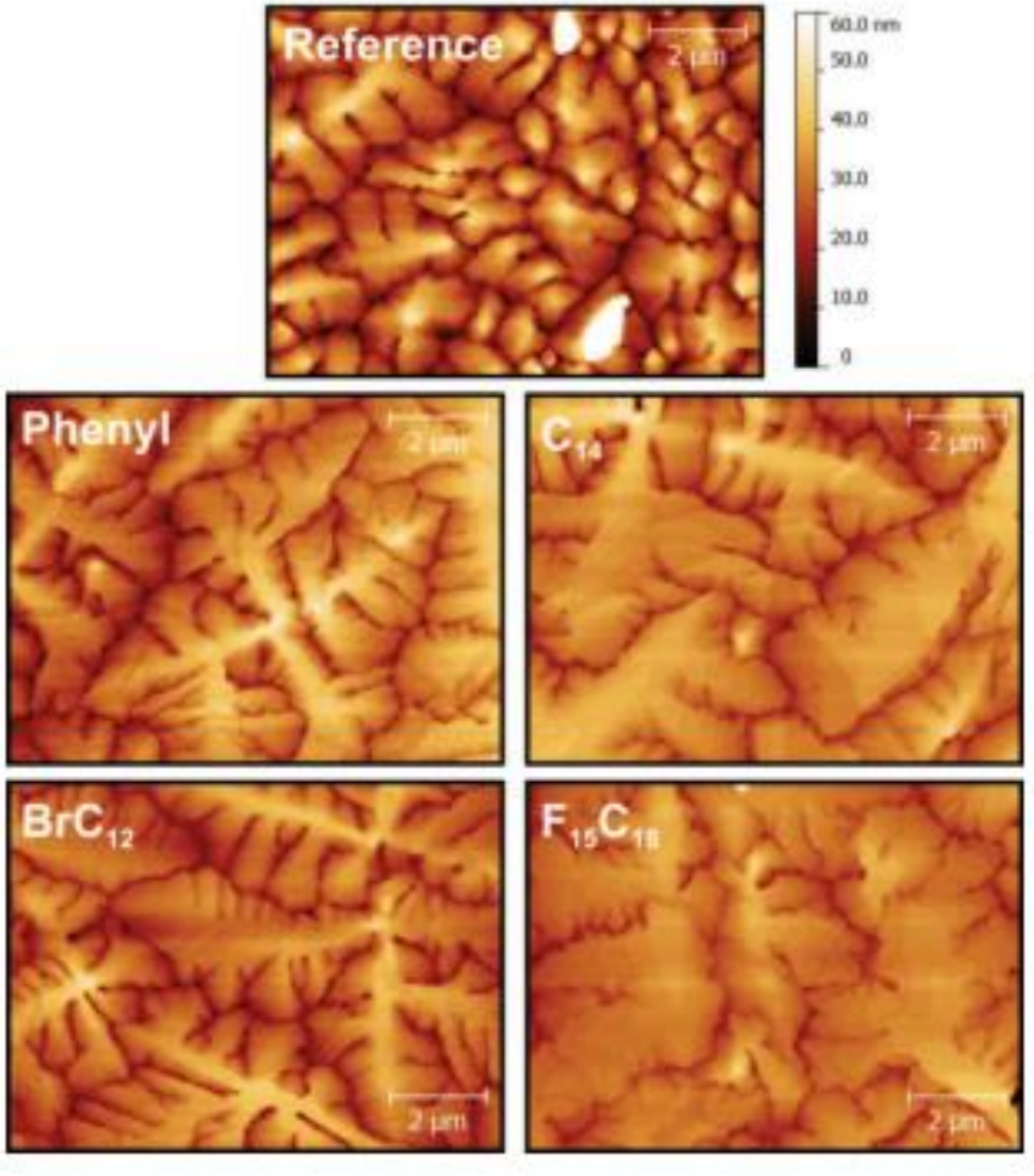

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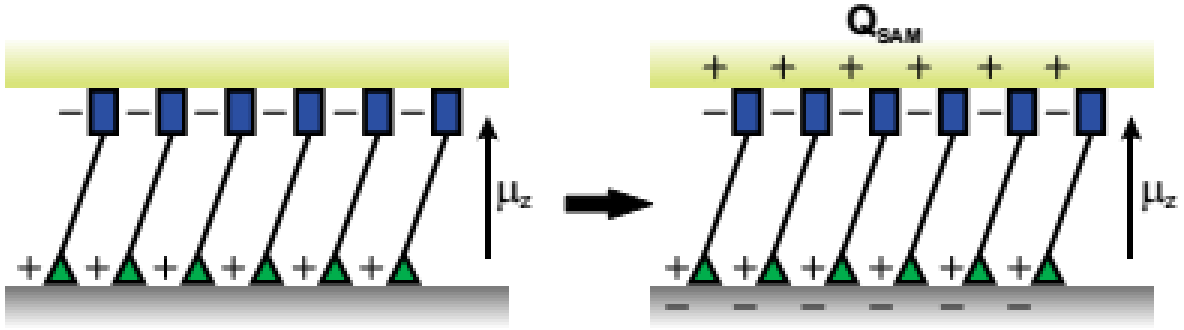

Figure 38: Schematic of charge rearrangement in the proximity of the SAM. The negative dipole moment perpendicular to the surface of the SAM induces mobile holes in semiconductor (Q_{SAM}).

If a vertical field is applied, Vgs, the charges concentration Qeff accumulated in the semiconductor is proportional to the applied voltage and to the dielectric capacitance *Ctot*:

$$Q_{eff} = V_{GS} C_{tot}$$

Dipoles at the insulator/semiconductor interface

$$C_{tot} = \left(\frac{1}{C_{ins}} + \frac{1}{C_{SAM}} \right)^{-1} \qquad (23)$$

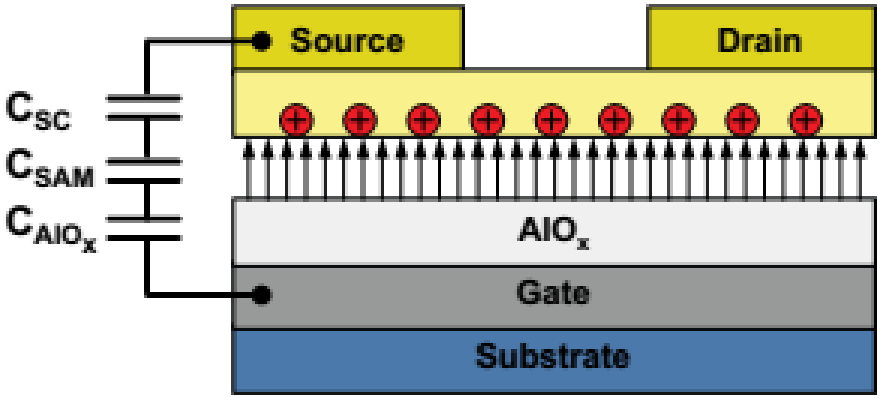

Figure 39: Effect of the electrostatic potential in the OTFT device. Additional mobile holes are induced in the semiconductor.

$$\Delta V_{GS} = V_{SAM} \frac{C_{SAM}}{C_{tot}} = -\Delta V_{th}$$

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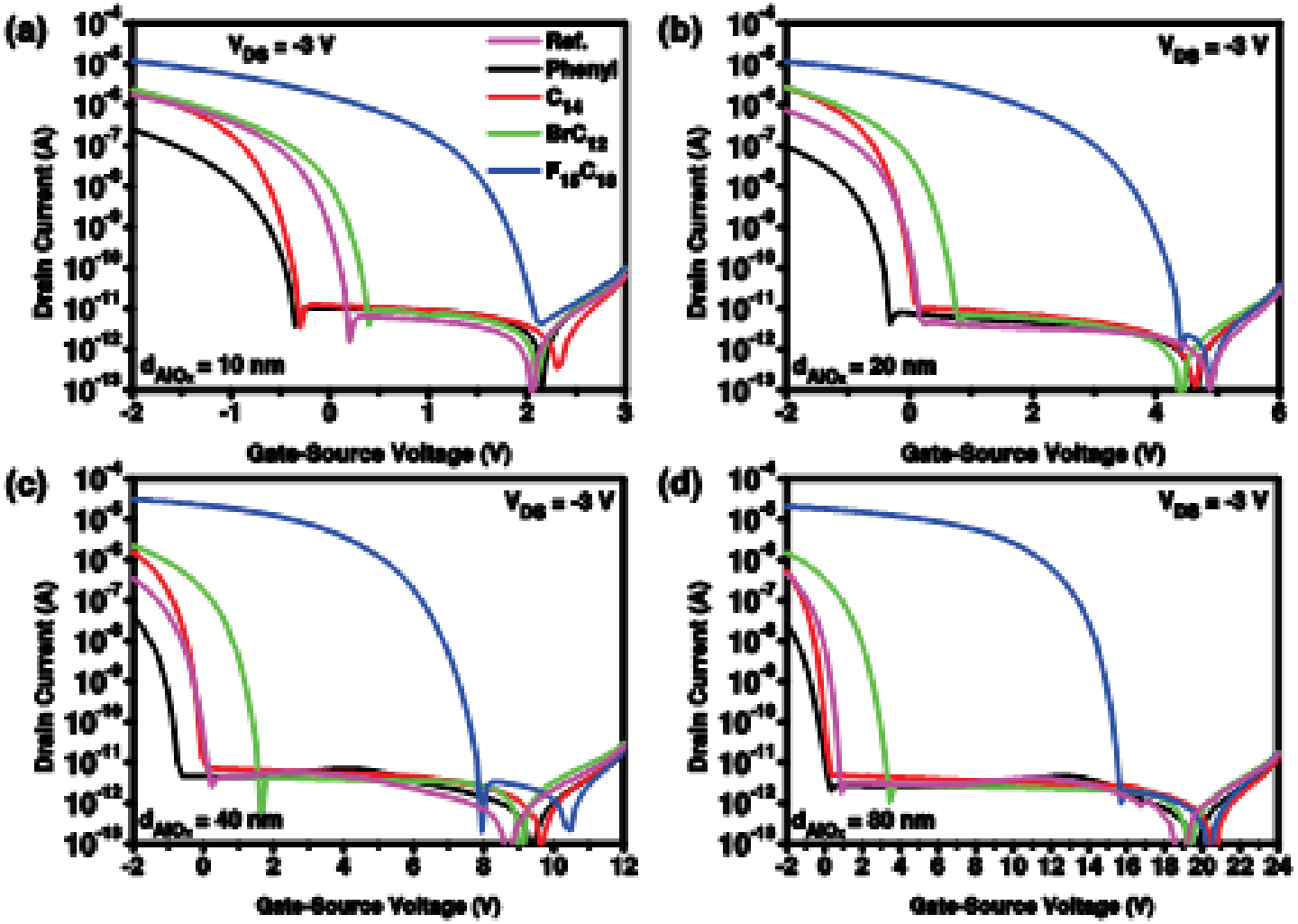

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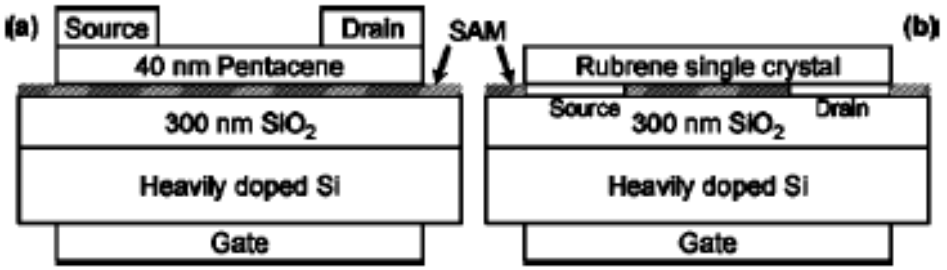
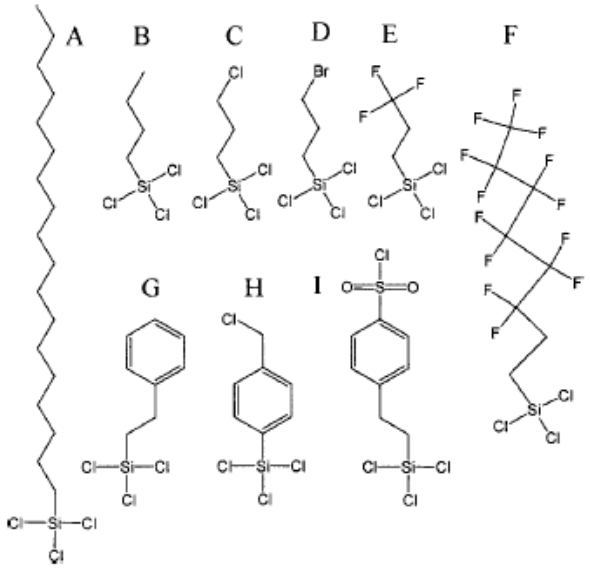
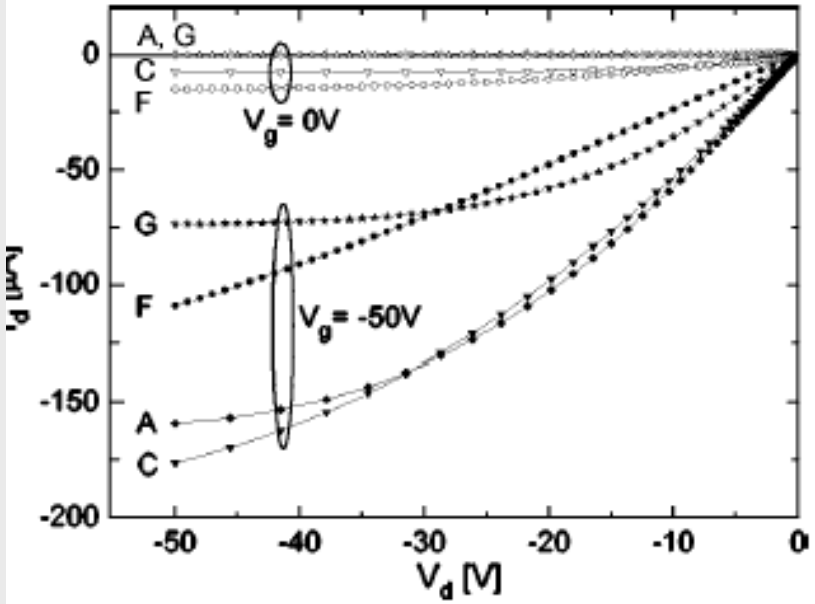
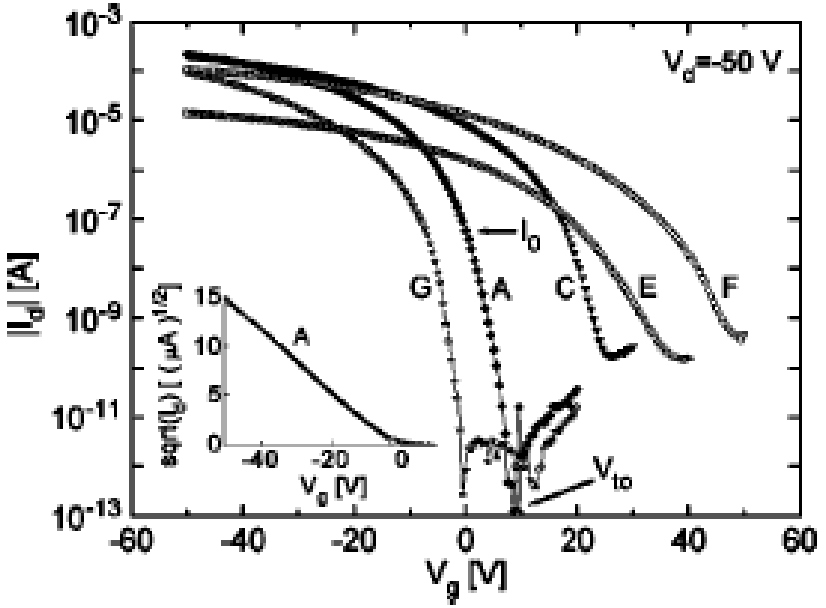








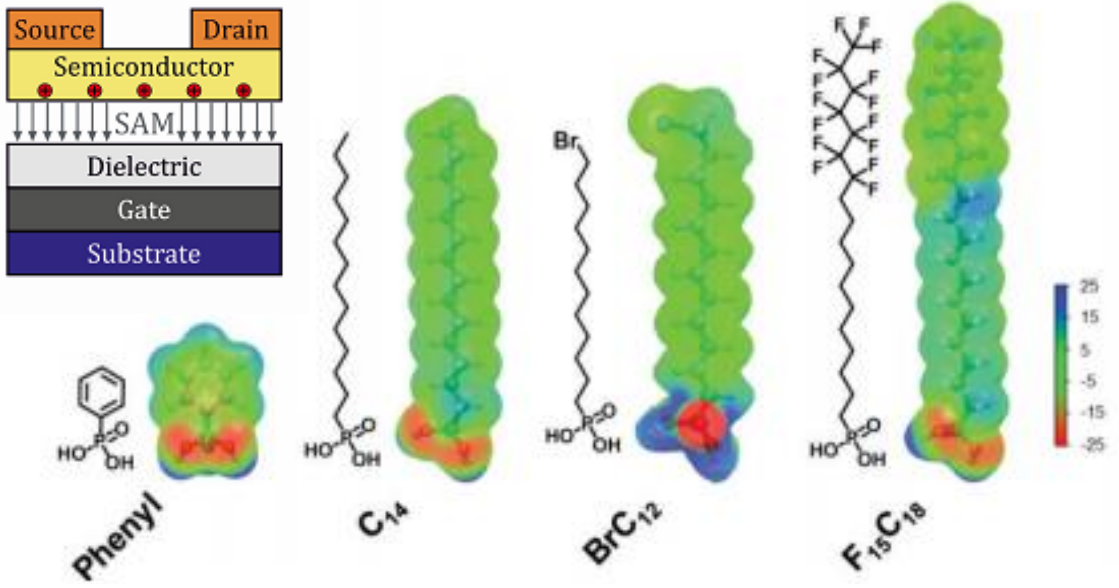
Dipoles at the insulator/semiconductor interface

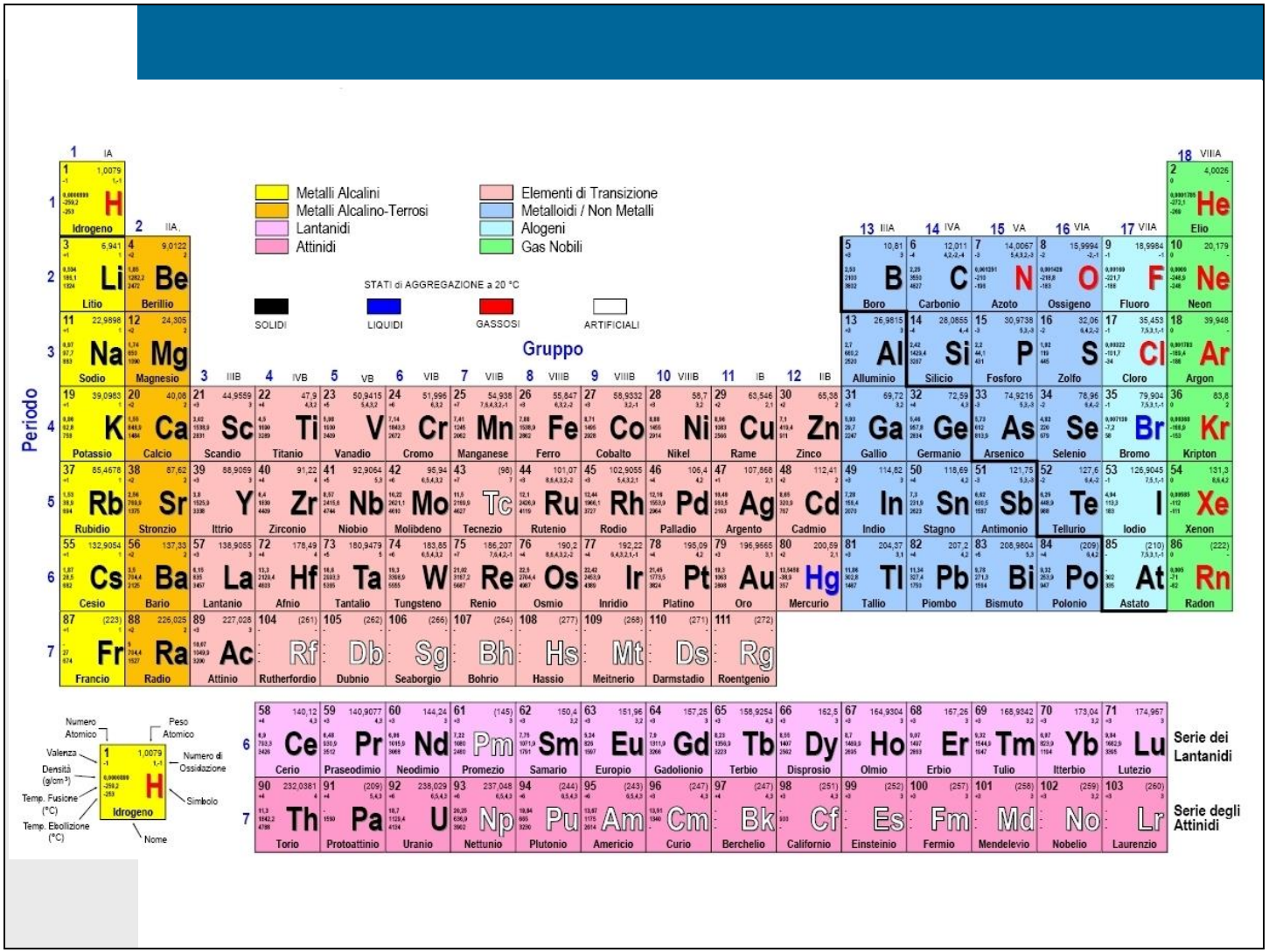
	Θ (deg)	μ (cm^2/V s)	V_t (V)	V_{to} (V)	S (V/dec.)	$\lvert I_0 \rvert$ (A)
(A) Octadecyltrichlorosilane	95	0.96(16)	−3.7(1.0)	4.7	0.9	10^{-8}
(B) Butyltrichlorosilane	93	0.61(11)	−4.3(0.5)	4.7	1.1	10^{-8}
(C) 3-Chloropropyltrichlorosilane	75	0.71(09)	1.5(1.8)	16	1.8	10^{-6}
(D) 3-Bromopropyltrichlorosilane	80	0.74(13)	2.8(2.8)	17	2	10^{-6}
(E) Trichloro(3,3,3-trifluoropropyl)silane	91	0.03(0.1)	22.7(5.2)	33	4.9	10^{-7}
(F) 1H,1H,2H,2H-Perfluorooctyl-trichlorosilane	105	0.15(0.2)	26(2.0)	44	4.9	10^{-6}
(G) Phenethyltrichlorosilane	92	0.71(11)	−12.7(1.2)	−1.5	0.9	10^{-12}
(H) 4-(Chloromethyl)phenyltrichlorosilane	88	0.56(12)	−7(1)	4	1.2	10^{-8}
(I) 2-(4-Chlorosulfonylphenyl)ethyltrichlorosilane	90	0.36(05)	25(3)	49	4.4	10^{-5}

Electronegative functional groups lead to a V_T variation towards more positive values

Pernstich et al. J. Appl. Phys. 96, 11, 2004
Jang et al. Appl. Phys. Lett. 90, 132104, 2007

Dipoles at the insulator/semiconductor interface

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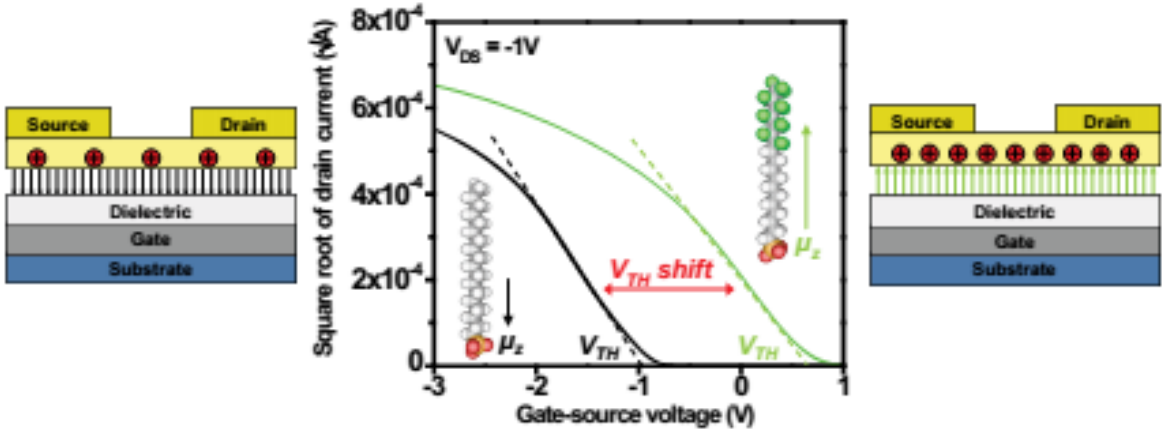

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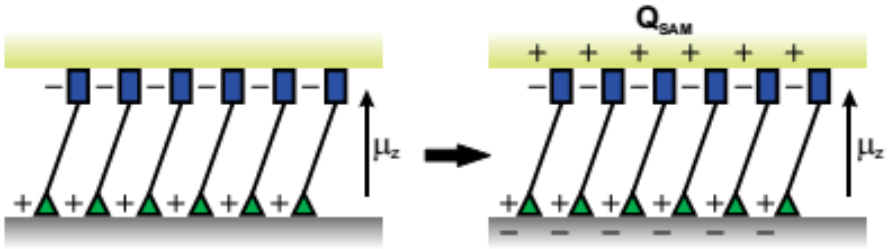

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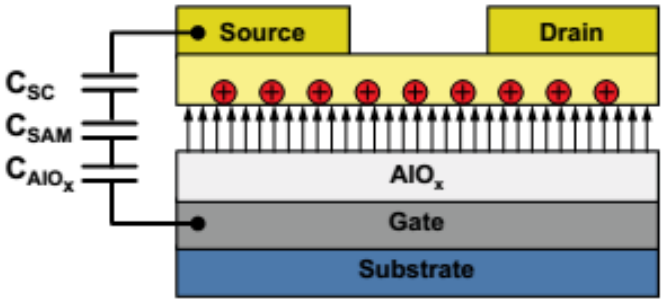

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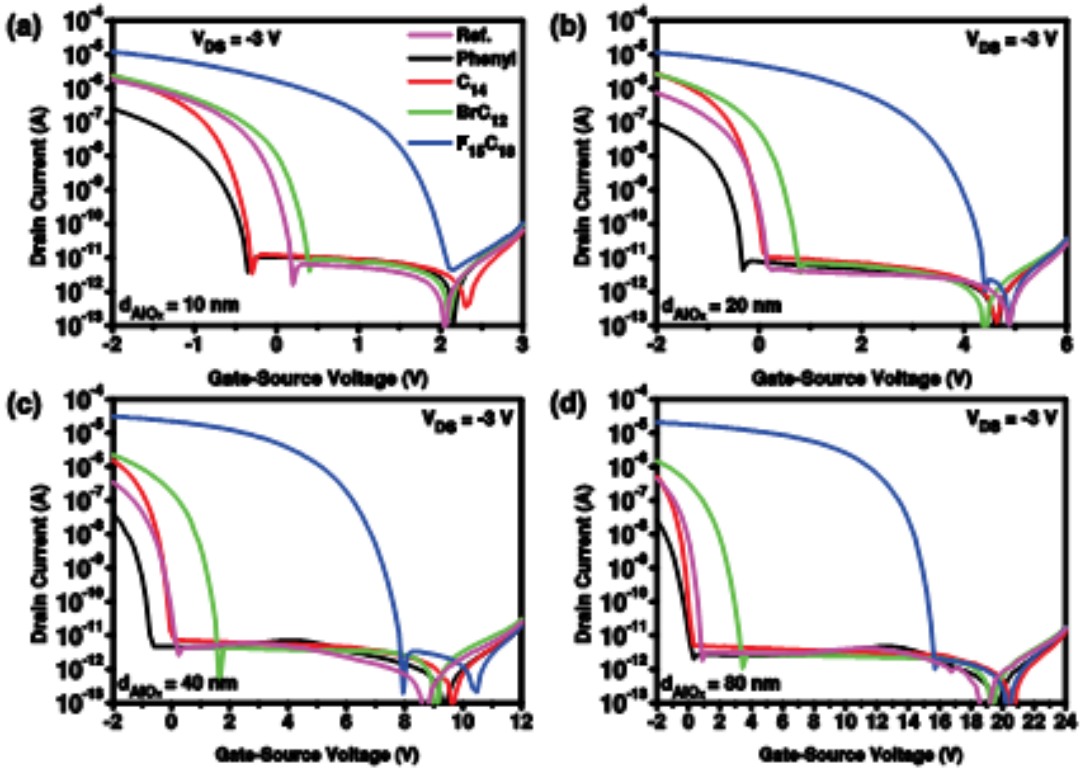

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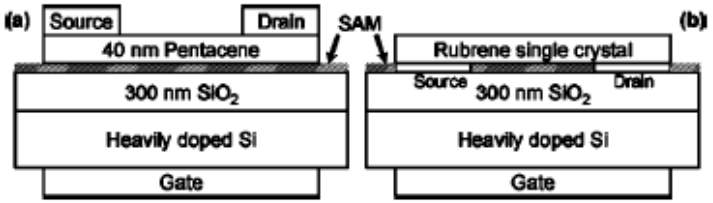

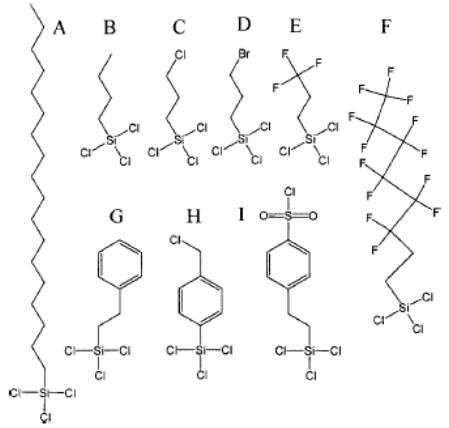

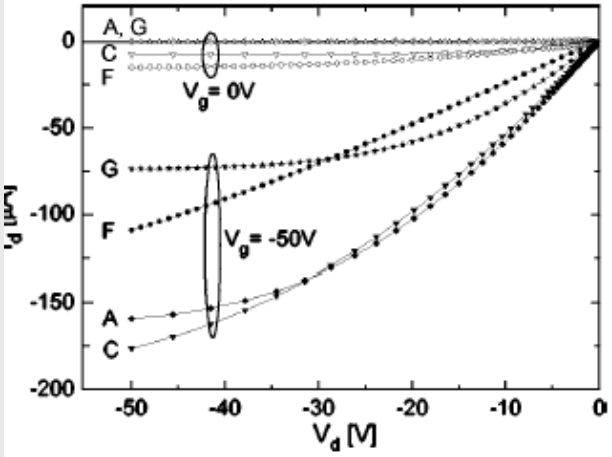

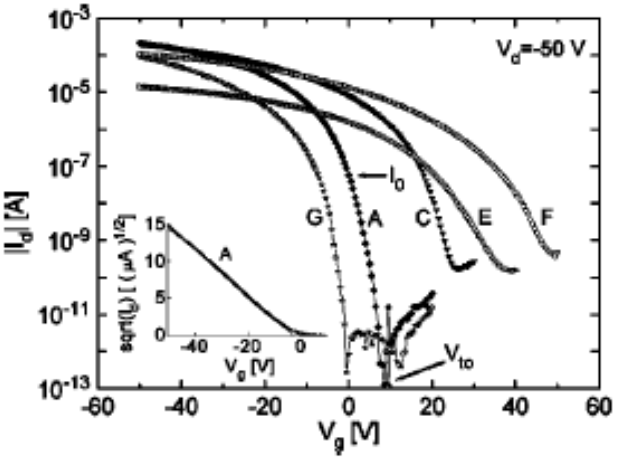

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(B) Butyltrichlorosilane	93	0.61(11)	−4.3(0.5)	4.7	1.1	10^{-8}
(C) 3-Chloropropyltrichlorosilane	75	0.71(09)	1.5(1.8)	16	1.8	10^{-6}
(D) 3-Bromopropyltrichlorosilane	80	0.74(13)	2.8(2.8)	17	2	10^{-6}
(E) Trichloro(3,3,3-trifluoropropyl)silane	91	0.03(0.1)	22.7(5.2)	33	4.9	10^{-7}
(F) 1H,1H,2H,2H-Perfluorooctyl-trichlorosilane	105	0.15(0.2)	26(2.0)	44	4.9	10^{-6}
(G) Phenethyltrichlorosilane	92	0.71(11)	−12.7(1.2)	−1.5	0.9	10^{-12}
(H) 4-(Chloromethyl)phenyltrichlorosilane	88	0.56(12)	−7(1)	4	1.2	10^{-8}
(I) 2-(4-Chlorosulfonylphenyl)ethyltrichlorosilane	90	0.36(05)	25(3)	49	4.4	10^{-5}

Electronegative functional groups lead to a V_T variation towards more positive values

Pernstich et al. J. Appl. Phys. 96, 11, 2004
Jang et al. Appl. Phys. Lett. 90, 132104, 2007

Bias stress

Bias Stress

Se il dipositivo viene sottoposto ad una polarizzazione continua le sue caratteristiche elettriche possono variare nel tempo

Diminuzione della corrente di uscita, indotta da uno shift della tensione di soglia

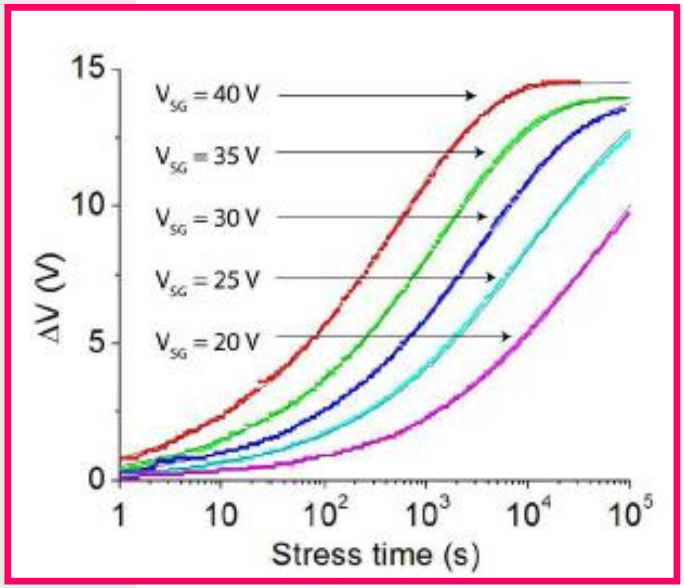
L'elevata concentrazione di stati trappola fa si che i portatori di carica vengano via via intrappolati e sottratti alla conduzione!

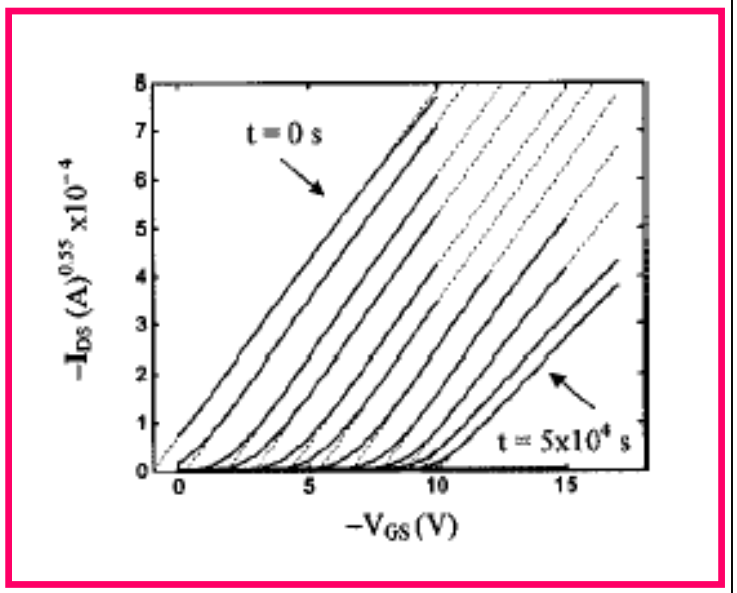
Vt tende a traslare verso valori più elevati in modulo

Bias Stress

Il fenomeno dipende prevalentemente dalla Vgs

Il fenomeno tende a saturare





Bias Stress

La variazione di Vt dovuta alla polarizzazione continua è dovuta all'intrappolamento di lacune

Considerando p la concentrazione di lacune iniziale e pt quella di lacune intrappolate

$$\Delta V_{th} = \frac{qp_t}{C_{ins}}$$

Affinchè avvenga intrappolamento deve esserci una lacuna libera, ma anche una trappola vuota, da cui il rate di intrappolamento diventa:

$$\frac{dp_t}{dt} = k(p - p_t)(N_t - p_t) \qquad \Delta V_{th}(t) \propto \left(1 - e^{\left(-\frac{t}{\tau}\right)^{\beta}}\right)$$

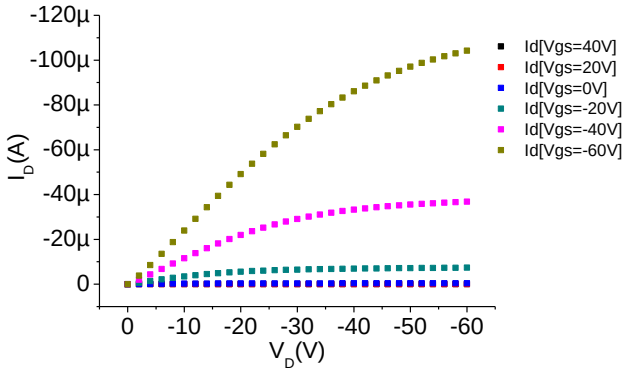
Bias Stress

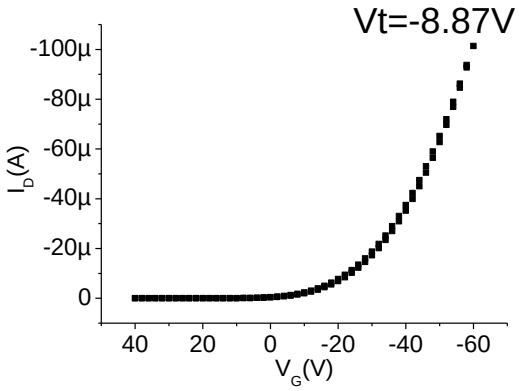
Se nel frattempo non subentrano altri fenomeni parassiti (es.: modifica permanente dello strato attivo → ossidazione del semiconduttore), il fenomeno è reversibile!

a) Rimuovere la polarizzazione e aspettare che gli stati trappola si svuotino

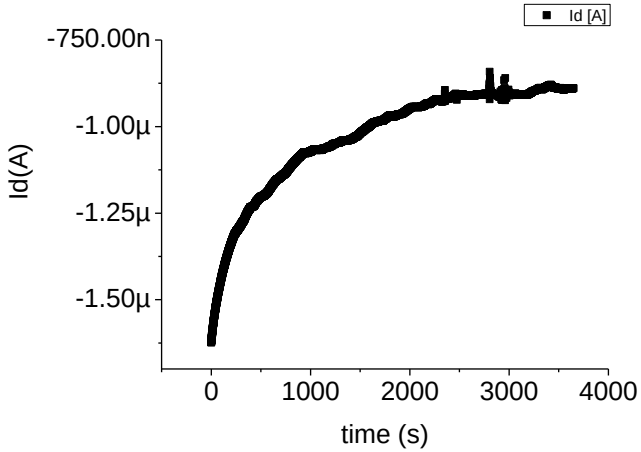
b) Applicare una polarizzazione opposta

Bias Stress – caso 1





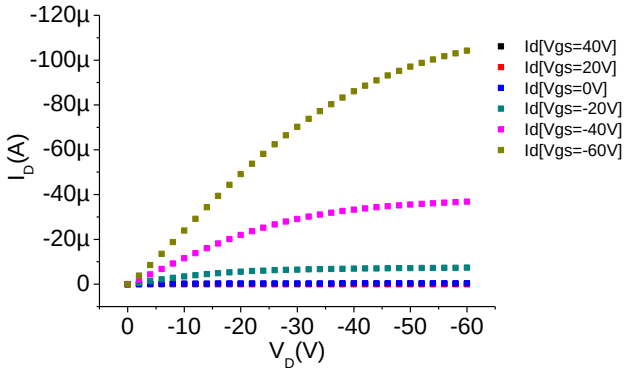
Vd=-20
Vg=-10
60 min

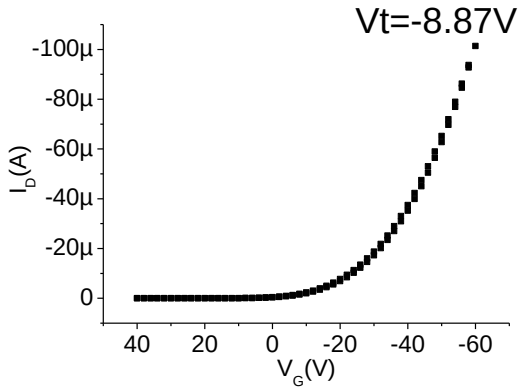


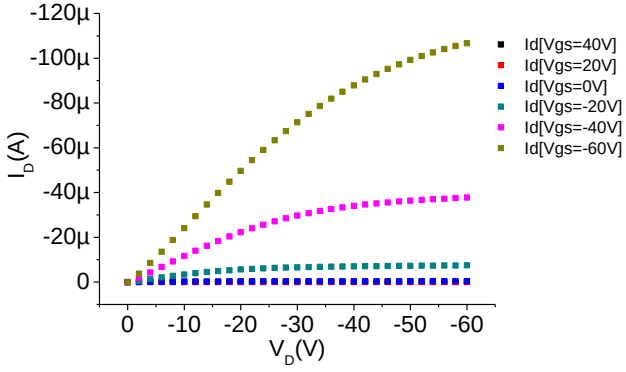
La corrente decresce

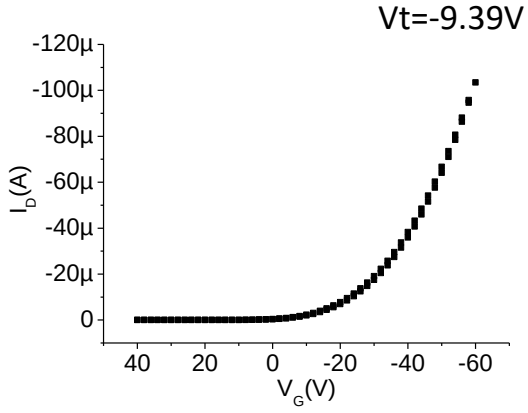
Vt shift

Bias Stress – caso 1

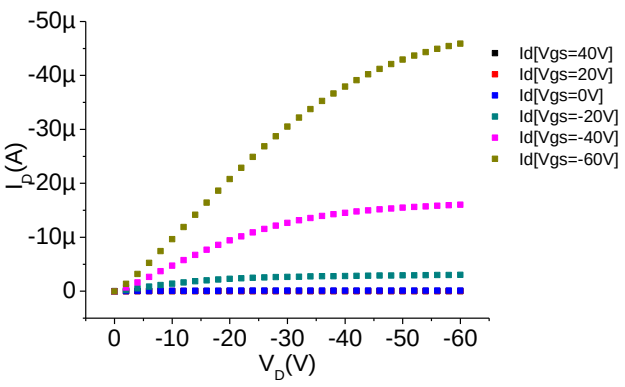


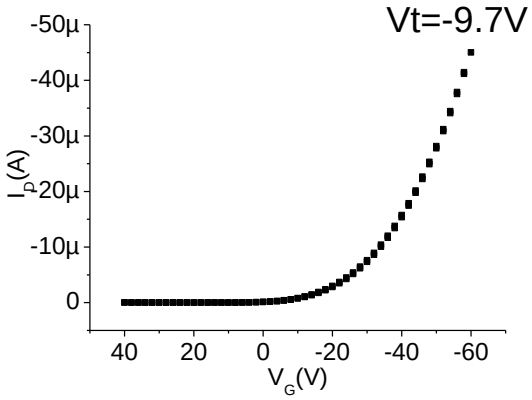




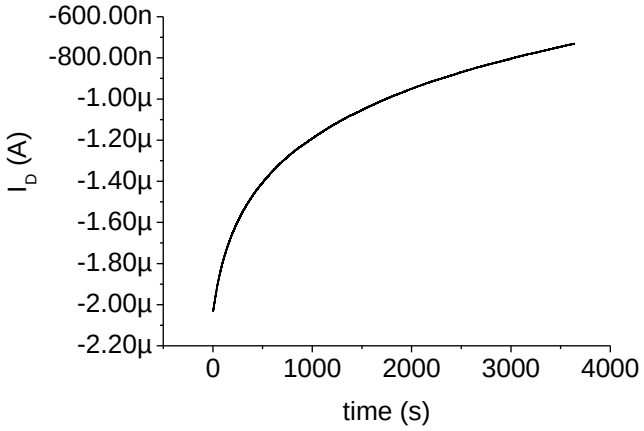


Bias Stress – caso 2





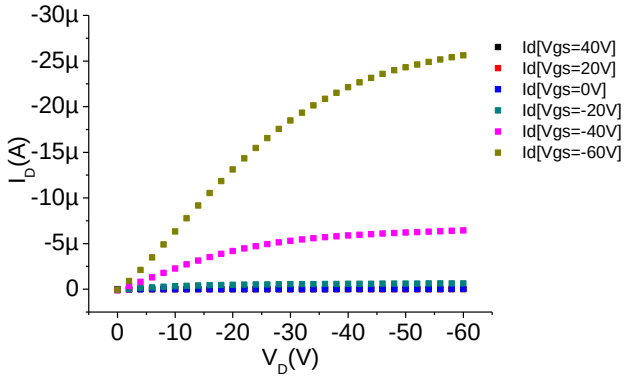
Vd=-5
Vg=-40
60 min

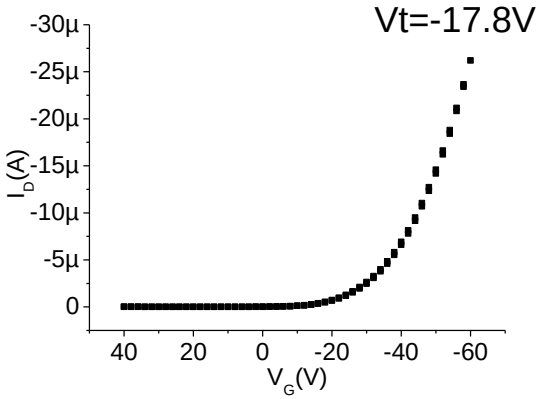


La corrente decresce

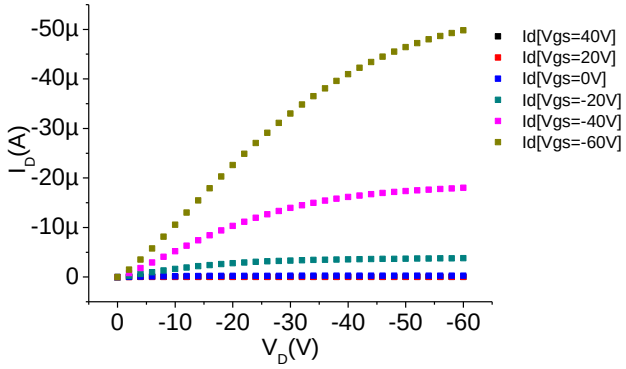
Vt shift

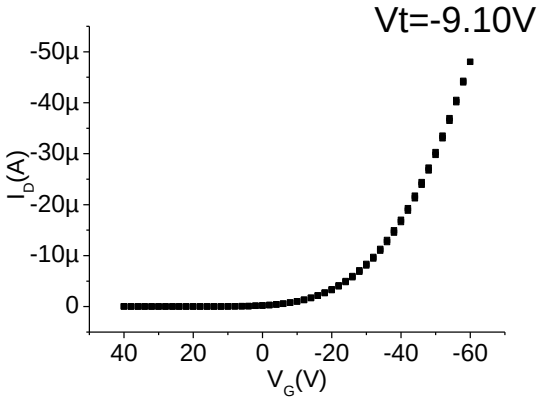
Bias Stress





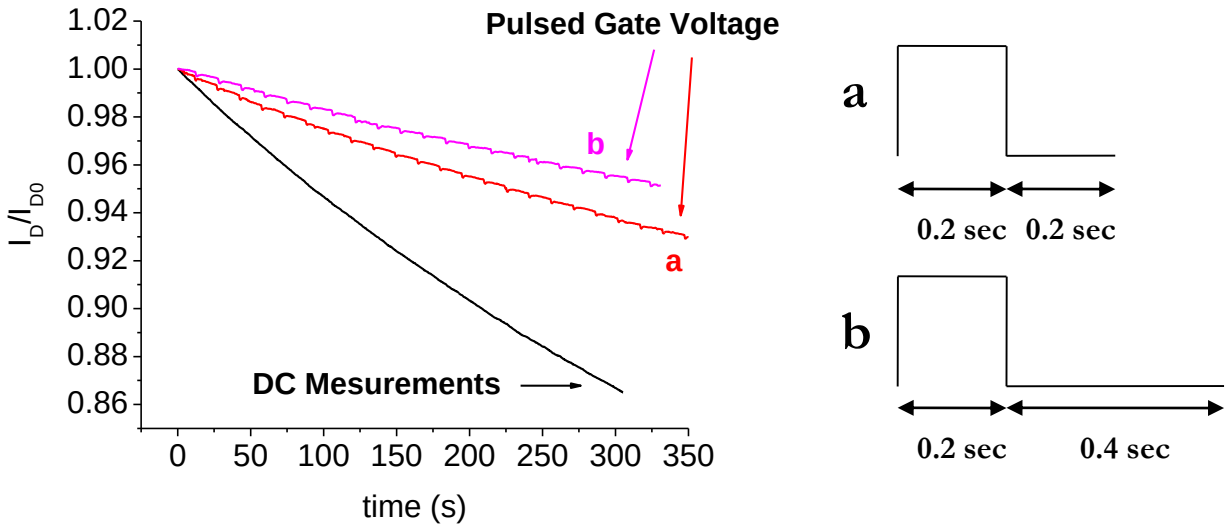
Se applico una polarizzazione positiva al gate (Vgs=+40V per 60 secondi) → detrappolamento! Vt ritorna al valore iniziale





Bias Stress

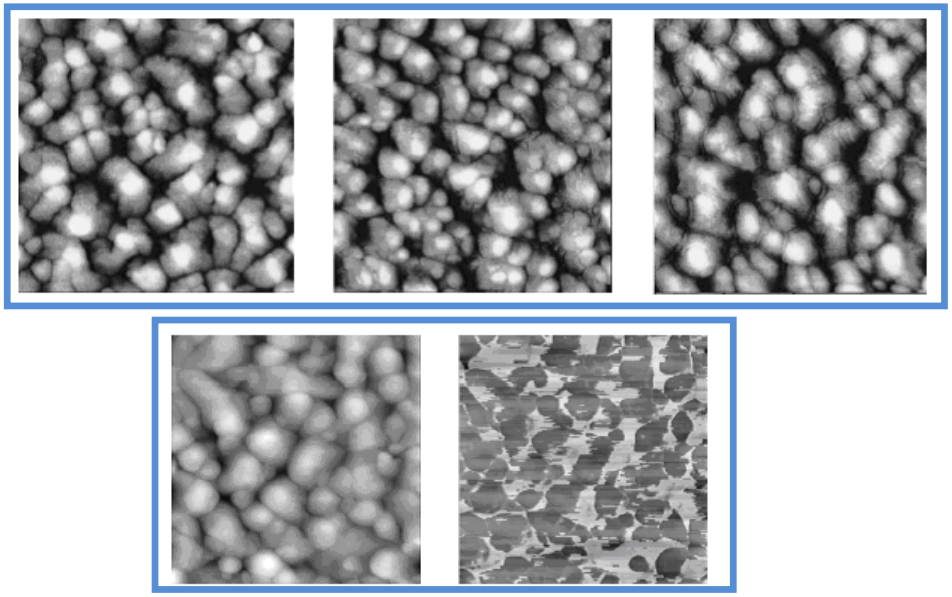
Il fenomeno di bias stress può essere fortemente ridotto applicando una polarizzazione impulsata al gate e settando opportunamente il duty cycle



Degradazione dello strato attivo

Degradazione dello strato attivo: H_2O

L'acqua (H_2O) penetra all'interno dello strato attivo del semiconduttore organico raggiungendo l'interfaccia isolante-semiconduttore, modificando la morfologia del film stesso



Incremento della densità di trappole ai bordi di grano

Degradazione dello strato attivo:H_2O

Quando il dispositivo si trova nello **stato di "on"**

La maggiore concentrazione di stati trappola vicino al canale porta ad una marcata riduzione della mobilità, e, di conseguenza, della corrente di uscita

Quando il dispositivo si trova nello **stato di "off"**

(il che significa tensione di gate è inferiore alla tensione di soglia), la presenza di un sottile film polare incrementa la conduttività tra source e drain, questo comporta un aumento della corrente di off e un decremento del rapporto $|I_{on}|/|I_{off}|$

Degradazione dello strato attivo: O_2

A causa della sua elettronegatività l'ossigeno attrae elettroni dalle molecole del semiconduttore → accumulo di lacune nel canale!

- *Aumento corrente di off*
- *Shift della tensione di soglia*

Processo reversibile

Inoltre, può portare ad un processo di ossidazione della molecola

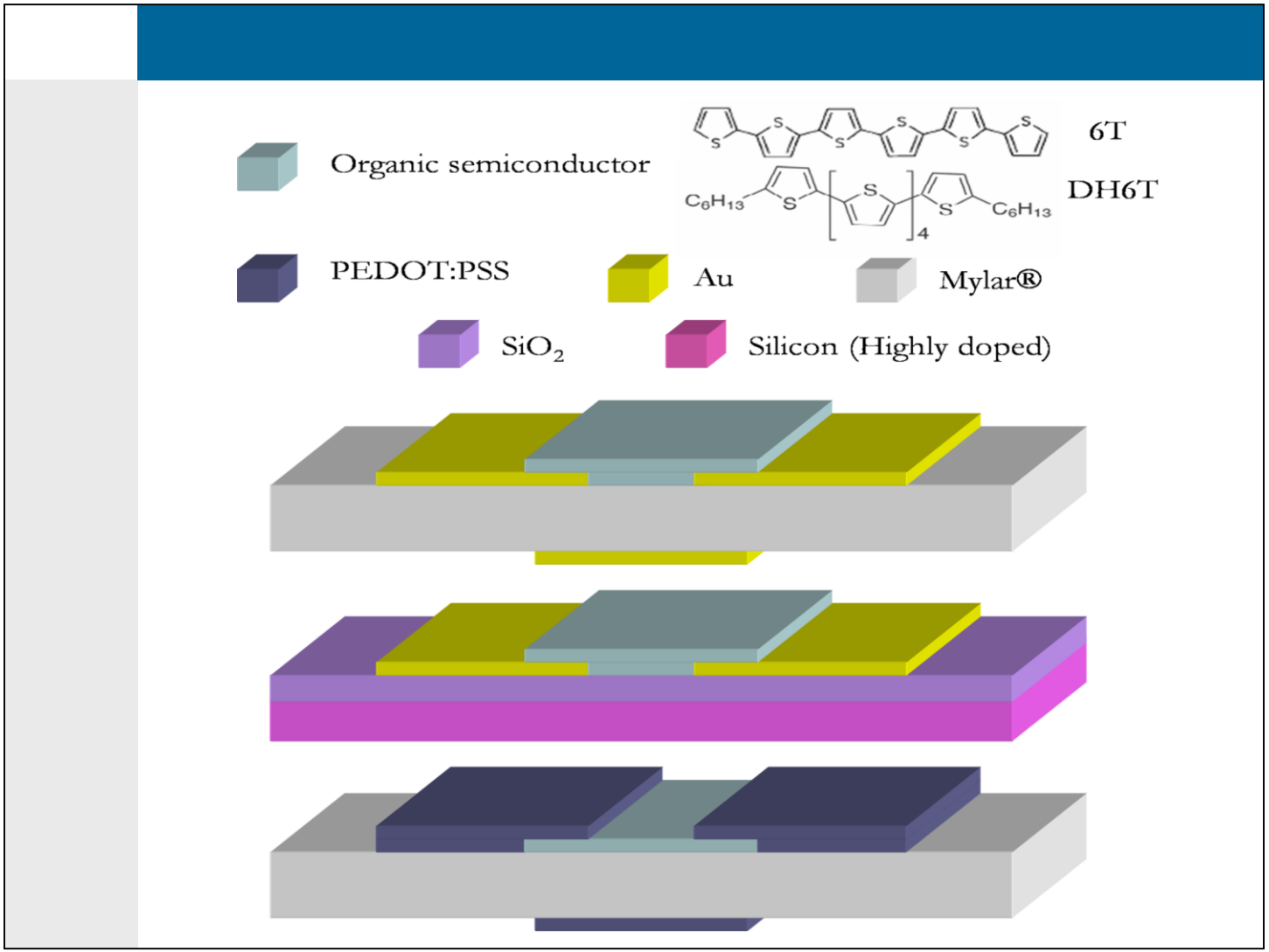
incrementando l'altezza di barriera nel processo di hopping

- *Diminuzione della mobilità*

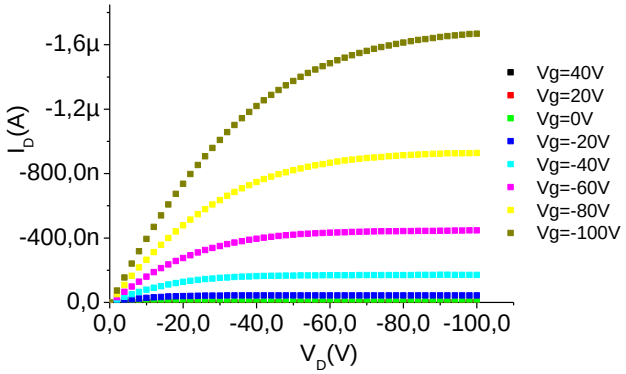
Processo irreversibile

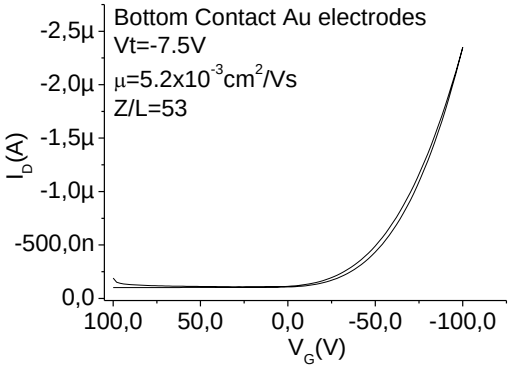
Incapsulamento

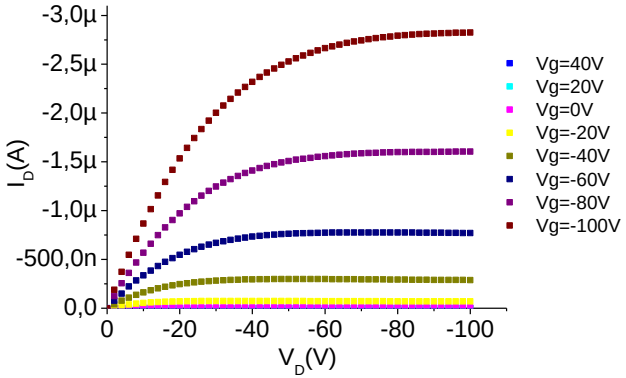
- La barriera deve essere sufficientemente robusta da permettere di maneggiare l'OTFT senza provocare danni, nonché proteggerlo da possibili urti, vibrazioni, etc.
- Il processo di deposizione deve essere compatibile con i materiali utilizzati per la realizzazione del dispositivo e in particolare non deve danneggiare lo strato attivo;
- La barriera deve essere flessibile
- Il rate di permeazione dell'acqua (Water Vapor Transmission Rate, WVTR) inferiore a $10^{-6}g/m^2$ day
- Il rate di permeazione dell'ossigeno (Oxygen Transmission Rate, OTR) tra 10^{-5} e $10^{-3}cm^3/m^2$ day per essere considerato un buon package
- La barriera deve essere stabile nel tempo.

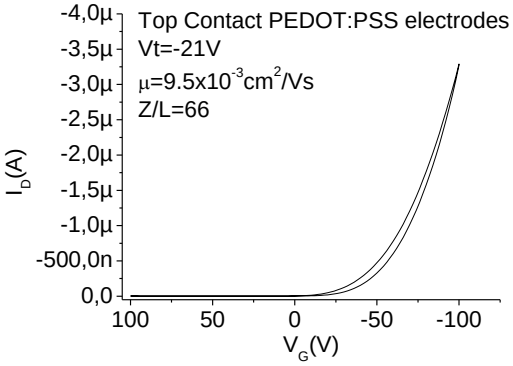

Organic semiconductor
6T
DH6T
PEDOT:PSS
Au
Mylar®
SiO_2
Silicon (Highly doped)

6T OFETs on Mylar

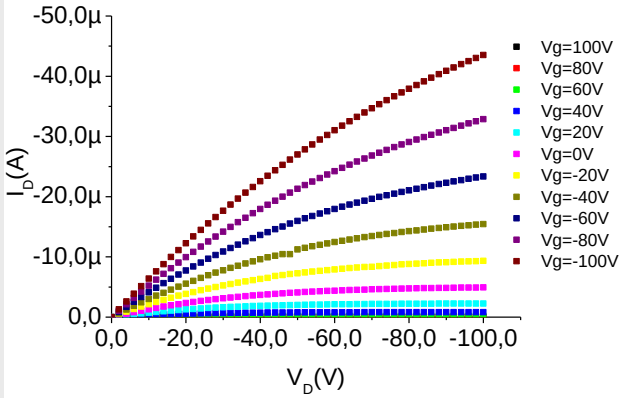


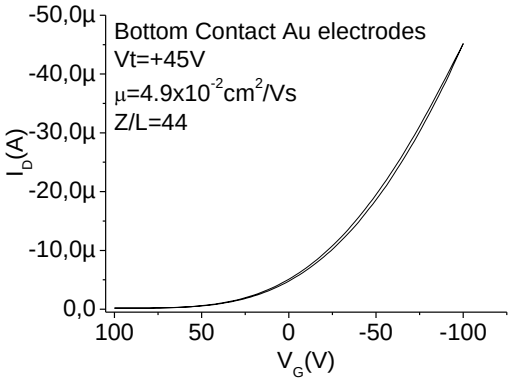


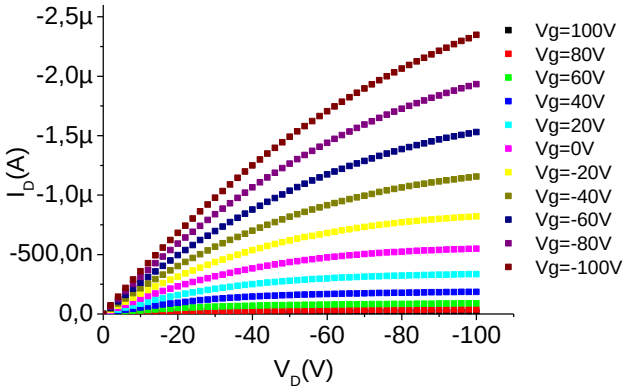


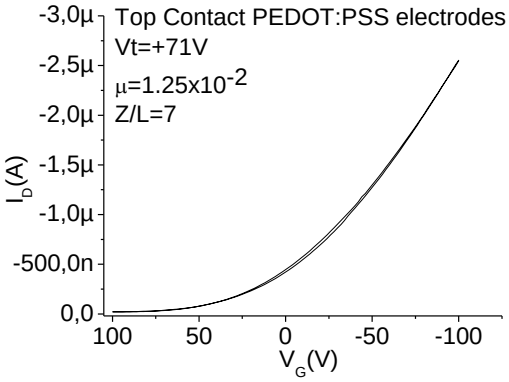


DH6T OFETs on Mylar

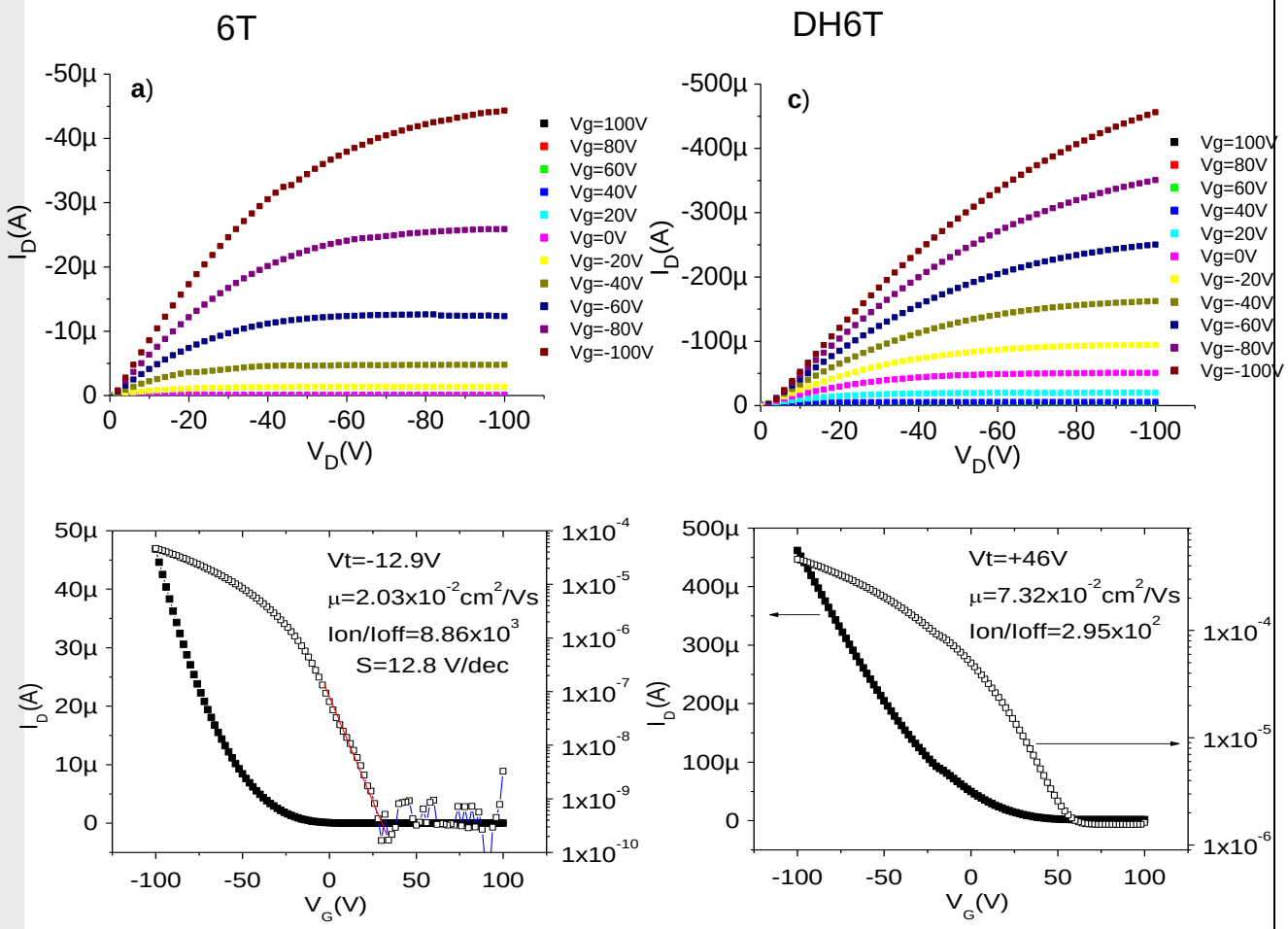








6T-DH6T OFETs on Silicon



6T vs. DH6T: results

Despite their very similar chemical structure, 6T and DH6T semiconductors lead to a very different electrical behaviour.

- Negative threshold voltages for 6T (accumulation device)
- High positive threshold voltages for DH6T (depletion device)
- DH6T devices: higher channel mobility

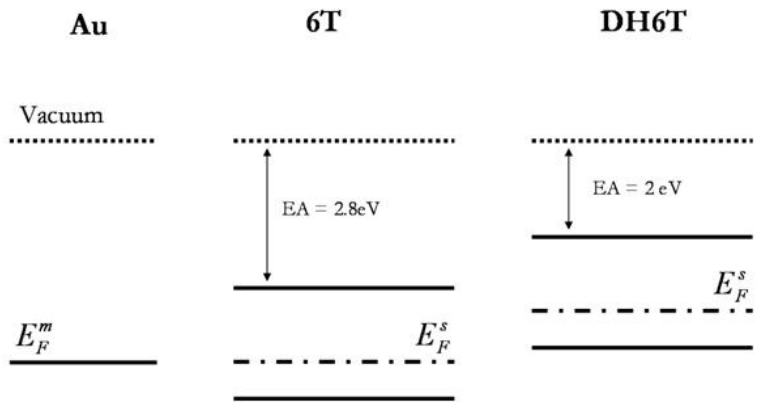
The presence of the alkyl chain as terminal substituents is the only difference between the two materials and has to be responsible for this behaviour.

Alkyl chain substituents effects

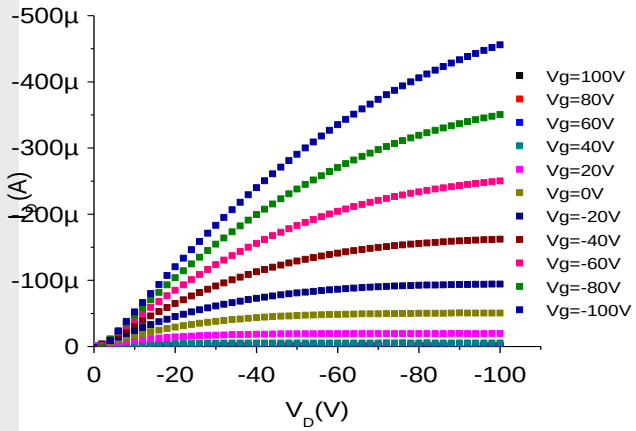
The 0.15 eV lower IE of DH6T results in a **lower hole injection barrier** at the DH6T/electrode interface compared to the 6T/electrode interface.

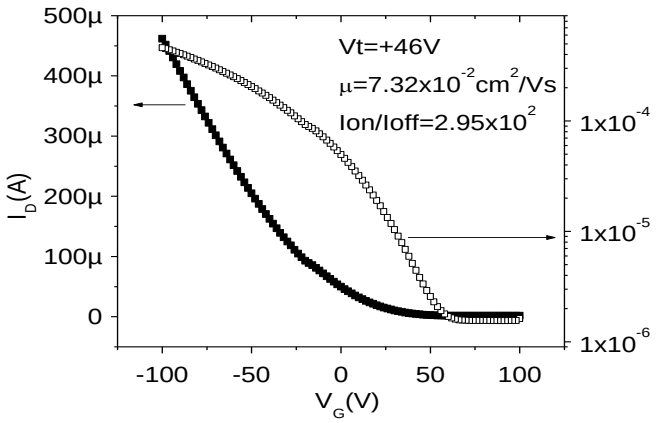
Consequently, hole injection into the DH6T film is more efficient than for 6T films, enabling a higher hole concentration in the DH6T channel at a certain gate voltage.

In addition, the lower IE of DH6T implies that **p-type doping by oxygen is more efficient** than for 6T.

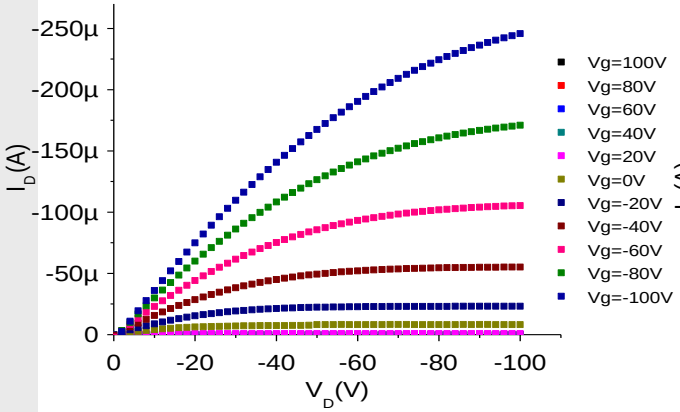


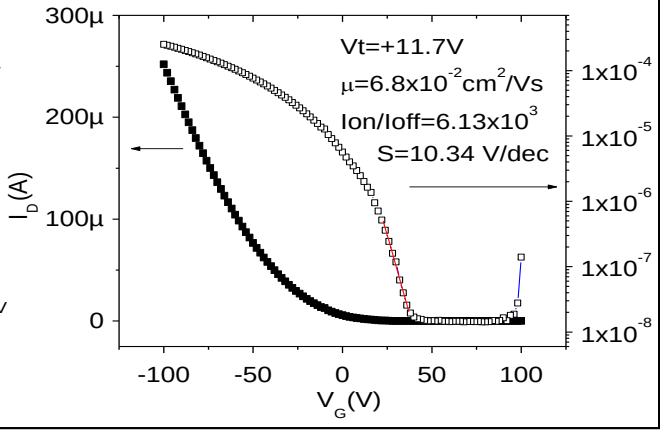
Oxygen doping process



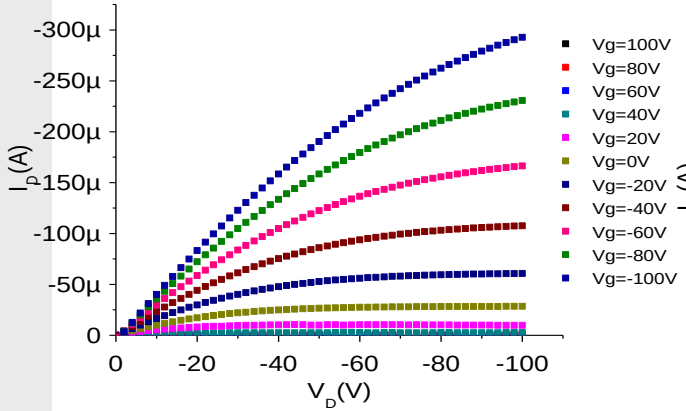


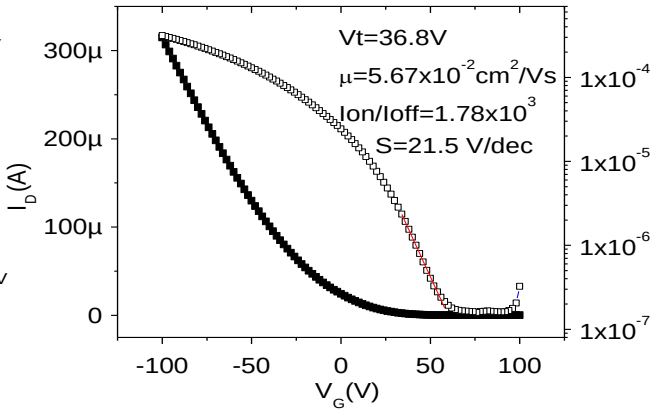
Dedoping effect after thermal annealing





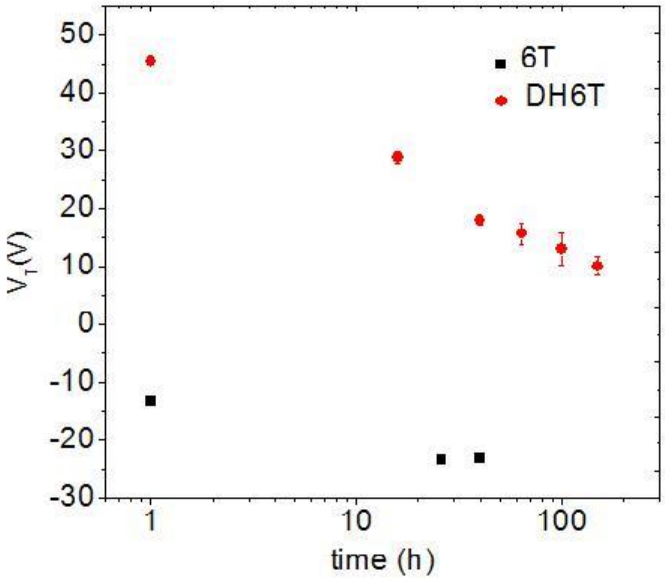
Oxygen doping process

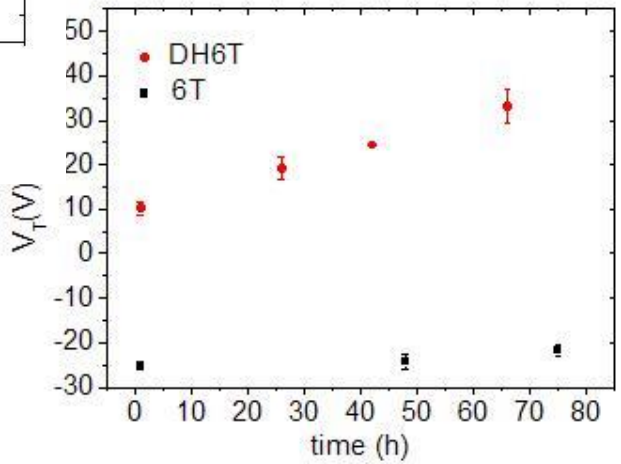




Redoping effect upon exposure to Air

Oxygen doping process





Effects on threshold voltage and mobility

The indirect doping effect is clearly confirmed the experiments reported in the previous slides.

A huge Threshold Voltage shift is visible upon sample annealing in inert gas for both DH6T; moreover, mobility is not significantly affected (within the error bar) and Ioff decreases of more of one order of magnitude, again confirming that dedoping is taking place.

Such a Threshold voltage shift was recorded both for 6T and DH6T samples, however, for the latter the voltage shift (as well as the Ioff decrease) is much more pronounced and faster, as could be predictable from the lower Ionization Energy of this material.

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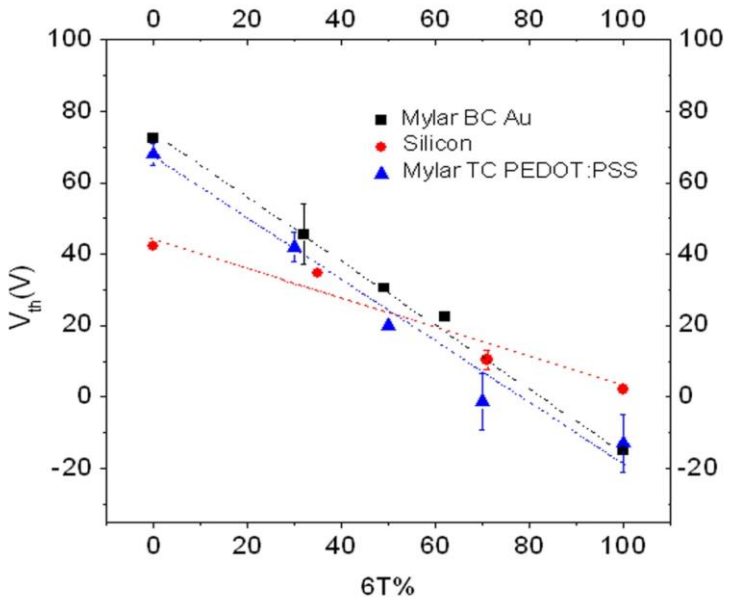
What if we co-deposit the two materials?

Tuning threshold voltage



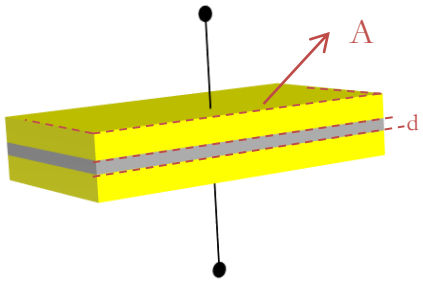
V_T varies linearly as function of 6T content within the mixed film

Low Voltage OFETs

Piero Cosseddu Ph. D.
Dept. Of Electrical and Electronic Engineering
University of Cagliari (Italy)

Towards low voltage OTFTs

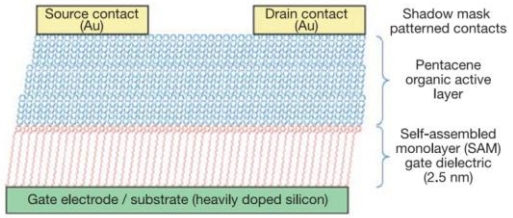
Is it possible to scale down the operational voltages in OTFTs?

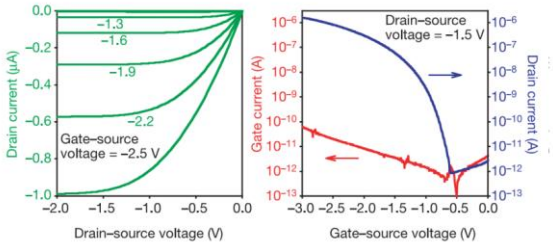


$$C_{ins} = \frac{\varepsilon_0 \varepsilon_r \uparrow}{d \downarrow} A$$

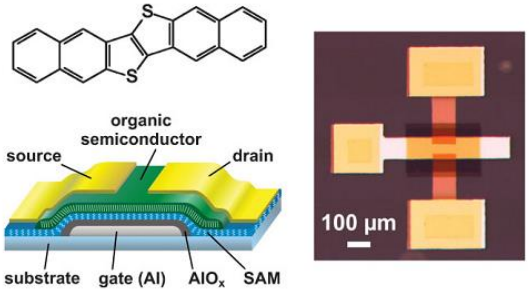
Increasing gate capacitance is the key factor for realizing low-voltage OFETs

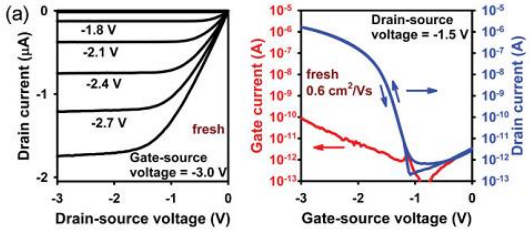
State of the art – SAMs and Polymers



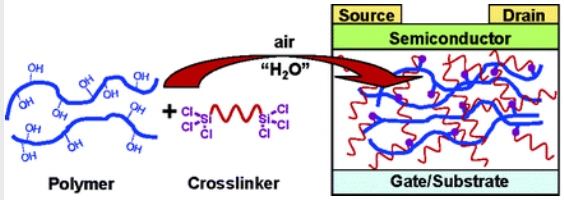


Halik et al., Nature, 2004, 431





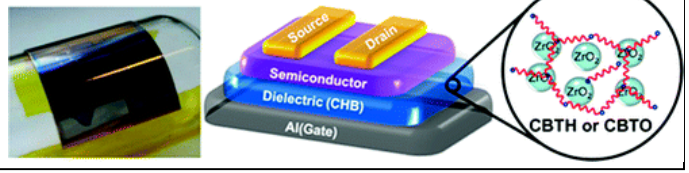
H. Klauk, et al. Nature 445, 745 2007 (2007)Zschieschang et al., Adv. Mater. 2010 , 22



CPB Dielectric

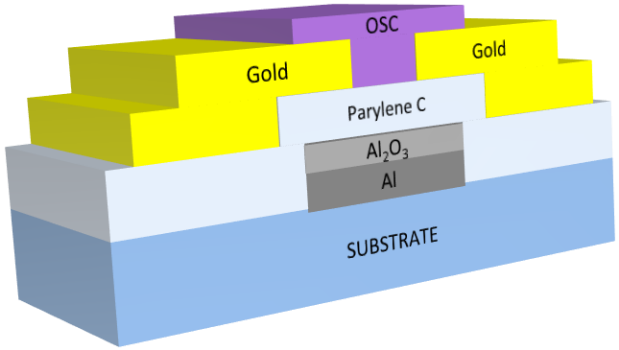
Young-geun Ha, et al. JACS, 2010, 132, 17426

Myung-Han Yoon, H. Yan, A. Facchetti, and T. J. Marks, JACS, 2005, 127, 10388



Low voltage OTFTs

Bottom gate, bottom contact structure on flexible PET substrate

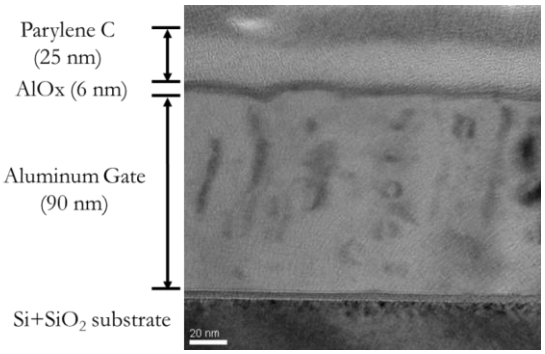


- **Gate: Aluminum**
- **Gate Dielectric:**

AlOx ***[UV-Ozone treatment at room temperature]***

Parylene C ***[deposited by CVD]***

[air-stable, robust, biocompatible and resistant to solvents; can be deposited in very thin films]

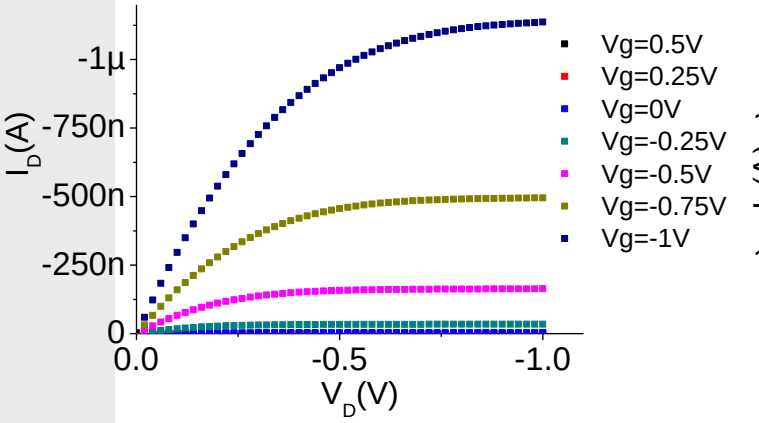


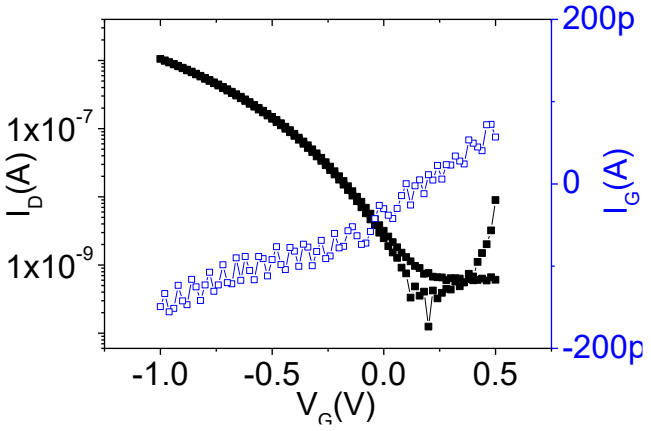
P. Cosseddu, et al. Appl. Phys. Lett. 100, 093305 (2012)

AlOx/Parylene C Double-Layer

Thermally evaporated pentacene as OS

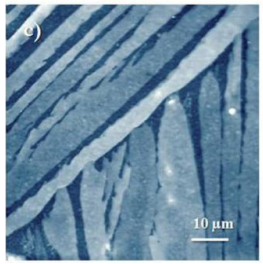
Insulating Structure	Capacitance [F/cm^2]	I_G [A] J_G[A/cm^2]	Vt [V]	μ [cm^2/Vs]	S [mV/dec]	Nt [cm^{-2}eV^{-1}]	OTFTs Yield [%]
AlOx	3.5 E-6	6 E-6 2.9 E-5	-1.2	3.3 E-3	360	1.1 E14	15%
AlOx + 25nm Parylene	1.3 E-7	4 E-10 1.9 E-9	-0.5	6 E-2	350	4 E12	95%





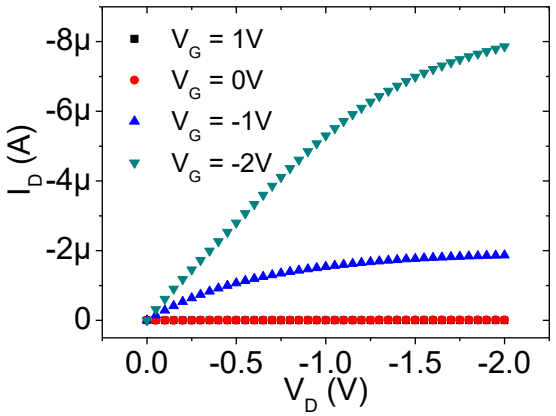
AlOx/Parylene C Double-Layer

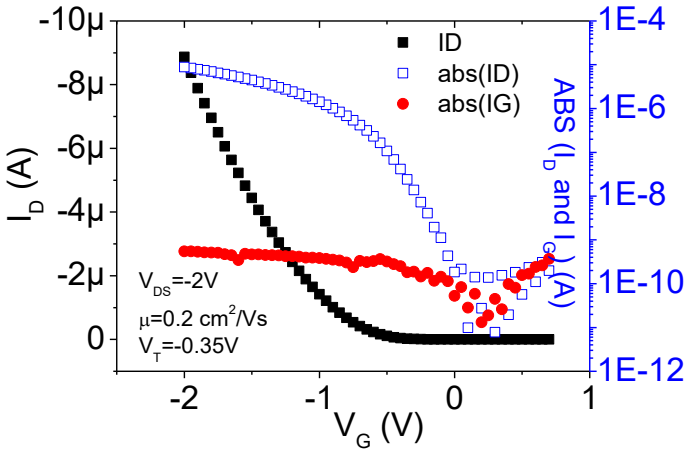
- *High yield*
- *Negligible hysteresis*
- *Very small leakage current*



TIPS-Pentacene

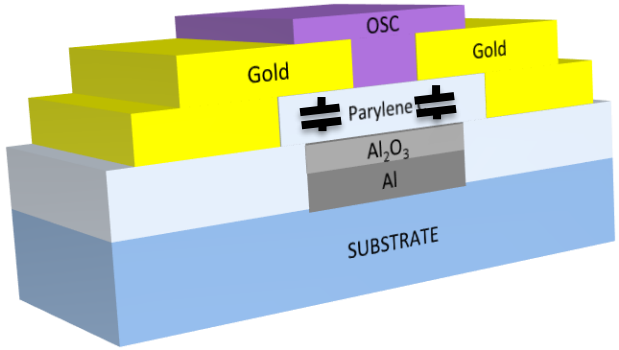
Insulating Structure	Capacitance [F/cm²]	I_G [A] J_G[A/cm²]	Vt [V]	µ [cm²/Vs]	S [mV/dec]	OTFTs Yield [%]
AlOx + Parylene	1.3 E-7	4 E-10 1.9 E-9	-0.2/-0.4	0.3	150	99%





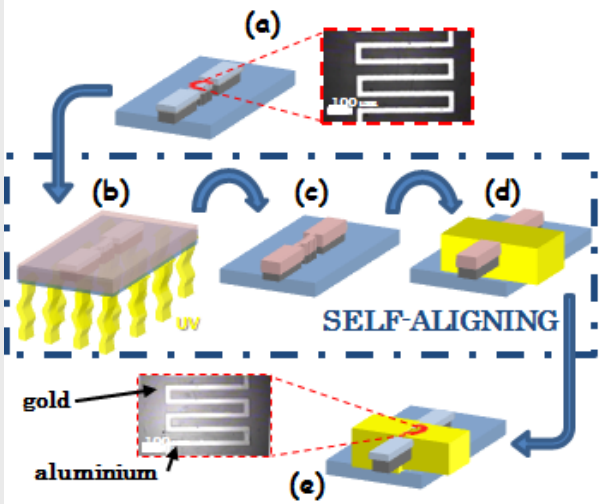
High Capacitance issues

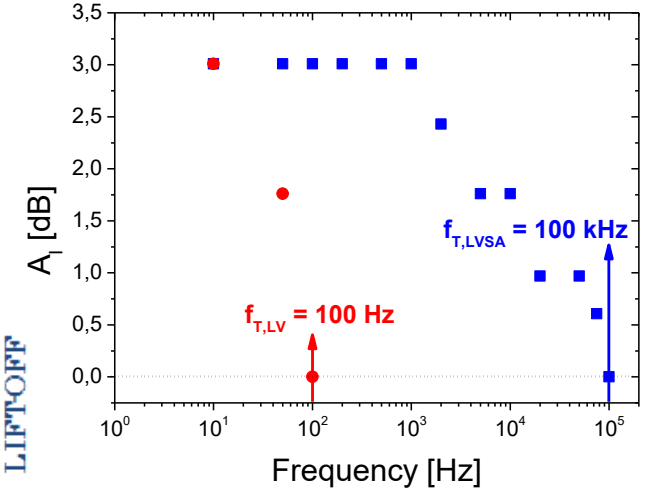
- *High gate dielectric capacitance means high parasitc capacitancies*
- *Overlapping between Source, Drain and Gate*

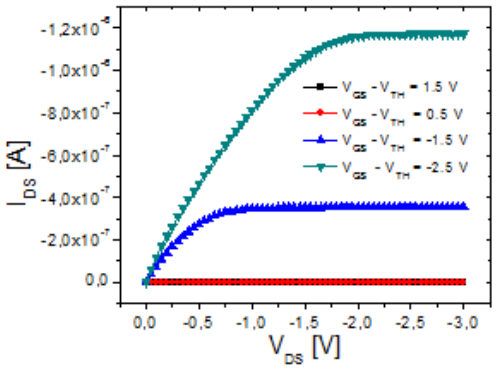


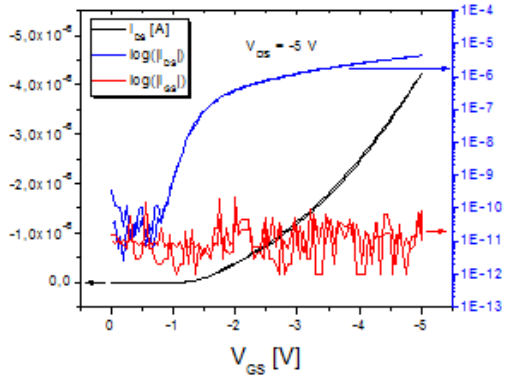
- *How to deal with this?*

Self-alignment process



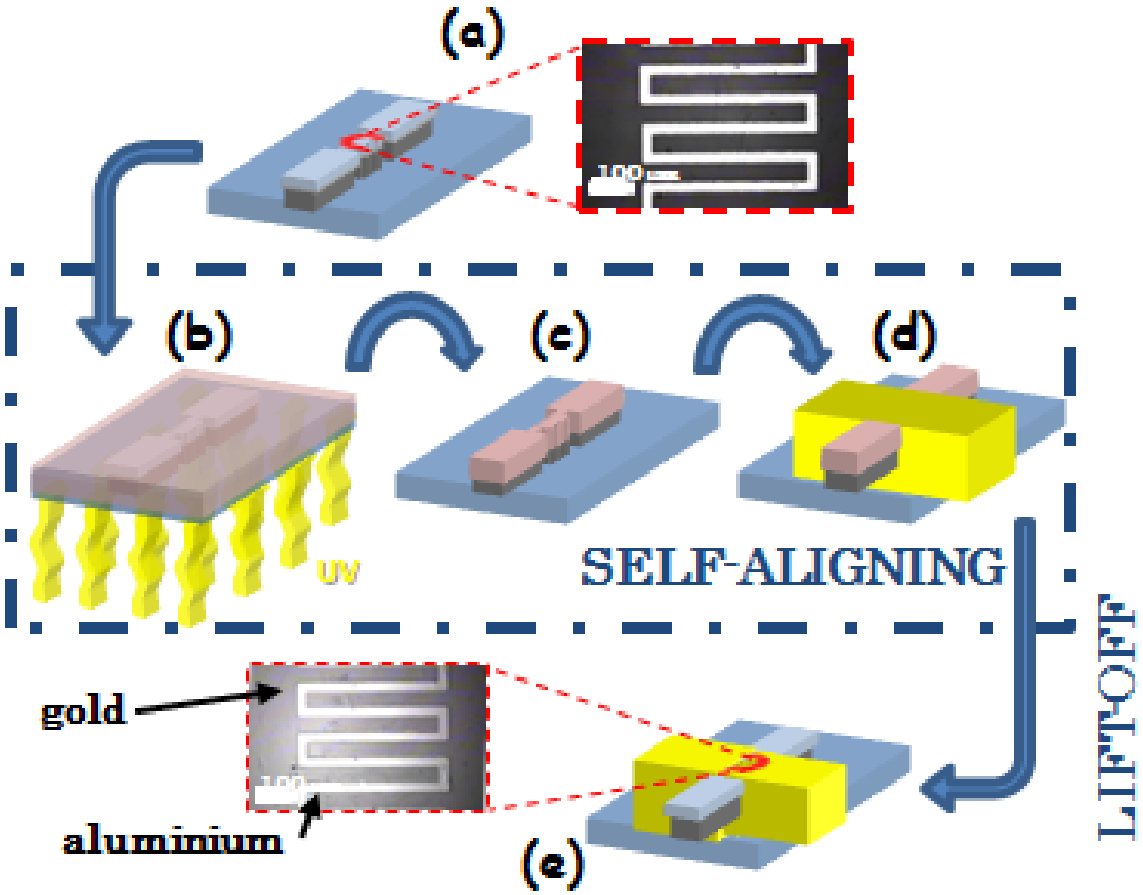




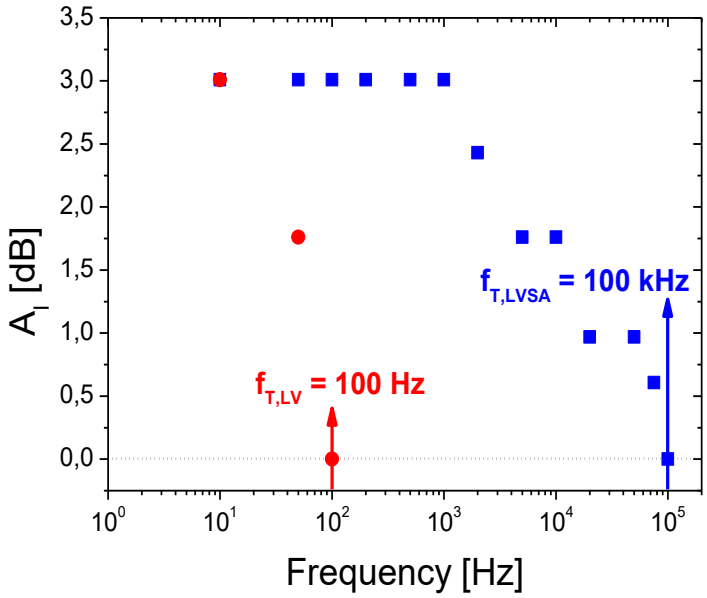


S. Lai, P. Cosseddu, G.C. Gazzadi, M. Barbaro e A. Bonfiglio, Org. Electr. 14, 754-761 (2013)

Self-alignment process

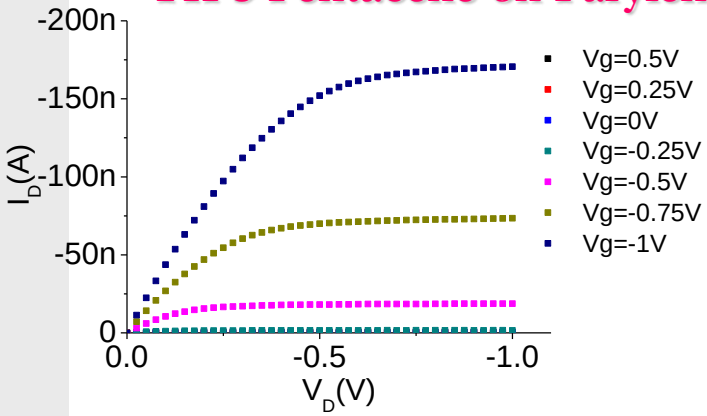


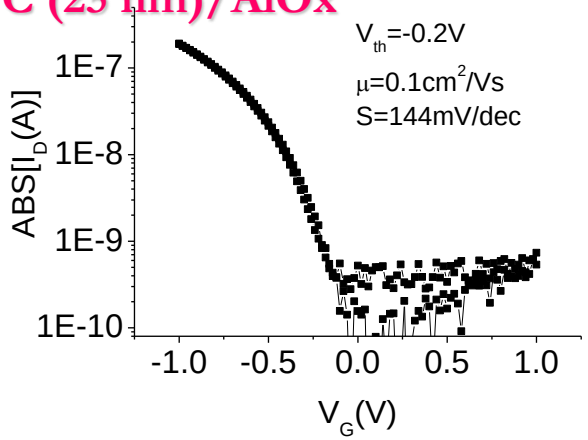
Self-alignment process



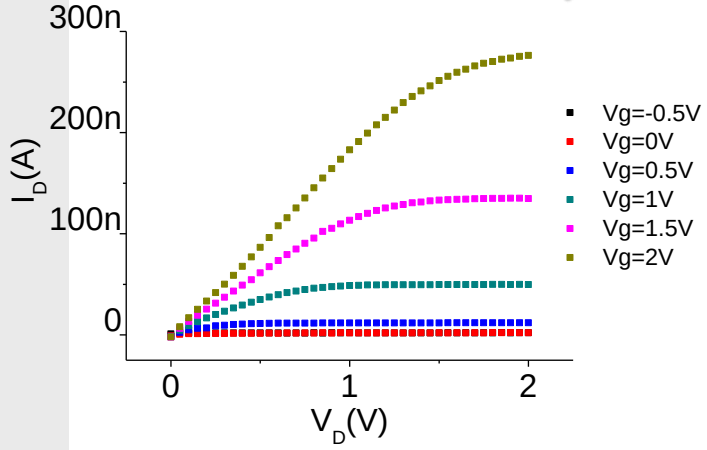
Low Voltage OFETs: Solution-Processable OSC

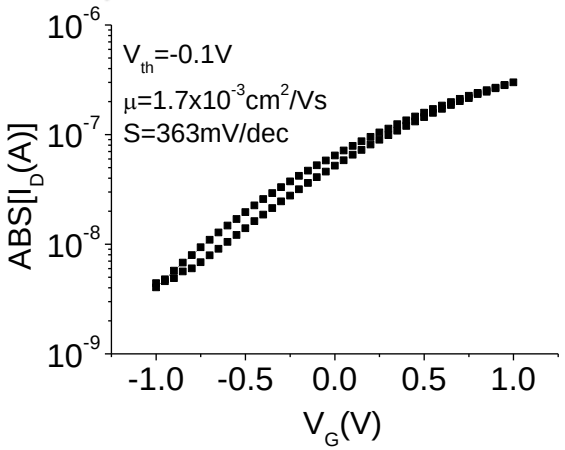
TIPS Pentacene on Parylene C (25 nm)/AlOx



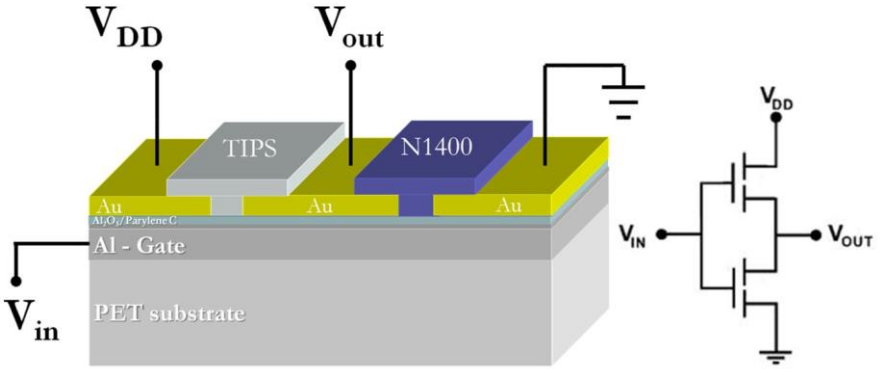


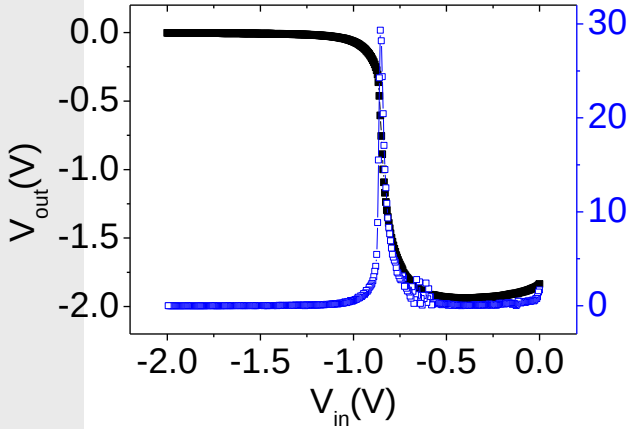
N1400 on Parylene C (25 nm)/AlOx

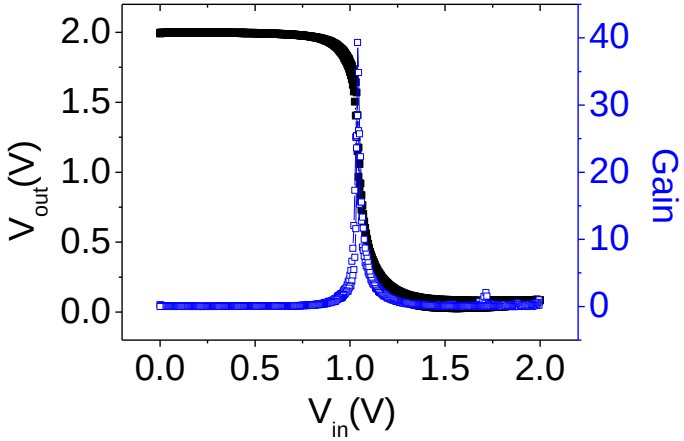




Low Voltage Complementary inverters







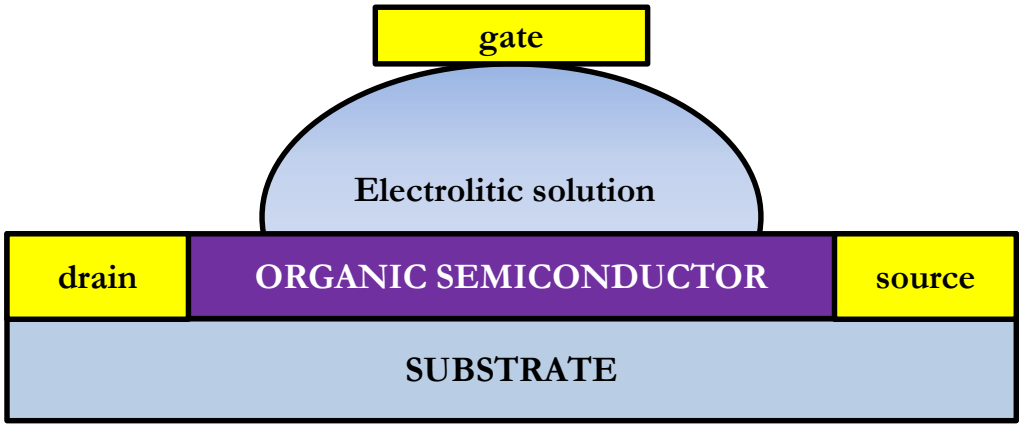
paper to be submitted

Electrolyte Gated Organic Field Effect Transistor EGOFET

Piero Cosseddu Ph. D.
Dept. Of Electrical and Electronic Engineering
University of Cagliari (Italy)

EGOFET: introduction

Electrolyte-**G**ated **O**rganic **F**ield-**E**ffect **T**ransistors



An *electrolitic solution* is a system composed by:

- a *solvent* in the liquid phase(generally water);
- a *solute* it ca be disassociated in an ionic state

Strong Electrolites: the fully disassociate

$$CA \xrightarrow{\text{acqua}} C^+ + A^-$$

Weak Electrolites: only partial desasspciation (reaction at the equilibrium)

$$CA \rightleftharpoons C^+ + A^-$$

Electrolite

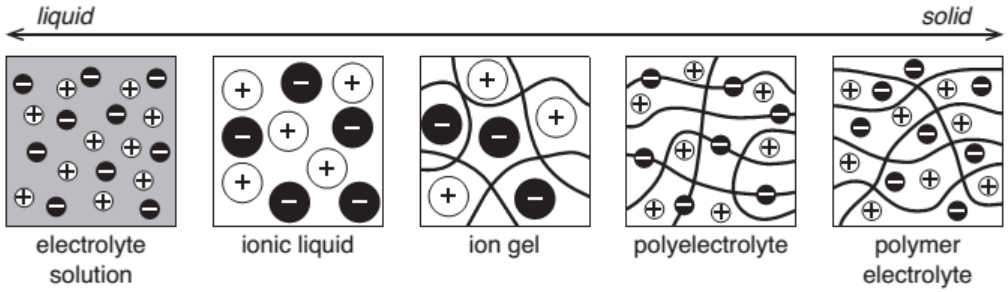


Figure 3.1 Schematic illustrations of different types of electrolytes, ordered from left to right by their physical appearance.

- Electrolitic solutions
- Ionic liquids
- Ion gels
- Polyelettroliti
- Polymer electrolites

Electrolyte

Electrolytic solutions

Salt solved in a liquid, generally a polar solvent

Acetonitrile, much more stable it does not give rise to chemical reactions

Also water is an electrolyte, H+ e OH- ions, very weak electrolite

Electrolyte

Ionic liquids

It is a slt in the liquid phase

Melting T below100°C

Can give rise to **very high conductivity**

Among the most employed electrolites

Electrolyte

Ion gels

The latter examples are not very suitable for the realization of solid state devices, per cui vengono generalmente **trattati** in modo da essere immobilizzati, per esempio **co-polymers to form gels**

Lower concentration of ions, lower conductivity

Electrolyte

Polyelectrolytes

Polymers containing an alectrolitic group in their chain

Such groups can disassociate in solution

The polymer gets ionized and there will be the counterions in solution

Electrolyte

Polymer electrolytes

It is a solid electrolyte!

Salt distributed in a polymeric matrix

PEO polyethileneoxide, the most employed

Very low conductivity, but can be employed for the fabrication of solid state devices

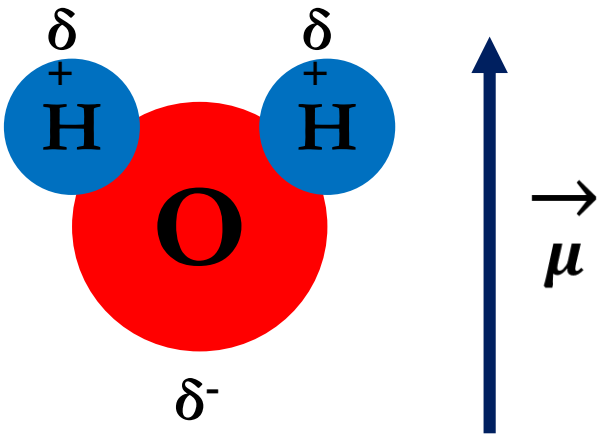
Es. flexible batteries

Polar molecules: have a permanent dipole moment due to the different electronegativity of the atoms.

Example: water molecule (Pauling scale)

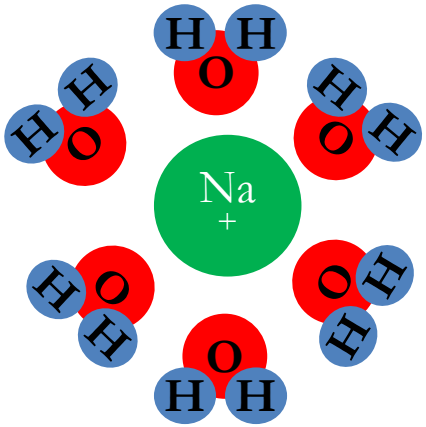
$\chi(O) = 3.44$

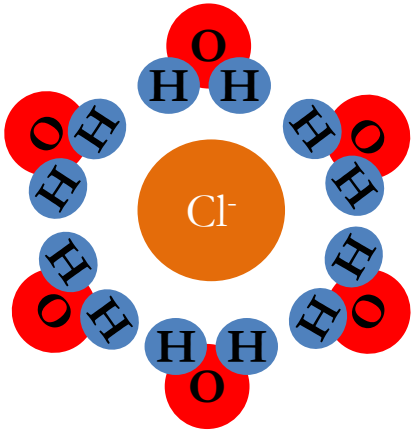
$X(H) = 2.20$



Solvation: interaction between the ions egenrated by dissociation and the solvent molecules. Each ion get surrounded by the solvent molecules

$$NaCl \xrightarrow{acqua} Na^+ + Cl^-$$





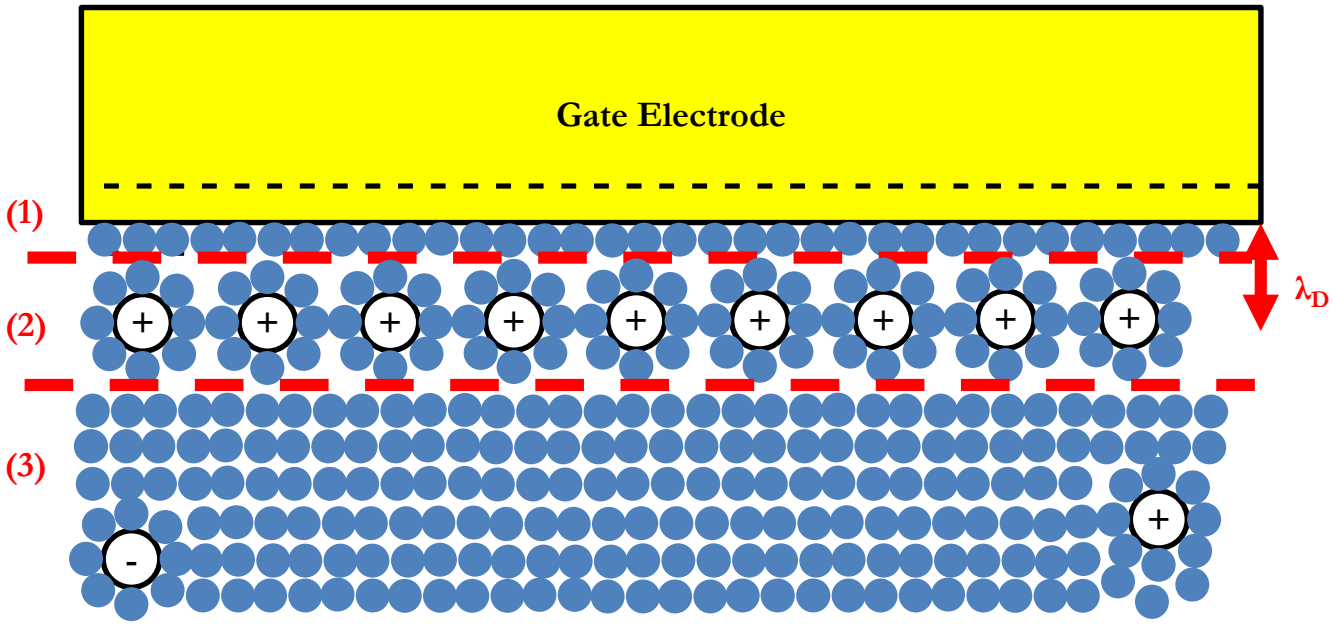
Electrolyte

Electrolytes are ion conductors and electron insulators

Upon contact with a charged ionblocking electrode, the electric potential difference between the electrode and the electrolyte gives rise to the **formation of a region consisting of two parallel layers of positive and negative charges called the electric double layer (EDL)**

The Helmholtz layer comprises **adsorbed dipole oriented solvent molecules** and **solvated ions**, which are assumed to approach the electrode at a *distance limited to the radius of the ion itself* and a single shell of solvated ions around each ion

Electrolytic Capacitance



(1) Helmholtz layer
(2) External Helmholtz layer
(3) «bulk»

λ_D → Debye length (~ Å)

Electrolyte

Thus, the Helmholtz layer and the electrode are **analogous to a parallel plate capacitor** separated by a distance of few Ångströms

The capacitance of the entire double layer is typically in the order of tens of μF cm^{-2}

Very high capacitances lead to low operating voltages

Electrolytic Capacitance

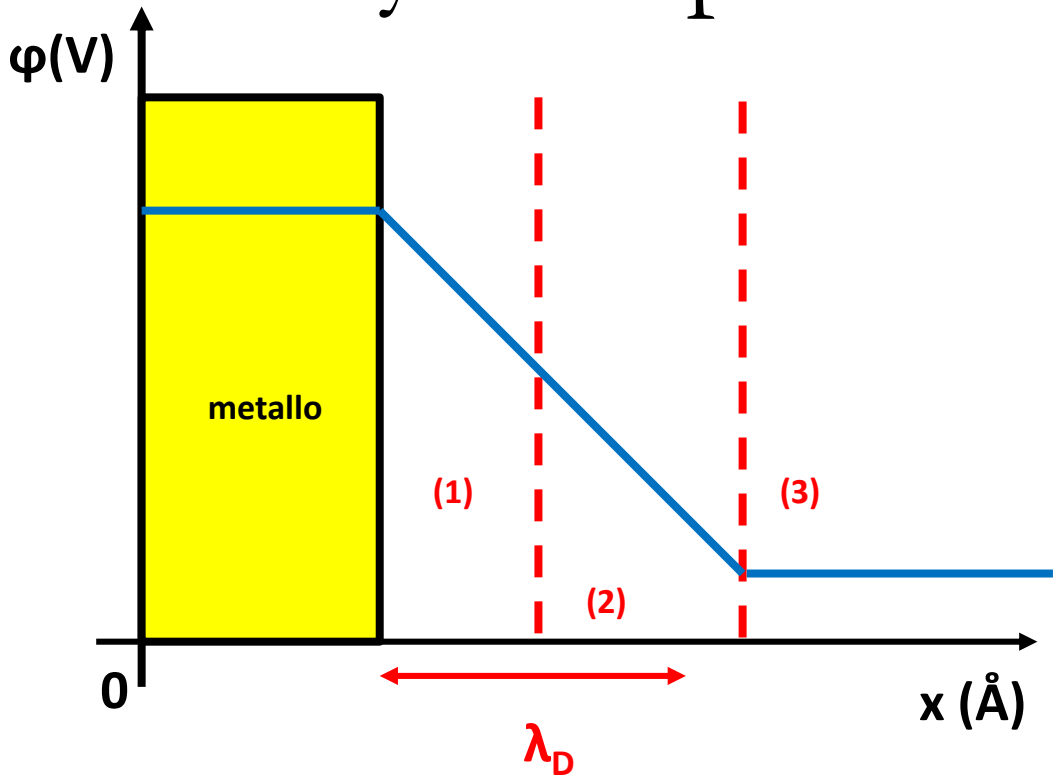
$$\frac{d^2\varphi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon}$$ Poisson equation

$$q_{dl} = \int_0^{+\infty} \rho(x)dx$$ Double layer charge

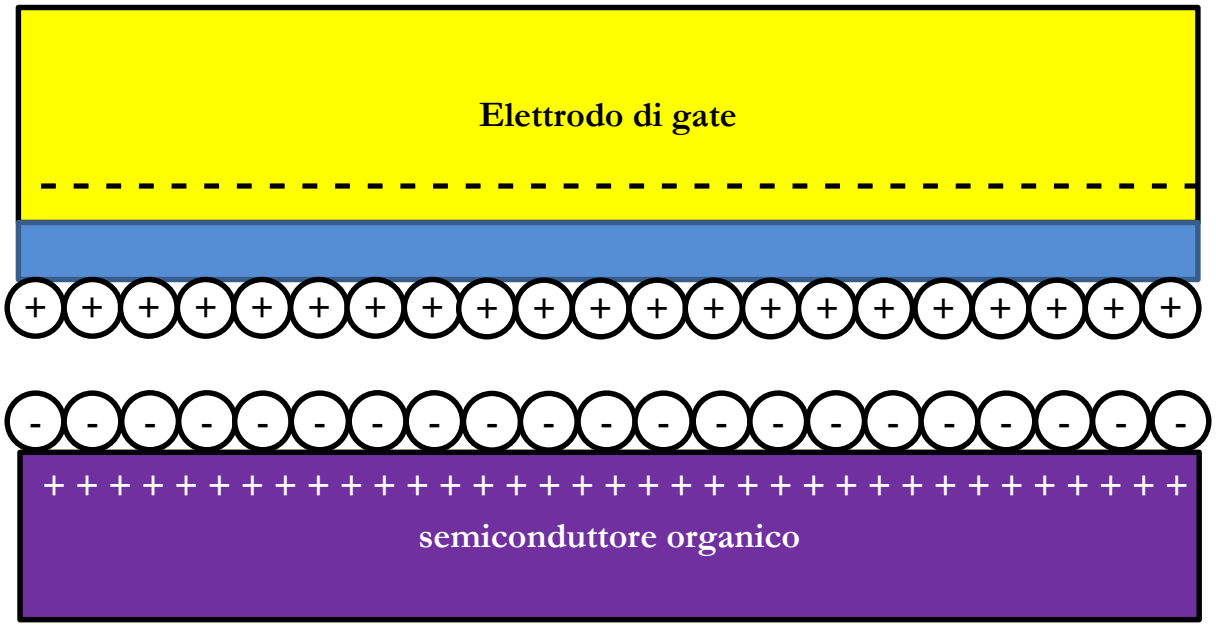
$$C_{dl} \cong \frac{\varepsilon}{\lambda_D} A$$ Double layer capacitance

EGOFET capacitance is order of magnitude higher than normal OFETs ones (10 – 100 μF · cm^{-2} vs 10 nF · cm^{-2}).

Electrolytic Capacitance



EGOFET: working principle



Holes concentration increase at the electrolite/semiconductor interface.

EGOFET

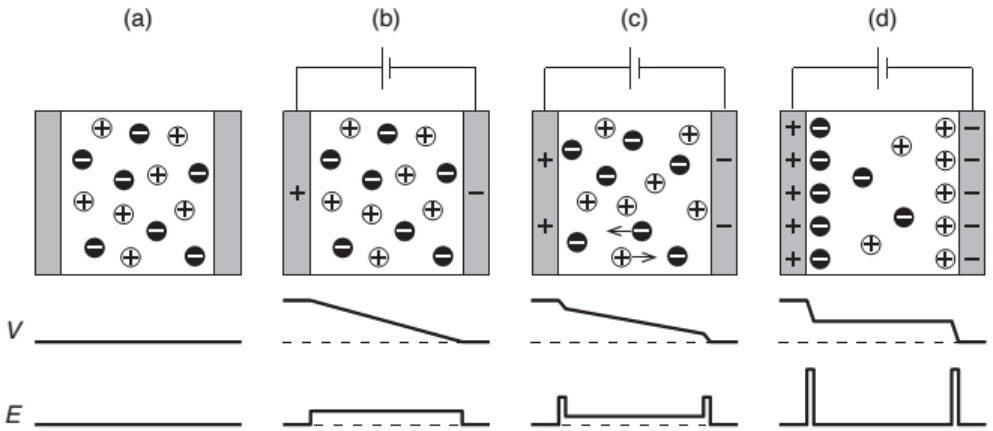


Figure 3.4 Schematic illustrations of the charge distribution, electric potential (*V*) and electric field (*E*) in the electrolyte layer of an electrolytic capacitor during charging. (a) The ions are evenly distributed when no voltage is applied. An applied voltage will induce a redistribution of the charges in the electrolyte. The situation in the electrolyte (b) before, (c) during and (d) after ionic relaxation is shown.

EGOFET

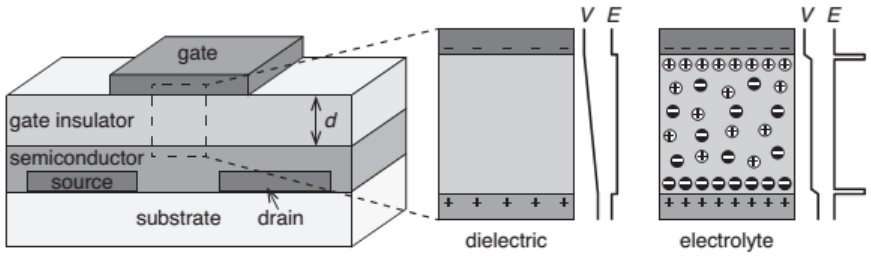
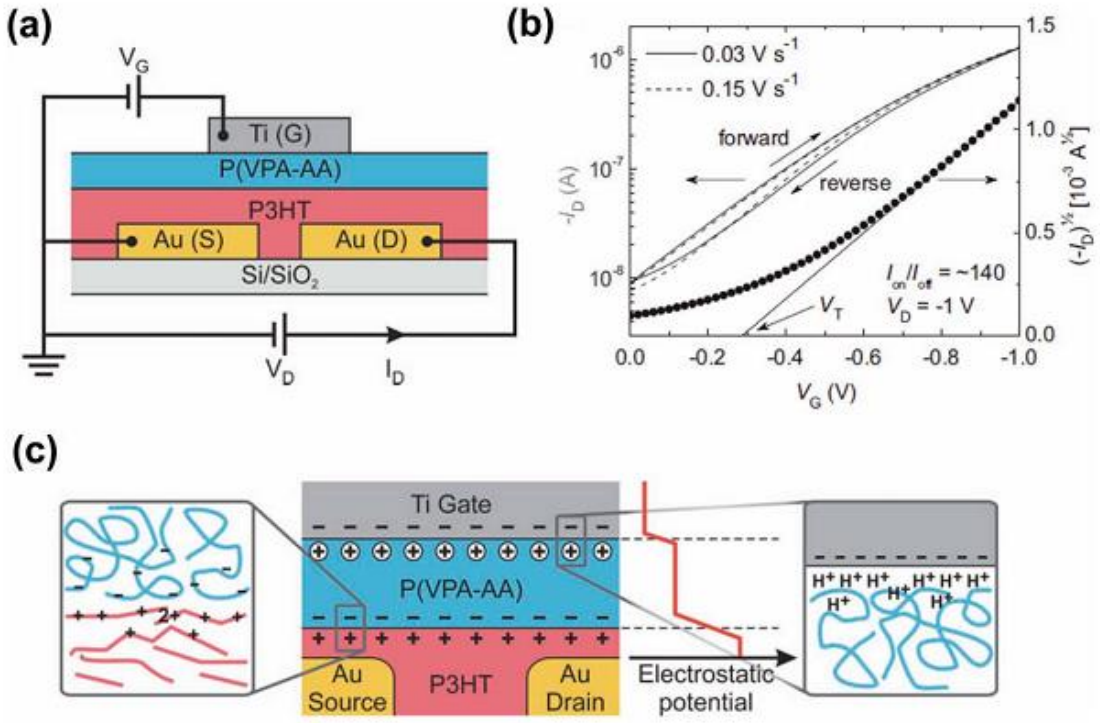


Figure 4.6 Schematic cross section of an organic thin-film transistor and illustrations of the voltage (*V*) and electric field (*E*) distributions in a dielectric and an electrolytic gate insulator when a negative gate voltage is applied.

In a normal dielectric layer the electric field varied lienearly within the film.

In al electrolitic layer the field is much more intense at the interfaces and almost negligible in the bulk

L'EGOFET


(a)
V_G
Ti (G)
P(VPA-AA)
P3HT
Au (S)
Au (D)
Si/SiO_2
V_D
I_D
(b)
0.03 V s^{-1}
0.15 V s^{-1}
forward
reverse
$-I_D$ (A)
$(-I_D)^{1/2}$ [10^{-3} $A^{1/2}$]
I_{on}/I_{off} = ~140
V_D = -1 V
V_T
V_G (V)
(c)
Ti Gate
P(VPA-AA)
Au Source
P3HT
Au Drain
Electrostatic potential
H^+

WGOFET

We do not necessarily need a strong electrolyte, also water can play the game

Water auto-protolysis:

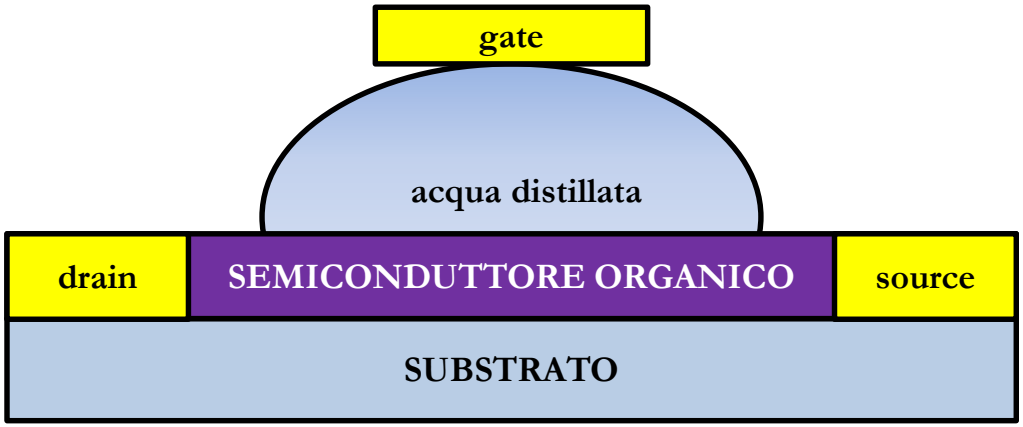
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

A T = 300 K

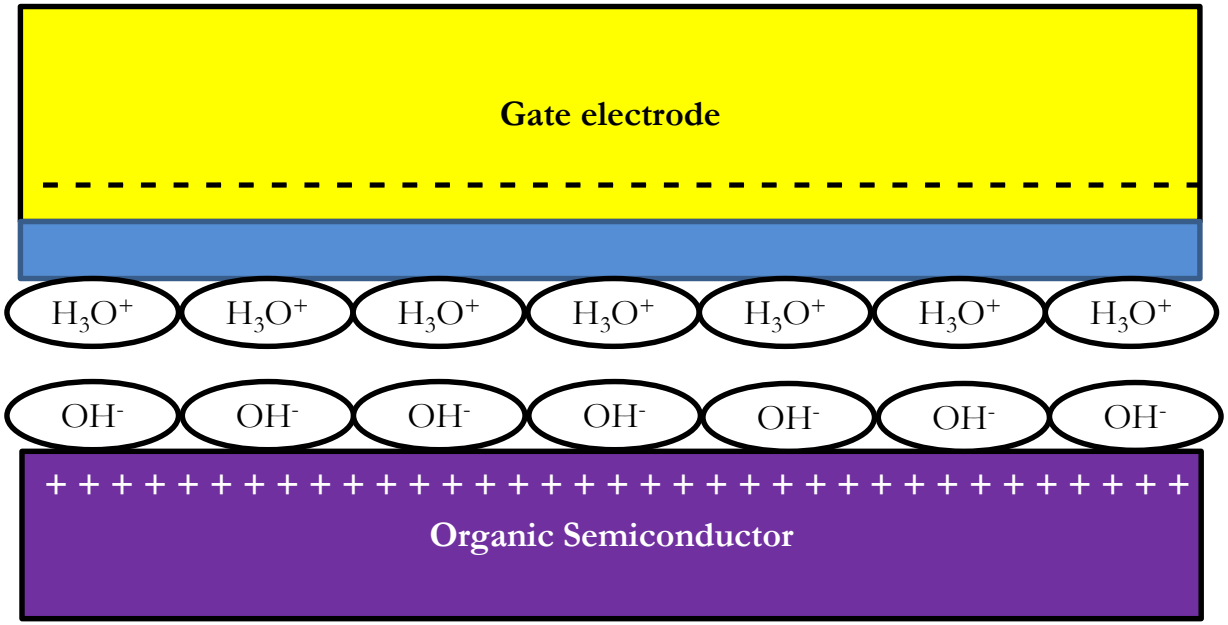
$$[H_3O^+] = [OH^-] = 10^{-7}\ M$$

WGOFET

Water – **G**ated **O**rganic **F**ield-**E**ffect **T**ransistor



WGOFET



Similarly to normal EGOFET the ions present in water can lead to the formation of the double layer and allow to gate the transistor

Organic Electro-Chemical Transistors (OECTs)

OECT: Introduction

We can intentionally modifiy the conductivity of some polymers by electrochemical doping

If a reversible redox process can be established, the polymer cna pass from a low conductance state to a high conductance one

This process can be employed for the fabrication of low voltage organic transistors:

Organic Electro-Chemical Transistors

OECT: Introduction

- Possono essere fabbricati su larga area
- Da fase liquida
- Tecniche a basso costo → Printing
- Materiali a basso costo → all plastic
- Basse tensioni di pilotaggio
- Basse Temperature di processing → substrati plastici
- Effetto elettrocromico → Display
- Se opportunamente modificati → sensing

OECT: Introduction

L'OECT work using organic polymers where charge transport is driven by electrones and also ions

Among them → PEDOT:PSS

Reversible redox process

This redox process is actually a doping and dedoping process of the polymer molecule that leads to an increase or decrease of carrier concentration → modulation of the conductivity

OECT: Introduction

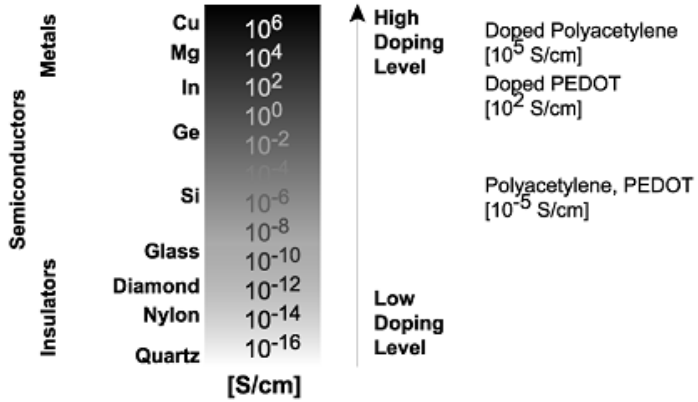


Figure 2. Conductivity levels of polyacetylene and PEDOT. In comparison, conductivity of some other materials is given, from very good insulators to metallic conductors.

OECT: Introduction

We already talked about doping before:

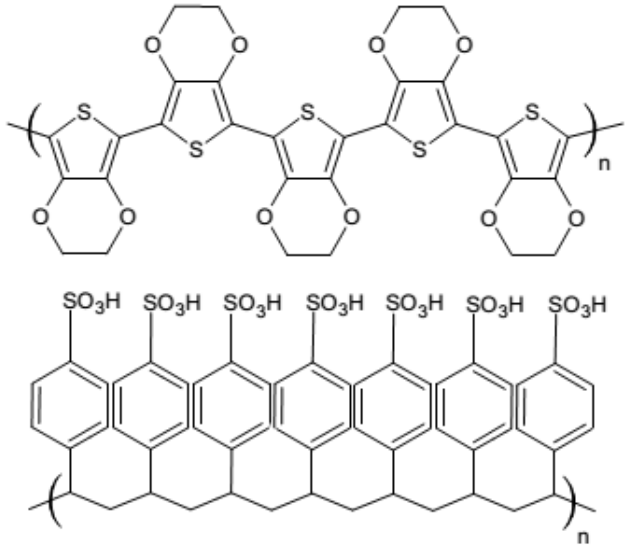
- Chemical doping
- Electrochemical doping
- Photo-induced doping
- Charge injection doping

Doping in conjugated molecules

Doping can be performed also chemically. For instance, it is possible to intentionally include in the molecule some functional groups which are electro-donors or electron-acceptors

PEDOT is an organic semiconductor,

PSS allows doping it and significantly increase its coductivity



Conductive polymers

PEDOT:PSS is formed by two different molecules, PEDOT and PSS

PEDOT is polythiophene conjugated polymer

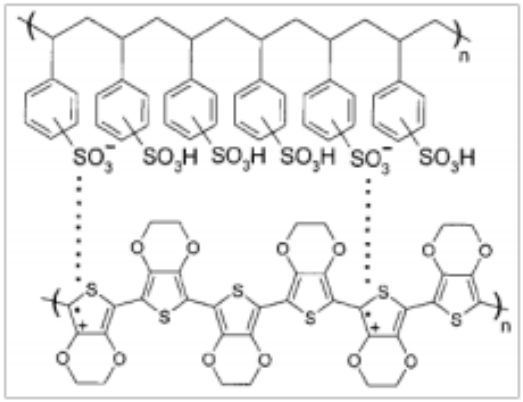
It is a semiconductor, and it is not soluble

PSS is a water soluble electrolite, it oxidized the PEDOT, removing an electron from is backbone

Therefore, PEDOT is positively charged, whereas PSS is negatively charged

Creation of a polar blend (solution) between the two molecules

$PEDOT^{+}:PSS^{-}$



Conductive polymers

In tohe words, **PSS acts as a dopant**, leading to significantly increase the number of holes in the PEDOT backbone

However PSS is an insulator!

This means that depending on the way the PSS is finally deposited on the film dramatically influences the charge transport within the film

PSS for instance can create insulating islands surrounding the PEDOT molecules, thus not allowing the created charge carrirs to move freely → bad percolation

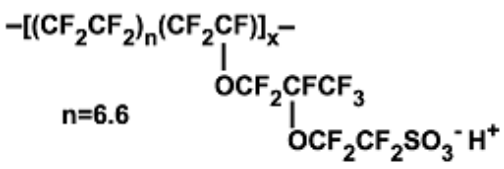
This issue can be significantly overcome by using post treatment processes, i.e. using some additives and thermal treatment to re-create the film morphology

L'electrolytes

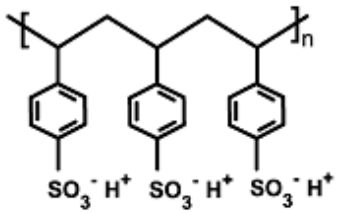
Different electrolytes can be used both in the solid or liquid phase

- Nafion
- Polys(tyrene sulfonic)acid (PSSH)
- Poly(etylene oxide) (PEO)
- Poly(vinyl alcohol) (PVA)

Nafion®



PSSH



Elctrochemical transistor

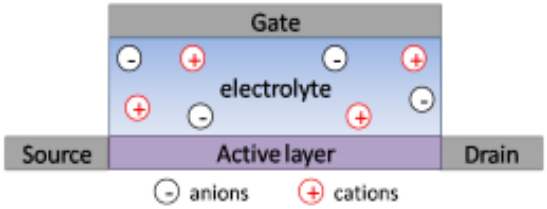
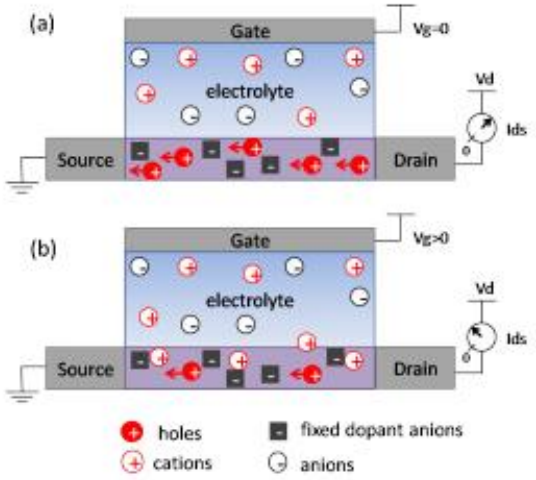


Figure 3.1: Schematic view of an OECT.



Il PEDOT:PSS is p-type doped (mobile holes, fixed ions). Let's ground the source electrodes and apply a certain voltage to the drain (Vd).

If no gate voltage is applied I'll measure PEDOT:PSS conductivity

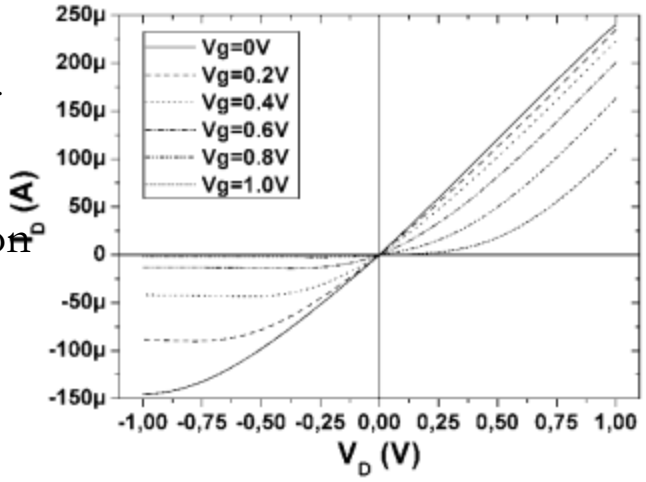
By applying a certain gate voltage I can electrochemically dope/dedope the PEDOT:PSS and modulate its conductivity.

OECT

When a positive Vgs is applied, the M^+ cations of the electrolyte are pushed into the semiconductor

Such ions will induce a **de-doping (riduction)** therefore → **decrease of the output current**

- Field effect induced by conductivity modulation of the channel
- OECT work in the depletion regime!
- Low working voltages

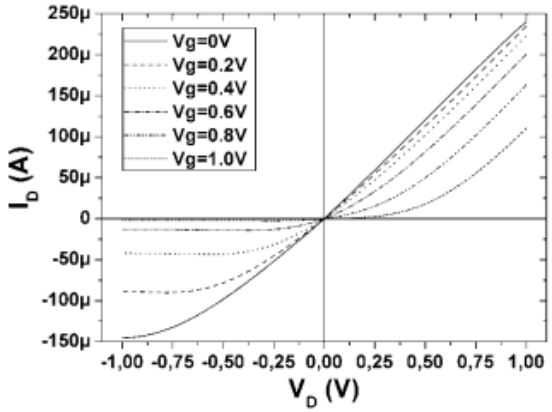


OECT

when $Vd < 0$ a portion of the channel can be entirely dedoped, this happen when the concentration of injected cations is equal to the concentration of initial dopants

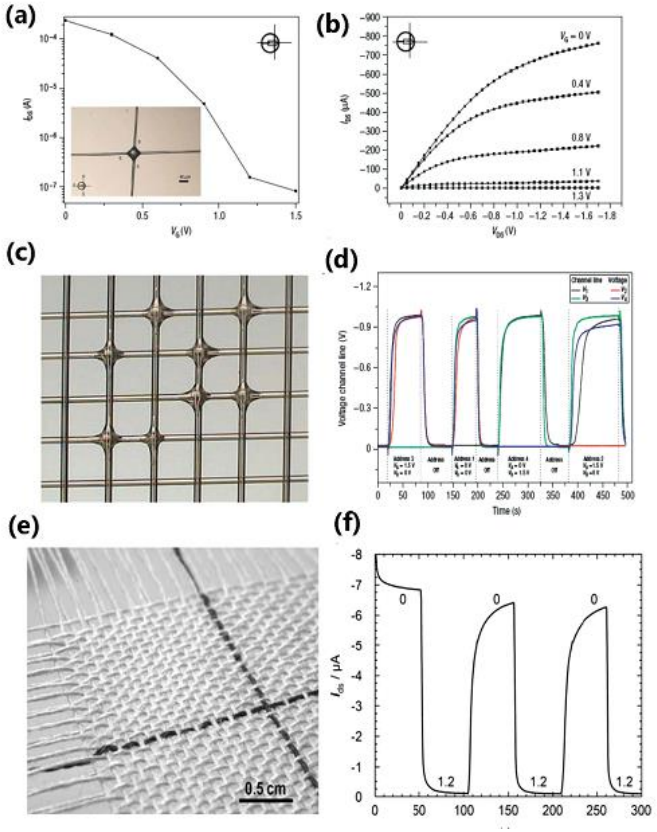
Therefore, if I keep on increasing drain voltage, **current will tend to saturate and the channel pinch off can be reached**

If gate electrode is ground connected or negatively biased PEDOT:PSS channel can be doped again and current will increase again



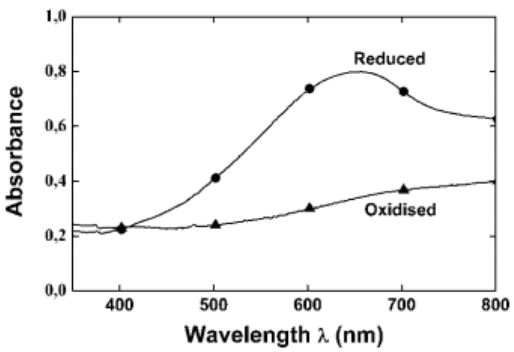
OECT

OCET on yarns

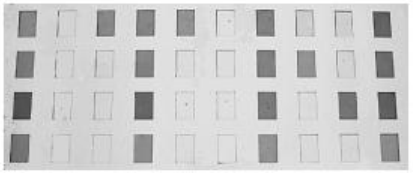


Electrochromic effect

- Doping a polymer means induce polarons into the molecule
- Localized states into the band gap changing the absorbance/emission spectrum of the molecule
- Lower energy absorption can be obtained
- Absorption peak towards higher wavelengths
- The film becomes almost transparent
- Color change!



a)



b)

Charge Transport Models in Organics

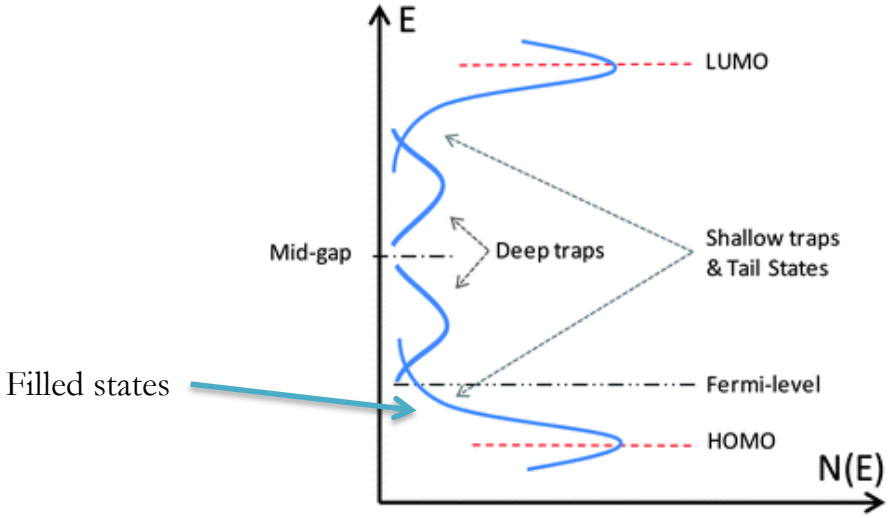
- Hopping Model (Miller-Abrahams)
- Multiple Trapping and Thermal Release

Band Transport

Crystal structure

- Continuous energetic bands
- Charge carriers move as free electron in a periodic potential, planar delocalized waves → very high mobility
- Scattering limited:
  - *Impurities*
  - *Phonons*
- Mobility decreases as temperature increases

Organic materials, different picture

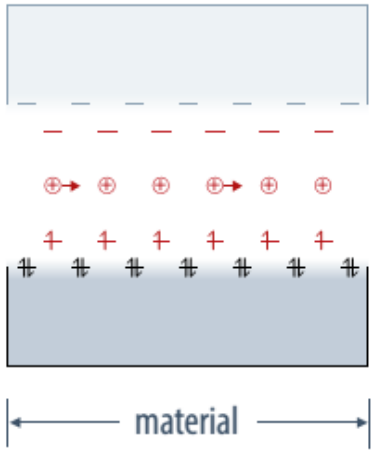


Impurities and disorder lead to a high concentration of trap states within the band gap, close to the edges of conduction and valence bands (shallow) or deeper in the gap (deep)

Band diagram is "smeared out"

Hopping Transport

Highly disordered structures



- Localized states
- Hopping dominated transport mechanism
- Thermal activation, mobility increases with T

Hopping model

Band like transport is very unlikely in organic materials due to the very low degree of order within the films

Charge transport is "hopping" like, charges hops between localized energetic states → Hopping Transport → phonon assisted

Localized states are due to defects of the materials or within the film and are generally localized in a small energetic range → high hopping probability

Hopping: Miller-Abrahams

Hopping rate from an occupied state i to an unoccupied one j, , with an energetic difference $\varepsilon_j - \varepsilon_i$ and a distance Rij:

$$W_{i,j} = \upsilon_0 \cdot \exp(-2\Gamma R_{i,j}) \begin{cases} \exp(-\dfrac{\varepsilon_i - \varepsilon_j}{k_B T}) & \varepsilon_i > \varepsilon_j \\ 1 & \varepsilon_i < \varepsilon_j \end{cases}$$

Tunneling

Boltzman factor (phonon absorption)

Γ^{-1} depends on the overlapping between the wave functions of the considered states, ν_0 pre-factor, esperimentally measured, k_B Boltzmann constant.

- Charge transport depends on the distance between states and on their distribution (density of states, DOS)
- Transport is thermally assisted

Hopping: Miller-Abrahams

It could happen that charge carries could hop more "easily" between states which are very distant but require a smaller activation energy, rather than between close states requiring a higher energy ***(Variable Range Hopping!)***

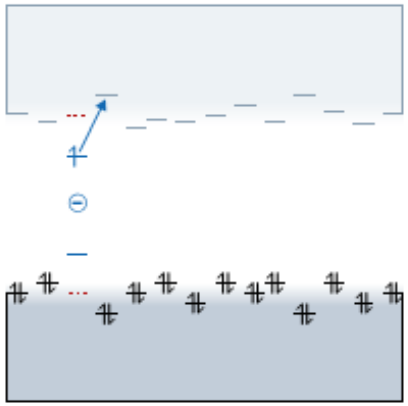
The first model was introduced by Mott, conductivity depends on temperature as follows:

$$\sigma(T) = \sigma_0 e^{-(T_0/T)^{1/\alpha}}$$

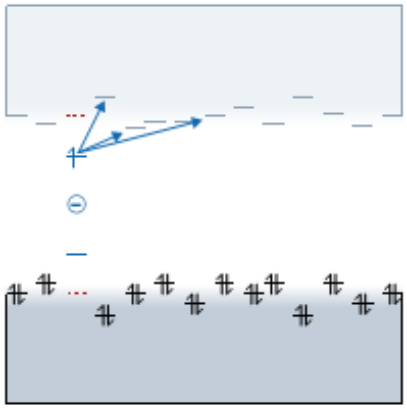
α between 1 and 4

Hopping: VRH Vissemberg e Matters

nearest neighbor hopping (NNH)



variable range hopping (VRH)



Hopping: VRH Vissemberg e Matters

Vissemberg e Matters developed a different version of VRH where DOS is an exponential distribution

The model takes also into account the dependance of mobility on the electric field (gate voltage dependance in transistors)

$$\sigma(\delta,T)=\sigma_0\left[\frac{\pi N_t \delta (T_0/T)^3}{(2\alpha)^3 B_c \Gamma(1-T/T_0)\Gamma(1+T/T_0)}\right]^{T_0/T}$$

$$\delta(x)=\delta_0 \exp\left[\frac{qV(x)}{kT}\right]$$

A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960)
D. Monroe, Phys. Rev. Lett. 54, 146 (1985)
M.C.J.M. Vissenberg and M. Matters, Phys. Rev. B 57, 12964 (1998)

Hopping: MTR

Some studies have demonstrated that also in some organic systems band like transport can occur

It can happen when the molecular order is very high, single crystals

Defect free structure, much lower concentration of trap states

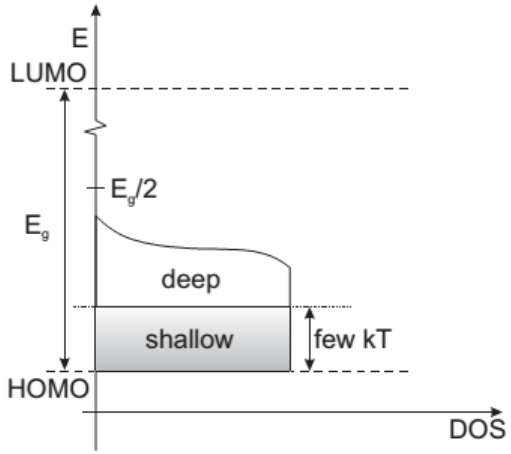
A new model must be provided

Multiple trapping and thermal release

MTR model was developed by Shur and Hack to better describe charge transport in amorphous

Afetrwards Horowitz extended such model also for organics

The model says that charge transport happens in extended states, but the most of the involved charge is trapped in localized states in the band gap

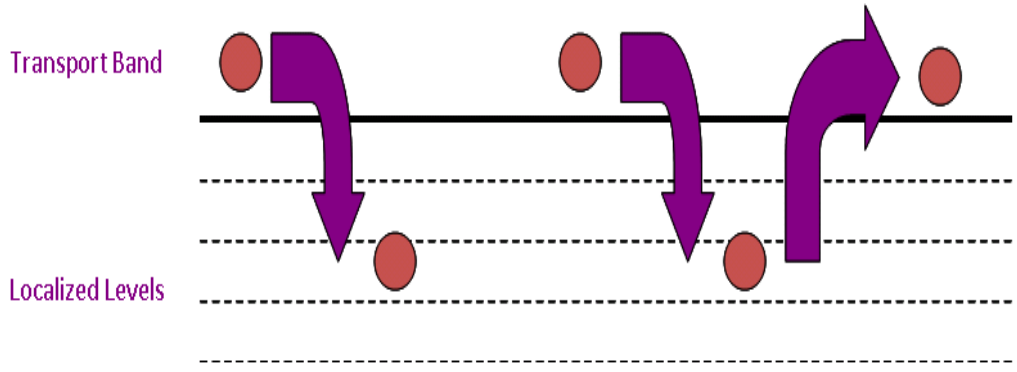


- *Deep states*
- *Shallow states*

Multiple trapping and thermal release

MTR → three transport levels:

- Transport
- Trapping
- Charge release



Charge transport is limetd by the presence of localized states which are very close to the HOMO and LUMO

Multiple trapping and thermal release

These states are due to defects, impurities etc.

Charge carriers are trapped during their transistion and are released afterwards thanks to thermal energy

Release dynamics depend on temperature, but also on the energy position of the state

As already said, temperature assists charges release from traps, also confering carriers kinetic energy by means of phonons

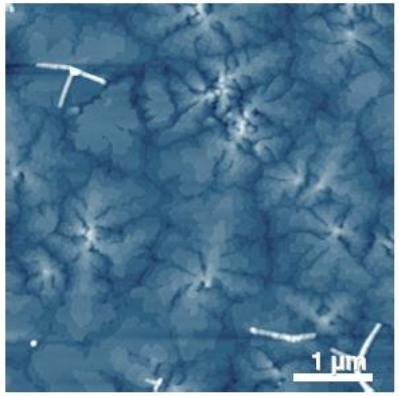
Multiple trapping and thermal release

Horowitz describes an organic film as it is characterized by two different regions:

- grains – high molecular order

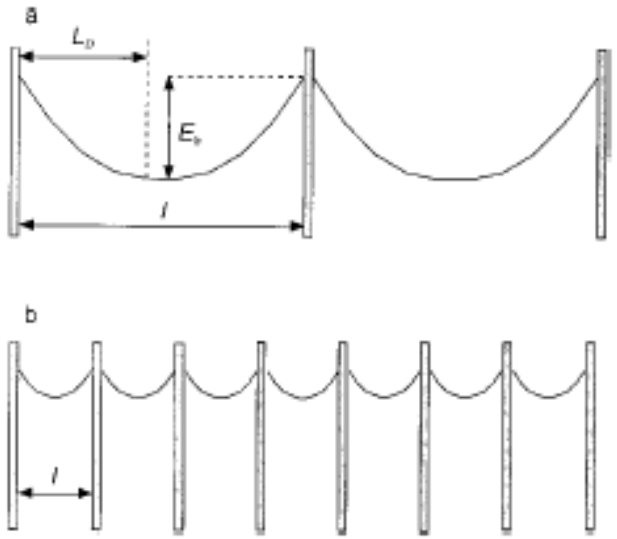
  transport through delocalized bands → *high mobility*

- Grain boundaries – high defects concentration, charge *trapping in localized (back-to-back diode like structure)* →*low mobility*



Pentacene su SiO_2

Hopping: MTR



$$L_D = \sqrt{\varepsilon_S kT / q^2 N}$$

Debye length

when $l < L_D$

Traps are uniformly distributed in the film

when $l > 2L_D$

Traps are mainly in the grain boundaries!

Hopping: MTR

$$\frac{1}{\mu} = \frac{1}{\mu_g} + \frac{1}{\mu_b}$$

Mobility depends on the mobility in the two regions

$\mu_g >> \mu_b$ → mobility is strongly limited by grain boundaries!

when $l < L_D$

$$\mu = \mu_0 \exp\left(-\frac{E_b}{kT}\right)$$

- Thermal activation
  Thermoionic emission
- μ_0 trap free mobility

Hopping: MTR

when $l > 2L_D$ for low T

$$\mu = \mu_0(T)\exp\left(-\frac{E_b}{E_0}\right)$$

No thermal activation
Tunneling

E_0 is a constant depending on polaron mass and defects concentration

When $l > 2L_D$ for high T

$$\mu = \frac{q\langle v\rangle l}{8kT}\exp\left(-\frac{E_b}{kT}\right)$$

Thermal activation
Thermoionic emission

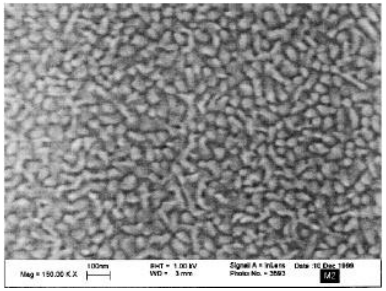
v = average electron speed

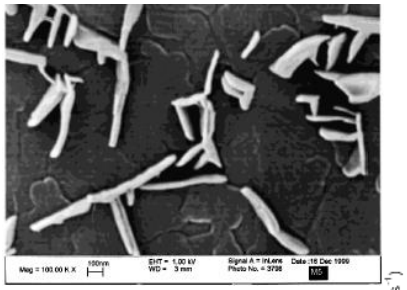
N.B. mobility linearly depends on the grain dimension (l) within the film

Hopping: MTR

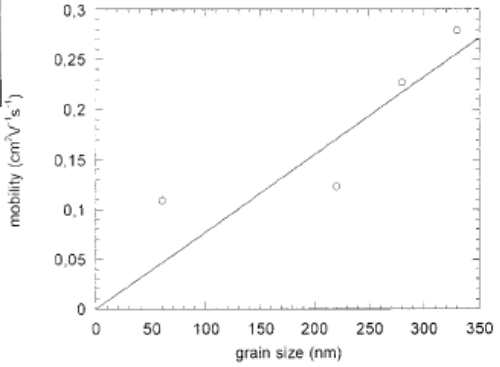
Electronic properties depend on the morphological/structural properties of the film!

Controlling film growth is very important:
Which are the parameters determining the film properties?
Investigation of structural/morphological features

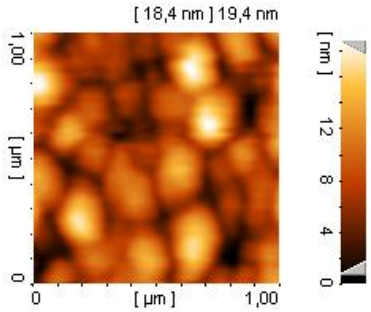
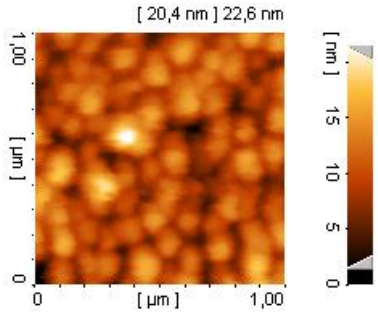
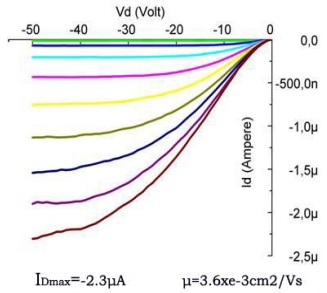
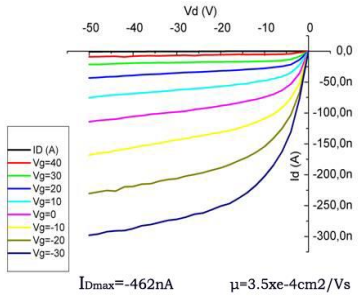


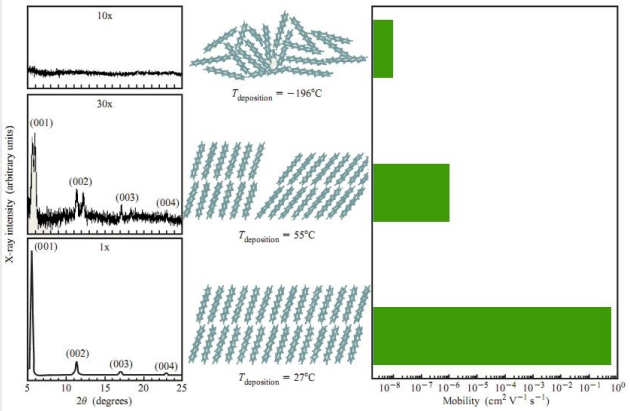


Substrate temperature [°C]	Grain size [nm]	Mobility [$cm^2 V^{-1} s^{-1}$]
room temperature	60	0.11
120	220	0.12
150	280	0.23
175	330	0.28



Correlation between morphological properties and mobility

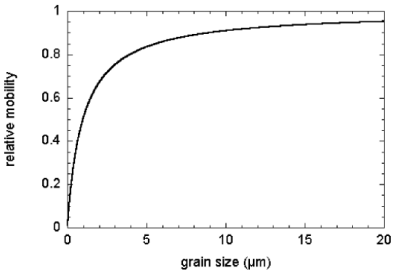
Rate 0.2 Å/sec *Spessore 300Å*	Transistor su Mylar®	Transistor su SiO_2
Morfologia		
I_D/V_D		

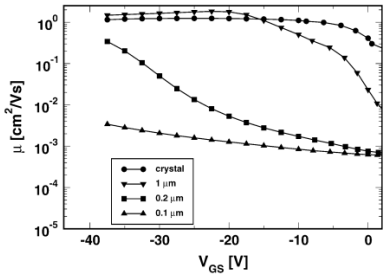


OFET mobility depends on structural and morphological properties of the active layer

Mobility depends on average grains dimensions (grain boundaries density)

Gate voltage dependance of mobility



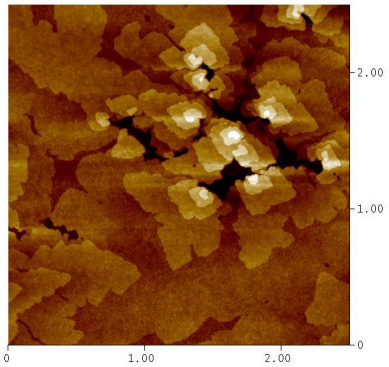


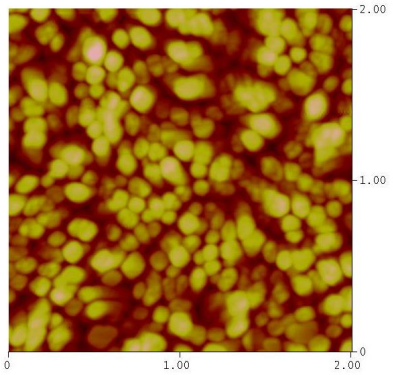
Materials
A few examples

Small molecules: Pentacene

Nelle molecole come il pentacene il trasporto di carica il trasporto di carica all'interno del fim dipende non solo dalla sovrapposizione degli orbitali π nella direzione dell'asse maggiore della molecola (**intra-chain charge transport**), ma anche dall'interazione tra orbitali π di molecole adiacenti (**inter-chain charge transport**).

Per cui il trasporto di carica è fortemente influenzato dalle proprietà morfologiche e strutturali del film depositato





Small molecules: Pentacene

band gap (as the most of organic semiconductors) around 2,2 eV.

Pentacene ionization energy(HOMO energy level) around 5.2 eV and electron affinity (LUMO level) around 3 eV.

It generally, in principle, forms an ohomic contact with Au, having a WF around 5.1 eV

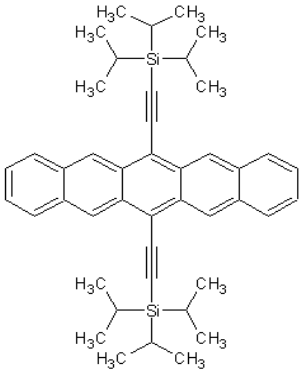
Lower barrier with respect to HOMO, higher barrier with LUMO

Good hole injection, but bad electron injection

Generally pentacene is p-type

Small molecules: Pentacene

6,13-Bis(triisopropylsilylethynyl)pentacene (Pentacene TIPS) similar to pentacene with two chains in the position 6 and 13



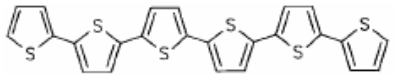
HOMO around 5.3 eV and LUMO around 3 eV, band gap around 2.3 eV

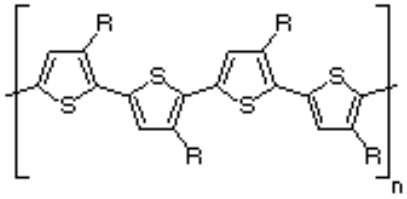
Similar to the previous one, p-type

Small molecules: oligothiopenes

thiophene monomer

Thiophene





quater-thiophene and **sexi-thiophene**

rod like molecules, as pentacene

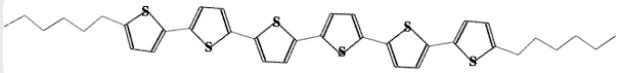
Energy gap around 2.0-2.2 eV

HOMO around 5 eV (p-type)

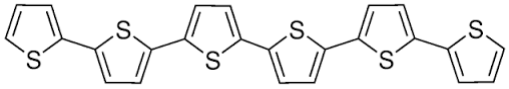
Can be functionalized in order to be soluble

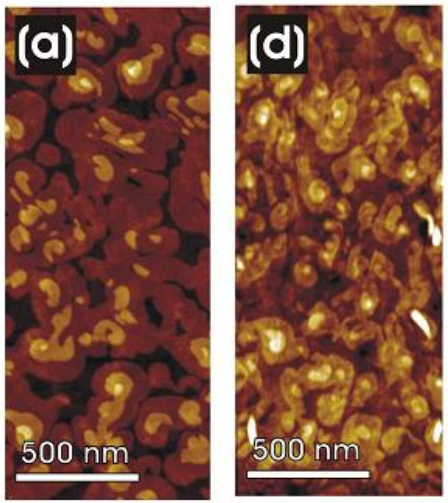
Small molecules: oligothiopenes

Dihexyl sexithiophene

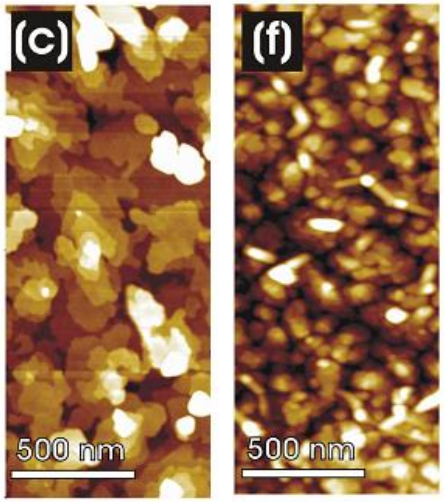


Sexithiophene





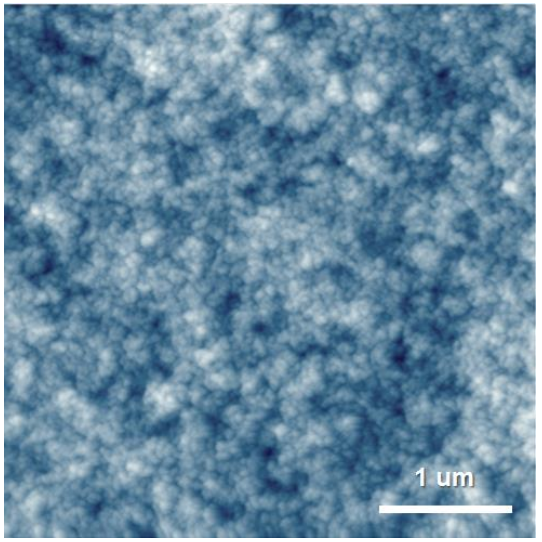
On SiO_2 On PET



On SiO_2 On PET

Polymers: polythiophenes (P3HT)

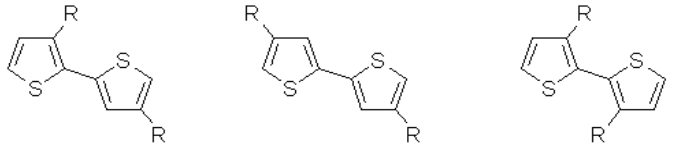
- poly (3-hexylthiophene) **P3HT**
- Soluble, tra i quali il chlorobenzene, il toluene and lo xylene.
- HOMO around 4.8 eV, very clos to Au WF
- Good hole injection, p-type
- Early Aging, due to lower ionization energy



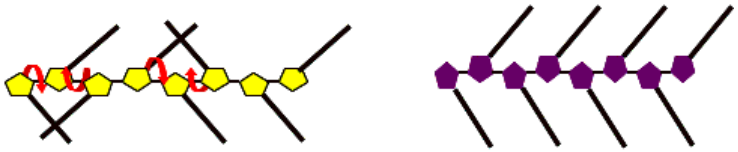
Regio-regolarity

P3HT is not symmetric!

Three different structures, depending on where the alkyl chains are attached



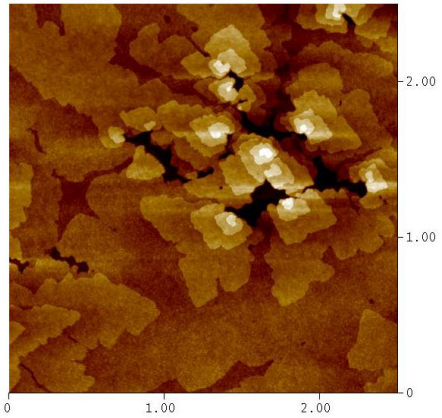
When there is amix of the different structure the polymer is called regio-irregular, if the structur is well controlled, regio-regular

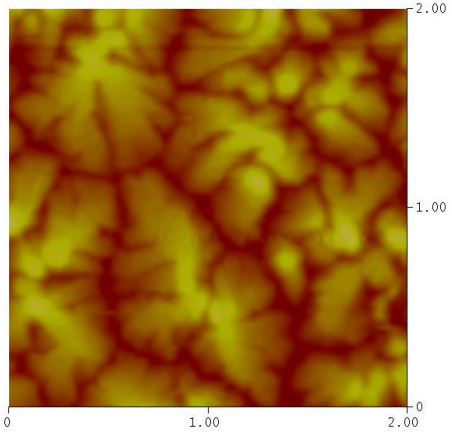


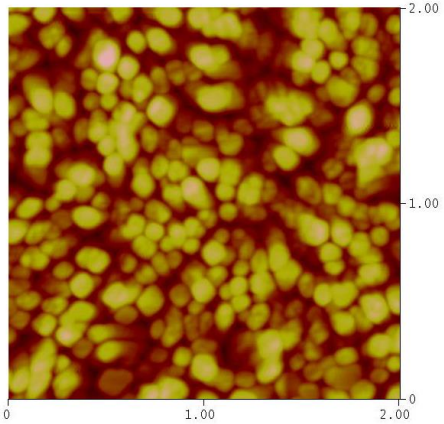
In order to have better morphology, leading to higher performances, a high regio-regularity is required

Morphological characterization

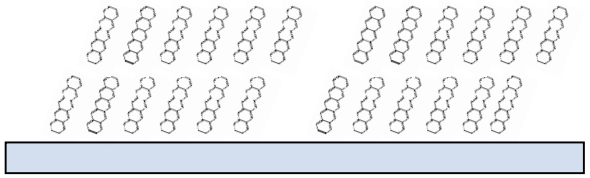
Differenti tipologie di morfologia



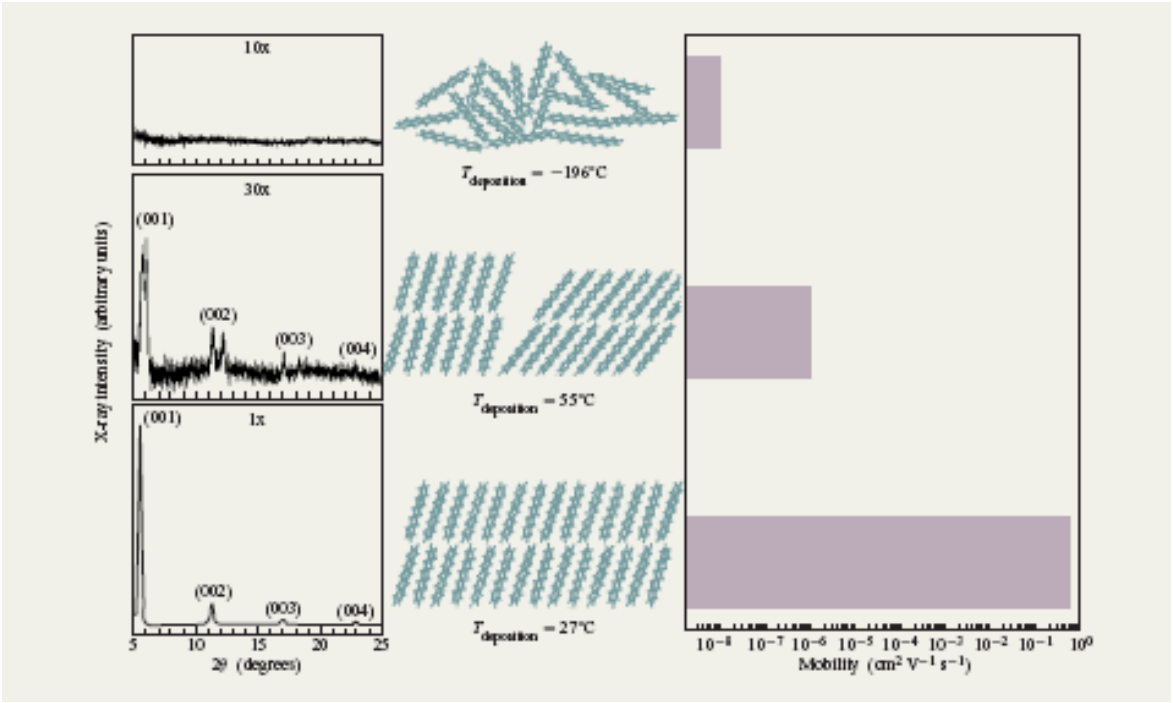


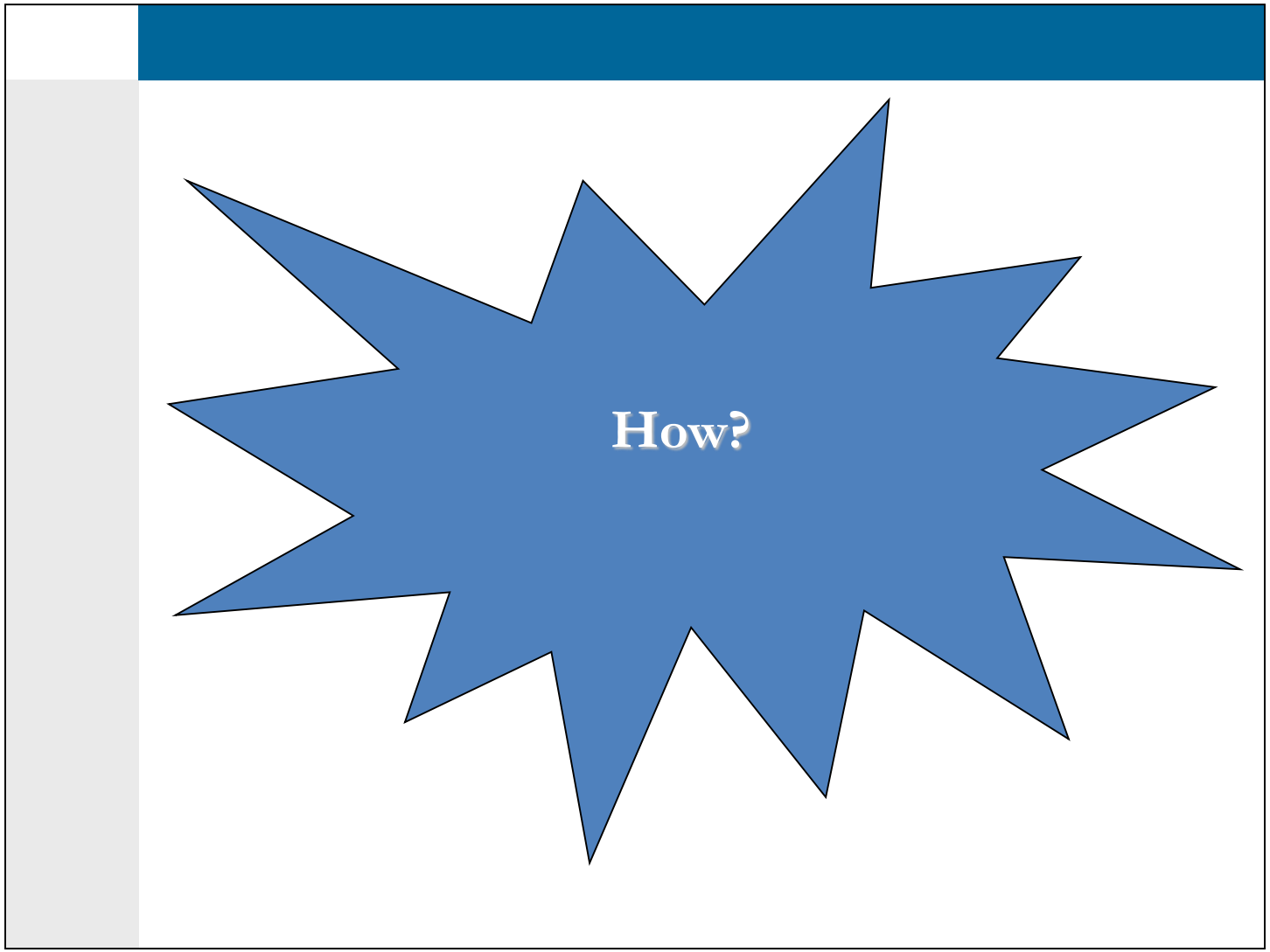


Same molecule can lead to different morphologies → different electrical properties

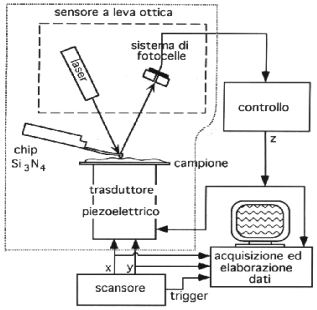
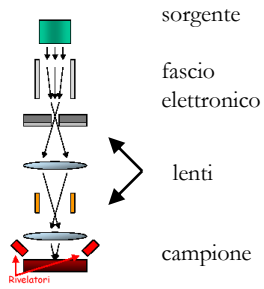
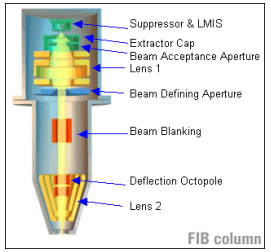


Morphology → transport




How?

instrumentation

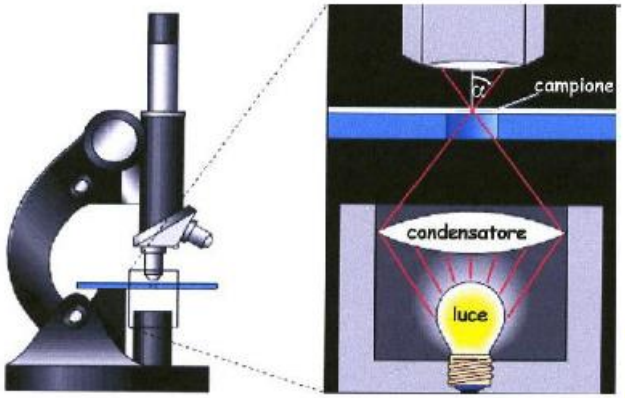
	SPM Scanning Probe Microscopy	SEM Scanning Electron Microscopy	FIB Focused Ion Beam
Scheme			
probe	cantilever	electrons	ions
Analysis	• morphology • spectroscopy	• morphology • spectroscopy	• morphology • spectroscopy • samples manipulation

instrumentation – optical microscope

La Microscopia Ottica

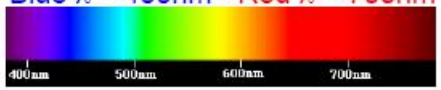
- Il limite di risoluzione di un microscopio può essere calcolato con la formula di Rayleigh

$$R = 0.61 \frac{\lambda}{\eta sen\alpha}$$



Luce visibile:

Blue λ = 400nm - Red λ = 700nm



Indice di rifrazione:

η = 1.0 Aria

η = 1.4 Olio

Risoluzione ≈ 0.22μm

Instrumentation - SEM

La Microscopia Elettronica

- Un sottile fascio di elettroni viene usato come sonda al posto della luce

relazione di De Broglie

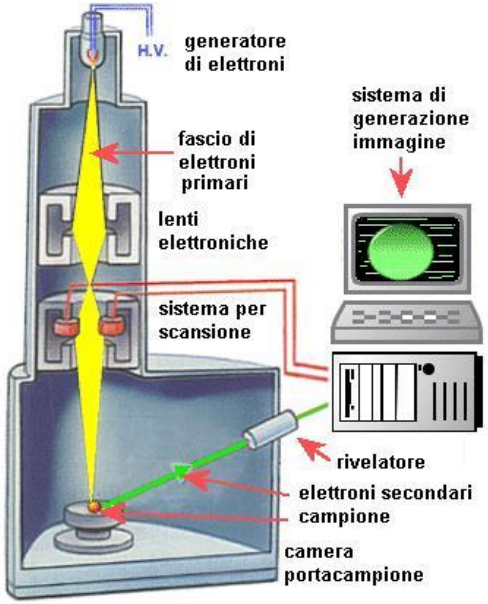
$$\lambda = h/mv$$

λ: Lunghezza d'onda associata alla particella
h: Costante di Plank 6.63×10^{-34} Js;
mv: momento della particella

La lunghezza d'onda dell'elettrone può essere ridotta aumentando il suo momento.

particle	Mass(kg)	Speed (ms^{-1})	Wavelength (pm)
1 eV electron	9.1×10^{-31}	5.9×10^{5}	1200
100 eV electron	9.1×10^{-31}	5.9×10^{6}	120
10 KeV electron	9.1×10^{-31}	5.9×10^{7}	12

Strumentazione - SEM



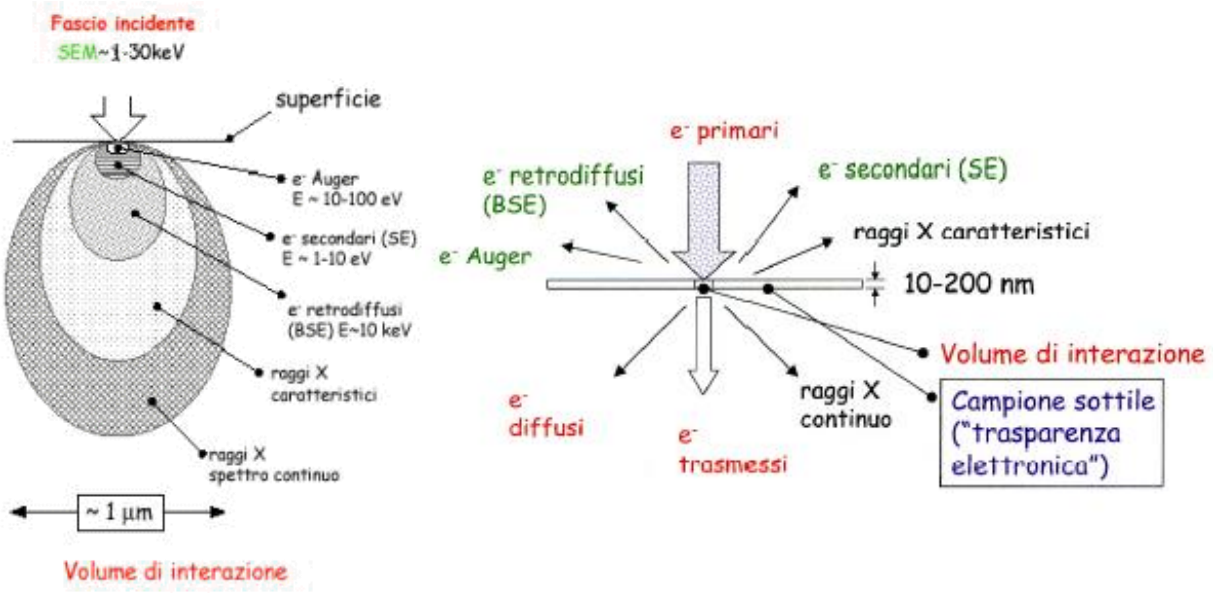
La sorgente emette elettroni per effetto termoionico.

Gli elettroni vengono accelerati da una differenza di potenziale e confinati tramite opportune lenti elettromagnetiche.

La scansione è determinata da un sistema di bobine a campo magnetico variabile.

Un secondo sistema di lenti focalizza meglio il fascio elettronico sul campione.

Instrumentation- SEM



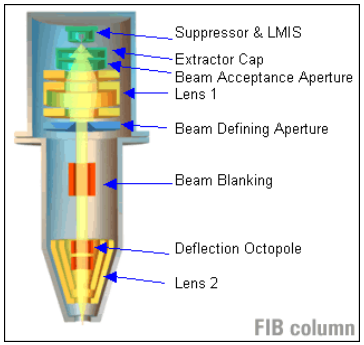
A detector attracts the scattered electrons and lead them into a CRD.

An image can be formed similarly as it used to happen in former TV screens

Instrumentation - FIB

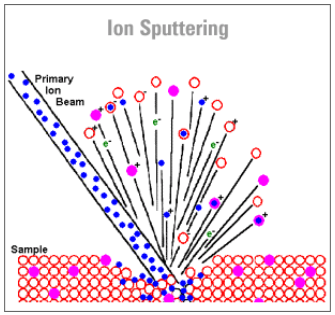
The source is a tungsten wire in a liquid metal (generally Gallium), LMIS

Beam creation is similar to SEM

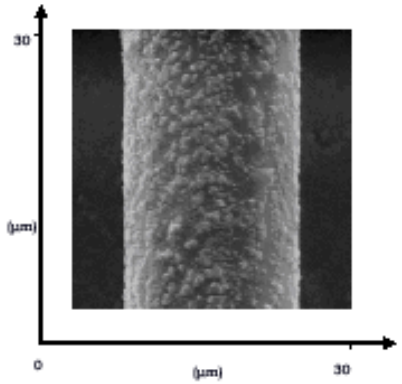


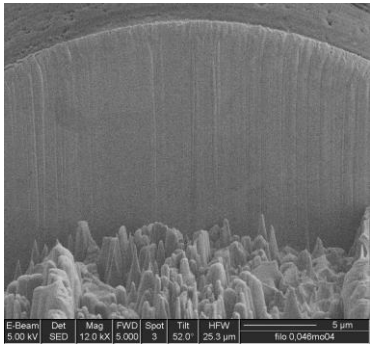
Ions are heavier than electron, more massive, can degrade sample surface

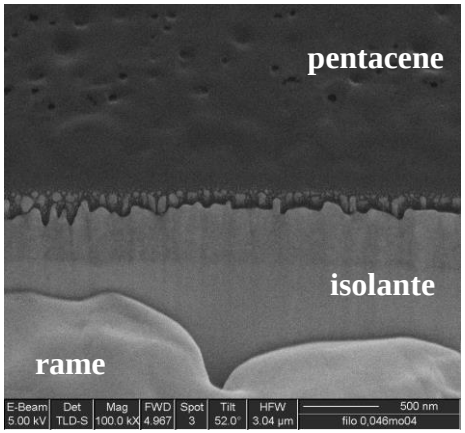
Such phenomenon can be used to make samples sections (Milling)



FIB


30
(µm)
0
(µm)
30


E-Beam 5.00 kV
Det SED
Mag 12.0 kX
FWD 5.000
Spot 3
Tilt 52.0°
HFW 25.3 µm
5 µm
filo 0,046mo04


pentacene
isolante
rame
E-Beam 5.00 kV
Det TLD-S
Mag 100.0 kX
FWD 4.987
Spot 3
Tilt 52.0°
HFW 3.04 µm
500 nm
filo 0,046mo04

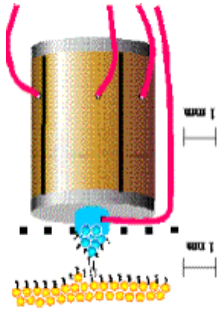
Scannig Probe Microscopy

A probe is used to scan the sample

A piezoelectric motor moves the sample with respect to the probe (or viceversa)

Such probe as a radius in the range of Ångstrom → very high resolution

Analizing such interaction probe/sample morphological informations can be obtained



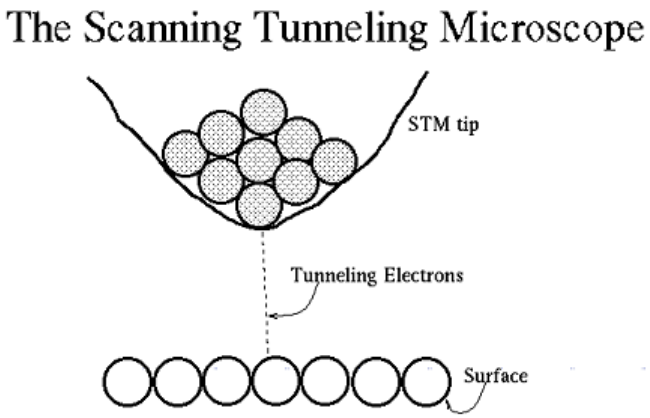
Probe-sample interaction:

- **Tunneling current→ Scanning Tunneling Microscopy (STM)**
- **Force→ Atomic Force Microscopy (AFM)**

Scanning Probe Microscope- STM

It was invented by **G. Binning e H. Rohrer** to study the conductivity of surfaces

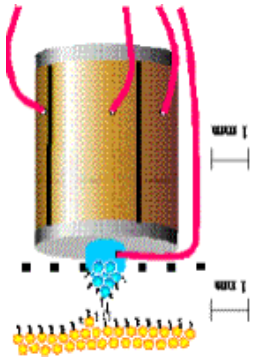
It is based on quantum mechanics effects, tunnelling current



Scanning Probe Microscope-AFM

The signal is the interaction force, leading to a **deflection of the probe**

From such deflection morphological information can be obtained



The deflection is measured point by point through a raster scan

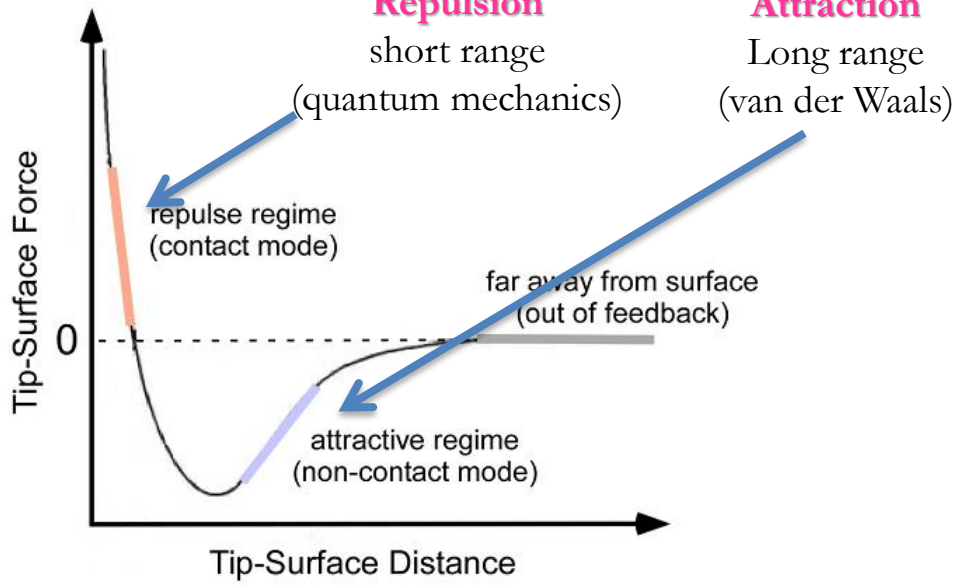
Involved forces

The interaction energy between two atoms depends on their distance and can be expressed by the Lennard – Jones expression:

$$w(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Repulsion
short range
(quantum mechanics)

Attraction
Long range
(van der Waals)



Scanning Probe Microscope-AFM

A laser beam is reflected from the back side of the probe (cantilever) into a photodetector system Al movimento del cantilever corrisponde quindi uno spostamento dello spot sullo schermo.

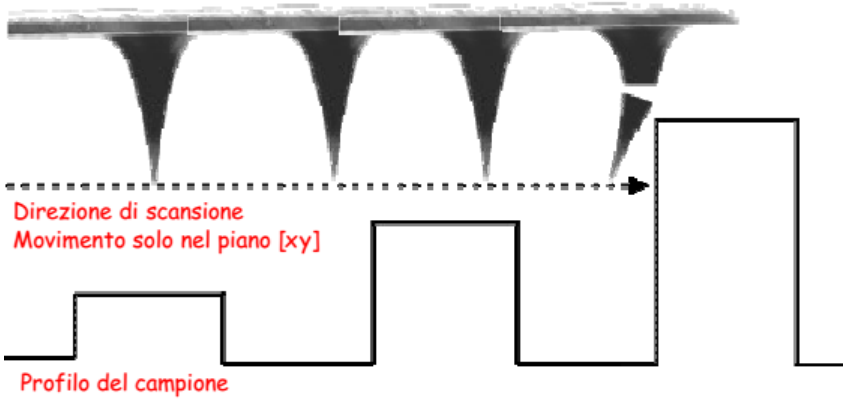
This induces a current variation in the photodetectors that can be turned into z deflections of the tip.

AFM – working principle

Contact mode: constant height

The cnatilever is at a fixed height during all the measurement. Its distance with respect of the surface will cange according to the surface roughness

By measuring the tip/sample repulsion forces, depending on the surface morphology, topographic information can be obtained.

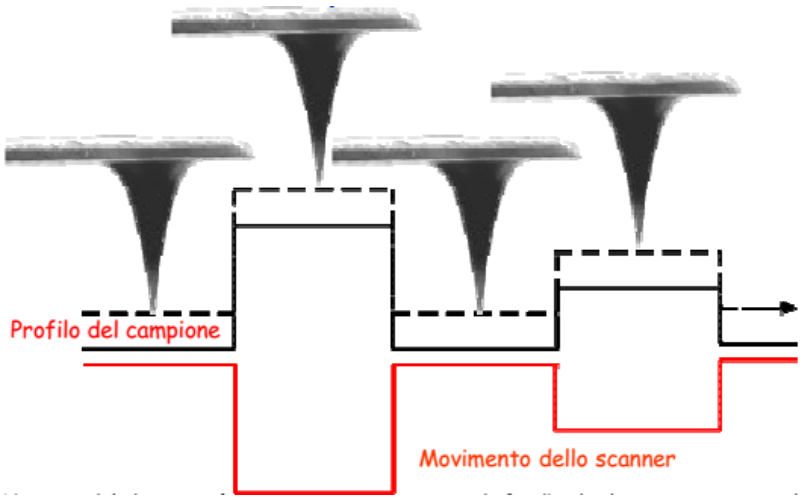


AFM – Modalità di funzionamento

Contact mode: constant force

In this case the vertical contact force is kept constant, that is given by the deflection times the cantilever elastic constant

$F=k\Delta z$



AFM – working principle

Non contact mode:

In this case the cantilever is at a distance around **10 nm** or more from the surface.

Van der Waals forces are playing the role

The cantilever is generally forced to oscillate close to the cantilever resonance frequency ω_0

The interaction lead to

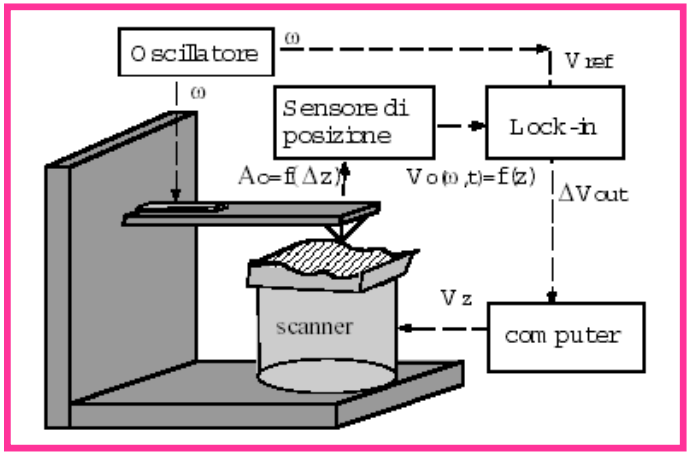
- Amplitude variations,
- Resonance frequency variation.

AFM – working principle

Non contact mode:

Interaction force is very small.

Generally used for bio-samples



AFM – working principle

Modalità semicontact mode:

A **combination between contact and non contact also called** *Tapping mode*.

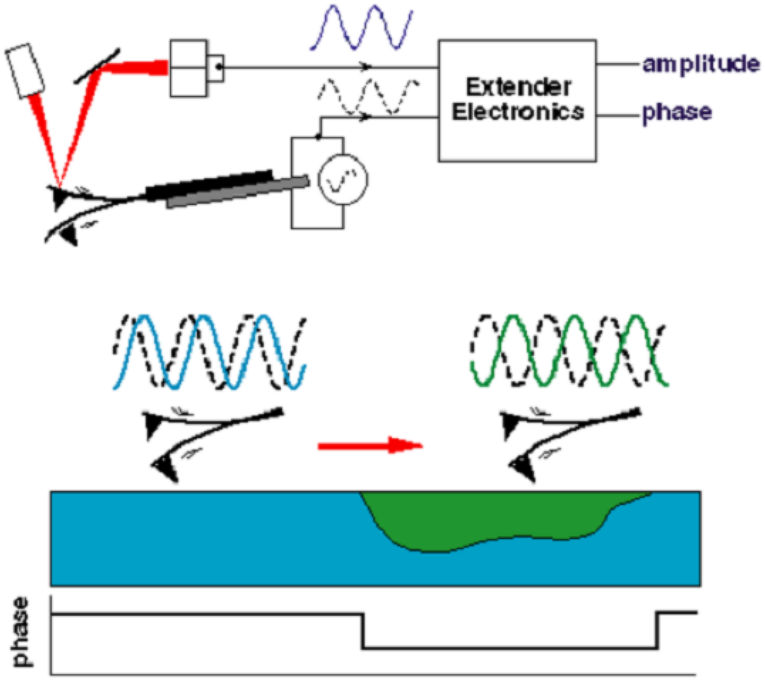
In this case the cantilevr is ascillating but at the end of its run it will touch the surface

In this case we are going to monitor the variations of the amplitude

AFM – working principle

Phase measurements

More sensitive to materials properties rather than topography



AFM – Confronto modalità di funzionamento

	Contact Mode	Tapping Mode	Non-Contact Mode
Advantages	• High scan speeds (throughput) • Rough samples with extreme changes in vertical topography can sometimes be scanned more easily in contact mode.	• Higher lateral resolution on most samples • Lower forces and less damage to soft samples • Lateral forces are virtually eliminated, so there is no scraping.	• No force exerted on the sample surface.
Disadvantages	• Lateral (shear) forces can distort features in the image. • The combination of lateral forces and high normal forces can result in reduced spatial resolution and may damage soft samples due to scraping between the tip and sample.	• Slightly slower scan speed than contact mode AFM.	• Lower lateral resolution, limited by the tip-sample separation • Slower scan speed than Tapping Mode and Contact Mode • Non-contact usually only works on extremely hydrophobic samples, where the adsorbed fluid layer is at a minimum.

Charge Transport Models in Organics

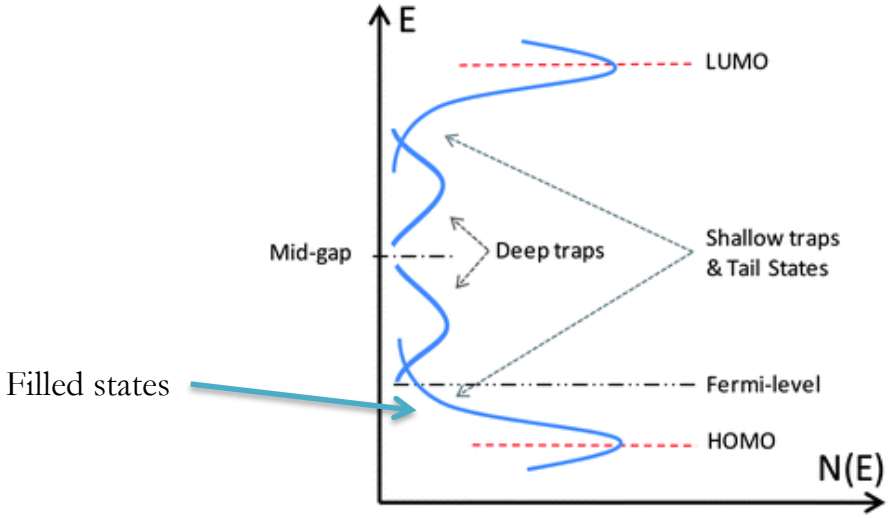
- Hopping Model (Miller-Abrahams)
- Multiple Trapping and Thermal Release

Band Transport

Crystal structure

- Continuous energetic bands
- Charge carriers move as free electron in a periodic potential, planar delocalized waves → very high mobility
- Scattering limited:
  - *Impurities*
  - *Phonons*
- Mobility decreases as temperature increases

Organic materials, different picture

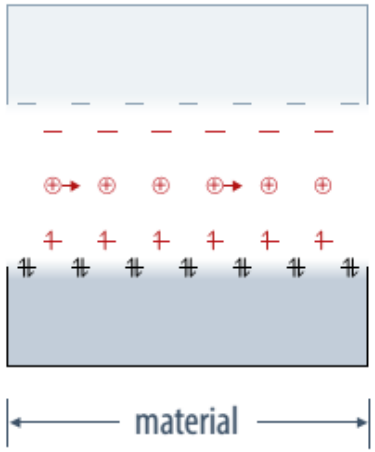


Impurities and disorder lead to a high concentration of trap states within the band gap, close to the edges of conduction and valence bands (shallow) or deeper in the gap (deep)

Band diagram is "smeared out"

Hopping Transport

Highly disordered structures



- Localized states
- Hopping dominated transport mechanism
- Thermal activation, mobility increases with T

Hopping model

Band like transport is very unlikely in organic materials due to the very low degree of order within the films

Charge transport is "hopping" like, charges hops between localized energetic states → Hopping Transport → phonon assisted

Localized states are due to defects of the materials or within the film and are generally localized in a small energetic range → high hopping probability

Hopping: Miller-Abrahams

Hopping rate from an occupied state i to an unoccupied one j, , with an energetic difference $\varepsilon_j - \varepsilon_i$ and a distance Rij:

$$W_{i,j} = \upsilon_0 \cdot \exp(-2\Gamma R_{i,j}) \begin{cases} \exp(-\dfrac{\varepsilon_i - \varepsilon_j}{k_B T}) & \varepsilon_i > \varepsilon_j \\ 1 & \varepsilon_i < \varepsilon_j \end{cases}$$

Tunneling

Boltzman factor (phonon absorption)

Γ^{-1} depends on the overlapping between the wave functions of the considered states, ν_0 pre-factor, esperimentally measured, k_B Boltzmann constant.

- Charge transport depends on the distance between states and on their distribution (density of states, DOS)
- Transport is thermally assisted

Hopping: Miller-Abrahams

It could happen that charge carries could hop more "easily" between states which are very distant but require a smaller activation energy, rather than between close states requiring a higher energy ***(Variable Range Hopping!)***

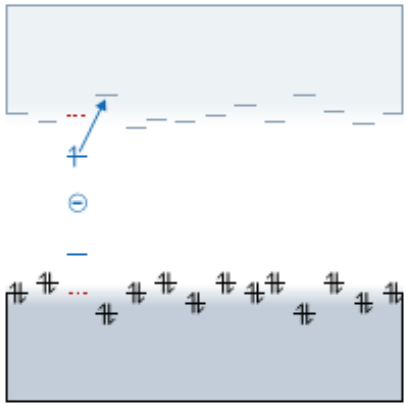
The first model was introduced by Mott, conductivity depends on temperature as follows:

$$\sigma(T) = \sigma_0 e^{-(T_0/T)^{1/\alpha}}$$

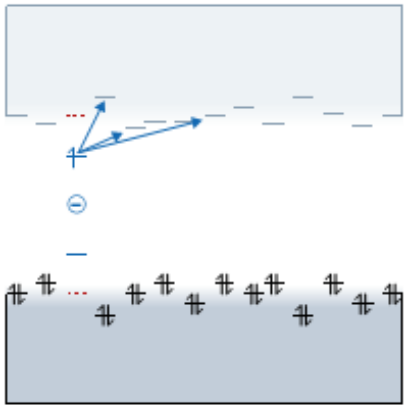
α between 1 and 4

Hopping: VRH Vissemberg e Matters

nearest neighbor hopping (NNH)



variable range hopping (VRH)



Hopping: VRH Vissemberg e Matters

Vissemberg e Matters developed a different version of VRH where DOS is an exponential distribution

The model takes also into account the dependance of mobility on the electric field (gate voltage dependance in transistors)

$$\sigma(\delta,T)=\sigma_0\left[\frac{\pi N_t \delta (T_0/T)^3}{(2\alpha)^3 B_c \Gamma(1-T/T_0)\Gamma(1+T/T_0)}\right]^{T_0/T}$$

$$\delta(x)=\delta_0 \exp\left[\frac{qV(x)}{kT}\right]$$

A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960)
D. Monroe, Phys. Rev. Lett. 54, 146 (1985)
M.C.J.M. Vissenberg and M. Matters, Phys. Rev. B 57, 12964 (1998)

Hopping: MTR

Some studies have demonstrated that also in some organic systems band like transport can occur

It can happen when the molecular order is very high, single crystals

Defect free structure, much lower concentration of trap states

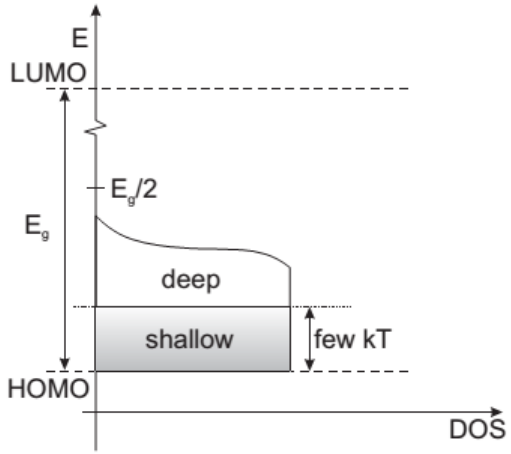
A new model must be provided

Multiple trapping and thermal release

MTR model was developed by Shur and Hack to better describe charge transport in amorphous

Afetrwards Horowitz extended such model also for organics

The model says that charge transport happens in extended states, but the most of the involved charge is trapped in localized states in the band gap

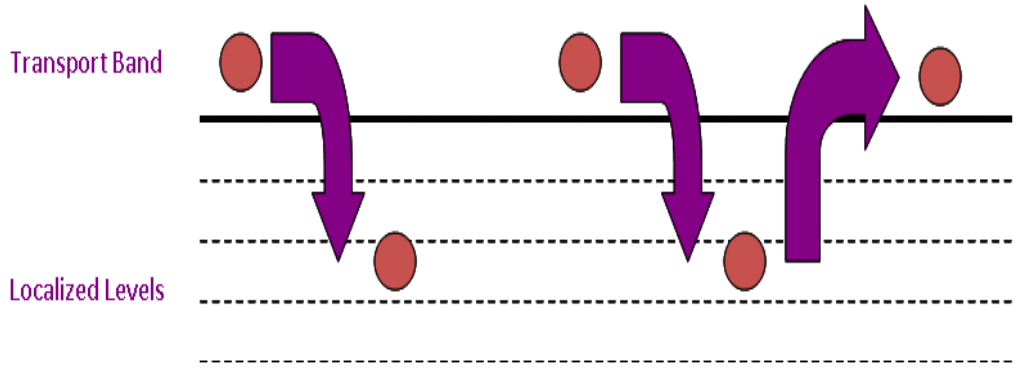


- *Deep states*
- *Shallow states*

Multiple trapping and thermal release

MTR → three transport levels:

- Transport
- Trapping
- Charge release



Charge transport is limetd by the presence of localized states which are very close to the HOMO and LUMO

Multiple trapping and thermal release

These states are due to defects, impurities etc.

Charge carriers are trapped during their transistion and are released afterwards thanks to thermal energy

Release dynamics depend on temperature, but also on the energy position of the state

As already said, temperature assists charges release from traps, also confering carriers kinetic energy by means of phonons

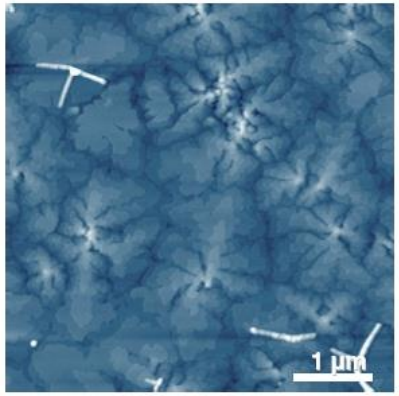
Multiple trapping and thermal release

Horowitz describes an organic film as it is characterized by two different regions:

- grains – high molecular order

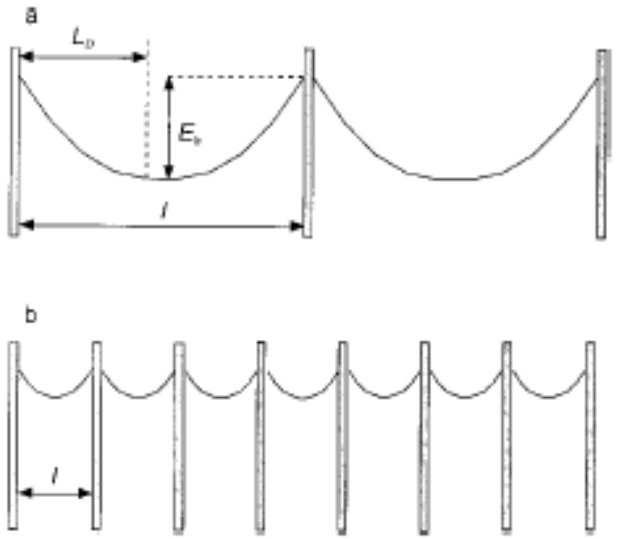
  transport through delocalized bands → *high mobility*

- Grain boundaries – high defects concentration, charge *trapping in localized (back-to-back diode like structure)* →*low mobility*



Pentacene su SiO_2

Hopping: MTR



$$L_D = \sqrt{\varepsilon_S kT / q^2 N}$$

Debye length

when $l < L_D$

Traps are uniformly distributed in the film

when $l > 2L_D$

Traps are mainly in the grain boundaries!

Hopping: MTR

$$\frac{1}{\mu} = \frac{1}{\mu_g} + \frac{1}{\mu_b}$$

Mobility depends on the mobility in the two regions

$\mu_g >> \mu_b$ → mobility is strongly limited by grain boundaries!

when $l < L_D$

$$\mu = \mu_0 \exp\left(-\frac{E_b}{kT}\right)$$

- Thermal activation
  Thermoionic emission
- μ_0 trap free mobility

Hopping: MTR

when $l > 2L_D$ for low T

$$\mu = \mu_0(T)\exp\left(-\frac{E_b}{E_0}\right)$$

No thermal activation
Tunneling

E_0 is a constant depending on polaron mass and defects concentration

When $l > 2L_D$ for high T

$$\mu = \frac{q\langle v\rangle l}{8kT}\exp\left(-\frac{E_b}{kT}\right)$$

Thermal activation
Thermoionic emission

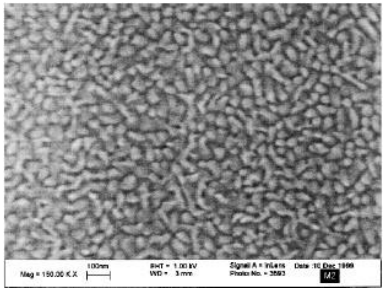
v = average electron speed

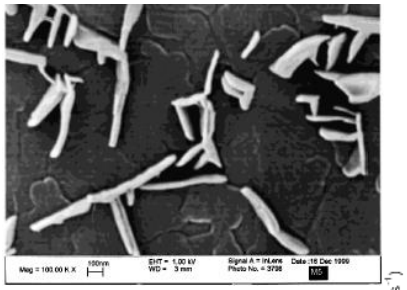
N.B. mobility linearly depends on the grain dimension (l) within the film

Hopping: MTR

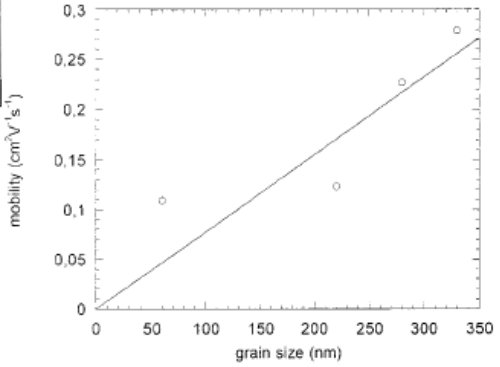
Electronic properties depend on the morphological/structural properties of the film!

Controlling film growth is very important:
Which are the parameters determining the film properties?
Investigation of structural/morphological features

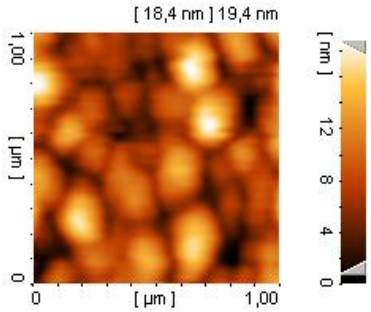
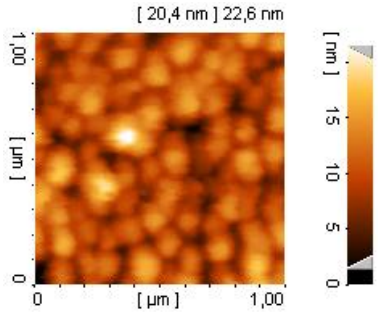
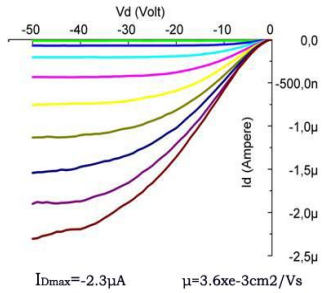
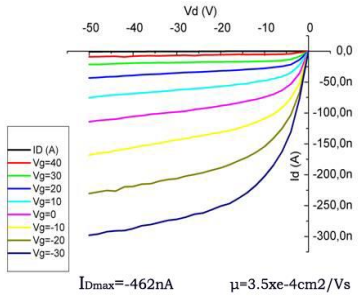


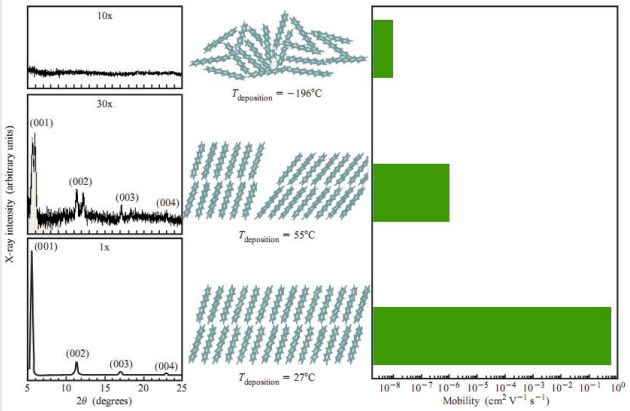


Substrate temperature [°C]	Grain size [nm]	Mobility [$cm^2 V^{-1} s^{-1}$]
room temperature	60	0.11
120	220	0.12
150	280	0.23
175	330	0.28



Correlation between morphological properties and mobility

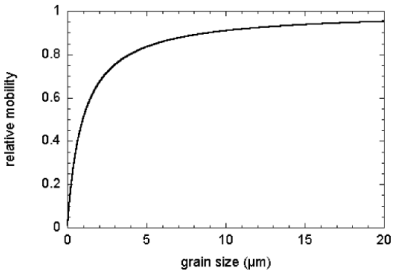
Rate 0.2 Å/sec *Spessore 300Å*	Transistor su Mylar®	Transistor su SiO_2
Morfologia		
I_D/V_D		

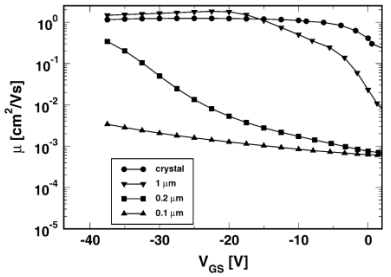


OFET mobility depends on structural and morphological properties of the active layer

Mobility depends on average grains dimensions (grain boundaries density)

Gate voltage dependance of mobility



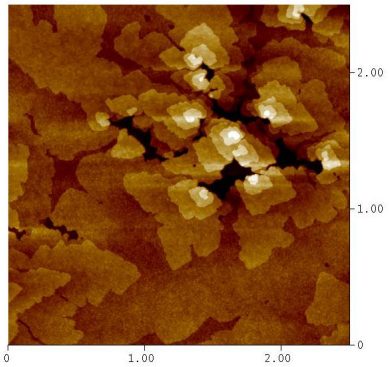


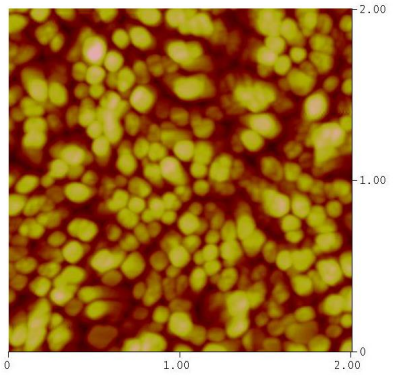
Materials
A few examples

Small molecules: Pentacene

Nelle molecole come il pentacene il trasporto di carica il trasporto di carica all'interno del fim dipende non solo dalla sovrapposizione degli orbitali π nella direzione dell'asse maggiore della molecola (**intra-chain charge transport**), ma anche dall'interazione tra orbitali π di molecole adiacenti (**inter-chain charge transport**).

Per cui il trasporto di carica è fortemente influenzato dalle proprietà morfologiche e strutturali del film depositato





Small molecules: Pentacene

band gap (as the most of organic semiconductors) around 2,2 eV.

Pentacene ionization energy(HOMO energy level) around 5.2 eV and electron affinity (LUMO level) around 3 eV.

It generally, in principle, forms an ohomic contact with Au, having a WF around 5.1 eV

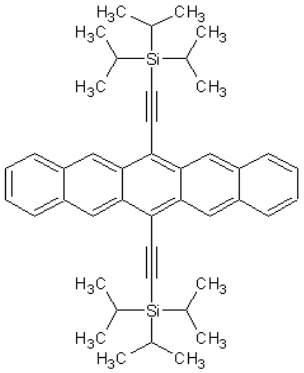
Lower barrier with respect to HOMO, higher barrier with LUMO

Good hole injection, but bad electron injection

Generally pentacene is p-type

Small molecules: Pentacene

6,13-Bis(triisopropylsilylethynyl)pentacene (Pentacene TIPS) similar to pentacene with two chains in the position 6 and 13



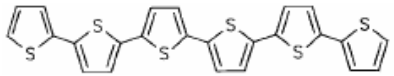
HOMO around 5.3 eV and LUMO around 3 eV, band gap around 2.3 eV

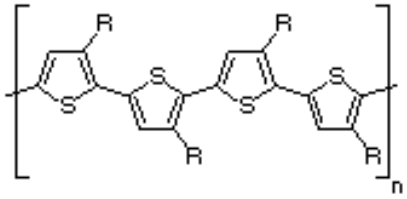
Similar to the previous one, p-type

Small molecules: oligothiopenes

thiophene monomer

Thiophene





quater-thiophene and **sexi-thiophene**

rod like molecules, as pentacene

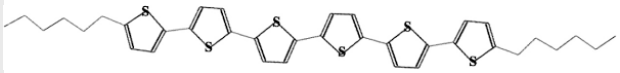
Energy gap around 2.0-2.2 eV

HOMO around 5 eV (p-type)

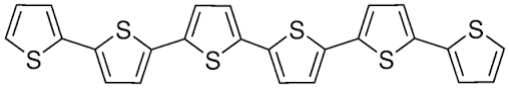
Can be functionalized in order to be soluble

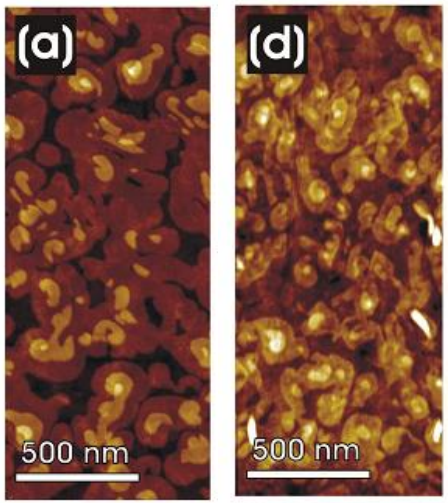
Small molecules: oligothiopenes

Dihexyl sexithiophene

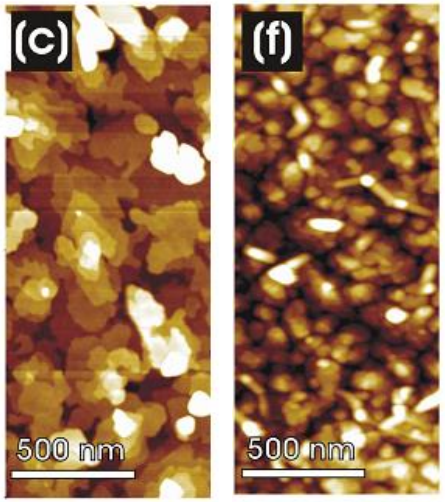


Sexithiophene





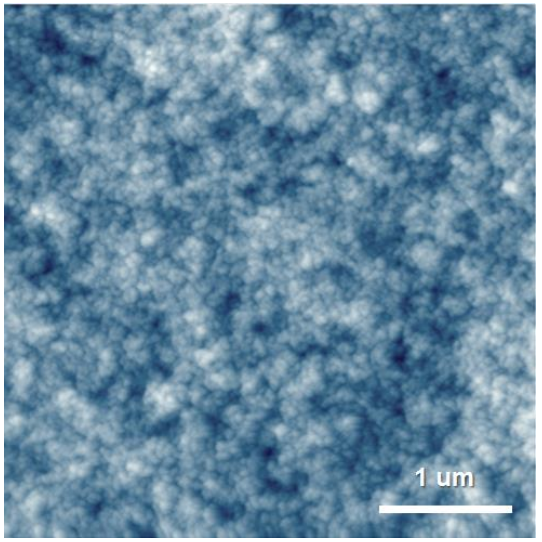
On SiO_2 On PET



On SiO_2 On PET

Polymers: polythiophenes (P3HT)

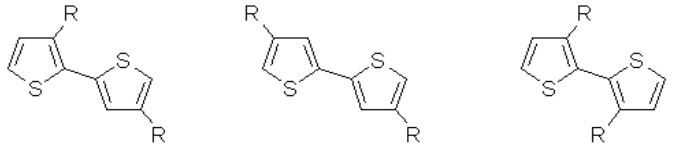
- poly (3-hexylthiophene) **P3HT**
- Soluble, tra i quali il chlorobenzene, il toluene and lo xylene.
- HOMO around 4.8 eV, very clos to Au WF
- Good hole injection, p-type
- Early Aging, due to lower ionization energy



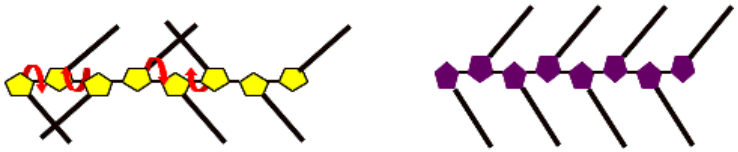
Regio-regolarity

P3HT is not symmetric!

Three different structures, depending on where the alkyl chains are attached



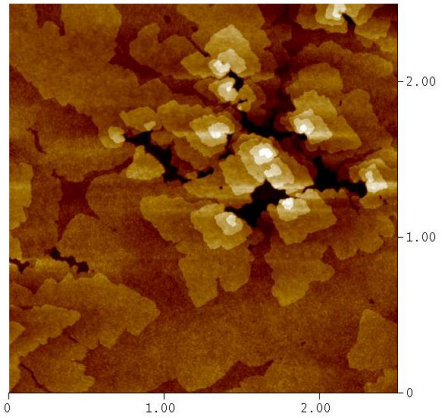
When there is amix of the different structure the polymer is called regio-irregular, if the structur is well controlled, regio-regular

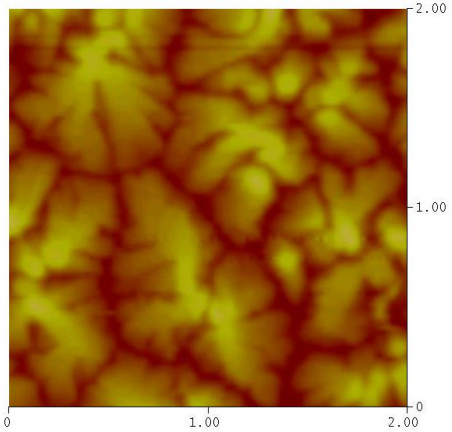


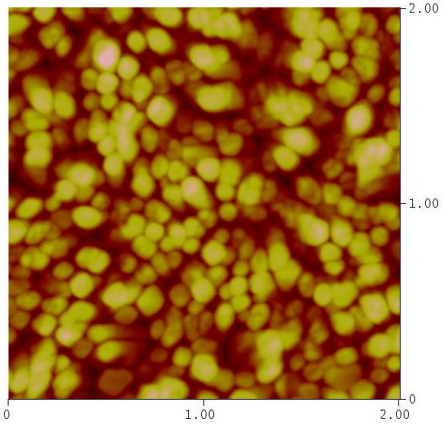
In order to have better morphology, leading to higher performances, a high regio-regularity is required

Morphological characterization

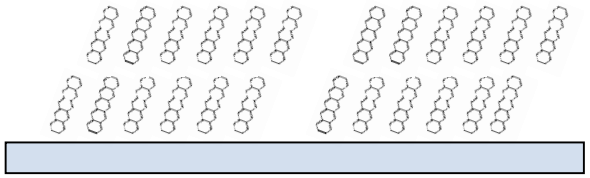
Differenti tipologie di morfologia



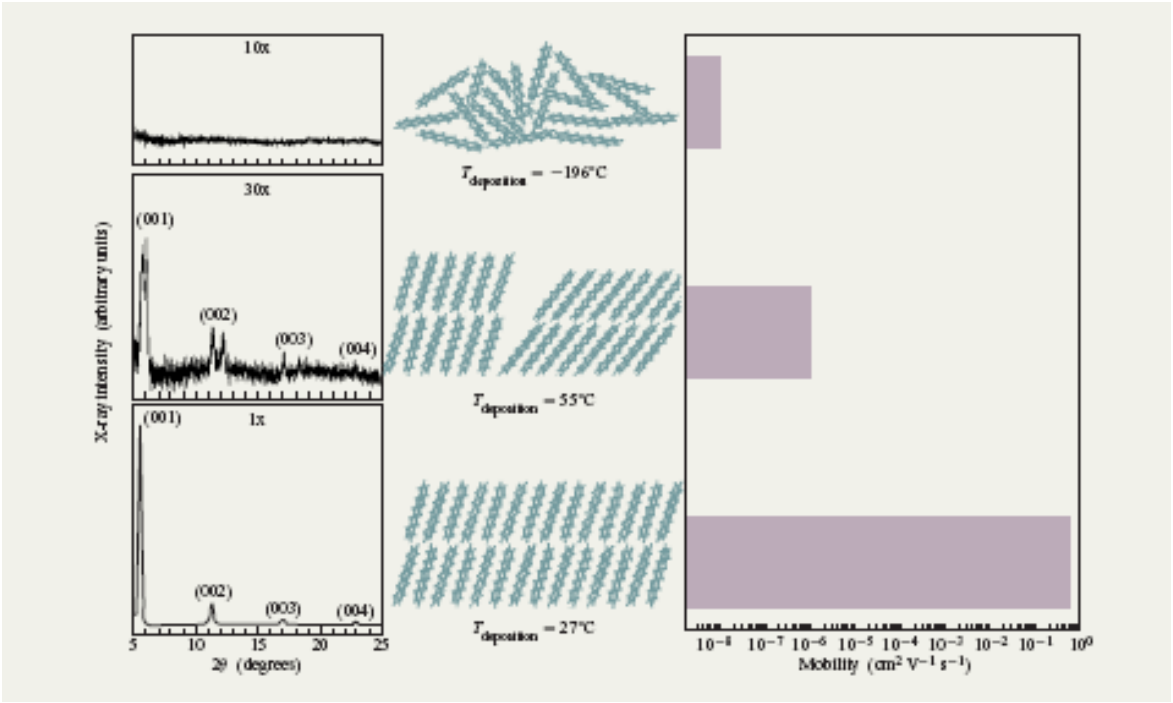


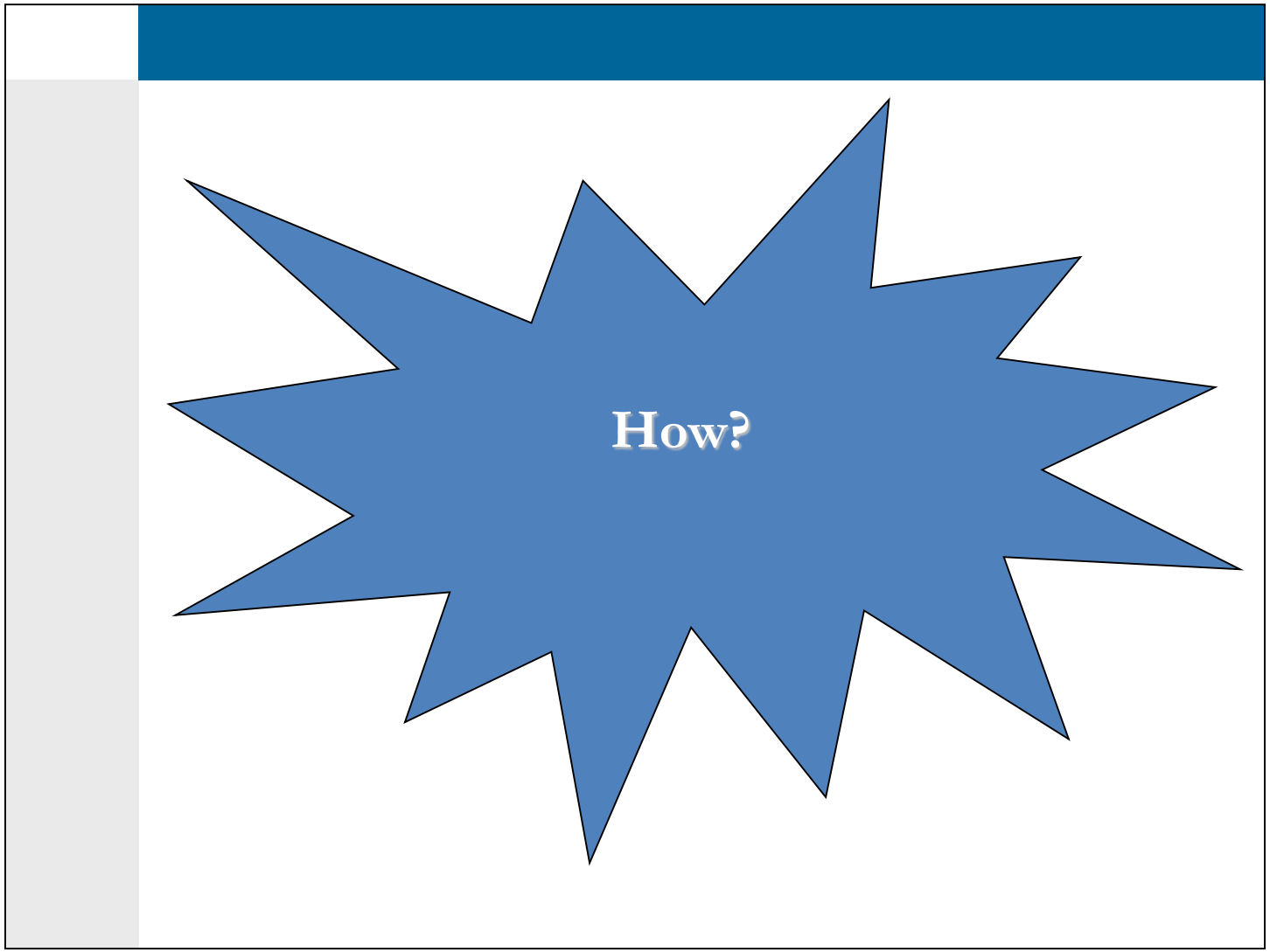


Same molecule can lead to different morphologies → different electrical properties

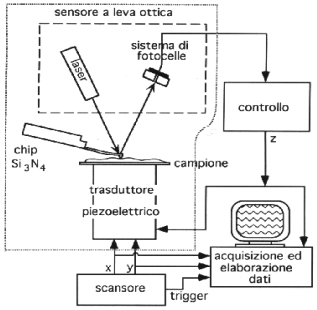
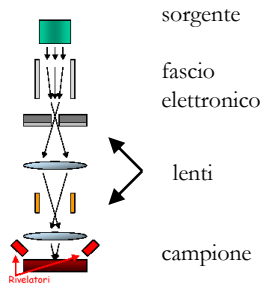
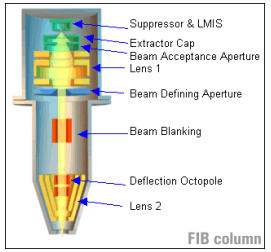


Morphology → transport




How?

instrumentation

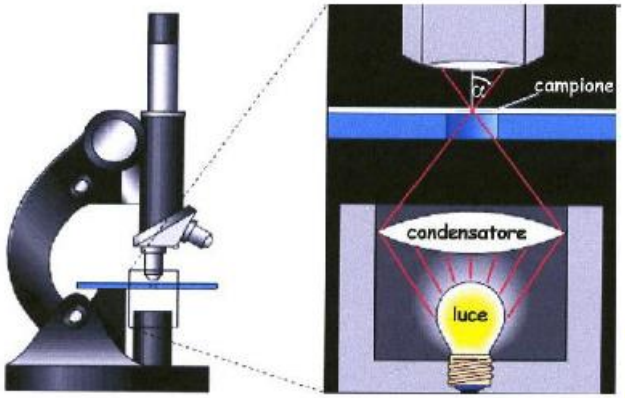
	SPM Scanning Probe Microscopy	SEM Scanning Electron Microscopy	FIB Focused Ion Beam
Scheme			
probe	cantilever	electrons	ions
Analysis	• morphology • spectroscopy	• morphology • spectroscopy	• morphology • spectroscopy • samples manipulation

instrumentation – optical microscope

La Microscopia Ottica

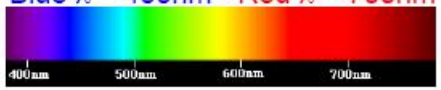
- Il limite di risoluzione di un microscopio può essere calcolato con la formula di Rayleigh

$$R = 0.61 \frac{\lambda}{\eta sen\alpha}$$



Luce visibile:

Blue λ = 400nm - Red λ = 700nm



Indice di rifrazione:

η = 1.0 Aria

η = 1.4 Olio

Risoluzione ≈ 0.22μm

Instrumentation - SEM

La Microscopia Elettronica

- Un sottile fascio di elettroni viene usato come sonda al posto della luce

relazione di De Broglie

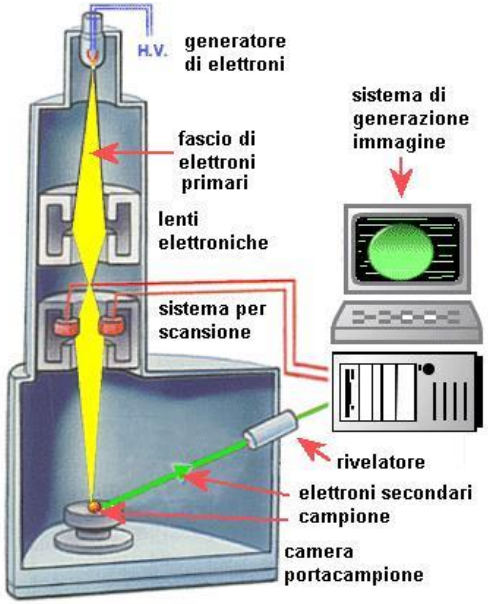
$$\lambda = h/mv$$

λ: Lunghezza d'onda associata alla particella
h: Costante di Plank 6.63×10^{-34} Js;
mv: momento della particella

La lunghezza d'onda dell'elettrone può essere ridotta aumentando il suo momento.

particle	Mass(kg)	Speed (ms^{-1})	Wavelength (pm)
1 eV electron	9.1×10^{-31}	5.9×10^{5}	1200
100 eV electron	9.1×10^{-31}	5.9×10^{6}	120
10 KeV electron	9.1×10^{-31}	5.9×10^{7}	12

Strumentazione - SEM



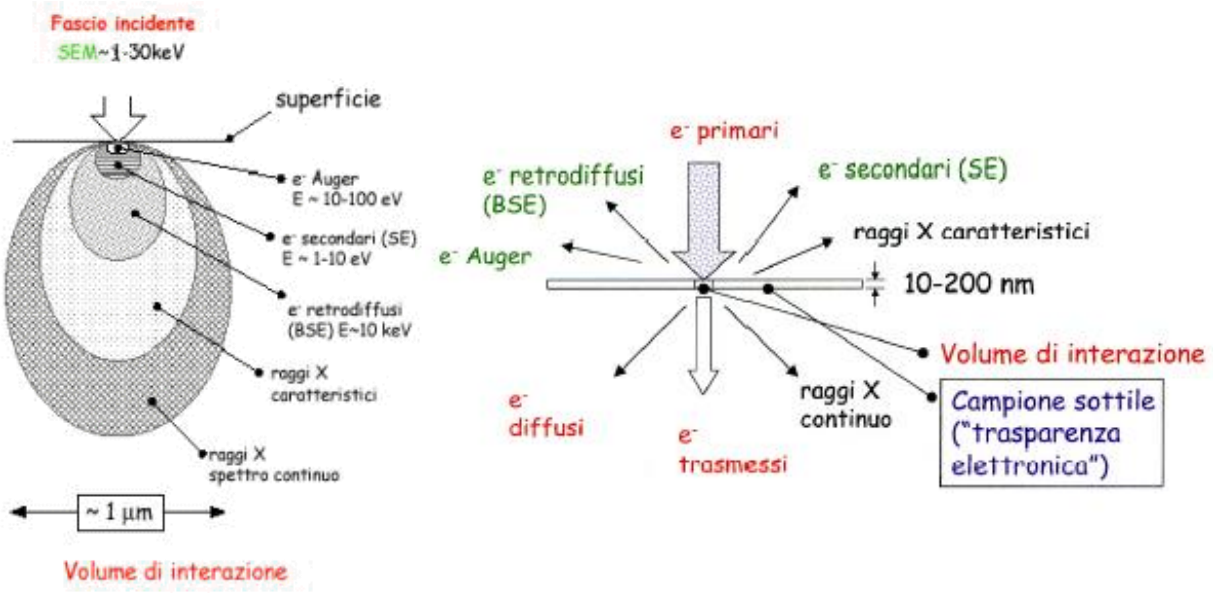
La sorgente emette elettroni per effetto termoionico.

Gli elettroni vengono accelerati da una differenza di potenziale e confinati tramite opportune lenti elettromagnetiche.

La scansione è determinata da un sistema di bobine a campo magnetico variabile.

Un secondo sistema di lenti focalizza meglio il fascio elettronico sul campione.

Instrumentation- SEM



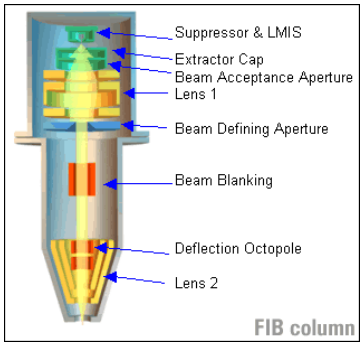
A detector attracts the scattered electrons and lead them into a CRD.

An image can be formed similarly as it used to happen in former TV screens

Instrumentation - FIB

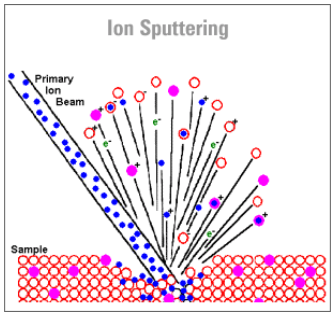
The source is a tungsten wire in a liquid metal (generally Gallium), LMIS

Beam creation is similar to SEM

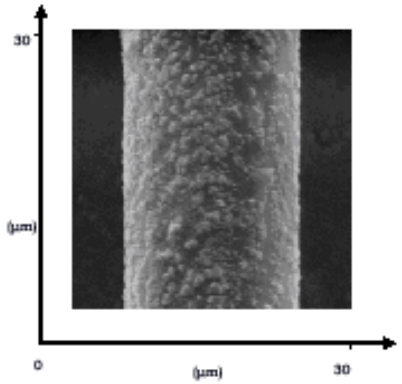


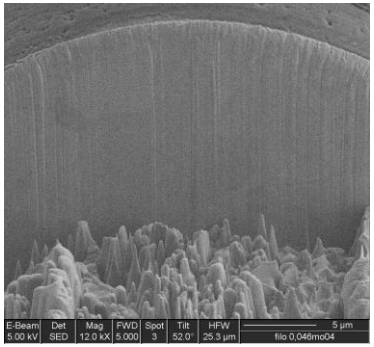
Ions are heavier than electron, more massive, can degrade sample surface

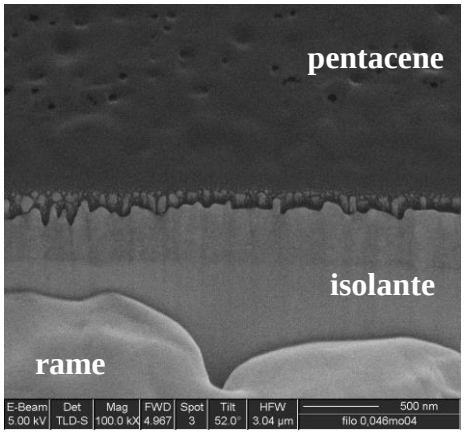
Such phenomenon can be used to make samples sections (Milling)



FIB


30
(µm)
0
(µm)
30


E-Beam 5.00 kV
Det SED
Mag 12.0 kX
FWD 5.000
Spot 3
Tilt 52.0°
HFW 25.3 µm
5 µm
filo 0,046mo04


pentacene
isolante
rame
E-Beam 5.00 kV
Det TLD-S
Mag 100.0 kX
FWD 4.987
Spot 3
Tilt 52.0°
HFW 3.04 µm
500 nm
filo 0,046mo04

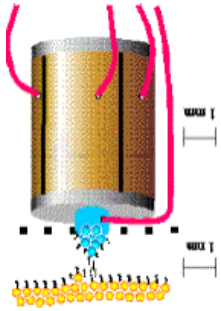
Scannig Probe Microscopy

A probe is used to scan the sample

A piezoelectric motor moves the sample with respect to the probe (or viceversa)

Such probe as a radius in the range of Ångstrom → very high resolution

Analizing such interaction probe/sample morphological informations can be obtained



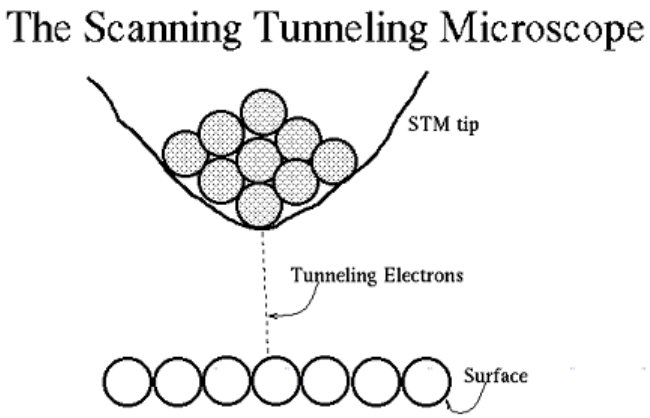
Probe-sample interaction:

- **Tunneling current→ Scanning Tunneling Microscopy (STM)**
- **Force→ Atomic Force Microscopy (AFM)**

Scanning Probe Microscope- STM

It was invented by **G. Binning e H. Rohrer** to study the conductivity of surfaces

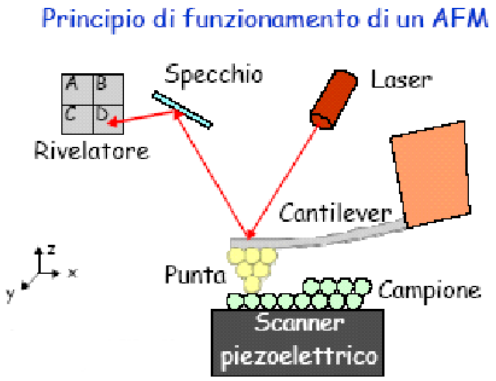
It is based on quantum mechanics effects, tunnelling current

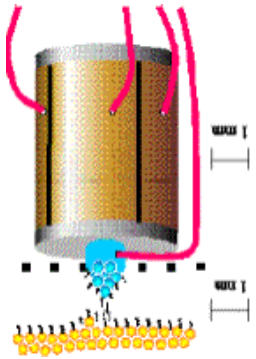


Scanning Probe Microscope-AFM

The signal is the interaction force, leading to a **deflection of the probe**

From such deflection morphological information can be obtained





The deflection is measured point by point through a raster scan

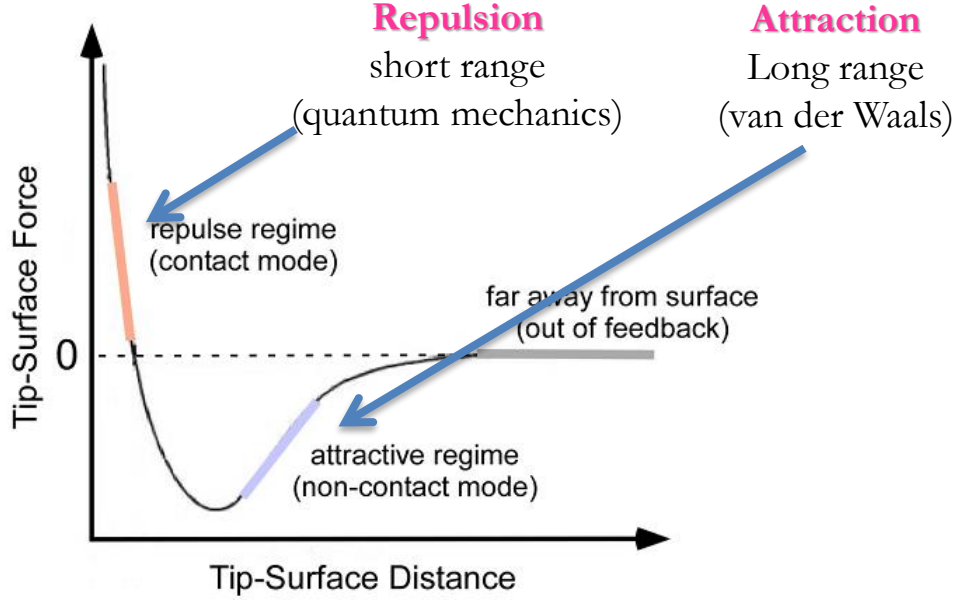
Involved forces

The interaction energy between two atoms depends on their distance and can be expressed by the Lennard – Jones expression:

$$w(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Repulsion
short range
(quantum mechanics)

Attraction
Long range
(van der Waals)



Scanning Probe Microscope-AFM

A laser beam is reflected from the back side of the probe (cantilever) into a photodetector system Al movimento del cantilever corrisponde quindi uno spostamento dello spot sullo schermo.

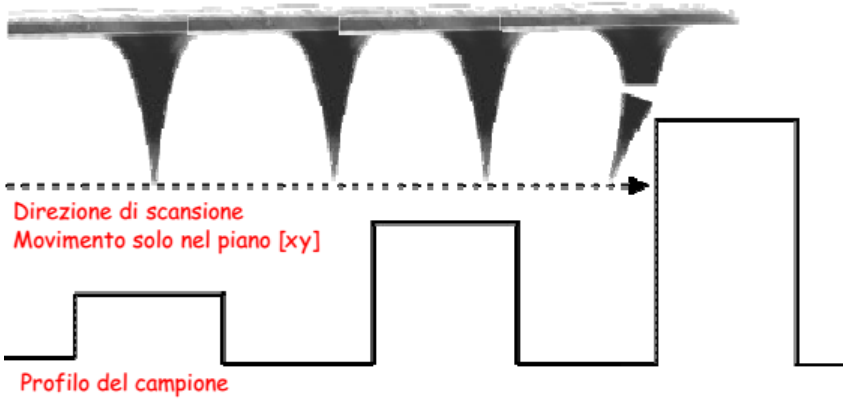
This induces a current variation in the photodetectors that can be turned into z deflections of the tip.

AFM – working principle

Contact mode: constant height

The cnatilever is at a fixed height during all the measurement. Its distance with respect of the surface will cange according to the surface roughness

By measuring the tip/sample repulsion forces, depending on the surface morphology, topographic information can be obtained.

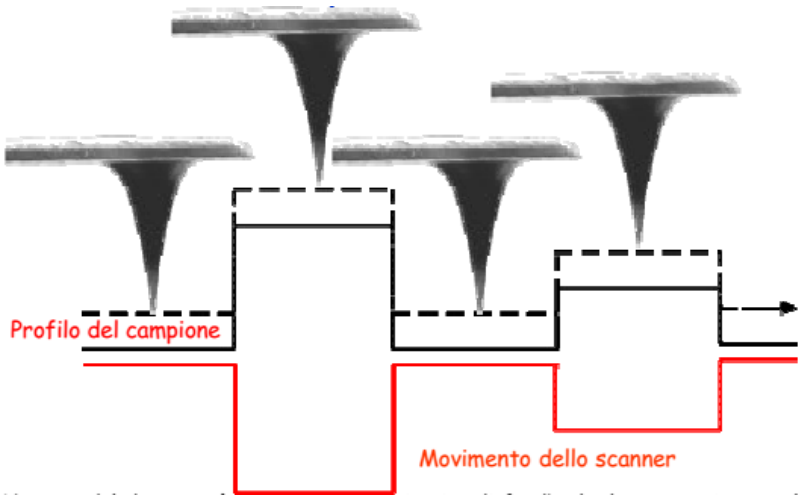


AFM – Modalità di funzionamento

Contact mode: constant force

In this case the vertical contact force is kept constant, that is given by the deflection times the cantilever elastic constant

$F=k\Delta z$



AFM – working principle

Non contact mode:

In this case the cantilever is at a distance around **10 nm** or more from the surface.

Van der Waals forces are playing the role

The cantilever is generally forced to oscillate close to the cantilever resonance frequency ω_0

The interaction lead to

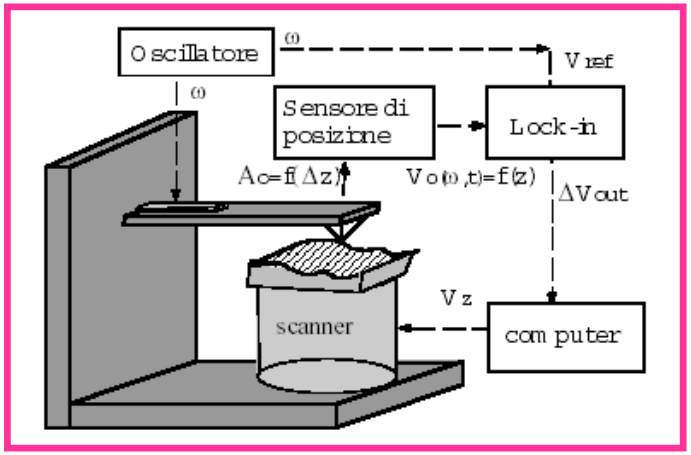
- Amplitude variations,
- Resonance frequency variation.

AFM – working principle

Non contact mode:

Interaction force is very small.

Generally used for bio-samples



AFM – working principle

Modalità semicontact mode:

A **combination between contact and non contact also called** *Tapping mode*.

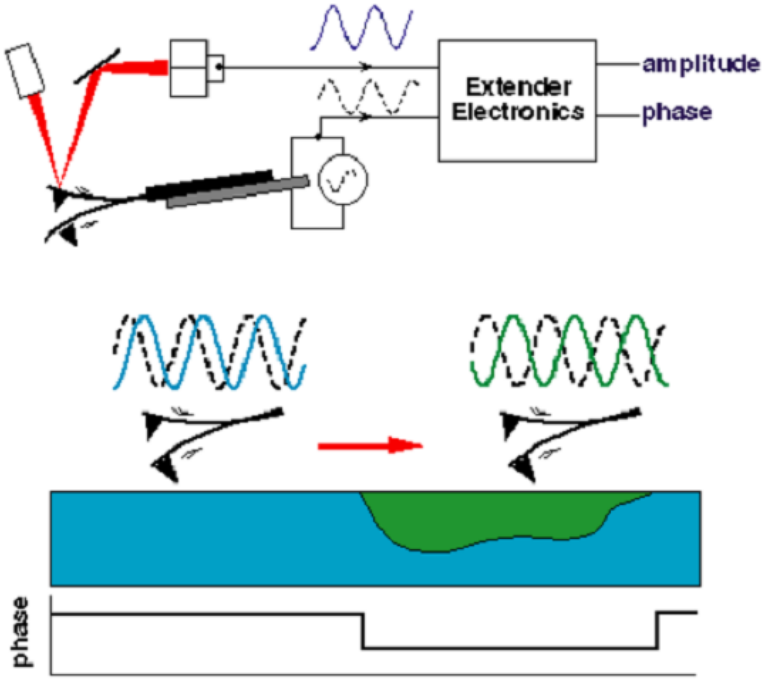
In this case the cantilevr is ascillating but at the end of its run it will touch the surface

In this case we are going to monitor the variations of the amplitude

AFM – working principle

Phase measurements

More sensitive to materials properties rather than topography



AFM – Confronto modalità di funzionamento

	Contact Mode	Tapping Mode	Non-Contact Mode
Advantages	• High scan speeds (throughput) • Rough samples with extreme changes in vertical topography can sometimes be scanned more easily in contact mode.	• Higher lateral resolution on most samples • Lower forces and less damage to soft samples • Lateral forces are virtually eliminated, so there is no scraping.	• No force exerted on the sample surface.
Disadvantages	• Lateral (shear) forces can distort features in the image. • The combination of lateral forces and high normal forces can result in reduced spatial resolution and may damage soft samples due to scraping between the tip and sample.	• Slightly slower scan speed than contact mode AFM.	• Lower lateral resolution, limited by the tip-sample separation • Slower scan speed than Tapping Mode and Contact Mode • Non-contact usually only works on extremely hydrophobic samples, where the adsorbed fluid layer is at a minimum.