Dispositivi e sensori a semiconduttore organico

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1: Semiconduttori organici

2: Organic Thin Film Transistors (OTFT)

3: Sensori basati sugli OTFT

Outline prima parte

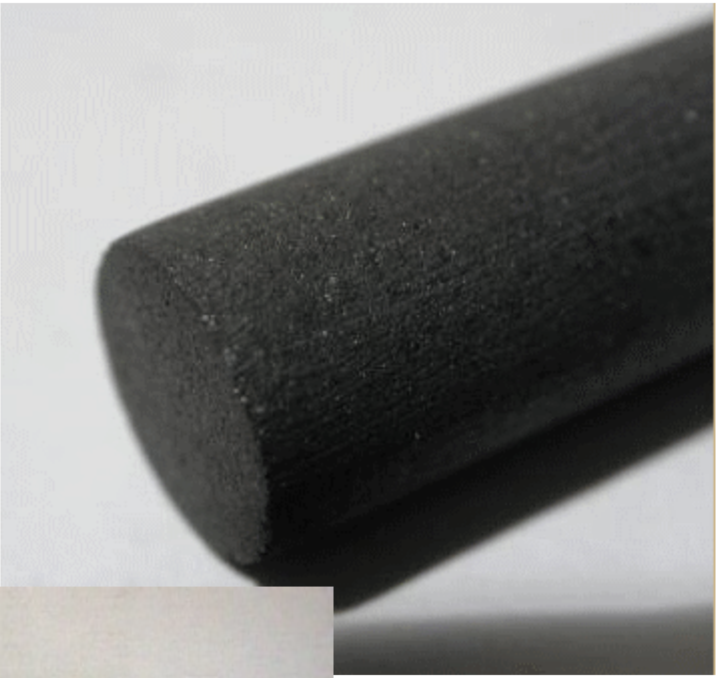
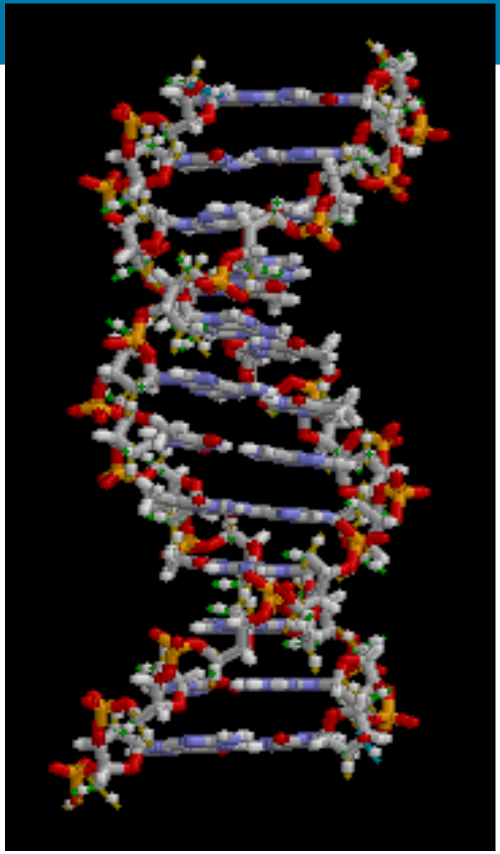
Proprieta' degli orbitali del Carbonio

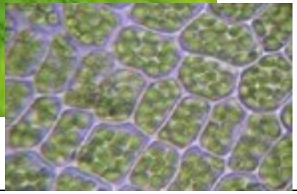
Molecole coniugate

Semiconduttori organici: orbitali molecolari e bandgap

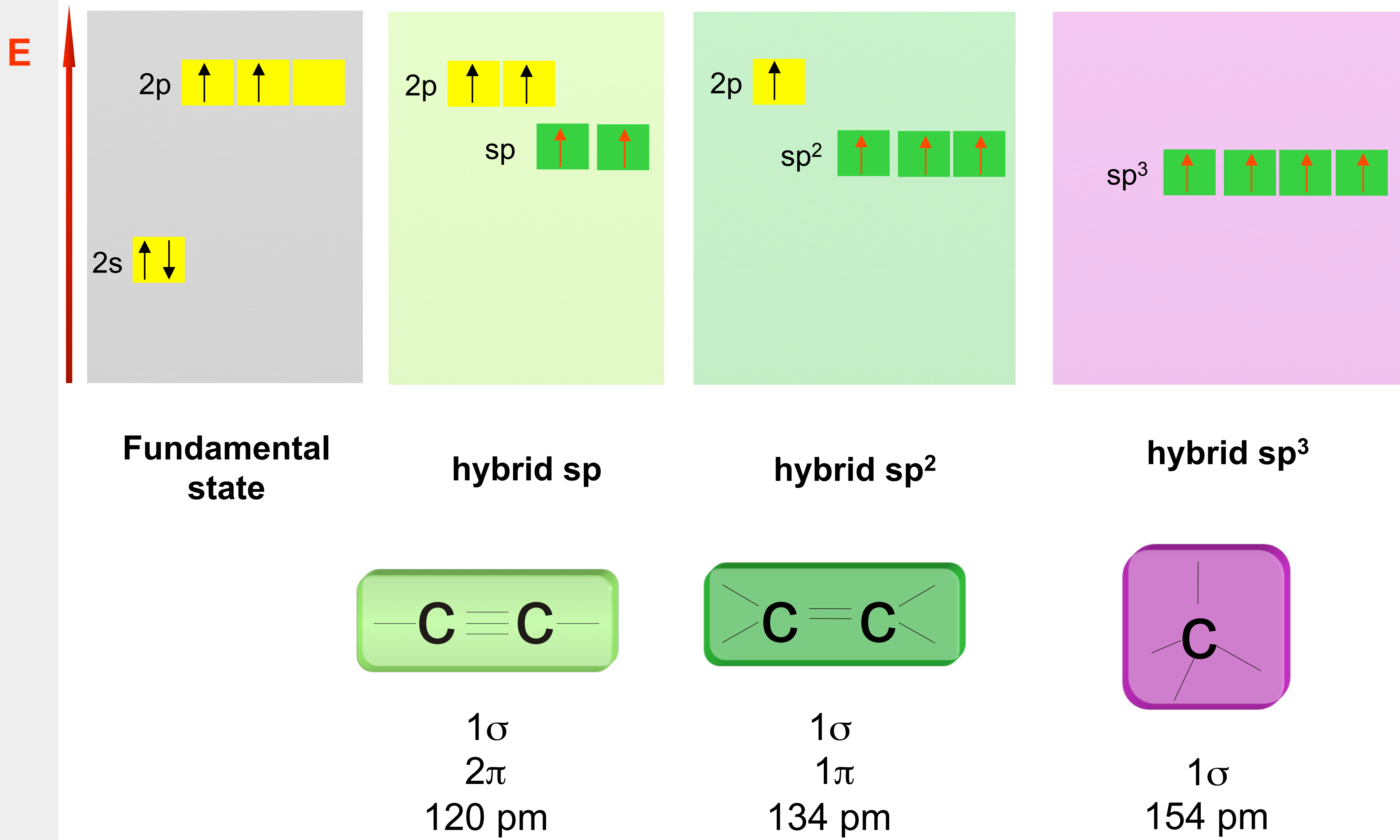
Portatori di carica e trasporto nei semiconduttori organici

Influenza della morfologia sul comportamento elettrico dei film sottili organici

Hybridization of orbitals in Carbon

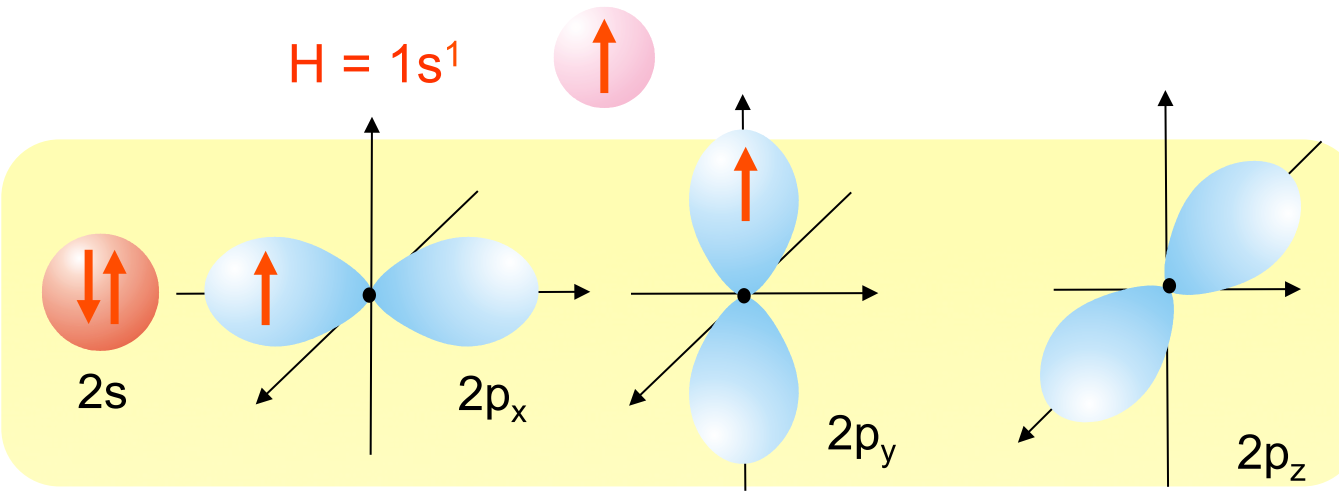


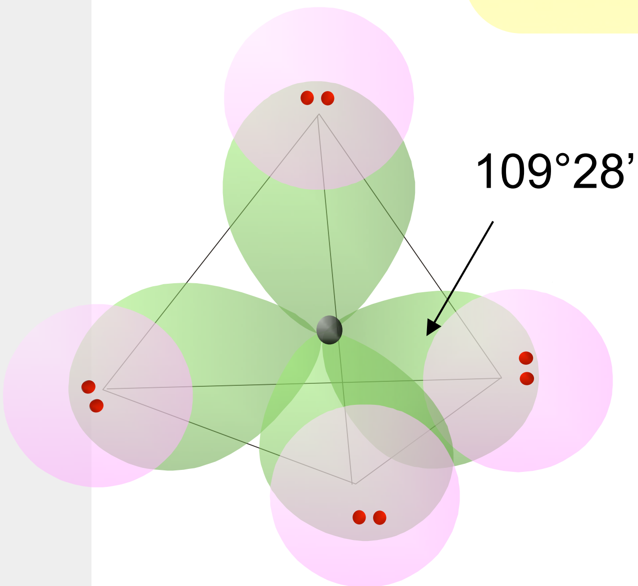
Hybridization of orbitals in Carbon

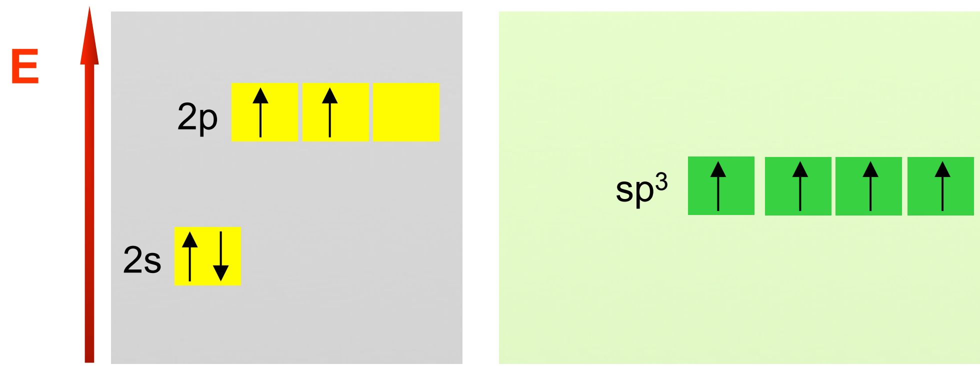
For instance: CH_4

$H = 1s^1$

$[He]2s^22p^2$





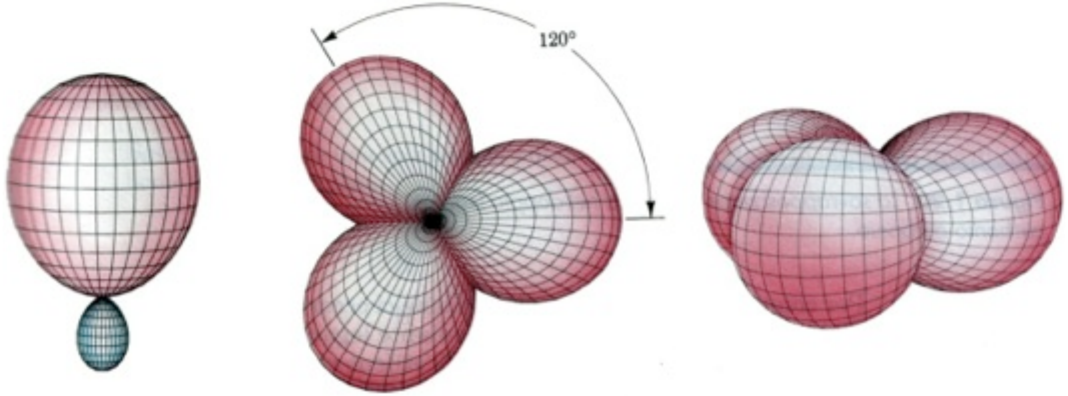


stato fondamentale

Ibrido sp^3

AB_4: tetraedrica

Hybridization of orbitals in Carbon



Hybrid orbital sp^2 Top view Side view

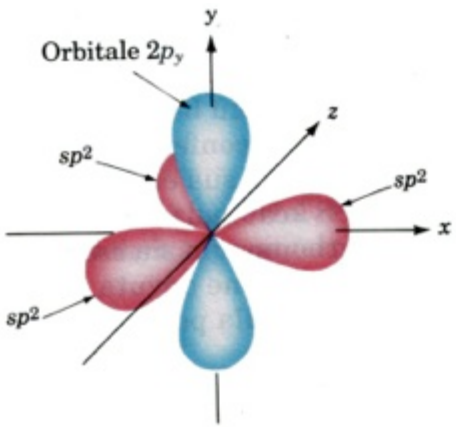


fig.1.1: un atomo di carbonio ibridizzato sp^2 [3].

Carbon-Carbon bonding

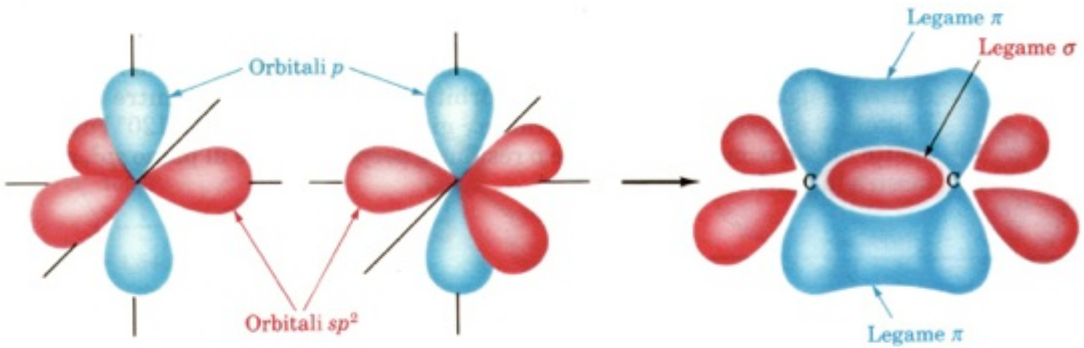
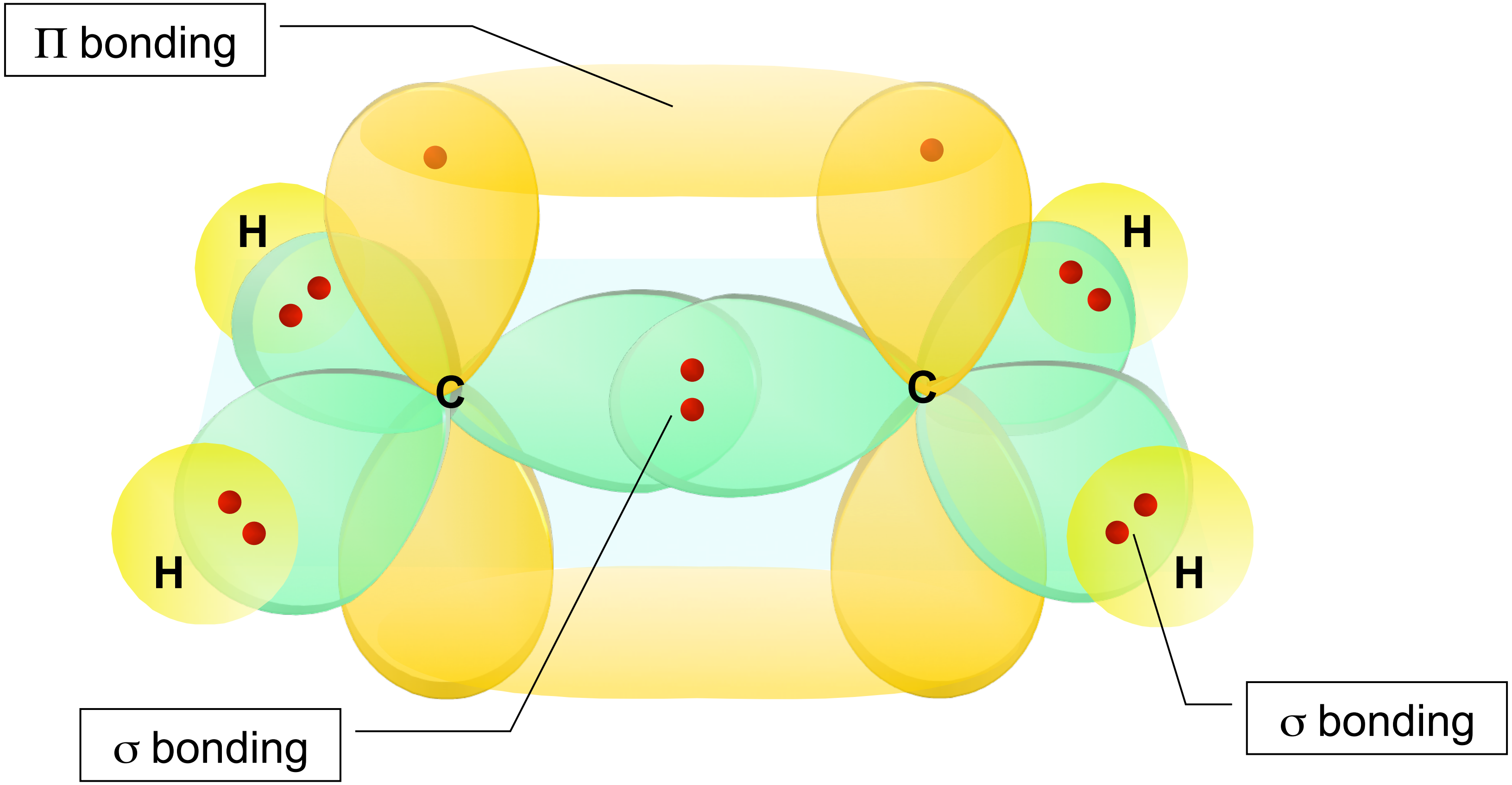
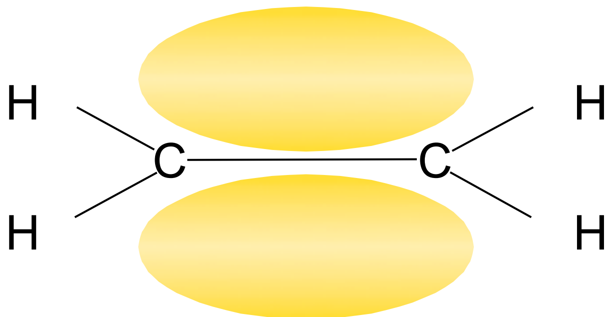


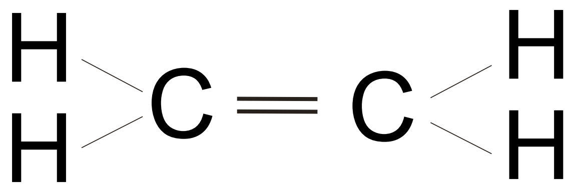
fig.1.2: la sovrapposizione orbitalica nel doppio legame carbonio-carbonio [3].

Molecular Orbital= linear combination of atomic orbitals (LCAO)

Carbon-Carbon bonding

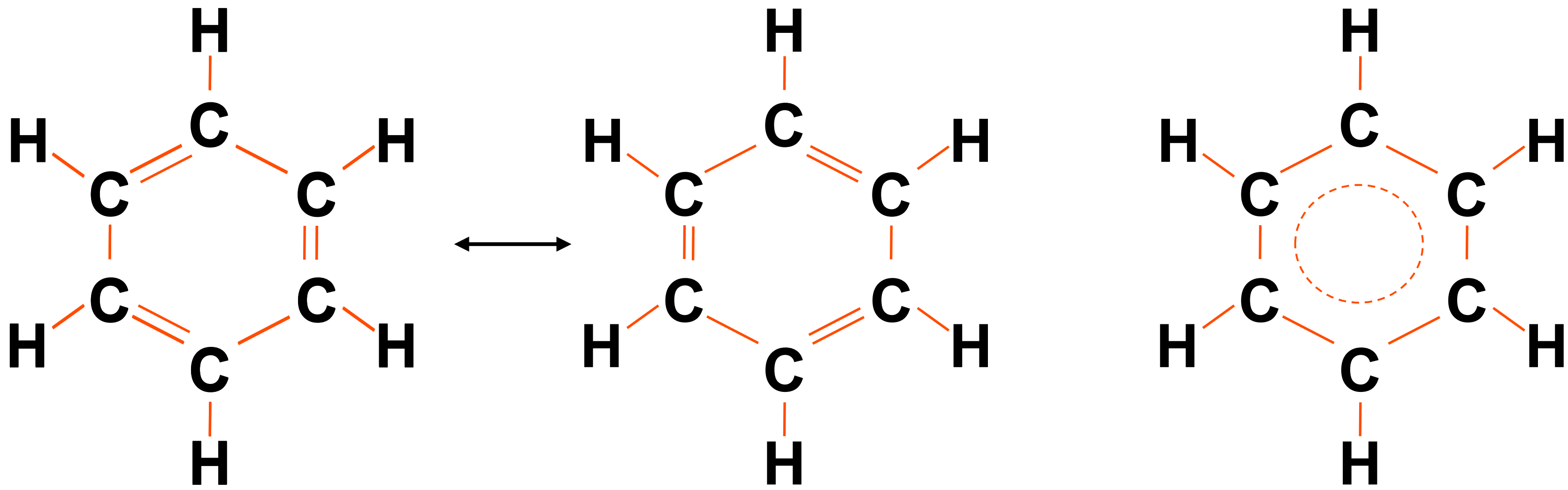




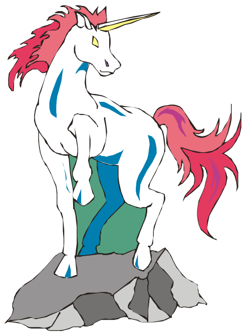


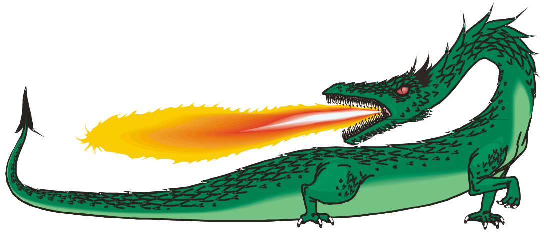
Coniugated molecules

C_6H_6

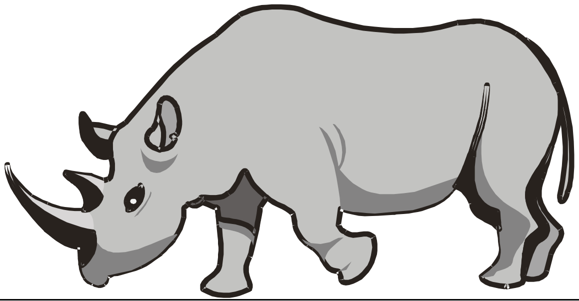


Limit formula



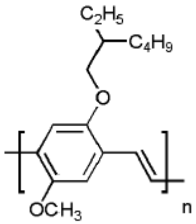


Limit formula

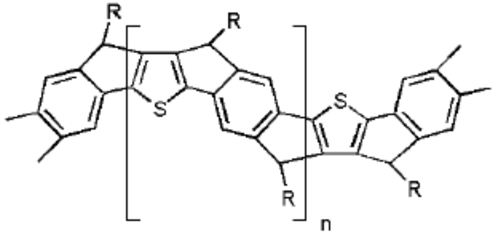


Real molecule

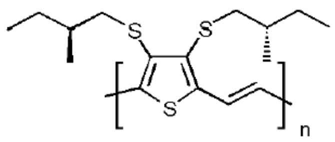
Coniugated molecules



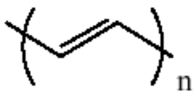
MEH-PPV



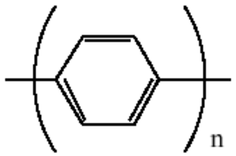
LPPPT



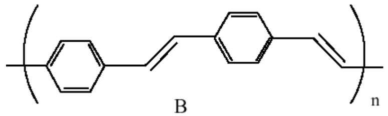
PTV



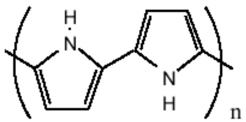
A



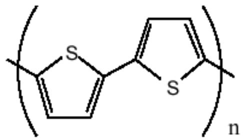
B



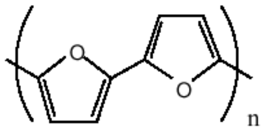
C



D



E



F

fig.1.6: struttura molecolare di: A) trans-poliacetilene (PA); B) poli-para-fenilene (PPP); C) poli-fenile-vinilene (PPV); D) poli-pirrolo (PPy); E) poli-tiofene (PT); F) poli-furano (PF) [4].

Band Gap

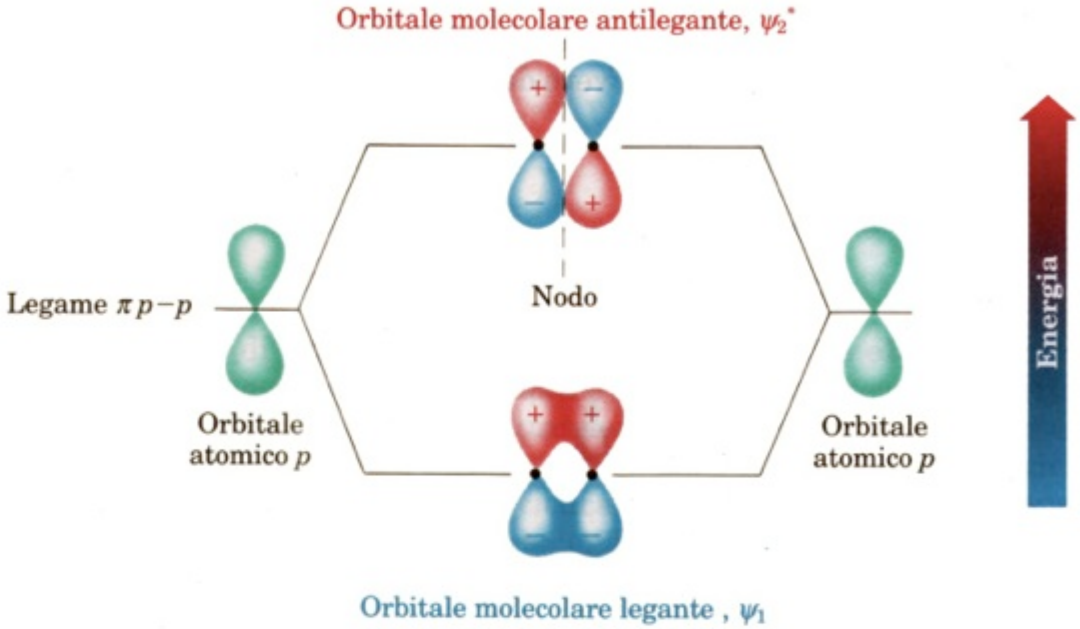
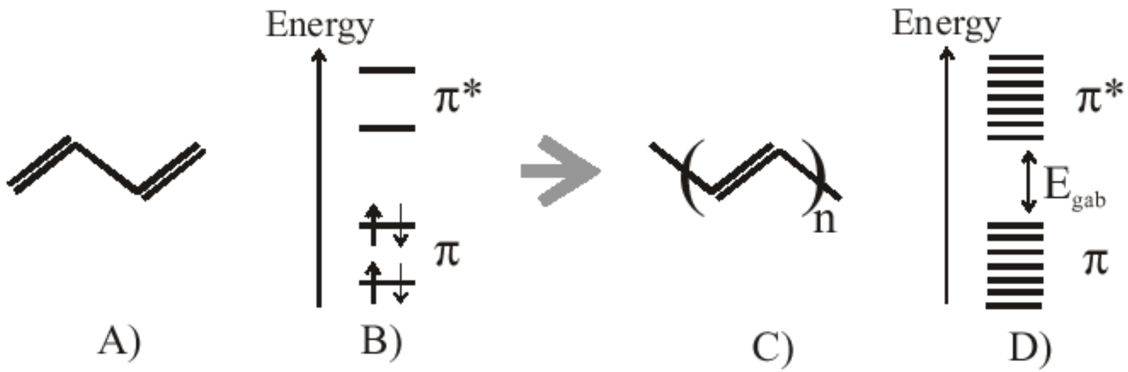


fig.1.7: orbitali molecolari π leganti e antileganti [3].

Legame	Energia di legame (kJ • mol^{-1})
C—C	350
C—H	410
C—O	350
C—S	260
C—F	440
C—Cl	330
C—Br	280
C—I	240



Legame	Energia di legame (kJ • mol^{-1})
Si—Si	180
Si—H	300
Si—O	370
Si—S	230
Si—F	540
Si—Cl	360
Si—Br	290
Si—I	210

Band Gap

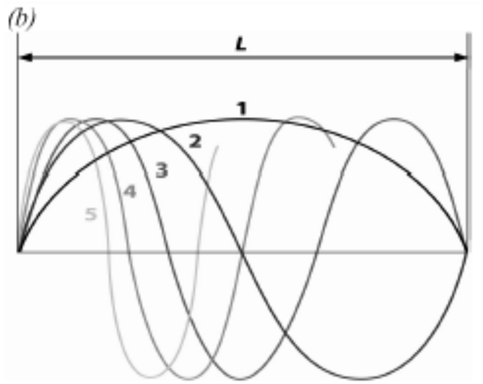


fig.1.10: funzioni d'onda dell'elettrone π nella buca di potenziale profonda infinito [6].

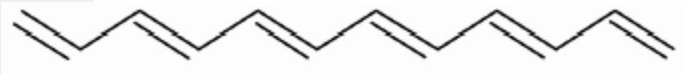
L = coniugation length = length of the shortest molecular segment with a perfect alternation of single and double bonds; N= number of atoms (each with 2 electrons); d = atomic distance

$$E_n = \frac{n^2 h^2}{8mL^2} \longrightarrow \quad E(HOMO) = \frac{\left(\frac{N}{2}\right)^2 h^2}{8m(Nd)^2} \qquad E(LUMO) = \frac{\left(\frac{N}{2}+1\right)^2 h^2}{8m(Nd)^2}$$

$$\longrightarrow E_G = E(LUMO) - E(HOMO) = \frac{(N+1)^2 h^2}{8m(Nd)^2} \approx \frac{h^2}{8md^2 N}$$

The highest N, the lowest the gap

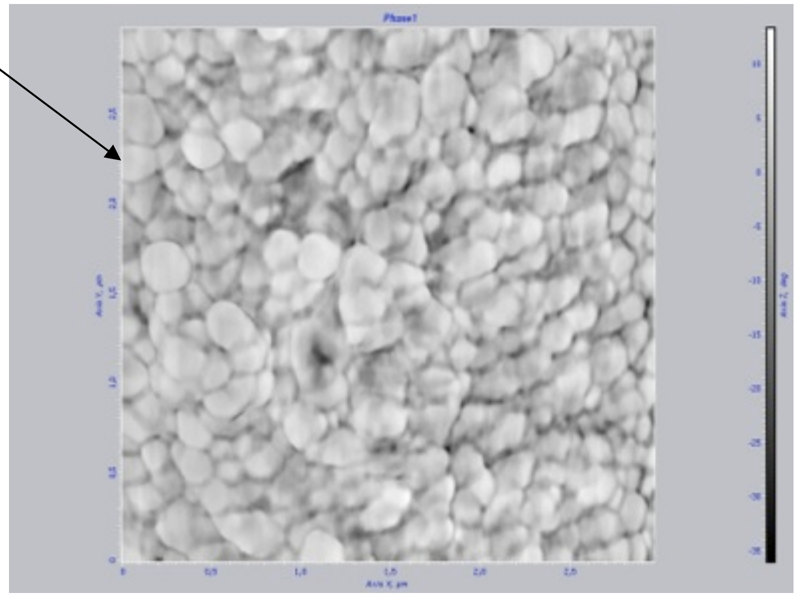
Charge transport in organic semiconductors



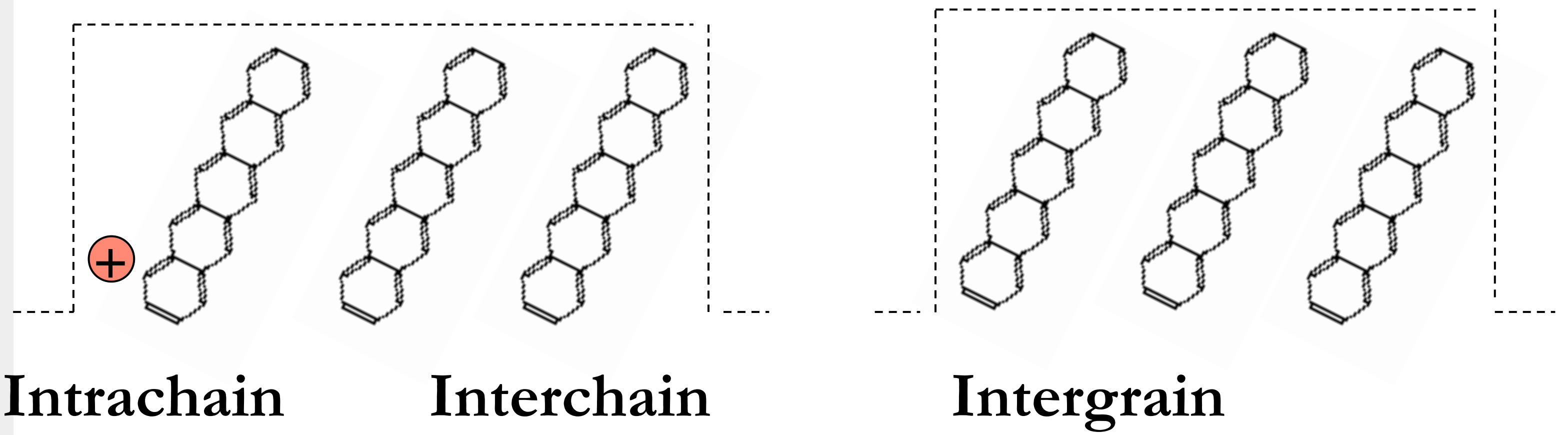
Å

nm

µm



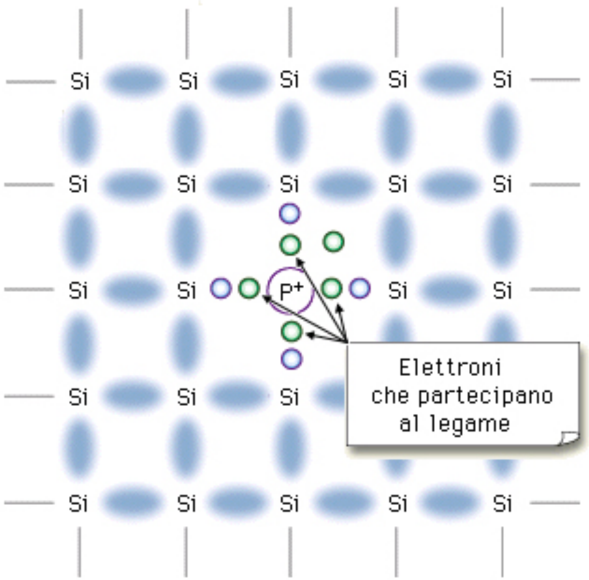
Charge transport in organic semiconductors

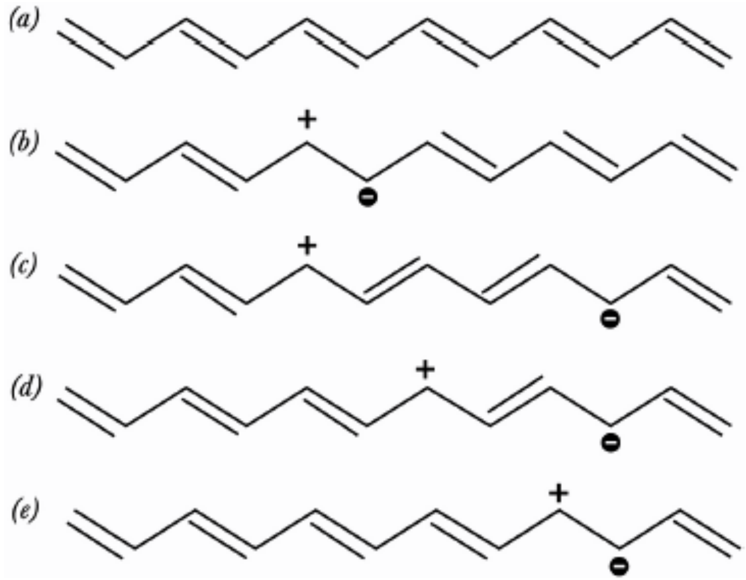


3 coesistent mechanisms+ charge injection from contacts

→ Measurements difficult to explain

Doping and charge transport





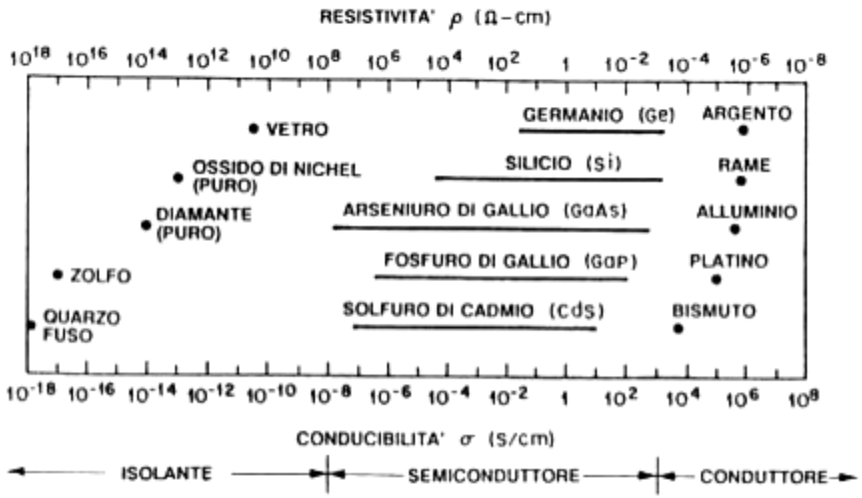
In inorganic semiconductor, doping is substitutional and causes an increase in free charge carrier concentration. These carriers move in a periodic potential with no interaction with the crystal (*band model*).
In organic, doping is not substitutional: supplementary charge physically interact with molecules causing a perturbation in the coniugated chain. This perturbation (charge + deformation induced by the charge) is called **polaron**

Doping and charge transport

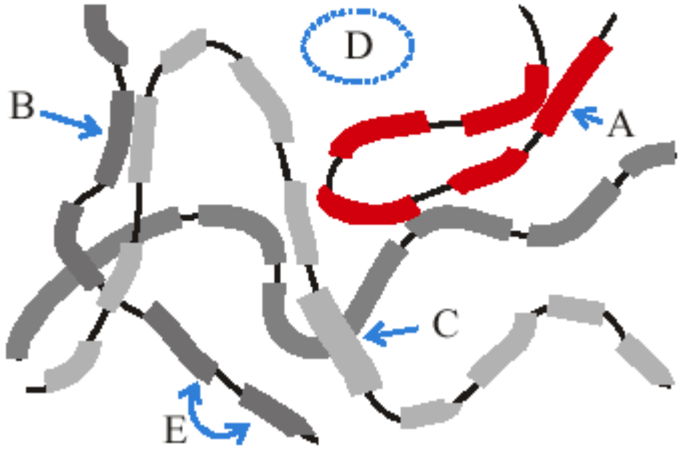
In analogy with inorganic semiconductors, the polaron can be roughly described as a charge free of moving along the chain strongly interacting with the semiconductor lattice

m eff (polaron) >> m eff (free charge carrier)

➔ mobility (polaron) << mobility (free charge carrier)



Intermolecular transport: hopping

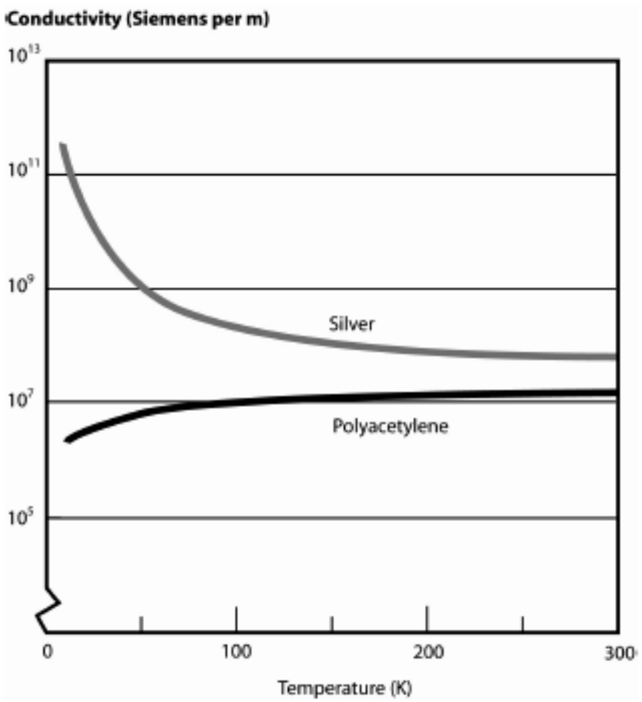


hopping = tunneling between crossing chains

To move, the charge carrier needs energy that can be provided by phonons (increasing with temperature)

$$\mu_D = \frac{e \cdot d^2}{2\tau_J \cdot k_B \cdot T} \quad \longrightarrow \quad \sigma(T) = \sigma o\,(T) \cdot exp[-(To/T)1/(1+d)]$$

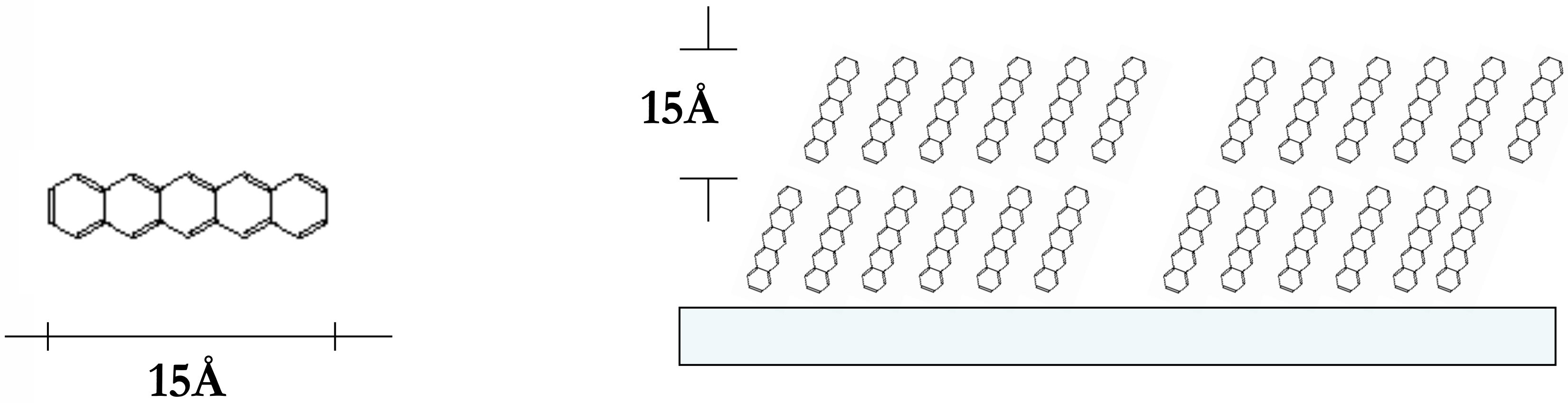
Intermolecular transport: hopping



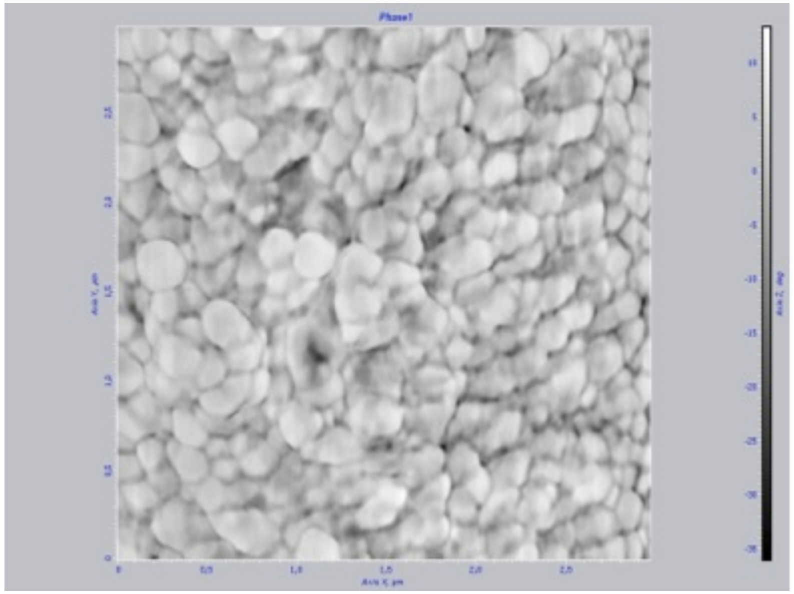
But, in organic materials there is a great variety of behaviour from material to material. A unifying theory has not yet been developed.

Intergrain transport: Pentacene (C_{22} H_{14})

- 5 benzene rings
- Non soluble. Deposited by evaporation
- Molecules stand perpendicular to the substrate.
- Molecules form separated domains (grains)



Intergrain transport: Pentacene ($C_{22}H_{14}$)



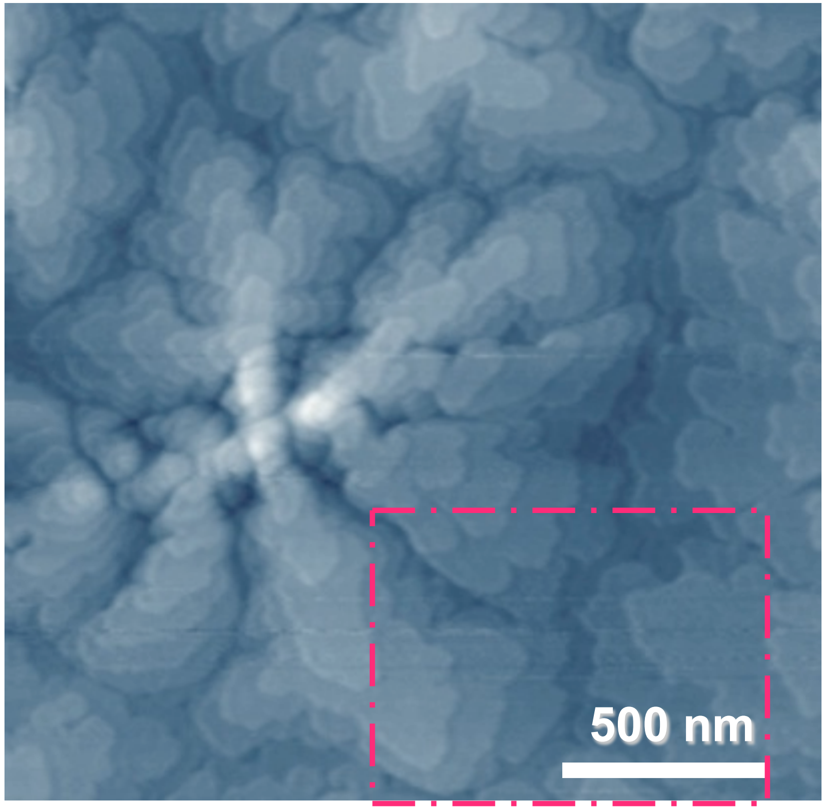
Conduction:

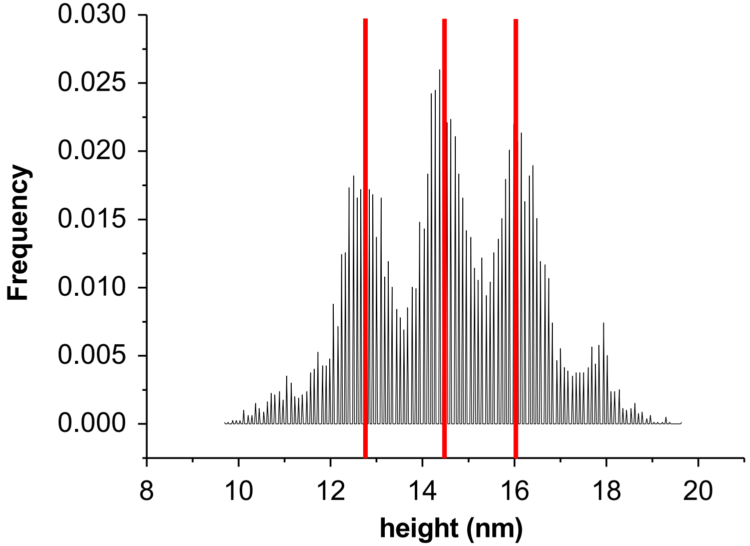
- hopping
- thermically activated
- limited by traps at grain boundaries

$$\frac{1}{\mu} = \frac{1}{\mu_{bulk}} + \frac{1}{\mu_{traps}}$$

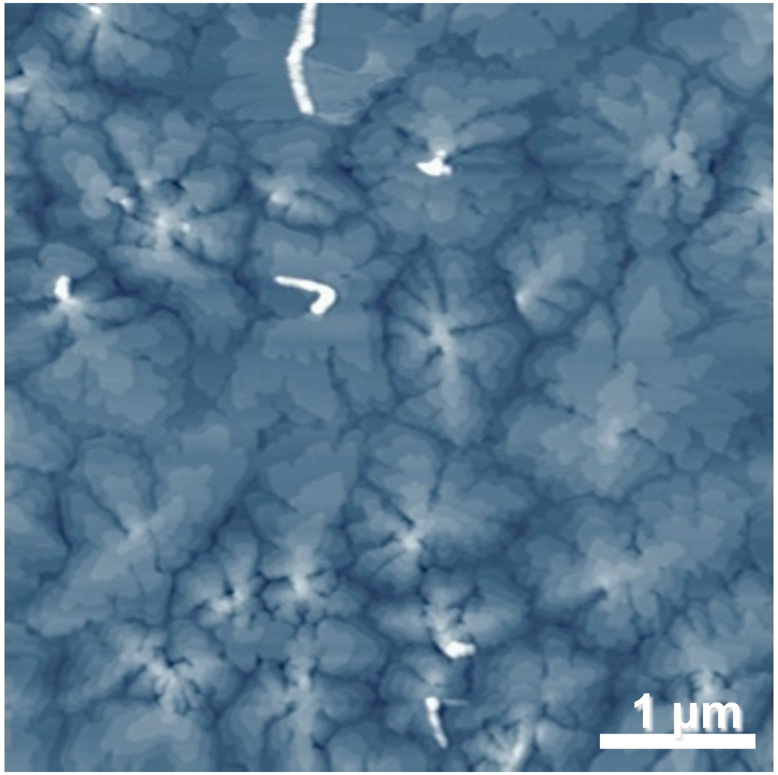
Correlation btw grain dimensions and mobility

Influence of surface morphology

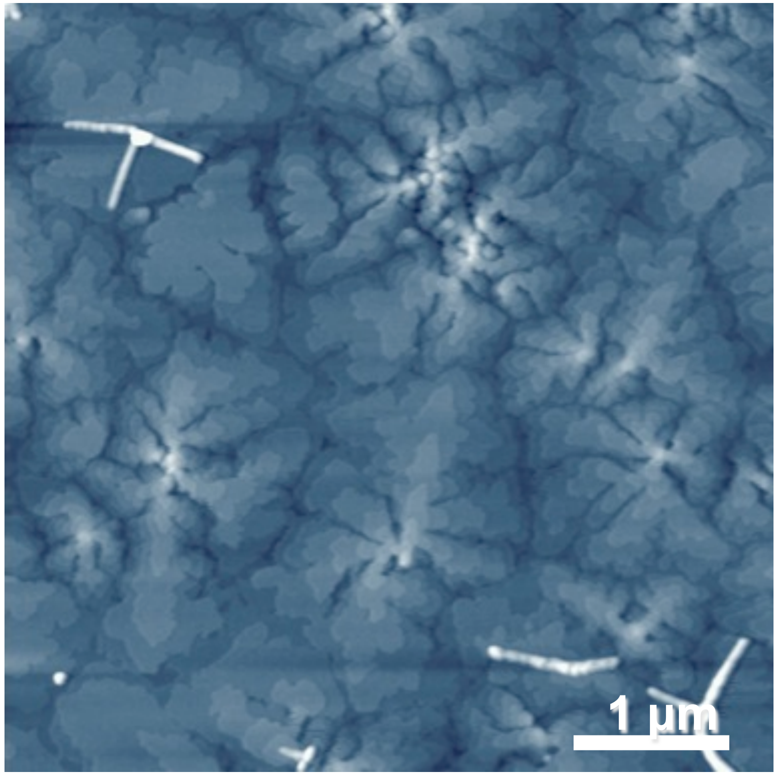




Influence of surface morphology

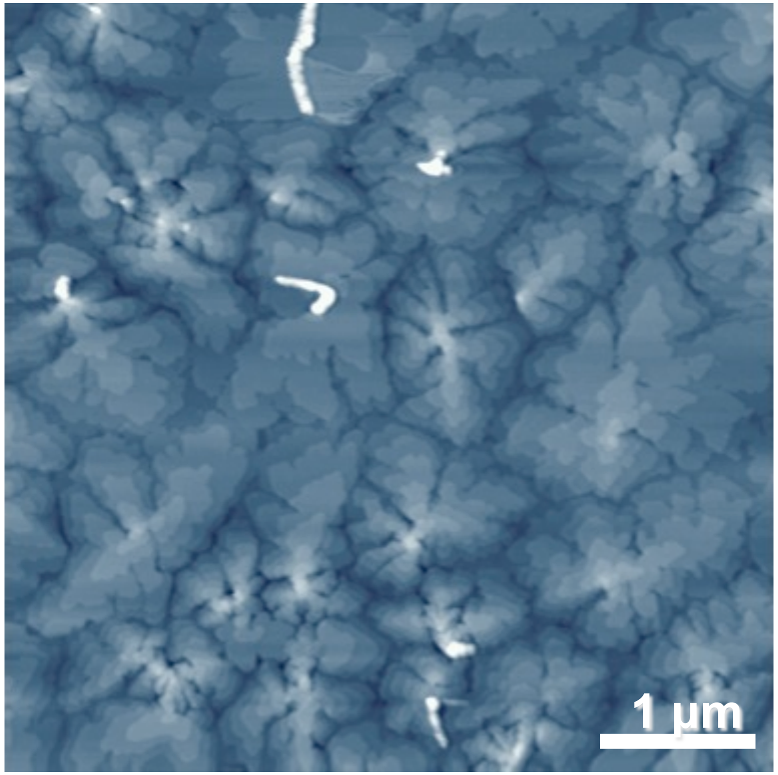


Pentacene on Mica

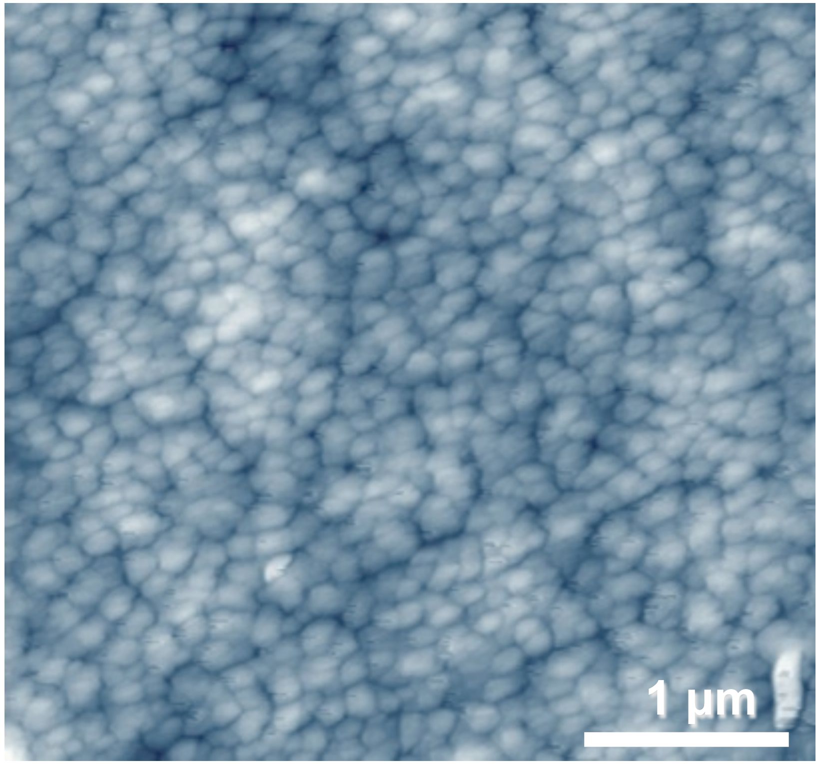


Pentacene on SiO_2

Influence of surface morphology



Pentacene on SiO_2



Pentacene on Mylar

Outline seconda parte

Organic Thin Film Transistors (OTFTs)

Contatti metallo-semiconduttore organico

Comportamento elettrico degli OTFT

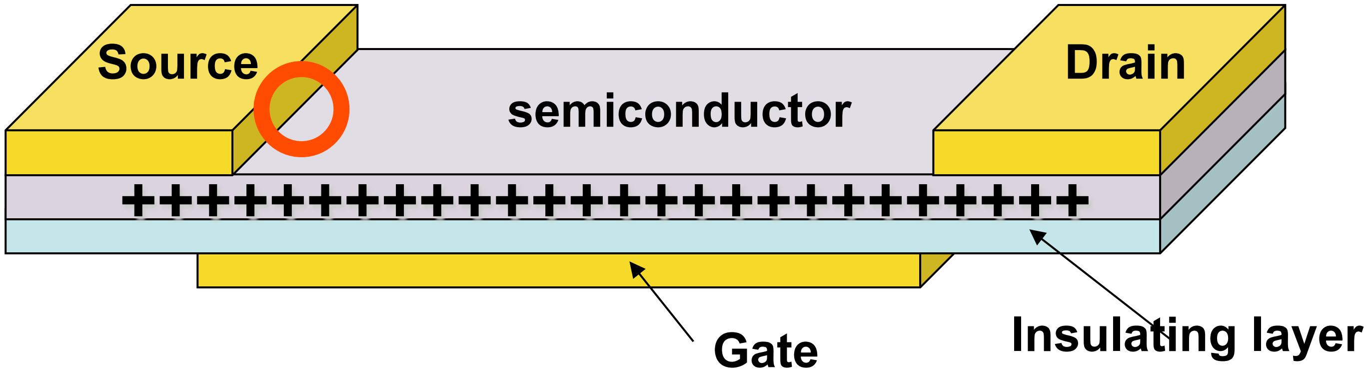
Modello elettrico del dispositivo

Tecnologia

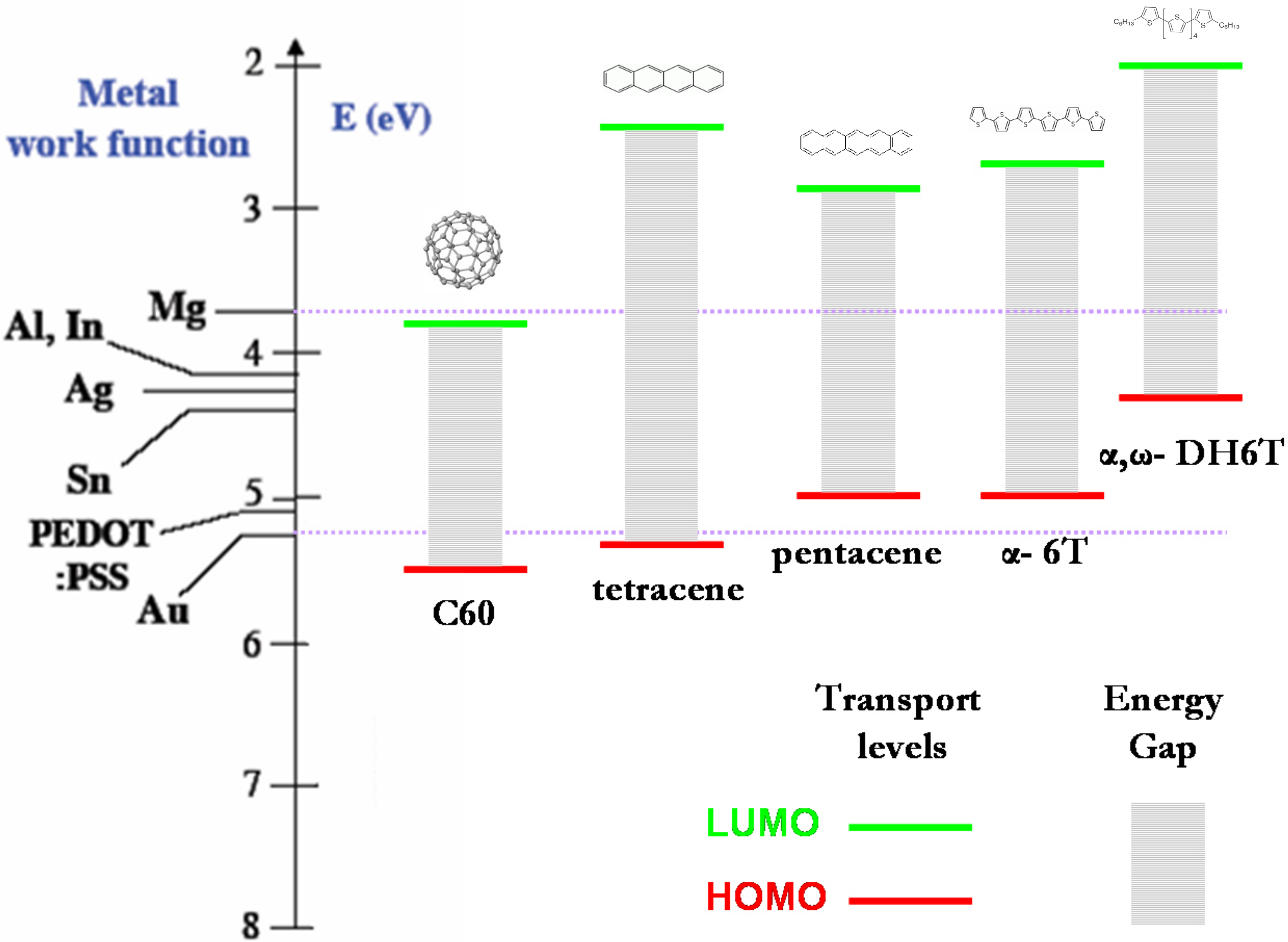
Field Effect Transistors

OTFT = ORGANIC THIN FILM TRANSISTOR

Interface metal - semiconductor

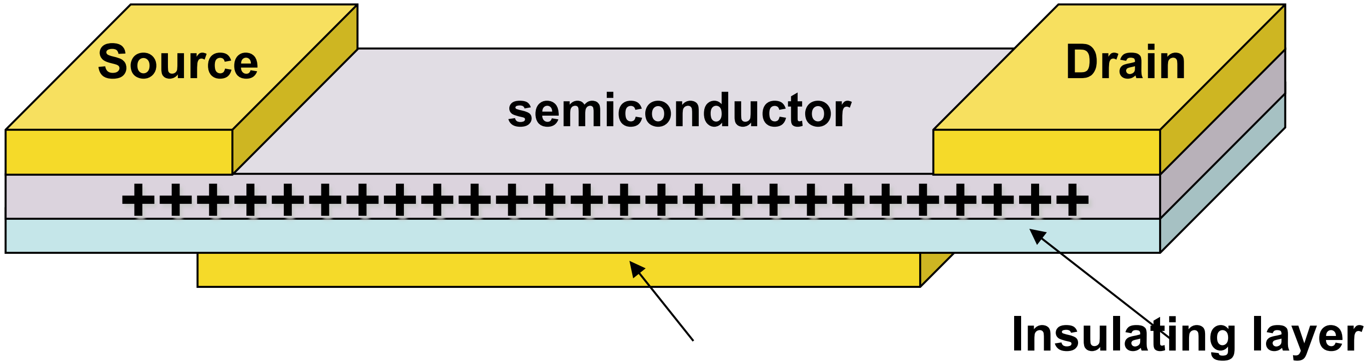


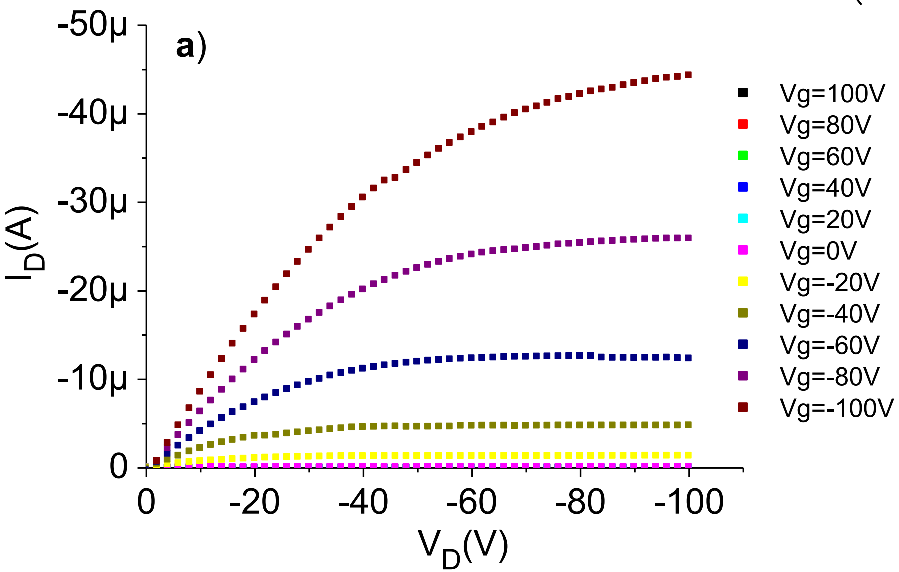
Charge injection from metal contacts



Thin Film Transistor

TFT model was first developed for poorly conductive semiconductors like amorphous Si





Tipically p-type!

How an OTFT works

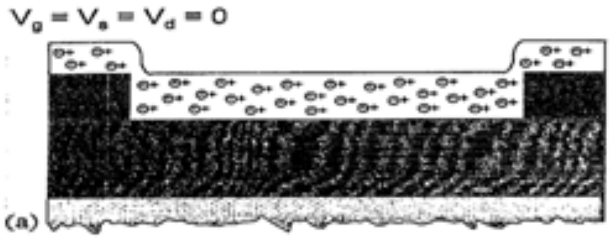


Fig. 2a

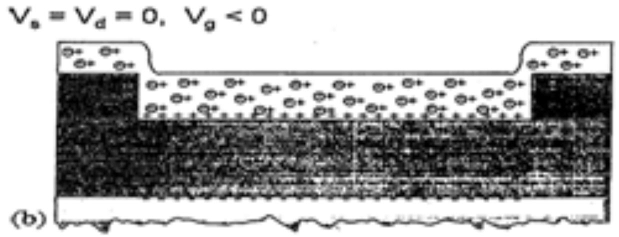


Fig. 2b

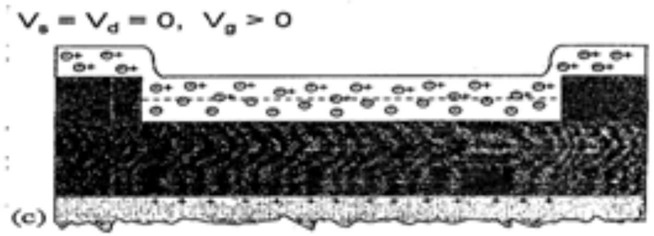


Fig. 2c

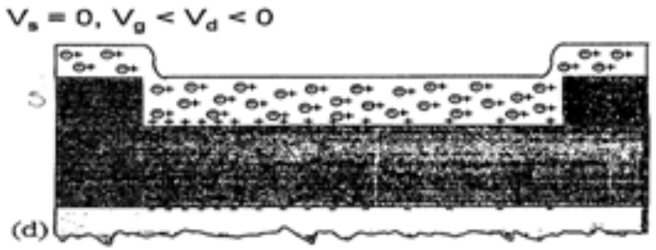


Fig. 2d

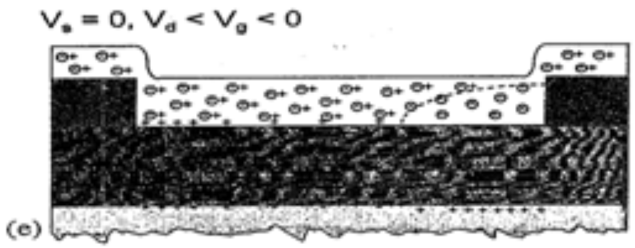
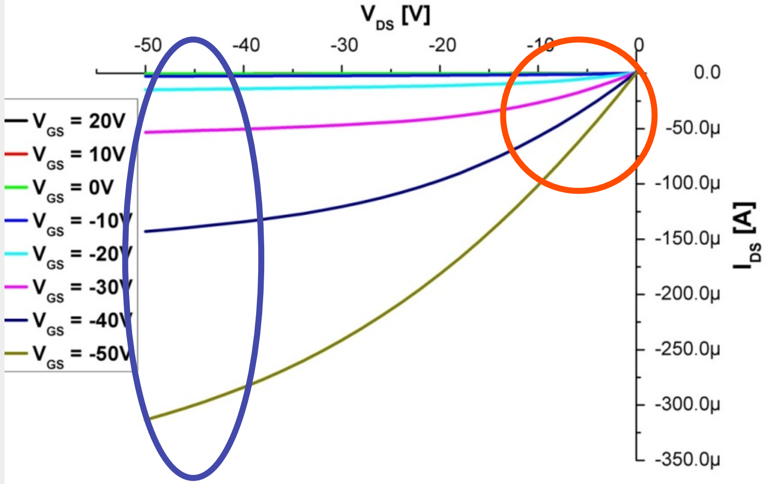


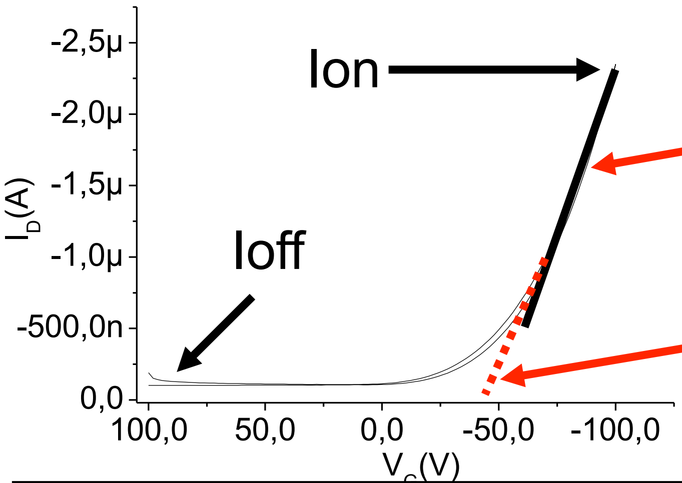
Fig. 2e

Equations and extraction of parameters



Linear region: $I_D = \mu C_{ox} \frac{Z}{L}(V_G - V_T)V_D$

Saturation region: $I_D = \frac{1}{2}\mu C_{ox} \frac{Z}{L}(V_G - V_T)^2$



$$\left.\frac{\partial I_D}{\partial V_G}\right|_{sat} = \mu C_{ox} \frac{Z}{L}(V_G - V_T)$$

Important parameters:

$\frac{I_{on}}{I_{off}}, \mu, V_T$

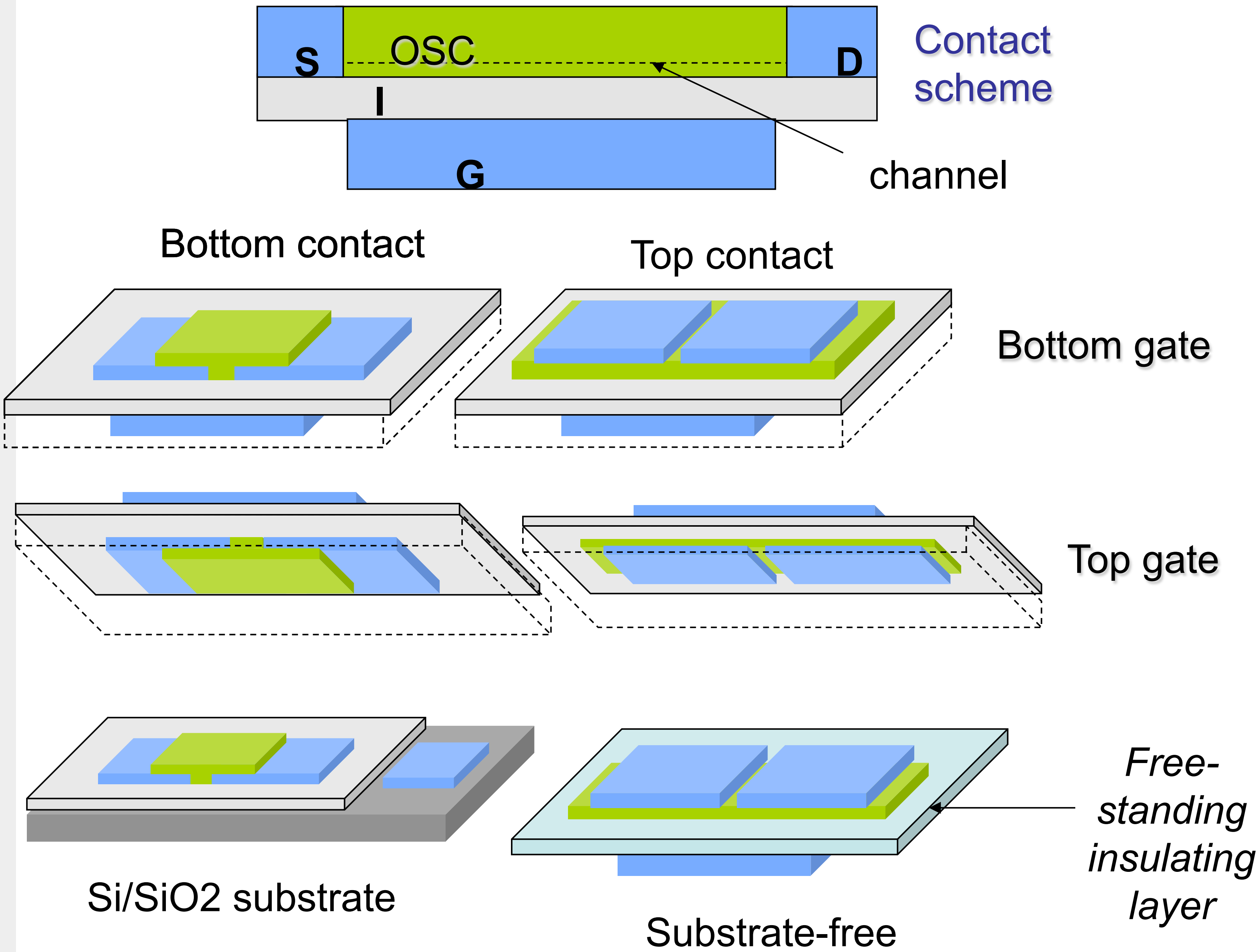
Typical values:

$\mu \sim 10^{-2}$: 10^{-1}

Ion/Ioff ~10^4 :10^5

V_T ~ -10:+10 V

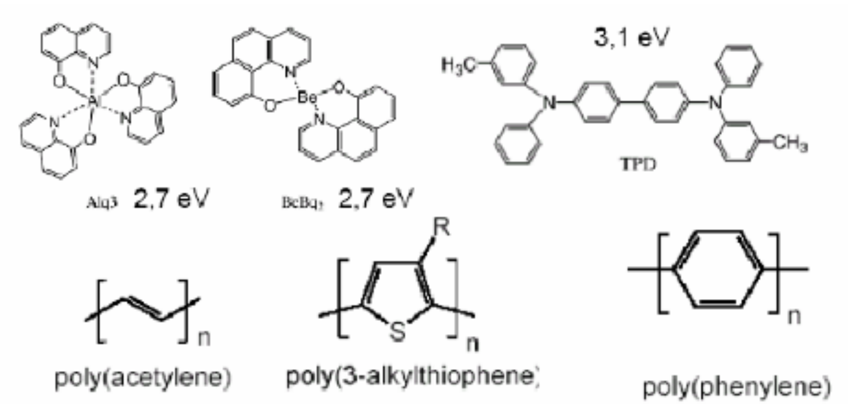
Structures and fabrication techniques



Materials and fabrication techniques

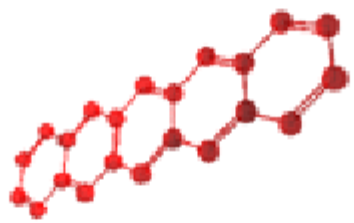
Materials:
Electrodes: metals, conductive polymers
Insulating layers: polyimide, PVA, PVP,…
Organic semiconductors

Solution processable
Polymers



Small molecules

(deposited by
evaporation)



Fabrication techniques - Spin Coating

Low cost technique for liquid phase materials

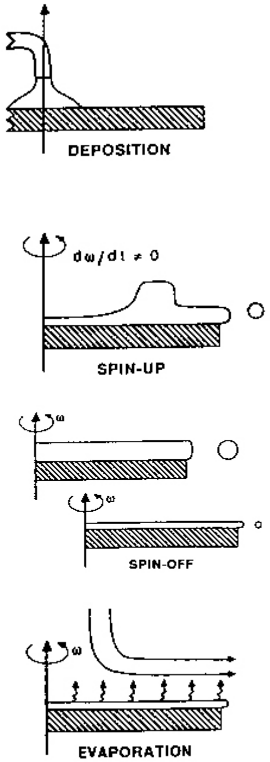
Deposition

Spin up

Spin off

Spin down

Thermal annealing (dewetting)

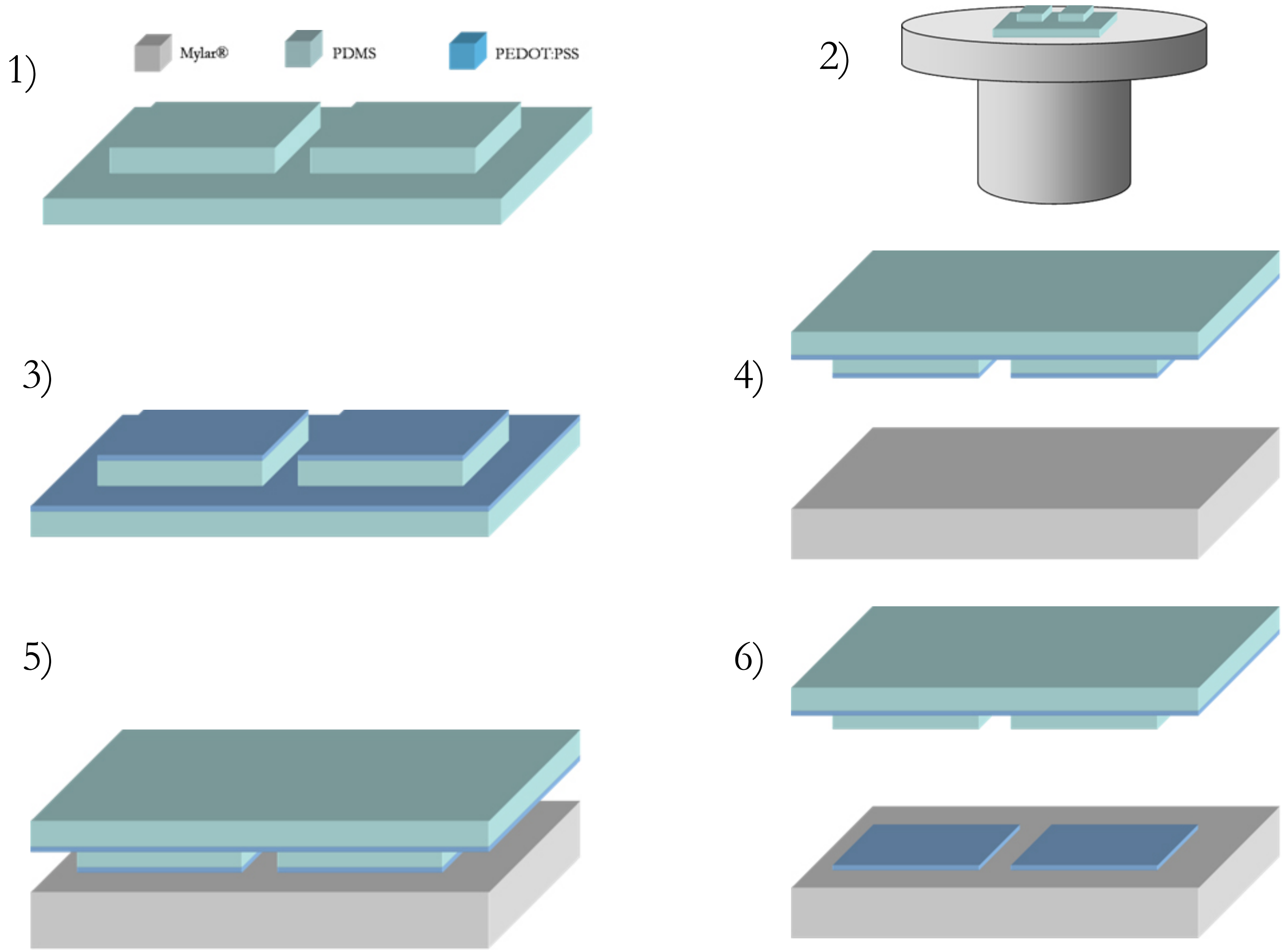


Process parameters:

1. Spin up time
2. Spin speed
3. Spin off time
4. Spin down time
5. Dewetting time
6. Dewetting T

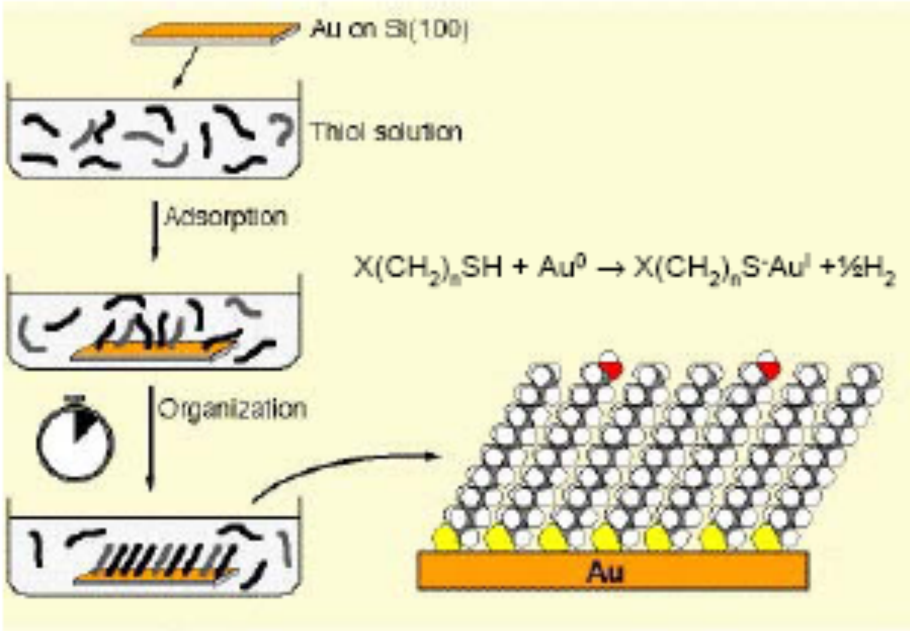
Adv: simple and low cost

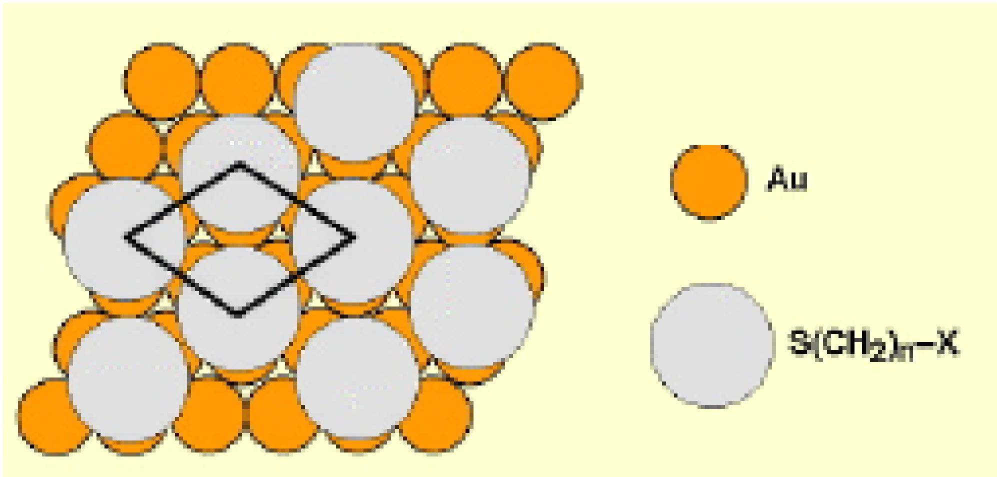
Fabrication technique – Soft Lithography



Fabrication technique – Soft Lithography

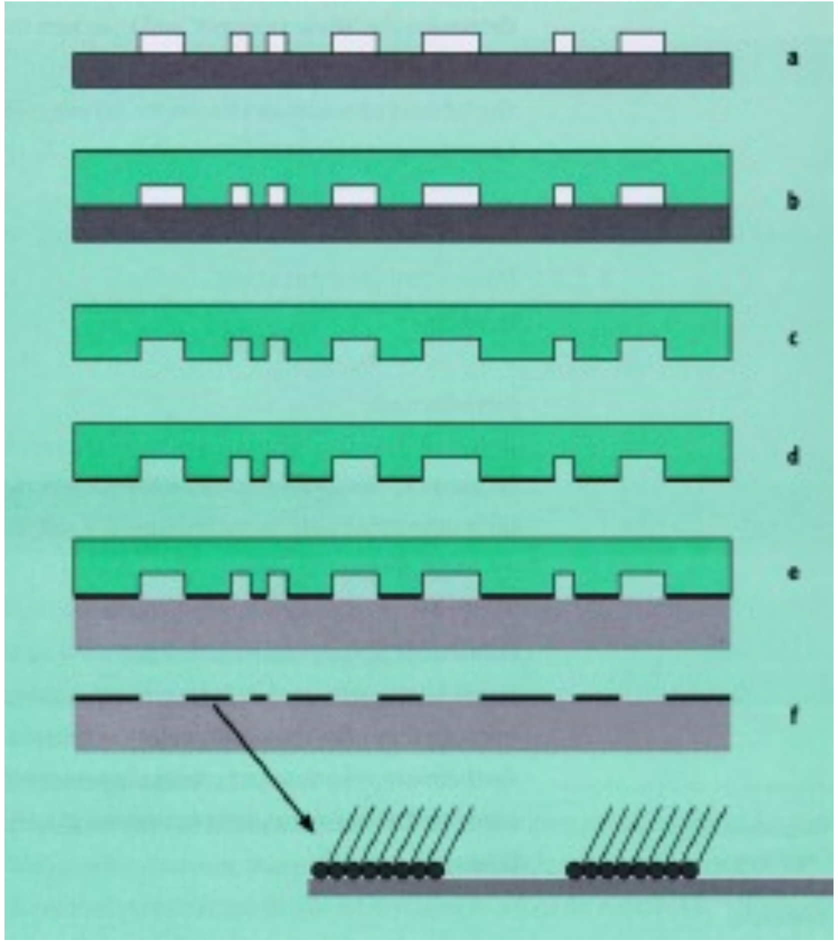
Inks instead of resist for patterning metals

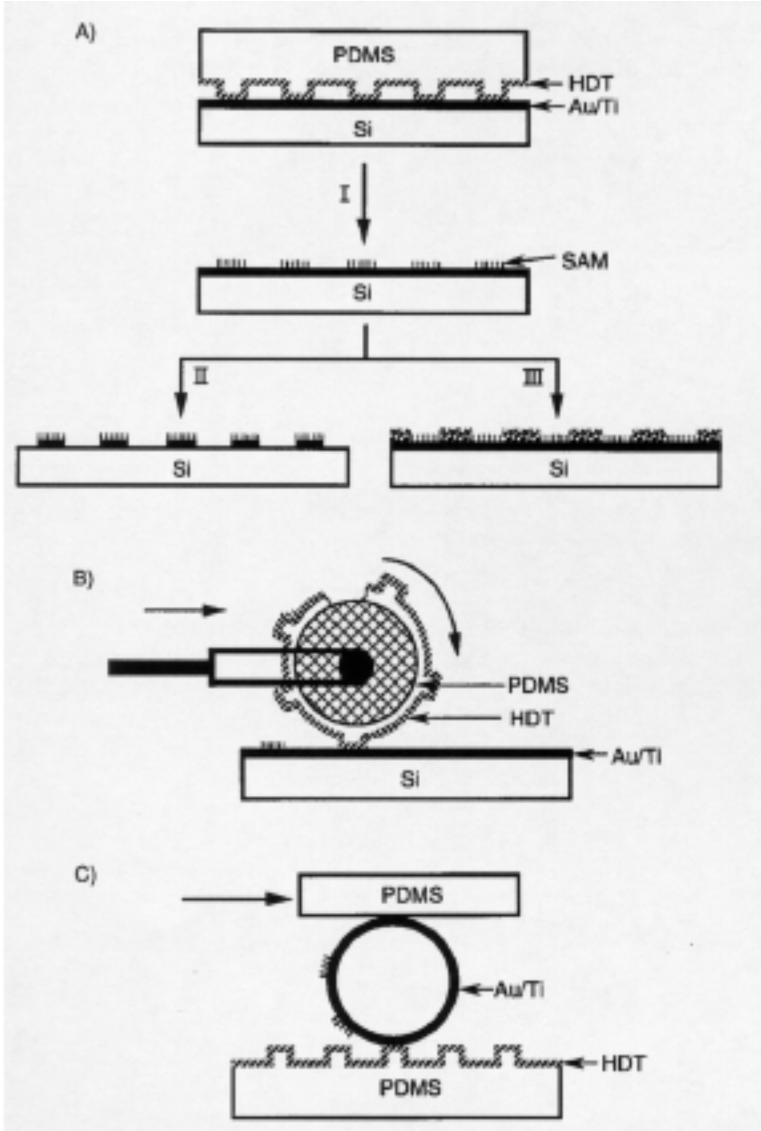




Fabrication technique – Soft Lithography

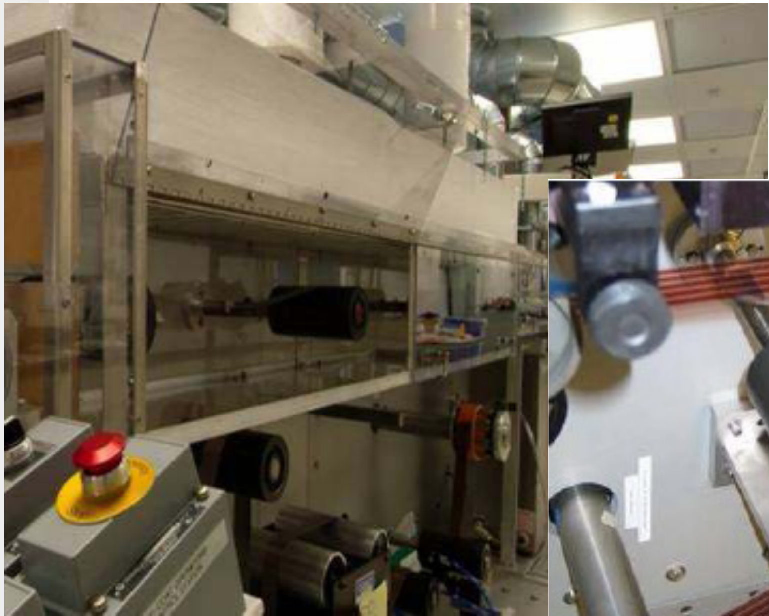
MicroContact Printing

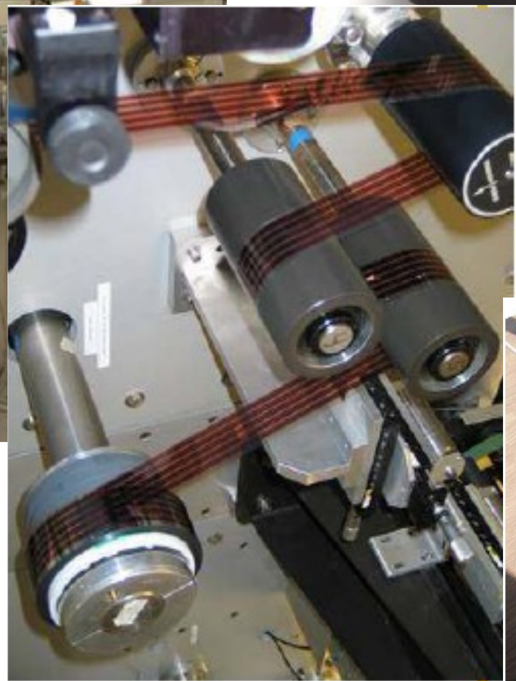




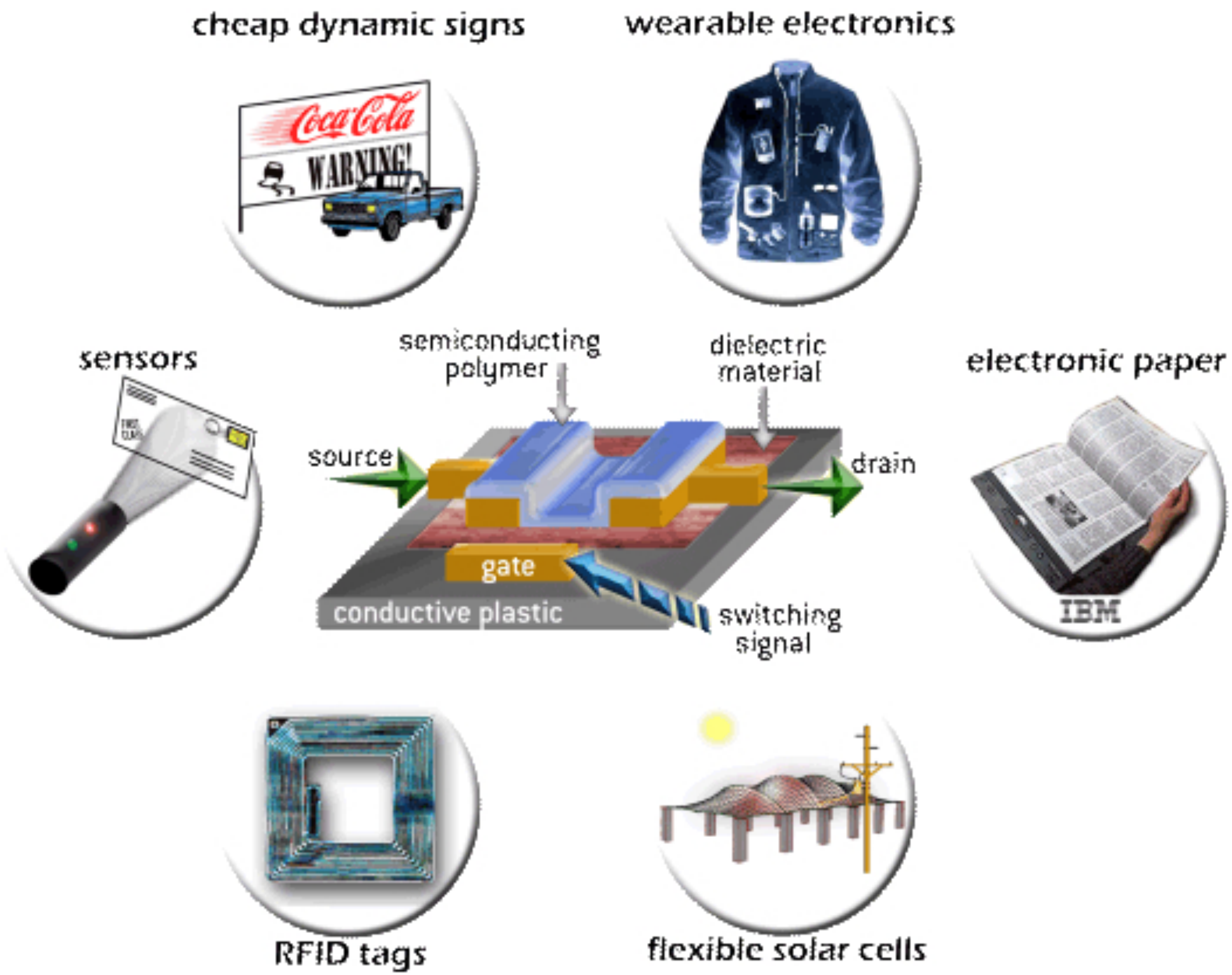
Printing & Roll to Roll

Printing





Possible applications for OTFTs



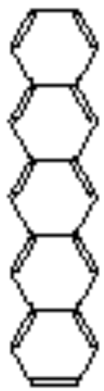
Outline terza parte

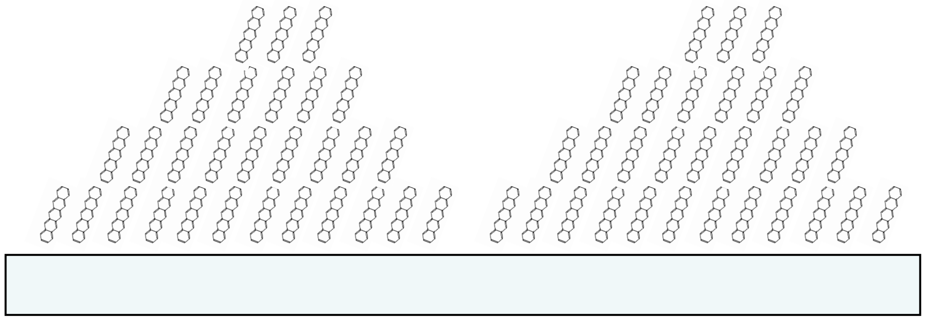
Sensori per variabili meccaniche

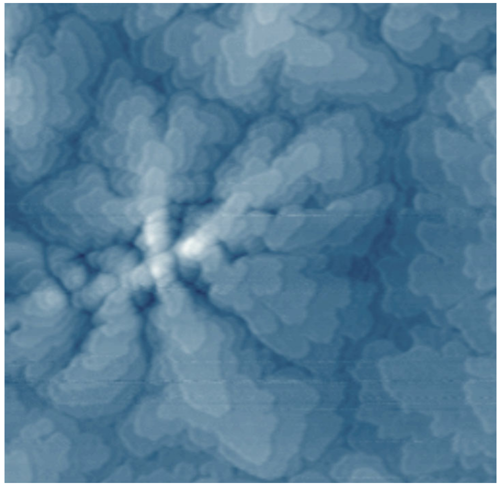
Sensori per variabili chimiche: ISOFET

Prospettive applicative

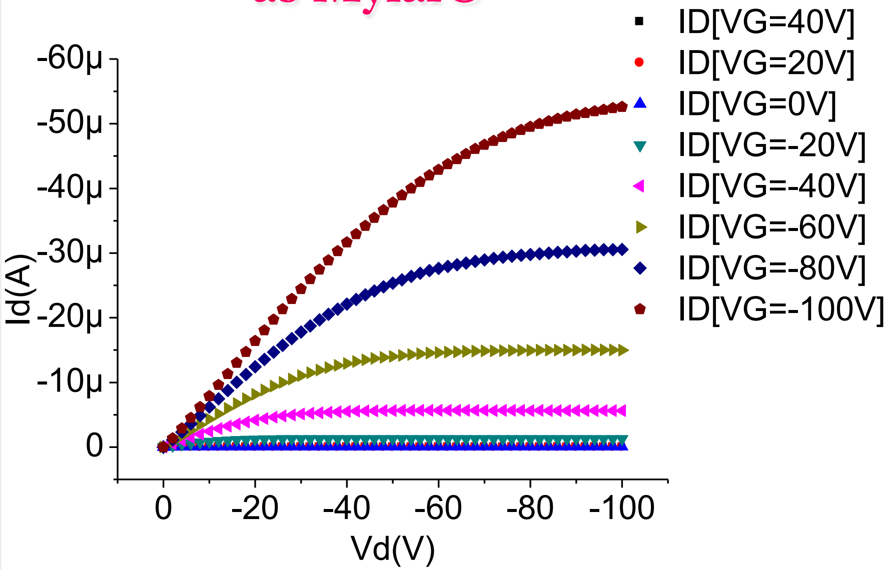
OFET based mechanical sensors

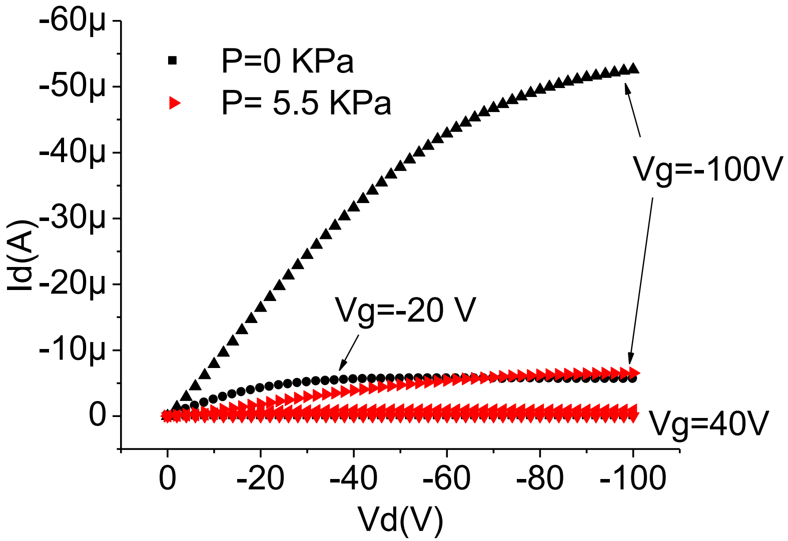






Nice molecular ordering, even when deposited on "non ideal" substrate as Mylar®

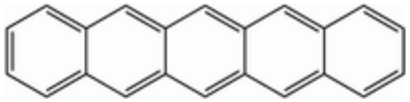




I_D always decreases when mechanical stimulus is applied

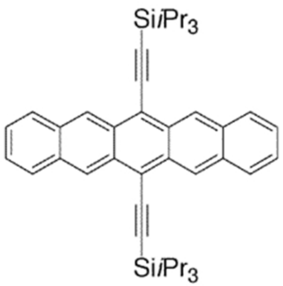
I. Manunza et al., Appl. Phys. Lett. 89, 143502 (2006)
I. Manunza et al., Bios. Bioelec. 22, 2775, (2007)

Different OS can be employed



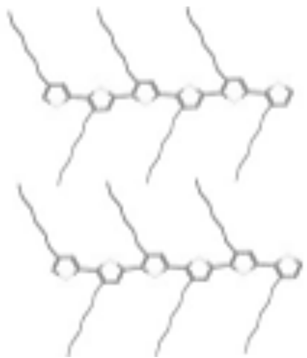
Pentacene

Not soluble



Tri-isopropylsilylethynyl (TIPS) Pentacene

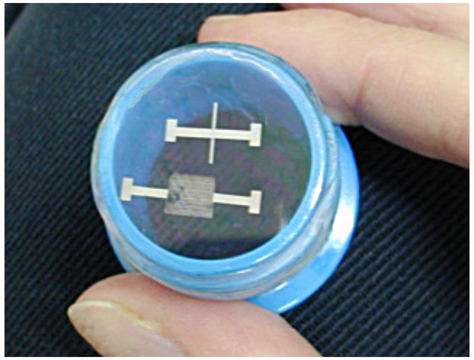
Soluble

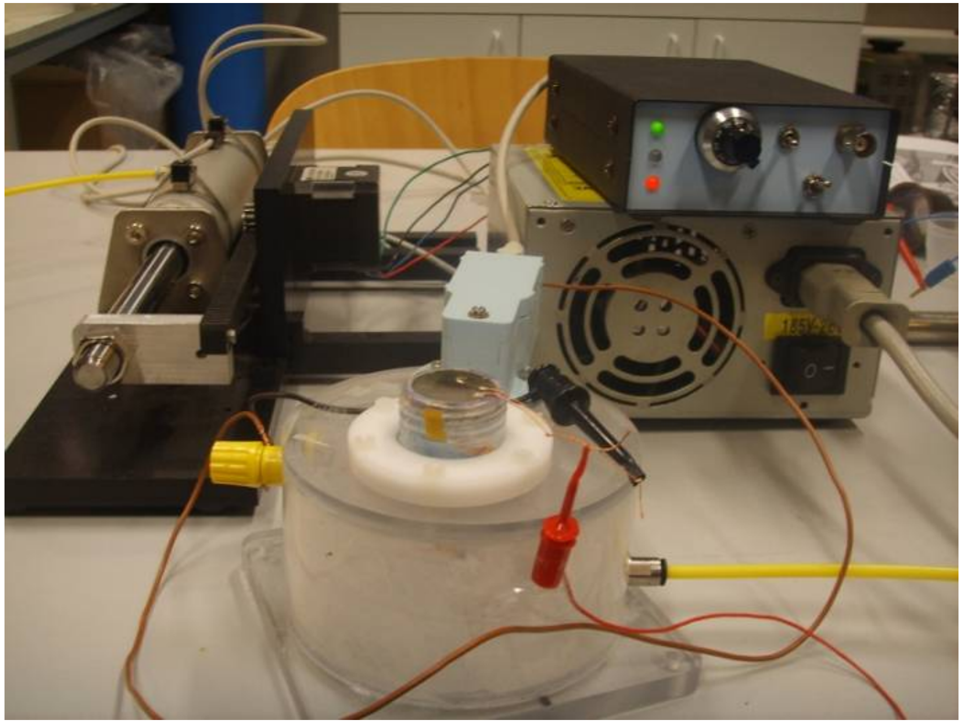


poly(3-hexylthiophene) (P3HT)

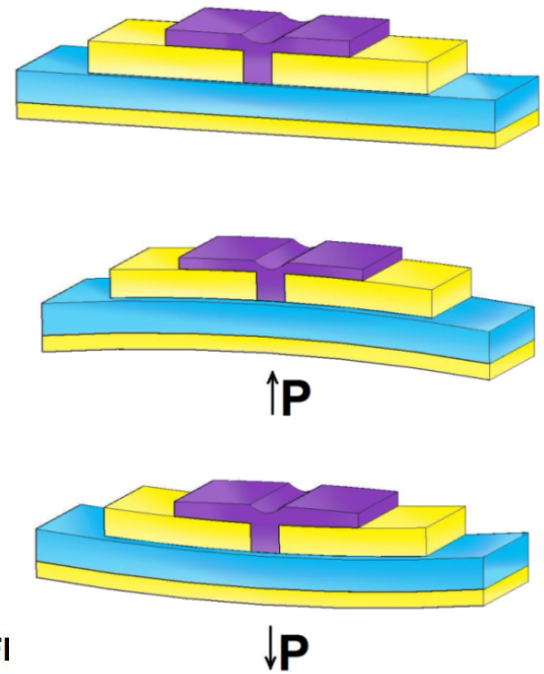
Soluble

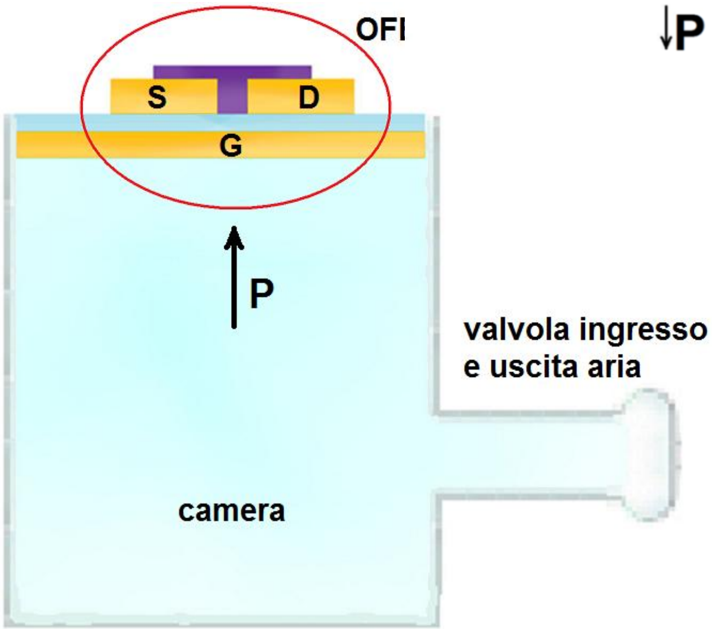
Pressure sensors: set up

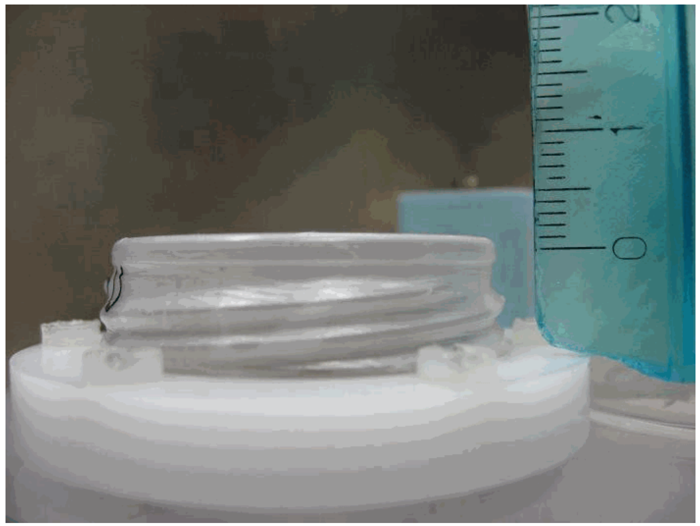




Pressure sensors: set up







Pressure Sensors: pentacene

Current decreases when pressure is applied

both for positive and negative P

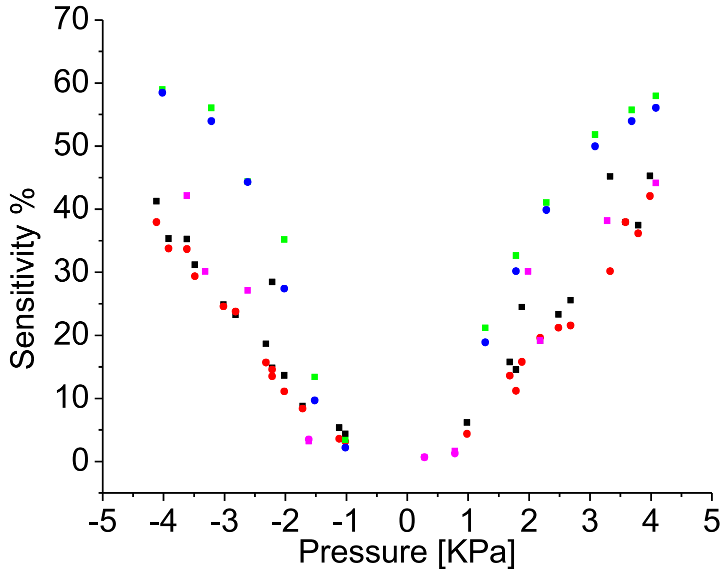
High sensitivity around 45 to 60%

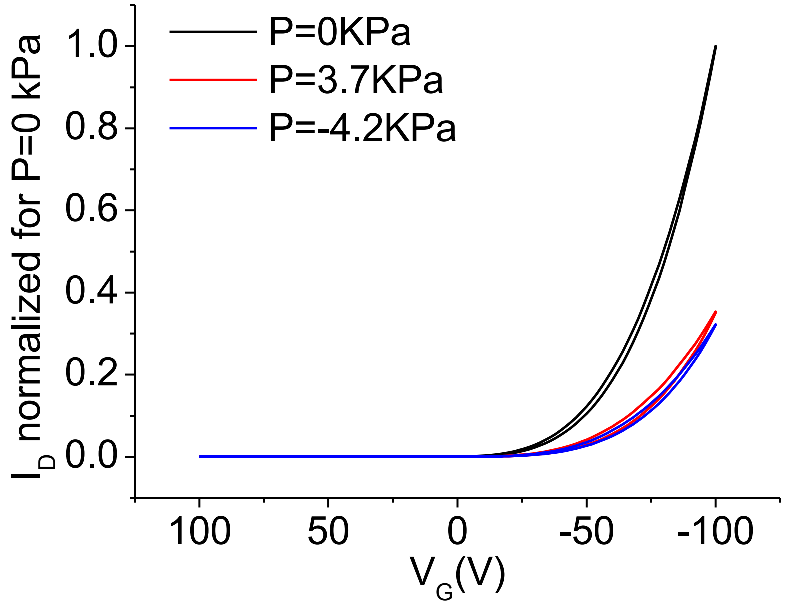
Response, rise and fall time ≈ 100ms

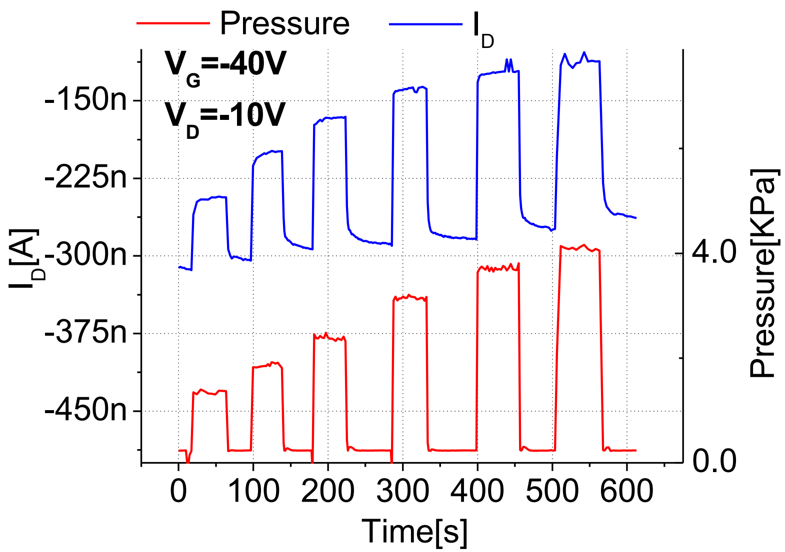
Short TS ↑> around 5-10s

↓> around 5-10s

Hysteresis increases for P>2.5kPa







Pressure Sensors: P3HT

Current decreases when pressure is applied both for positive and negative P

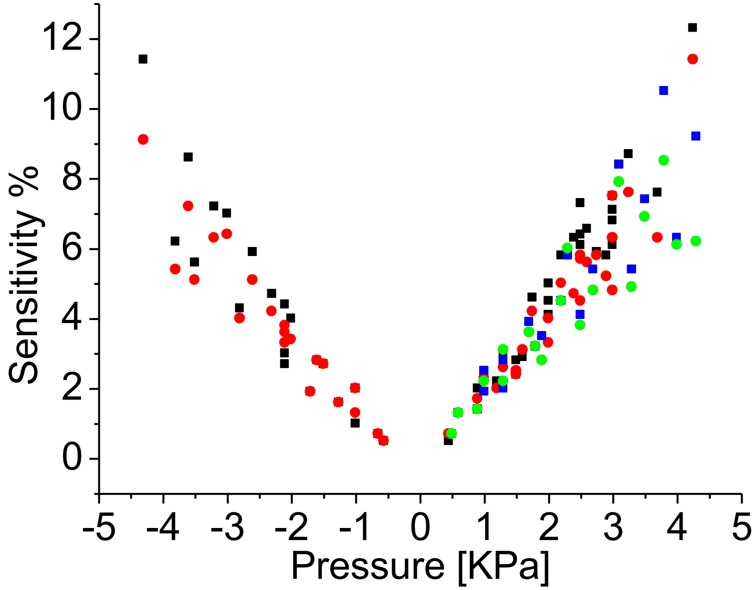
Low sensitivity, around 15%

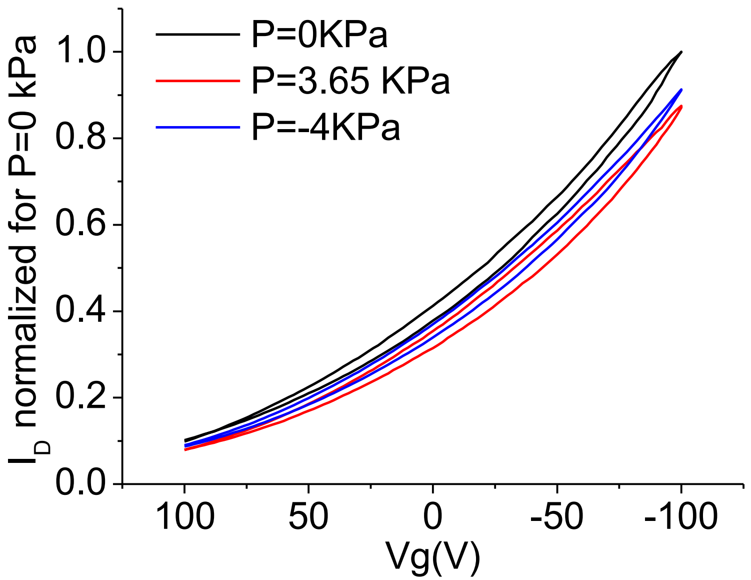
Response, rise and fall time ≈ 100ms

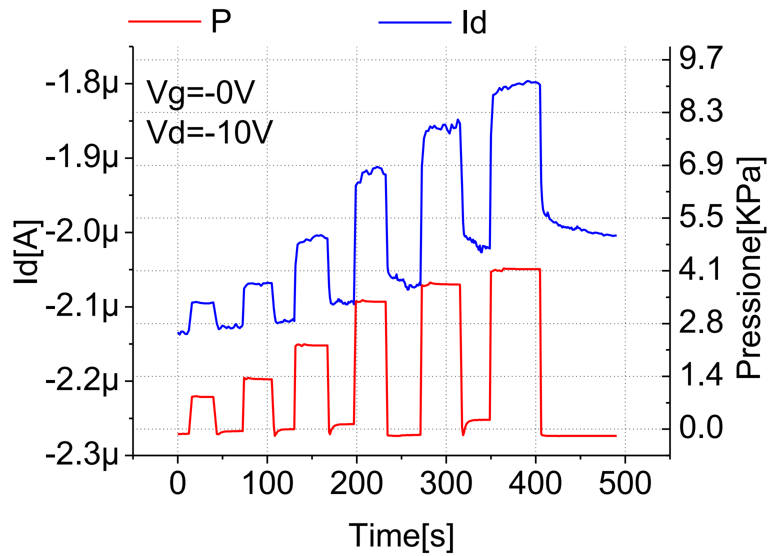
Short TS ↑ > around 5-10s

↓ > around 5-10s

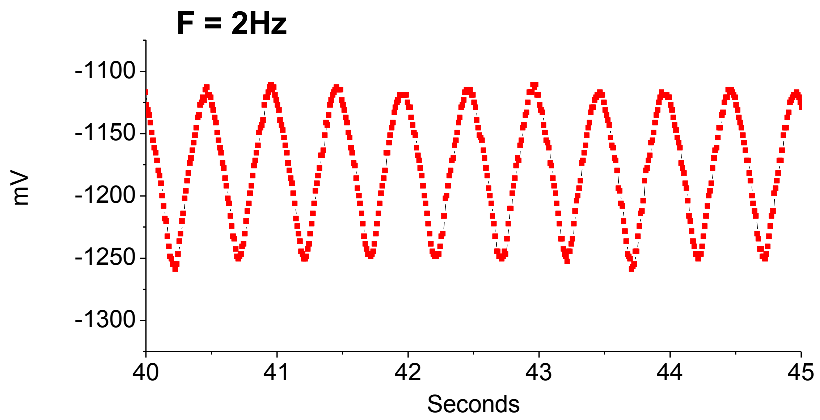
Hysteresis increases for P>2.5kPa

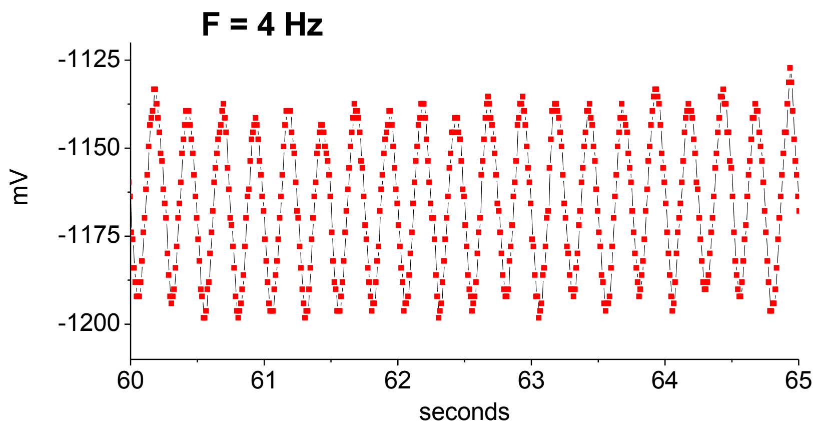


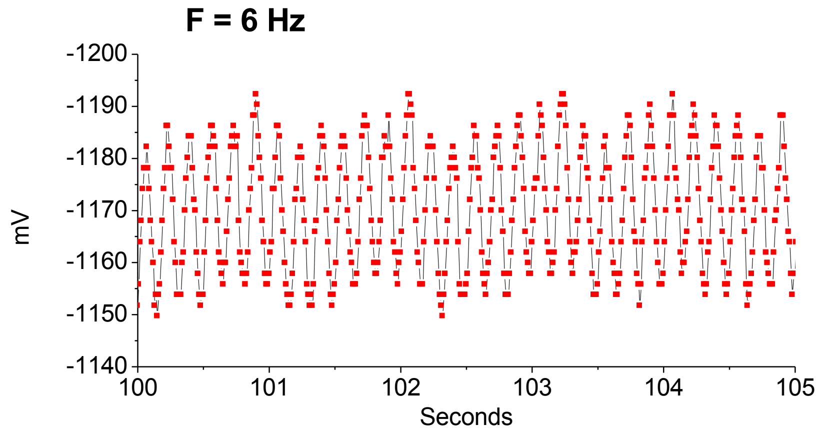


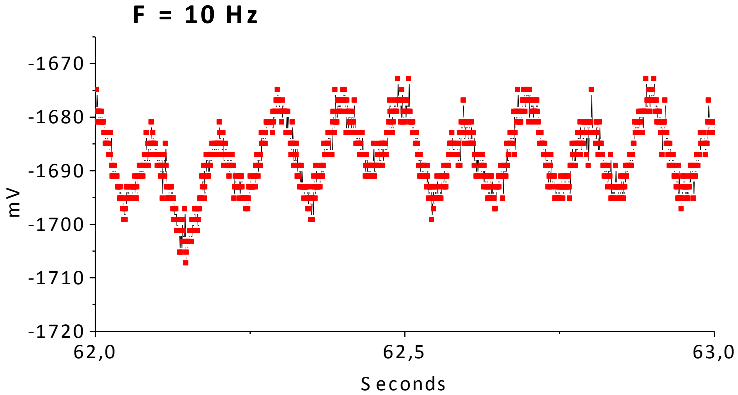


Pressure Sensors: dynamic characterization

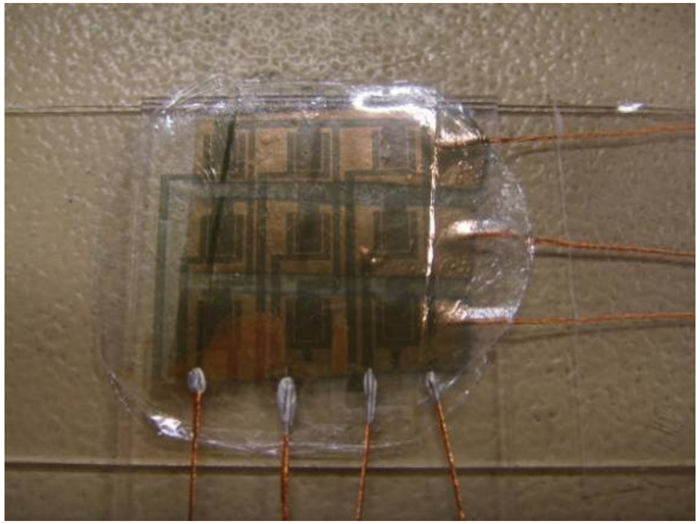






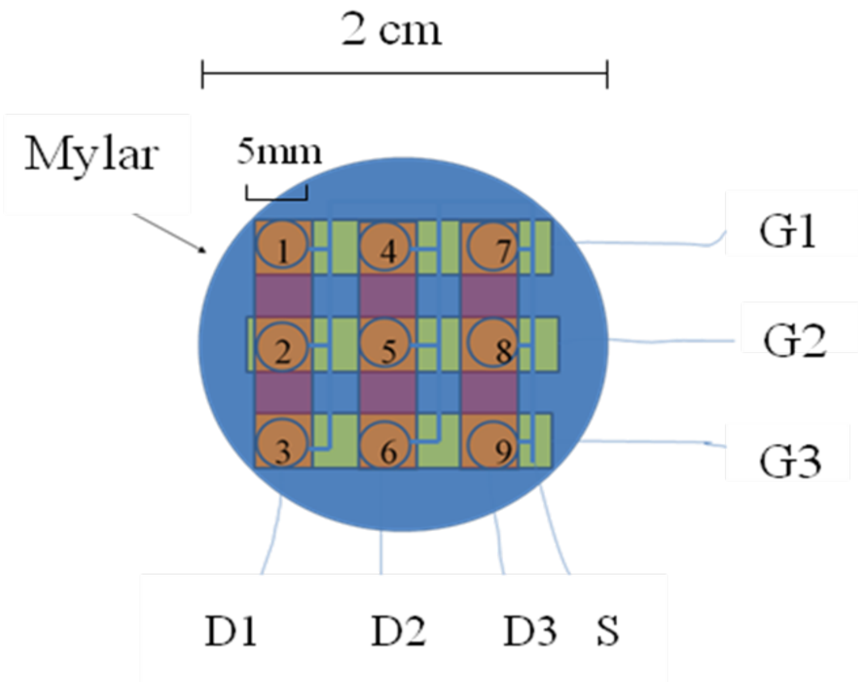


Some Examples: Matrixes of sensors



Up to 16 elements in 4cm^2 Area

For pressure distribution analyses



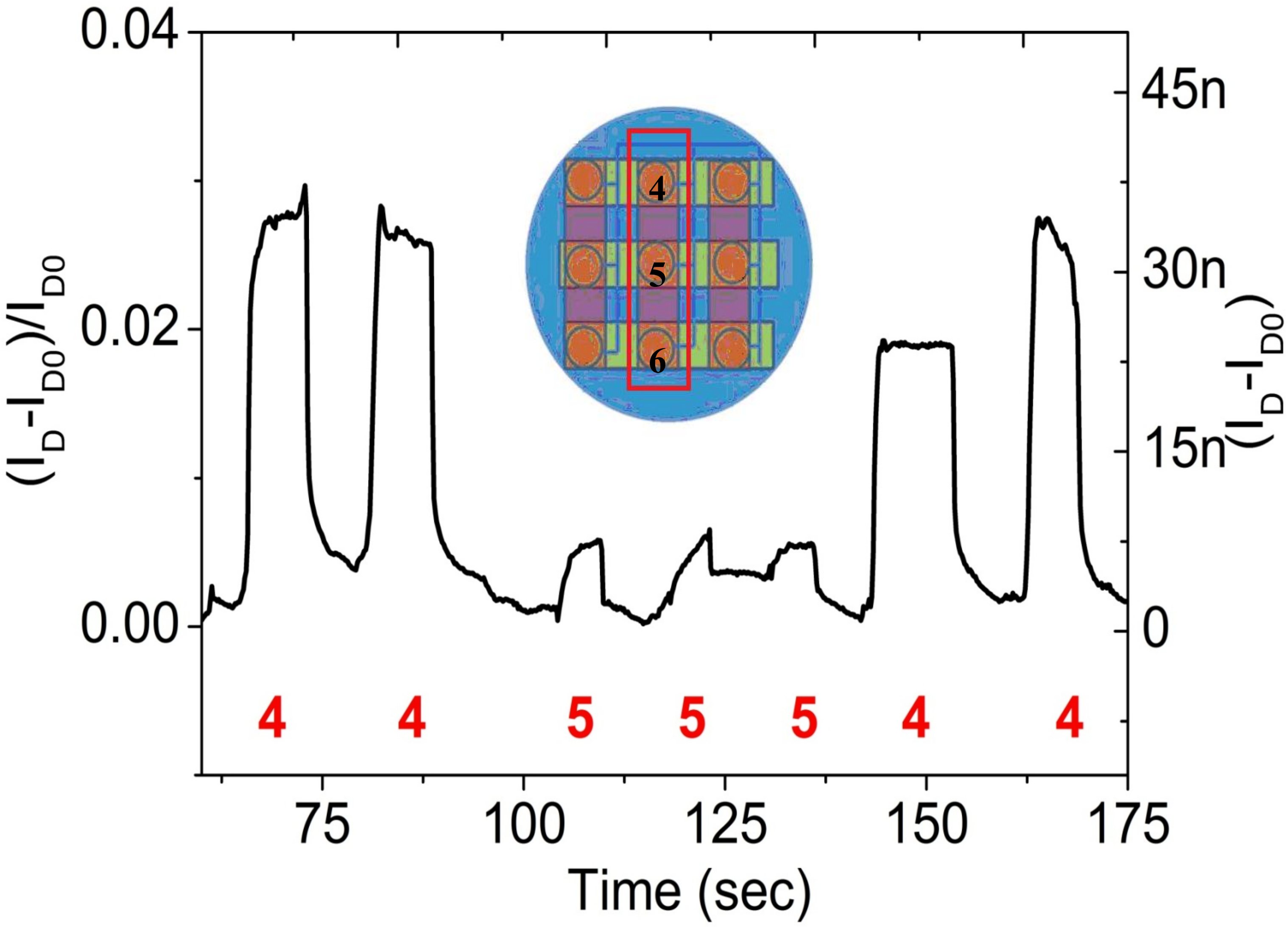
Common Ground (Source)

Rows → Common Gate

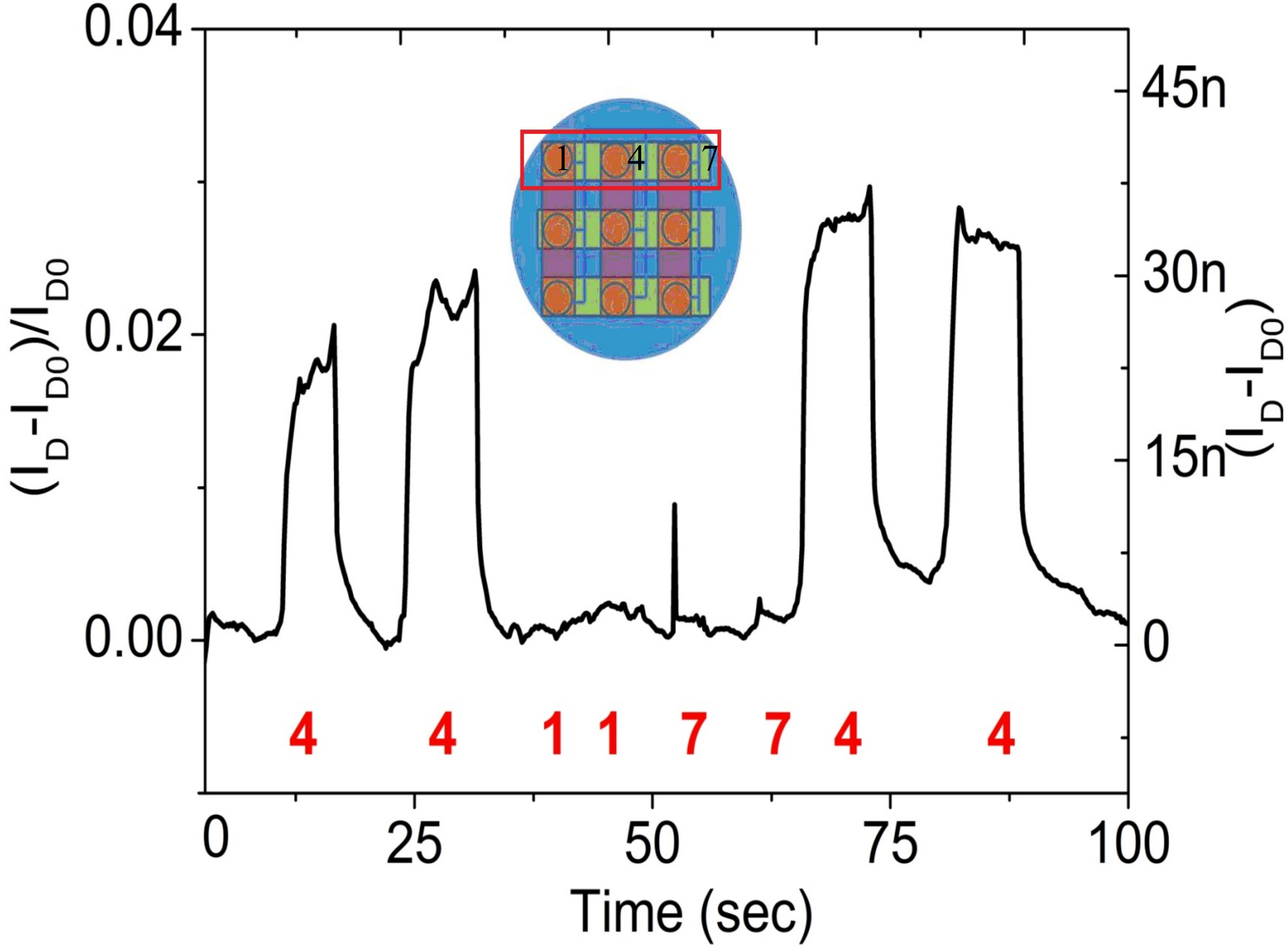
Columns → Common Drain

Every single element can be indipendently investigated

Some Examples: Matrixes of sensors

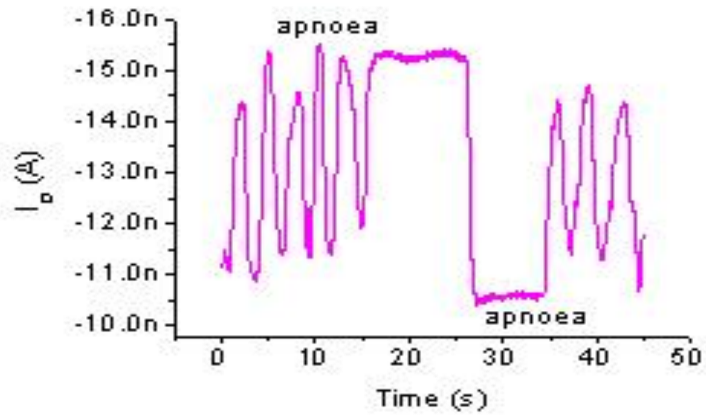


Some Examples: Matrixes of sensors

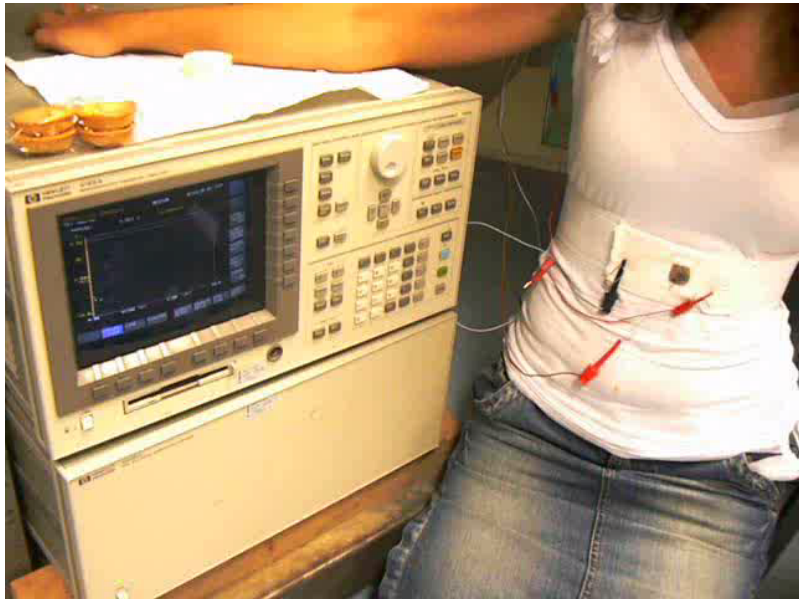


Some Examples: Breathing monitoring

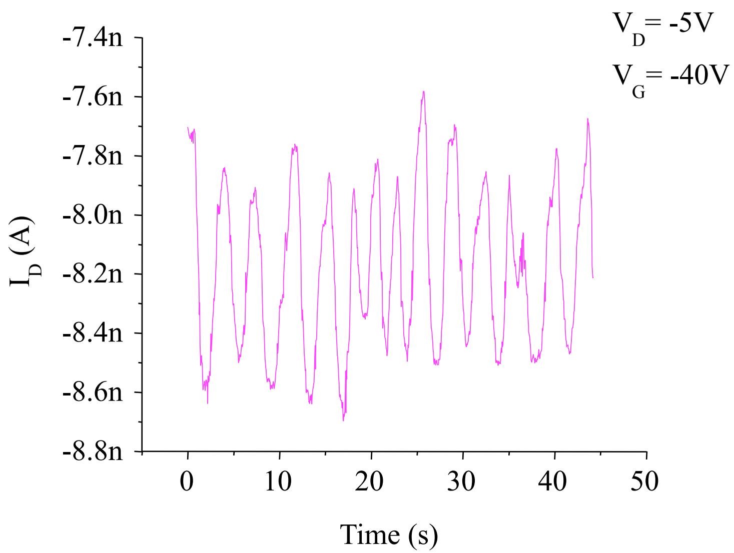
Sensor applied to a chest bandage for **breathing monitoring**



(b)

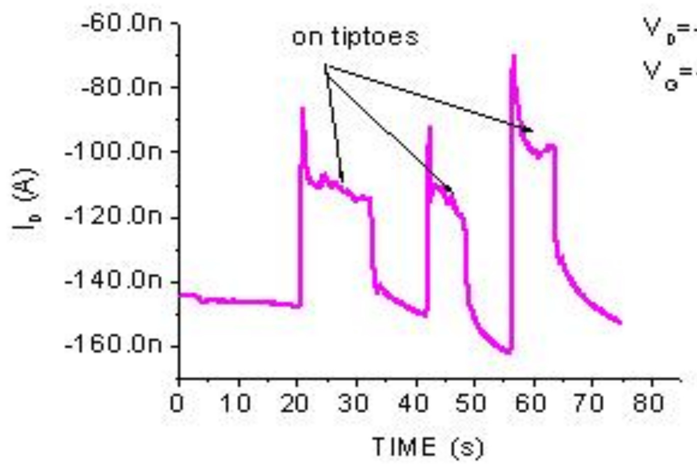


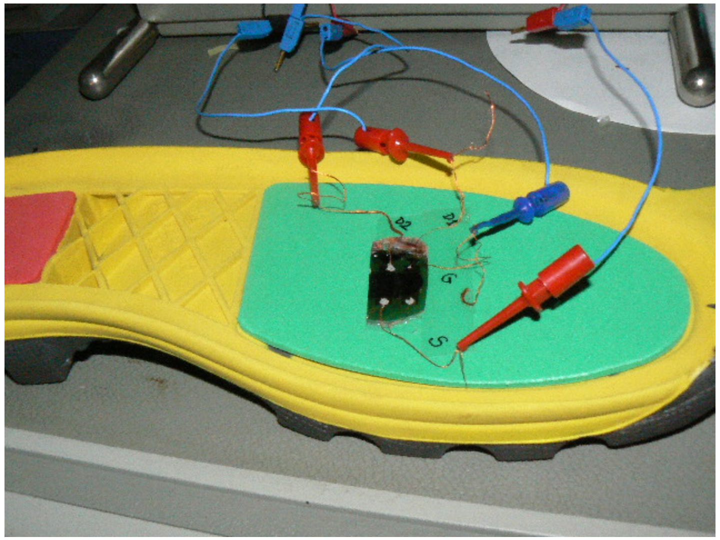
Regular breathing



Some Examples: Posture detection

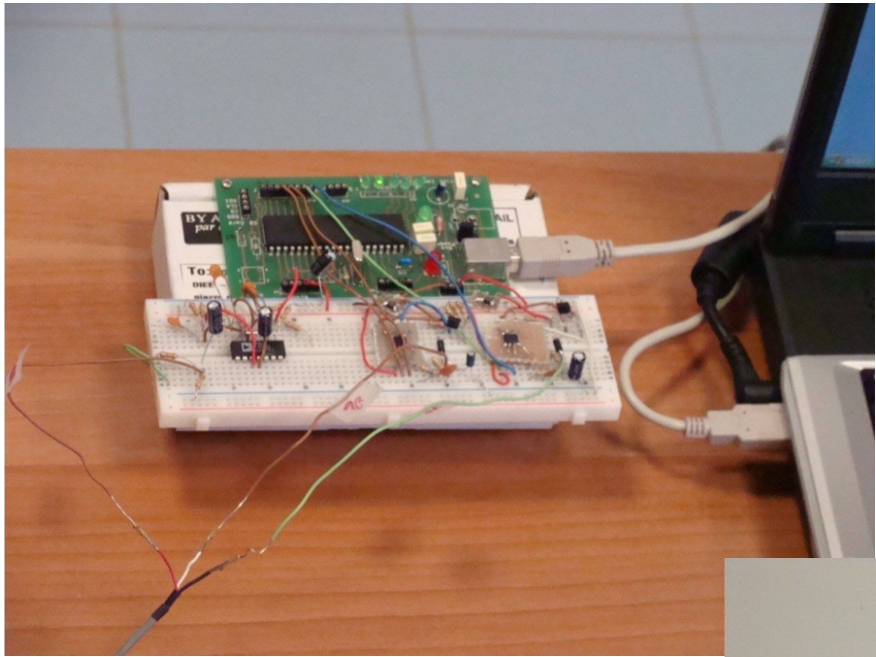
Sensor applied to a shoe sole for posture detection and monitoring



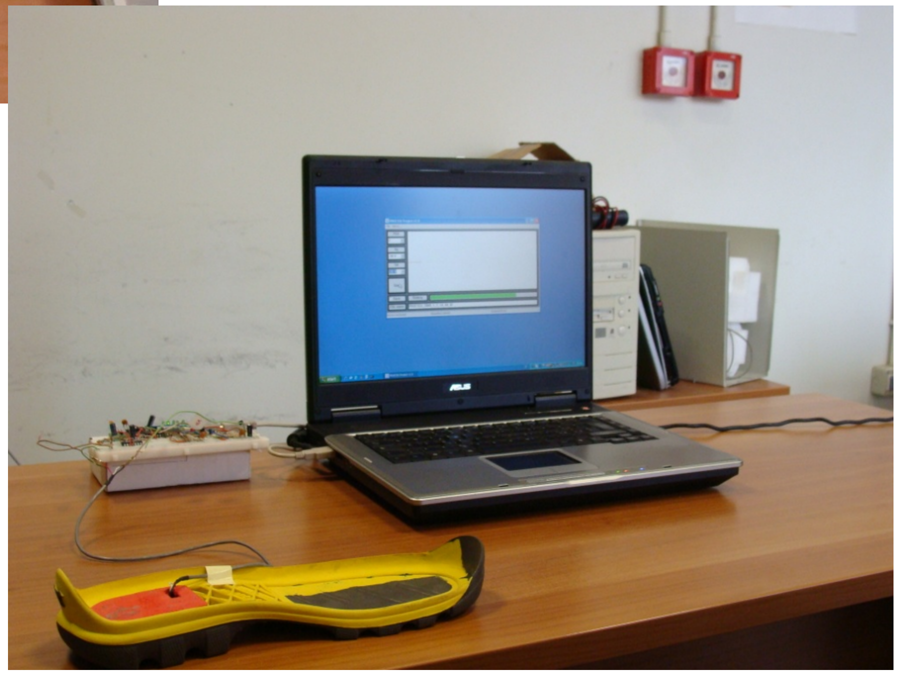


As can be noticed, output current varies as soon as pressure changes across the active surfaces

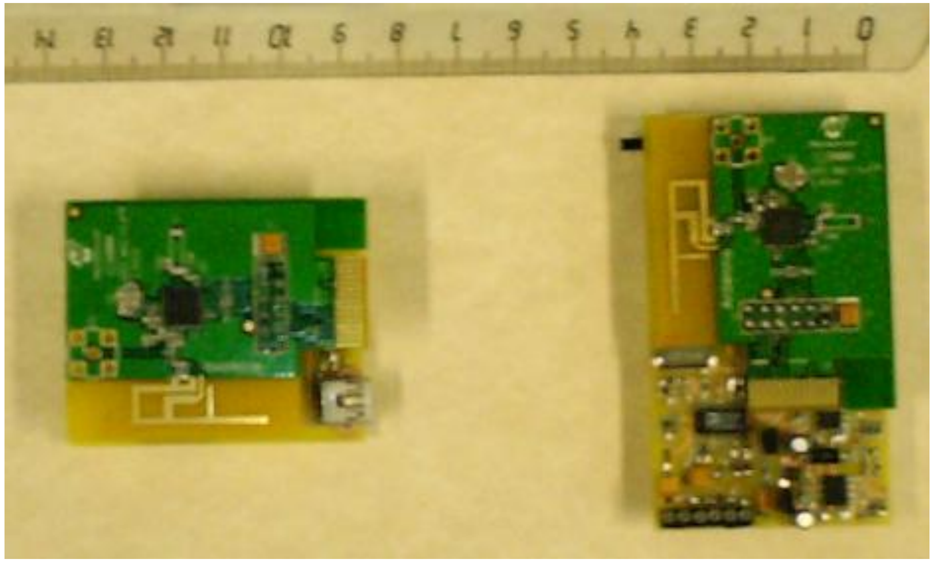
Some Examples: Posture detection

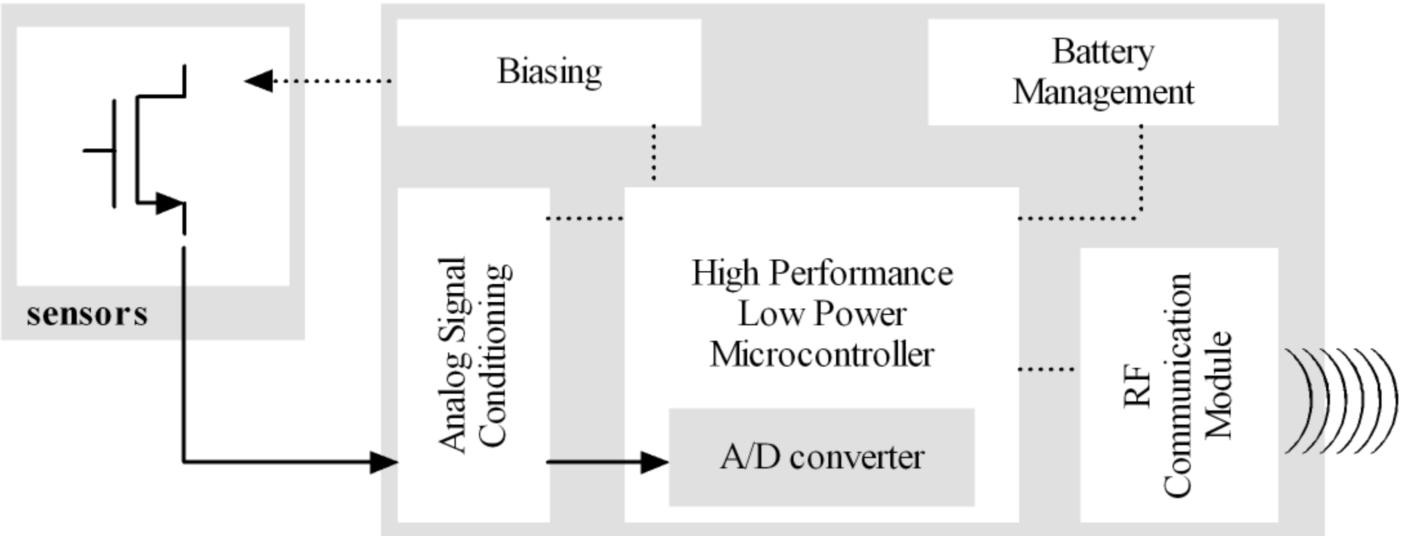


Prototype of the main board and measurement set up



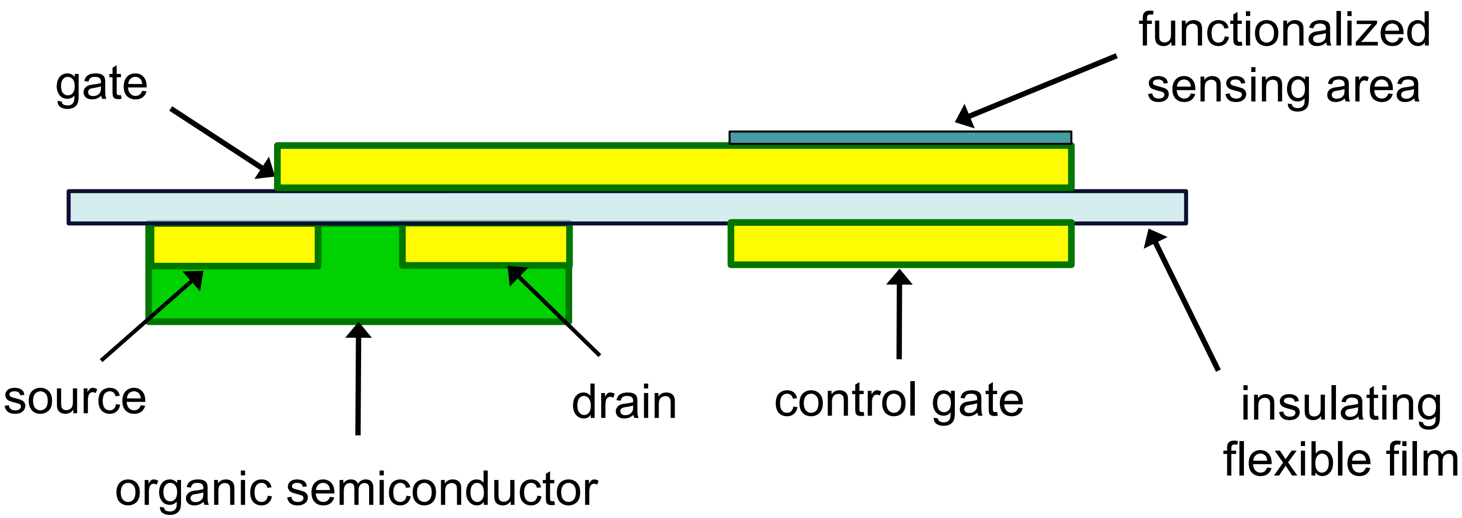
Some Examples: Posture detection



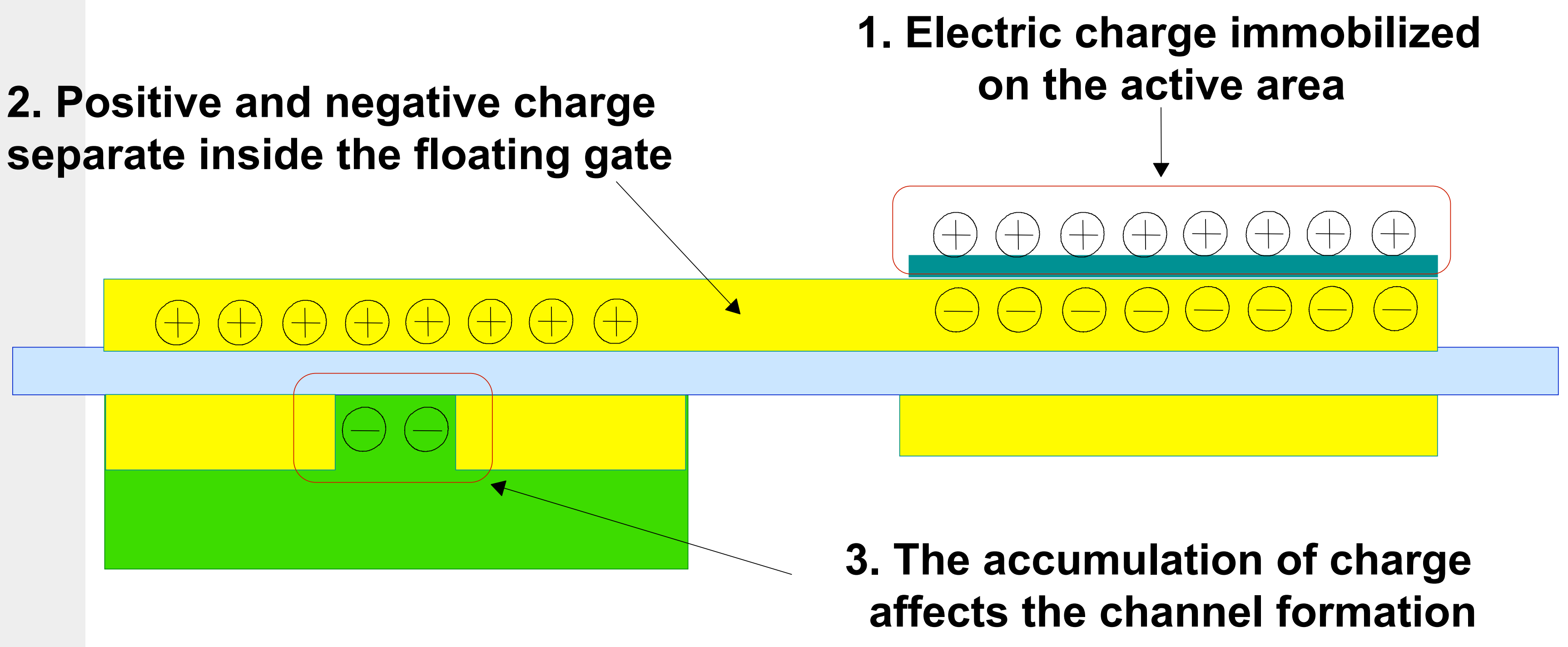


Chemical sensors: Device structure

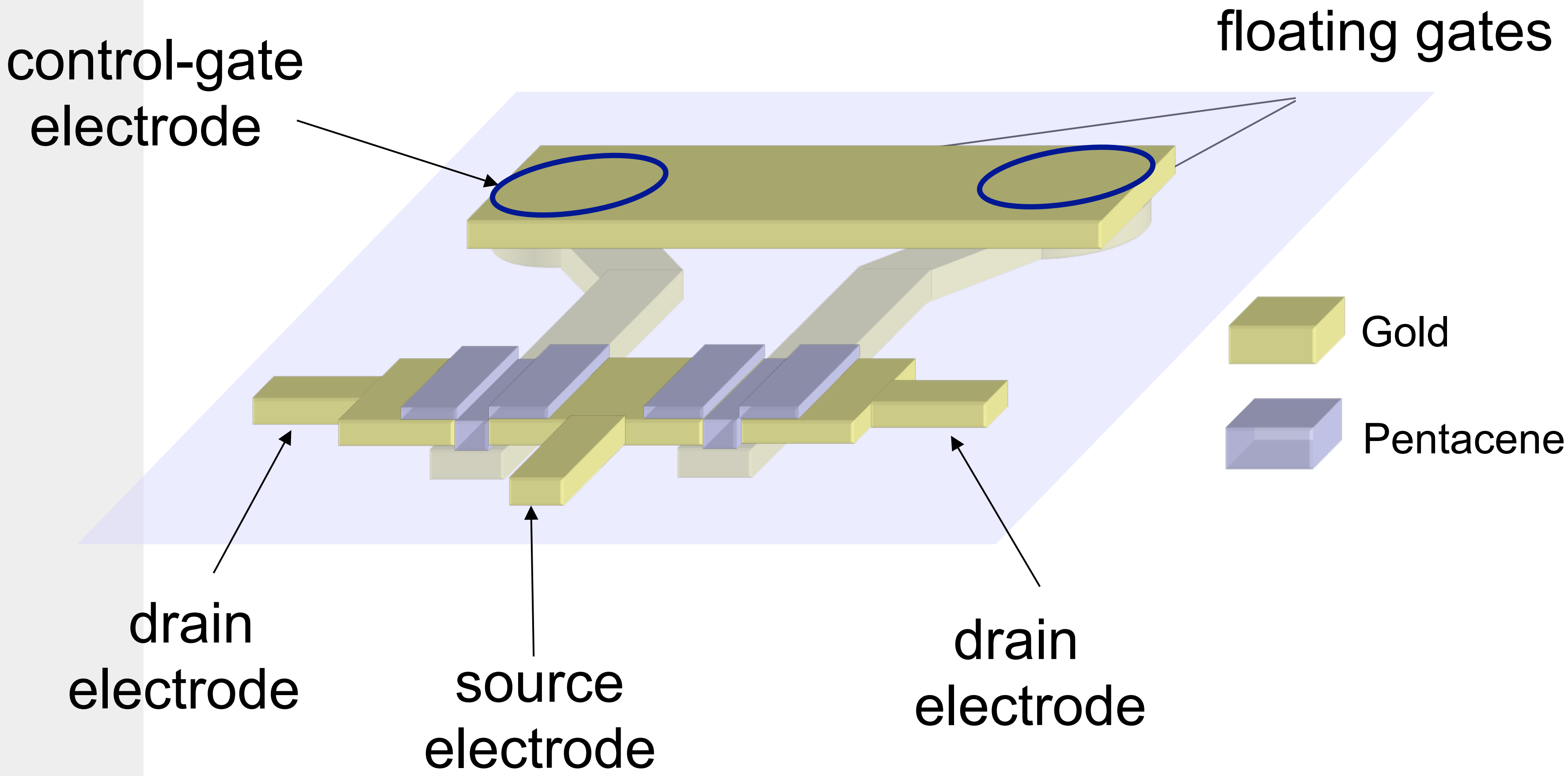
- The sensor structure is based on a fully *flexible organic field-effect transistor* (OFET)
- The device is assembled on a flexible film (Mylar®), which acts as gate insulator



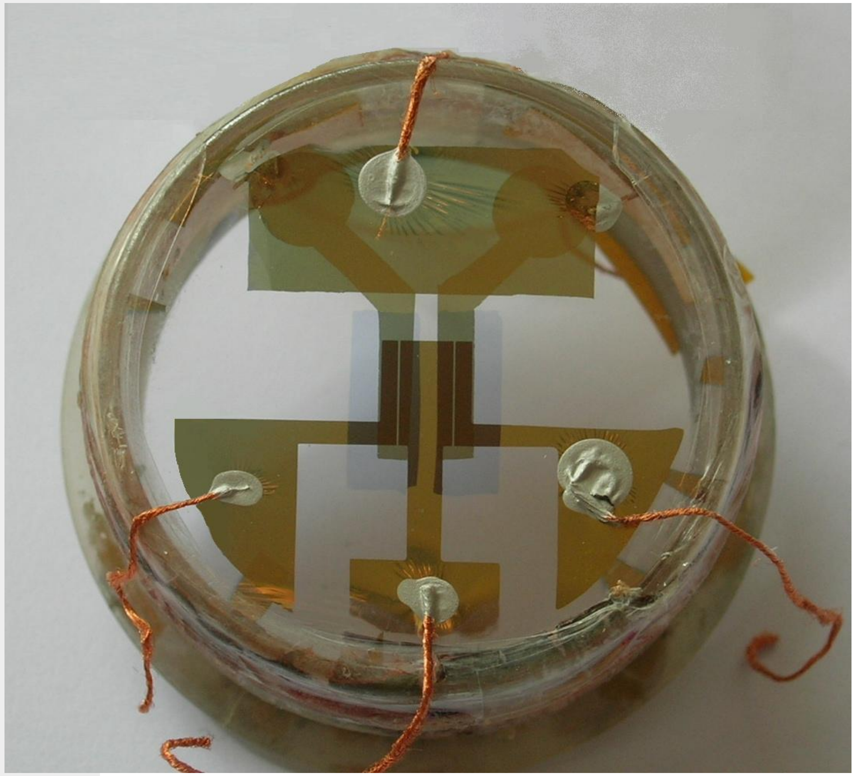
Working principle

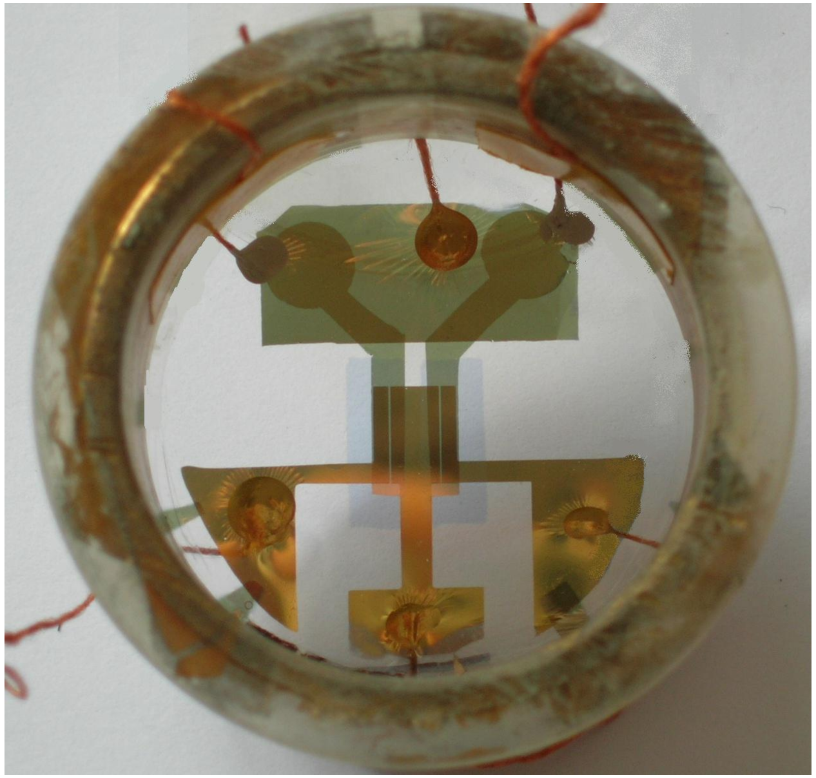


Device processing



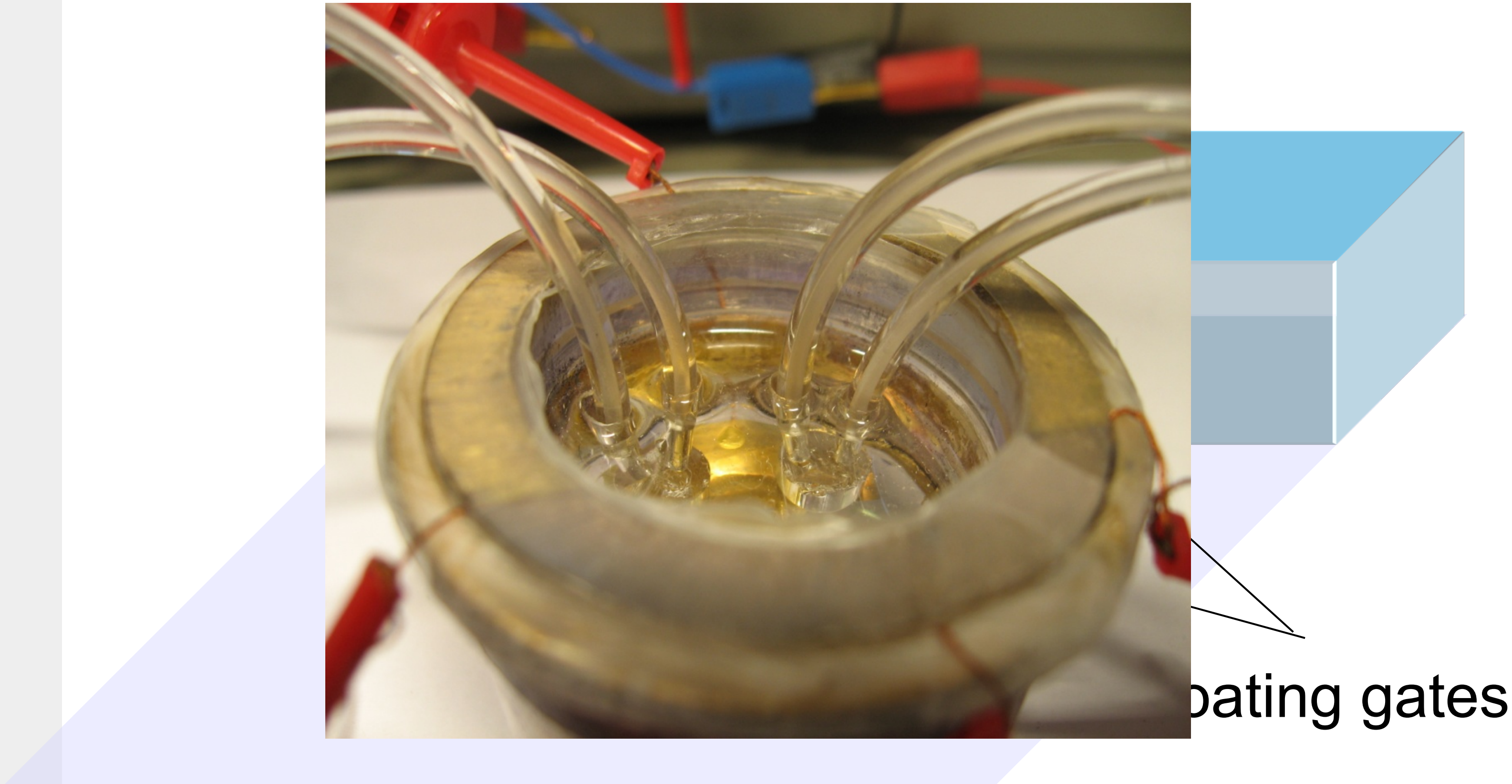
Fabricated device





Flow cell

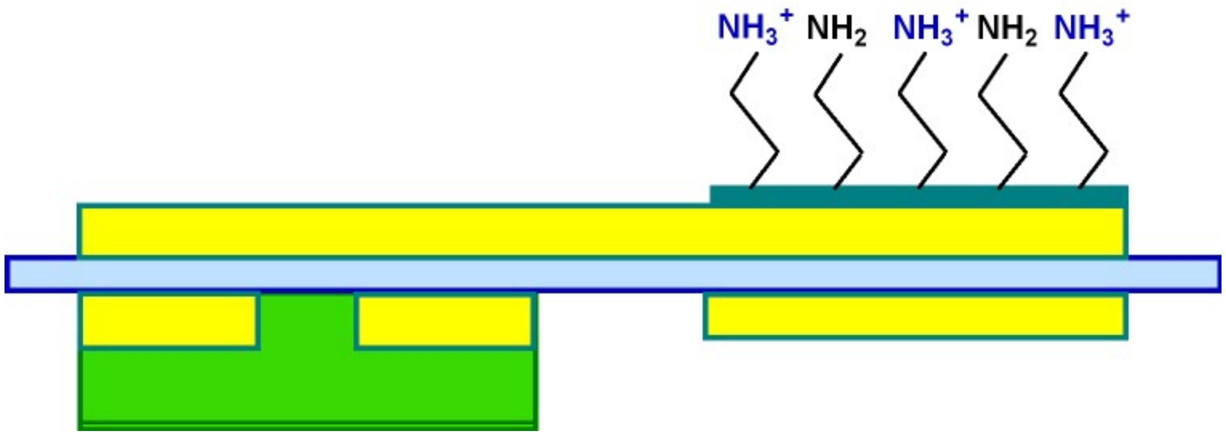
- A *custom flow cell* hosting two chambers with inlet and outlet channels, was developed to handle solutions involved in the assay



Ion-sensitive device: functionalization

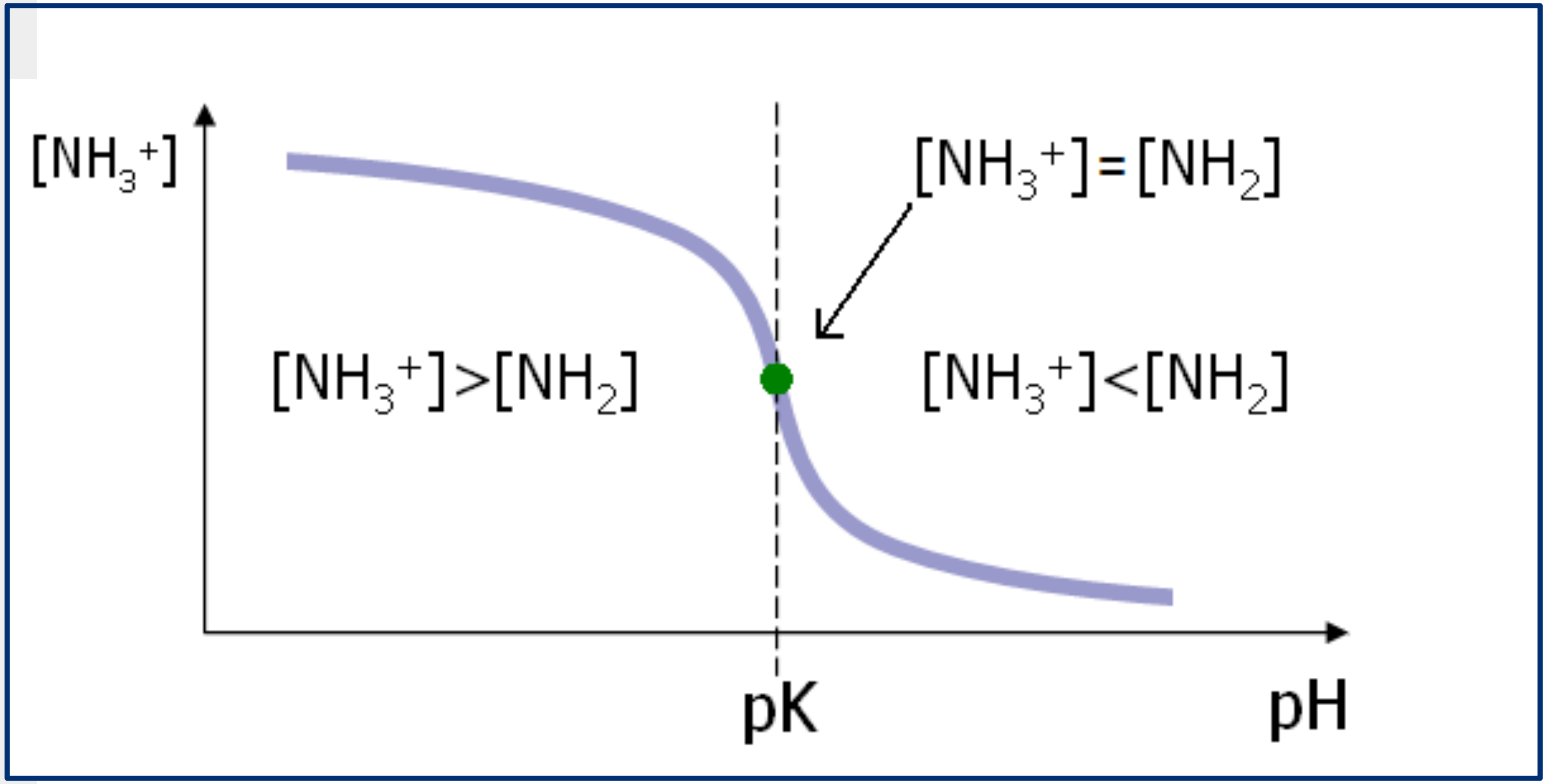
- The sensitivity is achieved functionalizing the floating gate by anchoring *NH_2 groups* on its surface
- The amino groups immobilized on the sensor protonize proportionally to the concentration of H3O+ ions in solution

- pH variations of the ionized functionalized surface floating gate by formation of a positive charge sheet on the actual gate
- The positive charge induces formation in the semiconductor → *higher threshold voltage*



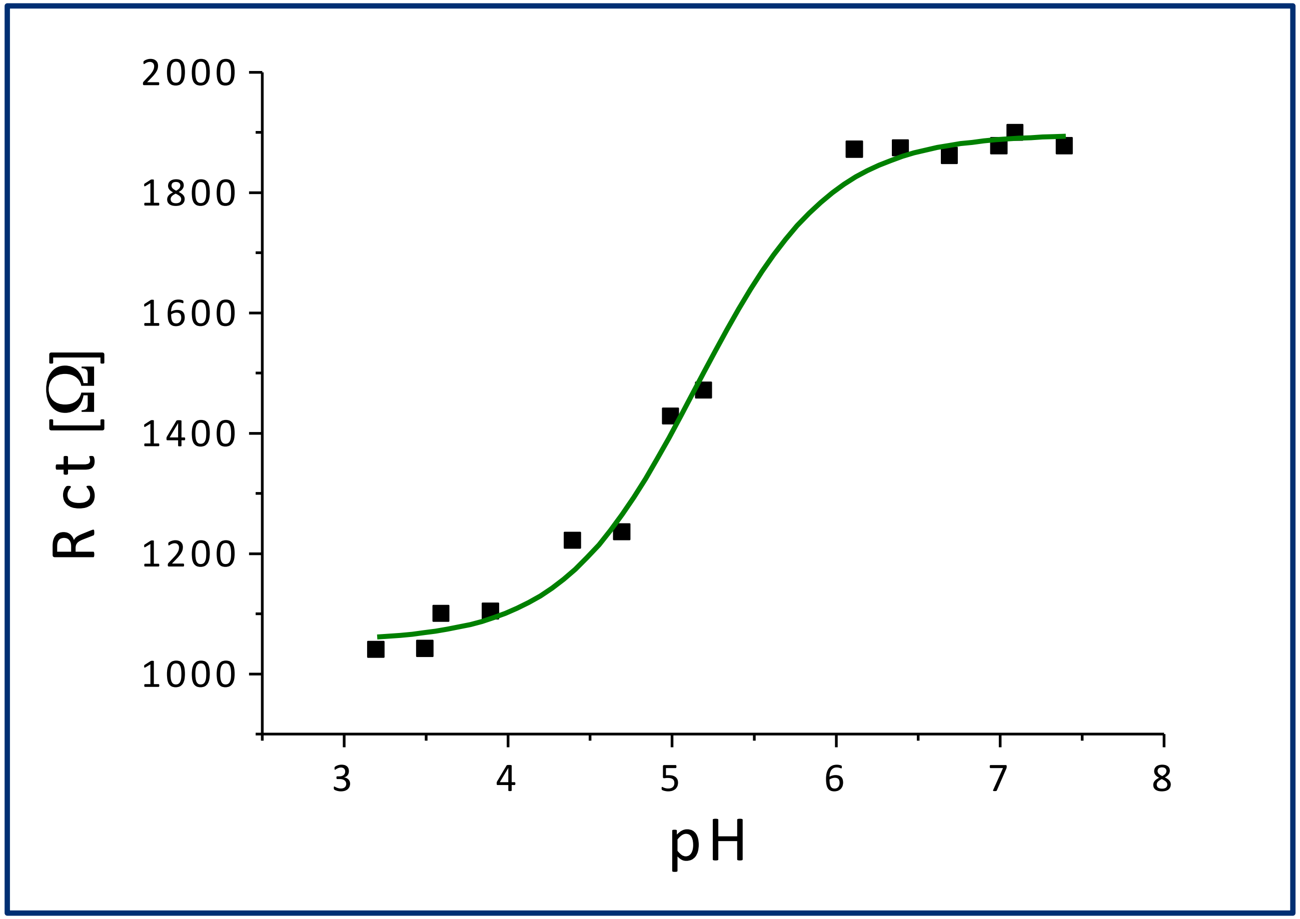
Ion-sensitive device: functionalization

Amino protonation curve - *Graphical representation*



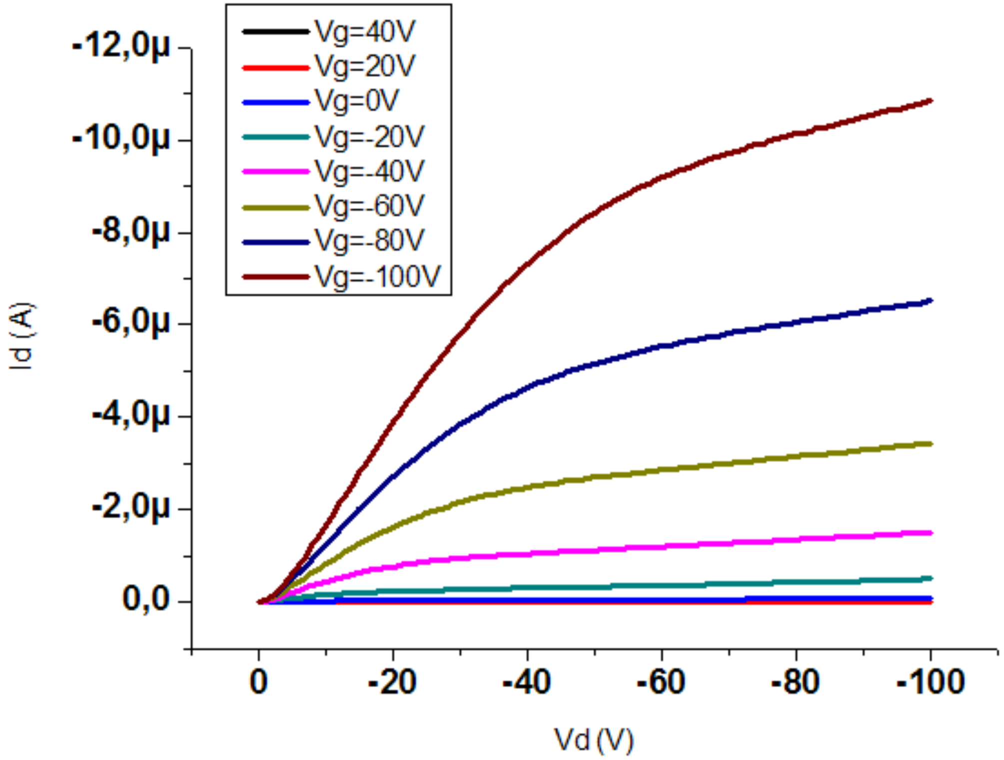
Ion-sensitive device: functionalization

Amino protonation curve – *Electrochemical Impedence Spectroscopy (EIS) measurements*



Ion-sensitive device: experimental results

- The device has the typical behavior of an organic *p-type* field effect transistor, working in *accumula*

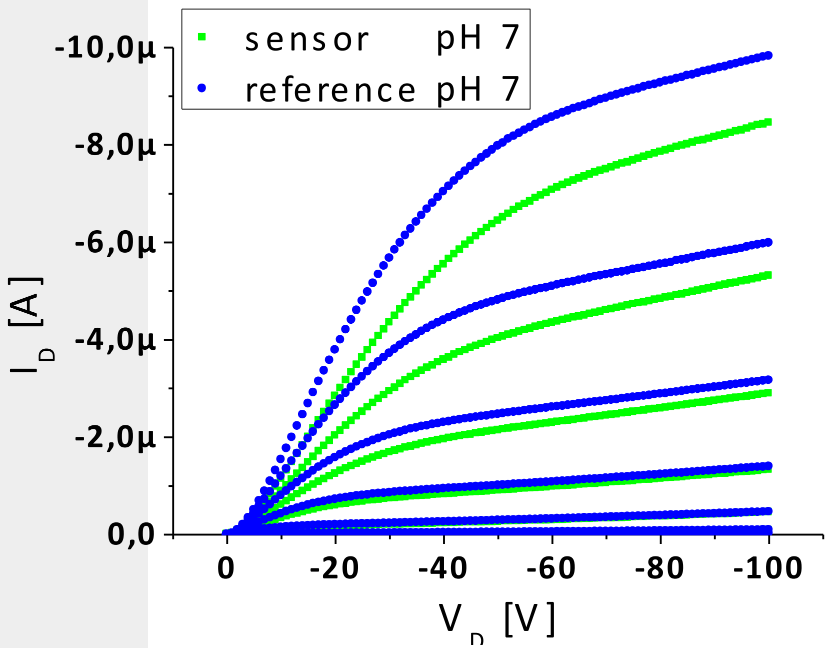


- The ion-s ... ıring the variation ... induced by the chan ... lution

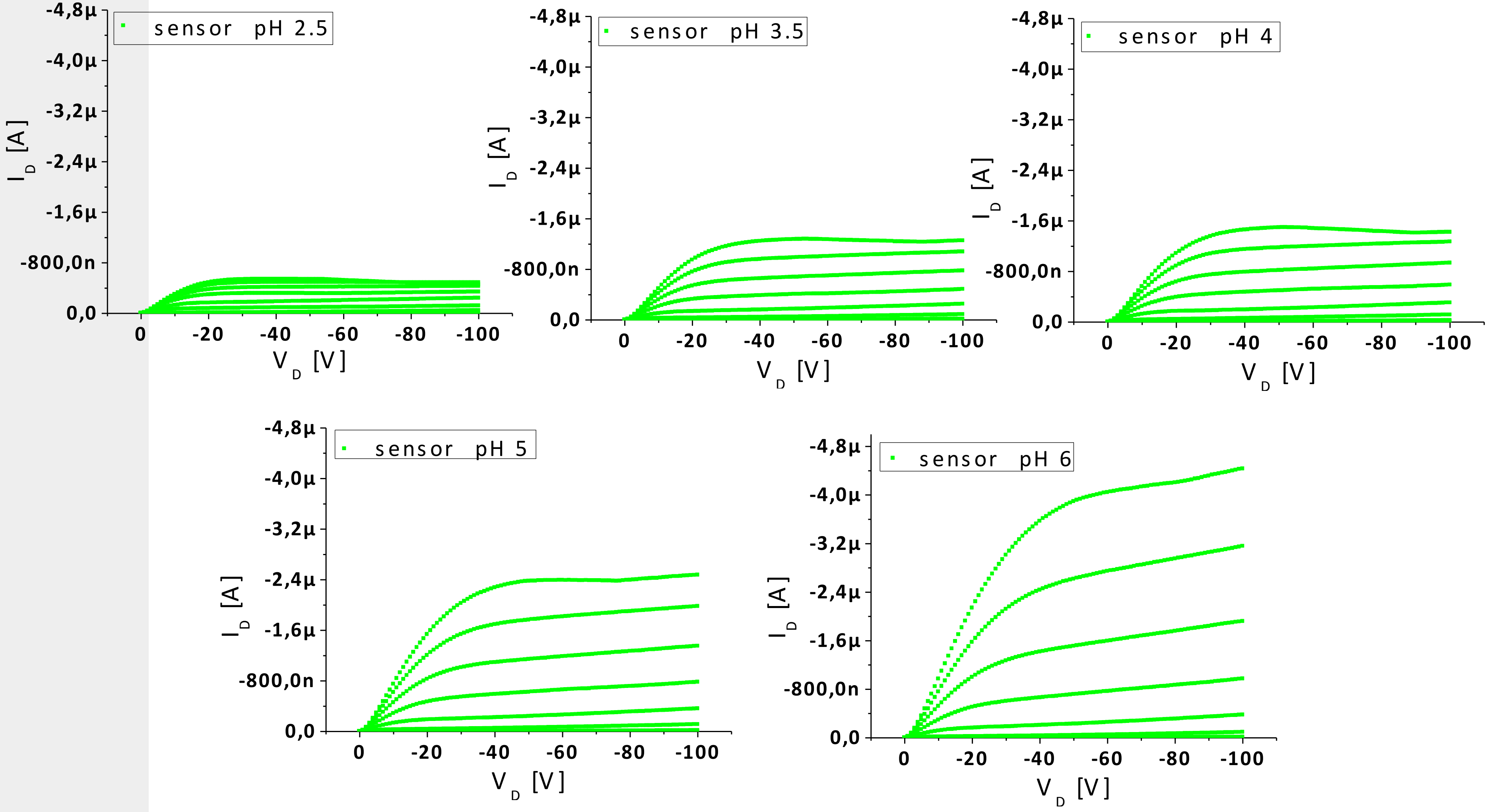
- The testi ... ɔing the solution ... ıs of the custom-developed fluidic system

Ion-sensitive device: experimental results

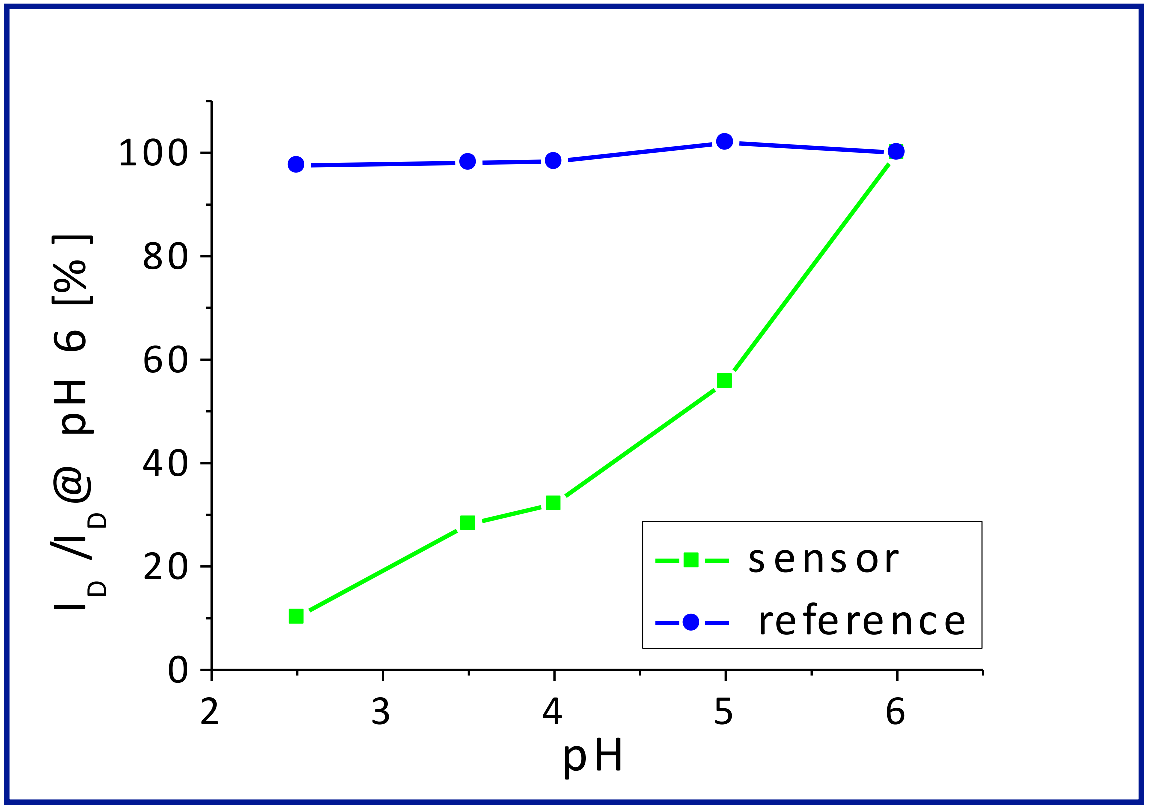
- The testing was performed by placing solutions at different pH values on the sensor, while keeping a solution at pH 7 on the reference



Ion-sensitive device: experimental results

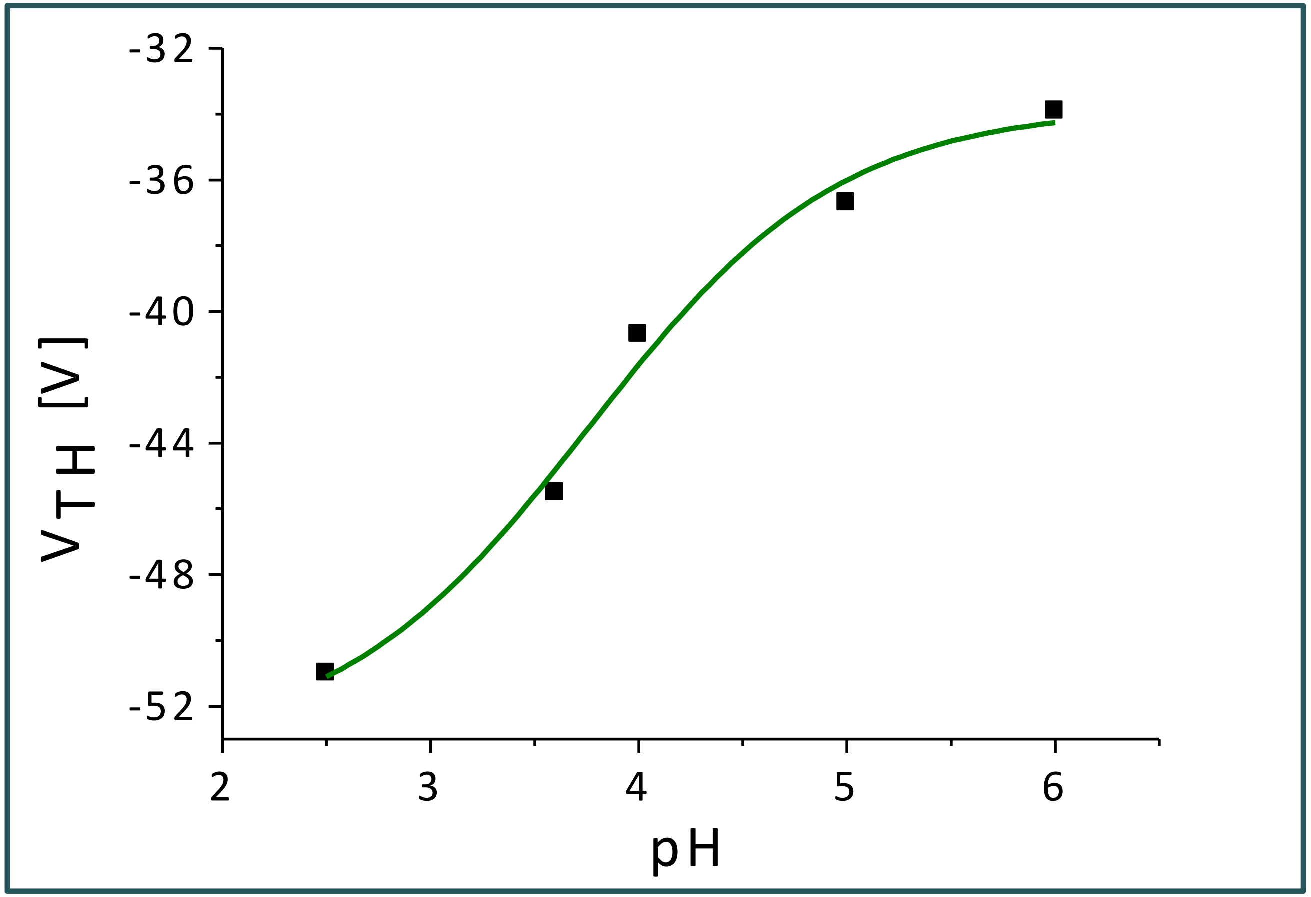


Ion-sensitive device: experimental results



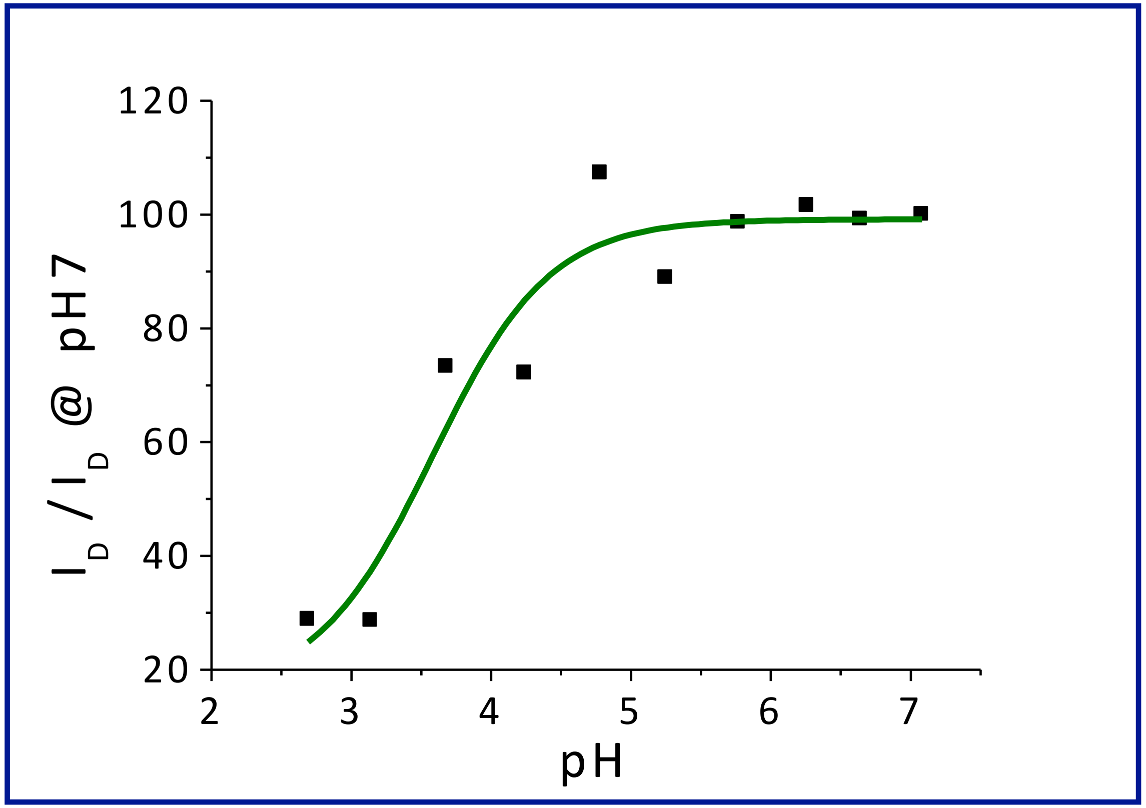
- Maximum *drain current* measured on both the sensor and the reference with varying pH (currents values normalized with reference to the current at pH 6)

Ion-sensitive device: experimental results



- Variation of the effective *threshold voltage* of the sensor with varying pH of the solution

Ion-sensitive device: experimental results



- Trend of the maximum sensor drain current with varying the pH towards more acid solutions

Conclusions: OFETs based sensors perspectives

– Electronic skin

– Biomedicine

Physiological parameter monitoring

– Smart textiles

– Wearable electronics