Dispositivi e sensori a semiconduttore organico

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1: Semiconduttori organici

2: Organic Thin Film Transistors (OTFT)

Outline prima parte

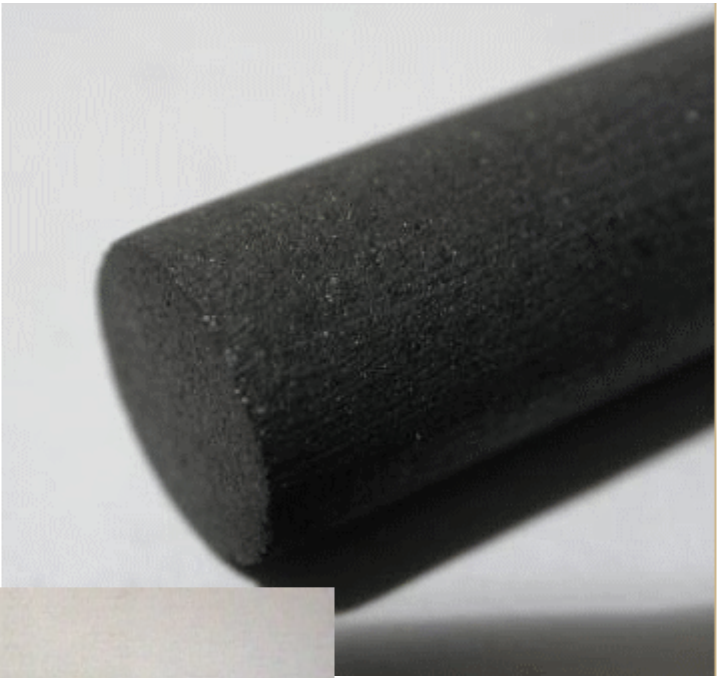
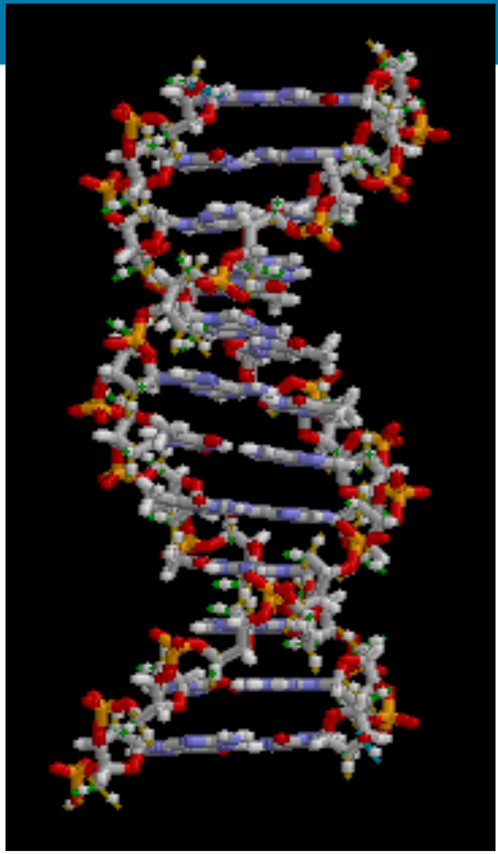
Proprieta' degli orbitali del Carbonio

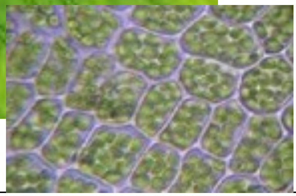
Molecole coniugate

Semiconduttori organici: orbitali molecolari e bandgap

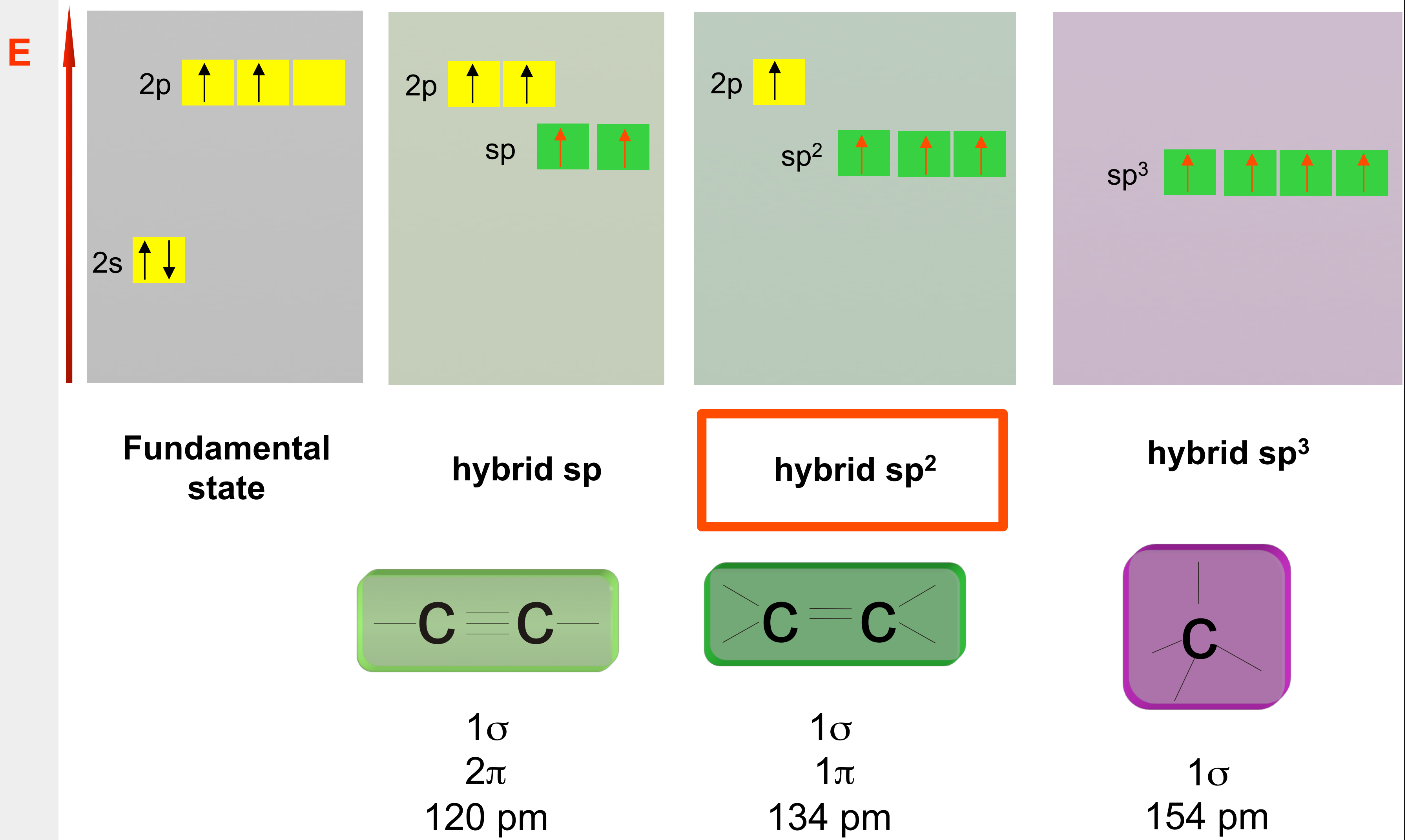
Portatori di carica e trasporto nei semiconduttori organici

Influenza della morfologia sul comportamento elettrico dei film sottili organici

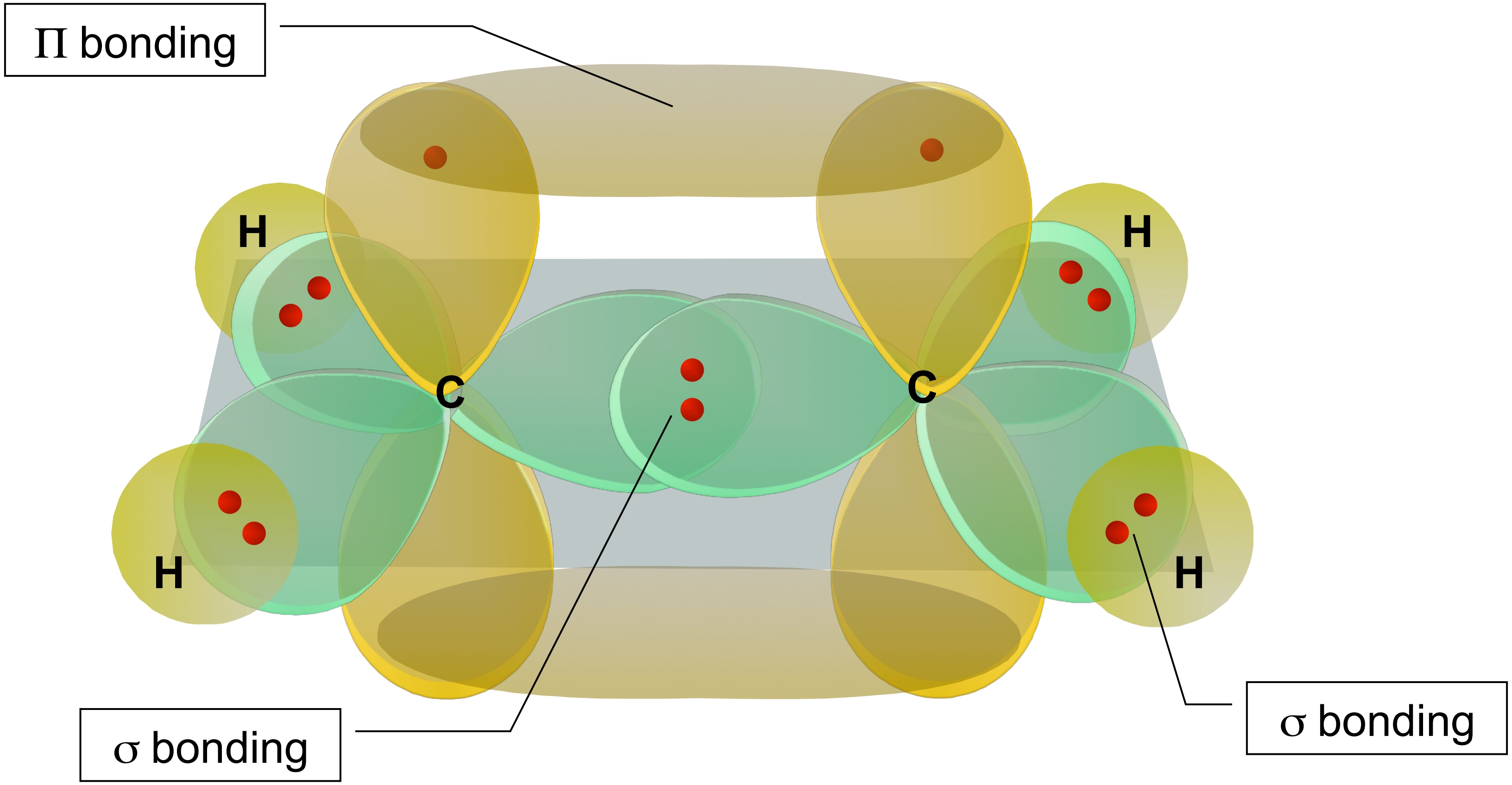




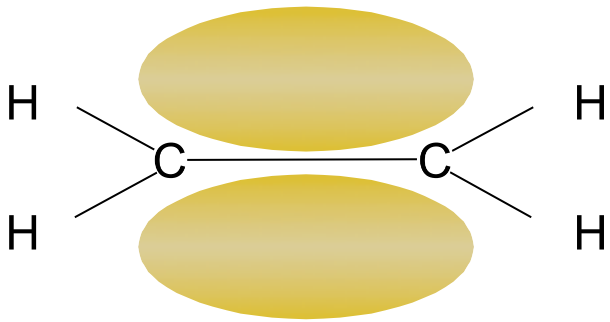



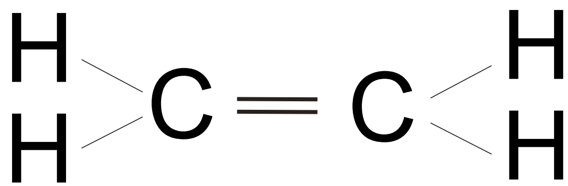
Hybridization of orbitals in Carbon



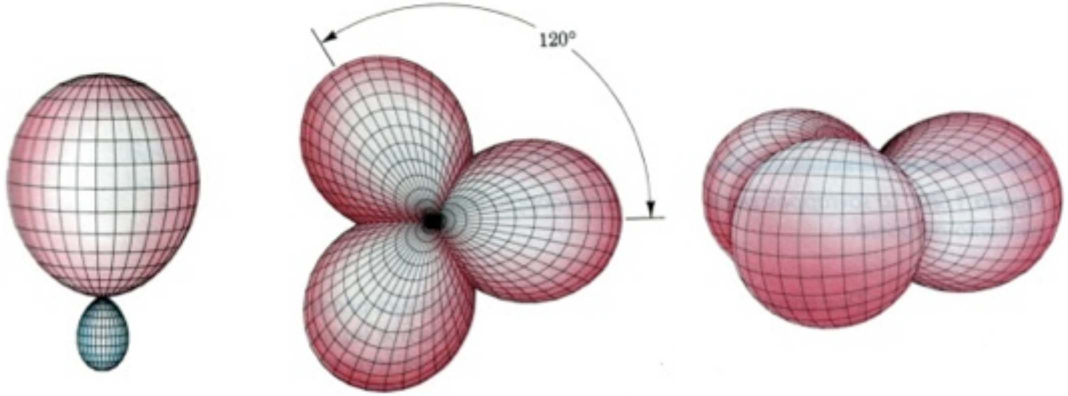
Carbon-Carbon bonding







Hybridization of orbitals in Carbon



Hybrid orbital sp^2 Top view Side view

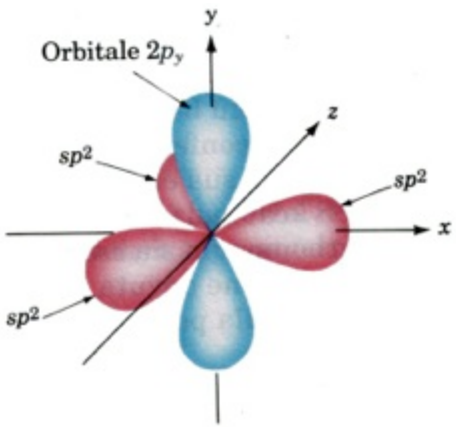


fig.1.1: un atomo di carbonio ibridizzato sp^2 [3].

Carbon-Carbon bonding

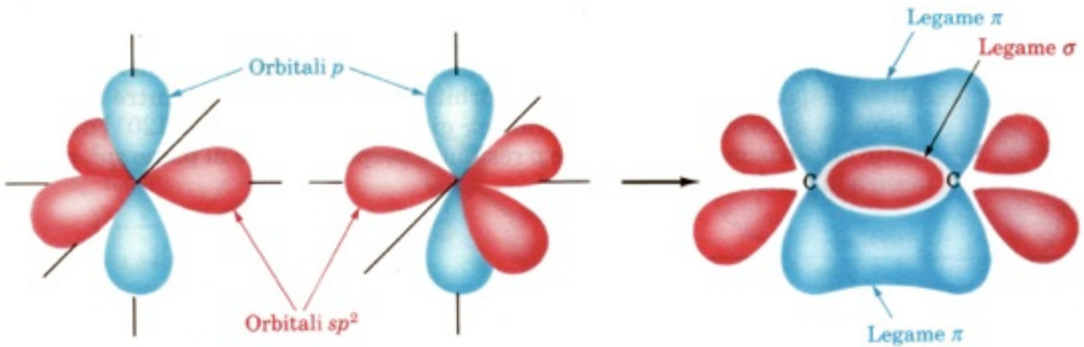
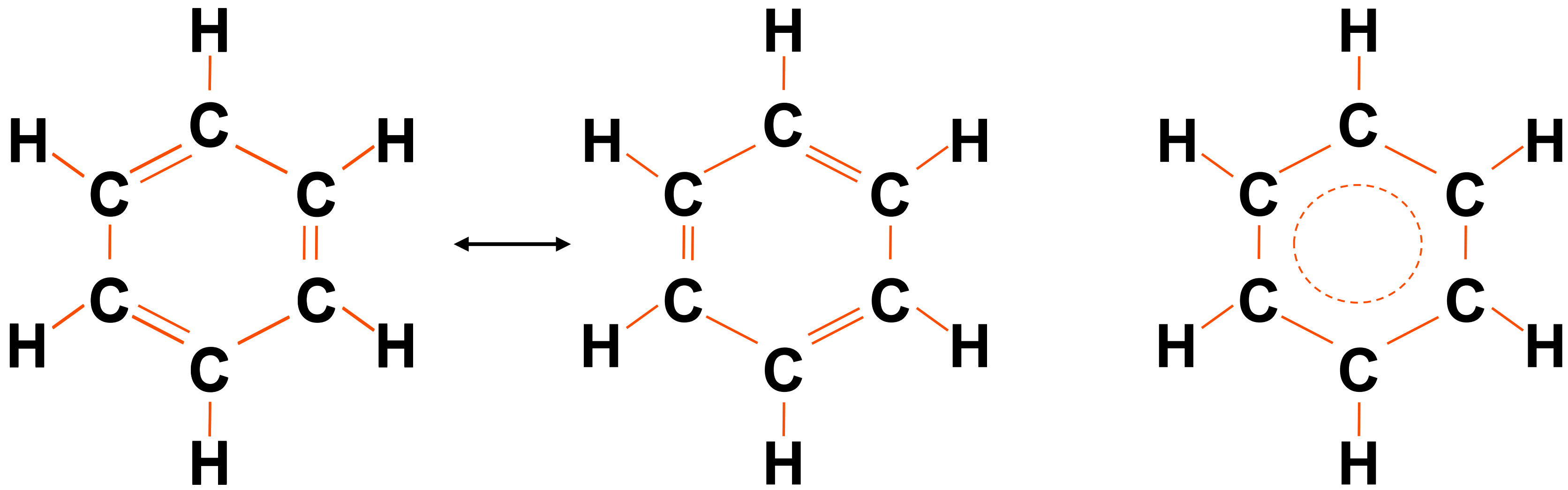


fig.1.2: la sovrapposizione orbitalica nel doppio legame carbonio-carbonio [3].

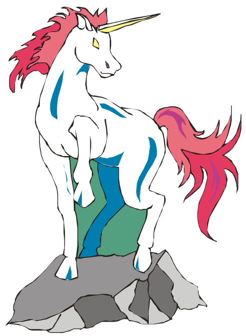
Molecular Orbital= linear combination of atomic orbitals (LCAO)

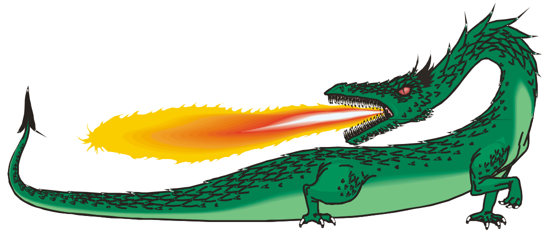
Coniugated molecules

C_6H_6

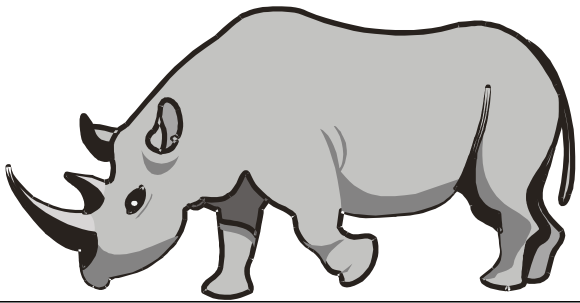


Limit formula



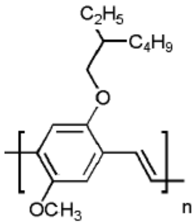


Limit formula

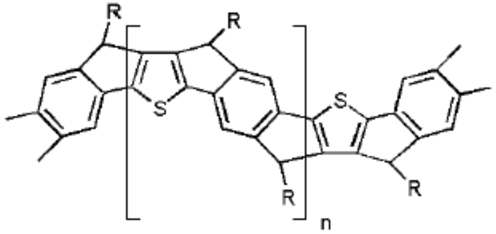


Real molecule

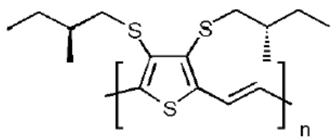
Coniugated molecules



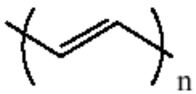
MEH-PPV



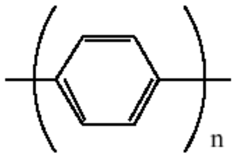
LPPPT



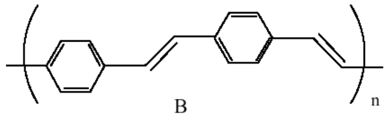
PTV



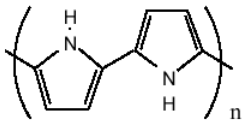
A



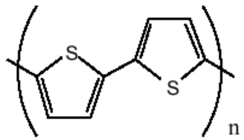
B



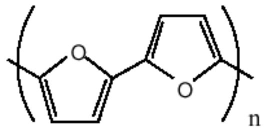
C



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

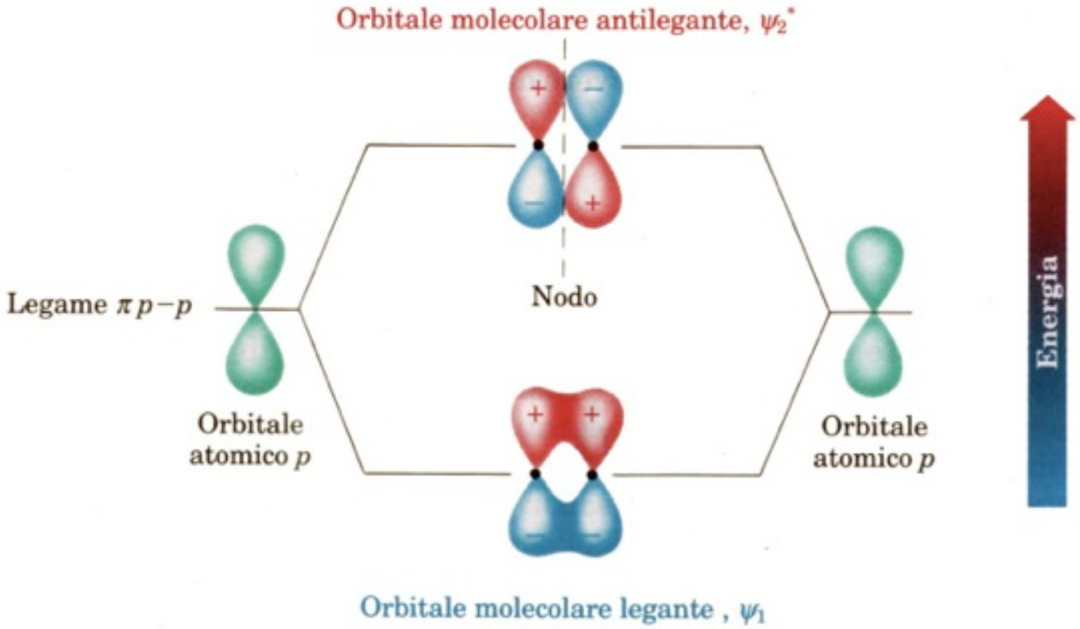
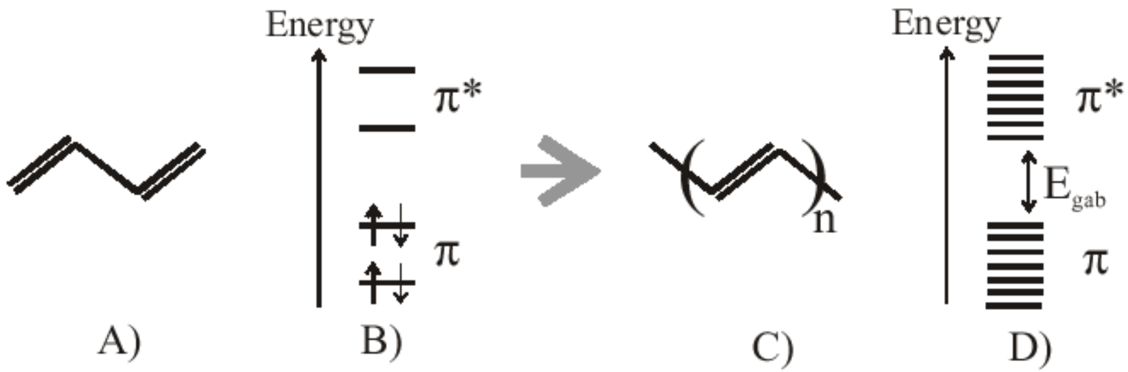


fig.1.7: orbitali molecolari π leganti e antileganti [3].

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

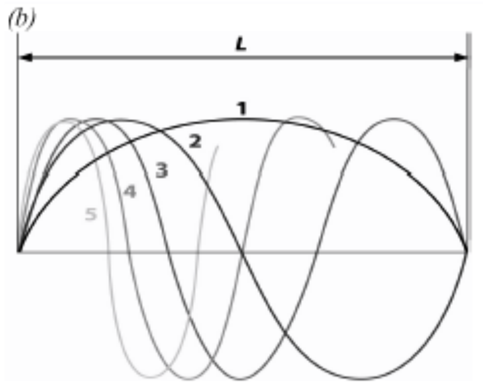


fig.1.10: funzioni d'onda dell'elettrone π nella buca di potenziale profonda infinito [6].

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

$$E_n = \frac{n^2 h^2}{8mL^2} \longrightarrow$$

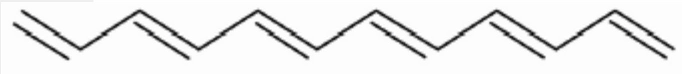
$$E(HOMO) = \frac{\left(\frac{N}{2}\right)^2 h^2}{8m(Nd)^2}$$

$$E(LUMO) = \frac{\left(\frac{N}{2}+1\right)^2 h^2}{8m(Nd)^2}$$

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

The highest N, the lowest the gap

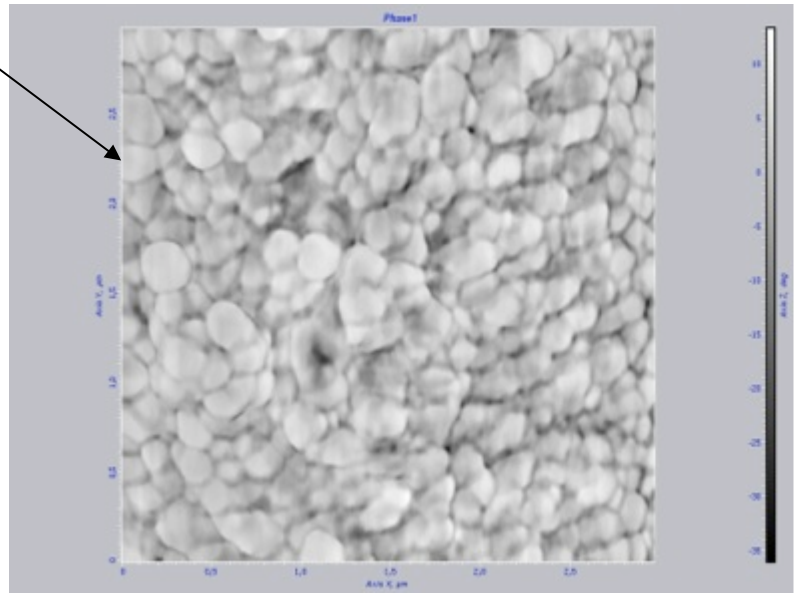
Charge transport in organic semiconductors



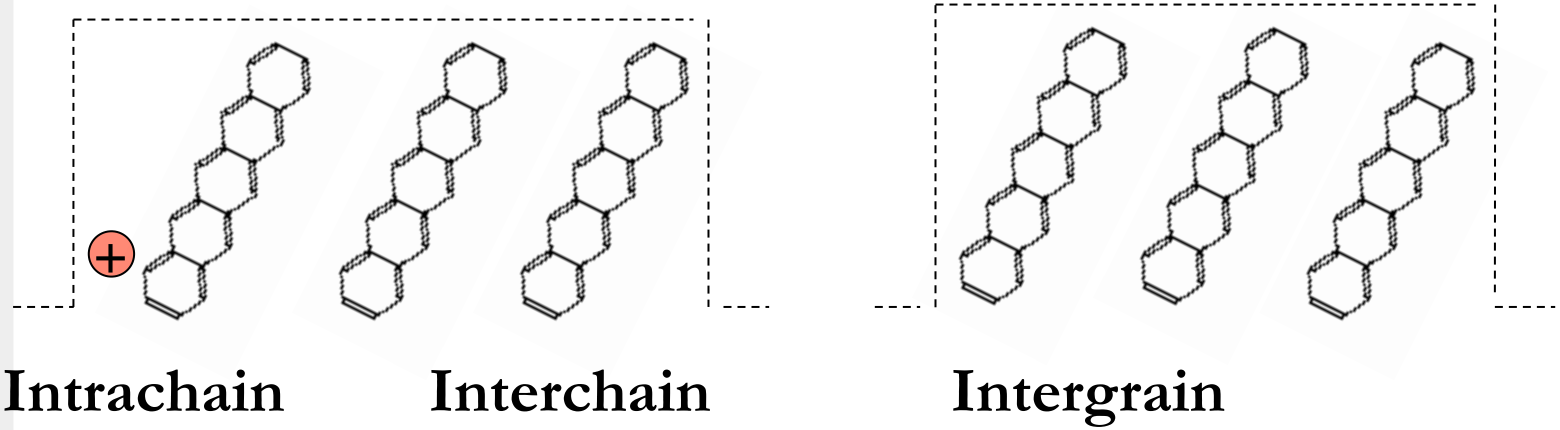
Å

nm

µm



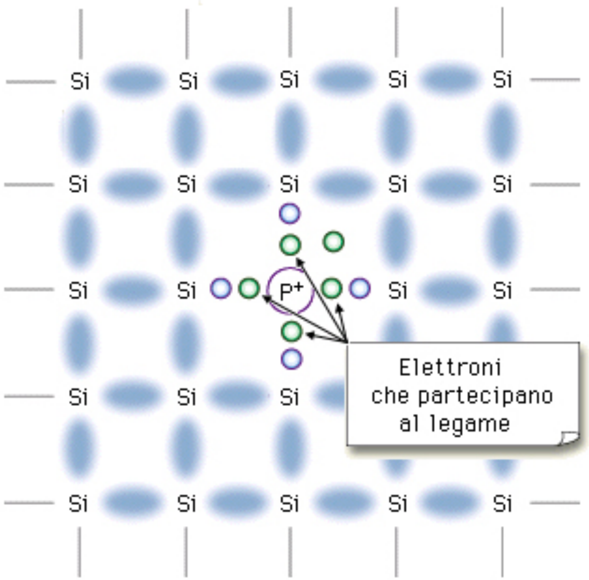
Charge transport in organic semiconductors

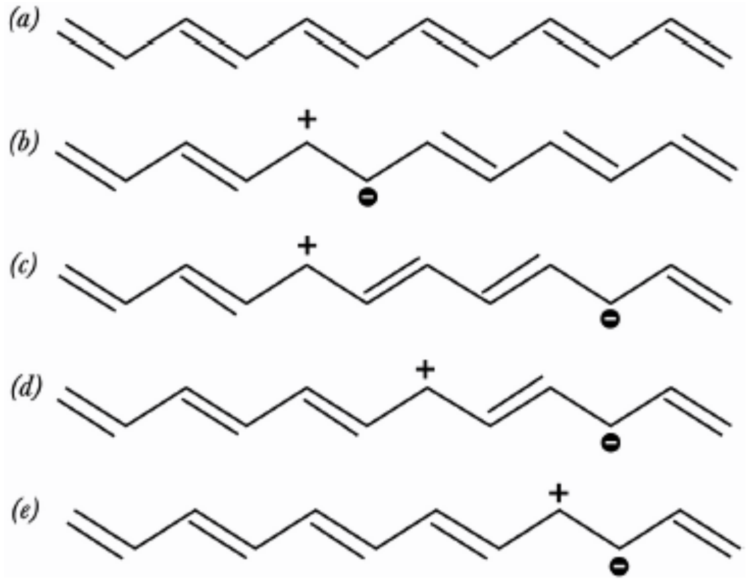


3 coesistent mechanisms+ charge injection from contacts

→ Measurements difficult to explain

Doping and charge transport



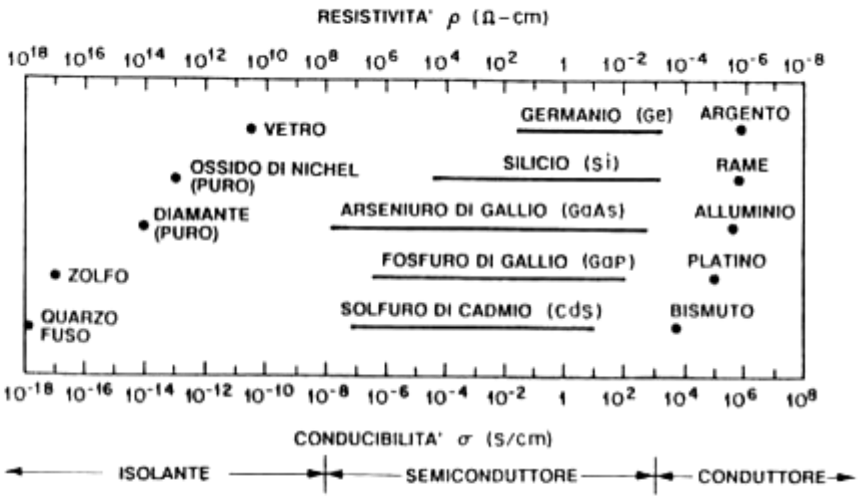


In inorganic semiconductor, doping is substitutional and causes an increase in free charge carrier concentration. These carriers move in a periodic potential with no interaction with the crystal (*band model*).
In organic, doping is not substitutional: supplementary charge physically interact with molecules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

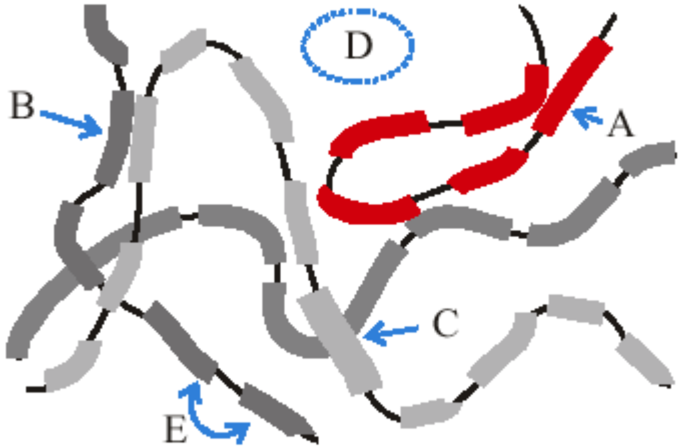
In analogy with inorganic semiconductors, the polaron can be roughly described as a charge free of moving along the chain strongly interacting with the semiconductor lattice

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

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



Intermolecular transport: hopping



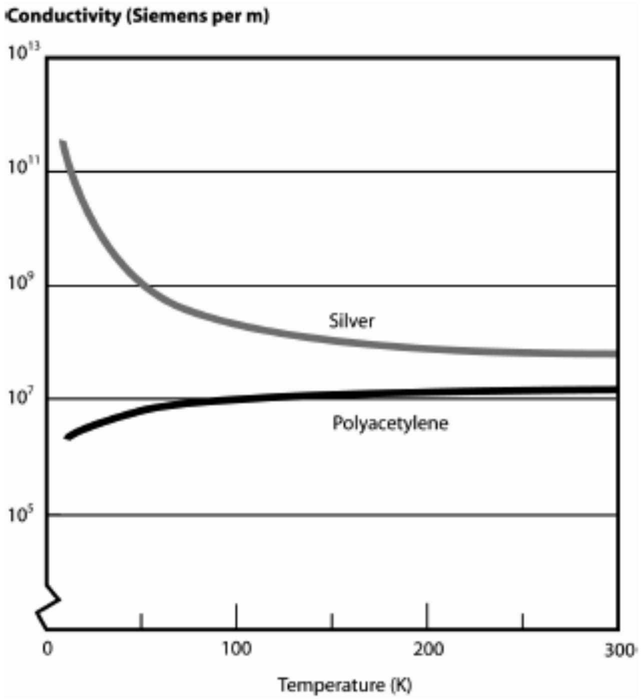
hopping = tunneling between crossing chains

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

$$\mu_D = \frac{e \cdot d^2}{2\tau_J \cdot k_B \cdot T}$$

→ *σ(T)= σo (T)·exp[-(To /T)1/(1+d)]*

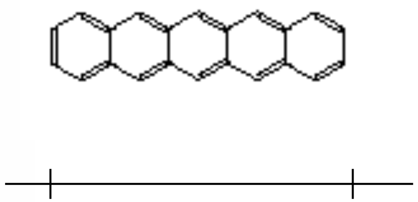
Intermolecular transport: hopping

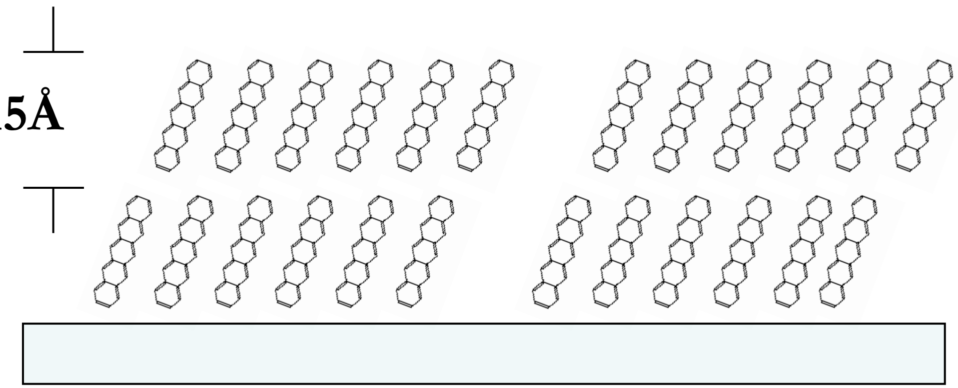


But, in organic materials there is a great variety of behaviour from material to material. A unifying theory has not yet been developed.

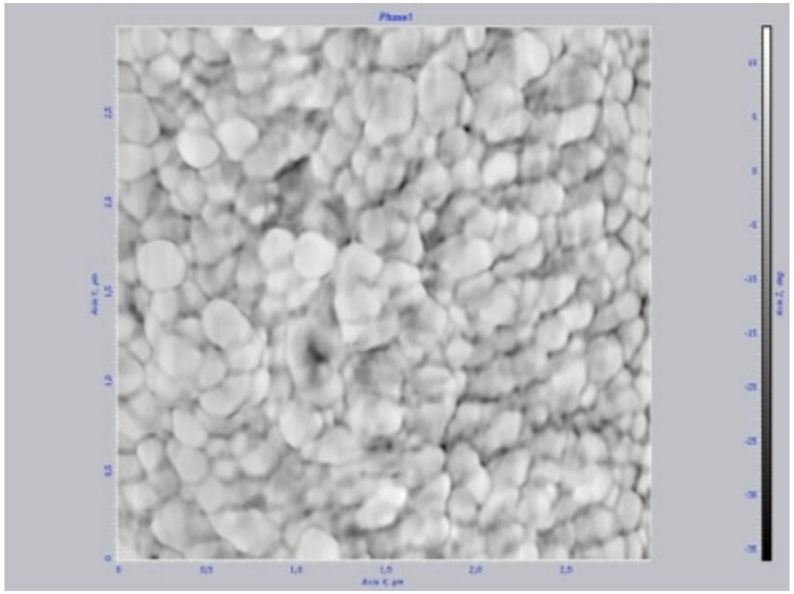
Intergrain transport: Pentacene (C_{22} H_{14})

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





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



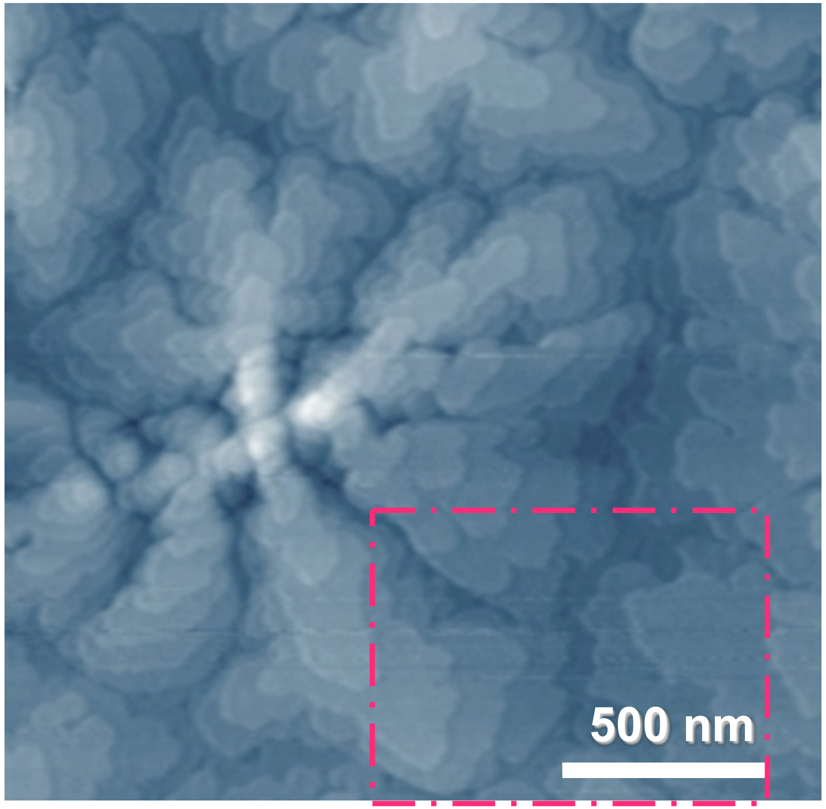
Conduction:

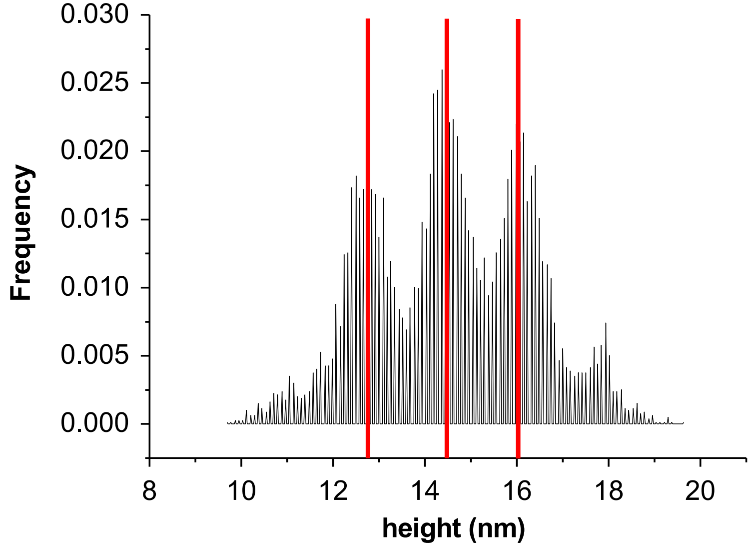
- hopping
- thermically activated
- limited by traps at grain boundaries

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

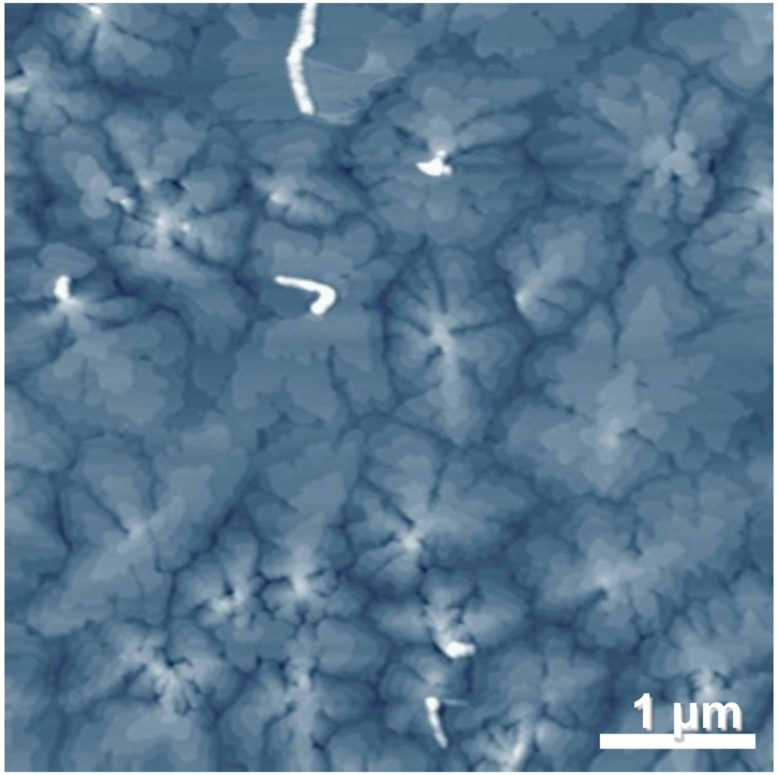
Correlation btw grain dimensions and mobility

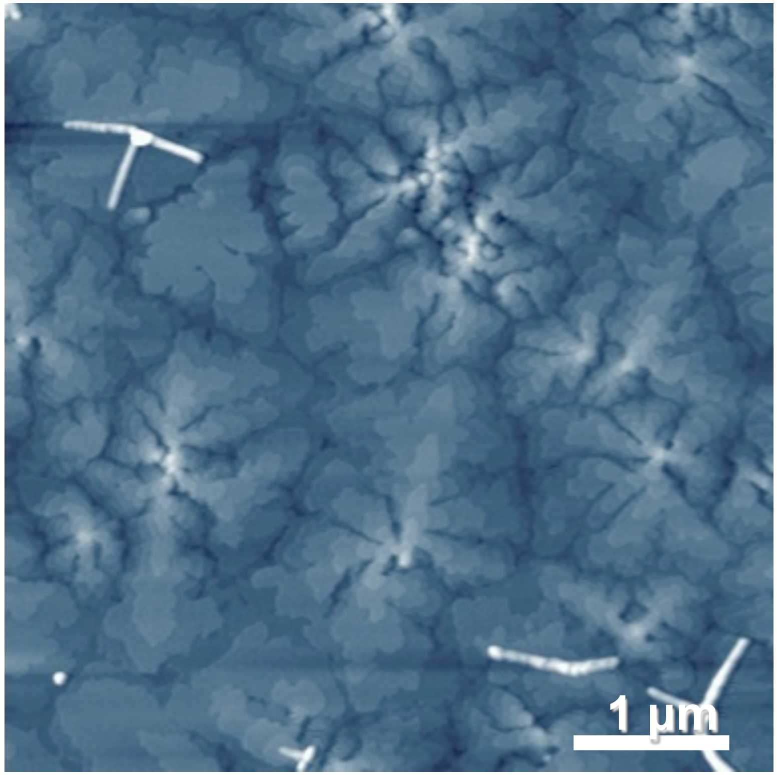
Influence of surface morphology





Influence of surface morphology

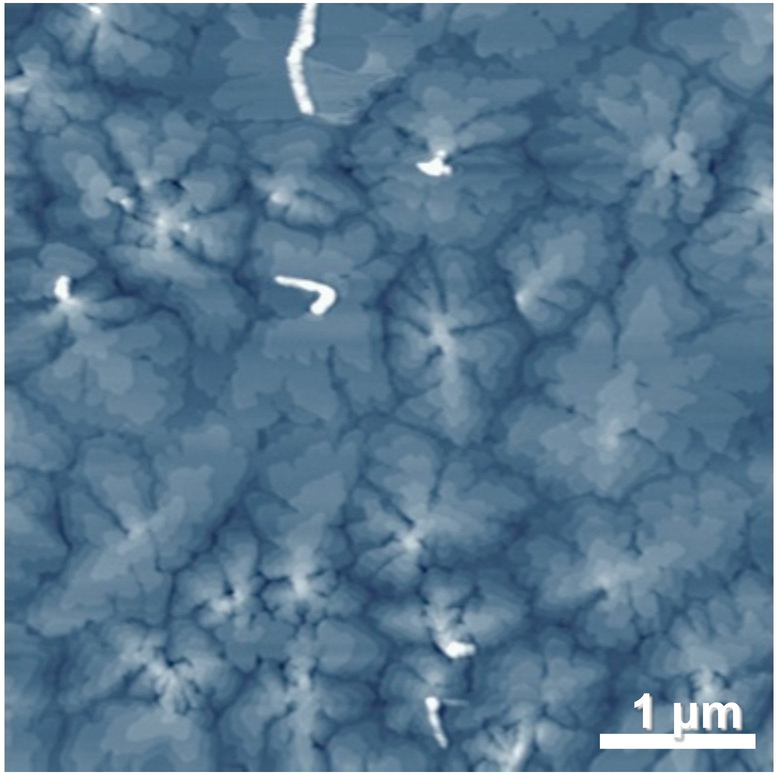


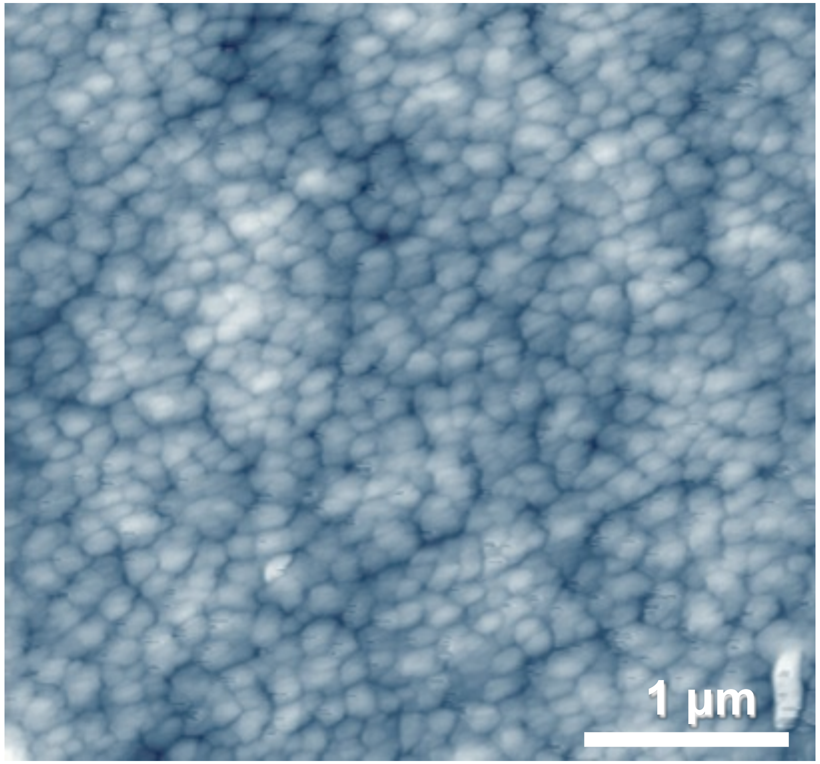


Pentacene on Mica

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

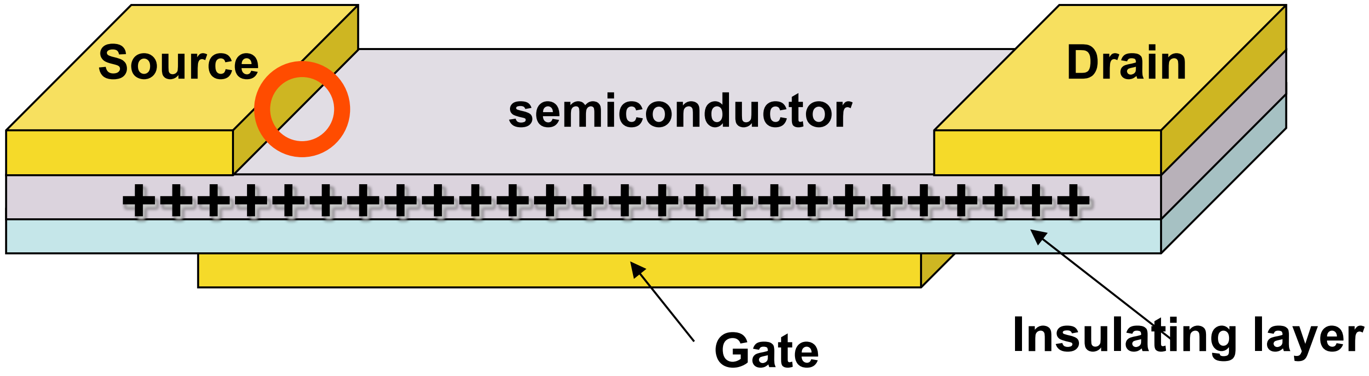
Modello elettrico del dispositivo

Tecnologia

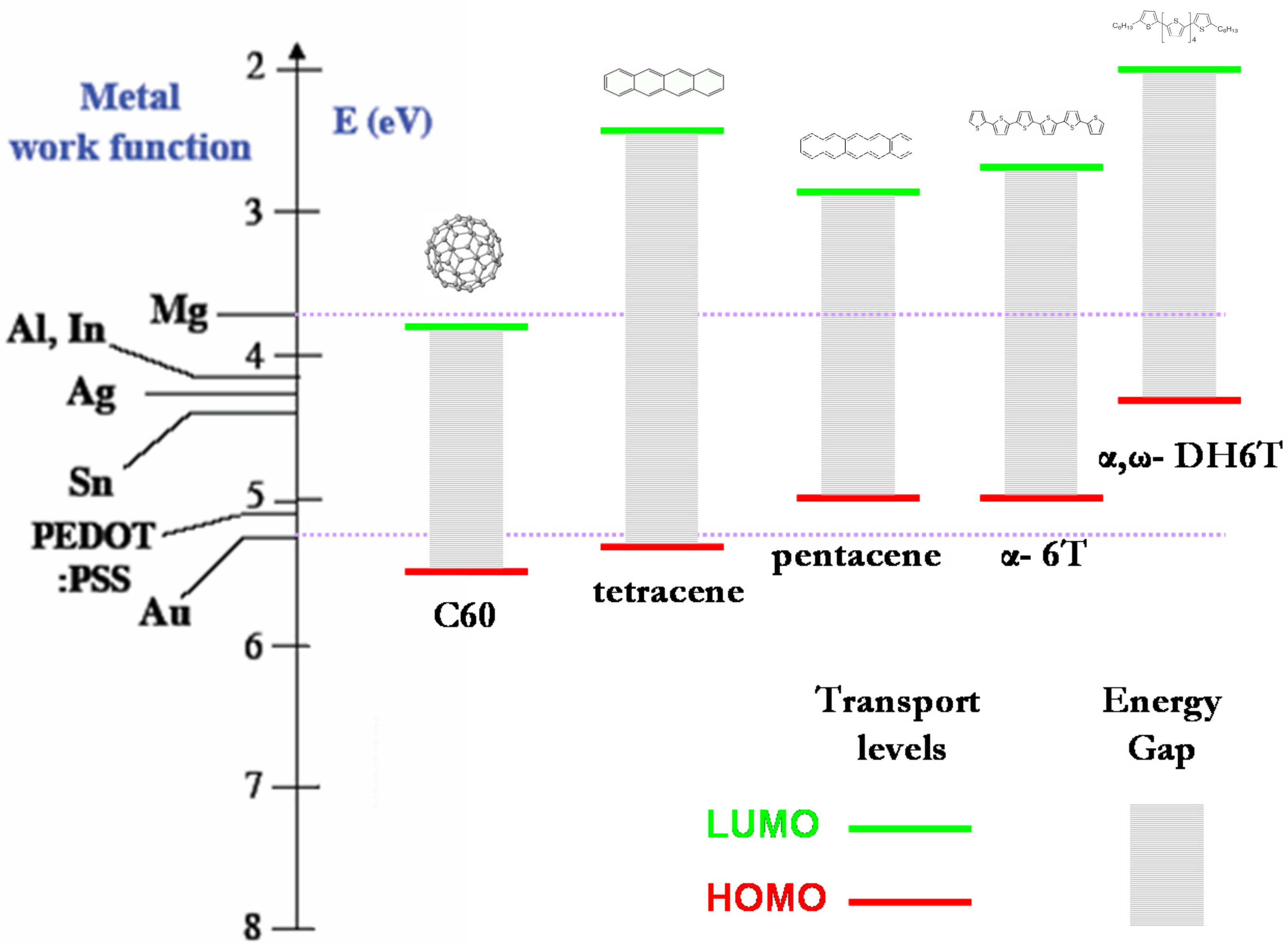
Field Effect Transistors

OTFT = ORGANIC THIN FILM TRANSISTOR

Interface metal - semiconductor

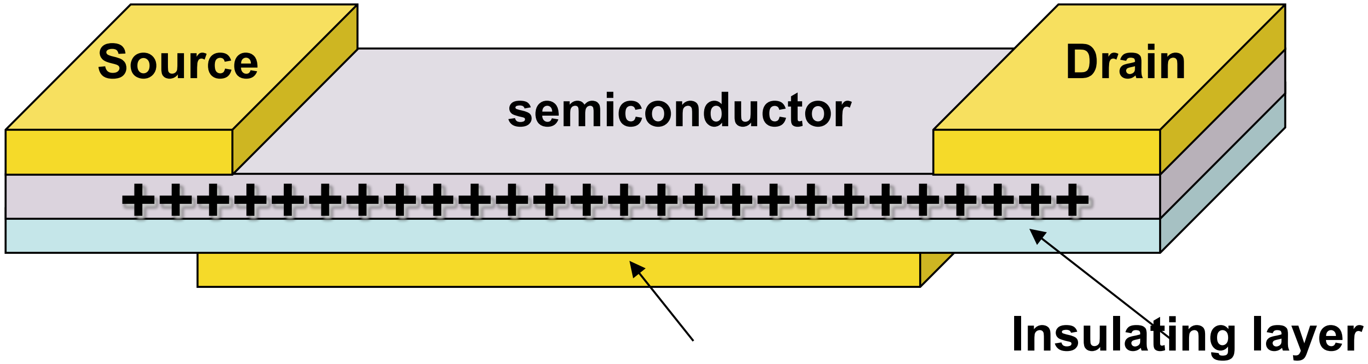


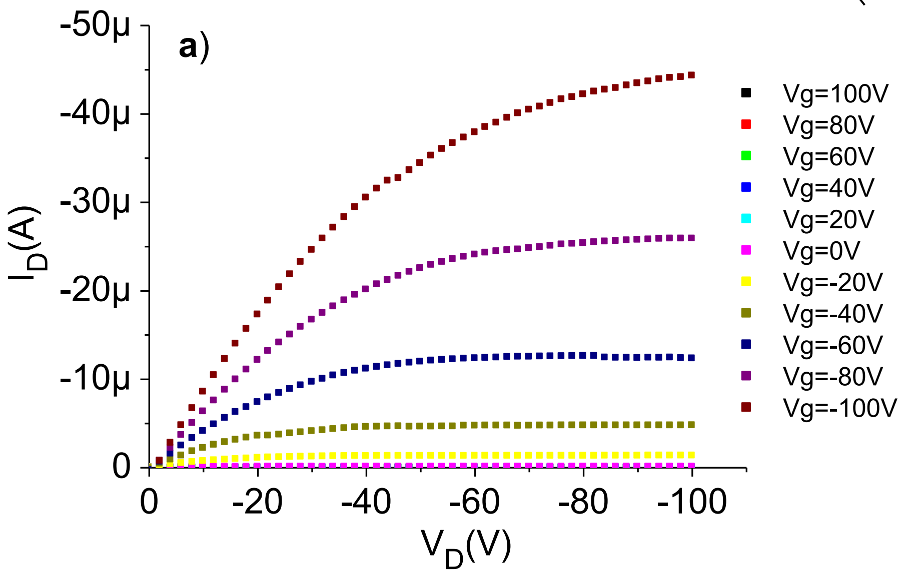
Charge injection from metal contacts



Thin Film Transistor

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





Tipically p-type!

How an OTFT works

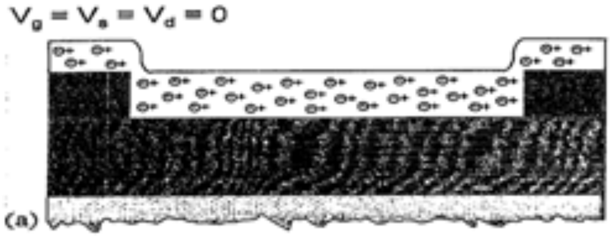


Fig. 2a

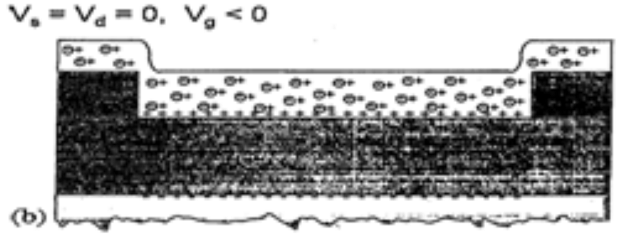


Fig. 2b

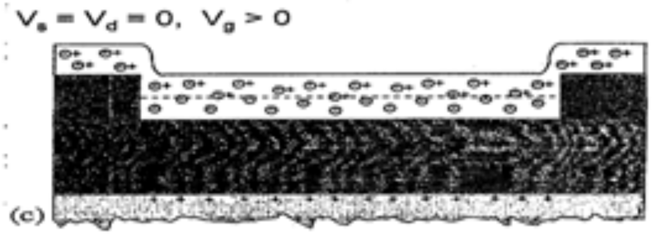


Fig. 2c

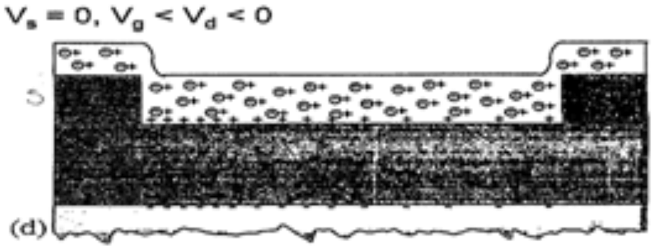


Fig. 2d

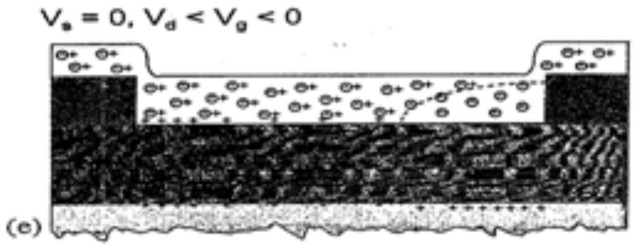
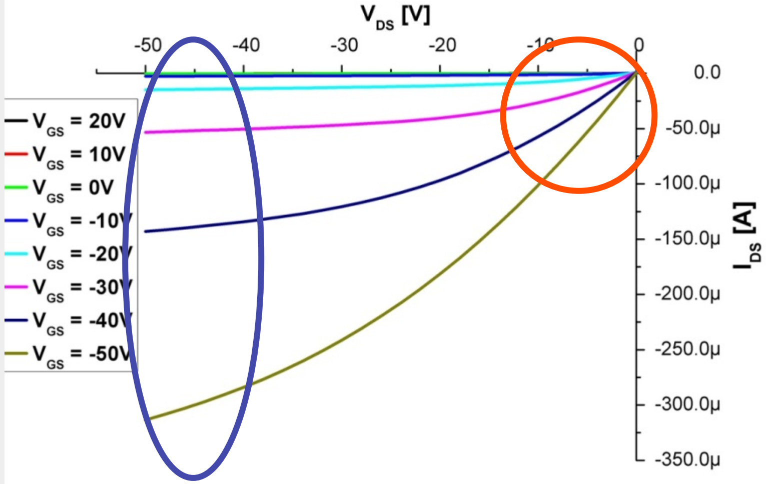


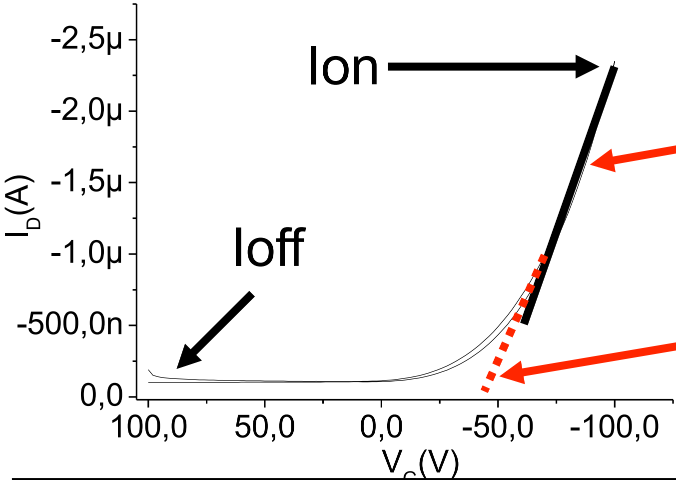
Fig. 2e

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:

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

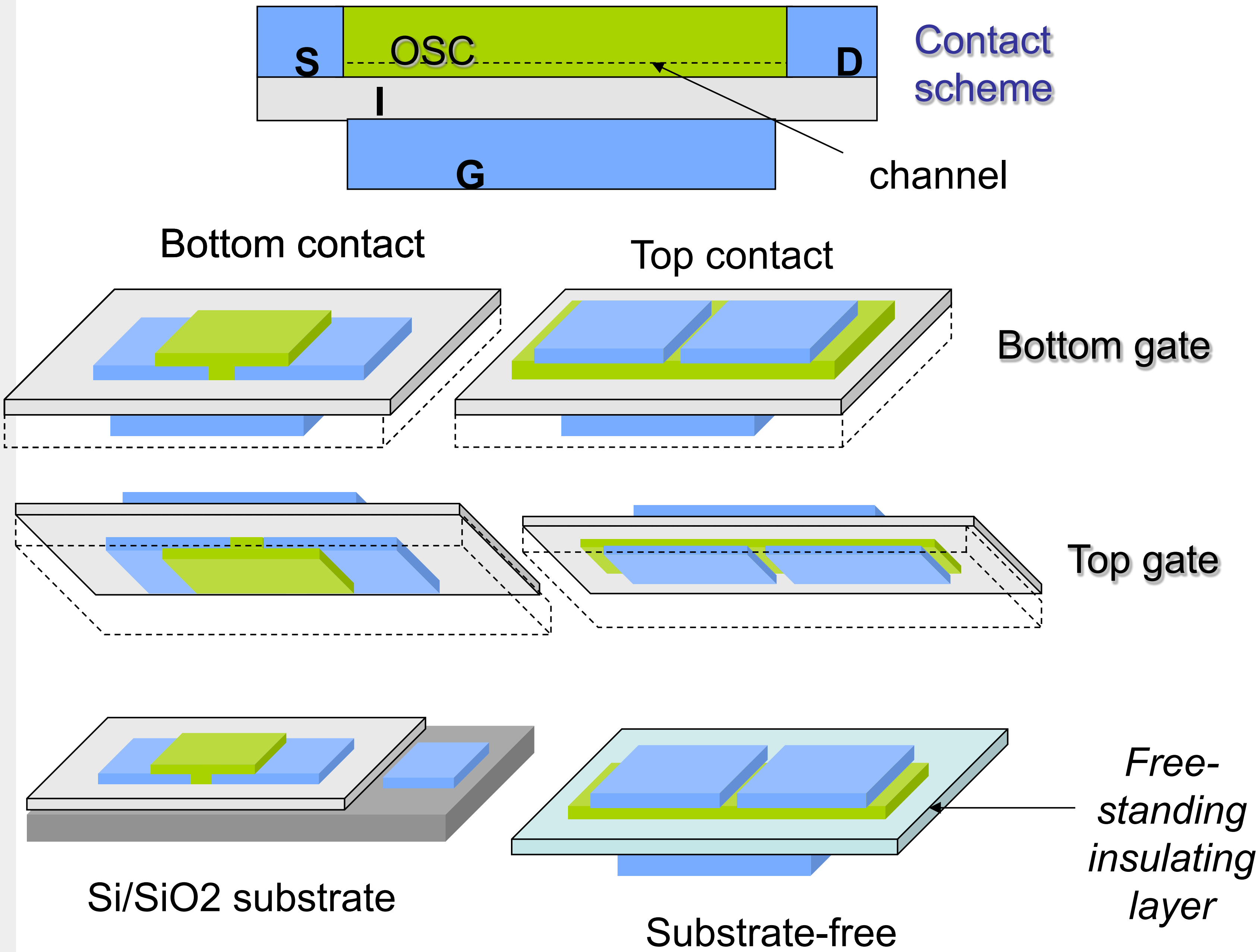
Typical values:

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

Ion/Ioff $\sim 10^4 : 10^5$

$V_T \sim$ -10:+10 V

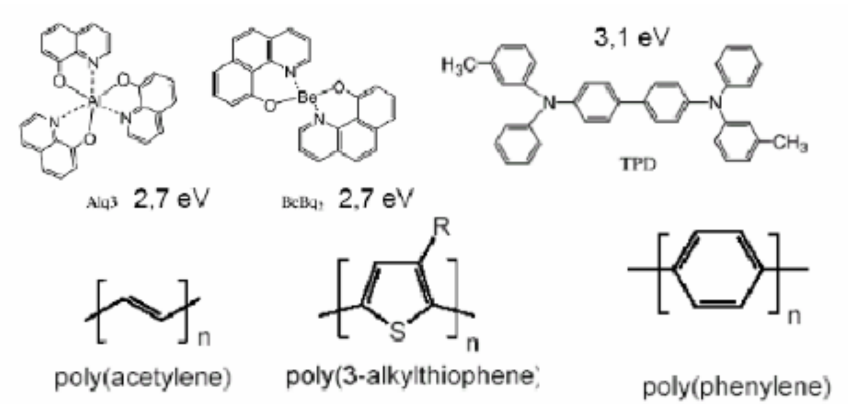
Structures and fabrication techniques



Materials and fabrication techniques

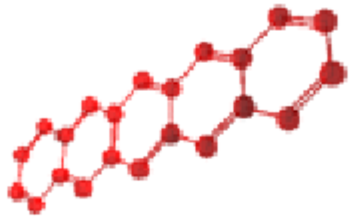
Materials:
Electrodes: metals, conductive polymers
Insulating layers: polyimide, PVA, PVP,…
Organic semiconductors

Solution processable
Polymers



Small molecules

(deposited by evaporation)



Fabrication techniques - Spin Coating

Low cost technique for liquid phase materials

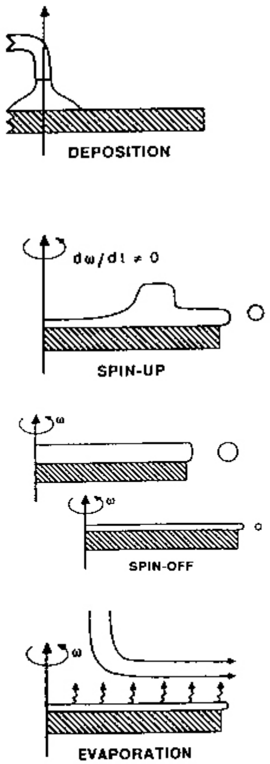
Deposition

Spin up

Spin off

Spin down

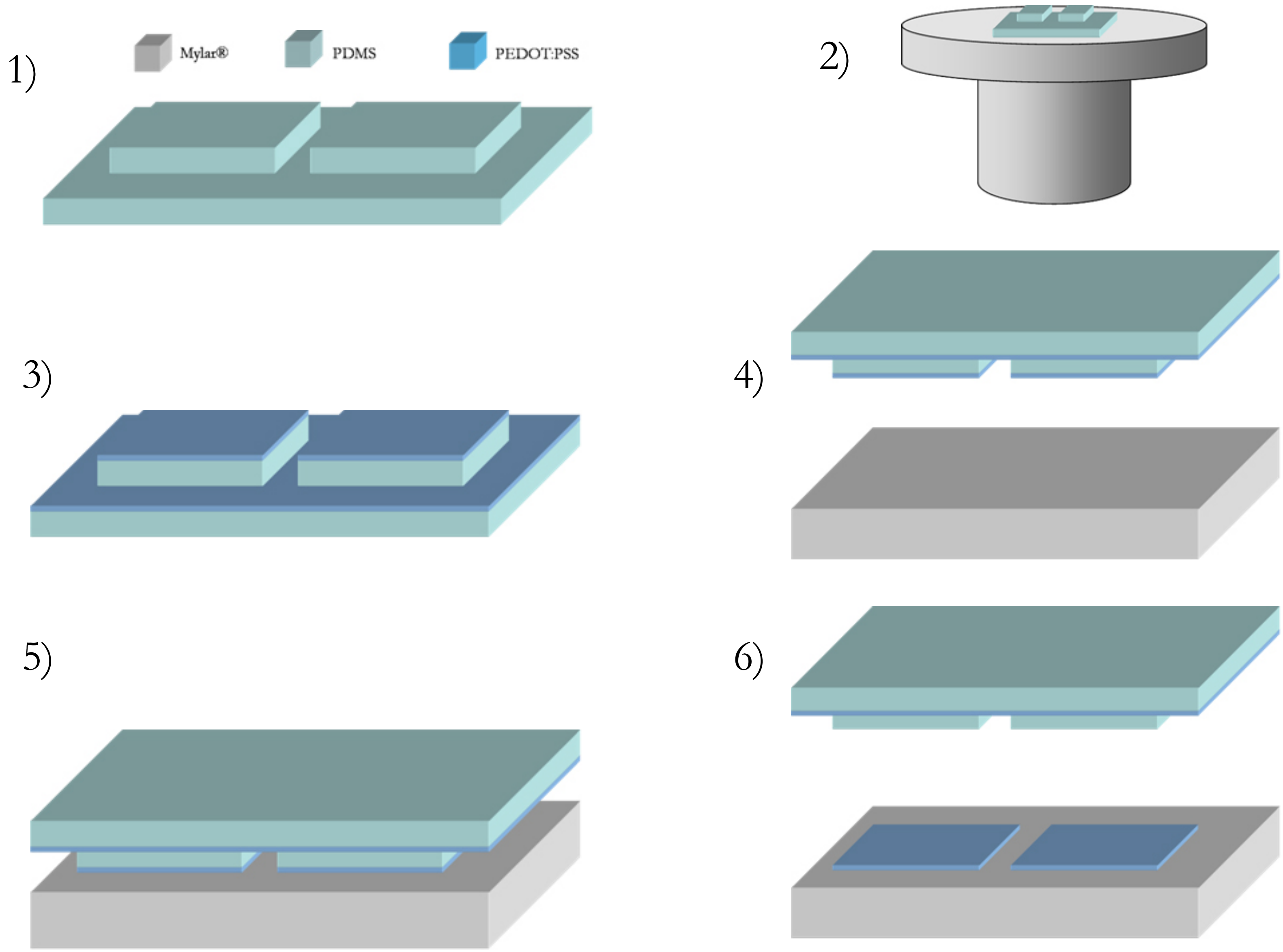
Thermal annealing (dewetting)



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

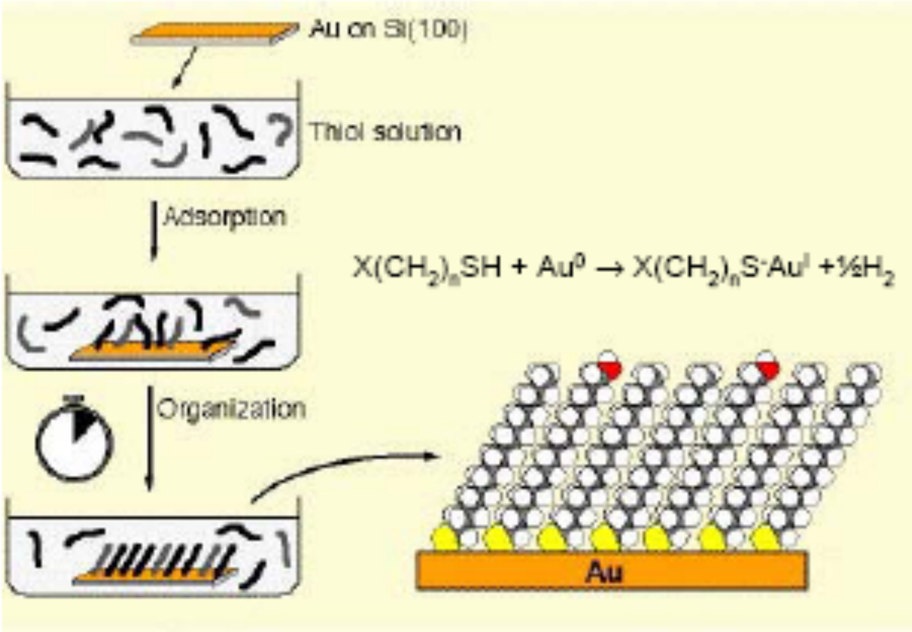
Adv: simple and low cost

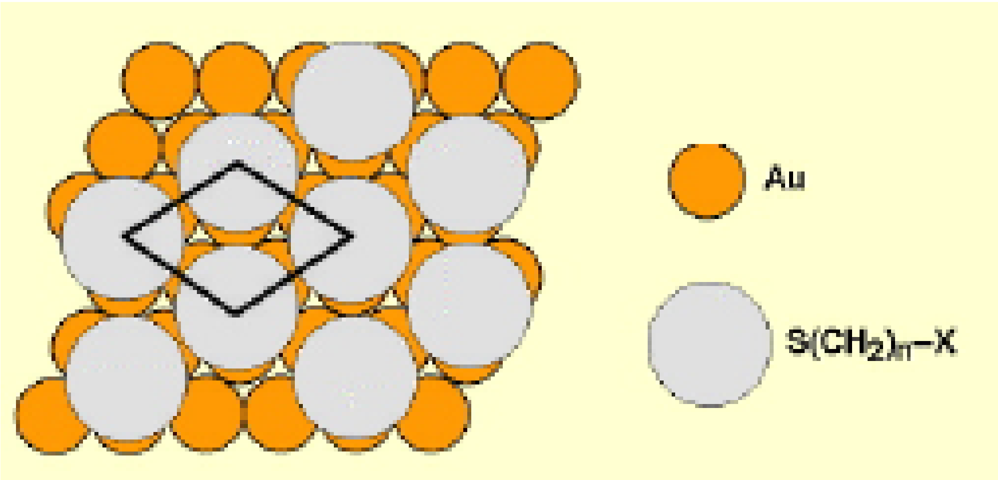
Fabrication technique – Soft Lithography



Fabrication technique – Soft Lithography

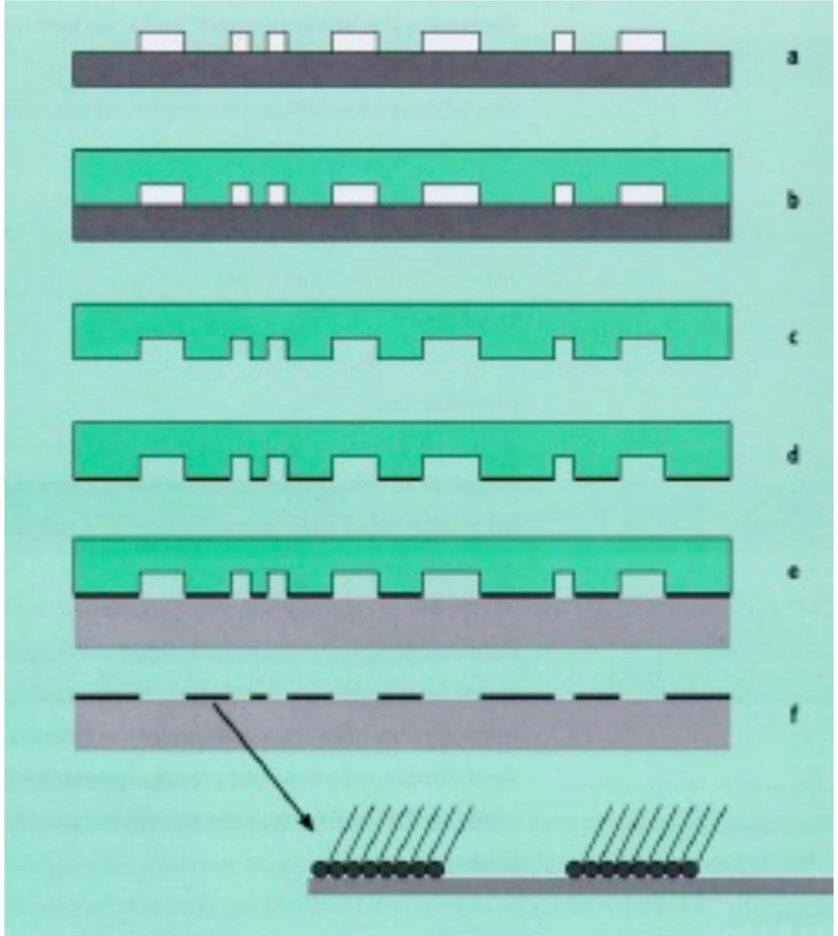
Inks instead of resist for patterning metals

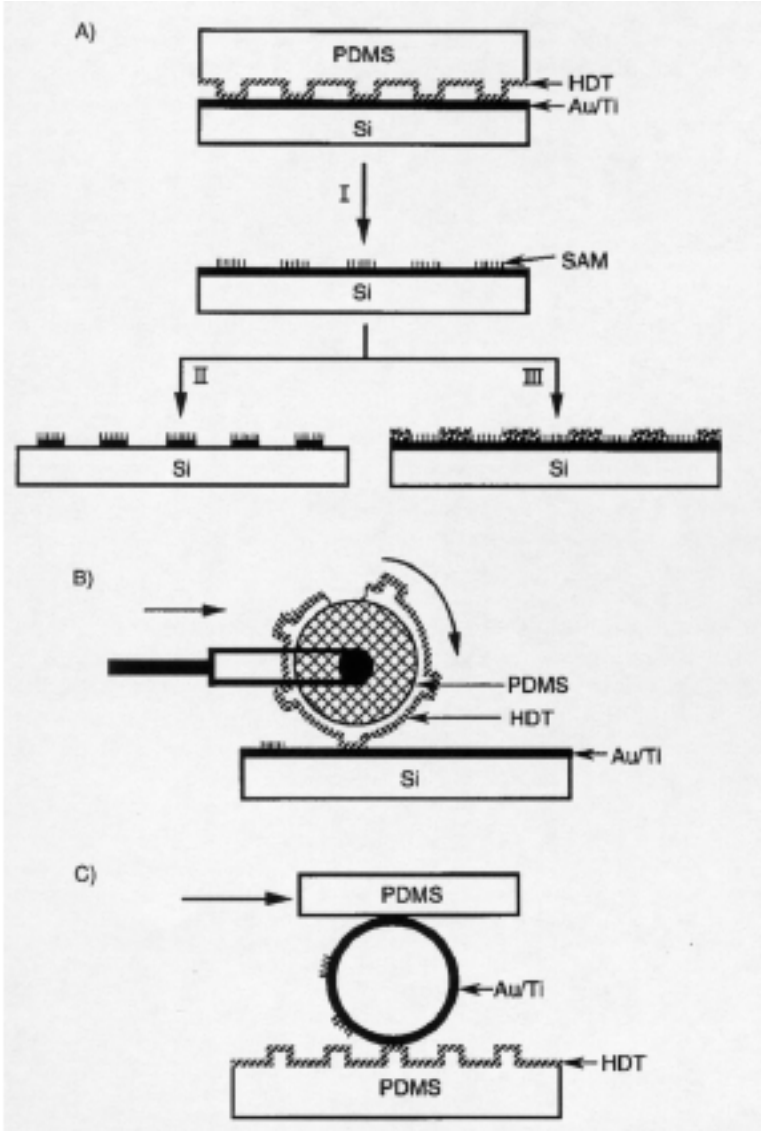




Fabrication technique – Soft Lithography

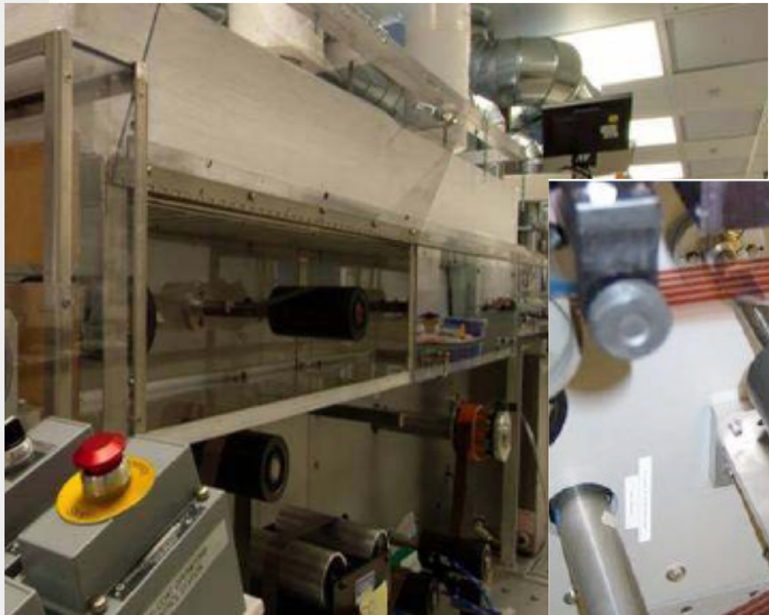
MicroContact Printing

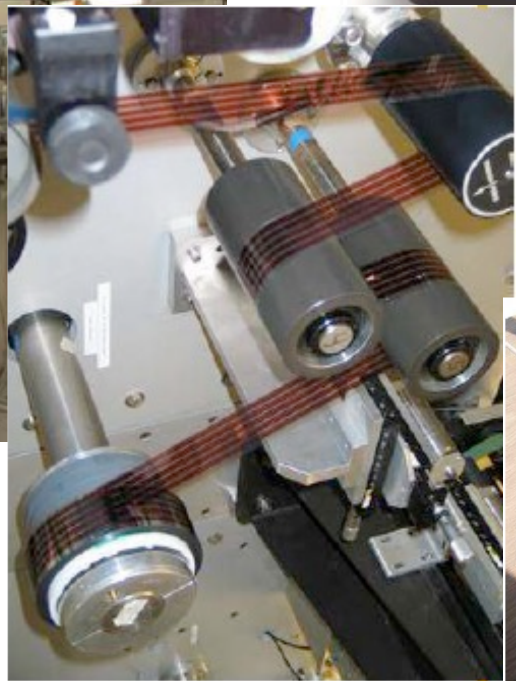


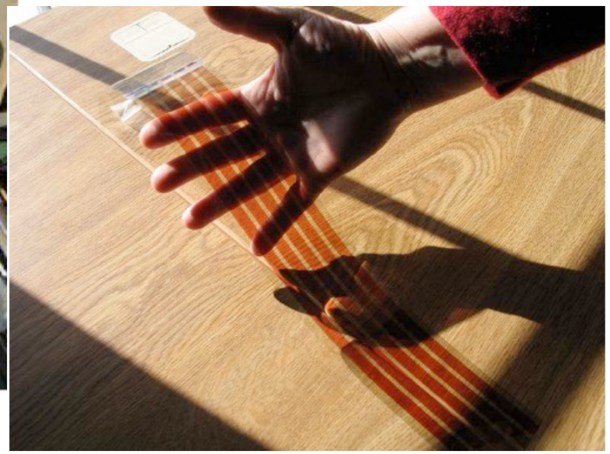


Printing & Roll to Roll

Printing







Possible applications for OTFTs