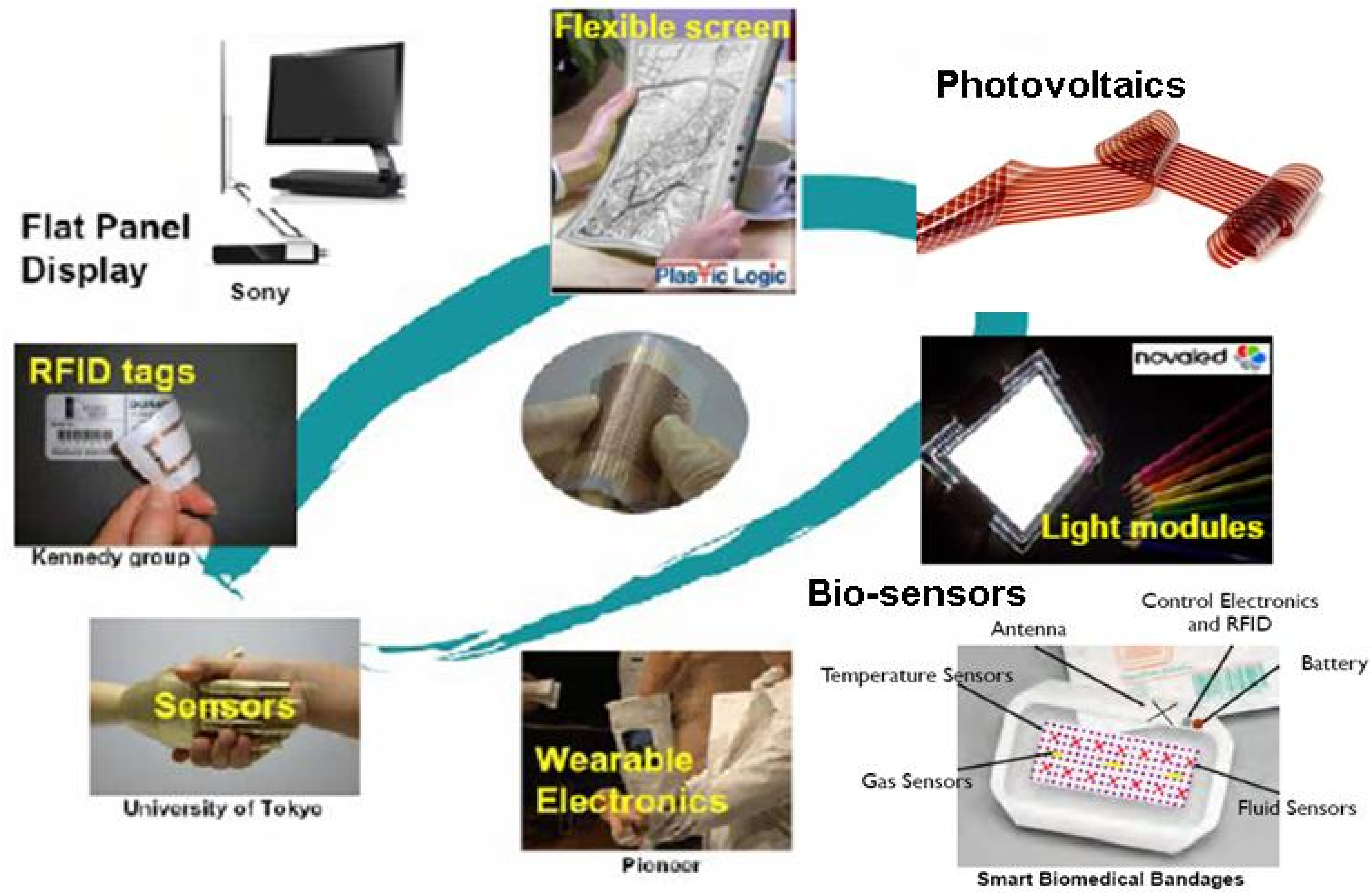
Radiation effects on Organic Semiconductors and Devices

Beatrice Fraboni

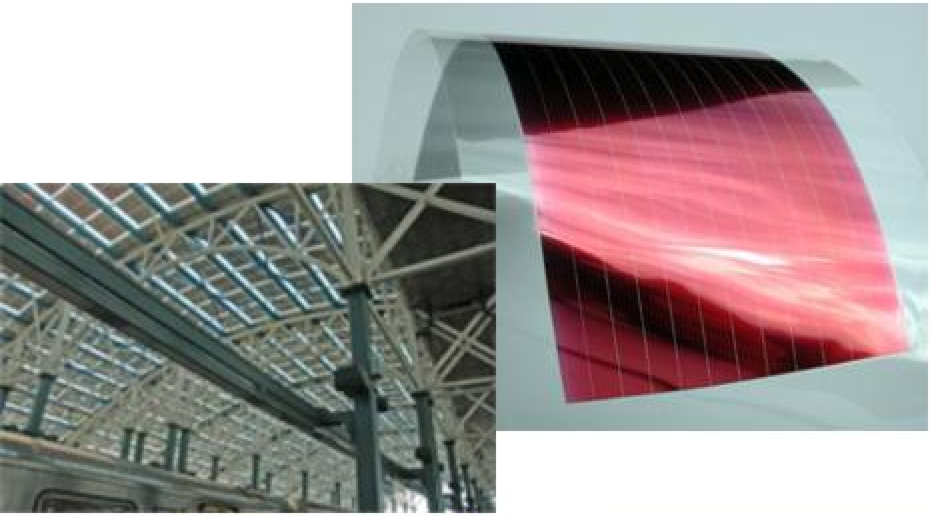
Department of Physics and Astronomy,
University of Bologna, Italy

V Scuola nazionale LNL – Legnaro - Aprile 2013

Organic electronics



Organic devices



Solar cells

OFETs

OLEDs

Outline

i) organic semiconducting materials: properties and charge transport

ii) organic thin film transistor (TFT): principle of operation

iii) radiation effects on organic TFTs and single crystal detectors

Organic semiconductors:

i) materials properties

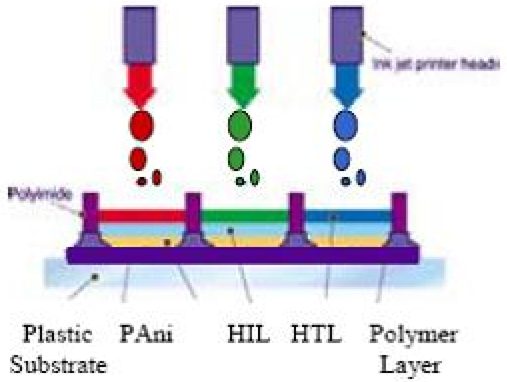
ii) charge transport

PERCHE' USARE SEMICONDUTTORI ORGANICI ?

- Flessibilità meccanica,
- Possibilità di coprire grandi superfici,
- emissione di luce nel visibile (… schermi), ad ampio angolo
- deposizione a bassa temperatura virtualmente su ogni tipo di substrato isolante, anche attivo,

Non per sostituire il Si!

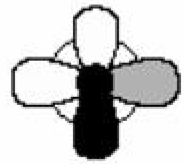
- **Spin coating, casting**
- **Molecular self assembling**
- **Ink-jet**
- **Stamping**
- **Nanoimprinting ...**

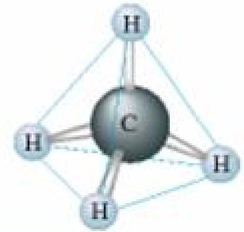


Il Carbonio

Ibridizza:

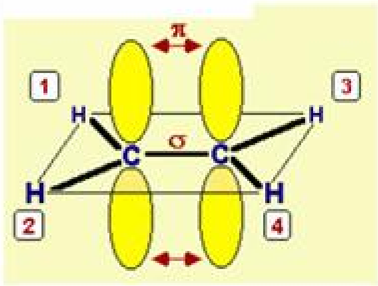
sp^3





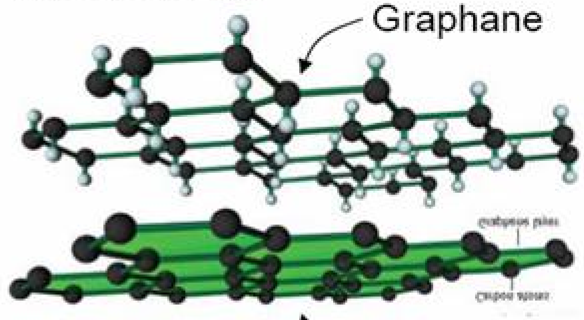
Diamante, Metano (CH_4)

sp^2



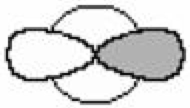
etilene

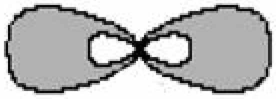
Graphane



Graphene

sp

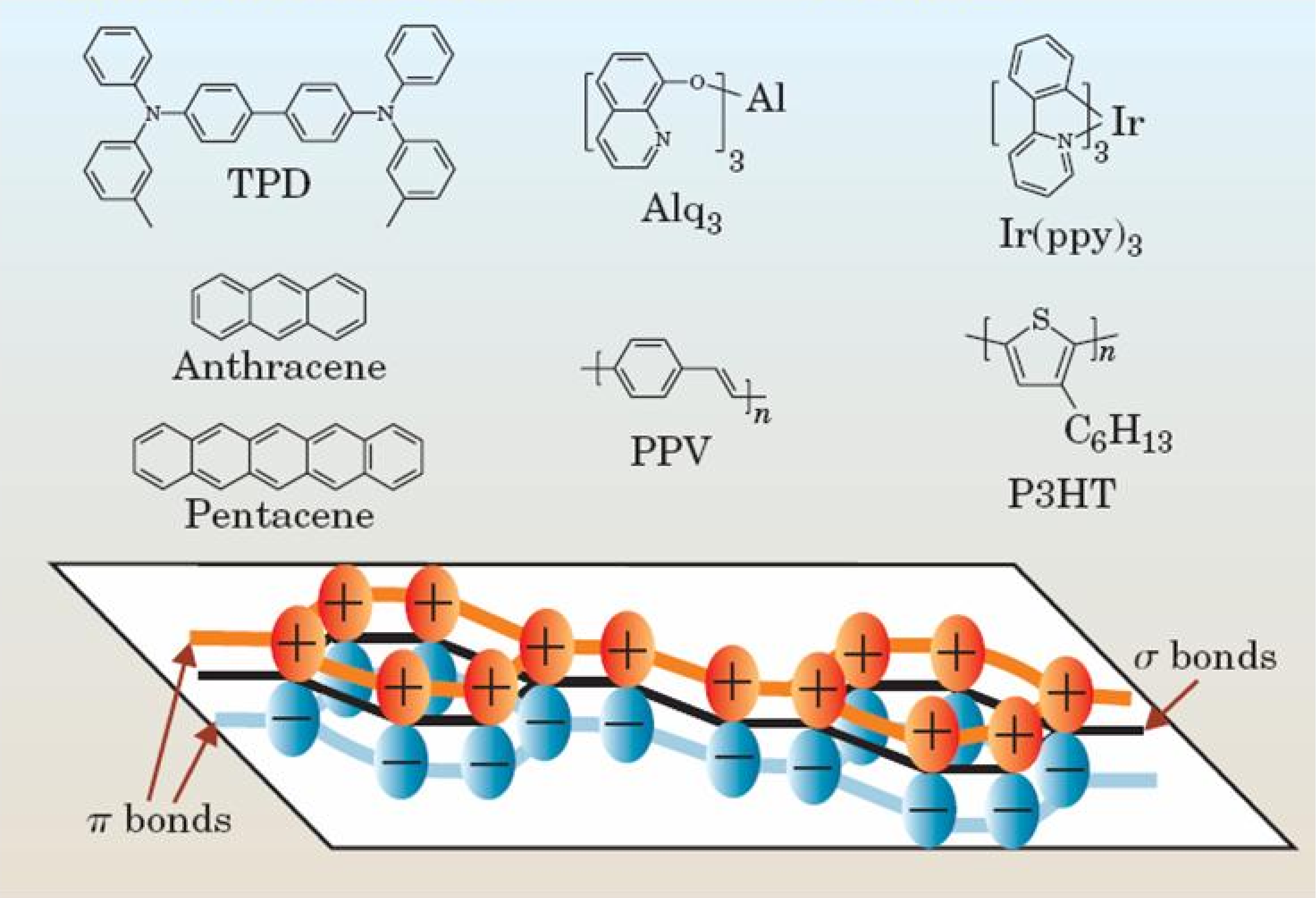




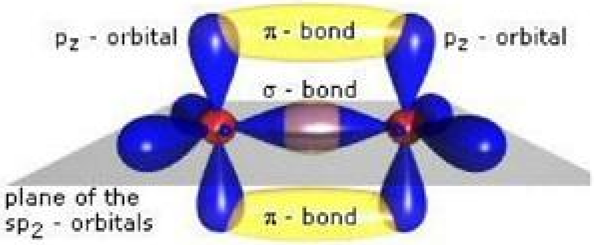
Si può quindi legare con altri atomi di carbonio in <u>strutture planari</u> con legami σ (forti) nel piano e legami π fuori dal piano

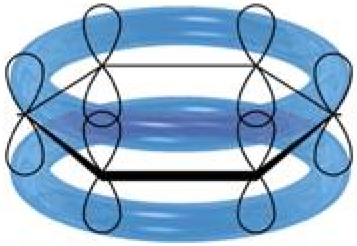
Semiconduttori organici

Small molecules / Polimeri

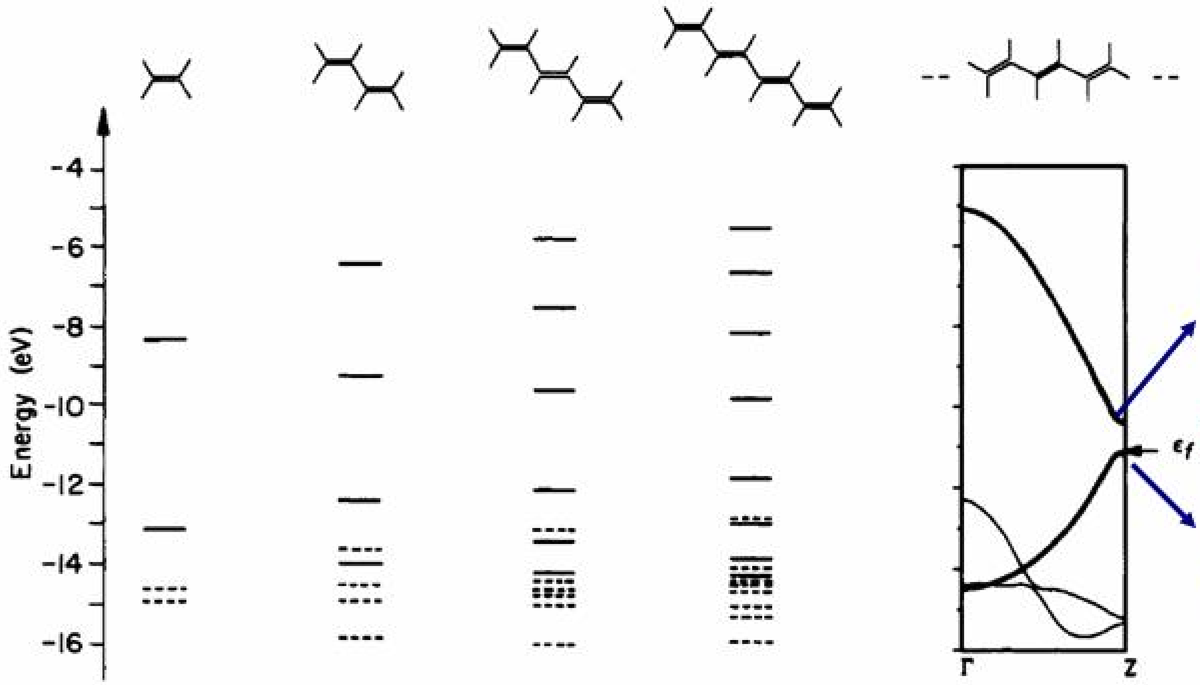


Formazione del band gap (HOMO-LUMO)





Al crescere della lunghezza della catena il materiale diventa sempre piu' conduttore ;
Eg si riduce ma non arriva mai a zero (Peierls distorsion)



Lowest unoccupied molecular orbital: LUMO

Energy gap

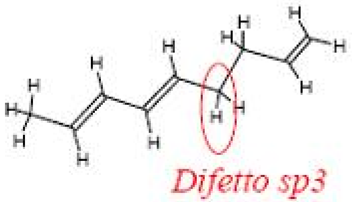
Highest occupied molecular orbital: HOMO

R.Hoffmann, *Macromolecules* 1991

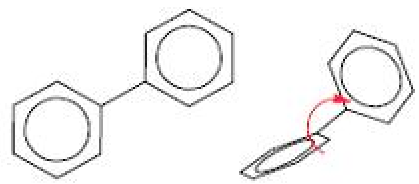
VARIAZIONE DI CONDUCIBILITA'

La coniugazione (e quindi la **CONDUCIBILITA'**) può essere diminuita a causa di:

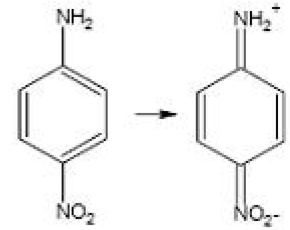
*Difetti chimici

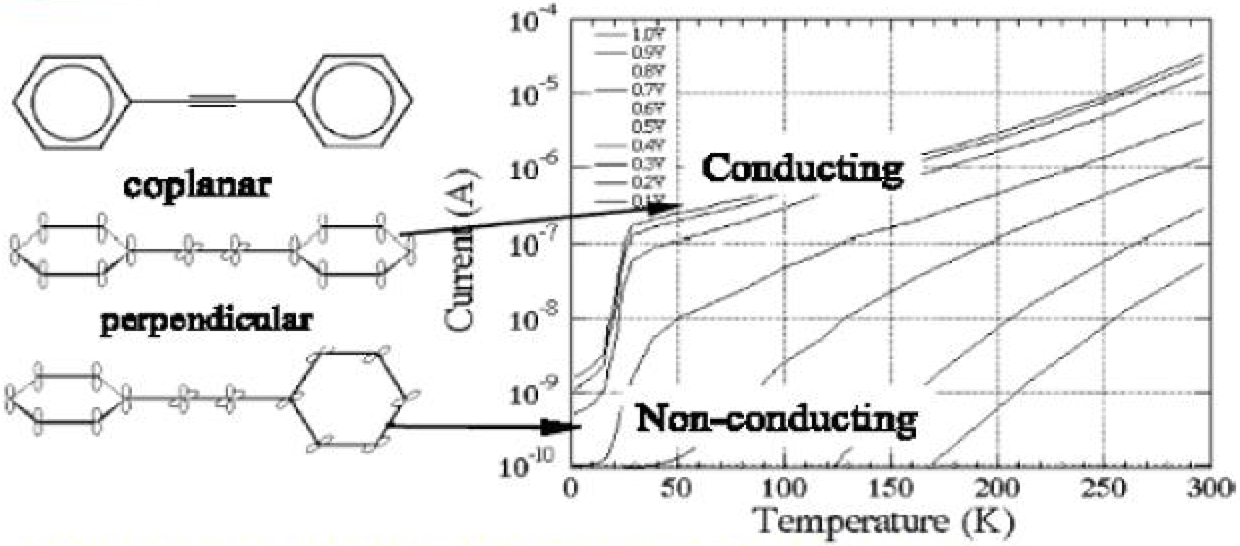


*Effetti conformazionali



*Presenza di sostituenti





J.Chen, M.A. Reed, A.M. Rawlett, J. M. Tour, *Science*, 286, 1150-1152, 1999

Band gap e DOS

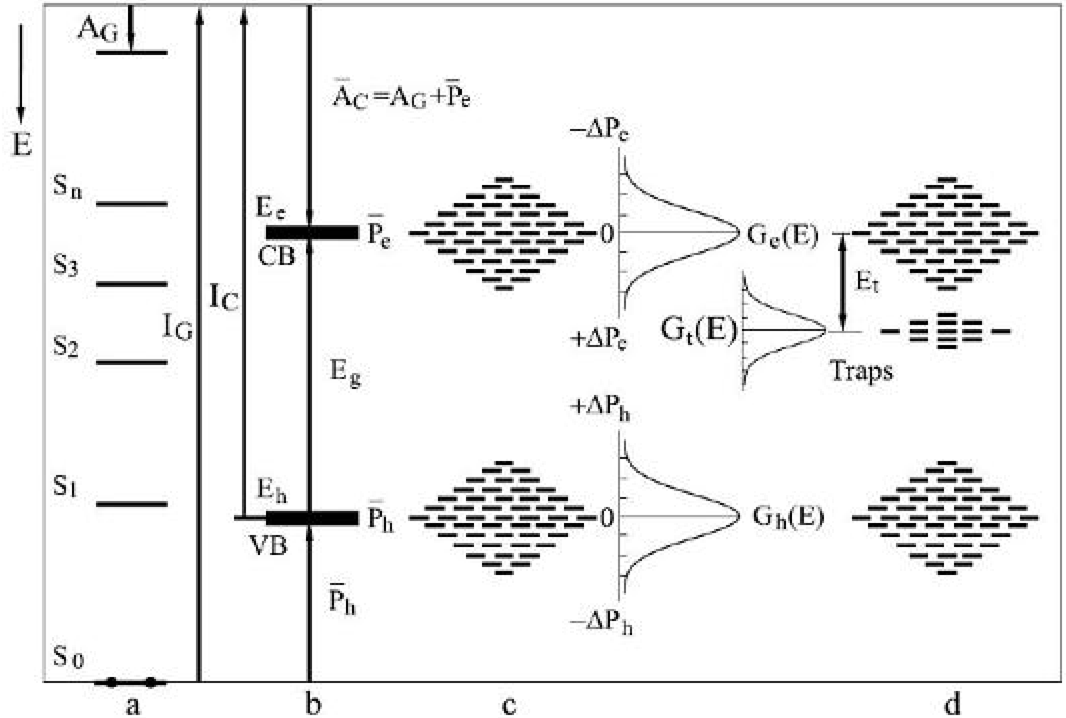


Figura 1.2: Diagramma energetico di un semiconduttore organico. a)livelli energetici molecola isolata. b)bande degli stati ionizzati in un cristallo ideale. c)livelli di stati ionizzati con una distribuzione statistica delle energie di polarizzazione(shallow level). d)Livelli energetici delle trappole nel band-gap(deep level).

Eh, Ee = energie caratteristiche delle bande dei polaroni rispettivamente,

positivi e negativi.

IG, IC = energia di ionizzazione della molecola isolata e del cristallo.

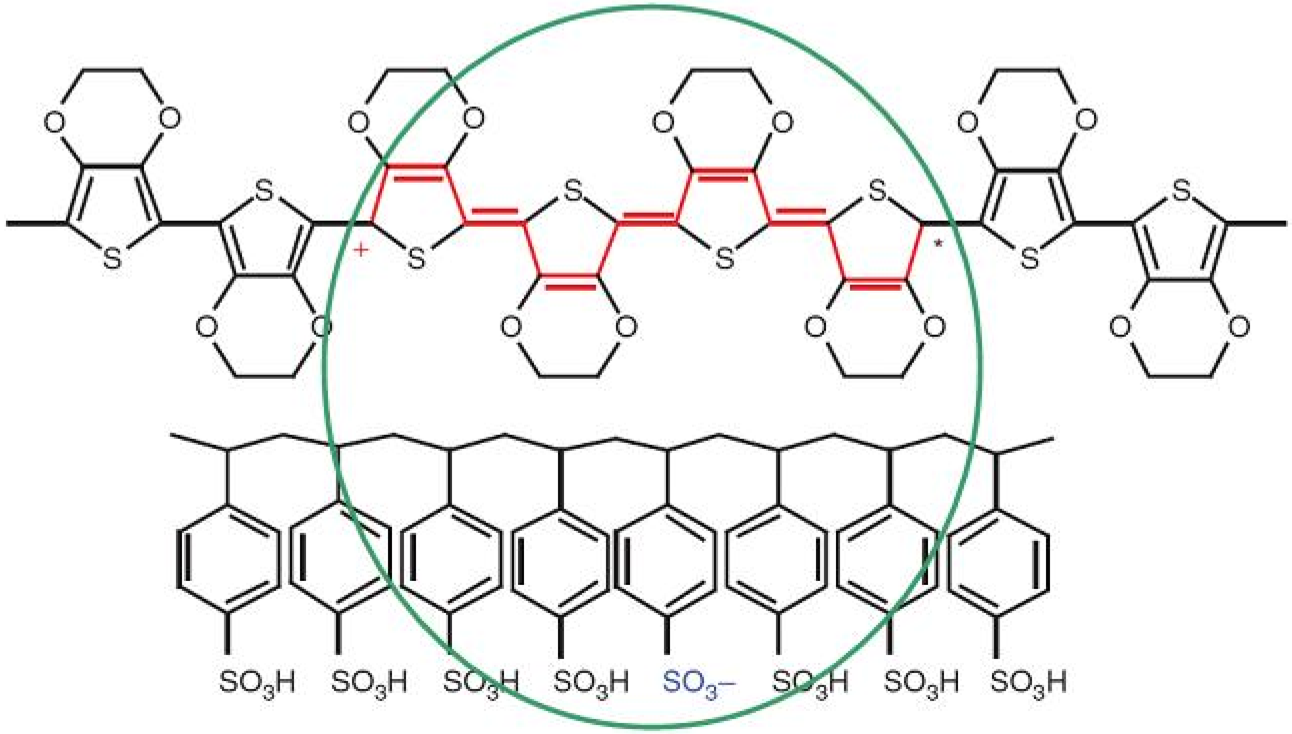
AG, AC = anita elettronica della molecola isolata e del cristallo.

Ph, Pe = energie di polarizzazione dei polaroni.

R.Freind, G.Malliaras, *Physics Today* 2005

Polaroni

poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrene sulfonate) (PSS)- a degenerately doped *p*-type semiconductor, in which holes in the conjugated polymer PEDOT (in red) are compensated by the PSS anions (in blue)



PEDOT

PSS

TRASPORTO DI CARICA

band-like **oppure** ***hopping*** **?**

C R I S T A L L I U L T R A P U R I

I portatori liberi possiedono un quasi momento $\hbar k$

Possibilità scattering e^- - fonone

> T → < μ

S O L I D I D I S O R D I N A T I

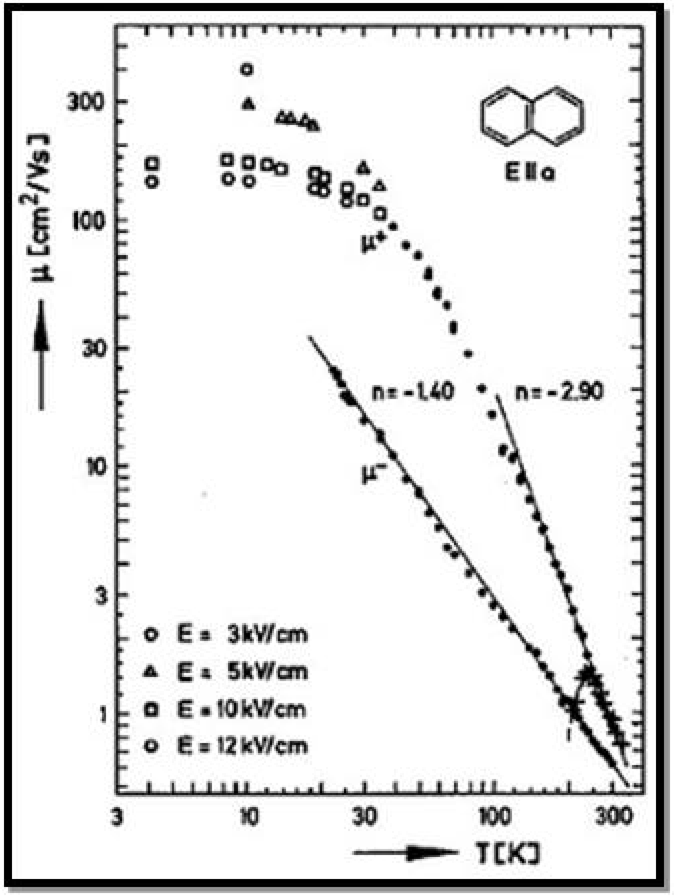
I portatori liberi sono localizzati nelle molecole

I portatori devono essere attivati per saltare da molecola a molecola ($\lambda \simeq a_o$)

> T → < μ

tipo di TRASPORTO ⇔ **μ vs T**

Trasporto band-like



Naftalene, cristallo singolo

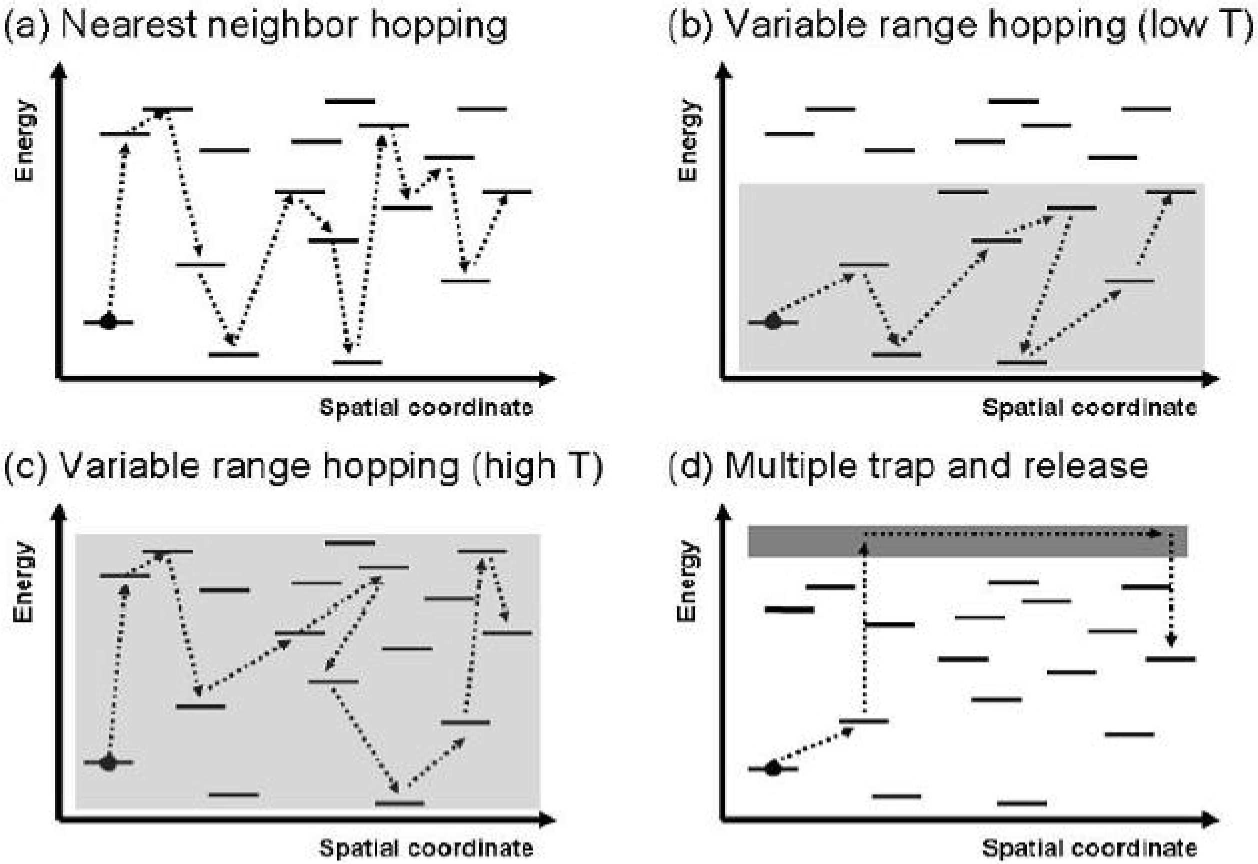
$$\mu \approx T^{\,n}$$

n < 0
n ≠ - 3/2

Energia
e
concentrazione
delle trappole

$$\mu(E) = \mu_0\sqrt{2}\left\{ + \left[1 + \frac{3\pi}{8(\frac{\mu_0 E}{c_s})^2}\right]^{1/2} \right\}^{-1/2}$$

Trasporto hopping

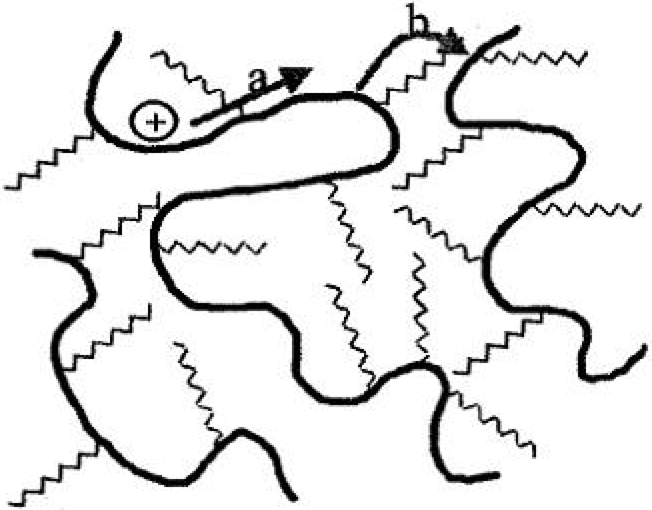


Materiali disordinati

(amorfi, polimeri, ecc...).
Il trasporto non e coerente, ma gli stati energetici sono spazialmente localizzati. Il movimento di cariche puo avvenire solo attraverso salti per effetto tunnel fra uno stato e l'altro

$$\mu_{hop} = \mu_0 \exp\left(-\frac{T_0}{T}\right)^2$$

Film di polimero amorfo



a- trasporto della carica lungo la catena - *facile*

b- trasporto della carica da una catena all'altra - *difficile*
Fenomeno reso ancora più complicato dal fatto che la distanza tra le catene ha una distribuzione casuale

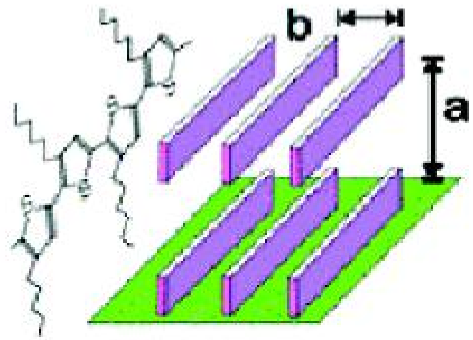
➡ Variable range hopping

➡ Bassa mobilità dei portatori, dettata dal fenomeno più lento.

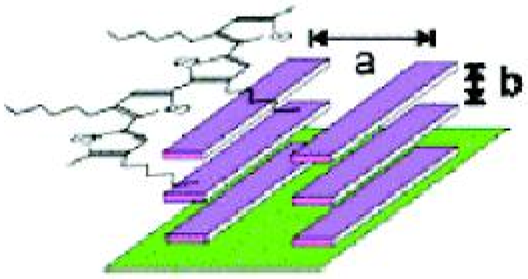
Film policristallino
(polimero o small molecule

La mobilità risente fortemente della orientazione del piano molecolare …

π – π stacking



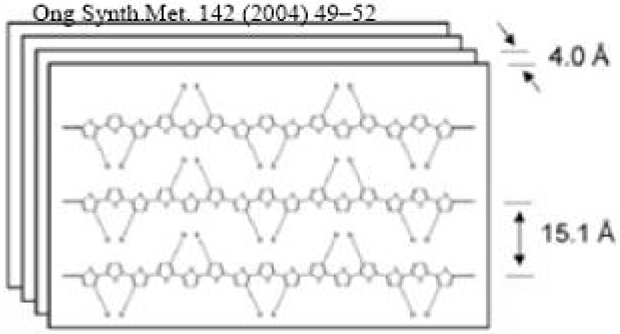
μ_{FE}=5.10^{-2} cm^2/V.s



μ_{FE}=2.10^{-4} cm^2/V.s

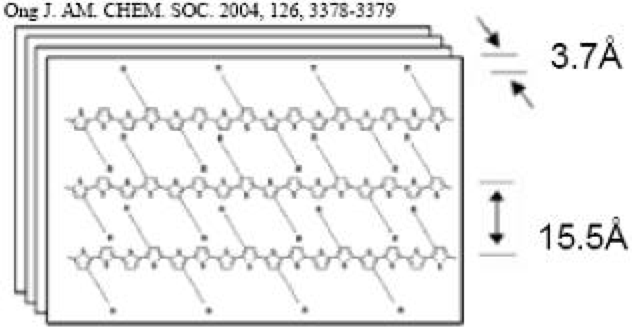
… e del tipo di molecole laterali

Ong Synth.Met. 142 (2004) 49–52



3×10^{-2} cm^2 / V.s

Ong J. AM. CHEM. SOC. 2004, 126, 3378-3379

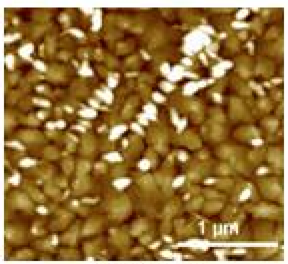


10^{-1}cm^2/Vs

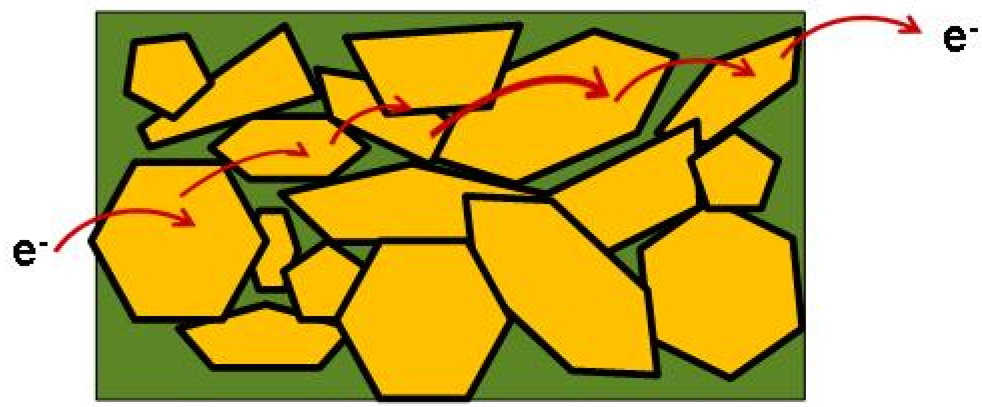
Cristalli organici singoli

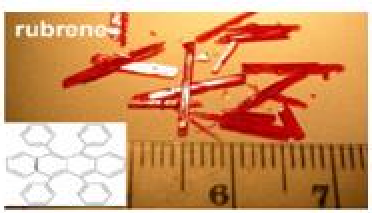
absence of defects related to grain boundaries, well defined geometrical disposition of molecules, high degree of order

band-like transport

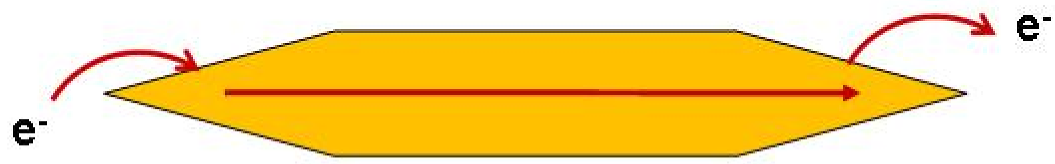


Vacuum-evaporated small molecules

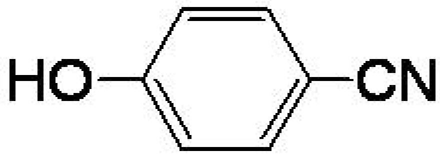


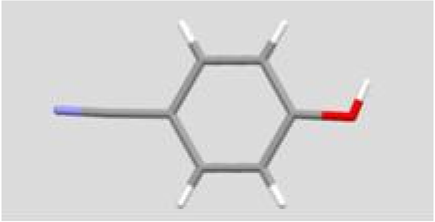


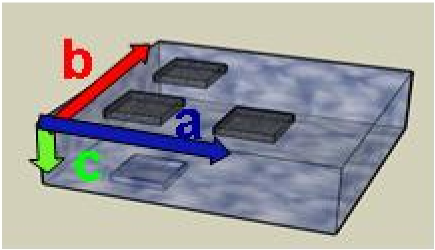
Vacuum-purified single crystals

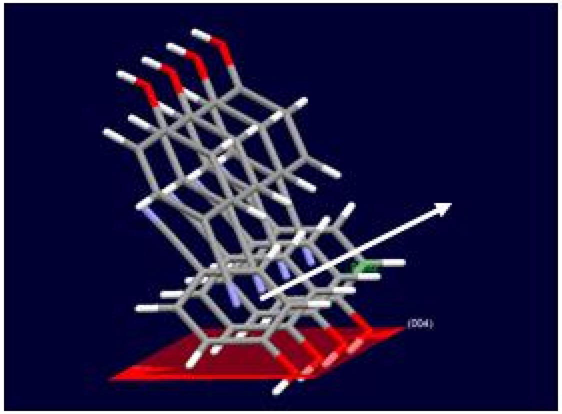


3D Anisotropic molecular packing



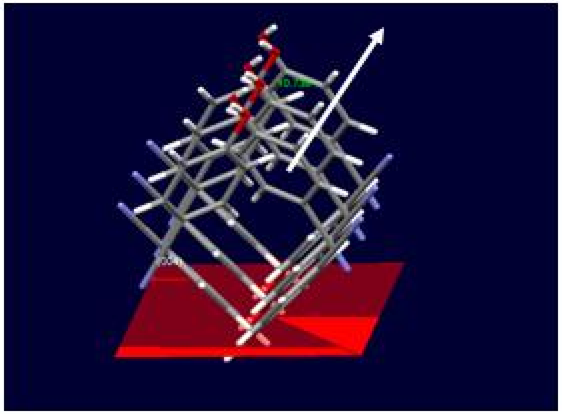




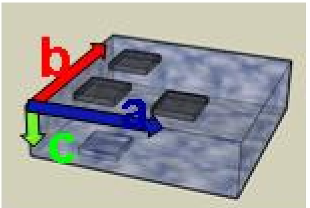


axis *a*

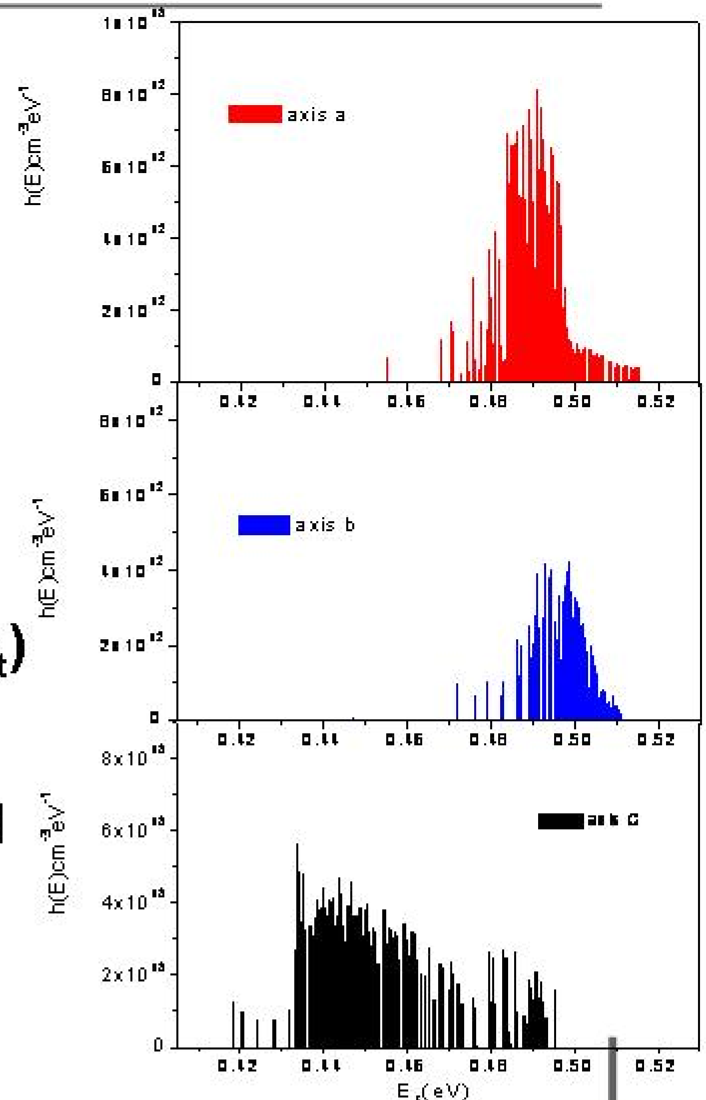
axis *b*



3D Anisotropic Charge Transport



Axis	$\mu_{SCLC/FET}$ (cm²/Vs)
a	1×10^{-1}
b	2×10^{-2}
c	2×10^{-4}



i) anisotropic electrical properties (μ, N_t, E_t)

ii) good mobility values, measured by
-space charge limited current (SCLC) method
-field effect transistor (FET)operation

B. Fraboni et al, Org. Electron., ***11****, 10 (2010)*

Conclusioni sui materiali organici

- Diversi tipi di molecole (single molecules, oligomers-small molecules, polymers) e strutture (amorfi, policristallini, cristalli singoli)
- Anisotropia di trasporto elettronico
- Diverse tecniche di deposizione inducono diverse strutture di impacchettamento che si riflettono in differenti proprietà di trasporto

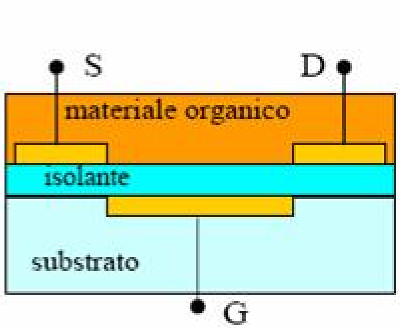
grande variabilità e versatilità di proprietà e prestazioni

Organic electronic devices

thin film transitors (TFTs)

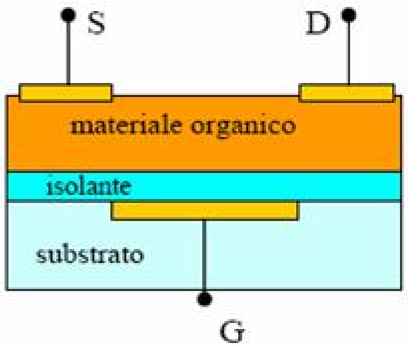
STRUTTURA di oFET

BOTTOM CONTACTS BOTTOM GATE



- Organico deposto alla fine sopra a tutto (molto usato in laboratorio)
- Nessun contatto di organico con i solventi usati per litografare S&D
- Uso della tecnologia del Silicio
- Resistenza serie non trascurabile

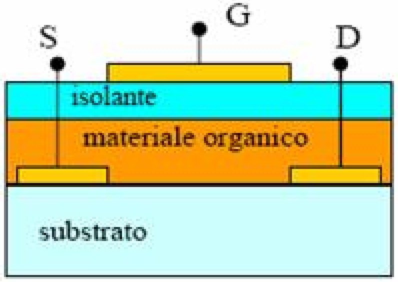
TOP CONTACTS BOTTOM GATE



- Small contact resistance
- Gate dielectric prior to organic

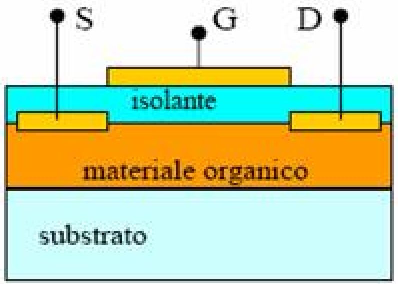
Gundlach et al., J.Appl.Phys. 100 (2006) 024509

TOP GATE BOTTON CONTACTS



- Semiconductor protected by gate and dielectric
- Small contact resistance
- Semiconductor must withstand subsequent processing
- Photolithography can be used to patter S/D

TOP GATE TOP CONTACTS

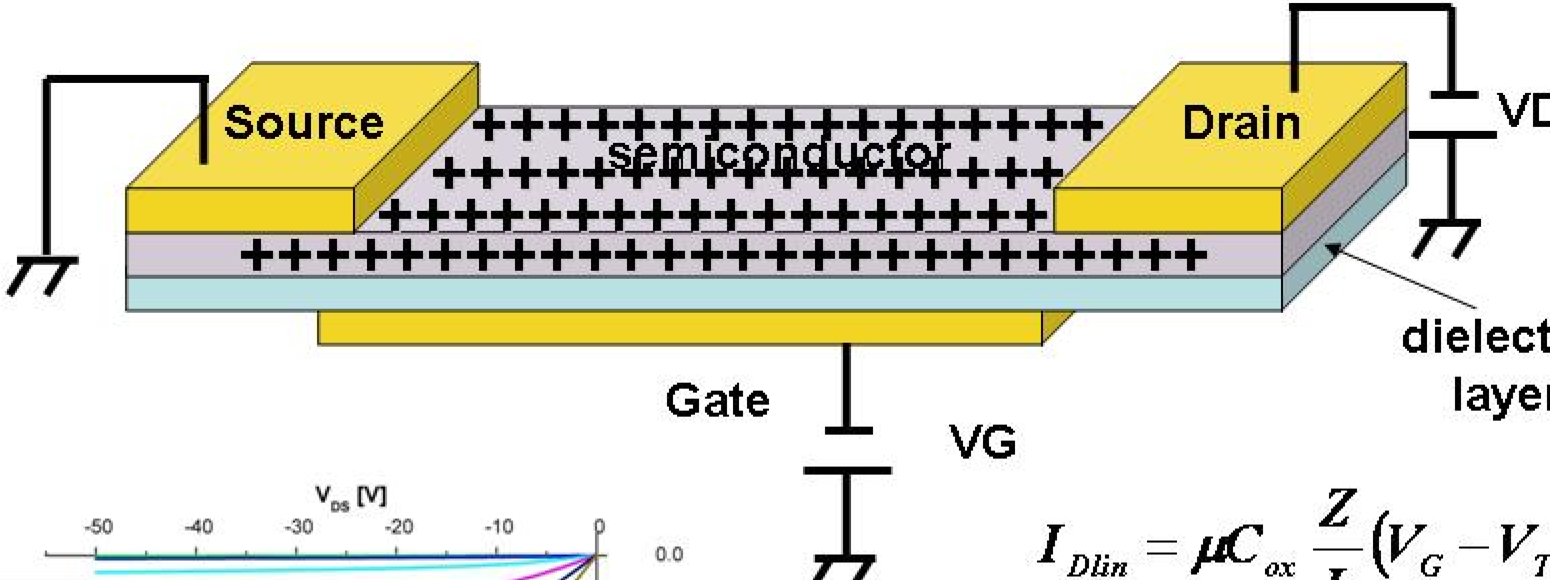


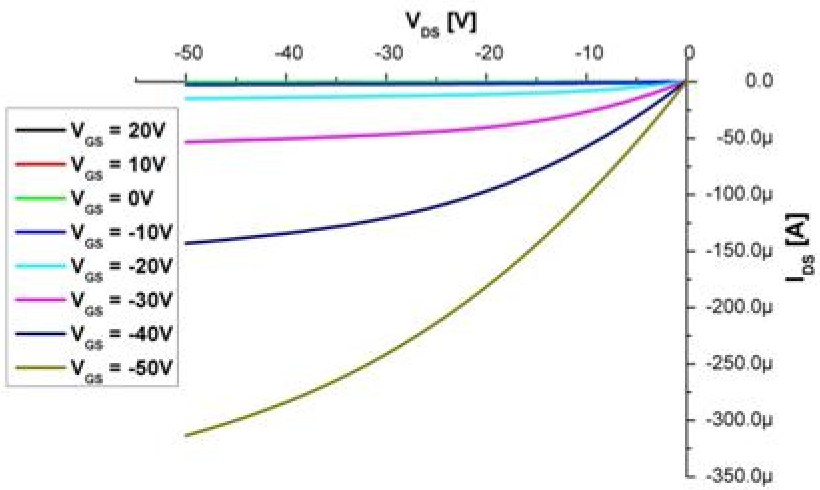
Complessità realizzativa crescente

Possibilità circuitali crescenti

All layers can be deposited at low temperature from solution and patterned ➡ low cost

Come funziona un OTFT





$$I_{Dlin} = \mu C_{ox} \frac{Z}{L}\left(V_G - V_T\right)V_D$$

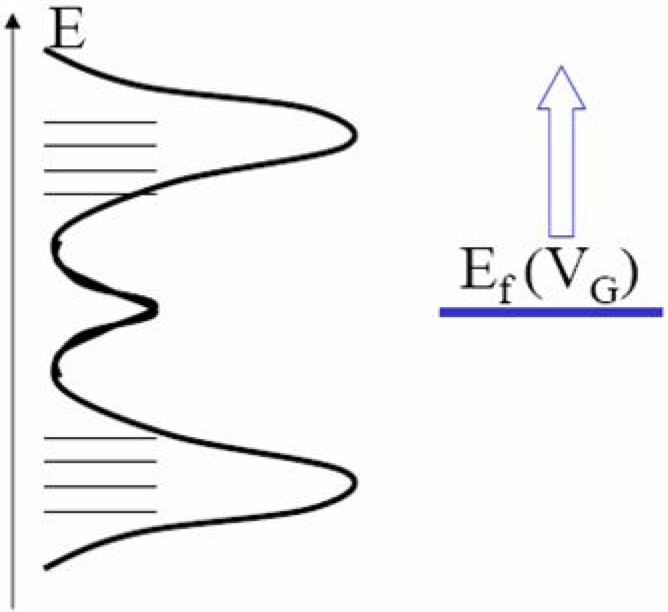
$$I_{Dsat} = \frac{1}{2}\mu C_{ox} \frac{Z}{L}\left(V_G - V_T\right)^2$$

Typical values:
$\mu \sim 10^{-1}$ cm^2/Vs
$V_T \sim \pm 5$ V

MOBILITA'

Dipendenza dalla tensione di Gate

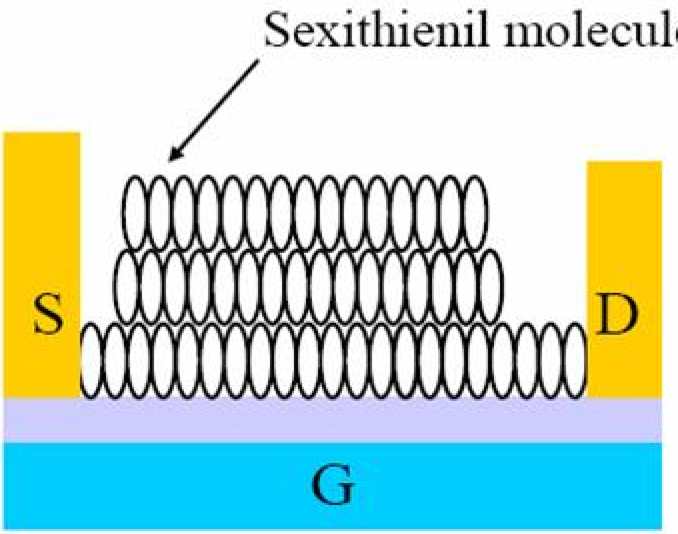
LA MOBILITÀ NON È COSTANTE CON LA TENSIONE DI GATE

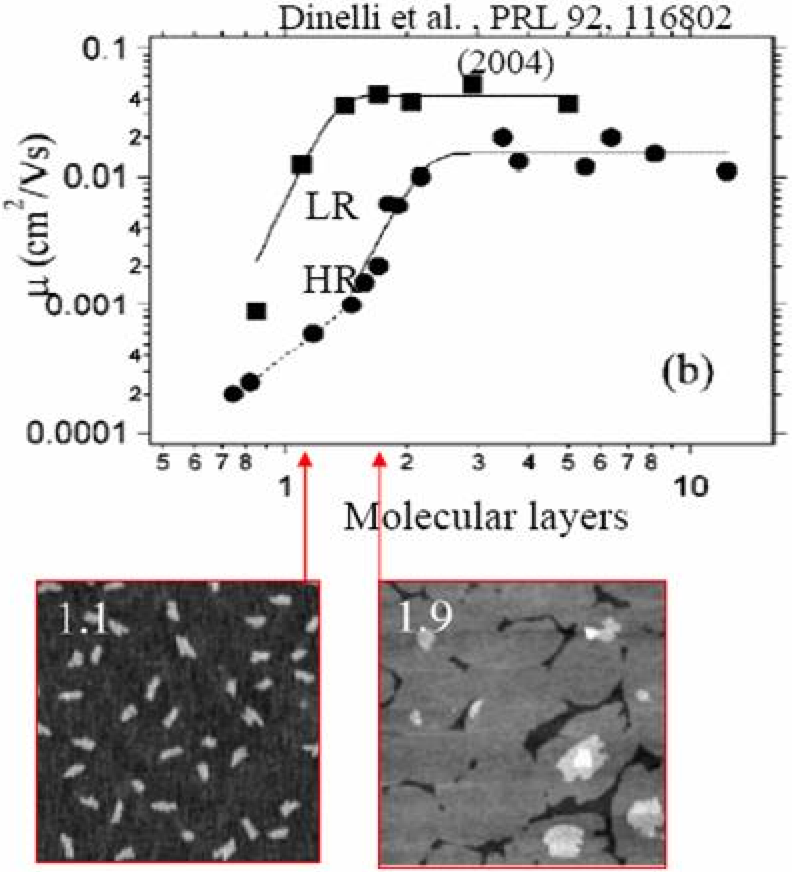


All'aumentare di $|V_G|$,

- aumenta la concentrazione di portatori
- E_f si sposta
- le trappole localizzate nel band gap ed i livelli molecolari (poco delocalizzati) sono sempre più pieni
- i portatori sono sempre più nella banda delocalizzata dove possono muoversi liberamente.

LOCALIZZAZIONE DEL TRASPORTO





Only the first two molecular layers, adjacent to gate dielectric, contribute to transport !

Prestazioni OTFTs

PICCOLE MOLECOLE Rubrene e pentacene (*cristalli*) ~ 1-20 cm^2/Vs

Deposte da fase vapore in vuoto; non solubili a meno di usare precursori. (*quindi tecnologia non industrializzabile a basso costo*).
Utile palestra per studiare le *proprietà intrinseche* di una specifica molecola.

OLIGOTIOFENI ~ 0.1 cm^2/Vs

Facile purificarli; solubili; l'aggiunta di catene alchiliche laterali favorisce l'impaccamento

POLITIOFENI < 0.1 cm^2/Vs

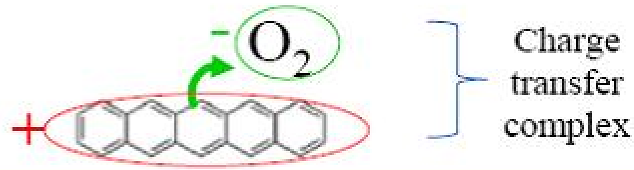
Solubilissimi; economici; se sintetizzati opportunamente (regioregolari) hanno buone prestazion

μ, Ion/off, confrontabile con a-Si

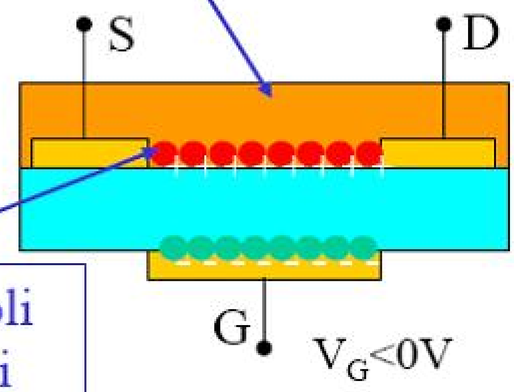
Materiale IDEALE : solution processable - high stability - good performance

Ruolo dei difetti nel bulk

unintentional doping



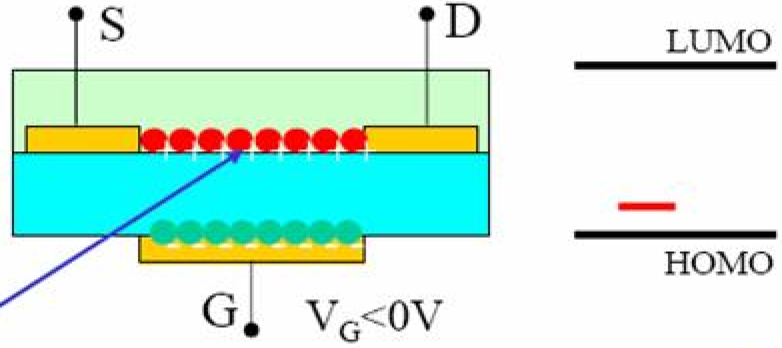
O_2 – unintentional doping
Cambia la conducibilità (ON/OFF ratio)



Le trappole cambiano i dipoli all'interfaccia con i contatti (diversa barriera per iniezione di portatori)

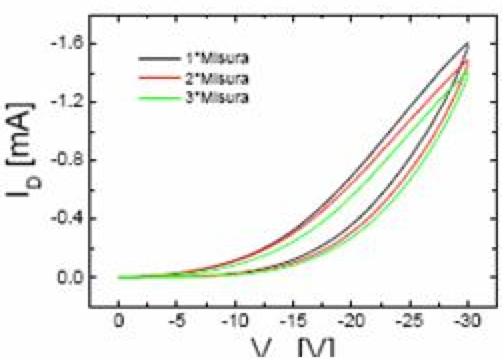
→ Contact resistance

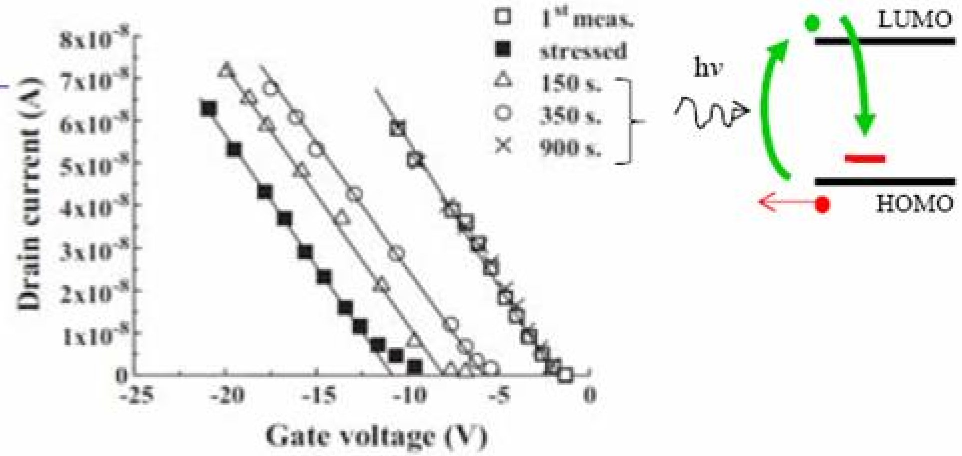
Ruolo dei difetti all'interfaccia



Recovery :
- non operation
- positive V_G
- illumination

Le trappole modificano V_T
(a pari V_G con il tempo porta meno corrente)
e causano isteresi
(sweep rate&temperature dep.)





Radiation effects on organic semiconductors and electronic devices

i) thin film transitors (TFTs)

ii) single crystal detectors

Radiation effects

Effects on non-conductive polymers have been studied:

molecular level

- C-H and C-C bonds breaking (>4eV required)
- hydrogen release
- chain scissioning
- crosslinking, graphetization
- radical formation

macroscopic level

- changes in density, hardening
- refractive index and absorption
- conductivity

D.Fink "Fundamentals of ion irradiated polymers" Springer 2007

Radiation effects

what happens to organic semiconductors ?

what happens to organic devices?

Little is known:

i) aromatic-ring-containing polymers show a higher conductivity modification

ii) aromatic-ring- containing molecules are more stable under ionizing radiation *[Ferry et al J. Phys.Chem 2012]*

Radiation effects on organic semiconductors and devices

Ion irradiation:

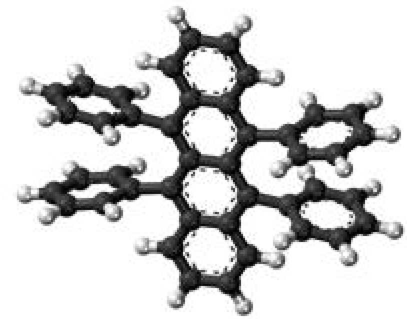
- high energy protons (1MeV) *[Zimmerling et al Phys.Rev.B 2012]*
- low energy Ne and N ions (<70keV) *[Fraboni et al Org.Electron 2011]*

X-ray irradiation:

- Cu target or Mo target 35-40kV *[Intaniwet Org.Electron 2011; Fraboni et al Adv.Mater.2012]*
- W target 50-70kV *[Keivanidis et al. Appl.Phys.Lett. 2008; Agostinelli et al Appl.Phys.Lett. 2008; Newmann et al. Appl.Phys.Lett. 2007]*
- Sinchrotron radiation 5-30KeV *[Fraboni et al in press 2013]*

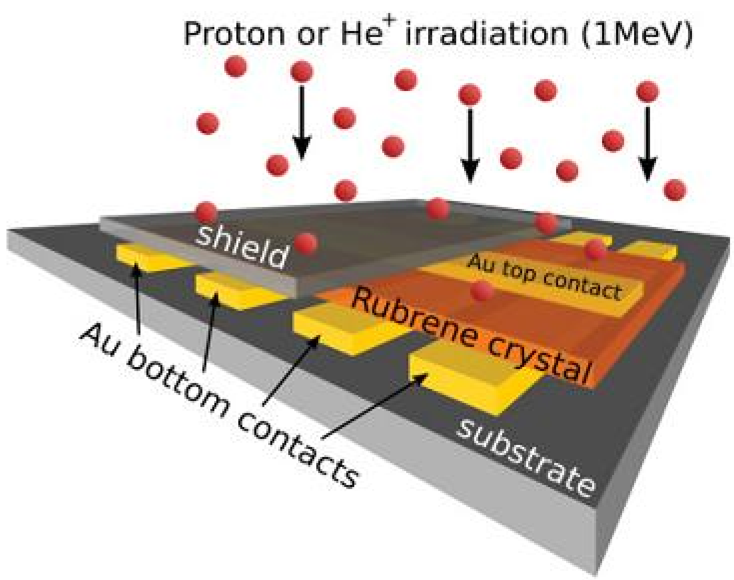
High energy ion irradiation of organic single crystals - I

Rubrene crystal (vapour grown) 1μm thick
Ions: proton or He+
Energy: 1MeV
Fluence: $1x10^{11} – 5x10^{12}$ cm^{-2}



Irradiation in the dark, HV
Full crystal penetration

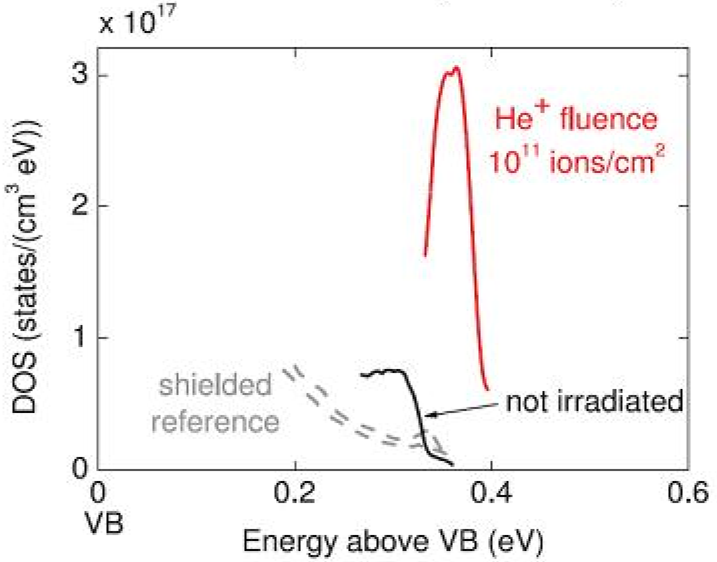
I-V-T curves analized with the SCLC model



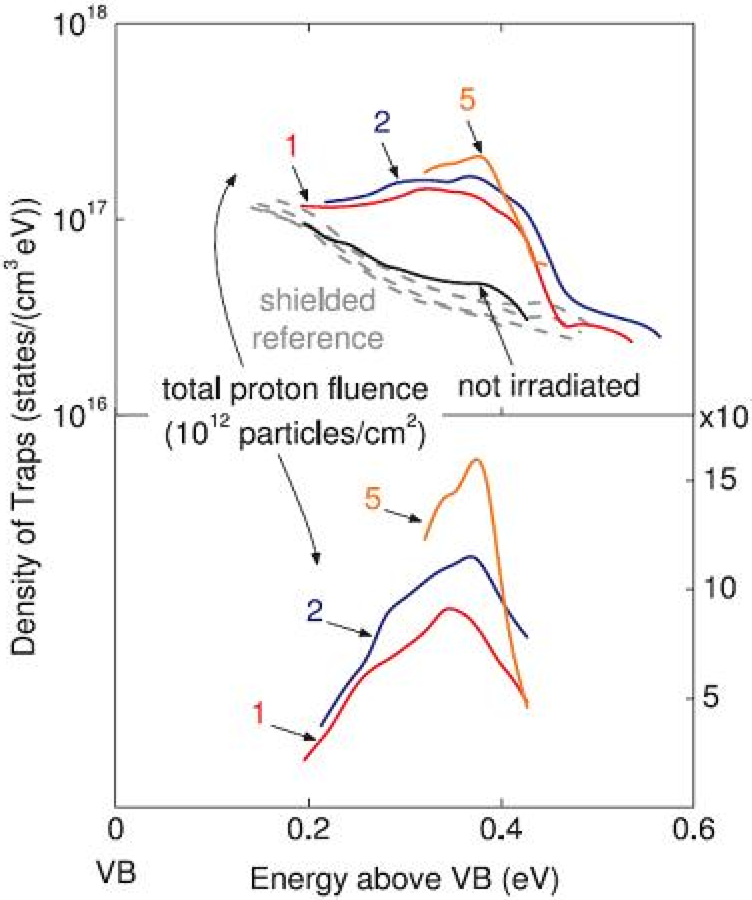
[Zimmerling et al Phys.Rev.B 2012]

High energy ion irradiation of organic single crystals - II

He^+ ions (10^{11}cm^2)

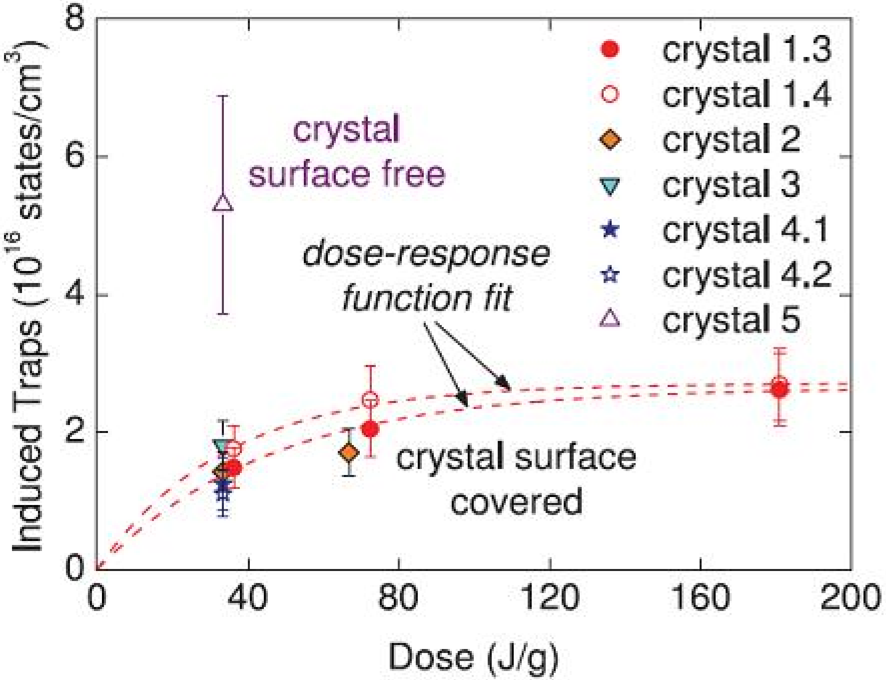


Protons



SCLC measurements identify two trap bands at 0.35eV, broader for proton irradiation

High energy ion irradiation of organic single crystals - III



Induced trap density as a function of absorbed radiation dose:

-With increasing dose, the trap density rises sublinearly and saturates at high dose.

- Crystal 5 was irradiated after the top contact had been peeled off, resulting in a roughly three to five times higher trap density compared to crystals irradiated with the surface covered by the PDMS/Cr/Au top electrode.

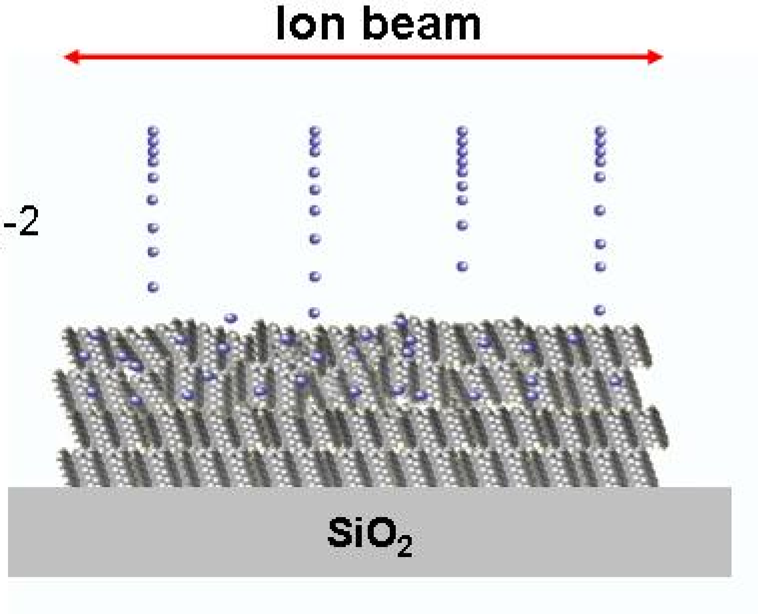
Saturation interpreted as **equilibrium interplay** between:

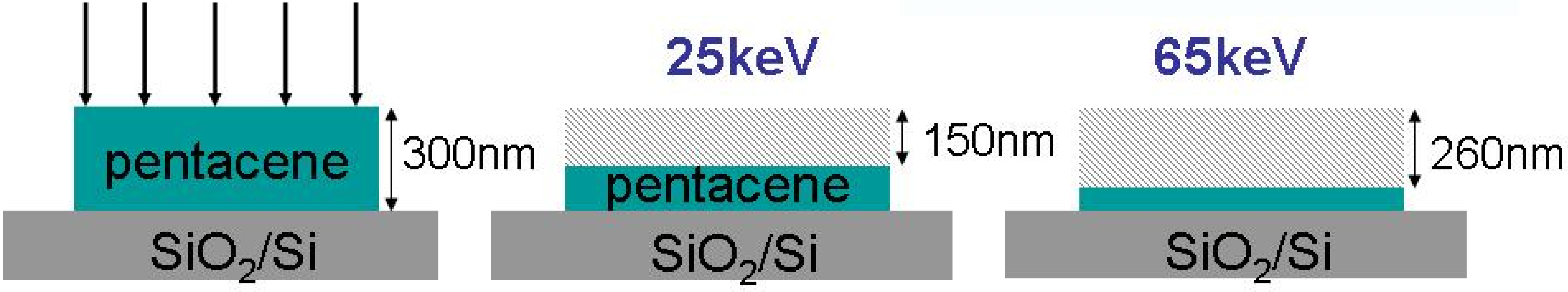
-Trap generation: breaking off of a H from the rubrene molecule (possibly associated to lattice distortion)

-Trap healing: H reattaches to the aromatic ring (some H atom may desorb from the surface if it is exposed/free

Low energy ion irradiation of pentacene OTFTs

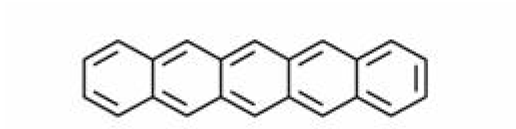
- **Ion:** $^{14}N^{+}$ or $^{20}Ne^{+}$
- **Dose range**: $1x10^{14} cm^{-2}$ to $5x10^{16} cm^{-2}$
- **Energy range:** 25keV to 65keV
- **Damage depth:** 150nm to 260nm (collision events –SRIM)



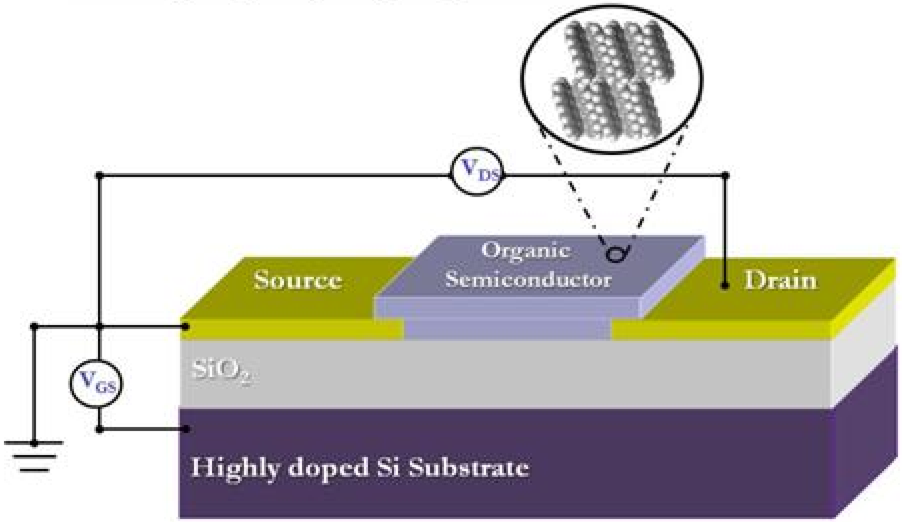


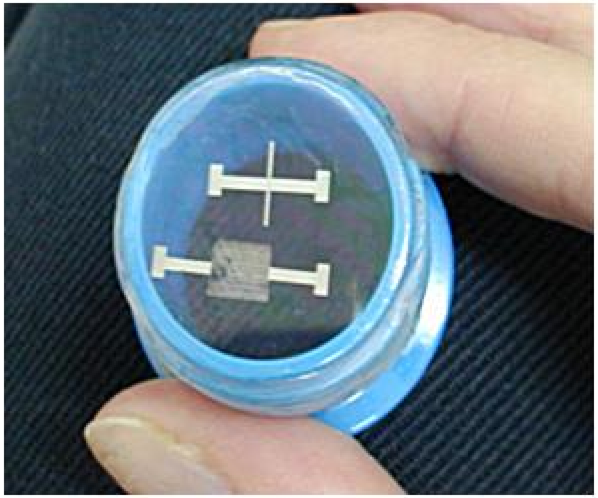
Fraboni et al. Org.Electron. ***12****, 1552 (2011)*

Pentacene OTFTs



$C_{22}H_{14}$



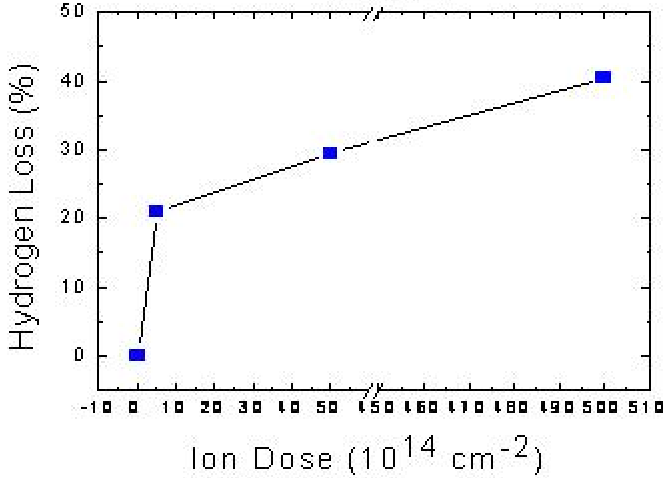


Hole mobility: $6 \times 10^{-2} cm^2/Vs$
Threshold voltage: -6V

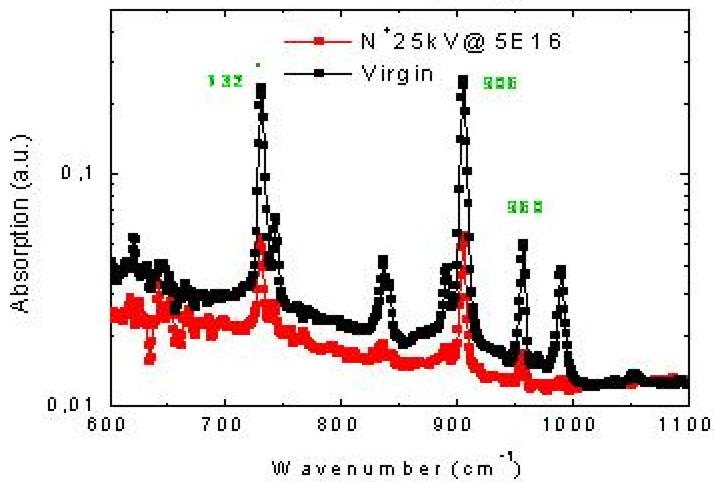
Active layer: thermally evaporated polycrystalline pentacene
typically 50nm thick, here 300 nm
Metal contacts: Au
Device dimensions: L=50μm and W=5mm

Ion irradiation effects: Structural

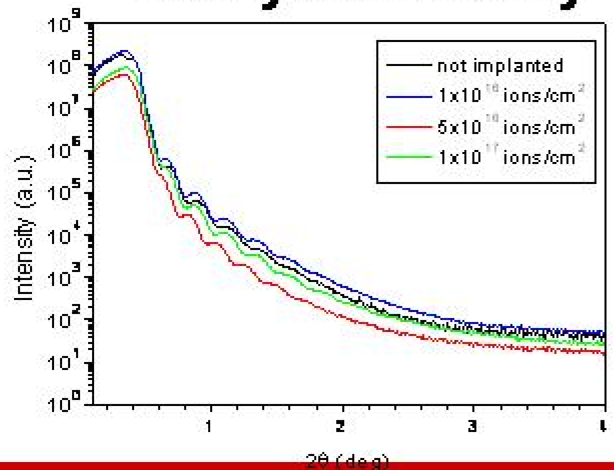
ERD



FTIR



X-Ray Reflectivity



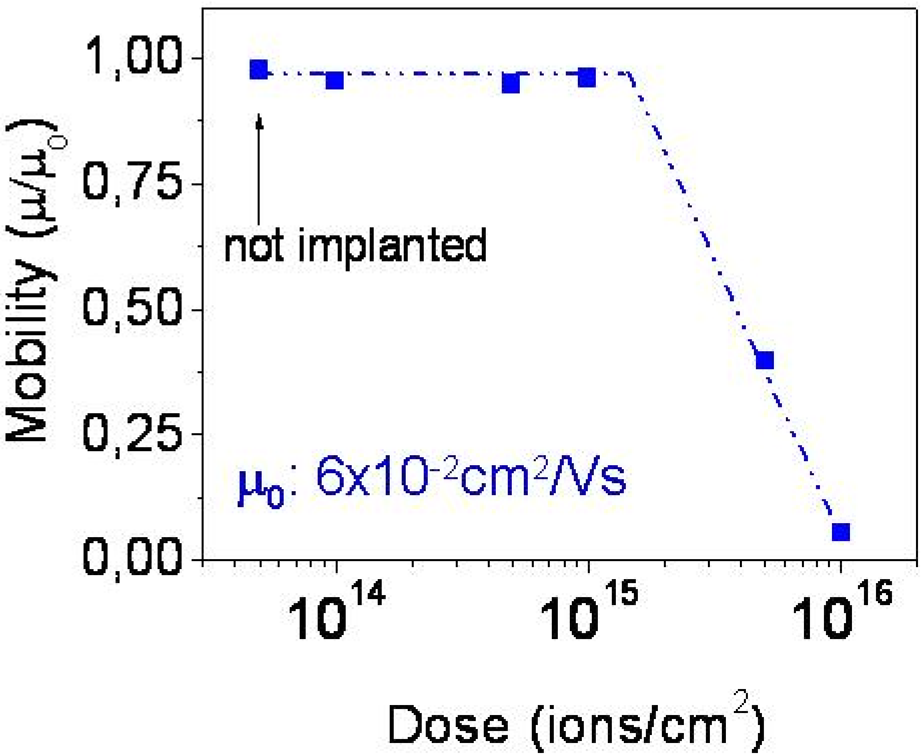
-dehydrogenation, carbonification

- No changes in film thickness

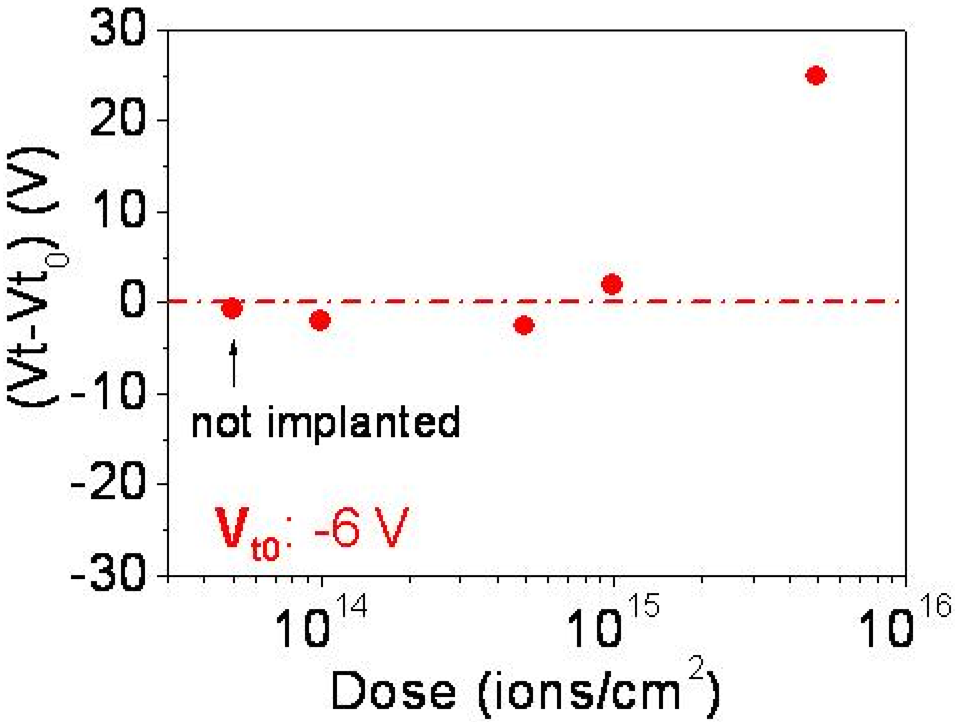
Ion irradiation effects:
Electrical (μ, V_t)

N^+ ions energy @ 25keV

Carrier mobility

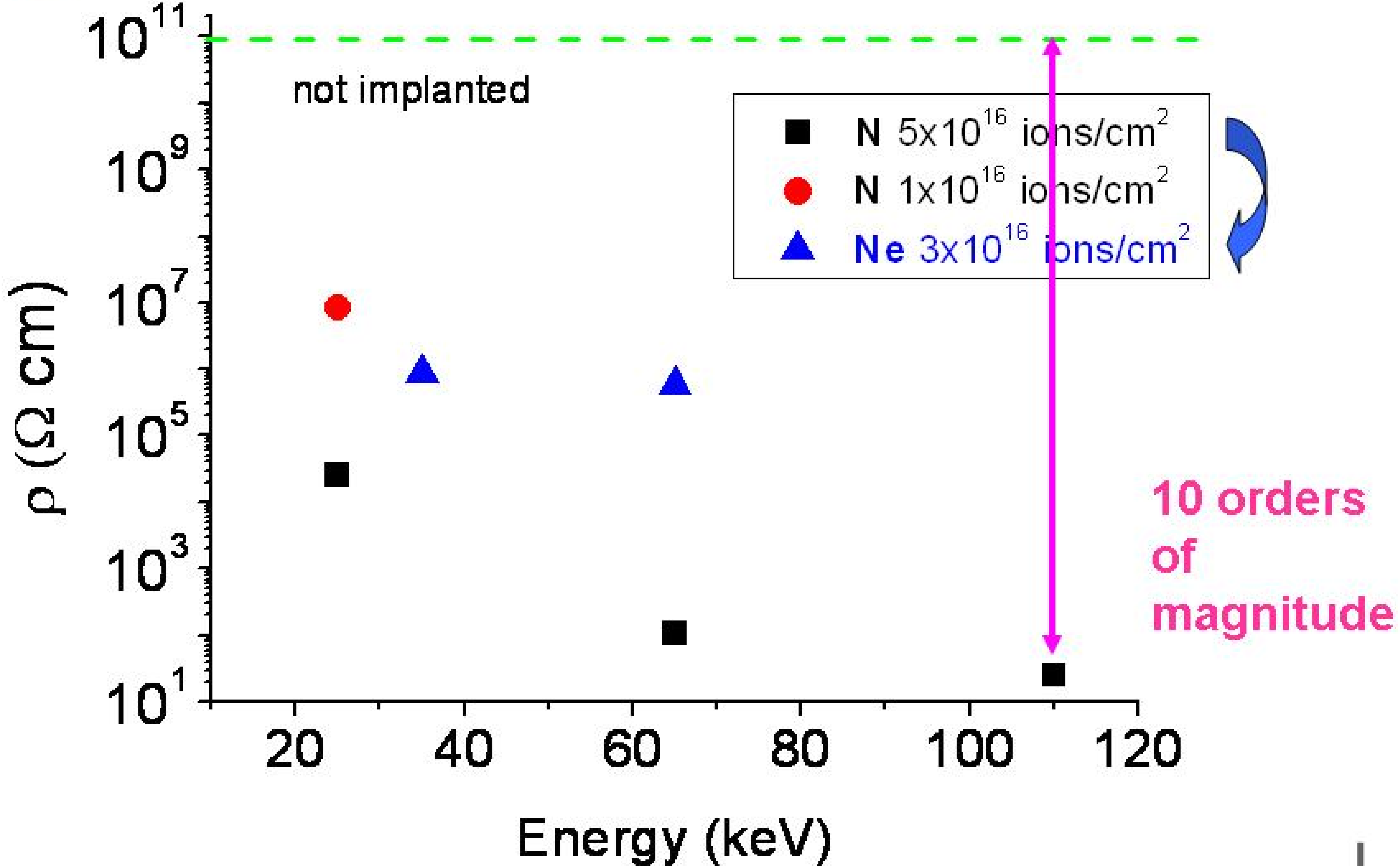


Threshold voltage

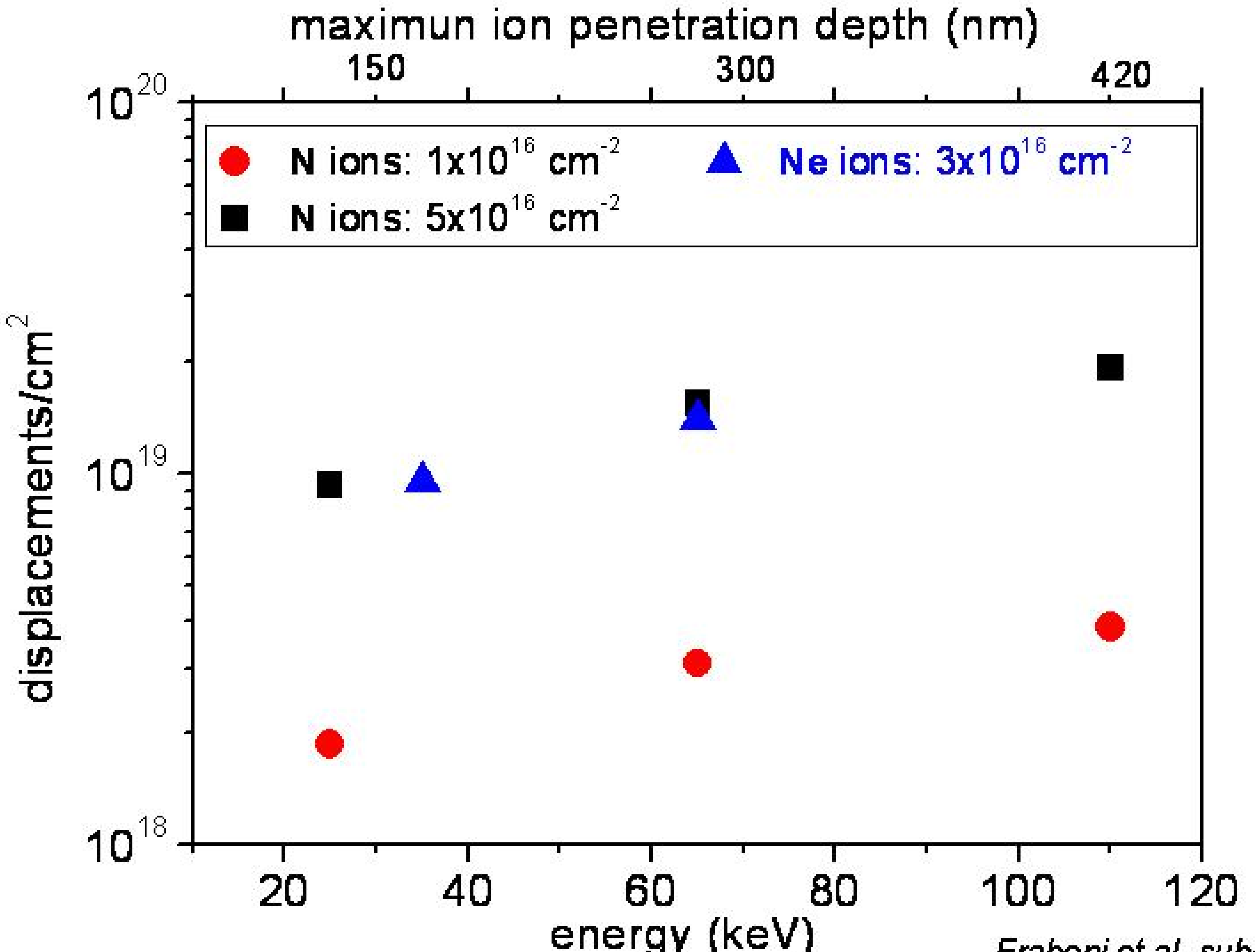


Fraboni et al. Synth.Met. ***161****, 2585 (2012)*

Electrical Resistivity modification



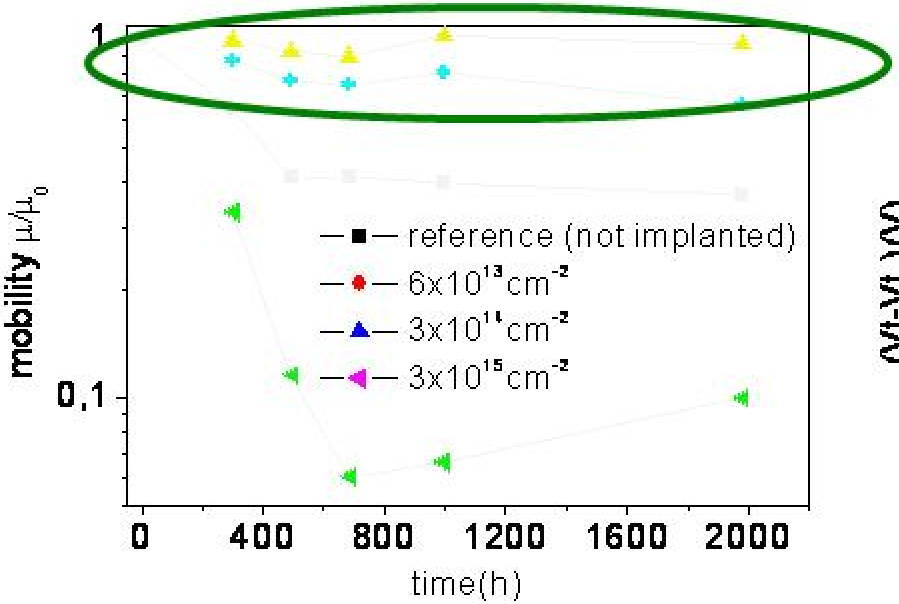
Damage induced by N and Ne ions



Fraboni et al. submitted

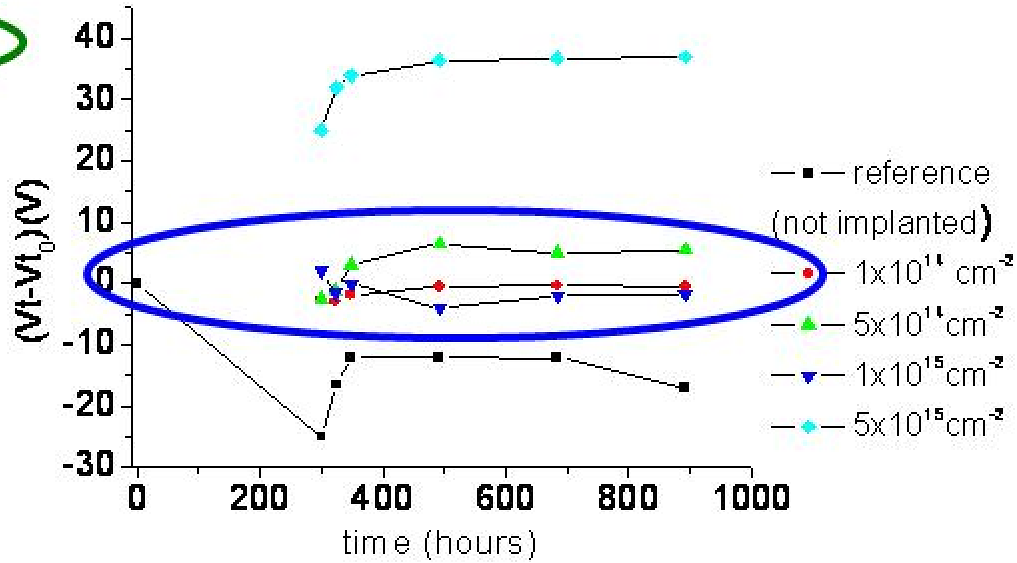
μ, V_T variation with time

Carrier mobility



Ne$^+$ ions @ 35keV

Threshold voltage

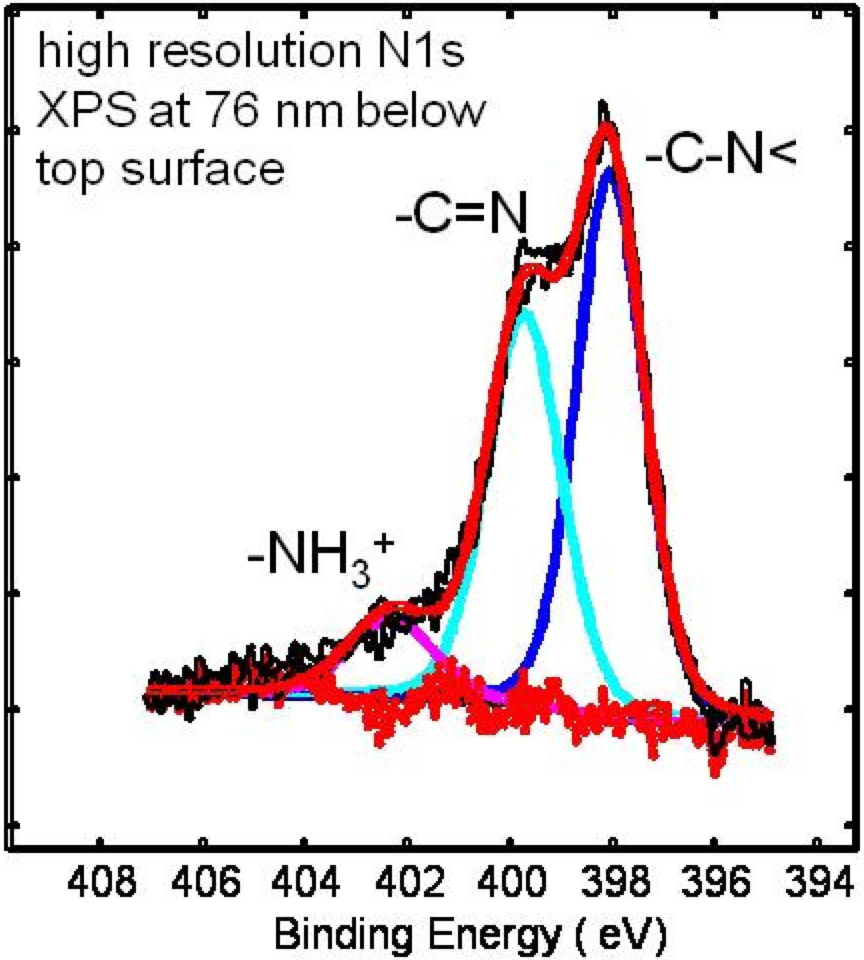


N$^+$ ions @ 25keV

Different behaviour of Ne and N ion/identical damage profile: not just radiation damage!

Fraboni et al. Org.Electron. ***12****, 1552 (2011)*

Depth-resolved XPS



- N^+ ions induce the formation of -CN and $-NH_3$ groups that may affect the charge density distribution within the film

- No detectable effects due to Ne irradiation (no bonding with the hydrocarbon matrix)

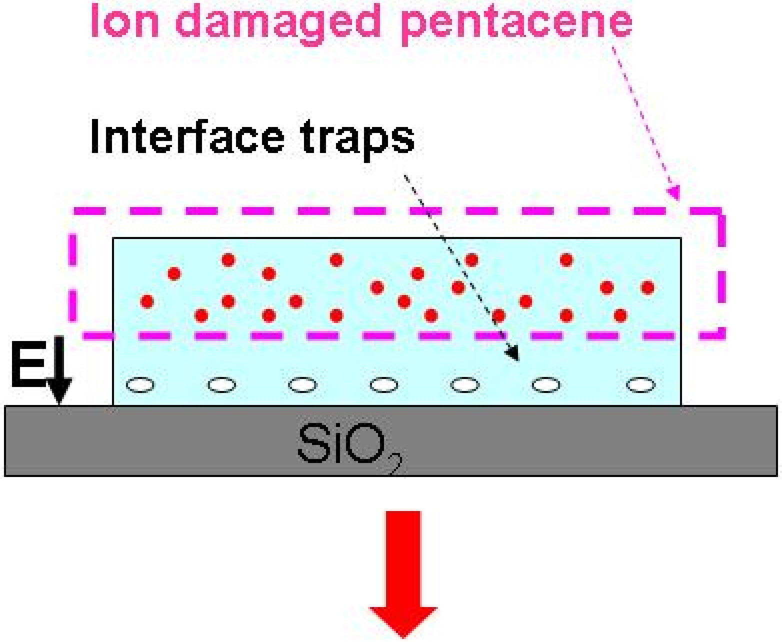
Role of interface trap states

- **N^+** ions induce the formation of charged groups that affect the charge density distribution within the film

- **Vt degradation** with time is due to charge trapping effects at the semiconductor/dielectric interface (chemical surface structure of most dielectric layer (e.g. -OH terminations in SiO_2) [*C.Huang et al.Adv. Funct. Mater. (2007)]*

- **N^+** irradiation of OTFTs stabilizes Vt

- the semiconductor/dielectric interface is not affected by the irradiation process



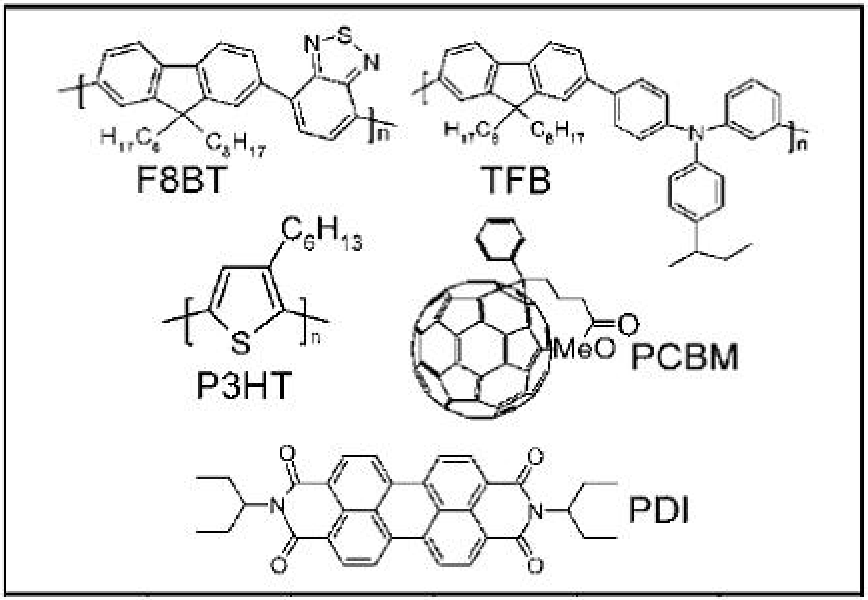
The irradiated charged layer induces an electric field that overrides interface trapping effects and stabilizes Vt

IMPLANTATION?

X-ray irradiation of semiconducting polimer OTFTs

Photodiodes coupled to scintillators

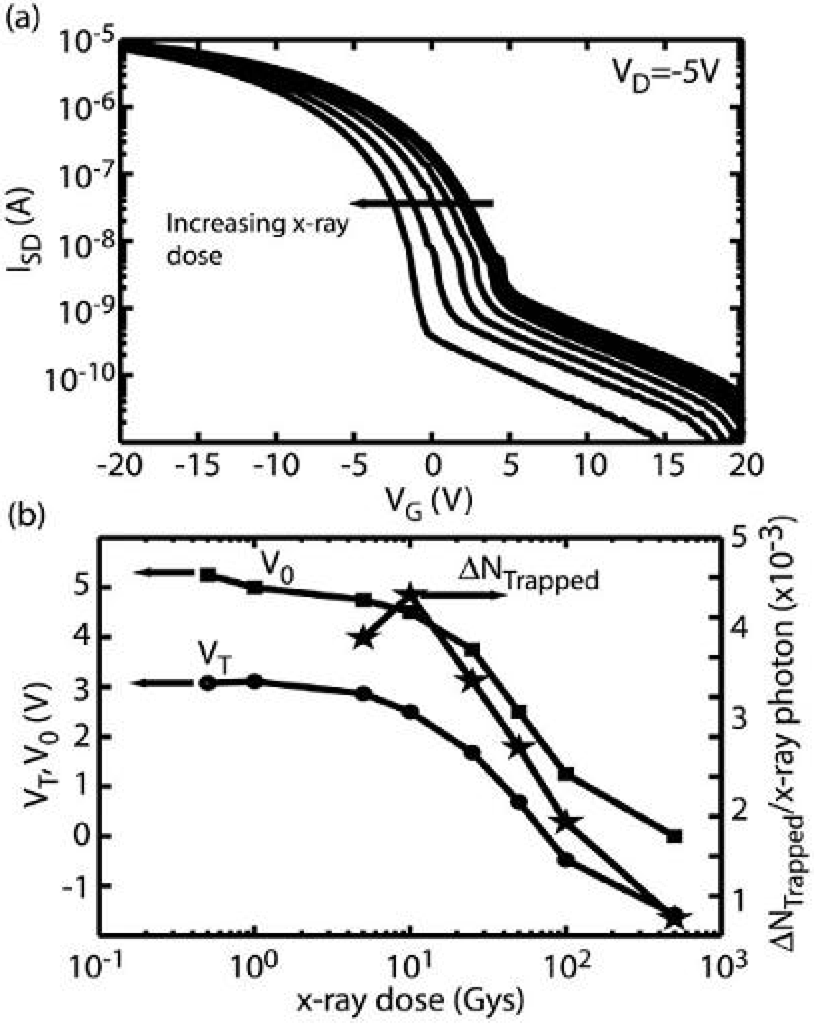
Materials:
Polytriamilines (PTAA)
Poly-phenylene-vylene (PPV)
P3HT:PCBM



- **X-ray:** W tube 70kV 15mA
- **Dose rate**: 18 mGy/s
- **Max total dose** :500Gy

[Keivanidis et al. Appl.Phys.Lett. 2008; Agostinelli et al Appl.Phys.Lett. 2008; Newmann et al. Appl.Phys.Lett. 2007]

X-ray irradiation of semiconducting polimer OTFTs



a Evolution of the *in situ* measured transfer characteristics of a PTAA transistor with X-ray exposure. From right to left, the characteristics are measured for x-ray doses of 0, 0.5, 1, 5, 10, 20, 50, 100, and 500 Gy.

b Variation of the onset V_0 and threshold V_T voltages with X-ray exposure. On the right-hand axis is plotted the estimated variation of the number of detrapping events $N_{Trapped}$ per incident x-ray photon.

X-ray irradiation of semiconducting polimer OTFTs

- chain scission and crosslinking. Surface graphitization
- thin films:

- No full absorption of the radiation
- strong interaction with the atmosphere (oxygen)

- secondary electrons effects, due to the X-ray interaction with the substrate
- Charge build-up in the dielectric (SiO_2)
- TFT bias stress effects

All these effects must be disentagled!

X-ray irradiation of pentacene OTFTs

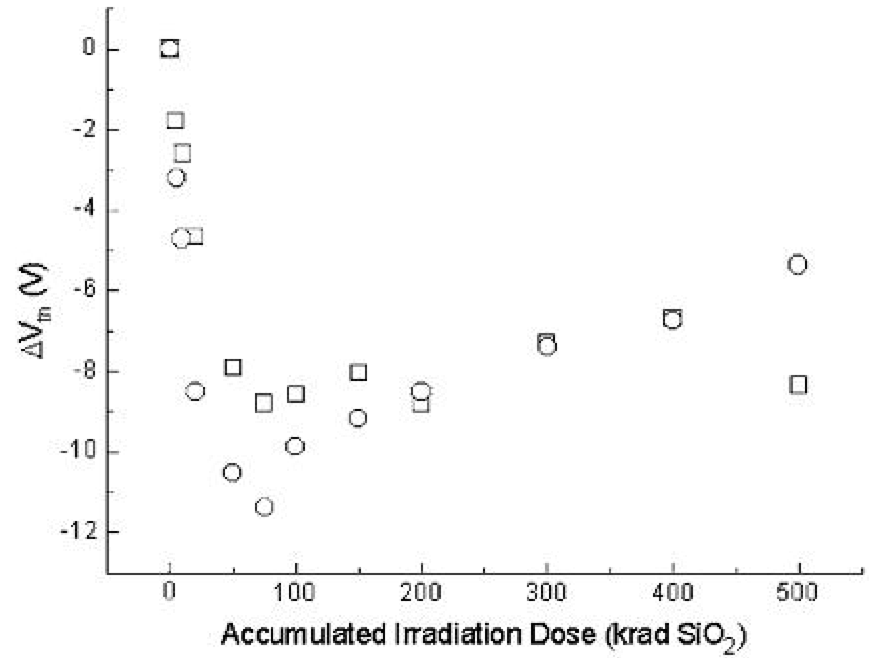
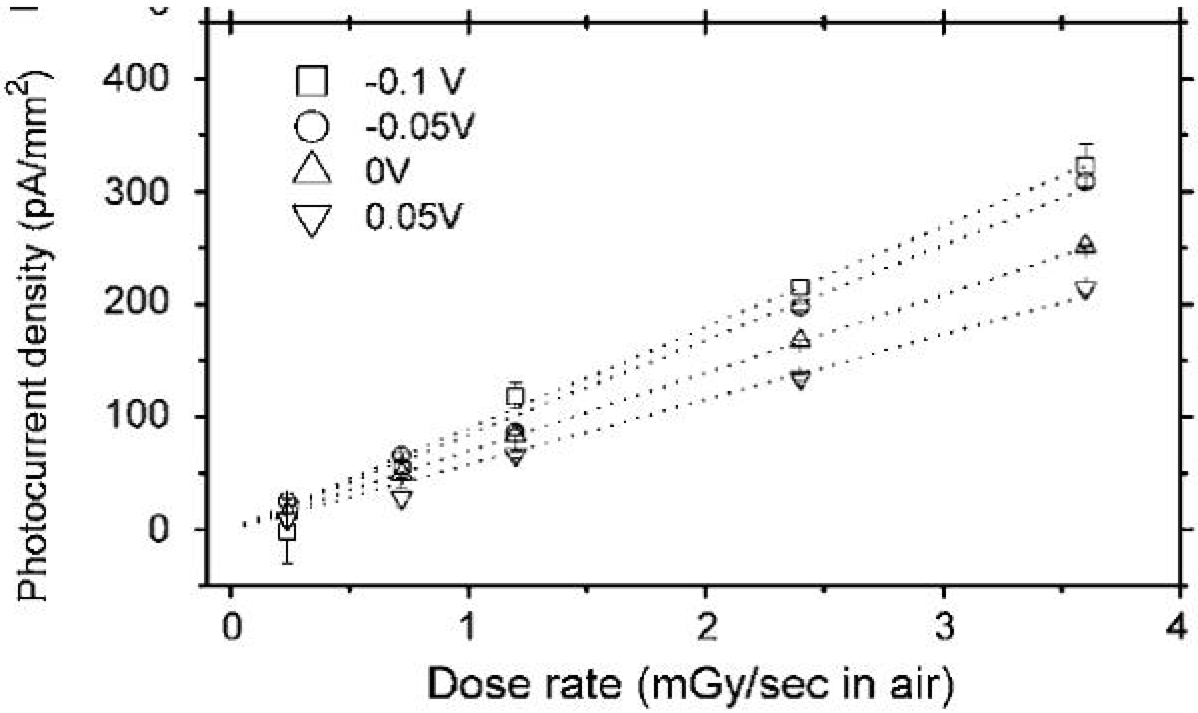


FIG. 3. Estimated variation of the threshold voltage due solely to effects of radiation deduced by subtraction: ΔV_{th} (irr) $=(\Delta V_{th})_{(\text{irradiation+bias stress})} - (\Delta V_{th})_{(\text{bias stress only})}$ (□) 1 MV cm^{-1} during stressing and stressing and irradiation, and (○) −1 MV cm^{-1} during stressing and stressing and irradiation.

[Devine at al, Appl.Phys.Lett.2006]

Interesting observations



- Radiation hard up to 500Gy

- Linear dependence of photocurrent response with increasing X-ray dose

Novel X-ray solid state detectors?

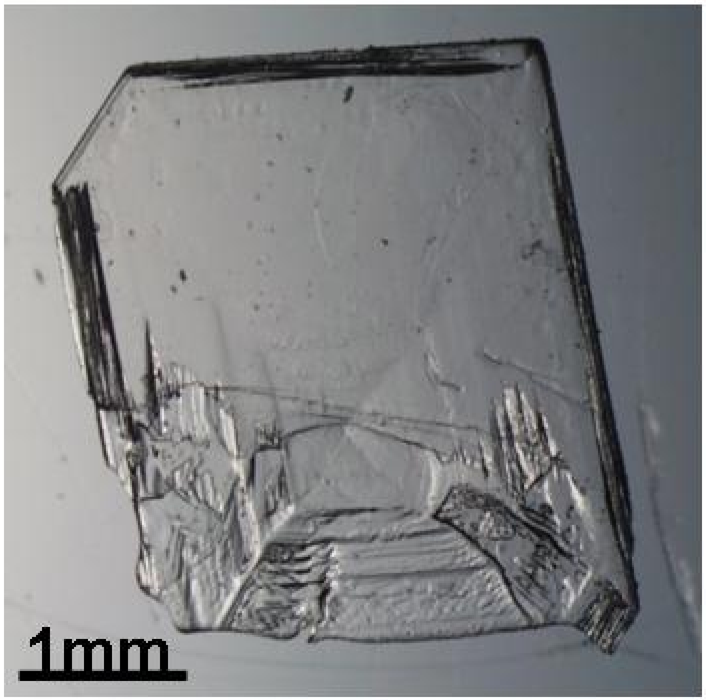
Organic semiconducting single crystals

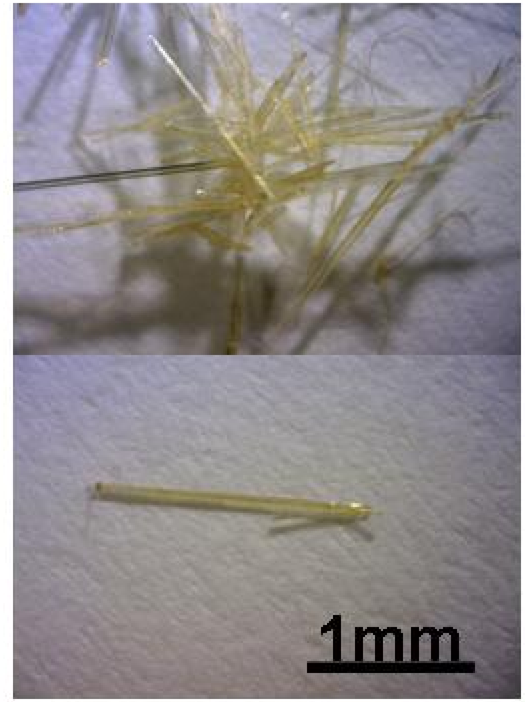
- absence of defects related to grain boundaries, well defined geometrical disposition of molecules, high degree of order

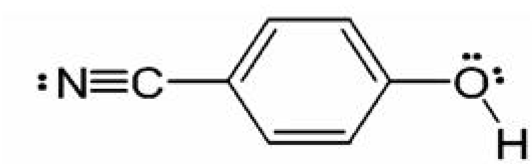
- Larger thickness and volume (up to mm^3)

- Long term stability in atmosphere

Solution Grown Single Crystals

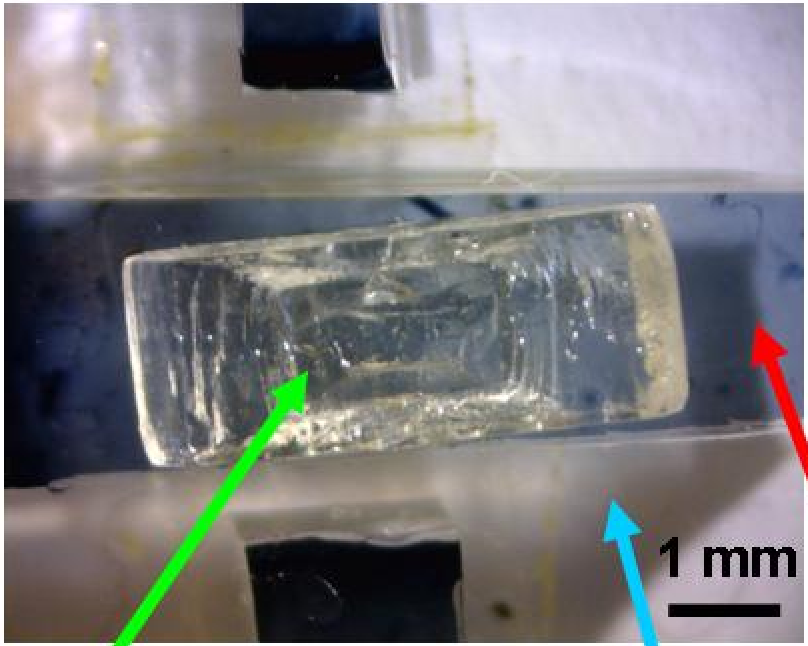




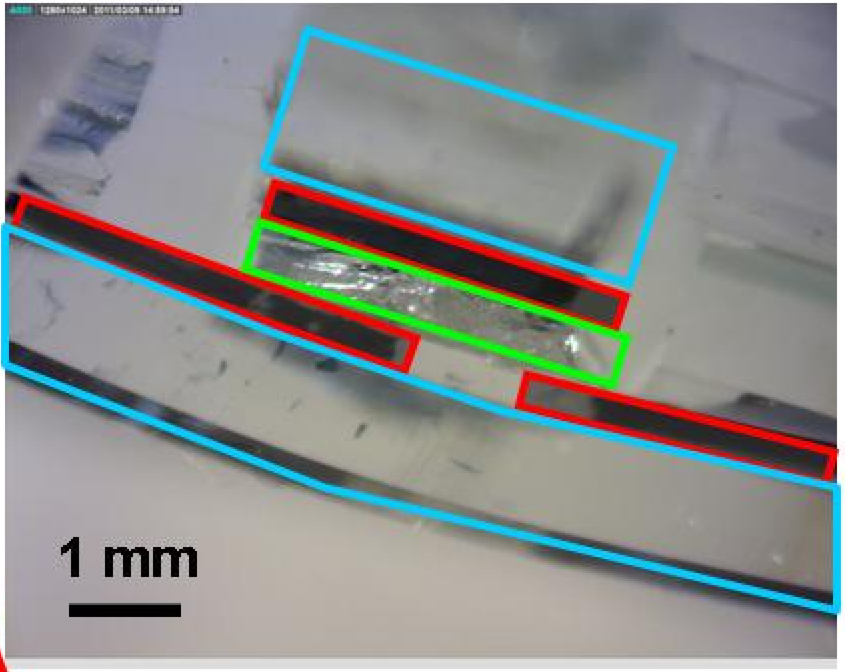


All-organic X-ray detector

Top view



X-section (complete device)



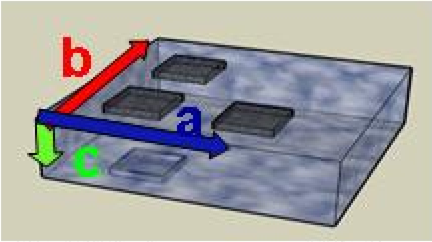
Optically transparent

B. Fraboni et al, Adv. Mater., **21**, 1835 (2009)

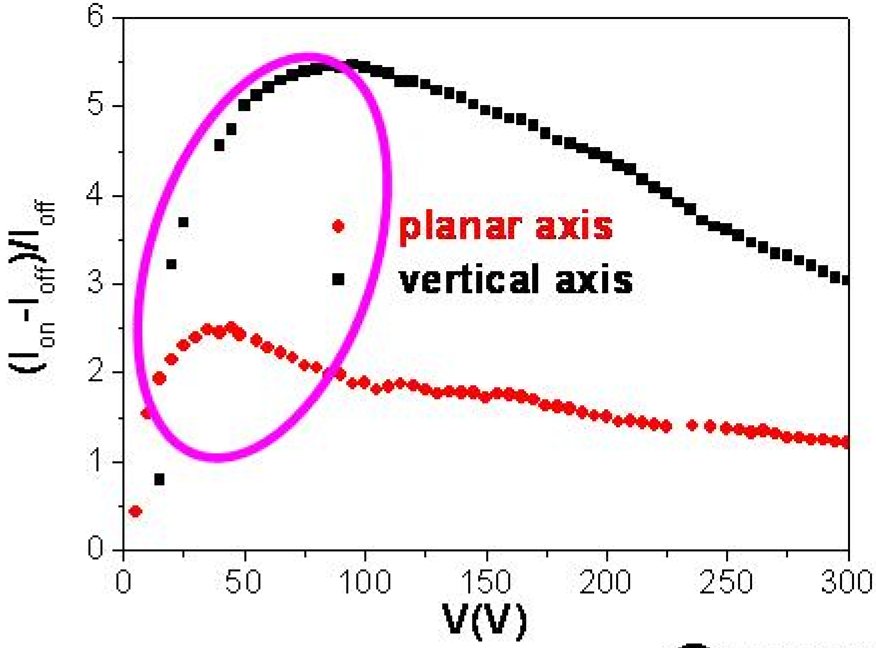
X-ray electrical response

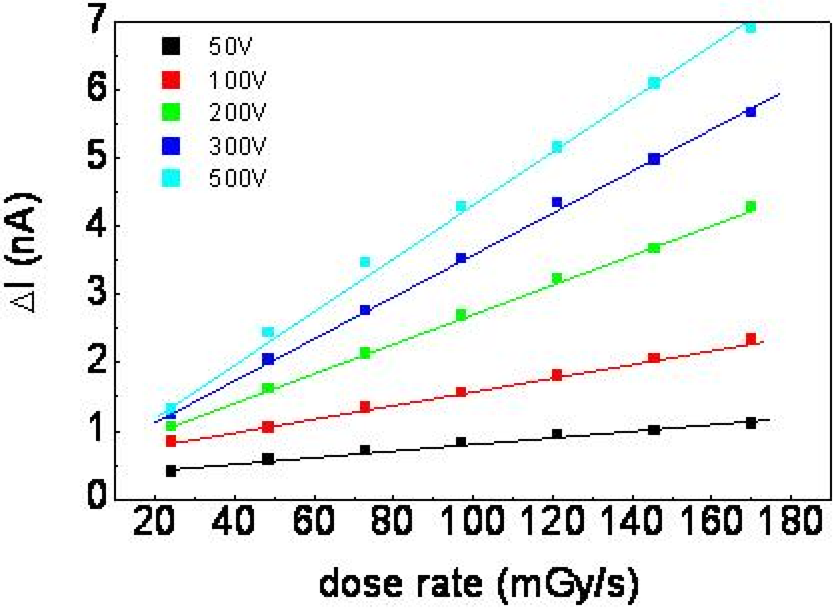
X-ray irradiation:

Mo tube - 35kV
Dose rate: 70mGy/s



Crystal thickness ≈ 300μm
Electrodes distance ≈ 300μm

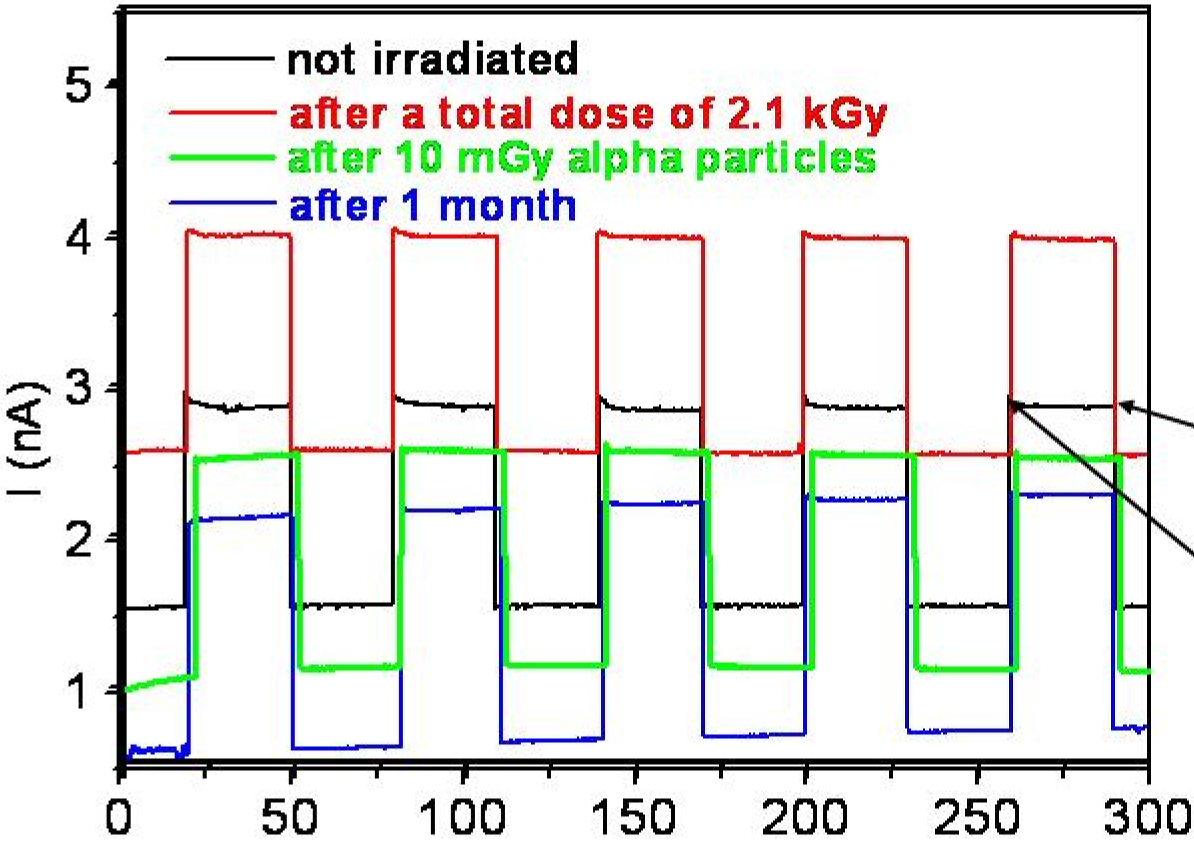


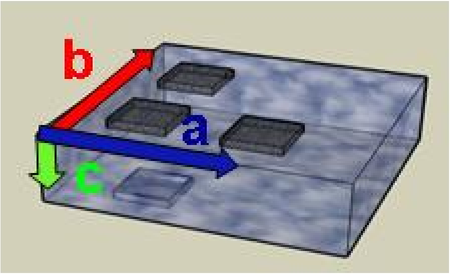


@ room temperature

B. Fraboni et al, Adv. Mater. (2012)

Radiation hardness: X-rays (total dose 2.1kGy) alpha (total dose 10mGy)





V=100V

B. Fraboni et al, Adv. Mater. (2012)

Vertical axis

Conclusions

- Organic semiconducting materials present extremely varied properties depending on their molecular structure, packing and growth methods that in turn affect their macroscopic structural and electrical and properties

- Organic electronic devices have peculiar operation conditions (e.g. in TFTs $\mu=\mu(V_G)$ and only few nm at the dielectric/semiconductor interface contribute) and can be affected by the interaction with the environment (thin films)

- The study of the effects of ionizing radiation on organic semiconductors and devices is still in its infancy: thorough experimental and theoretical studies are needed to interpret and exploit their huge potential (large area, low cost, conformable, low weight)