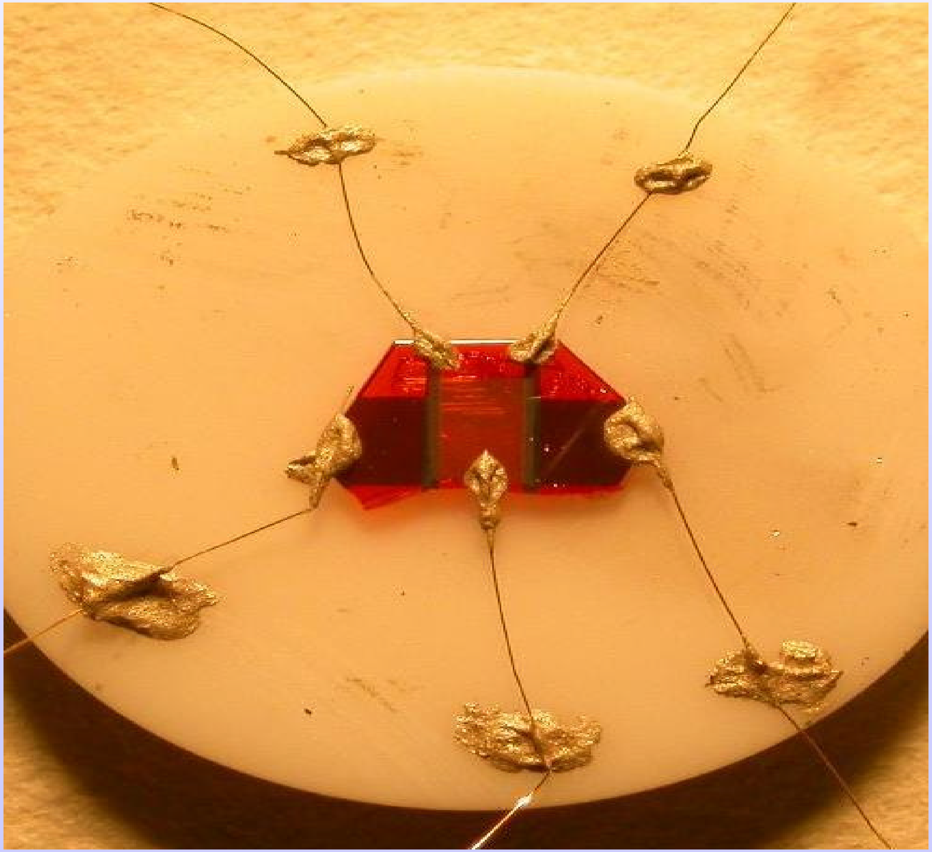
Single-Crystal Organic Field Effect Transistors



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Outline:

- Organic field-effect transistors (OFETs) as a tool for studying charge transport in molecular crystals.
- Performance of the thin-film OFETs
- Single-crystal OFETs: challenges and tricks
- The rubrene single-crystal OFETs: first results
- Transport of surface charge carriers in organic molecular crystals: unsolved problems

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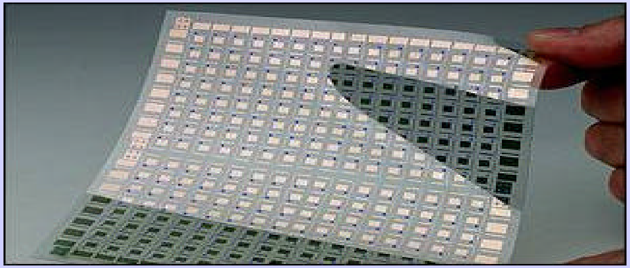
Field-effect doping and organic FETs

***Fundamental academic interest*:**

- **many isolators can be “field-effect doped”; the “doping” level in OFETs might be higher than that accessible with chemical methods;**
- **potentially, OFETs could be a very important tool for studying strongly-correlated 2D systems, 2D superconductivity, etc.;**
- **OFETs also can help to solve the puzzle of the crossover “polaronic transport Û band transport” in organic crystals.**

***Applications of OFETs*:**

(potentially) inexpensive, flexible, light-weight, suitable for large area applications



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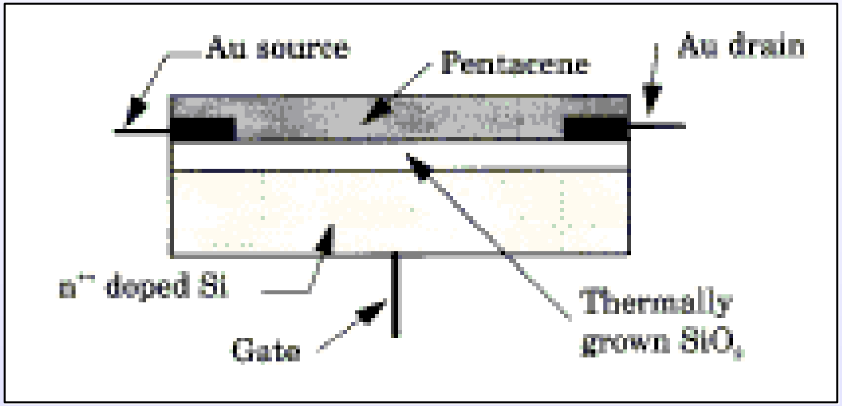
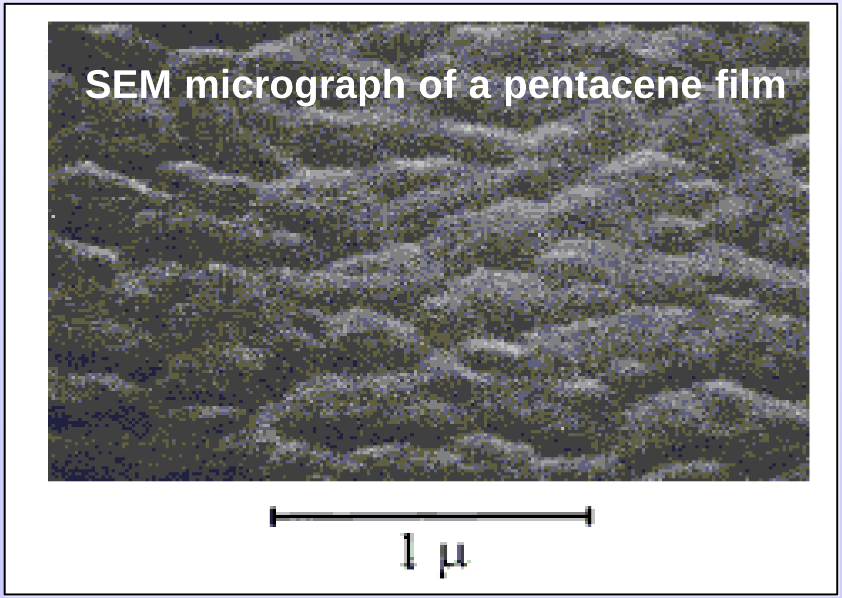
Thin-film OFETs




SEM micrograph of a pentacene film

Uniqueness of organic molecular compounds – in an intrinsically low density of charge traps at the interface, due to a weak, van der Waals bonding of molecules.

The thin-film OFET performance depends crucially on the film structure: presence of different phases, inter-crystalline boundaries, etc. reduces drastically the carrier mobility, and results in the other undesirable effects (e.g., dependence of μ on V_g and V_{SD}).

The best characteristics are realized in the devices where a thin organic film is deposited in high vacuum on an oxidized *Si* wafer (this compromises the whole idea of a cheap and flexible OFET).

Current status of the thin-film OFETs

On one hand, a decade of the research in thin-film OFETs has produced impressive results: the performance of the best thin-film OFETs is comparable to the α:Si FETs. In particular, for the best thin-film OFETs, $\mu \sim 1$ cm^2/V·s.

On the other hand, the further progress is limited by the morphology of organic films: orientational molecular disorder and inter-crystalline boundaries affect the mobility and other characteristics.

In this situation, it makes sense to explore the *single-crystal* OFETs, as an “ideal” system which is free of the bulk defects. The price considerations are not an issue in this case (the best thin-film OFETs are not cheap either…).

However, fabrication of the single-crystal OFETs is still a challenge...

Challenges of the single-crystal OFET fabrication (or why it took almost two years…)

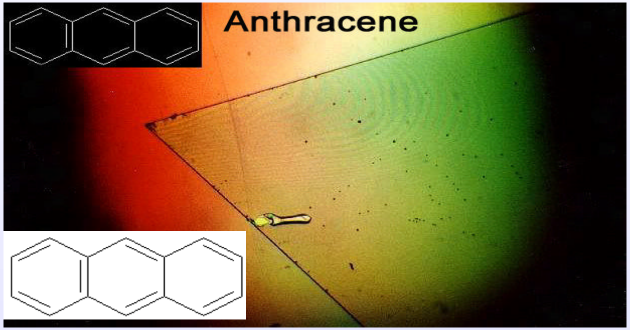
Epitaxial growth of single-crystal organic films has not been developed yet. At present, the only option is to form FETs on the surface of pre-fabricated organic molecular crystals. However, these crystals are very vulnerable and, very often, incompatible with the standard processes of thin-film technology (sputtering, photolithography, etc.).

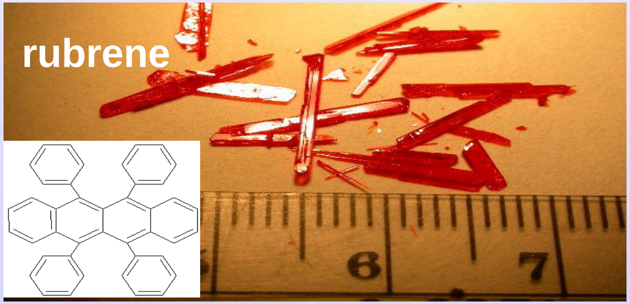
Technological stages:

- **purification of the starting organic material and growth of suitable organic crystals: “molecularly-flat” facets with a low density of charge traps**
- **deposition of the low-resistance source and drain contacts**
- **formation of the disorder-free interface between the organic crystal and the gate insulator.**

The OFET should be compatible with low-T measurements.

Organic molecular crystals



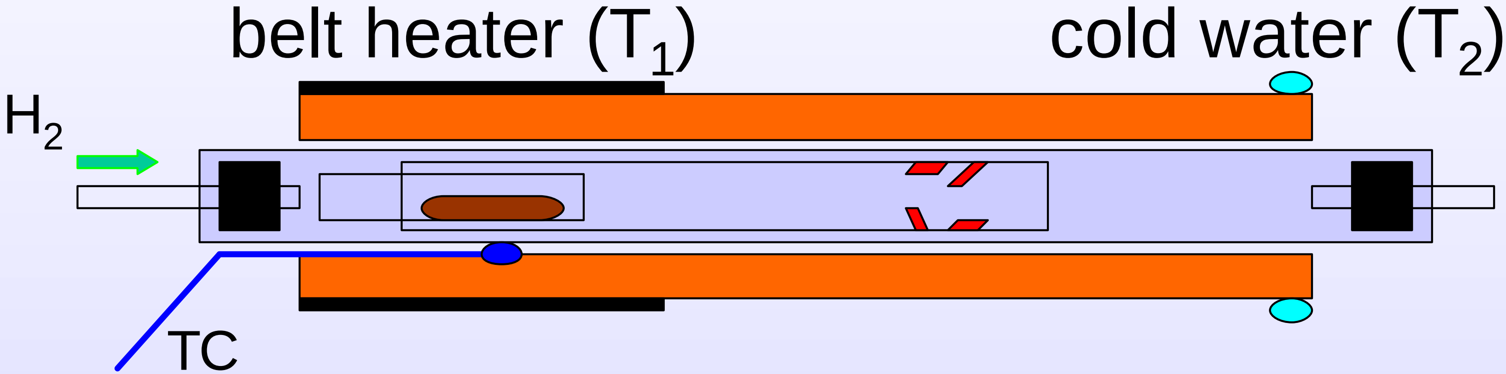


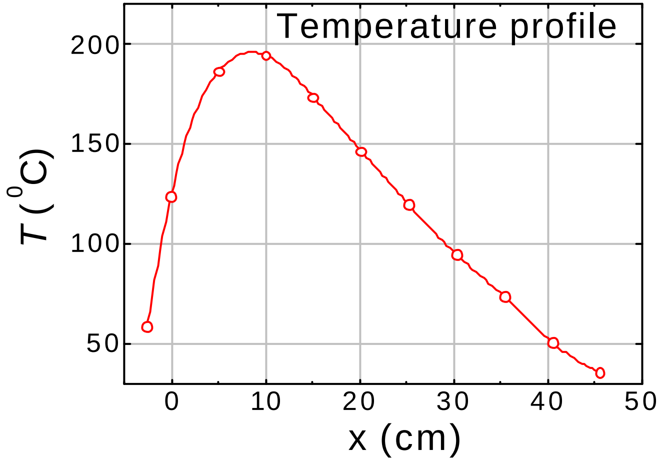
Organic molecules carry carbon 2p_z electronic wavefunctions (conjugated p-electron systems).

Usually, the van der Waals-bonded low molecular weight crystals are aromatic molecules deriving from the benzene ring (e.g., the naphthalene family).

From the viewpoint of the charge transport and optical properties, these crystals are wide-band semiconductors

PVT crystal growth and purification





Impurities affect strongly the electrical properties of organic crystals (similar to inorganic semiconductors).

The impurity concentration has to be reduced down to or even below the ppm level (1 ppm = 10^{-6} molecular fractional content): very slow growth and multiple re-growth cycles.

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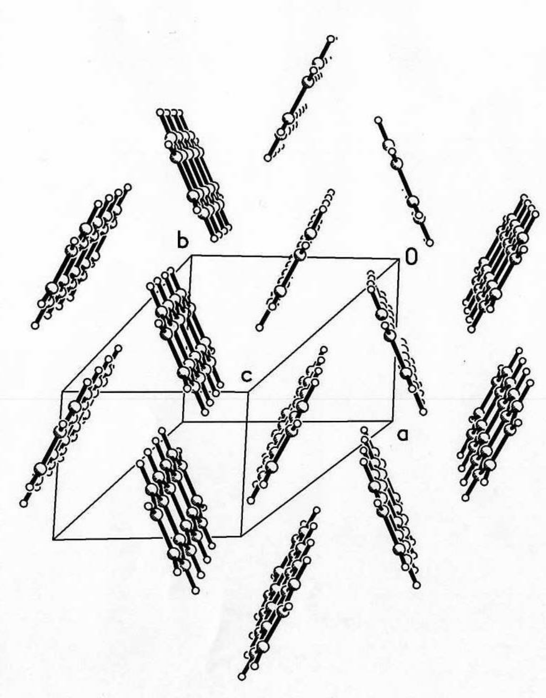
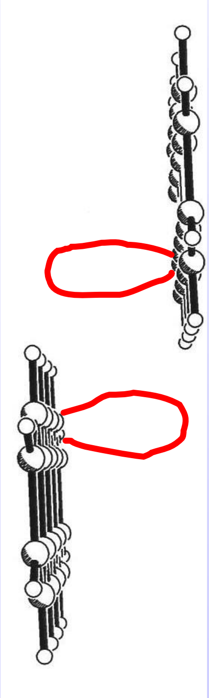
Molecular packing in organic crystals: tetracene

c-axis

The crystal structure of tetracene,
the so-called herringbone packing.

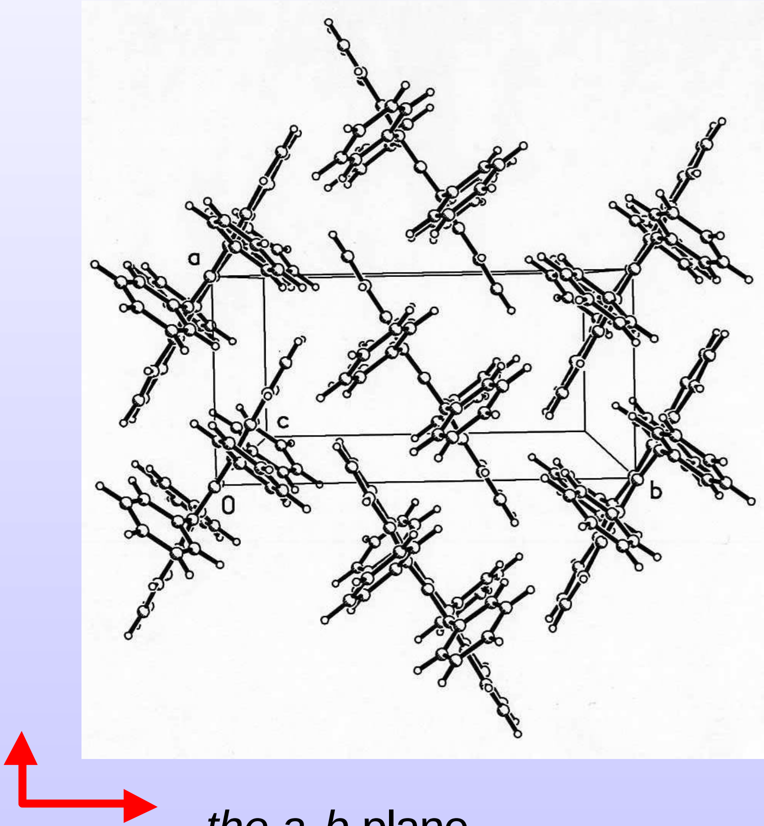




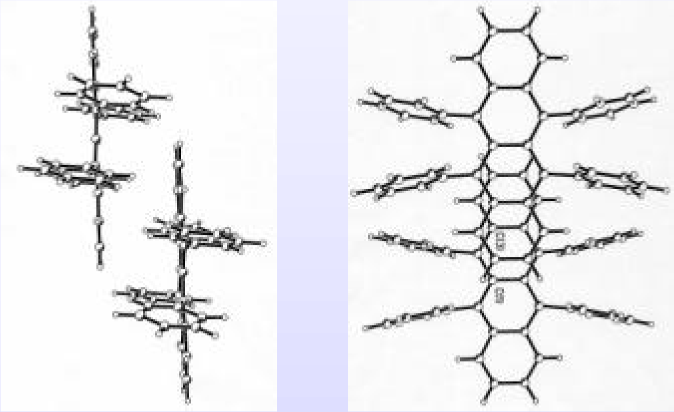
Note that the overlap of π-orbitals is small

a-*b* plane, flat crystal facet

Rubrene



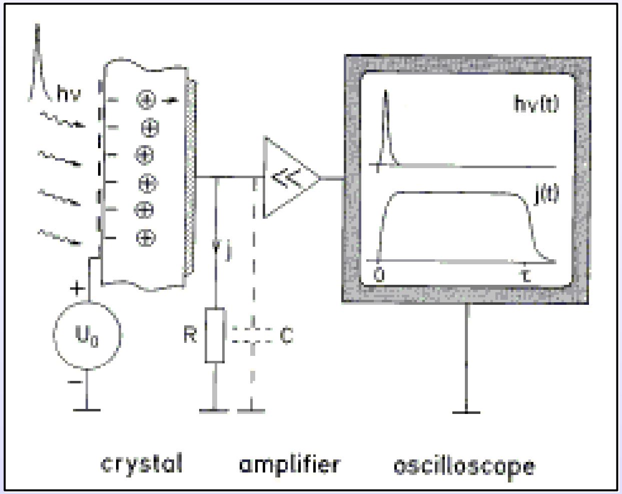
the a-*b* plane

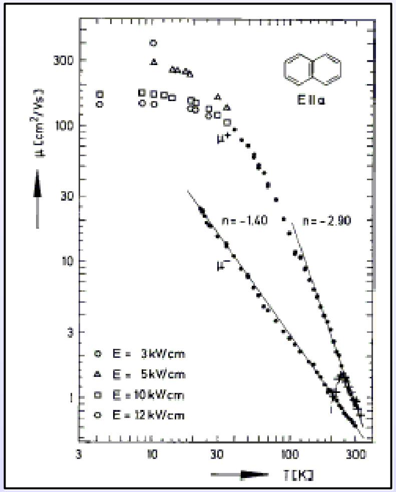


The overlap of π-orbitals seems to be greater than in tetracene, and the axes of the molecules are in the plane of layers –

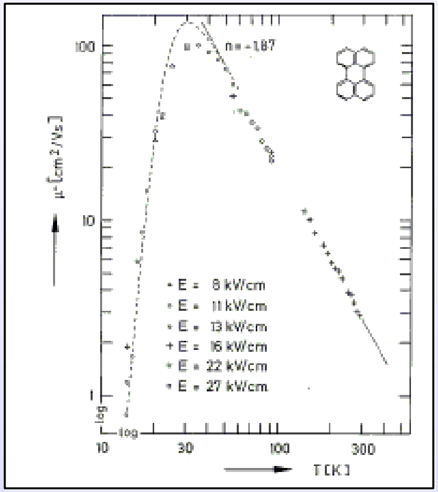
relevance of this fact to a larger mobility in rubrene FETs remains to be clarified…

“Bulk” charge transport in organic crystals





naphthalene



α - perylene

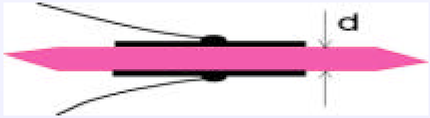
The crossover from the polaronic transport at higher temperatures to the band transport at lower temperatures:

“upon increasing temperature, increased phonon scattering slows down band transport, whence the local polarization interactions increase and, hence, the effective mass grows, in conjunction with band narrowing. Finally,…the thermally activated polaron-hopping transport becomes more efficient and takes over”.

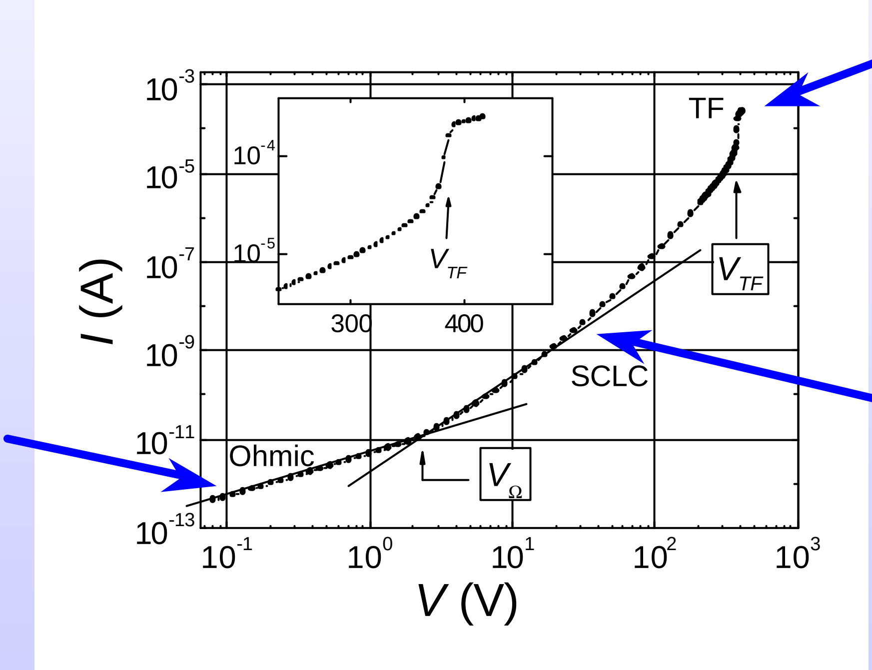
N. Karl, *Synt. Metals* **133-134**, 649 (2003)

N. Karl et al., *J. Vac. Sci. Technol*. **A 17**, 2318 (1999).

“Bulk” charge transport along the c-axis: the purity test



The I-V characteristic for rubrene (current flows in the direction perpendicular to the facets)



trap free regime
j_{TF} **= 9/8em(1/d)(V/d)^2**
at **$V > V_{TF}$ µ N_{traps} d^{2}**

Ohmic regime
$j = e\mu p_0(V/d)$

space-charge limited current
j = 9/8em(Q/d)(V/d)^2

The density of charge traps can be estimated from V_{TF}: $N_t \sim 10^{15}$ cm^{-3}

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Metallization of contacts

Two major issues:

(a) A metal should be a good injector of charge carriers (e.g., in the case of hole conductivity in OFETs on tetracene, rubrene, etc., gold and silver work well, while aluminum does not work at all)

(b) The resistance of the Schottky barrier at the organic/metal interface depends strongly on a method of contact fabrication. The rule of thumb: the less "invasive" the method, the better…

Examples of fabrication techniques,
which result in a low contact resistance:

- "rubber-stamp" deposition of gold
- water-based solution of colloidal graphite forms low-resistance contacts

Thermal deposition of metals requires extreme care for two reasons:

- the thermal load on a crystal should be minimized (large crystal-source distance, crystal cooling)
- even minor contamination of the channel surface by deposited metal reduces drastically the field effect.

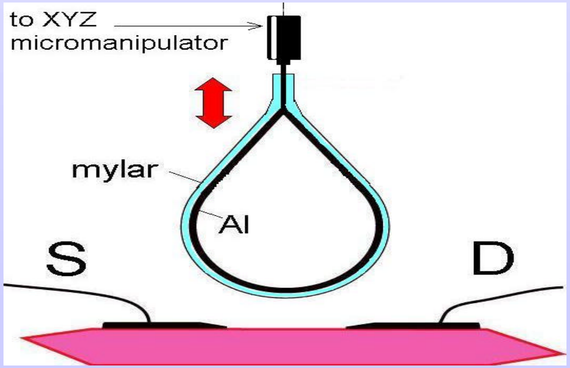
Gate insulator problem

Schon claimed that the conventional sputtering of Al_2O_3 worked well….

Sputtering "kills" the field effect almost instantaneously, because of bombardment of the surface by charged particles. The field effect vanishes in plasma even if the crystal is placed in the region of shadow, where no material is deposited on the surface…

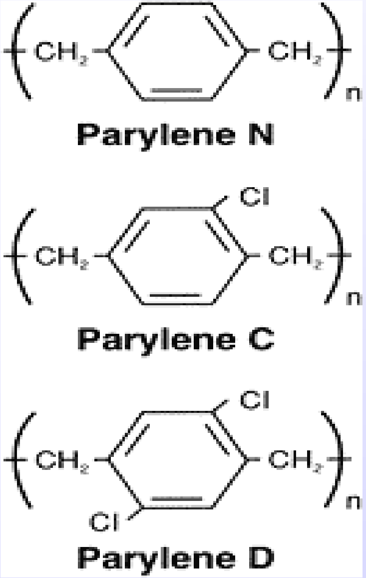
All our attempts to protect the organic surface by applying a bias voltage, experimenting with the deflecting electrodes, etc. failed, and, after a year, we gave up.

Thermal deposition of SiO also has not produced any promising results…



As a "quick and dirty" test for the field effect (e.g., for characterization of organic crystals), we used a 1-μm-thick aluminized mylar film – a loop made of such a film was pressed gently against the surface of a molecular crystal.

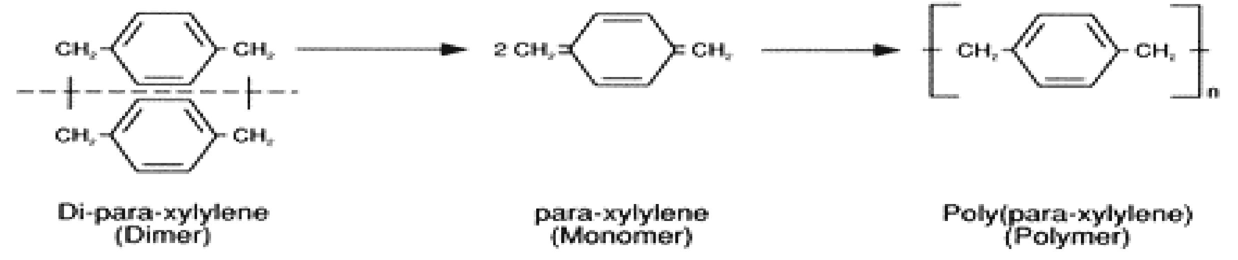
Parylene solution (pin-hole free conformal coating)



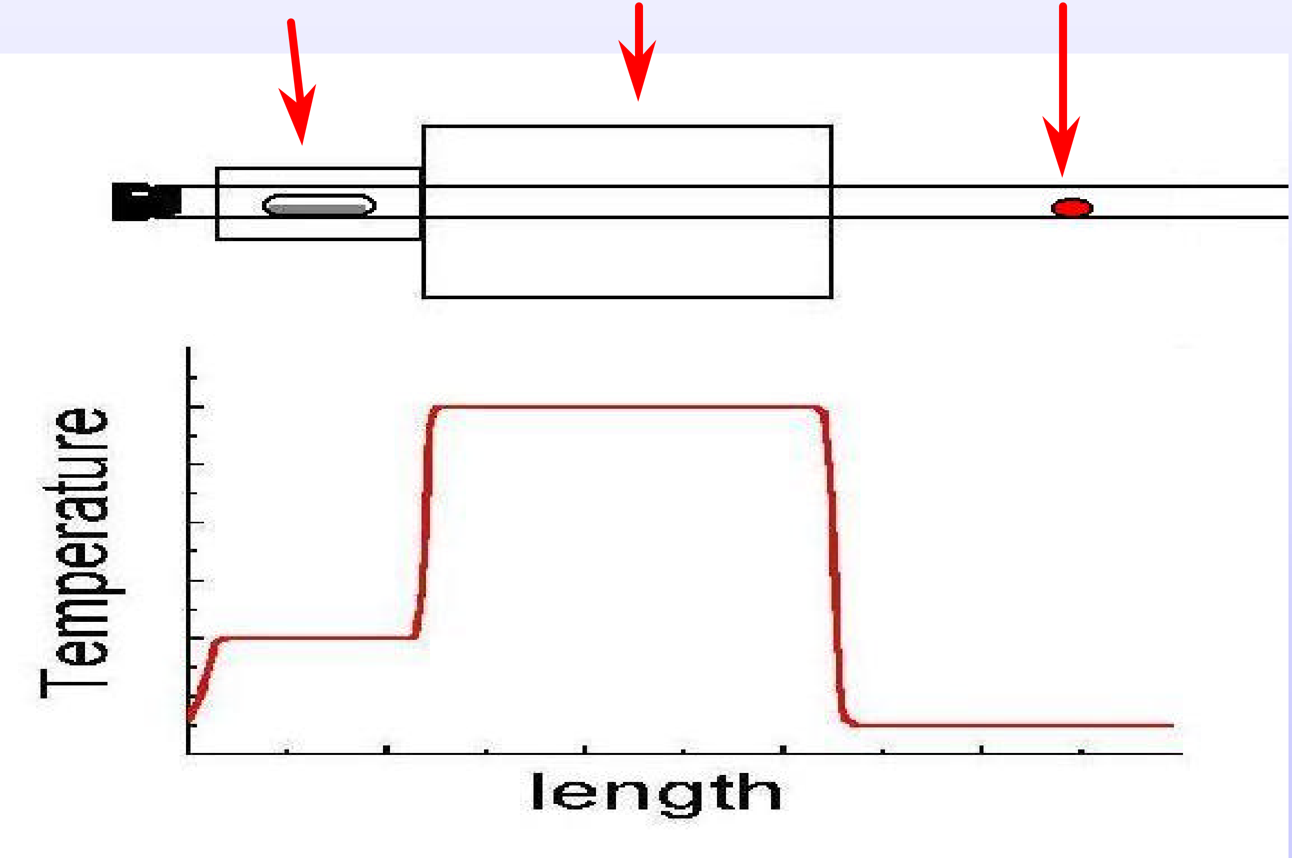
Parylene is the common name for a unique family of thermoplastic polymers used in the conformal coating process.

This vapor deposition process:

- a raw material (dimer) is heated in a vacuum system until the material sublimes to form a gaseous monomer.
- The gas of monomers flows into a deposition chamber containing the substrate to be coated.
- At the substrate surface, the gas converts into a solid polymer state, and forms of a completely conformal transparent polymer film.



Parylene deposition



Sublimation
100 ^oC

Pyrolysis
700 ^oC

Polymerization
25 ^oC

To LN_2 trap and pump

P ~ 0.1 mbar

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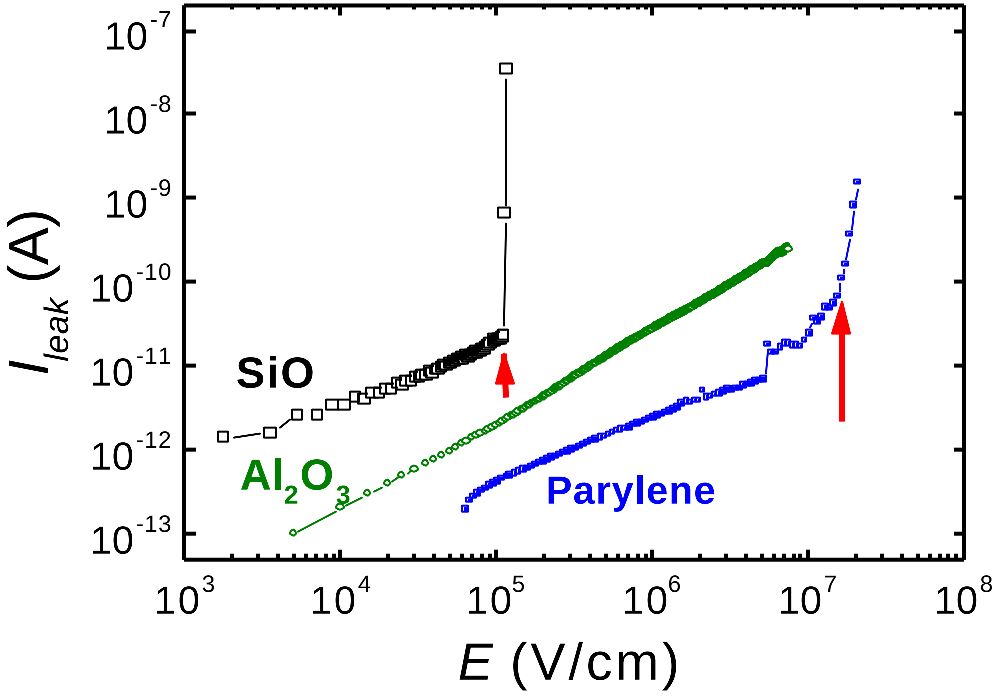
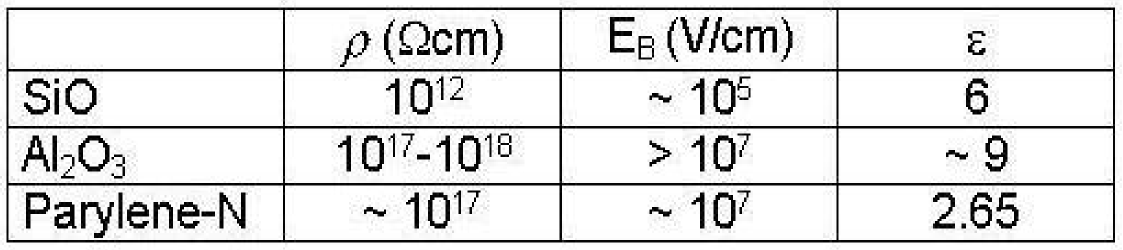
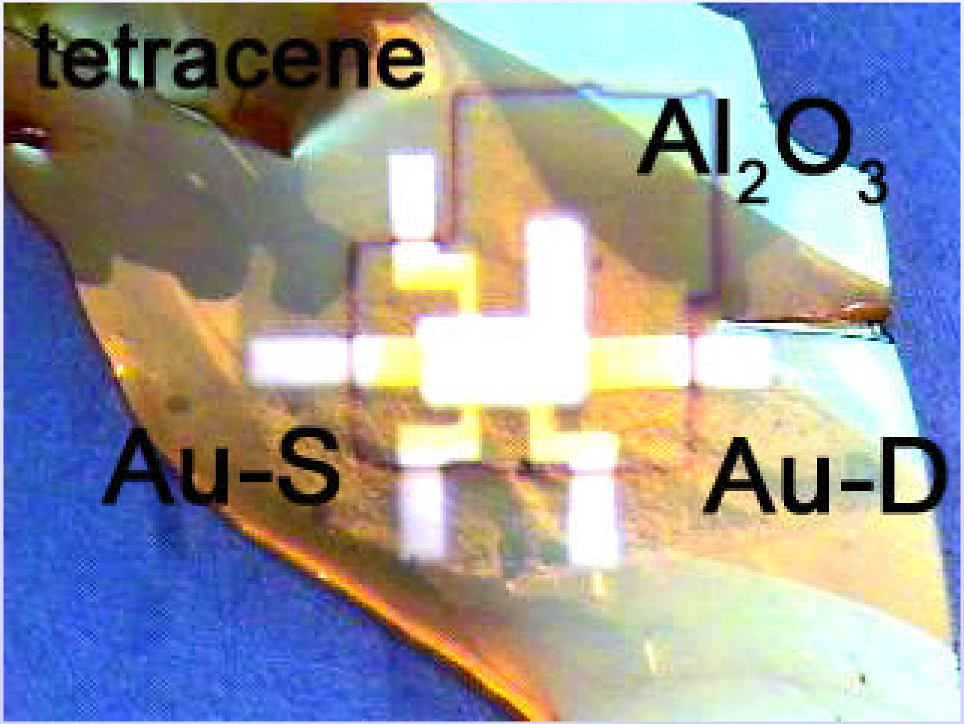
Breakdown characteristics





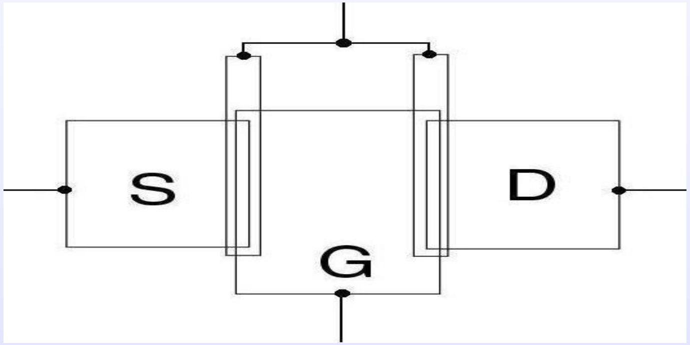
	ρ (Ωcm)	E_B (V/cm)	ε
SiO	10^{12}	~ 10^{5}	6
Al_2O_3	10^{17}-10^{18}	> 10^{7}	~ 9
Parylene-N	~ 10^{17}	~ 10^{7}	2.65

OFET on tetracene

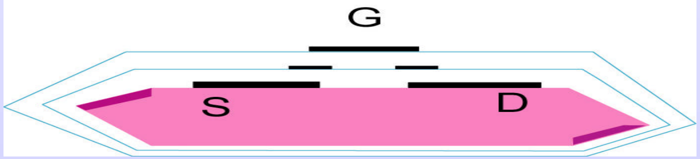


The OFET is “dead on arrival” – because of the Al_2O_3 gate insulator, but the photo shows all essential elements.

Double-gate OFET on rubrene

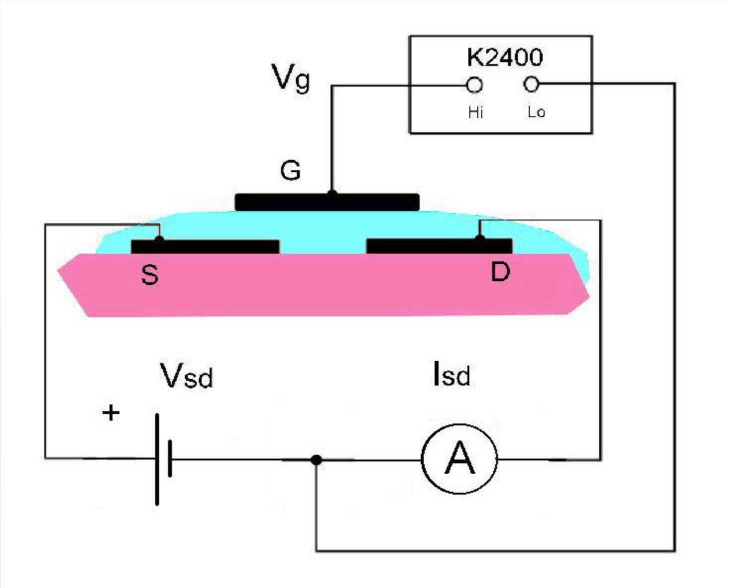


TOP VIEW

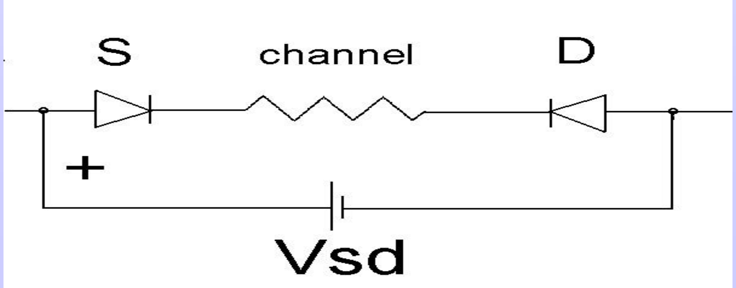


SIDE VIEW

2-probe and 4-probe configurations

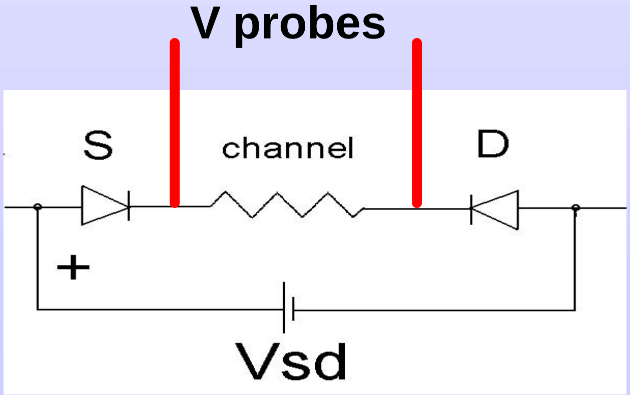


Conventional 2-probe measurements



The resistance of the Schottky barriers at the metal/organics interface is large, and it depends on both V_g and V_{SD}.

To eliminate the contact effects, we used the 4-probe configuration:



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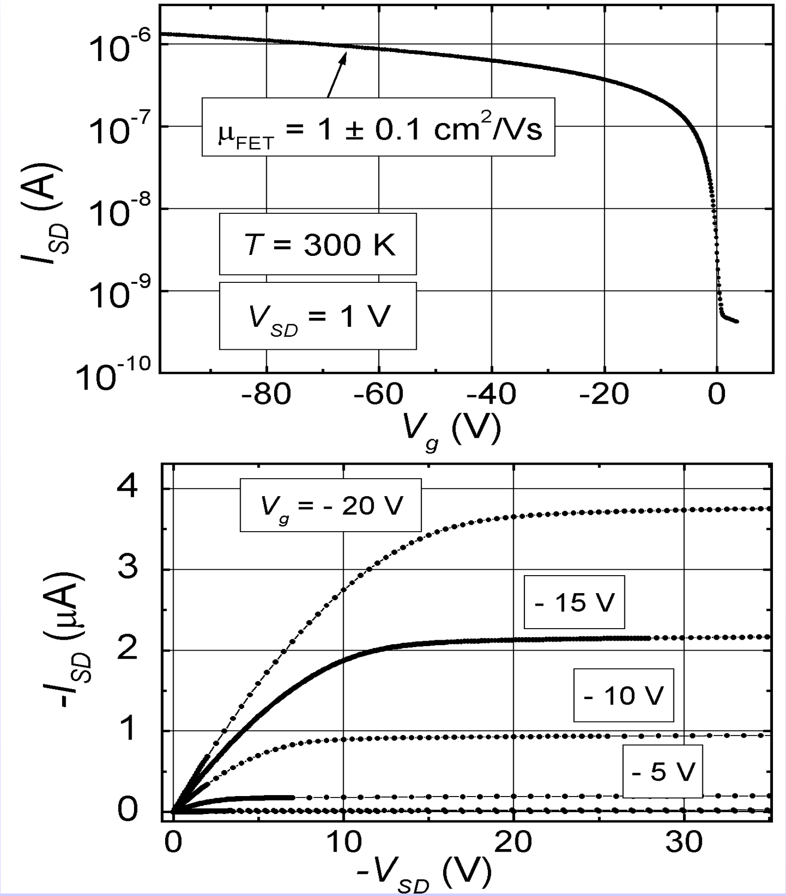
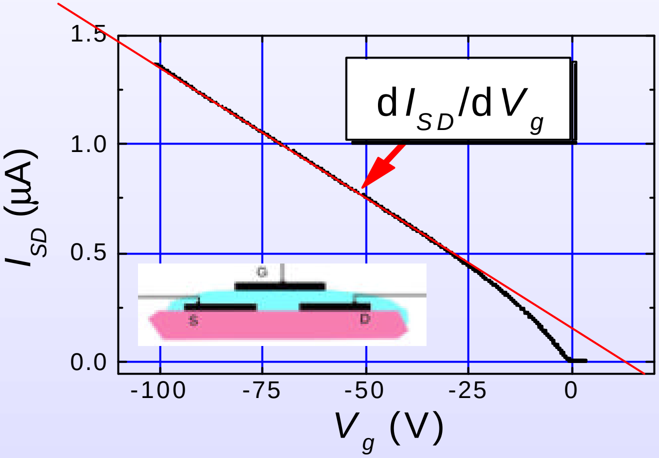
Transistor characteristics of rubrene OFETs





$$\sigma_{2D} = en_{2D}\mu$$

$$en_{2D} \propto CV_g$$

$$\mu \propto (\partial I_{SD}/\partial V_g)/V_{SD}$$

Unipolar FET with the hole conductivity

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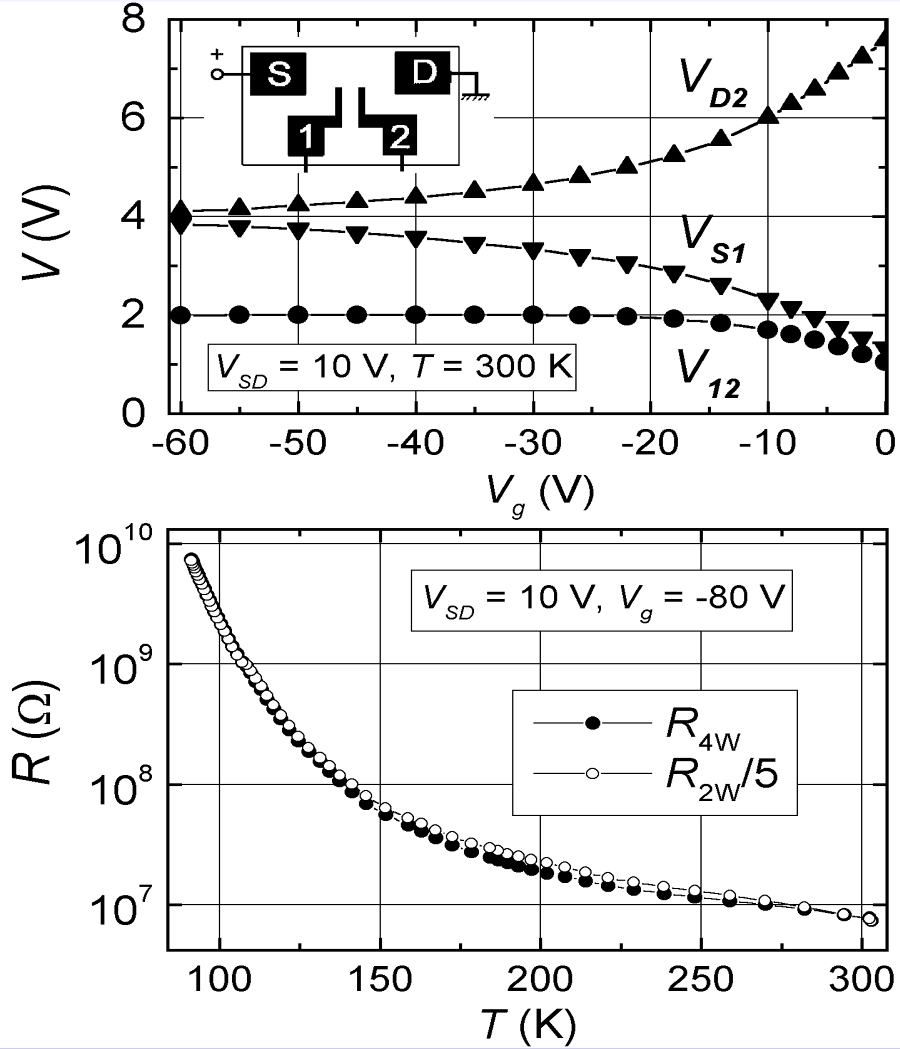
Can we trust the 2-probe measurements?



The resistance of Schottky barriers at the interface metal/organics diminishes with the increase of the carrier density (large |V_g|).

At room temperature, the contact resistance can be made negligibly small, provided a sufficiently large V_g is applied.

With cooling, however, the contact resistance increases significantly…

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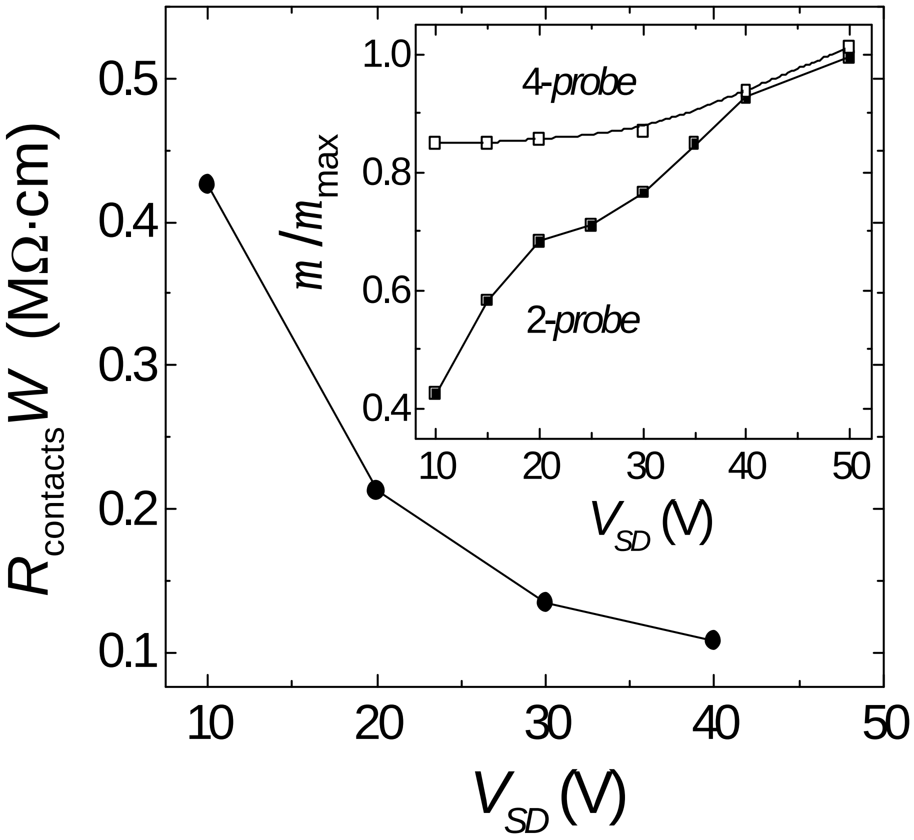
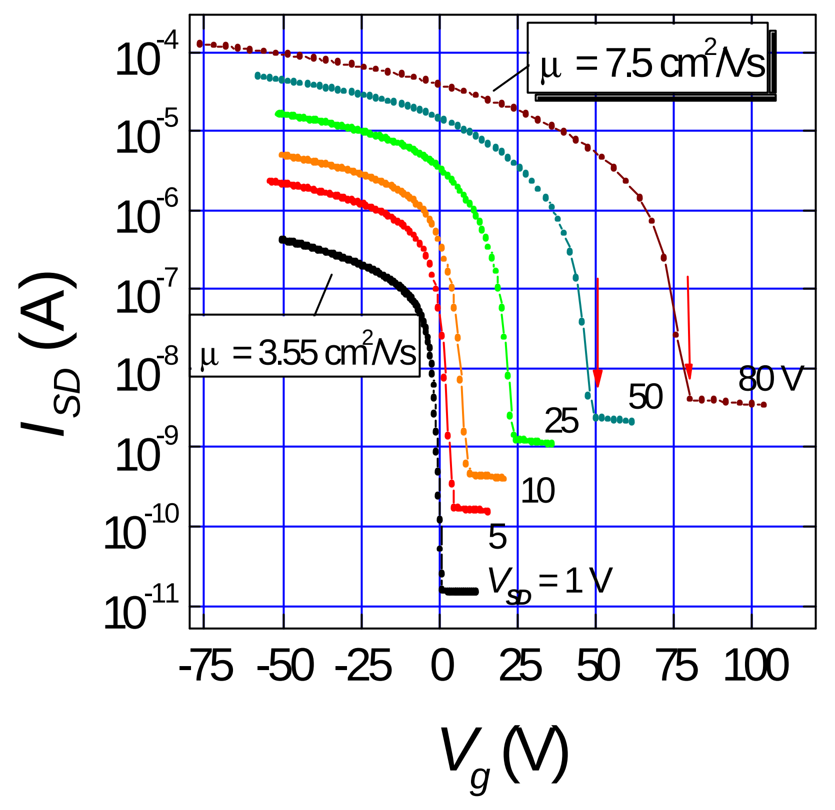
Contact effect in 2-probe measurements



The contact resistance is also a function of the source-drain voltage: it decreases with increasing V_{SD}. For this reason, in the low-T measurements, a large V_{SD} is usually applied.

The "apparent" carrier mobility in the 2-probe measurements depends on V_{SD}, while the "4-probe" mobility is almost V_{SD}-independent.

Threshold-free operation of rubrene OFETs



Two-probe measurements at room temperature

Application of V_{SD} in the presence of the gate electrode only 1 mm away from the interface creates a strong electric field normal to the crystal surface, and induces propagation of the conducting channel from source to drain.

The onset of the field-effect conductivity – at $V_g^{onset} = V_{SD}$.

threshold-free operation Û the density of charge traps is very low for rubrene facets, at least at T = 300K (for tetracene and TCNQ, the threshold is non-zero even at room temperature).

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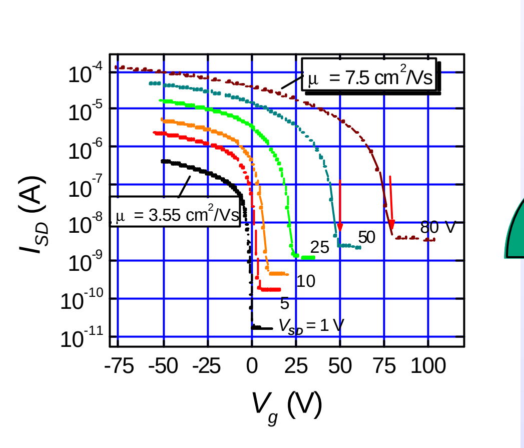
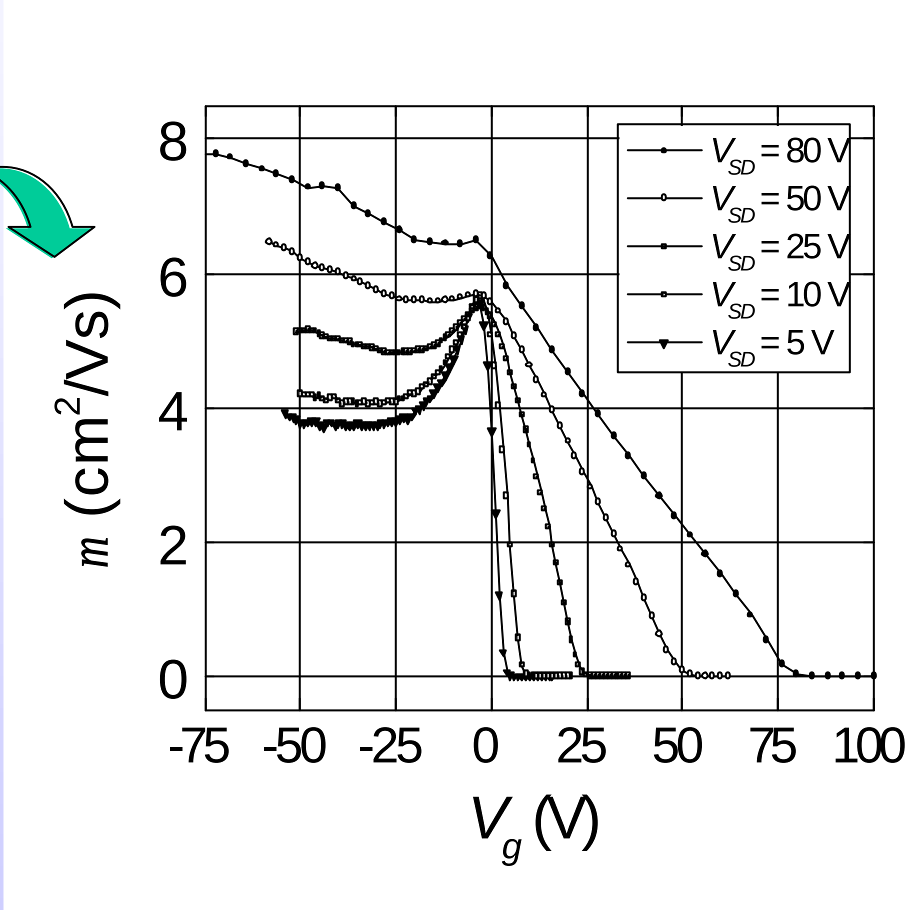
(almost) V_g-independent mobility





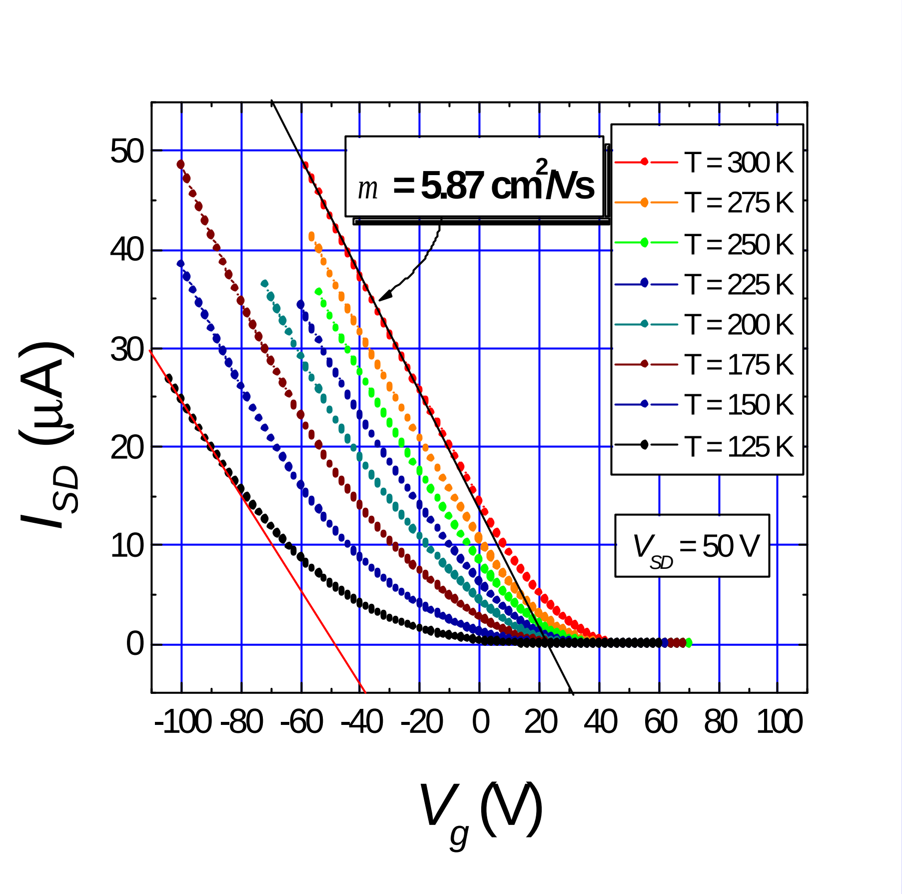
Roughly, m does not depend on the hole density.

For comparison, in the thin-film OFETs, m typically varies by a factor of 10 with V_g.

Room-temperature performance of rubrene FETs

- **Mobility** – **approx. 10 times greater than in thin-film OFETs and a :Si MOSFETs, does not depend on *n* and V_{SD}.**
- **Threshold** – **none**
- **On/off ratio** – **can be > 10^{7}.**
- **Sub-threshold slope** – **an order of magnitude better than in thin-film OFETs and a :Si MOSFETs.**

What happens with cooling?



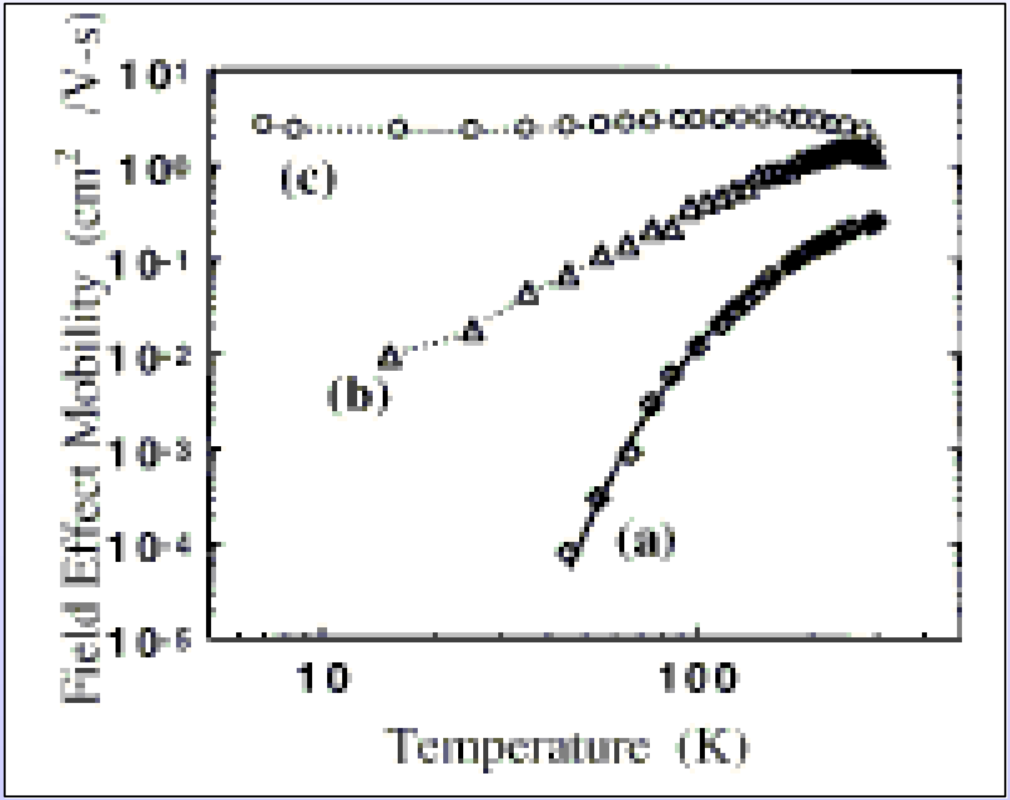
Apparent increase of the threshold – mostly due to the increase of the contact resistance at low *T*.

The mobility changes insignificantly with *T*, if m is large enough at *T*=300 K (³ 1 cm²/Vs).

Note that a weakly temperature-dependent mobility in a 2D system with $R_\square$ >1 MW is a non-trivial fact – still “classical” transport…

2-probe measurements

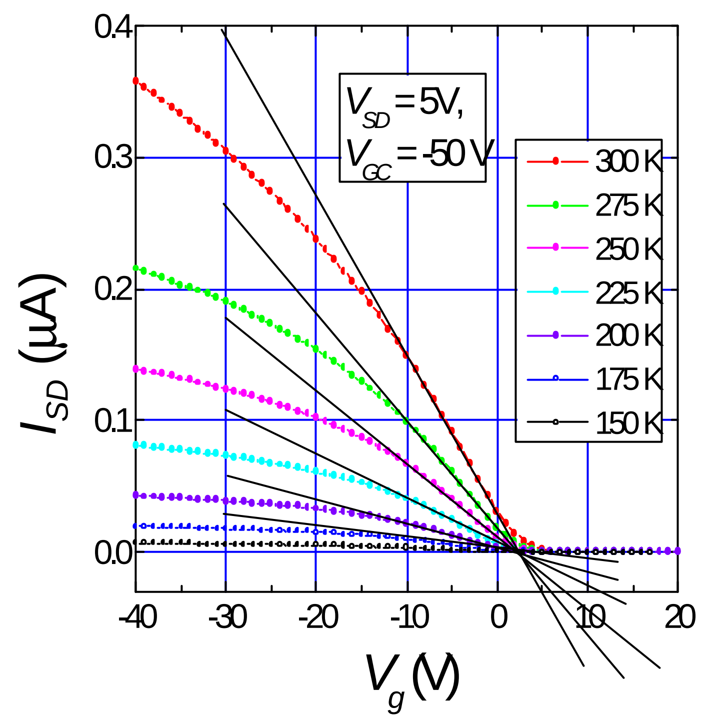
m(*T*) in thin-film OFETs

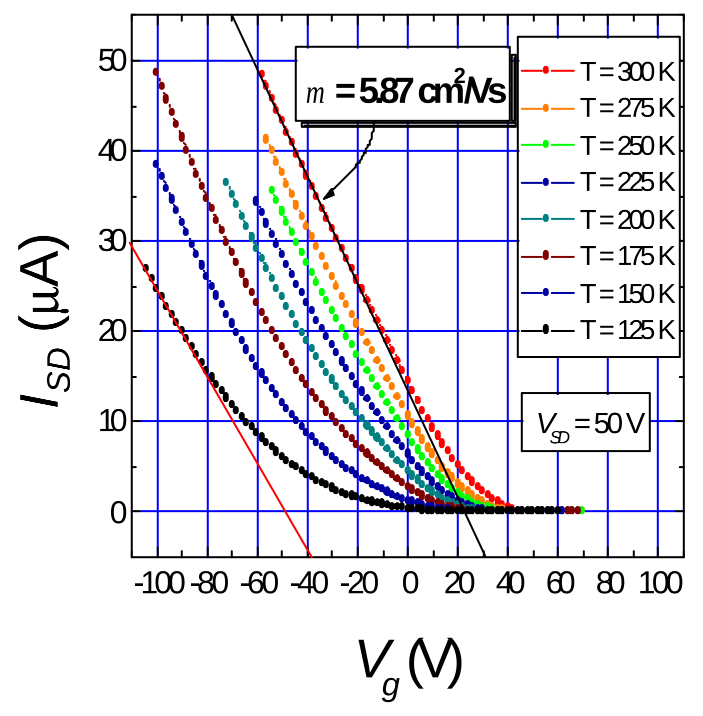


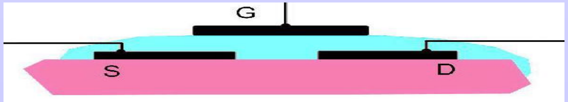
The field-effect mobility in OFETs based on highly-oriented pentacene films.

Nelson et al., *APL* **72**, 1854 (1998).

Double-gate FET vs. single-gate FET







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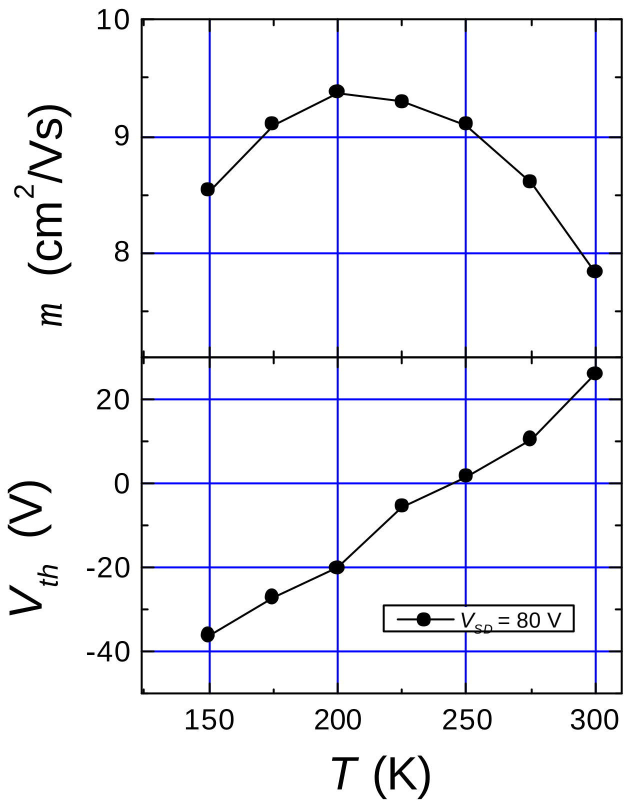
What happens with cooling (cont.)



The results of more careful, 4-probe measurements:

- **the dependence m(*T*) is weak and non-monotonic (competition between two mechanisms?)**

- **the threshold does increase with cooling (depopulation of the charge traps?)**

Summary

- **We have developed a technique for fabrication of single-crystal organic FETs (crystal growth, low-resistance contact fabrication, gate insulator deposition). The devices are suitable for low-temperature experiments.**

- **The single-crystal OFETs outperform both the thin-film OFETs and a:*Si* MOSFETs (mobility, sub-threshold slope, etc.). Comparison between single-crystal and thin-film OFETs helps to identify the characteristics of the latter devices, associated with the structural defects in thin organic films.**

- **The physics of the charge transport in the OFETs is still a "terra incognita", which, despite some technical problems, might be a very exciting field in the future…**

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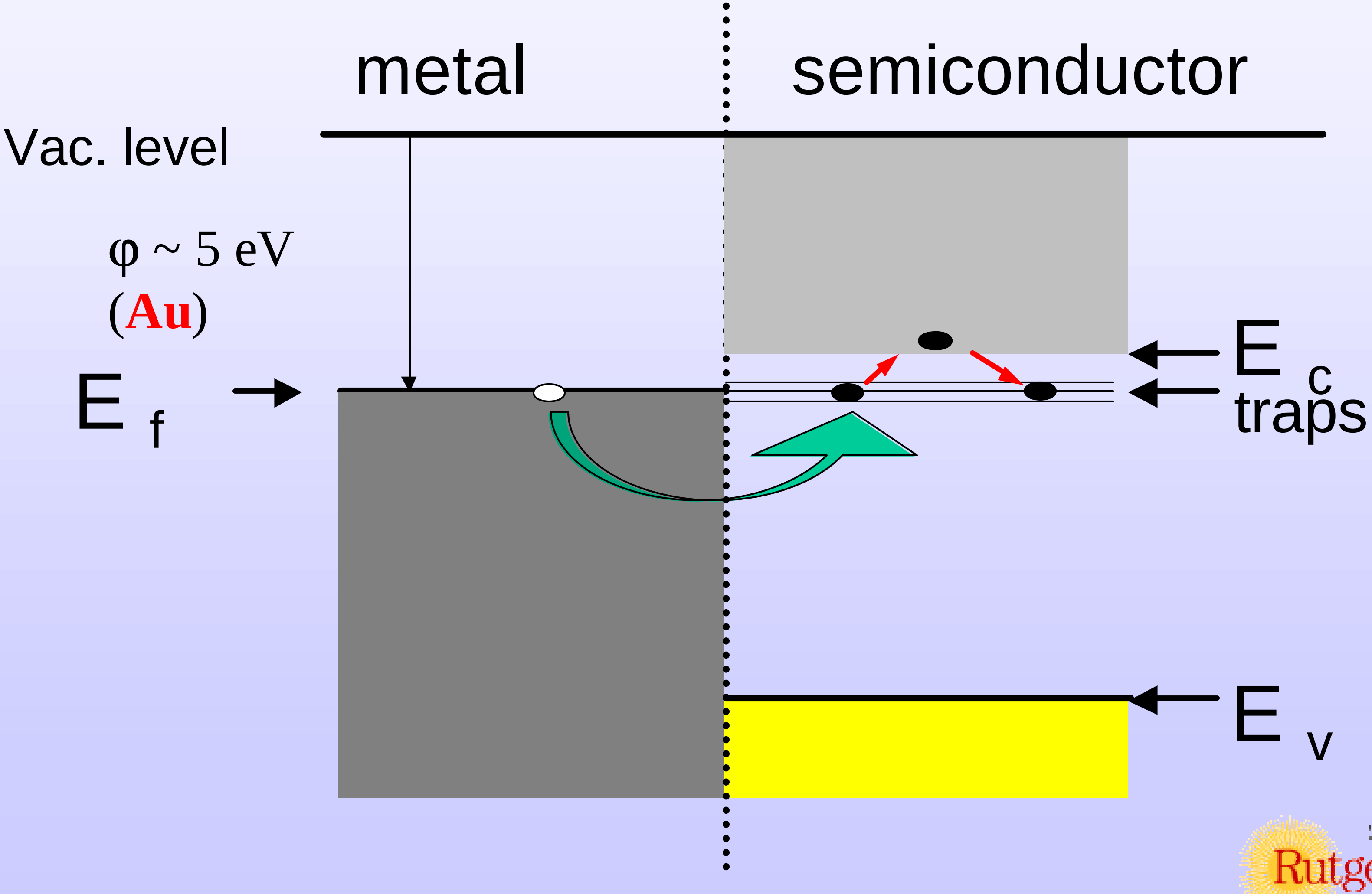
Open issues

- **The mechanism of conductivity in OFETs at high temperatures (polarons?),**
  - **characterization of the charge carriers (m*, etc.)**
  - **the role of molecular packing in organic crystals.**

- **Realization of a high mobility of surface carriers at low *T***
  - **observation of a crossover to a “band” transport**
  - **quantum effects in the conductivity.**

- **Non-trivial photoconductivity**

Electron-injecting contact



metal

semiconductor

Vac. level

φ ~ 5 eV

(**Au**)

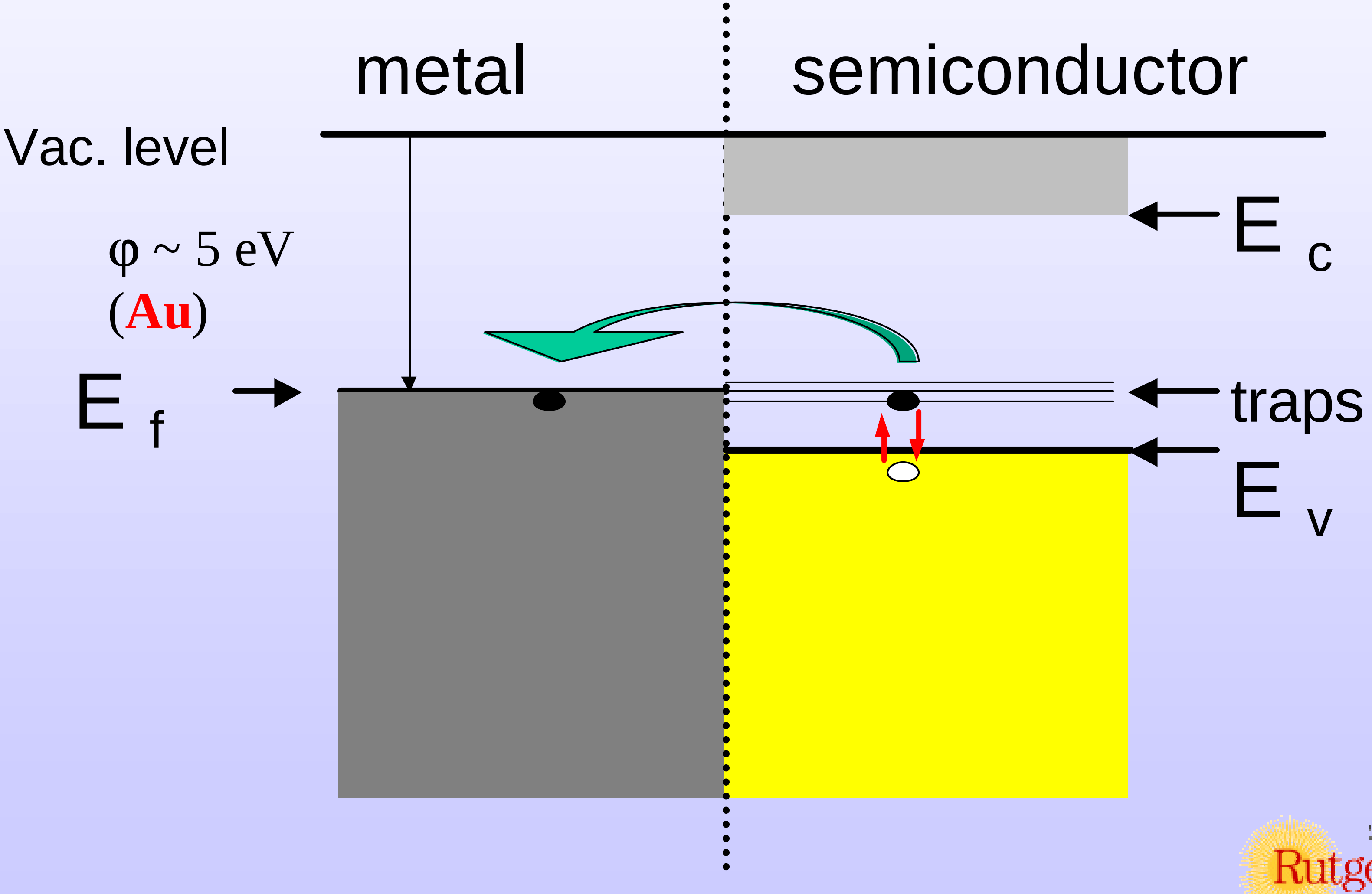
E_f

E_c

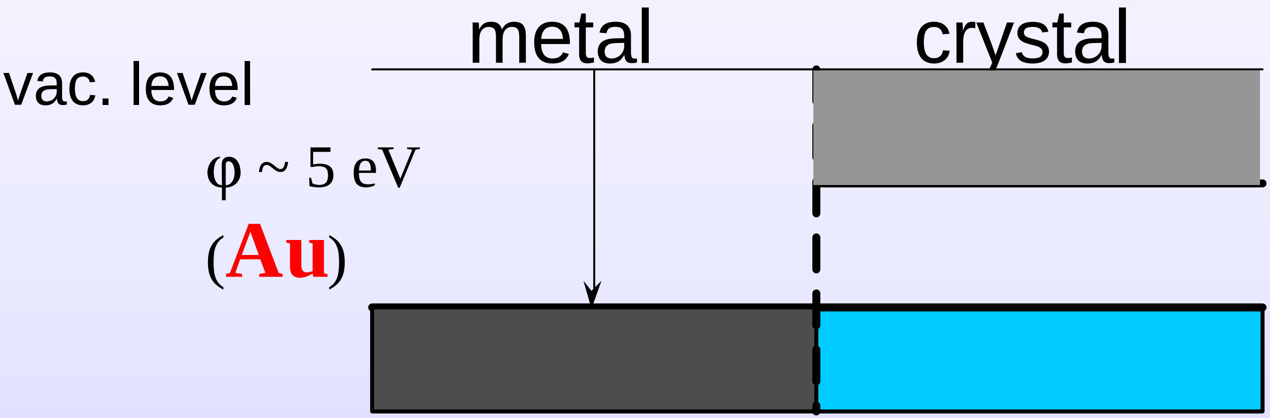
traps

E_v

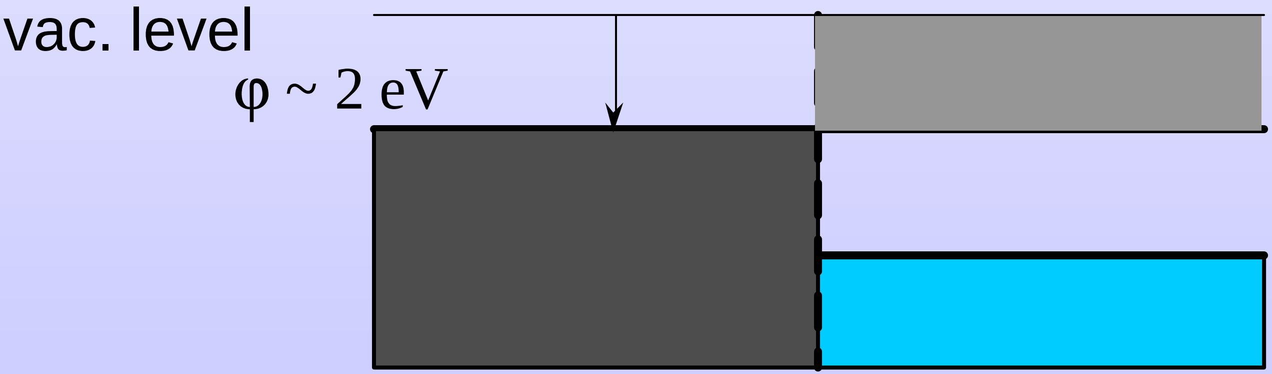
Hole-injecting contact



Contacts “metal-organics”

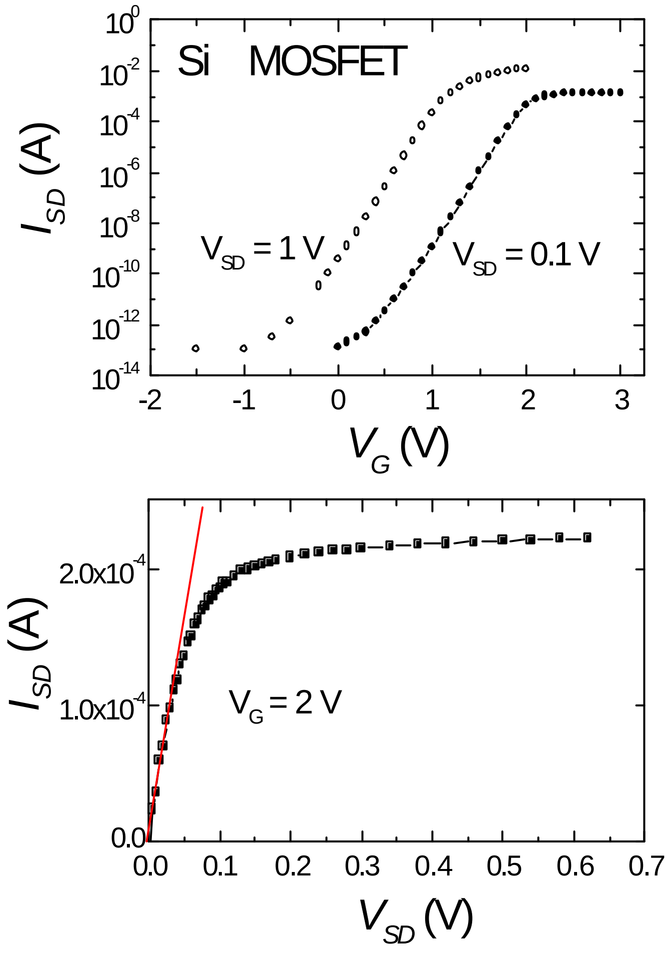


hole-injecting contact



electron-injecting contact

Commercial Si MOSFET



On/Off = 10^{10}

$\mu > 100\ \mathrm{cm^2/Vs}$

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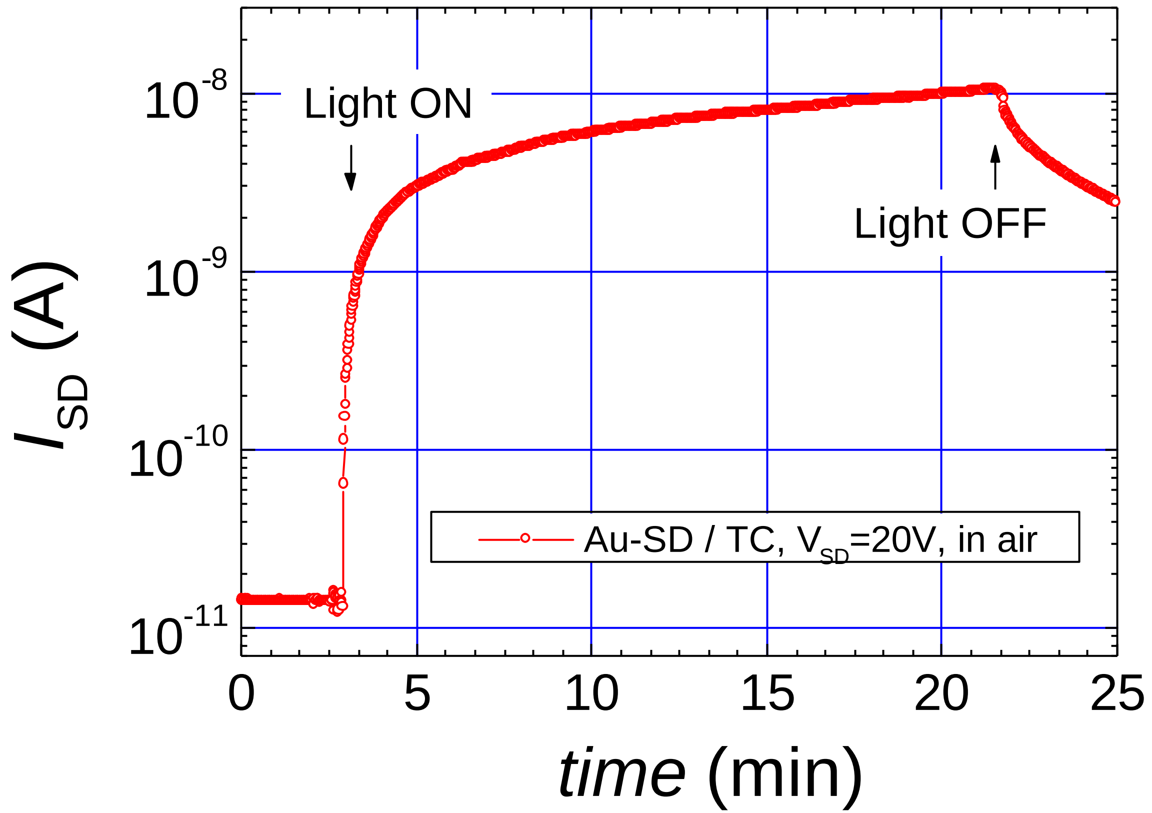
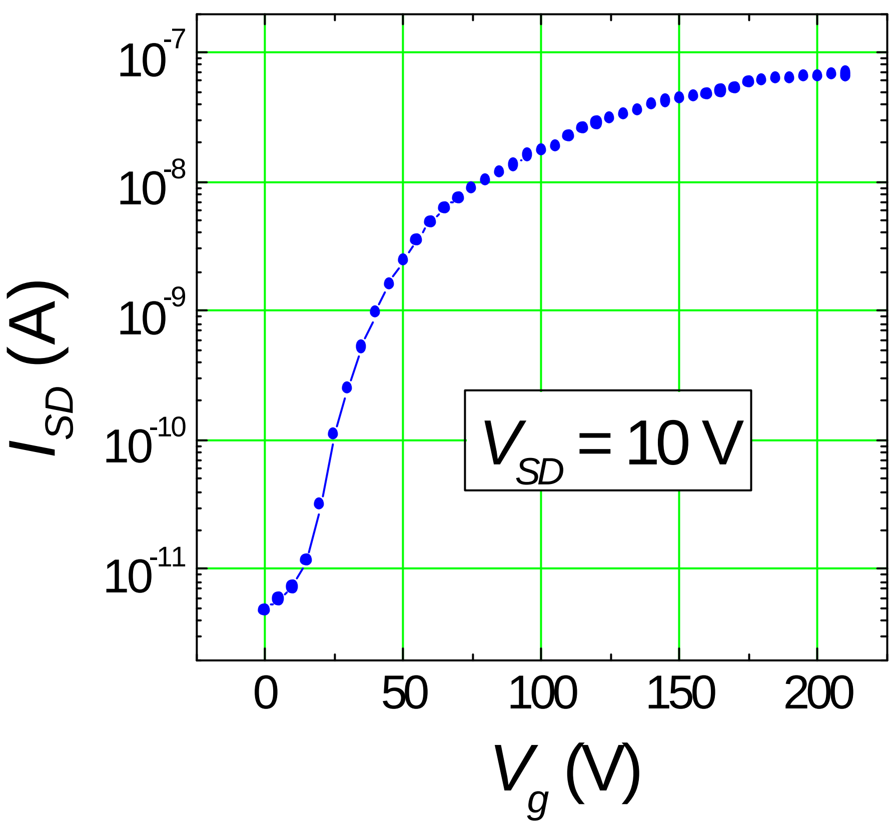
Photoconductivity



n-type conductivity in TCNQ-FET



m **~ $5\text{x}10^{-2}$ cm^2/Vs**

(the best previously reported result for TCNQ - m **~ $3\text{x}10^{-5}$ cm^2/Vs)**

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