



Tutorial: Organic Single Crystals 101

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<http://iamdn.rutgers.edu/>

**Fall MRS 2012
Nov. 25, 2012 (Boston, MA)**

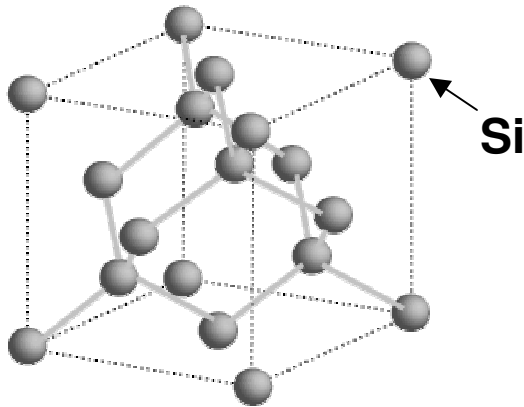
Outline:

1. Various types of semiconductors important in modern technology.
2. Phenomenological description of charge carrier mobility.
3. Importance of organic single crystal research for Organic Electronics.
4. Experimental methods of mobility determination:
 - 4.1. Time of Flight (TOF) measurements;
 - 4.2. Space-charge limited current (SCLC) measurements;
 - 4.3. Organic Field-Effect Transistor (OFET) measurements.
5. Organic single-crystal FETs:
 - 5.1. OFETs with parylene insulator;
 - 5.2. OFETs with org. crystals laminated on Si/SiO₂ wafer;
 - 5.3. OFETs based on PDMS elastomeric stamps;
 - 5.4. OFETs by vacuum lamination.
6. OFET operation modes: Linear vs. Saturation regimes.
7. 4-probe OFET measurements - addressing Schottky contact resistance.
8. Mobility anisotropy and non-activated transport in single-crystal OFETs.
9. Importance of deep and shallow traps.
10. Photo-induced phenomena in OFETs.

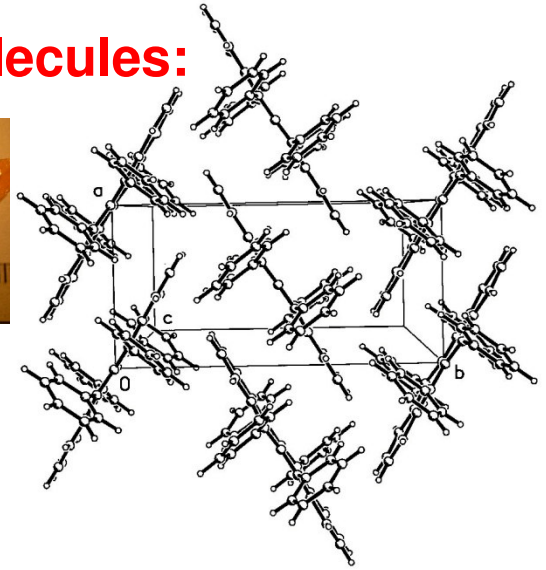
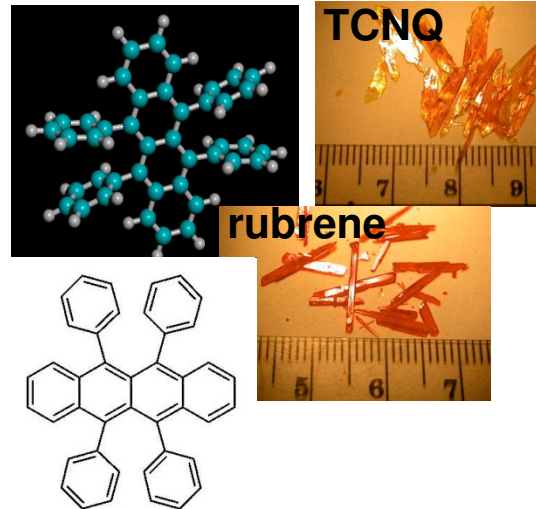
<http://www.physics.rutgers.edu/~podzorov/index.php>

1. Different types of semiconductors

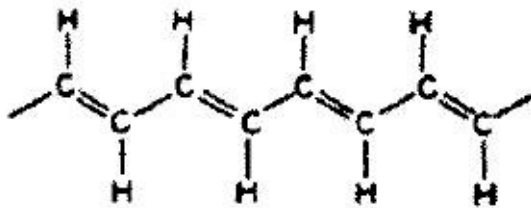
1. Inorganic: Si, Ge, GaAs



2. Organic small-molecules:



3. Conjugated Polymers

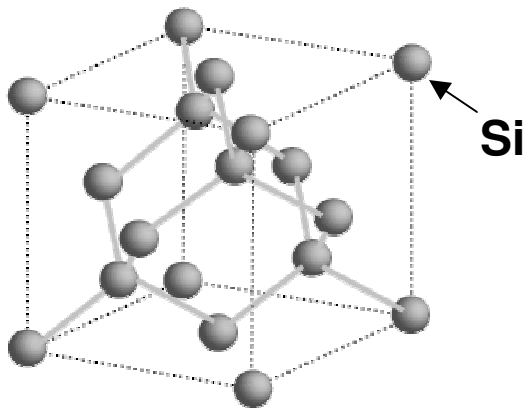


Two types of bonding in organic materials:

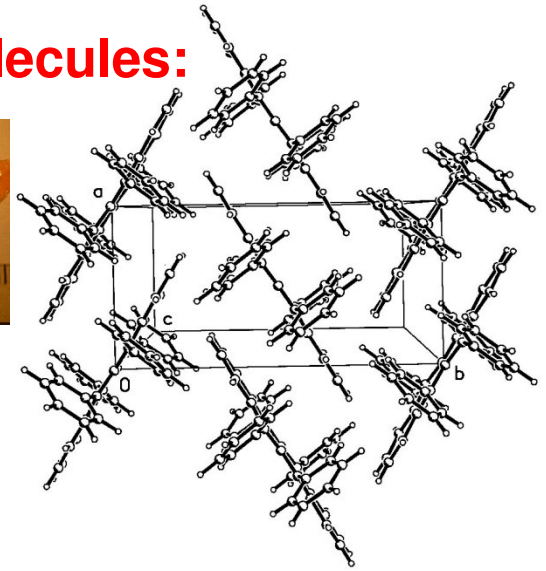
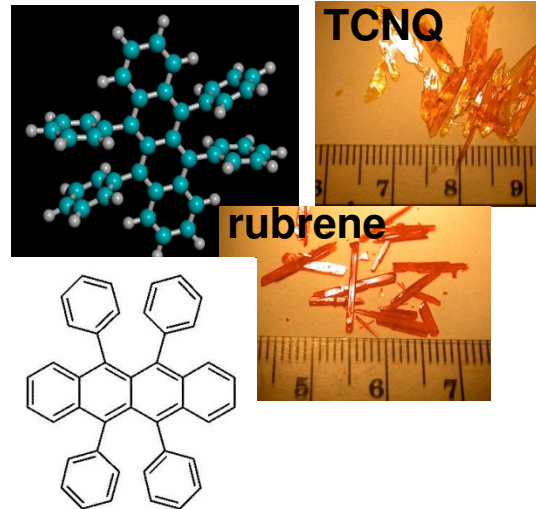
1. Intra-molecular: C-C or C-H
2. Inter-molecular: van der Waals

1. Different types of semiconductors

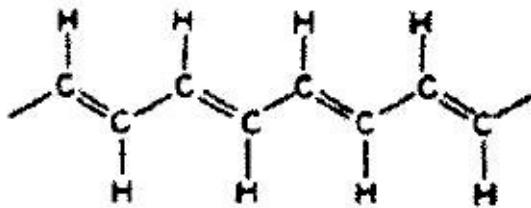
1. Inorganic: Si, Ge, GaAs



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Two types of bonding in organic materials:

1. Intra-molecular: C-C or C-H

2. Inter-molecular: van der Waals

Comparison of electronic properties of inorganic and organic semiconductors

Si, Ge, GaAs	small-molecule organics
strong covalent bonding	weak van der Waals bonding
↓	↓
large bandwidth, $W \sim 10$ eV	narrow bands, $W \sim 0.1 - 0.3$ eV
↓	↓
high mobility of electrons and holes, $\mu \sim 500$ cm ² /Vs	low mobility of small polarons, $\mu \sim 1 - 10$ cm ² /Vs

Small-molecule organic materials for OFETs: wide-gap undoped semiconductors (for rubrene, the HOMO-LUMO gap = 2.2 eV)

Why mobility is important?

Definition of mobility

Because drift velocity of charge carrier is $v = \mu E$, and hence the higher the μ , the faster the electronic circuits.

2. Phenomenological description of mobility

In a viscous medium, drift velocity is proportional to external force:

$$v = \mu F$$

For a charged particle moving under the influence of an external electric field in a medium that exerts a “friction force” on the particle, drift velocity is proportional to the external electric field:

$$v = \mu E$$

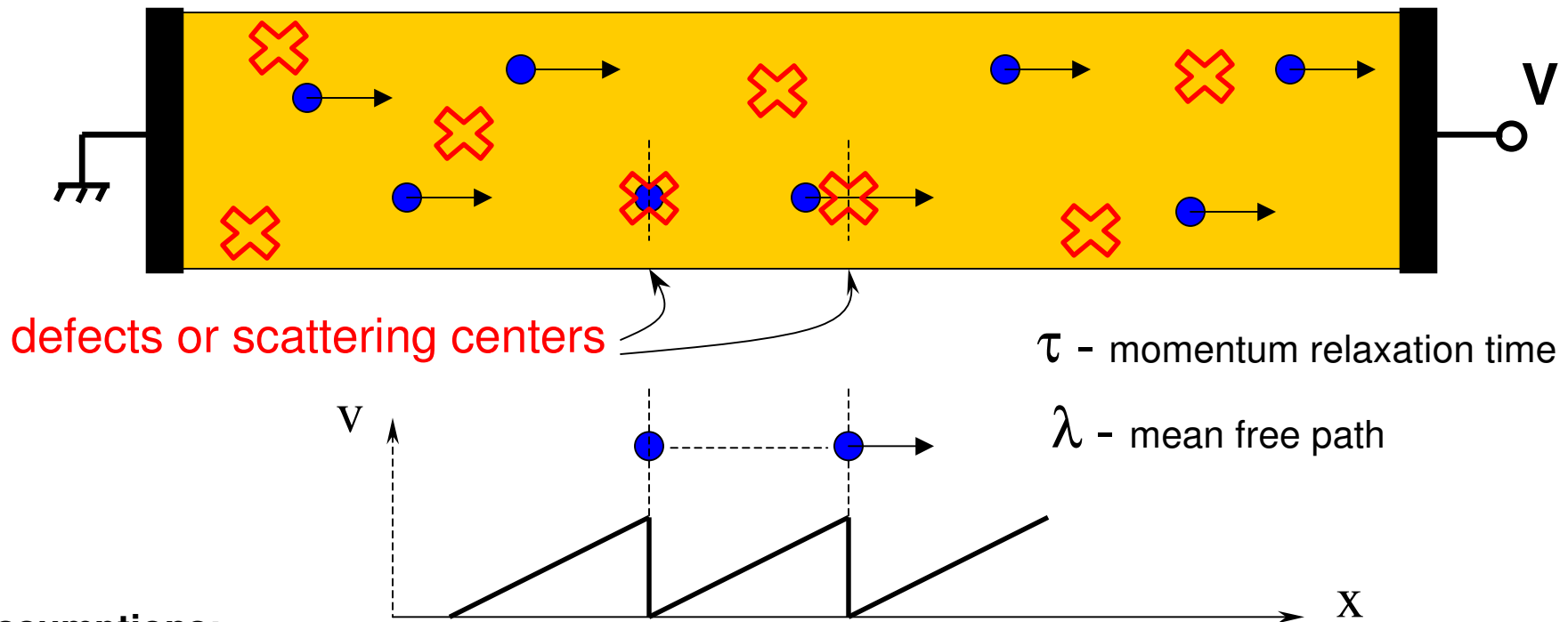
Definition of mobility

Units of μ ? [cm²V⁻¹s⁻¹]

Mobility is a quasi-static physical characteristics defined for a stabilized (constant) average drift velocity of the carrier motion in a material, established as the result of balance between the external driving force and the “friction force” .

In other words, mobility is a purely *dc* characteristics of the material important for conductivity.

Mobility: Drude model



Assumptions:

1. Charge carriers are delocalized (mean free path is much greater than lattice constant, $\lambda \gg a$);
2. Scattering occurs NOT on the ionic skeleton of the lattice, but on phonons (dynamic disorder) and irregular structural defects, e.g., impurities, dopants, etc, (static disorder);
3. Scattering is completely inelastic (kinetic energy of the charge is lost in collision, velocity becomes zero);

Mobility, momentum relaxation time and mean free path

Drift velocity: $v = \mu E = (e\tau/m^*)E \sim 1 \text{ m/s}$

$$\text{Mobility: } \mu = e\tau/m^*$$

Mean free path: $\lambda = \tau v$, where v is thermal velocity

Thermal velocity: $v = (3kT/m^*)^{1/2} \sim 10^5 \text{ m/s at RT}$

$$\text{Mobility: } \mu = e\lambda/(vm^*)$$

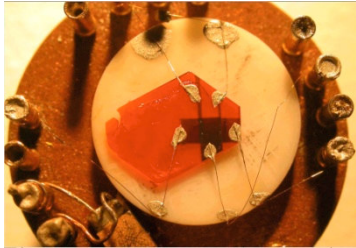
The T-dependence of the mobility depends on the effective mass, scattering mechanisms (phonons, charged impurities, screening, etc). In most of the band semiconductors:

$$\mu(T) \propto T^{-n}, \text{ where } n > 0, \lambda \gg a$$

meaning that μ increases when T is lowered. For organic semiconductors, this simple theory fails, because λ becomes comparable to the lattice constant at $T > 100 \text{ K}$.

G. Horowitz in *Organic Field-Effect Transistors*,
Ed. Z. Bao and J. Locklin, pp. 27-72 (Taylor & Francis, 2007).

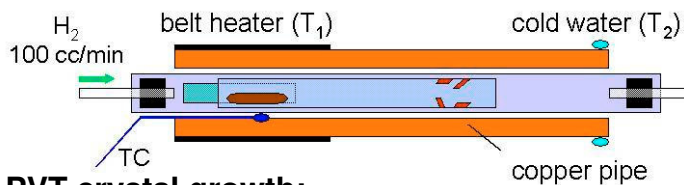
3. Importance of organic single crystal research for Org. El.



High- μ single-crystal OFETs:

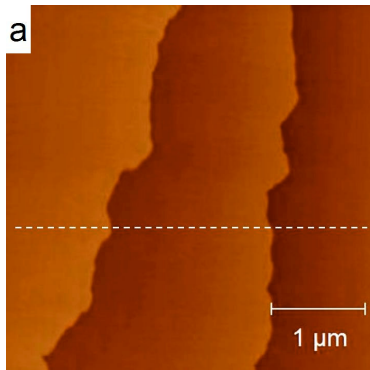
Podzorov *et al.*,
APL **83** 3504 (2003)

- No grain boundaries;
- Self-purifying crystal growth =
= very low impurity content;
- Unprecedented structural order;
- Extremely good surface crystallinity;
- Very good interface quality due to
several recently developed fabrication
techniques for s.-c. OFETs.



PVT crystal growth:

R. A. Laudise, Ch. Kloc, P. G. Simpkins and T. Siegrist,
J. Cryst. Growth (1998).

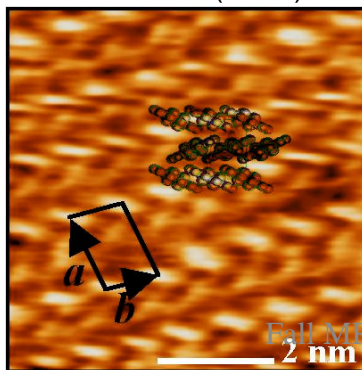


AFM:

B. Lee, T. J. Choi, S-W. Cheong and
V. Podzorov, *Adv. Funct. Mater.* (2009)

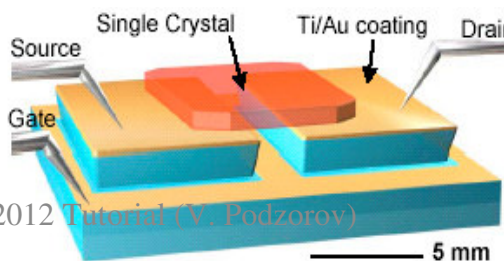
STM:

E. Menard, *et al.*,
Adv. Mater. (2006)



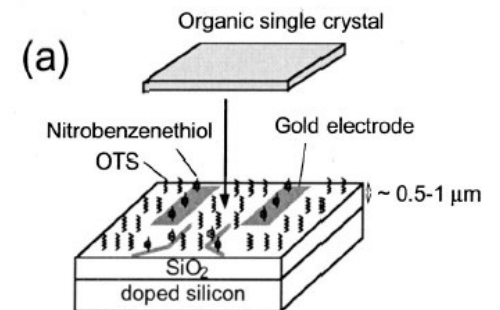
PDMS-stamp OFETs:

Podzorov, *et al.*, *PRL* (2004)
Menard, *et al.*, *Adv. Mater.* (2004)
Sundar, *et al.*, *Science* (2004)

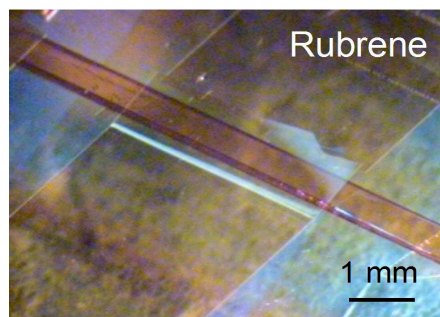
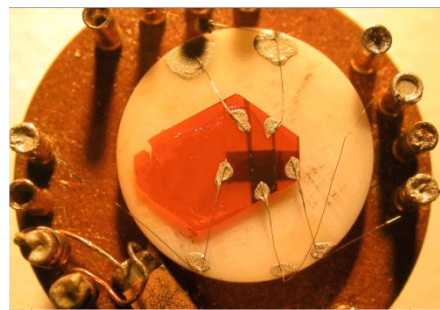
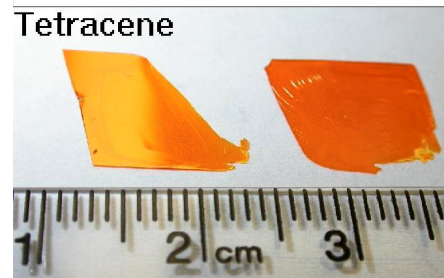
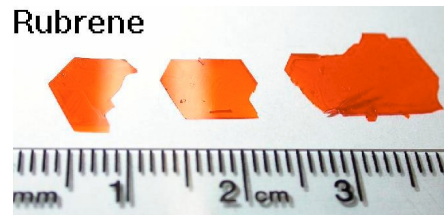


Si/SiO₂-stamp OFETs:

Morpurgo *et al.*, *APL* (2003)
Takeya, Batlogg *et al.*, *JAP* (2003)



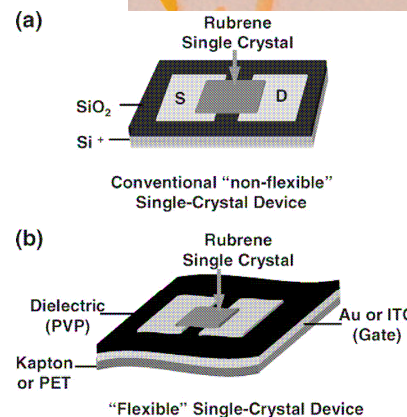
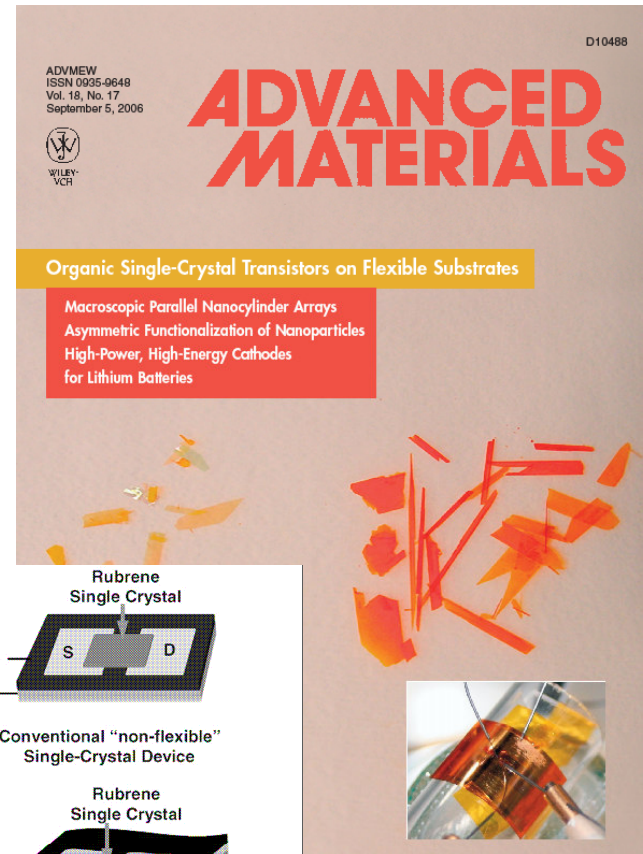
Variable morphology: convenient for different studies



Rutgers (2003-2010)

Thick & bulky

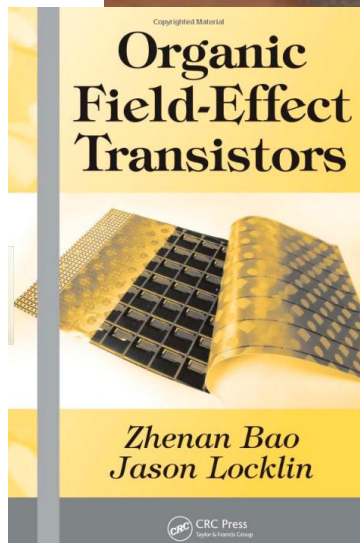
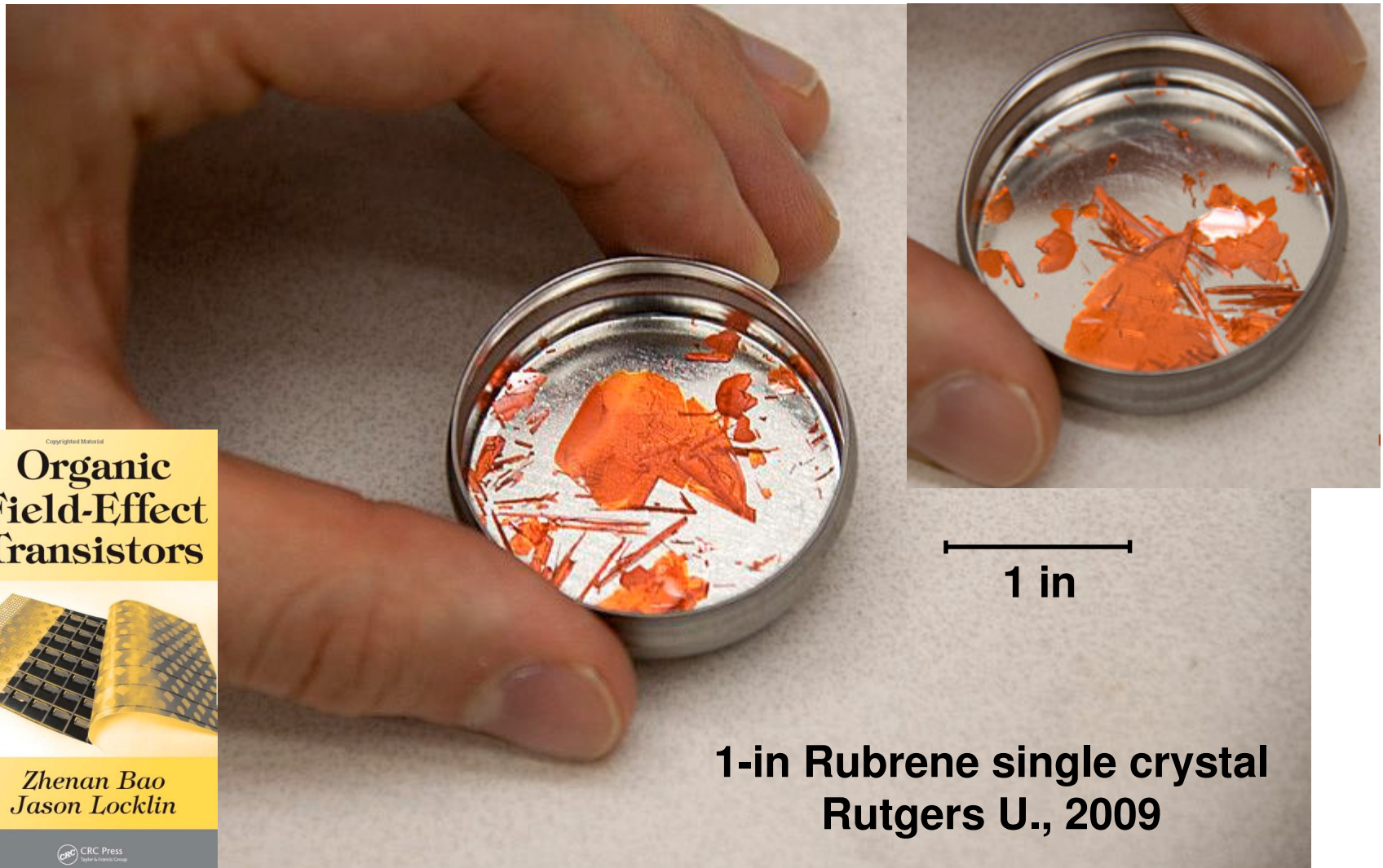
Ultrathin,
< 500 nm



A. L. Briseno *et al.*, *Adv. Mater.* **18**, 2320 (2006)

V. Podzorov, book chapter in *Organic Field-Effect Transistors*, Ed. Z. Bao and J. Locklin, pp. 27-72 (Taylor & Francis, 2007).

Rubrene single crystals



**1-in Rubrene single crystal
Rutgers U., 2009**

1. *Organic Field-Effect Transistors*, Ed. Z. Bao and J. Locklin, (Taylor & Francis, 2007)
2. R. W. I. de Boer, M. E. Gershenson, A. F. Morpurgo and V. Podzorov, "Organic single-crystal field-effect transistors", *Phys. Stat. Solidi* **201**, 1302 (2004)

Fall MRS-2012 Tutorial (V. Podzorov)

Single-crystal Organic Electronic Devices

Single-crystal organic devices have been recognized as a powerful tool for the basic research in Organic Electronics

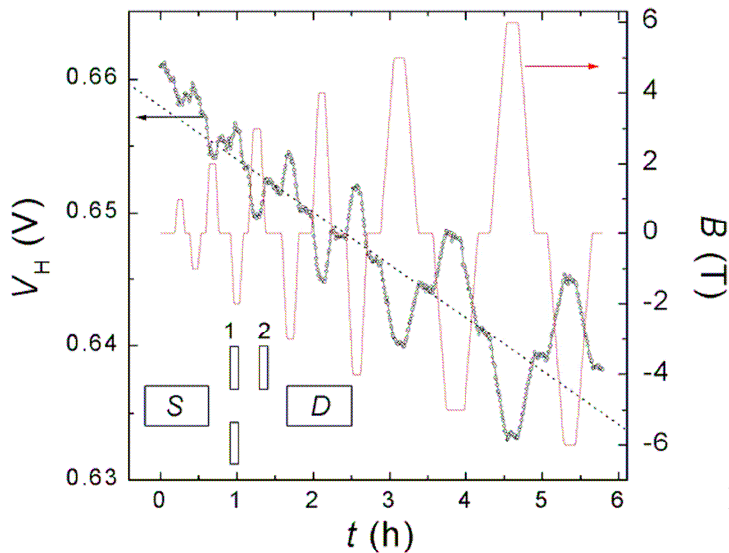
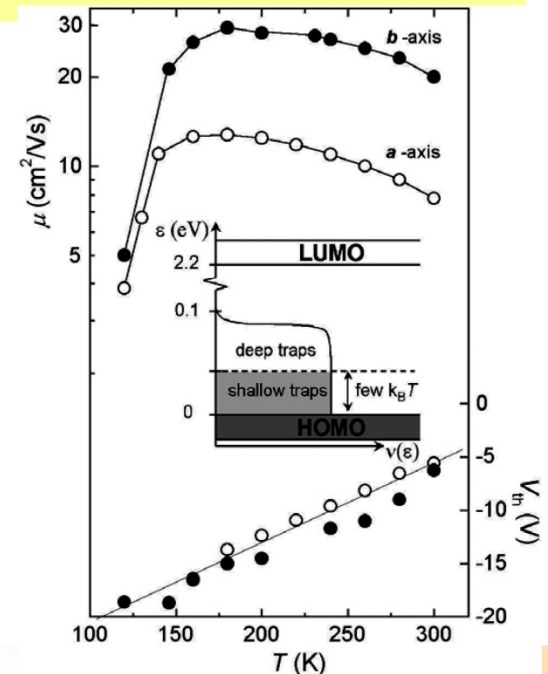
Some of the important results:

- record high mobility in organic transistors;
- observation of non-activated transport and anisotropy of μ ;
- observation of band-like semiconductor Hall effect;
- Interfacial Froelich polarons;
- very large exciton diffusion length.

Podzorov *et al.*,
PRL **93**, 086602 (2004)

Morpurgo *et al.*, *Nature Mater.*, (2009)

Najafov *et al.*,
Nature Mater. **9**, 938 (2010)



Podzorov *et al.*,
PRL **95**, 226601 (2005)

Takeya & Iwasa *JJAP* (2005)

Sekitani & Someya *APL* (2007)

Bao & Reese,
Materials Today (2007)

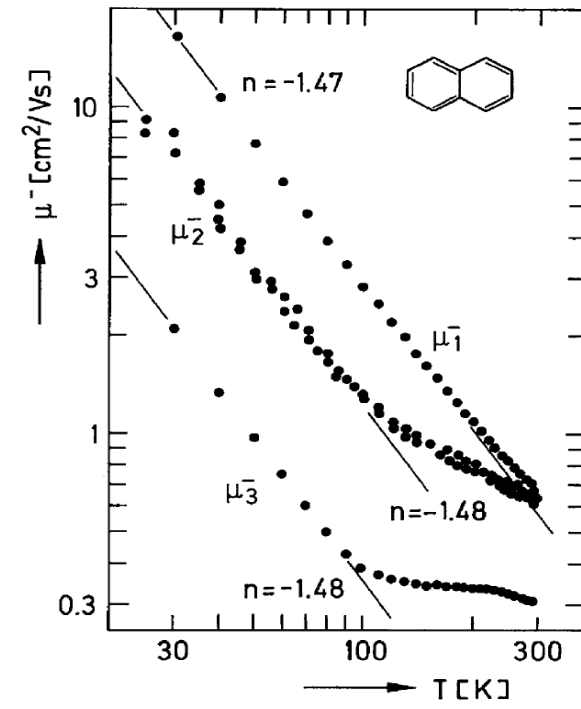
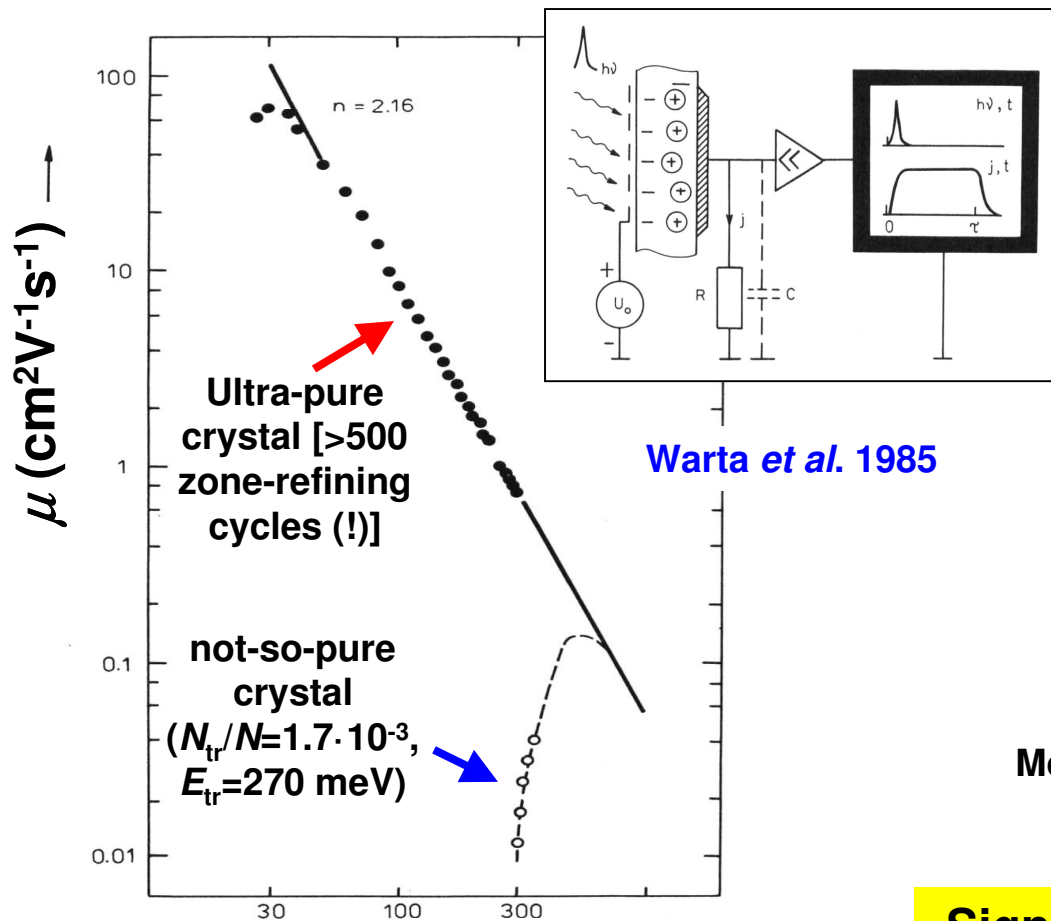
Fall MRS-2012 Tutorial (7. October 2012)



4. Experimental methods of mobility determination

1. Time of Flight (TOF)
2. Space-Charge Limited Current (SCLC)
3. Organic Field-Effect Transistor (OFET)

4.1. TOF experiments with ultra-pure bulk crystals



Mobility of the negative charge carriers in naphthalene (Karl *et al.*, 1985)

Theoretical treatment: $T(\text{K}) \rightarrow$

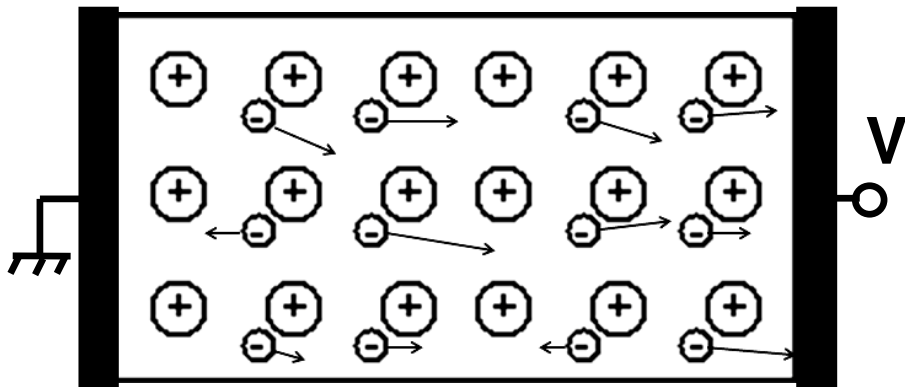
- Kenkre (PRL),
- Bredas *et al.* (JACS, Chem. Rev., PNAS)
- Hannewald & Bobbert (PRB, APL)
- Troisi & Orlandi PRL (2006), Adv. Mater. (2007)
- Fratini & Ciuchi PRL (2009)

Signatures of intrinsic transport:

- $\mu(T) = aT^{-n}$, where $n \sim 1.2 - 2.9$
- anisotropy of μ

4.2. Space-charge limited current (SCLC) measurements: SCLC meas. is a 2-probe I - V measurement in undoped (intrinsic) SC or insulator

The difference between Ohmic conductors and intrinsic semiconductors/insulators:



Metals, doped SC, etc: el. neutral bulk

Ohmic regime holds:

$$j = \sigma E = en\mu E$$

n - mobile carrier density is constant

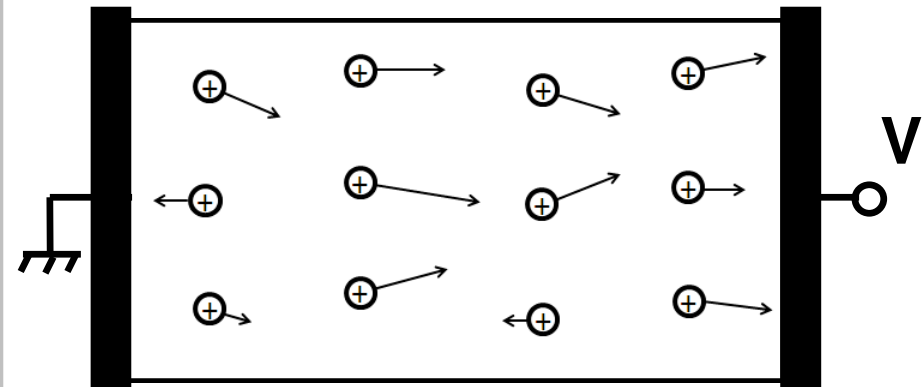
μ - carrier mobility is constant (on average)

$$\text{So, } j = en\mu(V/L)$$

This also comes from the Poisson eq.:

$$dE(x)/dx = en_{\text{tot}}(x)/\epsilon,$$

since $n_{\text{tot}}=0$, $E = V/L = \text{const.}$



**Undoped SC, insulators:
non-zero charge in the bulk**

Non-Ohmic regime:

$$j = \sigma E = en\mu E = e\mu n(x)E(x)$$

j is constant (does not depend on x)

From the Poisson eq.:

$$dE(x)/dx = en(x)/\epsilon = j/(\epsilon\mu E(x)),$$

$$E(x)dE = j/(\epsilon\mu)dx$$

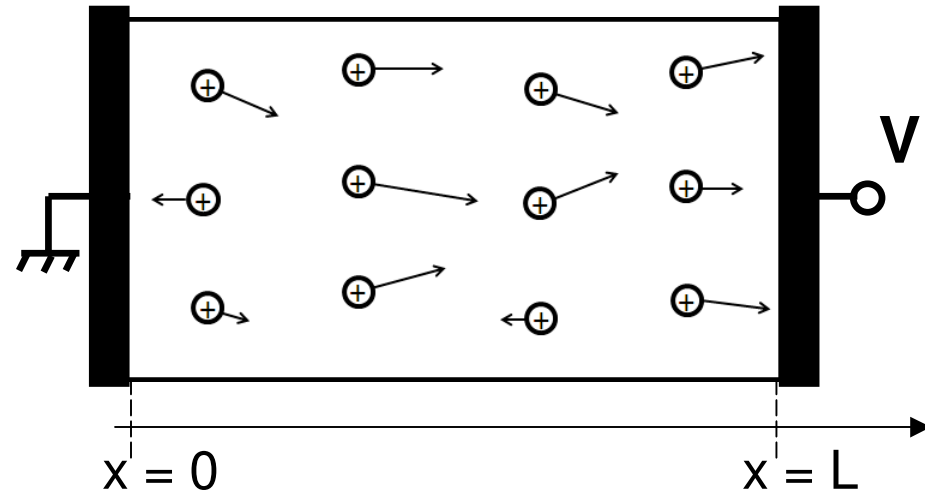
$$E(x) = (2j/\epsilon\mu)^{1/2}\sqrt{x}$$

$$n(x) = (\epsilon j/2e^2\mu)^{1/2}/\sqrt{x}$$

4.2. Space-charge limited current (SCLC) measurements

$$E(x) = (2j/\epsilon\mu)^{1/2}\sqrt{x}$$

$$n(x) = (\epsilon j/2e^2\mu)^{1/2}/\sqrt{x}$$



$$\Delta\phi = V = \int_0^L E(x)dx = (2j/\epsilon\mu)^{1/2} \int_0^L \sqrt{x}dx = (2j/\epsilon\mu)^{1/2}(2/3)(L)^{3/2}$$

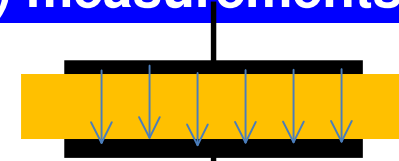
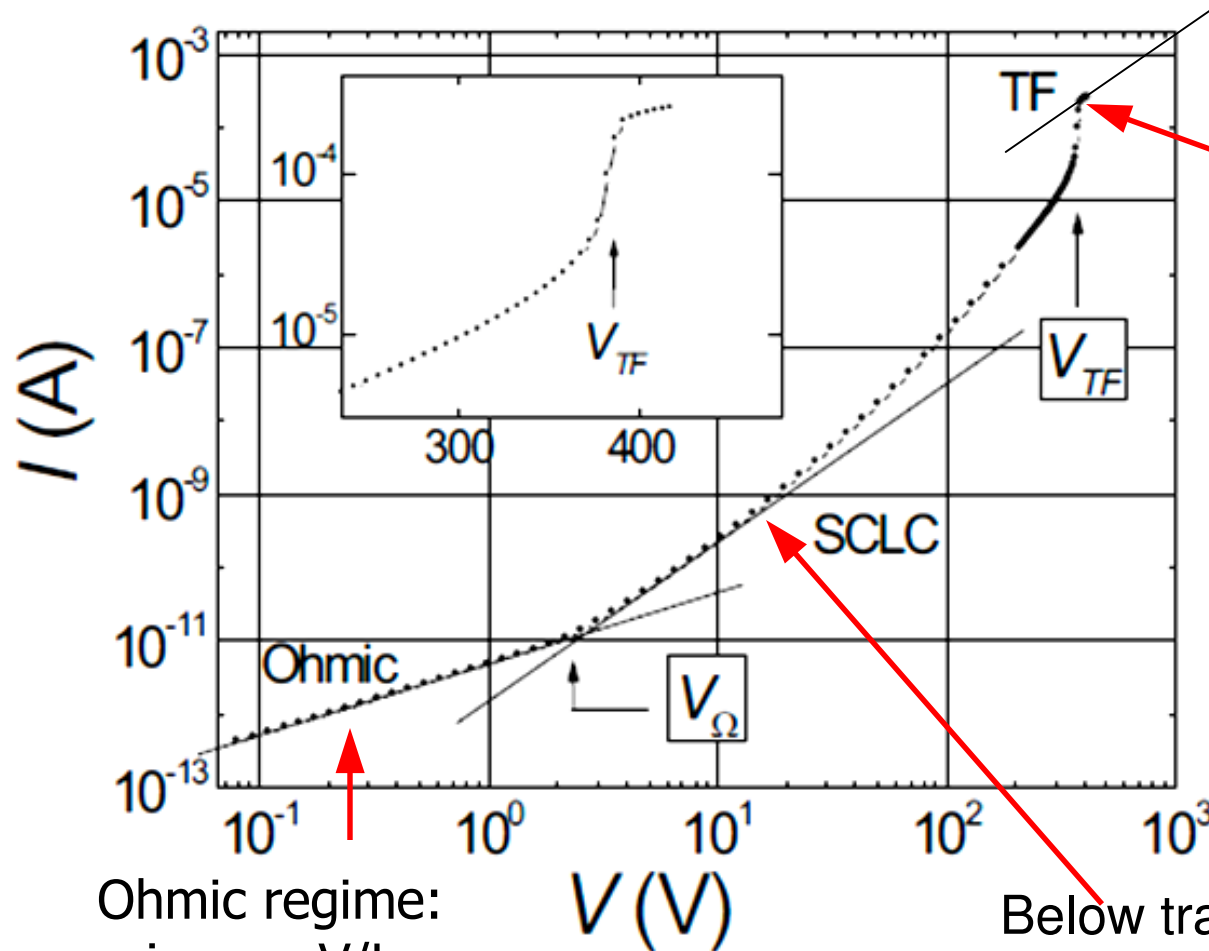
$$j = (9/8)\epsilon\mu V^2/L^3$$

Mott-Gurney law
for SCLC transport in
intrinsic trap-free S.C.

K. C. Kao and W. Hwang,
Electrical Transport in Solids,
Pergamon, Oxford (1981)

4.2. Space-charge limited current (SCLC) measurements

Podzorov *et al.*, *Appl.Phys.Lett.* **83**, 3504 (2003)



Above trap filling threshold:

$$j = (9/8)\epsilon\mu V^2/L^3$$

quadratic

Threshold voltage for trap filling can be easily estimated:

$$V_{TF} = (eN_{tr}/\epsilon)L^2$$

where N_{tr} is trap density

Ohmic regime:

$$j = en\mu V/L$$

linear

Below trap filling threshold:

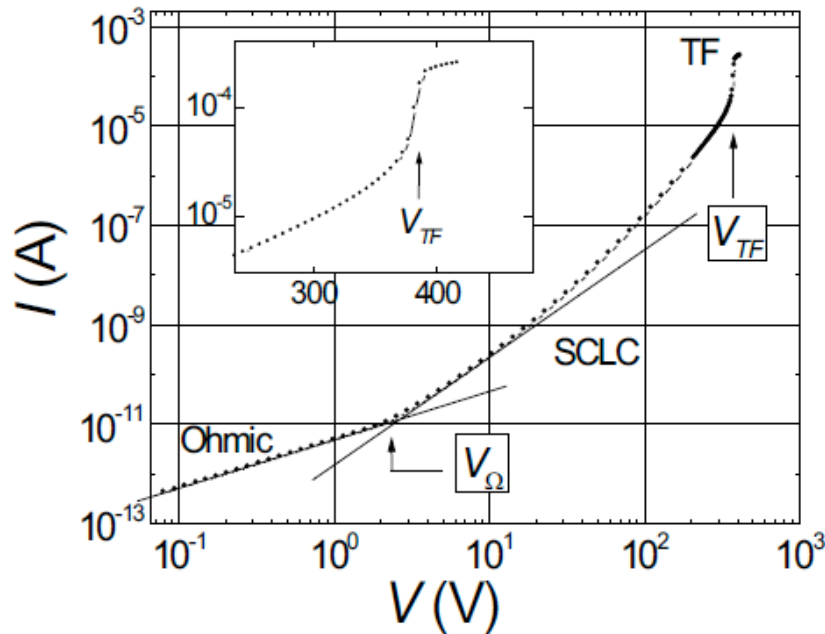
$$j \propto V^2$$

quadratic,

but the exact expression contains many unknown parameters

K. C. Kao and W. Hwang,
Pergamon, Oxford (1981)

4.2. Space-charge limited current (SCLC) measurements



de Boer, Gershenson, Morpurgo and Podzorov, “Organic single-crystal field-effect transistors” *Phys. Stat. Solidi* **201**, 1302 (2004)

Fig. 7 I - V characteristic of a ~ 10 μm -thick rubrene crystal, measured along the c -axis. The inset is a blow-up of the crossover to the trap free regime (also in a double-log scale). From the crossover to the trap-free regime, the density of deep traps $N_t^d \simeq 10^{15} \text{ cm}^{-3}$ can be estimated [23].

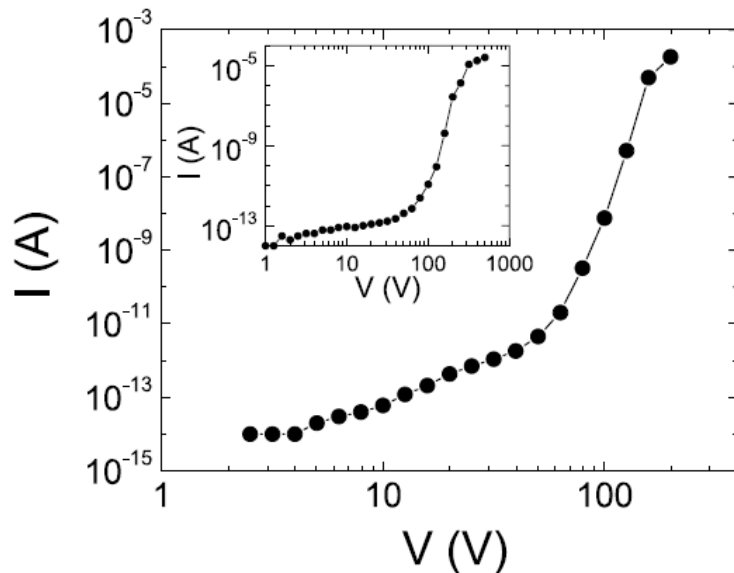
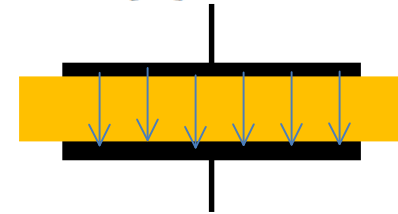
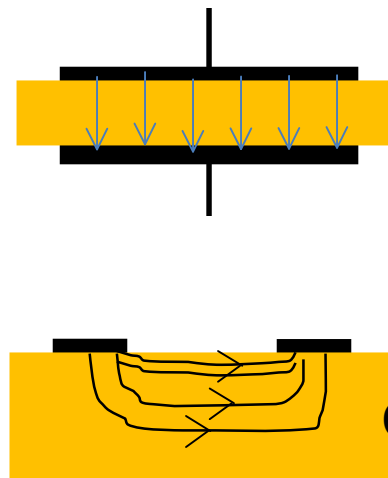
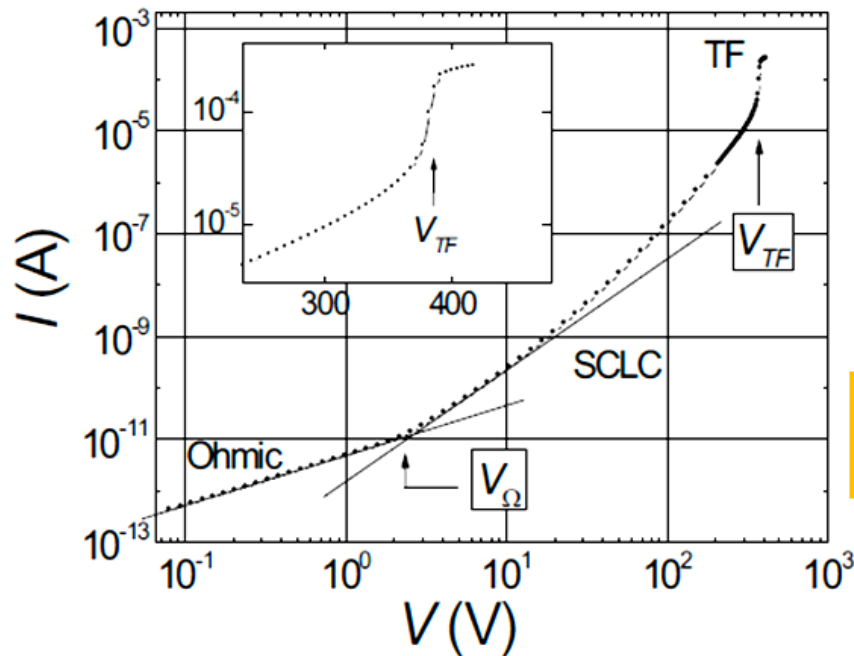


Fig. 8 Typical result of a DC I - V measurement perpendicular to the a - b plane of a tetracene single-crystal, with a thickness $L = 30$ μm and a mobility $\mu_{\text{min}} = 0.59 \text{ cm}^2/\text{Vs}$. The inset shows a similar measurement on a different crystal ($L = 25$ μm , $\mu_{\text{min}} = 0.014 \text{ cm}^2/\text{Vs}$), in which a crossing over into an approximately quadratic dependence on voltage is visible at high voltage. In both cases, a very steep current increase occur around of just above 100 V that we attribute to filling of deep traps. We observed a steep increase in current in most samples studied.



4.2. Space-charge limited current (SCLC) measurements

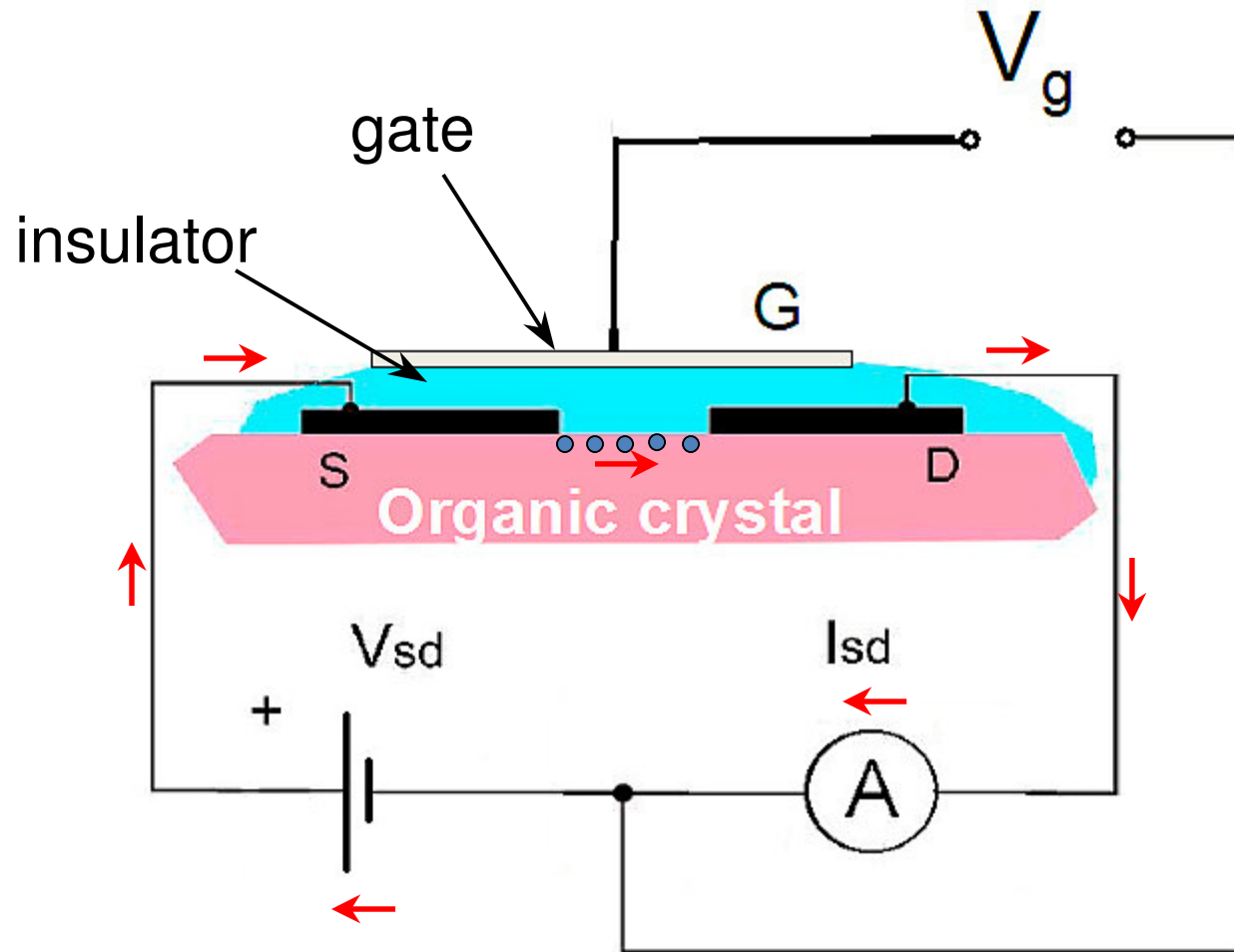
1. Reliable extraction of parameters (μ , N_{tr} , etc) from SCLC measurements can ONLY be done in the **trap-filling regime** (the 3rd regime at $V > V_{TF}$), if it is clearly and systematically observed. Only in this regime calculations can be done without assumptions;
2. One must also clearly see the transition from Ohmic (1st regime) to the carrier injection SCLC regime (the 2nd regime) – a **“knee”** in a double-log plot must be clearly present;
3. These measurements can be **trustable ONLY in a sandwich geometry**. Co-planar geometry is not reliable, because crude assumptions are necessary.



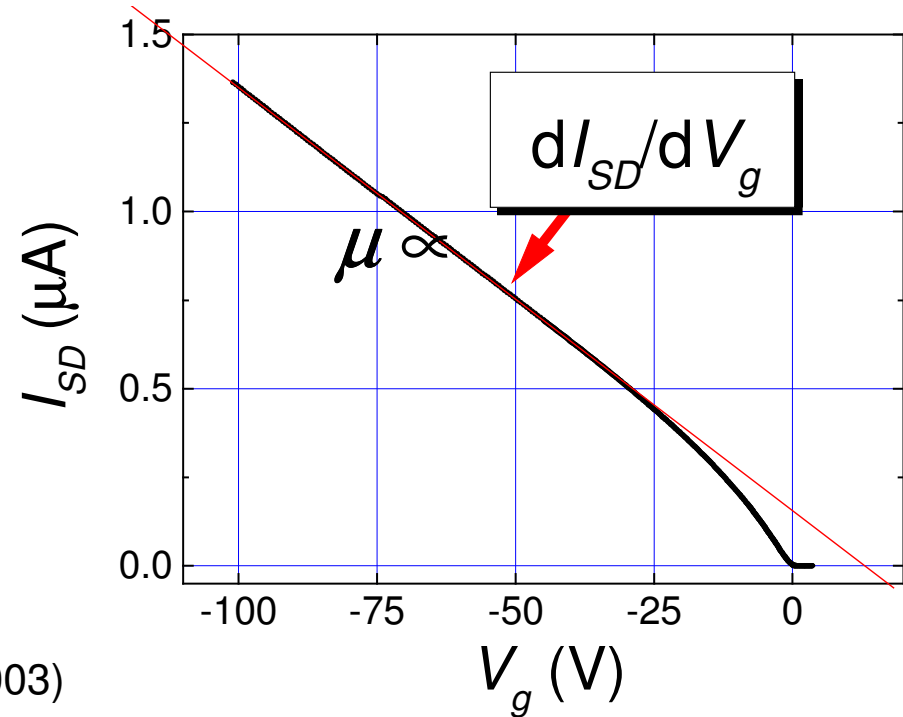
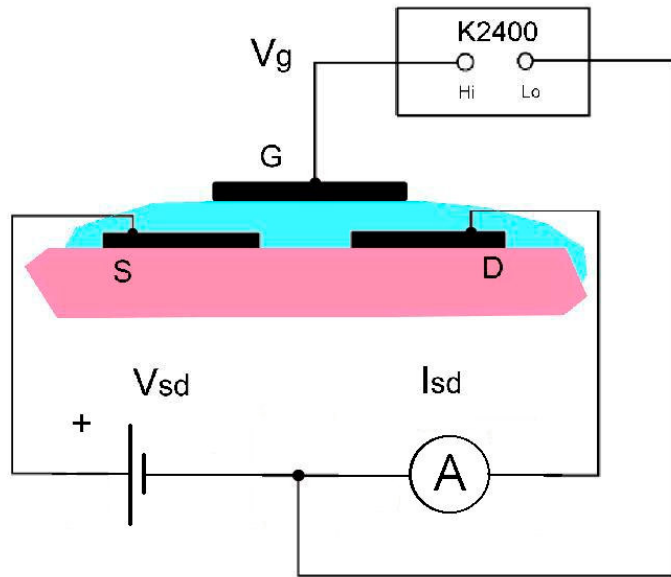
Sandwich geometry - **OK**

Co-planar geometry - **Not OK**

4.3. Field-Effect Transistor (FET) geometry

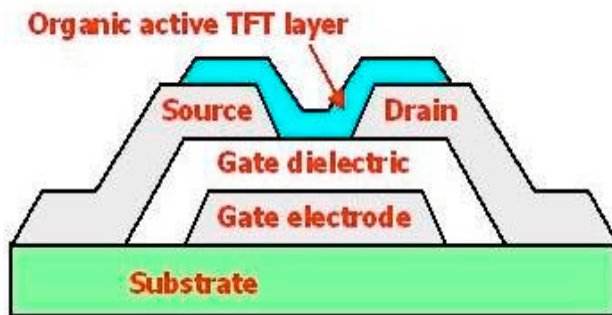


Field-Effect Transistors as a tool to study surface transport



Podzorov *et al.*, *Appl.Phys.Lett.* **82**, 1739 (2003)

Podzorov *et al.*, *Appl.Phys.Lett.* **83**, 3504 (2003)



$$\sigma_{2D} = e \mu n_{2D} = (I_{SD}/V_{SD})(L/W)$$

$$en_{2D} \propto C_i V_g$$

$$\mu = [L/(C_i W V_{SD})] \cdot (\partial I_{SD}/\partial V_g)$$

M. Shtein, J. Mapel, J. B. Benziger,
S. R. Forrest *et al.*, *APL* **81**, 268 (2002)

Challenges of the single-crystal OFET fabrication

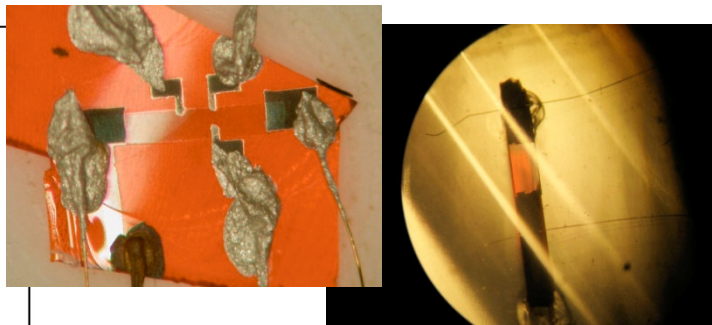
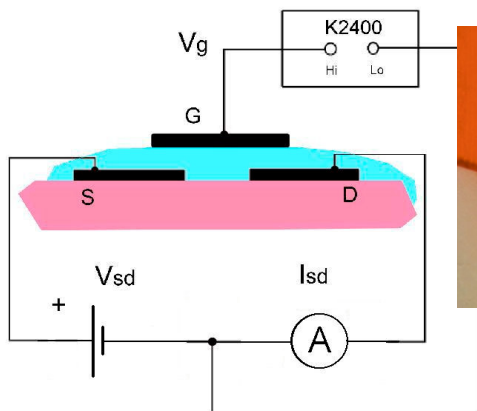
The organic crystals are incompatible with the standard processes of thin-film technology (sputtering, photolithography, etc.)

Technological challenges:

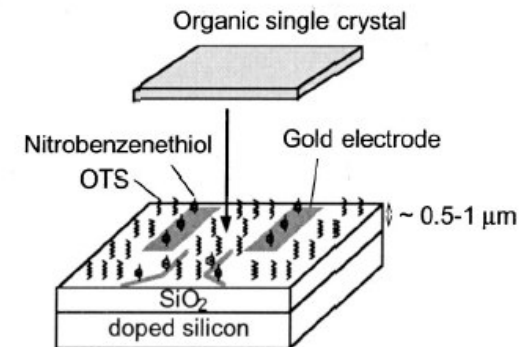
- ultra-pure crystals with low density of defects;
- low-resistance metallic contacts to undoped semiconductors;
- disorder-free interface btw the gate insulator and organic crystal.

Two approaches:

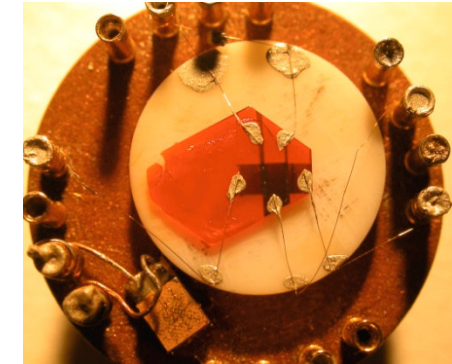
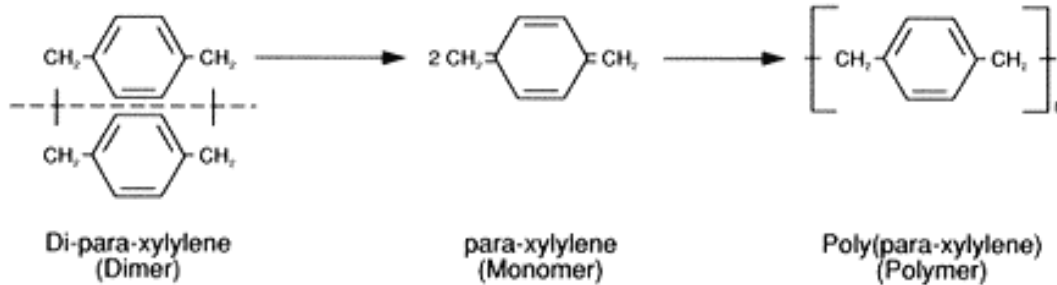
- 1) Fabrication of FET structure directly at the surface of organic crystals (free-standing FETs);
- 2) Electrostatic or van der Waals bonding of organic crystal to “gate/source/drain” structure (a transistor “stamp”).



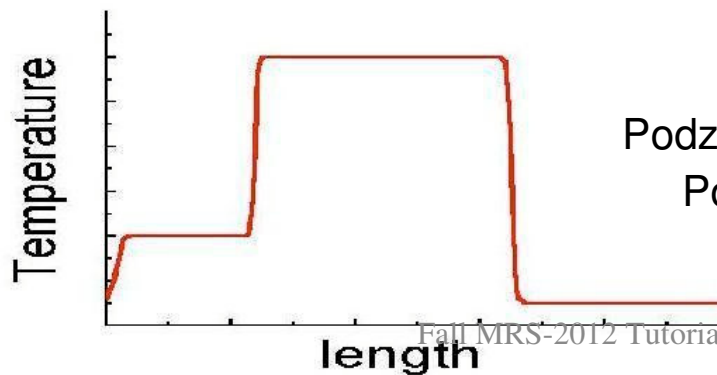
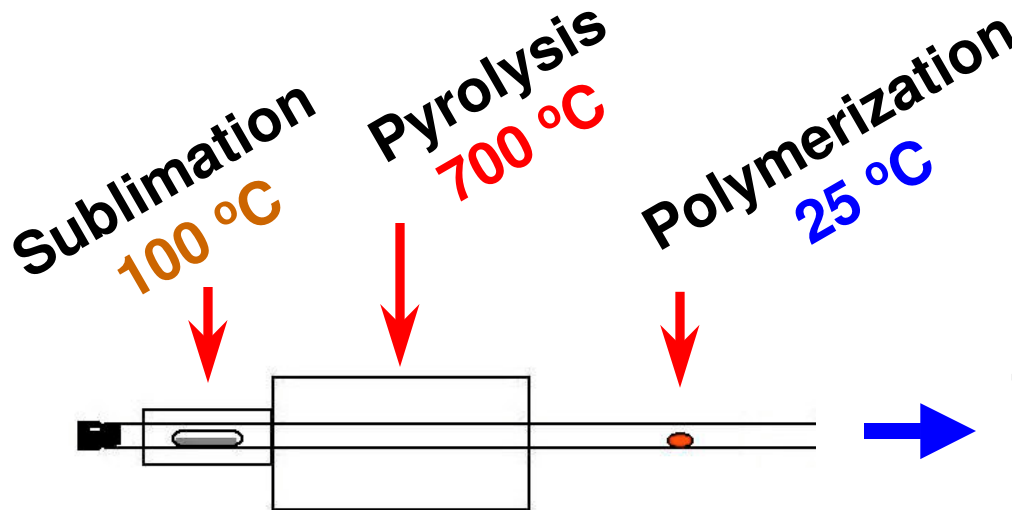
Fall MRS-2012 Tutorial (V. Podzorov)



5.1. OFETs with parylene dielectric: damage-free coating

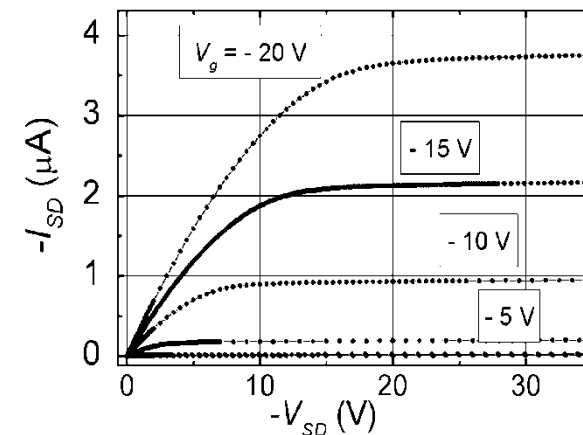
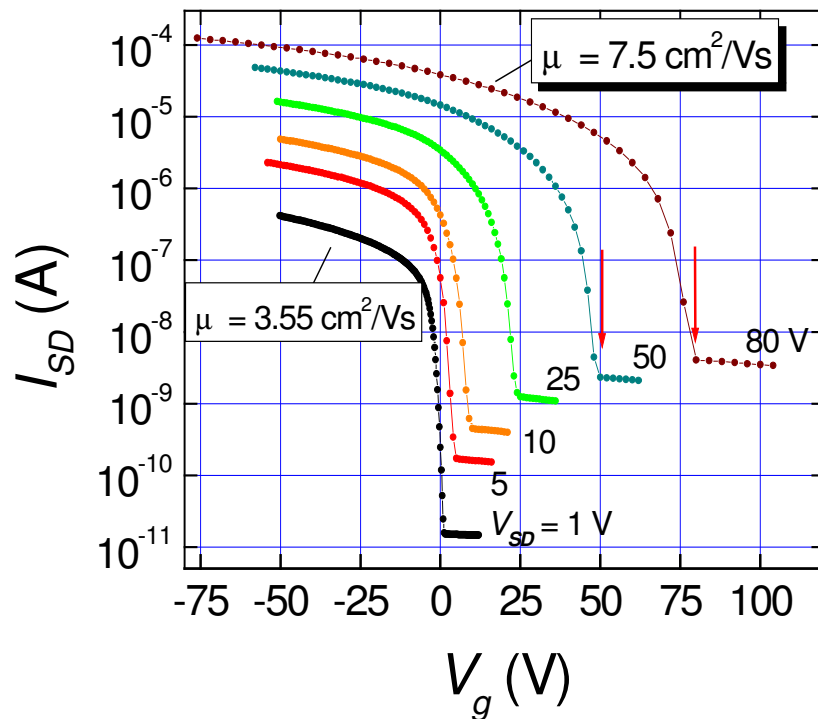


free standing devices with high mobility



Podzorov *et al.*, *Appl.Phys.Lett.* **82**, 1739 (2003)
 Podzorov *et al.*, *Appl.Phys.Lett.* **83**, 3504 (2003)

5.1. Characteristics of rubrene S.C. OFETs with parylene insulator



Mobility – up to $8 \text{ cm}^2/\text{Vs}$, 5-10 times greater than in the best organic TFTs and $\alpha\text{-Si:H}$ MOSFETs;

Threshold – nearly zero;

Sub-threshold slope – 10 times better than in organic TFTs and $\alpha\text{-Si:H}$ MOSFETs.

Podzorov *et al.*, *Appl. Phys. Lett.* **82**, 1739 (2003)

Podzorov *et al.*, *Appl. Phys. Lett.* **83**, 3504 (2003)

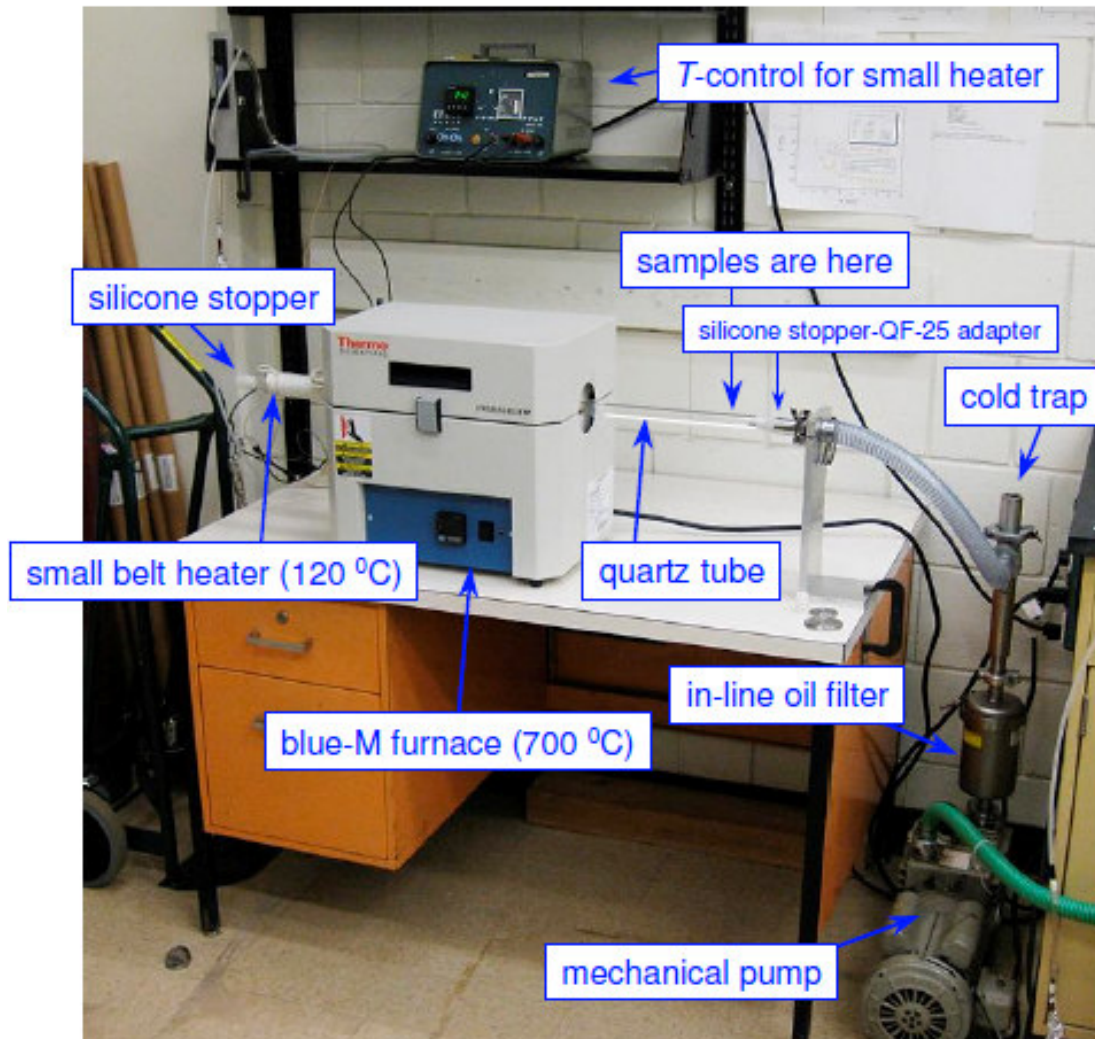
Advantages:

1. Low-k dielectric;
2. Conformal coater;
3. Crystals of any size and shape can be used;
4. Immuned from pinholes, even if the gate is deposited over sharp edges;
5. Works with graphite contacts;
6. The method is inexpensive;

Disadvantages:

There are no real disadvantages, except **it needs to be set up!**

5.1. OFETs with parylene dielectrics: damage-free coating



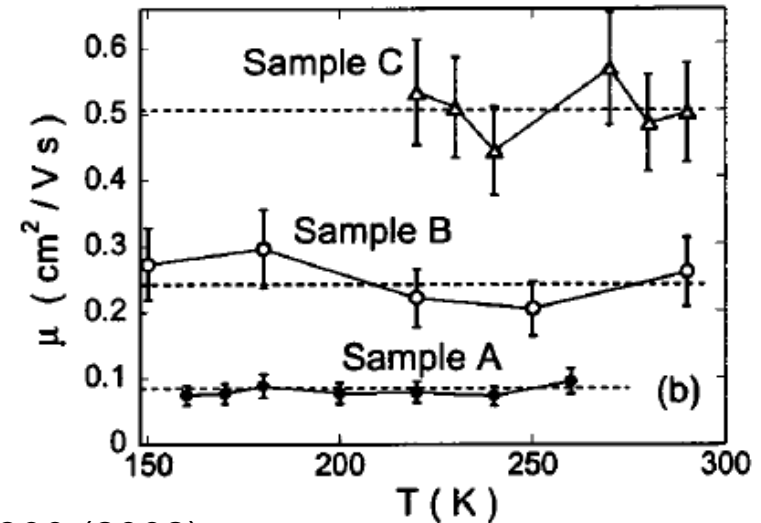
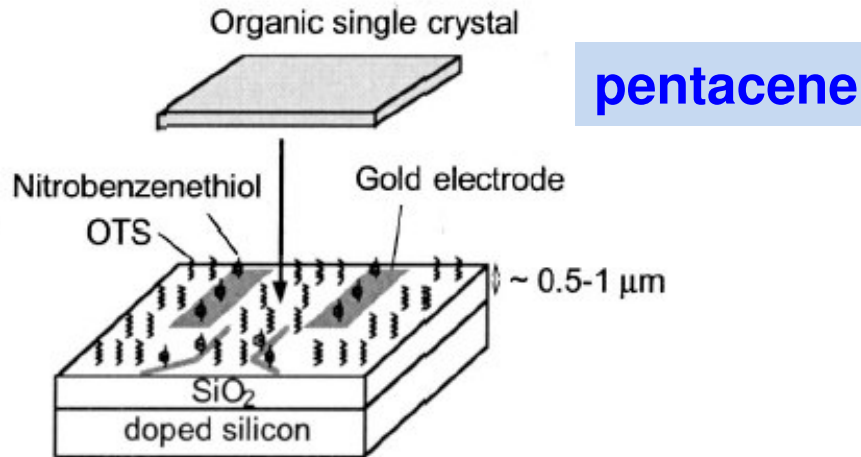
A simple home-made parylene deposition setup

Main elements:

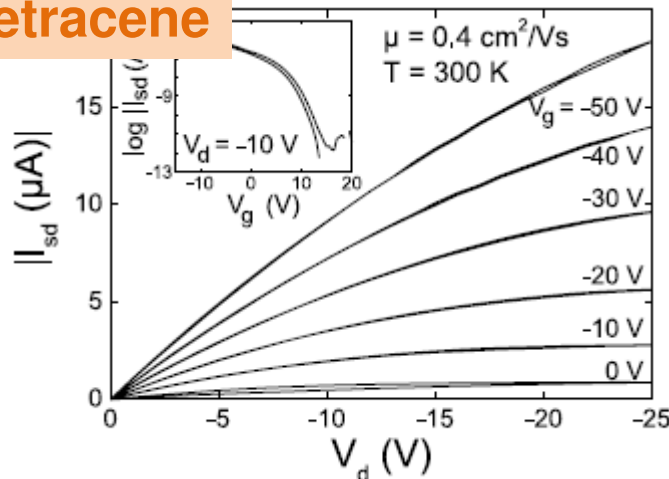
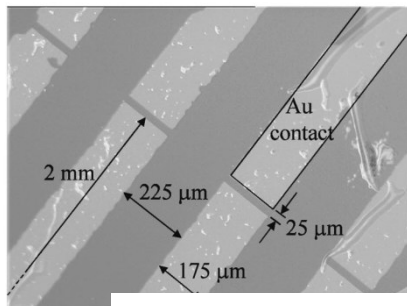
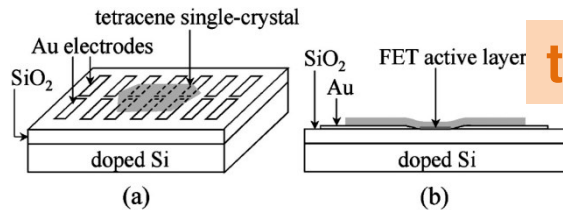
1. Quartz tube;
2. Small tube furnace (Blue-M);
3. Mech. pump with a cold trap.

Detailed technical notes on how to deposit parylene dielectric films are available at: <http://www.physics.rutgers.edu/~podzorov/index.php>

5.2. OFETs with crystals laminated on Si/SiO₂ wafers



Takeya, Batlogg *et al.*, *J. Appl. Phys.* **94**, 5800 (2003)



de Boer, Morpurgo *et al.*, *Appl. Phys. Lett.* **83**, 4345 (2003)

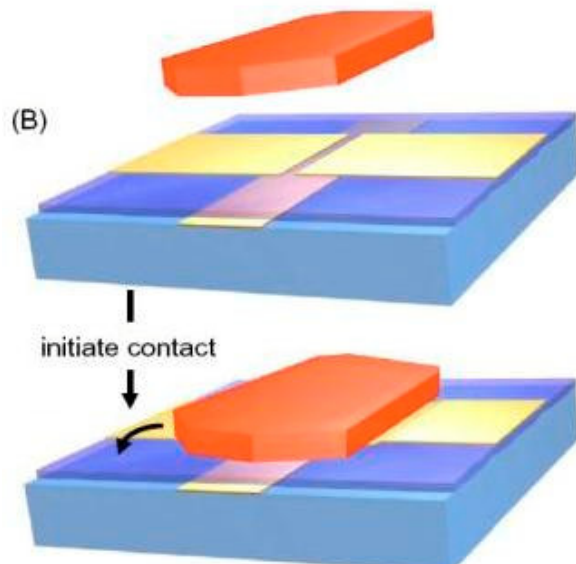
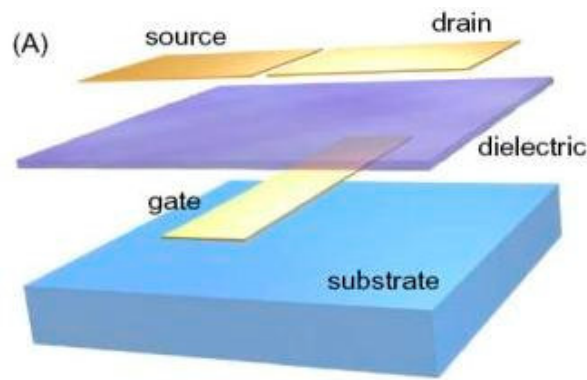
Advantages:

1. Lithographic contacts;
2. SAM treatment possible.

Disadvantages:

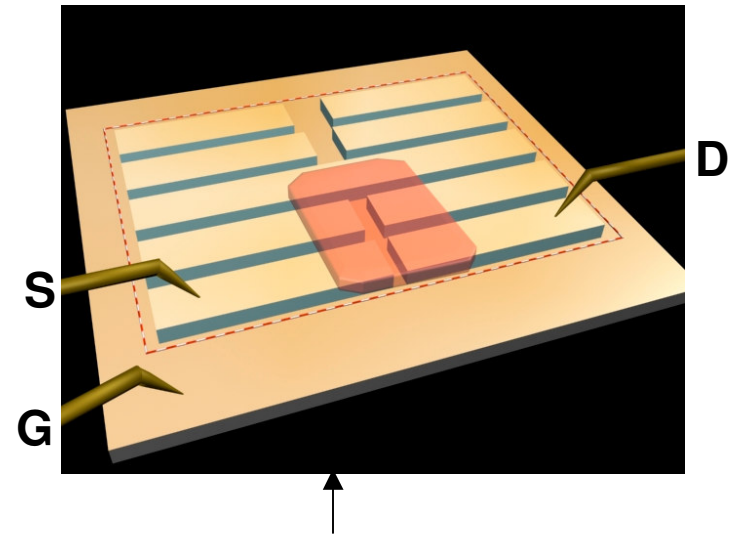
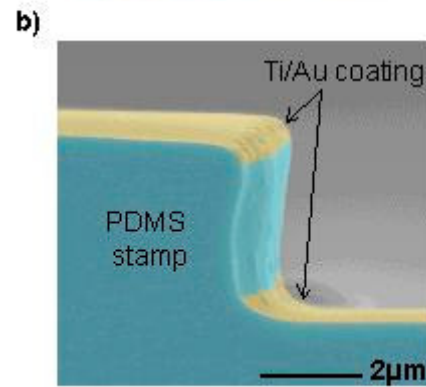
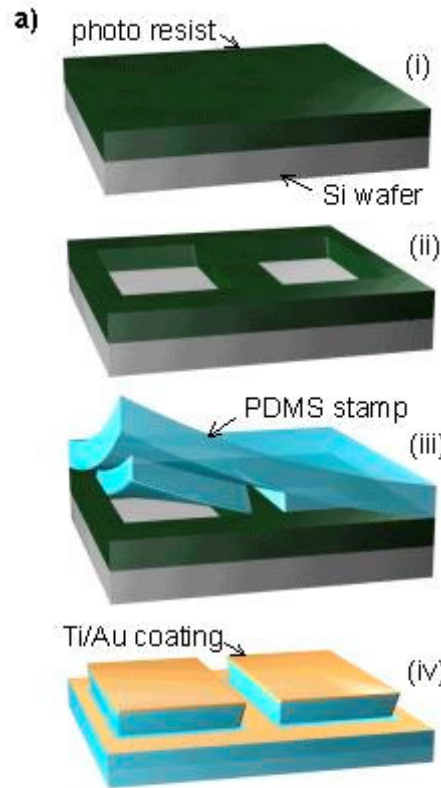
1. Only very thin and flat crystals can be used;
2. Gold/org. contacts are usually very resistive;
3. Gated area is not limited only to the channel.

5.3. OFETs using PDMS elastomeric stamps



PDMS S.C. OFETs

V. Sundar *et al.*,
Science **303**, 1644 (2004)



Air-gap S.C. OFETs

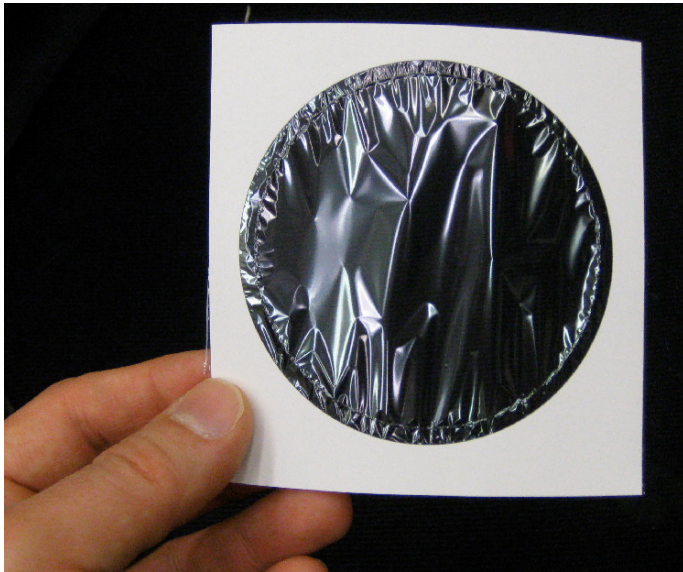
E. Menard *et al.*,
Adv. Mater. **16**, 2097 (2004)

V. Podzorov *et al.*,
Phys. Rev. Lett. **93**, 086602 (2004)

5.4. OFETs by vacuum lamination

vacuum lamination of free-standing insulating membranes

Mylar (Chemplex Inc.)



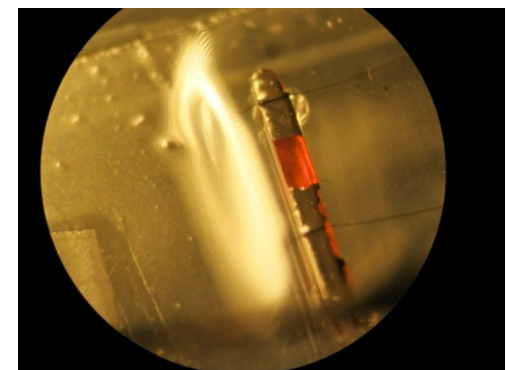
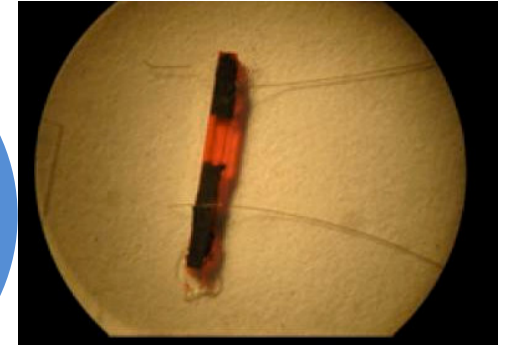
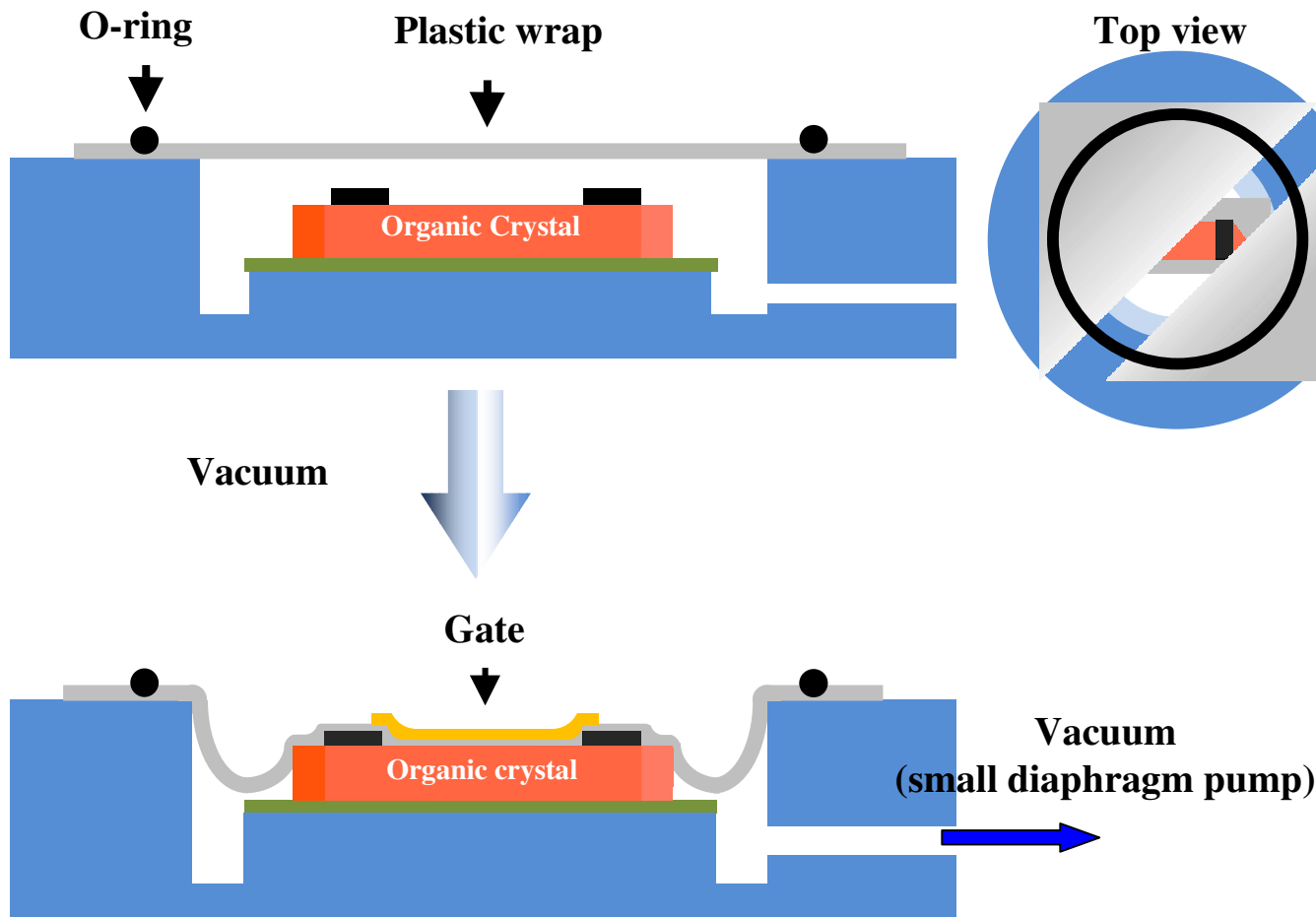
Food Wrap



	Mylar [®]	Glad [®] food wrap
d	2.5 μm	11 μm
C_i	1.14 nF/cm ²	0.18 nF/cm ²
ϵ_r	3.26	2.26



5.4. OFETs by vacuum lamination



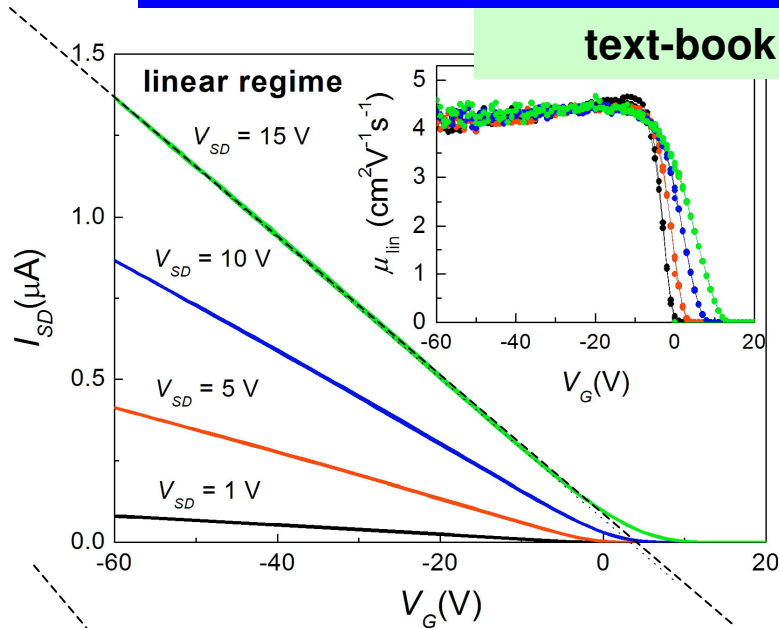
**Simple and fast: takes less than 10 min
to prepare high-performance OFETs**

H. T. Yi, *et al.*, *Adv. Mater.* **23**, 5807 (2011)

<http://www.physics.rutgers.edu/~podzorov/index.php>

5.4. OFETs by vacuum lamination

text-book characteristics of single-crystal OFETs

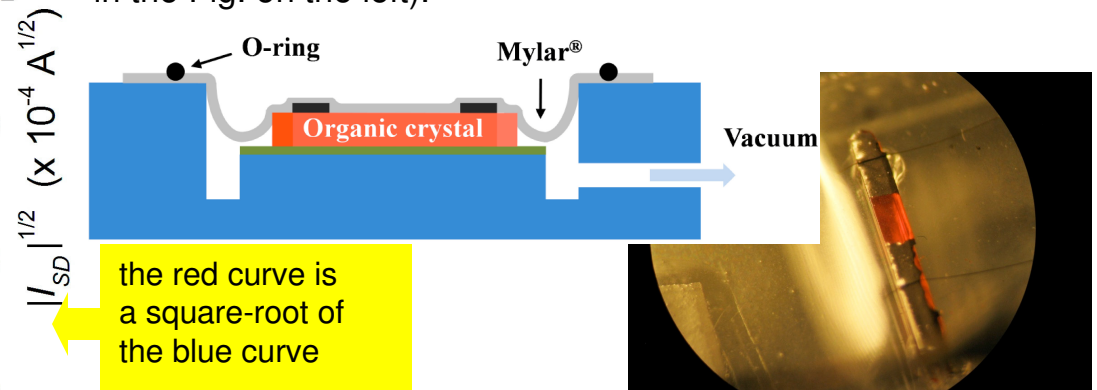
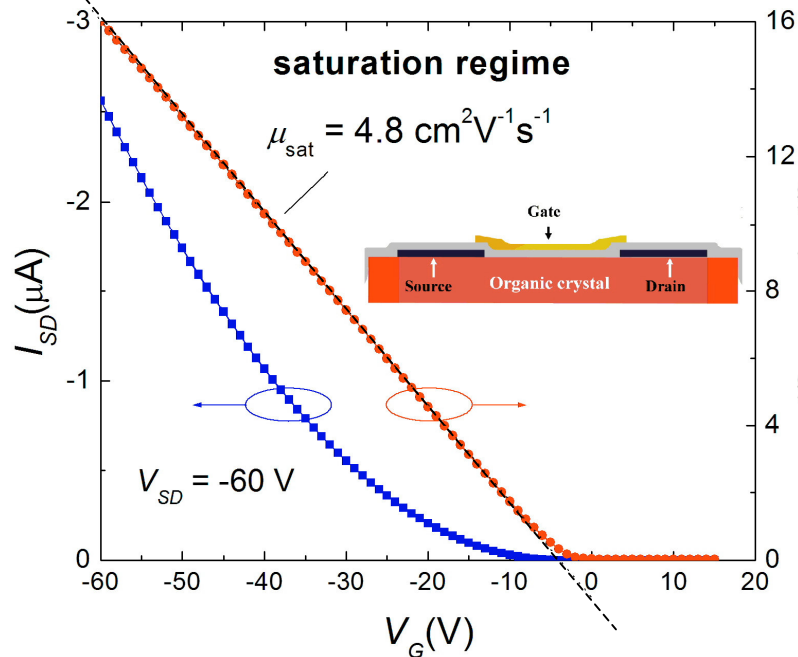


Shockley's gradual channel model:

$$I_{SD}^{linear} = \frac{W}{L} \mu C_i (V_G - V_T) V_D \quad (|V_G| \gg |V_{SD}|)$$

$$I_{SD}^{saturation} = \frac{W}{L} \mu C_i \left[\frac{(V_G - V_T)^2}{2} \right] \quad (|V_G| < |V_{SD}|)$$

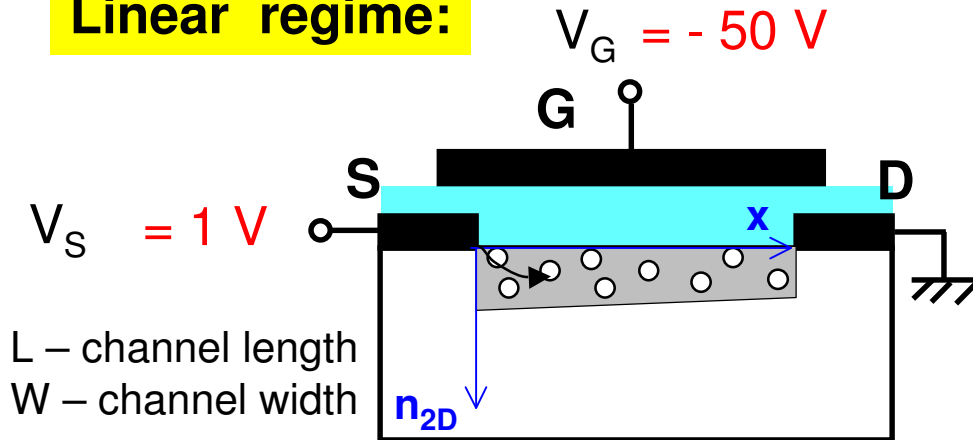
1. Perfectly linear transfer and saturation characteristics, as expected in correctly operating OFETs;
2. Mobility is independent of the carrier density (or, V_G);
3. Negligible contact resistance;
4. Nearly zero-threshold operation;
5. Negligible hysteresis (V_G is swept back and forth in the Fig. on the left).



H. T. Yi, *et al.*, *Adv. Mater.* **23**, 5807 (2011)
<http://www.physics.rutgers.edu/~podzorov/index.php>

6. OFET operation modes: Linear vs. Saturation regimes

Linear regime:



$$V_G < 0 \text{ and } |V_G| \gg |V_S|$$

- $n_{2D}(x)$ is almost constant along the channel (carrier density and potential are distributed uniformly);
- none of the contacts are pinched off (depleted);
- longitudinal el. field \ll gate el. field. (graduate channel approx.)

Only in this case the linear Ohmic equations can be safely applied:

$$\sigma_{2D} = e \mu n_{2D}$$

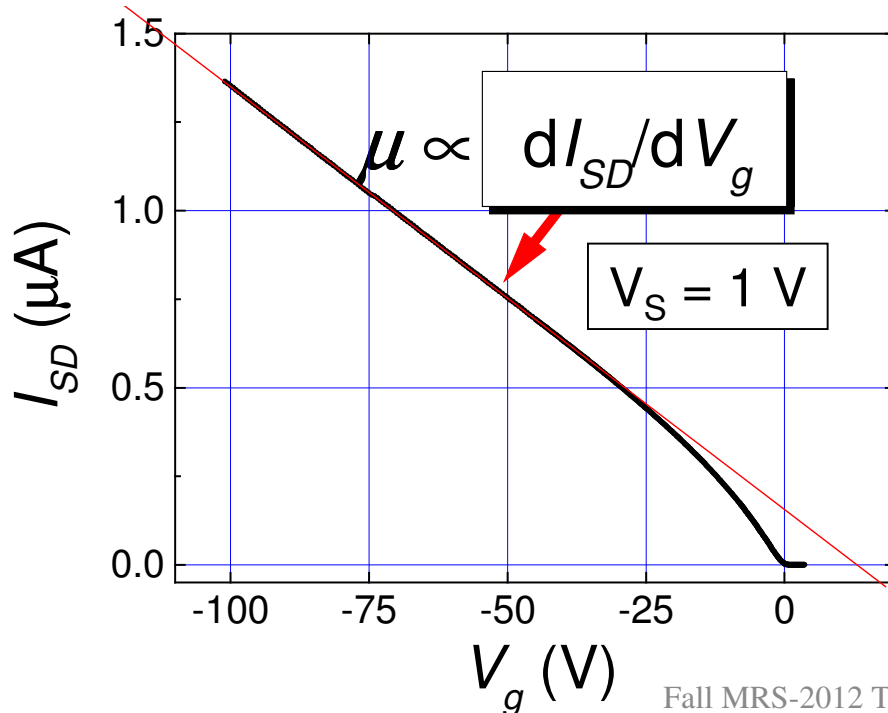
$$en_{2D} = C_i(V_G - V_{TH}), \quad V_{TH} = \text{const.}$$

$$\sigma_{2D} = \mu C_i(V_G - V_{TH}) = (I_{SD}/V_S)(L/W)$$

$$I_{SD} = (W/L)V_S\mu C_i(V_G - V_{TH})$$

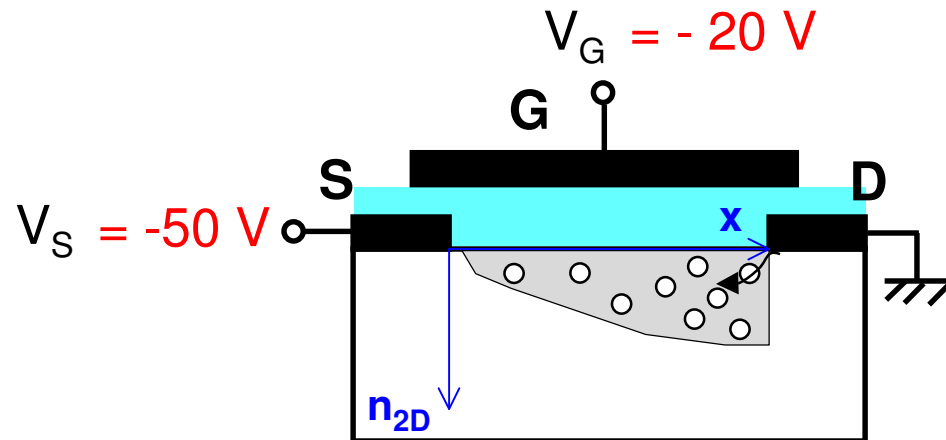
By taking derivative w. resp. to V_G we get:

$$\mu_{lin} = (L/W)(1/C_i)(1/V_S)(\partial I_{SD}/\partial V_G)$$



6. OFET operation modes: Linear vs. Saturation regimes

Saturation regime:



$$V_G < 0, V_S < 0 \text{ and } |V_S| > |V_G|$$

- $n_{2D}(x)$ is highly non-uniform;
- carrier-injecting contact is Drain;
- source Schottky contact is depleted;
- potential drop along different sections of the channel is varied;
- in some sections (for example, at narrow depleted region near Source), longitudinal el. field \gg gate el. field (gradual channel approx. is invalid).

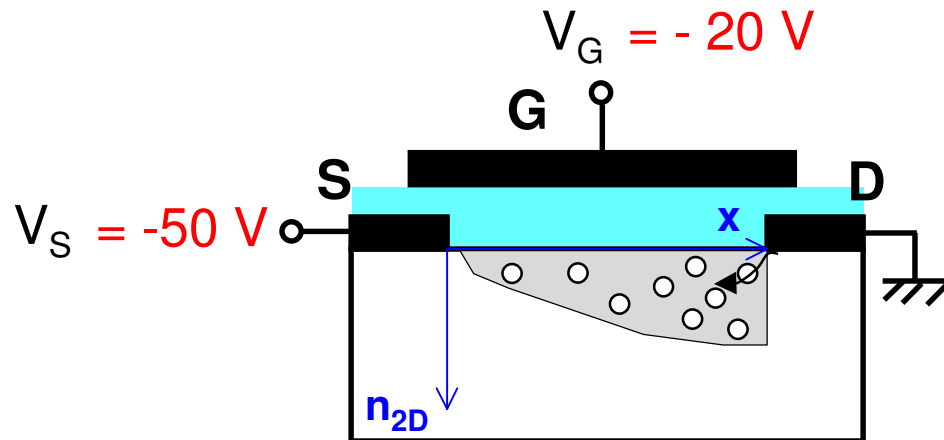
For these reasons, saturation regime is generally not a good regime for mobility measurements, especially in the cases of disordered (polycrystalline and amorphous) OFETs.

It can only be used, if the following assumptions are justified:

- μ is independent of carrier density and therefore is constant along the channel;
- the depleted contact is assumed to have a negligible contact resistance, and hence the gradual channel approximation still holds.

6. OFET operation modes: Linear vs. Saturation regimes

Saturation regime:



$$V_G < 0, V_S < 0 \text{ and } |V_S| > |V_G|$$

- $n_{2D}(x)$ is highly non-uniform;
- carrier-injecting contact is Drain;
- source Schottky contact is depleted;
- potential drop along different sections of the channel is varied;
- in some sections (for example, at narrow depleted region near Source), longitudinal el. field \gg gate el. field (graduate channel approx. is invalid).

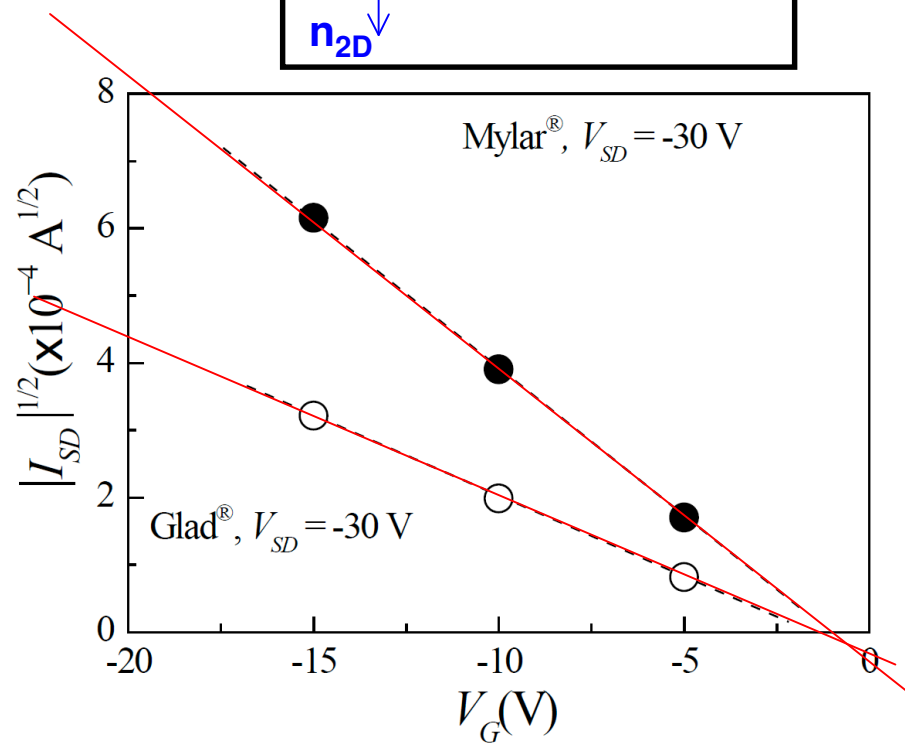
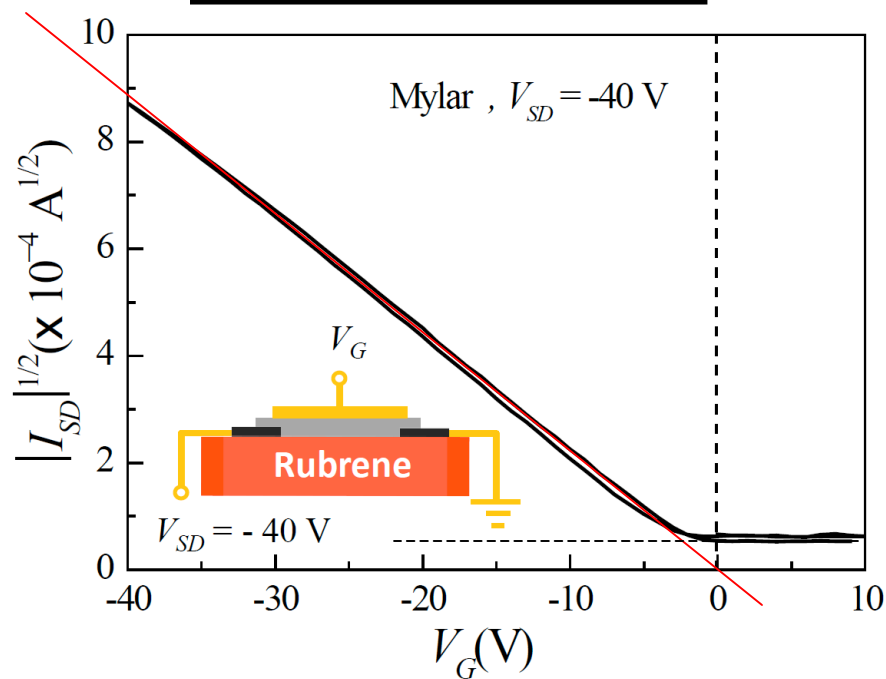
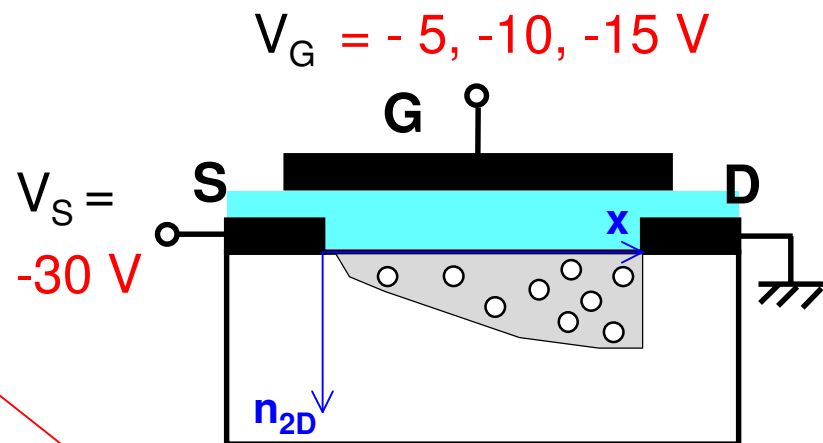
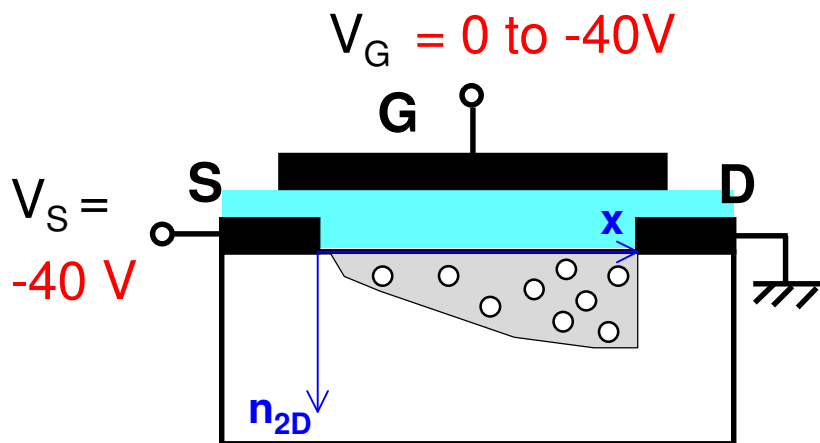
If the assumptions on the prev. page are justified, then it's possible to show

that in a saturation regime: $I_{SD} = -(W/2L)\mu C_i(V_G - V_{TH})^2$

and, hence, $\sqrt{-I_{SD}} \propto V_G$ - this dependence must be a straight line.

6. Correctly looking saturation regime: rubrene OFETs

Perfectly linear $(-I_{SD})^{0.5}$ vs. V_G has to be observed!



6. Problems with saturation regime measurements

Generally, saturation regime is not a good regime for mobility measurements, especially for disordered (polycrystalline and amorphous) OFETs.

$$I_{Dlin} = \frac{Z}{L} C_i \mu \left[(V_G - V_T) V_D - \frac{V_D^2}{2} \right], \quad (2.2.1)$$

$$I_{Dsat} = \frac{Z}{2L} C_i \mu (V_G - V_T)^2. \quad (2.2.2)$$

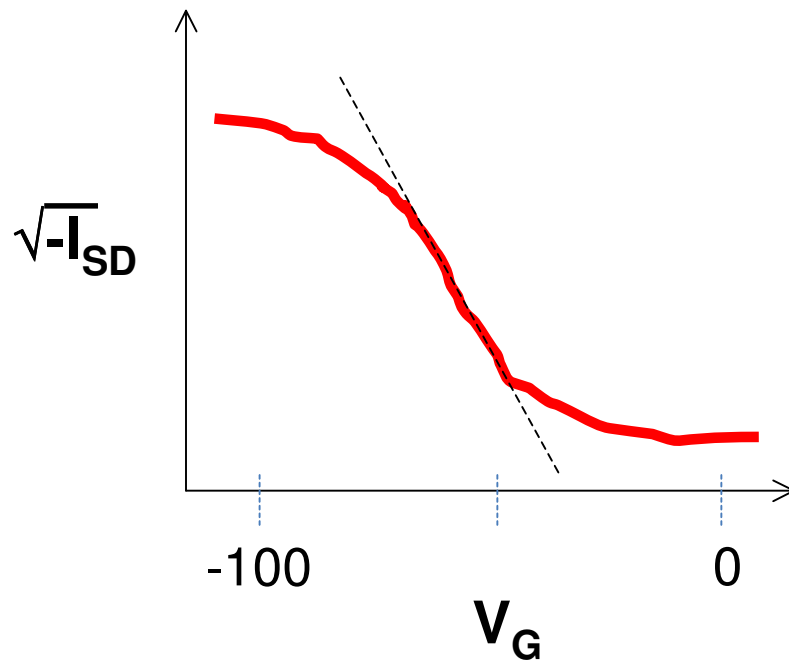
Equations (2.2.1) and (2.2.2) rests on the following assumptions: (1) The transverse electric field induced by the gate voltage is largely higher than the longitudinal field induced by the gate bias (so-called gradual channel approximation); (2) the mobility is constant all over the channel. Assumption (1) is justified by the geometry of the device; that is, the distance from source to drain is most often much larger than the thickness of the insulator. Assumption (2) is more or less fulfilled in a conventional inorganic semiconductor. However, this is far from true in organic solids, as will be shown in this chapter. For this reason, the use of Equation (2.2.2) to extract the mobility may lead to an incomplete, if not erroneous, description of charge transport in organic semiconductors. Alternative approaches to circumvent

G. Horowitz in *Organic Field-Effect Transistors*,
Ed. Z. Bao and J. Locklin, pp. 27-72 (Taylor & Francis, 2007).

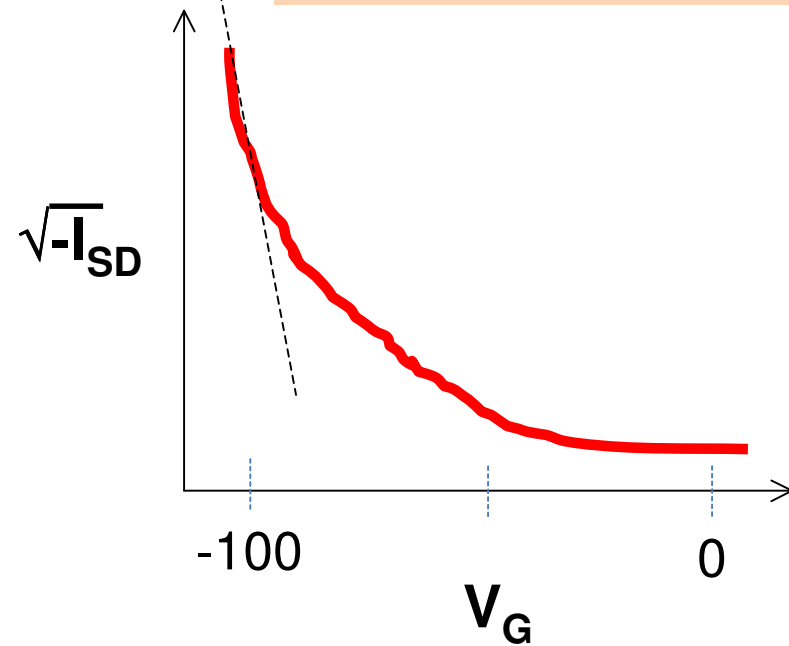
Fall MRS-2012 Tutorial (V. Podzorov)

6. Problems with saturation regime measurements

S-shape curves



Super-linear curves



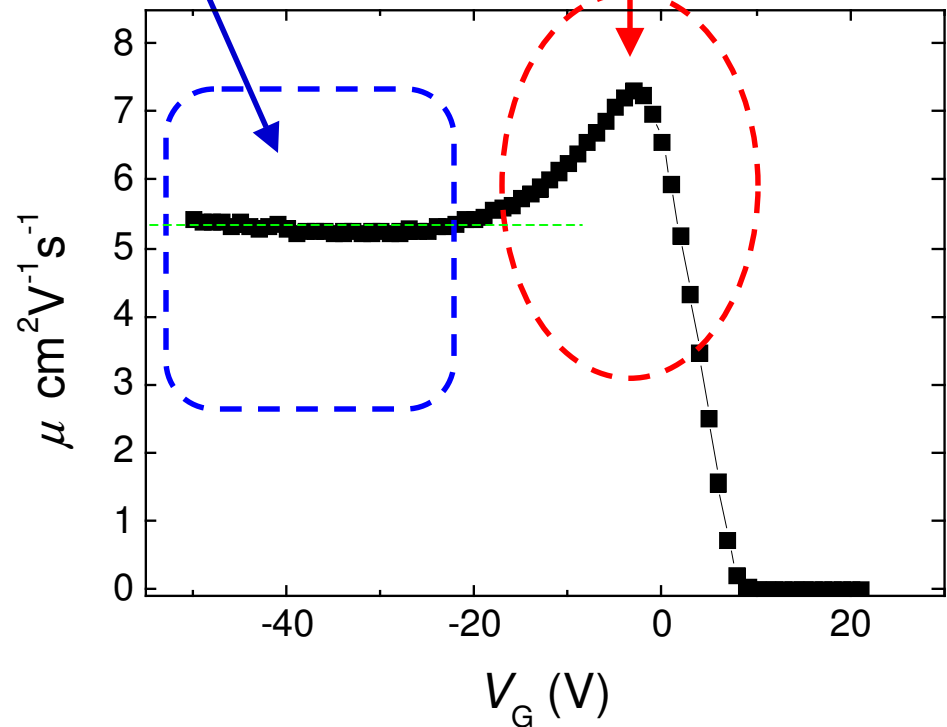
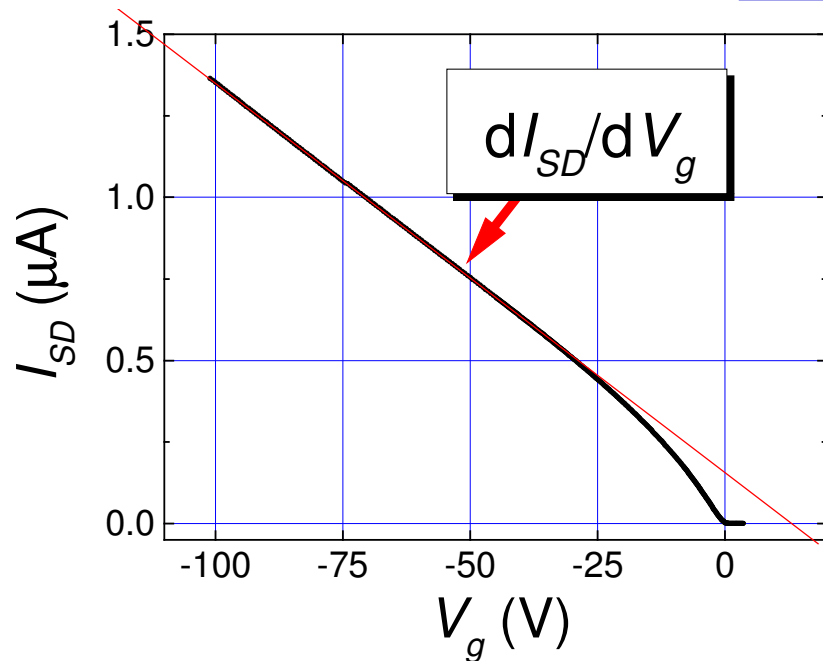
If you see such data in literature, this simply means that the devices do not work properly. The correct regime for mobility measurement is the linear regime.

6. Linear regime and linear μ in rubrene OFETs

To determine mobility correctly, it is important to use the linear transconductance regime, that is a plateau region on $\mu(V_g)$ dependence.

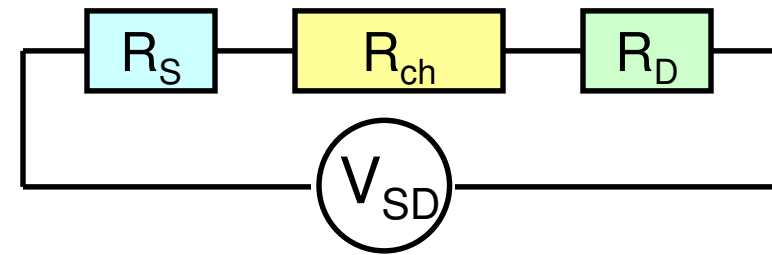
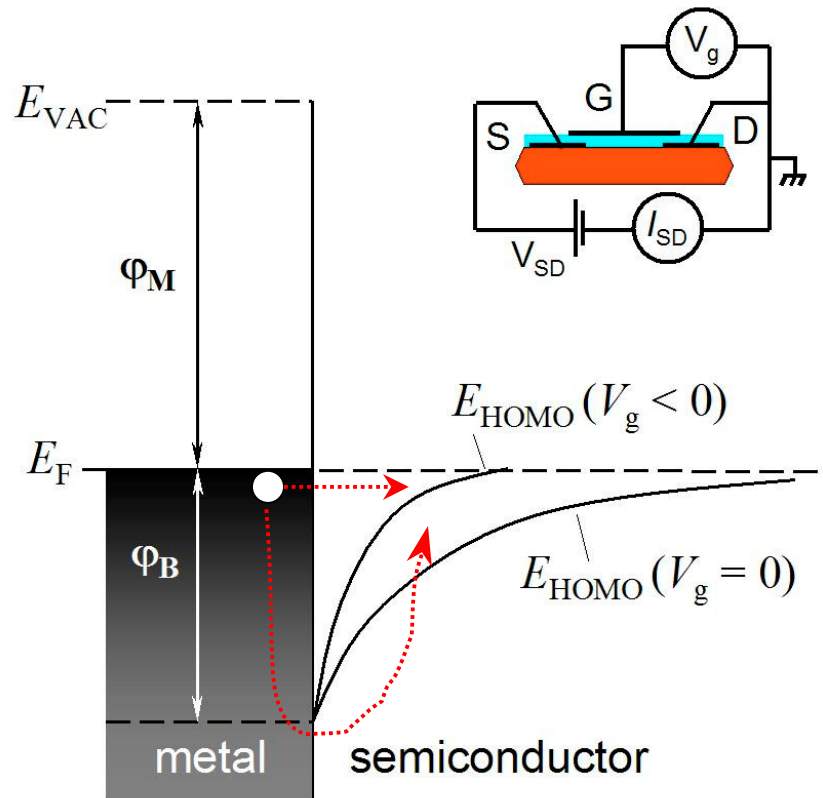
Linear regime:
true mobility

Non-linear,
sub-threshold regime:
the “hump” is likely a
contact effect



Podzorov *et al.*,
Appl.Phys.Lett. **83**, 3504 (2003)

7. 4-probe OFET measurements: Schottky contact resistance



V_{SD} is fixed (it is total voltage applied).
Actual voltage drop across the channel
is not necessarily equal to V_{SD}

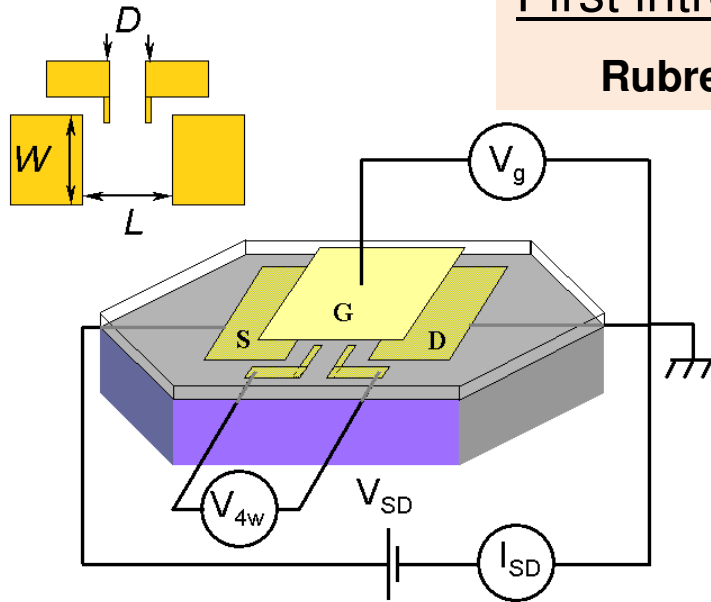
$$R = R_{cont} + R_{ch}$$

Schottky barrier: thermionic emission of carriers

7. 4-probe OFET measurements

First introduced in OFETs in:

Rubrene by Podzorov *et al.*, *Appl. Phys. Lett.* **82**, 1739 (2003)



Also used in:

P3HT OFETs Merlo, Frisbie *J. Polymer Science: Part B: Polymer Physics* (2003)

Pentacene S.C. OFETs Takeya, Batlogg *et al.*, *J. Appl. Phys.* (2003)

n-type TFTs Chesterfield, Frisbie *J. Appl. Phys.* (2004).

Rubrene Morpurgo *et al* *APL* (2004)

$$\sigma \equiv \frac{I_{SD}}{V_{4w}} \frac{D}{W} \quad \text{- contact-independent channel conductivity}$$

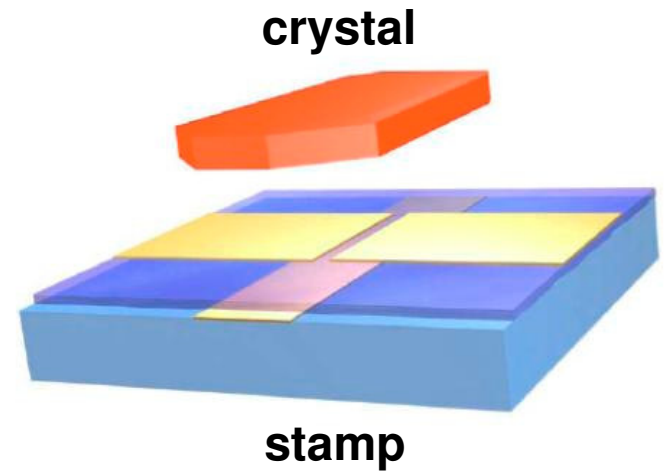
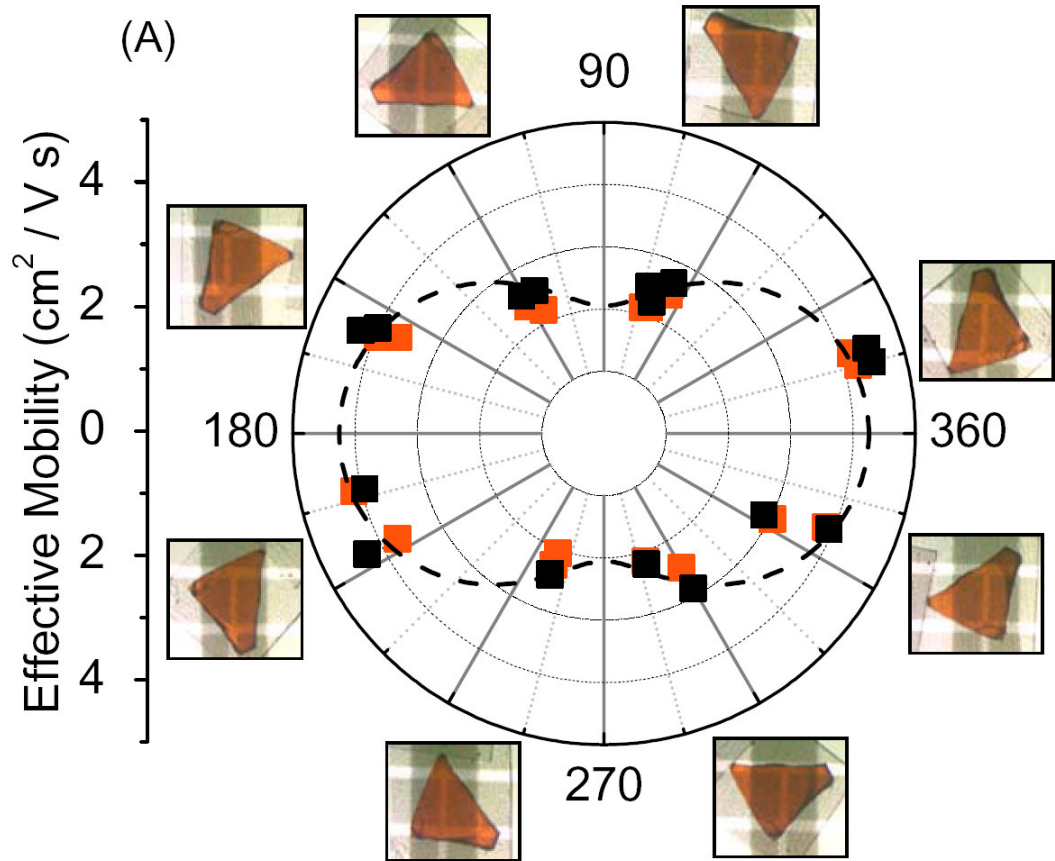
$$\mu_{4w} = \left(\frac{1}{C_i} \right) \left(\frac{d(I_{SD} / V_{4w})}{dV_g} \right) \frac{D}{W} \quad \text{- contact-independent channel mobility}$$

$$R_C = \frac{V_{SD}}{I_{SD}} - \frac{L}{D} \frac{V_{4w}}{I_{SD}} \quad \text{- contact resistance}$$

V. Podzorov, book chapter in *Organic Field-Effect Transistors*, Ed. Z. Bao and J. Locklin, pp. 27-72 (Taylor & Francis, 2007).

8. Mobility Anisotropy

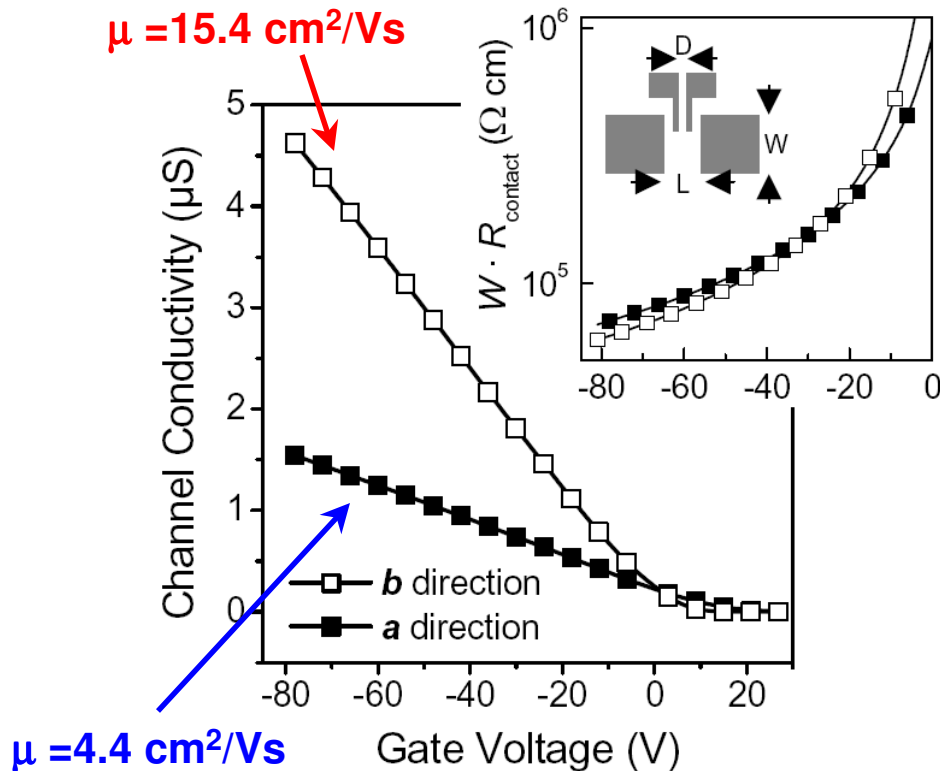
Rubrene FETs, 2-probe measurements, RT



V. Sundar *et al.*, *Science* **303**, 1644 (2004)

8. Mobility Anisotropy

4-probe measurements, RT



Rubrene FETs, RT

4-probe measurements with the “contact” PDMS stamps at room temperature

$$V_{SD} = 10V$$

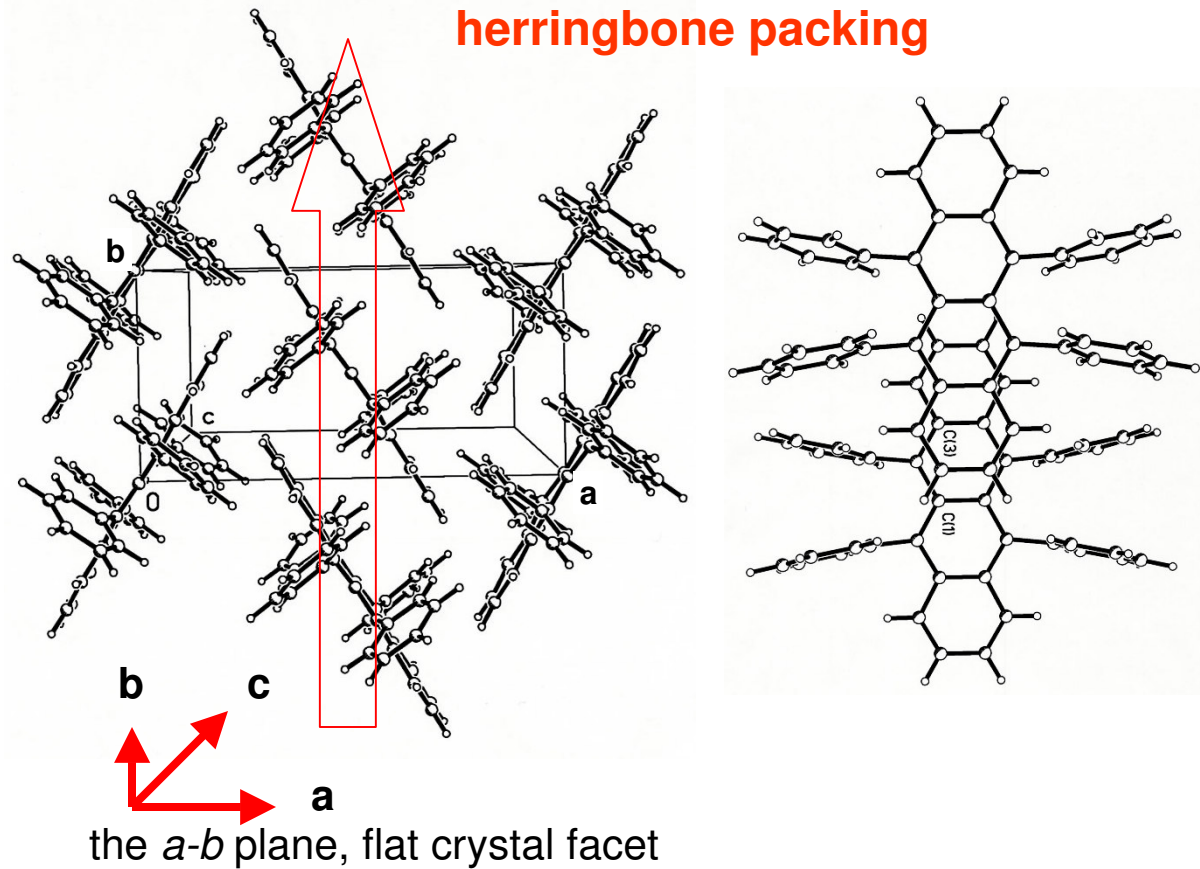
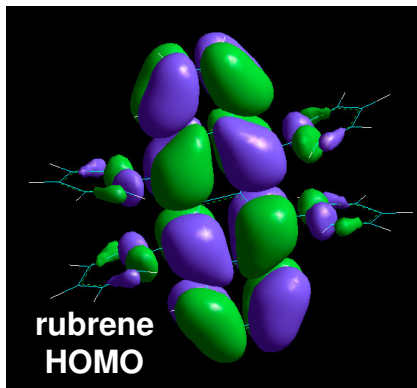
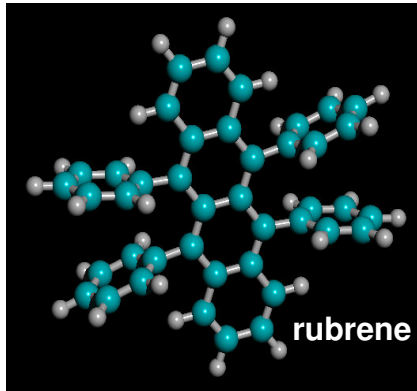
$$L = 0.75 \text{ mm}, W = 1.45 \text{ mm},$$

$$D = 0.25 \text{ mm}, C_i = 0.65 \text{ nF/cm}^2$$

The mobility along the **b** axis is 3-4 times greater than that along the **a** axis.

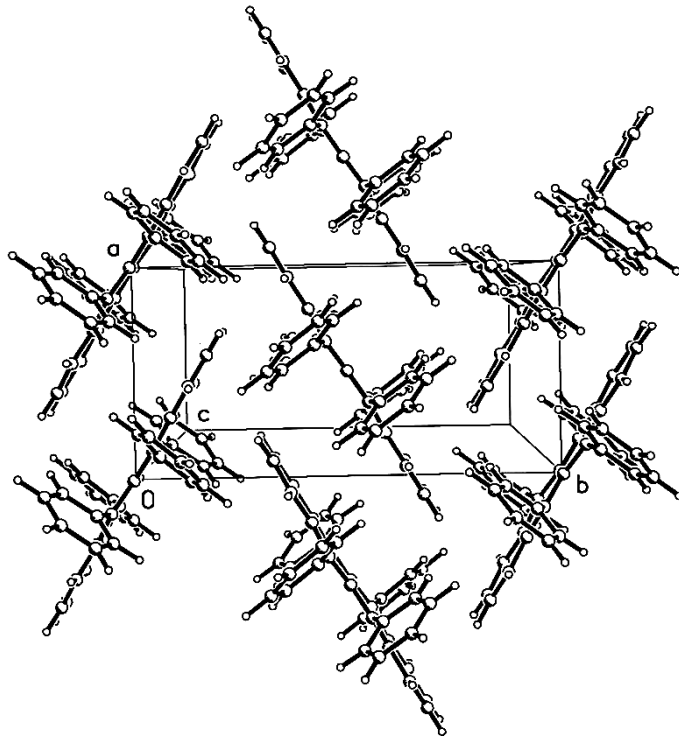
V. Sundar *et al.*, *Science* **303**, 1644 (2004)

8. Molecular Packing in Rubrene

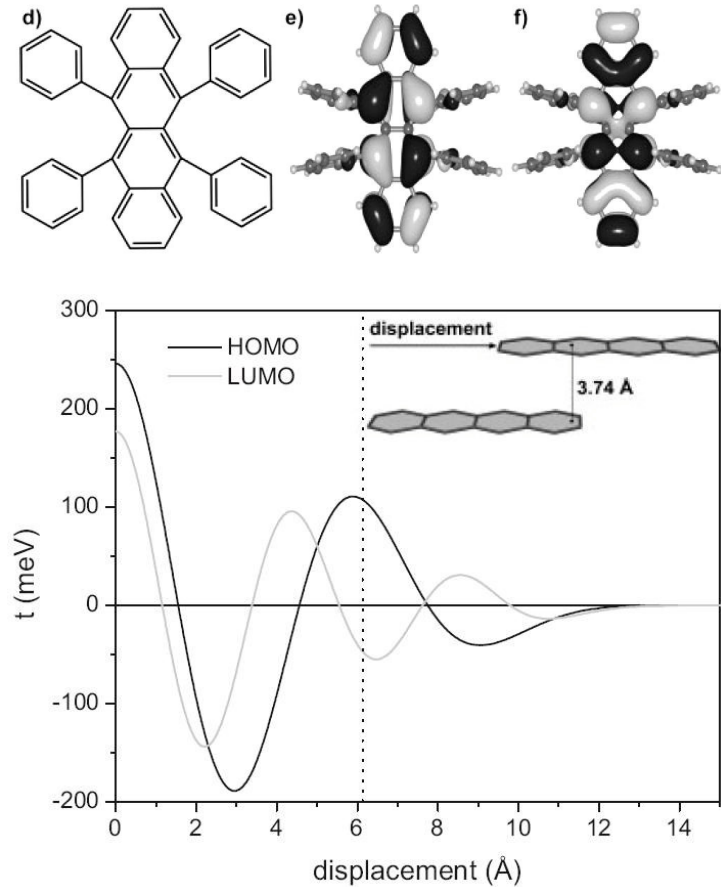


Strong π - π overlap along the *b* axis \Rightarrow
 $\mu \sim 20 \text{ cm}^2/\text{Vs}$, a record for the *RT* mobility in organic semiconductors

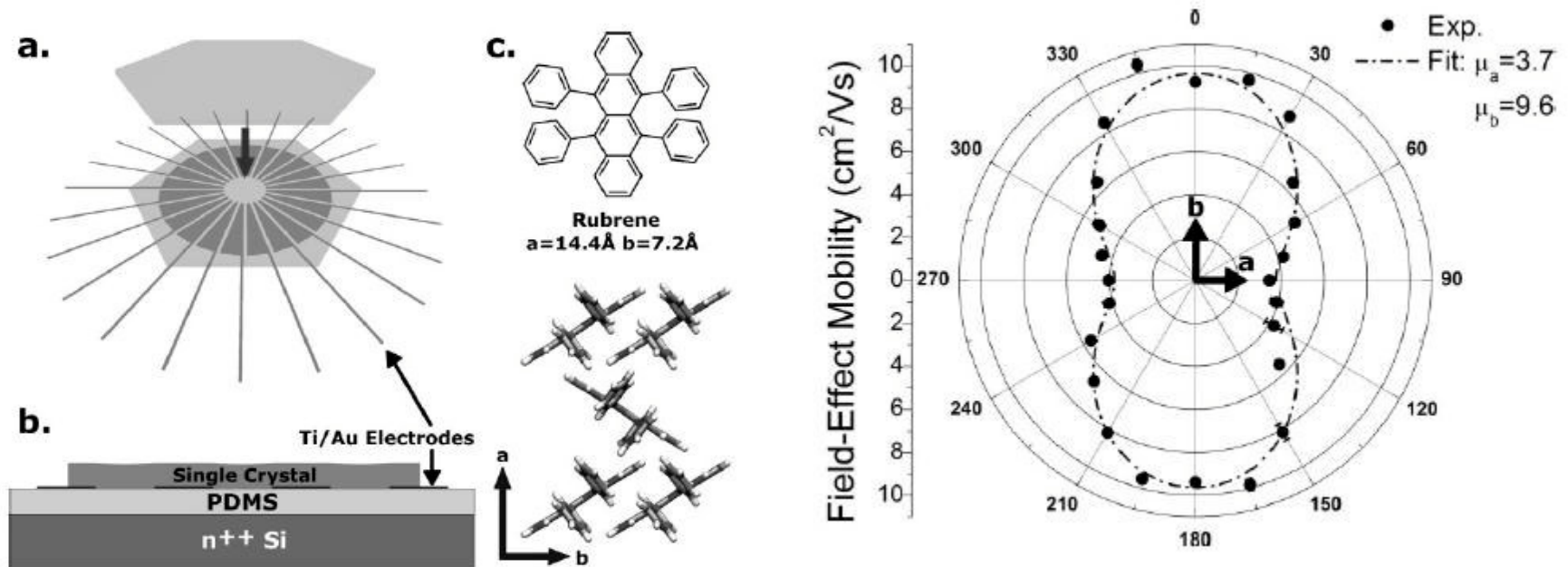
8. Inter-molecular bonding (van der Waals): π -orbital overlap between adjacent molecules



D. A. da Silva Filho, E.-G. Kim, J.-L. Bredas
Adv. Mater. **17**, 1072 (2005)

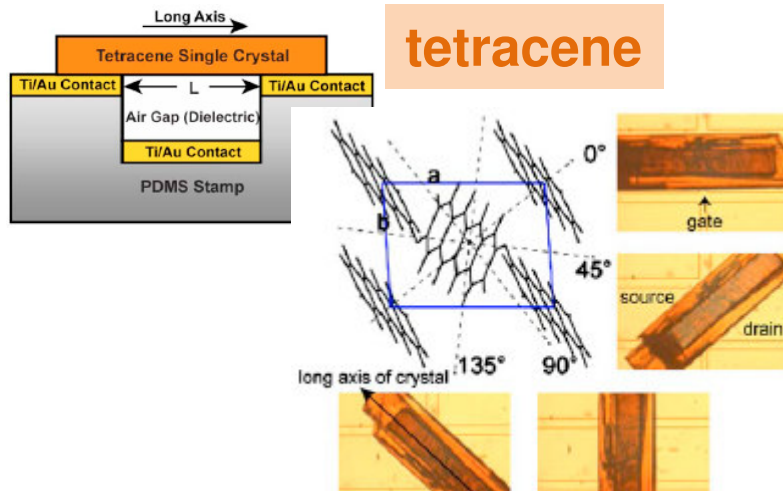


8. High resolution measurements of mobility anisotropy in rubrene



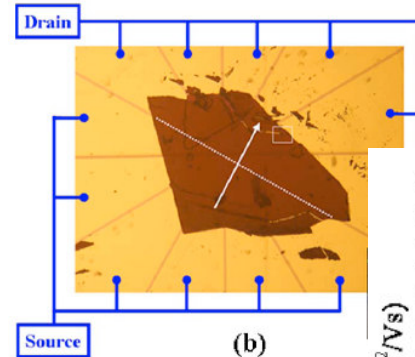
C. Reese & Z. Bao, *Adv. Mater.* **19**, 4535 (2007)

8. Mobility anisotropy measurements in other single-crystal OFETs

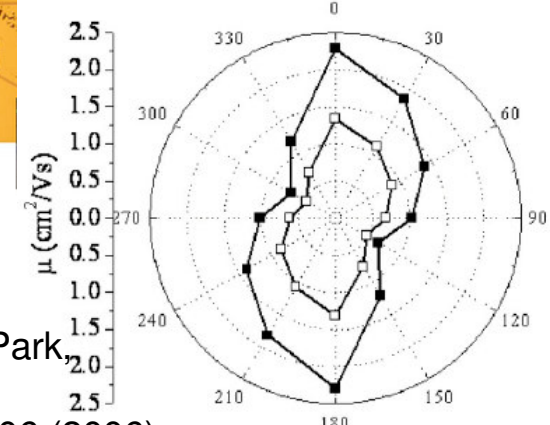


tetracene

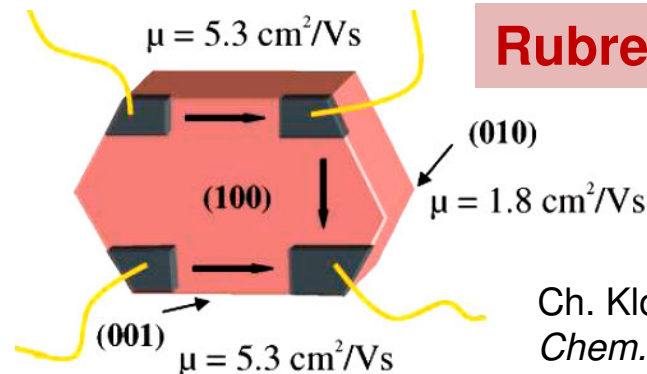
Y. Xia & C. D. Frisbie, Anisotropy in tetracene, *Appl. Phys. Lett.* **90**, 162106 (2007)



pentacene



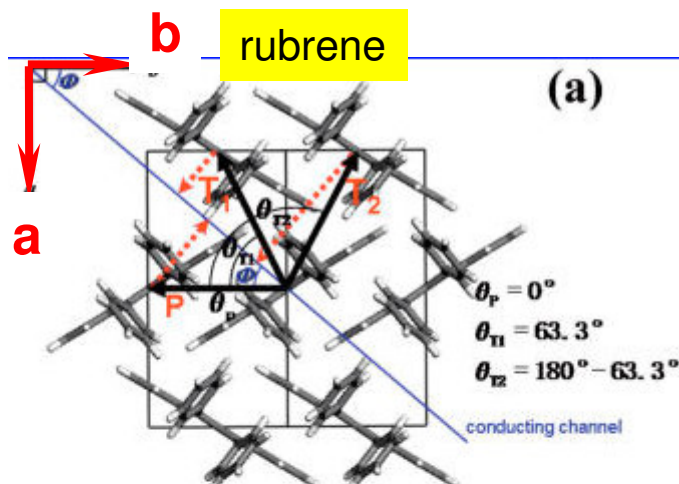
J. Y. Lee, S. Roth, Y. W. Park, Anisotropy in pentacene, *Appl. Phys. Lett.* **88**, 252106 (2006)



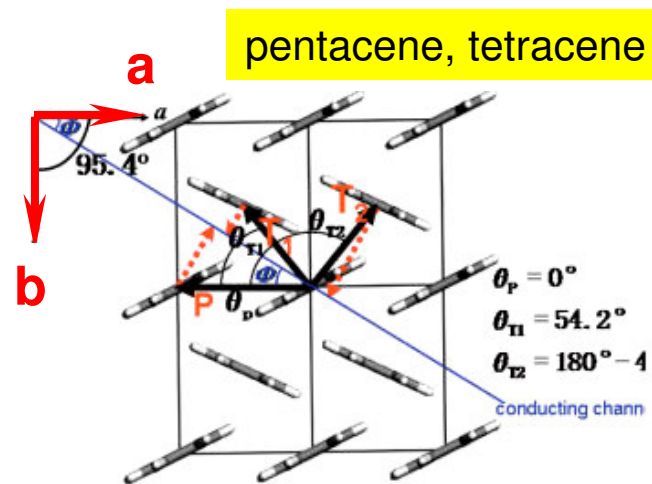
Rubrene

Ch. Kloc *et al*, Anisotropy in rubrene, *Chem. Mater.* **18**, 244 (2006)

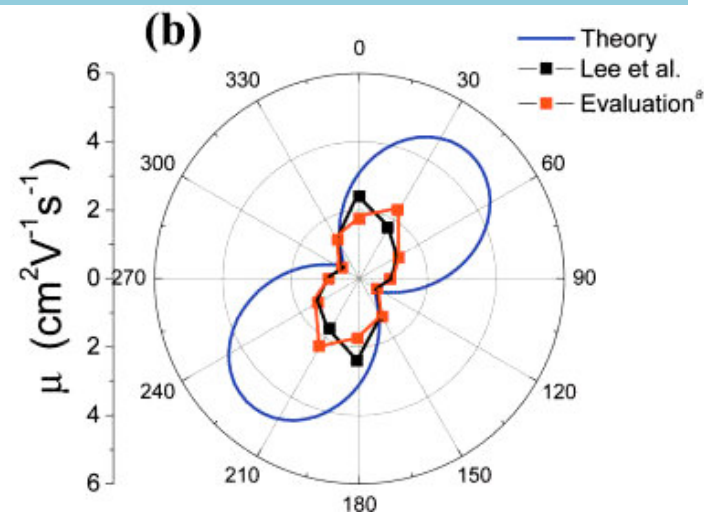
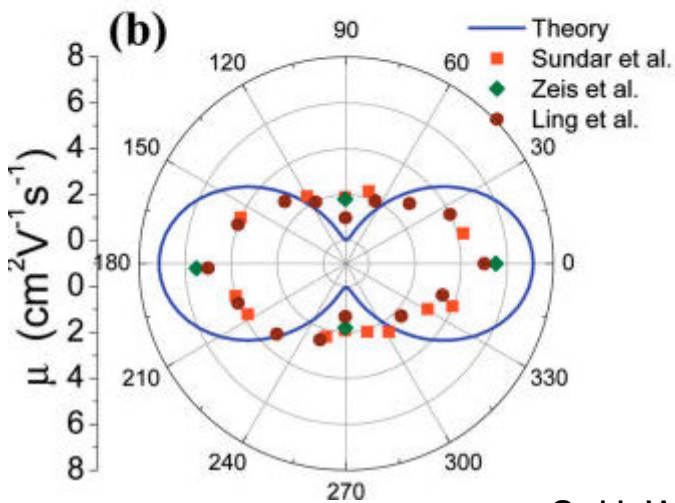
8. Theoretical calculations of mobility anisotropy



Mobility maximum is along **b** axis



Mobility maximum is in **a-b** direction

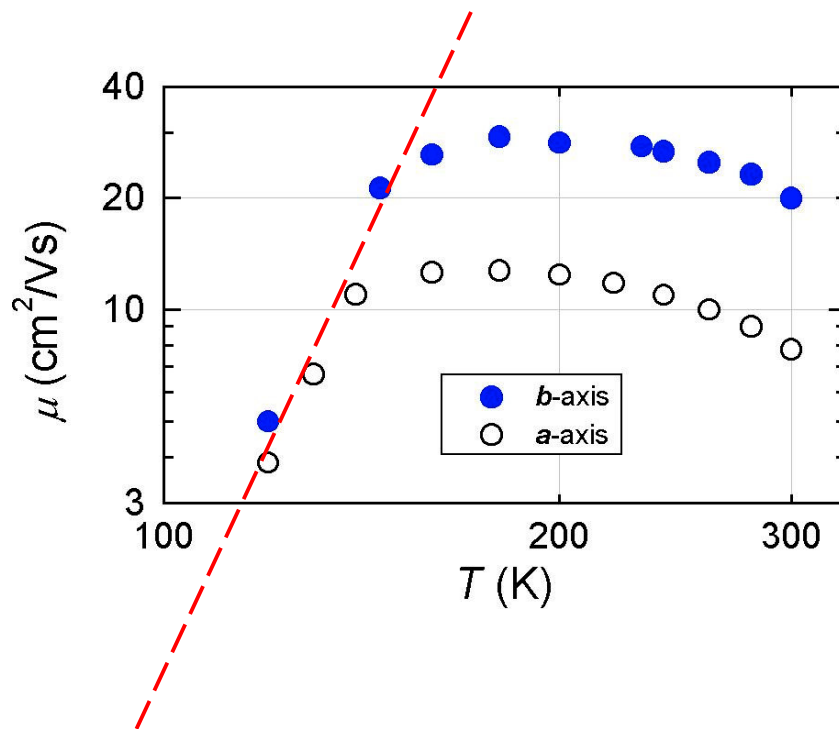


S.-H. Wen, W. A. Goddard III, et al,
 First-Principles Investigation of Anisotropic Hole Mobilities in Organic Semiconductors,
J. Phys. Chem. B 113, 8813 (2009)

Fall MRS-2012 Tutorial (V. Podzorov)

8. Non-activated $\mu(T)$, anisotropy and anisotropy vanishing in the trapping regime in rubrene

In the “activation” regime $\mu = \mu_0 \exp\left(-\frac{T_0}{T}\right)$, the anisotropy vanishes.



This is consistent with predictions of the multiple trap and release model:

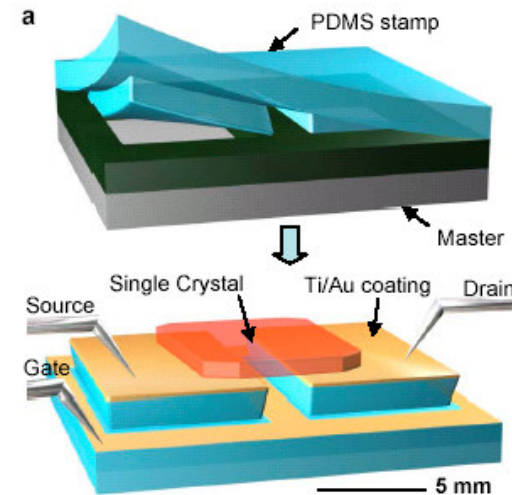
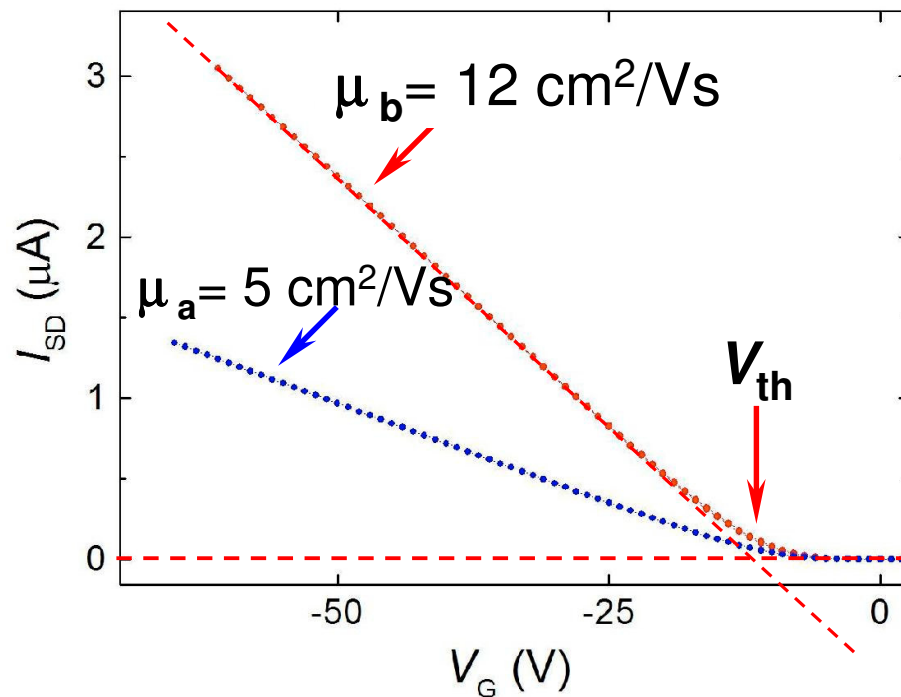
$$\mu_{eff} = \mu_0 \frac{\tau}{\tau + \tau_{tr}}$$

μ_0 - intrinsic trap-free mobility,
 τ - avrg. time of travel between traps ($\tau \sim \mu_0^{-1}$), τ_{tr} – the time spent on a shallow trap.

For the case $\tau_{tr} \gg \tau$,

V. Podzorov *et. al.*, *Phys. Rev. Lett.* **93**, 086602 (2004) μ_{eff} is isotropic.

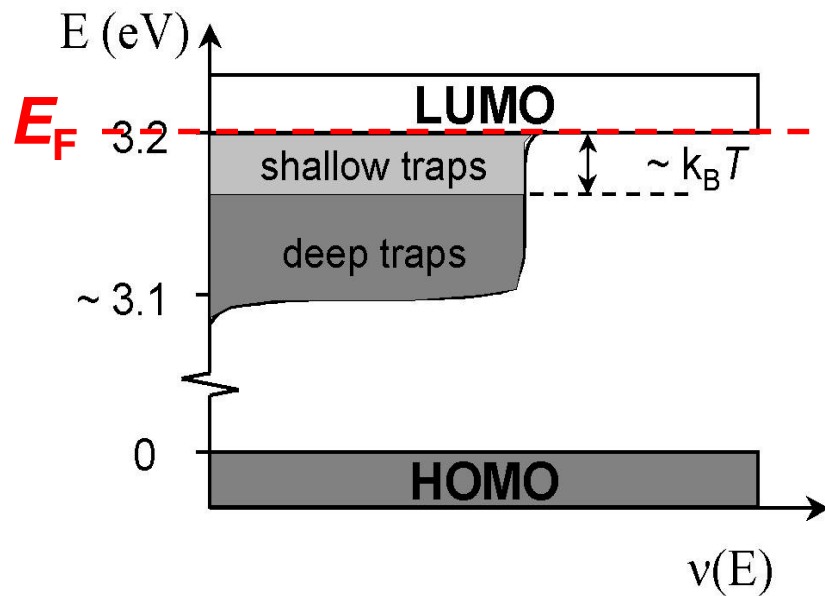
9. Importance of μ anisotropy and non-activated transport



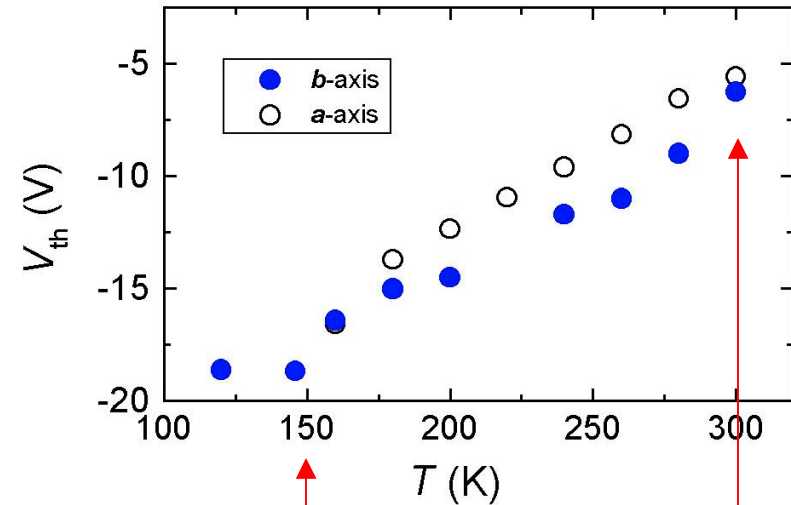
E. Menard *et al.*,
Adv. Mater. **16**, 2097 (2004)

Threshold voltage V_{th} and mobility μ in OFETs are two important parameters defined by the deep and shallow traps, respectively.

9. Threshold voltage is defined by the deep trap density



$$N_{tr} = \frac{C_i \cdot V_{th}}{e}$$



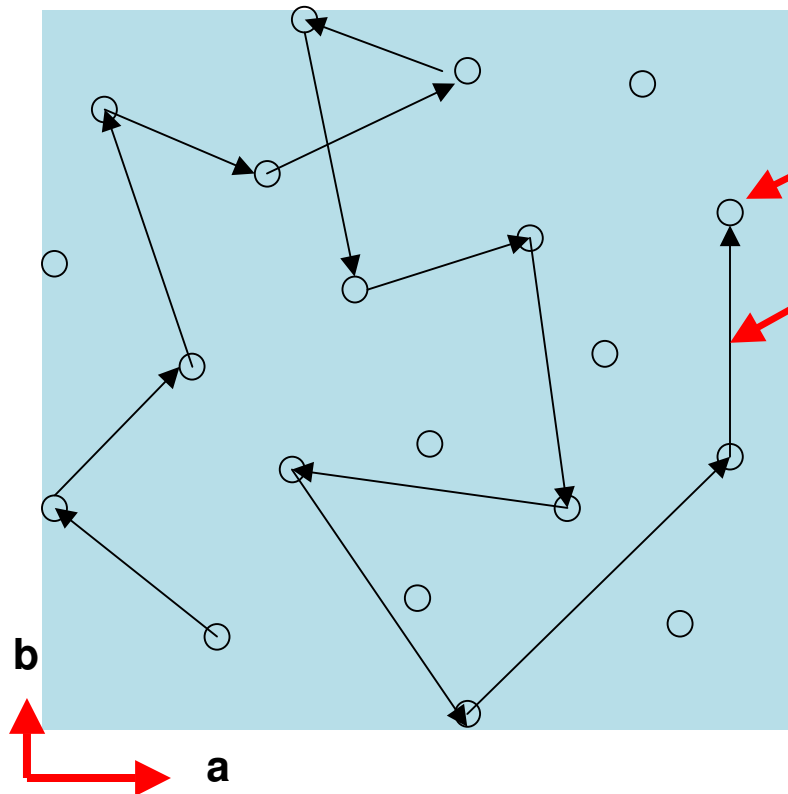
$$N_{\text{deep}}(150\text{K}) = 2 \cdot 10^{10} \text{ cm}^{-2}$$

$$N_{\text{deep}}(300\text{K}) = 0.7 \cdot 10^{10} \text{ cm}^{-2}$$

V. Podzorov *et. al.*,
Phys. Rev. Lett. **93**, 086602 (2004)

**Useful general method for the analysis of
deep traps in OFETs**

9. Mobility is defined by intrinsic (molecular packing) and non-intrinsic (trapping on shallow traps) factors



τ_{tr} – average time spent on a shallow trap

τ - time of traveling between traps ($\tau \sim \mu_0^{-1}$)

According to MTR model:

$$\mu_{eff} = \mu_0 \frac{\tau}{\tau + \tau_{tr}}$$

$\tau \gg \tau_{tr}$

Intrinsic:

$$\mu_{eff} = \mu_0$$

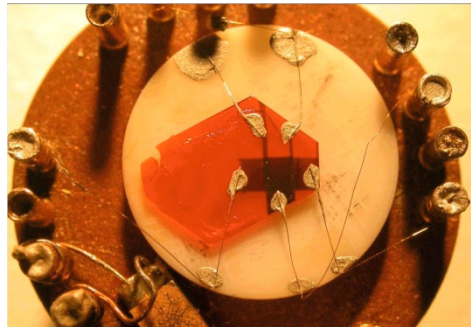
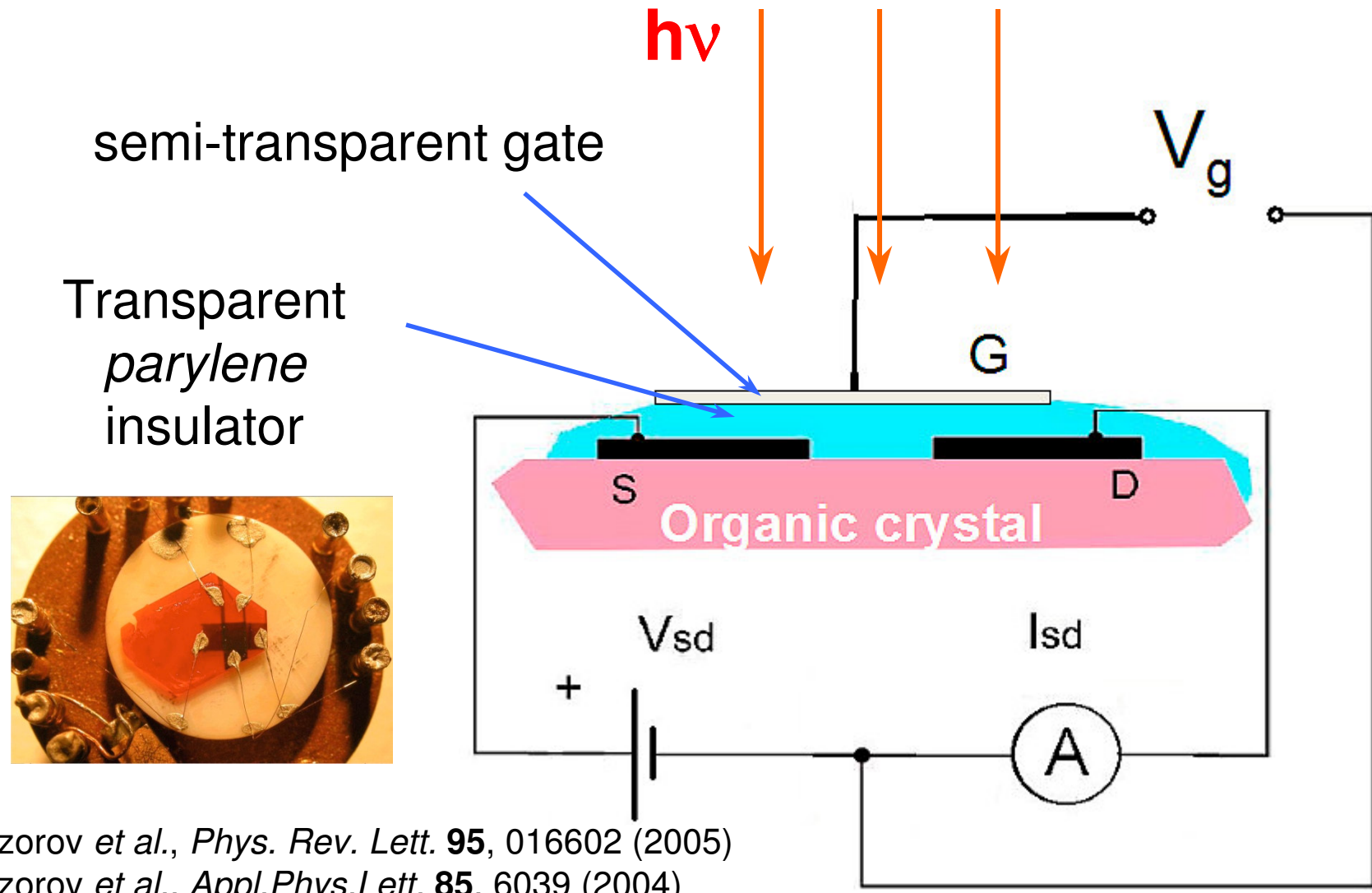
$\tau \ll \tau_{tr}$

Trap-dominated:

$$\mu_{eff} = \mu_0 (\tau / \tau_{tr})$$

- 1). Mobility anisotropy is a very good signature of intrinsic, not dominated by shallow traps operation of an OFET;
- 2). Observation of non-activated transport is also sign of intrinsic operation.

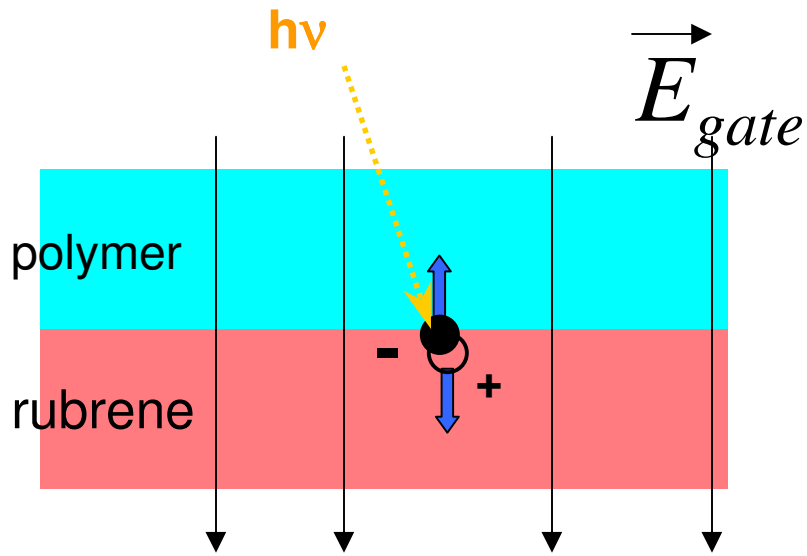
10. Photo-induced phenomena in single-crystal OFETs



Podzorov *et al.*, *Phys. Rev. Lett.* **95**, 016602 (2005)
Podzorov *et al.*, *Appl. Phys. Lett.* **85**, 6039 (2004)
Calhoun *et al.*, *Phys. Rev. Lett.* **98**, 096402 (2007)

10. Positive or negative threshold shifts in rubrene OFETs controlled by the gate voltage and illumination

Photo-induced charge transfer at the semicond.-insulator interface

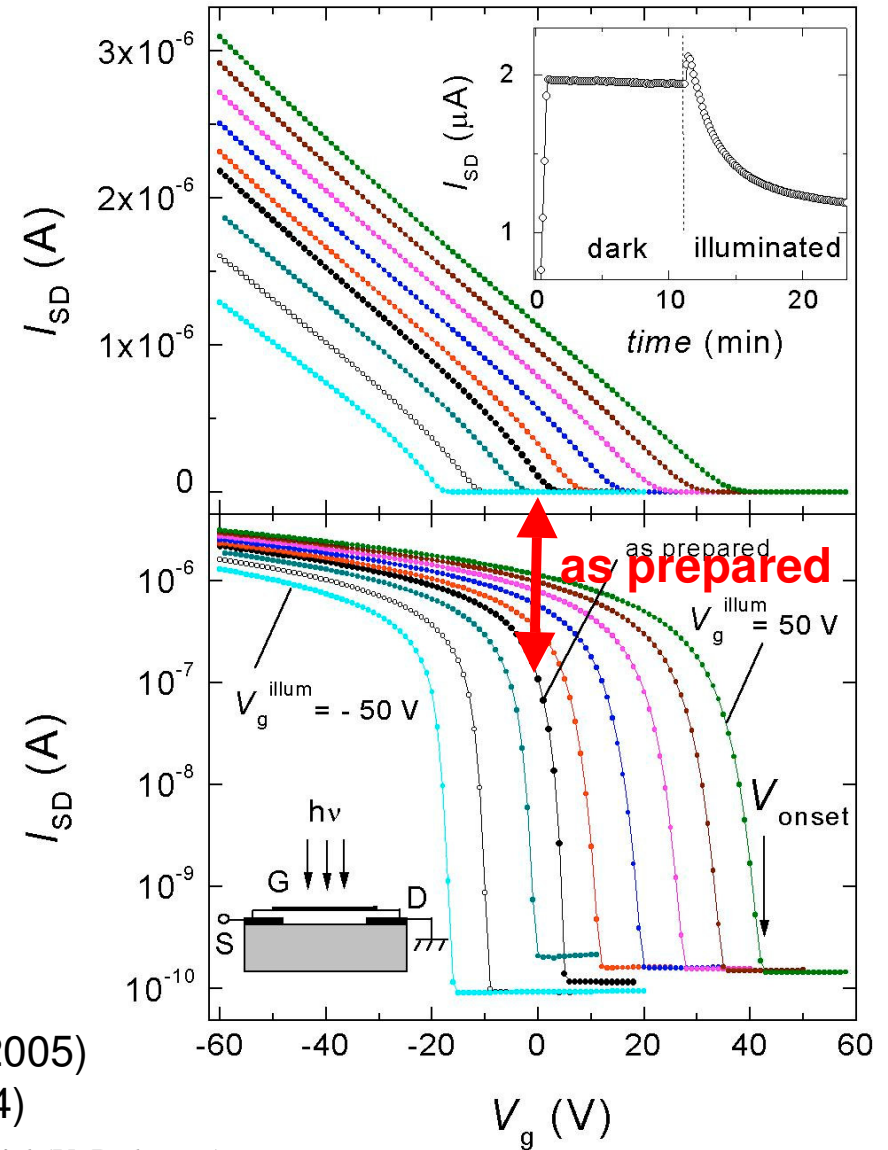


$$e \cdot (dn/dt) = \chi(\lambda) \cdot \Phi \cdot E_g$$

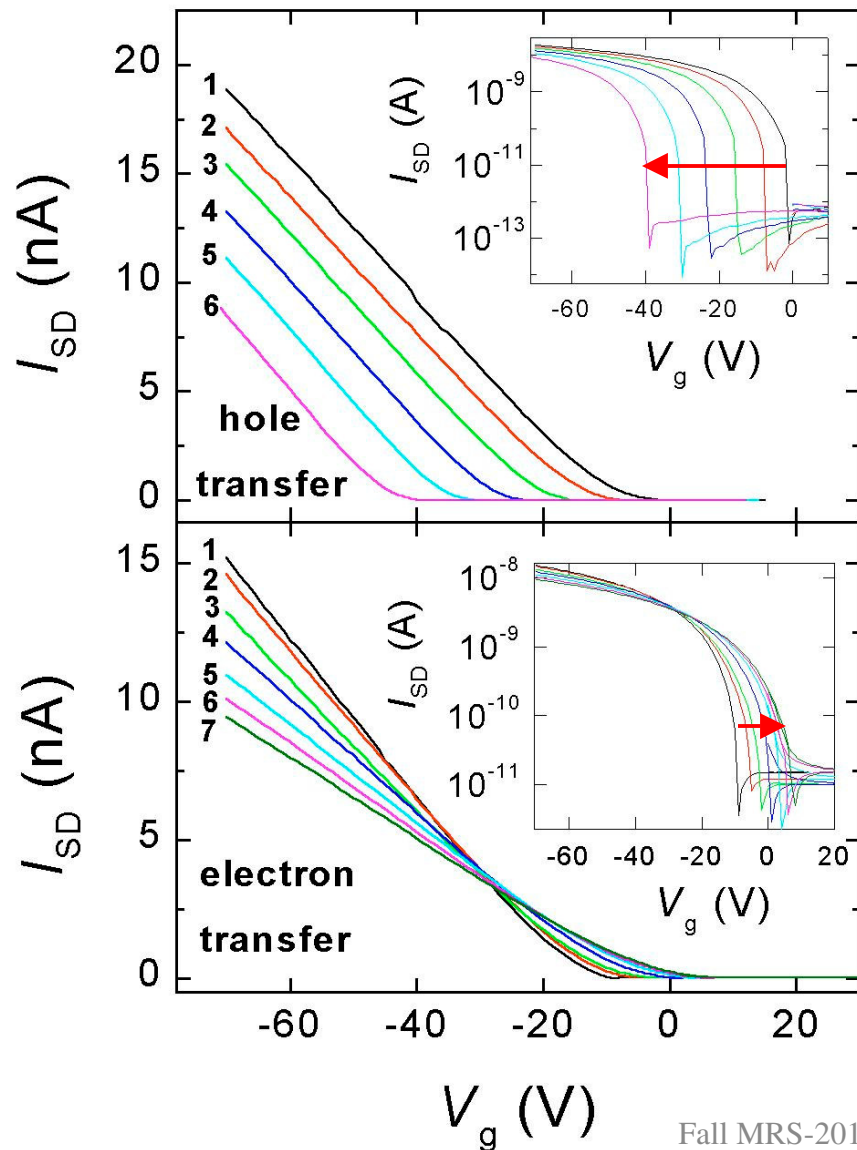
$$E_g = V_g/d - en(t)/\epsilon\epsilon_0$$

V. Podzorov *et al.*, *Phys. Rev. Lett.* 95, 016602 (2005)

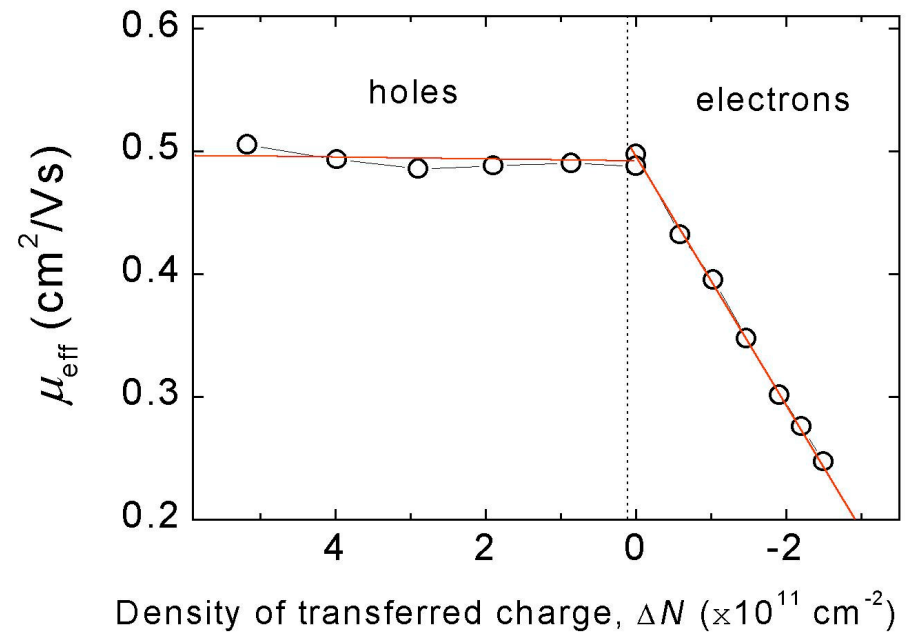
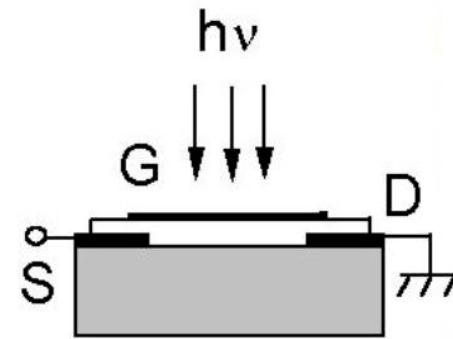
V. Podzorov *et al.*, *Appl. Phys. Lett.* 85, 6039 (2004)



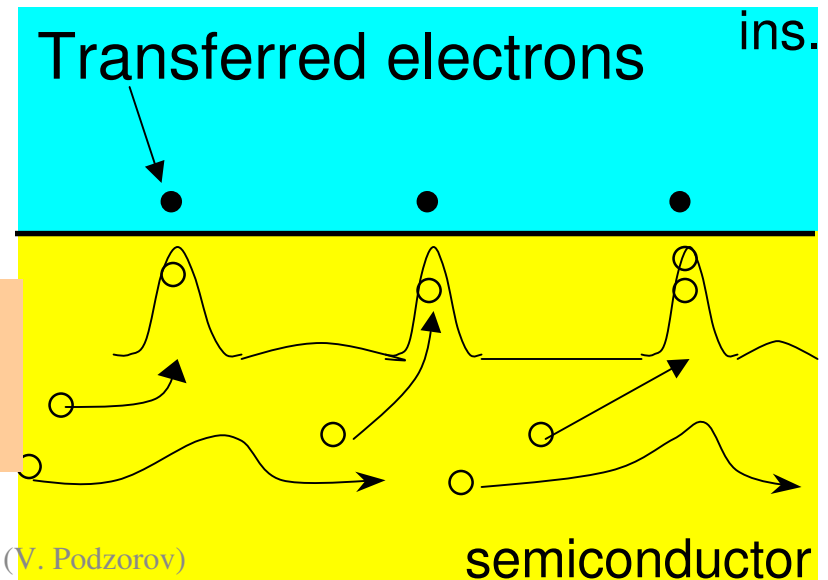
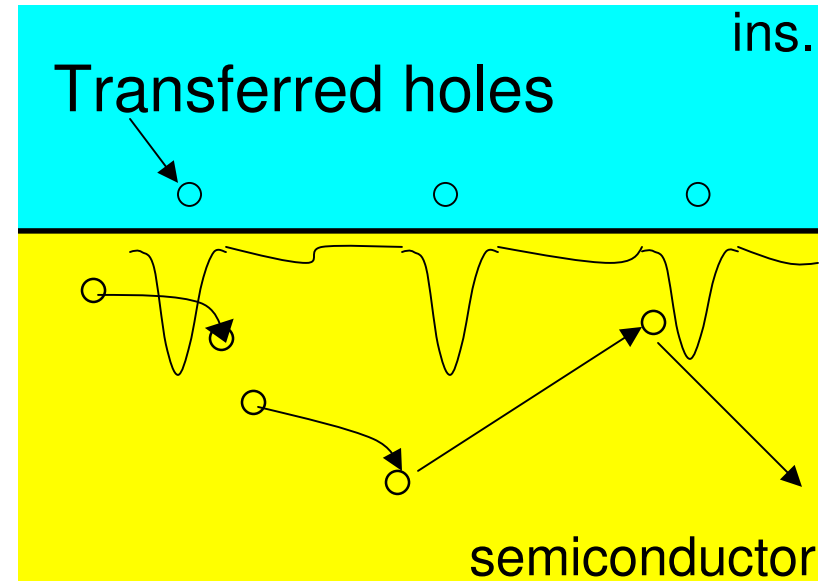
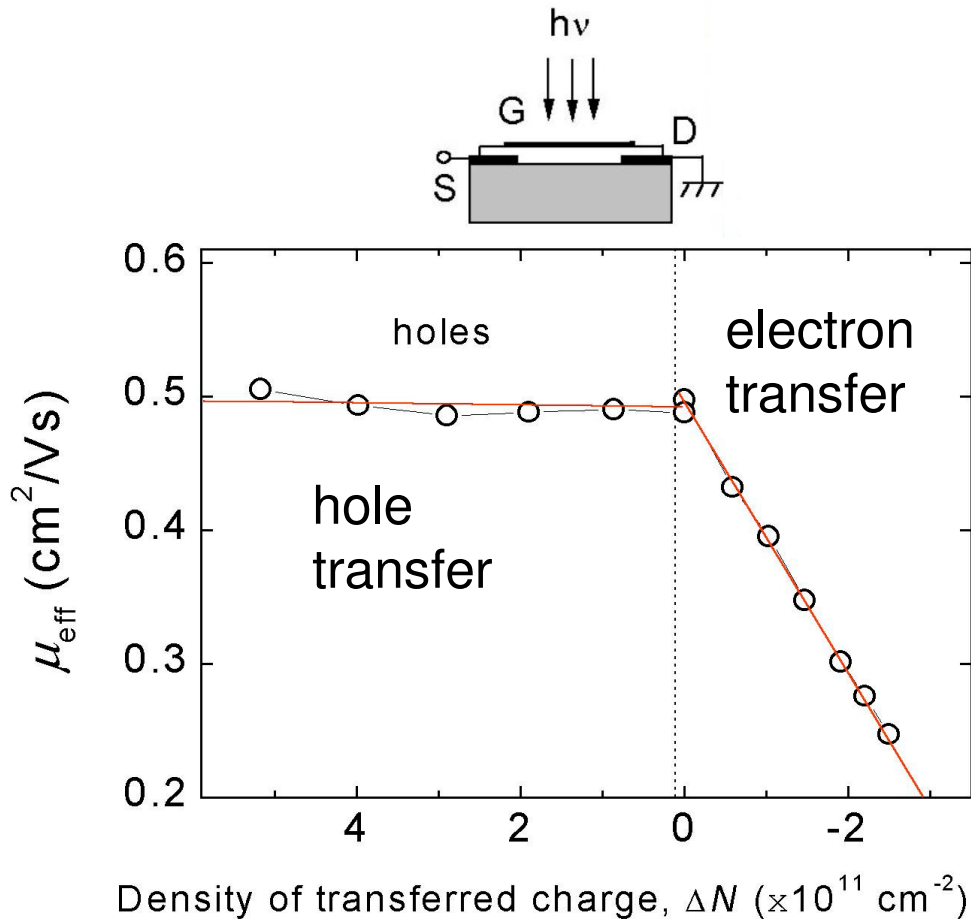
10. Photo-induced charge transfer in trap-dominated OFETs (the case of tetracene single-crystal OFETs)



Calhoun *et al.*, *Phys. Rev. Lett.* **98**, 096402 (2007)



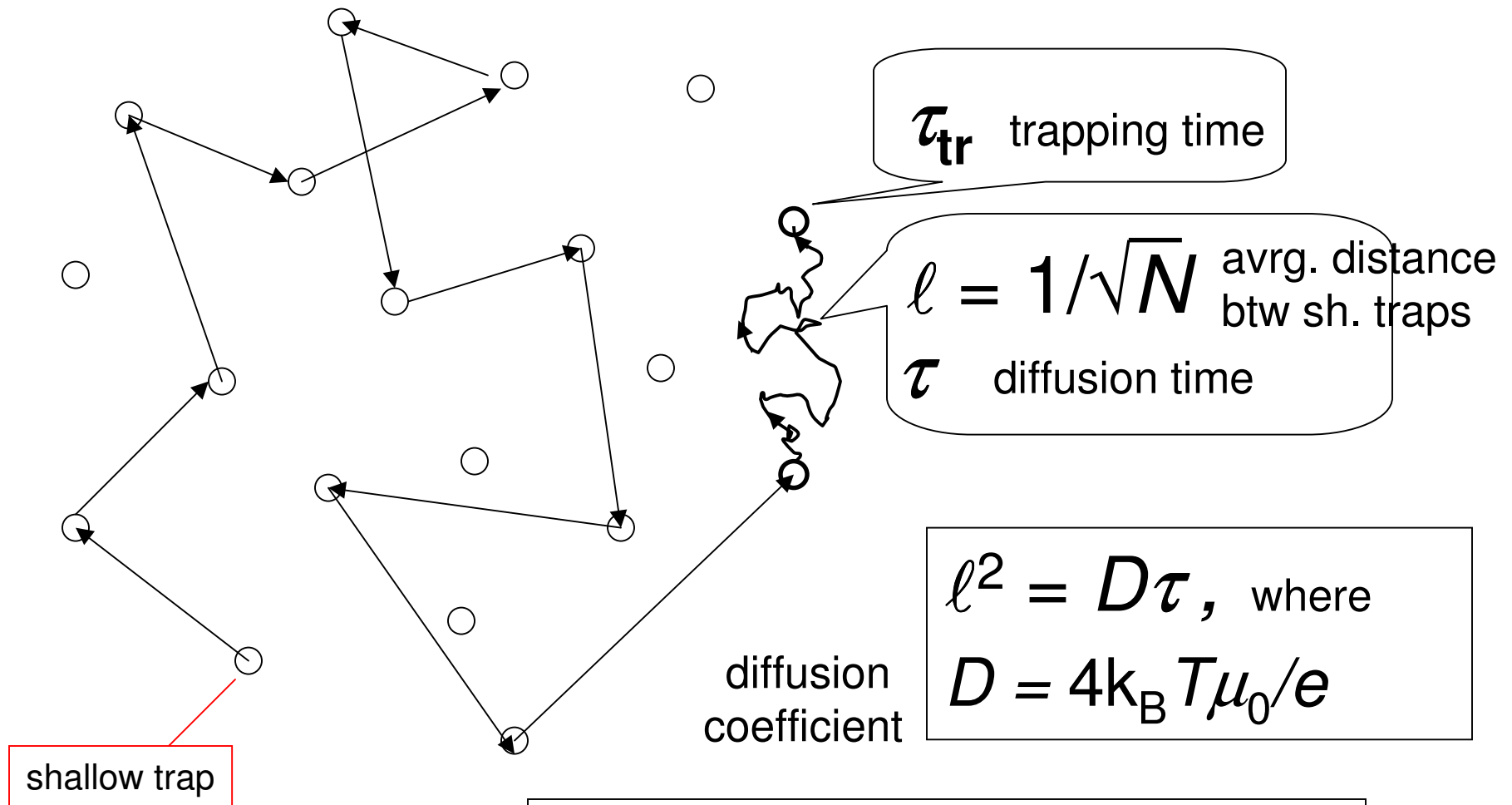
10. Photo-induced charge transfer in trap-dominated OFETs



This behavior can be used to extract the **density of shallow traps** and **trapping time**, inaccessible in other methods.

Calhoun *et al.*, *Phys. Rev. Lett.* **98**, 096402 (2007)

10. Photo-induced charge transfer in trap-dominated OFETs

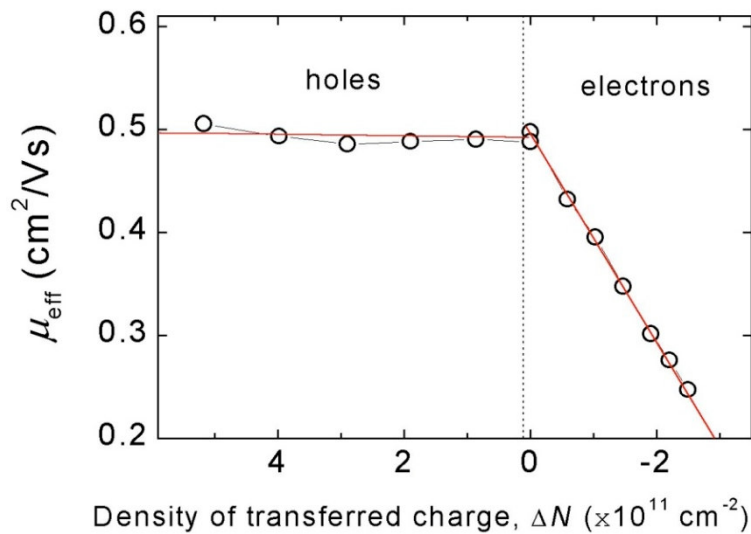


In multiple trap and release (MTR) model, the effective mobility is:

$$\mu_{\text{eff}} = \mu_0 \frac{\tau}{\tau + \tau_{tr}}$$

10. Photo-induced charge transfer in trap-dominated OFETs

$$\mu_{\text{eff}}(\Delta N) = \frac{\mu_{\text{eff}}^{(0)}}{1 + (4k_B T/e)\mu_{\text{eff}}^{(0)} \cdot \tau_{\text{tr}} \cdot \Delta N}$$



Average shallow trapping time:
 $\tau_{\text{tr}} \approx 50 \text{ ps}$

Shallow trap density in as-prepared OFETs:
 $N = 3.5 \cdot 10^{11} \text{ cm}^{-2}$

Calhoun *et al.*, *Phys. Rev. Lett.* **98**, 096402 (2007)

Some conclusions on photo-induced phenomena in OFETs

- It is demonstrated that the main response of high-quality OFETs to photoexcitation is a photo-induced charge transfer between the semiconductor and the gate dielectric resulting in a positive or negative threshold voltage shift, depending on the polarity of the gate voltage applied during the illumination.
- Besides importance for applications, these phenomena can be used to extract basic information on shallow traps, such as trapping time and the density of shallow traps, inaccessible by other methods.
- The method based on the photo-induced charge transfer in OFETs gives information directly relevant to the shallow traps and charge transport in OFETs, because the field-effect is used as a probe.
- Overall, single-crystal OFETs provide a powerful tool for the studies of photophysics of organic semiconductors.

For more materials, technical notes and recipes please visit our web page

<http://www.physics.rutgers.edu/~podzorov/index.php>

Podzorov Group

Investigating novel semiconductors at Rutgers University

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About Us

We are a research group based in Rutgers University Physics Department in Piscataway, New Jersey, where we study the physics of novel semiconductors. Our research tends to revolve around the following themes:

1. Fundamentals of charge carrier transport in organic semiconductors (OFETs).
2. The fundamental optical properties of highly ordered organic semiconductors (exciton dynamics, photo-conductivity and the photovoltaic effect).
3. Molecular self-assembly at functional interfaces.
4. Novel inorganic layered semiconductors (dihalcogenides and graphene).



Latest News (click individual entry for abstract)

1. An amazing effect of photo-triggered diffusion of molecular oxygen in a crystalline organic semiconductor is reported.
2. The origin of the bias-stress instability in single-crystal OFETs is revealed.
3. A very large exciton diffusion length ($L_{EX} \sim 3-8 \mu\text{m}$) is observed in highly ordered organic semiconductors.
4. A molecular self-assembly of silanes on organic semiconductors is discovered.
5. D. J. Elliman from the group of Prof. D. C. Fritchie (University of Minnesota)

Fall MRS-2012 Tutorial (V. Podzorov)

Credits to students, post-docs, collaborators and funding agencies

Students & Postdocs:

Dr. Y. Chen
Dr. H. T. Yi
Dr. H. Najafov
B. Lee
D. Fu
K. Czelen

**Post-doc applications
are welcome!**

Collaborations:

J. Anthony (*U. of Kentucky*)
C. D. Frisbie (*U. of Minnesota*)
J. Rogers (*U. Illinois*)
I. McCulloch (*Imperial College, London, UK*)
D. Basov (*UCSD*)
I. Biaggio (*Lehigh, U.*)
Y.-T. Tao & Y.-C. Chang (*Acad. Sinica, Taiwan*)

