

Intro to Organic Electronics

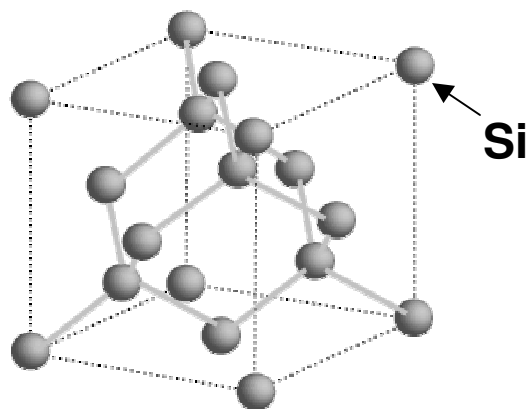
Vitaly Podzorov

Surface Science Course

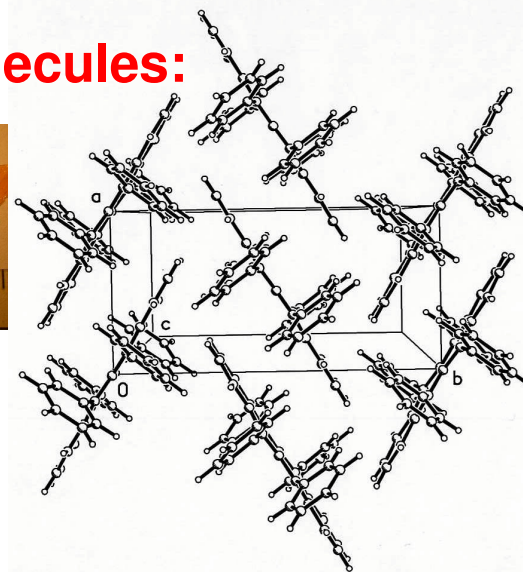
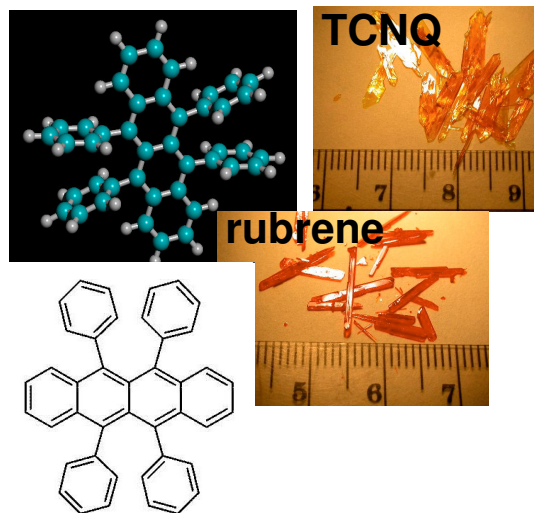
Dec. 6, 2010

Different types of Semiconductors

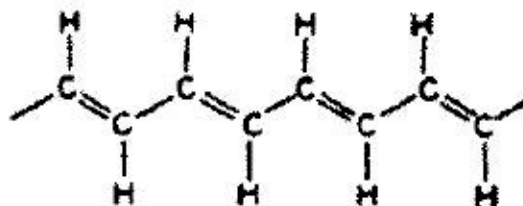
1. Inorganic: Si, Ge, GaAs



2. Organic small-molecules:



3. Conjugated Polymers



Prototypes of Organic Electronic devices:



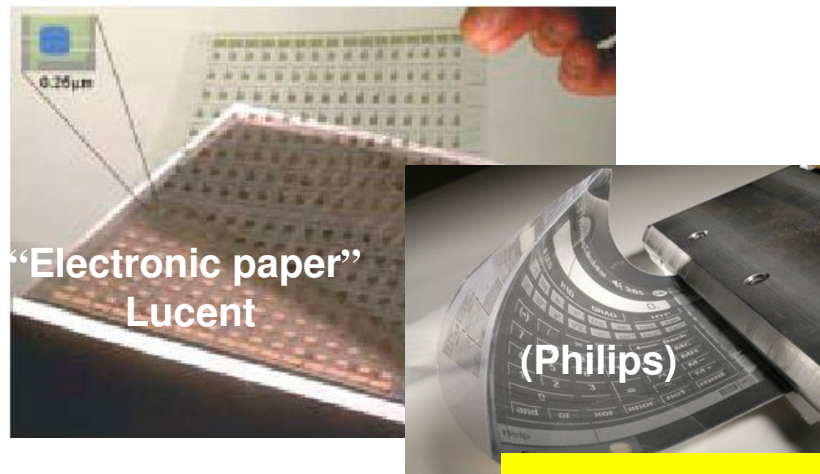
OLEDs:

S. R. Forrest in *Nature* 428, 911 (2004)

Organic Photo-Voltaics:

Electronic paper:

C. Reese et al., *Materials Today*, Sept. 2004

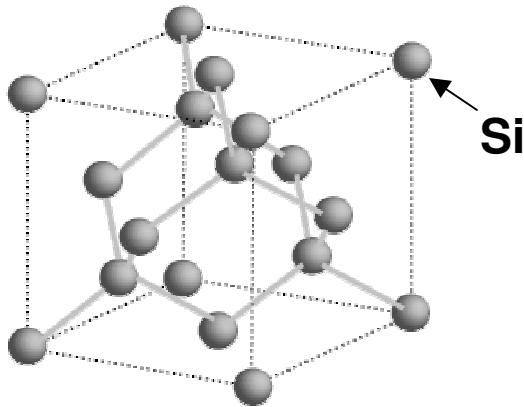


Show demonstration

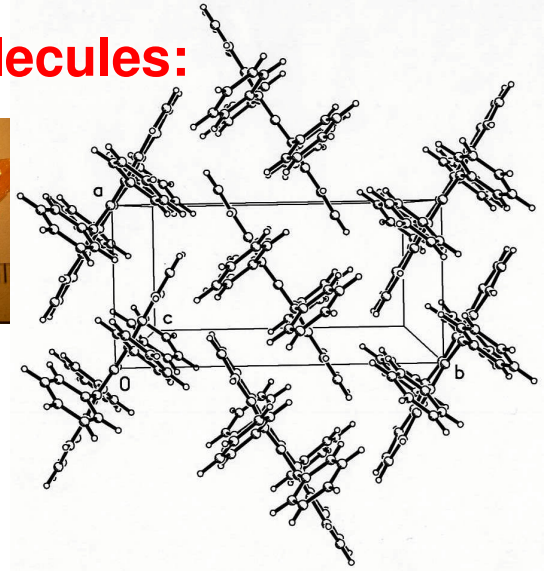
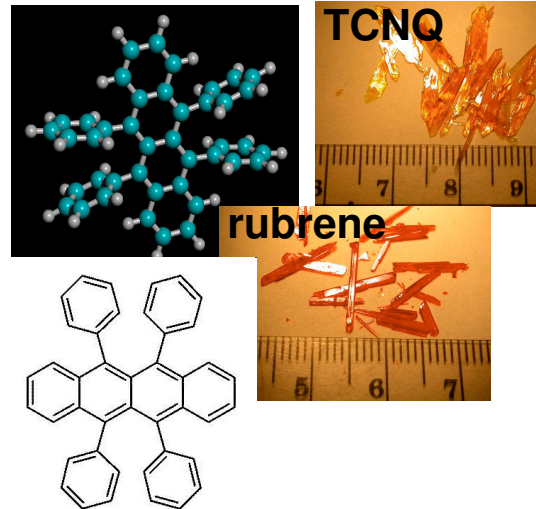


Different types of Semiconductors

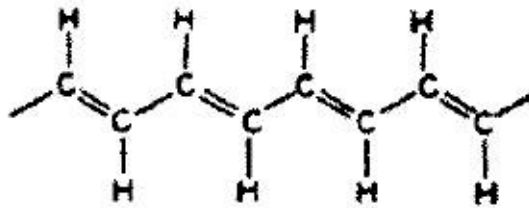
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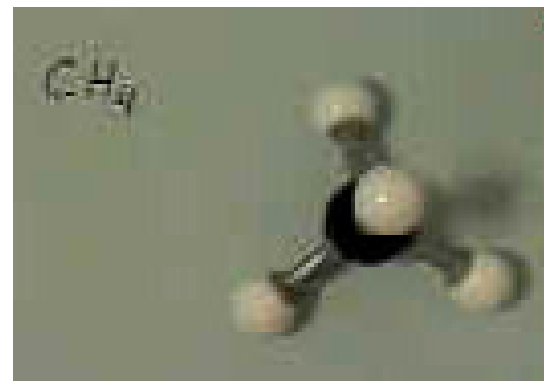
Two types of bonding in organic materials:

1. Intra-molecular: C to C, C to H;
2. Inter-molecular: van der Waals

Intra-molecular bonding: carbon bonds

Electron configuration for C: $1s^2 2s^2 2p^2$

How can this arrangement of electrons in the orbitals of a carbon atom be related to the arrangement of electrons in CH_4 to give a tetrahedral shape?

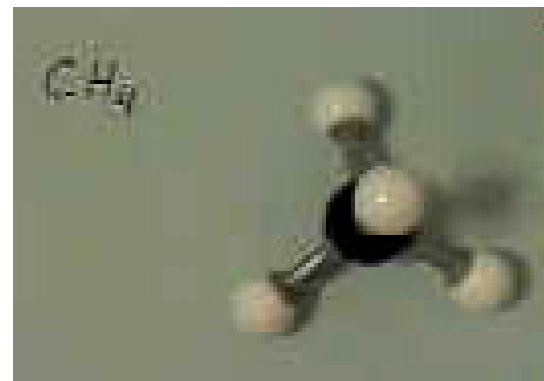


Tetrahedral methane

Intra-molecular bonding: carbon bonds

Electron configuration for C: $1s^2 2s^2 2p^2$

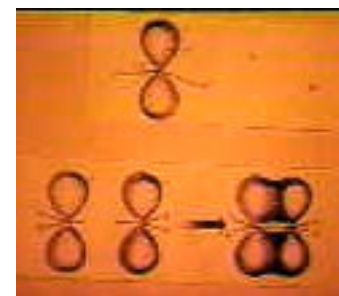
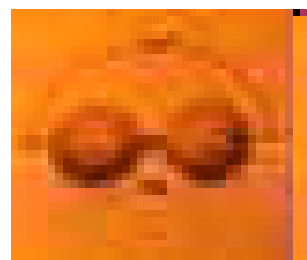
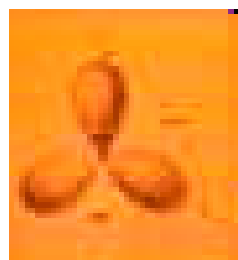
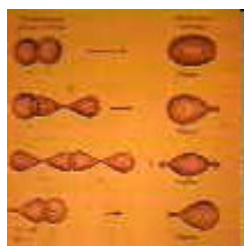
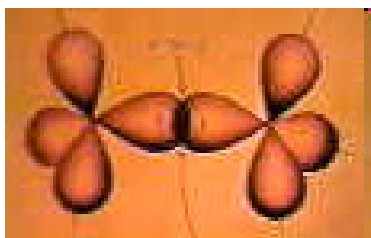
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Tetrahedral methane

Hybridization! - change from atomic orbitals to bonding orbitals.

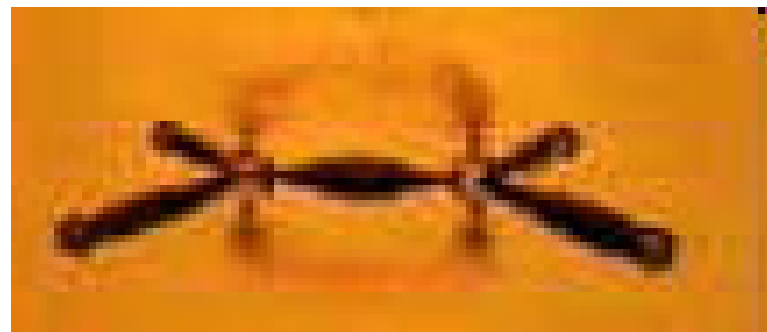
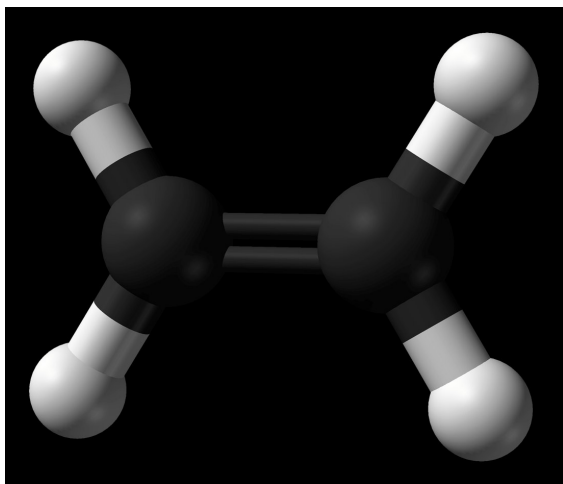
Discuss sp^3 , sp^2 , sp hybridization, σ -bonds, π -bonds, delocalization of π electrons



Example of a double bond: ethylene

This diagram tries to represent all of the sigma and pi bonds in ethylene (C_2H_4). This is perhaps the best way to represent that a double bond consists of a sigma bond and a pi bond.

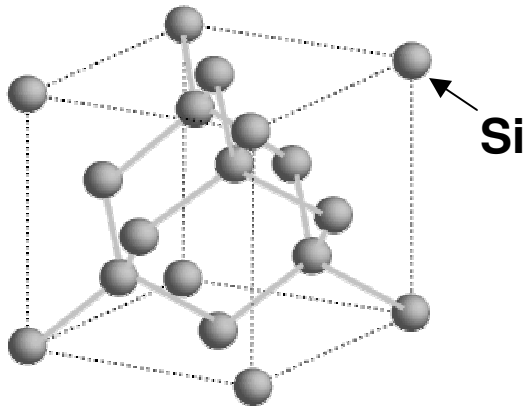
It may possibly look like three bonds to you, but it is not. There is a sigma bond in the center and a pi bond above and below that. Altogether that represents a double bond.



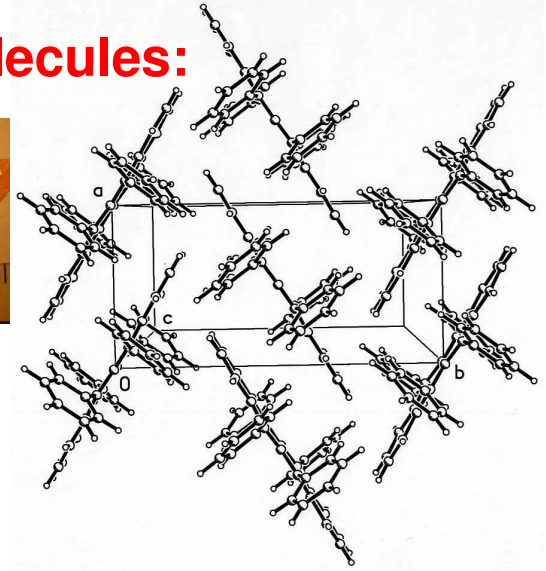
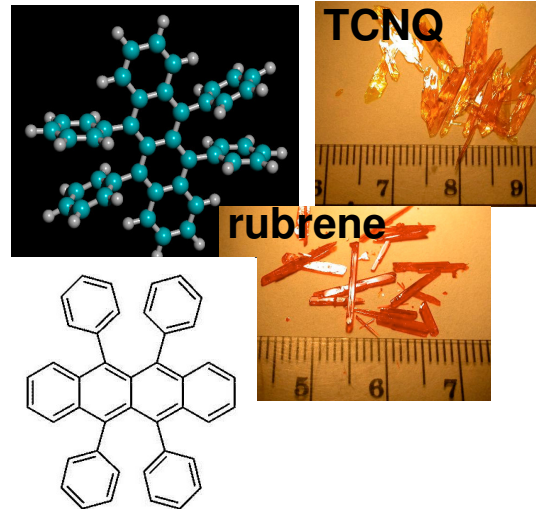
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Different types of Semiconductors

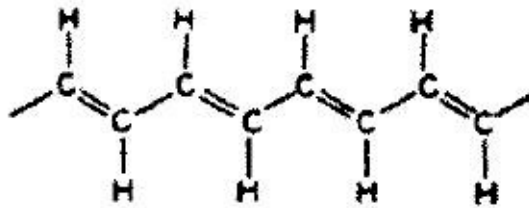
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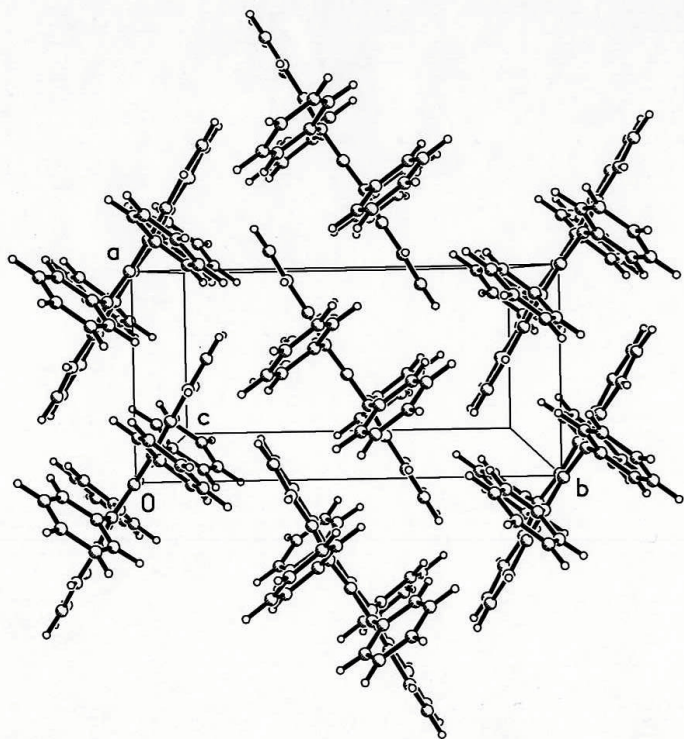
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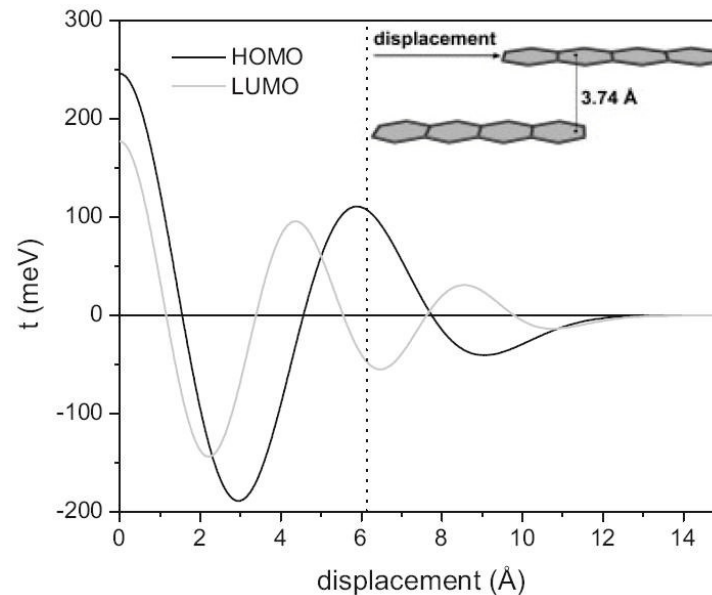
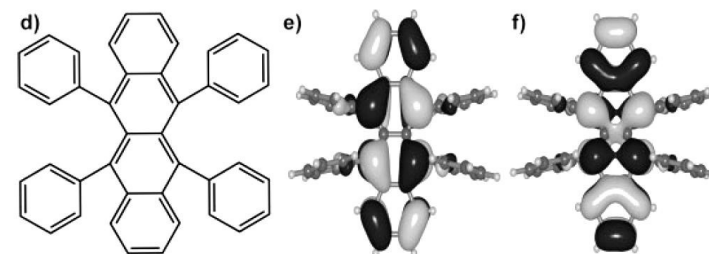
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



Inter-molecular bonding (van der Waals): Pi-orbital overlap between adjacent molecules



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



Electronic Properties of Small-Molecule Organics

Si, Ge, GaAs	small-molecule organics
strong covalent bonding	weak van der Waals bonding
	
large bandwidth, $W \sim 10$ eV	narrow bands, $W \sim 0.1$ eV
	
high mobility of electrons and holes, $\mu \sim 500$ cm²/Vs	low mobility of small polarons, $\mu \sim 1-10$ cm²/Vs

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

Phenomenological definition of mobility.

In a “viscous” medium, drift velocity is proportional to the force:

$$v = \mu F$$

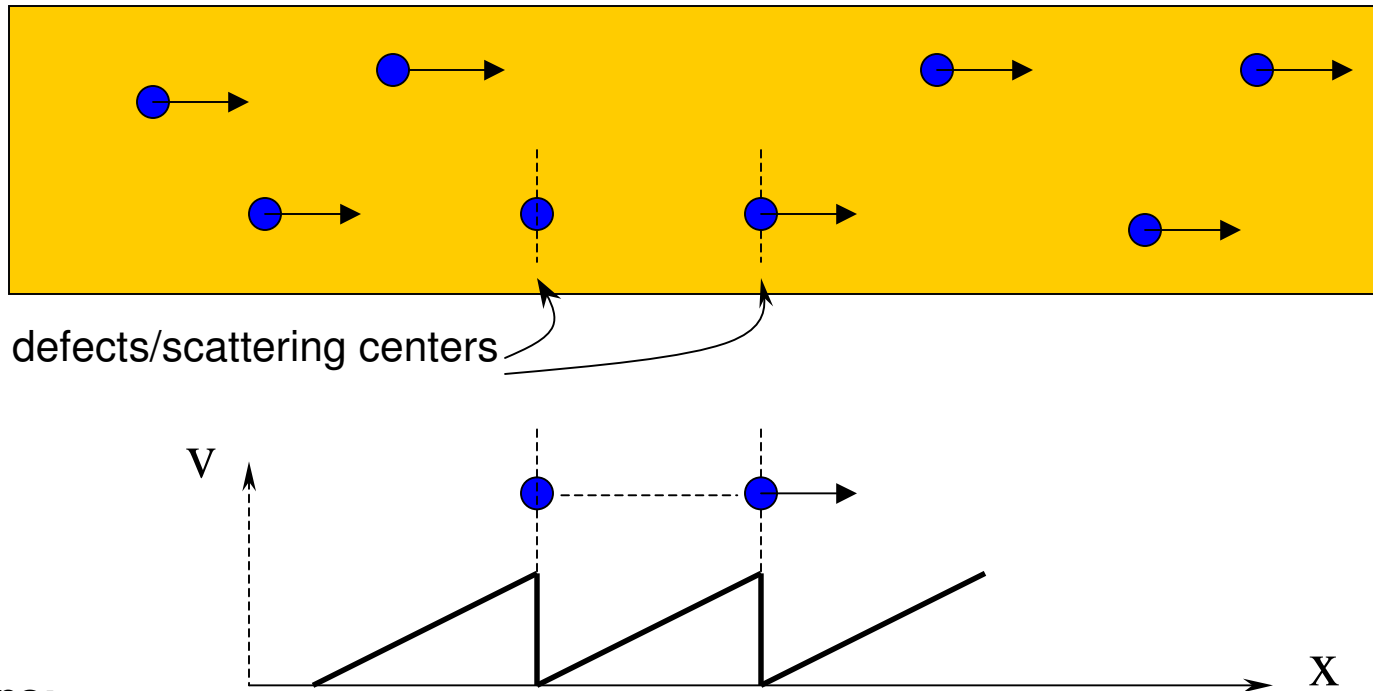
For charged particles in an electric field, drift velocity is proportional to the electric field:

$$v = \mu E$$

Units of μ ?

$$\mu \text{ [cm}^2\text{/Vs]}$$

Definition of 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);

Write down differential equation

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

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

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

$$v = (3kT/m^*)^{1/2} \quad (10^5 \text{ m/s at room temperature})$$

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

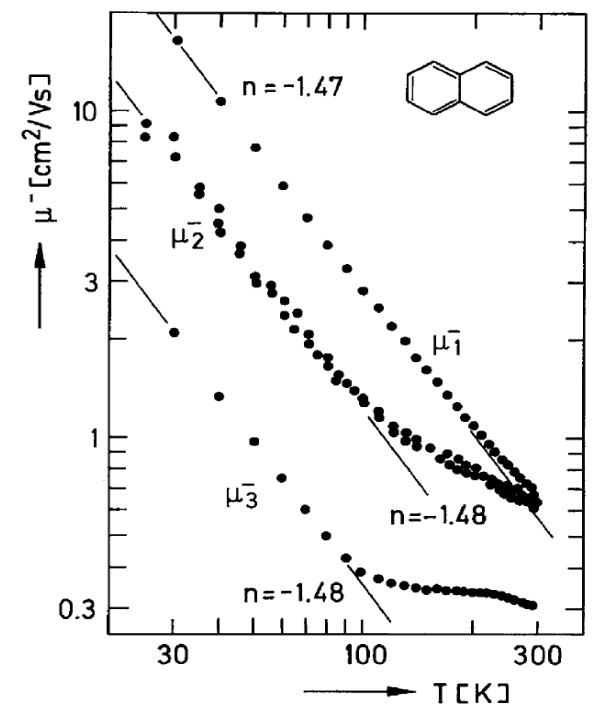
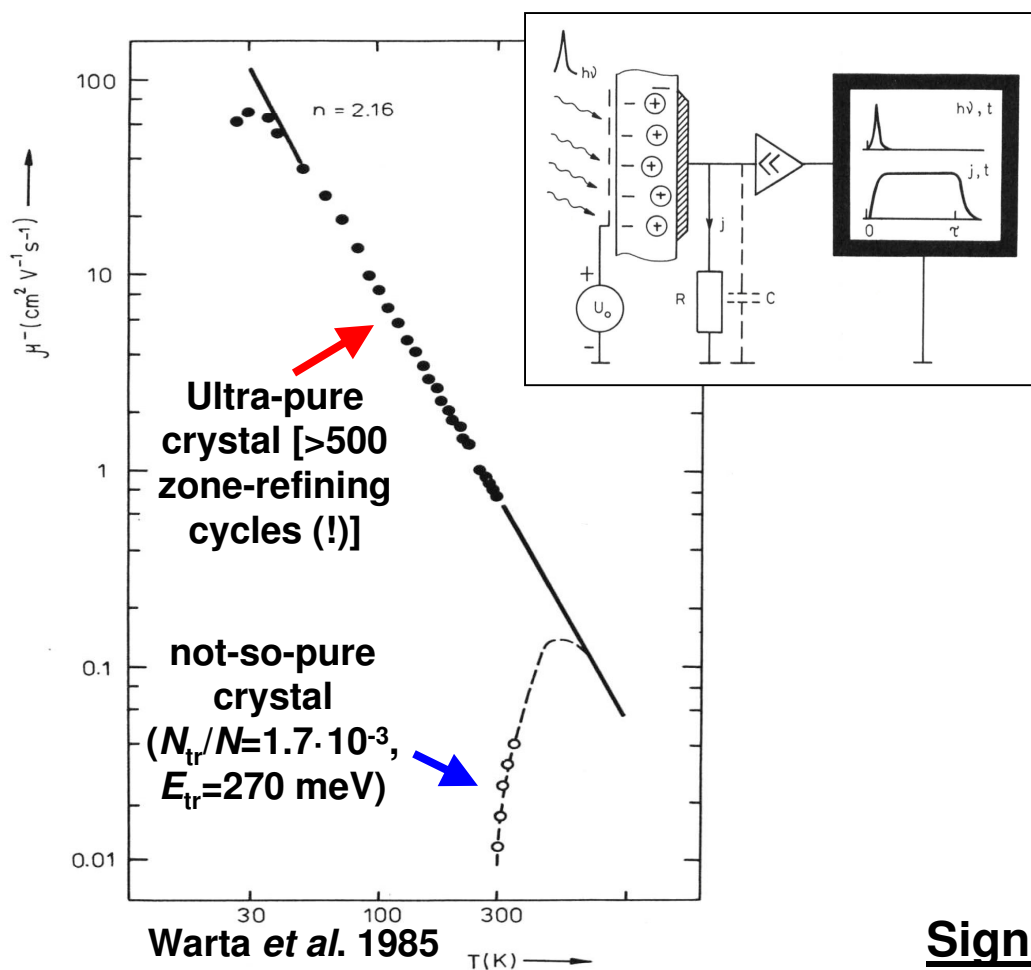
The T-dependence of the mobility depends on the effective mass, scattering mechanisms (phonons, charged impurities, screening, etc). In most of the band semiconductors:

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

meaning that μ increases when T is lowered.

For organic semiconductors, this simple theory fails, because λ becomes comparable to the lattice constant at $T > 100$ K.

TOF experiments with ultra-pure bulk crystals



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

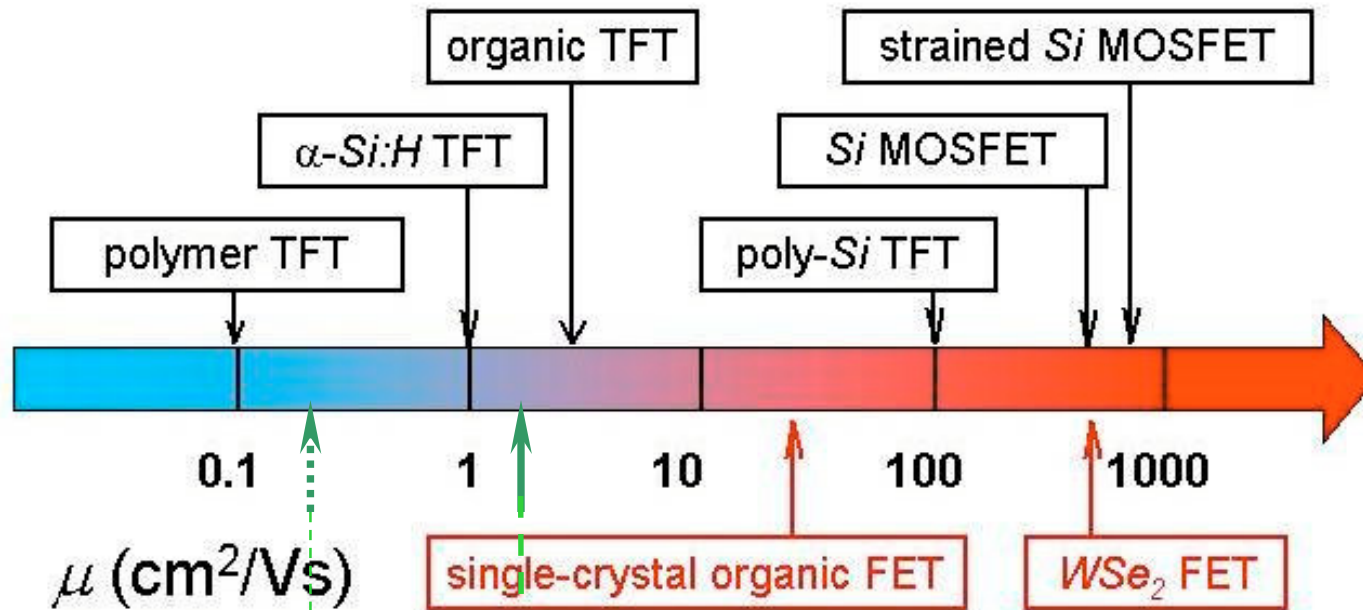
Theoretical treatment:

Kenkre (PRL),
 Bredas (JACS, Chem. Rev., PNAS)
 Hannewald & Bobbert (PRB, APL)
 Palstra (Synth. Met.)

Signatures of intrinsic transport:

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

Organic vs. Inorganic Semiconductors



$\mu \sim 0.01\text{-}0.1 \text{ cm}^2/\text{Vs}$ in **polymer TFTs**: Z. Bao *et al.*, *APL* **69** 4108 (1996)
 Sirringhaus *et al.* *Nature* **401**, 685 (1999)
 Salleo *et al.*, *APL* **81** 4383 (2002)

$\mu \sim 1 \text{ cm}^2/\text{Vs}$ in **p-type OTFT**: Gundlach, Nelson, Klauk & Jackson in *APL*, and
 in *IEEE Trans. Elec. Devices* & 3M

$0.2 \text{ cm}^2/\text{Vs}$ in **n-type OTFT**: Chesterfield *et al.*, *Adv. Mater.* **15**, 1278 (2003)

$\mu \sim 2 \text{ cm}^2/\text{Vs}$ in **single-crystal n-type OFETs**: Menard *et al.*, *Adv. Mater.* **16**, 2097 (2004)

$\mu \sim 10 - 20 \text{ cm}^2/\text{Vs}$ in **single-crystal p-type OFETs**: Podzorov *et al.*, in *APL*, and *PRL*;

$\mu \sim 500 \text{ cm}^2/\text{Vs}$ in **WSe₂**: Podzorov *et al.*, *APL* **84**, 3301 (2004)

Polarization in Molecular Crystals

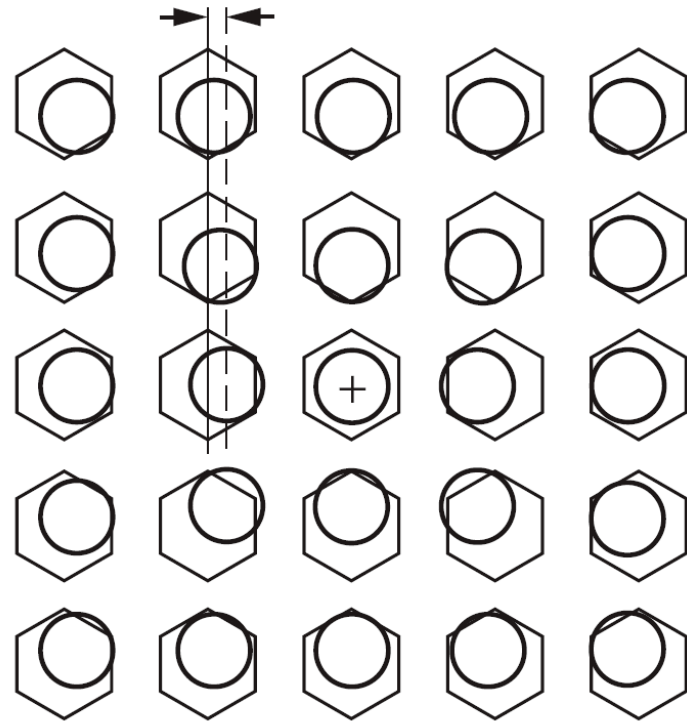
The main reason why the band model is unable to account for charge transport in organic semiconductors is that it fails to account for a crucial phenomenon in these materials: polarization.

“Dressed” charge, and the formed quasi-particle is called a *polaron*. In conjugated solids, the main polarization effect is that on the clouds formed by the π -electrons.

To analyze probability of polaron formation we should define two typical time-scales:

- (1) the residence time τ_{res} corresponds to the average time a charge will reside on a molecule;
- (2) the electronic polarization time τ_{el} is the time it takes for the polarization cloud to form around the charge.

Estimation of these time scales uses Heisenberg’s uncertainty principle.



Comparison of possibility of forming a polaron in org. and inorg. semiconductors

For the residence time, the pertinent energy is the width W of the allowed band, typically 0.1 eV in an organic semiconductor and 10 eV in an inorganic semiconductor, which gives a residence time of 10^{-14} s for the org. semiconductor and 10^{-16} s for an inorganic semiconductor.

As for the electronic polarization time, the corresponding energy is that of an electron transition — that is, the energy gap (~ 1 eV) — so the time of the order of 10^{-15} s in both cases.

Residence Time and Various Polarization Times

		Energy (eV)	Time (s)
Residence τ_{res}	Inorganic SC	10	10^{-16}
	Molecular SC	0.1	10^{-14}
Polarization	Electronic τ_{el}	1	10^{-15}
	Molecular τ_v	0.1	10^{-14}
	Lattice τ_l	< 0.01	$> 10^{-13}$

Polarization effect on band structure

As a result of a strong polarization effect (polaronic effect) the energy levels are significantly shifted (band structure is modified).

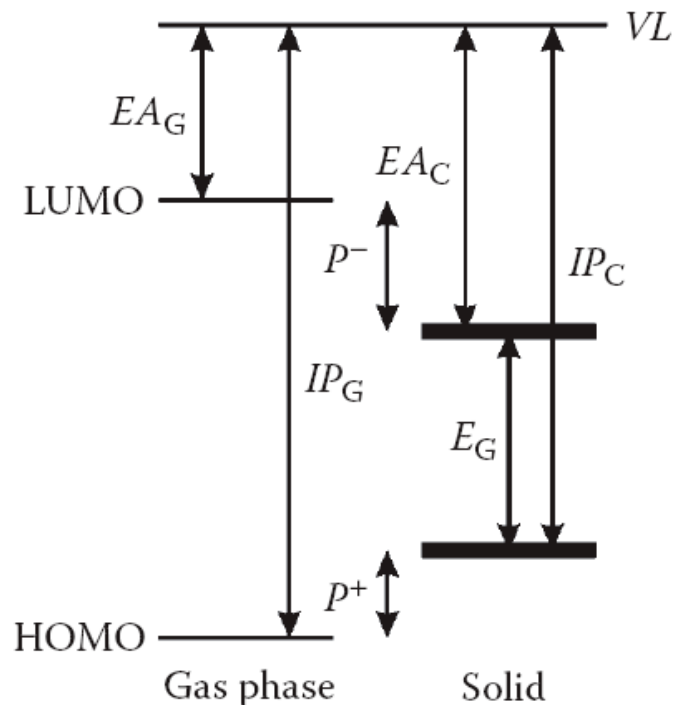


FIGURE 2.2.6 Energy scheme of the electronic polaron in a molecular crystal. VL is the vacuum level, EA the electronic affinity, and IP the ionization potential. P^+ and P^- are the polarization energy for positive and negative charge, respectively, and E_G the transport band gap. (From Silinsh, E.A. and Capek, V., *Organic molecular crystals: Interaction, localization, and transport phenomena*, AIP Press, New York, 1994.)

Molecular Polaron

Complementary to the electronic polarization, a charge carrier in a molecular solid also polarizes the intramolecular vibration modes of the molecule on which it is located, as well as dipole active modes of the neighboring molecules. This forms an extended ionic state. As already mentioned, the corresponding relaxation time is comparable to the residence time. The new quasi-particle associated with this process is called *molecular polaron*.

The temperature dependence of the effective mass of the molecular polaron:

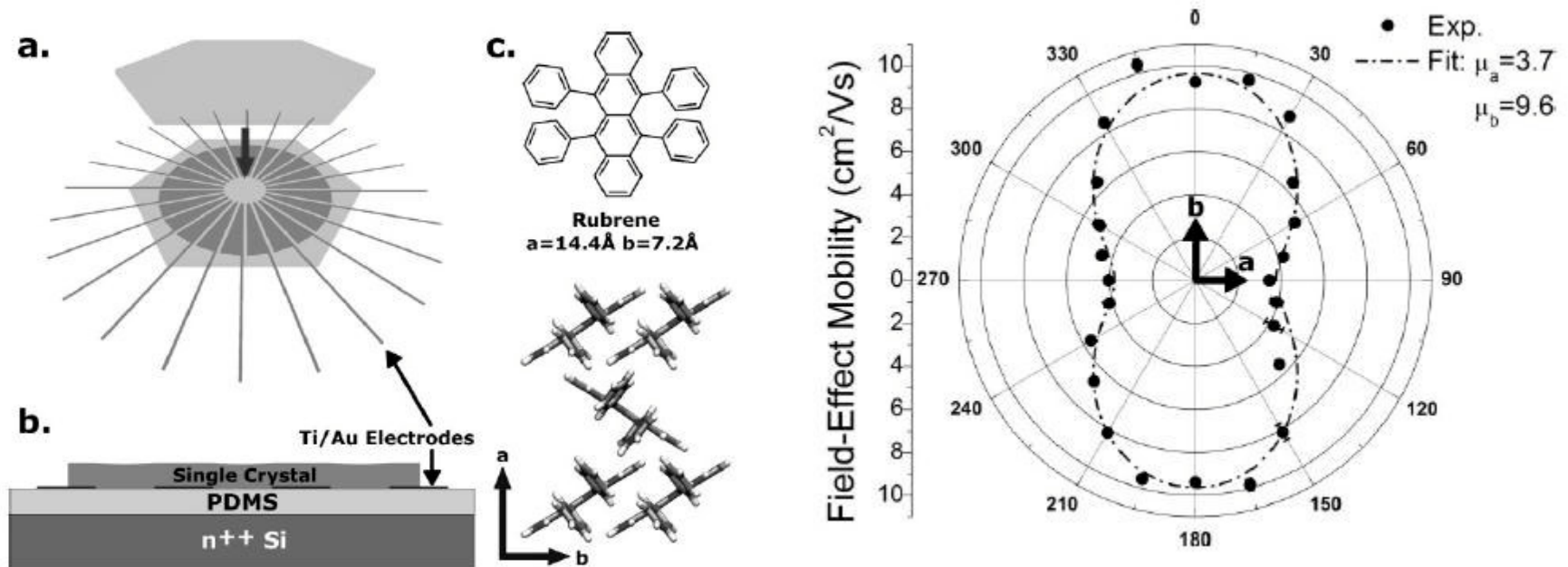
$$m_{\text{eff}}(T) = m_{\text{eff}}(0)e^{T/T_0}$$

The polaron becomes lighter as T is lowered!

Hence, mobility, $\mu = e\tau/m^*$, increases.

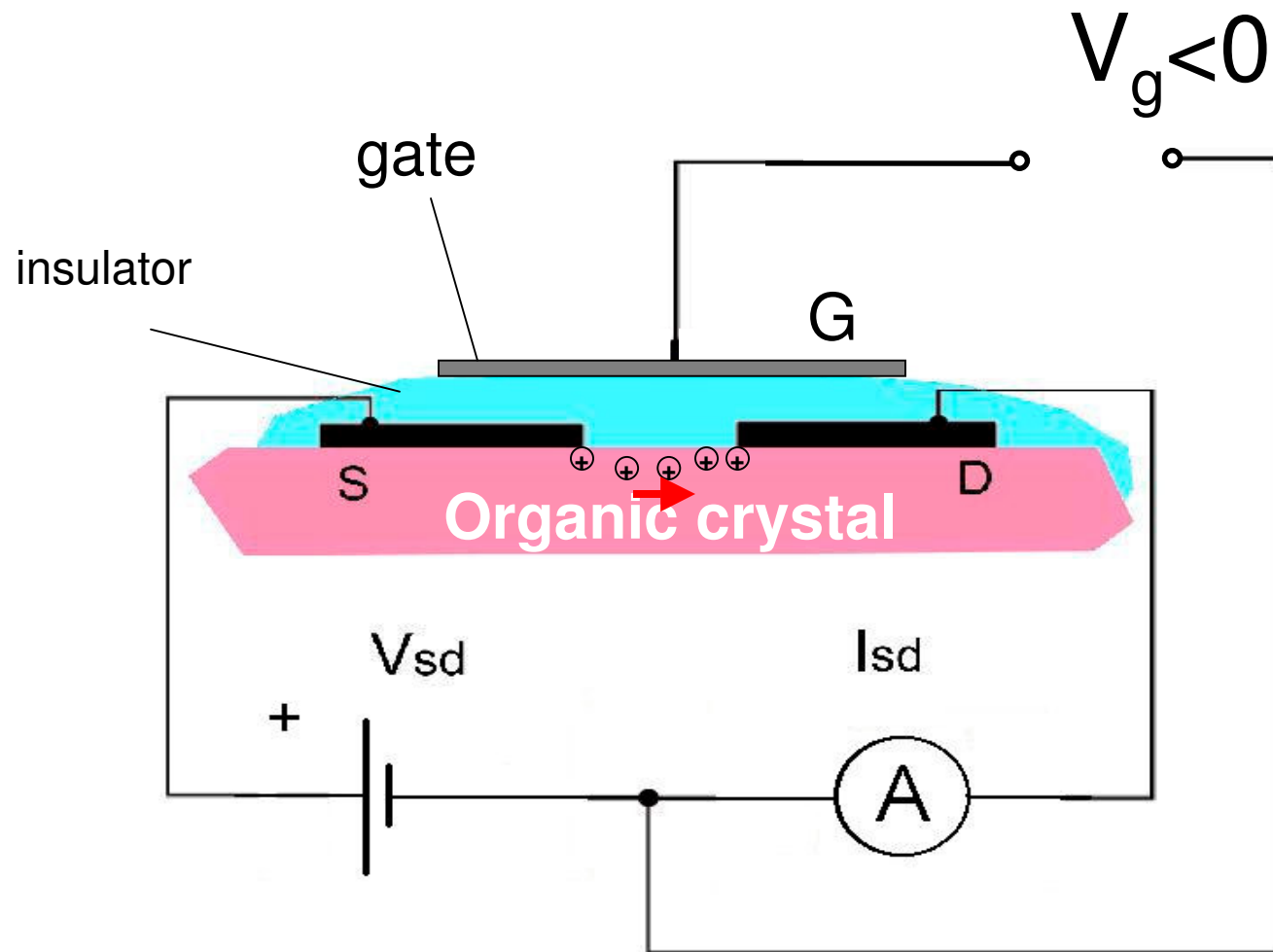
Experimental methods of mobility measurements

1. Time of flight (TOF);
2. Space charge limited current;
3. OFET.

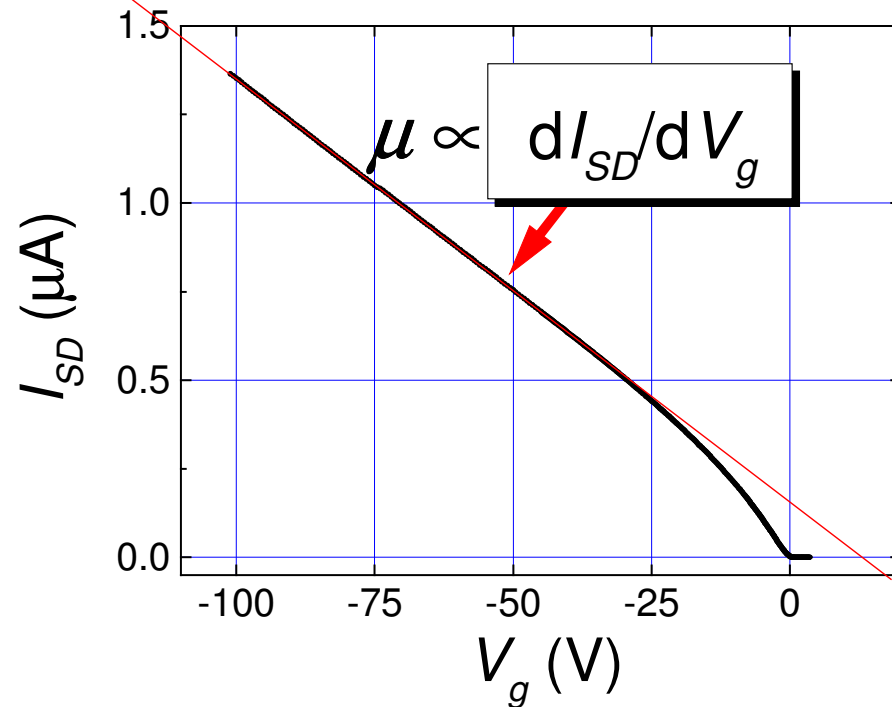
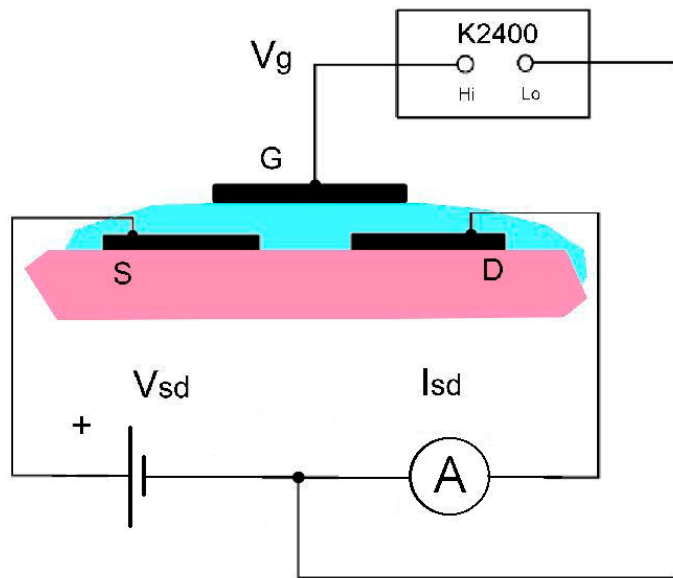


C. Reese & Z. Bao, *Adv. Mater.* **19**, 4535 (2007)

Generic Field-Effect Transistor (FET) geometry



Field-Effect Transistors as a tool to study the surface charge transport



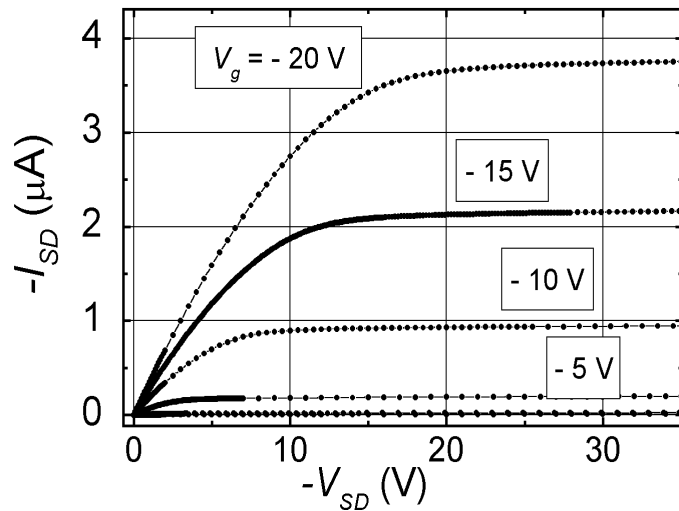
Derive this

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

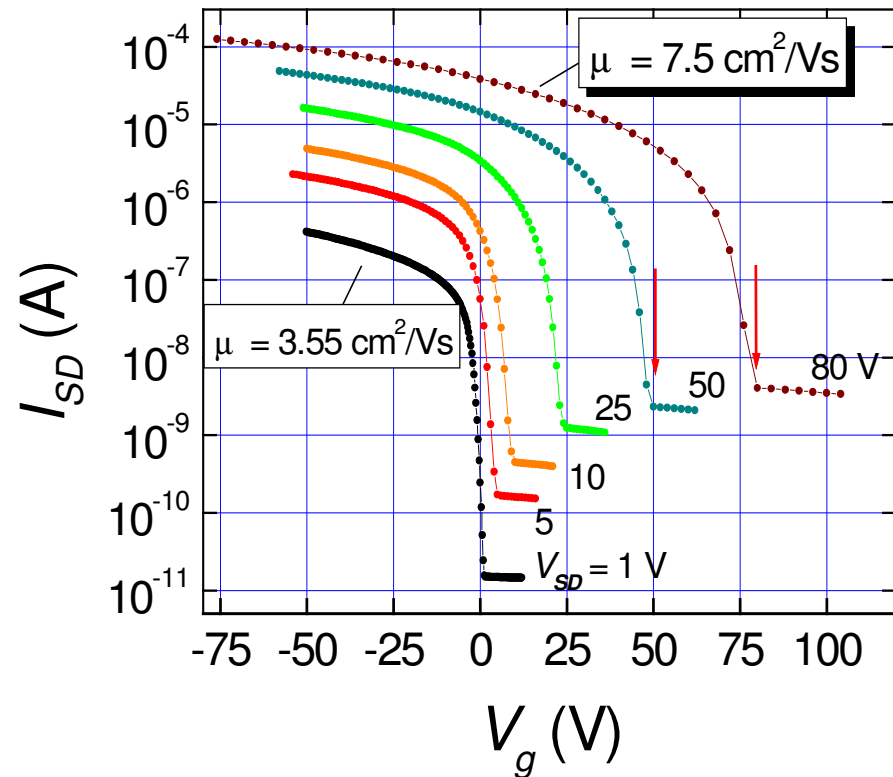
$$e n_{2D} \propto C_i V_g$$

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

Single-crystal OFETs with parylene insulator

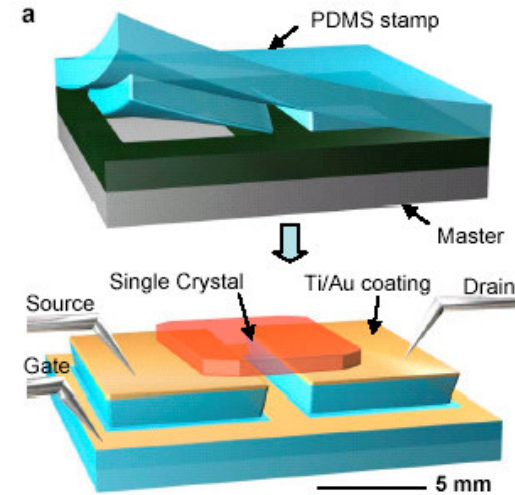
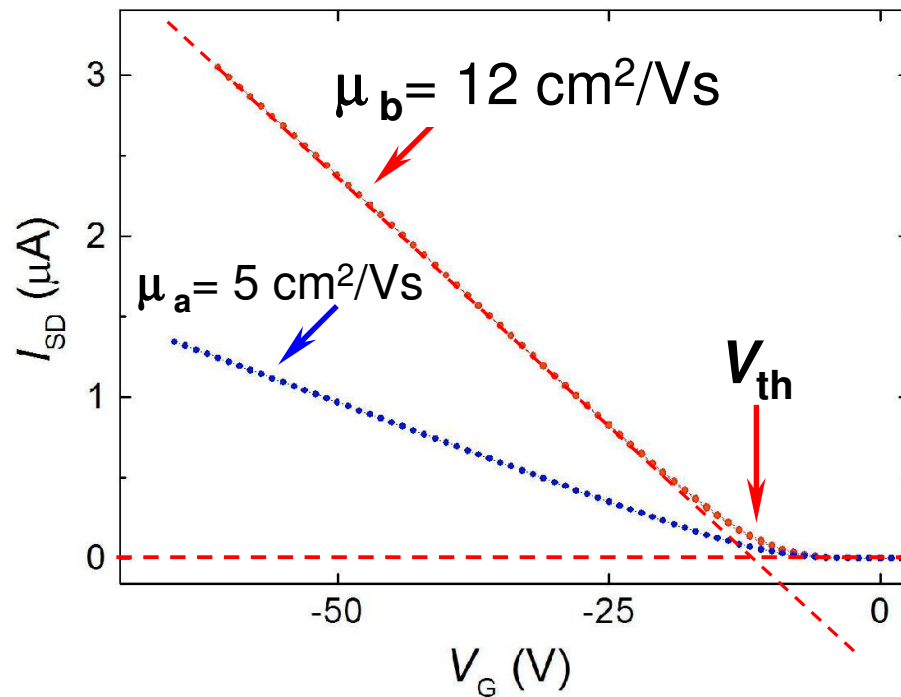


- **Mobility** – up to $8 \text{ cm}^2/\text{Vs}$, 3-5 times greater than in the best organic TFTs and $\alpha\text{-Si:H}$ MOSFETs
- **Threshold** – nearly zero at 300K
- **Sub-threshold slope** – 10 times better than in organic TFTs and $\alpha\text{-Si:H}$ MOSFETs.



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

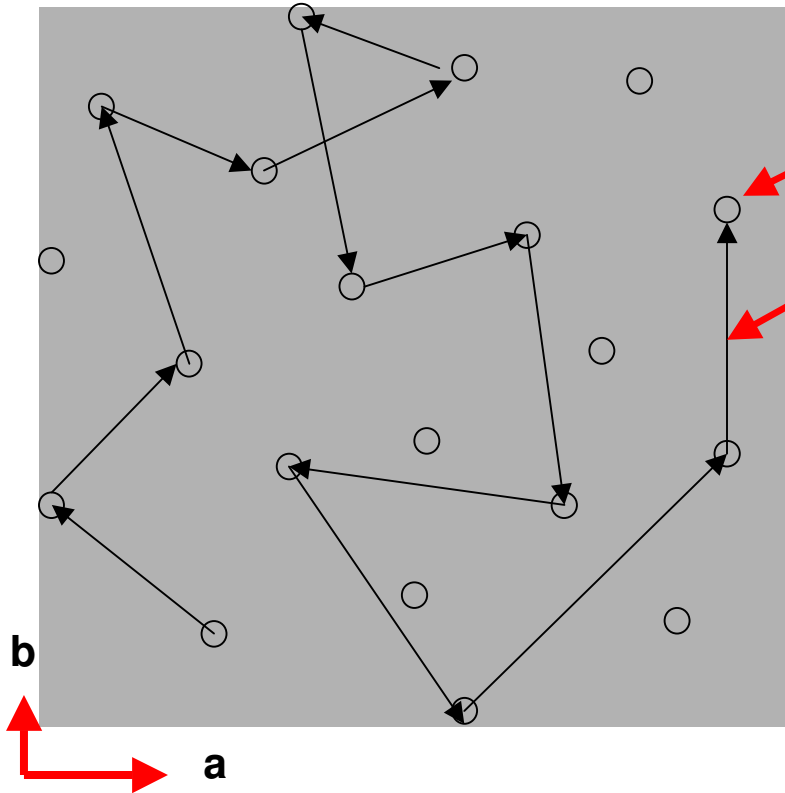
Mobility and Threshold Voltage: μ and V_{th}



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

V_{th} and μ are two important parameters of OFETs determined by the deep and shallow traps, respectively.

Importance of μ anisotropy and non-activated transport: mobility is defined by the intrinsic factors, such as molecular packing and by shallow traps.



τ_{tr} – 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:

$\mu_{eff} = \mu_0$

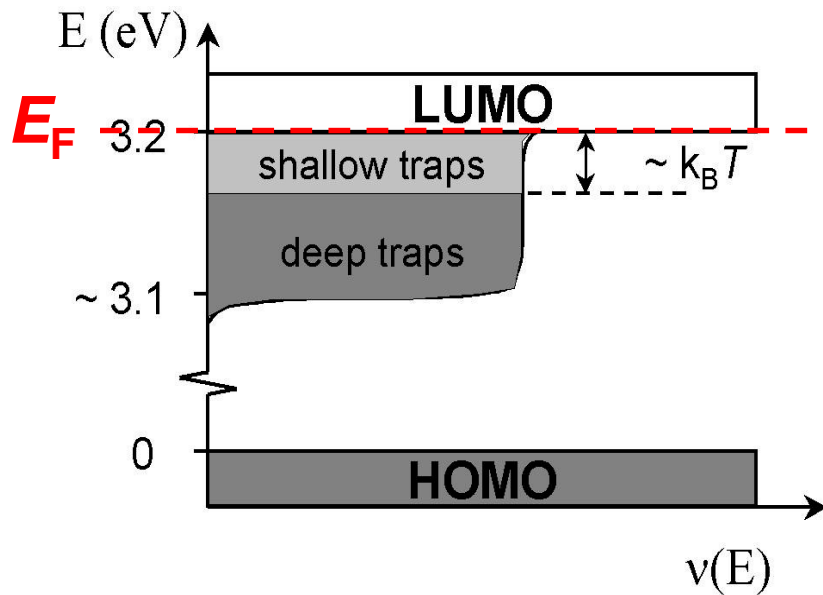
$\tau \ll \tau_{tr}$

Trap-dominated:

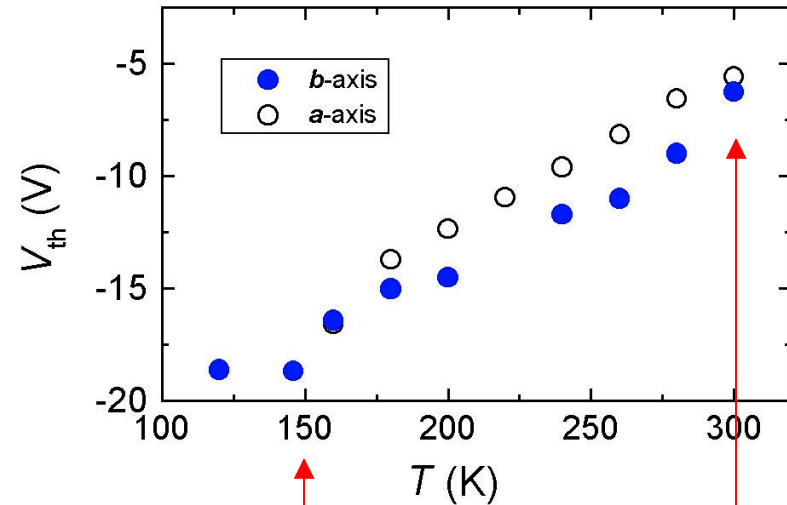
$\mu_{eff} = \mu_0(\tau/\tau_{tr})$

- 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.

Threshold voltage is defined by the deep trap density



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



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

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

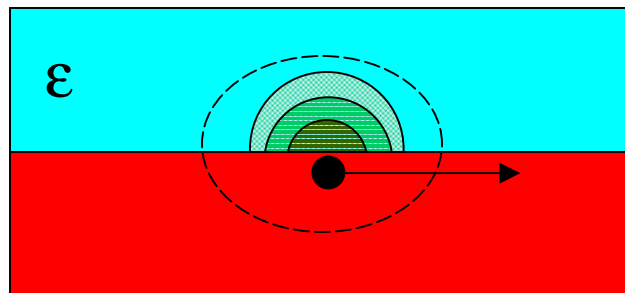
Useful general method for the analysis of deep traps in OFETs

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

Charge carrier transport at different carrier densities

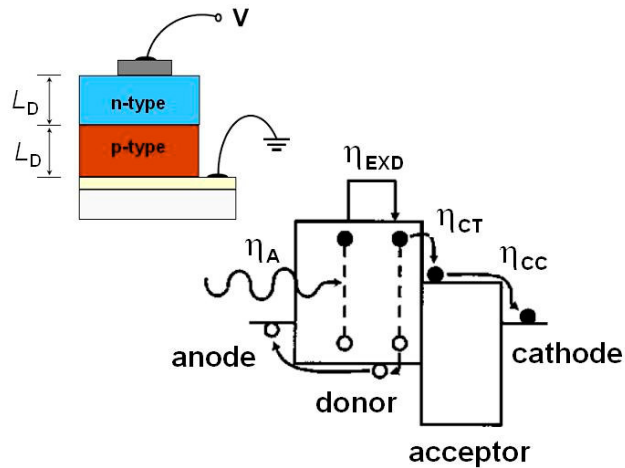
	n_{2D} (cm^{-2})	corresponding insulator
Dilute:	$10^9 - 10^{11}$	air-gap OFETs
Medium:	$10^{11} - 10^{12}$	polymer and SiO_2 dielectrics
High:	$10^{12} - 10^{14}$	<u>high-k dielectrics</u> or <u>electrolytes</u>

I. N. Hulea *et al.*, *Nature Mat.* **5**, 985 (2006)



M. J. Panzer and C. D. Frisbie,
Appl. Phys. Lett. **88**, 203504 (2006).

Basics of excitonic solar cells



- Typical **exciton diffusion length** in organics is small: $L \sim 10 - 50 \text{ nm}$
- Typical absorption constant $\alpha = 10^4 \text{ cm}^{-1}$, which means most light is absorbed in $\sim 1 \mu\text{m}$



Contradictory requirements !
Because L is small, the PV cells have to be made very thin, and most of the light is lost



Relatively poor efficiency of conventional organic solar cells