Week 1-9

Electronic Properties 3

Field effect mobility

Doping

Metal-Organic Contacts

Chapter 4.4-4.6.2

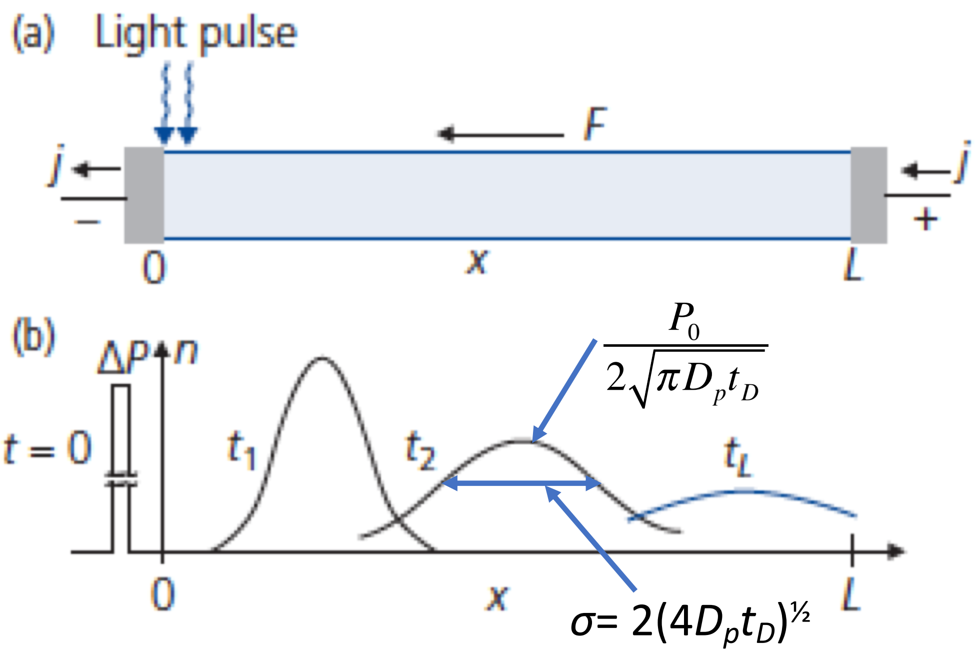
Organic Electronics
Stephen R. Forrest

Extracting the Diffusion Constant

Shockley-Haynes method (time of flight)

- Bias sample at quasi-equilibrium to avoid injection (Ohmic at $V_a \rightarrow 0$).
- Light pulse generates excitons that separate into charges at $t = 0$
- Measure arrival time (t_D) of the photogenerated current pulse.

$$\boxed{t_D = \frac{L^2}{\mu V_a}}$$



Start with diffusion equation: $\frac{\partial p}{\partial t} = D_p \frac{\partial^2 p}{\partial x^2}$

With solutions: $p(x,t) = \left[\frac{P_0}{2\sqrt{\pi D_p t}}\right]\exp\left(-x^2/4D_p t\right)$ (A single μ ⇒ Gaussian spreading)

The peak decreases with t_D, and it spreads with half width at $1/e$ from max.: $\sigma = 2(4D_p t_D)^{1/2}$

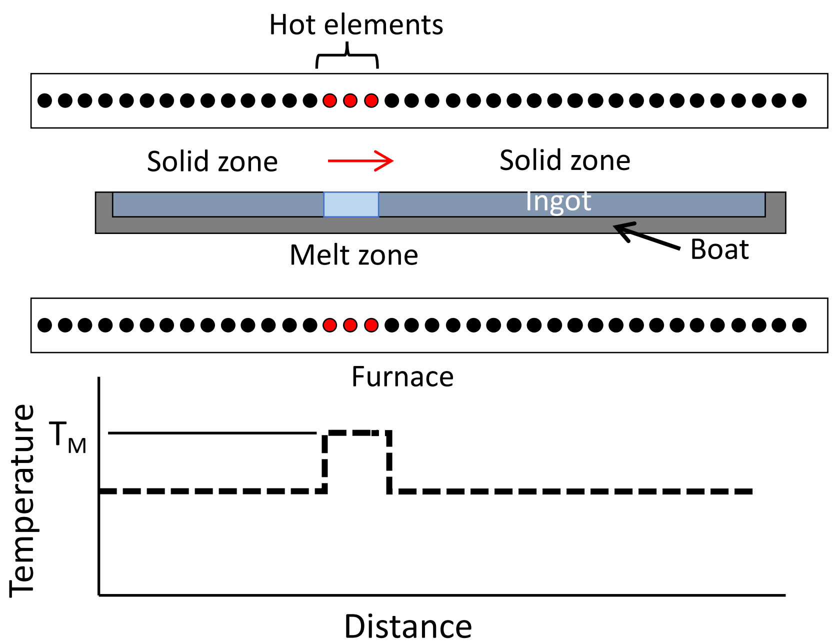
The <u>width</u> of the current pulse gives the diffusion constant of the charge, D.

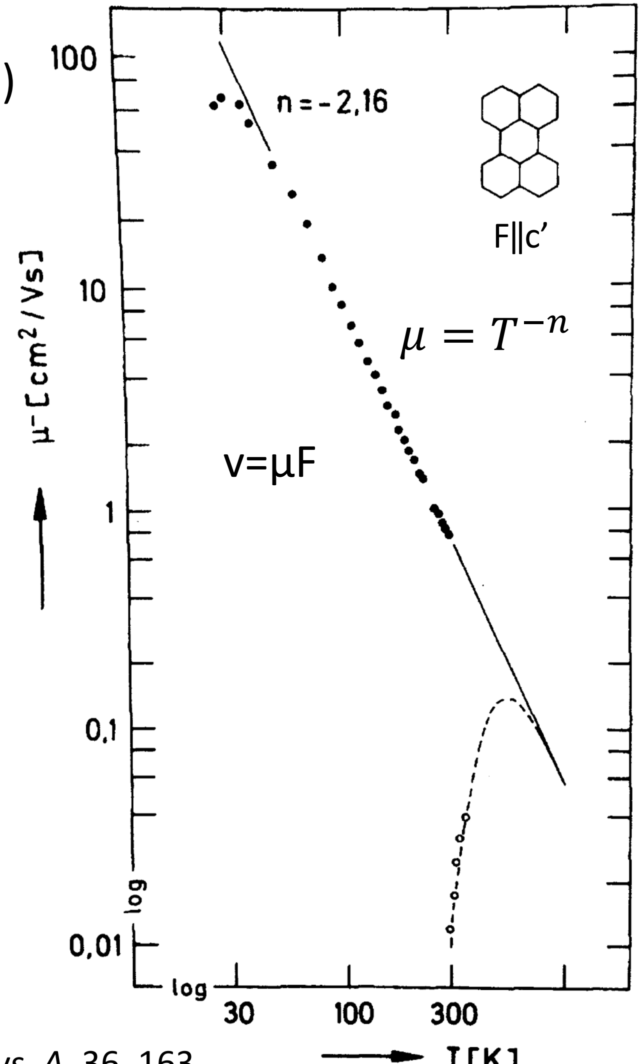
D_p should be consistent with the Einstein relation ⇒ μ

Non-Dispersive Mobility in Ultrapure Organics

n = 1.5 band transport
n = 2 acoustic phonon scattering

High purity achieved via zone refining (see Ch. 5)

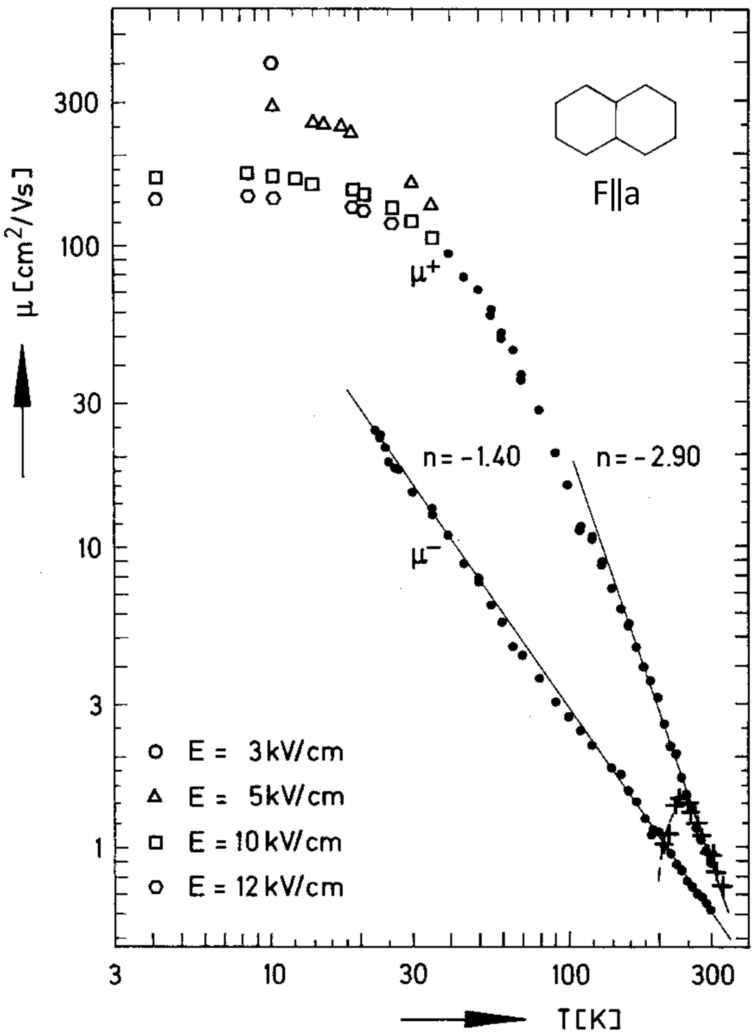


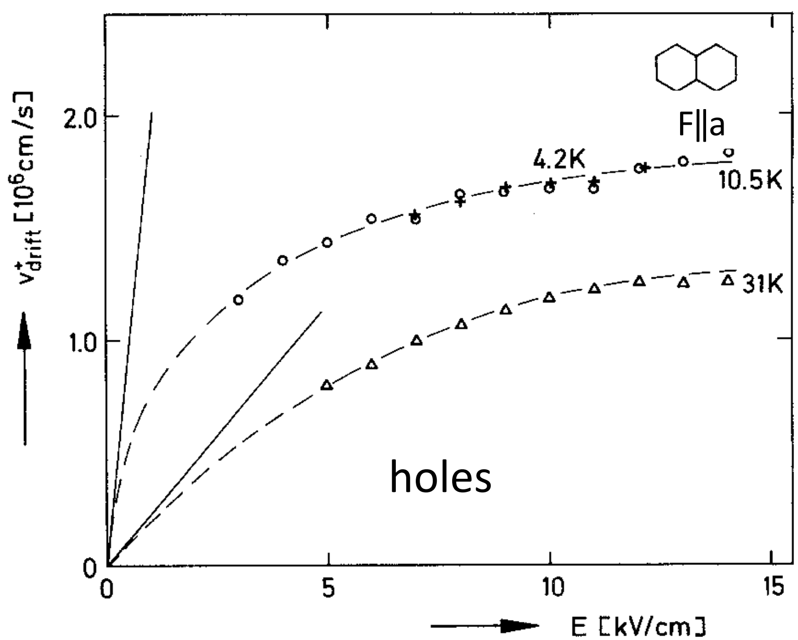


W. Warta, R. Stehle & N.Karl, 1985. *Appl. Phys. A,* 36, 163.

Band Transport in Organics

- Ultra-purified naphthalene





- Mobility *vs*. majority carrier type

  e.g. If the mobility of holes > electrons,
  does NOT imply the material is *p*-type
- The “type” of a material depends on the polarity of the **majority** carrier

Time of Flight Experiment
Ultrapurified Naphthalene Crystals

- Current pulse

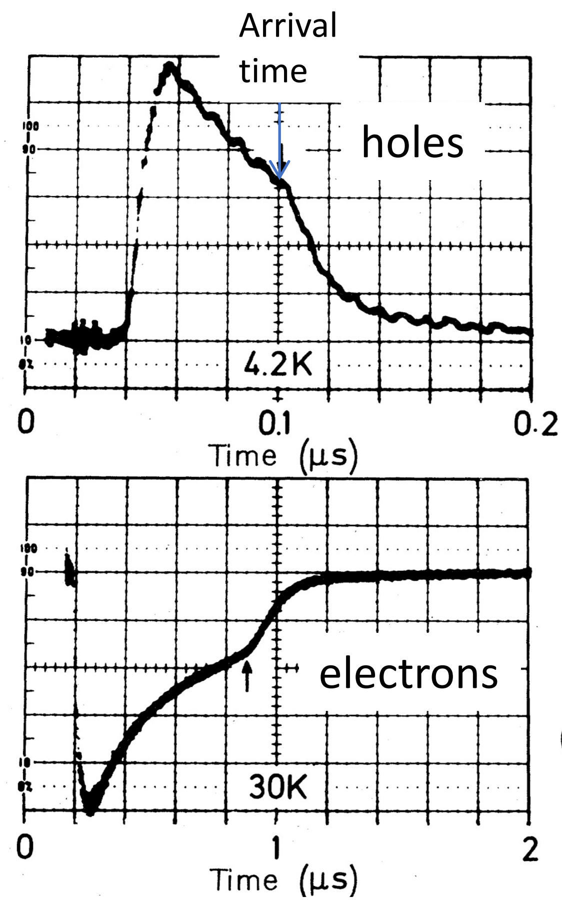
$v > 10^6$ cm/s!

$\lambda = v\tau$

$\tau = \mu m^*/q$

$v = (3k_BT/m^*)^{½}$

$\Rightarrow \lambda = (\mu/q)(3m^*k_BT)^{½}$



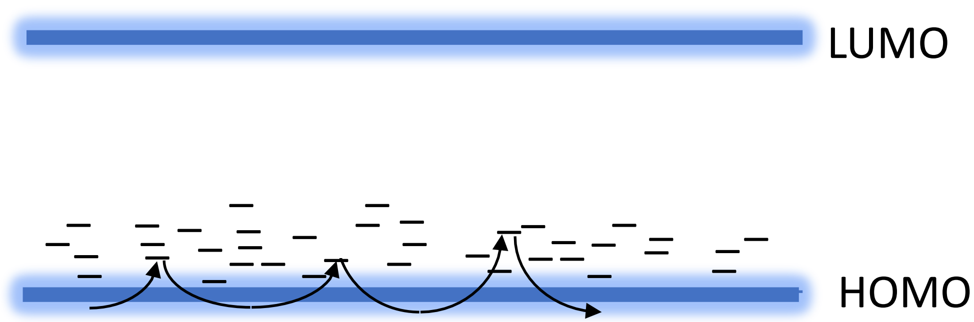
From the data on naphthalene:

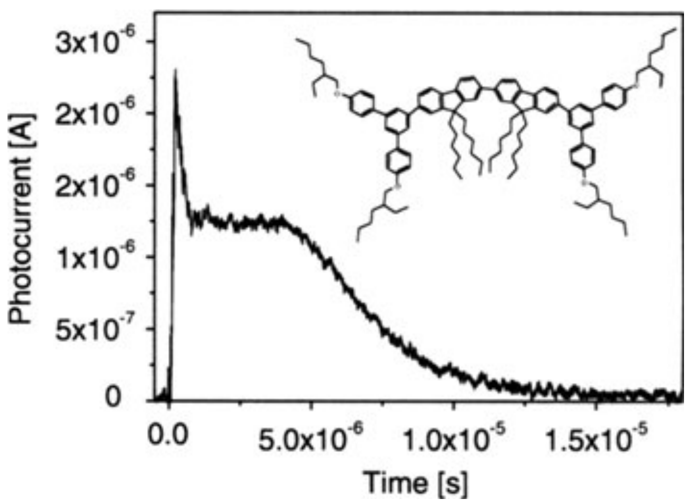
$m^* \sim 3\text{-}15 m_0$

$\lambda \sim 8a$: definitely in the band transport regime

TOF Mobility with Traps

- In the presence of defect states, charges continually trap and de-trap during transit
  - The mobility is not a good number—there are several mobilities, one for each carrier
  - Results in **dispersive transport**

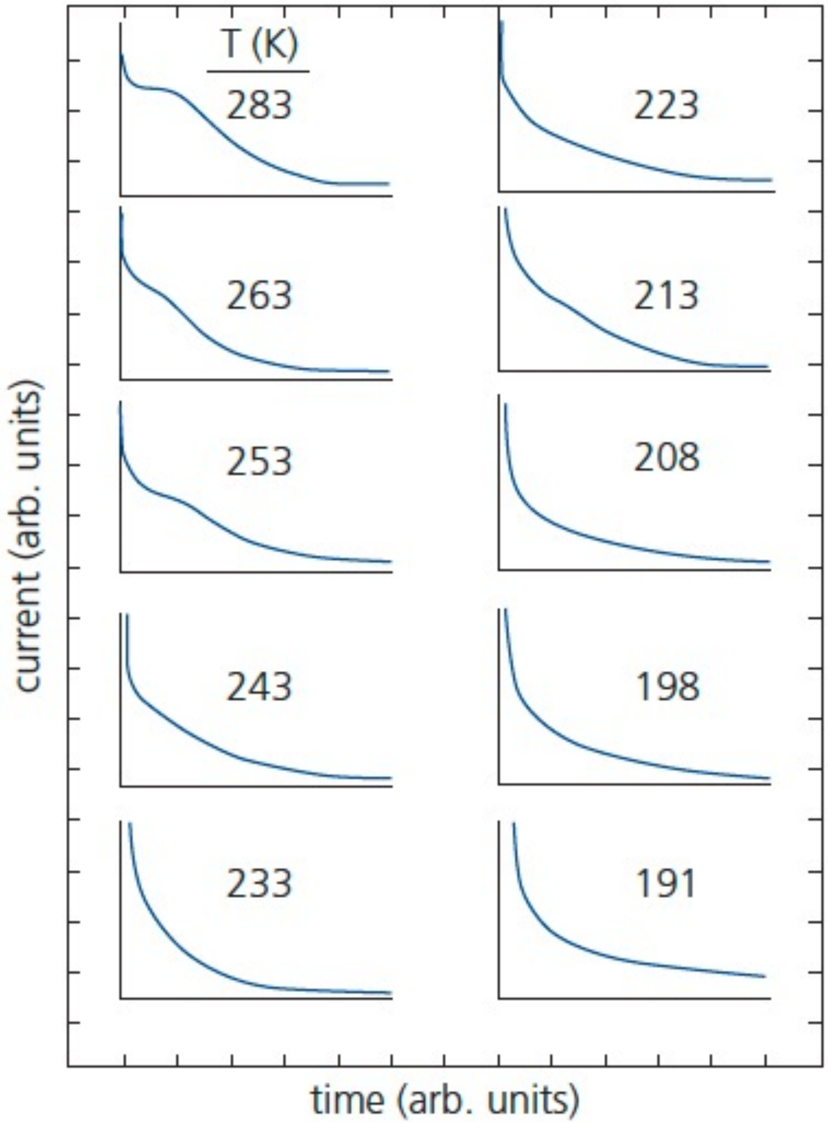




Gambino S, et al. (2008) Org Electron 9, 220

- Initial spike: Charge motion prior to energetic relaxation in the DOS if the RC time constant is short (i.e. reactance small)
- Plateau and broad tail indicate dispersive transport: many different arrival times from trapping/de-trapping during transit.

Evolution of dispersive transport



- Transport becomes increasingly dispersive with decreasing T
- Diffusion is thermally activated

⇒ Transport by thermally activated hopping

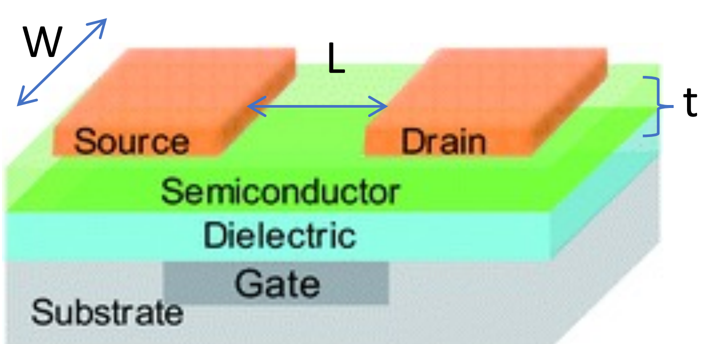
Time of flight hole current in the polymer, DEH

Borsenberger et al., Phys. Rev. B, 46, 12145 (1992).

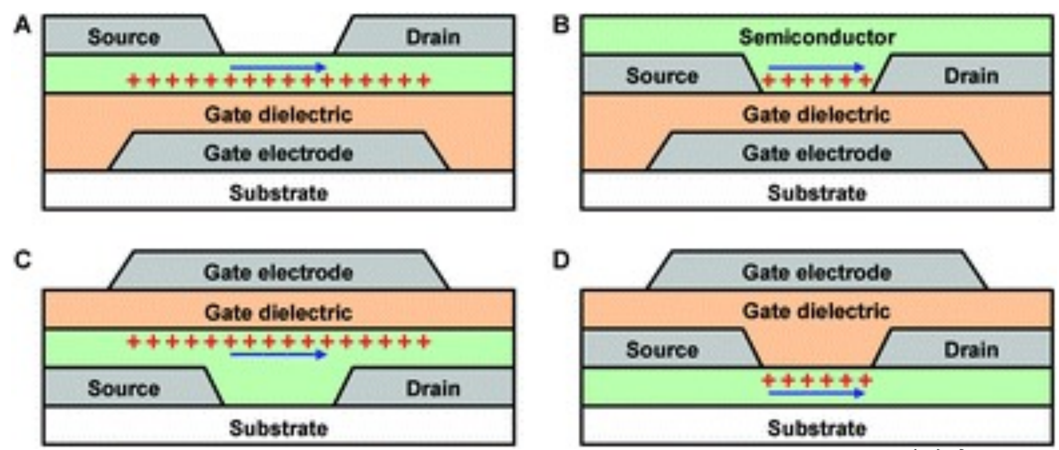
Measuring Field Effect Mobility

Transfer characteristics of thin film transistors (OTFTs)

- This measures an interface property, **not** bulk mobility
- Can be strongly influenced by interface trapping
- Can be AC or DC Measurement
  - Almost always used in less reliable DC mode



Basic "Bottom gate, top source-drain OTFT"



Different contact arrangements

How an OTFT works

(More on this in Semester 2: This is quick introduction)

The charge induced by a gate voltage, V_G, at very low drain voltage, V_D, and hence low channel current (i.e. ohmic):

$$Q(x) = n(x)qt = C_G\left(V_G - V(x)\right)$$

Charge layer thickness

But contact resistance, charge trapping, grain boundaries, etc. prevent channel conduction until a threshold voltage V_T is reached:

$$Q(x) = n(x)qt = C_G\left(V_G - V_T - V(x)\right)$$

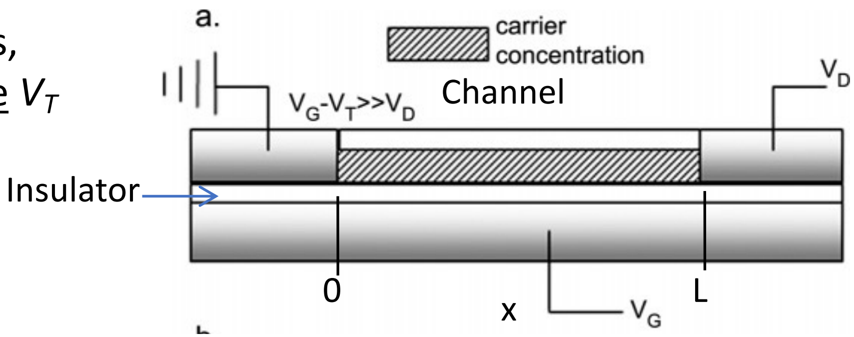
At low voltage, conduction is ohmic ⇒we can use the average channel voltage drop $V_D/2$. Also, following Ohm's Law:

$$I_D = A\sigma F = W\underbrace{(n_{ave}qt)}_{Q_{ave}}\mu\frac{V_D}{2L}$$

Or, in the linear regime of operation:

$$\boxed{I_D = \frac{W}{L}C_G\mu\left(V_G - V_T - \frac{V_D}{2}\right)V_D = \frac{W}{L}C_G\mu\left((V_G - V_T)V_D - \frac{V_D^2}{2}\right)}$$

Bottom contact/bottom gate



Extracting the Mobility

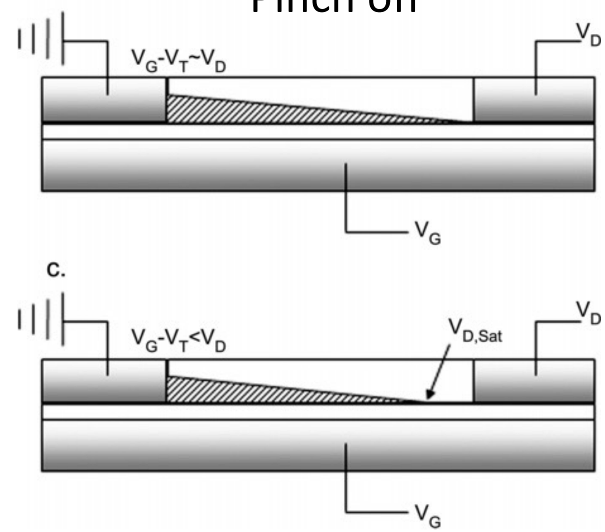
In the linear regime (V_G-V_T>>V_D), we calculate the transconductance:

$$g_m = \left.\frac{\partial I_D}{\partial V_G}\right|_{V_D} = \frac{W}{L} C_G \mu_{lin} V_D$$

Or the output conductance:

$$g_o = \left.\frac{\partial I_D}{\partial V_D}\right|_{V_G} = \frac{W}{L} C_G \mu_{lin} \left(V_G - V_T\right)$$

Pinch off



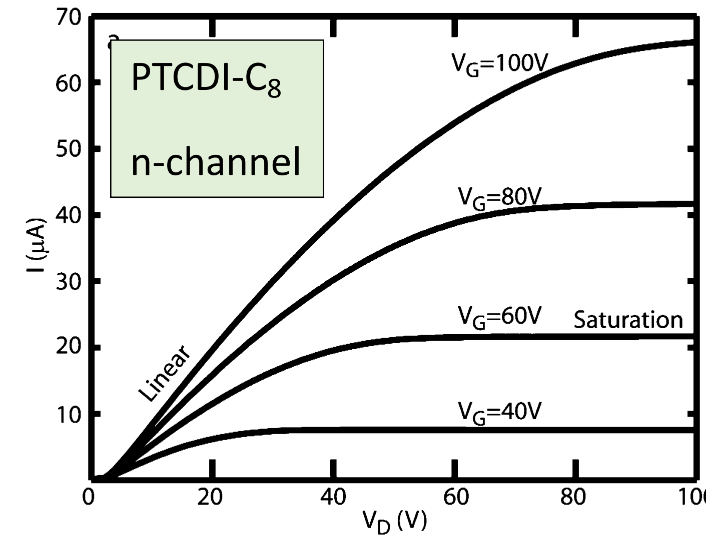
Due to contact and other parasitic resistances, μ_{lin} can give errors, so mostly use saturation characteristics:
⇒When V_D=V_G-V_T channel pinches off
⇒No longer potential drop between drain and pinch-off point
⇒No more current (except leakage) enters channel with increasing V_D, hence we are in the saturation regime.

Then: $$I_D == \frac{W}{2L} C_G \mu_{sat} \left(V_G - V_T\right)^2$$

Plot of $I_D^{1/2}$ vs. V_G gives both μ_{sat} and V_T

DC Characteristics of an OTFT

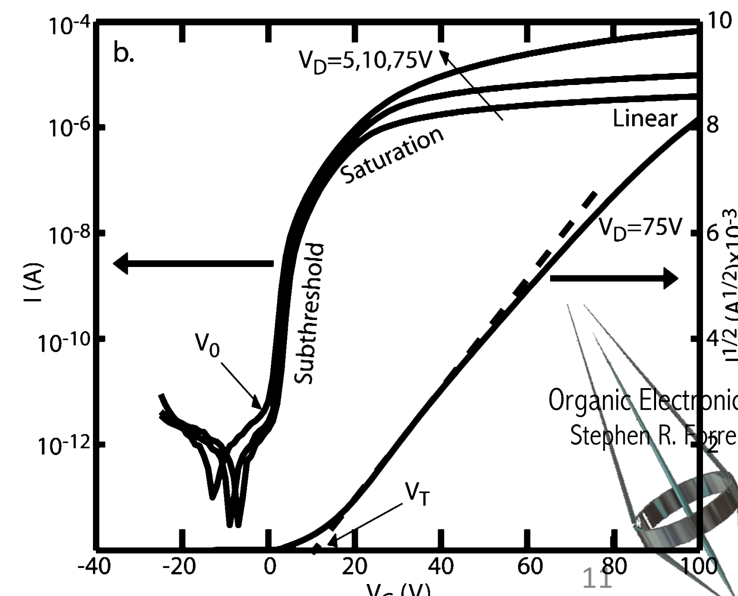
- Pentacene most frequently employed small molecule for OTFT
- μ_{sat}~1-1.5 cm²/V-s
- DC mobility as high as 40 cm²/V-s measured in rubrene using OTFTs: is it reliable? (Takeya, et al. Appl. Phys. Lett. **90** 102120 (2007))
- OTFTs measure <u>interface conductance</u>, not mobility.



- BUT OTFTs can also be used in AC mode (equivalent to a TOF measurement)

$$f_T = \frac{1}{2\pi RC} = \frac{g_m}{2\pi\left(C_G + C_p\right)} = \frac{W}{2\pi L}\frac{C_G}{\left(C_G + C_p\right)}\mu_{sat,AC}\left(V_G - V_T\right)$$

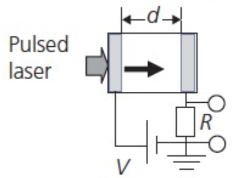
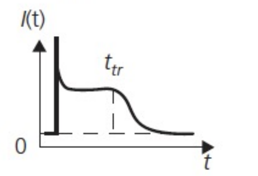
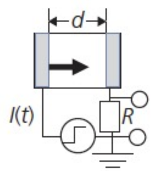
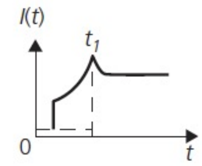
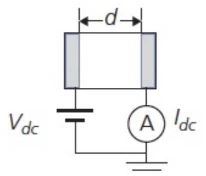
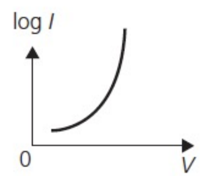
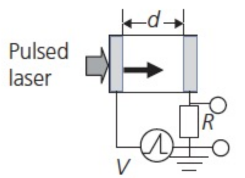
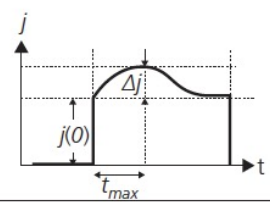
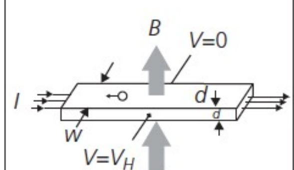
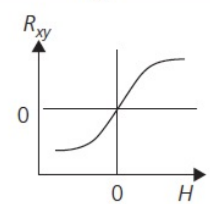
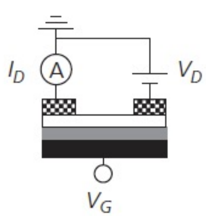
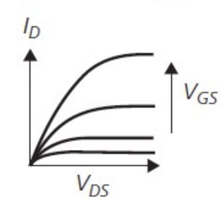
Parasitic capacitance



- However, this method rarely employed in organics.

(see Kitamura and Arakawa, Appl. Phys. Lett. 95 023502 (2009))

There are many ways to measure μ

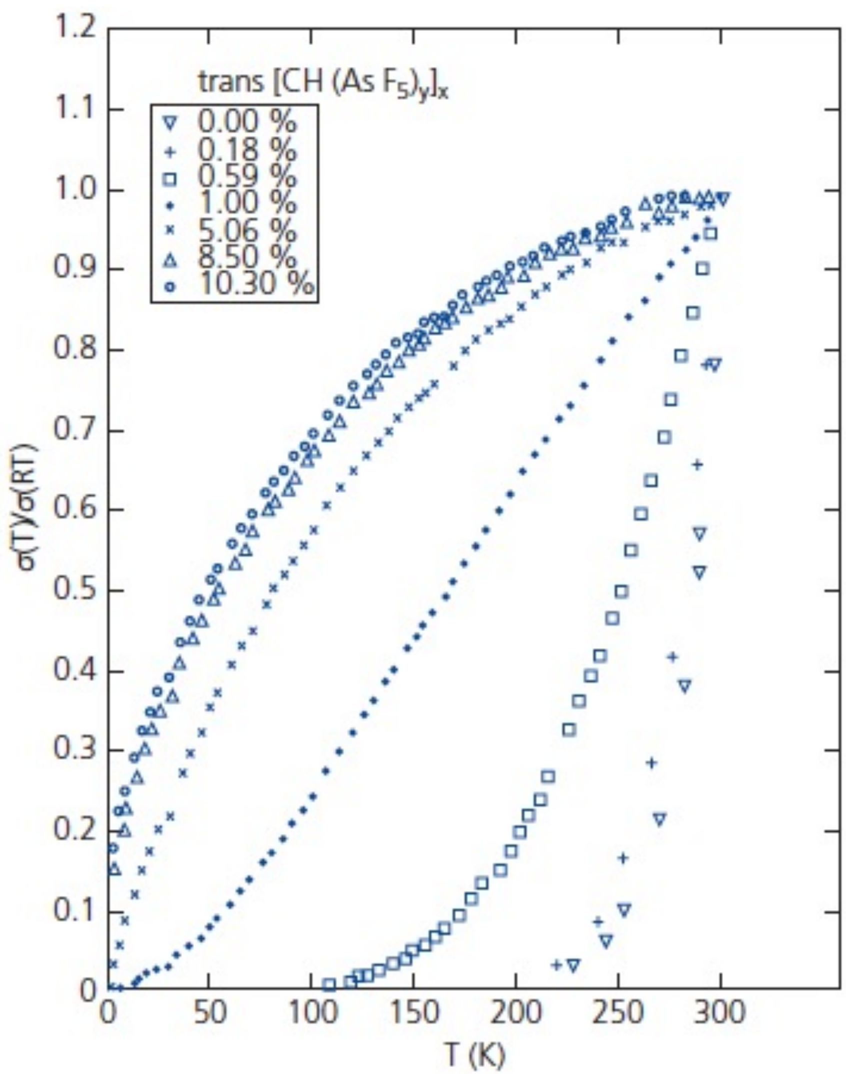
Technique	Sample Geometry	Typical Data
1. TOF (Time-of-flight)		
2. DISLC (Dark-injection space-charge-limited current)		
3. *J-V* Analysis (current-voltage characteristics)		
4. CELIV (Charge extraction by linearly increasing voltage)		
5. Hall Effect		
6. OTFT (Organic Thin Film Transistor)		

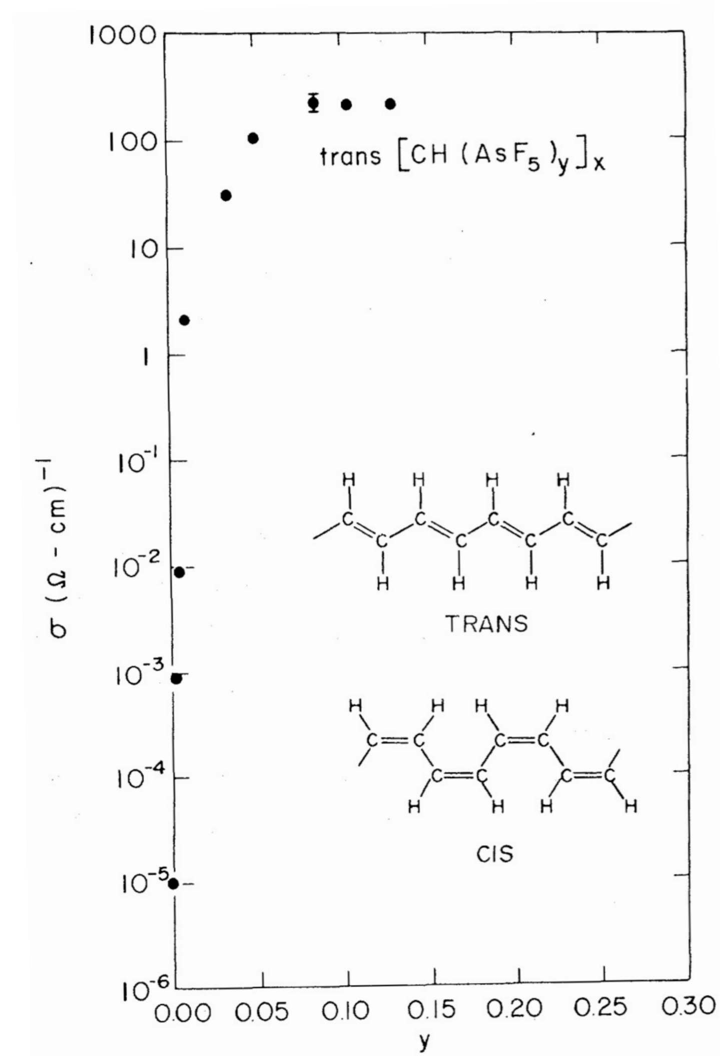
<u>Typical ranges (at RT)</u>

(cm^2/V-s)

- **Small molecule:**
  Amorphous: 10^{-5}-10^{-2}
  Crystalline: 10^{-2}-1
- **Polymer:**
  10^{-5}-10^{-1}
- No systematic difference between μ_n or μ_p
- Many more high hole vs. electron mobility materials

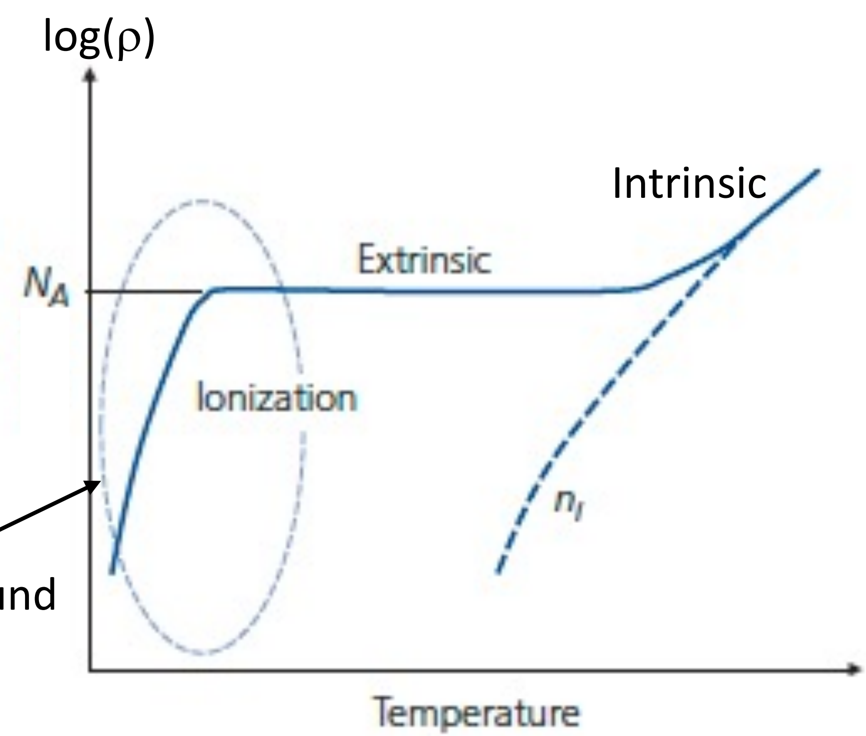
Doping of Organics to Increase Conductivity





Heeger, Shirakawa, MacDiarmid, et al. Phys. Rev. Lett., **39** 1098 (1977)

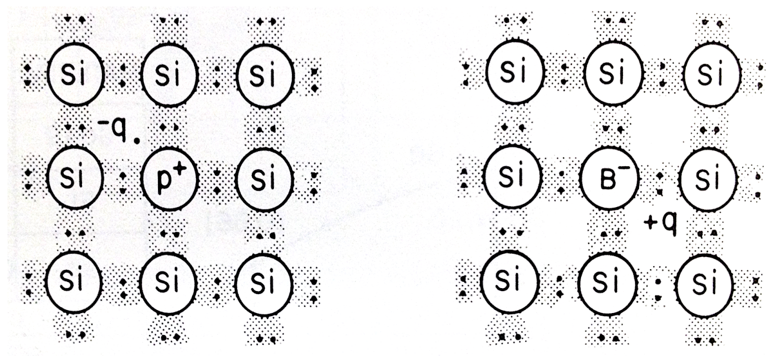
Temperature Dependence of Charge Density



impurity ionization region is found for data for polyacetylene

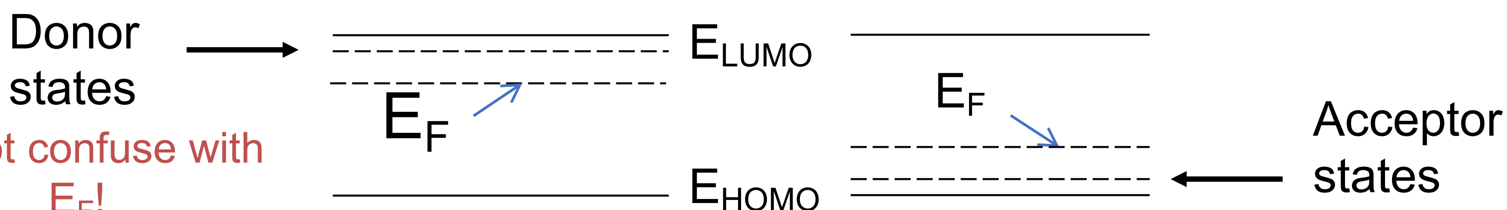
Doping in Organics: Not entirely similar to inorganics

Substitutional doping in inorganics



(a) (b)

But no shared bonds in organics!



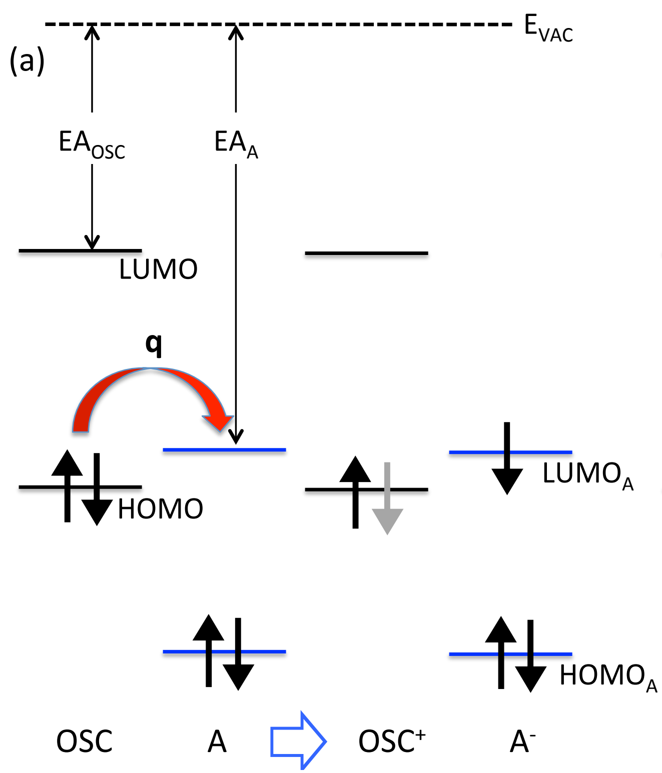
Do not confuse with E_F!

$$n = N_{LUMO} \exp\left(\frac{E_F - E_{LUMO}}{k_B T}\right) \qquad p = N_{HOMO} \exp\left(\frac{E_{HOMO} - E_F}{k_B T}\right)$$

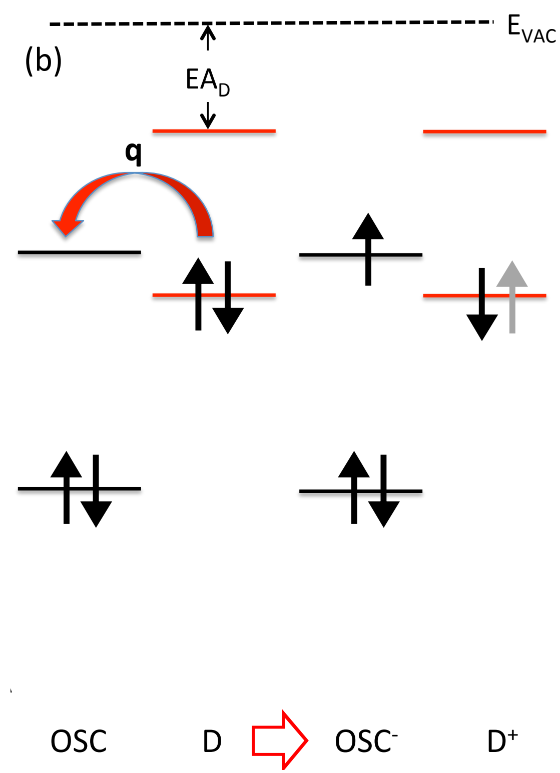
$\Rightarrow$ Law of mass action: $n_i^2 = N_{HOMO} N_{LUMO} \exp\left[-\frac{E_G}{k_B T}\right]$

Doping at the molecular level

Involves charge transfer between dopant and host

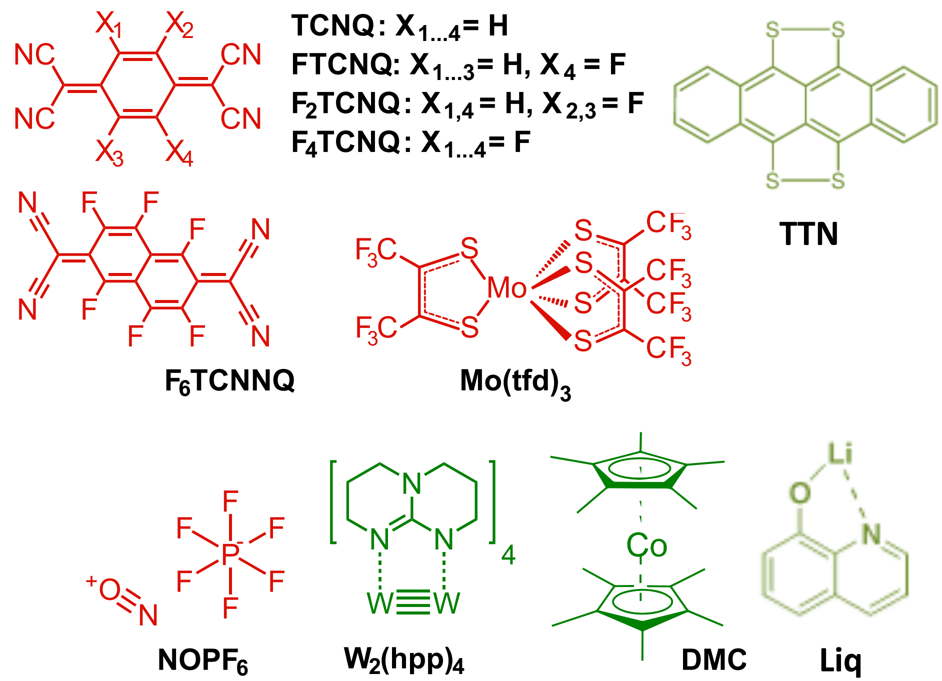


p-type doping



n-type doping

Example *molecular* dopants



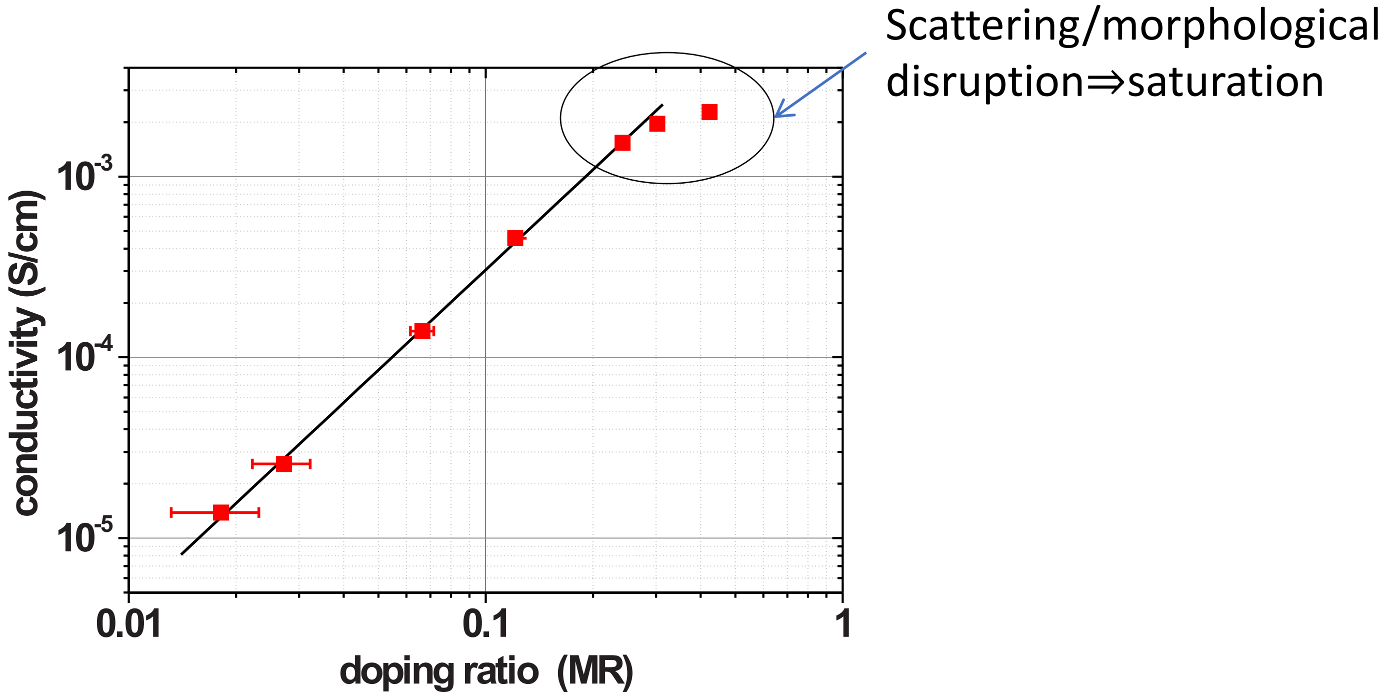
red=acceptors; green=donors

But there are metallic dopants too: Cs, Li, etc.

LiF + Al cathodes common in OLEDs:

$$\mathrm{LiF} + \mathrm{Al} \rightarrow \mathrm{Li}^{+} + e^{-} + \mathrm{AlF}$$

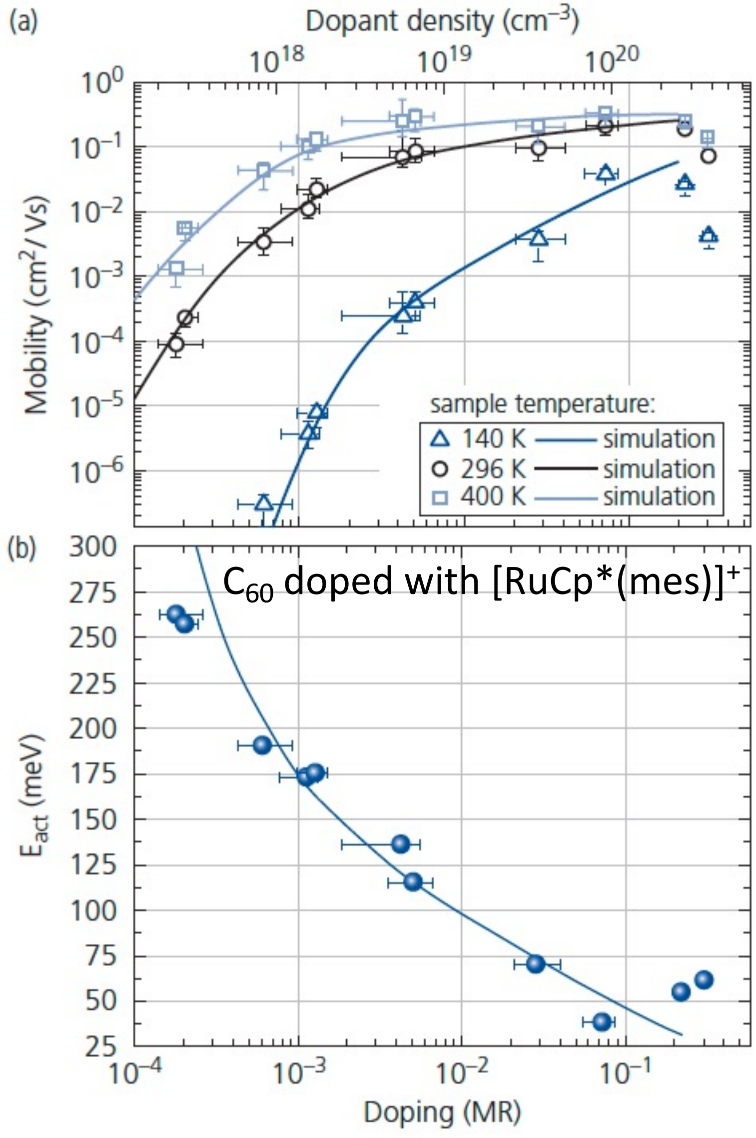
Difficult to get a high conductivity
(it takes *a lot* of dopant)



N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine with **F_4-TCNQ**.

Olthof et al., J. Appl. Phys., 106, 103711 (2009)

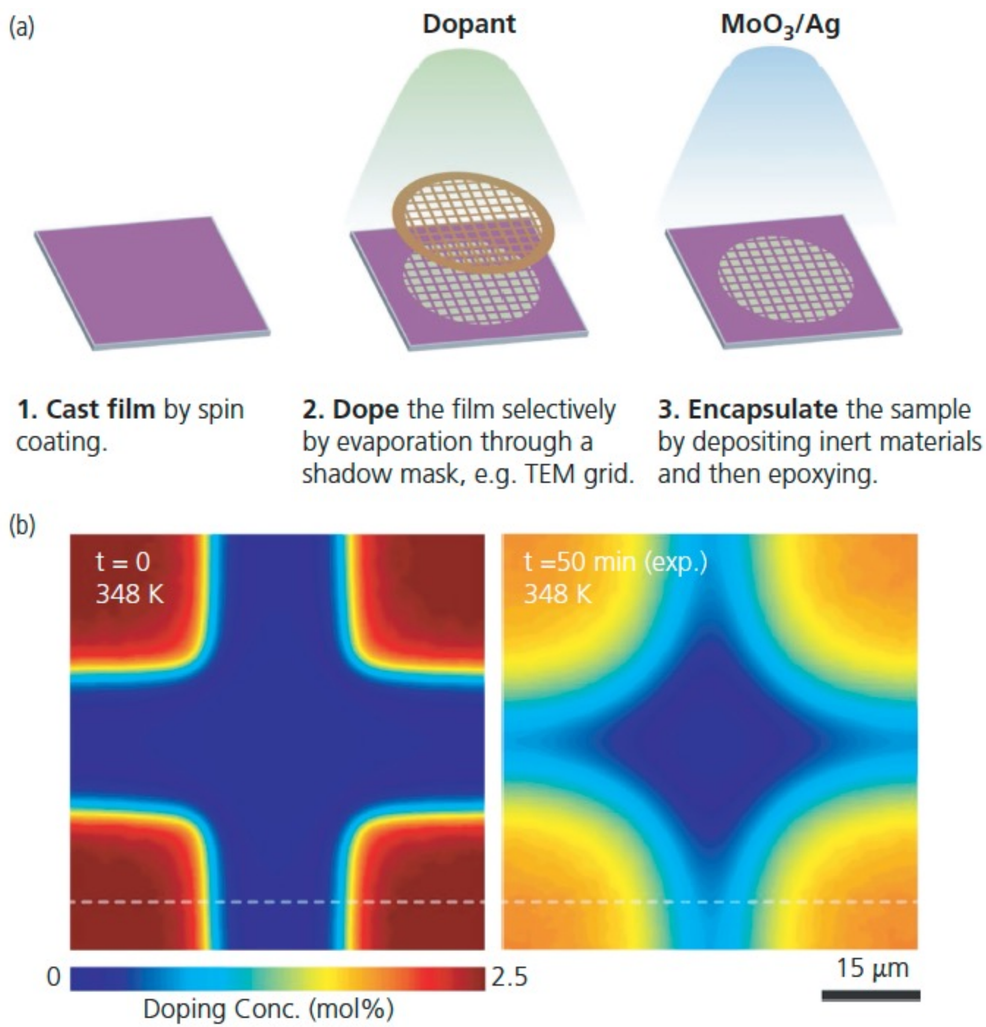
Problem 1: High doping reduces mobility



- Disorder in crystal introduces scattering
- As T increases, scattering reduces as DOS mobility edge moves toward energy gap edge

Olthof et al. Phys. Rev. Lett., 109, 176601 (2012).

Problem 2: Dopants diffuse with time and temperature



Li et al, Macromolec. 50, 5476 (2017)

Recombination

Charge diffusion equations

$$\frac{\partial n}{\partial t} = \frac{1}{q}\nabla \cdot \mathbf{j}_e - R_e + G_e \qquad \frac{\partial p}{\partial t} = -\frac{1}{q}\nabla \cdot \mathbf{j}_h - R_h + G_h$$

Using Fick's Law

$$\mathbf{j}_e = qD_e \nabla n$$

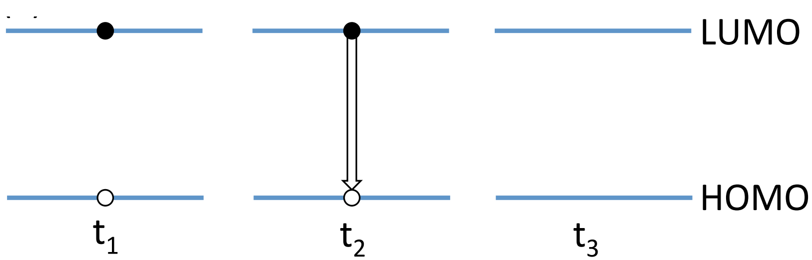
$$\mathbf{j}_h = -qD_h \nabla p$$

Gives:

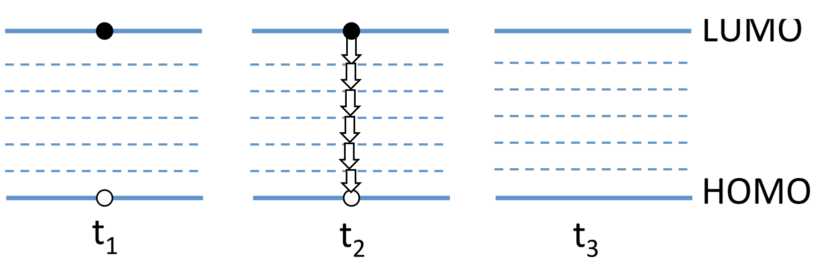
$$\frac{\partial n}{\partial t} = D_e \nabla^2 n - R_e + G_e \qquad \frac{\partial p}{\partial t} = D_h \nabla^2 p - R_h + G_h$$

Direct HOMO-LUMO Recombination and via Midgap States

Direct (Band-to Band) Recombination

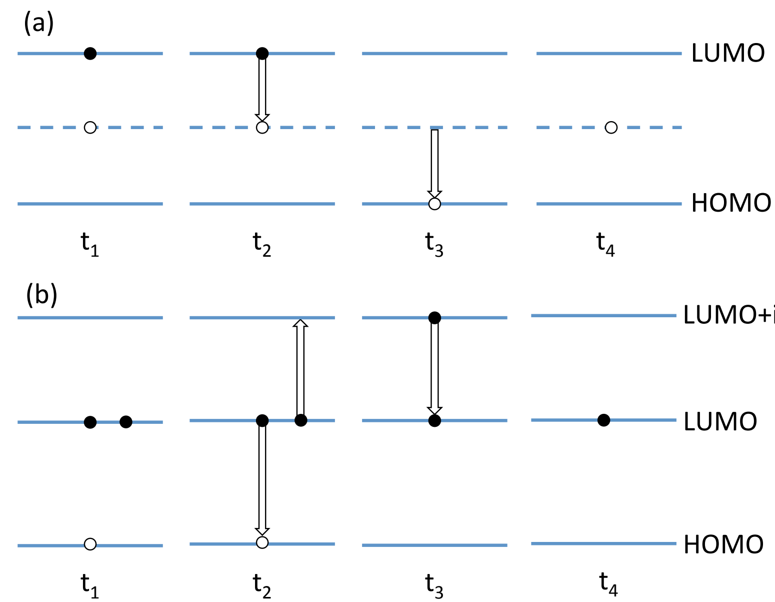


Multiple Step Recombination



$$R_e^{dir} = \frac{n - n_0}{\tau_e} = \frac{\Delta n}{\tau_e}$$

Shockley-Read-Hall Recombination

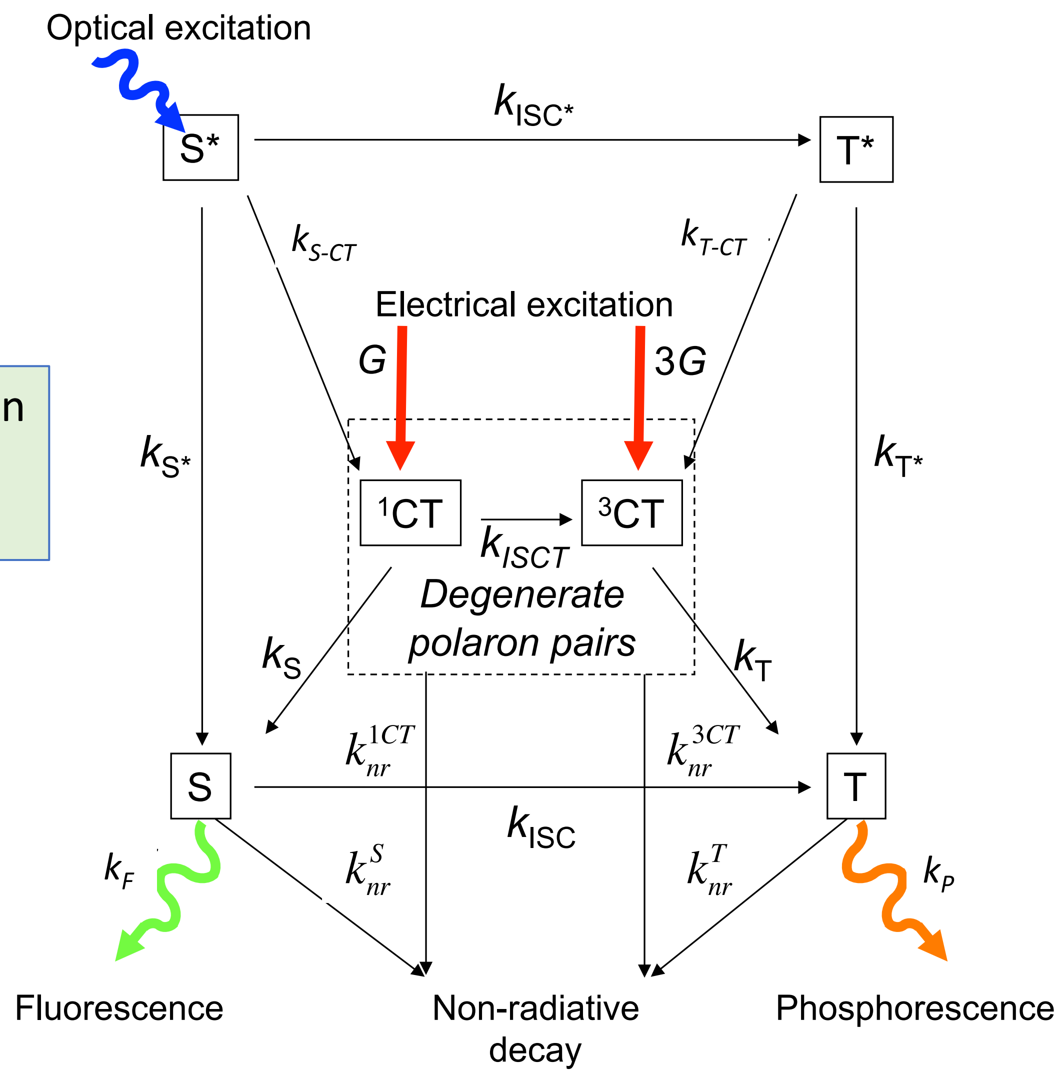


equilibrium restoring force

$$R^{SRH} = \frac{np - n_i^2}{\tau_e\left(p + p_1\right) + \tau_h\left(n + n_1\right)}.$$

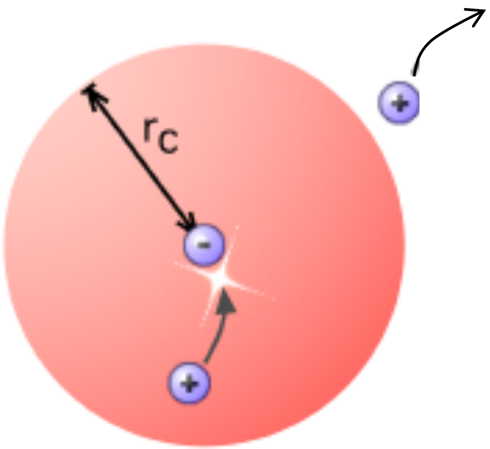
Geminate & Bimolecular Recombination

Geminate = exciton recombination
Bimolecular = 2 charges combine to form exciton



Langevin (Bimolecular) Recombination

- When two carriers meet….



Capture radius: When Coulomb = thermal energy

$$r_c = \frac{q^2}{4\pi\varepsilon_r\varepsilon_0 k_B T}.$$

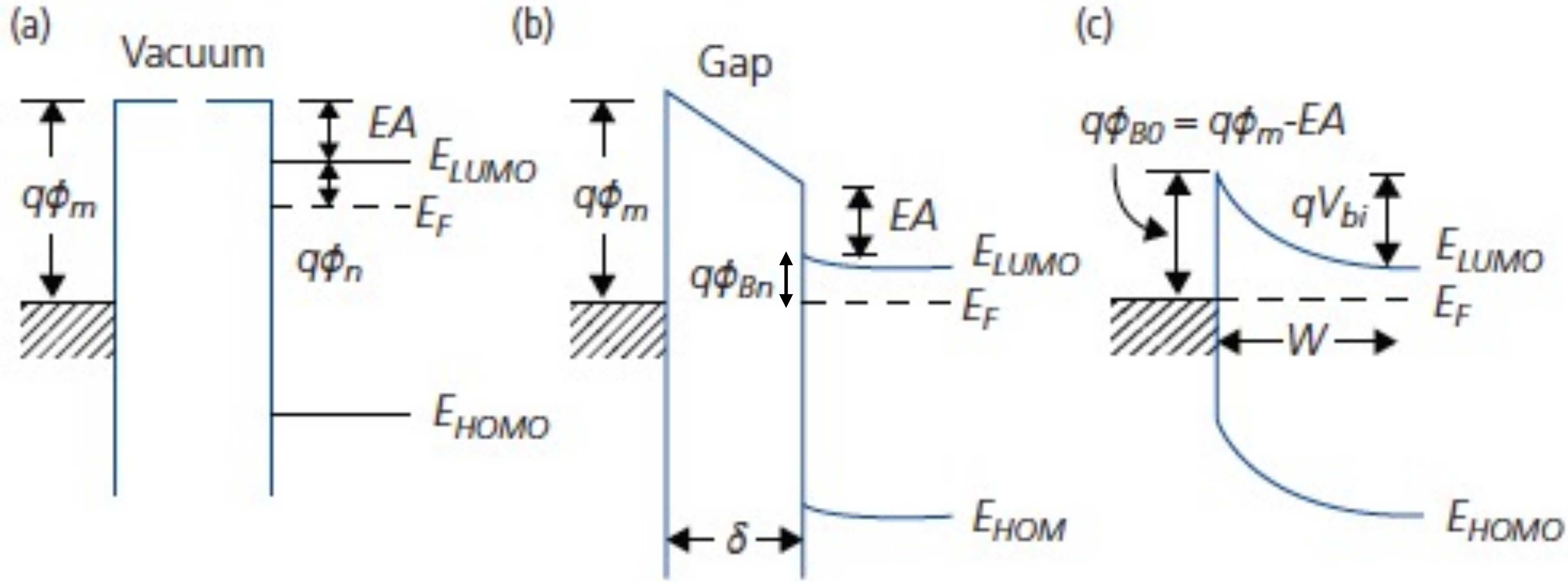
Langevin recombination rate constant:

$$\gamma_L = \frac{q}{\varepsilon_r\varepsilon_0}(\mu_e + \mu_h) = \frac{q}{\varepsilon_r\varepsilon_0}\mu_T.$$

Yielding the recombination rate (and hence current)

$$R^L = \gamma_L\left(pn - n_i^2\right)$$

Injection From Contacts
Schottky barrier formation



Traps Play a Big Role in Determining Barrier Heights at Metal-Semiconductor Junctions

Metal Work Functions

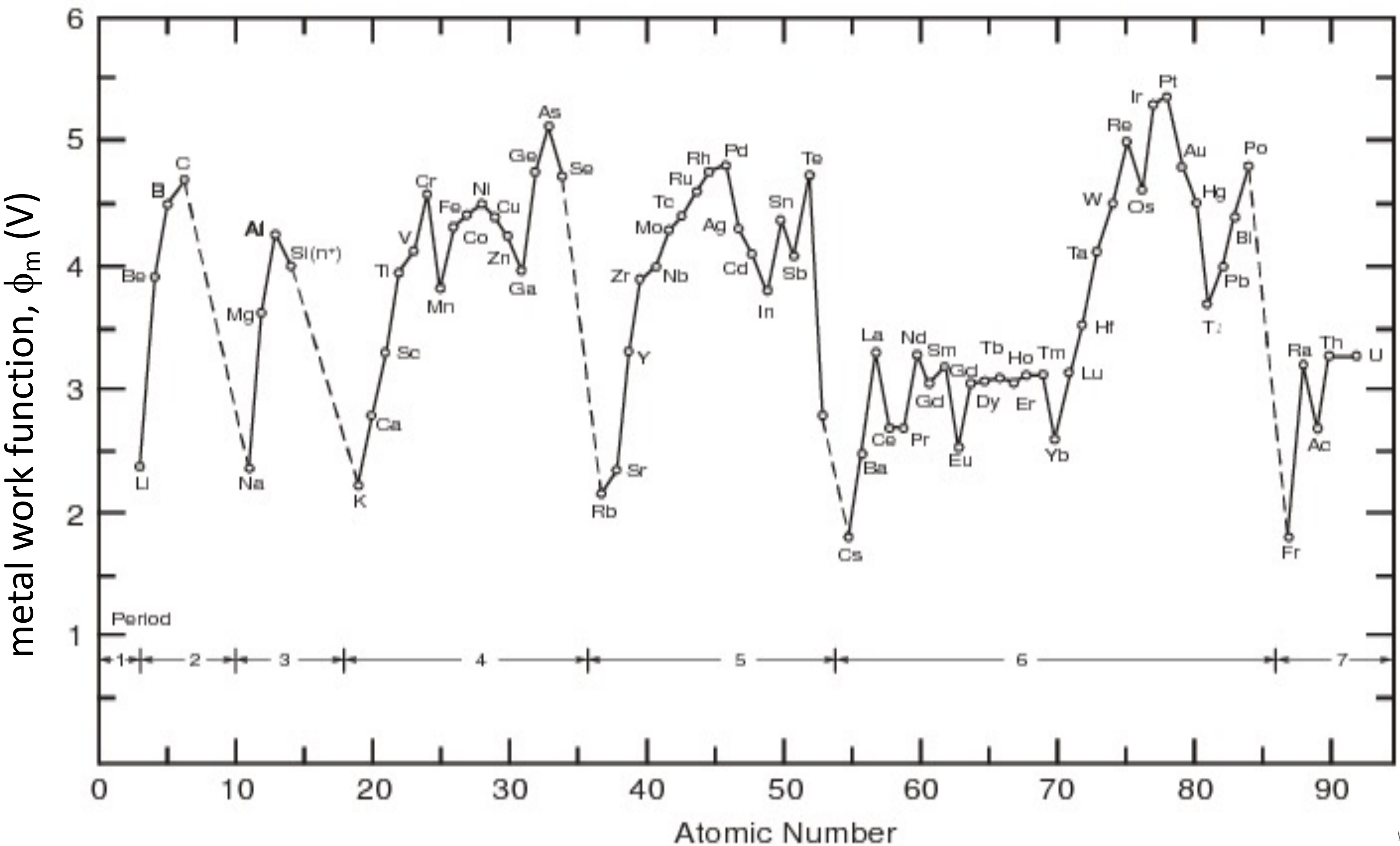


Fig. 6. Metal Work Function for a Clean Metal Surface in a Vacuum Versus Atomic Number [Sze 1985].

ganic Electronics
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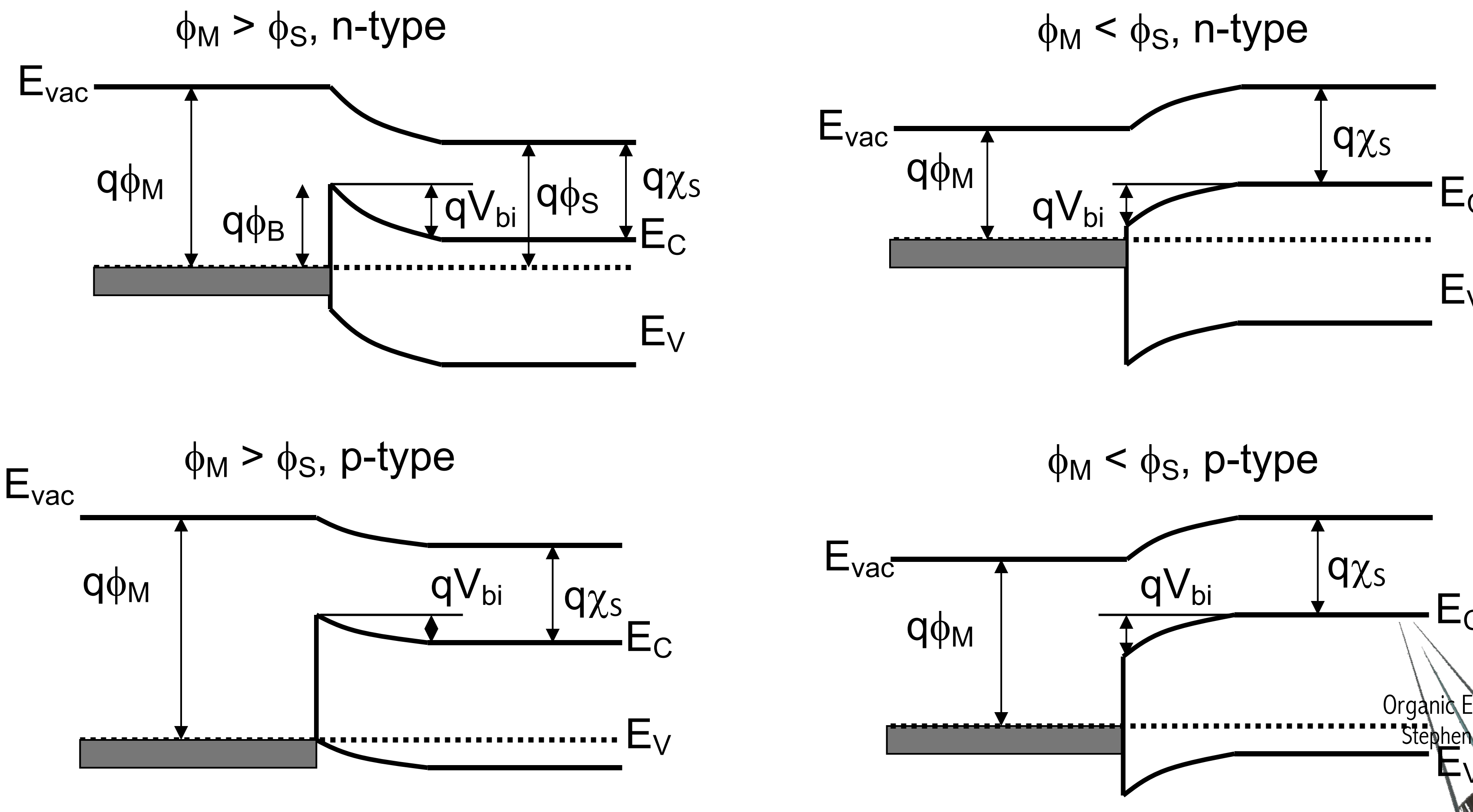
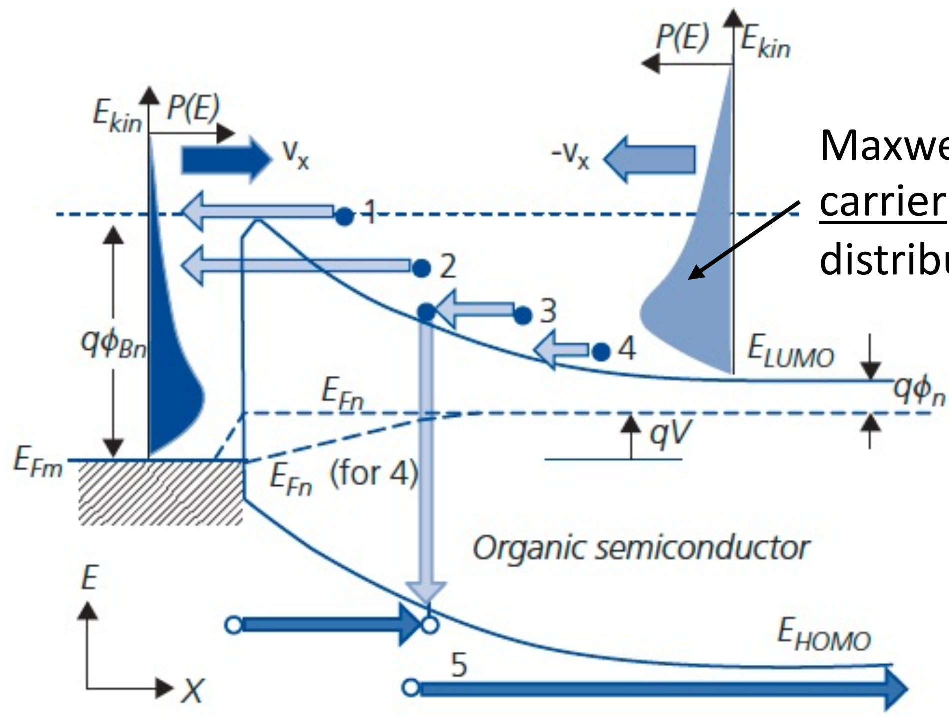
Schottky barrier formation and the built-in potential

$$V_{bi} = \phi_M - \phi_S = \phi_M - \left[\chi + \frac{1}{q}\left(E_C - E_f\right) \right]$$



Current sources across Metal-Org. Junction

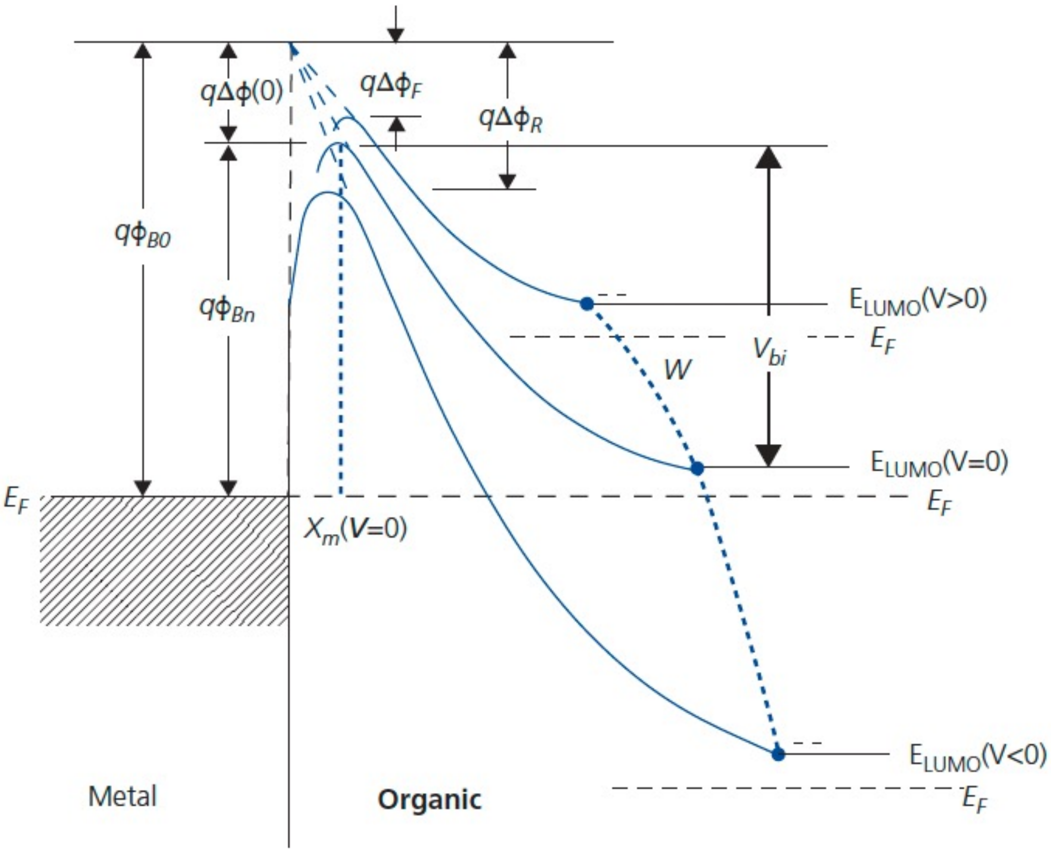


Maxwell-Boltzman <u>majority carrier</u> kinetic energy distribution

1. Thermionic emission
2. Tunneling
3. Majority carrier recombination
4. Majority carrier diffusion
5. Minority carrier (hole) diffusion

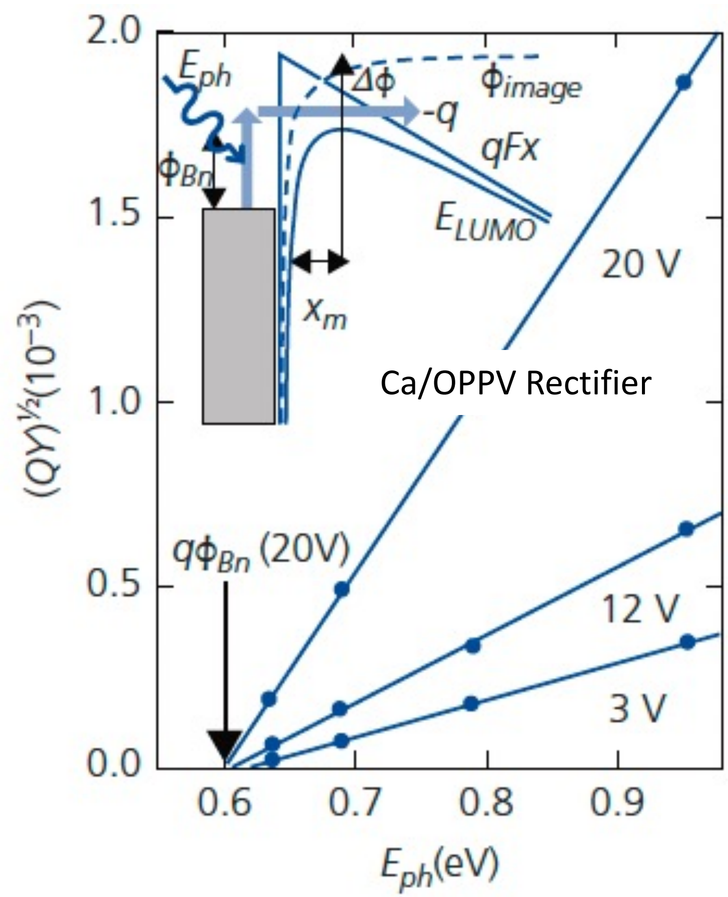
Barrier Lowering Under Applied V

Theory



Barrier lowering and increasing depletion occur with voltage

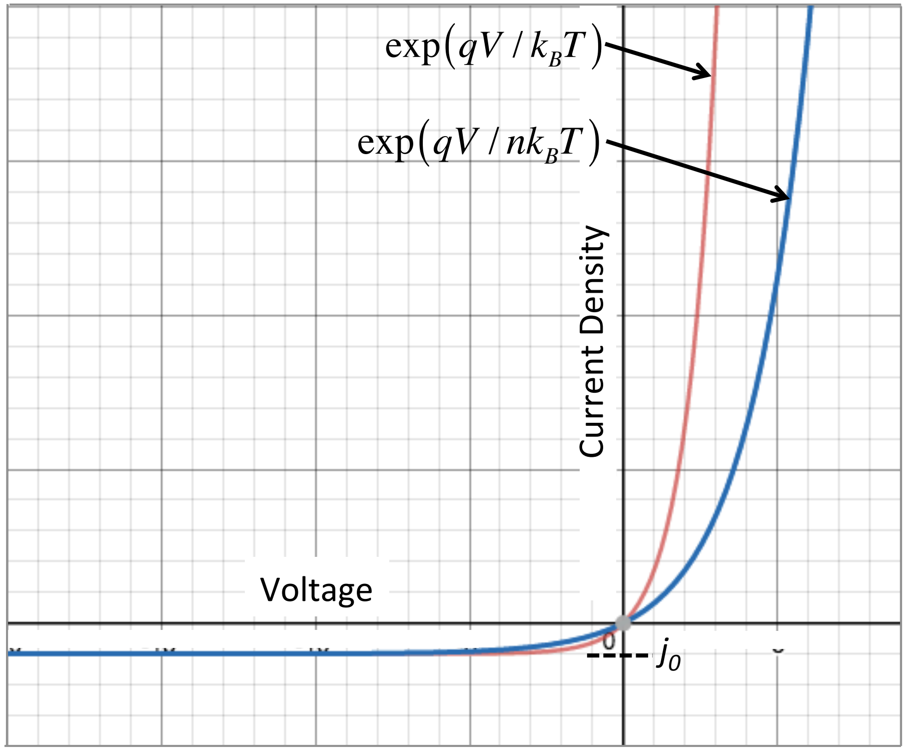
Experiment



Photoemission over barrier vs. voltage yields barrier height and lowering

Rikken, et al. Appl. Phys. Lett., 65, 219 (1994).

j-V Characteristics of M-O Junctions



$$j = j_0\left(\exp\left(qV/k_BT\right) - 1\right)$$

$$j_0 = j_{0TE} = A^*T^2\exp\left(-q\phi_{B0}/k_BT\right) \qquad A^* = \frac{4\pi q m^* k_B^2}{h^3}$$ (Richardson Constant)

Junction and Schottky Diodes
A qualitative comparison

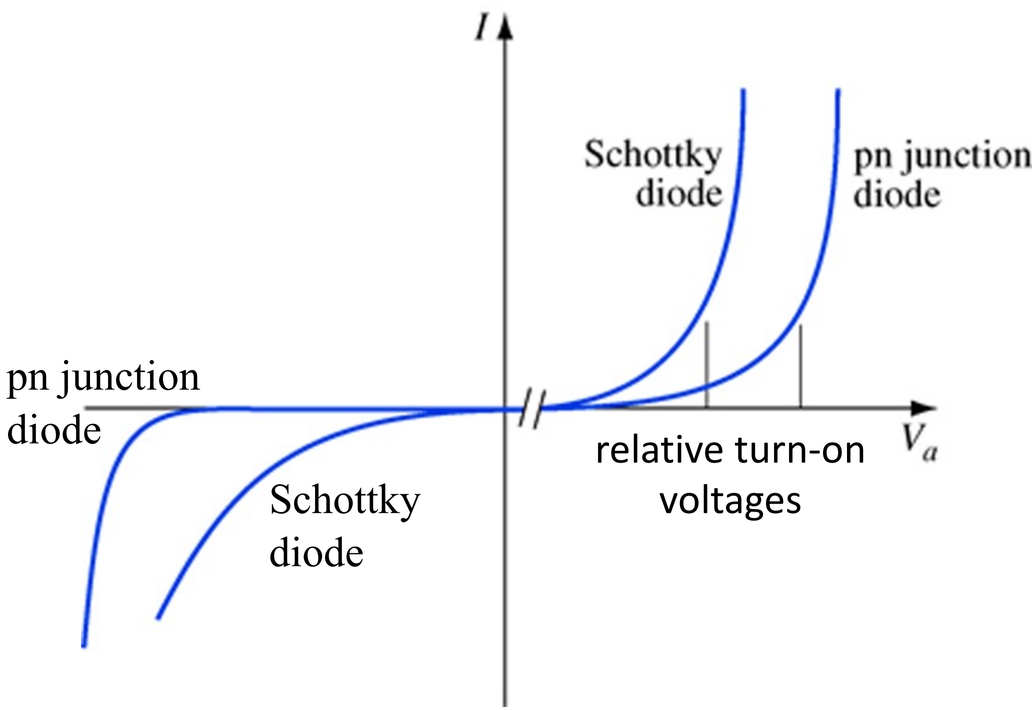


Image charge barrier lowering and tunneling make reverse characteristics of Schottky diodes more voltage dependent than ideal diodes