Electrical Properties of Organic Semiconductors

2014. 4. 17.

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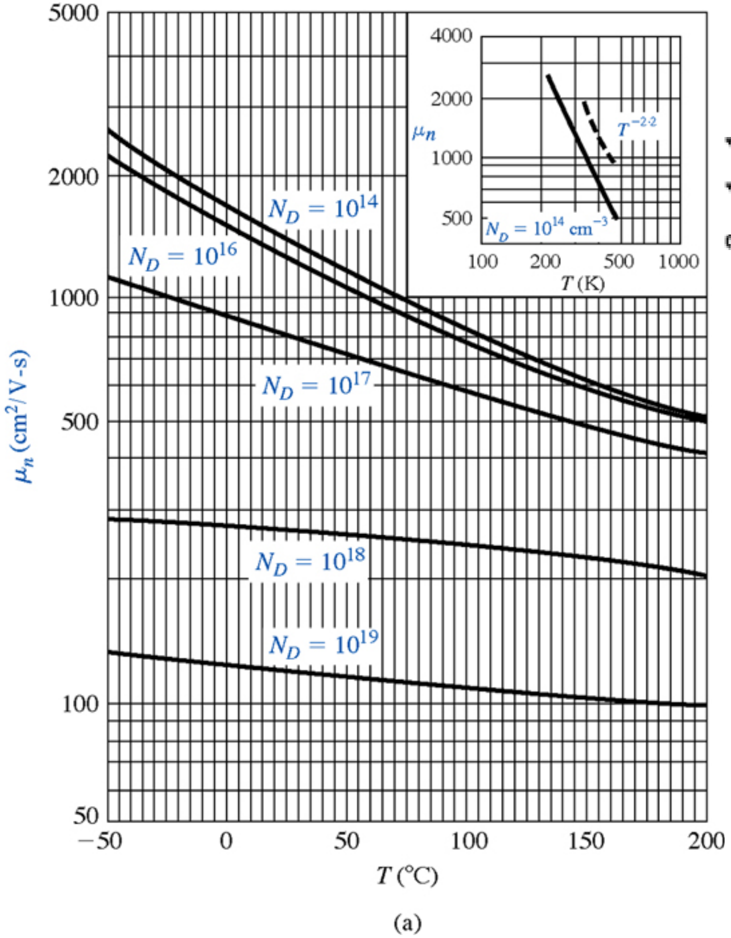
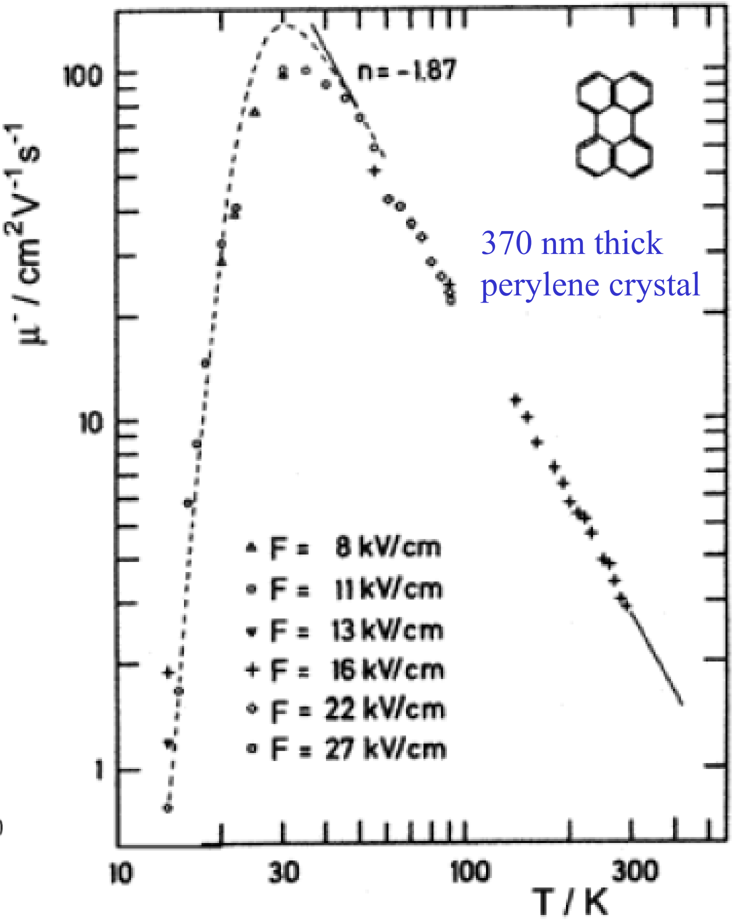
Charge Transport in Si and Organic Crystals

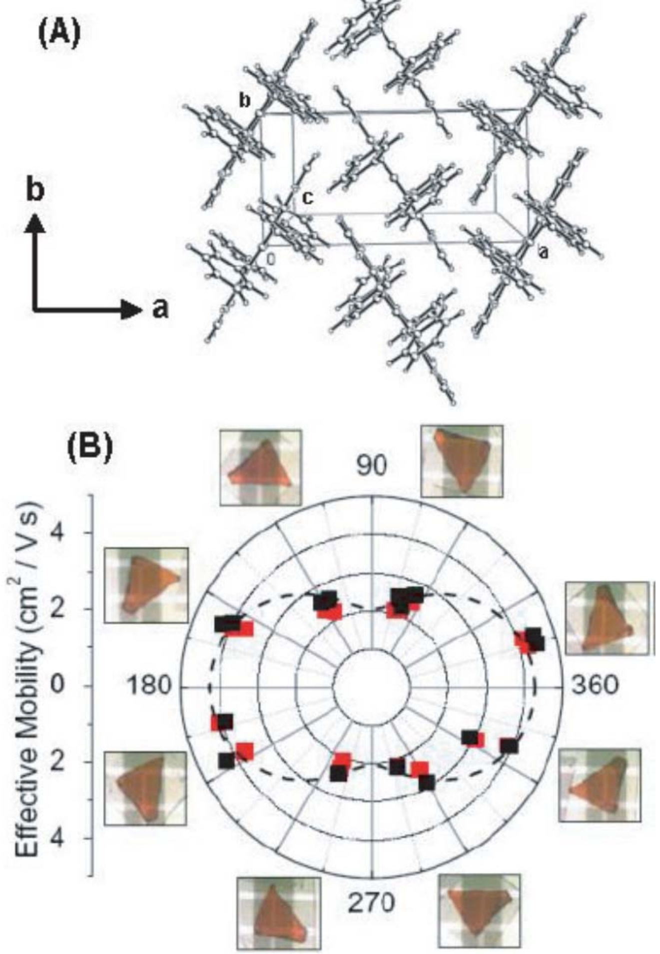
Electron mobility of Si



Electron mobility of Perylene



Rubrene crystal: The angular dependence of the mobility measured at room temperature.



Band-like transport of carriers.
Carrier mobility is limited by scatterings with phonons, impurities, etc.

$$\mu(T) \approx \mu_o T^{-n}$$

R. W. I. de Boer, M. E. Gershenson, A. F. Morpurgo, and V. Podzorov, phys. stat. sol. (a) 201, 1302 (2004).

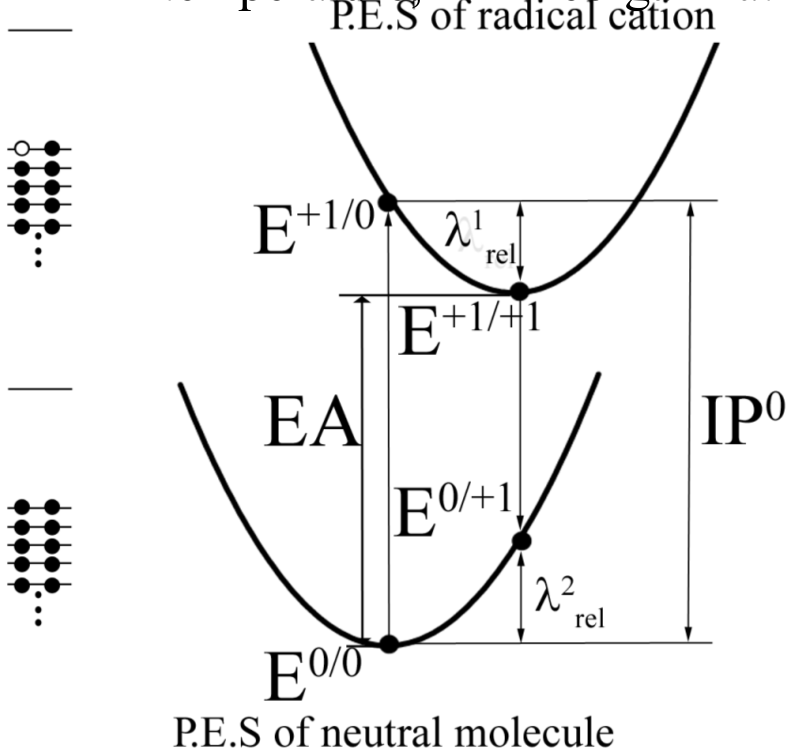
Rate of Charge Transfer

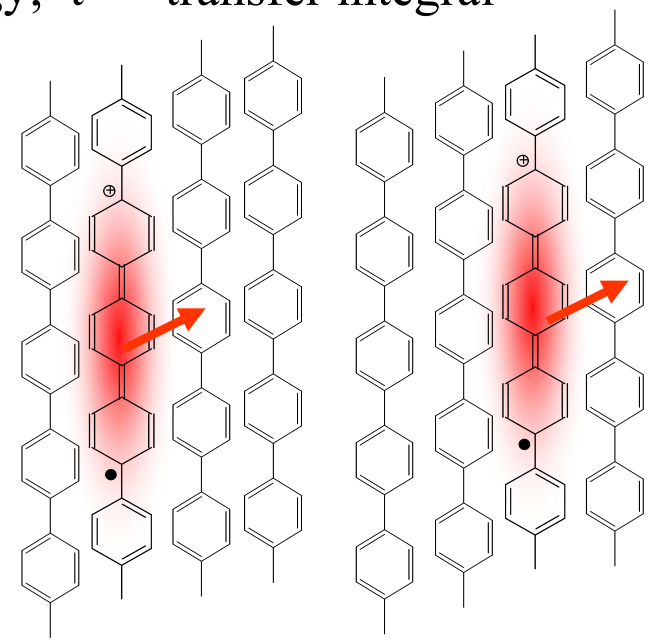
The rate of charge transfer is limited by the reorganiztion of the molecules.

According to the semiclassical Marcus theory in the high temperature limit, the electron - transfer (hopping) rate, k_{ET}, can be described as,

$$k_{ET} = A \cdot \exp\left[-\frac{(\lambda - 2t)^2}{4\lambda k_B T} \right]$$

T = temperature; λ = reorganization energy; t = transfer integral

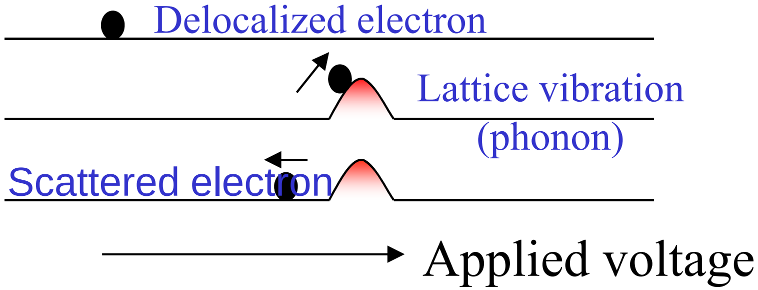




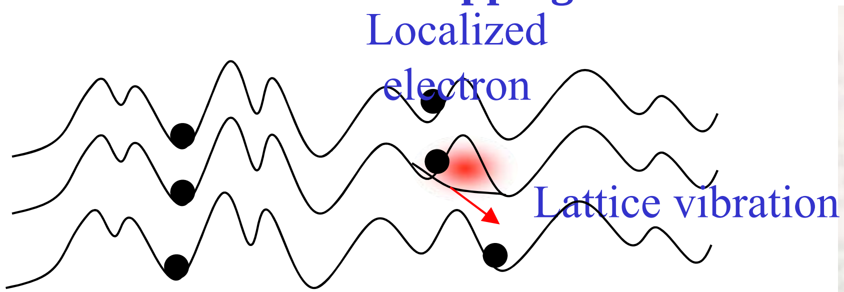
Polaron hopping

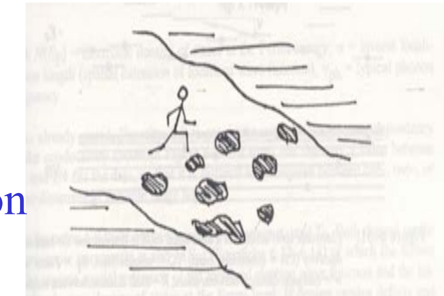
Carrier mobility

Band-like conduction

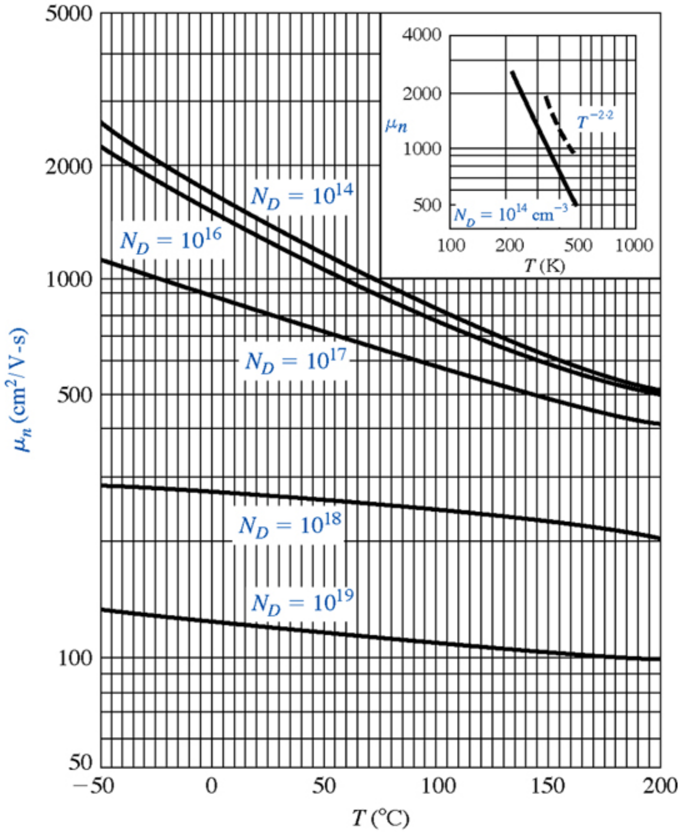


Hopping conduction

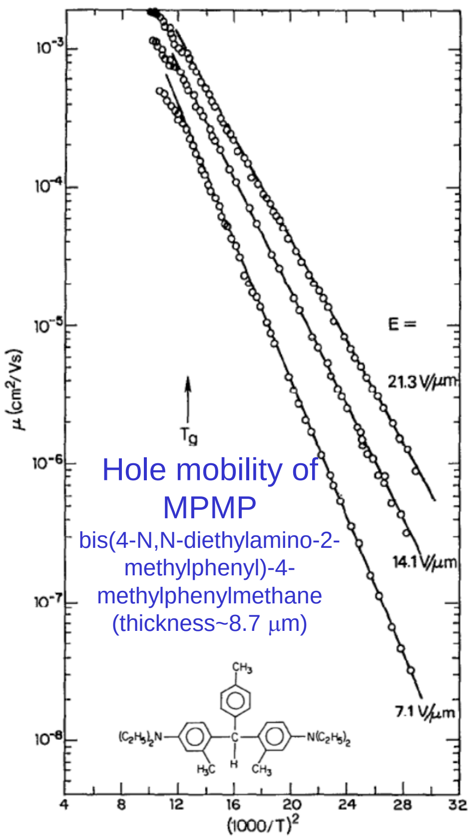


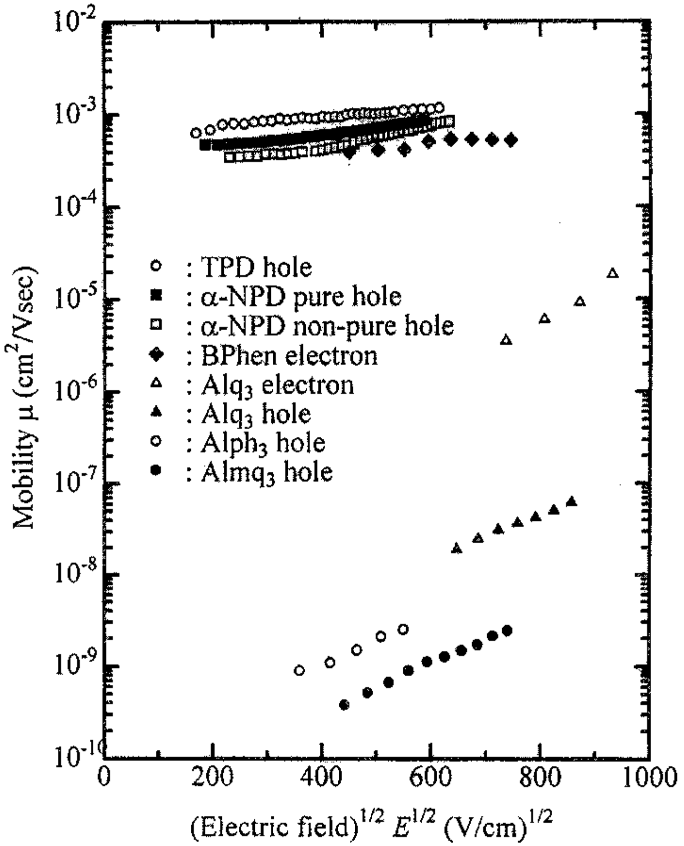


Electron mobility of Si



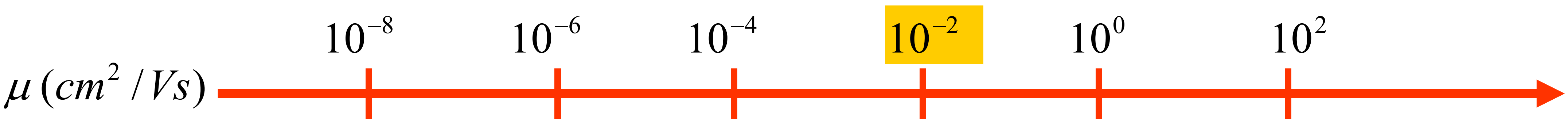
e & h mobility of organic materials

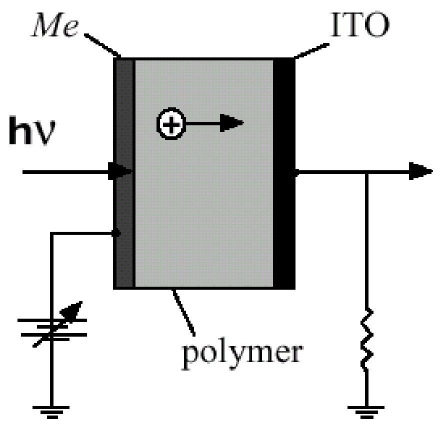




P. M. Borsenberger, L. Pautmeier and H. Bässler, J. Chem. Phys. 95, 1258 (1991)

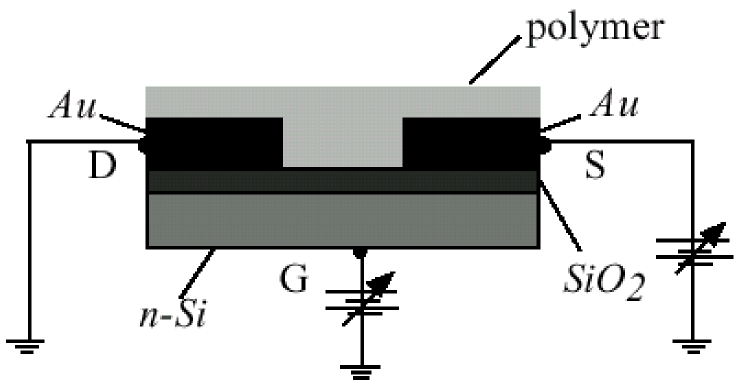
Mobility Measurement Techniques





$$\tau = \frac{d^2}{\mu V}$$

$$\therefore \mu = \frac{d^2}{V\tau}$$



TOF
Mobility in the bulk
d = 0.5~5 μm

FET
Mobility in a thin layer
d ~ 50 nm

Other mobility measurement techniques

- Dark injection in the space-charge limited current regime
- I-V characteristics of space charge limited current
- Transient EL
- SHG measurement [T. Manaka, E. Lim, R. Tamura, M. Iwamoto, *Nature Photon.* **1,** 581–584 (2007).]

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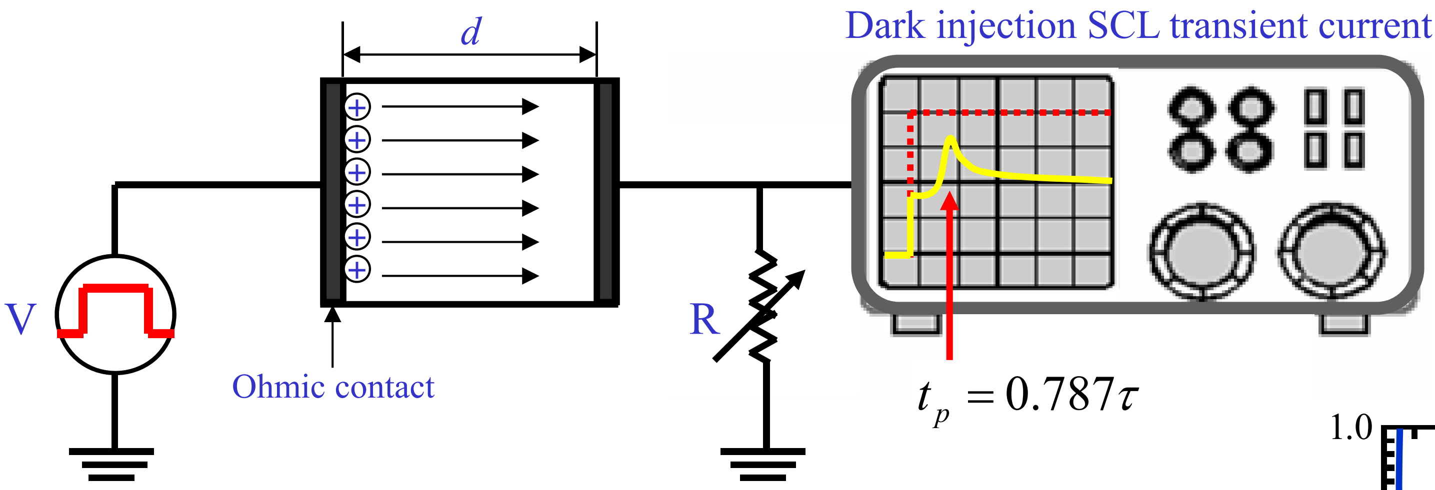
Transient SCLC



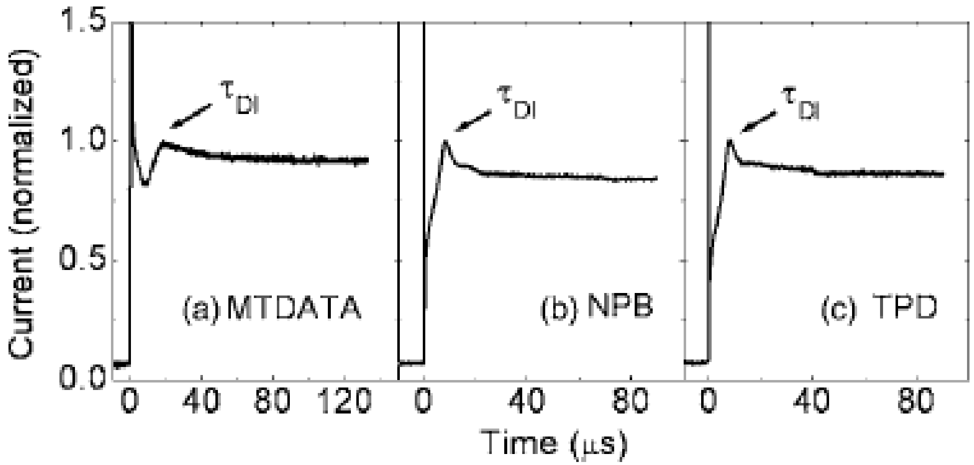
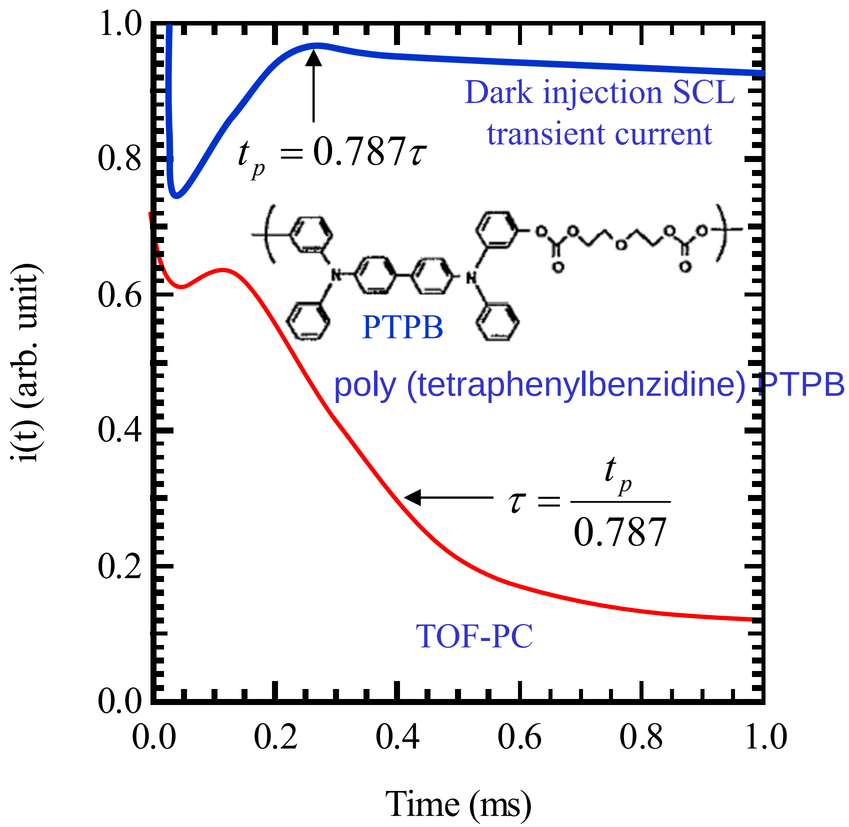


FIG. 5. Room temperature DI signals for MTDATA, NPB, and TPD under applied field strengths of 0.10, 0.09, and 0.09 MV/cm, respectively. The film thicknesses for MTDATA, NPB, and TPD were 0.76, 4.11, and 5.13 μm, respectively.

S.C. Tse, S.W. Tsang, and S.K. So, J. Appl. Phys. 100, 063708 (2006).



M. Abkowitz, J. S. Facci, and M. Stolka, Appl. Phys. Lett. 63, 1892 (1993).

Mobility Measurement Techniques: dark charge injection

In a monopolar and single-layer configuration, the carrier transit time is shorter than in the absence of space-charge effects due to the enhancement of the electric field at the leading edge of the carrier packet.

$$t_{tr} = 0.786 \frac{d}{\mu E}$$

The transient current overshoots its steady-state value by a factor of 1.21 and starts at 0.44 times the steady-state value

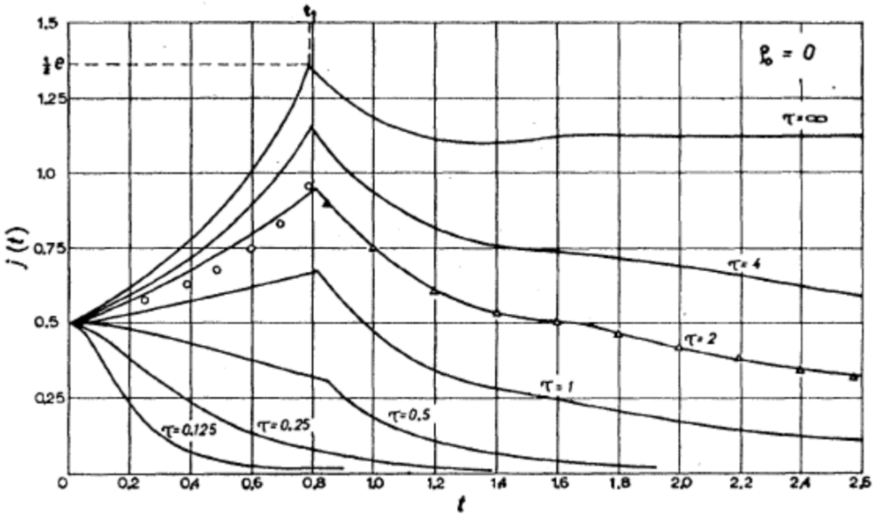
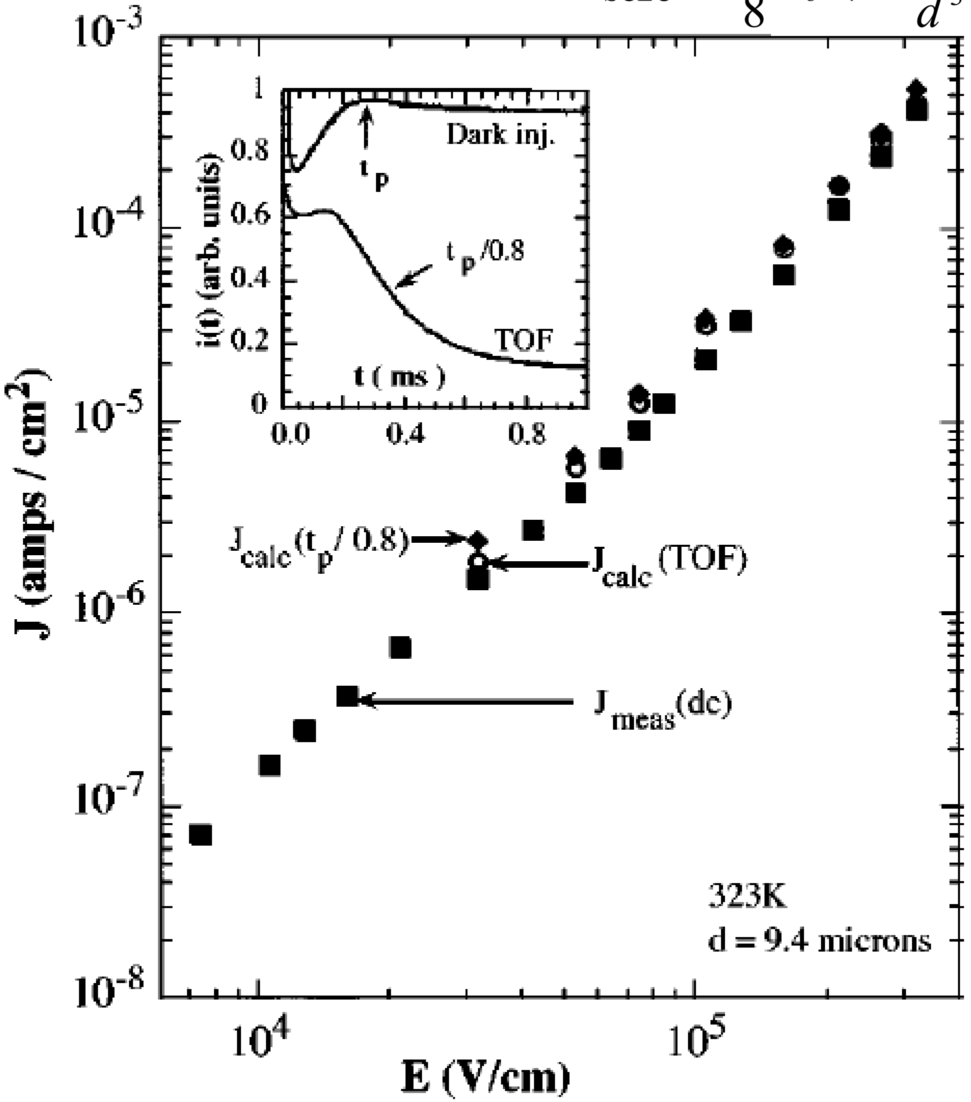


FIG. 5. The time dependence of the SCLC density for insulating crystals characterized by various trapping times, and $\theta_0 = 0$.

A. Many and G. Rakavy, Phys. Rev. **126**, 1980 (1962)

$$J_{SCLC} = \frac{9}{8}\varepsilon_o \varepsilon_r \mu \frac{V^2}{d^3}$$



M. Abkowitz, J. S. Facci, J. Rehm, J. Appl. Phys. 1998, 83, 2670.

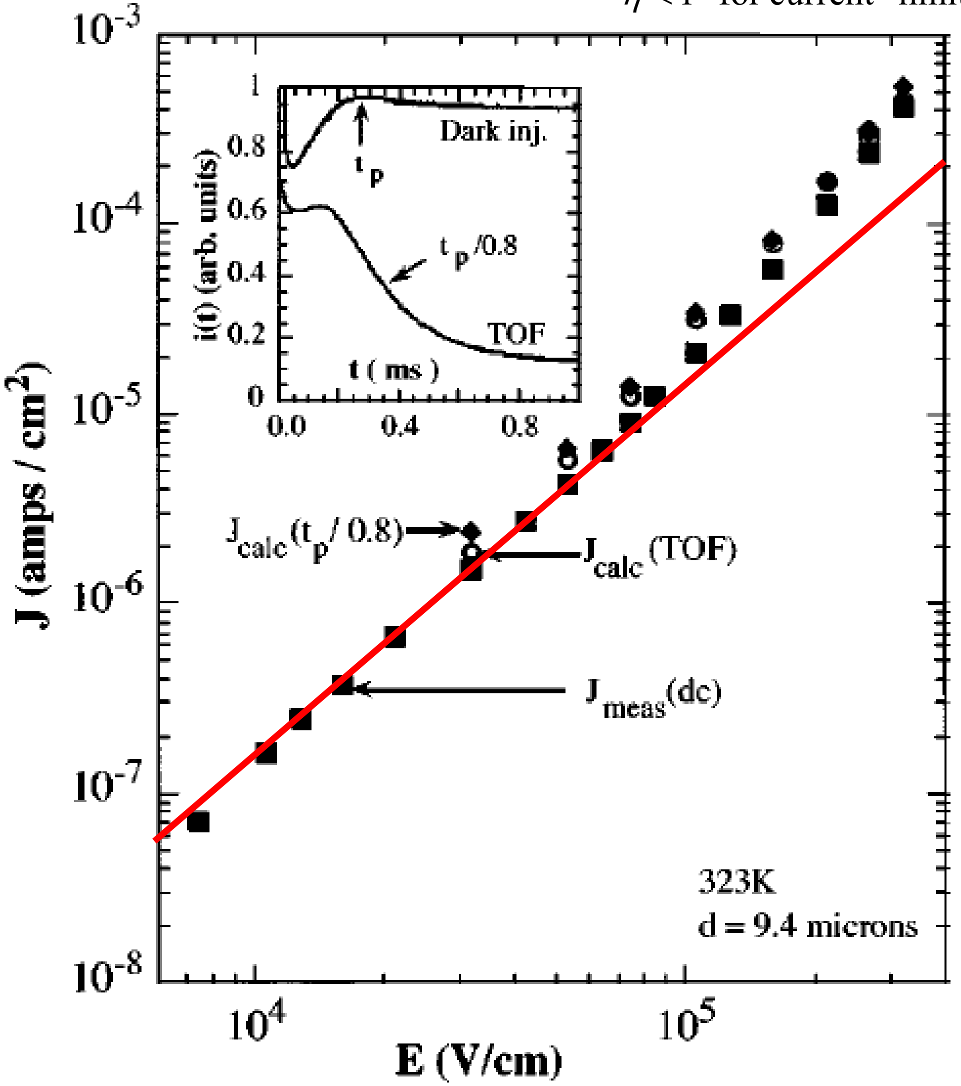
Carrier injection efficiency

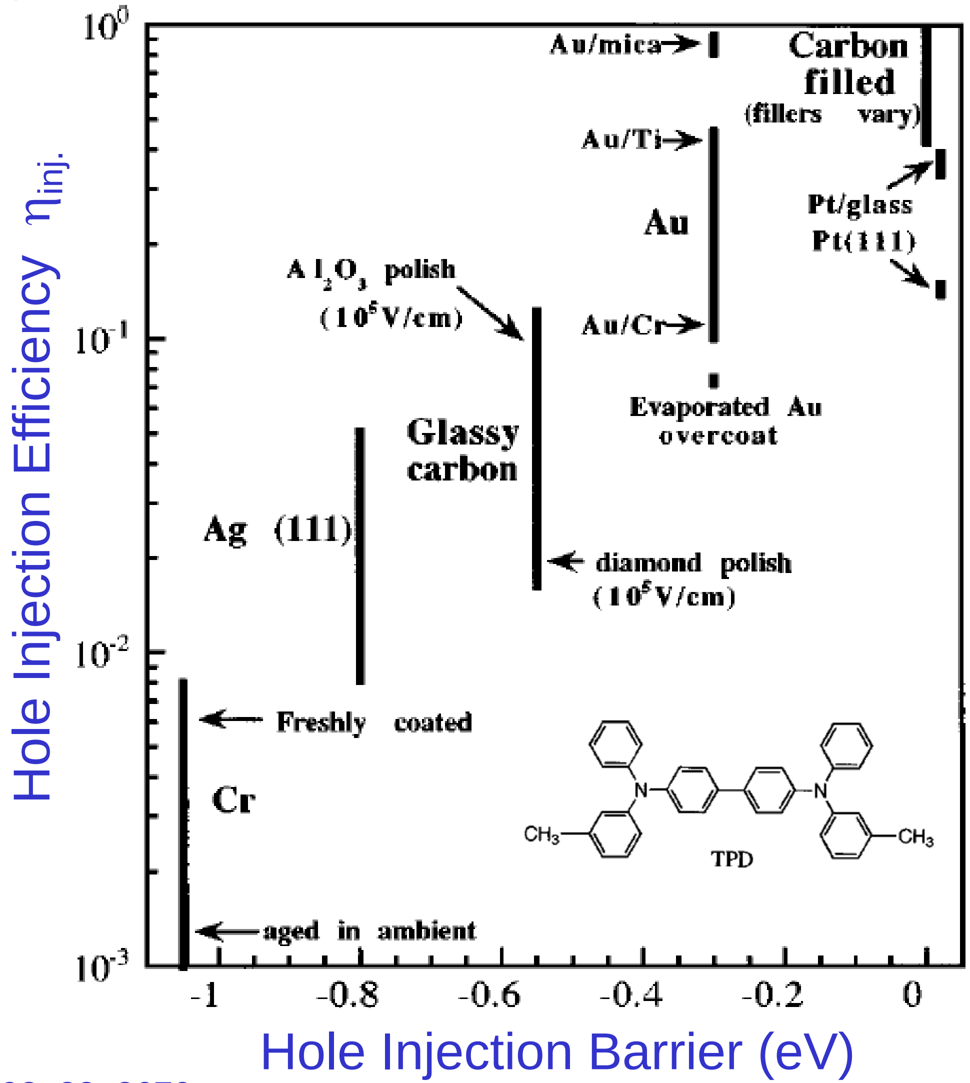
$$J_{SCLC} = \frac{9}{8}\frac{\varepsilon_o \varepsilon_r \mu V^2}{d^3}$$

$$\text{Injection efficiency}: \eta = \frac{\text{injected current}}{SCLC}$$

$\eta = 1$ for ohmic contact

$\eta < 1$ for current - limiting contact

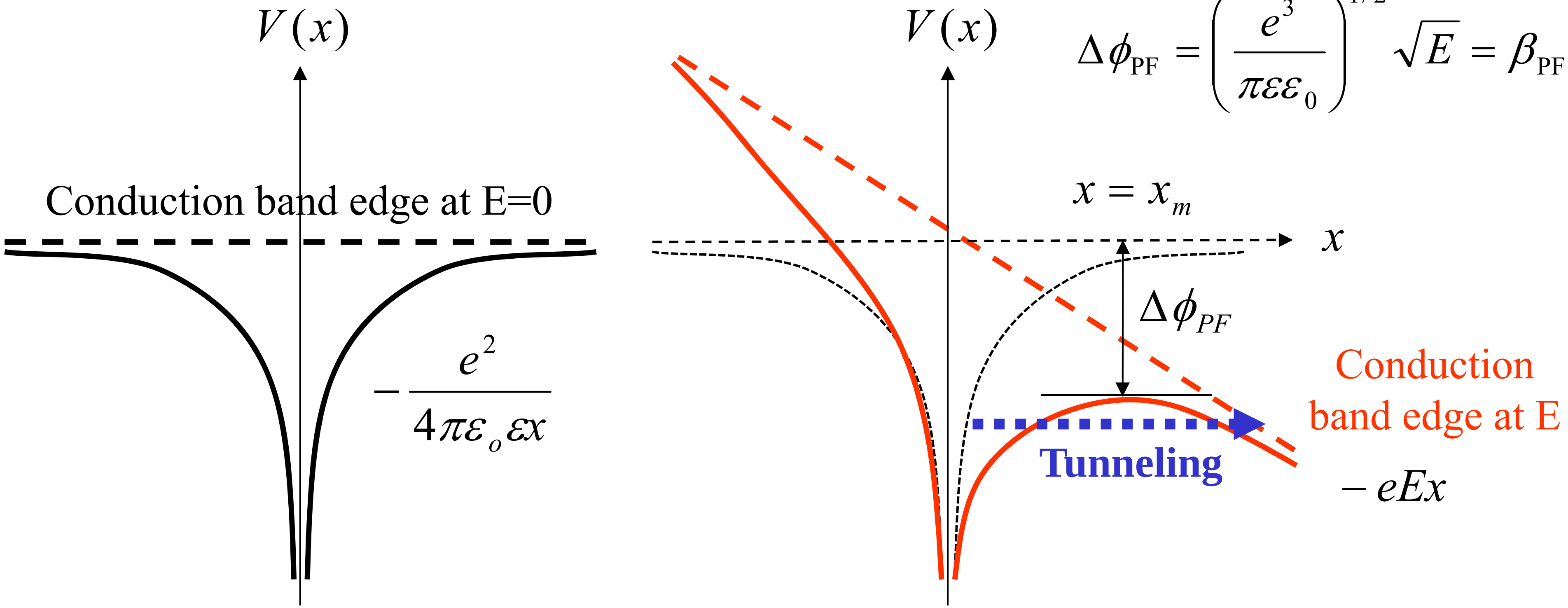




M. Abkowitz, J. S. Facci, J. Rehm, J. Appl. Phys. 1998, 83, 2670.

(1) Poole-Frenkel Model

$$\Delta\phi_{PF} = \left(\frac{e^3}{\pi\varepsilon\varepsilon_0}\right)^{1/2}\sqrt{E} = \beta_{PF}\sqrt{E}$$



Zero field (E=0)

E≠0

$$\mu(F,T) = \mu_{PF}\exp\left(-\frac{\Delta E}{k_B T}\right)\exp\left(\frac{\beta_{PF}\sqrt{E}}{k_B T}\right)$$

$$\beta_{PF} = \sqrt{\frac{e^3}{\pi\varepsilon\varepsilon_0}}$$

ΔE : Activation energy at E=0

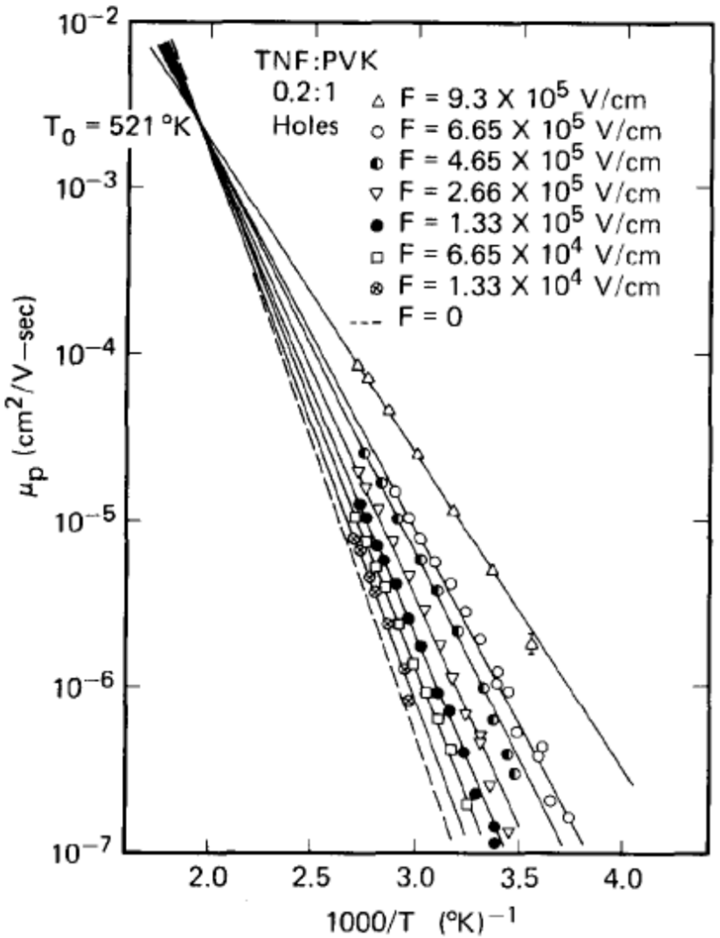
μ_{PF} : PF Mobility

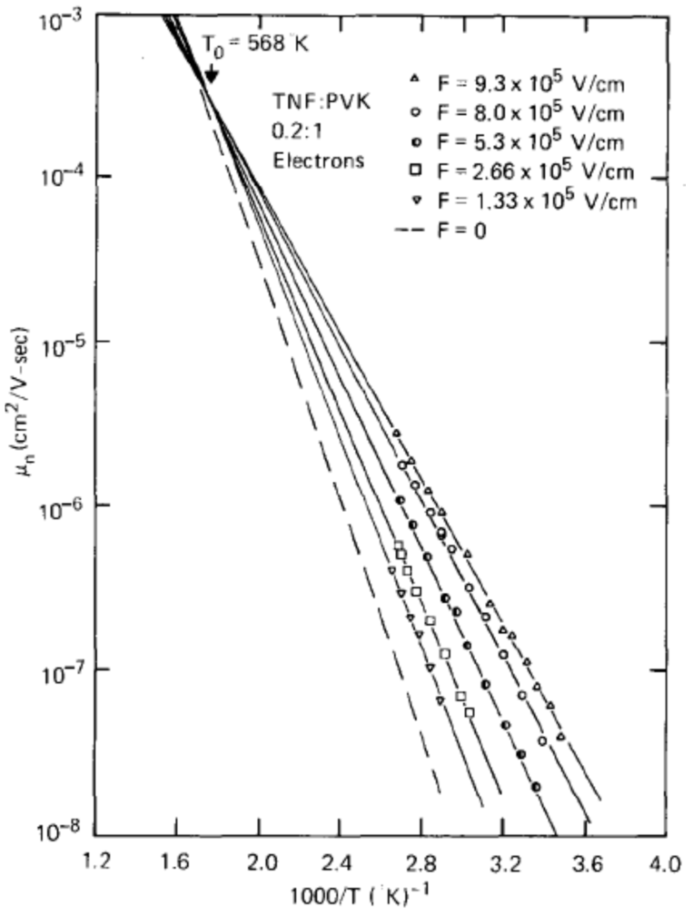
β_{PF} : PF constant

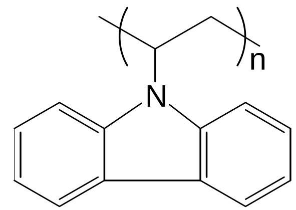
(2) Gill's modified Poole-Frenkel model

$$\mu(F,T) = \mu_{PF} \exp\left(-\frac{\Delta E}{k_B T_{eff}}\right) \exp\left(\frac{\beta_{PF}\sqrt{E}}{k_B T_{eff}}\right) \qquad \frac{1}{T_{eff}} = \frac{1}{T} - \frac{1}{T_0}$$

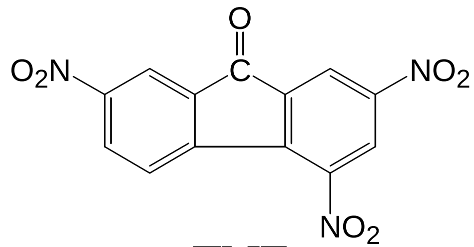
T_0 : Empirical parameter







PVK
poly-n-vinylcarbazole
(hole conductor)



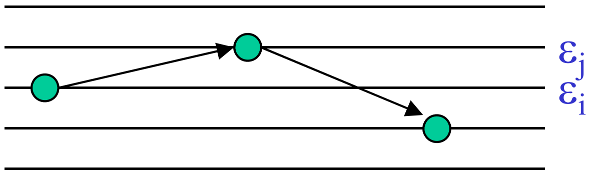
TNF
2,4,6-trinitro-9-fluorenone
(electron acceptor)

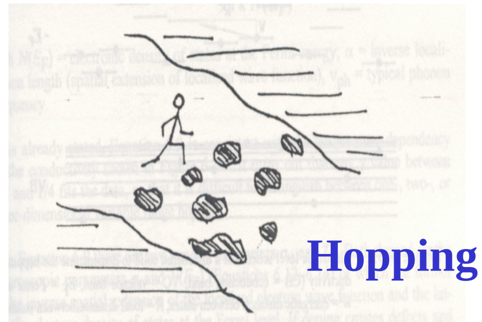
W. D. Gill, J. Appl. Phys. **43**, 5033 (1972).

(3) Bassler's Gaussian Disorder Model

- The energy of each site is distributed in accordance with the Gaussian distribution
- Energies of adjacent sites are uncorrelated and motion between sites is Markovian (no phase memory)
- The transition rates for phonon-assisted tunneling (Miller and Abrahams):

$$W_{ij} = \nu_{ph} \exp(-2\alpha R_{ij}) \begin{cases} \exp\left(-\dfrac{\varepsilon_i - \varepsilon_j}{kT}\right), & \varepsilon_i > \varepsilon_j \\ 1, & \varepsilon_i < \varepsilon_j \end{cases}$$

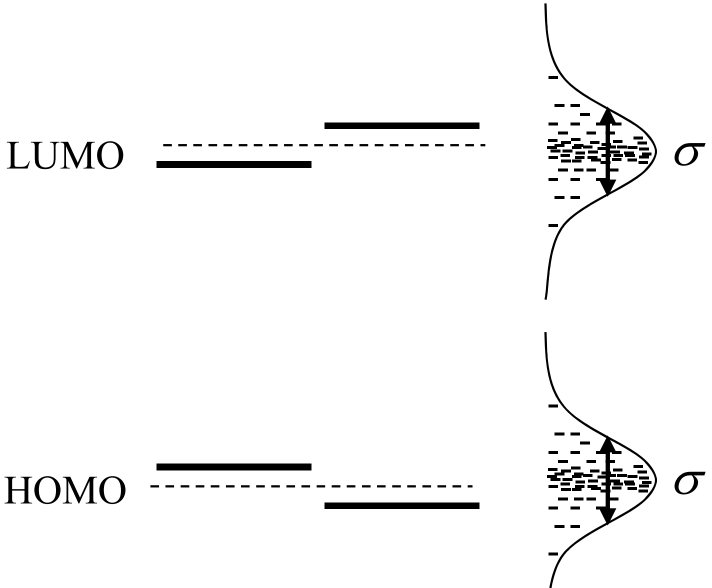


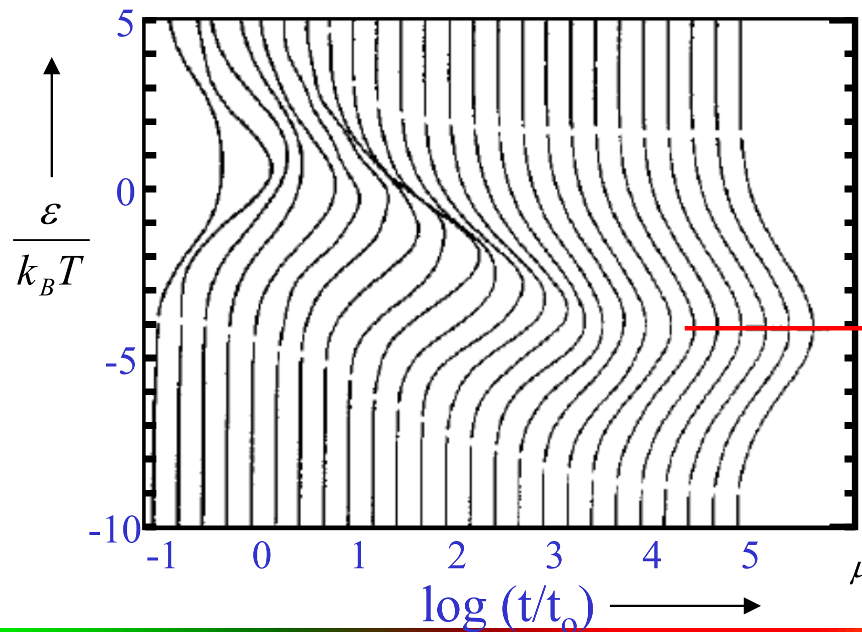


A. Miller, E. Abrahams, Phys. Rev. **120** (1960) 745.

α = inverse localization length, R_{ij} = distance between the localized states, ε_i = energy at the state i.

- Since the hopping rates are strongly dependent on both the positions and the energies of the localized states, *hopping transport is extremely sensitive to structural as well as energetic disorder.*



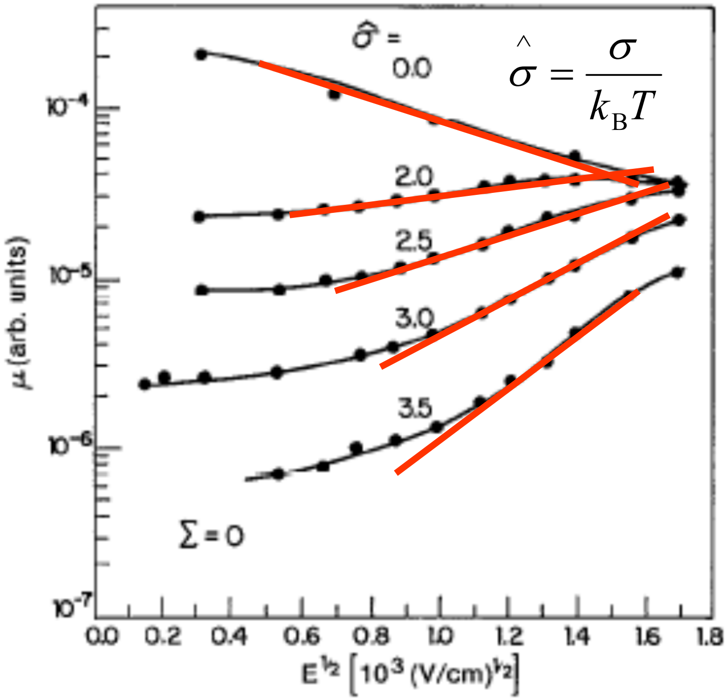


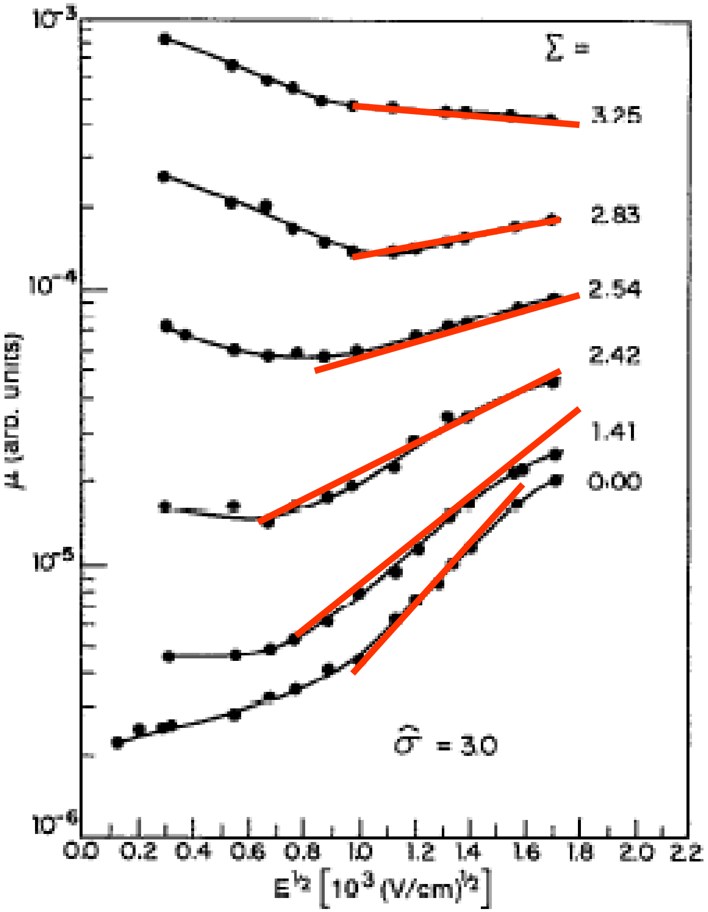
$$\frac{\langle \varepsilon_\infty \rangle}{k_B T} = -\frac{\sigma^2}{k_B T}$$

$$\mu = \mu_o \exp\left[-\left(\frac{T_o}{T}\right)^2\right], \quad T_o = \frac{2\sigma}{3k}$$

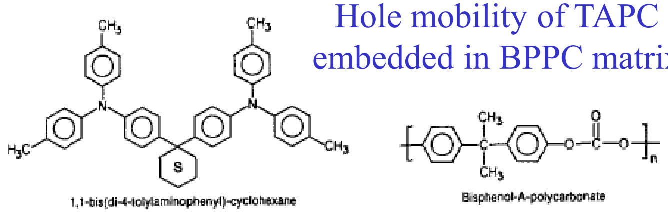
H. Bässler, Phys. Status Solidi B **175**, 15 (1993).

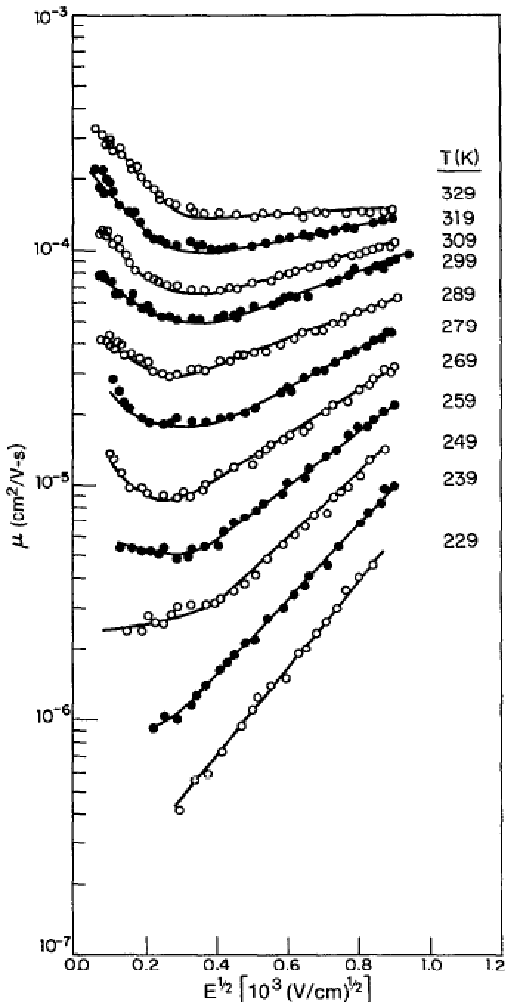
Bassler's Gaussian Disorder Model





Hole mobility of TAPC embedded in BPPC matrix





σ : Energetic disorder

Σ : Positional disorder

C : Constant ~2.9x10^{-4} (cm/V)$^{1/2}$

μ_o : High temperature limit of the mobility

$$\mu(E,T) = \mu_o \exp\left[-\left(\frac{2\sigma}{3k_B T}\right)^2\right]\exp\left\{C\left[\left(\frac{\sigma}{k_B T}\right)^2 - 2.25\right]\sqrt{E}\right\},\ (\Sigma \le 1.5)$$

$$\mu(E,T) = \mu_o \exp\left[-\left(\frac{2\sigma}{3k_B T}\right)^2\right]\exp\left\{C\left[\left(\frac{\sigma}{k_B T}\right)^2 - \Sigma^2\right]\sqrt{E}\right\},\ (\Sigma > 1.5)$$

$$\mu_o(\rho) = a_o \rho^2 \exp(-2\rho/\rho_o),$$

where ρ = average inter-site distance

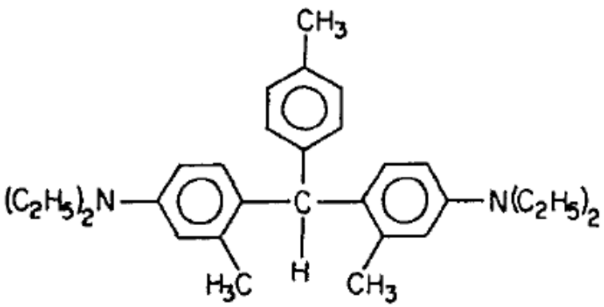
and ρ_o = carrier localization radius

H. Bässler, Phys. Status Solidi B **175**, 15 (1993).

M. Stolka, J. F. Janus and D. M. Pai, J. Phys. Chem. **88**, 4707 (1984).

P. M. Borsenberger, L. Pautmeier and H. Bassler, J. Chem. Phys. **94**, 5447 (1991).

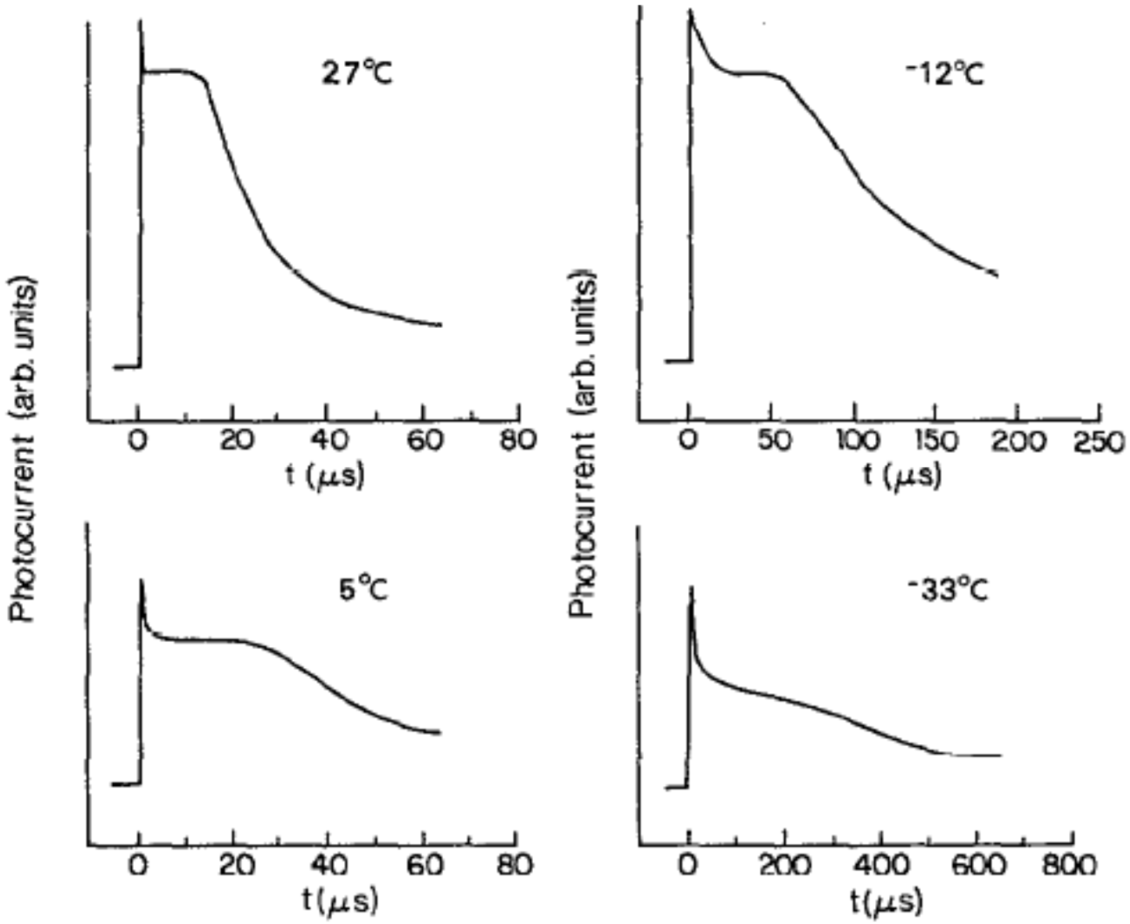
Charge Transport in Disordered Polymers

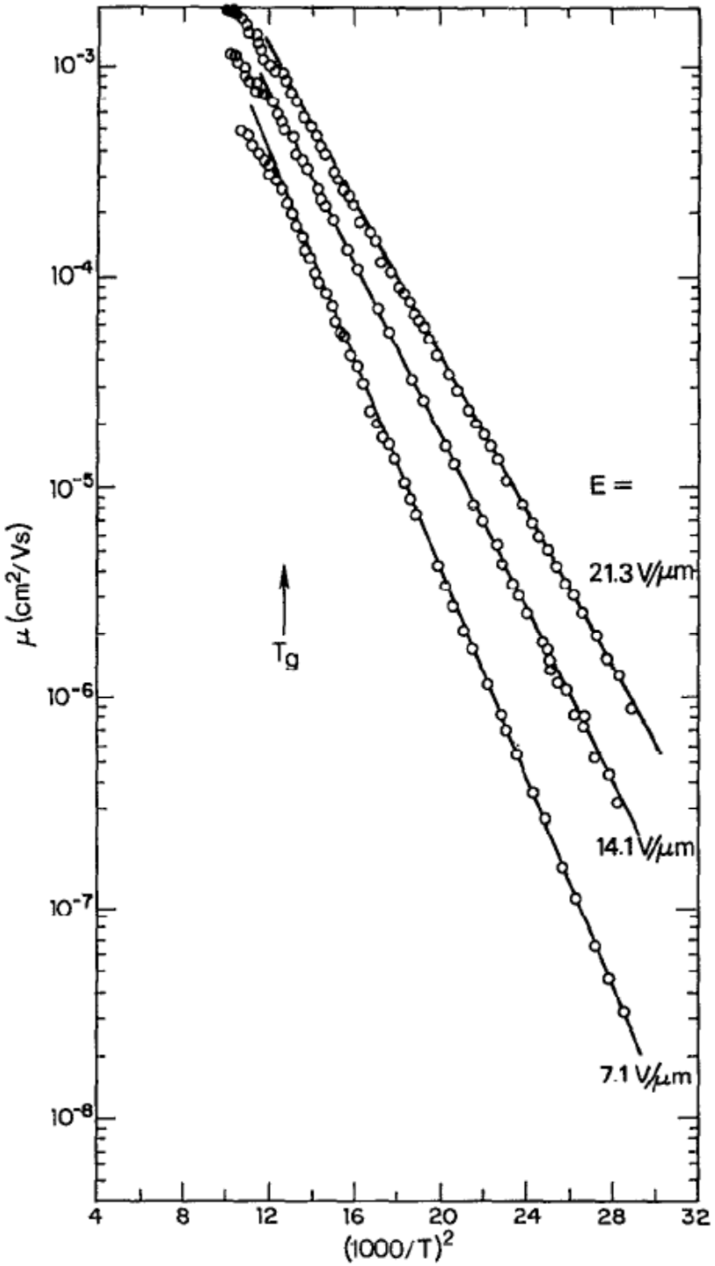


Hole mobility of MPMP

MPMP

bis(4-N,N-diethylamino-2-methylphenyl)-4-methylphenylmethane
(thickness~8.7 μm)





P. M. Borsenberger, L. Pautmeier and H. Bässler, J. Chem. Phys. **95**, 1258 (1991)

Disorder parameters

Disorder parameters

- σ: The width of the DOS. Random distribution of both permanent and van der Waals dipoles lead to local fluctuations in electric potential → increase s by an amount proportional to the square root of the dipole concentration and to the strength of the dipole moment. → reduce the carrier mobility. The smaller dipolar interaction is better for the carrier transport.
- Σ: The degree of positional disorder. Amorphous morphology of molecular solids or doped polymers lead to the variation in the intermolecular distances.

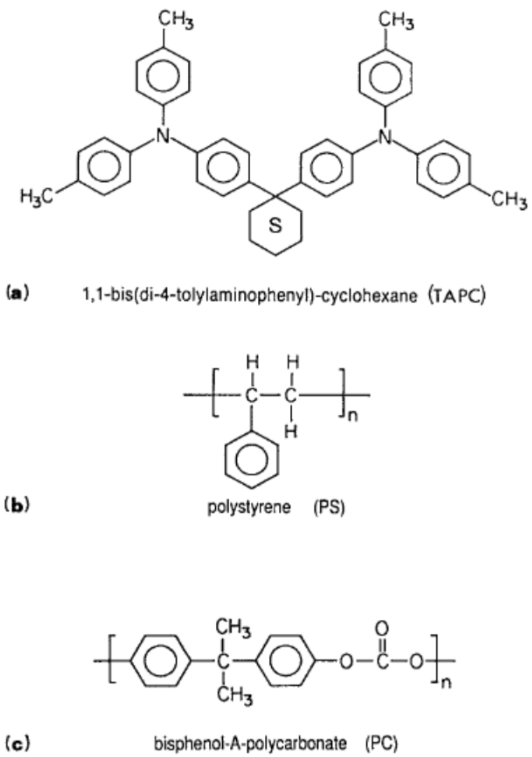


FIG. 1. Molecular structures of compounds used in this study.

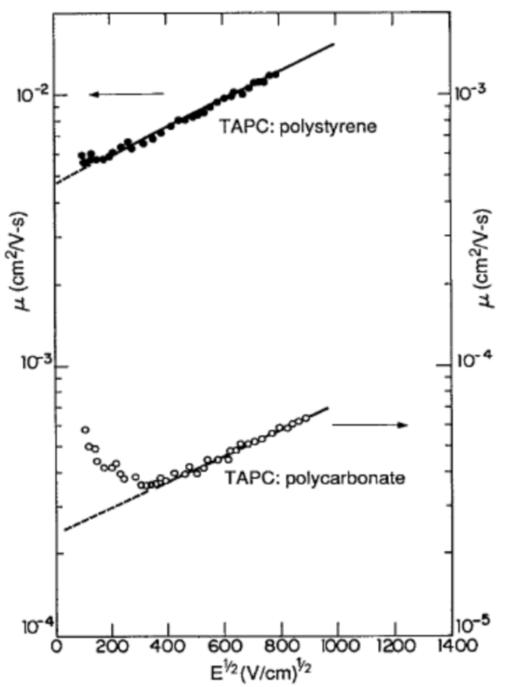


FIG. 2. Logarithm of the mobility vs $E^{1/2}$ for TAPC doped polystyrene and TAPC doped polycarbonate measured at 295 K.

P. M. Borsenberger and H. Bässler, J. Chem. Phys. **95**, 5327 (1991).

$\mu_{\text{TAPC doped polystyrene}} \gg \mu_{\text{TAPC doped polycarbonate}}$

Dipole moment:

- TAPC [1,1-bis(di-4-tolylaminophenyl)cyclohexane] = 1.0 D
- PC (bisphenol-*A*-polycarbonate) = 1.0 D
- PS (polystyrene) = 0.1 D

- Larger dipolar interaction increases both σ and Σ.
- The elimination of random dipolar fields due to static dipole moments of PC reduces both σ and Σ and thereby increases the mobility.

Influence of impurity on the carrier mobility

Electron and hole mobilities of anthracene

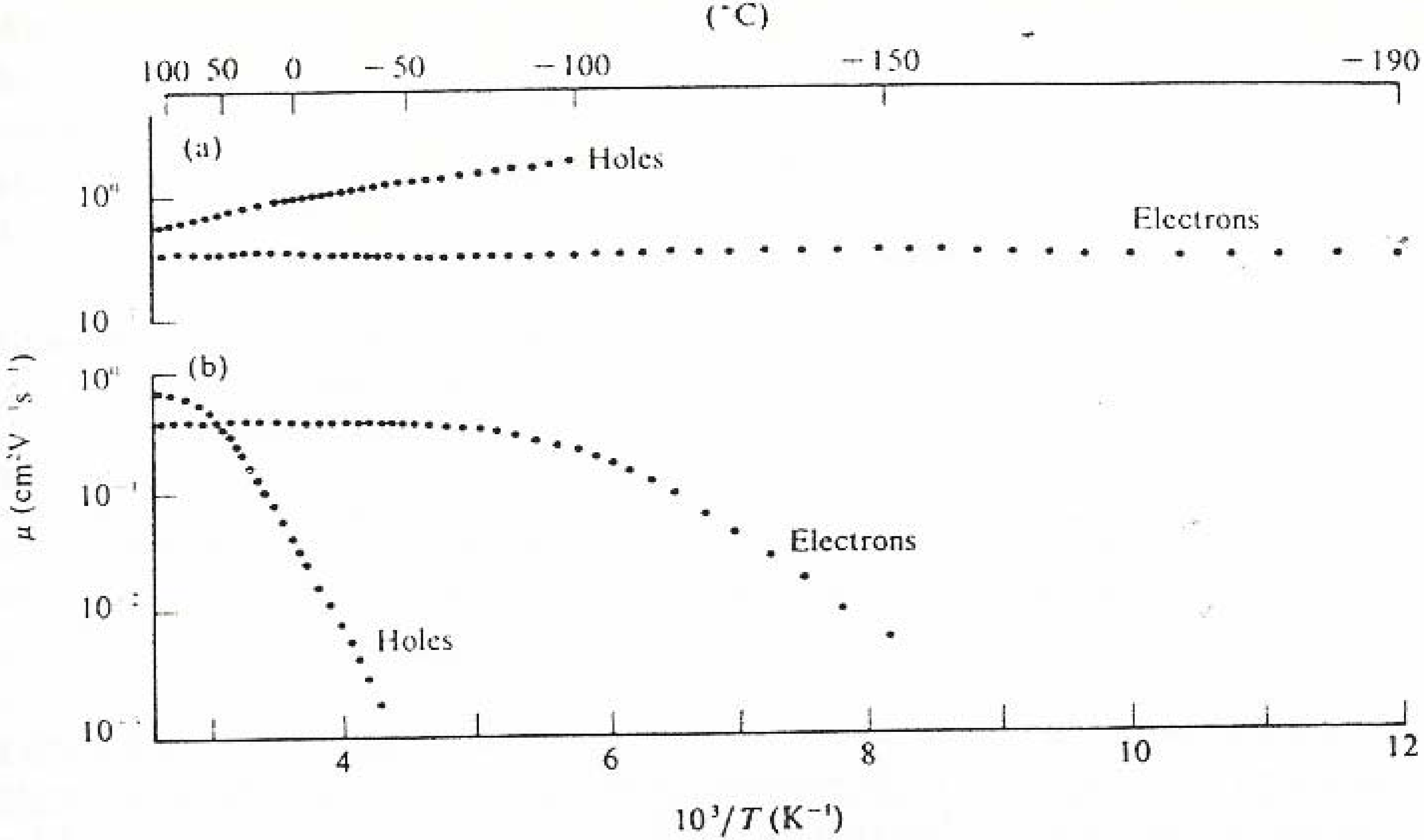
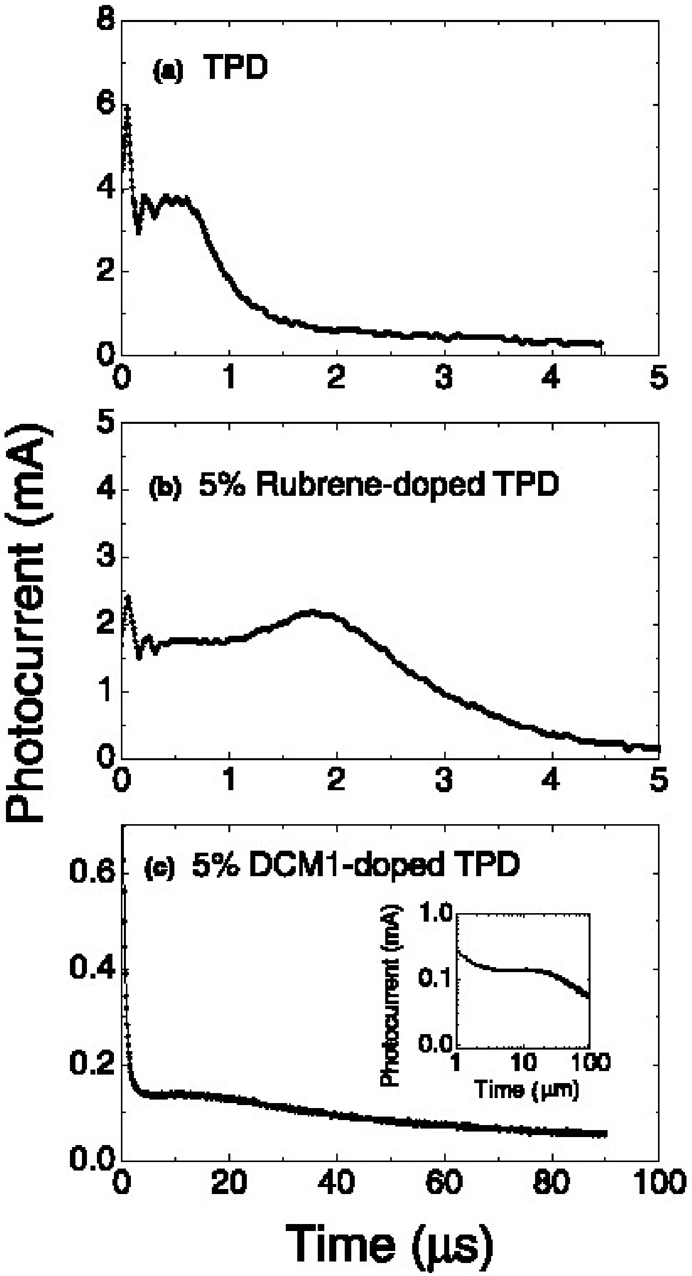
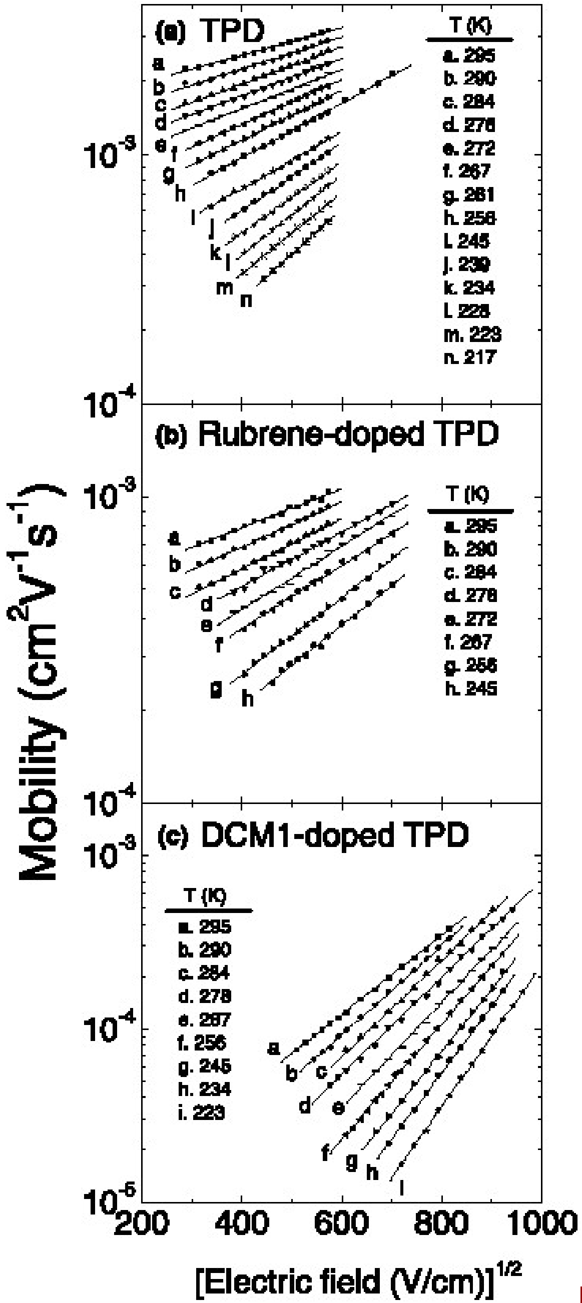


Fig. II.F.14. The influence of 10^{-7} mol/mol tetracene doping on the anthracene c' charge carrier mobilities. (a) Undoped crystal mobilities; (b) doped crystal mobility. Note the asymmetry between the hole and electron trapping, and the trap depths calculated using Eq. II.F.2.32. (Karl 1980a)

Mobility – Doping Relation





Doping reduces carrier mobility and affects I-V-EL characteristics.

Ref. H.H. Fong et al.
Chem. Phys. Lett. 353 (2002) 407

Charge –voltage characteristics of organic semiconductors

- Current
  - Injection limited
    - **Thermionic emission**

      $$J = J_s[\exp(\frac{eV}{k_B T}) - 1] \quad J_s = A^* T^2 \exp(\frac{-e\phi_{bn}}{k_B T})$$

    - **Tunneling**

      $$J \approx E^2 \exp(\frac{-b}{E}) \quad b = \frac{8\pi\sqrt{2m^*}(q\phi)^{3/2}}{3qh}$$

  - Bulk Limited
    - **Ohmic (Doped semiconductor)**

      $$J = ep\mu E$$

    - **SCLC (undoped semicond. or Insulator)**

      $$J_{SCLC} = \frac{9}{8}\varepsilon_o \varepsilon_r \mu \frac{V^2}{d^3}$$

Carrier injection at the contact

Thermionic Emission

$$J = J_s[\exp(\frac{eV}{nk_BT}) - 1]$$

$$J_s = A^*T^2 \exp(\frac{-e\phi_{bn}}{k_BT})$$

effective Richardson constant for thermionic emission

$$A^* = \frac{4\pi e m_n^* k_B}{h^3} = 120(\frac{m^*}{m}) \text{ A/cm}^2/\text{K}^2$$

Schottky effect $\Delta\Phi = \sqrt{\frac{e^3 F}{4\pi\varepsilon\varepsilon_o}}$

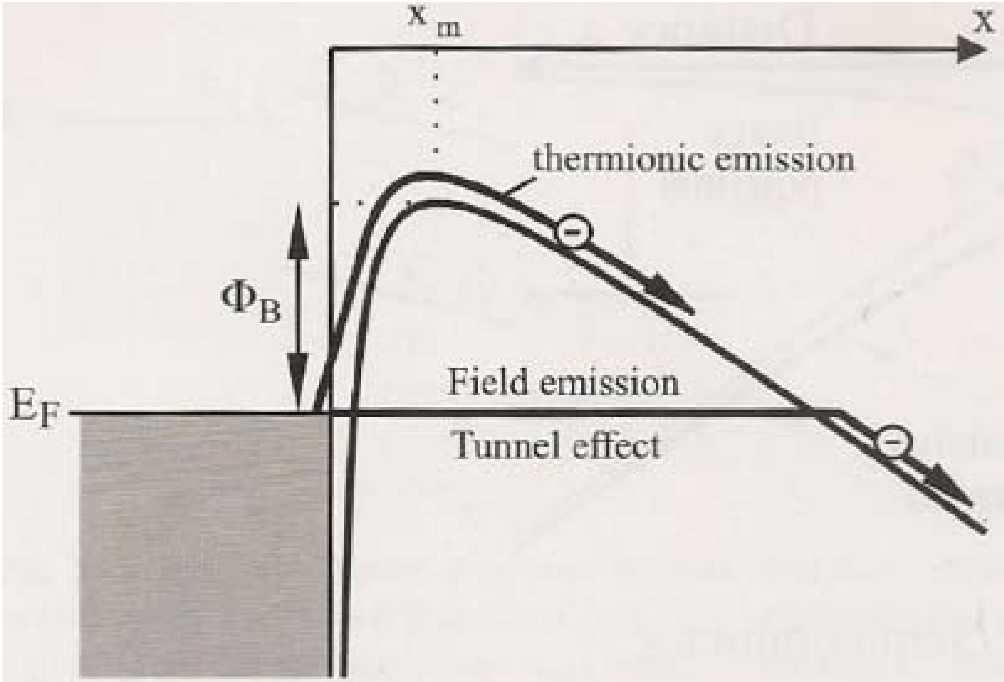


Fig. 8.24 Thermionic emission and field emission.

Fowler-Nordheim Tunneling

$$J_s \approx E^2 \exp(\frac{-b}{E}) \quad b = \frac{8\pi\sqrt{2m^*}(q\phi)^{3/2}}{3qh}$$

Carrier Injection : Fowler-Nordheim Tunneling

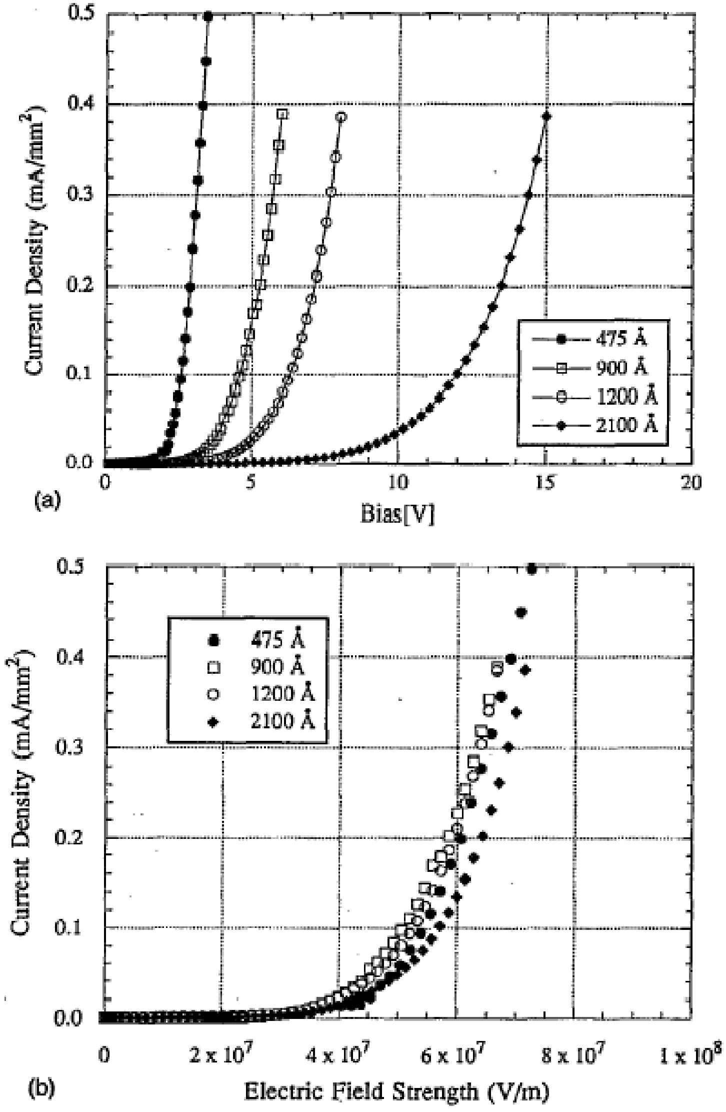


FIG. 2. (a) Thickness dependence of the *I-V* characteristics in an ITO/MEH-PPV/Ca device. (b) Electric field *v* current dependence for the above devices.

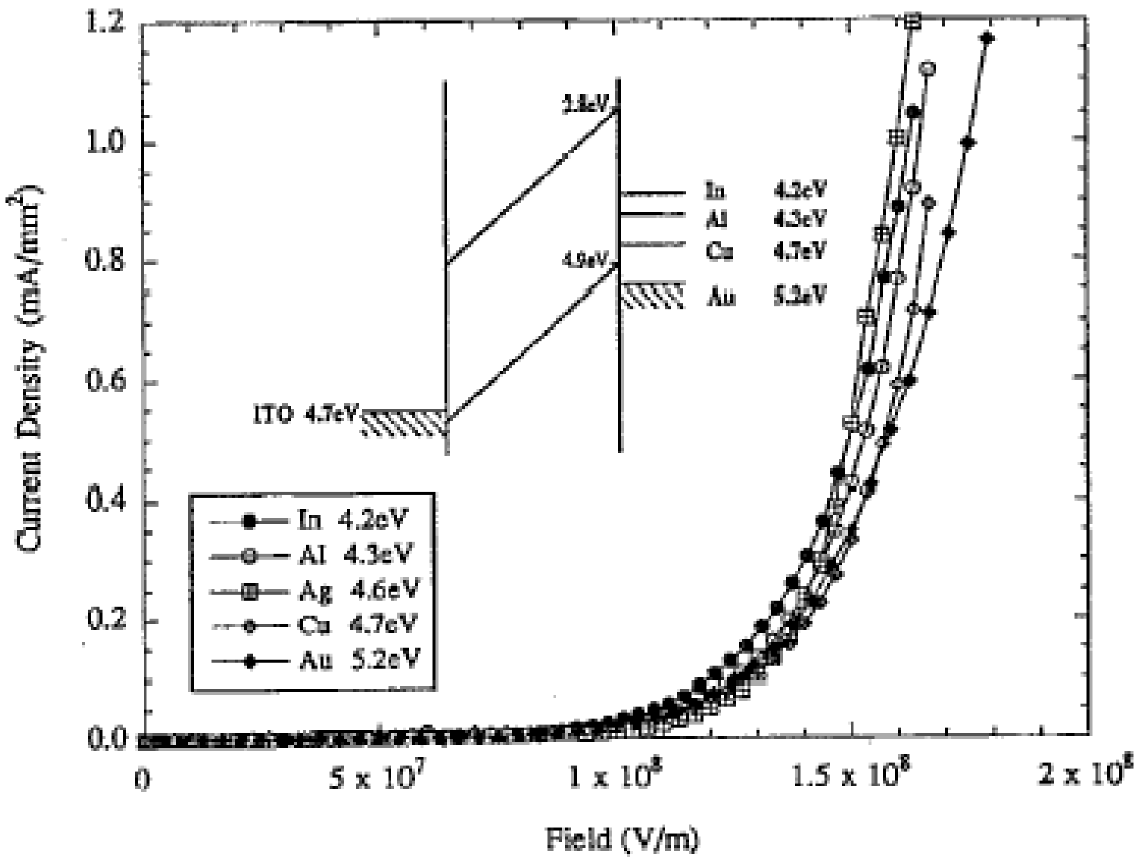


FIG. 3. *I-V* characteristics of 1200 Å thick "hole-only" devices. Inset shows band models indicating the relative position of the Fermi energies of the various materials.

I. D. Parker, J. Appl. Phys. **75**, 1656 (1994).

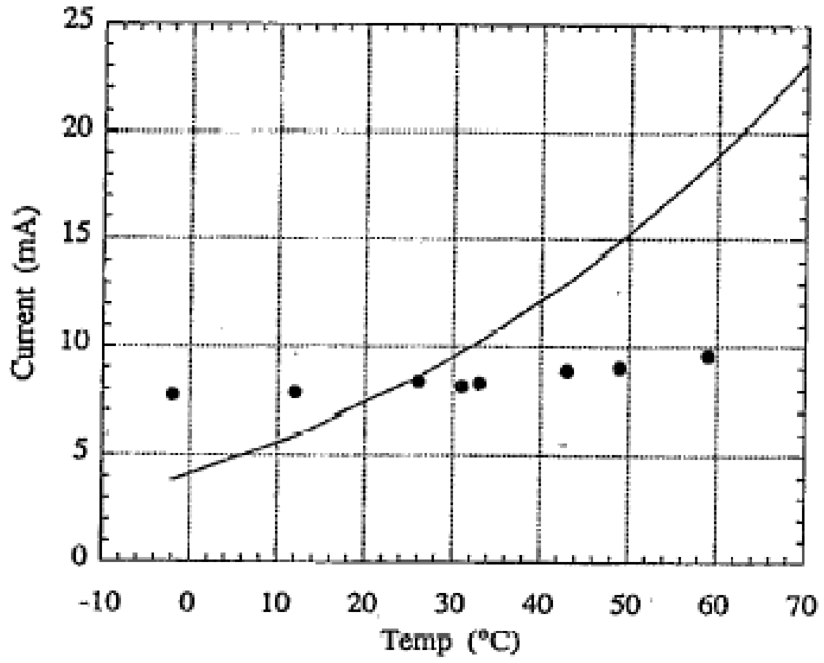


FIG. 5. Temperature dependence of a 1200 Å thick ITO/MEH-PPV/Au device operating at 17 V bias. For comparison, the solid line indicates the *I-V* characteristics of a 0.2 eV Schottky barrier device.

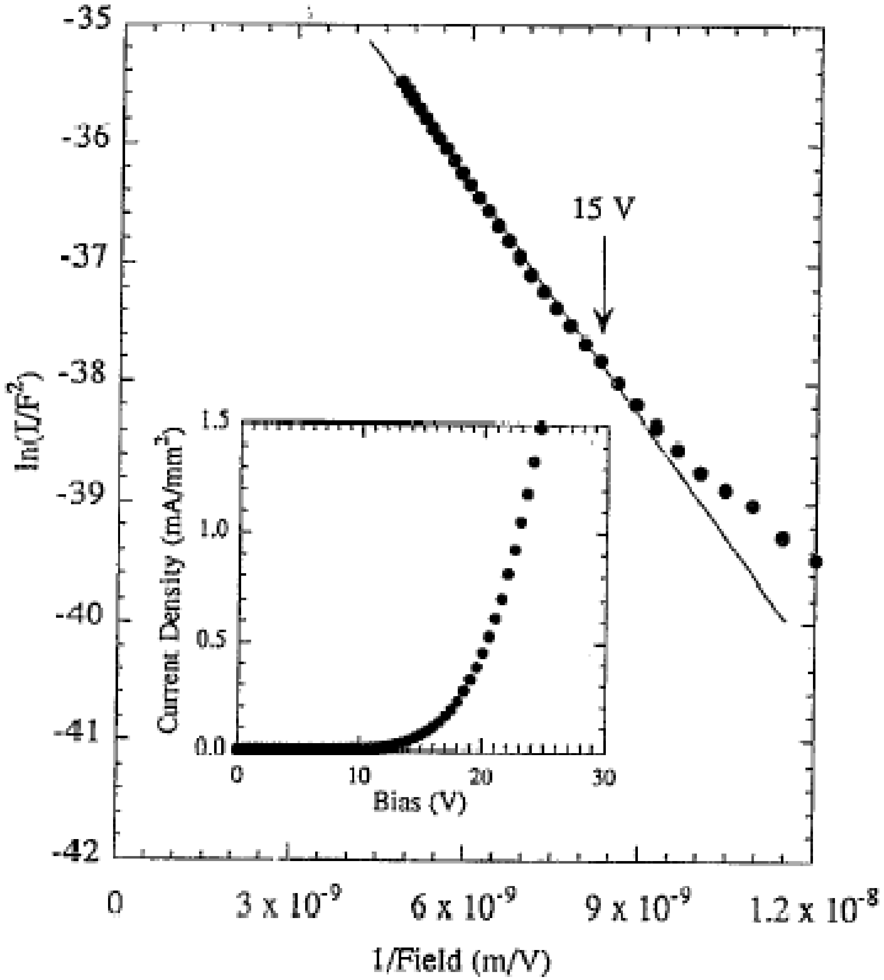


FIG. 6. Fowler–Nordheim plot for a 1200 Å thick ITO/MEH-PPV/Au device. Inset shows the *I-V* characteristics of the device.

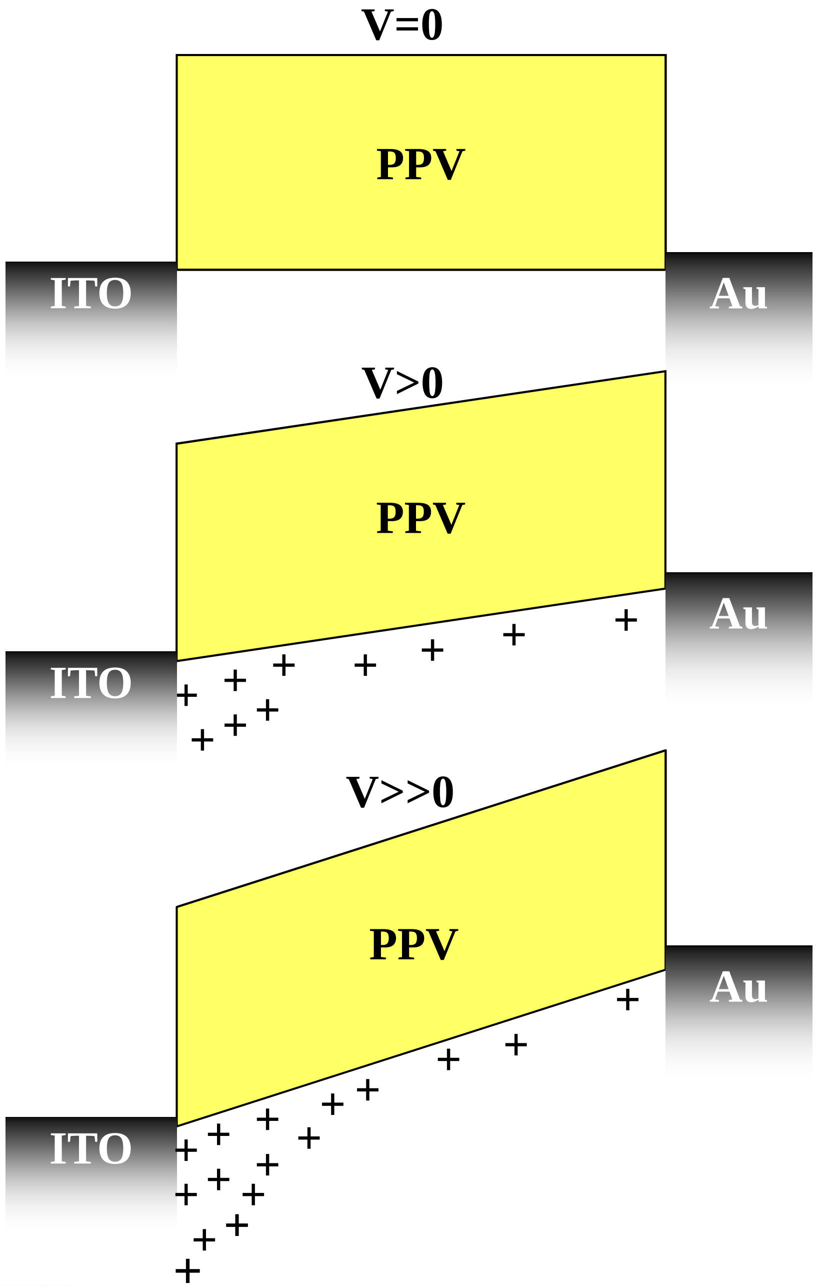
Fowler-Nordheim Tunneling

$$J_s \approx E^2 \exp\left(\frac{-b}{E}\right)$$

$$b = 8\pi(2\,m^*)^{1/2}\,(q\Phi)^{3/2}/3qh$$

I. D. Parker, J. Appl. Phys. **75**, 1656 (1994).

Space-charge-limited current (SCLC)



Space-charge-limited current (SCLC)

OLED acts as a capacitor

$$J_{SCLC} \approx (\text{charge density}) \times \text{velocity}$$

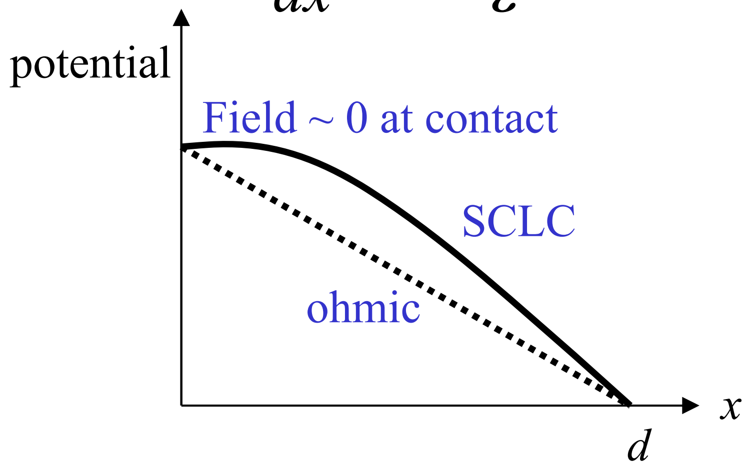
$$= \left(\frac{CV}{d \cdot \text{area}}\right) \times (\mu E)$$

$$= \frac{\varepsilon_o \varepsilon_r}{d^2} \cdot V \cdot \mu \cdot \frac{V}{d}$$

$$= \frac{\varepsilon_o \varepsilon_r \mu V^2}{d^3}$$

$$J_{SCLC} = \frac{9}{8} \varepsilon_o \varepsilon_r \mu \frac{V^2}{d^3}$$

$$\frac{d^2 V}{dx^2} = -\frac{\rho}{\varepsilon}$$



SCLC: no trap

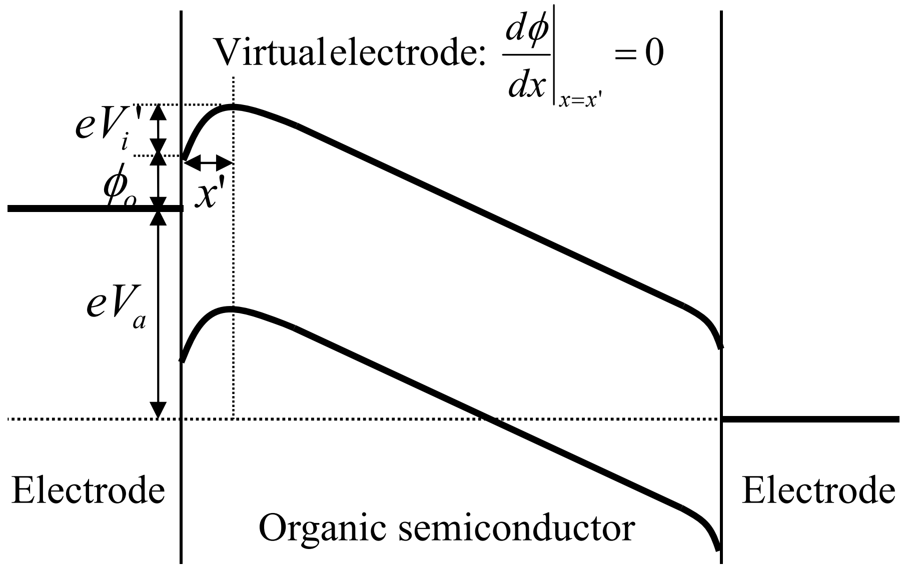
Distribution function of trap density

$h(E,x) = N_t(E)S(x).$

Poisson equation : $\dfrac{dF(x)}{dx} = \dfrac{\rho}{\varepsilon} = \dfrac{q[p(x) + p_t(x)]}{\varepsilon}.$

Current flow equation : $J = q\mu_p p(x)F(x).$

$$p_t(x) = \int_{E_l}^{E_u} h(E,x) f_p(E)dE, \quad p(x) = N_v \exp[-\frac{E_{F_p}}{k_B T}].$$



For $p_t(x) = 0,$

$$2F(x)\frac{dF(x)}{dx} = \frac{d[F(x)]^2}{dx} = \frac{2J}{\varepsilon\mu_p}. \quad \therefore [F(x)]^2 - [F(x=0)]^2 = [F(x)]^2 = \frac{2J}{\varepsilon\mu_p}x.$$

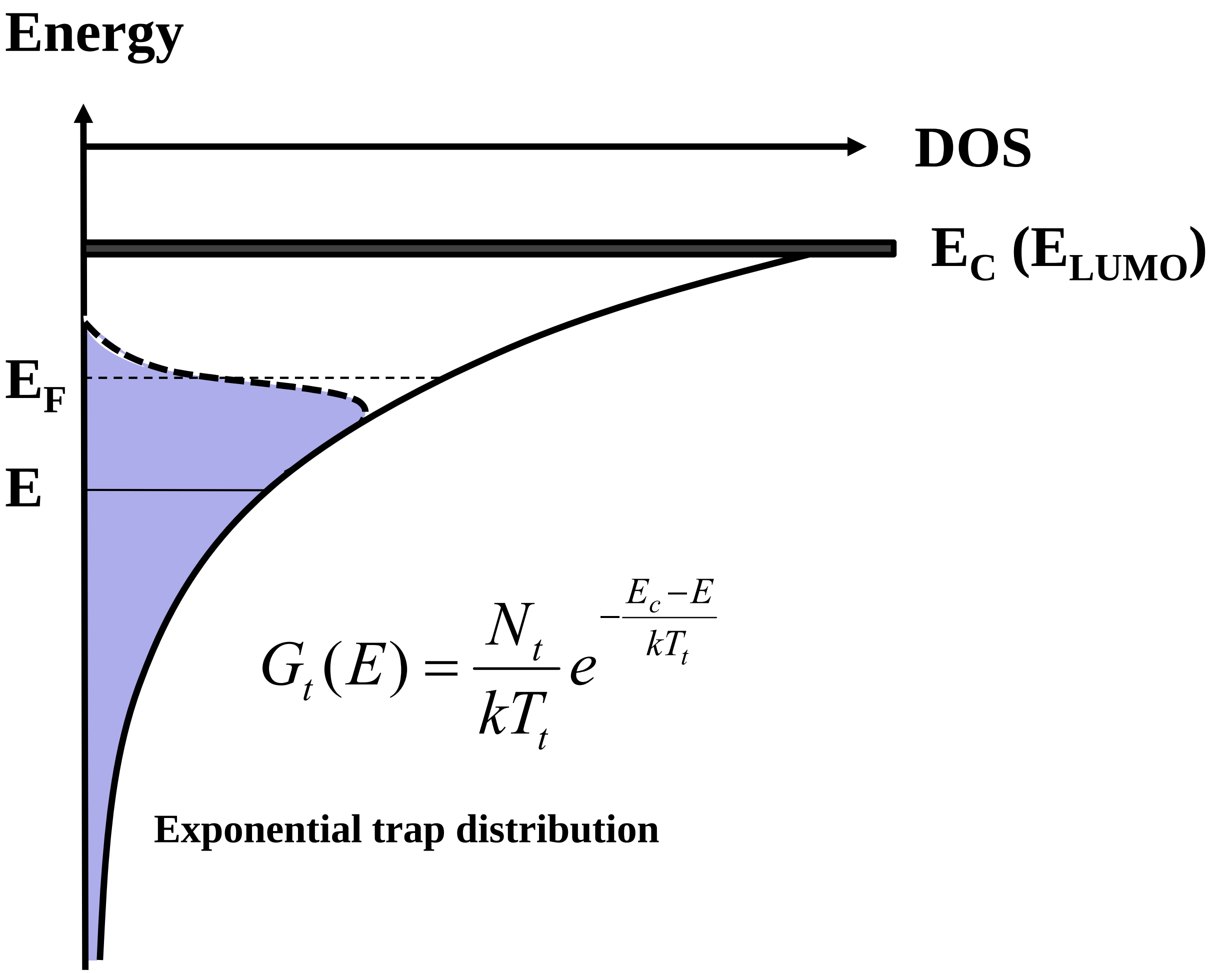
The distance W_a between the actual electrode surface and the virtual anode ($-dV/dx=F=0$) is so small that we can assume $F(x=W_a \rightarrow 0)=0$ for simplicity.

$$\therefore F(x) = \sqrt{\frac{2J}{\varepsilon\mu_p}x}.$$

Boundary condition, $V = \int_0^d F(x)dx.$

$$J = \frac{9}{8}\varepsilon\mu_p \frac{V^2}{d^3}. \quad \text{Mott-Gurney law.} \quad \text{(no trap)}$$

SCLC: exponential trap density



$$G_t(E) = \frac{N_t}{kT_t} e^{-\frac{E_c - E}{kT_t}}$$

$$n_f = N_c e^{-\frac{E_c - E_F}{kT}}$$

$$n_t = \int_{-\infty}^{E_c} \frac{N_t}{k_B T_t} e^{-\frac{E_c - E}{kT}} f_{FD}(E) dE$$

$$\approx \int_{-\infty}^{E_F} \frac{N_t}{k_B T_t} e^{-\frac{E_c - E}{kT}} dE$$

$$= N_t e^{-\frac{E_c - E_F}{kT_t}}$$

$$\therefore n_t \approx N_t \left(\frac{n_f}{N_c}\right)^{\frac{T}{T_t}} = N_t \left(\frac{n_f}{N_c}\right)^{\frac{1}{m}}$$

$$m = \frac{T_t}{T}$$

SCLC: exponential trap density

$$\text{Poisson equation}: \frac{dF(x)}{dx} = \frac{q[n_f(x)+n_t(x)]}{\varepsilon_o\varepsilon} \approx \frac{qn_t(x)}{\varepsilon_o\varepsilon} \approx \frac{qN_t}{\varepsilon_o\varepsilon}\left(\frac{n_f}{N_c}\right)^{1/m}.$$

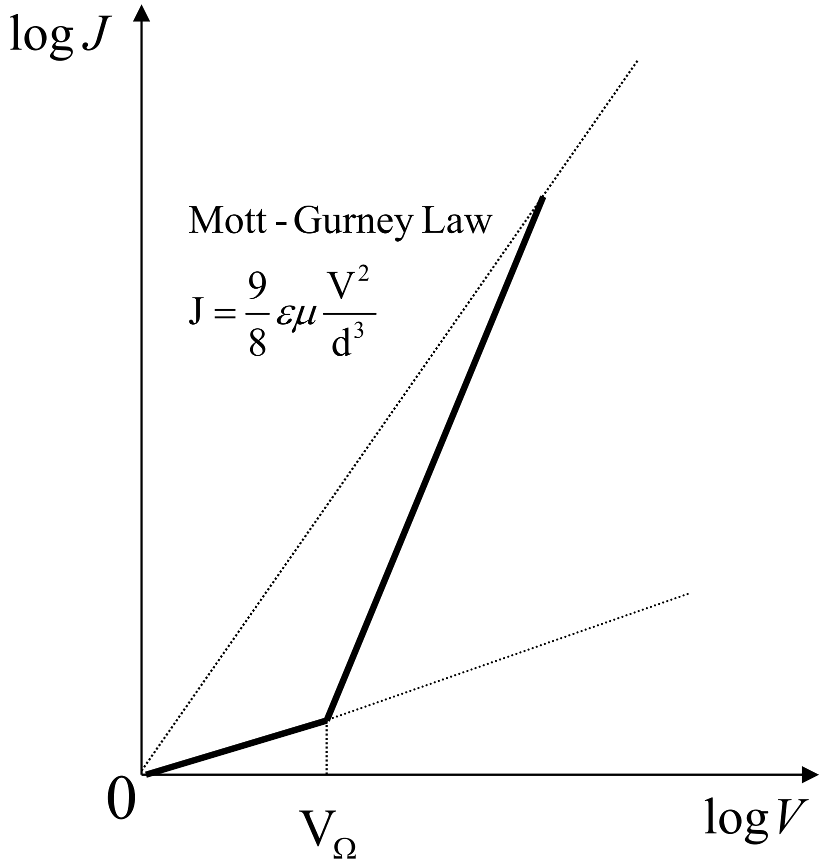
$$\text{Current flow equation}: J = q\mu n_f(x)F(x).$$

$$F^{1/m}\frac{dF(x)}{dx} = \frac{N_t}{\varepsilon_o\varepsilon}\left(\frac{J}{q\mu N_c}\right)^{1/m}.$$

$$\therefore \frac{m}{m+1}F^{\frac{m+1}{m}} = \frac{N_t}{\varepsilon_o\varepsilon}\left(\frac{J}{q\mu N_c}\right)^{1/m}x.$$

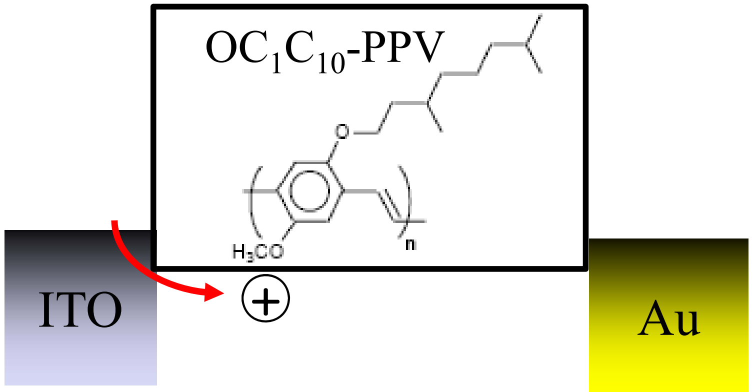
$$\therefore F(x) = \left(\frac{m+1}{m}\frac{N_t}{\varepsilon_o\varepsilon}\right)^{\frac{m}{m+1}}\left(\frac{J}{q\mu N_c}\right)^{\frac{1}{m+1}}.$$

$$\text{Boundary condition}, V = \int_0^d F(x)dx.$$

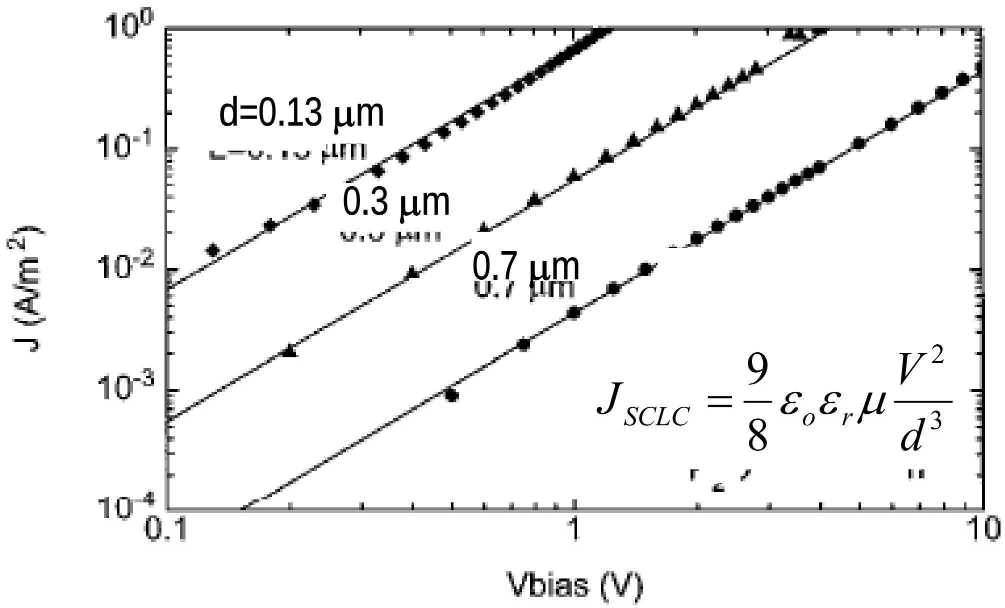


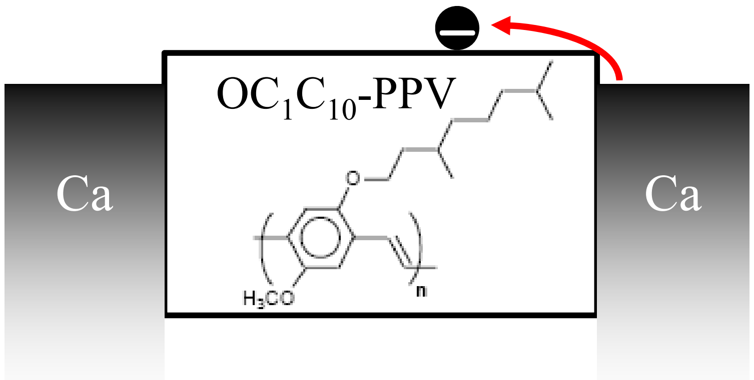
$$J = q^{1-m}\mu N_c\left(\frac{2m+1}{m+1}\right)^{m+1}\left(\frac{m}{m+1}\frac{\varepsilon_o\varepsilon}{N_t}\right)^m\frac{V^{m+1}}{d^{2m+1}}, \qquad m = \frac{T_t}{T}.$$

SCLC: an example

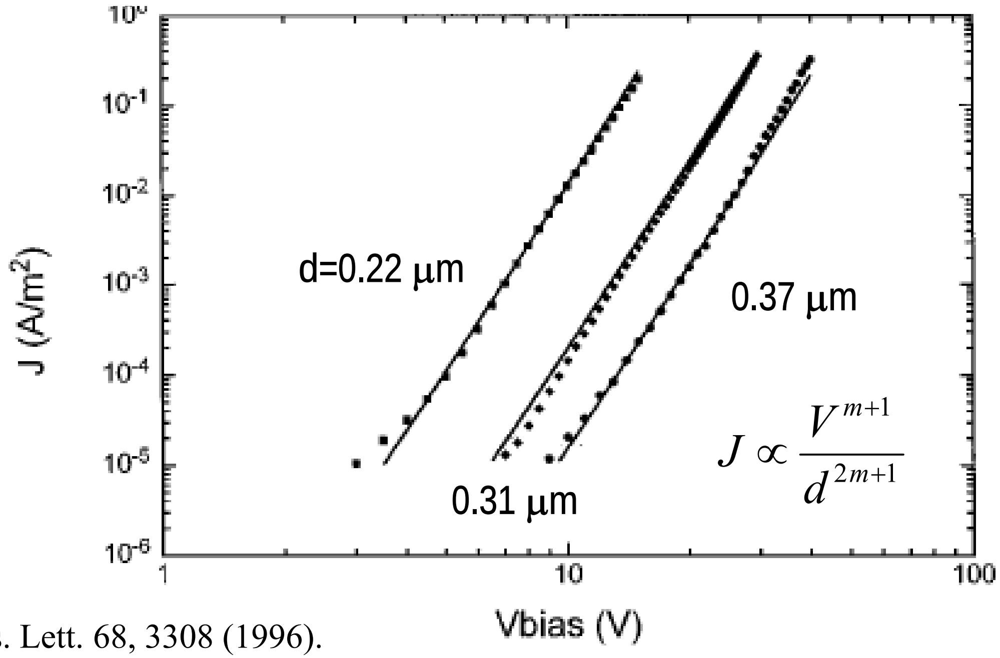


(a) Hole only device



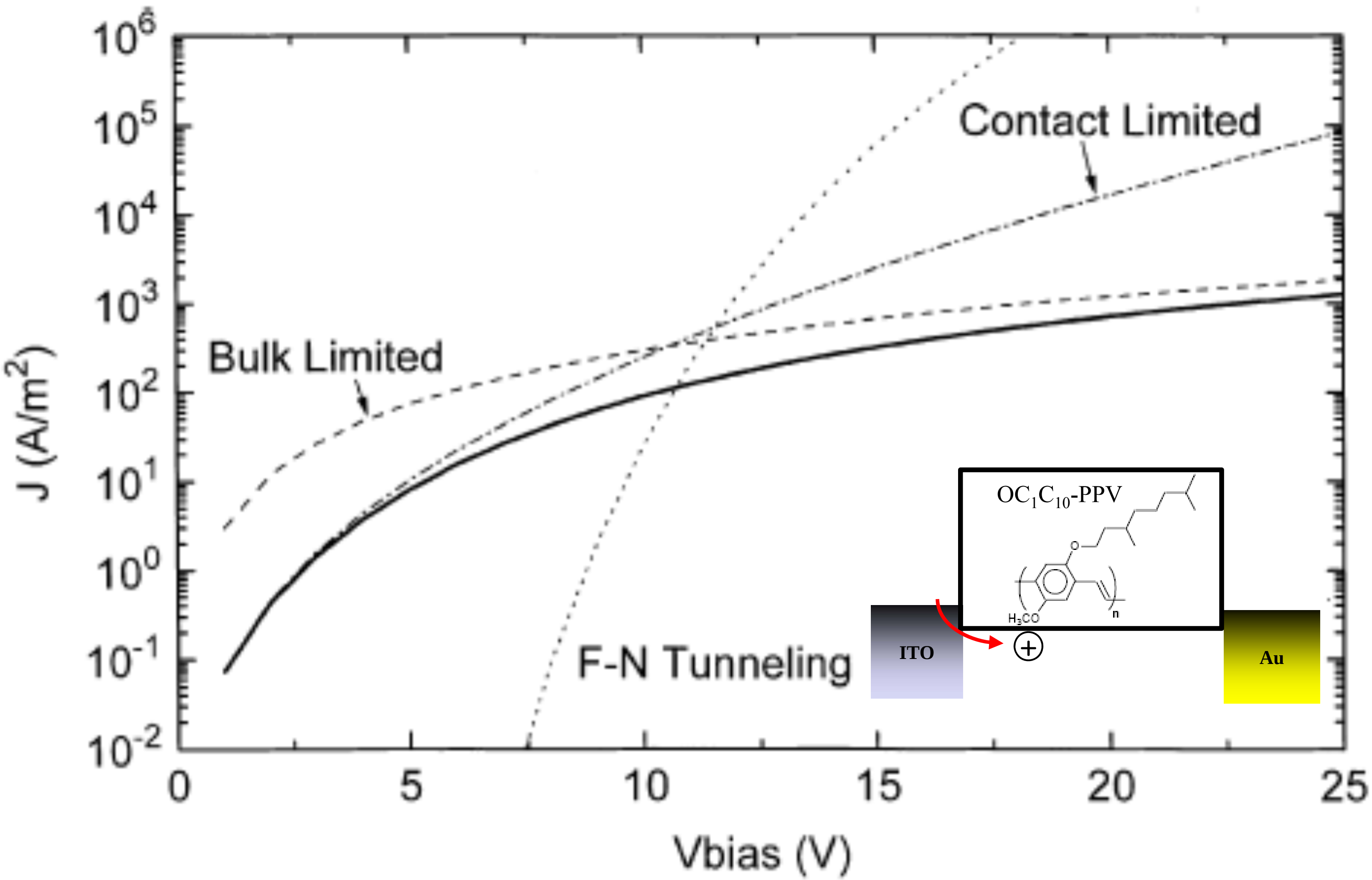


(b) Electron only device



P. W. M. Blom M. J. M. de Jong, and J. J. M. Vleggaar, Appl. Phys. Lett. 68, 3308 (1996).

SCLC: comparison with other models



P. W. M. Blom M. J. M. de Jong, and J. J. M. Vleggaar, Appl. Phys. Lett. 68, 3308 (1996).