Organic Electronic Devices

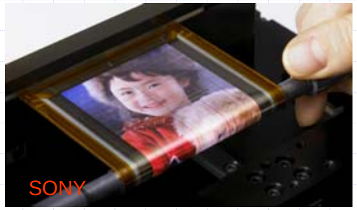
Organic LED Display

Organic LED Lighting

Large area
Low-cost (like an ink)
High contrast (Self luminous)
Liquid crystal 10^3→Organic EL 10^6
Flexible
Thin
Light-weight

Organic Electronic Devices

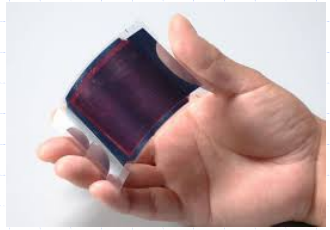
Organic LED + Organic transistor



Flexible

Flexible scanner

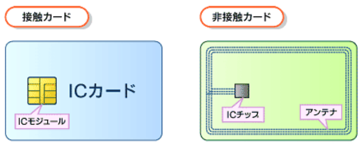
Organic Electronics
- **LED (Electroluminescence)**
- **Transistor**
- **Solar cell (Photovoltaics)**



Organic solar cell

Organic Electronic Devices

Printed Electronics



RF ID tag

Low cost
Easy process

↓

Printed electronics **Inkjet printing ...**

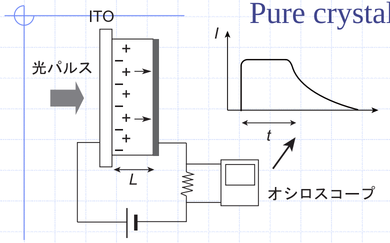
↓

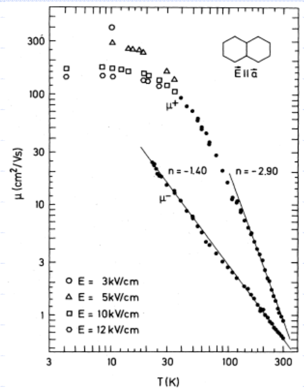
Fabricate IC by ink

Photoconductivity

Time of Flight (TOF)

Pure crystals





TOF Mobility (cm^2/Vs)

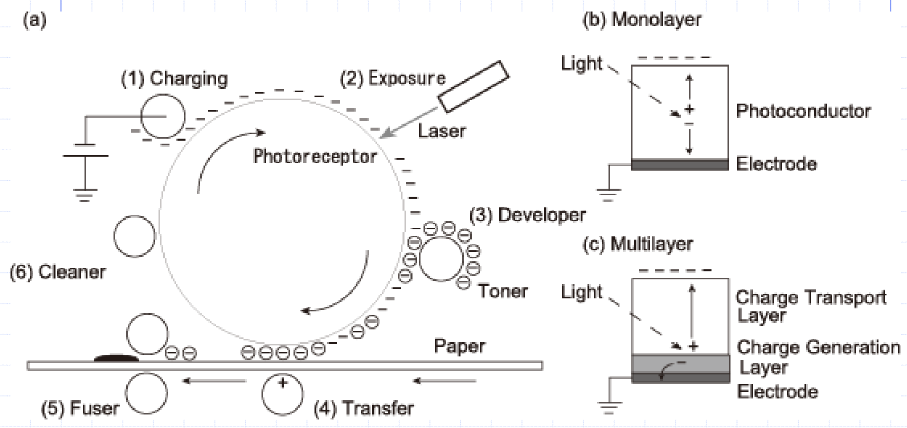
	Hole *a*/*b*/*c*	Electron *a*/*b*/*c*
Naphthlene	0.94/1.48/0.32	0.62/0.64/0.44
Anthracene	1.13/2.07/0.73	1.73/1.05/0.39
Perylene	Activated	2.37/5.53/0.78
Terphenyl	0.6/-/0.80	0.34/1.2/0.25

N. Karl, *Landort-Börnstein Numerical Data and Functional Relationships in Science and Technology*, New Series Group III 17a-i (1985).

Photoconductivity

Electrophotography C. F. Carlson (1938)

Copy·Lase printer

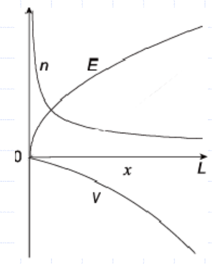


Space-charge-limited current (SCLC)

Carrier injection into an insulator

J* = *en*μ*E ➡ $\frac{\partial E}{\partial x} = \frac{en}{\varepsilon} = \frac{J}{\varepsilon \mu E}$

Integrate ➡ $E = \left(\frac{2J}{\varepsilon\mu}\right)^{1/2} x^{1/2}$

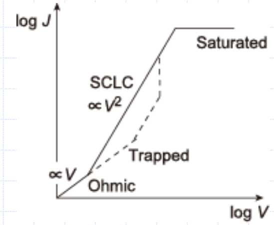


***n* is accumulated around x = 0.**
***E* is steep at x = 0.**

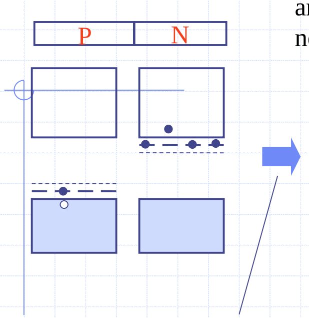
Integrate for x up to the thickness *L* → *V*

$$V = \int_0^L E dx = \left(\frac{8J}{9\varepsilon\mu}\right)^{1/2} L^{3/2} \quad ➡ \quad J = \frac{9}{8}\varepsilon\mu\frac{V^2}{L^3}$$

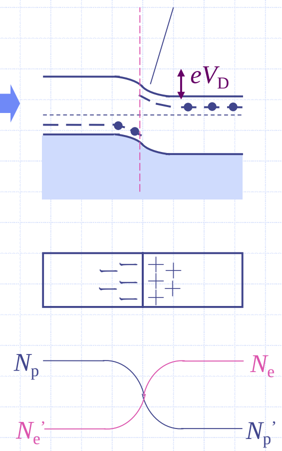
***J* ∝ *V*² Non ohmic**
→ Mobility *μ*



PN junction



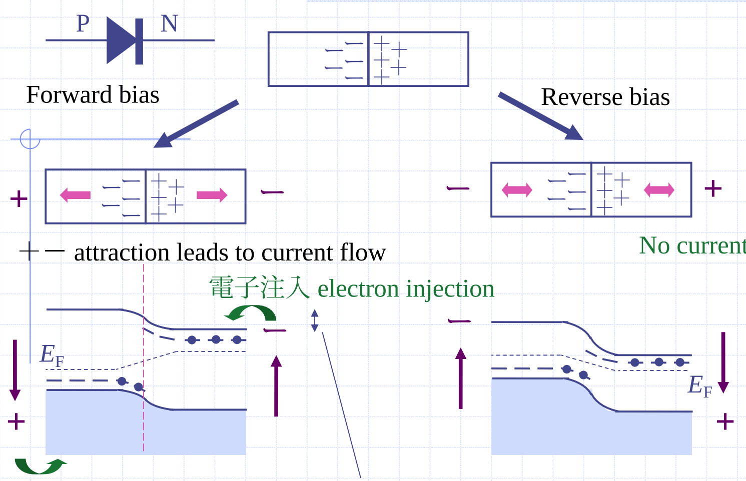
Majority carrier is depleted around the junction to have net positive charge. →欠乏層 (Depletion Layer)



Junction polarizes so as to have opposite charges to the majority carriers.

Most resistance come from the depleted junction.

Potential surface bends so as to make E_F = const.



+ − attraction leads to current flow

No current flows

電子注入 electron injection

ホール注入
hole injection

Potential is lowered to V_D-V.

Majority carrier in N $N_e = N_e^0 e^{-\frac{E_C - E_F}{k_B T}}$

Minority carrier in P $N_e' = N_e^0 e^{-\frac{E_C - E_F + eV_D}{k_B T}} \Rightarrow N_e' = N_e e^{-\frac{eV_D}{k_B T}}$

Under bias V, this leads to $N_e' = N_e e^{-\frac{e(V_D - V)}{k_B T}}$

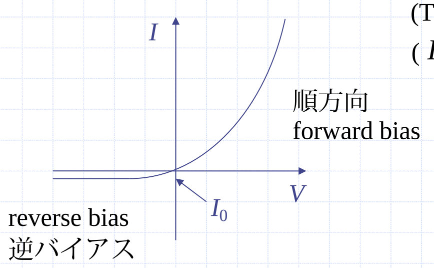
Majority carrier transport from N to P (electron diffusion current) $\propto N_e$

Minority carrier transport from P to N (electron generation current) $\propto N_e'$

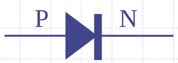
Total current $I \propto N_e' - N_e = I_0 (e^{eV/k_B V} - 1)$

(The same equation for holes)

($I_0 = N_e e^{-eV_D/k_B T}$ does not depend on V.)



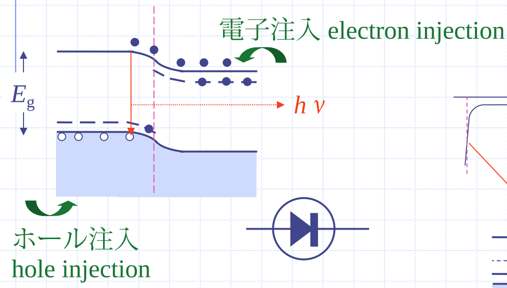
Current flows only for forward bias。
(Diode)



Diodes for specialized uses

Light Emitting Diode

Recombination of injected carriers at forward bias generates light.

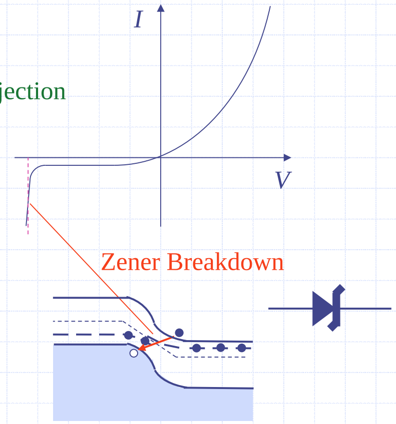


EL：Electroluminescence

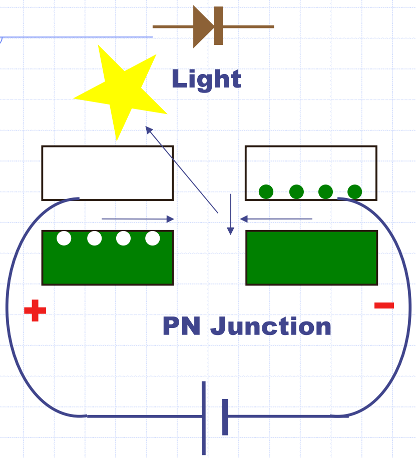
$h\nu$ depends on E_g.

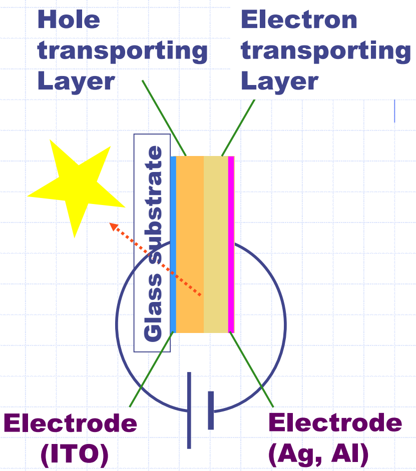
Zener Diode

Standard voltage at the reverse bias.

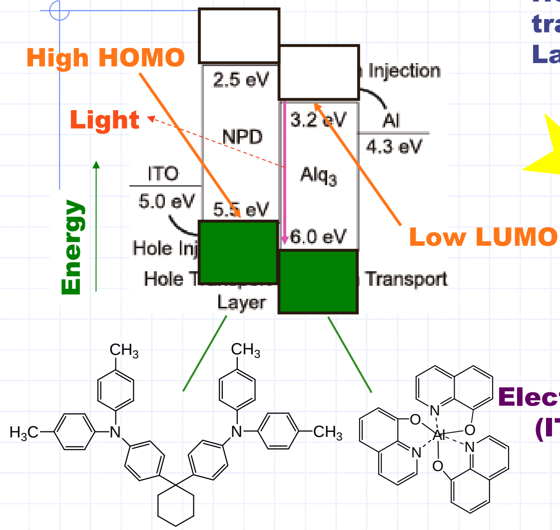


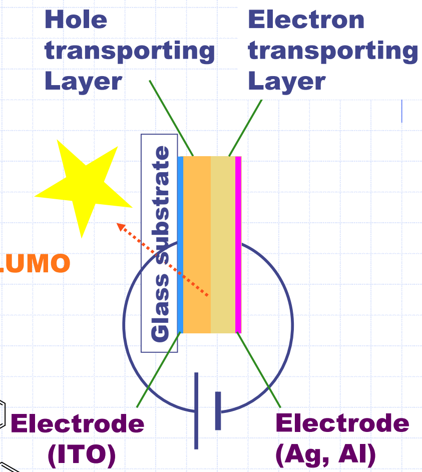
Light Emitting Diode (LED)
Organic EL (Electroluminescence)

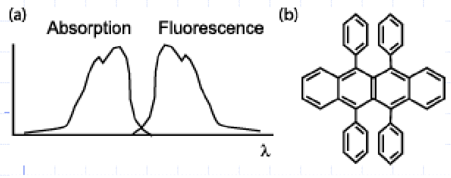




Light Emitting Diode (LED)
Organic EL (Electroluminescence)

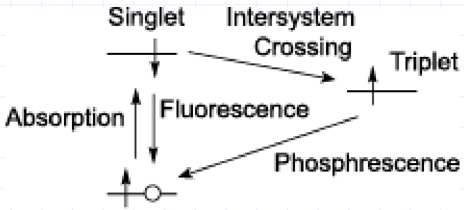






Fluorescence quantum yield

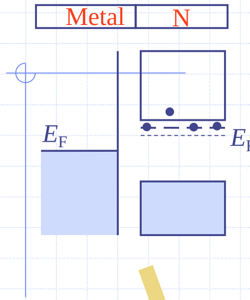
Benzene	**0.07**	**Naphtharene**	**0.23**	**Anthracene**	**0.36**
Tetracene	**0.21**	**Pyrene**	**0.65**	**Perylene**	**0.94**
Rubrene	**～1.0**	**Fluorene**	**0.80**		
Biphenyl	**0.18**	**Terphenyl**	**0.93**	**PPV**	**0.08**
TPD	**0.35**	**Alq_3**	**0.25**	**Sexithiophene**	**0.40**

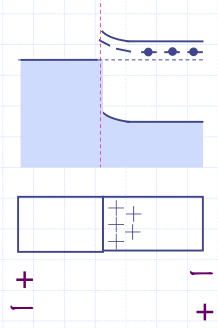


Fluorescence from singlet 25%
Phosphorescence from triplet 75%

Metal-semiconductor junction

Metal E_F < E_F in N-type semiconductor





Adjust E_F

Depletion layer

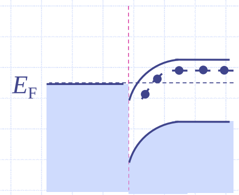
Shottokey Diode

Forward

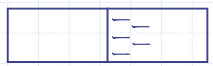
Reverse

Shottokey Barrier

Meta E_F > E_F in N-type SC：Ohmic contact



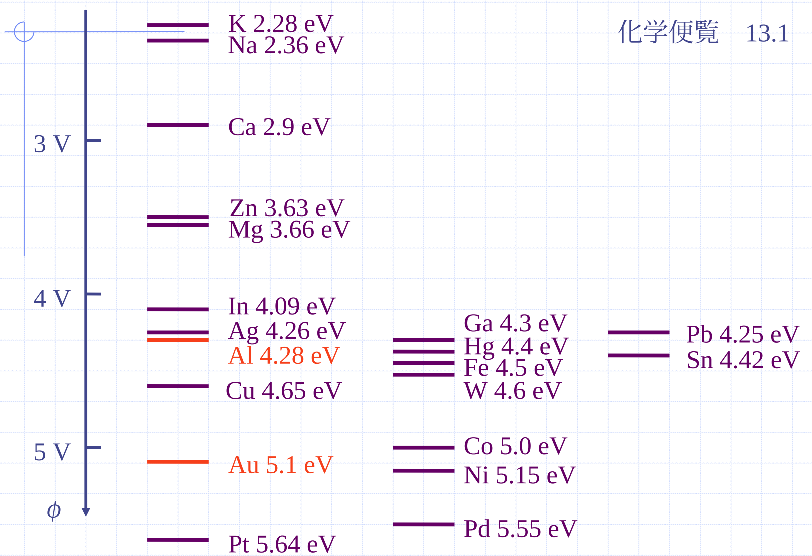
Accumulation layer in majority carrier



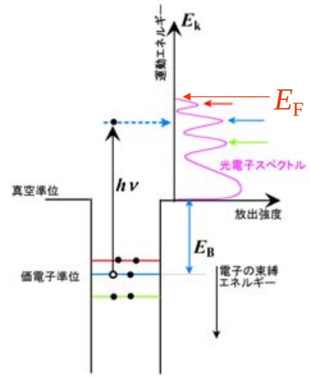
Current flow for both biases.

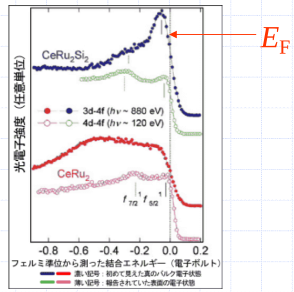
Work function of Metals (Position of E_F)
cf. Ionization potential for semiconductors

化学便覧 13.1



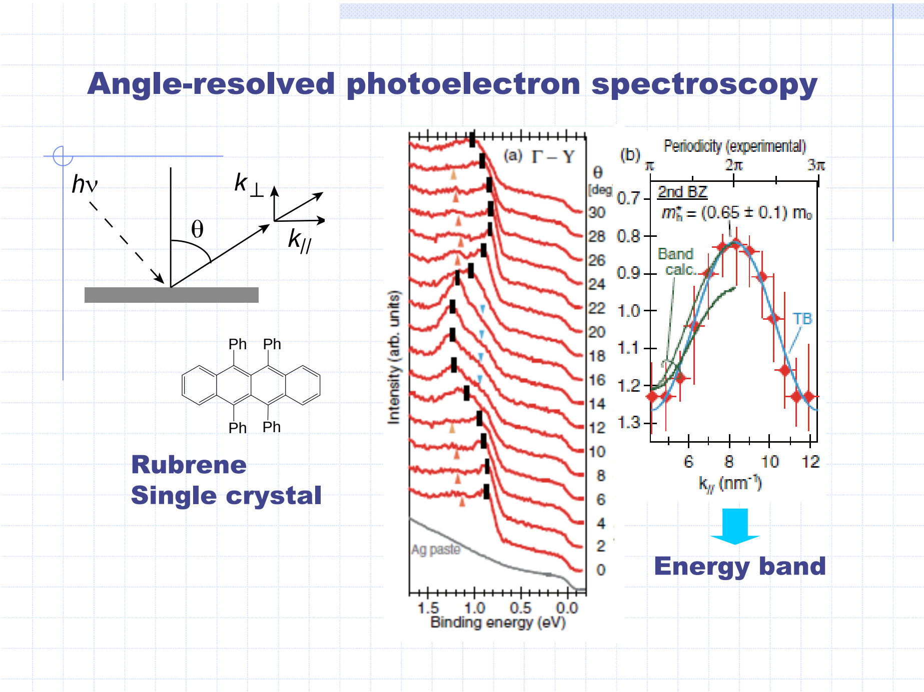
Photoeletron spectroscopy

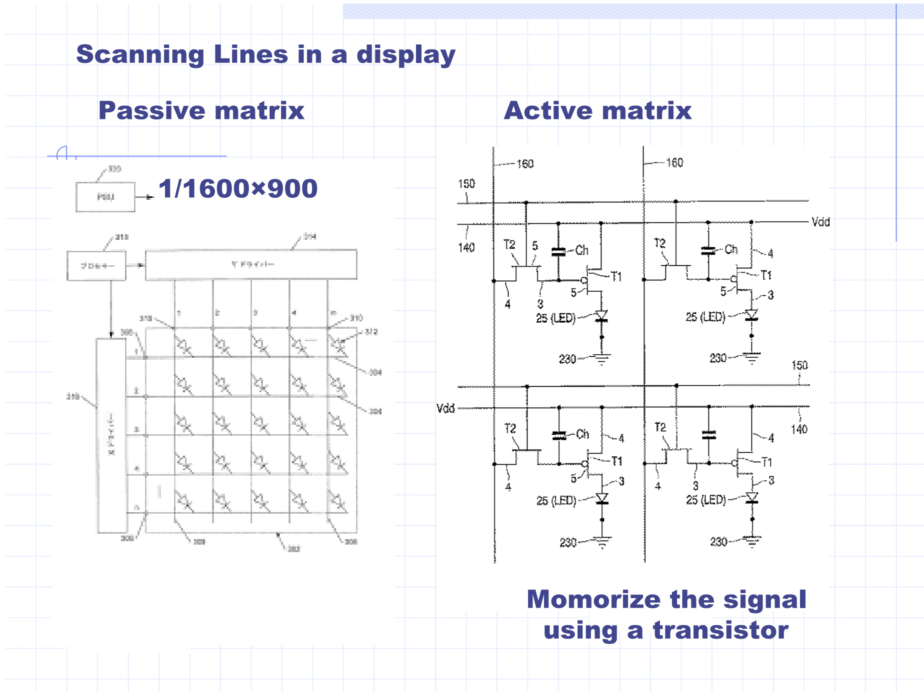


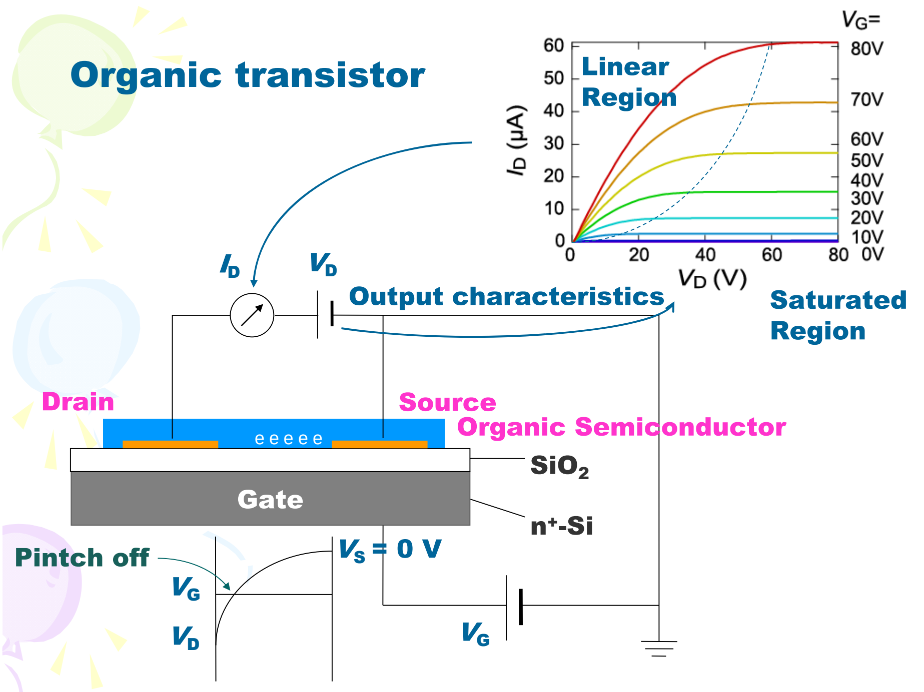


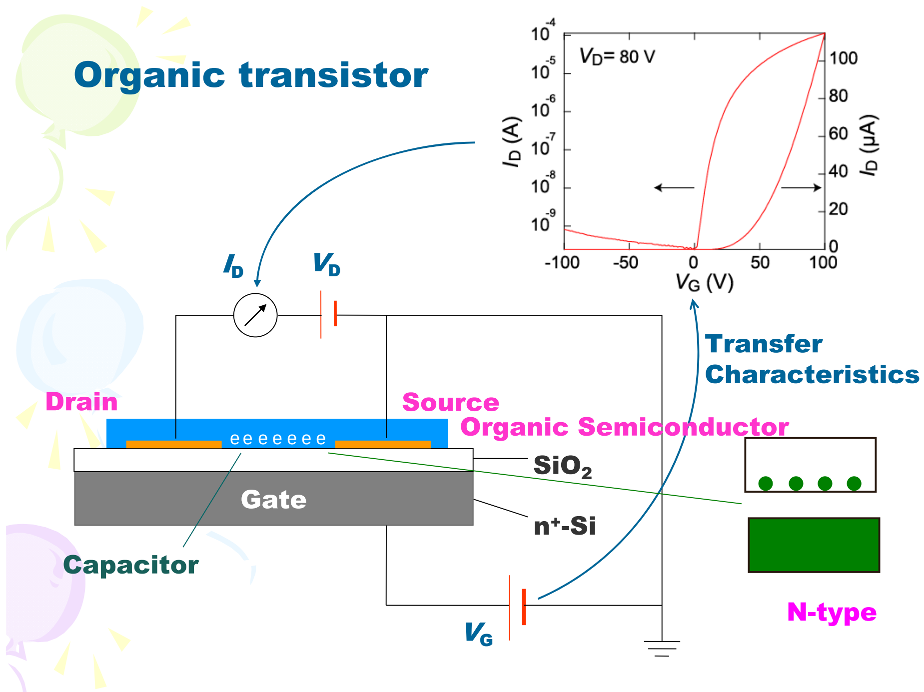
$$E_B = h\nu - E_K$$

Ionization potential

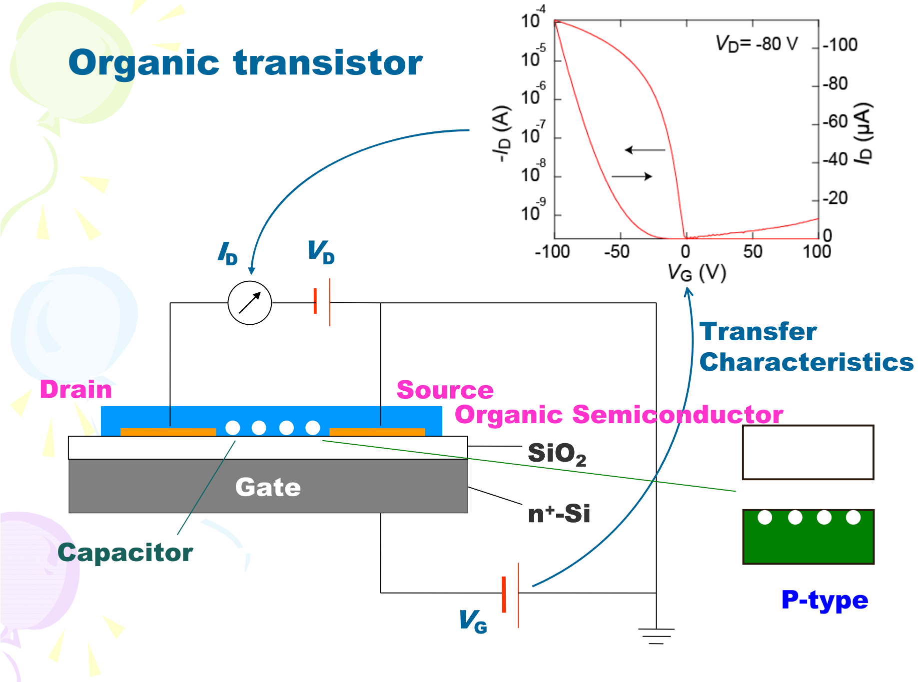

Angle-resolved photoelectron spectroscopy
hν
k⊥
θ
k//
Ph Ph
Ph Ph
Rubrene
Single crystal
(a) Γ − Y
θ [deg]
Intensity (arb. units)
Ag paste
Binding energy (eV)
(b)
Periodicity (experimental)
2nd BZ
m*h = (0.65 ± 0.1) m0
Band calc.
TB
k// (nm-1)
Energy band


Scanning Lines in a display
Passive matrix
Active matrix
1/1600×900
Vdd
T2
T1
Ch
25 (LED)
Momorize the signal
using a transistor


Organic transistor
VG=
80V
70V
60V
50V
40V
30V
20V
10V
0V
Linear Region
ID (μA)
VD (V)
Output characteristics
Saturated Region
ID
VD
Drain
Source
Organic Semiconductor
eeeee
SiO2
Gate
n+-Si
Pintch off
VS = 0 V
VG
VD
VG


Organic transistor
VD= 80 V
ID (A)
ID (μA)
VG (V)
ID
VD
Transfer Characteristics
Drain
Source
Organic Semiconductor
eeeeeee
SiO2
Gate
n+-Si
Capacitor
VG
N-type

Organic transistor



Quantitative transistor characteristics (Gradual Channel Approximation)

Charge on the interface

$Q = C(V_G - V_T)$

Voltage $V(x)$ depends on x

$Q(x) = C(V_G - V_T - V(x))$

$ne \rightarrow Q(x)$ **in** $\sigma = ne\mu$

Electric field $E_x = -dV(x)/dx$

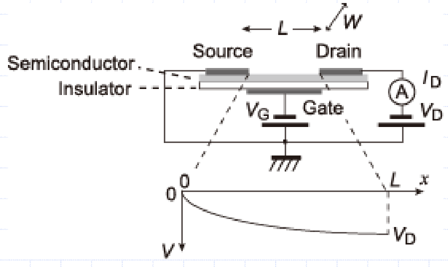
$$I_D = WQ(x)\mu(-dV(x)/dx)$$

Integrate using $Q(x)$

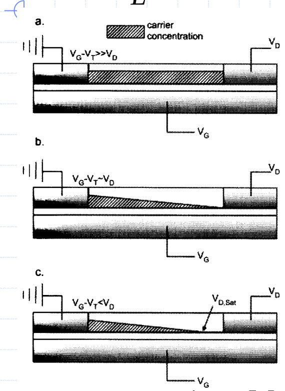
$$\int_0^L I_D dx = \int_0^{V_D} WC\mu(V_G - V_T - V(x))dV$$

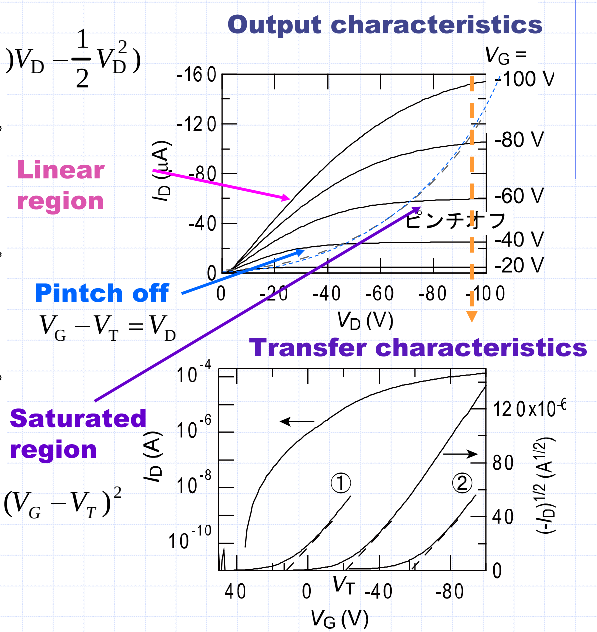
I_D**=constant**

$$I_D = C\mu\frac{W}{L}[(V_G - V_T)V_D - \frac{1}{2}V_D^2]$$



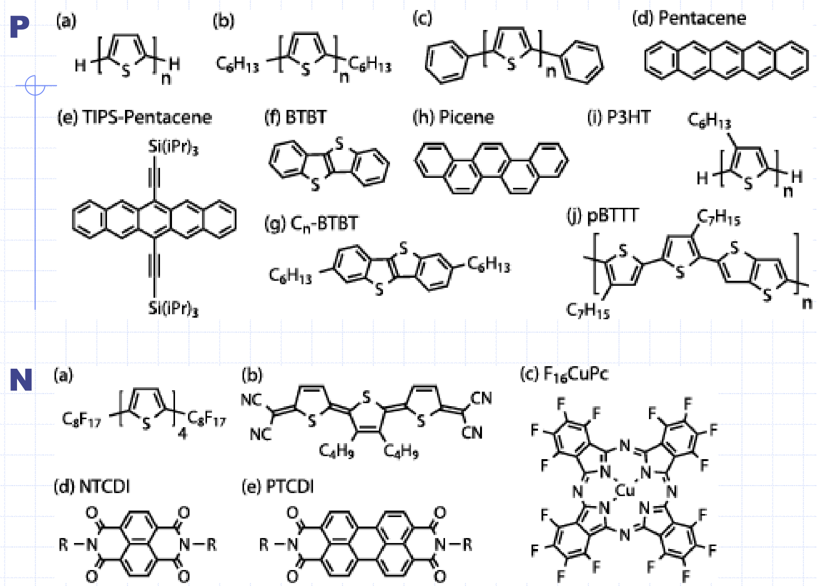
$$I_D = \frac{W\mu C}{L}((V_G - V_T)V_D - \frac{1}{2}V_D^2)$$



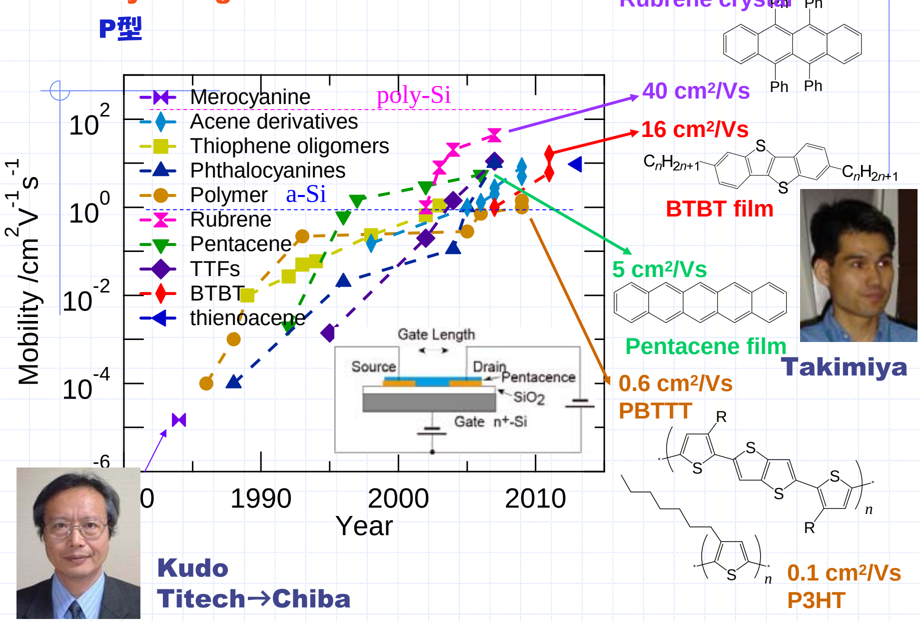


$$I_D = \frac{1}{2}C\mu\frac{W}{L}(V_G - V_T)^2$$

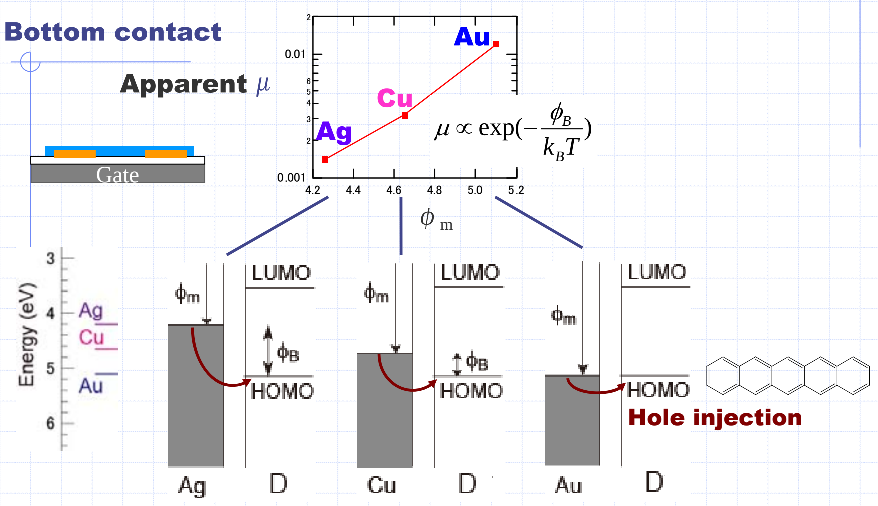
Organic Transistor Materials

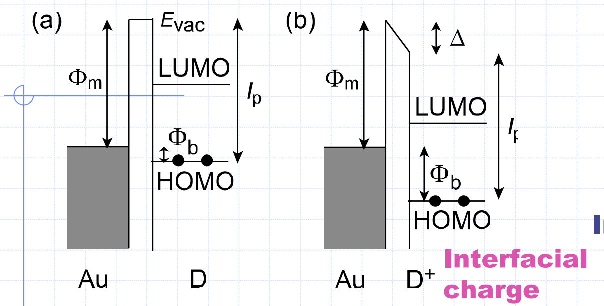


Hiatory of organic transistor materials



Metal work function ϕ_m → Schottky barrier ϕ_b





Donor：D⁺

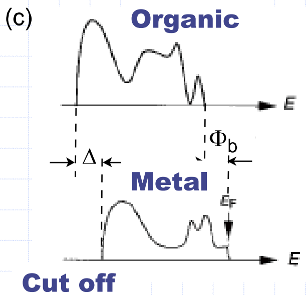
Lower the energy

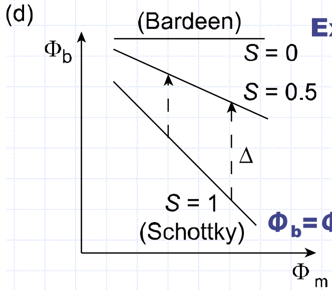
Increase barrier

Acceptor：A⁻

Increase the energy

Increase barrier



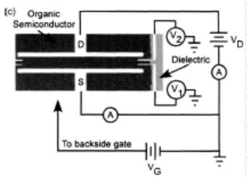


Exception Au/A (Au is a good electrode for N)

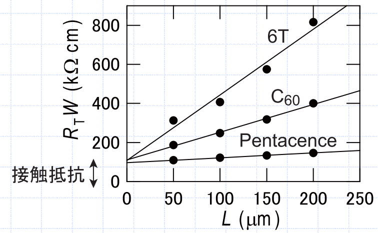
$\Phi_b = \Phi_m - \Phi_s$

接触抵抗の測定

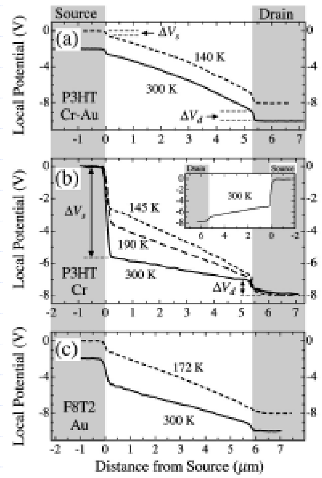
①四端子法



②トランスファーライン法



③ Scanning Probe Potentiomery



森・長谷川 有機トランジスタの評価と応用II (2008)

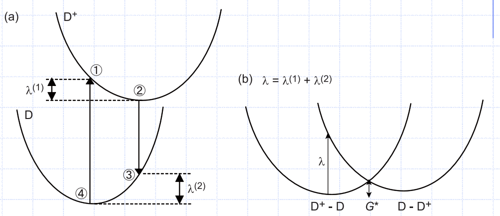
移動度μの理論計算

マーカス理論 (Marcus theory)

$$\mu = \frac{ea^2}{k_B T} k_{ET}$$

$$k_{ET} = \frac{2\pi}{\hbar} t^2 \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp[-\frac{\lambda}{4k_B T}]$$

①中性分子Dの形のD+
②構造最適化したD+
③D+の構造でのD
④構造最適化したD



D+−D → D−D+

再配向エネルギー (reorganization energy)

$\lambda = \lambda^{(1)} + \lambda^{(2)}$

電荷移動反応のポテンシャルエネルギーが放物線的
→ 活性化エネルギー $G^* = \lambda / 4$

λ : 0.1〜0.3 eV程度

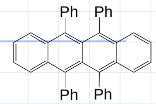
Bredas, *Chem. Rev*. **104**, 4971 (2004); **107**, 926 (2007).

Table 4. B3LYP/6-31G** Estimates of the Relaxation Energies Obtained from eqs 41 and 42 for the Thiophene Oligomers T*n* (with *n* the Number of Thiophene Rings)

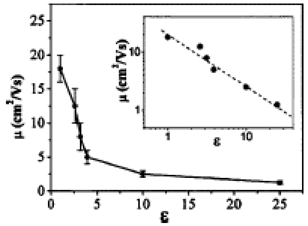
molecule	$\lambda^{(1)}_{rel}$ (meV)	$\lambda^{(2)}_{rel}$ (meV)
T1	200	204
T2	187	237
T3	162	211
T4	153	192
T5	142	172
T6	136	165
T7	126	147
T8	119	137

Single-crystal organic transistor

Rubrene



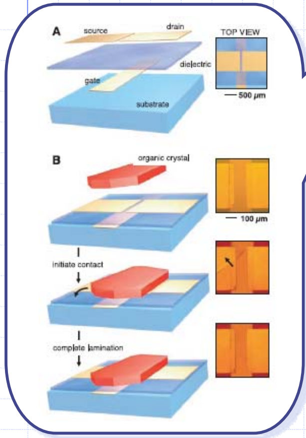
Single crystal
2003 1 cm²/Vs
2003 8 cm²/Vs
2004 20 cm²/Vs
(air-gap stamp

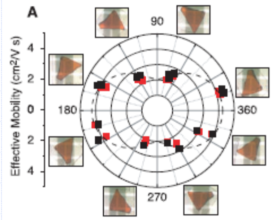


Dielectric constant of gate

cf. $C = \frac{\varepsilon S}{d}$

Stassen, *APL*, 85, 3899 (2004).



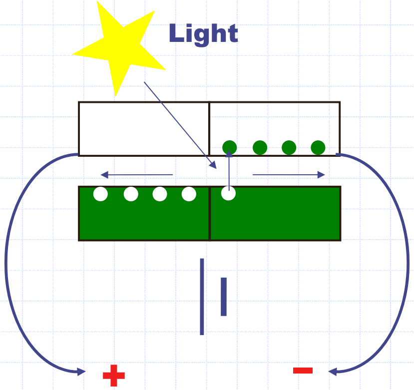


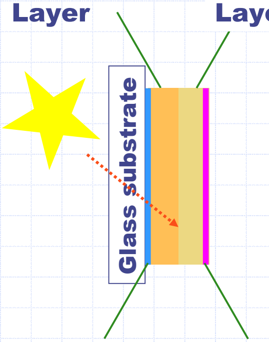
Sunder, *Science*, 303, 1644 (2004).

Single-crystal anisotropy

Organic solar cell Reverse operation

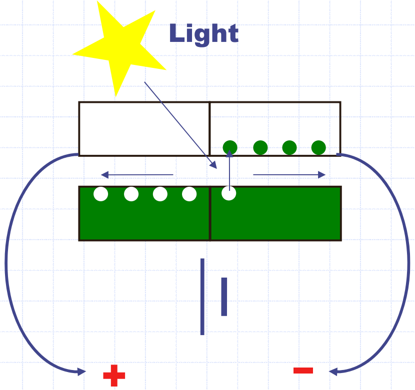
Electricity ← Light

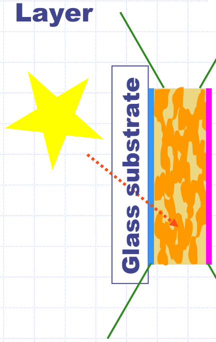




Organic solar cell Reverse operation

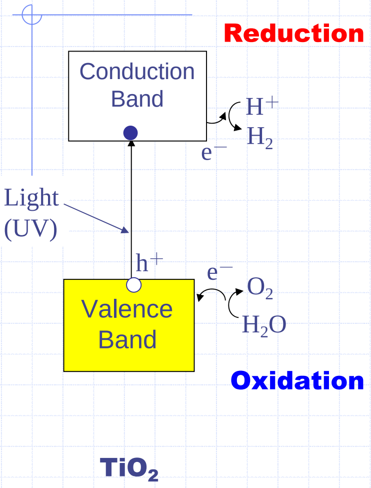
Electricity ← Light



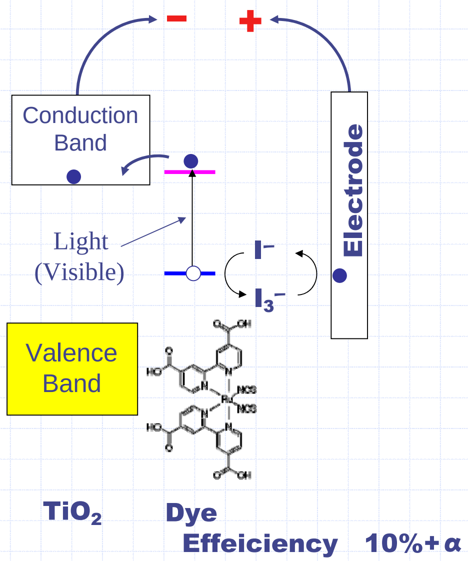


Scramble → Bulk heterojunction
Yield 〜10%

Photocatalyst



Dye sensitized solar cell



Dye sensitized solar cell

Efficiency

Si film	**15%**
Si crystal	**25%**
Compound semiconductor	**>30%**
Organic film	**10%**
Dye sensitized	**10%+α**
Perovskite	**20%**