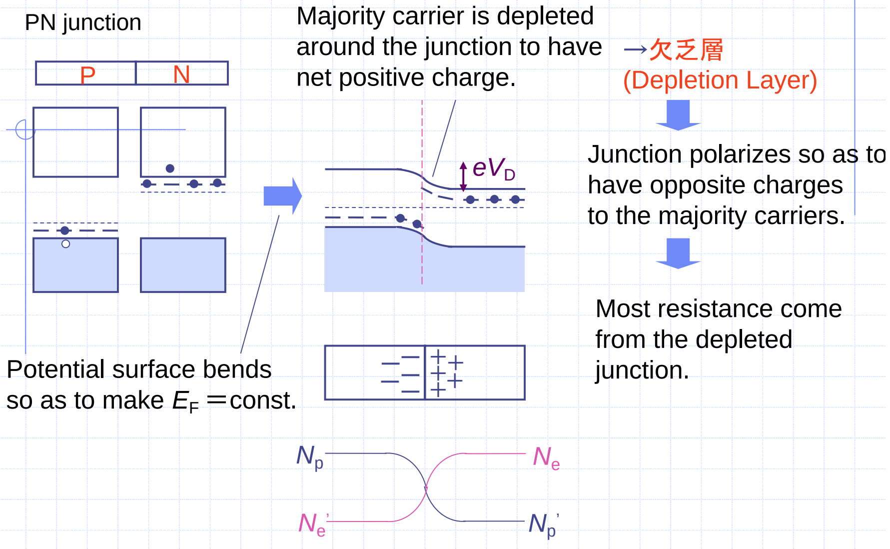
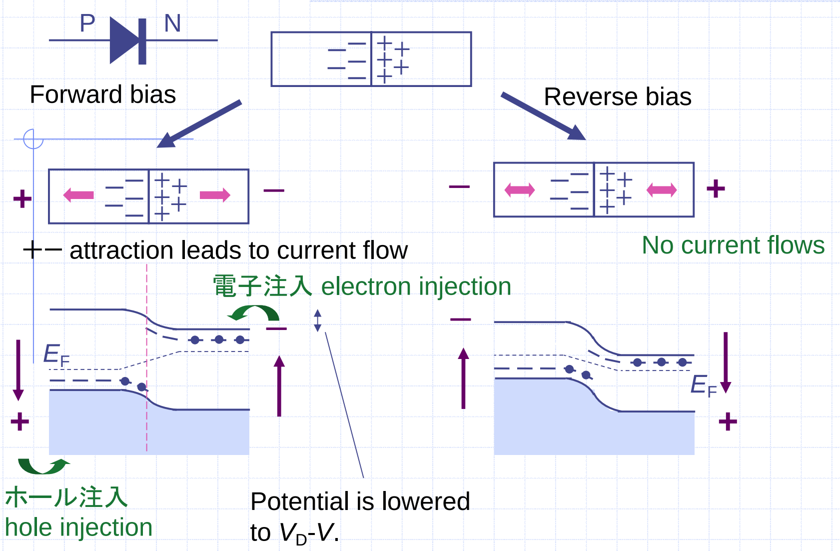
Energy and Semiconductors

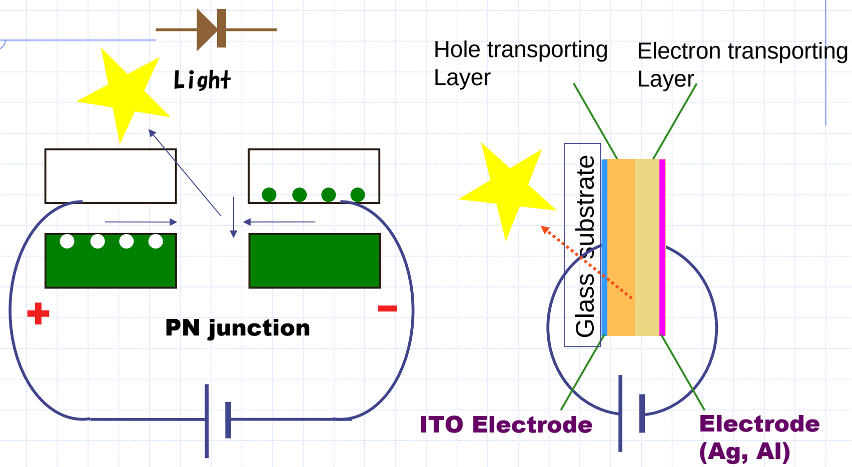
Takehiko Mori
Department of Materials Science and Engineering

Organic light emitting diode
Energy levels in organic materials cf. photocatalyst
Conversion of enegy scales
Light ⇔ chemical ⇔ thermal ⇔ magnetic energy
Doped organic materials = Charge-transfer complexes
Organic superconductors
Organic transistors
Organic solar cells





有機発光ダイオード Light Emitting Diode (LED)
有機EL (Electroluminescence)



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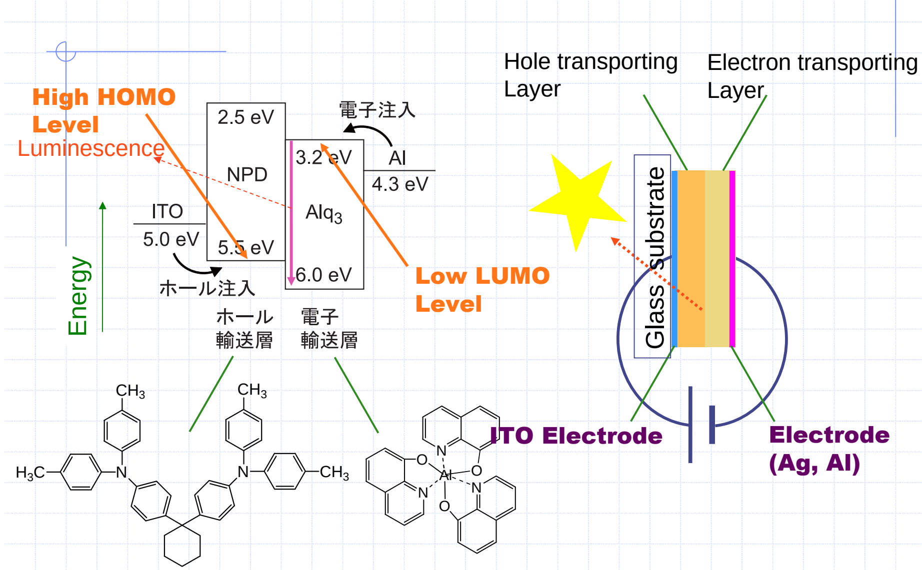
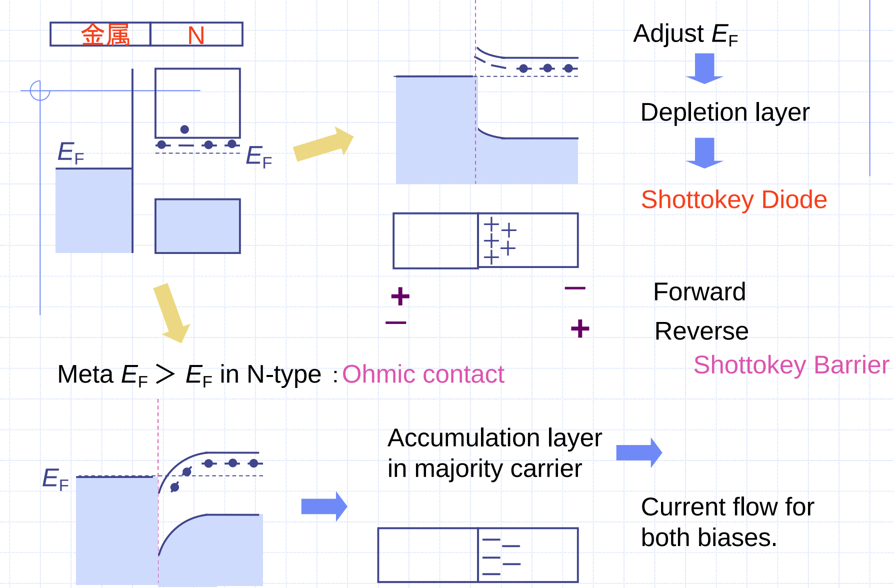
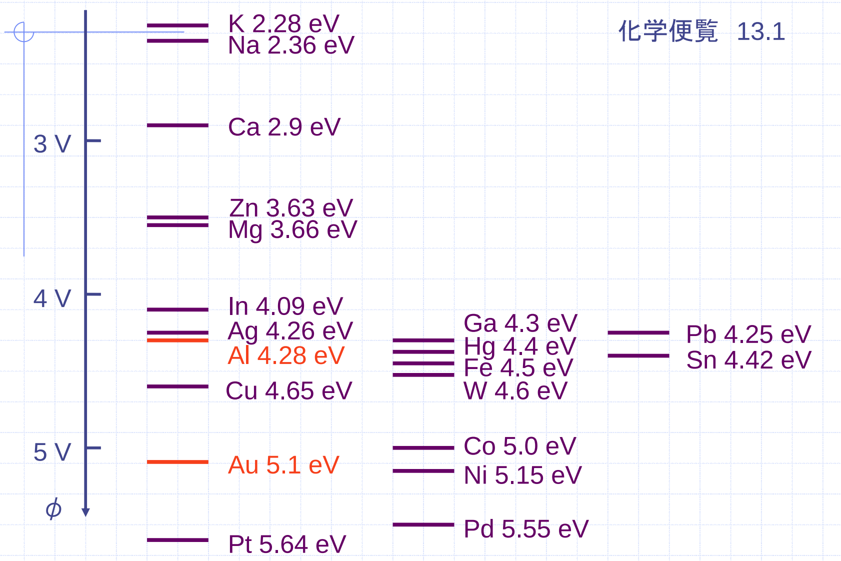
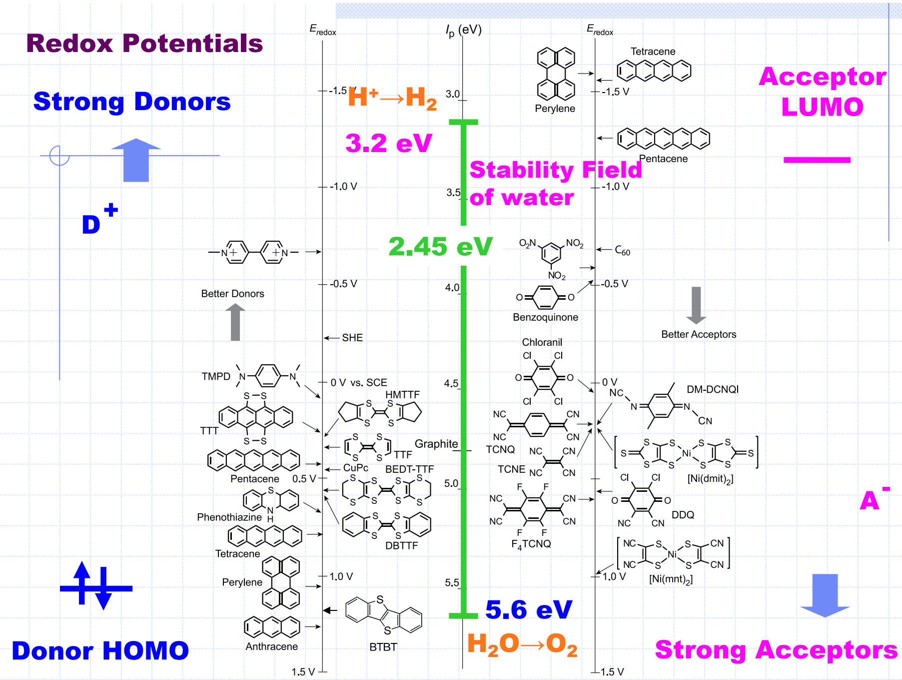


Metal-semiconductor junction



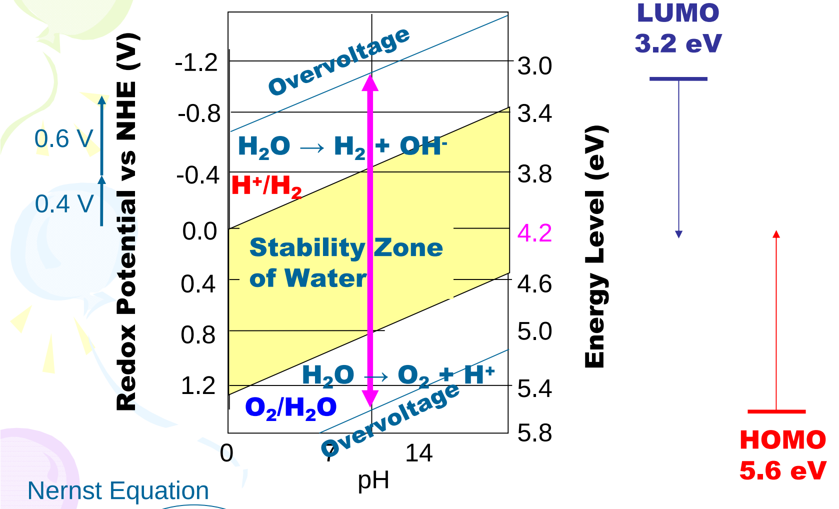
Work function of Metals (Position of E_F)
cf. Ionization potential for semiconductors





Stability Zone of Water

Schriver, Atkins, Inorganic Chemistry



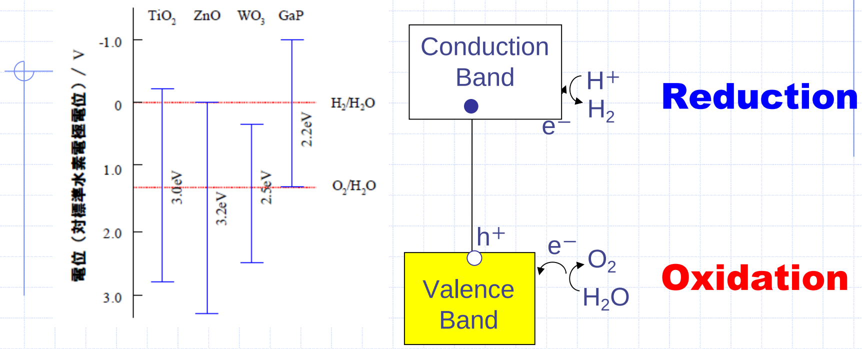
Nernst Equation

$$E = E^0 + \frac{RT}{F}\ln[H^+]$$

0.4 V

Photocatalyst

(Honda·Fujishima Effect)



Electrochemical Redox Potential (cyclic voltammetry)

Standard Calomer Electrode Hg_2Cl_2 vs. SCE = 0.24 V NHE

vs. Ag/AgCl = 0.22 V NHE

Ferrocene＝0.38 V vs. SCE

Energy Level ＝ E_{redox}(vs. SCE) + 4.4 V

＝ E_{redox}(vs. Ferrocene) + 4.8 V

森 分子エレクトロニクスの基礎 p322

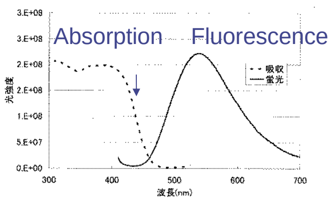
(velocity)＝(wavelength)(frequency) → $c = \lambda\nu$

Photon energy **$E = eV = h\nu$**

$eV = hc/\lambda$

$$E = \frac{(6.62\times10^{-34}\ \mathrm{Js})(3\times10^{8}\ \mathrm{m/s})}{(1.6\times10^{-19}\ \mathrm{J/eV})\lambda} = \frac{(1.24\times10^{-6}\ \mathrm{m\cdot eV})}{\lambda} = \frac{(1240\,\mathrm{nm\cdot eV})}{\lambda}$$

or 1 eV = 1.24 μm $\boxed{E = \frac{(1240\,\mathrm{nm\cdot eV})}{\lambda}}$

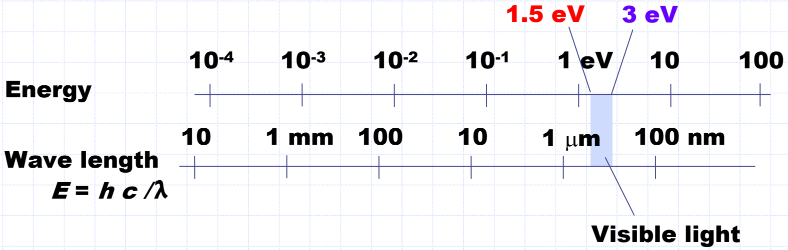


for example Alq3 2.8 eV → 443 nm

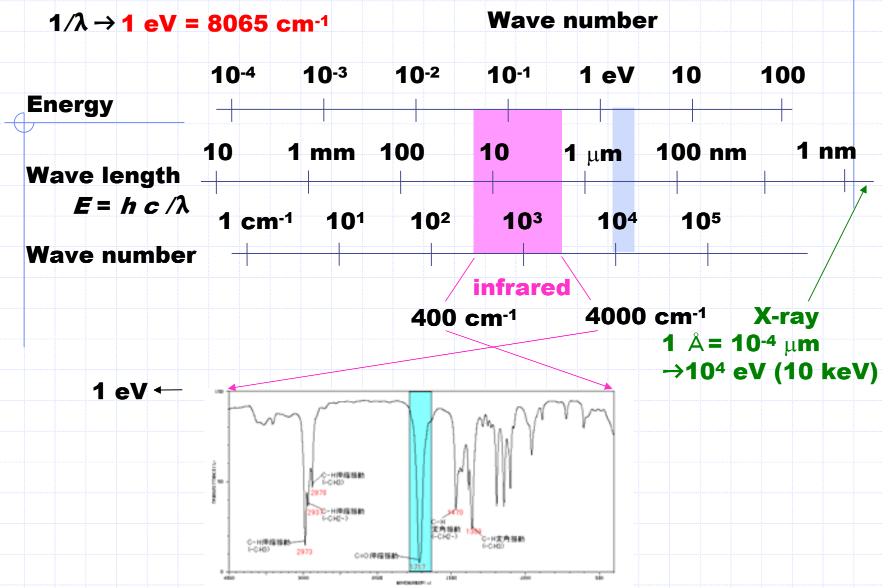
Absorption edge

Visible light: 400 ~ 800 nm

3.1 ~ 1.5 eV



$1/\lambda \rightarrow$ 1 eV = 8065 cm^{-1}



Infrared spectrum ← molecular vibration

1 eV = eN_A = (1.6x10^{-19} J)(6x10^{23} /mol) = 96000 J/mol

Avogadro Number Faraday constant

Faraday constant = Charge of 1 mol electrons (C/mol)

= eV ⇔ J/mol conversion

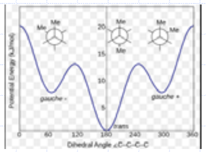
Energy 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1 eV 10 100

Wave length 10 1 mm 100 10 1 μm 100 nm

$E = hc/\lambda$

J/mol 10^1 10^2 10^3 10^4 10^5 10^6

Conformation 10 kJ/mol **100 kJ/mol**



Chemical Reactions

Enthalpy of combustion

H_2: 286 kJ/mol

Enthalpy of vaporization

H_2O: 41 kJ/mol

Photoexcitation

→ Chemical reactions

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1 eV = $k_B T$ = (1.6x10^{-19} J)/(1.38x10^{-23} J/K)=11600 K

Energy 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1 eV 10 100

Wave length 10 1 mm 100 10 1 μm 100 nm

$E = hc/\lambda$

Wave number 1 cm^{-1} 10^1 10^2 10^3 10^4 10^5

Temperature 1 K 10^1 10^2 10^3 10^4 10^5

$E = k_B T$

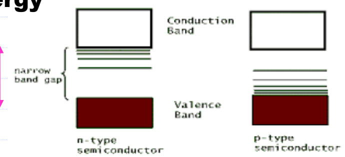
room temperature **10^4 K**

1 cm^{-1}～1 K ～1 T **Magntic field ←Zeemen energy**

$E = k_B T$ **$E = \mu_B H$**

Semiconductor gaps

1~2 eV



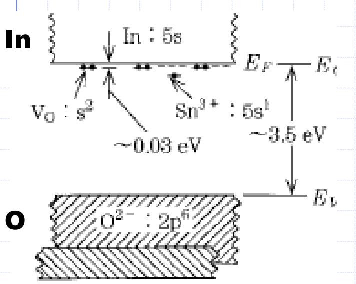
Transparent conductors **Doped wide-gap semiconductors**

Liquid crystal display

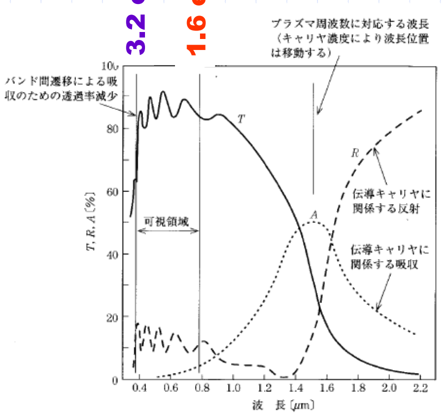
LED display

Solar cell

ITO In_2O_3 In^{3+} (+Sn^{4+})



3.2 eV **1.6 eV**



Various transparent conductors

In_2O_3 several %Sn doped → ITO (Indium tin oxide)

In (3+) → Sn (4+) Electron doped cf. Si(4+) → As(5+)

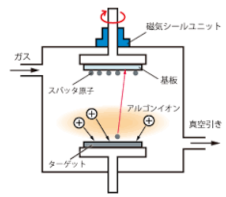
Oxygen defficient → In^0 from charge nuetrality

→ Electron doped

Electron doped in most oxides

Films from magnetron sputtering

2 x 10^{-4} Ωcm, E_g ~ 3.3 eV



SnO_2 Rutile、oxygen defficiency

ZnO Wurzite、oxygen defficiency

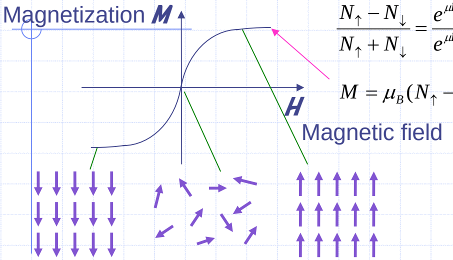
$Ti_{1-x}Nb_xO_2$ Rutile

$SrTiO_3$ Perovskite、oxygen difficiency

12CaO·7Al_2O_3 Partly reduced, electron doped (Electrolyde)

$E = \mu_B H$ = (9.27x10^{-24} J/T)/(1.6x10^{-19} J/eV)=0.58x10^{-4} eV/T

1 eV = 0.58x10^{-4} T or 1 K = 0.67 T → 1 K ~ 1 T



$$\frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} = \frac{e^{\mu H/k_BT} - e^{-\mu H/k_BT}}{e^{\mu H/k_BT} + e^{-\mu H/k_BT}} = \tanh\frac{\mu_B H}{k_B T}$$ ← 1 T ~ 300 T ← 1 K ~ 300 K

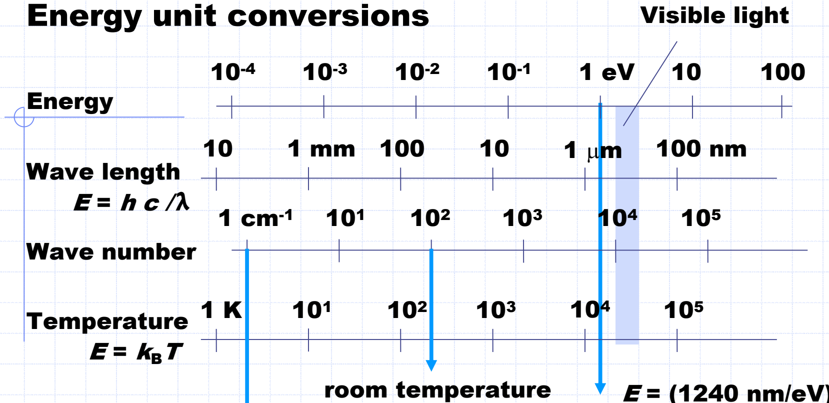
$$M = \mu_B(N_\uparrow - N_\downarrow) = N\mu_B \tanh\frac{\mu_B H}{k_B T}$$

1 T

8 T

45 T

Energy unit conversions



1 cm^{-1}~1 K ~1 T

Magntic field

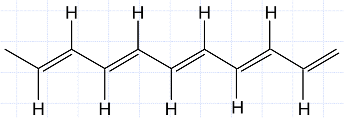
$E = k_B T$ $E = \mu_B H$

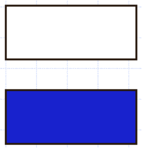
1 eV = 1.24 μm $eV = hc/\lambda$
= 8065 cm^{-1}
= 11605 K $E = k_B T$
= 0.96x10^5 J/mol or C/mol
eN_A Faraday const. =1 mol charge

1 eV ~ 1 μm ~10^4 cm^{-1} ~10^4 K ~ 100 kJ/mol

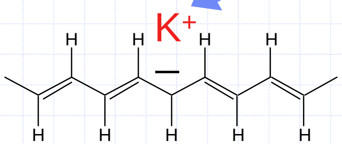
Doped Polyacetylene

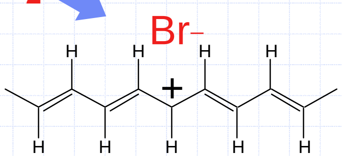
10^{-5} S/cm



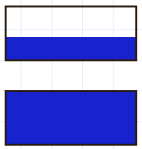


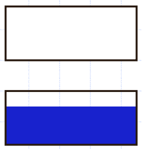
K → K$^+$ Br_2 → Br^-





300 S/cm

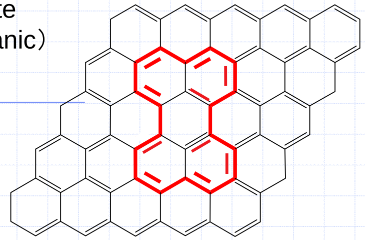


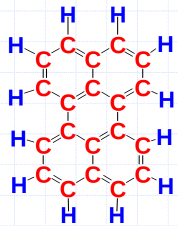


Negative Positive

Electron dope (N型) Hole dope (P型)

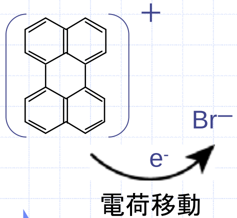
Graphite
(Inorganic)





First Electrically Conducting Organics

perylene

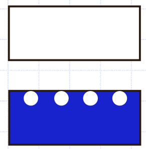


Charge-transfer complex
電荷移動錯体

Br doped Perylene shows high electric conductivity
First conducting charge-transfer salt
Akamatsu, Inokuchi, Matsunaga,

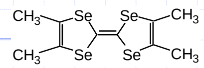
Nature, **173**, 168 (1954).

0.1 S/cm

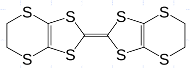


Components of Organic Superconductors

Donors

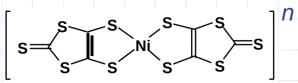


Tetramethyltetraselenafulvalene
TMTSF



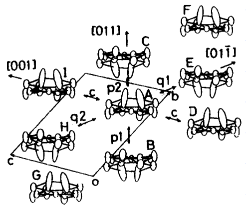
Bis(ethylenedithio)tetrathiafulvalene
BEDT-TTF

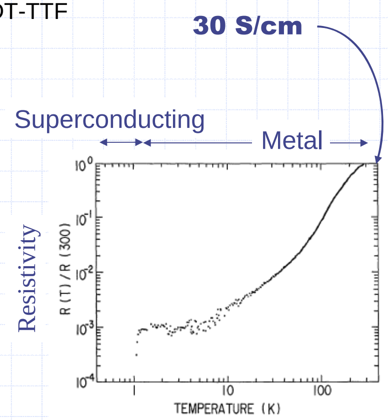
Acceptor



$[Ni(dmit)_2]^{n-}$

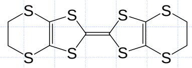
β-$(BEDT\text{-}TTF)_2I_3$ 1/2+ –

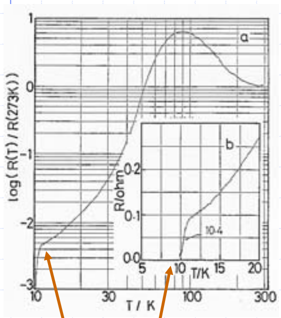




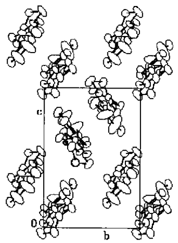
κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$

1/2+ + – –





Superconductivity at 10.4 K (1987)



Electrochemical Crystal Growth

BEDT-TTF → $BEDT\text{-}TTF^{+}$

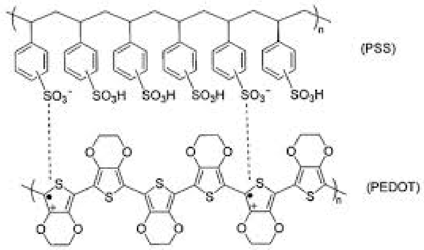
$[Cu(NCS)_2]^{-}$

→ $(BEDT\text{-}TTF)_2Cu(NCS)_2$

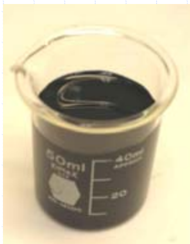
Polyacetylene → Polythiophene

PEDOT:PSS

poly(ethylenedioxythiophene) : polystyrene sulphonate)

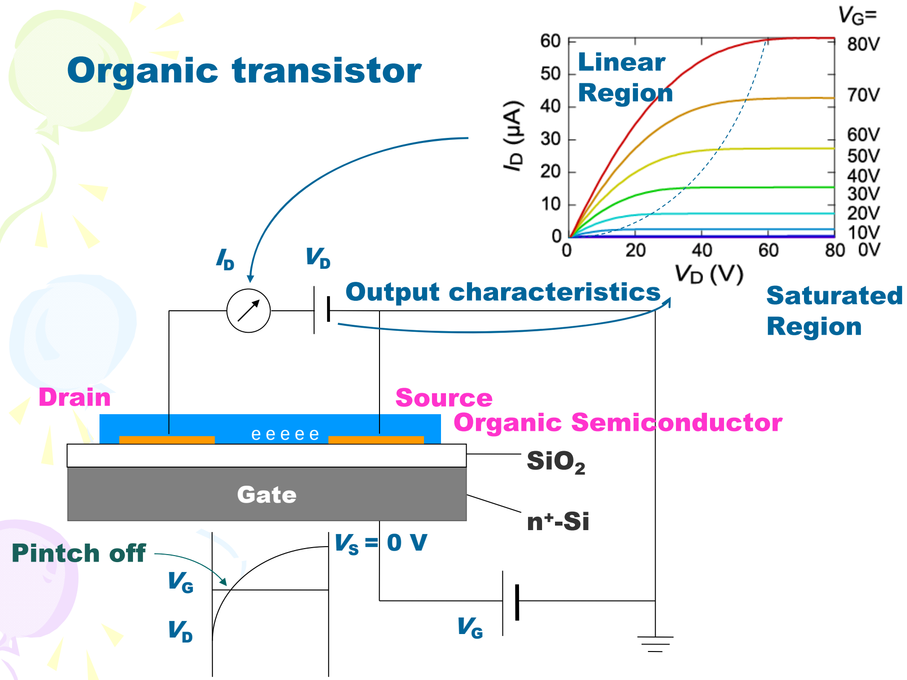


Conductivity σ ~ 300 S/cm
S = Ω^{-1} Siemens

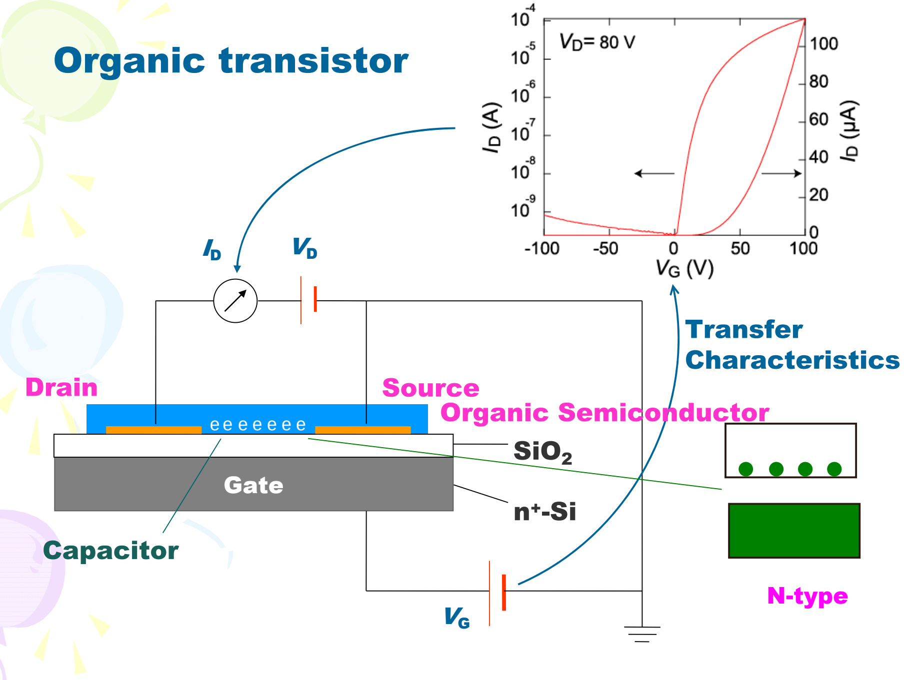


Water solution

Organic transistor



Organic transistor



Quantitative transistor characteristics (Gradual Channel Approximation)

Charge on the interface

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

Voltage $V(x)$ depends on x

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

$ne \to Q(x)$ in $\sigma = ne\mu$

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

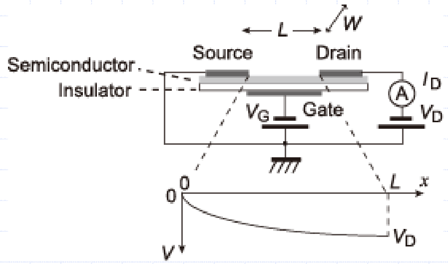
$$I_D = WQ(x)\mu(-dV(x)/dx)$$

Integrate using $Q(x)$

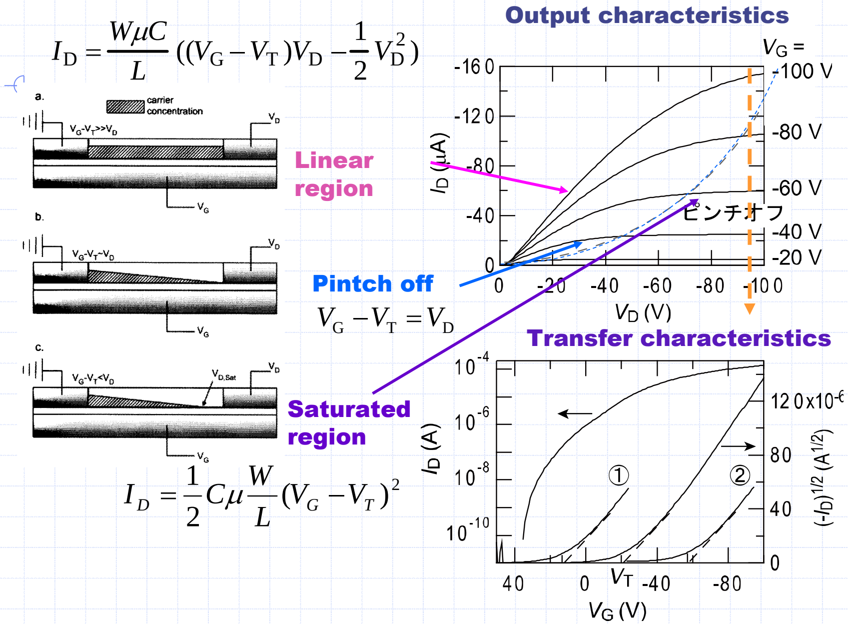
$$\int_0^L I_D dx = \int_0^{V_D} WC\mu(V_G - V_T - V(x))dV$$

I_D=constant

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



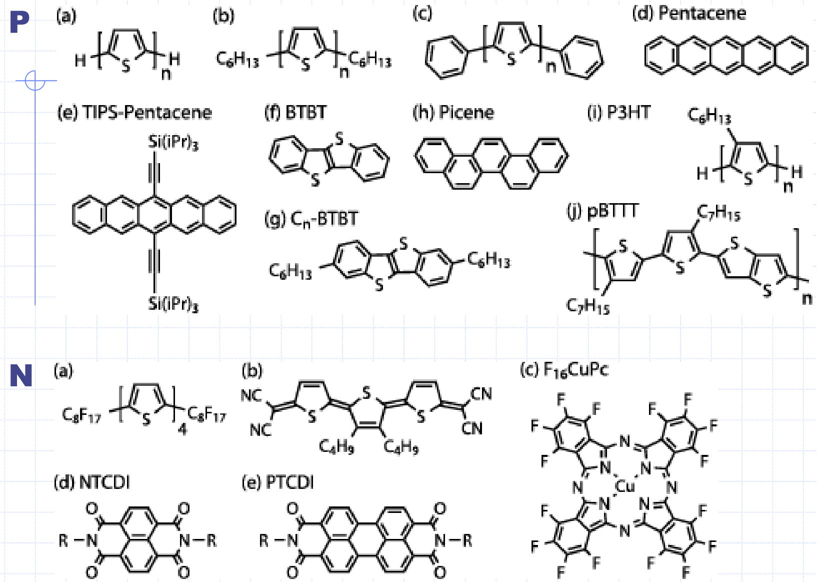
$$I_D = \frac{W\mu C}{L}((V_G - V_T)V_D - \frac{1}{2}V_D^2)$$

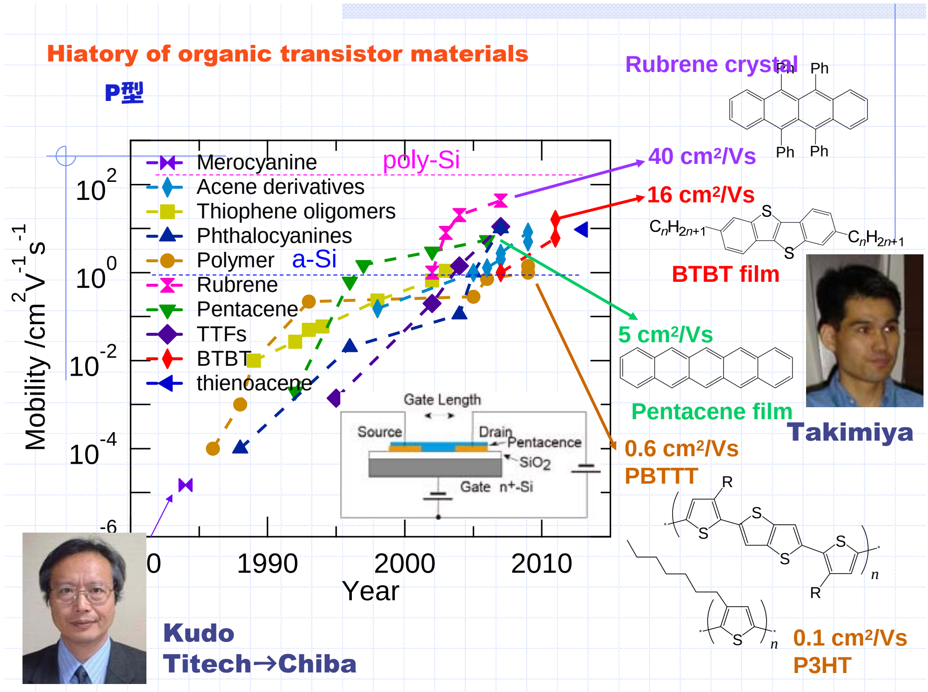


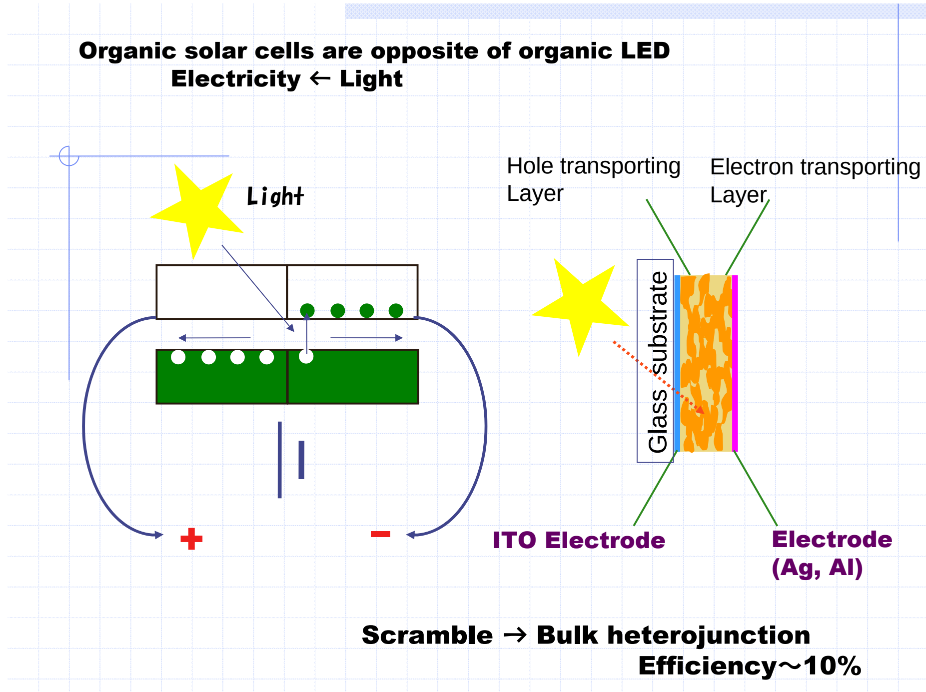
$$V_G - V_T = V_D$$

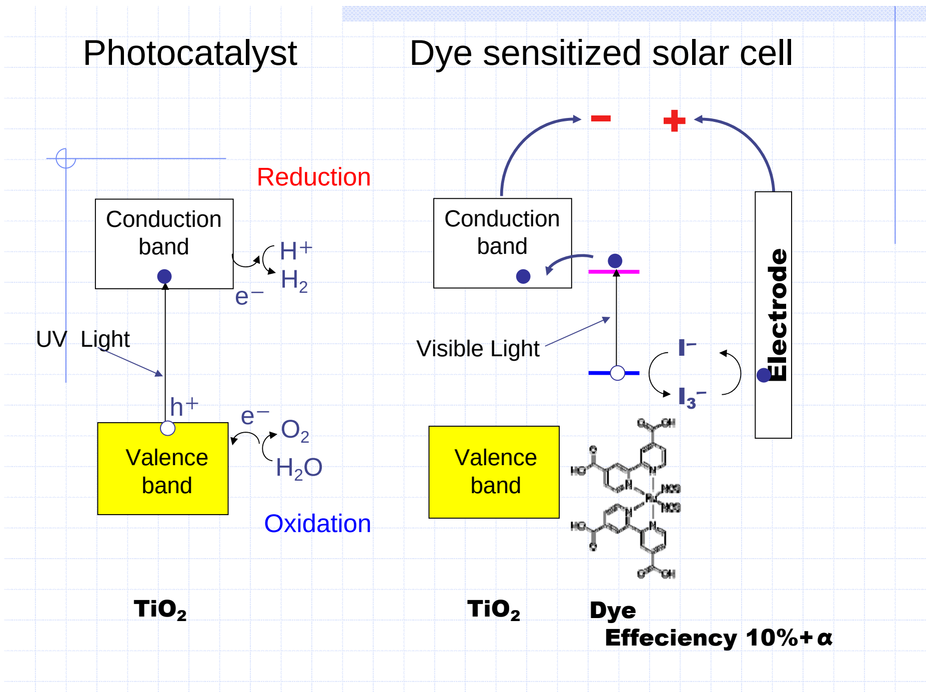
$$I_D = \frac{1}{2}C\mu\frac{W}{L}(V_G - V_T)^2$$

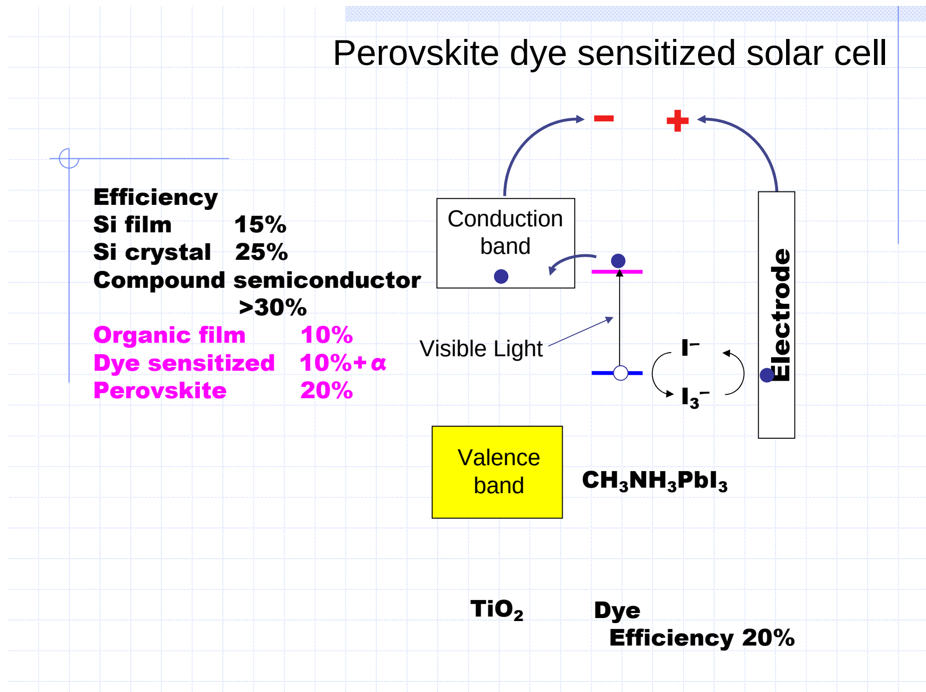
Organic Transistor Materials




Hiatory of organic transistor materials
P型
Rubrene crystal
Ph Ph
Ph Ph
Merocyanine
Acene derivatives
Thiophene oligomers
Phthalocyanines
Polymer
Rubrene
Pentacene
TTFs
BTBT
thienoacene
poly-Si
a-Si
10^2
10^0
10^{-2}
10^{-4}
10^{-6}
Mobility /cm^{2}V^{-1}s^{-1}
1990
2000
2010
Year
Gate Length
Source
Drain
Pentacene
SiO_2
Gate n+-Si
40 cm²/Vs
16 cm²/Vs
C_nH_{2n+1}
C_nH_{2n+1}
BTBT film
5 cm²/Vs
Pentacene film
Takimiya
0.6 cm²/Vs
PBTTT
R
S
n
0.1 cm²/Vs
P3HT
Kudo
Titech→Chiba


Organic solar cells are opposite of organic LED
Electricity ← Light
Light
Hole transporting Layer
Electron transporting Layer
Glass substrate
+
−
ITO Electrode
Electrode (Ag, Al)
Scramble → Bulk heterojunction
Efficiency～10%


Photocatalyst
Dye sensitized solar cell
Reduction
Conduction band
H^+
H_2
e^-
UV Light
h^+
e^-
O_2
H_2O
Valence band
Oxidation
TiO_2
Conduction band
Visible Light
−
+
I^-
I_3^-
Electrode
Valence band
TiO_2
Dye
Effeciency 10%+α


Perovskite dye sensitized solar cell
Efficiency
Si film 15%
Si crystal 25%
Compound semiconductor >30%
Organic film 10%
Dye sensitized 10%+α
Perovskite 20%
Conduction band
Visible Light
−
+
I^-
I_3^-
Electrode
Valence band
$CH_3NH_3PbI_3$
TiO_2
Dye
Efficiency 20%