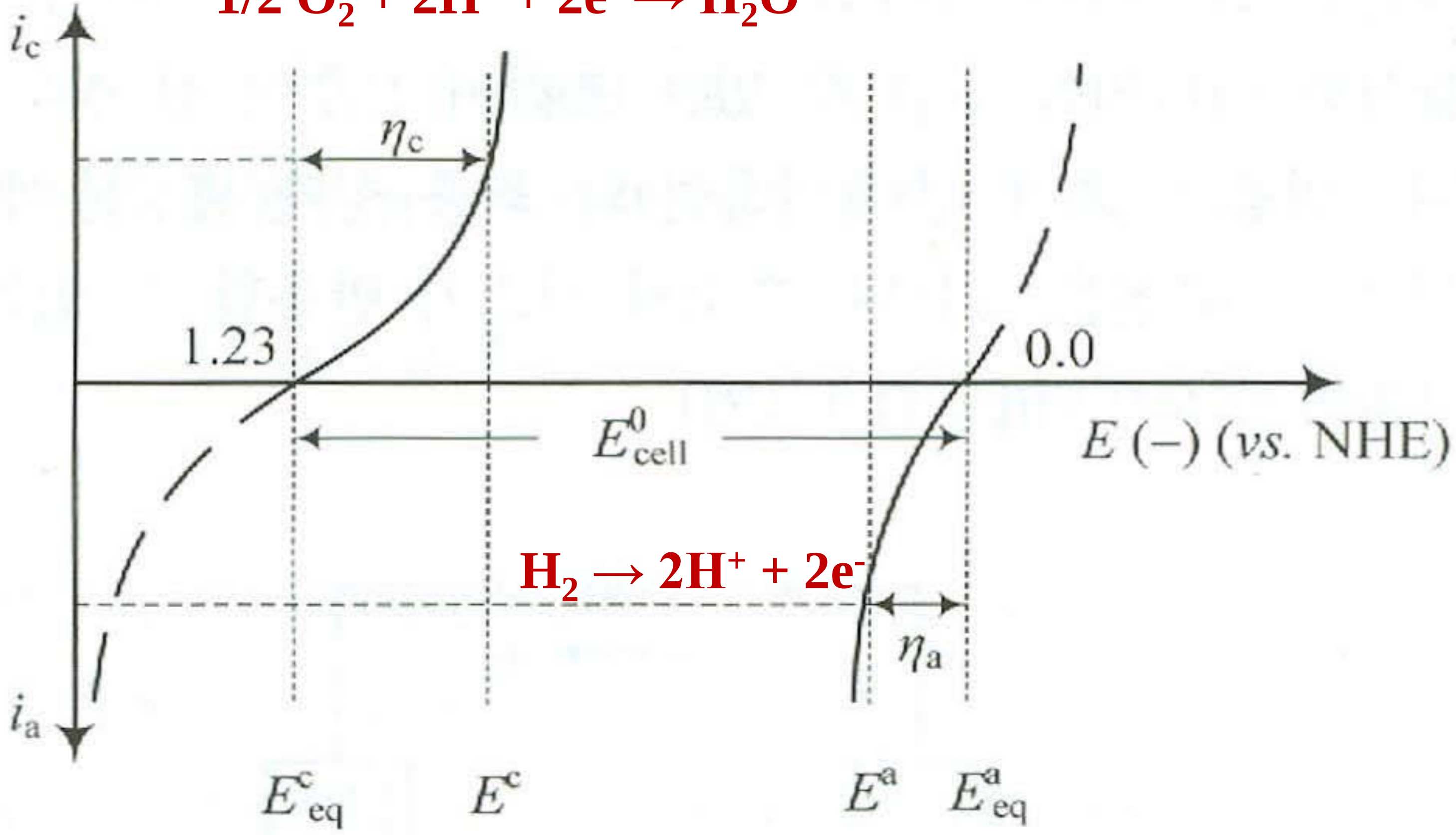
16. Photoelectrochemistry (Bard, ch. 18)

A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, Wiley, 2001.

Electrochemical Energy Devices

$1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$



$H_2 \rightarrow 2H^+ + 2e^-$

FC/electrolyzer: hydrogen + oxygen [air) ↔ water + electric energy

Respiration/photosynthesis: glucose + oxygen (air) ↔ CO_2 + water + energy

Photoelectrochemical cell

Energy storage (battery)

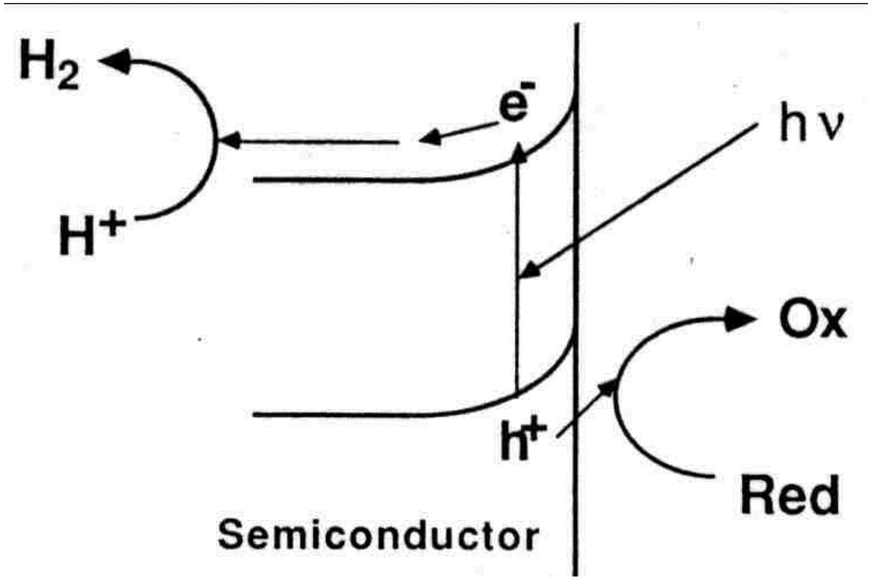
Photoelectrochemistry at semiconductors

Radiation energy ⇔ electrical or chemical energy

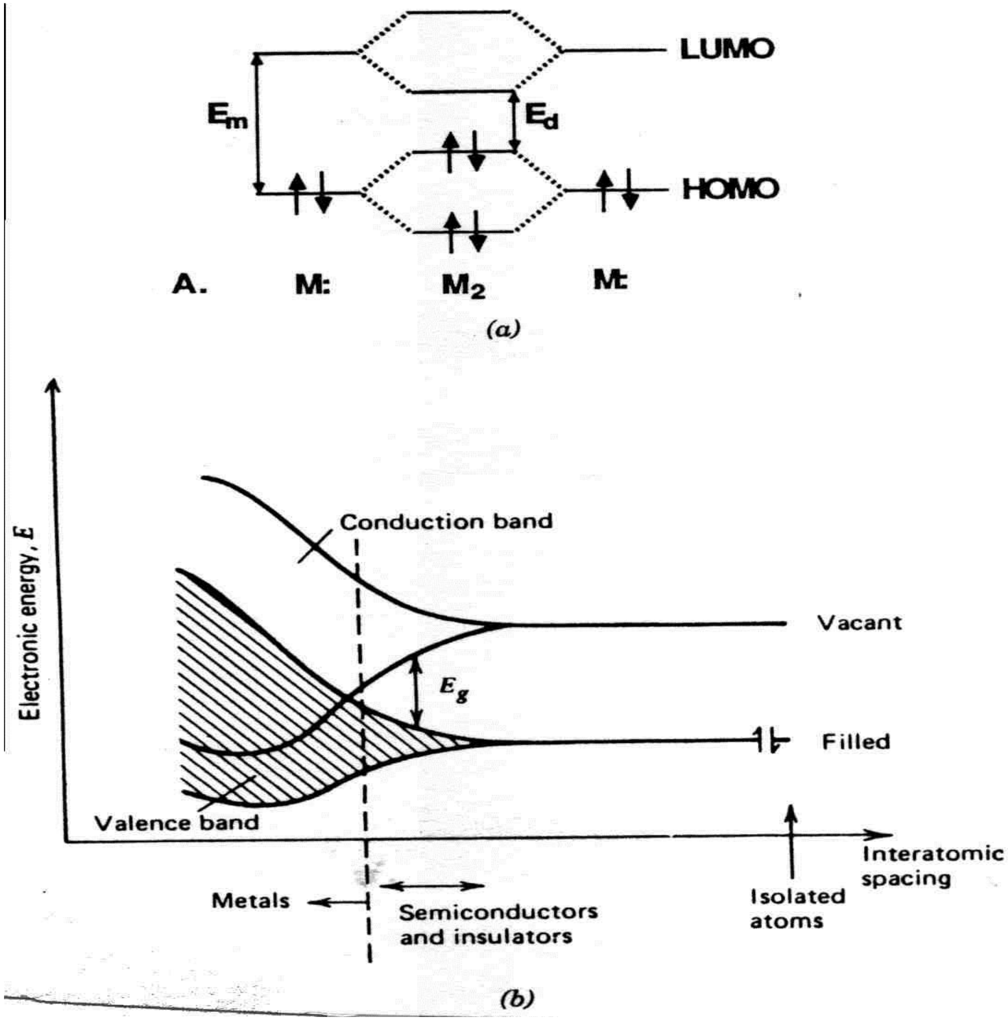
- **photoelectrochemical system**: absorption of light by the system (e.g., sun light) → chemical reactions & flow of current

- semiconductor:

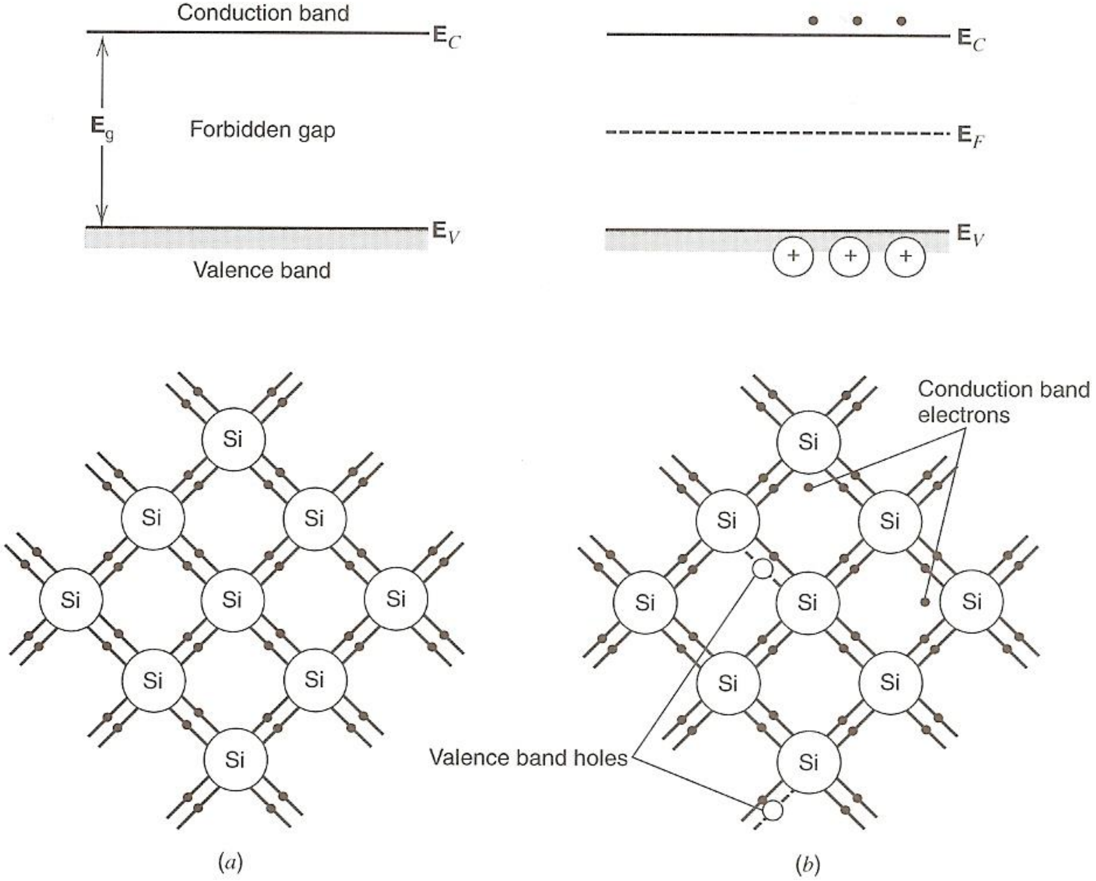
absorb photons → electron-hole pairs ⇒ oxidation/reduction reactions → products
(photocurrent)



Semiconductor electrodes
Band model



intrinsic semiconductor; undoped



(*a*) (*b*)

- intrinsic semiconductor; # of e^-(n_i) & h^+(p_i) per cm^3 at T

$$n_i = p_i = (N_C N_V)^{1/2} \exp\left[-\frac{E_g}{2kT}\right]$$

$$N_C = 2\left(\frac{2\pi m_n kT}{h^2}\right)^{3/2} = (4.83 \times 10^{15})(m_e{}^*T)^{3/2}$$

$$N_V = 2\left(\frac{2\pi m_p kT}{h^2}\right)^{3/2} = (4.83 \times 10^{15})(m_h{}^*T)^{3/2}$$

Where T(K), m_n, m_p; reduced masses of e^- & h^+, $m_e{}^*$, $m_h{}^*$; relative effective masses where $m_e{}^* = m_n/m_0$, $m_h{}^* = m_p/m_0$ (m_0; rest mass of an electron)

$n_i = p_i \sim 2.5 \times 10^{19} \exp(-E_g/2kT)$ cm^{-3} (near 25℃)

For Si, $n_i = p_i \sim 1.4 \times 10^{10}$ cm^{-3}
$E_g > 1.5$ eV → few carriers: electrical insulators

TABLE 6.2.1. Energy Gaps (E_g) of Selected Materials

Substance	E_g (eV)	Substance	E_g (eV)
Ge	0.67	Fe_2O_3	~2.3
$CuInSe_2$	0.9	CdS	2.42
Si	1.12	ZnSe	2.58
WSe_2	~1.1	WO_3	2.8
$MoSe_2$	~1.1	TiO_2 (rutile)	3.0
InP	1.3	TiO_2 (anatase)	3.2
GaAs	1.4	ZnO (zincite)	3.2
CdTe	1.50	$SrTiO_3$	3.2
CdSe	1.74	SnO_2	3.5
GaP	2.2	ZnS (zinc blende)	3.54
		C (diamond)	5.4

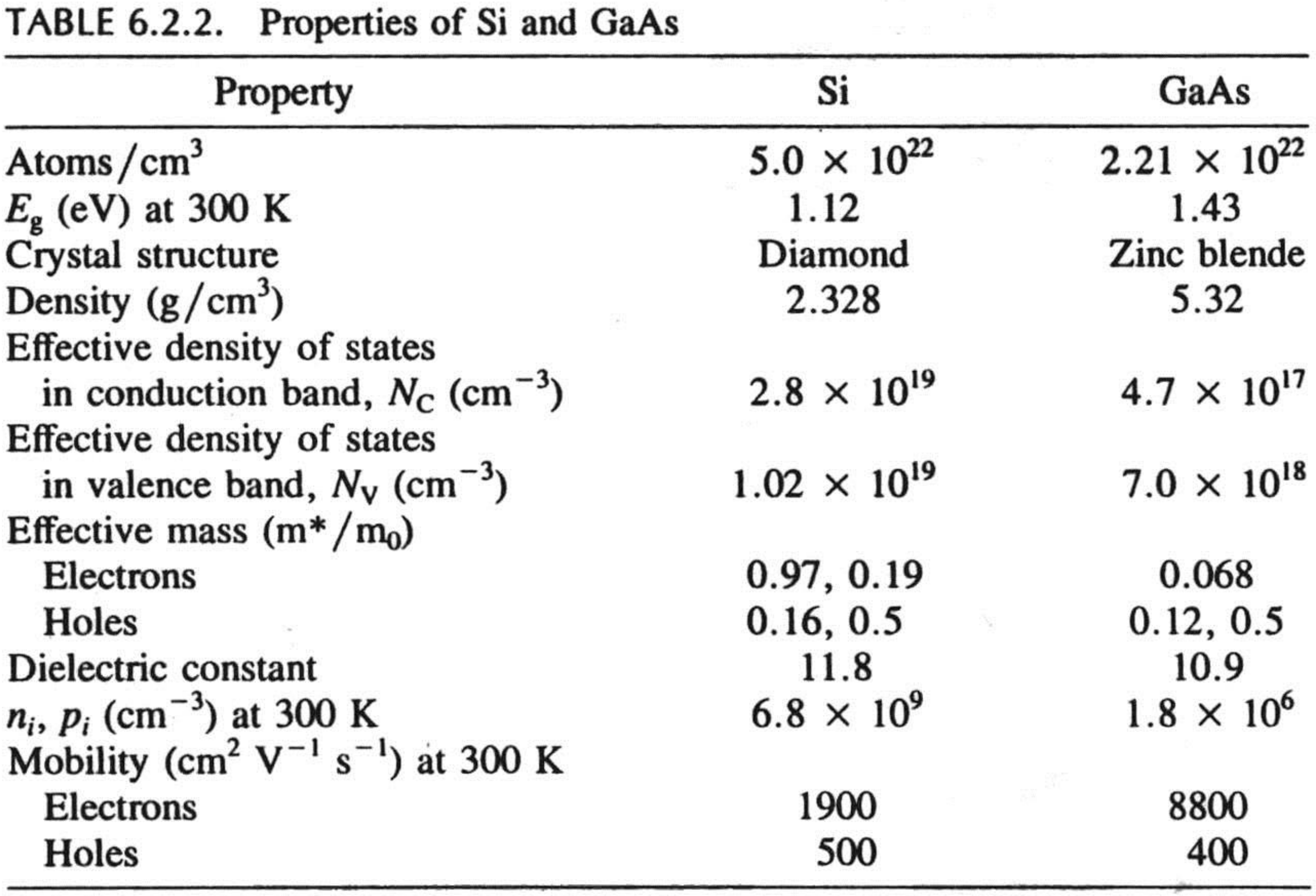


TABLE 6.2.2. Properties of Si and GaAs

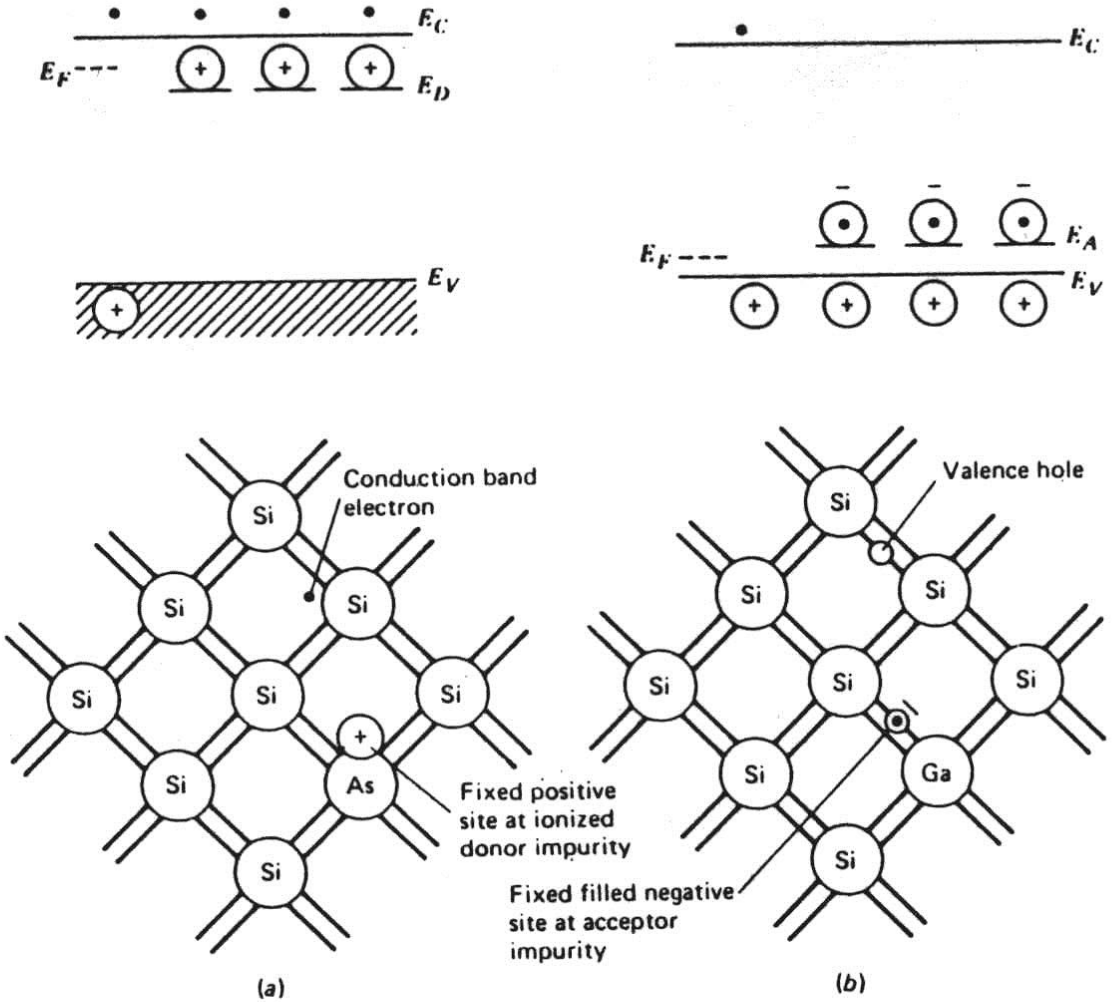
Property	Si	GaAs
Atoms/cm^3	5.0×10^{22}	2.21×10^{22}
E_g (eV) at 300 K	1.12	1.43
Crystal structure	Diamond	Zinc blende
Density (g/cm^3)	2.328	5.32
Effective density of states in conduction band, N_C (cm^{-3})	2.8×10^{19}	4.7×10^{17}
Effective density of states in valence band, N_V (cm^{-3})	1.02×10^{19}	7.0×10^{18}
Effective mass (m^*/m_0)		
Electrons	0.97, 0.19	0.068
Holes	0.16, 0.5	0.12, 0.5
Dielectric constant	11.8	10.9
n_i, p_i (cm^{-3}) at 300 K	6.8×10^9	1.8×10^6
Mobility (cm^2 V^{-1} s^{-1}) at 300 K		
Electrons	1900	8800
Holes	500	400

- Mobilities (μ, cm^{2}V^{-1}s^{-1}) vs. diffusion coefficient (cm^{2}s^{-1})

$D_i = kT\mu_i = 0.0257\mu$ at 25°C, $i = n, p$

Extrinsic semiconductors; doped

- dopants or impurity; ~ppm, typical donor densities (N_D) are 10^{15}-10^{17} cm^{-3}



n-type

p-type

n-type: total density (n) of electrons in CB

$n = p + N_D$, p; hole density (thermal activation of VB atoms)

most cases for moderate doping $N_D >> p$, $n \sim N_D$

For any materials (intrinsic or extrinsic)

$$np = N_C N_V \exp \frac{-E_g}{kT} = n_i^2 = p_i^2$$

For n-type SC

$$p = \frac{N_C N_V}{N_D} \exp \frac{-E_g}{kT} = \frac{n_i^2}{N_D}$$

e.g., 10^{17} cm^{-3} As doped Si → electron density ~10^{17} cm^{-3}, hole density ~ 460

→ majority carrier: electron

p-type

dopant (acceptor) density; N_A, electron density (by thermal promotion); n →

total density of holes (p)

$$p = n + N_A$$

when $N_A >> n$, $p = N_A$ → hole; majority carriers

$$n = n_i^2/N_A$$

e.g., Si: $N_A = 5 \times 10^{16}$ acceptor/cm^3, $n \sim 4000$ cm^{-3}

•compound semiconductor (e.g., GaAs or TiO_2); n-type or p-type → replacement of impurity atoms to the constituent lattice atoms, impurity atoms in an interstitial position, lattice vacancy or broken bond

e.g., n-TiO_2: oxygen vacancies in the lattice

- extrinsic SC; E_F move up & down depending upon doping

$$E_F = E_V + kT \ln\left(\frac{N_V}{N_A}\right) \qquad \text{(p-type semiconductor)}$$

and donors move E_F up toward the conduction band:

$$E_F = E_C - kT \ln\left(\frac{N_C}{N_D}\right) \qquad \text{(n-type semiconductor)}$$

e.g., 10^{17} cm^{-3} As doped Si → $N_D \sim 10^{17}$ cm^{-3}, $N_C = 2.8 \times 10^{19}$ cm^{-3}, 25 °C
$\Rightarrow E_F = E_C - (25.7 \times 10^{-3}$ eV$) \ln(N_C/N_D) \sim E_C - 0.13$ eV
- if $N_D < N_C$, $N_A < N_V \rightarrow$ SC
- if higher doping levels; Fermi level moves into VB or CB $\Rightarrow$ show metallic conductivity

e.g., transparent SnO_2 (E_g = 3.5 eV) + heavily doping with Sb(III) ($N_D > 10^{19}$ cm^{-3}) $\Rightarrow$ the material becomes conductive

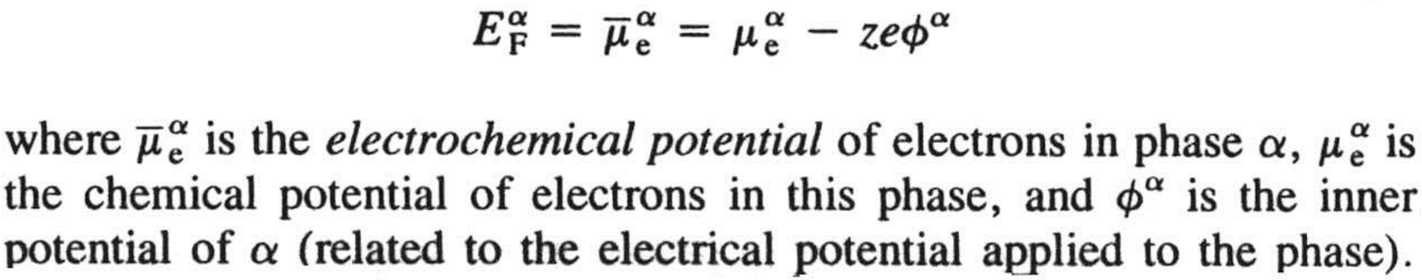
Fermi level

1) probability that an electronic level at energy E is occupied by an electron at thermal equilibrium f(E) → Fermi-Dirac distribution function

$$f(E) = \frac{1}{1 + \exp[(E - E_F)/kT]}$$

- Fermi level E_F; value of E for which f(E) = 1/2 (equally probable that a level is occupied or vacant)
- At T = 0, all levels below E_F ($E < E_F$) are occupied (f(E) → 1); all levels $E > E_F$ vacant
- intrinsic SC: E_F in the middle of CB and VB edges

2) alternative definition of E_F for a phase α : “electrochemical potential”



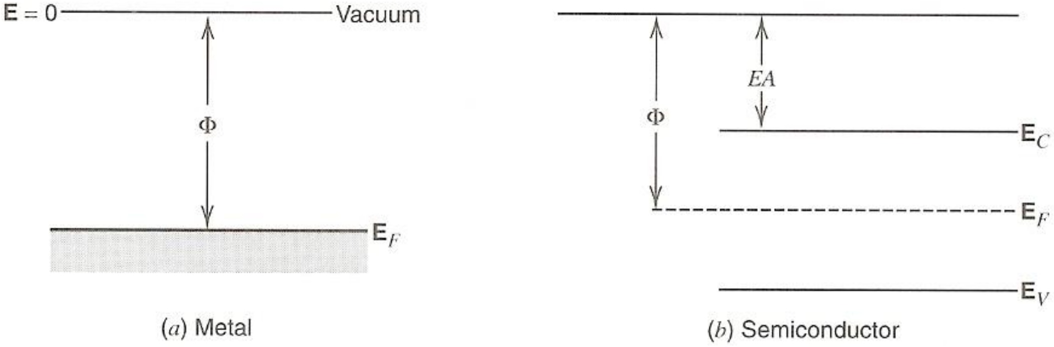
$$E_F^\alpha = \bar{\mu}_e^\alpha = \mu_e^\alpha - ze\phi^\alpha$$

where $\bar{\mu}_e^\alpha$ is the *electrochemical potential* of electrons in phase α, μ_e^α is the chemical potential of electrons in this phase, and ϕ^α is the inner potential of α (related to the electrical potential applied to the phase).

- useful in thermodynamic considerations of reactions and interfaces; at equilibrium electrically, the electrochemical potential of electrons in all phases must be same by charge transfer → same Fermi level
- Fermi levels difference between two phases; function of the applied potential

- Fermi level (uncharged phase) vs. work function (Φ)

$$\Phi = -E_F$$



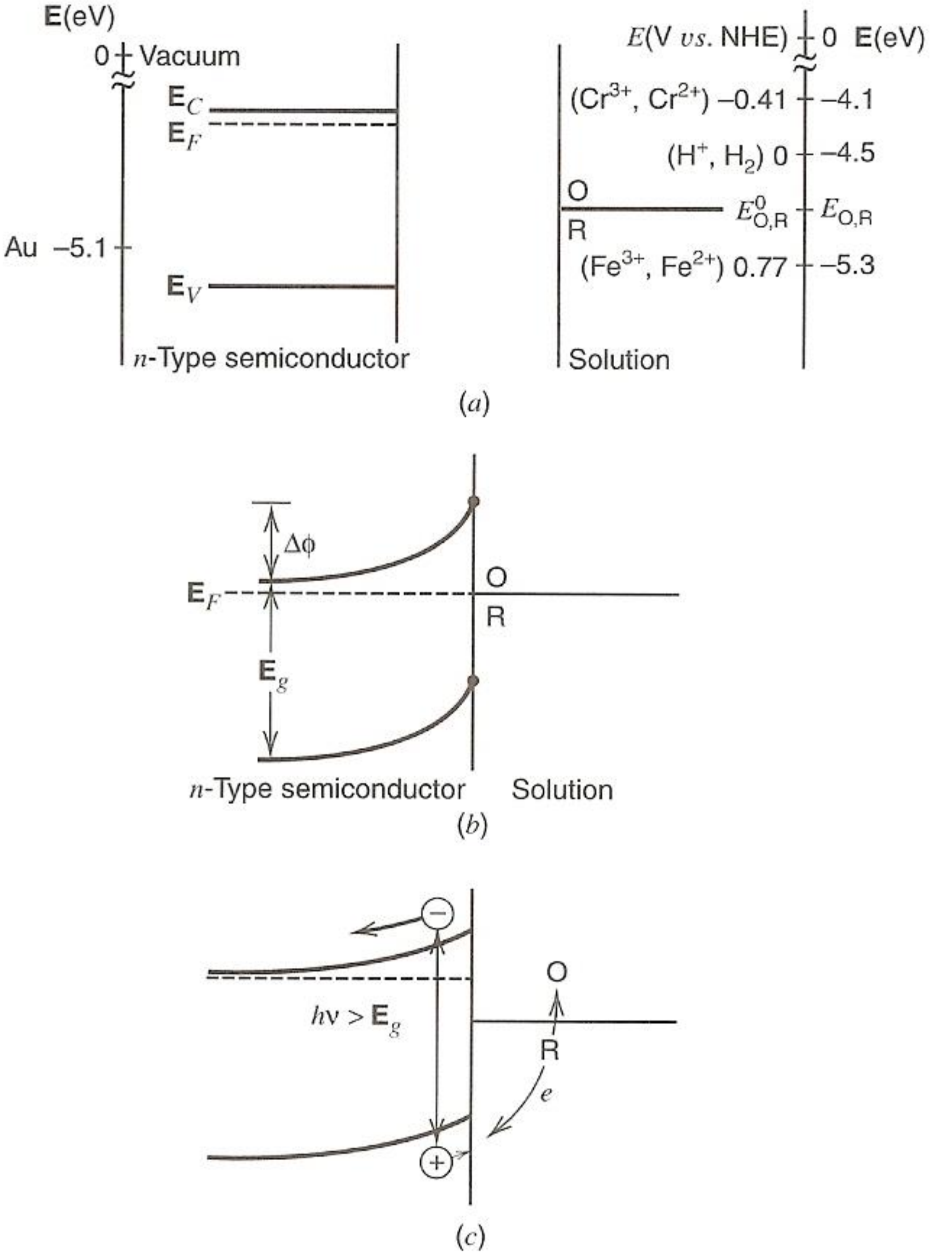
(*a*) Metal (*b*) Semiconductor

Semiconductor/solution interface

- electron transfer at the interface (same principles as those given above) + chemical reaction (if possible, e.g., decomposition of SC , oxide film formation) → complicate
  - Si; SiO_2 (if oxygen or oxidant in solution); hinder electron transfer

- The distribution of charge (e^-/h^+ in SC & ions in solution) and potential; depend on their relative Fermi level
- Fermi level in solution: electrochemical potential of electrons in solution phase ( )
  - governed by the nature and concentration of the redox species present in the solution and is directly related to the solution redox potential as calculated by the Nernst equation
  - at the point of zero charge, no surface state, no specifically adsorbed ions, no excess charge → the distribution of carriers (e^-, h^+, anions, cations) is uniform from surface to bulk, and the energy bands are flat "<u>flat band potential</u>" (E_{fb}) ; no space charge layer in SC & no diffuse layer in solution

n-type


E(eV)
0 Vacuum
E$_C$
E$_F$
Au −5.1
E$_V$
n-Type semiconductor
E(V vs. NHE) 0 E(eV)
(Cr^{3+}, Cr^{2+}) −0.41 −4.1
(H$^+$, H$_2$) 0 −4.5
O
R
$E^0_{O,R}$
$E_{O,R}$
(Fe^{3+}, Fe^{2+}) 0.77 −5.3
Solution
(a)
Δφ
E$_F$
O
R
E$_g$
n-Type semiconductor
Solution
(b)
hν > E$_g$
O
R
e
(c)

- potential difference (by applied voltage or Fermi level difference) ; charged interface → space charge layer (thickness W); potential difference ΔV, dopant density N_D

$$W\ (\mathrm{cm}) \approx 1.05 \times 10^{3} \left[\frac{\varepsilon \Delta V(\mathrm{V})}{N_{\mathrm{D}}(\mathrm{cm}^{-3})} \right]^{1/2}$$

50 ~ 2000 Å

- <u>band bending</u>: because of non uniform carrier density in SC (upward (with respect to the bulk SC) for a positively charged SC and downward for a negatively charged one) → electric field in the space charge region → direction of motion

The capacitance of the space charge layer

$$C_{sc} = (2kTn_i\varepsilon\varepsilon_0)^{1/2} \cdot \frac{e}{2kT}\,\frac{-\lambda e^{-Y} + \lambda^{-1}e^{Y} + (\lambda - \lambda^{-1})}{[\lambda(e^{-Y} - 1) + \lambda^{-1}(e^{Y} - 1) + (\lambda - \lambda^{-1})]^{1/2}}$$

where $\lambda = n_i/N_D$ and $Y = e\Delta\phi/kT$. This equation can be simplified under the conditions that a depletion layer exists (i.e., $\lambda e^{-Y} << \lambda^{-1}$). For an n-type semiconductor, when $\lambda^{-1} >> \lambda$, this equation can be written with some rearrangement as

$$\frac{1}{C_{sc}^2} = \frac{2}{e\varepsilon\varepsilon_0 N_D}\left(-\Delta\phi - \frac{kT}{e}\right)$$

Mott-Schottky plot

which at 25°C, for C_{sc} in $\mu F/cm^2$, N_D in cm^{-3}, and $\Delta\phi = E_{fb} - E$ in volts is

$$\frac{1}{C_{sc}^2} = \frac{1.41 \times 10^{20}}{\varepsilon N_D}[E - E_{fb} - 0.0257]$$

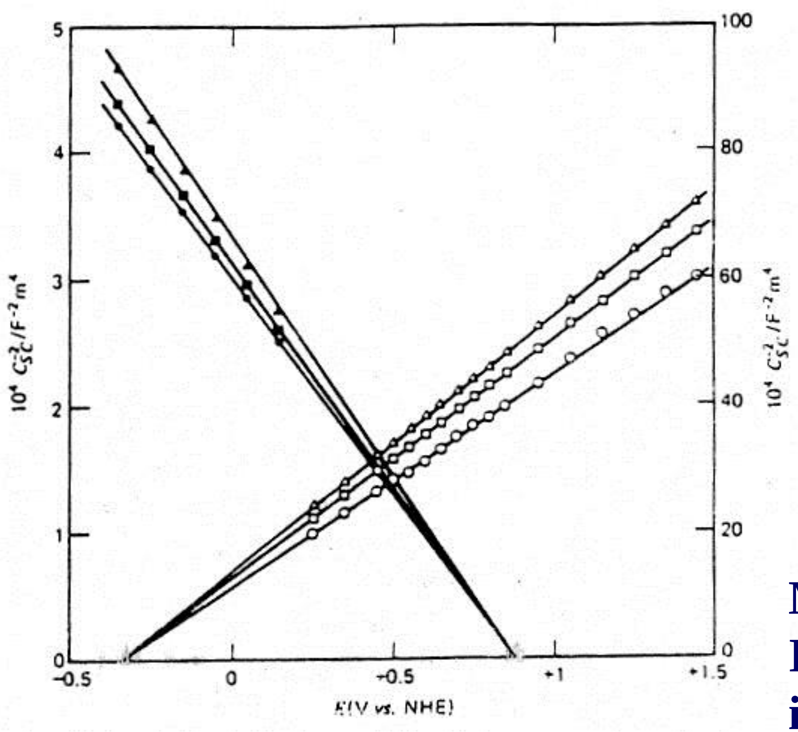
Mott-Schottky plot: useful in characterizing SC/liquid interface where a plot of $(1/C_{SC}^2)$ vs. E should be linear → values of E_{fb} and N_D from the intercept and slope

space charge capacitance C_{sc} → Mott-Schottly equation

$$1/C_{sc}^{2} = (2/e\varepsilon\varepsilon_{0}N)^{1/2}(-\Delta\phi - kT/e)$$

ε: dielectric constant, N: donor or acceptor densities, e: quantity of charge, $-\Delta\phi = E-E_{fb}$

A plot of $1/C_{sc}^{2}$ vs. potential E should be linear → E_{fb}, doping level N



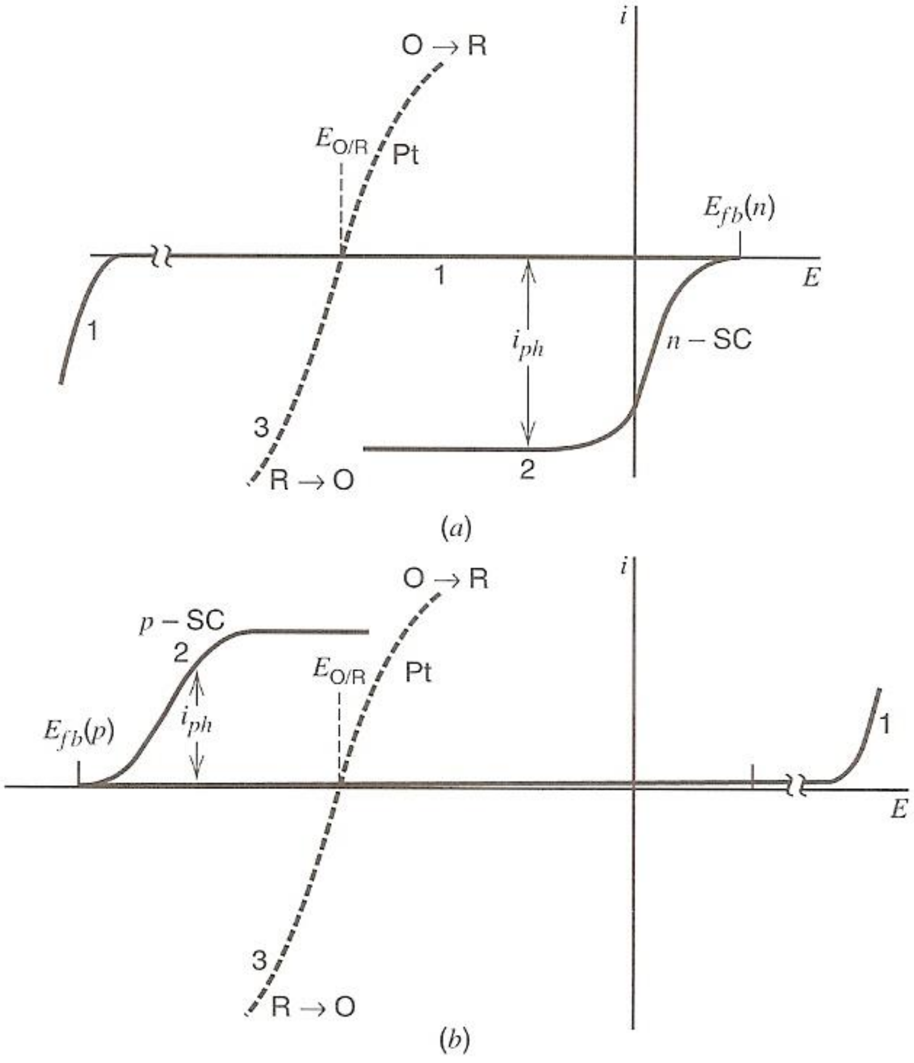
Mott-Schottky plots for n- and p-type InP
in 1 M KCl + 0.01 M HCl

Photoeffects at semiconductor electrodes

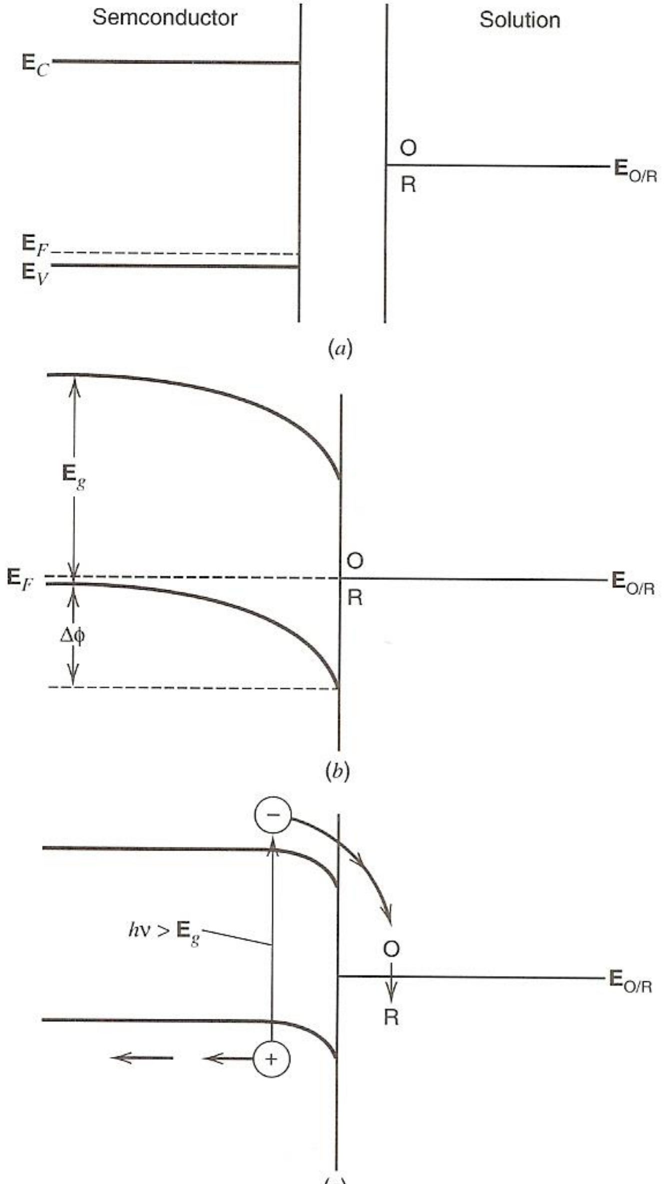
1: dark
2: irradiation
3: Pt electrode

n-type

p-type



p-type


Semconductor
Solution
E_C
O
R
$E_{O/R}$
E_F
E_V
E_g
O
E_F
$E_{O/R}$
R
$\Delta\phi$
−
$h\nu > E_g$
O
$E_{O/R}$
R
+

(a)

(b)

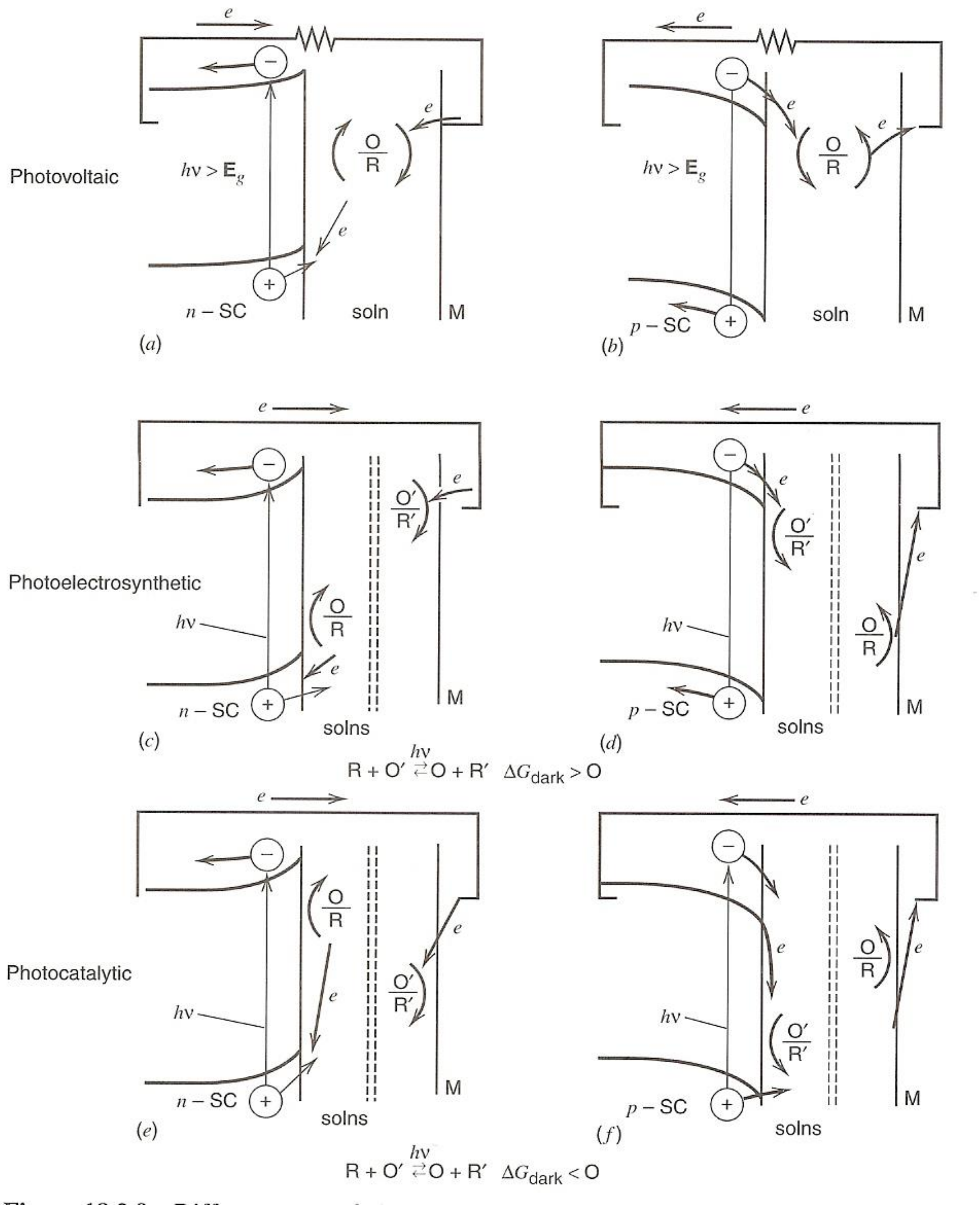
(c)

Photoelectrochemical cells

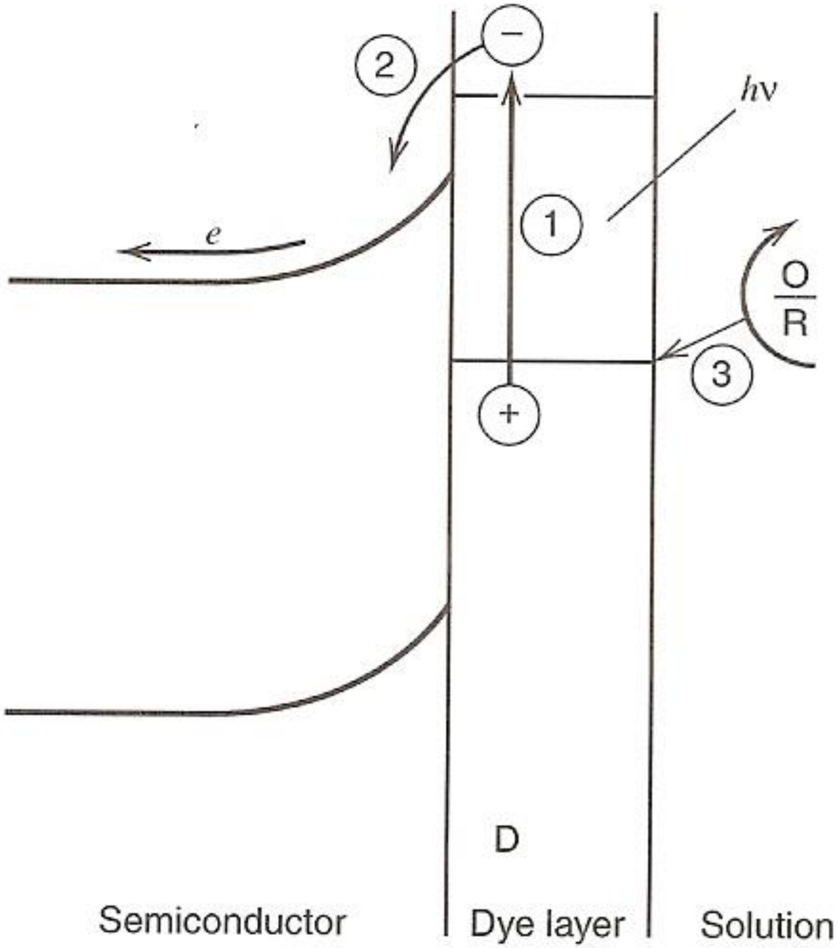
Photovoltaic cells:
convert light to electricity

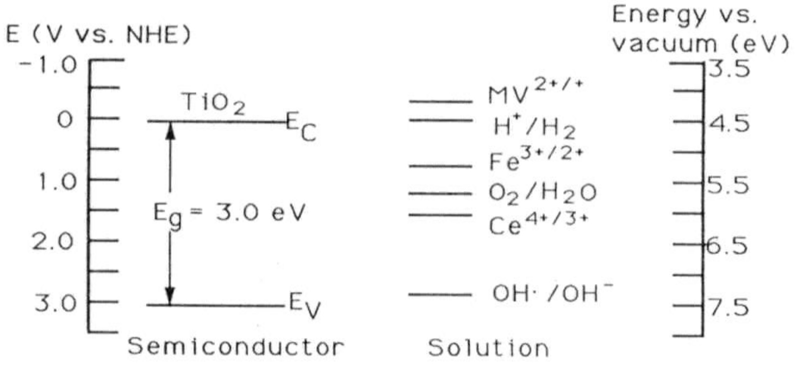
Photoelectrosynthetic cells:
Radiant E to chemical energy

Photocatalytic cells:
Light E to overcome
activation E of the process

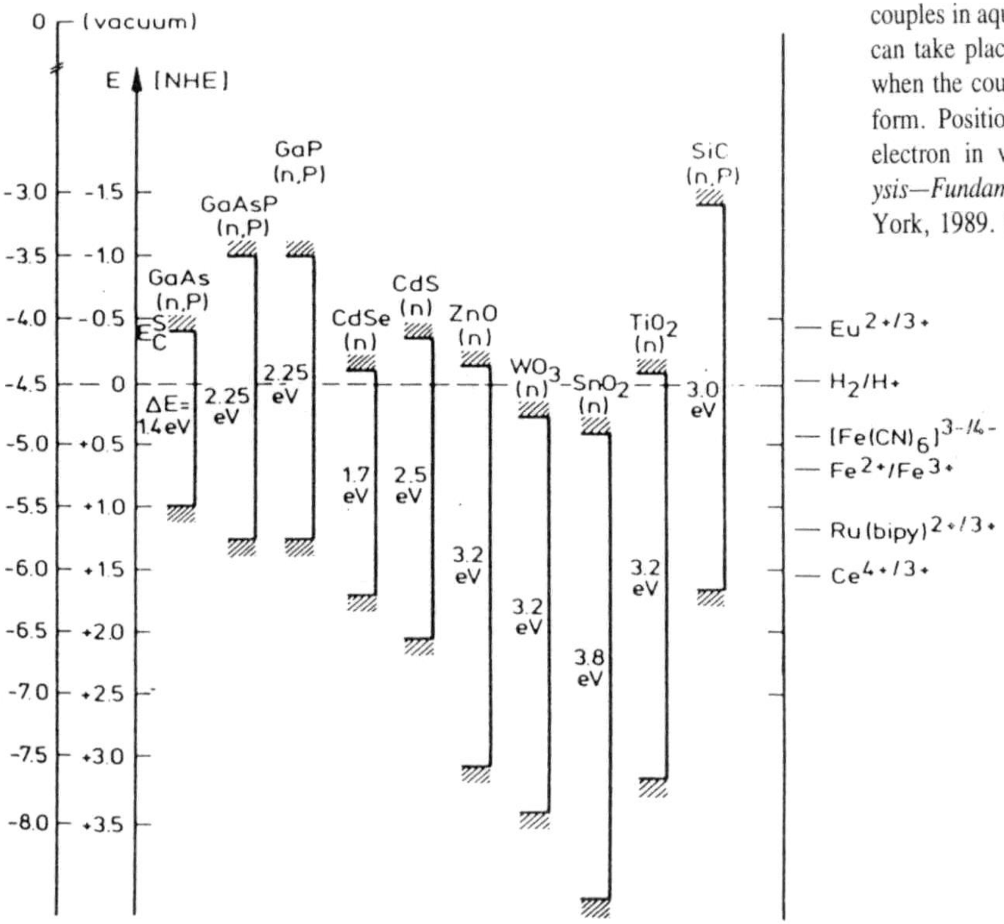


Band gap vs. wavelength → limit to utilize sunlight (e.g., TiO_2 (3.0 eV))
→ dye sensitization of a semiconductor





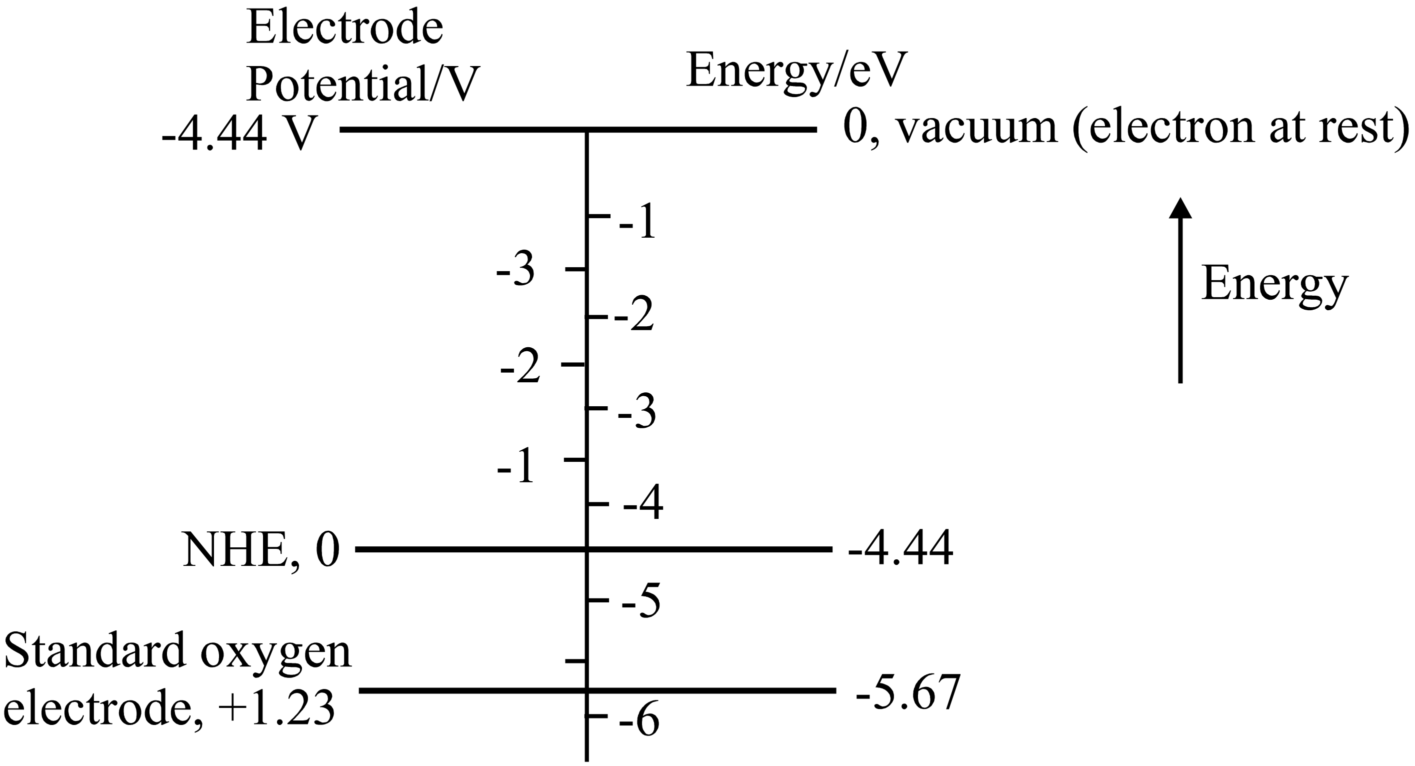
(a)



(b)

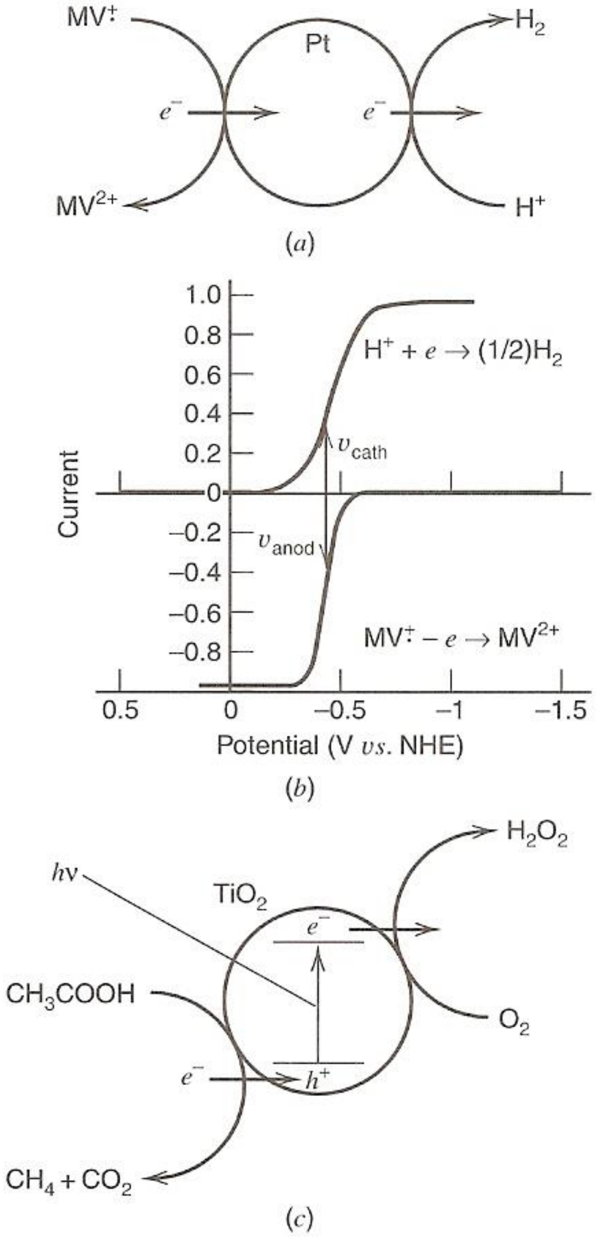
Band-edge positions of semiconductors with respect to several redox couples in aqueous solution at pH 1. (*a*) TiO_2 in rutile form. Reduction by a CB electron can take place when the redox couple lies below E_C; oxidation by a VB hole occurs when the couple lies above E_V. (*b*) Other semiconductors; here TiO_2 is in the anatase form. Positions are given both as potentials versus NHE and as energies versus the electron in vacuum. [Reprinted with permission from M. Grätzel, in *Photocatalysis—Fundamentals and Applications*, N. Serpone and E. Pelizzetti, eds., Wiley, New York, 1989. Copyright © 1989 John Wiley & Sons.]

Potential vs. energy (vs. vacuum)



Semiconductor particles

Grains
Nanocrystalline films
Quantum particles
(Q-particles or quantum dots)



I-V Curves in Fuel Cell, Battery, Solar Cell(Photoelectrochemical Cell)