15. Photoelectrochemistry (ch. 18)

1. Electrogenerated Chemiluminescence
2. Photoelectrochemistry at Semiconductors

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

Photoelectrochemistry

Radiation energy ⇐ electrical or chemical energy
e.g., ECL, electrochromic device, EL, sensors

General Concepts of luminescence

- **the type of excitation**

- Photoluminescence: light emission by UV or visible light
- Radioluminescence (scintillation): excited by radioactive substances
- Cathodoluminescence: excited by high velocity electron bombardment
- X-ray luminescence: by X-rays
- Chemiluminescence: by chemical reactions
- Electrochemiluminescence or electrogenerated chemiluminescence: by electrochemical reactions
- Electroluminescence: by electric voltage

- **Luminescent materials** (or luminophors): substances which exhibit luminescence

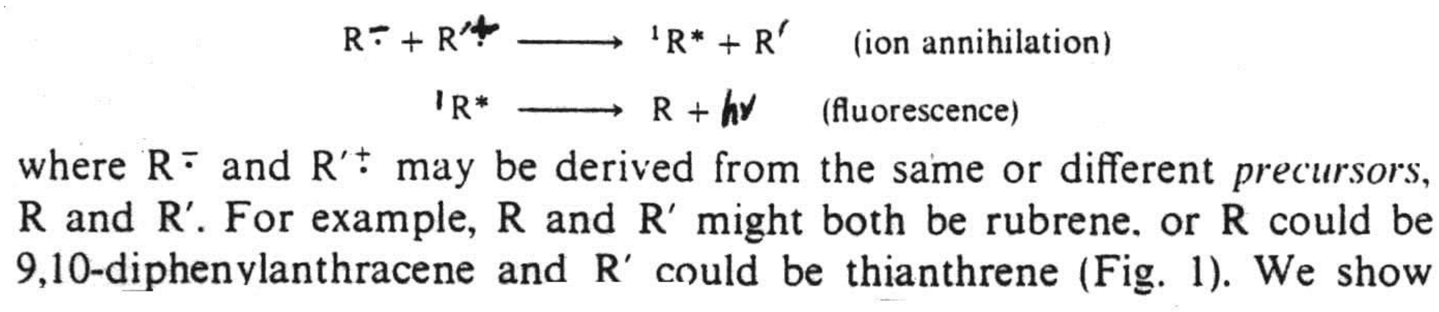
- organic (organoluminophors)
- inorganic (phosphors)

1. Electrochemiluminescence (or electrogenerated chemiluminescence, ECL)

- solution phase chemiluminescence resulting from electron transfer reactions, often involving aromatic radical ions

- general reaction mechanisms

- <u>S route</u>: “energy sufficient” (energy released by the electron transfer process is sufficient to raise a product to the emitting state)



$$R^{\cdot -} + R'^{\cdot +} \longrightarrow {}^1R^* + R' \qquad \text{(ion annihilation)}$$

$$ {}^1R^* \longrightarrow R + h\nu \qquad \text{(fluorescence)}$$

where $R^{\cdot -}$ and $R'^{\cdot +}$ may be derived from the same or different *precursors*, R and R′. For example, R and R′ might both be rubrene, or R could be 9,10-diphenylanthracene and R′ could be thianthrene (Fig. 1). We show

- <u>T route</u>: “energy deficient” (the energy available in electron transfer is substantially less than that required to reach the emitting state), triplet intermediates

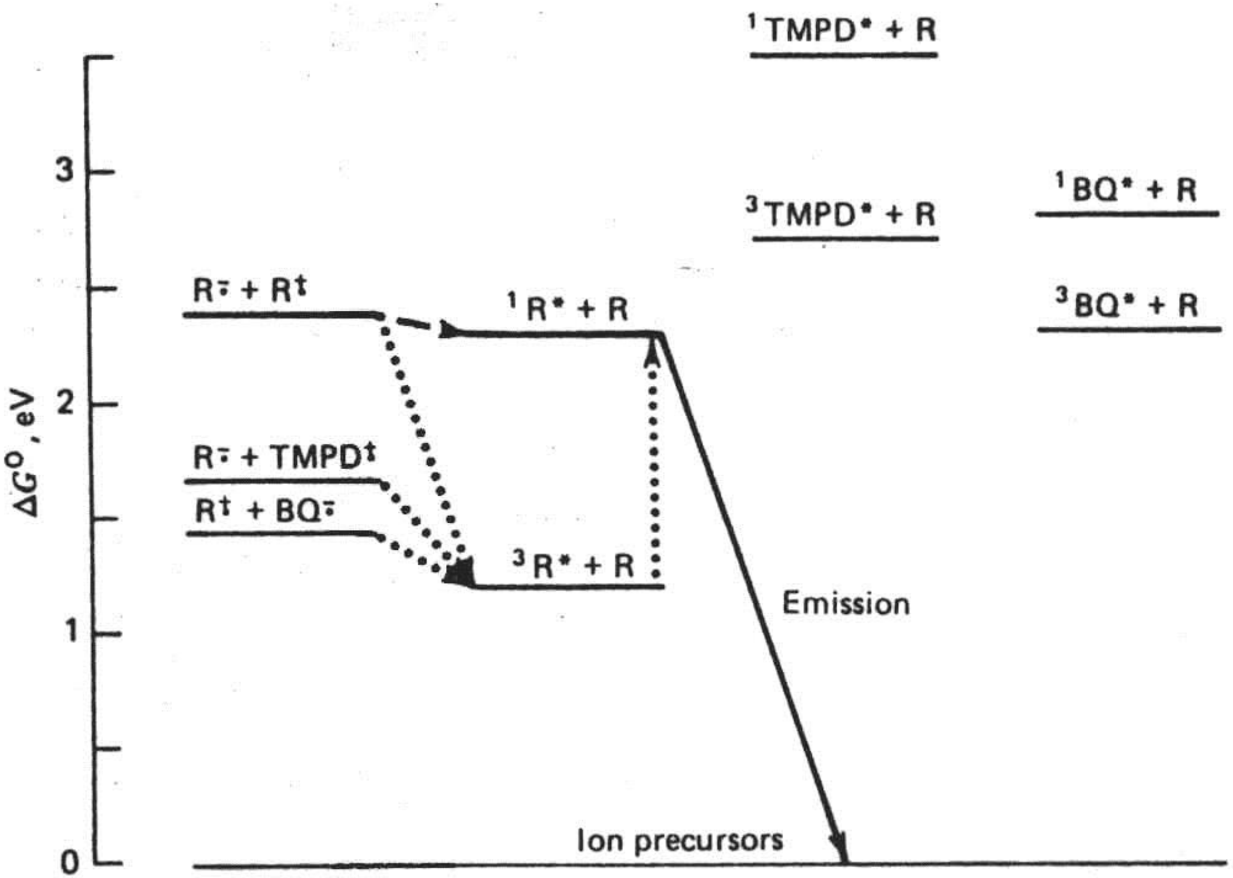
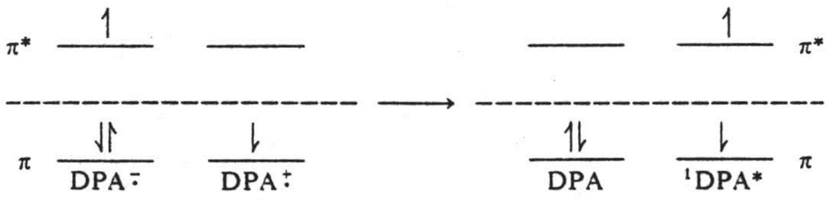


Figure 14.4.1

Energetics for chemiluminescent reactions of rubrene radical ions. All energies measured with respect to ground-state neutral species. Dashed arrow shows *S* route. Dotted arrows show *T* route. Promotion from ^{3}R* + R to ^{1}R* + R requires another rubrene triplet.



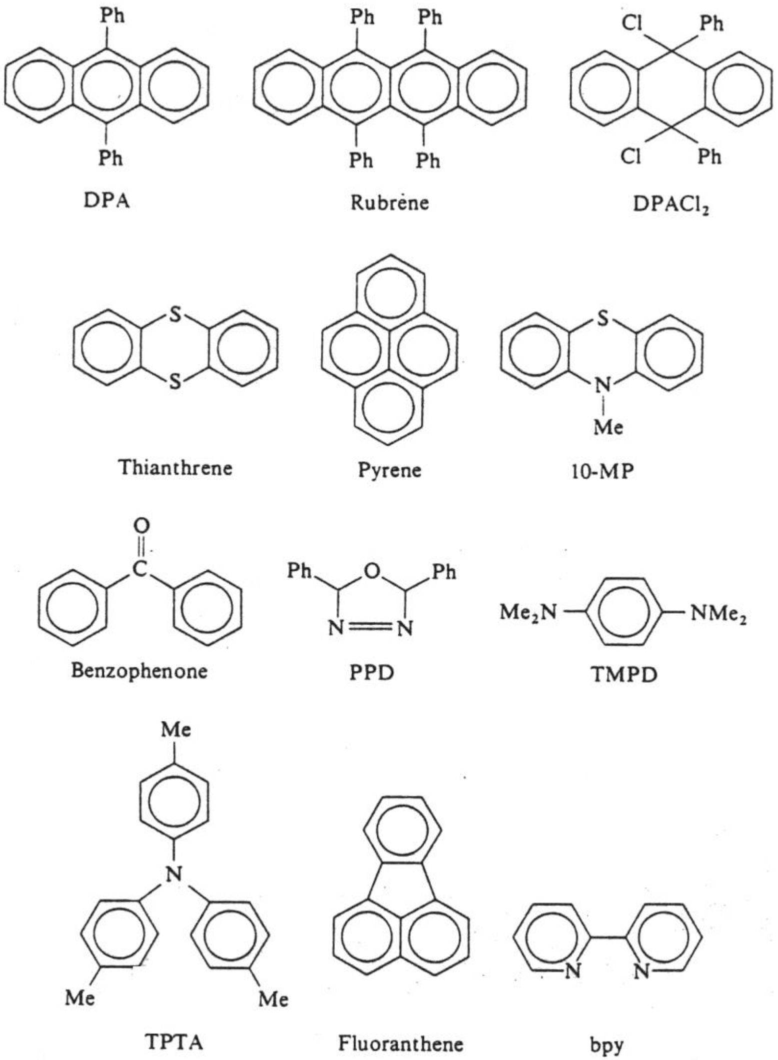


Fig. 1. Structures of compounds.

- experimental techniques

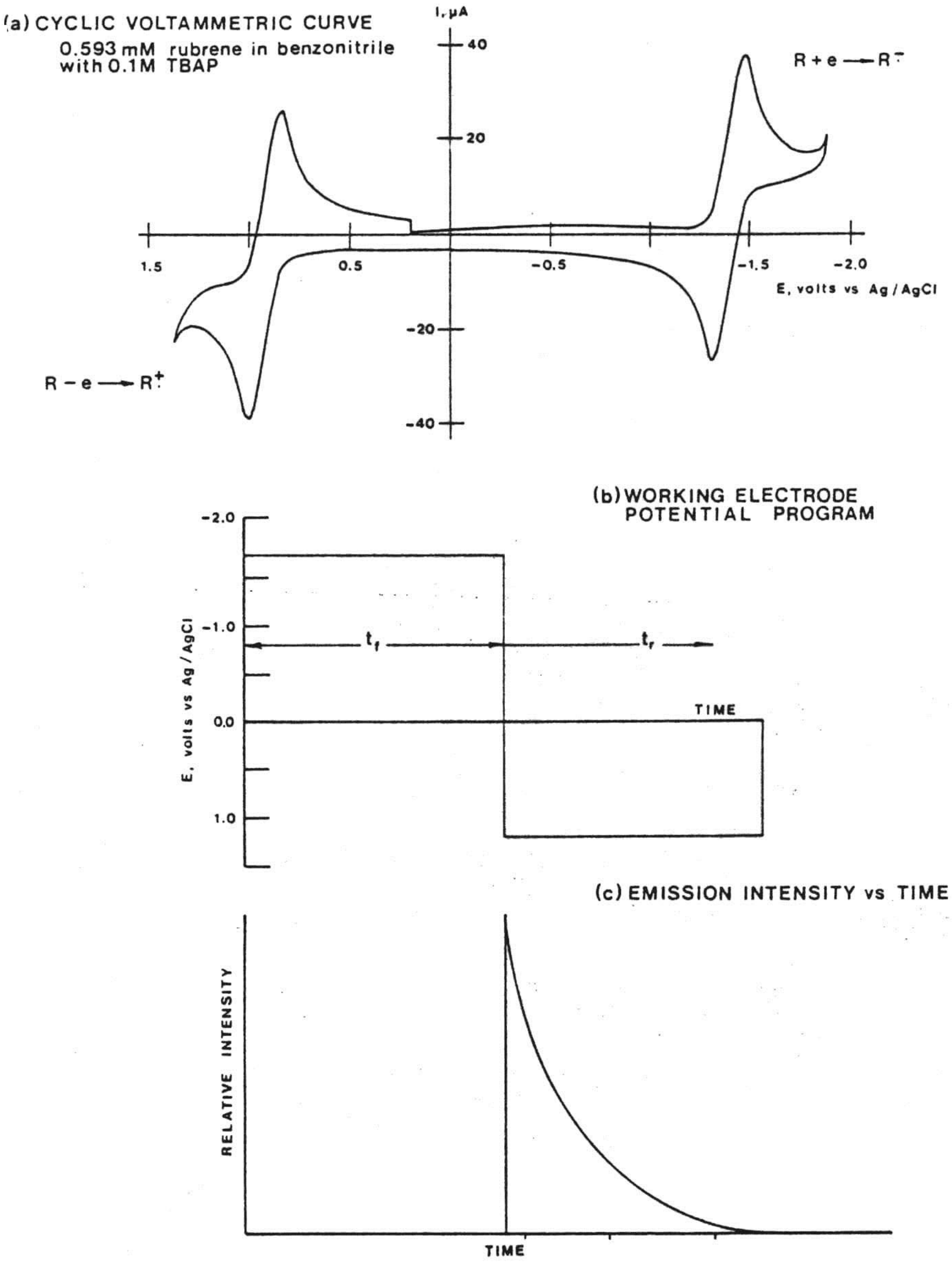
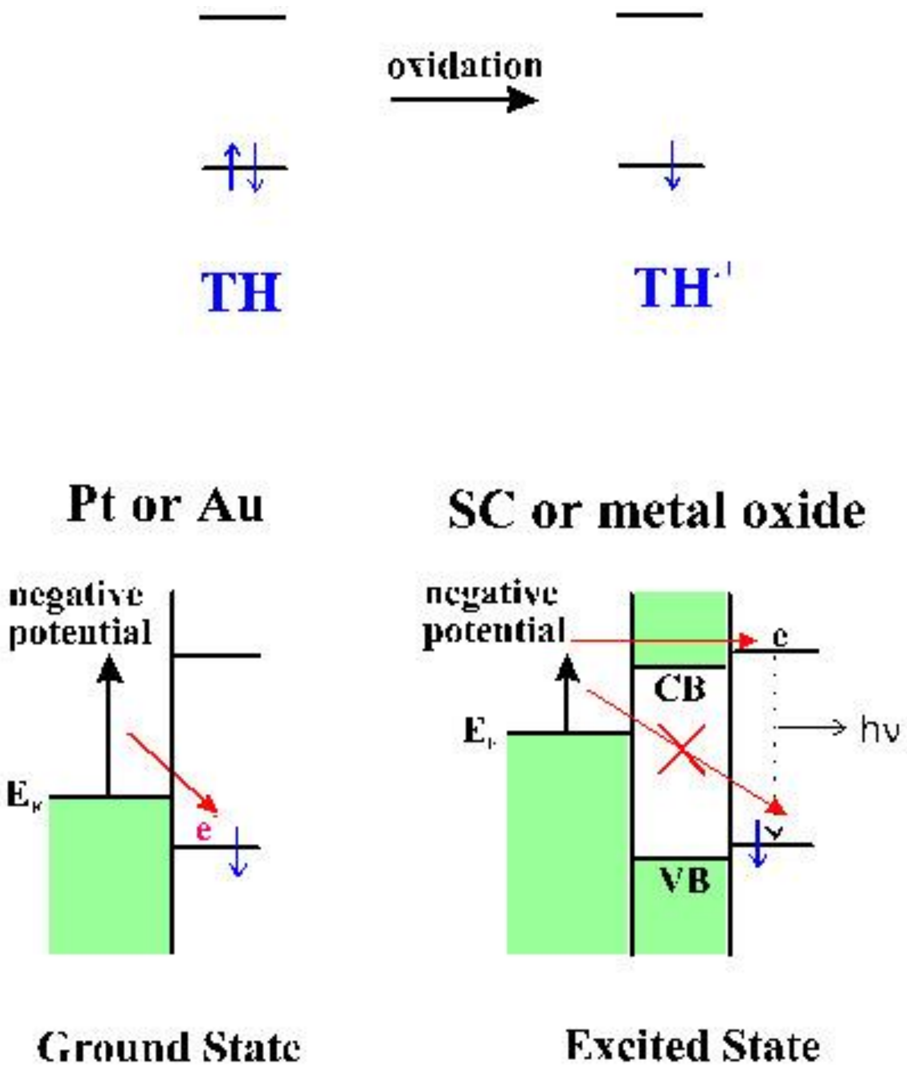
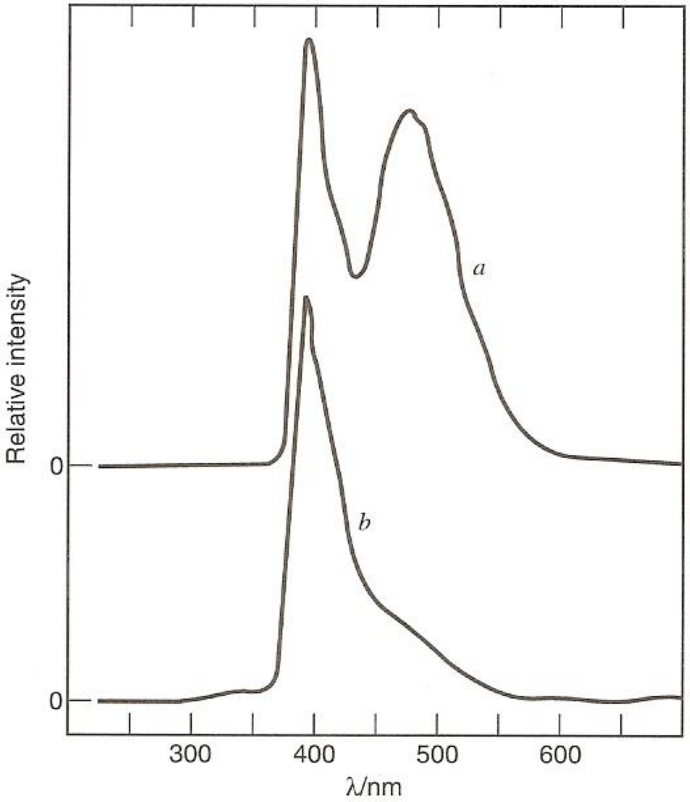


Fig. 3. The generation of ECL in a sequential step experiment. From Faulkner and Bard (1977), with permission from Marcel Dekker, Inc.

- ECL at semiconductors



ECL in Pyrene (Py) and TMPD solution: 400 nm & 450 nm

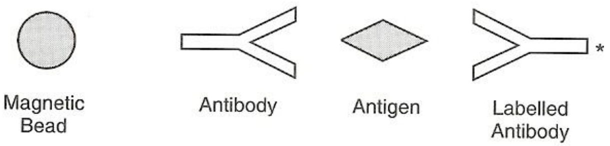


(a) ECL (b) Fluorescence (excitation at 350 nm)

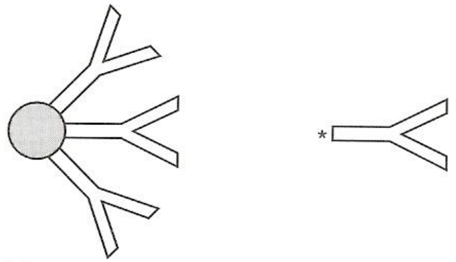
Analytical applications of ECL

Light intensity is proportional to concentration → analysis using ECL
-Very sensitive: very low light level
-No light source is needed: electrochemical excitation

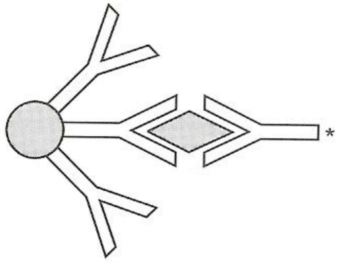
Most frequently used ECL-active label: $Ru(bpy)_3^{2+}$

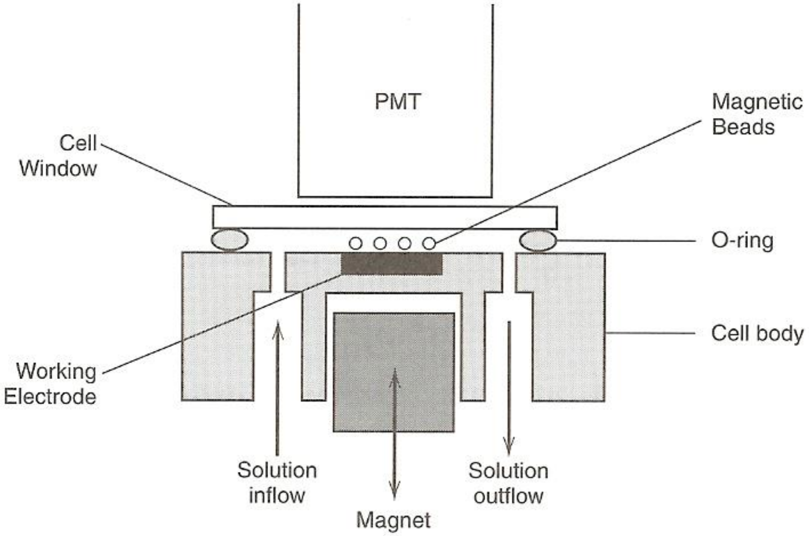


(*a*) Sample with no antigen (labelled antibody not attached to bead)

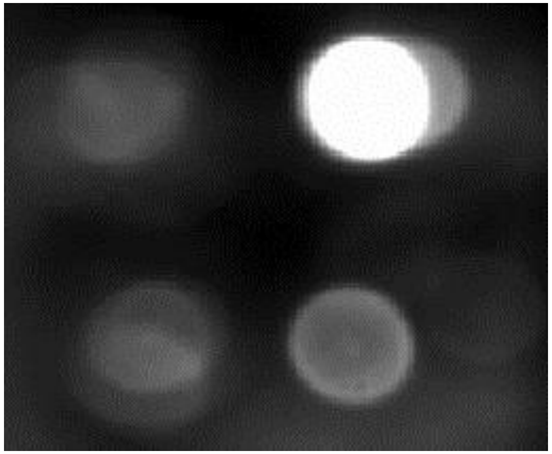


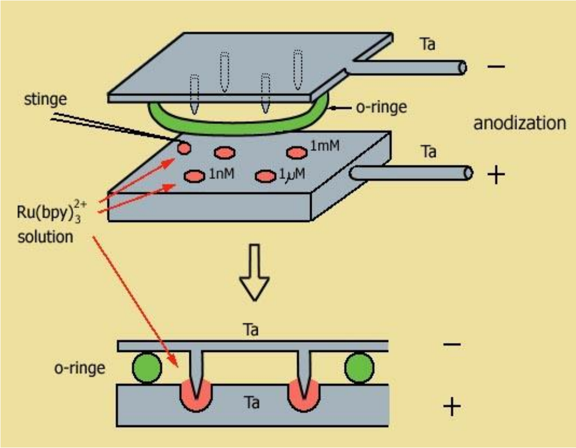
(*b*) Sample with antigen (labelled antibody attaches to bead)

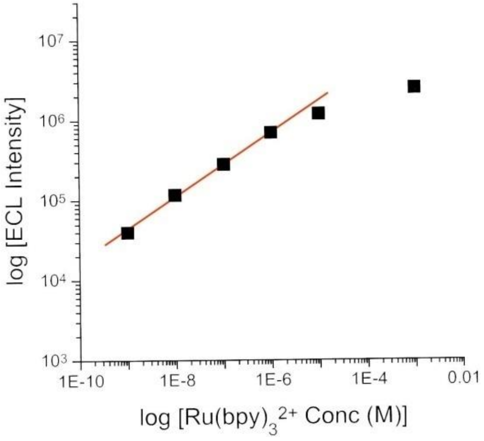




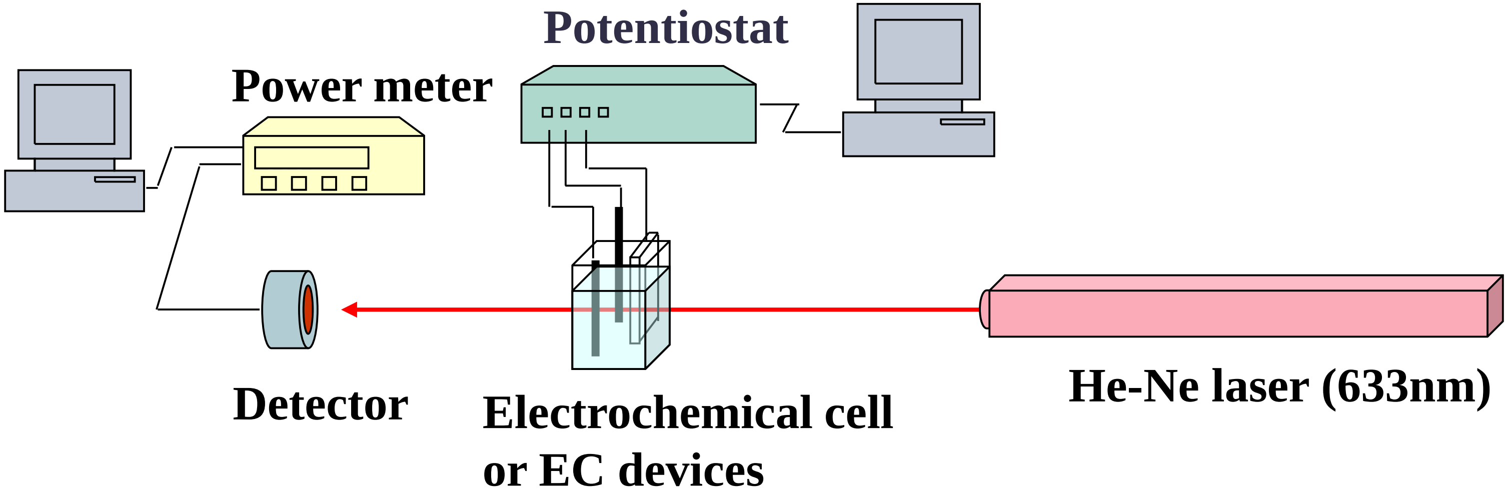
Electro(chemi)luminescent Devices







In-situ transmittance test



Potentiostat

Power meter

Detector

Electrochemical cell
or EC devices

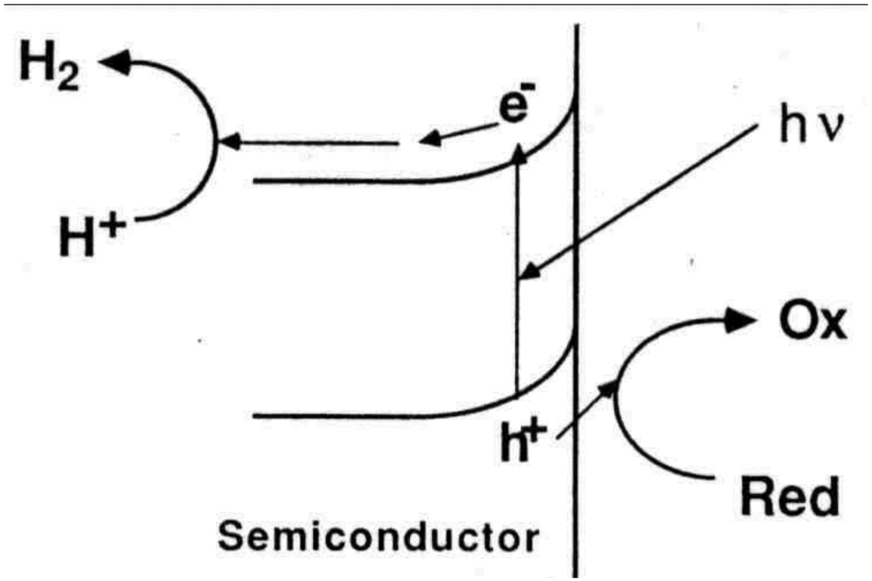
He-Ne laser (633nm)

2. 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)

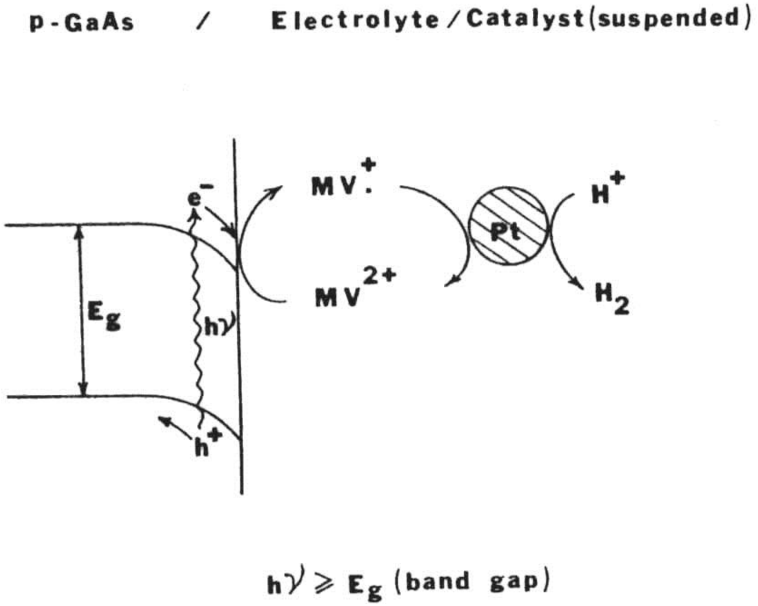


- Hydrogen fuel production (H^+ or H_2O reduction): i) kinetically difficult → catalyst, ii) recombining electrons and holes and lowering the efficiency of the photoreaction unless rapid chemical reaction

$$2H^+ + Red \rightarrow H_2 + Ox$$

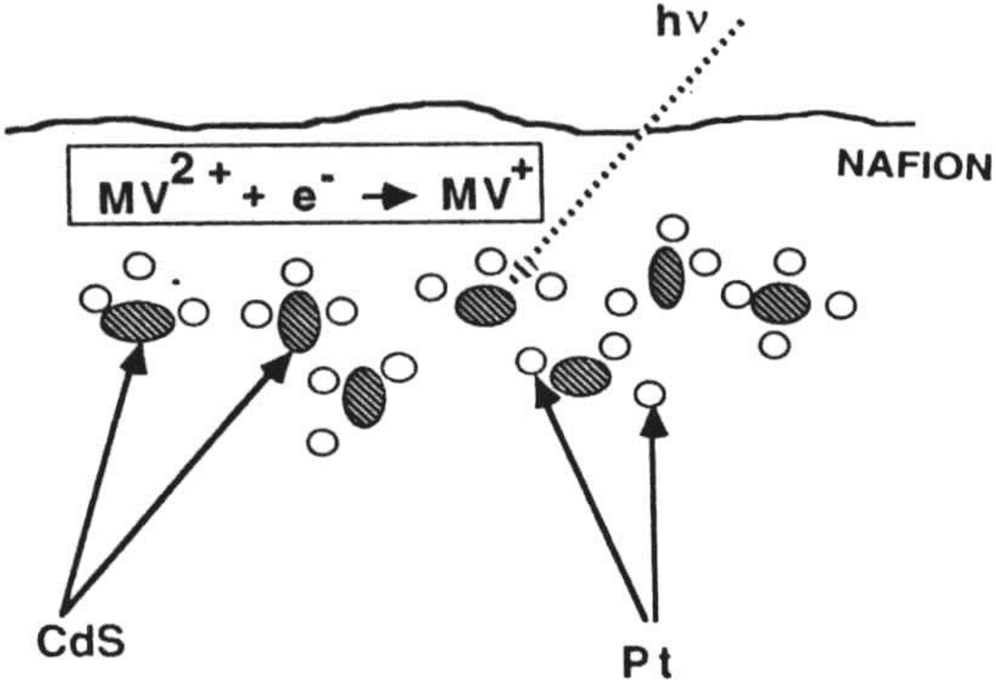
Red: sacrificial (electron) donor

e.g., Photoproduction of H_2 on p-GaAs with methyl viologen & colloidal Pt (*J. Am. Chem. Soc*., 102, 1488 (1980))

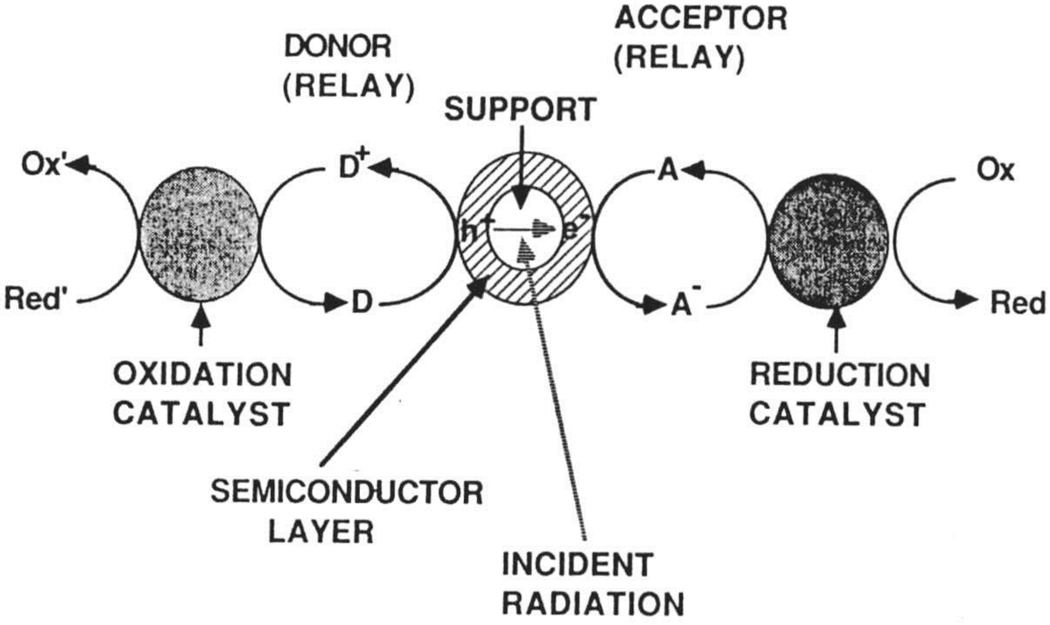


Very slow H_2 photoreaction on GaAs (high hydrogen overpotential) → fast reaction of $MV^{2+/1+}$ + Pt (fast hydrogen evolution) → viologen + polymer/self assembly etc

e.g., CdS particles in Nafion



- General photoelectrochemical system for conversion of solar energy(sunlight) to useful chemical products



$$\text{Ox} + \text{Red}' + h\nu \rightarrow \text{Red} + \text{Ox}'$$

e.g., $H_2O \rightarrow 2H_2 + O_2$ or H_2, Cl_2, OH^- from NaCl solution

TABLE 6.1.1. Representative Half-Reactions of Interest in Photoelectrochemistry

Reductions			Oxidations		
Ox	Red	Application	Red′	Ox′	Application
H^+	H_2	Fuel generation	Cl^-	Cl_2	Disinfection
CO_2	CH_4	Fuel generation	Br^-	Br_2	Energy storage
Cu^{2+}	Cu	Metal removal	Organic	CO_2	Wastewater treatment
Ag^+	Ag	Metal recovery	CN^-	CNO^-	Wastewater treatment
Pt(IV)	Pt	Catalyst preparation	H_2O	O_2	Inexpensive reductant
O_2	H_2O_2	Synthesis	$CH_3CO_2^-$	CO_2, $CH_3\cdot$	Synthesis

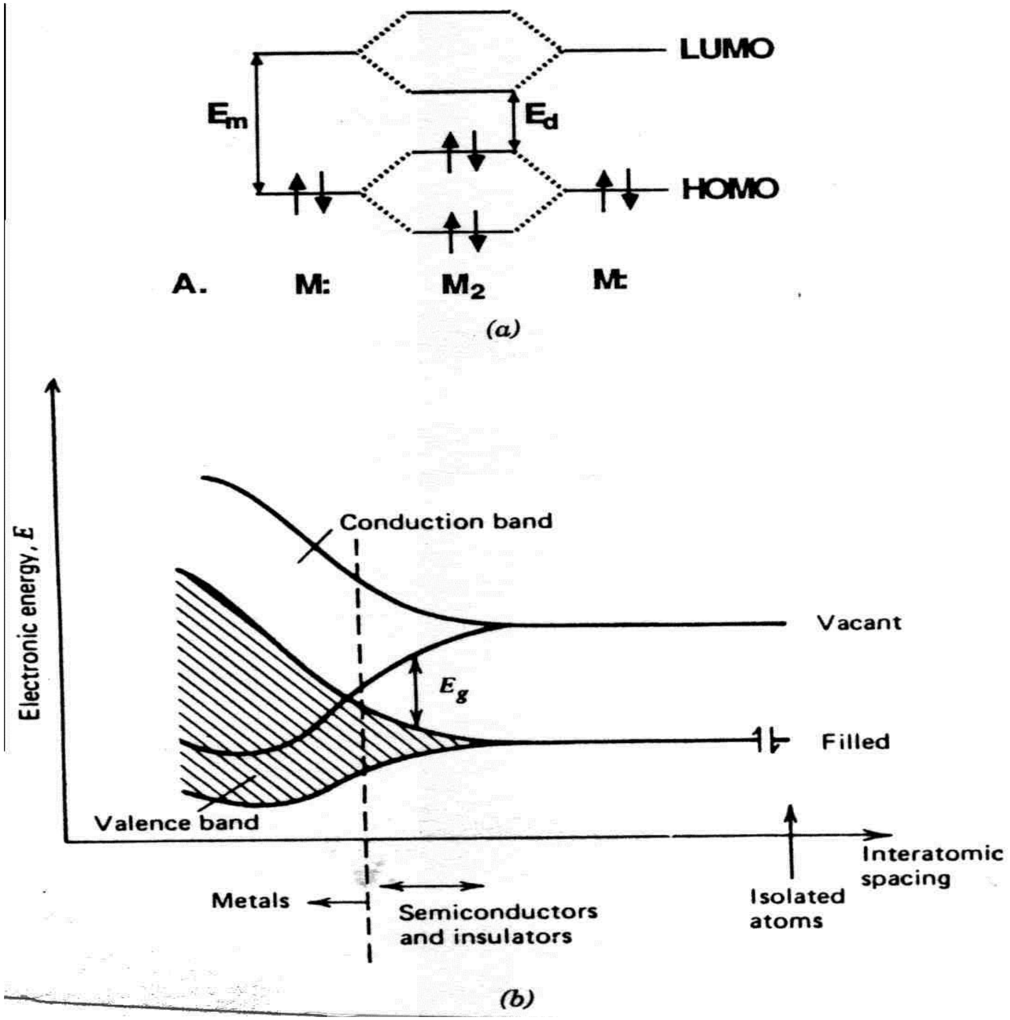
- Energy transduction step

1) adsorption of a photon of incident light & conversion to an electron-hole pair (e^-h^+)

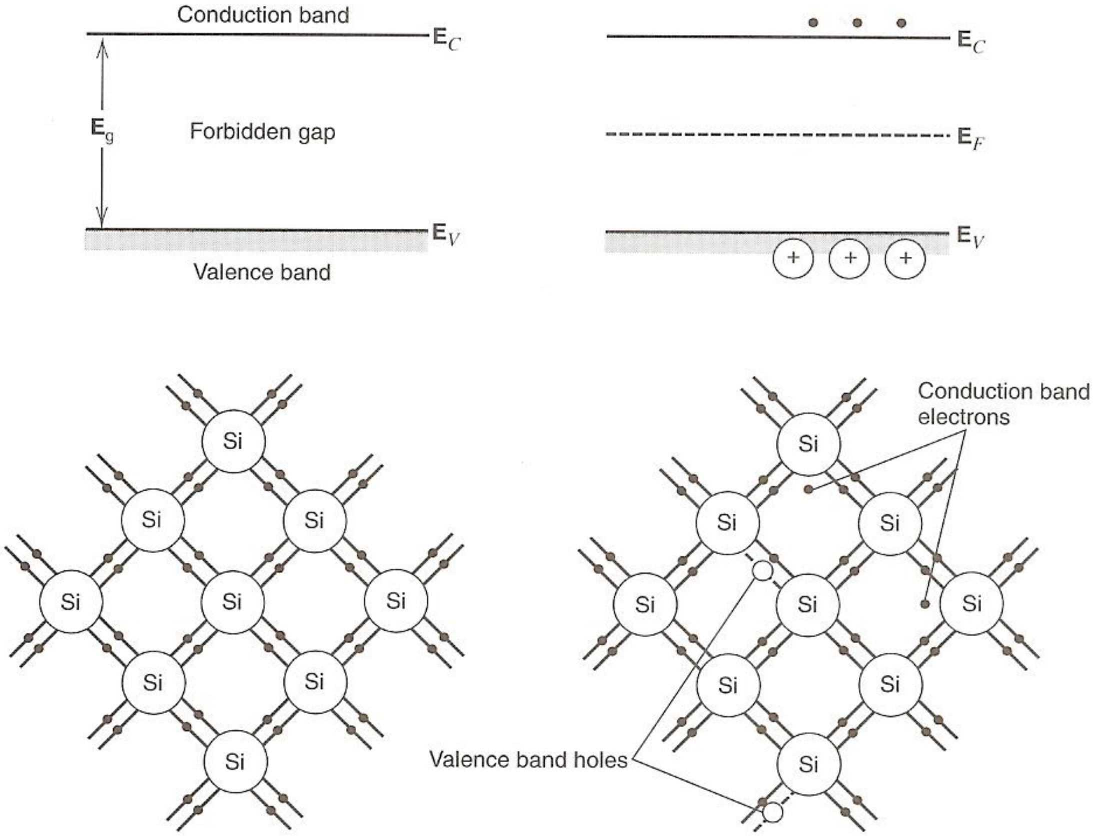
2) electron & hole react with relays or mediators (serve the role of capturing e^- & h^+ , thereby preventing the backreaction (recombination of e^- & h^+ to produce heat))

3) conducting these charges to catalyst centers where the final reactions occur

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

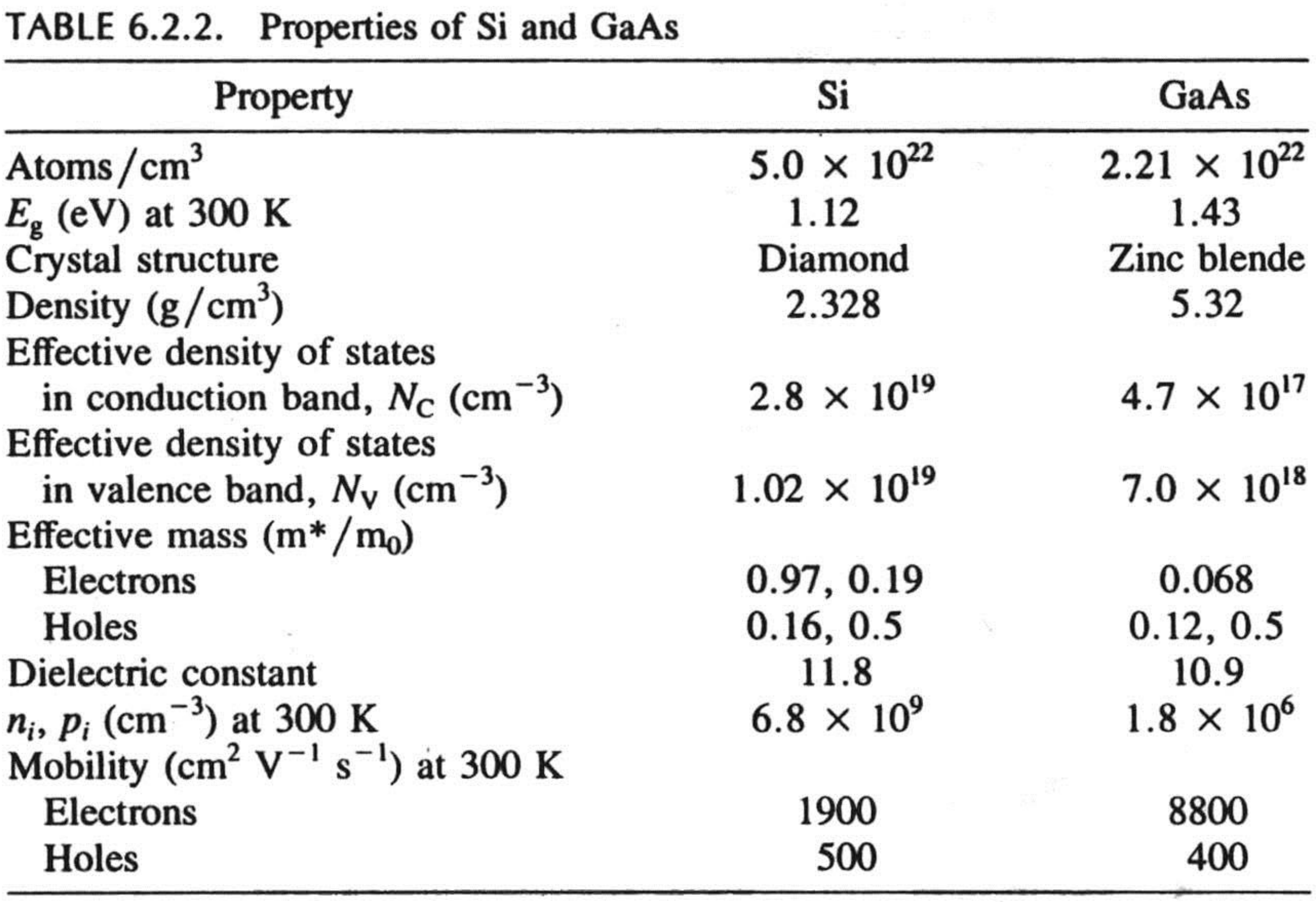


TABLE 6.2.2. Properties of Si and GaAs

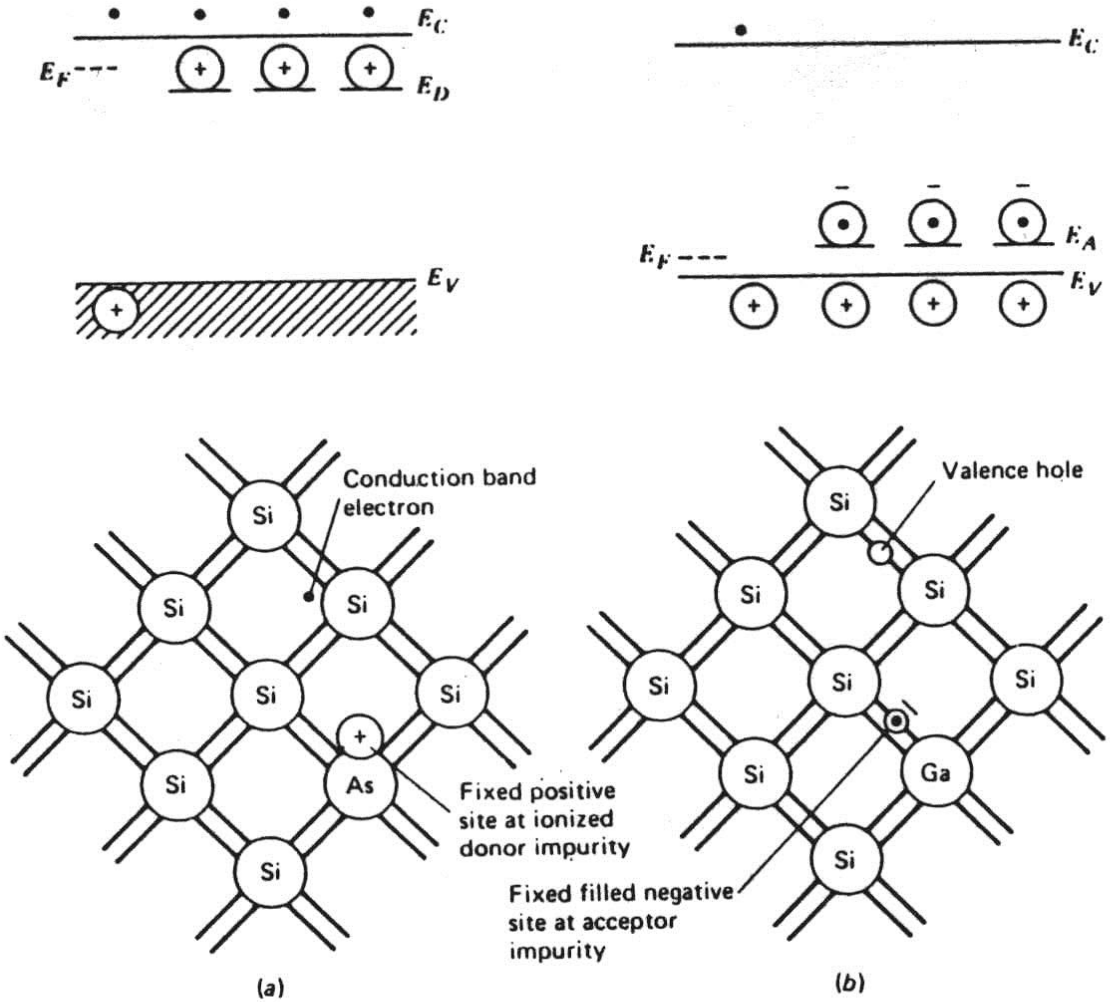
Property	Si	GaAs
Atoms/cm^3	5.0×10^{22}	2.21×10^{22}
E_g (eV) at 300 K	1.12	1.43
Crystal structure	Diamond	Zinc blende
Density (g/cm^3)	2.328	5.32
Effective density of states in conduction band, N_C (cm^{-3})	2.8×10^{19}	4.7×10^{17}
Effective density of states in valence band, N_V (cm^{-3})	1.02×10^{19}	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}

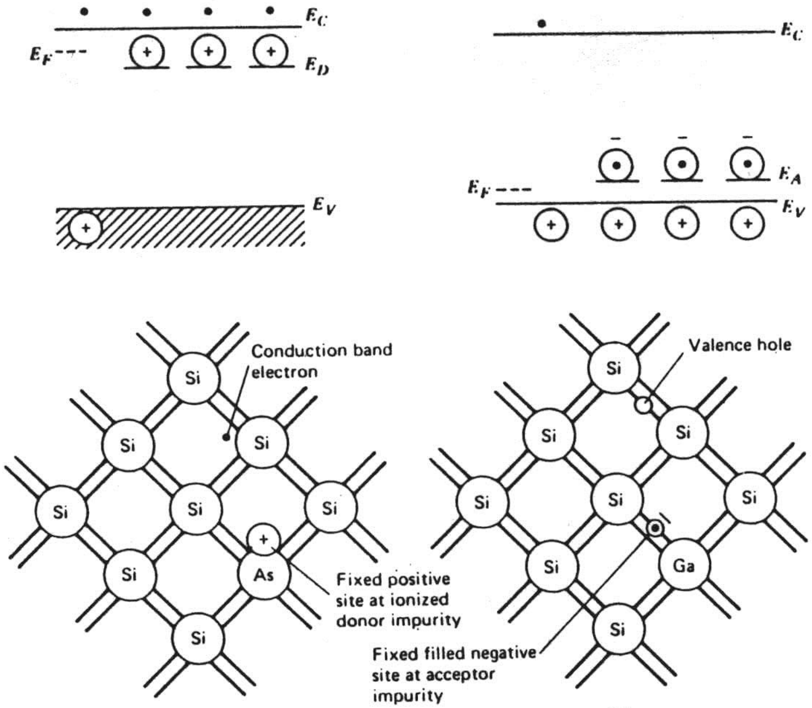


n-type

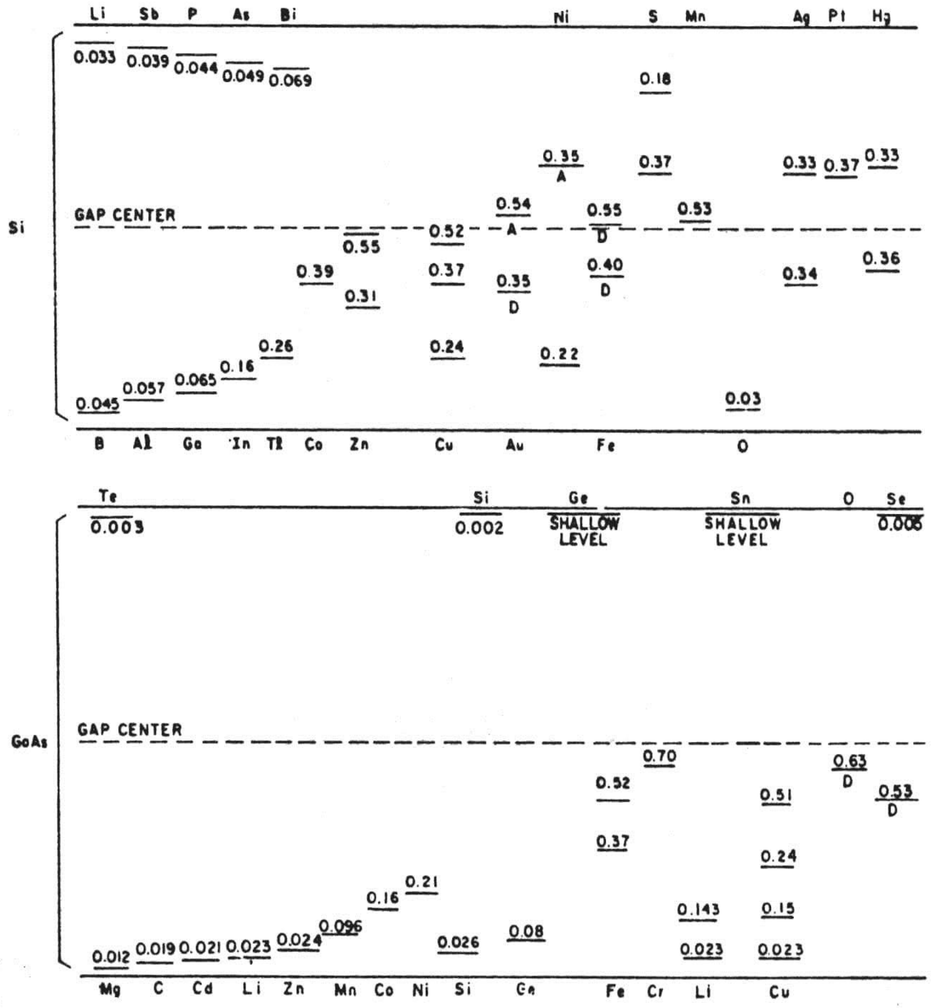
p-type

- Extrinsic semiconductors; doped

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



(a) (b)



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 $\sim 10^{17}$ 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

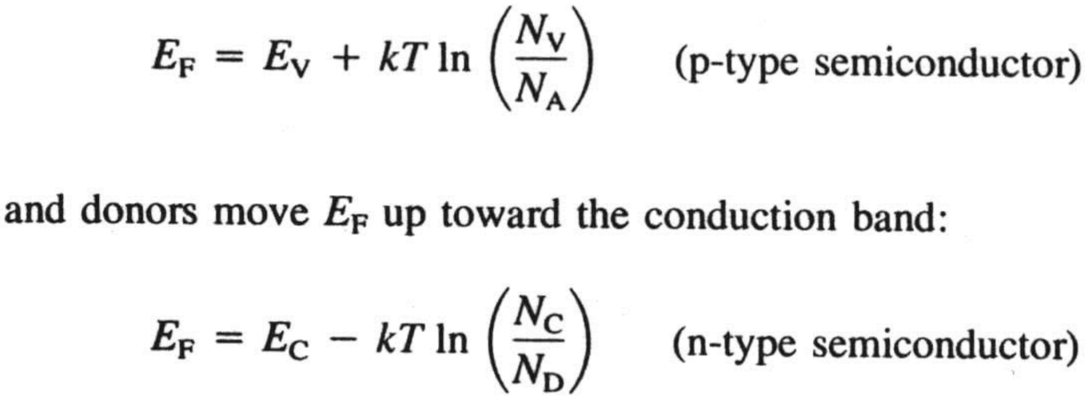
$$n = n_i^2/N_A$$

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 ~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 $N_D < N_C$, $N_A < N_V$ → SC
- if higher doping levels; Fermi level moves into VB or CB ⇒ show metallic conductivity

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

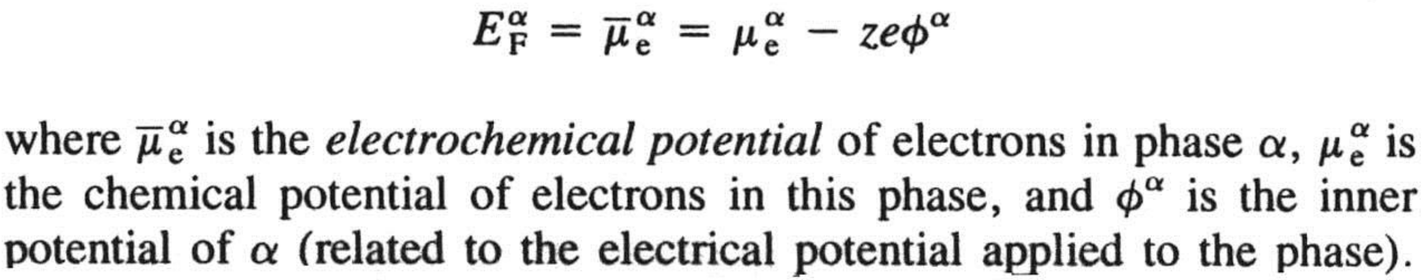
Fermi level

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

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

- 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"



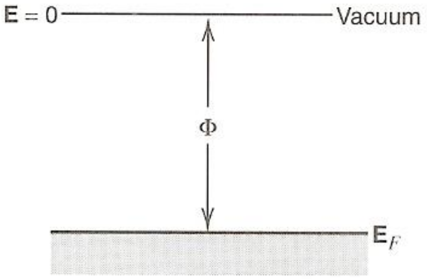
$$E_F^\alpha = \overline{\mu}_e^\alpha = \mu_e^\alpha - ze\phi^\alpha$$

where $\overline{\mu}_e^\alpha$ 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).

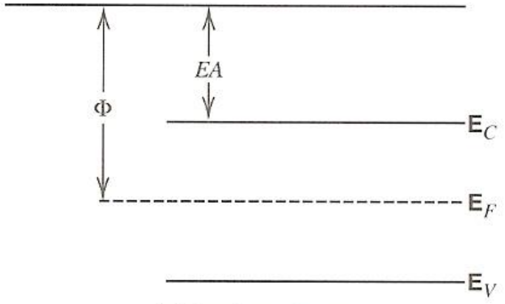
- useful in thermodynamic considerations of reactions and interfaces; at equilibrium electrically, the electrochemical potential of electrons in all phases must be same by charge transfer → same Fermi level
- Fermi levels difference between two phases; function of the applied potential

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

$$\Phi = -E_F$$



(*a*) Metal



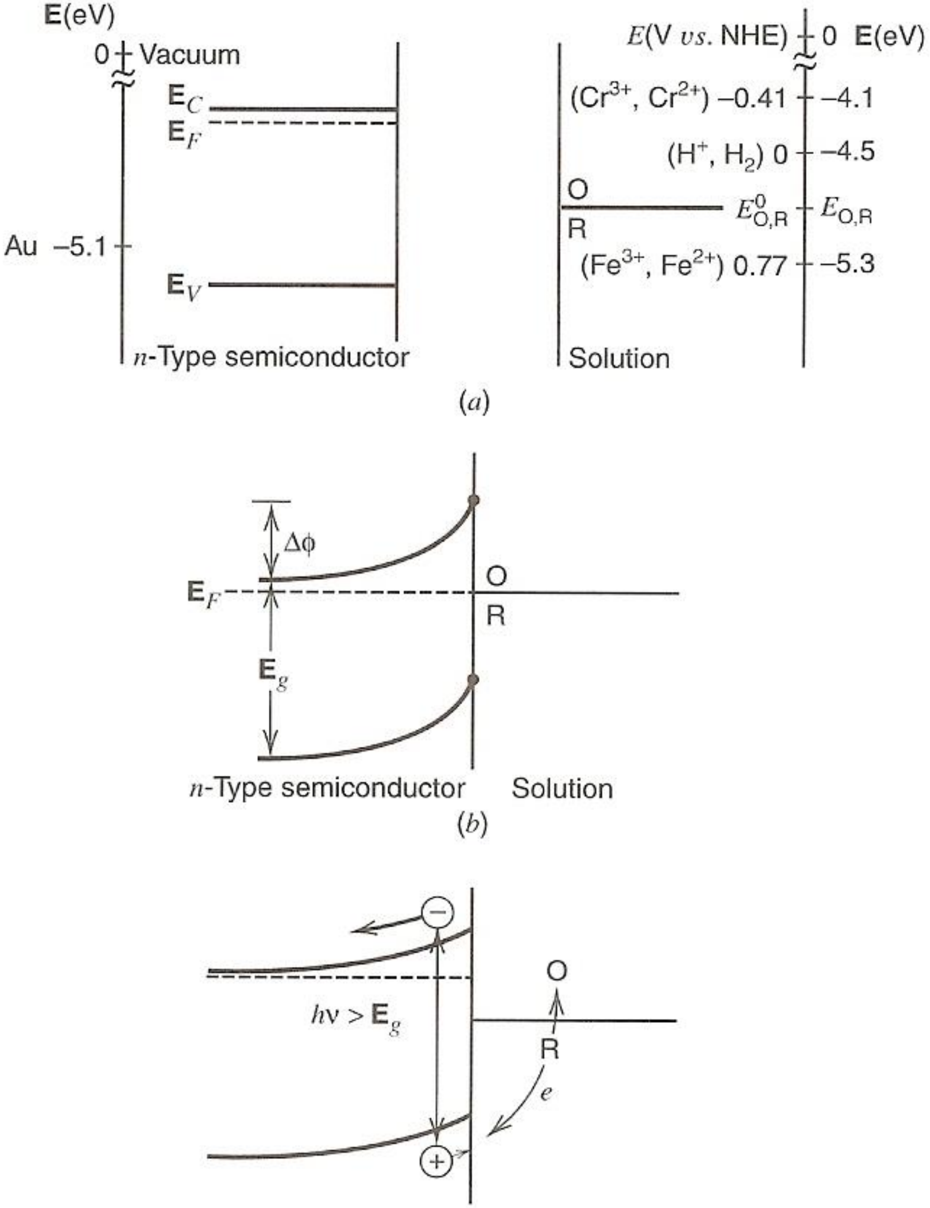
(*b*) Semiconductor

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 " flat band potential" (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)
(Cr3+, Cr2+) −0.41 −4.1
(H+, H2) 0 −4.5
O
R
E0O,R EO,R
(Fe3+, Fe2+) 0.77 −5.3
Solution
Δφ
E_F
O
R
E_g
n-Type semiconductor
Solution
hν > E_g
O
R
e

(*a*)

(*b*)

(*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

- band bending: 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 μF/cm^2, N_D in cm^{-3}, and $\Delta\phi = E_{fb} - E$ in volts is

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

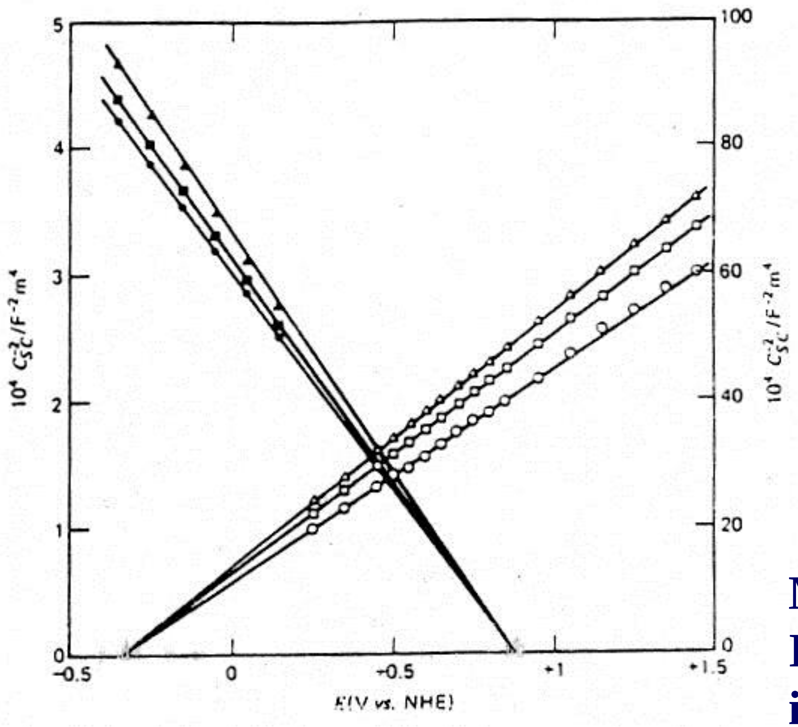
Mott-Schottky plot: useful in characterizing SC/liquid interface where a plot of $(1/C_{SC}^2)$ vs. E should be linear → values of E_{fb} and N_D from the intercept and slope

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

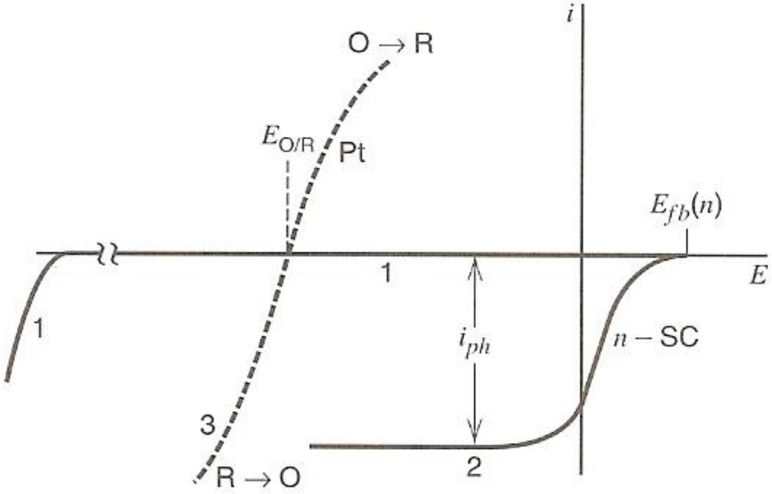


Mott-Schottky plots for n- and p-type InP
in 1 M KCl + 0.01 M HCl

Photoeffects at semiconductor electrodes

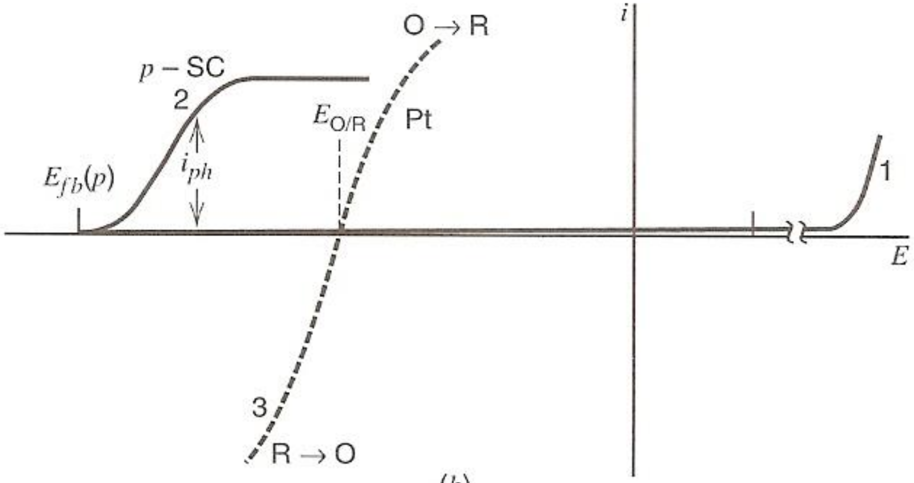
1: dark
2: irradiation
3: Pt electrode

n-type



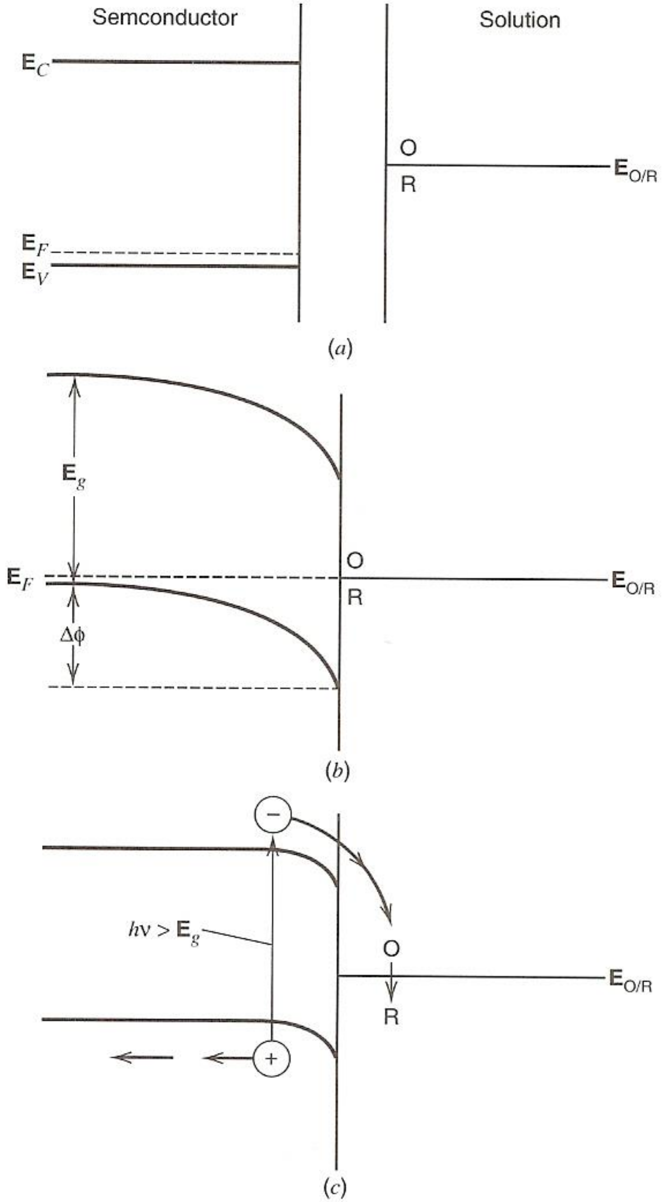
(a)

p-type



(b)

p-type

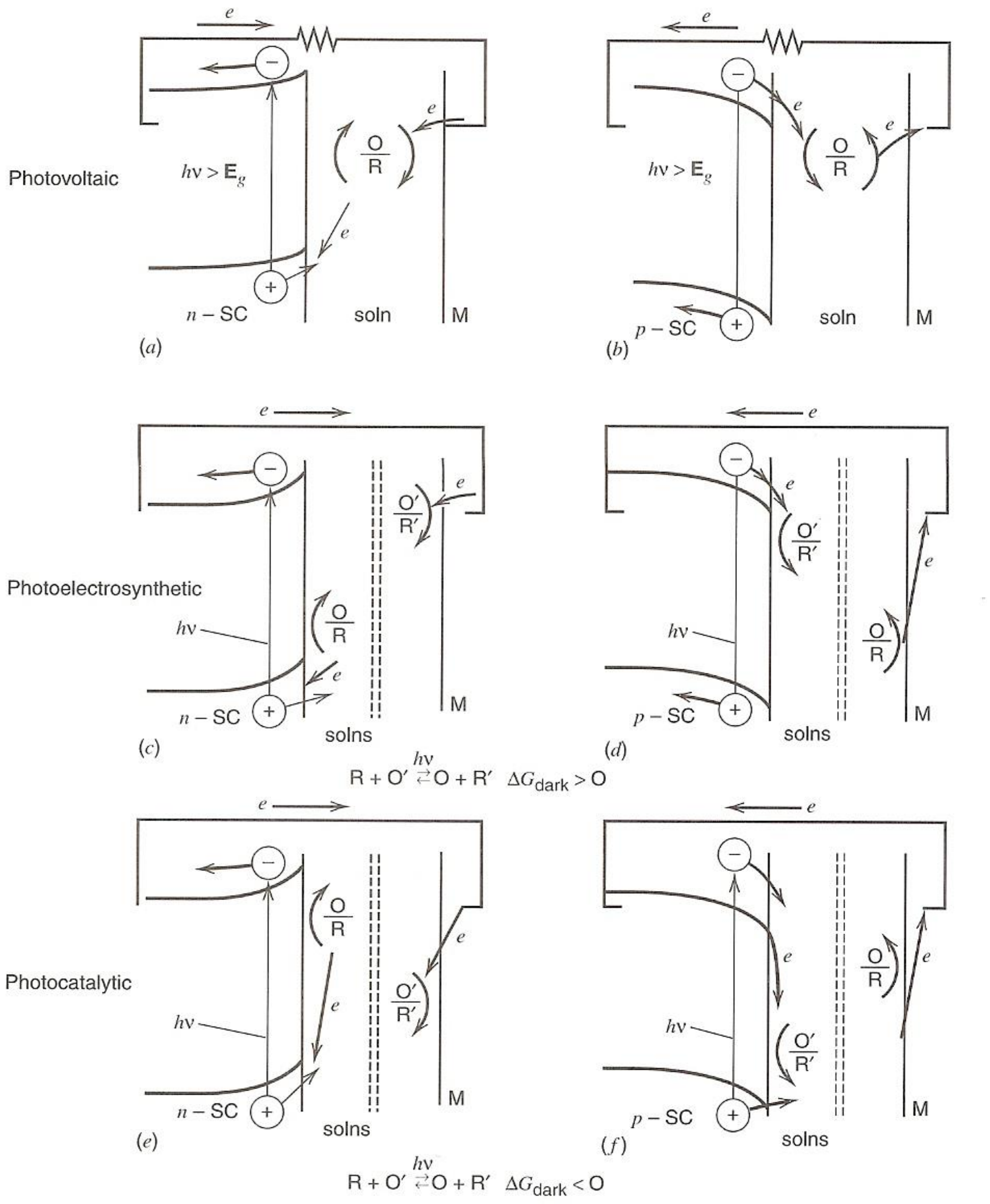

Semconductor
Solution
E_C
O
R
$E_{O/R}$
E_F
E_V
(a)
E_g
E_F
O
R
$E_{O/R}$
$\Delta\phi$
(b)
−
$h\nu > E_g$
O
R
$E_{O/R}$
+
(c)

Photoelectrochemical cells

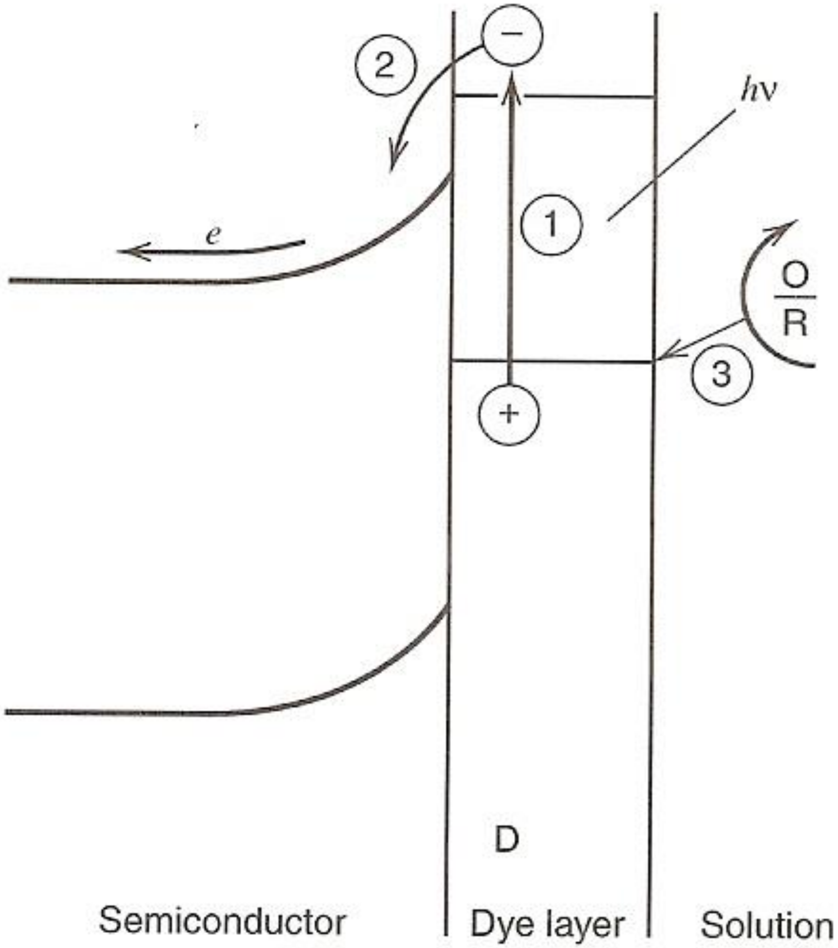
Photovoltaic cells:
convert light to electricity

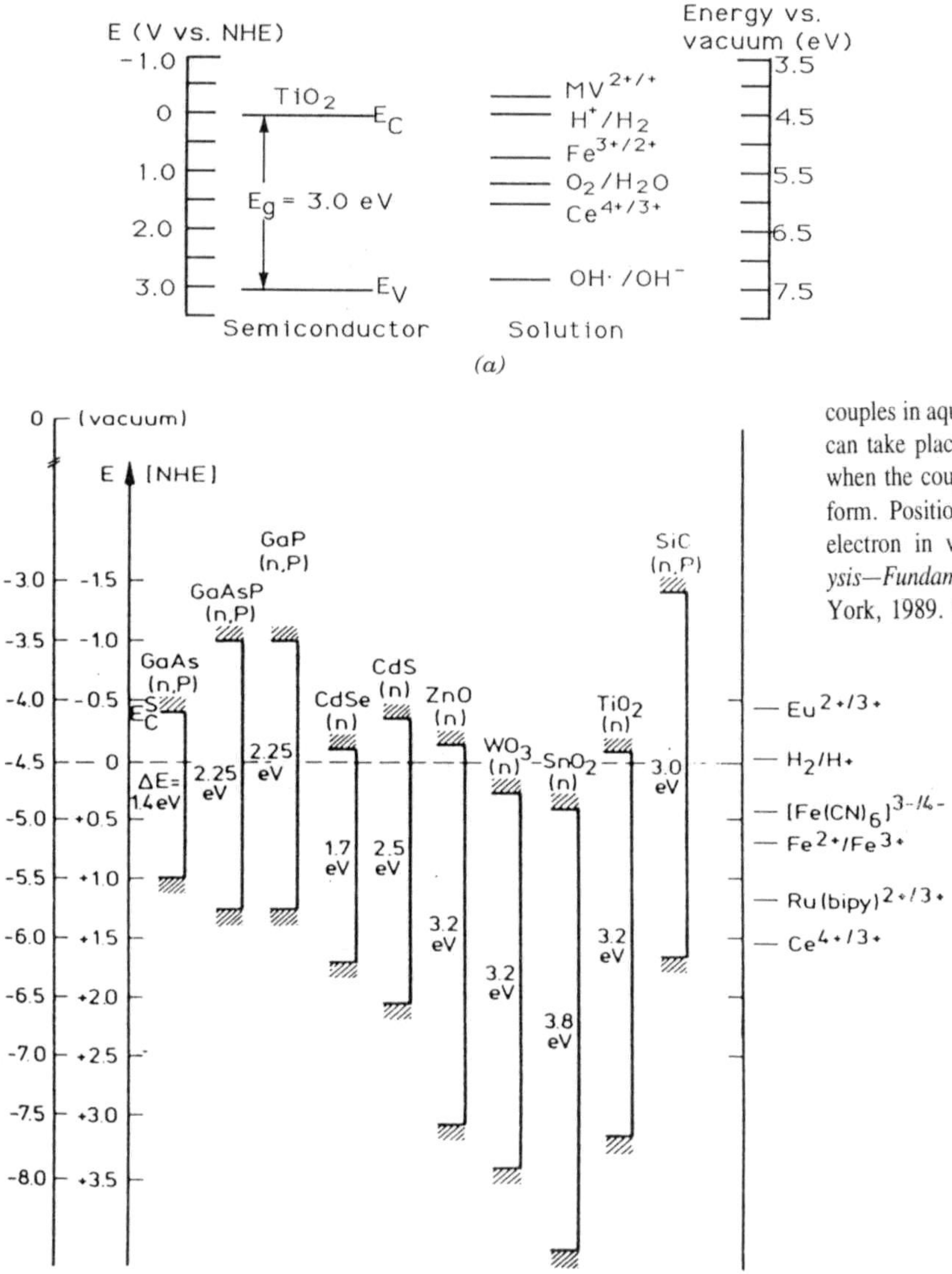
Photoelectrosynthetic cells:
Radiant E to chemical energy

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



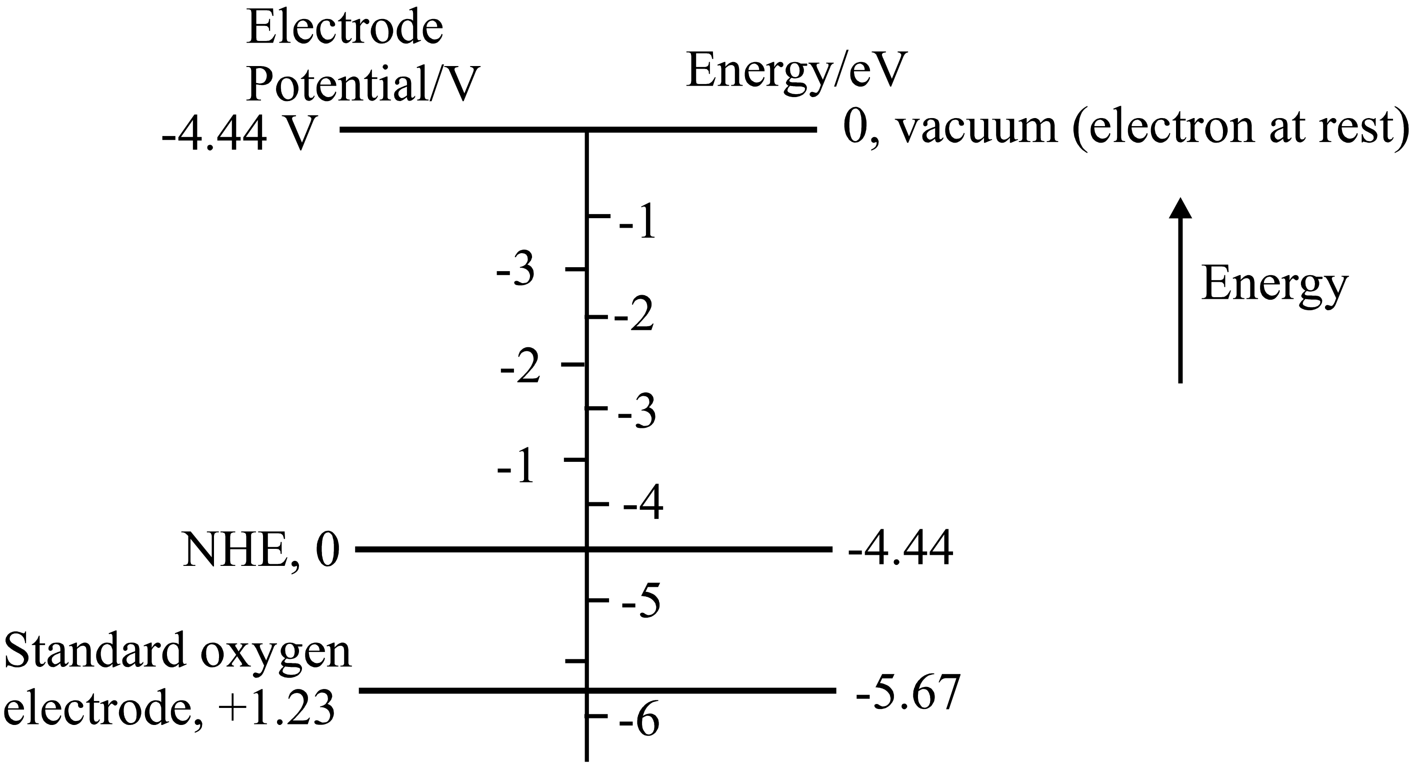


(a)

(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)



Photoelectrochemical photovoltaic cells

- basic idea

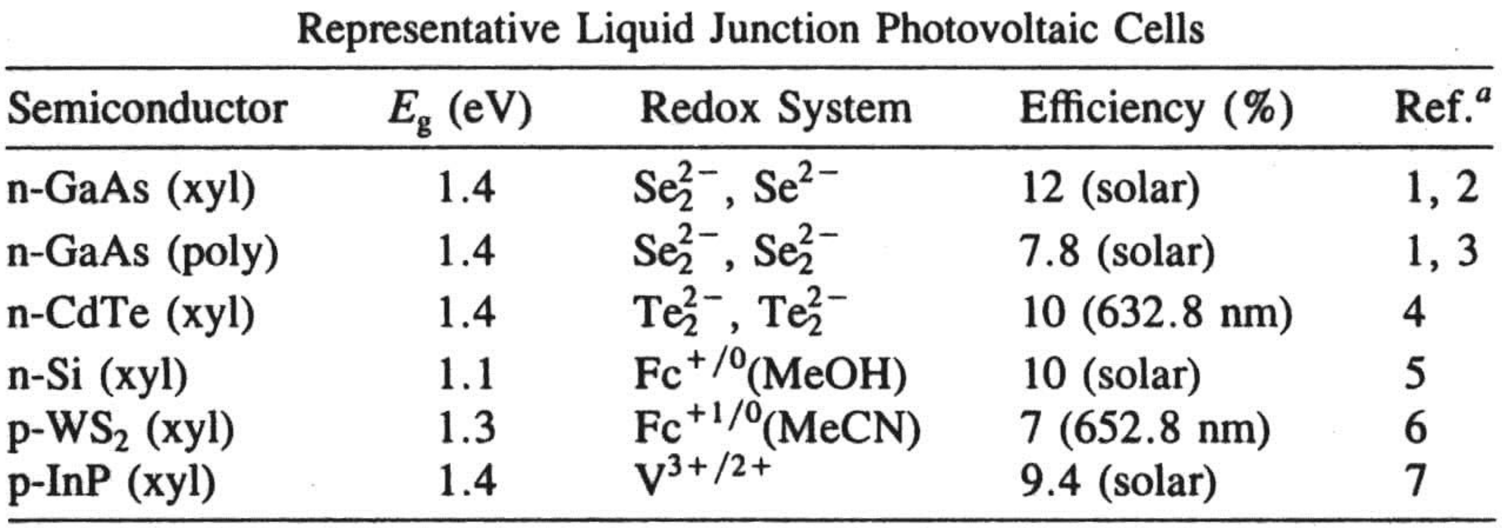
- SC & counter electrodes in the same solution containing the redox couple D/D^+

- no net chemical reaction occurs in the solution during irradiation; hole oxidize D to D^+ & electrons reduce D^+ to D

- net effect: conversion of the radiant energy to electrical energy (h^+ and e^-) in the external circuit connecting the two electrodes

- Conversion efficiency depends on the quantum efficiency of the carrier generation, the rates of interfacial electron transfer, the rate of carrier recombination, internal cell resistance

- Photoelectrochemical photovoltaic cells

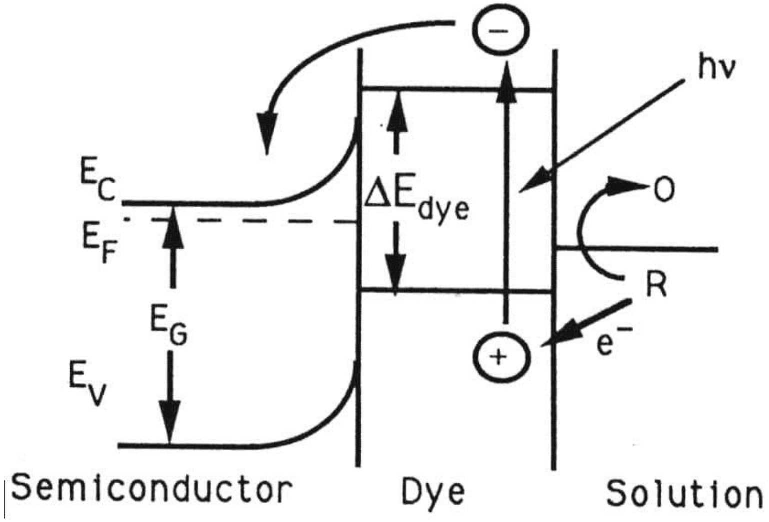


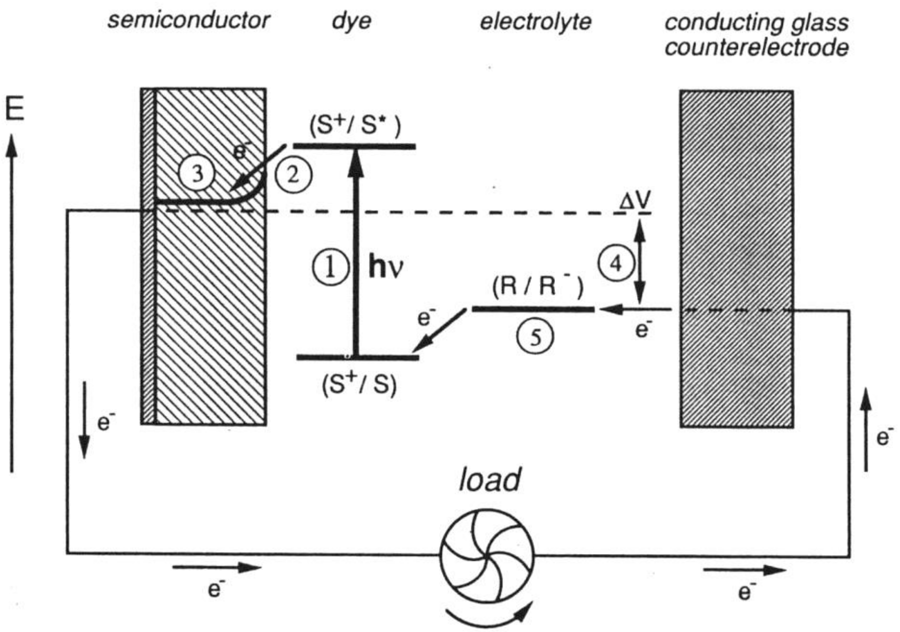
Representative Liquid Junction Photovoltaic Cells

Semiconductor	E_g (eV)	Redox System	Efficiency (%)	Ref.[a]
n-GaAs (xyl)	1.4	Se_2^{2-}, Se^{2-}	12 (solar)	1, 2
n-GaAs (poly)	1.4	Se_2^{2-}, Se_2^{2-}	7.8 (solar)	1, 3
n-CdTe (xyl)	1.4	Te_2^{2-}, Te_2^{2-}	10 (632.8 nm)	4
n-Si (xyl)	1.1	$Fc^{+/0}$(MeOH)	10 (solar)	5
p-WS_2 (xyl)	1.3	$Fc^{+1/0}$(MeCN)	7 (652.8 nm)	6
p-InP (xyl)	1.4	$V^{3+/2+}$	9.4 (solar)	7

- photoactive dyes adsorbed or covalently attached to the electrode surface

- to sensitize the electrode to visible light and produce photocurrents under irradiation with light of smaller energy than that corrsponding to the SC band gap
- principle: absorption of light in the dye layer (smaller energy than SC band gap) → injection of electrons to CB of SC; hole in dye filled by electron transfer from solution species (R to O)





Dye sensitization of semiconductor electrode. (*A*) Principles. (*B*) Schematic representation of TiO_2/dye/I^-, I_2/ITO cell (see text) (ΔV corresponds to the open-circuit photovoltage developed in the cell; S, dye sensitizer; S*, electronically excited sensitizer; S^+, oxidized sensitizer; R, iodine; R^-, iodide). [Reprinted, with permission from *Nature*, from B. O'Regan and M. Grätzel, *Nature*, **353,** 737 (1991). Copyright 1991 Macmillam Magazines Limited.]

e.g., liquid junction photovoltaic cell
dye sensitized SC: TiO_2

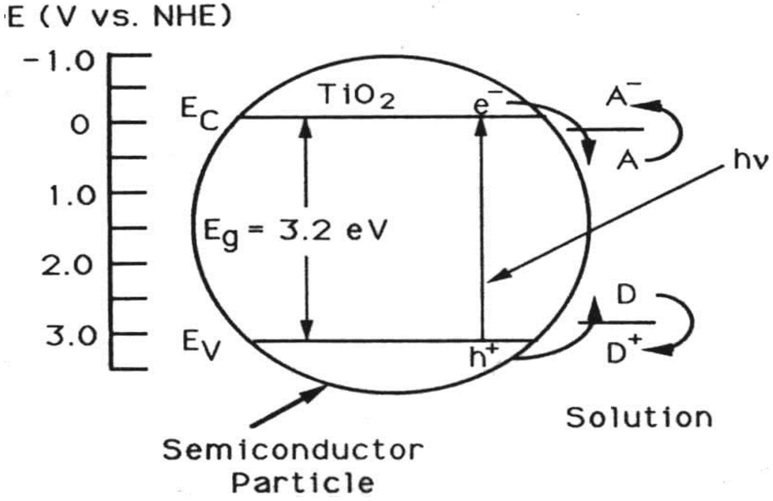
Particulate SC systems

e.g., solar energy to produce fuels or to remove pollutants from water

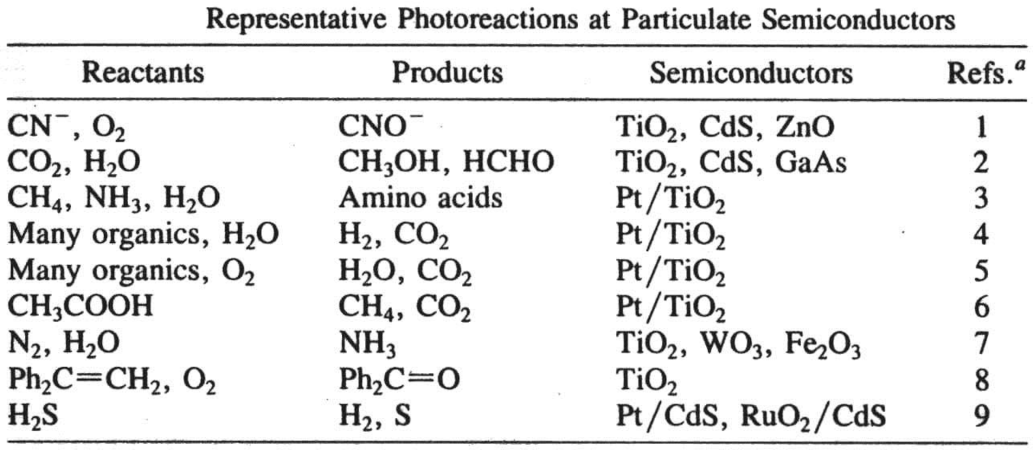
• principles

- behave as microelectrode: carry out both anodic and cathodic half-reactions at different sites on the particle surface

e.g., TiO_2 particle: CN^- oxidation by O_2 (CN^- oxidation + O_2 reduction) by e^-h^+ pair



-particle dimensions < space charge layer ; charge separation by electric charge does not play a major role in promoting e^--h^+ separation
- trapping of charge at surface state maybe important in charge separation



Representative Photoreactions at Particulate Semiconductors

Reactants	Products	Semiconductors	Refs.[a]
CN^-, O_2	CNO^-	TiO_2, CdS, ZnO	1
CO_2, H_2O	CH_3OH, HCHO	TiO_2, CdS, GaAs	2
CH_4, NH_3, H_2O	Amino acids	Pt/TiO_2	3
Many organics, H_2O	H_2, CO_2	Pt/TiO_2	4
Many organics, O_2	H_2O, CO_2	Pt/TiO_2	5
CH_3COOH	CH_4, CO_2	Pt/TiO_2	6
N_2, H_2O	NH_3	TiO_2, WO_3, Fe_2O_3	7
$Ph_2C{=}CH_2$, O_2	$Ph_2C{=}O$	TiO_2	8
H_2S	H_2, S	Pt/CdS, RuO_2/CdS	9

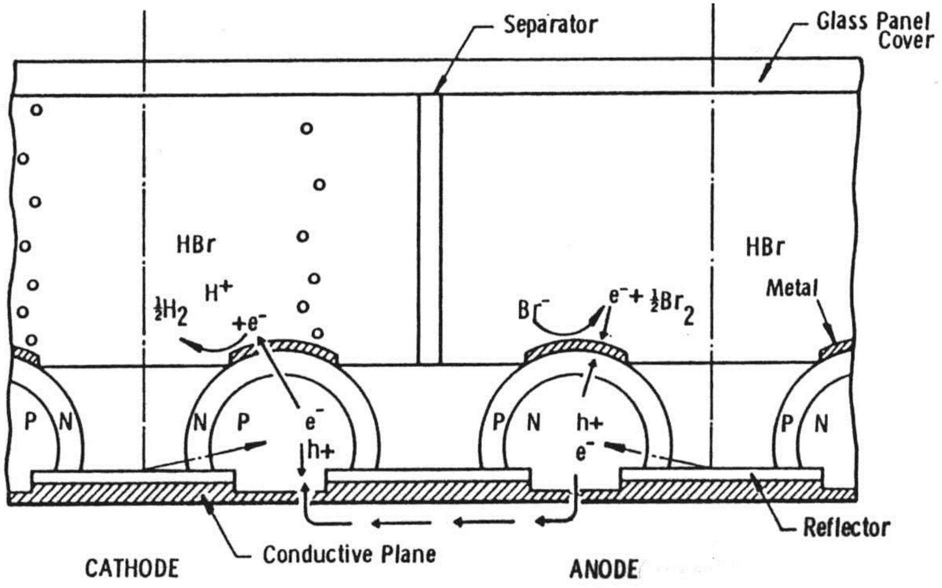
• supported SC particles
- why? Prevent the flocculation & settling out of very small particles
- if transparent support: high area thin films & small SC particle
- support materials

polymer films or membranes: e.g., Nafion with Cd^{2+}/H_2S (CdS)
Inorganics (SiO_2, clays, zeolites)
Organic supports: micelles, langmuir-Blodgett film with CdS

- Multijunction photoelectrochemical systems

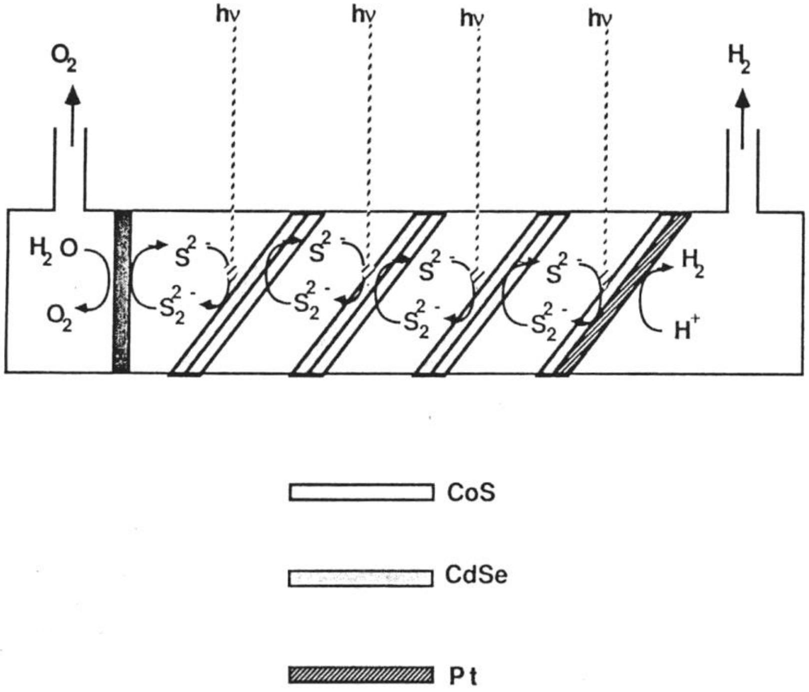
- limited single junction: splitting of water (< 0.8 V open circuit photovoltage), p/n junction Si (~o.55 V), electric eel (one organ; 0.1 V → in series, 500 V)

- e.g., Texas Instrument Solar Energy System



Small (250 μ) Si spheres (n-Si coated p-Si & p-Si coated n-Si)/glass matrix + catalyst; irradiation of the p/n junction produce 1.1 V → decompose HBr to H_2 + Br_2 ; other part; H_2 + Br_2 produce electricity

- CdSe/Ti/CoS



Schematic diagram of a multielectrode array consisting of CdSe/CoS panels in series arranged in a cell for the photosplitting of water to H_2 and O_2 without an external bias. All solutions contain 1 *M* NaOH. The inner solutions also contain 1 *M* S and 1 *M* Na_2S (66). [Reprinted from A. J. Bard, *Ber. Bunsenges. Phys. Chem.* **92,** 1187 (1988). Copyright 1988 VCH Verlagsgesellschaft.]

Nano(or quantum, Q-) particles

- size quantization effect in Q-particles

- particle size sufficiently small: electronic properties differ from that of bulk material
- quantom dot, quantum wire, quantum particle
- nano thickness layers: superlattices (different materials sandwiched)

- band energetics of Q-particles

- increase band gap
- CB up and VB down: electrons are better reductants & holes are better oxidants in Q-particles

e.g., enhanced photoredox chemistry at smaller particles of PbSe and HgSe

Semiconductor particles

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