Lecture Note #15 (Spring, 2022)

Photoelectrochemical cells

1. Semiconductor basics
2. Semiconductor-electrolyte interface
3. Light absorption
4. Photoelectrochemical effects
5. Photoelectrochemical cells

Fuller & Harb (textbook), ch.15, Bard & Faulkner, ch. 18

Semiconductor basics

Figure 15.1 Illustration of energy bands formed in a crystalline solid.

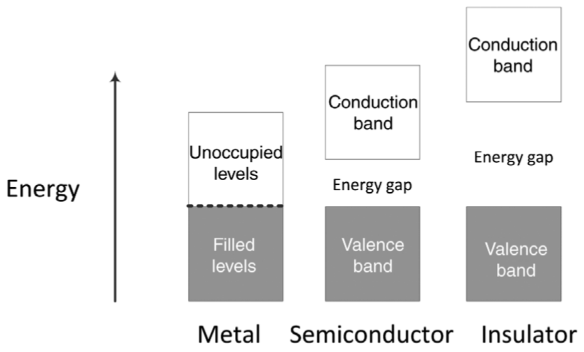


Figure 15.2 Energy bands and energy (band) gaps for different types of solid materials.

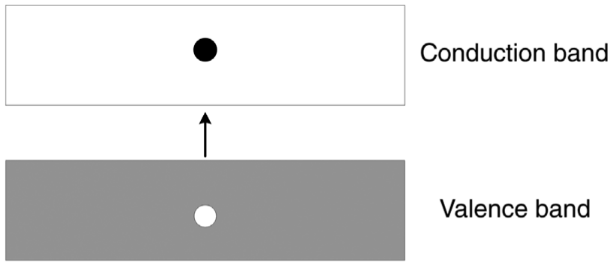


Figure 15.3 Excitation of an electron from the valence band to the conduction band of a semiconductor.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.
© 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc.
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

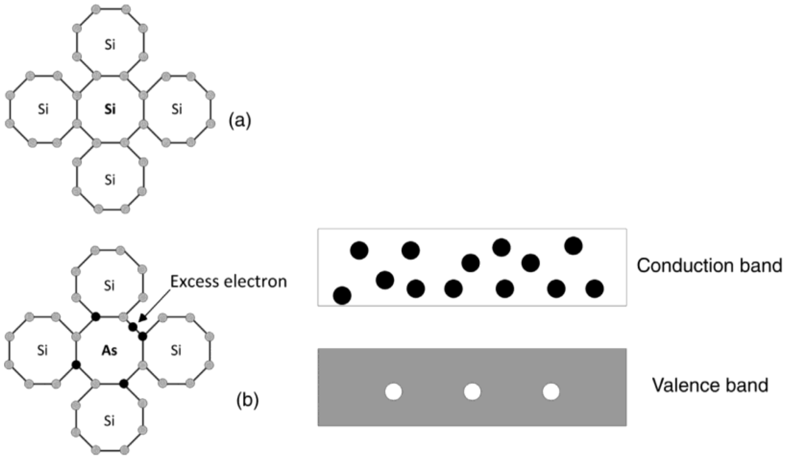


Figure 15.4 (a) Undoped Si. (b) An illustration of an *n*-type extrinsically doped Si with electrons as the majority carriers.

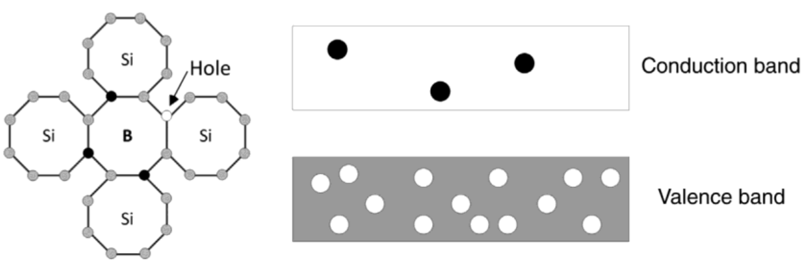


Figure 15.5 Illustration of a *p*-type extrinsically doped semiconductor with holes as the majority carriers.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.
© 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc.
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

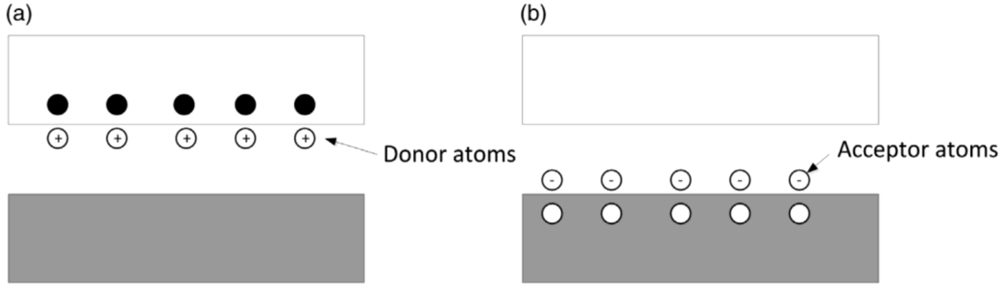


Figure 15.6 Illustration of energy levels and ionization for (a) *n*-type and (b) *p*-type dopants.

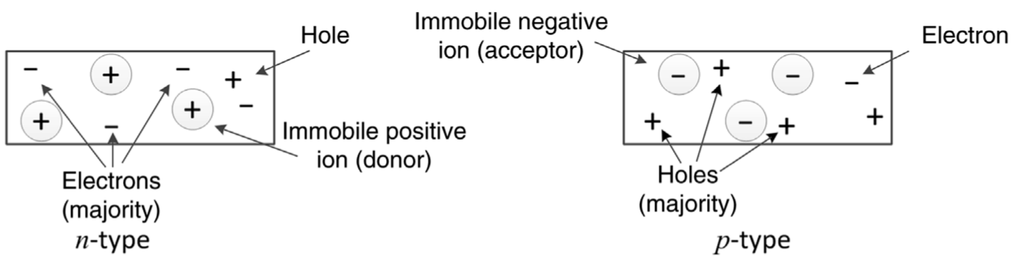


Figure 15.7 Carriers and immobile ions in extrinsic semiconductors.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.
© 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc.
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

n: # of free electrons (cm^{-3})
p: # of holes (cm^{-3})
n_i: # of free electrons (cm^{-3}) in the intrinsic(undoped) SC
N_D: # of donor atoms (cm^{-3})
N_A: # of acceptor atoms (cm^{-3})

$n \sim N_D$ for n-type SC
$p \sim N_A$ for p-type SC

$np = n_i^2$

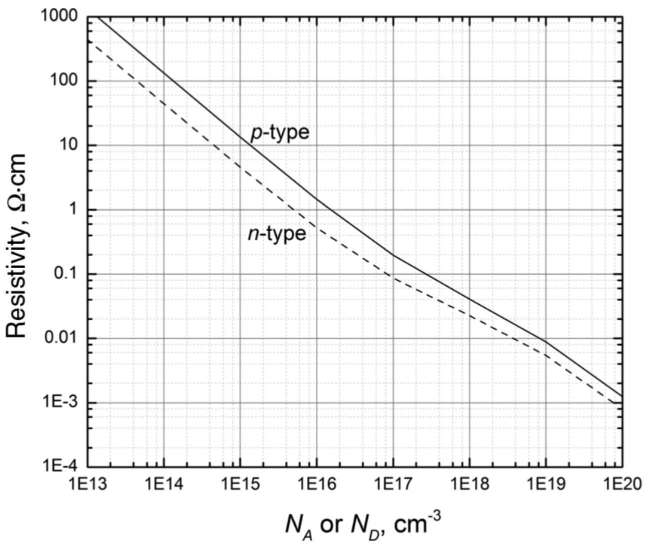


Figure 15.8 Resistivity of silicon at room temperature as function of dopant concentration. For *n*-type, the dopant is phosphorous; for *p*-type, it is boron.

Illustration 15.1

Energy scales

$$E_{vacuum}[eV] = -4.44 - qE^0$$

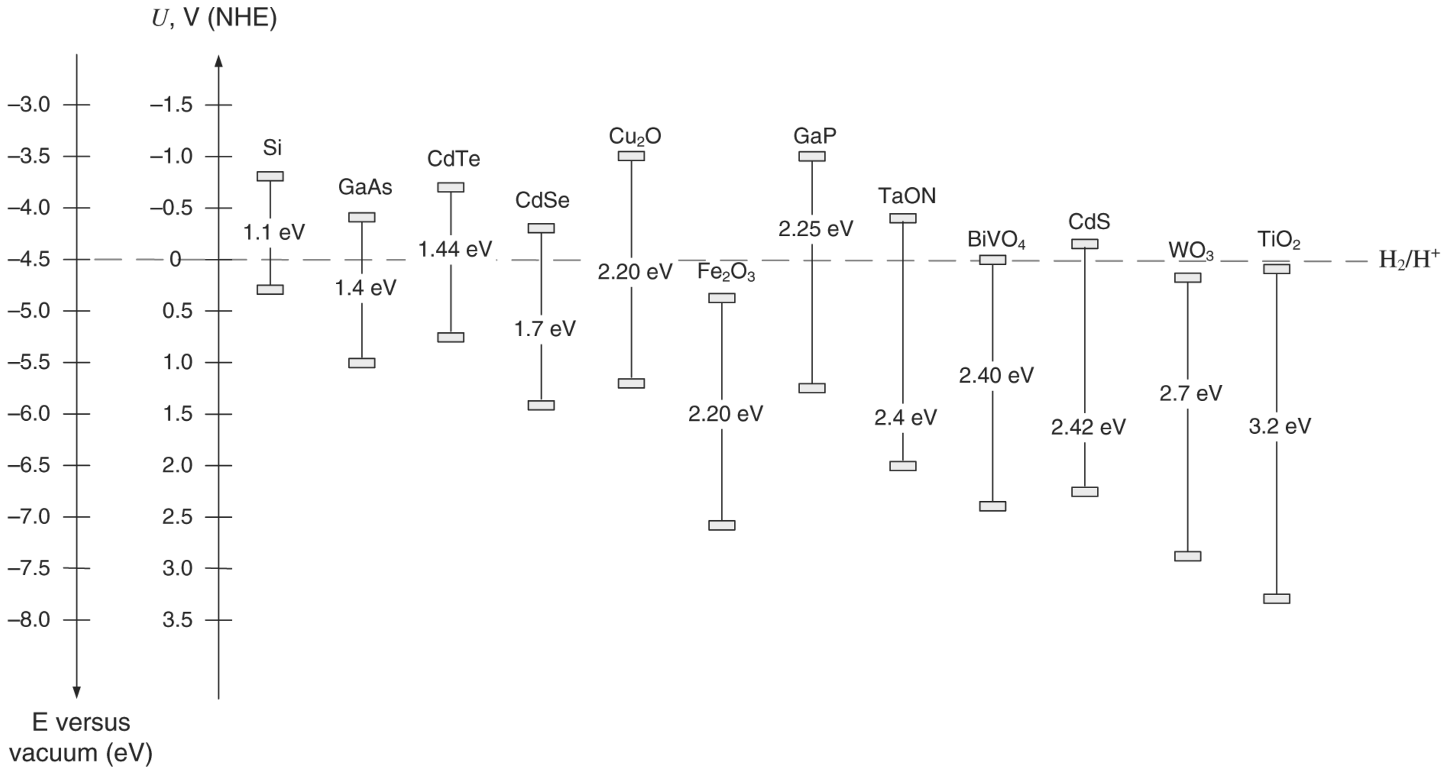


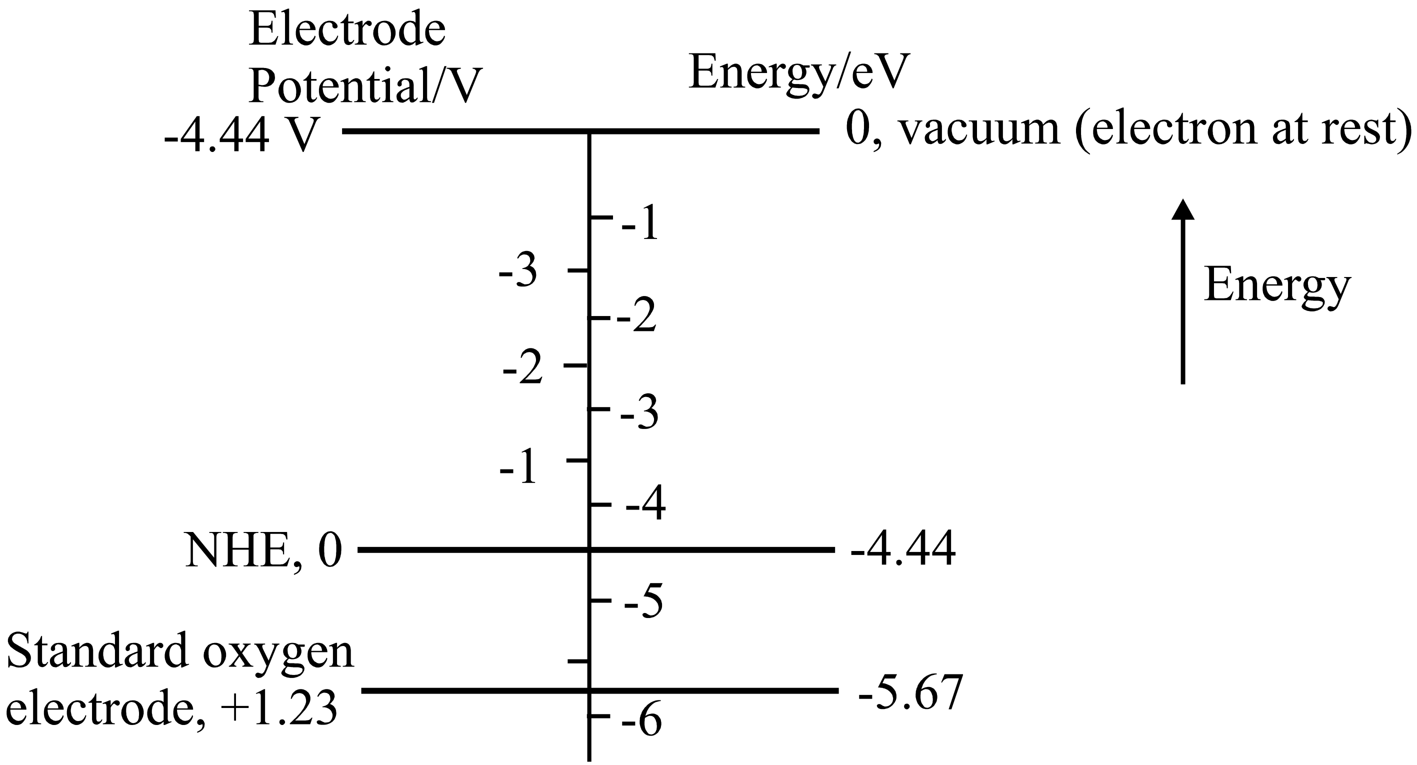
Figure 15.9 Band gap energies at 300 K as well as location of the band edges for various semiconductors. Both vacuum and hydrogen scales are shown. Solids with band gaps larger than about 3 eV are effectively insulators.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

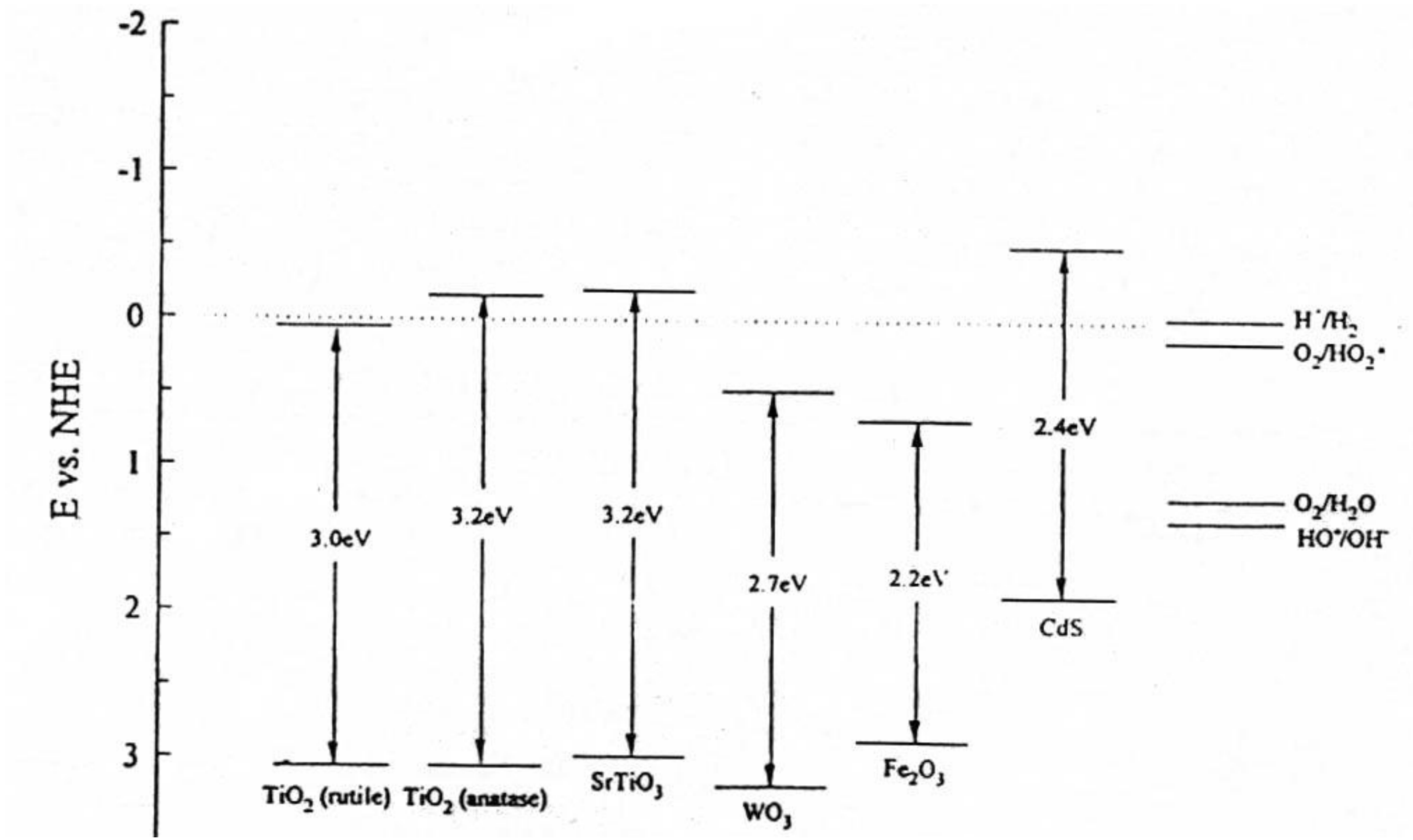
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Illustration 15.2

Potential vs. energy (vs. vacuum)



Example: Potential vs. energy (vs. vacuum)



HOMO and LUMO of organic materials or polymers can be displayed in the same way

유기물이나 고분자의 HOMO, LUMO도 동일하게 표시 가능

Semiconductor-electrolyte interface

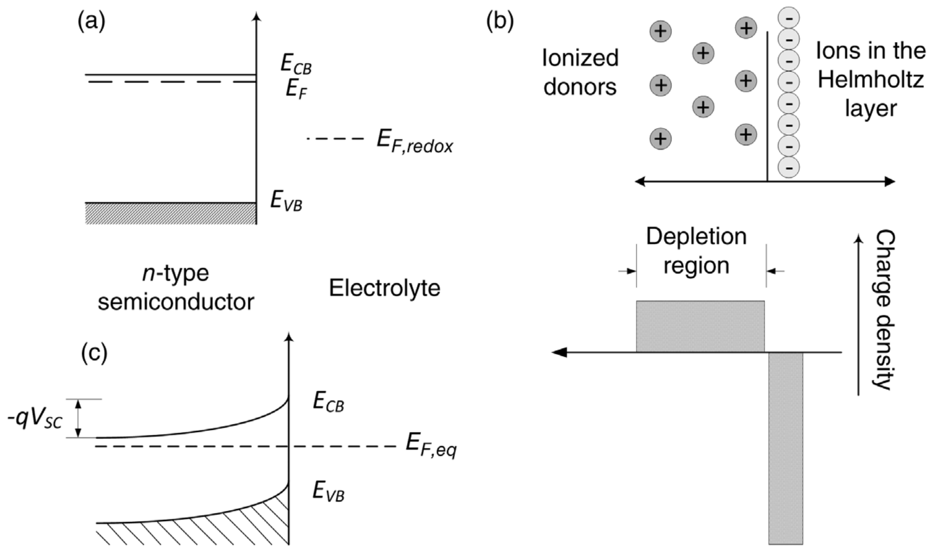
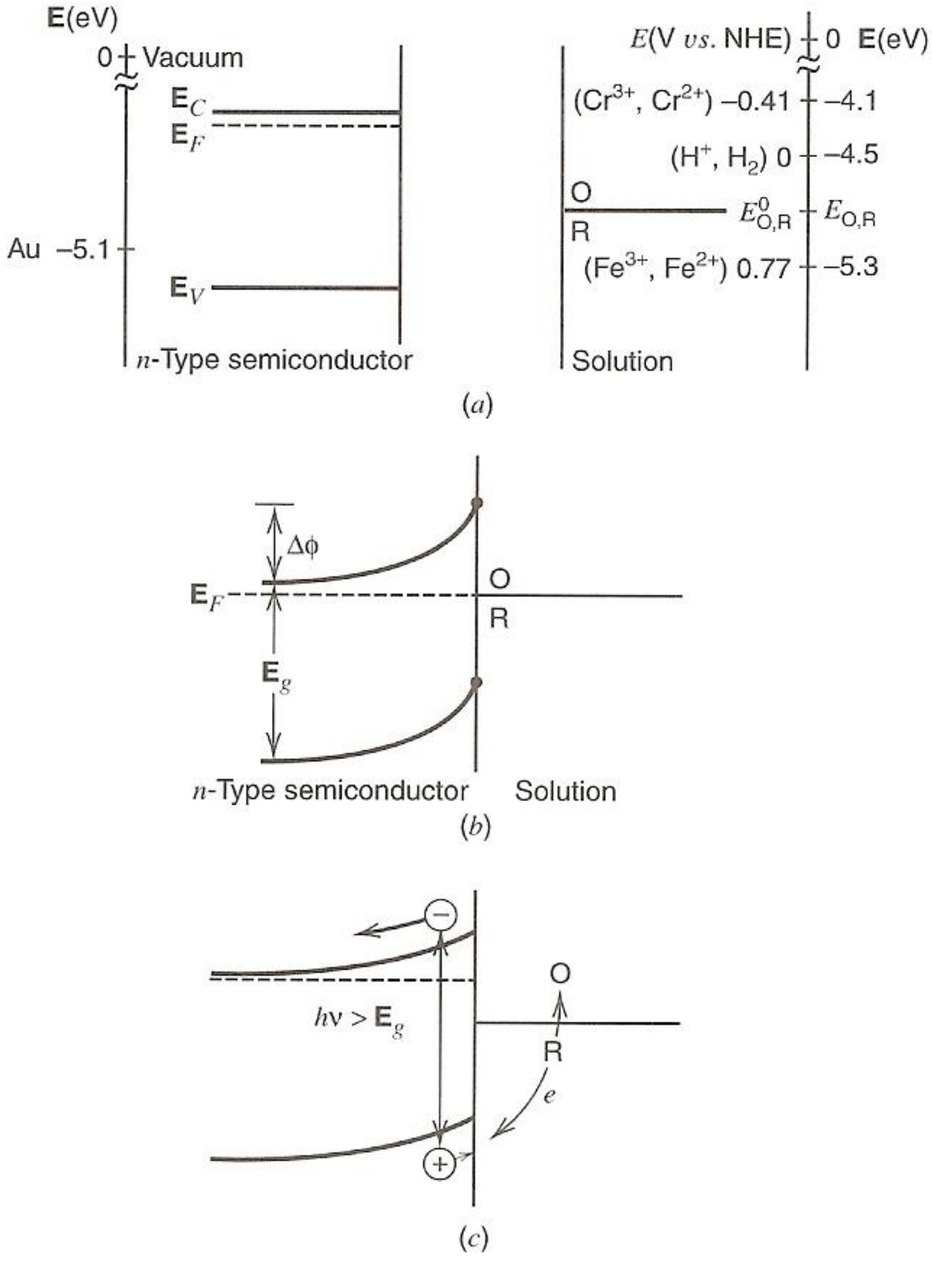


Figure 15.10 (a) Initial electron energy levels of semiconductor and redox couple, where the energy of the CB electron is higher than that of the redox couple. (b) Illustration of the physical distribution of charge after transfer of charge from *n*-type semiconductor (leaving a net positive charge on the left) to the electrolyte (on the right). (c) Band bending (different electron energy) at the interface after energy levels have equilibrated by the transfer of electrons between phases.

n-type



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

p-type

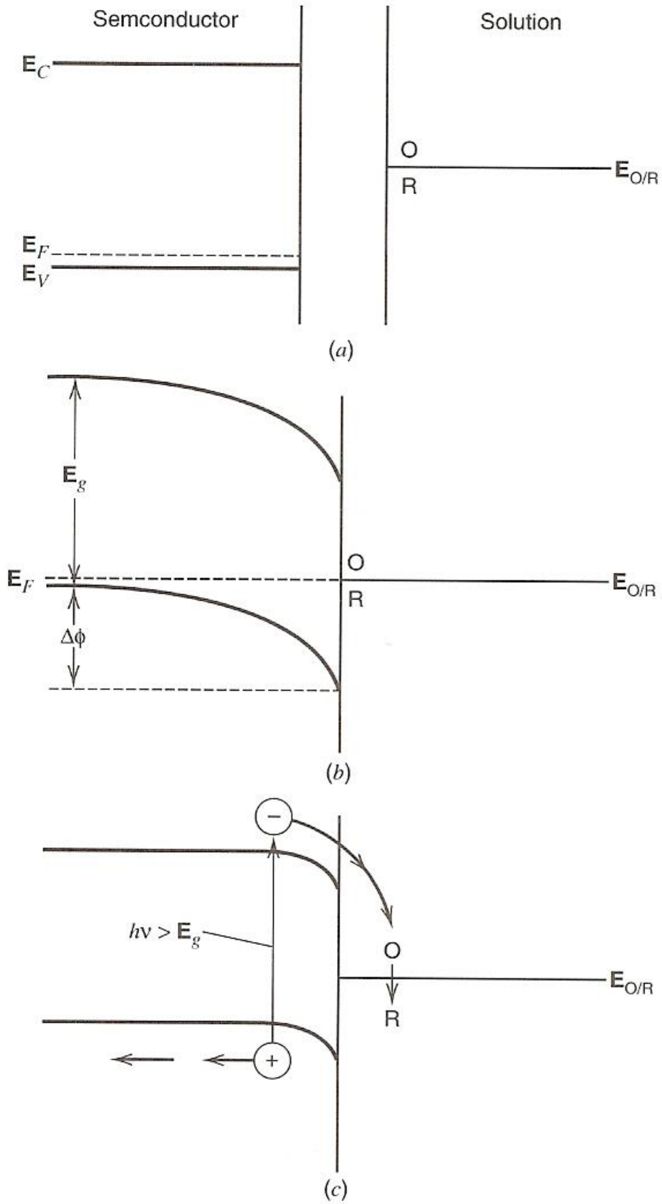


Illustration 15.3

Light absorption

E (eV) = 1,240 / λ(nm)

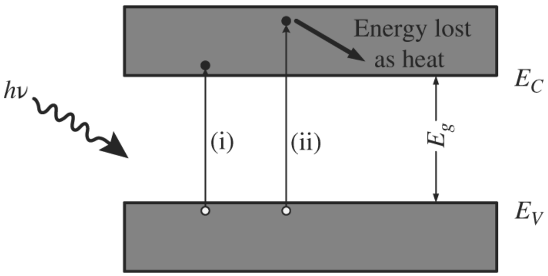


Figure 15.15 Optical absorption to excite electrons to the conduction band (i) where the photon energy is equal to the energy of the band gap, and (ii) where the photon energy is greater than the band gap energy.

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

A.J. Bard, Integrated Chemical Systems, Wiley, 1994.

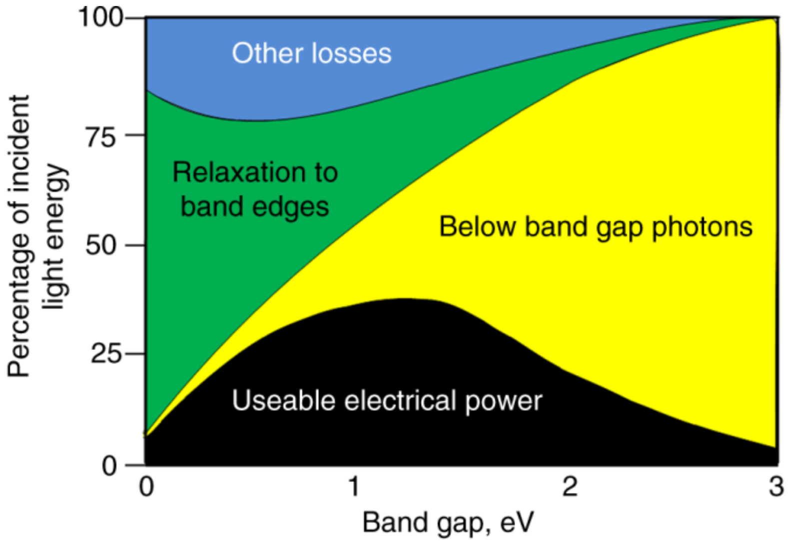


Figure 15.18 Useable electric power generated from light energy.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Illustration 15.5

Photoelectrochemical effects

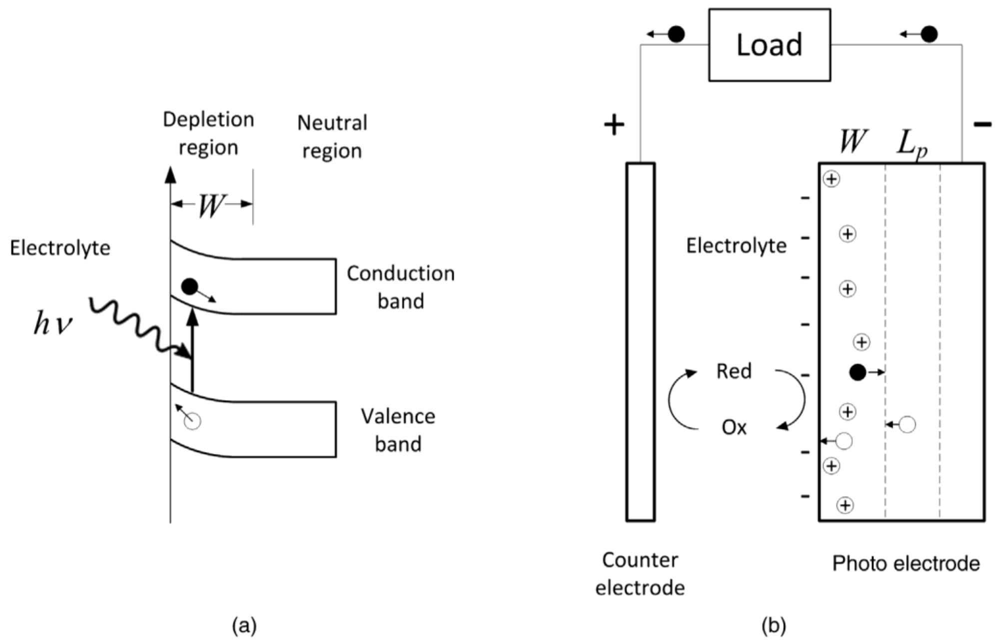


Figure 15.19 Generation and separation of electron–hole pairs through light absorption in the depletion region of an *n*-type semiconductor. (a) Band structure. (b) Physical situation.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

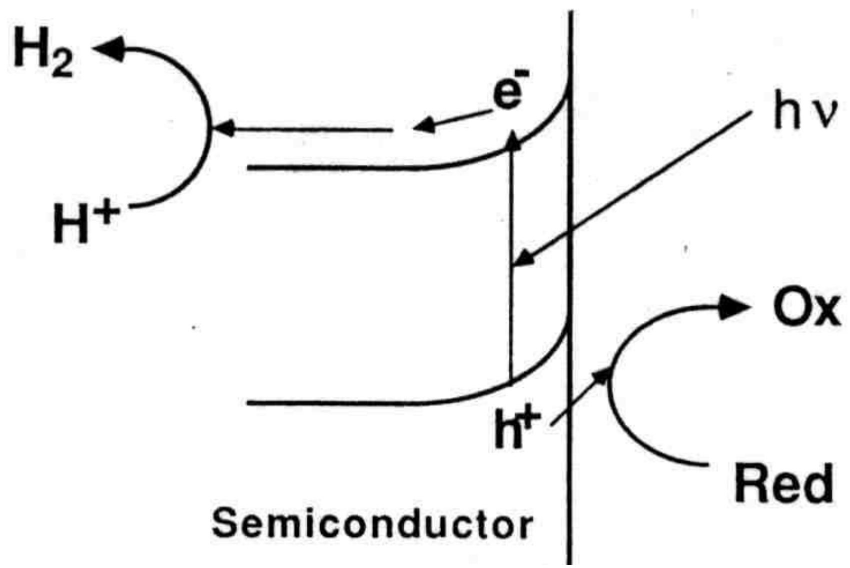
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Photoelectrochemistry at semiconductors

Radiation energy ⇔ electrical or chemical energy

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

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

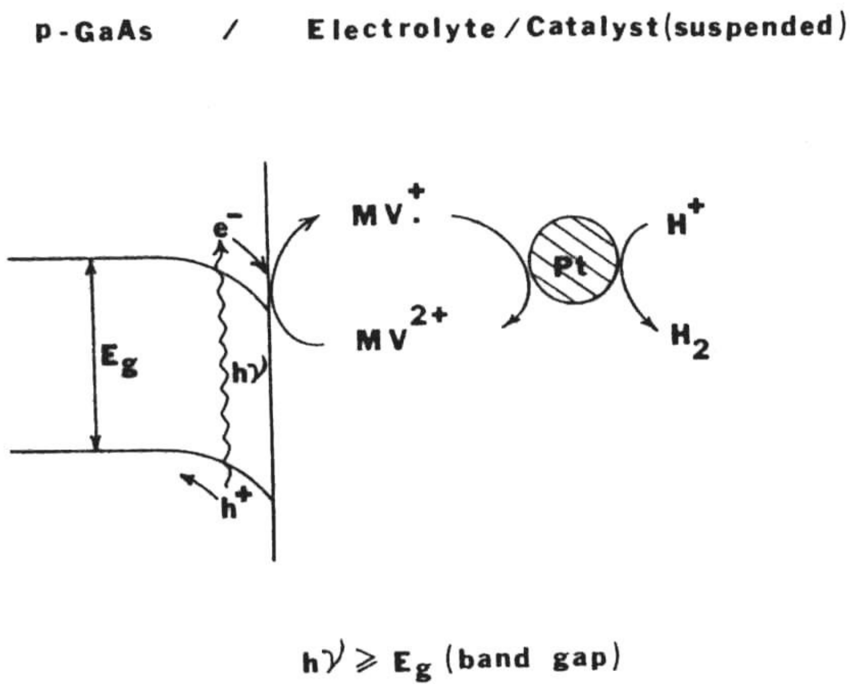


Hydrogen fuel production (H^+ or H_2O reduction): i) kinetically difficult $\rightarrow$ catalyst, ii) recombining electrons and holes and lowering the efficiency of the photoreaction unless rapid chemical reaction

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

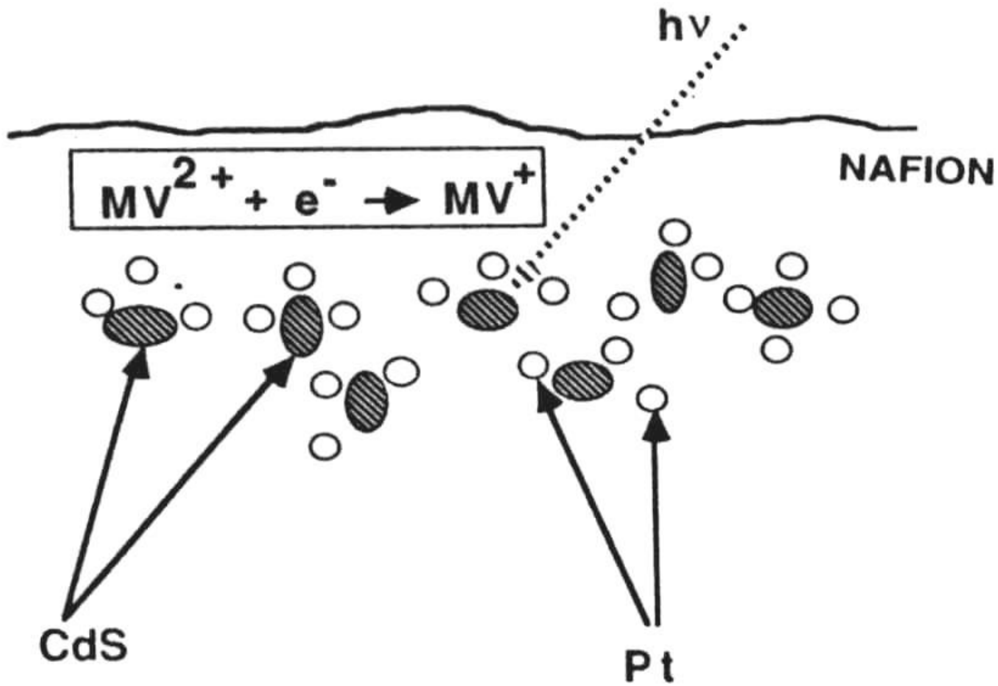
Red: sacrificial (electron) donor

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

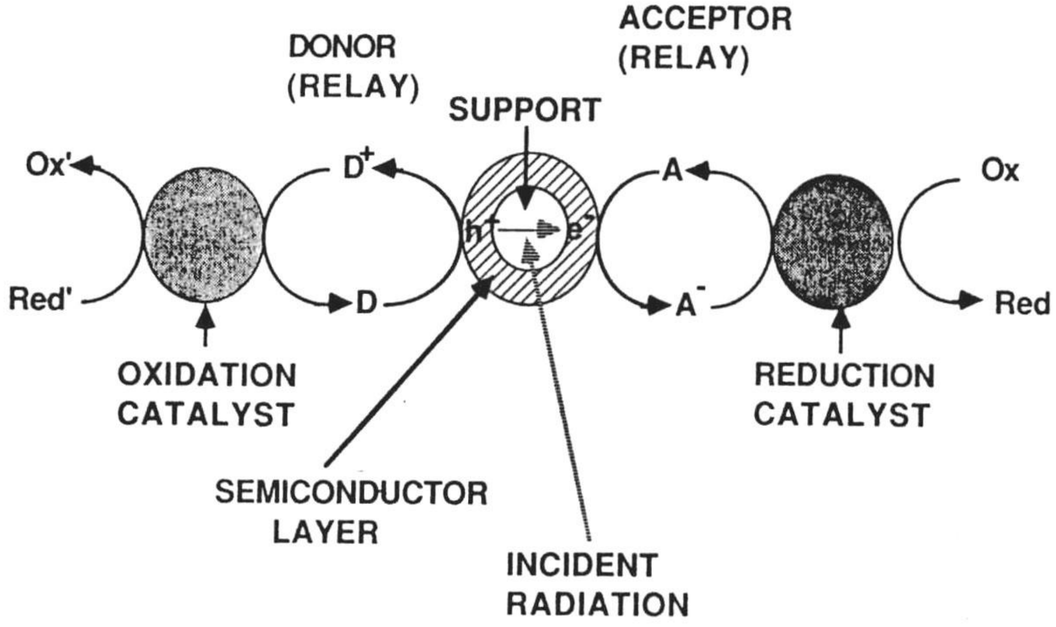


Very slow H_2 photoreaction on GaAs (high hydrogen overpotential) → fast reaction of $MV^{2+/1+}$ + Pt (fast hydrogen evolution) → viologen + polymer/self assembly etc

e.g., CdS particles in Nafion



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



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

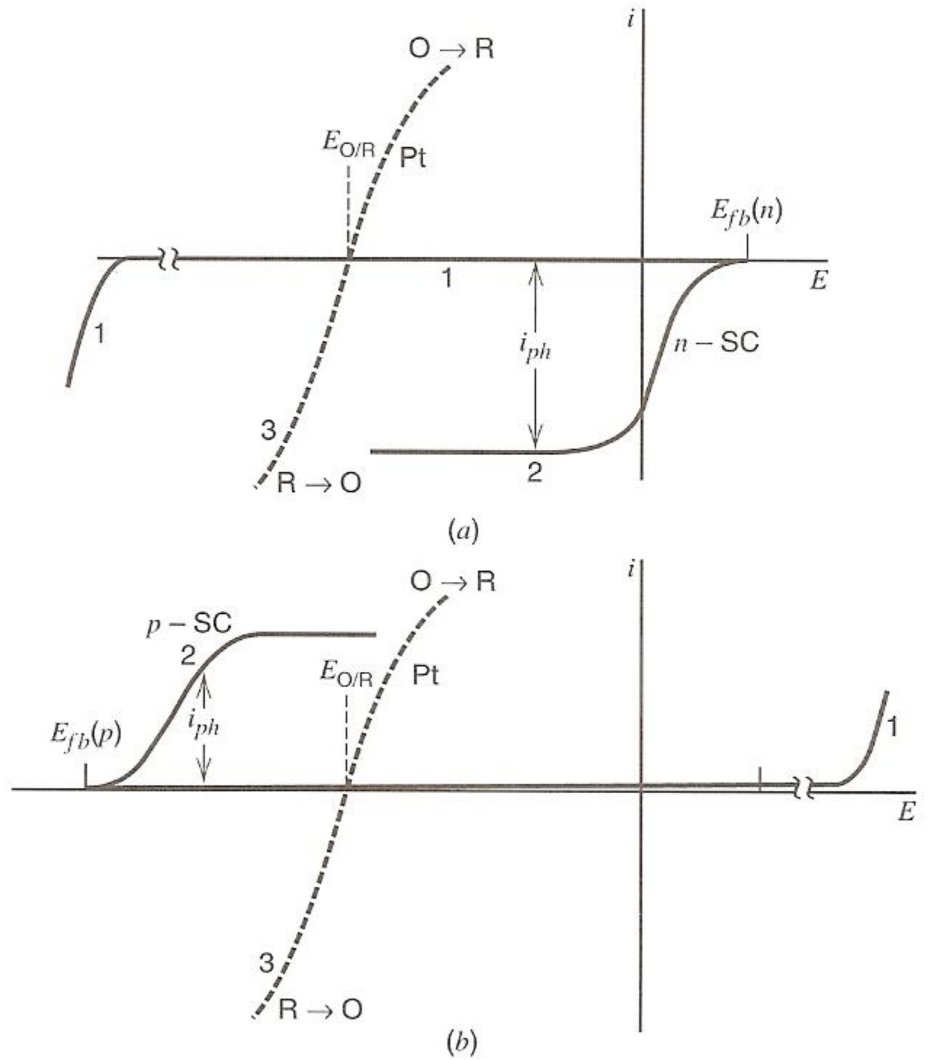
e.g., $H_2O \rightarrow 2H_2 + O_2$ or H_2, Cl_2, OH^- from NaCl solution

Photoeffects at semiconductor electrodes

1: dark
2: irradiation
3: Pt electrode

n-type

p-type



Photoelectrochemical cells

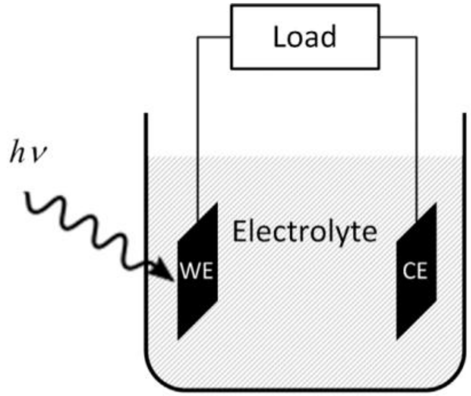


Figure 15.21 Schematic diagram of a photoelectrochemical cell.

Illustration 15.7

Maximum power

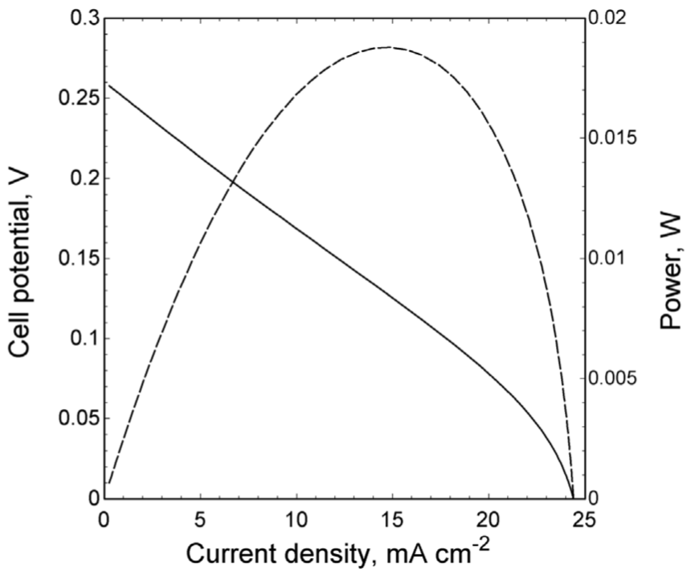
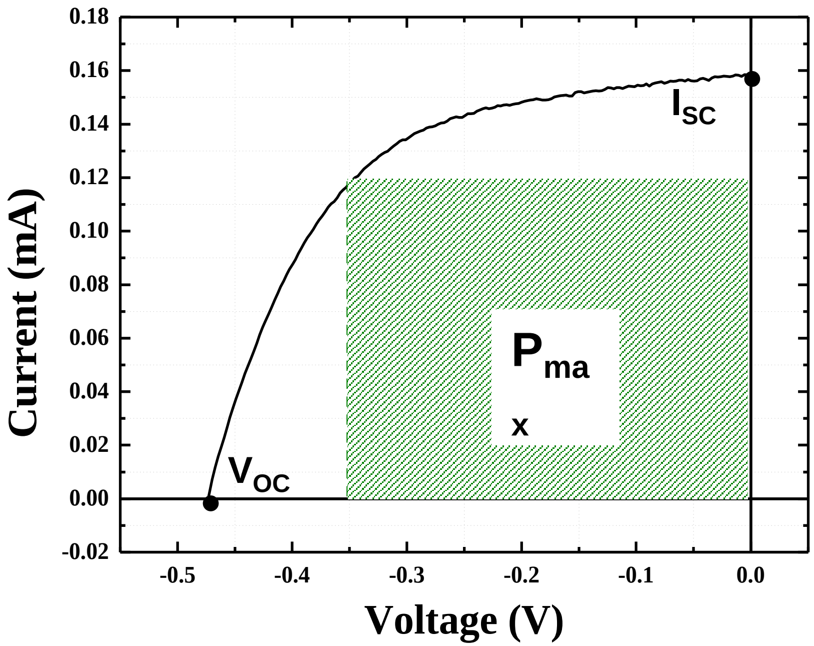


Figure 15.22 *i*–*V* curve, and on right ordinate, power versus cell potential for the cell from Illustration 15.7.

Cell efficiency

Power curve (I-V curve)



I_{SC} : Short-circuit current

→ Current value when V=0

V_{OC} : Open-circuit voltage

→ Voltage value when I=0

P : Power output of the cell

$$P=IV$$

F.F : Fill factor

$$F.F = \frac{P_{max}}{I_{SC}V_{OC}} = \frac{I_m V_m}{I_{SC}V_{OC}}$$

The overall efficiency

$$\eta = \frac{P_{max}}{P_r} = \frac{F.F\ I_{SC}V_{OC}}{P_r}$$

(P_r : Radient power input)

Types of PEC cells

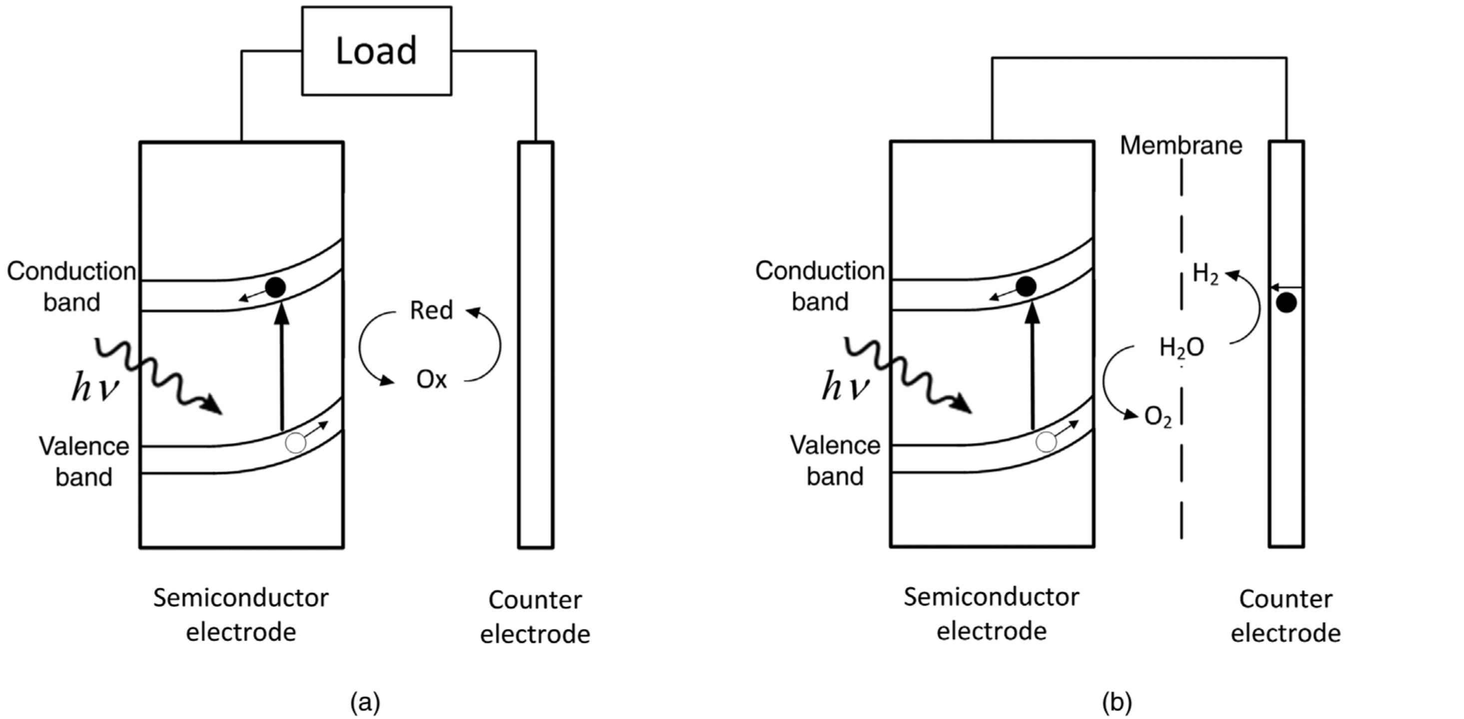


Figure 15.23 Energy diagrams for (a) a regenerative and (b) a photoelectrolytic cell. *Source:* Adapted from Grätzel 2001.

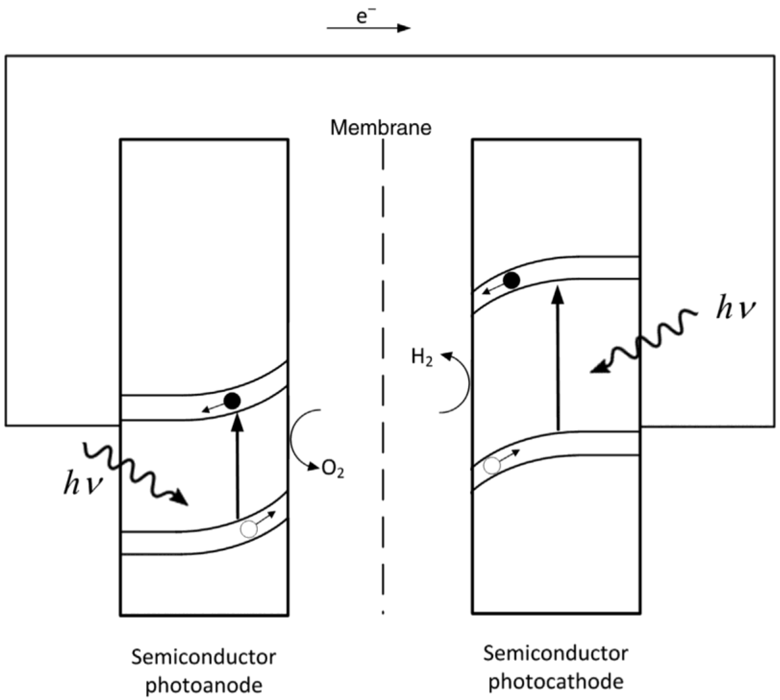
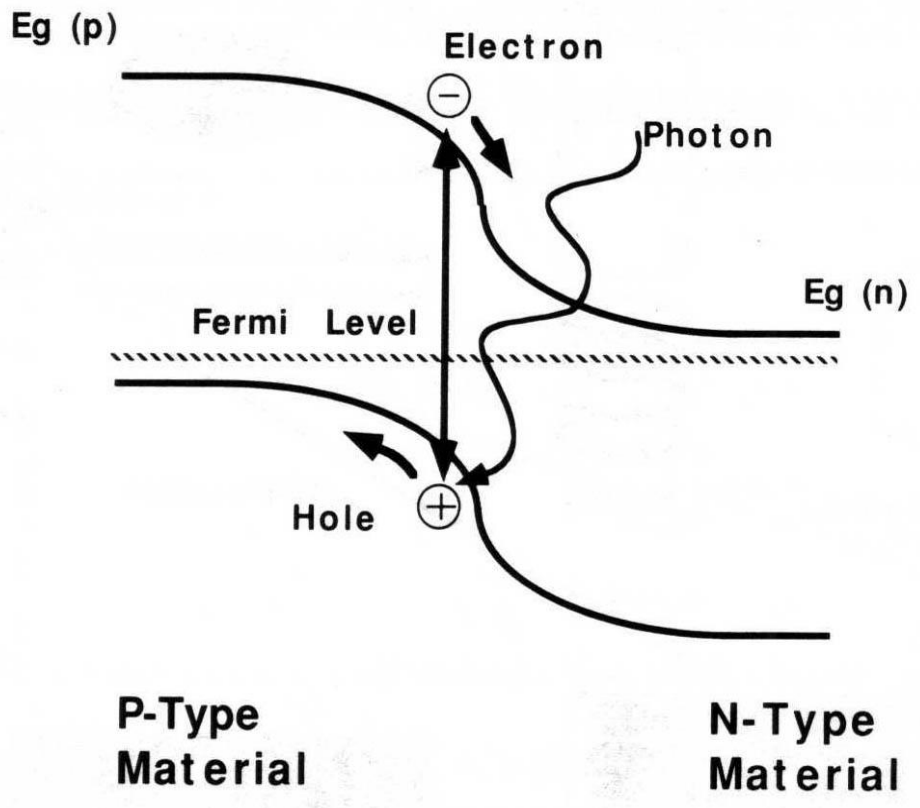


Figure 15.24 Photoelectrolytic cell with two photoelectrodes.

Illustration 15.8

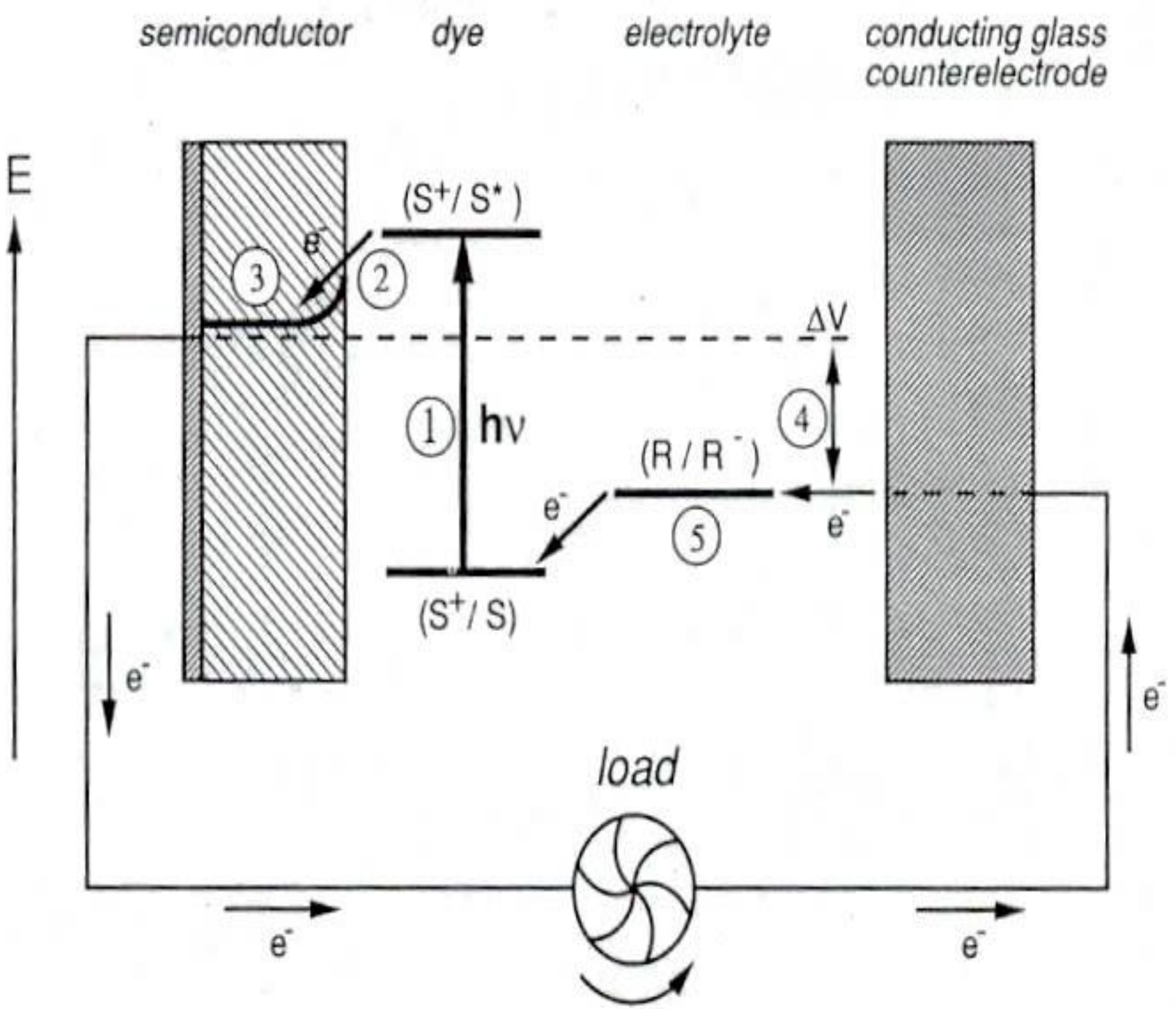
cf. solar photovoltaic conversion & solar photovoltaic cell

Principle of p/n solar cell



Simple Si P/N Solar Cell/ Diode

Dye-Sensitized Solar Cell (염료감응태양전지)



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

A.J. Bard, Integrated Chemical Systems, Wiley, 1994.

Electrolytic processes for a sustainable future

Electrolytic fuel generation

- Solar fuels such as hydrogen: Hydrogen production using photoelectrochemical cell (ch.15 in the textbook)

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

A.J. Bard, Integrated Chemical Systems, Wiley, 1994.