Photoelectrochemistry (ch. 18)

Semiconductor electrodes

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

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

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°C)

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

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)

For n-type SC

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 ~ 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

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

- 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 ($f(E) \rightarrow 1$); all levels $E > E_F$ vacant
- intrinsic SC: E_F in the middle of CB and VB edges

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

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 $N_D < N_C$, $N_A < N_V$ → 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

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

- 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)

$$\Phi = -E_F$$

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

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

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

Mott-Schottky plot

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

Photoeffects at semiconductor electrodes

1: dark
2: irradiation
3: Pt electrode

n-type

p-type

p-type

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

Semiconductor particles

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