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ELCOREL Workshop, Oud Poelgeest Castle, Oegstgeest

An Introduction to Semiconductor Electrochemistry

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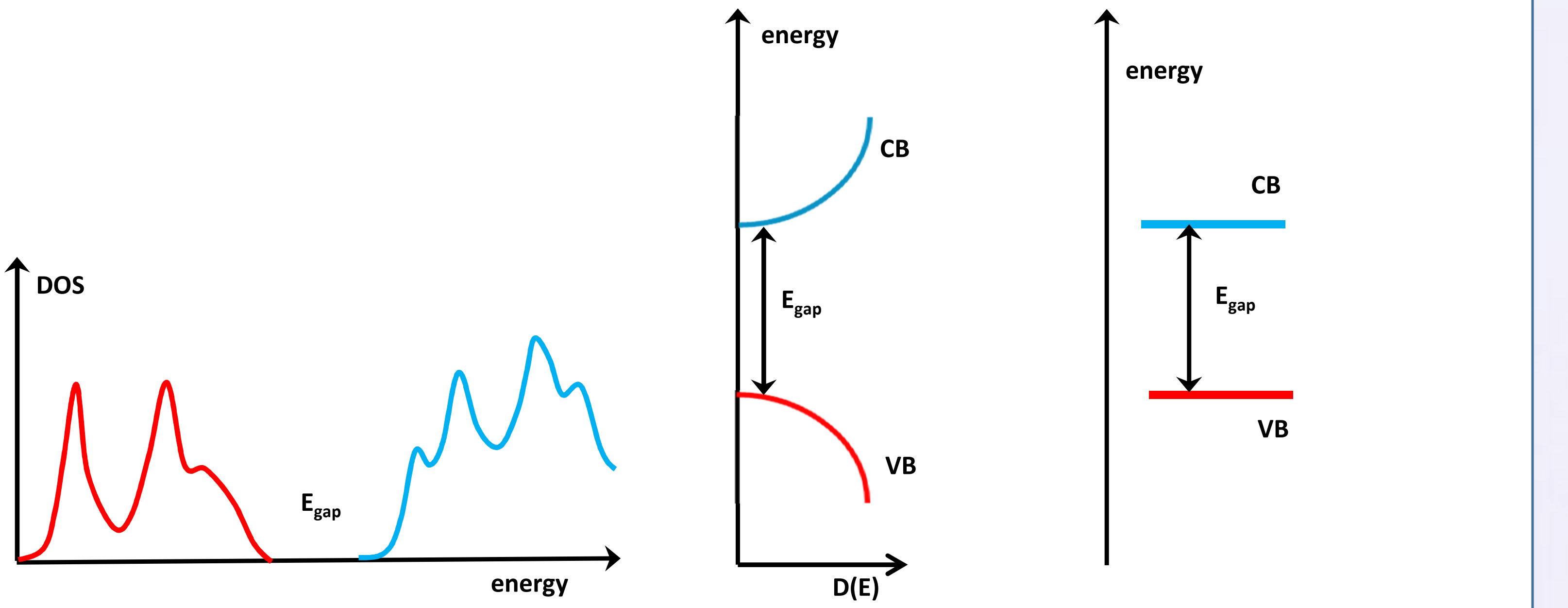
Basic Ideas: Band Diagrams



density of states　　parabolic approximation　　simplified band diagram

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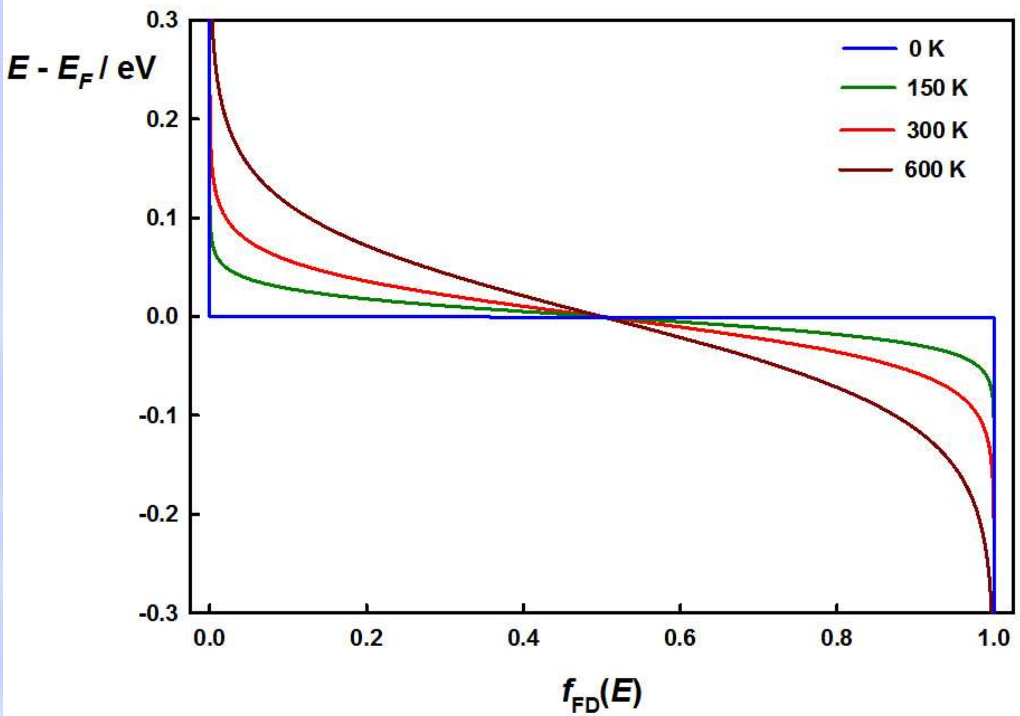
Fermi-Dirac Function Determines Concentrations of Electrons and Holes in Electronic Energy Levels

$$f_{FD}(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}$$

E_F **– the Fermi level**

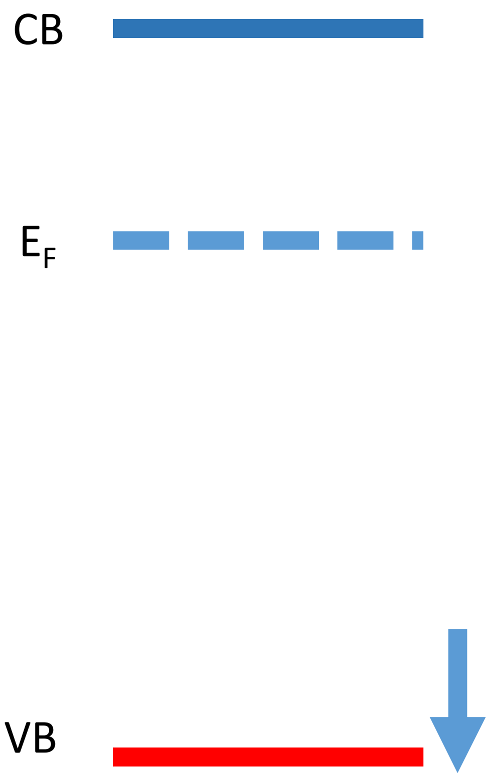


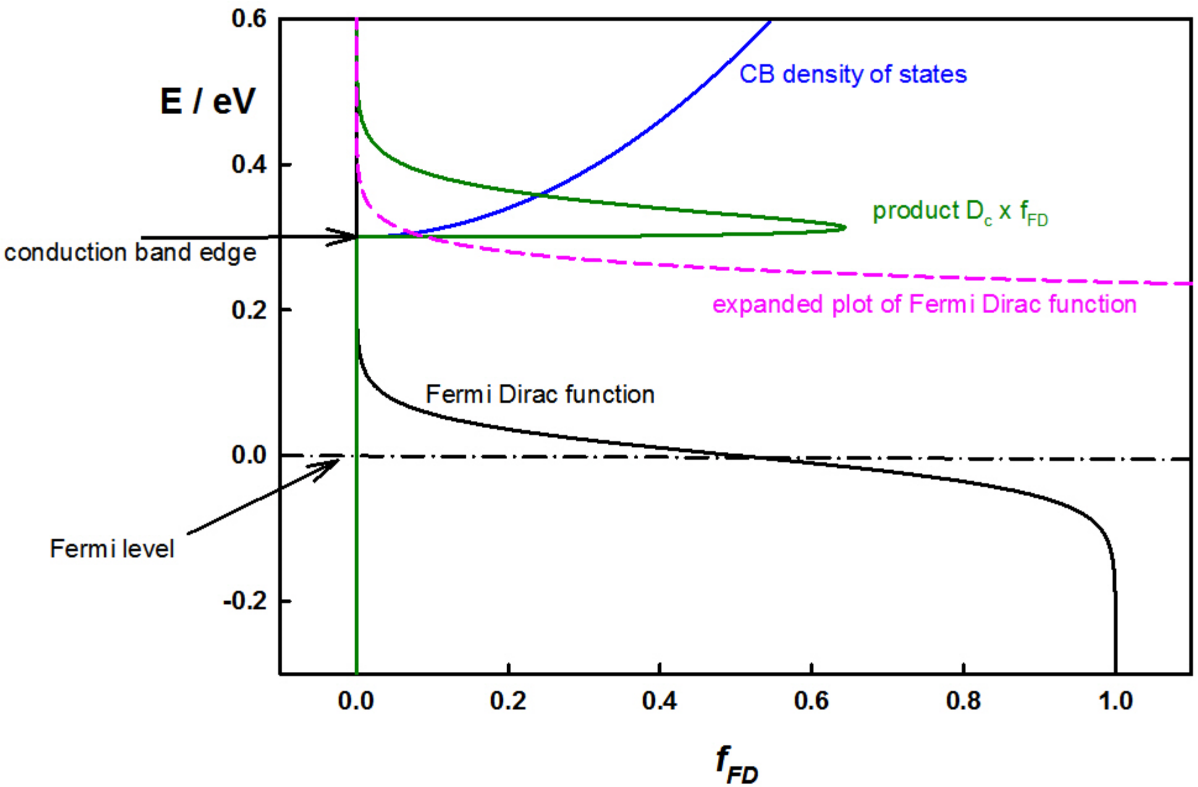
To obtain the **total concentrations of electrons and holes** we need to integrate the product of the occupation probability $f_{FD}(E)$ and the density of electronic states in the conduction or valence bands, D_C and D_V

$$n = \int_{E_C}^{\infty} D_C(E) f(E)\, dE = N_C \exp -\left(\frac{E_C - E_F}{k_B T}\right)$$

$$p = \int_{-\infty}^{E_V} D_V(E)\left[\left(1 - f(E)\right)\right] dE = N_V \exp\left(\frac{E_V - E_F}{k_B T}\right)$$

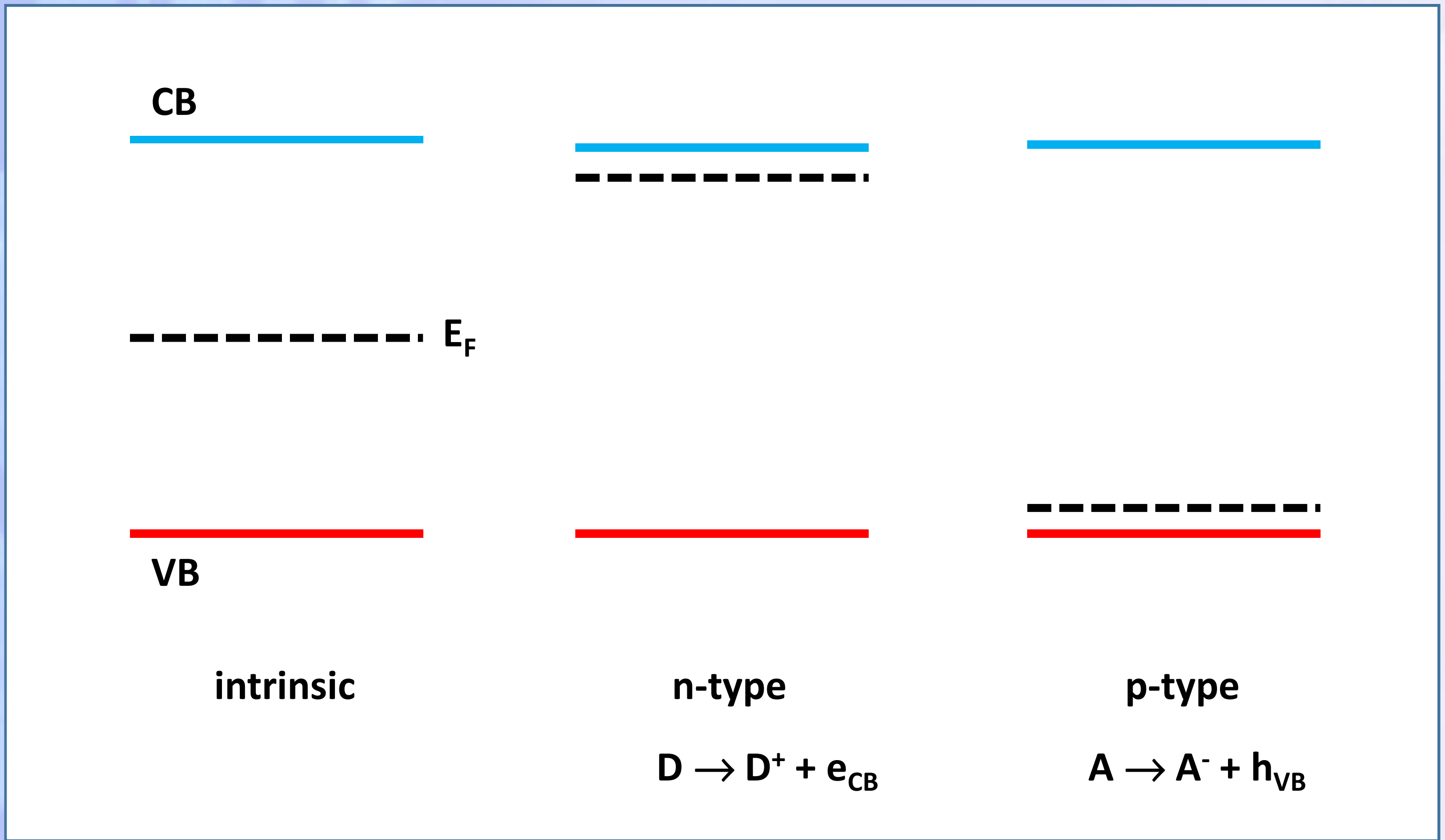
In **thermal equilibrium** $$np = N_C N_V \exp -\left(\frac{E_{gap}}{k_B T}\right)$$



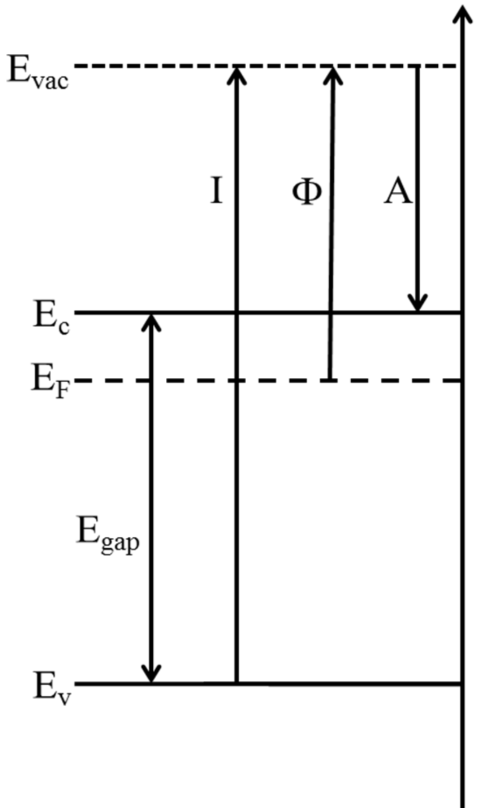


Integrate the green curve to obtain the concentration of electrons

Intrinsic and Doped Semiconductors



Energy diagram for an n-type semiconductor



E_{vac} – vacuum energy level.

E_c conduction band edge energy.

E_v – valence band edge energy.

E_{gap} – energy gap.

A – electron affinity.

I – ionization energy.
Φ - work function.

Φ E_F Fermi energy.

The Fermi level, Free Energy and the Electrochemical Potential of Electrons and Holes

$$\bar{\mu}_i = \left(\frac{\partial \bar{G}}{\partial n_i}\right)_{T,P,n_j,\varphi}$$

Electrochemical potential or Partial Molar Gibbs Free Energy of Charged Species

$$\bar{\mu}_i = \mu_i + z_i F \varphi$$

chemical potential → μ_i

potential dependent term → $z_i F \varphi$

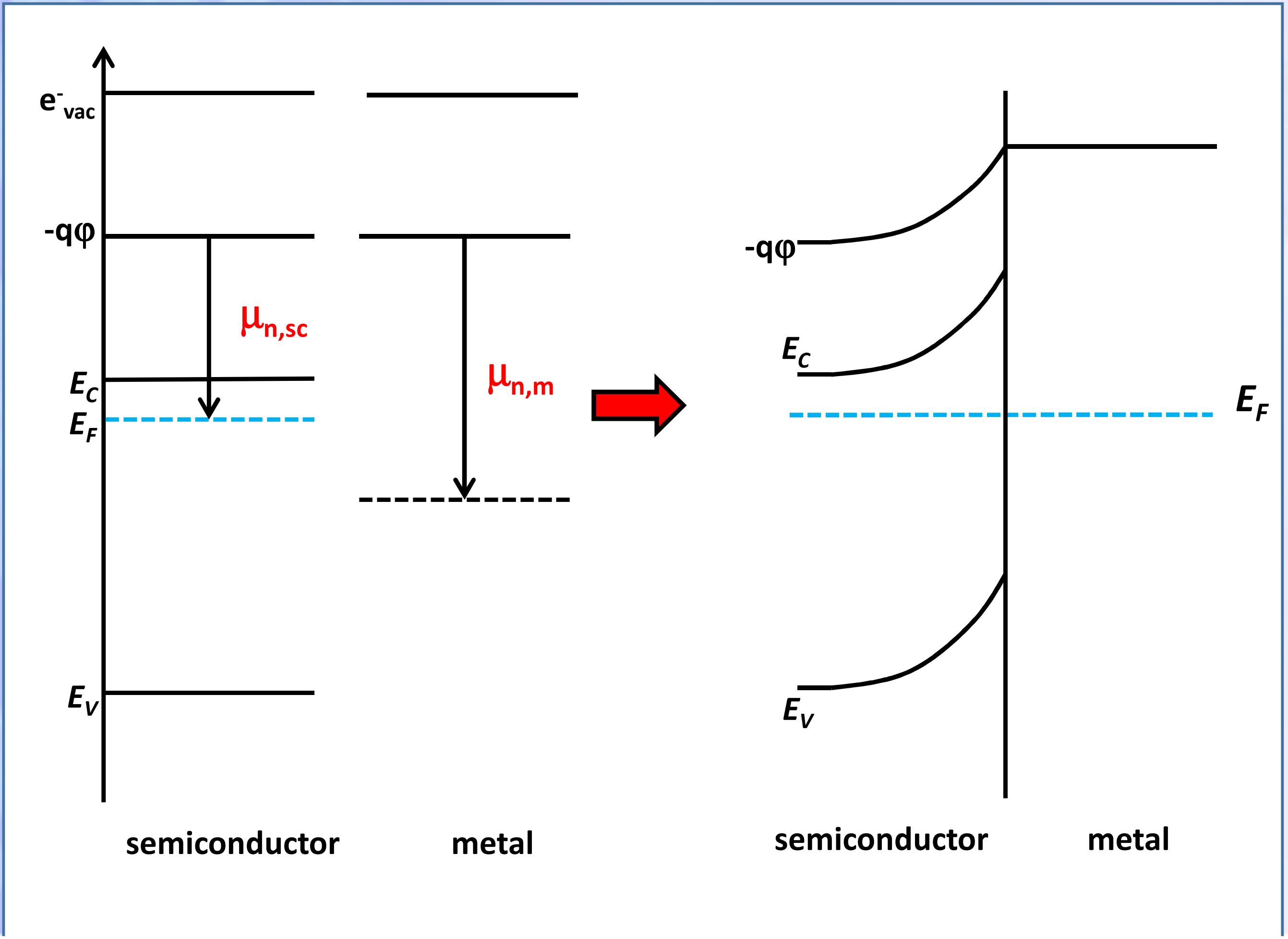
$$\mu_n = \mu_n^0 + k_B T \ln \frac{n}{N_C} \qquad \mu_p = \mu_p^0 + k_B T \ln \frac{p}{N_V}$$

$$\bar{\mu}_n = E_F \qquad \bar{\mu}_p = -E_F$$

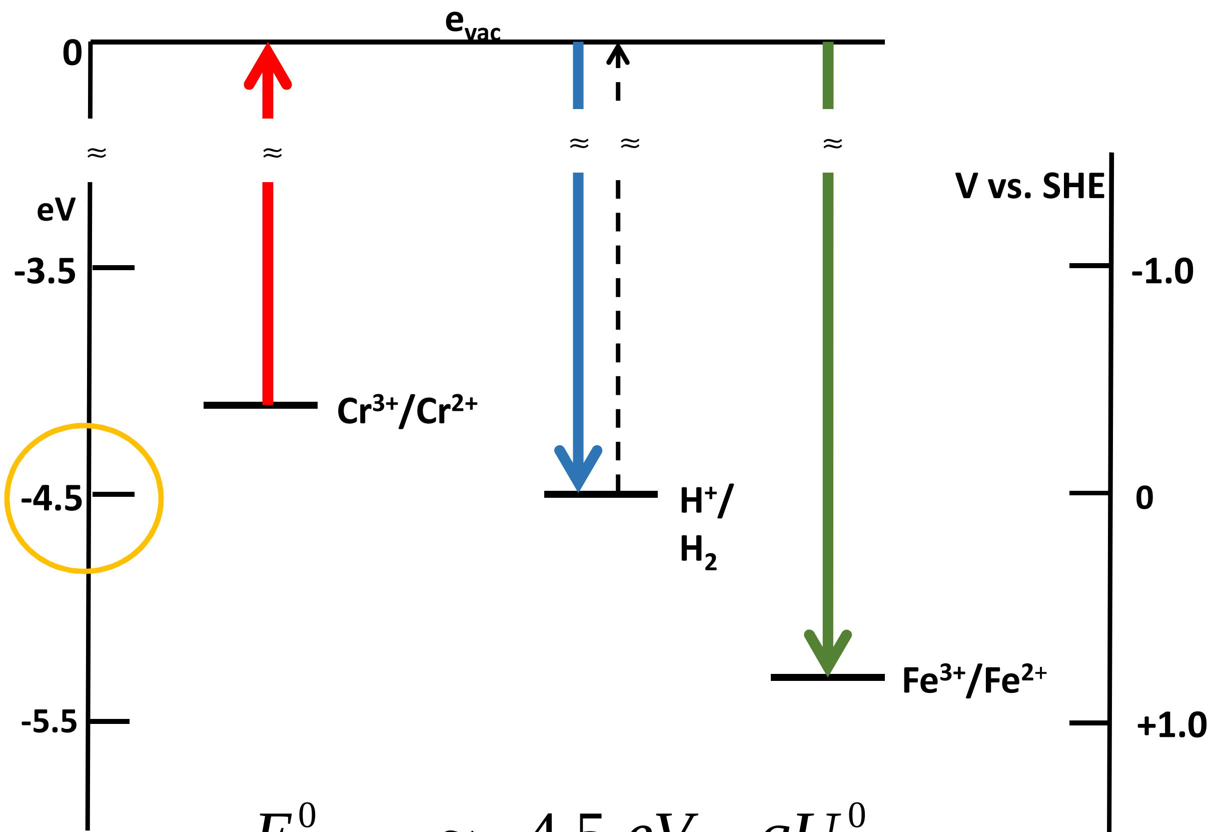
N_c and N_V – effective density of states

thermodynamic standard states

Equilibration of Fermi Levels in Solid State Junction
Formation of a Schottky Barrier

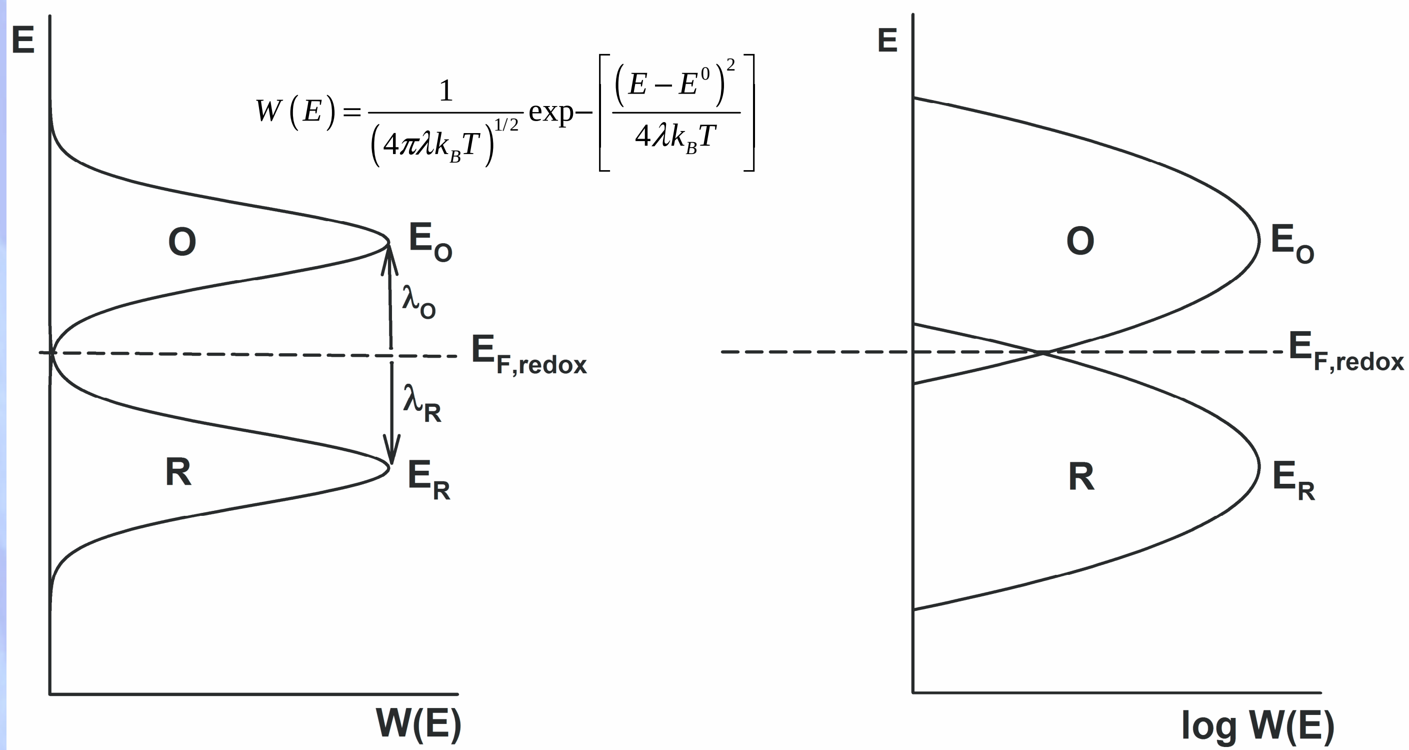


Vacuum Energy Scale and Electrode Potential Scale



$$E^0_{F,redox} \approx -4.5\ eV - qU^0_{redox}$$

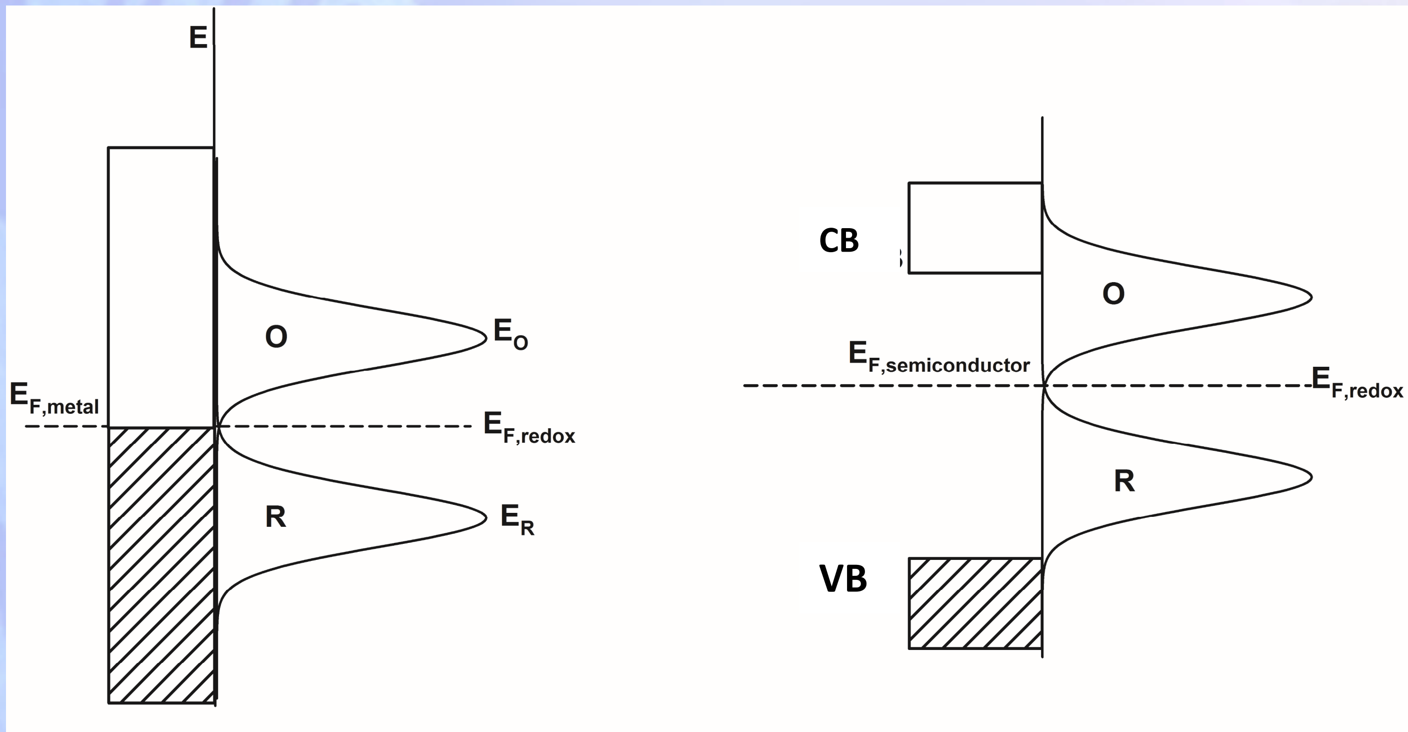
Outer Sphere Redox Systems – Marcus Theory



Redox Fermi level

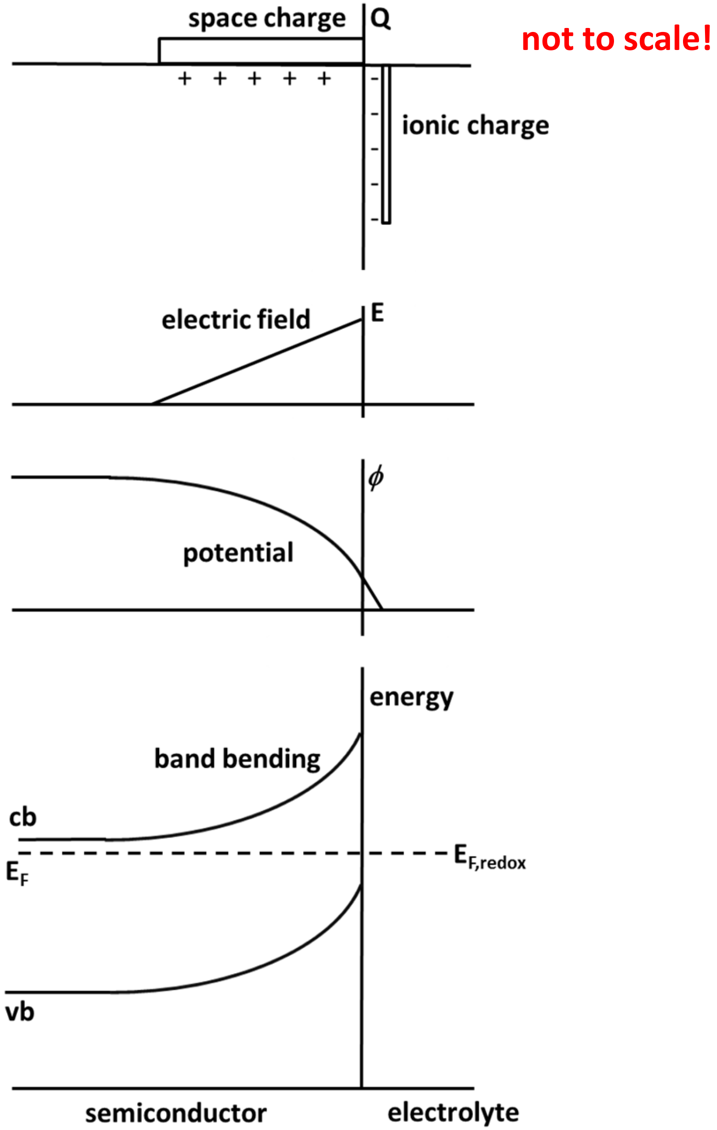
$$E_{F,redox}=\bar{\mu}_R-\bar{\mu}_O=\left(\bar{\mu}_R^{o}-\bar{\mu}_O^{o}\right)+k_BT\ln\frac{N_R}{N_O}$$

Equilibration of Fermi Levels in Electrolyte Junctions



metal/redox

semiconductor/redox

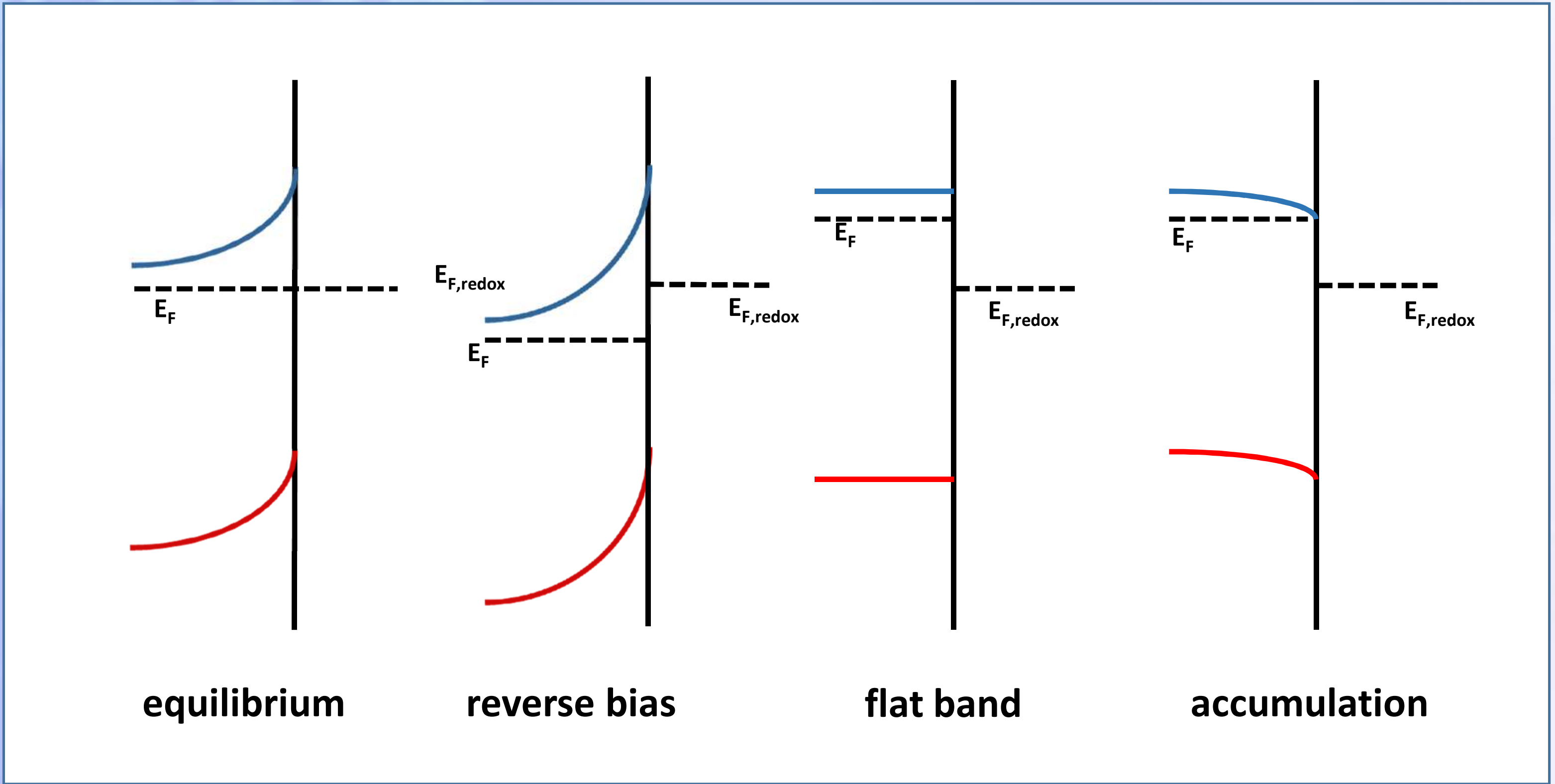


Charge, Field and Potential Distribution in the Case where a Depletion Layer or Space Charge Region (SCR) is formed

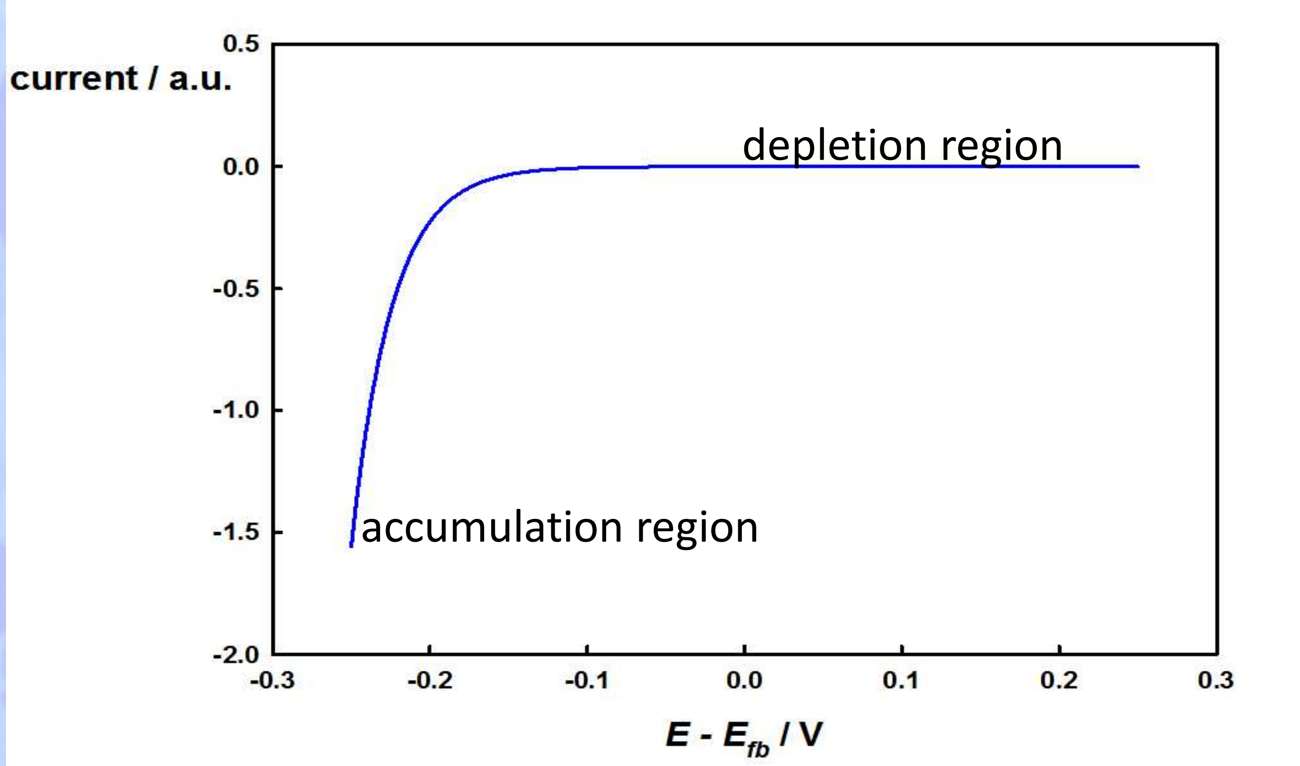
$$W_{SCR} = \left(\frac{2\Delta\phi_{SCR}\varepsilon\varepsilon_0}{qN_d}\right)^{1/2}$$

The charge distribution corresponds to a space charge capacitance

Band Bending as a Function of Applied Potential



In the dark the electrode behaves as a diode

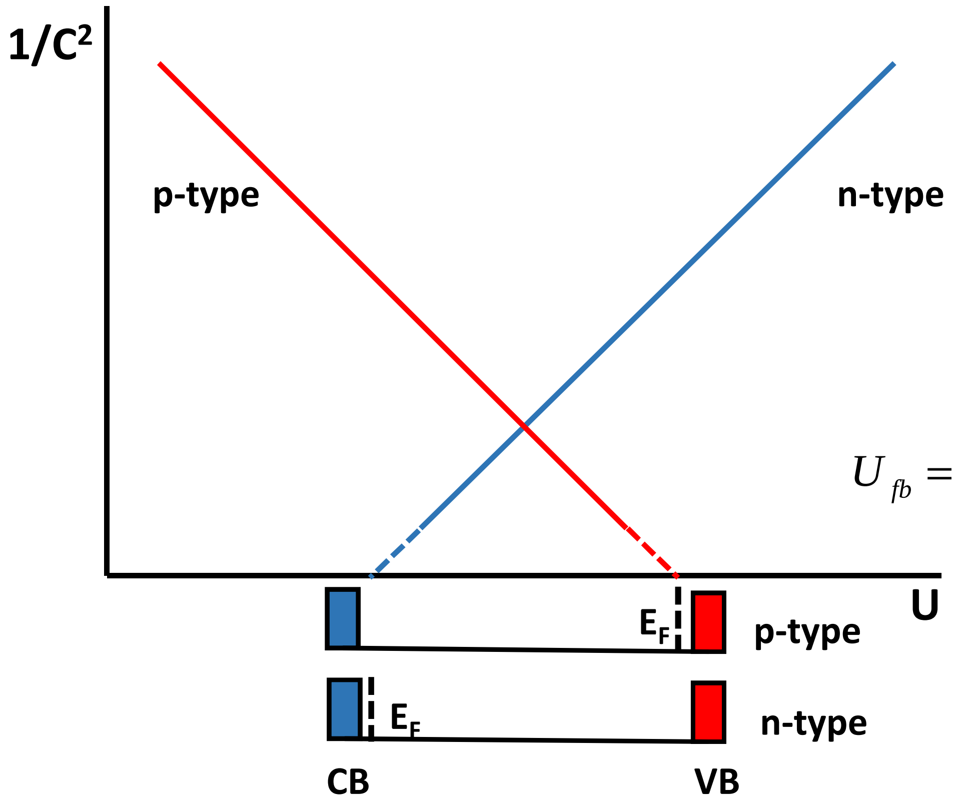


n-type electrode

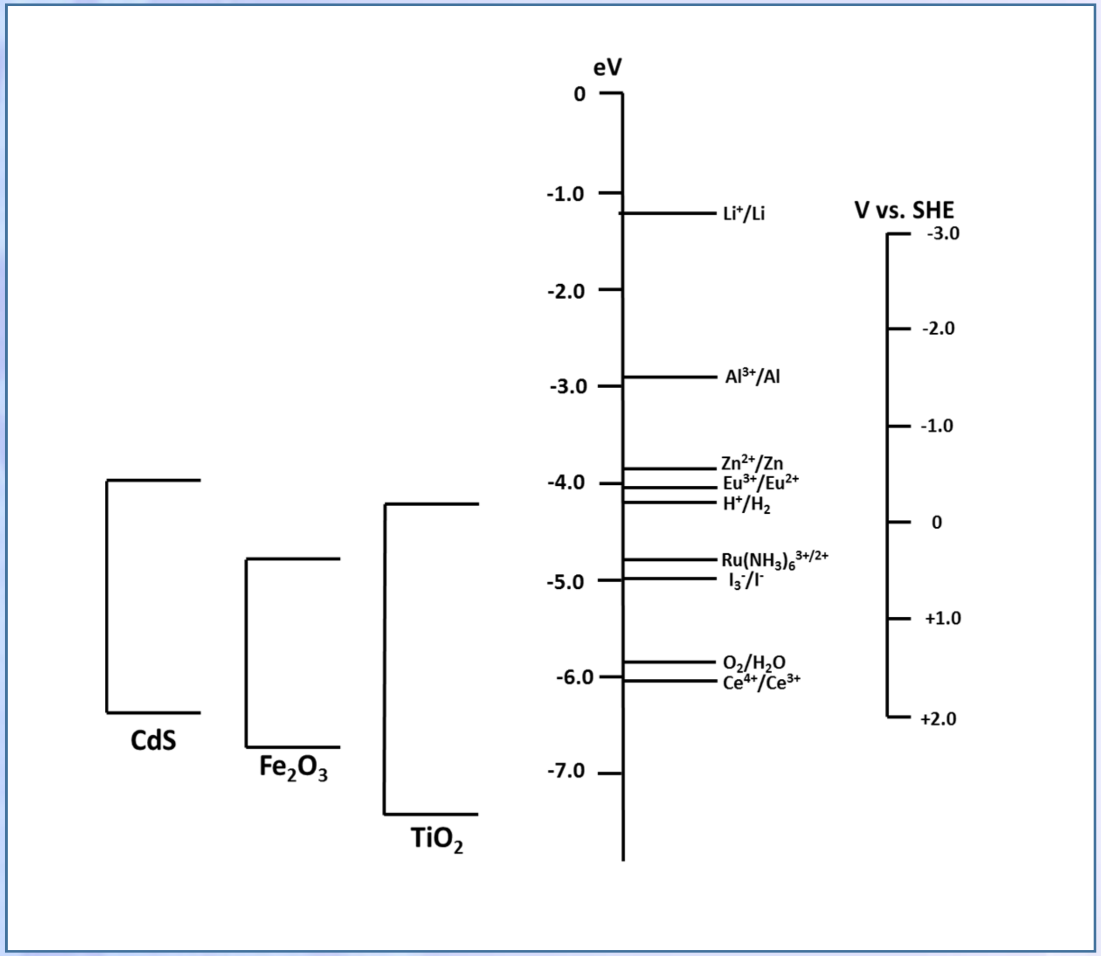
Mott Schottky Plots of the Space Charge Capacitance

$$\frac{1}{C_{sc}^{2}} = \frac{2}{qN_{d}\varepsilon_{SC}\varepsilon_{0}}\left[\Delta\phi_{sc} - \frac{k_{B}T}{q}\right]$$

$$U_{fb} = U_{fb}(pH0) - 0.059\,pH$$

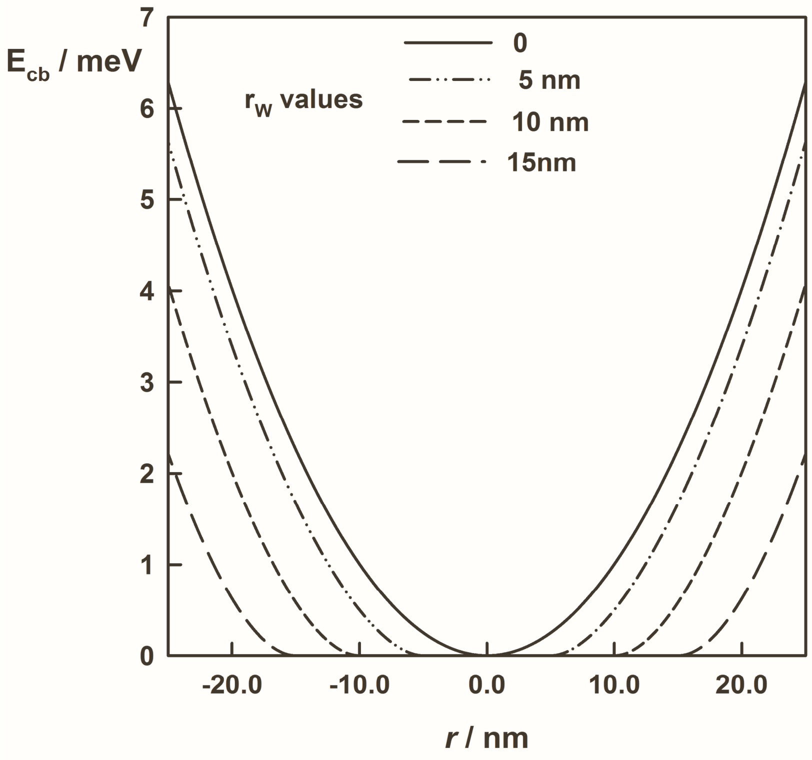


Band Edge Positions at pH = pH_{pzc}

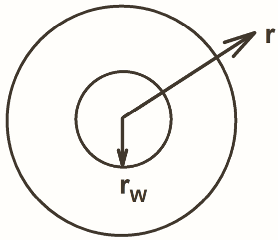


Nanostructured Electrodes

Space Charge in Spherical Particles



$$\phi(r) = \frac{qN}{6\varepsilon\varepsilon_0}\left(r - r_W^2\right)\left(1 + \frac{2r_W}{r}\right)$$

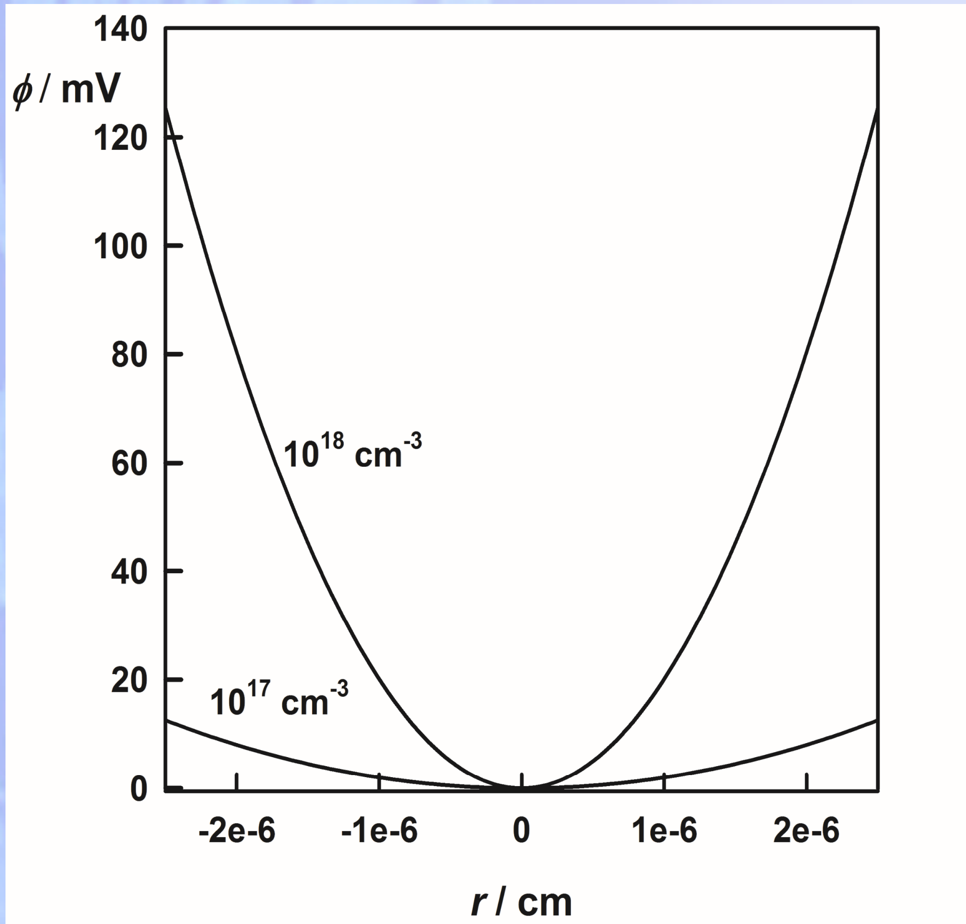


Band bending for a spherical anatase particle ($N_d = 10^{17}$ cm^{-3}, r = 25 nm, ε = 30) as a function of r_W .

r_W defines the edge of the space charge region.

The **maximum band bending of ca. 6 meV** is reached when r_W is reduced to zero, i.e. the space charge region extends to the centre of the particle.

Influence of Doping Density on Space Charge in Spherical Particles



Band bending for complete depletion in spherical anatase particles with different doping densities (r = 25 nm, ε = 30, doping density as shown).

In the case of the lower doping, band bending is limited to only **a few mV**.

For the higher doping, saturation occurs when the potential drop across the depletion layer reaches ca. 120 mV. **The effects of band banding cannot be neglected in this case.**

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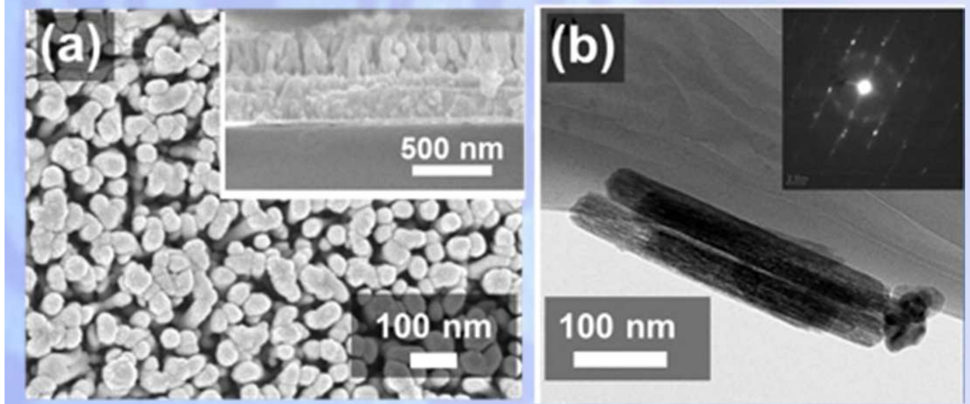
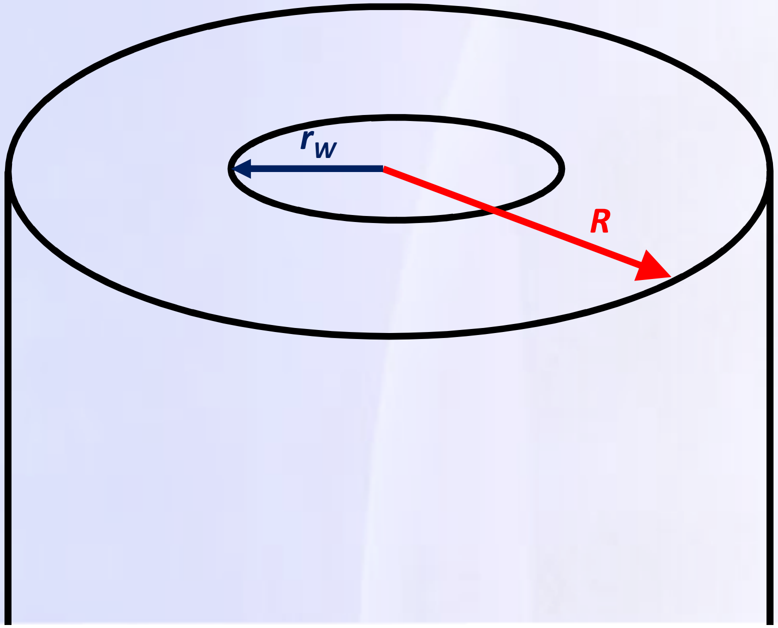
Space Charge in Nanorod Electrodes



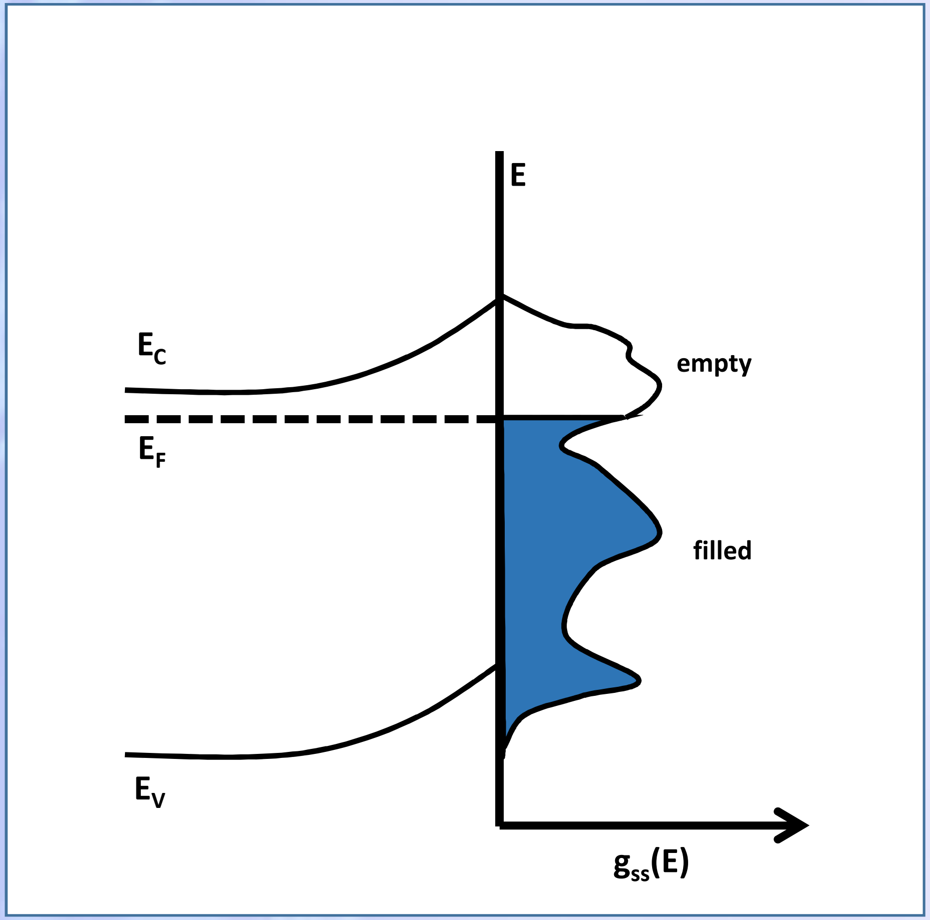
Fe_2O_3 nanorod arrays

$$C_{sc,rod} = \frac{\varepsilon\varepsilon_0}{R\,ln\left(\frac{R}{r_W}\right)}$$

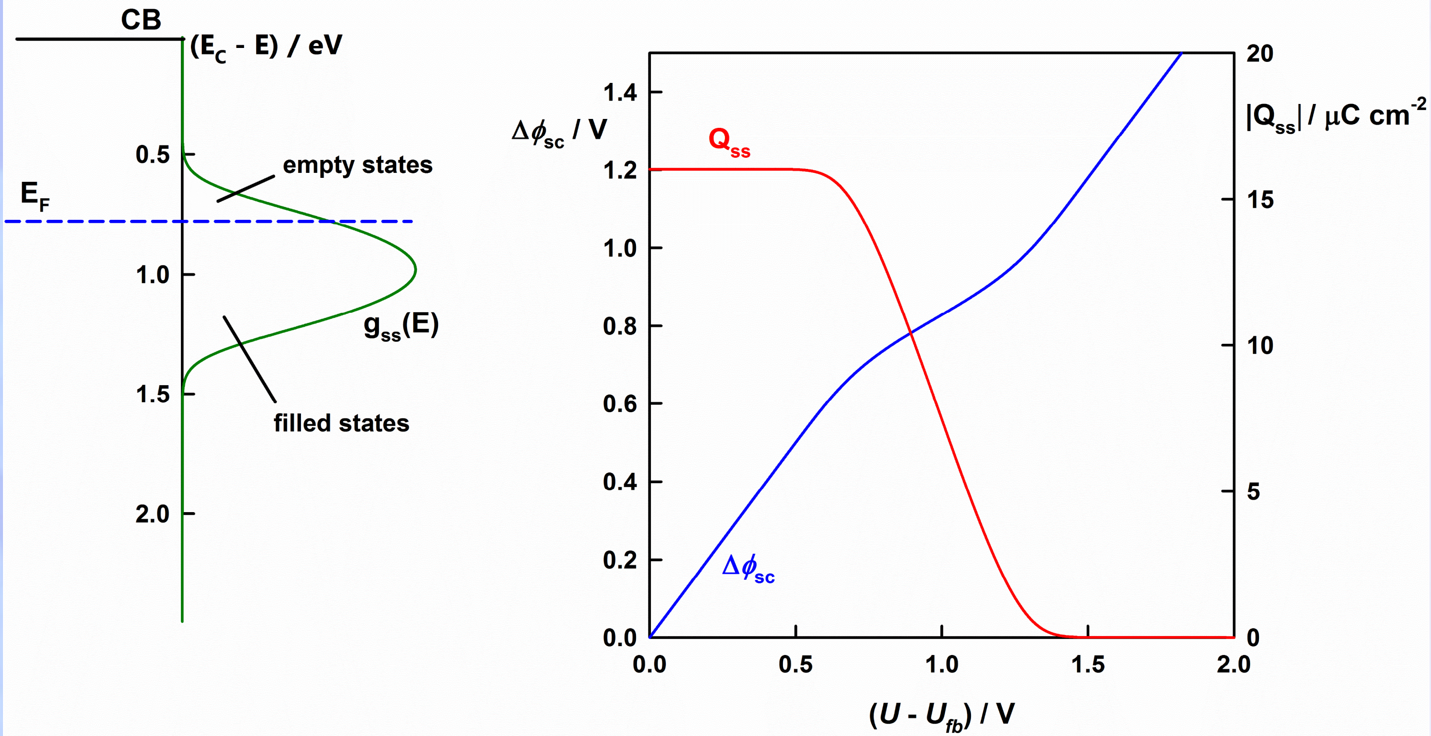
$$\Delta\phi_{SC} = -\frac{qN}{2\varepsilon\varepsilon_0}\left[\frac{1}{2}\left(R^2 - r_W^2\right) + R^2 \ln\left(\frac{r_W}{R}\right)\right]$$



Non-Ideal Systems: Surface States



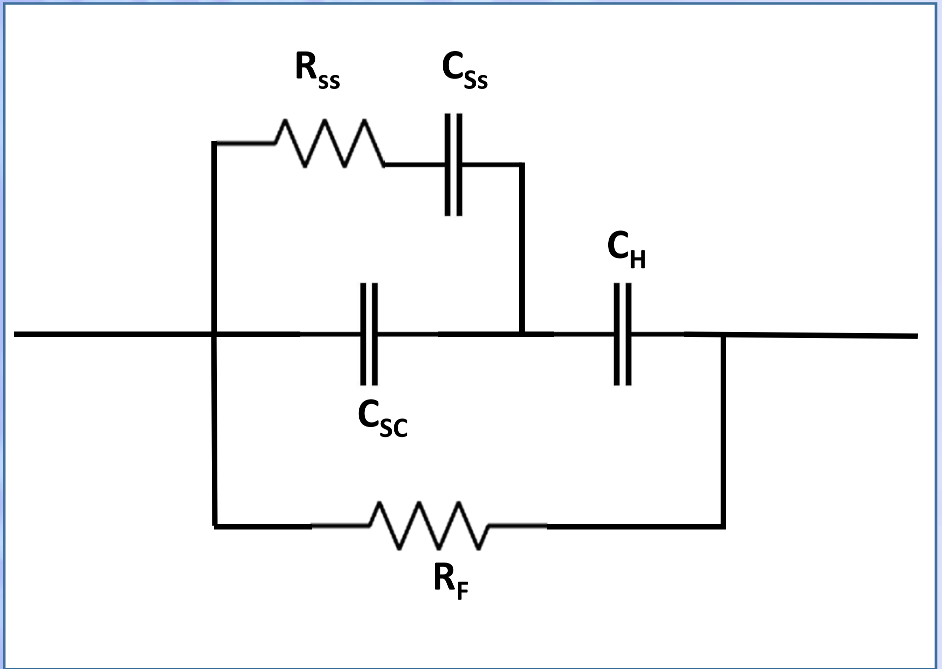
Surface States and Fermi Level Pinning

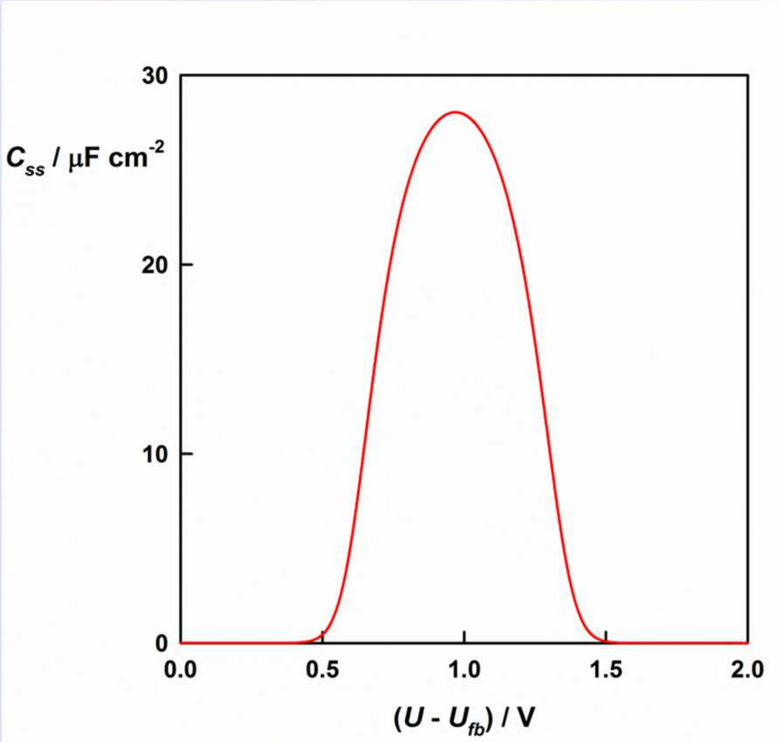


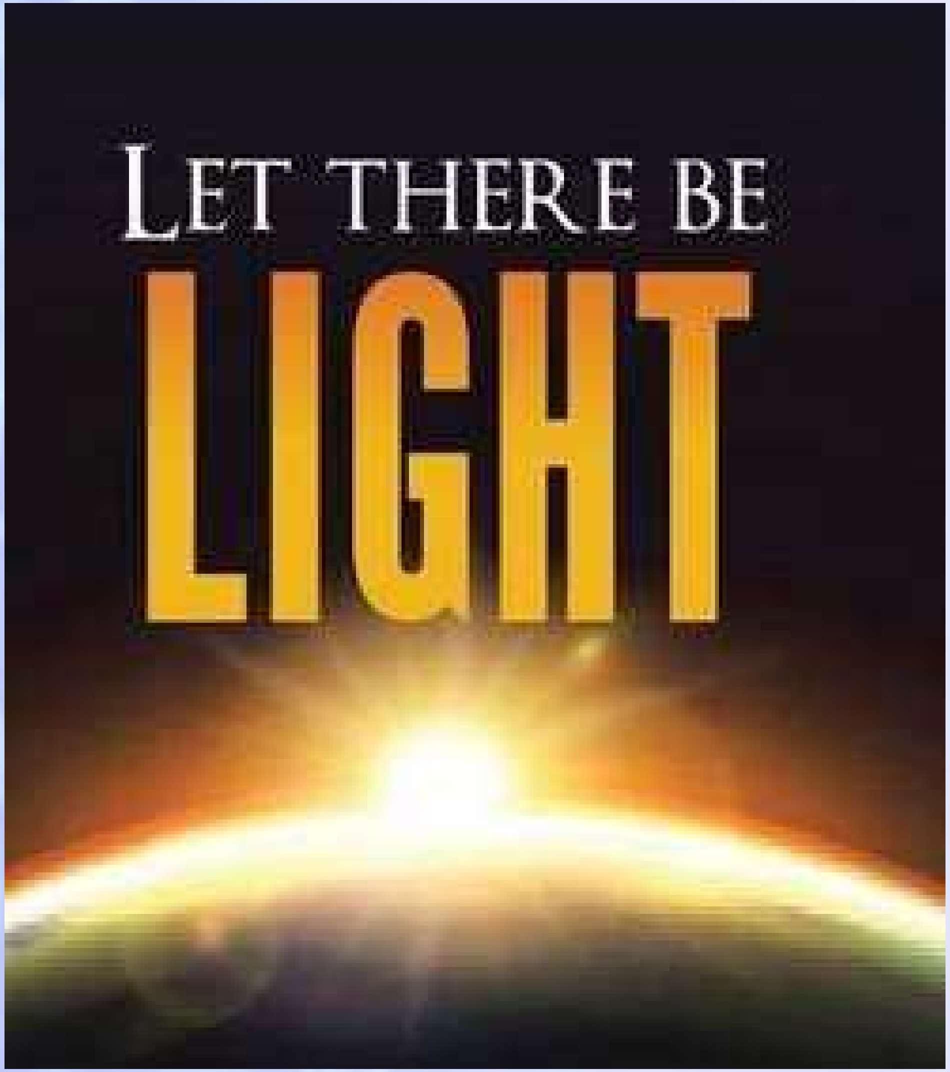
surface state distribution

charge in surface state
and potential drop across the space charge region

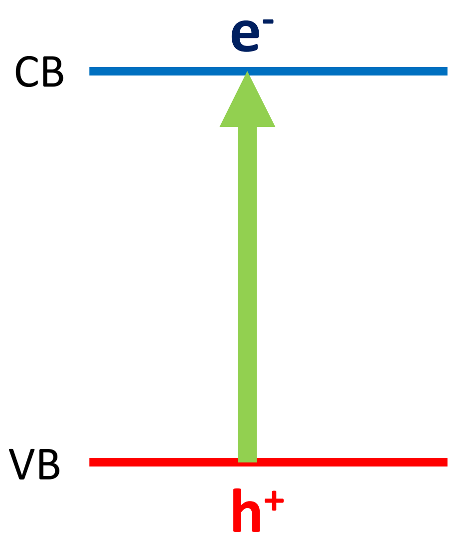
Equivalent Circuit Including Surface State Capacitance






LET THERE BE
LIGHT

What happens when we illuminate a semiconductor electrode?



We create electron-hole pairs

Thermal equilibrium no longer applies

$$n_{eq} \rightarrow n_{eq} + \Delta n$$

$$p_{eq} \rightarrow p_{eq} + \Delta p$$

$$\Delta n = \Delta p$$

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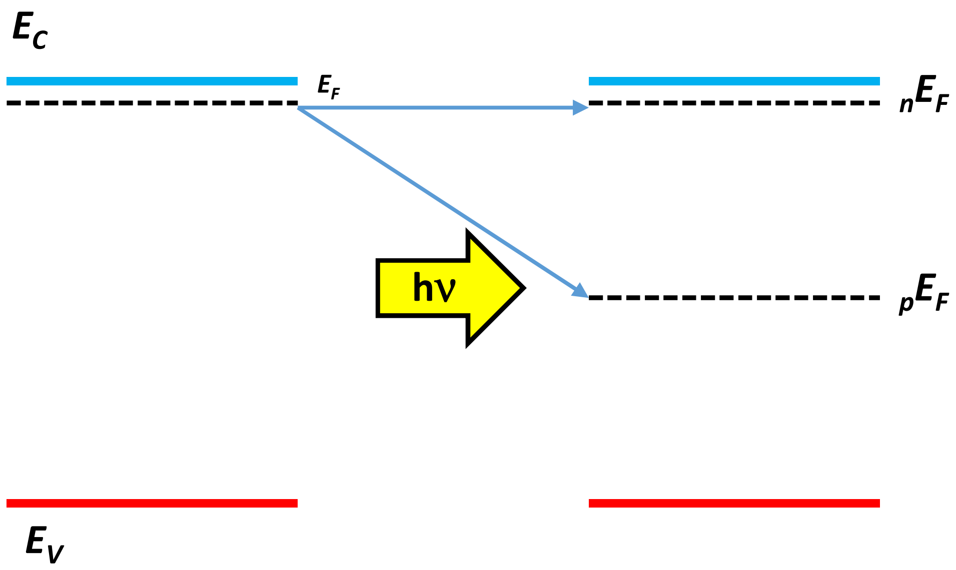
Quasi-Fermi Levels and Fermi Level Splitting



$$n + \Delta n = N_C \exp - \left(\frac{E_C - {}_nE_F}{k_B T} \right)$$

majority carriers - small change

$$p + \Delta p = N_V \exp \left(\frac{E_V + {}_pE_F}{k_B T} \right)$$

minority carriers - large change

stored free energy $\mu_{eh} = \mu_n + \mu_p = {}_nE_F - {}_pE_F$

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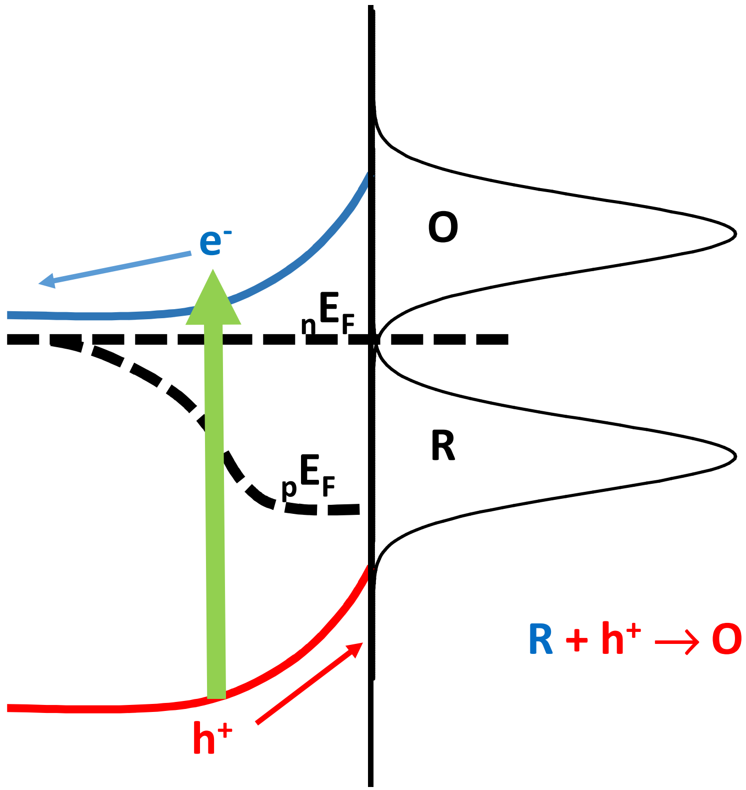
Quasi Fermi Level in Illuminated Semiconductor-Electrolyte Junction

photocurrent due to reaction of **minority carriers** (holes)





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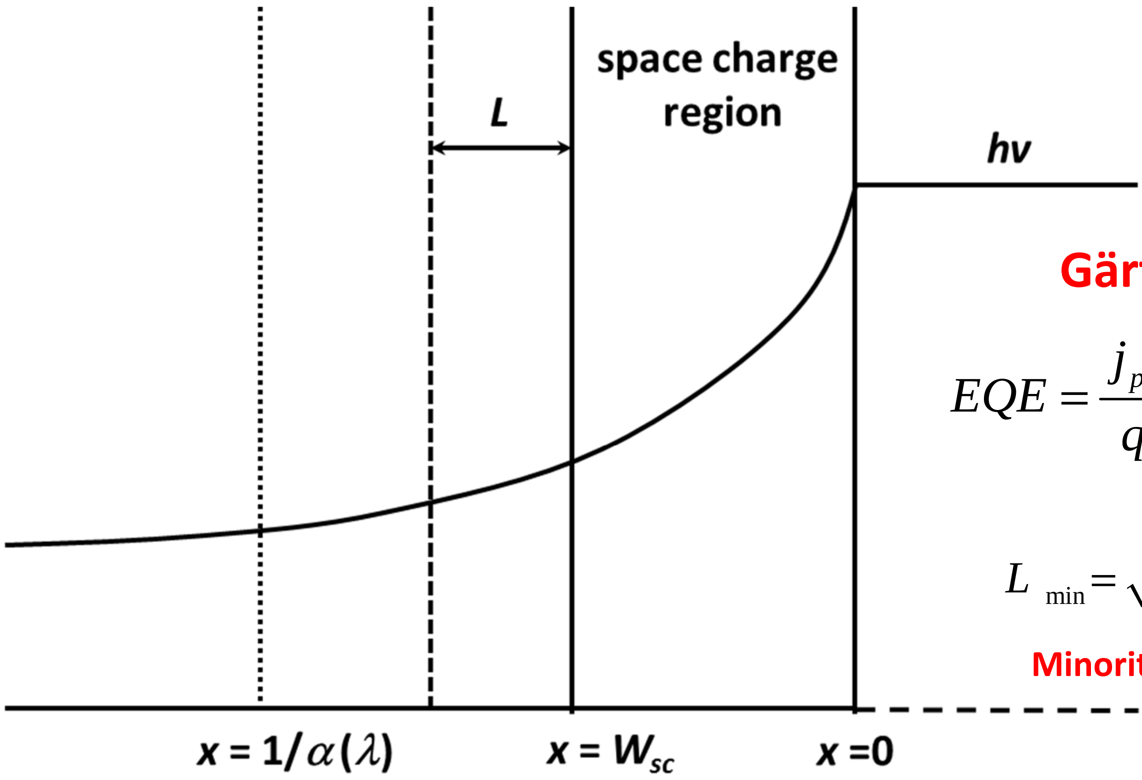
Generation and Collection of Minority Carriers



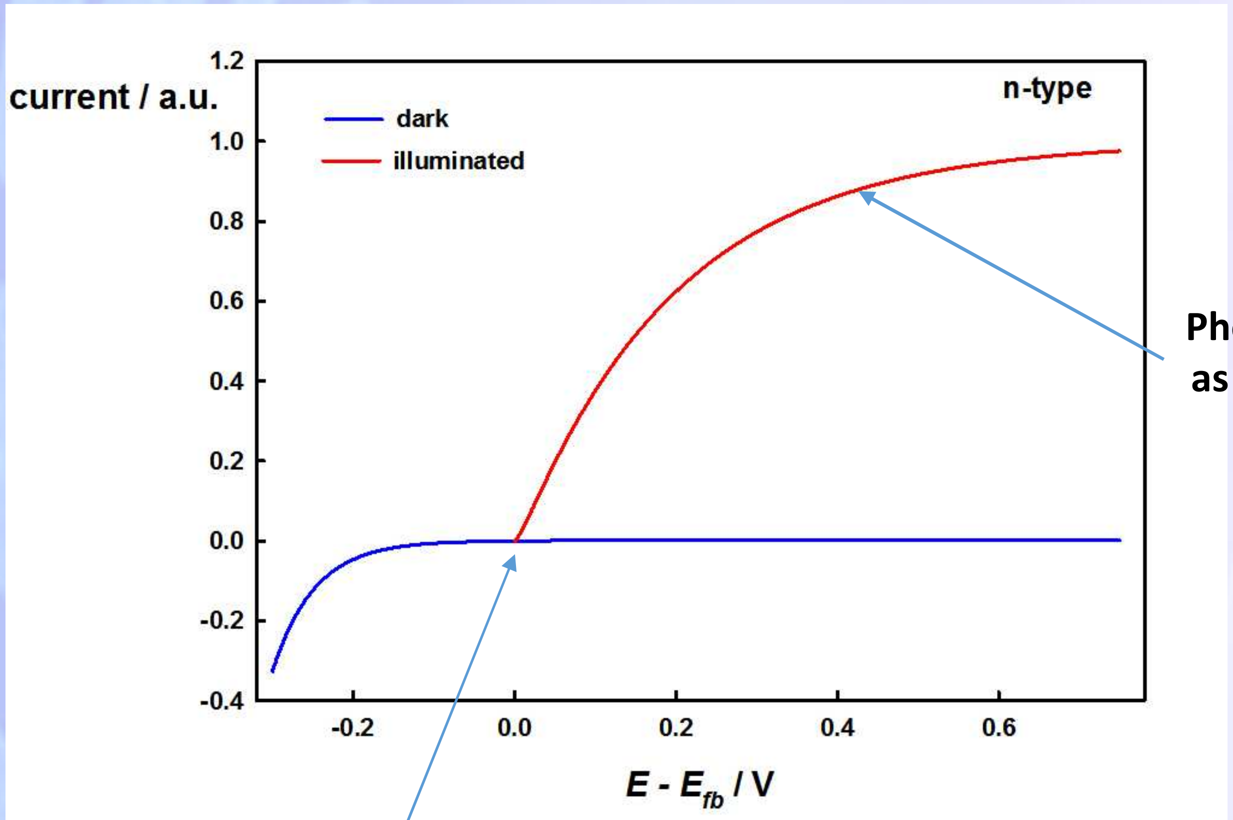
Gärtner Equation

$$EQE = \frac{j_{photo}}{qI_0} = 1 - \frac{\exp-(\alpha W_{SC})}{1+\alpha L_{\min}}$$

$$L_{\min} = \sqrt{D_{\min}\tau_{\min}} = \sqrt{\frac{k_B T}{q}\mu_{\min}\tau_{\min}}$$

Minority carrier diffusion length

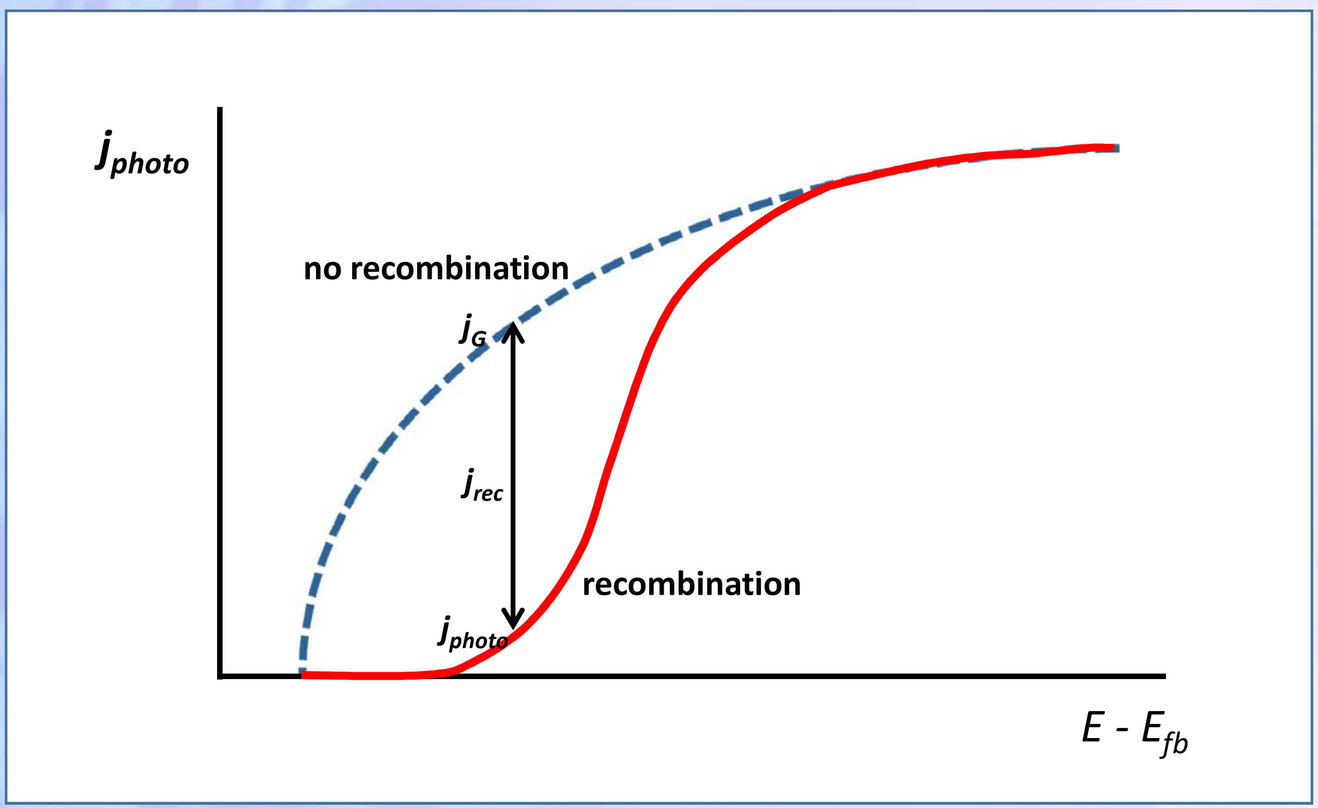
Anodic Photocurrent for n-type Electrode



Photocurrent increases as space charge region gets wider

Simple theory predicts photocurrent onset at flat band potential

Delayed Photocurrent Onset Due to Surface Recombination of Electrons and Holes



End of the first lecture….