Кинетика процессов в конденсированных фазах и на межфазных границах.

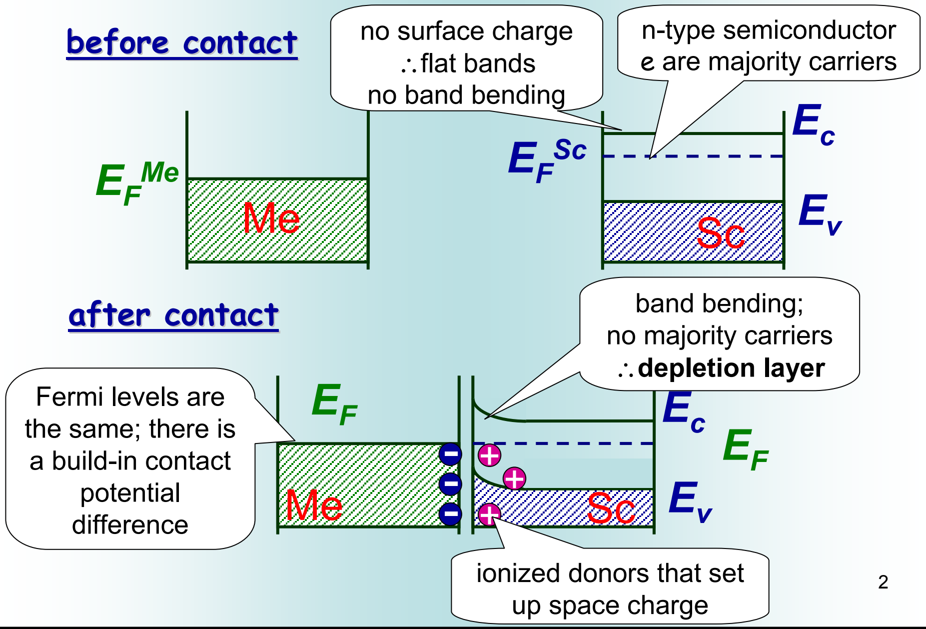
Границы раздела и кинетика реакций на полупроводниковых электродах.

Lecture 2. Semiconductor/Solution Interface. Mott-Schottky Plots. Electron transfer via Valence and Conduction Bands.

Dr. O.A. Semenikhin

МГУ-2017

Metal/Semiconductor Interface



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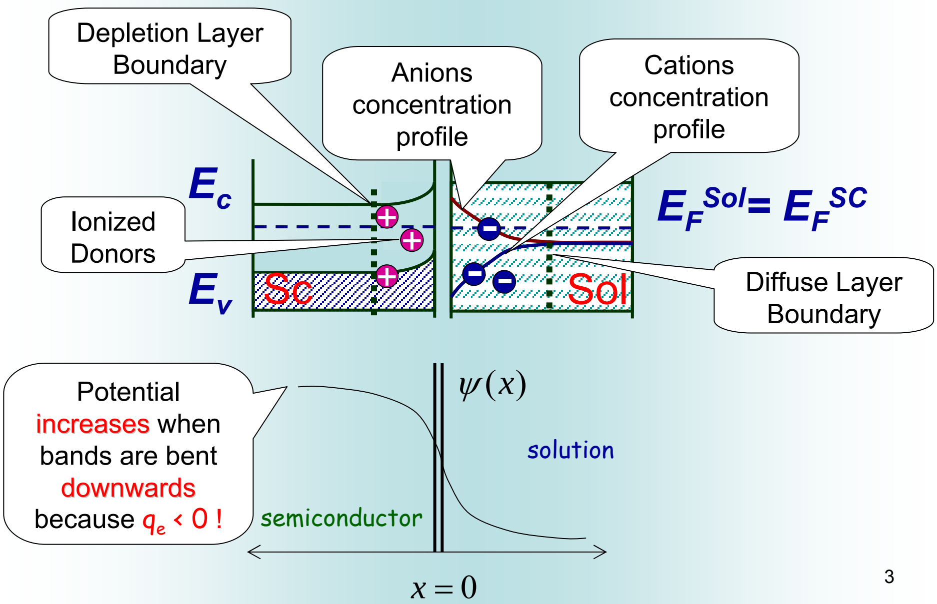
Semiconductor/Solution Interface



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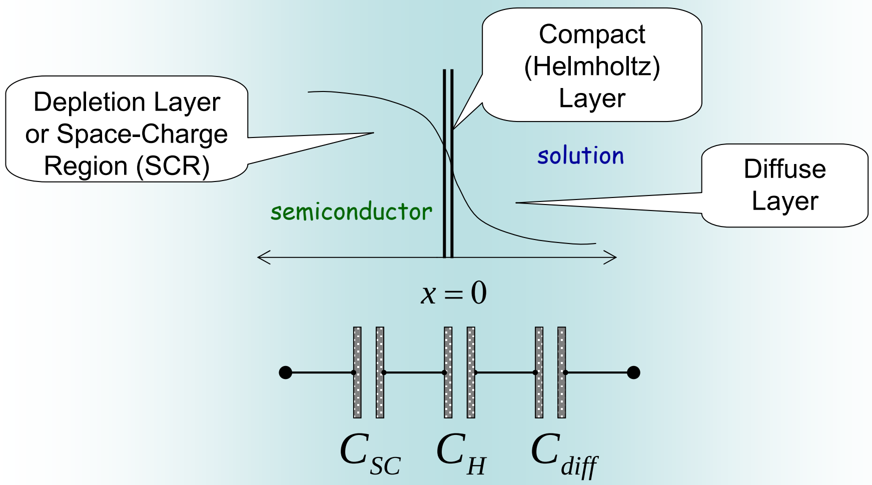
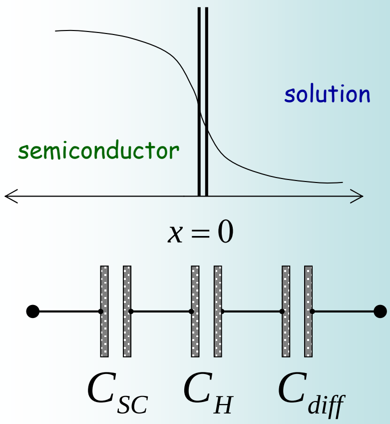
Semiconductor/Solution Interface



$$\boxed{\frac{1}{C_{\text{int}}} = \frac{1}{C_H} + \frac{1}{C_{diff}} + \frac{1}{C_{SC}}}$$

4

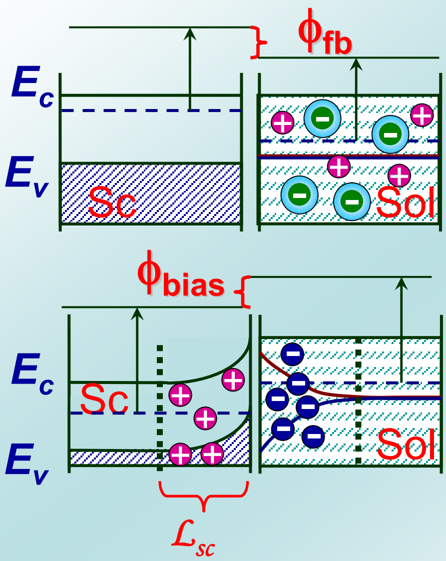
Semiconductor/Solution Interface: Interfacial Capacitance



$$\boxed{\frac{1}{C_{\text{int}}} = \frac{1}{C_H} + \frac{1}{C_{diff}} + \frac{1}{C_{SC}}}$$

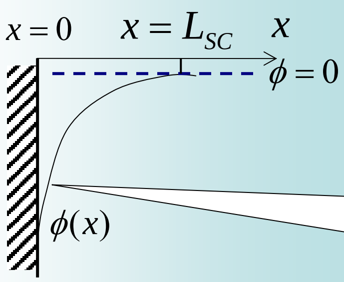
- Capacitance of a semiconductor-electrolyte solution interface consists of three components:
  - capacitance of diffuse layer in the solution;
  - capacitance of compact (Helmholtz) layer at the interface;
  - capacitance of space-charge layer in the semiconductor.
- Of the three components, we have already discussed C_H and C_{diff}.
- We can eliminate C_{diff} if we use sufficiently high electrolyte concentration.
- For semiconductor electrodes, $1/C_{SC}$ is most often much higher than $1/C_H$, and it is C_{SC} that determines C_{int}.
- We need to know how C_{SC} depends on potential.

Flat-Band Potential



- As with the Me/Sc interface, we can bias the interface so that we compensate the build-in contact potential difference.
- There will be no interface charging and no band bending in the semiconductor phase.
- The electrode potential at which such a situation happens is called **flat-band potential**.
- Alternatively, we can bias the interface in other direction and repulse mobile carriers deeper into semiconductor bulk.
- The band bending will increase and so will the **width** $\mathcal{L}_{sc}$ of the **space-charge layer** in the semiconductor.

Width of the Space-Charge Layer



The bulk of semiconductor is electrically neutral outside the SCL

Potential profile in the semiconductor; at the interface $\phi < 0$ vs. bulk; surface charged negatively

Poisson Equation

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\varepsilon\varepsilon_0}$$

charge density in the semiconductor

dielectric constant of the semiconductor

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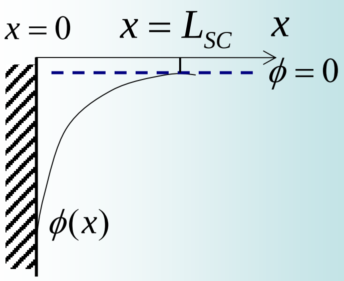
Width of the Space-Charge Layer



$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\varepsilon\varepsilon_0}$$

for depletion layer

$$\rho(x) = e_0 N_D$$

ionized donor density

elementary charge

$$\phi(x) = -\frac{e_0 N_D}{2\cdot\varepsilon\varepsilon_0}x^2 + ax + \phi(0); \quad a = \left.\frac{\partial\phi}{\partial x}\right|_{x=0} = -E(0)$$

$$\partial\frac{\phi(x)}{\partial x} = -\frac{e_0 N_D}{\varepsilon\varepsilon_0}x + a;$$

There is no space charge beyond $x=L_{sc}$ and $\phi, d\phi/dx=0$

when x=Lsc: $\left.\frac{\partial\phi}{\partial x}\right|_{x=Lsc} = 0 \qquad \frac{e_0 N_D}{\varepsilon\varepsilon_0}L_{sc} = a$

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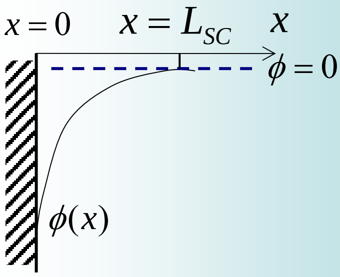
Width of the Space-Charge Layer



$$\frac{d^2\phi}{dx^2}=-\frac{e_0 N_D}{\varepsilon\varepsilon_0}\quad\Big|\times 2\cdot\frac{d\phi}{dx}$$

$$2\cdot\frac{d\phi}{dx}\cdot\frac{d^2\phi}{dx^2}=-\frac{2e_0 N_D}{\varepsilon\varepsilon_0}\cdot\frac{d\phi}{dx}$$

$$2\cdot\frac{d\phi}{dx}\cdot\frac{d^2\phi}{dx^2}=\frac{d}{dx}\left[\frac{d\phi}{dx}\right]^2;\quad \frac{d\phi}{dx}\equiv -E(x)$$

E=-grad(ϕ)
Definition of electric field

$$\frac{d}{dx}[E(x)]^2=\frac{2e_0 N_D}{\varepsilon\varepsilon_0}\cdot E(x)$$

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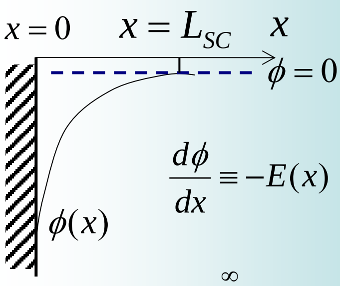
Width of the Space-Charge Layer



$$\frac{d}{dx}[E(x)]^2=\frac{2e_0 N_D}{\varepsilon\varepsilon_0}\cdot E(x)$$

$$\frac{d\phi}{dx}\equiv -E(x)$$

$$[E(x)]^2\Big|_0^\infty=\frac{2e_0 N_D}{\varepsilon\varepsilon_0}\cdot\int_o^\infty E(x)\cdot dx$$

$$[E(\infty)]^2=0;\int_o^\infty E(x)\cdot dx=\int_o^\infty -\frac{d\phi}{dx}\cdot dx=\phi(0)$$

Both electric field and potential equal to zero at x=∞

$$-[E(0)]^2=\frac{2e_0 N_D}{\varepsilon\varepsilon_0}\cdot\phi(0)$$

$$E(0)=a=\sqrt{\frac{2e_0 N_D}{\varepsilon\varepsilon_0}}\cdot\sqrt{|\phi(0)|}$$

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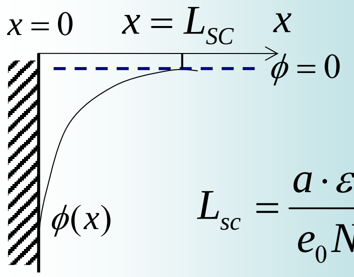
Width of the Space-Charge Layer



$$E(0)=a=\sqrt{\frac{2e_0N_D}{\varepsilon\varepsilon_0}}\cdot\sqrt{|\phi(0)|}$$

$$L_{sc}=\frac{a\cdot\varepsilon\varepsilon_0}{e_0N_D} \qquad L_{sc}=\sqrt{\frac{2\varepsilon\varepsilon_0}{e_0N_D}|\phi(0)|}$$

The width of the space-charge layer increases as a square root of the potential drop across the SCL

at $\phi=\phi_{fb}$ there is no SCL and $\phi(0)=0$.

$\therefore$ potential drop across the SCL $\phi(0)=\phi-\phi_{fb}$

$$L_{sc}=\sqrt{\frac{2\varepsilon\varepsilon_0}{e_0N_D}|\phi-\phi_{fb}|}$$

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Space-Charge Region

- The width of the space charge region can be also expressed through the Debye length:

$$L_{sc}=\sqrt{\frac{2\varepsilon\varepsilon_0}{e_0N_D}\cdot\Delta\psi} \qquad L_D=\sqrt{\frac{\varepsilon\varepsilon_0k_BT}{e_0^2n_0}}$$

$$L_{sc}=\sqrt{\frac{\varepsilon\varepsilon_0}{e_0N_D}\cdot\frac{k_BT}{e_0}}\times\sqrt{\frac{2\cdot\Delta\psi}{\left(\frac{k_BT}{e_0}\right)}}$$

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Space-Charge Region

- For a doped semiconductor,

$$n_0 = N_D$$

- and $$L_{sc} = L_D \times \sqrt{\frac{2 \cdot \Delta\psi}{k_B T / e_0}}$$

- At T=298 K

$$k_B T / e_0 = 0.029\ \mathrm{V}$$

- and therefore the Debye length is equal to the width of the space charge layer when the potential drop across the SCR is half of this value, or ca, 15 mV at 298K.
- In semiconductor devices, the potential drops are typically much greater and Lsc can be up to several micrometers.

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Capacitance of the Space-Charge Layer

$$C = \frac{\varepsilon\varepsilon_0}{L_{sc}} \qquad L_{sc} = \sqrt{\frac{2\varepsilon\varepsilon_0}{e_0 N_D}\left|\phi - \phi_{fb}\right|}$$

$$C^{-2} = \frac{2}{e_0 N_D \varepsilon\varepsilon_0}\left|\phi - \phi_{fb}\right|$$

The capacitance of the space-charge power minus 2 (that is, unity over capacitance squared) is directly proportional to the potential drop across the SCL. Being plotted vs. the electrode potential, the C^{-2} dependence yields a straight line with an intercept of ϕ_{fb} and a slope inversely proportional to the donor concentration N_D

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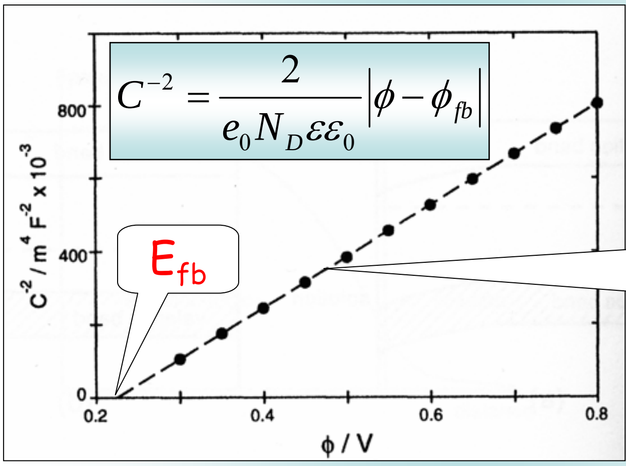
Capacitance of the Space-Charge Layer



Slope equal to

$$\frac{2}{e_0 N_D \varepsilon\varepsilon_0}$$

Such dependencies are called Mott-Schottky plots

An Example of Experimental Mott-Schottky Plots

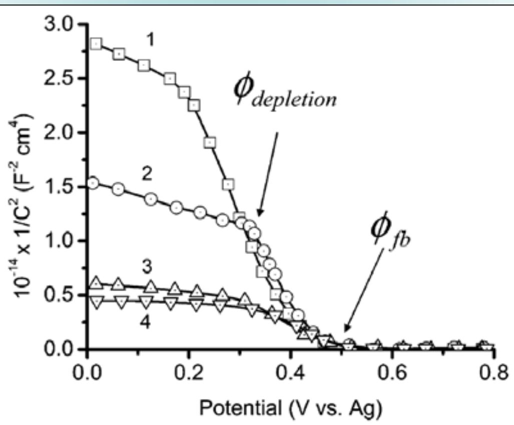
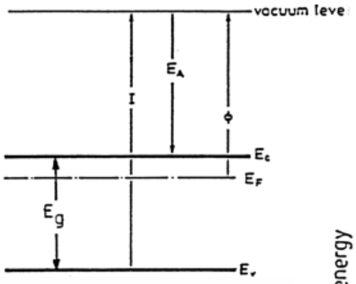


Figure 4. Mott−Schottky plots for PBT films of different thicknesses: (1) 40.2 nm, (2) 27.2 nm, (3) 19.1 nm, and (4) 13.2 nm. Potential modulation frequency was 900 Hz.

O.A. Semenikhin et al. *J. Phys. Chem. B, Vol. 110, No. 41, 2006*

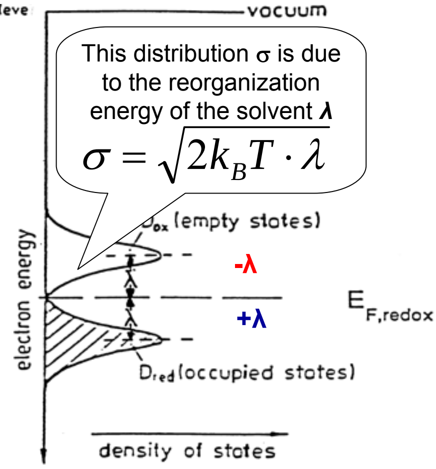
Kinetics of Dark and Light Processes at Semiconductor/Solution Interface



$$D_{ox} = \exp\left[-\frac{(E - E_{F,redox} - \lambda)^2}{4kT\lambda}\right]$$

$$D_{red} = \exp\left[-\frac{(E - E_{F,redox} + \lambda)^2}{4kT\lambda}\right]$$

λ is usually 0.5 – 2 eV



For the electron transfer to occur, the energy levels of the initial and final electronic states must coincide: the Franck-Condon principle.

Image Source: Arthur J. Nozik; *J. Phys. Chem.* **1996,** 100, 13061-13078.

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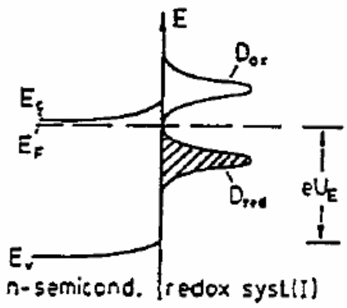
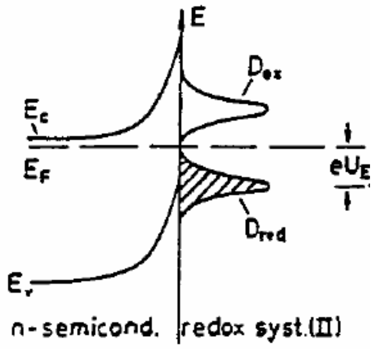
Semiconductor/Solution Interface



Electron exchange through conduction band



Hole exchange through valence band

Redox System II had more positive E^{redox} before contact

Image Source: Arthur J. Nozik; *J. Phys. Chem.* **1996,** 100, 13061-13078.

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J-E curves for p- and n-GaAs

GaAs, 6M HCl, Cu^{2+}/Cu^{+}
Currents only via valence band

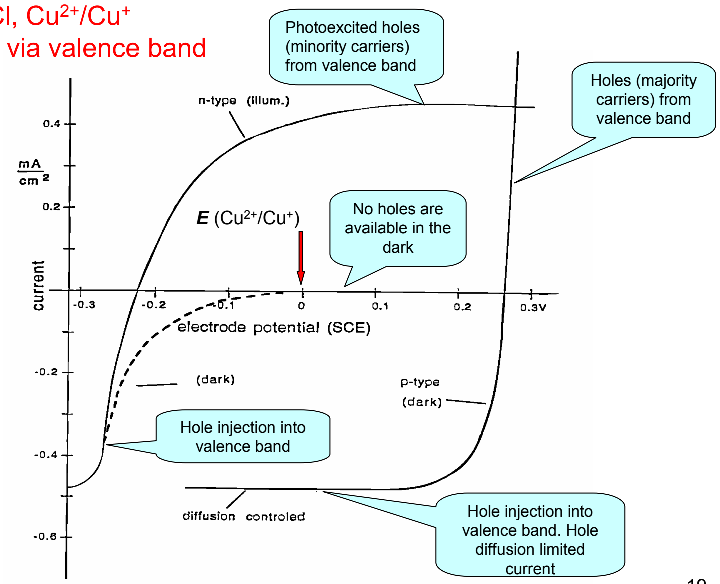

Image Source: Arthur J. Nozik; *J. Phys. Chem.* **1996,** 100, 13061-13078.

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Positions of Semiconductor Bands

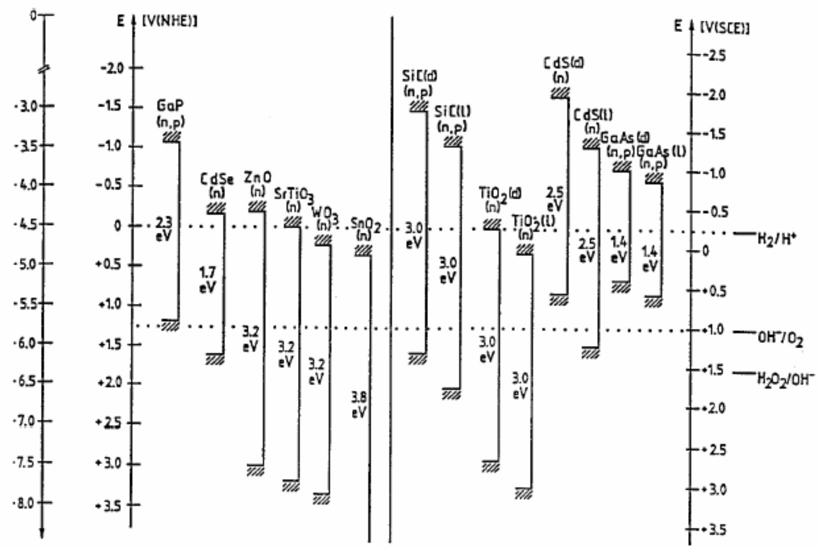

Image Source: Arthur J. Nozik; *J. Phys. Chem.* **1996,** 100, 13061-13078.

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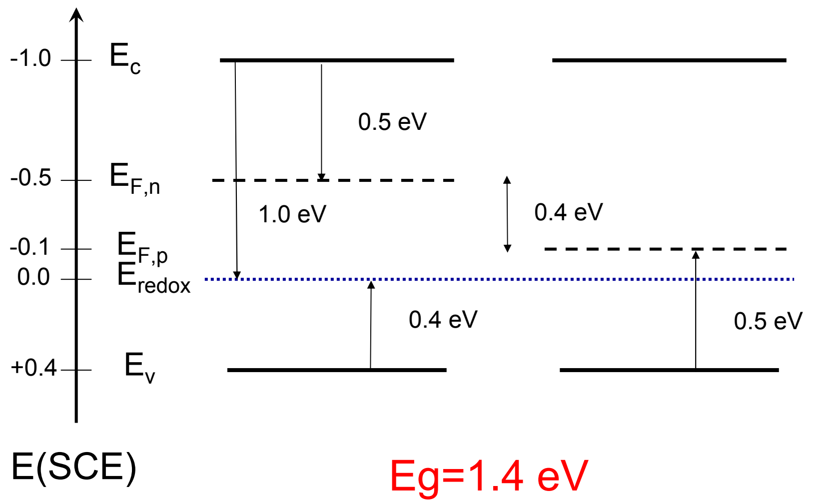
Energy Diagrams for p- and n-GaAs



Eg=1.4 eV

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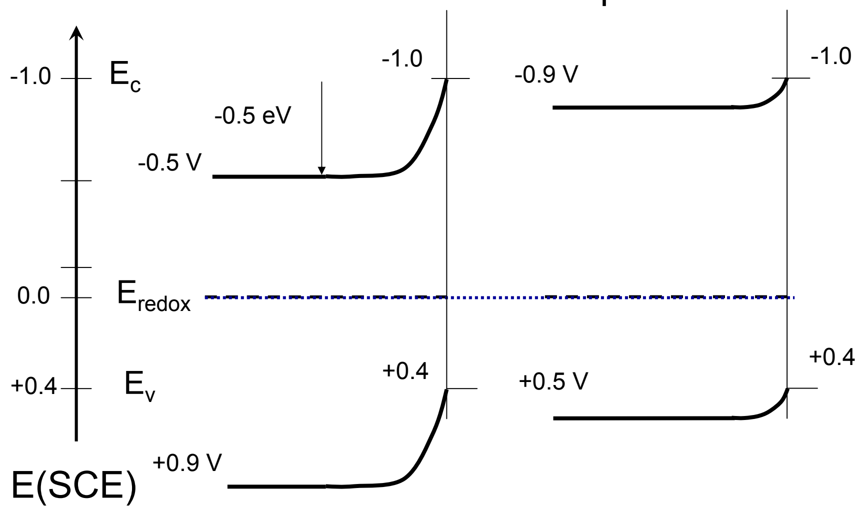
Energy Diagrams for p- and n-GaAs



Equilibrium

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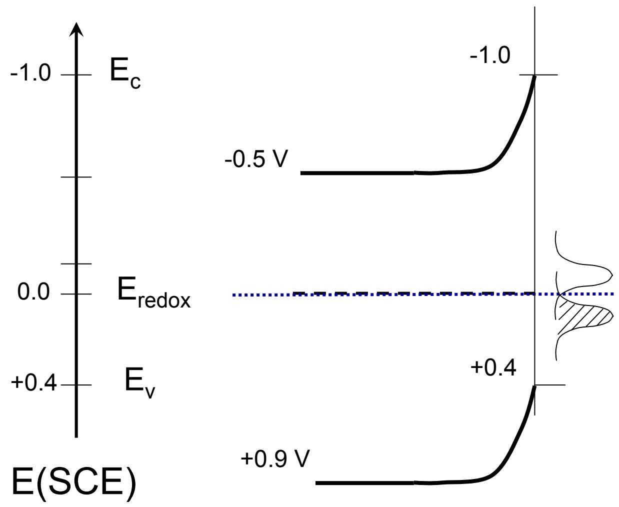
Energy Diagrams for p- and n-GaAs

Equilibrium



No dark current. Electrochemical potentials of electrons are equal in the semiconductor and in the solution.

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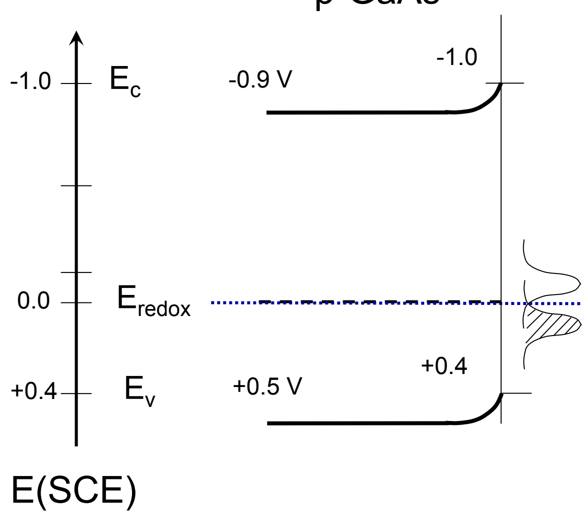
Energy Diagrams for p- and n-GaAs

Equilibrium



No dark current. Electrochemical potentials of electrons are equal in the semi-conductor and in the solution.

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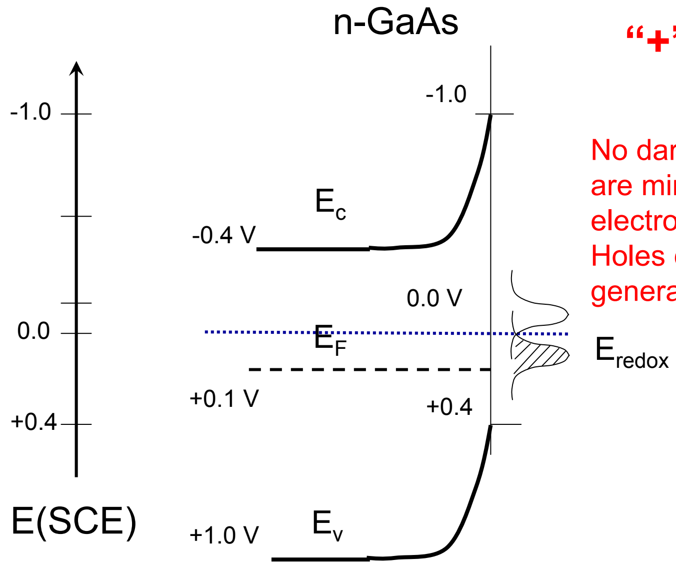
Energy Diagrams for p- and n-GaAs



“+”-ve bias

No dark current. Holes are minority carriers and electrons are depleted. Holes can be photo-generated though…

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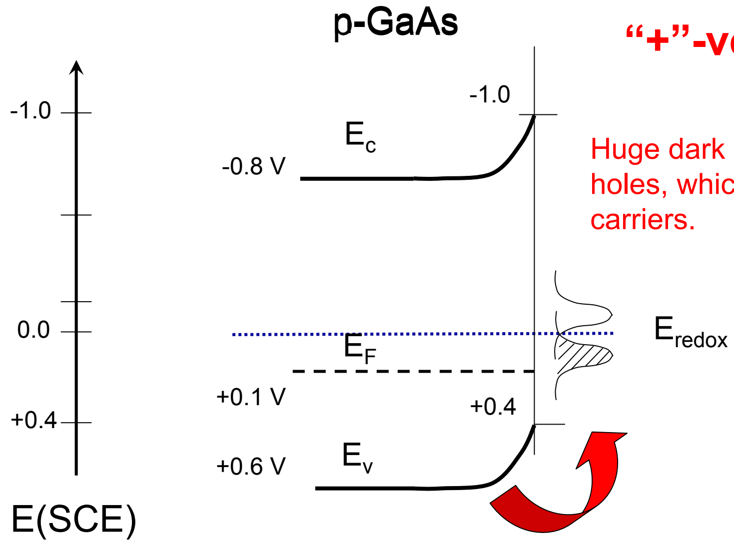
Energy Diagrams for p- and n-GaAs



“+”-ve bias

Huge dark current of holes, which are majority carriers.

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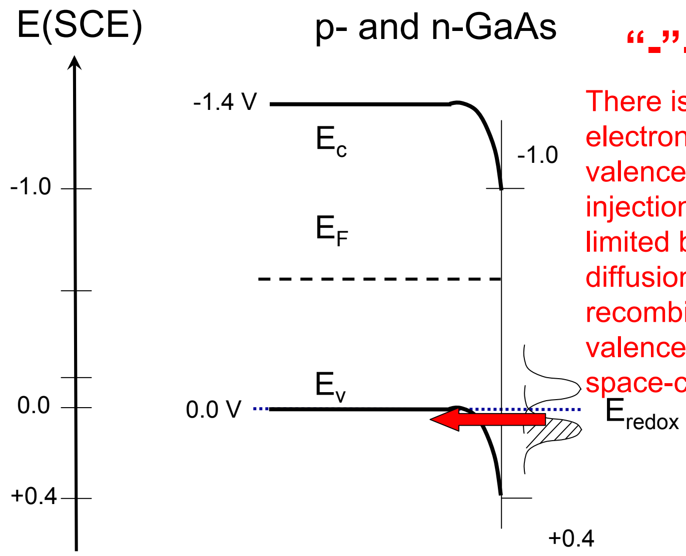
Energy Diagrams for p- and n-GaAs



"-"-ve bias

There is a dark current of electron tunnelling into the valence band (hole injection) . The current is limited by the hole diffusion and recombination in the valence band outside the space-charge layer.

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