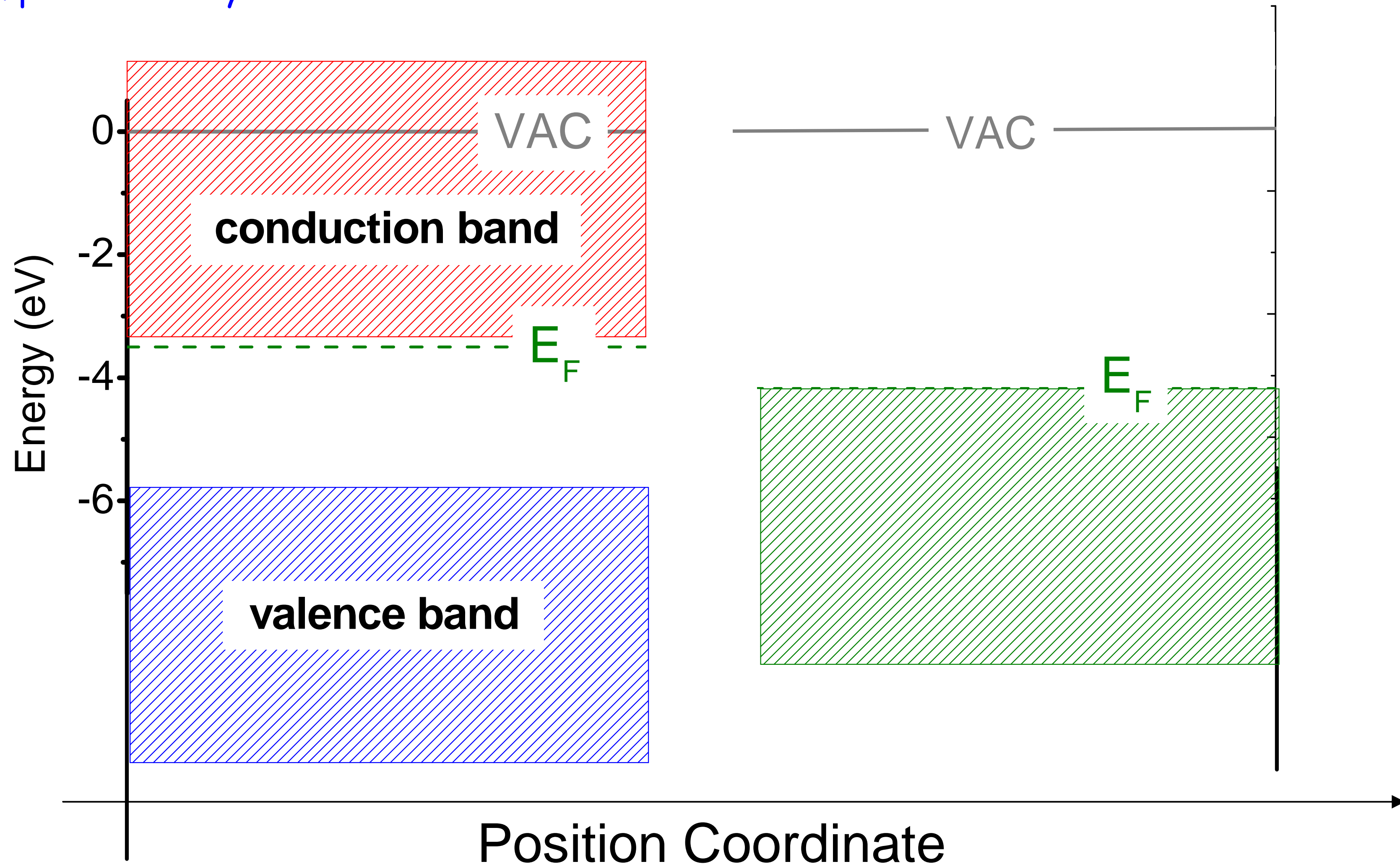
Formation and Equilibration of Interfaces

STEP 1: The alignment of electronic states is determined by the very nature of both interface components (vacuum level alignment)……………….

Example: Schottky Contact

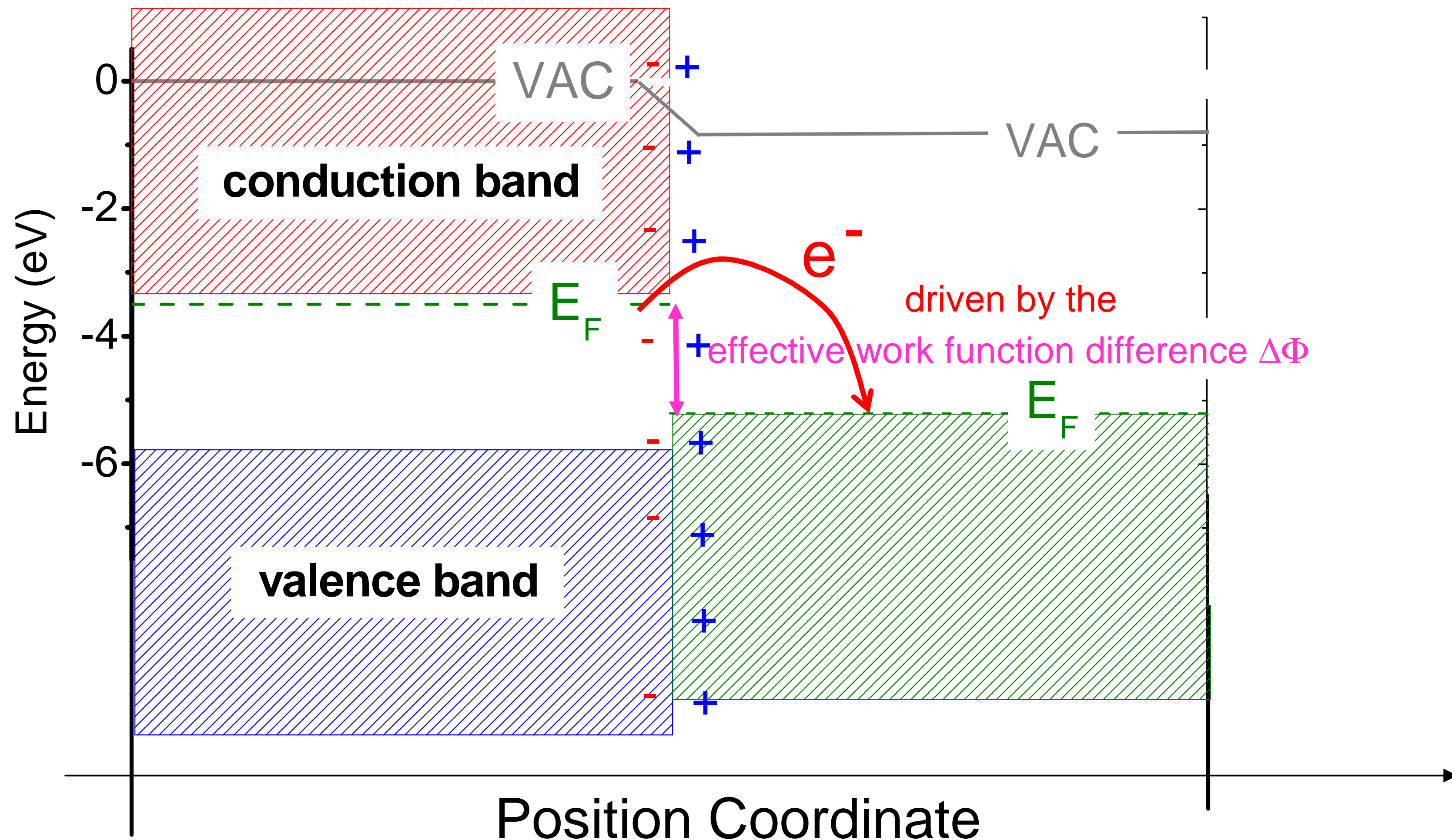


Formation and Equilibration of Interfaces

STEP 1 (still) ....plus the chemical reaction between them (set-up of interface dipoles)

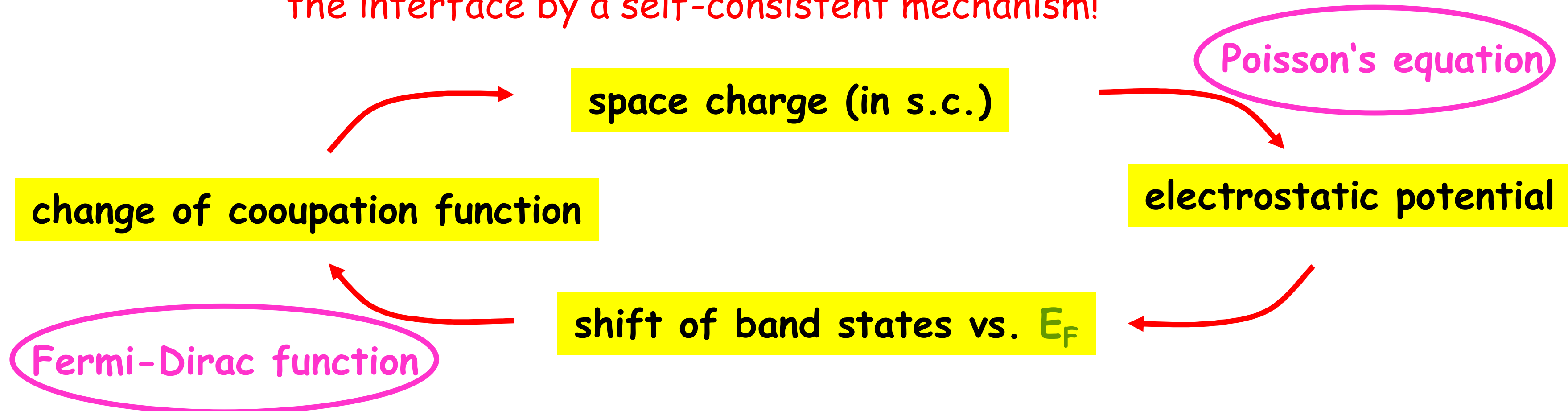
STEP 2: chemical equilibrium is achieved by the exchange of free charge................

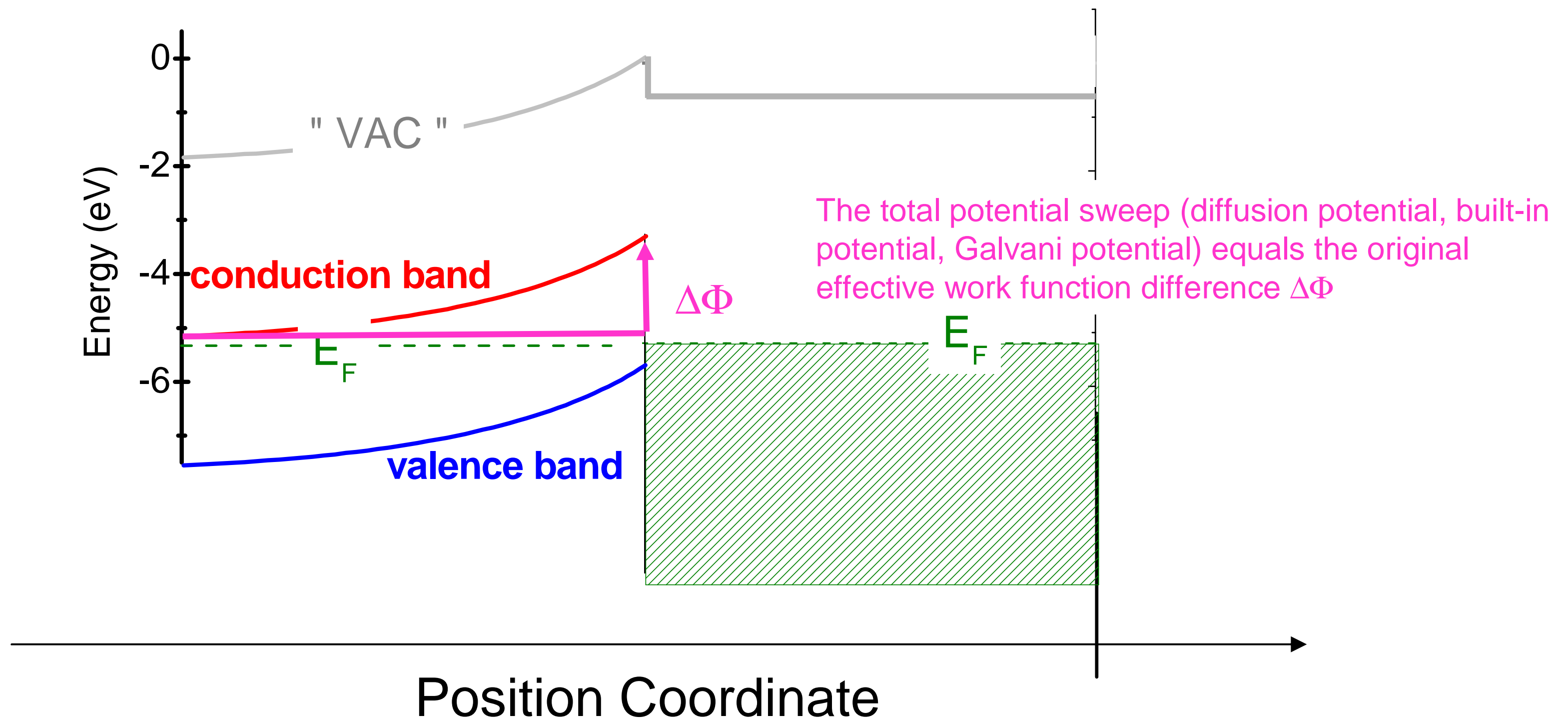
Example: Schottky Contact



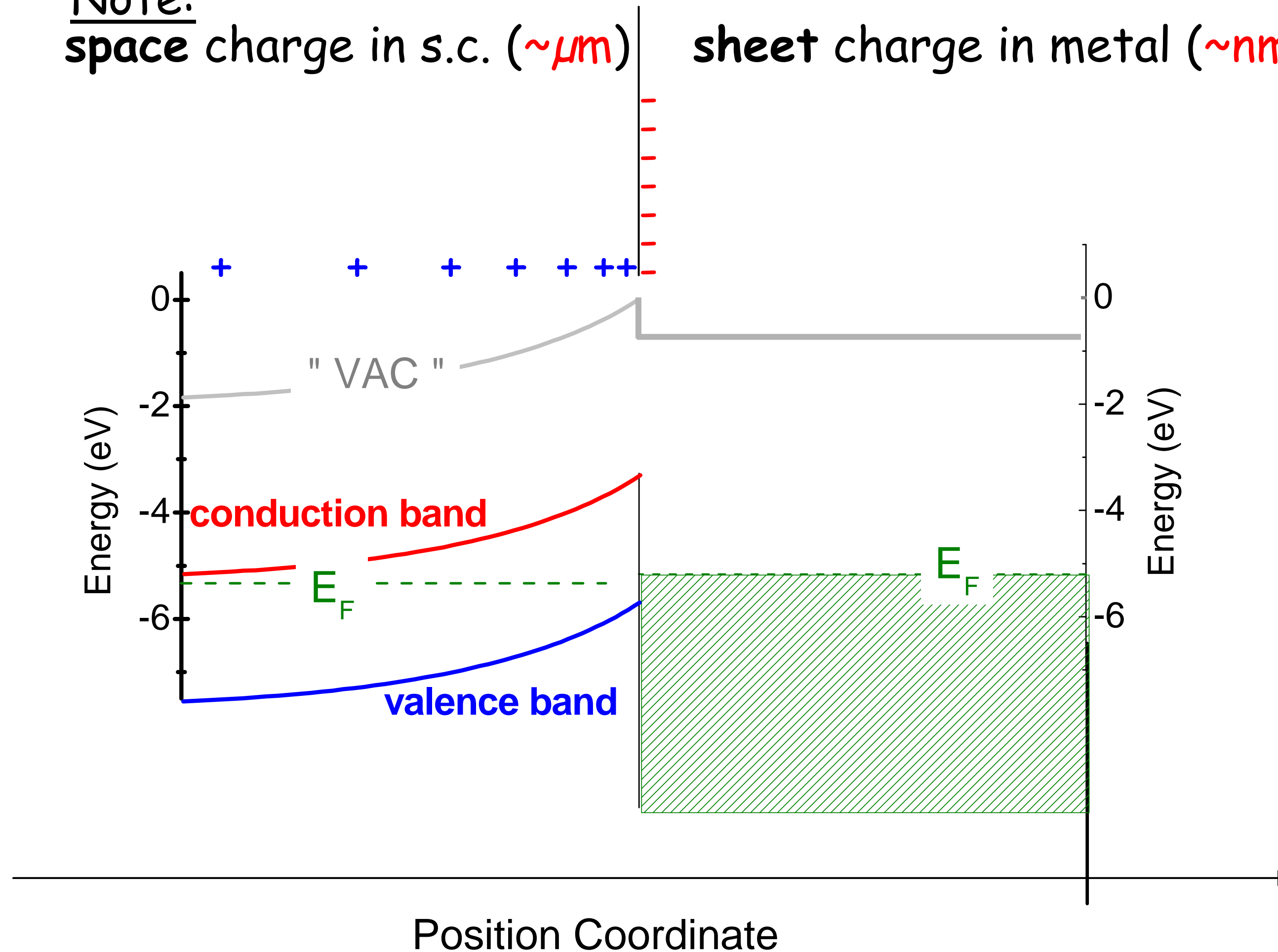
Formation and Equilibration of Interfaces

STEP 2: chemical equilibrium is achieved by the exchange of free charge across the interface by a self-consistent mechanism!





Space Charge and Potential



Role of metal can also be taken by:

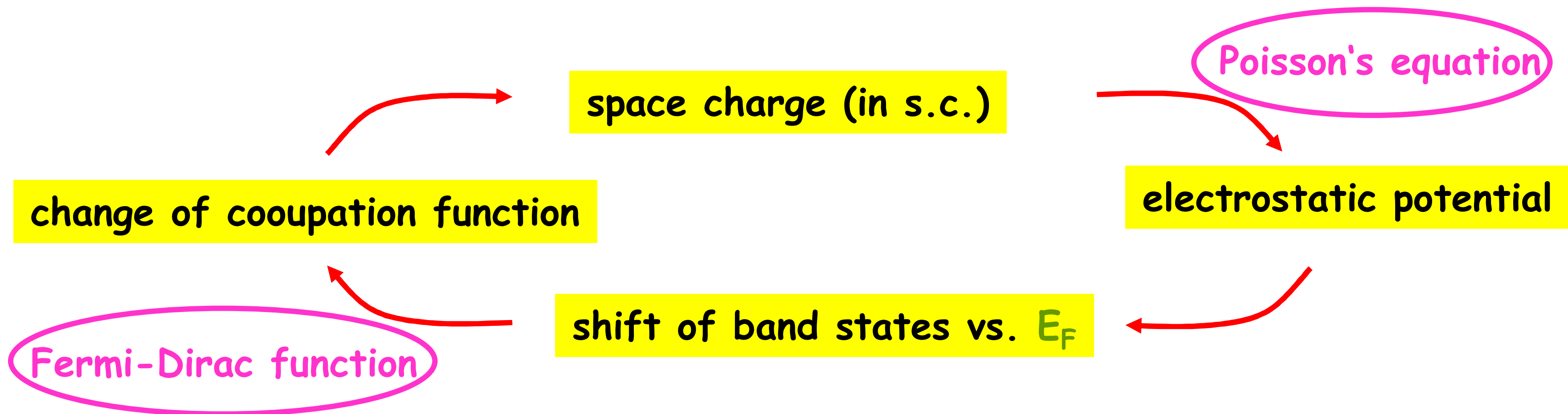
- surface states or defects
- adsorbates
- electrolytes
- metals across a dielectric

The Semiconductor Side

of the

Layer Stack

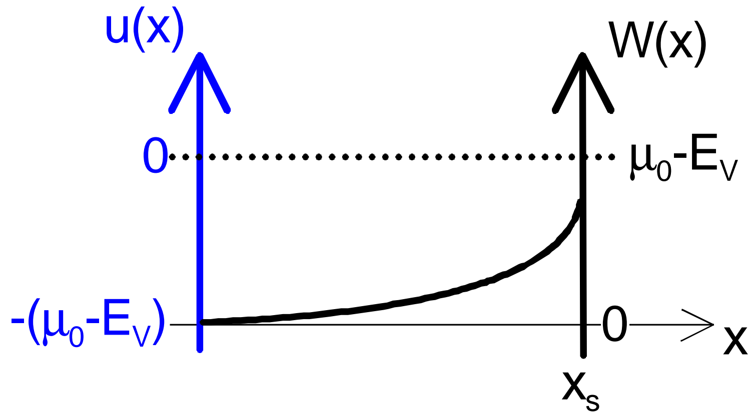
Profiles of Space Charge, Field and Potential

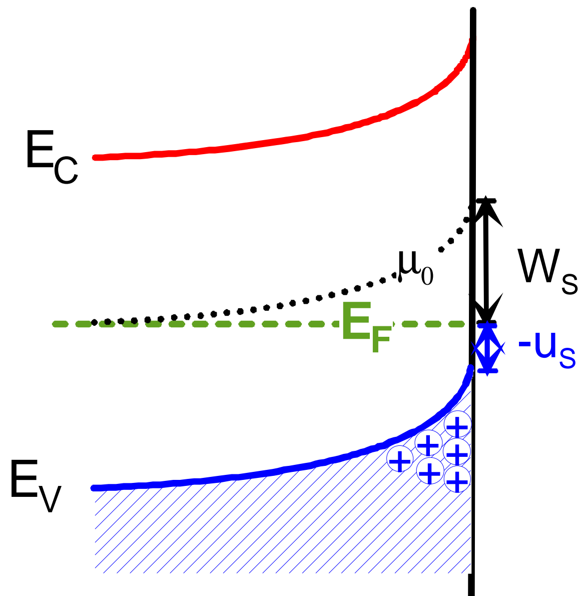


Task: find the consistent solutions of

- electron n (hole p) and space charge density $\rho(x)$
- electrostatic potential (energy) $W(x)$
- electric field $F(x)$

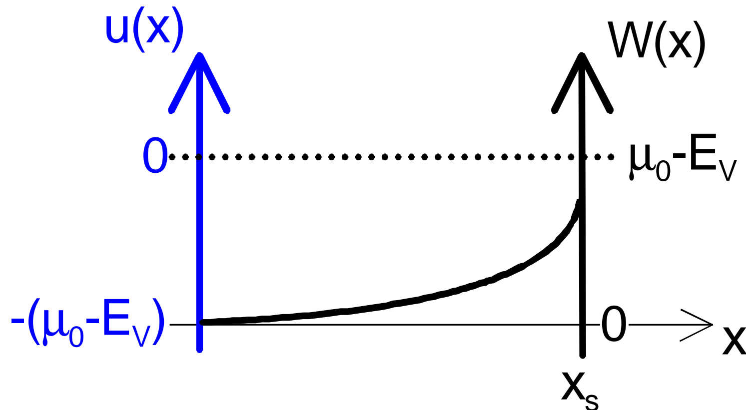
Definitions and Conventions

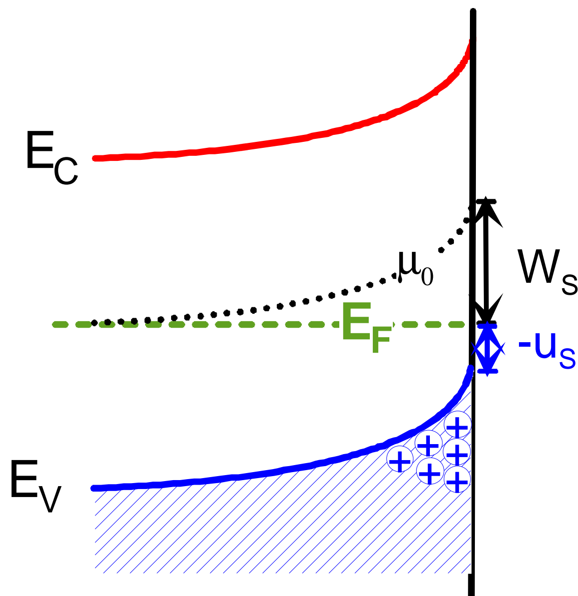




- μ_0 charge neutrality level (= characteristic band state energy, like E_V)
- potential zero can be freely chosen for convenience, e.g. use
  $W(x) = \mu_0(x) - E_F$ or
  $u(x) = E_V - E_F$

Potential ⟶ Space Charge Density





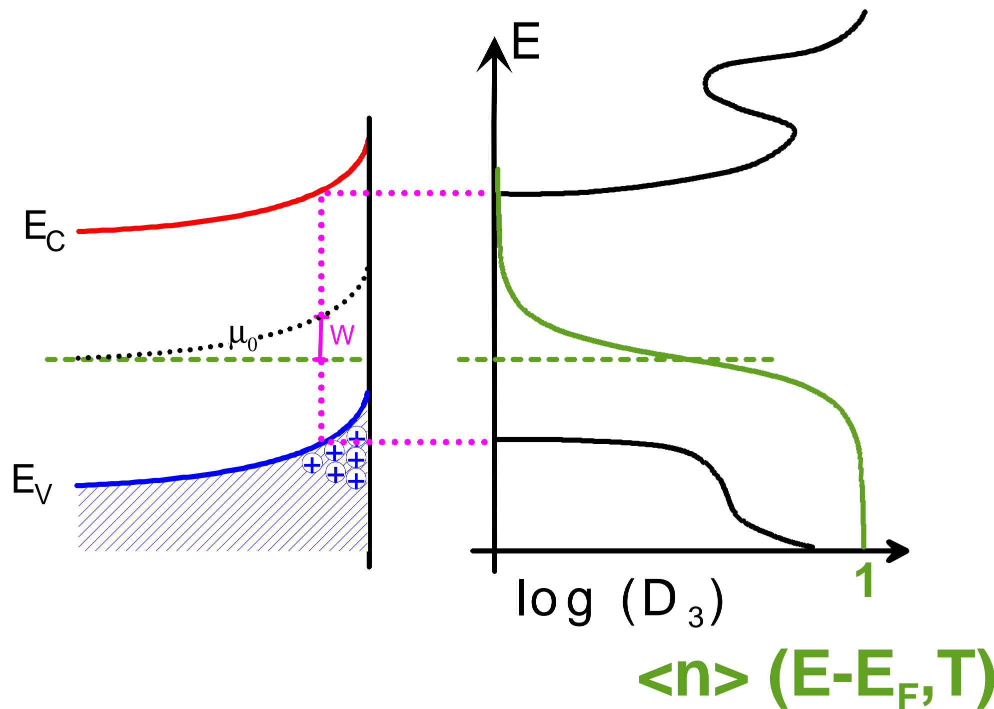
- μ_0 charge neutrality level (= characteristic band state energy, like E_V)
- potential zero can be freely chosen for convenience, e.g. use
  $W(x) = \mu_0(x)-E_F$ or
  $u(x) = E_V - E_F$
- space charge density for homogeneous s.c only function of potential:

$$\rho(W) = -e\left\{\int_{-\infty}^{\infty} \frac{D_3(E)}{1+\exp\left(\frac{W+E-\mu_0(T)}{kT}\right)}dE - \int_{-\infty}^{\infty} \frac{D_3(E)}{1+\exp\left(\frac{E-\mu_0(T)}{kT}\right)}dE\right\}$$

Space charge function:

- temperature dependent
- depends on choice of potential zero
  (e.g. ρ=0 for W=0, but not neccessary!)
- will be simplified for specific cases!

Background: The Space Charge Function



<n> $(E-E_F,T)$

$$<n>(E-E_F) = \frac{1}{1+\exp\left(\frac{E-E_F}{kT}\right)}$$

where locally $E_F=\mu_0(T)-W$

$$\rho(W) = -e\left\{\int_{-\infty}^{\infty} \frac{D_3(E)}{1+\exp\left(\frac{W+E-\mu_0(T)}{kT}\right)}dE - \int_{-\infty}^{\infty} \frac{D_3(E)}{1+\exp\left(\frac{E-\mu_0(T)}{kT}\right)}dE\right\}$$

Electron density at potential W

Electron density required for charge neutrality !

Special Case: Intrinsic Semi-infinite Semiconductor

density of states: $D_C(E) = 4\pi\left(2m_e^*/h^2\right)^{3/2} \cdot \sqrt{E - E_C}$ with m_e^* effective electron mass

electron density: with <n>(E) using Boltzmann's approximation

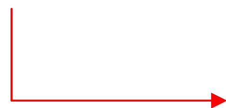
$$n(E) \approx 4\pi\left(2m_e^*/h^2\right)^{3/2} \cdot \int_{E_C}^{\infty} \sqrt{E - E_C} \cdot \exp\left(-\frac{E - E_C + E_C - \mu_0 + W}{kT}\right) dE$$

$$= 4\pi\left(2m_e^*/h^2\right)^{3/2} \exp\left(-\frac{E_C - \mu_0 + W}{kT}\right) \cdot \int_{E_C}^{\infty} \sqrt{E - E_C} \cdot \exp\left(-\frac{E - E_C}{kT}\right) dE$$

$$= 4\pi\left(2m_e^*/h^2\right)^{3/2} \exp\left(-\frac{E_C - \mu_0 + W}{kT}\right) \cdot (kT)^{3/2} \underbrace{\int_0^{\infty} \sqrt{\frac{E - E_C}{kT}} \cdot \exp\left(-\frac{E - E_C}{kT}\right) d\left(\frac{E - E_C}{kT}\right)}_{\Gamma\left(\frac{3}{4}\right) = \frac{\sqrt{\pi}}{2}}$$

$$= \underbrace{2\left(\frac{2\pi\, m_e^* kT}{h^2}\right)^{3/2}}_{} \exp\left(-\frac{E_C - \mu_0 + W}{kT}\right)$$

$$n = N_C(T) \cdot \exp\left(-\frac{E_C - \mu_0 + W}{kT}\right)$$



effective conduction band density of states
(weakly temperature dependent!)

Special Case: Intrinsic Semi-infinite Semiconductor

electron density:

$$n = N_C(T) \cdot \exp\left(-\frac{E_C-\mu_0}{kT}\right) \cdot \exp\left(-\frac{W}{kT}\right)$$

effective conduction band density of states

hole density:

$$p = N_V(T) \cdot \exp\left(\frac{E_V-\mu_0}{kT}\right) \cdot \exp\left(\frac{+W}{kT}\right)$$

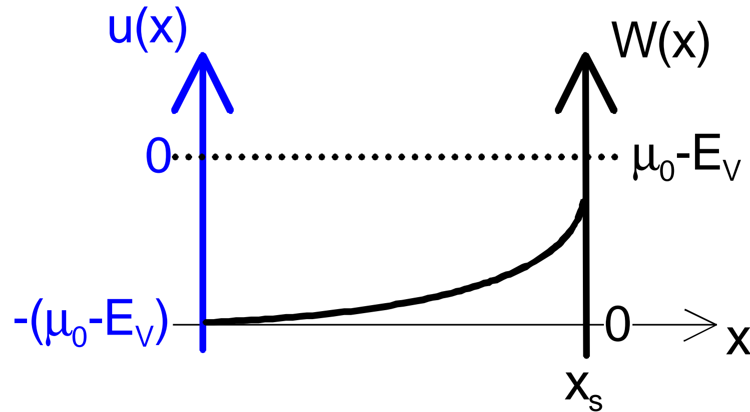
effective valence band density of states

always: $$n \cdot p = n_i^2 = N_C N_V \cdot \exp\left(\frac{E_C-E_V}{kT}\right)$$

intrinsic, W=0 and
$n = p = n_i$:

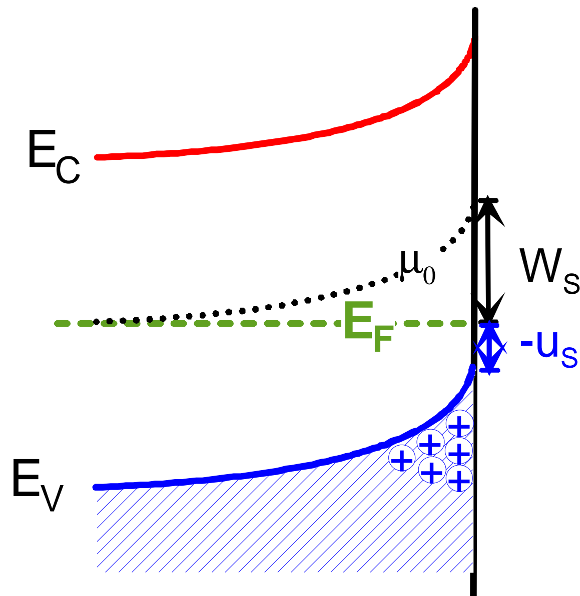
$$\mu_0 = \frac{E_C+E_V}{2} - \frac{kT}{2} \cdot \ln\left(\frac{N_C}{N_V}\right)$$

Special Case: Intrinsic Semi-infinite Semiconductor



$$n = N_C(T) \cdot \exp\left(-\frac{E_C + W - \mu_0}{kT}\right) = n_i \cdot \exp\left(-\frac{W}{kT}\right)$$

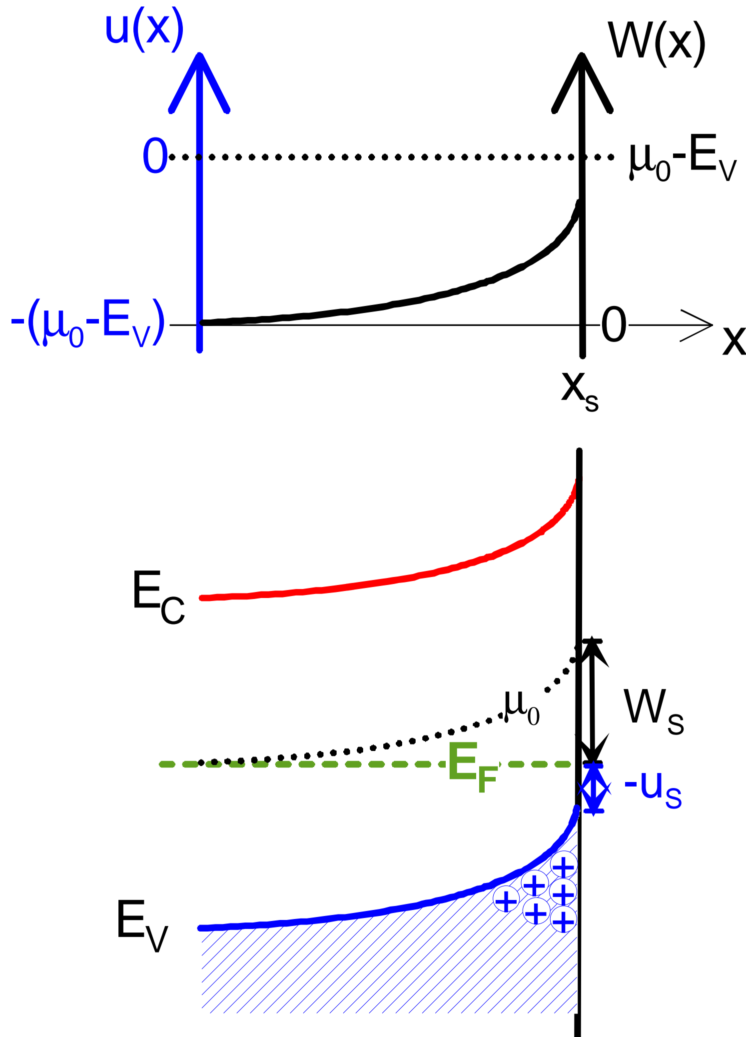
$$p = N_V(T) \cdot \exp\left(\frac{E_V + W - \mu_0}{kT}\right) = n_i \cdot \exp\left(+\frac{W}{kT}\right)$$



Space charge function:

$$\rho(W) = e(p - n) = 2\,e\,n_i \cdot \sinh\left(\frac{W}{kT}\right)$$

Space Charge Denisty → Potential



Gauss' law of electrostatics:

$$\operatorname{div} \vec{D} = \operatorname{div}\left(\varepsilon\varepsilon_0 \vec{E}\right) = \rho$$

with

$$\vec{E} = -\operatorname{grad} \Phi = \frac{1}{e} \operatorname{grad} W$$

in one dimension:

$$W''(x) = \frac{e}{\varepsilon\varepsilon_0} \rho(x)$$

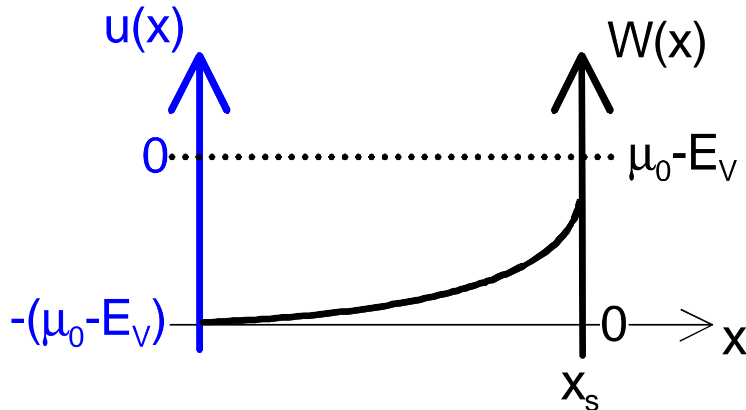
Poisson's equation
+ space charge function:

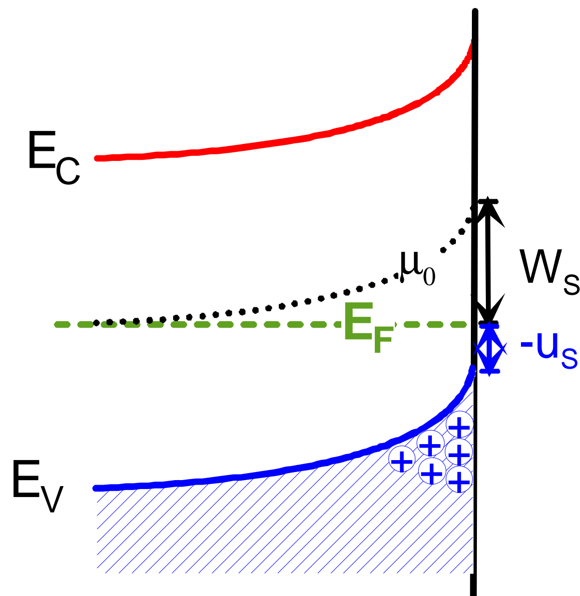
$$W'' = \frac{e}{\varepsilon\varepsilon_0} \rho(W)$$

Ordinary, inhomogeneous diff. eq. of second order for the potential profile W(x).

→ Two integration constants C_1 and C_2

Space Charge Density → Potential





$$W'' = \frac{e}{\varepsilon\varepsilon_0}\rho(W)$$

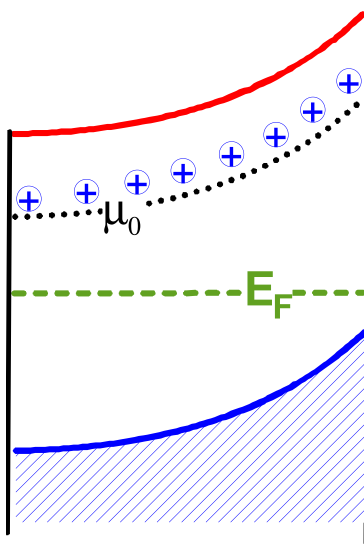
NOTE:

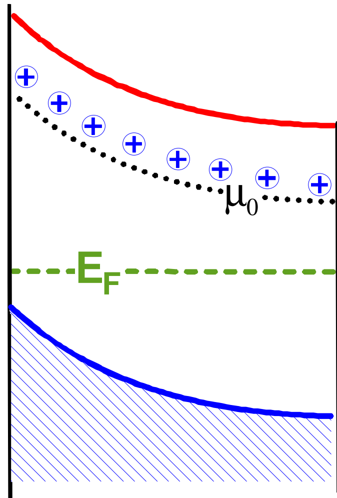
- Does not contain space charge **denstity** ρ**(x)** (= charge profile), but only space charge **function** (=general relation ρ **<-> W**).

- space charge **denstity** ρ**(x)** determines the **curvature of the potential**, not the slope (= electric field) and not the value. **Not even the sign of the electric field!**

Space Charge Density ⟶ Potential

Example: ρ = **const > 0**



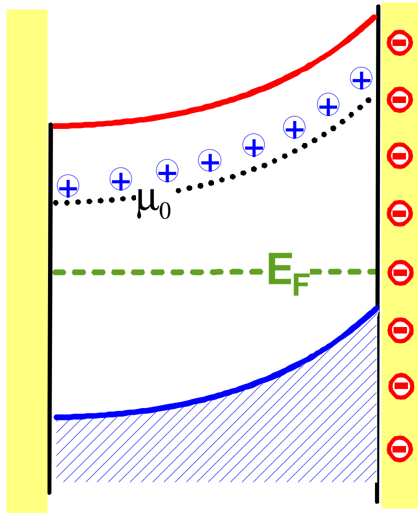


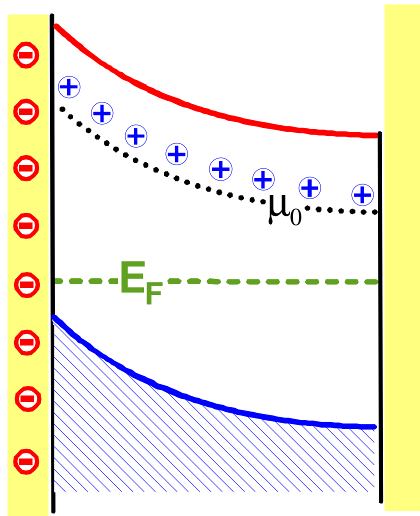
$$W'' = \frac{e}{\varepsilon\varepsilon_0}\rho(W)$$

- space charge **density** ρ**(x)** determines the **curvature of the potential**, not the slope (= electric field) and not the value. **Not even the sign of the electric field!**

Space Charge Density ⟶ Potential

Example: ρ **= const > 0**





$$W'' = \frac{e}{\varepsilon\varepsilon_0}\,\rho(W)$$

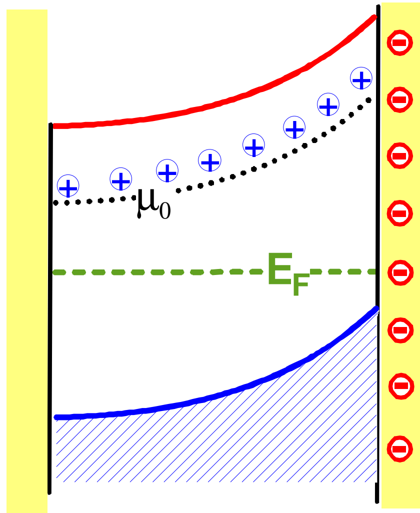
NOTE:

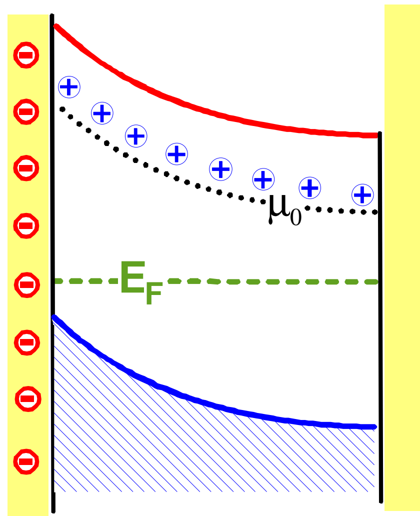
- space charge **density** ρ**(x)** determines the **curvature of the potential**, not the slope (= electric field) and not the value. **Not even the sign of the electric field!**

- **Charge exchange with the external electron reservoir**, representing the boundary conditions for the differential equation, finally determines the charge/field/potential profiles !

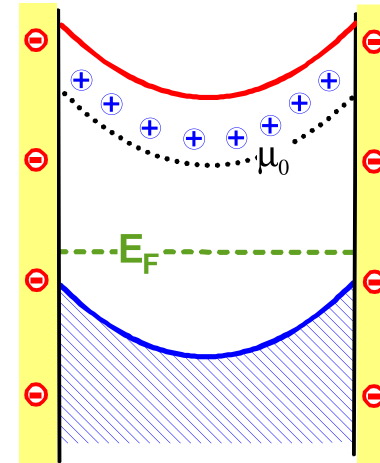
Space Charge Density ⟶ Potential

Example: ρ = const > 0





Or even:



Determination of electric field additionally needs two **boundary conditions**
(= external charge or potential!)

First Integral: the Potential-Field Relation

u(x)

W(x)

0

$\mu_0 - E_V$

$-(\mu_0 - E_V)$

0

x

x_s

E_C

μ_0

W_S

E_F

$-u_S$

E_V

$$W'' = \frac{e}{\varepsilon\varepsilon_0}\rho(W)$$

$$\Leftrightarrow$$

$$W' = \pm\sqrt{\left|2\frac{e}{\varepsilon\varepsilon_0}\cdot\left(\int \rho(W)\,dW + C_1\right)\right|}$$

Proof:

$$\left(\frac{dW}{dx}\right)^2 = 2\frac{e}{\varepsilon\varepsilon_0}\cdot\left(\int \rho(W)\,dW + C_1\right)$$

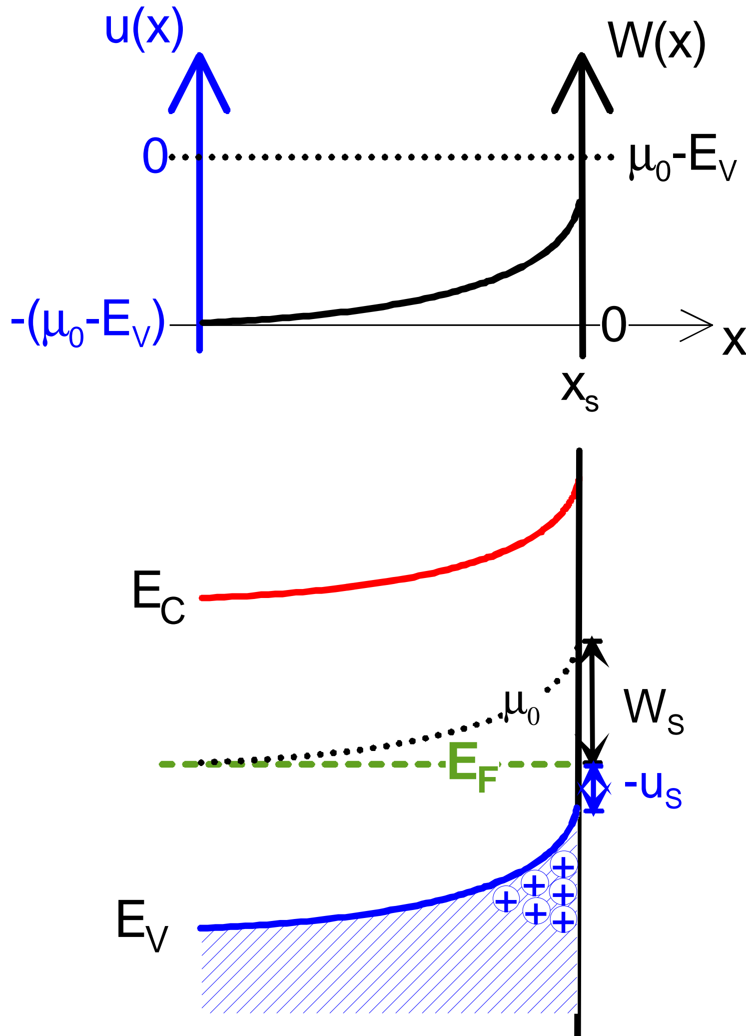
$$\frac{d}{dx}\bigg|\quad \left(\frac{dW}{dx}\right)^2 = 2\frac{e}{\varepsilon\varepsilon_0}\cdot\left(\int \rho(W)\,dW + C_1\right)\quad\bigg|\frac{d}{dW}\cdots\cdots\frac{dW}{dx}$$

$$2\left(\frac{dW}{dx}\right)\cdot\frac{d^2W}{dx^2} = 2\frac{e}{\varepsilon\varepsilon_0}\rho(W)\cdot\frac{dW}{dx}$$

$$W'' = \frac{e}{\varepsilon\varepsilon_0}\rho(W)$$

q.e.d.

First Integral: the Potential-Field Relation



$$W' = \pm\sqrt{\left|2\frac{e}{\varepsilon\varepsilon_0}\cdot\left(\int\rho(W)\,dW + C_1\right)\right|}$$

Diff. eq. of **1. order** only, but with one explicit integration constant C_1.

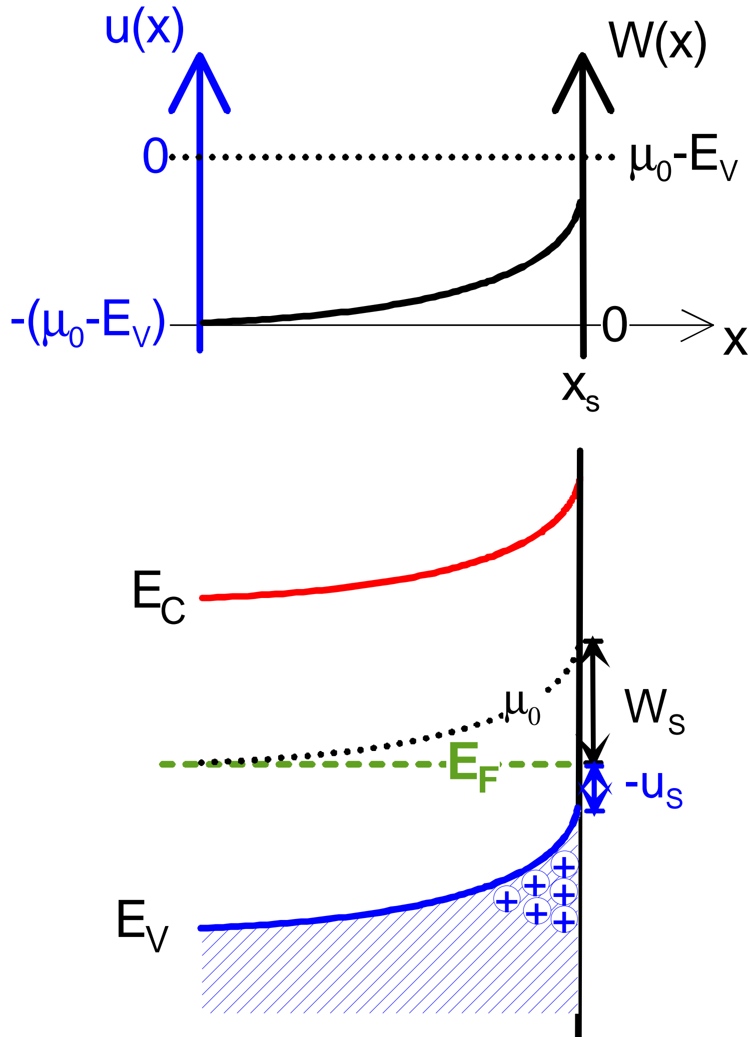
- C_1 can be determined by proper choice of position axis **via symmetry** of the problem (see example below!), thus evaluating the **first boundary condition**.
- With C_1 fixed, universal relation between electric field F and potential W holds **everywhere**!

$$F_{C_1}(W) = \pm\sqrt{\left|\frac{2}{e\varepsilon\varepsilon_0}\cdot\left(\int\rho(W)\,dW + C_1\right)\right|}$$

→ **All achieved by one integration step finding**

$$R(W) = \int\rho(W)\,dW$$

Special Case: The Intrinsic S.C.



Space charge function:

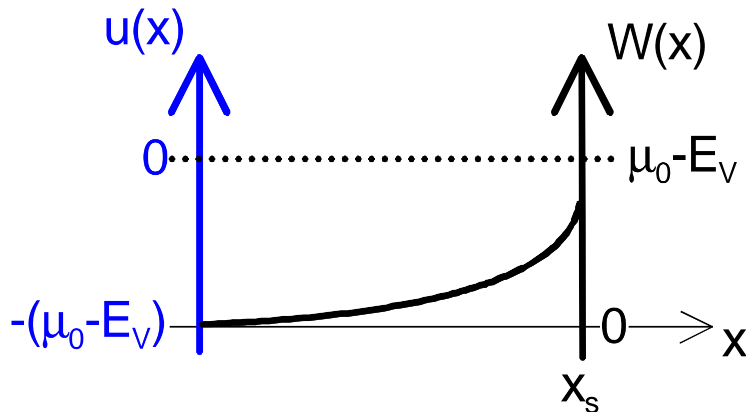
$$\rho(W) = 2\,e\,n_i \cdot \sinh\left(\frac{W}{kT}\right)$$

$$\int \rho(W)\,dW = 2en_i \cdot kT \cdot \cosh\left(\frac{W}{kT}\right)$$

$$W' = \pm\sqrt{\left|2\frac{e}{\varepsilon\varepsilon_0}\cdot\left(\int \rho(W)\,dW + C_1\right)\right|}$$

$$W' = \pm\sqrt{\left|\frac{4kTe^2 n_i}{\varepsilon\varepsilon_0}\cdot\left(\cosh\left(\frac{W}{kT}\right) + C_1\right)\right|}$$

C_1 from Symmetry: Semi-infinite



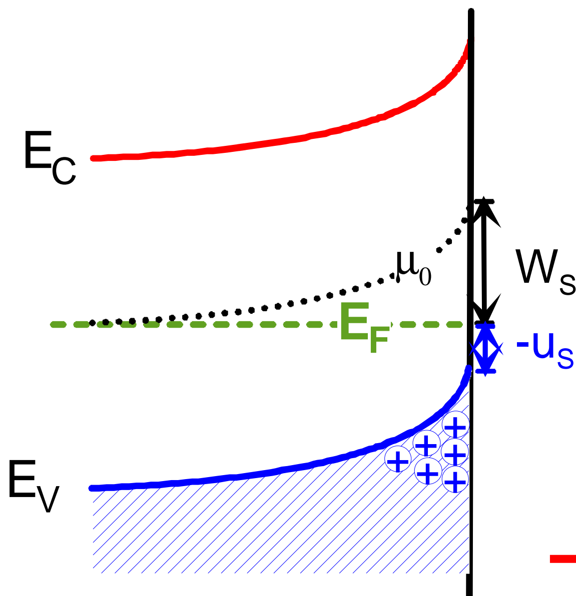
$$W' = \pm\sqrt{\left|\frac{4kTe^2 n_i}{\varepsilon\varepsilon_0}\cdot\left(\cosh\left(\frac{W}{kT}\right)+C_1\right)\right|}$$

$$W' \overset{!}{=} 0 \quad \text{when} \quad \rho(W) \sim \sinh(W/kT) = 0$$

$$W' \overset{!}{=} 0 \quad \text{when} \quad W = 0$$

→ $$C_1 = -1$$

and with $$\cosh(y) - 1 = 2\cdot\sinh^2\left(\tfrac{y}{2}\right)$$

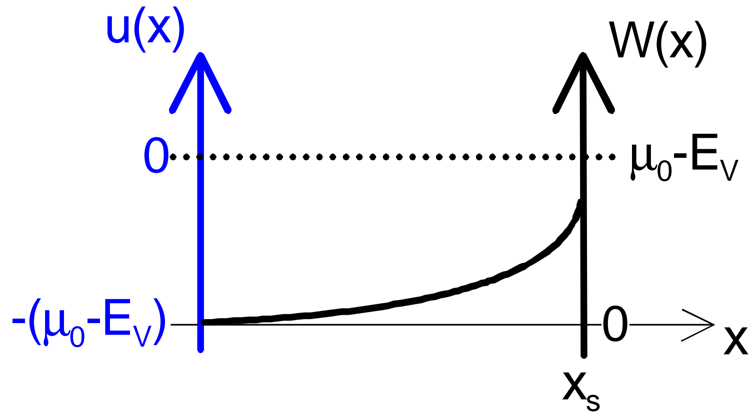


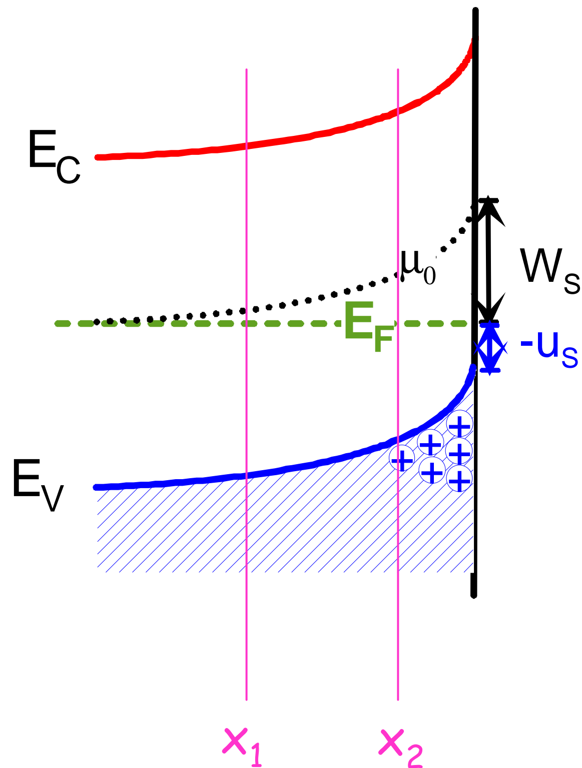
$$eF(W) = W' = \pm\sqrt{\frac{8kTe^2 n_i}{\varepsilon\varepsilon_0}}\sinh\left(\frac{W}{2kT}\right)$$

→ Potential-field relation for an intrinsic semi-inifinite semiconductor, valid at every position!

NOTE: + sign [- sign] for bulk extending towards - ∞ [+∞]!

Total Charge per Area





Gauss' law:

$$W''(x) = \frac{e}{\varepsilon\varepsilon_0}\rho(x)$$

$$\int_{x_1}^{x_2} W''(x)\,dx = W'(x_2) - W'(x_2)$$

$$= \int_{x_1}^{x_2} \frac{e}{\varepsilon\varepsilon_0}\rho(x)\,dx = \frac{e}{\varepsilon\varepsilon_0}\Sigma_{x_1,x_2}$$

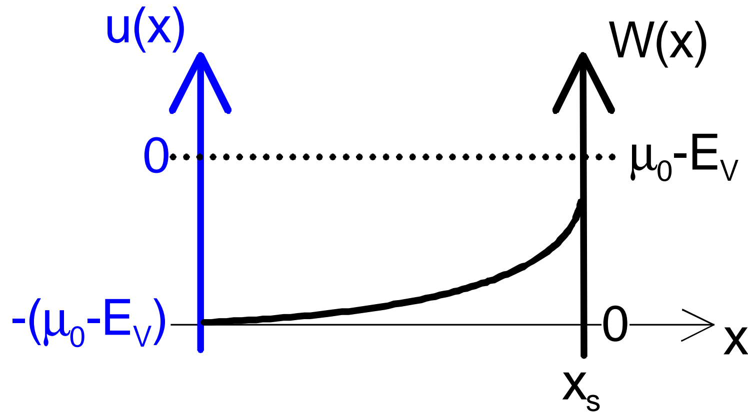
$$\Sigma_{x_1,x_2} = \frac{\varepsilon\varepsilon_0}{e}\left[W'(x_2) - W'(x_1)\right]$$

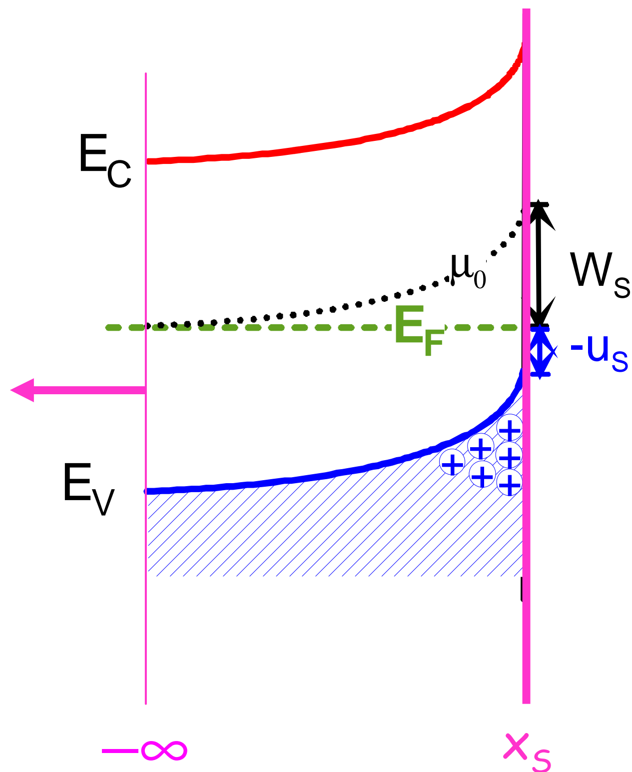
Total charge per area in any profile range

Corresponds to

Field change across the profile range

Total Charge per Area for Semi-infinite Symmetry





Choose:

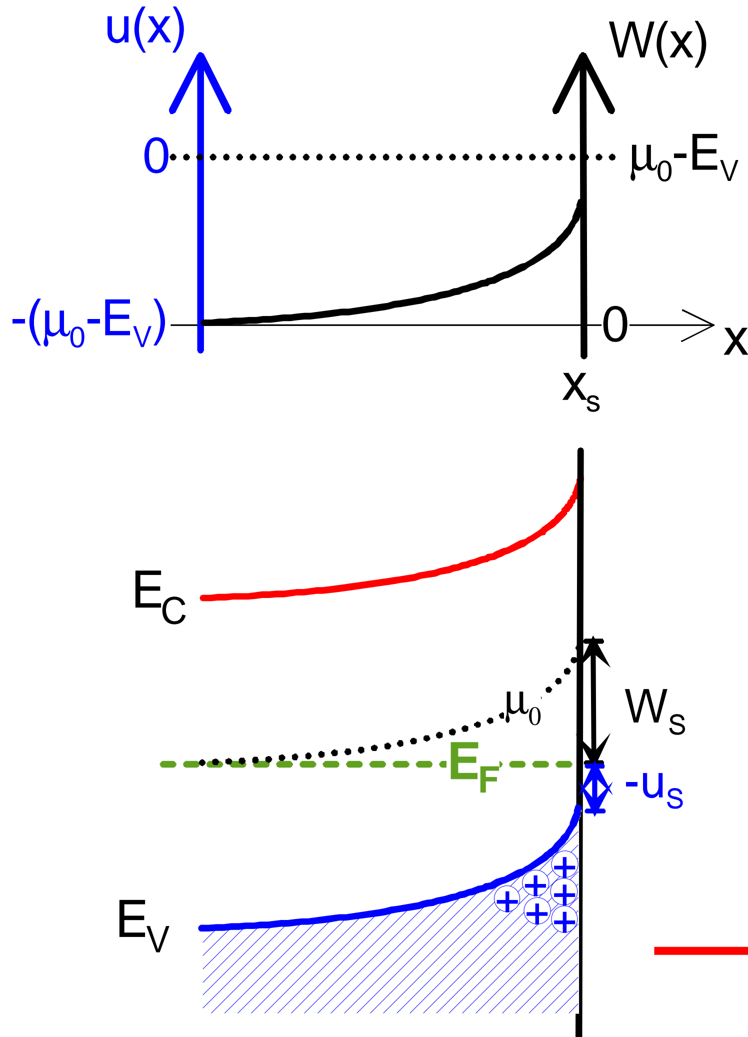
$$x_1 = -\infty \quad \text{and} \quad x_2 = x_S$$

surfac or interface!

$$\Sigma_{-\infty, x_S} = \Sigma = \frac{\varepsilon\varepsilon_0}{e} W'(x_S) = \varepsilon\varepsilon_0 F(x_S)$$

Total charge per area — corresponds to — Electric field at the surface (interface)

Total Charge vs. Surface Potential



$$\Sigma = \varepsilon\varepsilon_0 F(x_S)$$

Combine with potential-field relation:

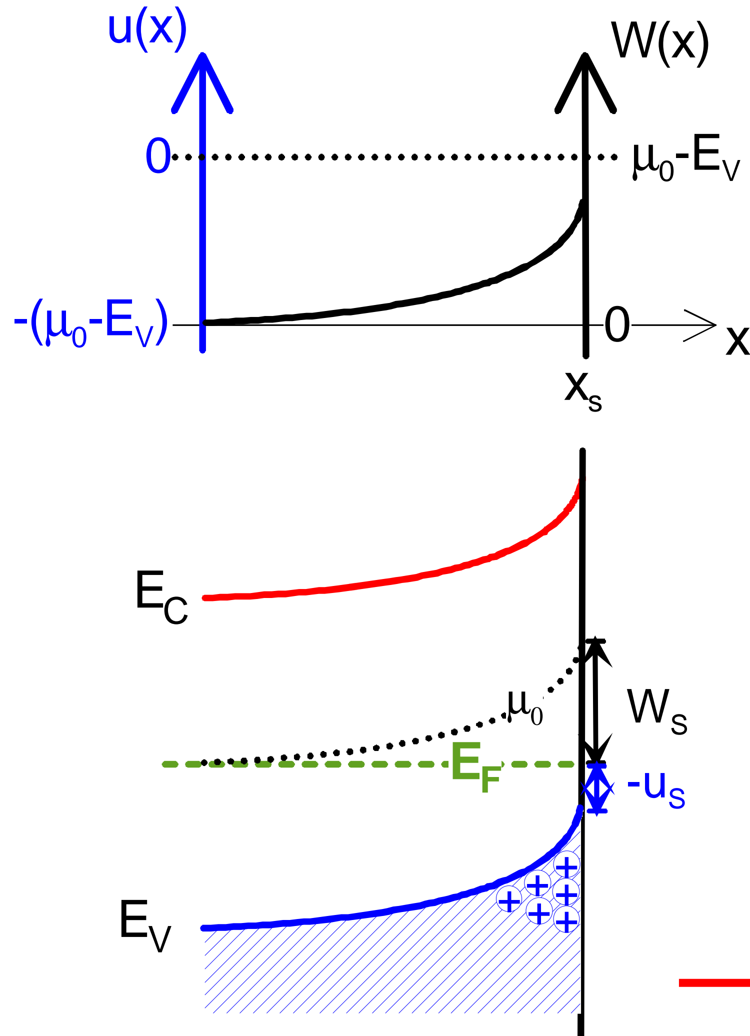
$$F_{C_1}(W) = \pm\sqrt{\frac{2}{e\varepsilon\varepsilon_0}\cdot\Big(\underbrace{\textstyle\int \rho(W)\,dW}_{R(W)} + C_1\Big)}$$

$$\Sigma = \pm\sqrt{\frac{2\varepsilon\varepsilon_0}{e}\cdot\left(R(W_S) + C_1\right)}$$

Total charge per area in the total profile (simply) related to surface (interface) electric field!

Note: i.) all without solving Possion's equation yet!!
ii.) valid only for semi-infinite symmetry and C_1 chosen appropriately!

Special Case: the Intrinsic, Semi-infinite S.C.



$$R(W) = \int \rho(W)\, dW = 2en_i \cdot kT \cdot \cosh\left(\frac{W}{kT}\right)$$

and $$C_1 = -1$$

into

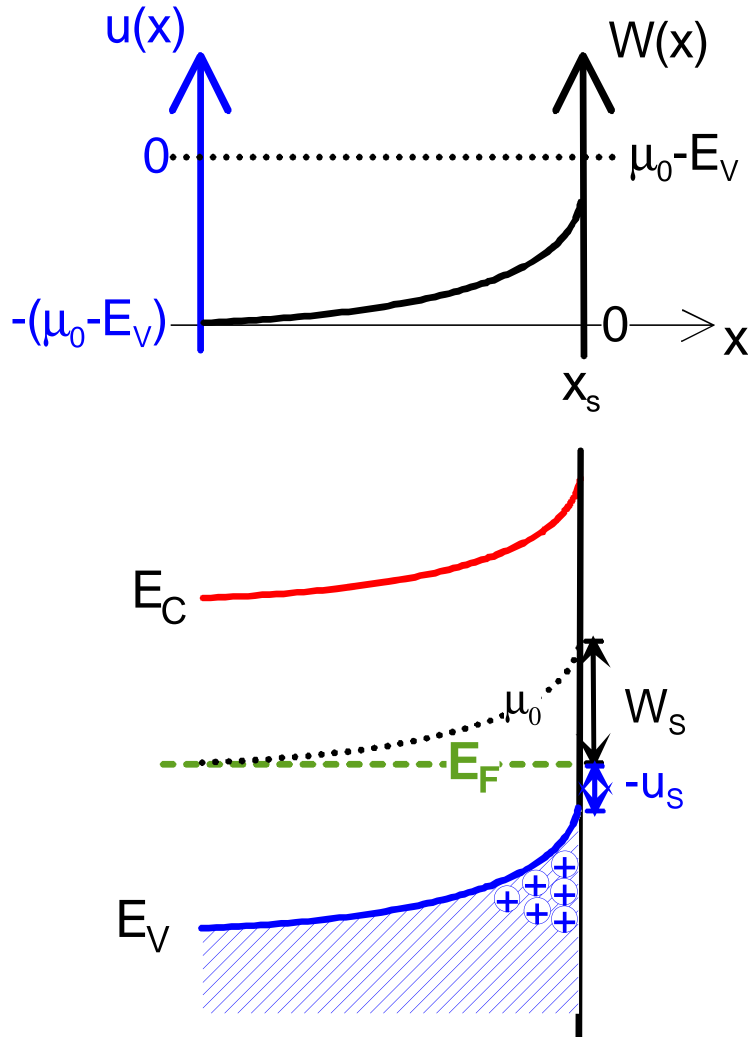
$$\Sigma = \pm\sqrt{\frac{2\varepsilon\varepsilon_0}{e} \cdot \left(R(W_S) + C_1\right)}$$

$$\Sigma = \sqrt{8kT\varepsilon\varepsilon_0 n_i}\, \sinh\left(\frac{W_S}{2kT}\right)$$

Total charge per area in an intrinsic semi-inifinite semiconductor;

only determined by the surface potential!

The Further Route to the Potential Profile W(x)



$$W' = \pm\sqrt{2\frac{e}{\varepsilon\varepsilon_0}\cdot\left(\int\rho(W)\,dW + C_1\right)} = e\cdot F_{C_1}(W)$$

$$\frac{dW}{dx} = e\cdot F_{C_1}(W)$$

$$\int\frac{1}{e\cdot F_{C_1}(W)}dW = \int dx$$

$$x(W) = \int\frac{1}{e\cdot F_{C_1}(W)}dW + C_2$$

Invert x(W) to yield poatential profile!

Determine C_2 from second boundary condition:, e.g. W_S , W_S' , Σ_S

Here, the overlayer with its charge exchange comes in!!

General Properties of the Potential Profiles W(x)

$$x(W) - C_2 = \pm \int \frac{1}{\sqrt{2 \frac{e}{\varepsilon\varepsilon_0} \cdot \left(\int \rho(W)\, dW + C_1 \right)}}\, dW$$

Requires double integration and inversion!

→ difficult and unhandy, approximations to ρ(W) in most cases advisable!

Yet some general conclusions possible:

- **C_1 in most cases from symmetry (first boundary condition)**
- **Potential profile can be formulated as a general function $W(x-C_2)$.**
- **With potential profile, also field profile $F(x) \sim W'(x)$ and space charge profile $\rho(x) \sim W''(x)$ are found.**
- **Charge exchange with overlayer(s) causes only a shift of the position axis for W, i.e. determines the postition x_s of the surface relative to C_2.**
- **Sign ambiguity +/- removed by surface-to-bulk orientation**

To Finish the Story: Intrinsic, Semi-infinite S.C.

Integrate: $$\pm\left[x(W)-C_2\right]=\int\frac{1}{e\cdot F_{C_1}(W)}dW=\sqrt{\frac{\varepsilon\varepsilon_0}{8kTe^2n_i}}\cdot\int\frac{1}{\sinh\left(\frac{W}{2kT}\right)}dW$$

$$=\underbrace{\sqrt{\frac{kT\varepsilon\varepsilon_0}{2e^2n_i}}}_{\lambda_i}\cdot\ln\left[\tanh\left(\frac{|W|}{4kT}\right)\right]$$

Invert:...... $$|W(x)|=2kT\cdot\ln\left[\frac{1+e^{\pm(x-C_2)/\lambda_i}}{1-e^{\pm(x-C_2)/\lambda_i}}\right]=2kT\cdot\ln\left[\frac{1+e^{(x-C_2)/\lambda_i}}{1-e^{(x-C_2)/\lambda_i}}\right]$$

($x< C_2$ for bulk towards - ∞)

$$W(x)=\pm\,2kT\cdot\ln\left[\frac{1+e^{(x-C_2)/\lambda_i}}{1-e^{(x-C_2)/\lambda_i}}\right]$$

→ Finally, the potential profile!

To Finish the Story: Intrinsic, Semi-infinite S.C.

+ for hole accumulation

$$W(x) = \pm 2kT \cdot \ln\left[\frac{1+e^{(x-C_2)/\lambda_i}}{1-e^{(x-C_2)/\lambda_i}}\right]$$

Note: for C_2-x >> λ_i, i.w. small potentials:

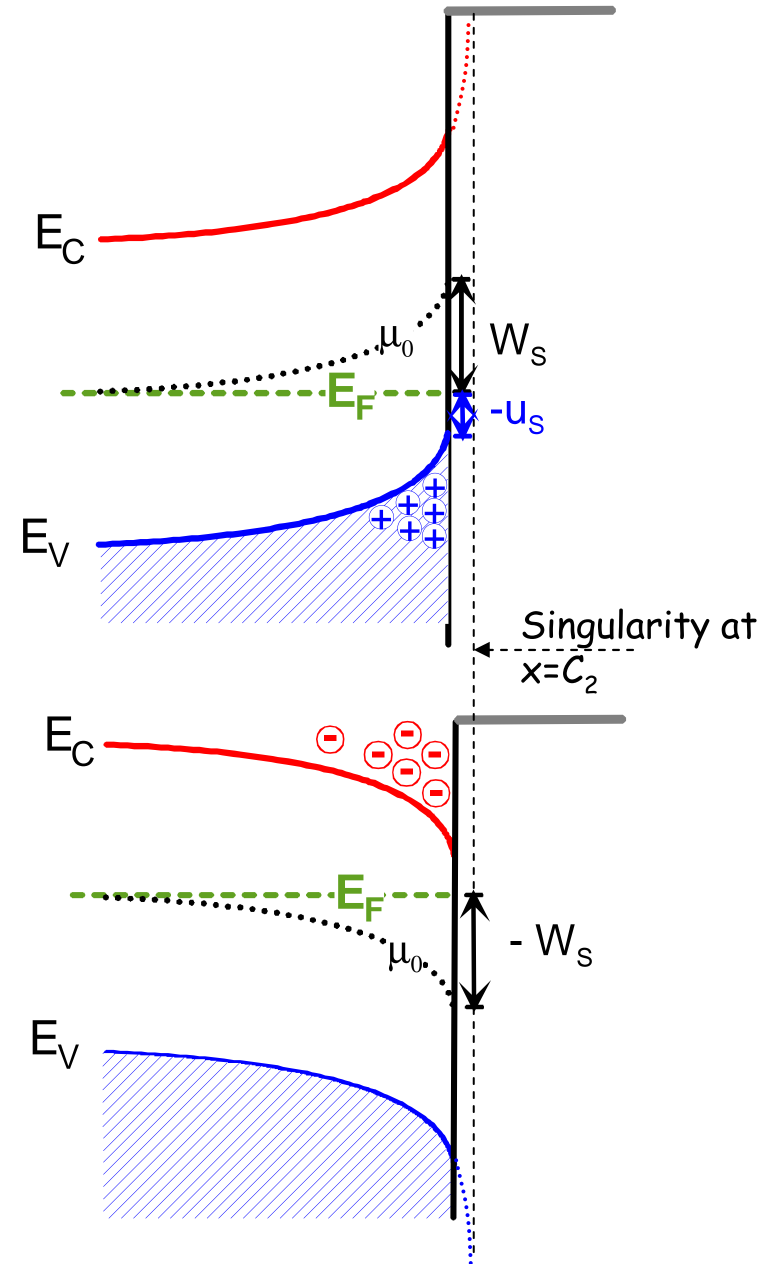
$$\frac{1+e^{(x-C_2)/\lambda_i}}{1-e^{(x-C_2)/\lambda_i}} \approx 1 + 2 \cdot e^{(x-C_2)/\lambda_i}$$

and

$$\ln\left[1 + 2 \cdot e^{(x-C_2)/\lambda_i}\right] \approx 2 \cdot e^{(x-C_2)/\lambda_i}$$

→ PROFILE EXPONENTIAL! *

- for electron accumulation



* Error < 5 % for |W| < 1.5 kT

To Finish the Story: Intrinsic, Semi-infinite S.C.

Potential:

$$W(x) = \pm 2kT \cdot \ln\left[\frac{1+e^{(x-C_2)/\lambda_i}}{1-e^{(x-C_2)/\lambda_i}}\right]$$

Electric Field:

$$F(x) = \frac{1}{e}W'(x) = \mp \frac{2kT}{e\lambda_i} \cdot \frac{1}{\sinh\left(\frac{x-C_2}{\lambda_i}\right)}$$

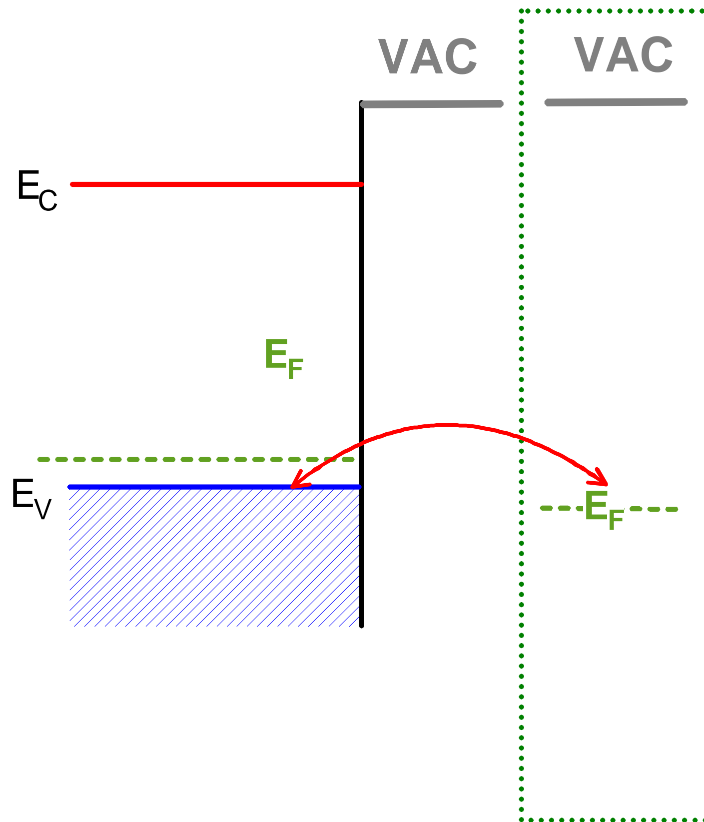
Space charge Density:

$$\rho(x) = \frac{1}{e}W''(x) = \pm 4en_i \cdot \frac{\cosh\left(\frac{x-C_2}{\lambda_i}\right)}{\sinh^2\left(\frac{x-C_2}{\lambda_i}\right)}$$

NOTE:

- **Singularities at C_2 -> C_2 is a point in front of the semiconductor!**
- **Position of ‚singularity point' C_2 relative to surface incorporates the second boundary condition, i.e. the charge exchange!**

Approximate Cases: the ‚Unipolar` Semiconductor



Fermi level of the overlayer such that charge exchange only with one band possible.

Semiconductor with ‚infinite band gap'.

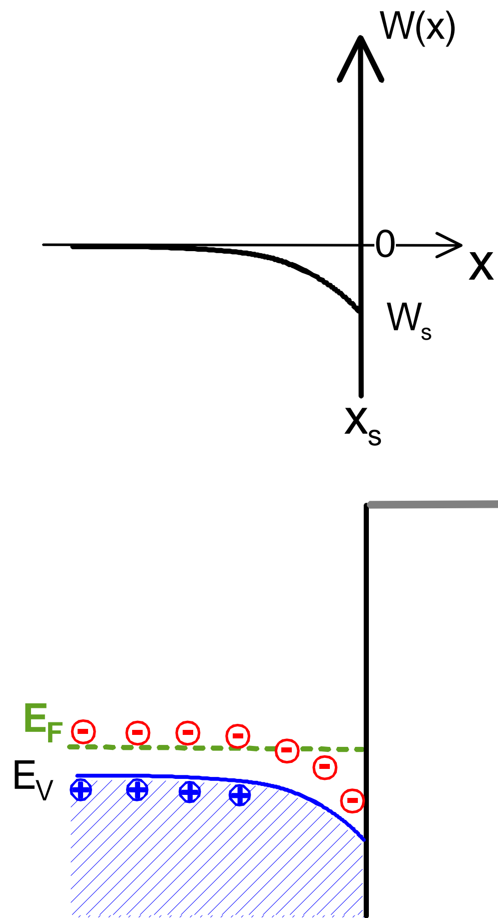
Two possibilities: Charge carrier depletion or accumulation.

Intrinsic or doped semiconductor

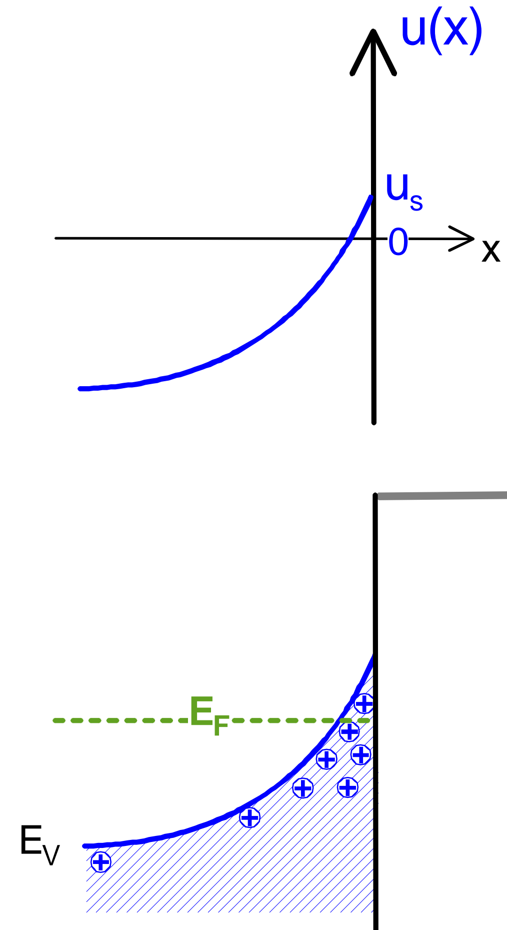
Overlayer, e.g:

- surface states or defects
- adsorbates
- electrolytes
- metals across a dielectric

Approximate Cases: the ,Unipolar` Semiconductor



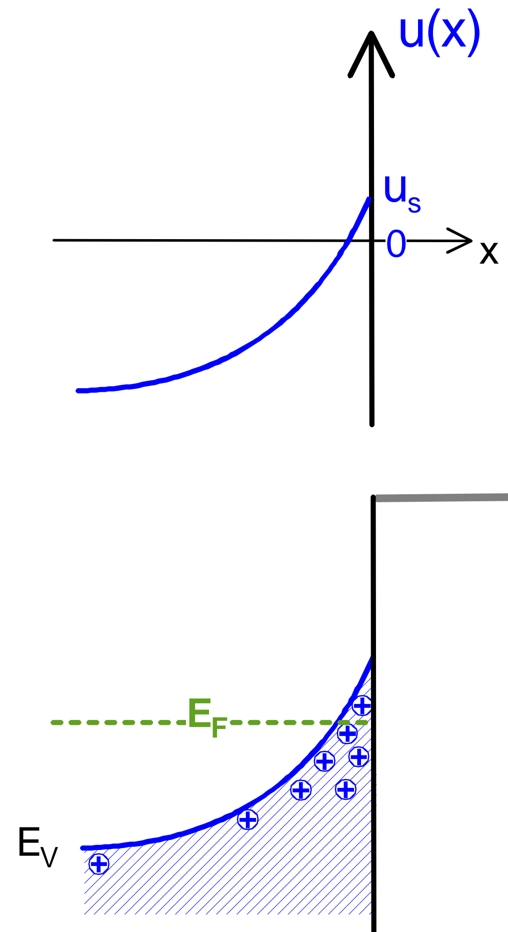
(Hole) depletion of a doped semiconductor



(Hole) accumulation of an intrinsic semiconductor

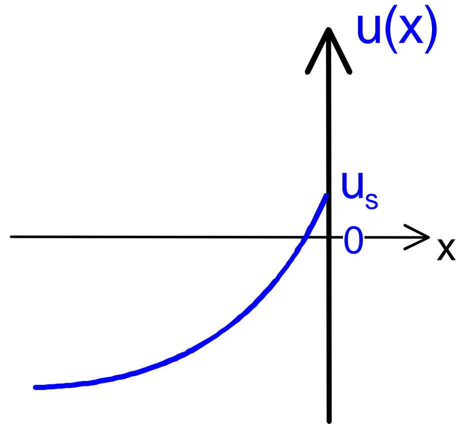
Case I:

Accumulation



(Hole) accumulation of an intrinsic semiconductor

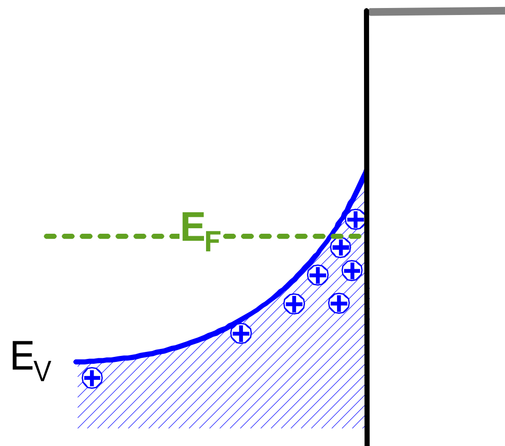
Simplified Description: Hole Accumulation



Space charge function:

$$\rho(u) = e\,N_V \cdot \exp\left(\frac{u}{kT}\right)$$

$$\int \rho(u)\,du = eN_V kT \cdot \exp\left(\frac{u}{kT}\right)$$

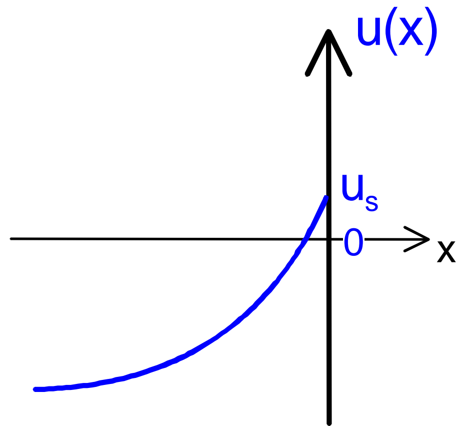


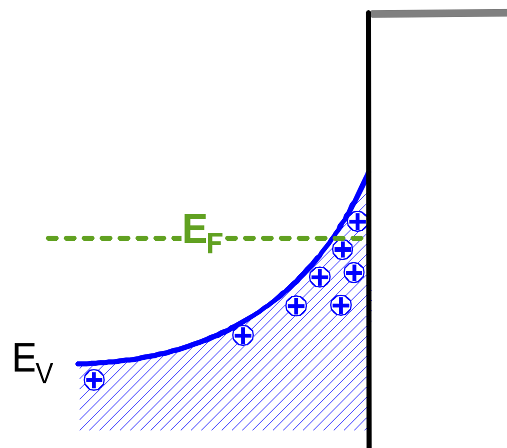
like before,
but simpler....

Note the unphysical asymptotic behaviour: ρ=0 only for u=-∞ (infinite band gap!)

→ approximation only valid until E_F reaches μ_0 !

Simplified Description: Hole Accumulation





Potential-field relation:

$$eF(u) = u' = \sqrt{\frac{2kTe^2N_V}{\varepsilon\varepsilon_0}} \exp\left(\frac{u}{2kT}\right)$$

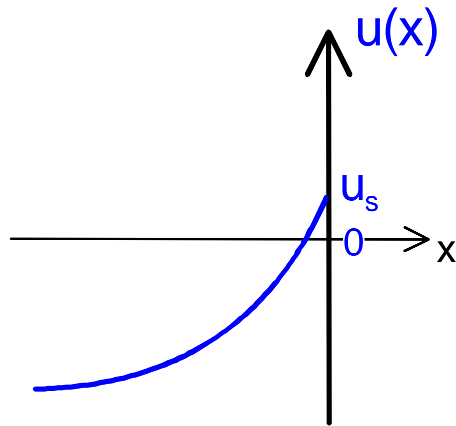
and with that:

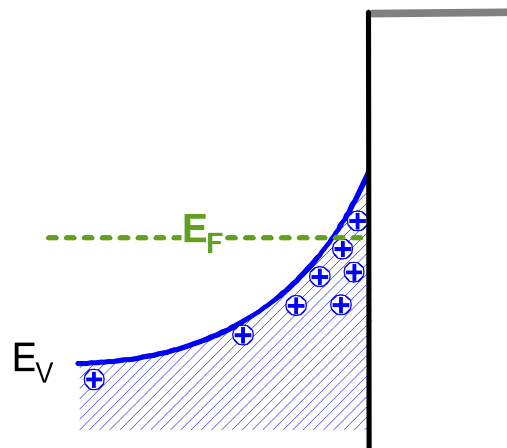
$$\Sigma = \underbrace{\sqrt{2kT\varepsilon\varepsilon_0 N_V}}_{\Sigma_V} \exp\left(\frac{u_S}{2kT}\right)$$

temperature dependent material constant

Total charge per area in the profile exponentially related to surface potential

Total Charge vs. Surface Potential





$$\Sigma = \underbrace{\sqrt{2kT\varepsilon\varepsilon_0 N_V}}_{\Sigma_V} \exp\left(\frac{u_S}{2kT}\right)$$

temperature dependent material constant

at R.T for	Silicon	Diamond
E_G	1.1 eV	5.5 eV
ε	11.8	5.8
N_V	$6.6 \cdot 10^{19}$cm^{-3}	$2.7 \cdot 10^{19}$cm^{-3}
Σ_V	$e \cdot 4.6 \cdot 10^{12}$cm^{-2}	$e \cdot 2.1 \cdot 10^{12}$cm^{-2}
Surface atoms	$6.8 \cdot 10^{14}$cm^{-2}	$1.6 \cdot 10^{15}$cm^{-2}

for the (100) surface

Charge / Field / Potential Profiles

Potential:

$$u(x) = -2kT \cdot \ln\left[C_2 - \frac{x}{\lambda_V}\right]$$

Electric Field:

$$F(x) = \frac{1}{e}u'(x) = \frac{2kT}{e\lambda_V} \cdot \frac{1}{\left(C_2 - \frac{x}{\lambda_V}\right)}$$

Space charge Density:

$$\rho(x) = \frac{\varepsilon\varepsilon_o}{e}u''(x) = eN_V \cdot \frac{1}{\left(C_2 - \frac{x}{\lambda_V}\right)^2}$$

- simple analytic functions
- charge exchange with external reservoir described by the surface position relative to the singularity point C_2
- $\lambda_V = \sqrt{2kT\varepsilon\varepsilon_0/(e^2N_V)}$ temperature dependent material parameter:

5.7 Å for Si, 7.7 Å for Diamond at R.T.

Universal Representation of Diffusion Profiles

On a depth scale in reduced units $\tilde{x} = x / \lambda_V$ and with $C = -C_2$:

Potential:

$$\tilde{u} = \frac{u}{2kT} = -\ln(\tilde{x} - C)$$

Electric Field:

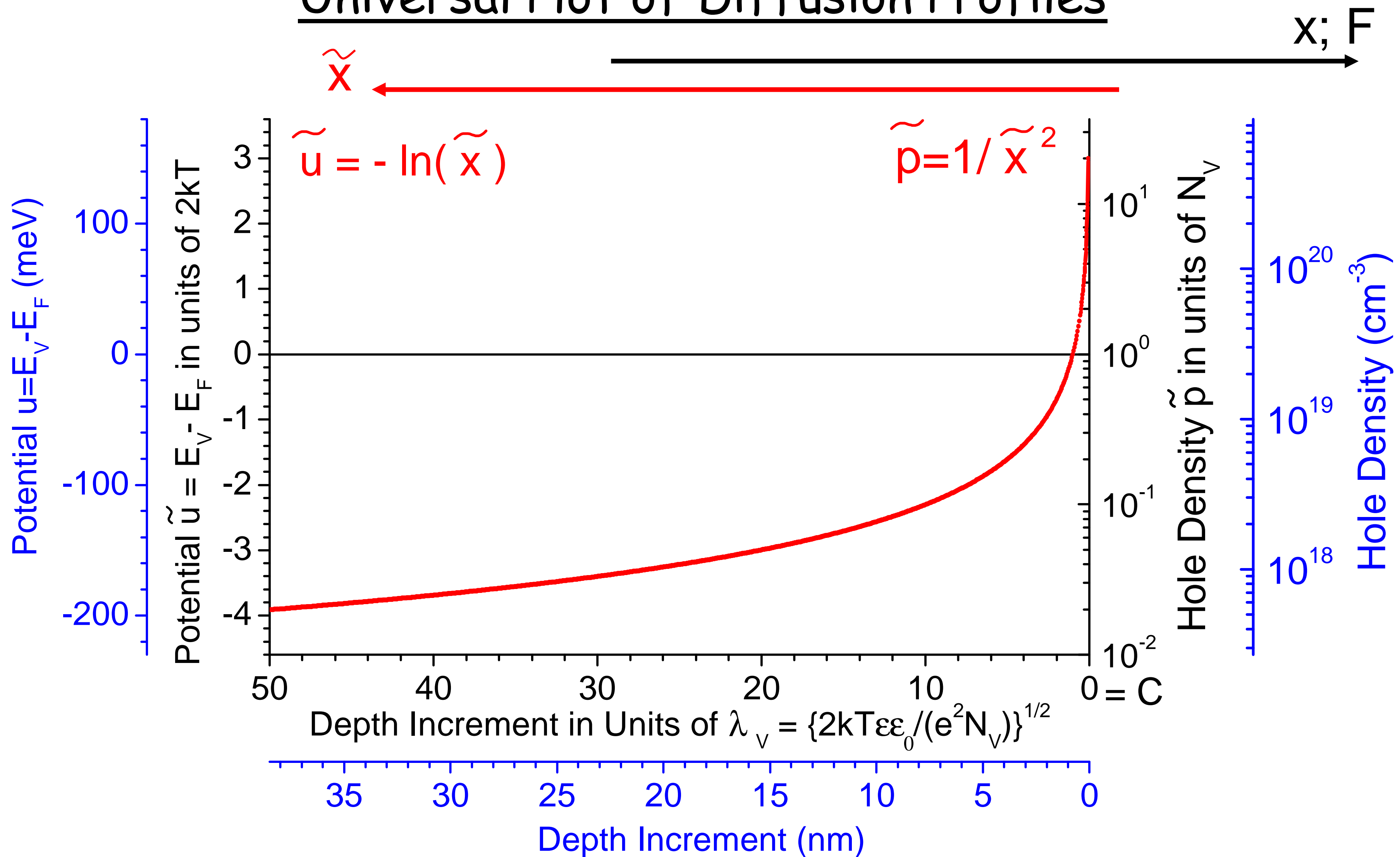
$$\tilde{F} = \frac{F}{2kT/(e\lambda_V)} = \frac{1}{\tilde{x} - C} = \tilde{\Sigma} = \frac{\Sigma}{\sqrt{2kT\,\varepsilon\varepsilon_0\,N_V}}$$

Space charge Density:

$$\tilde{\rho} = \frac{\rho}{eN_V} = \frac{1}{(\tilde{x} - C)^2} = \tilde{p} = \frac{p}{N_V}$$

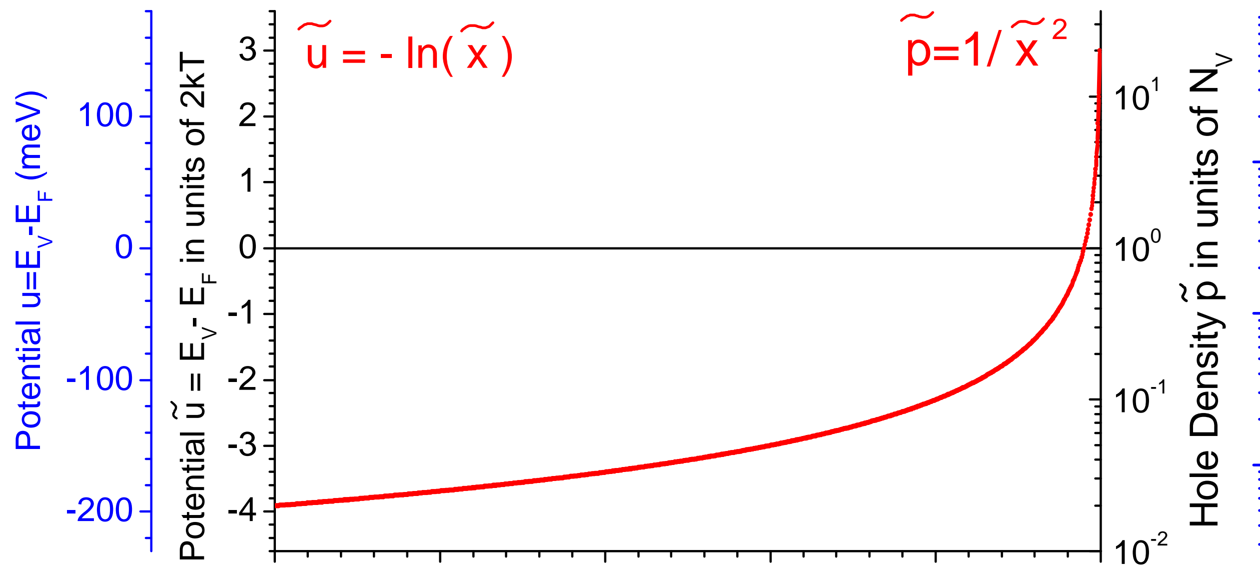
Note: Follows, of course, also from the general case of the intirinsic s.c. by approximating the hyperbolic functions by exponentials, valid for $(C_2 - x)/\lambda_V << 1$ **,**
and using $u = W - (\mu_0 - E_V)$ **,** $\mu_0 = (E_C + E_V)/2 - kT/2 \cdot \ln(N_C / N_V)$ **,** $\lambda_V = 2\sqrt{n_i / N_V} \cdot \lambda_i$

Universal Plot of Diffusion Profiles



- Displays any profile for any intrinsic S.C.; just choose surface coordinate !
- Charge are carriers self-confined by their own charge + surface charge.

blue scales: for Diamond at R.T



Charge exchange

$$\tilde{x}_S - C$$

Can be specified by:

$$\tilde{x}_S - C = e^{\frac{2kT}{u_s}}$$

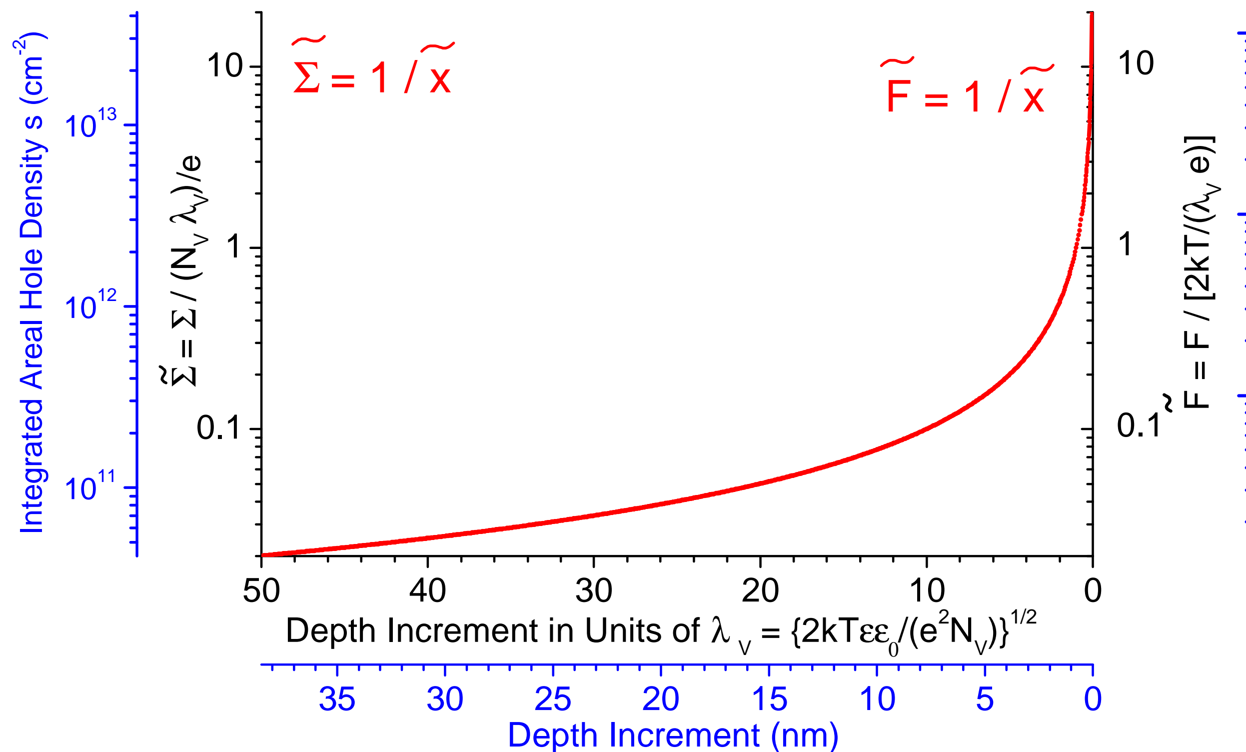
surface potential

$$\tilde{x}_S - C = \frac{2kT/(e\,\lambda_V)}{F_S} = \frac{\sqrt{2kT\varepsilon\varepsilon_0 N_V}}{\Sigma_S}$$

surface field or total charge

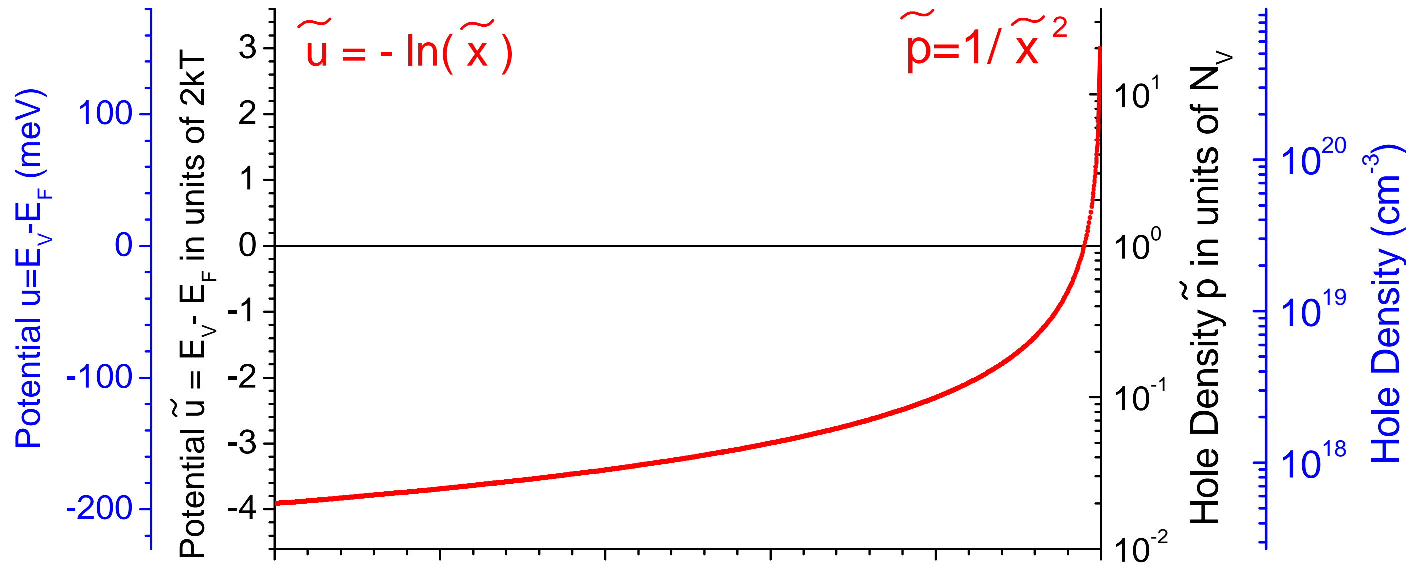
$$\tilde{x}_S - C = \frac{\sqrt{eN_V}}{\sqrt{\rho_S}} = \frac{\sqrt{N_V}}{\sqrt{p_S}}$$

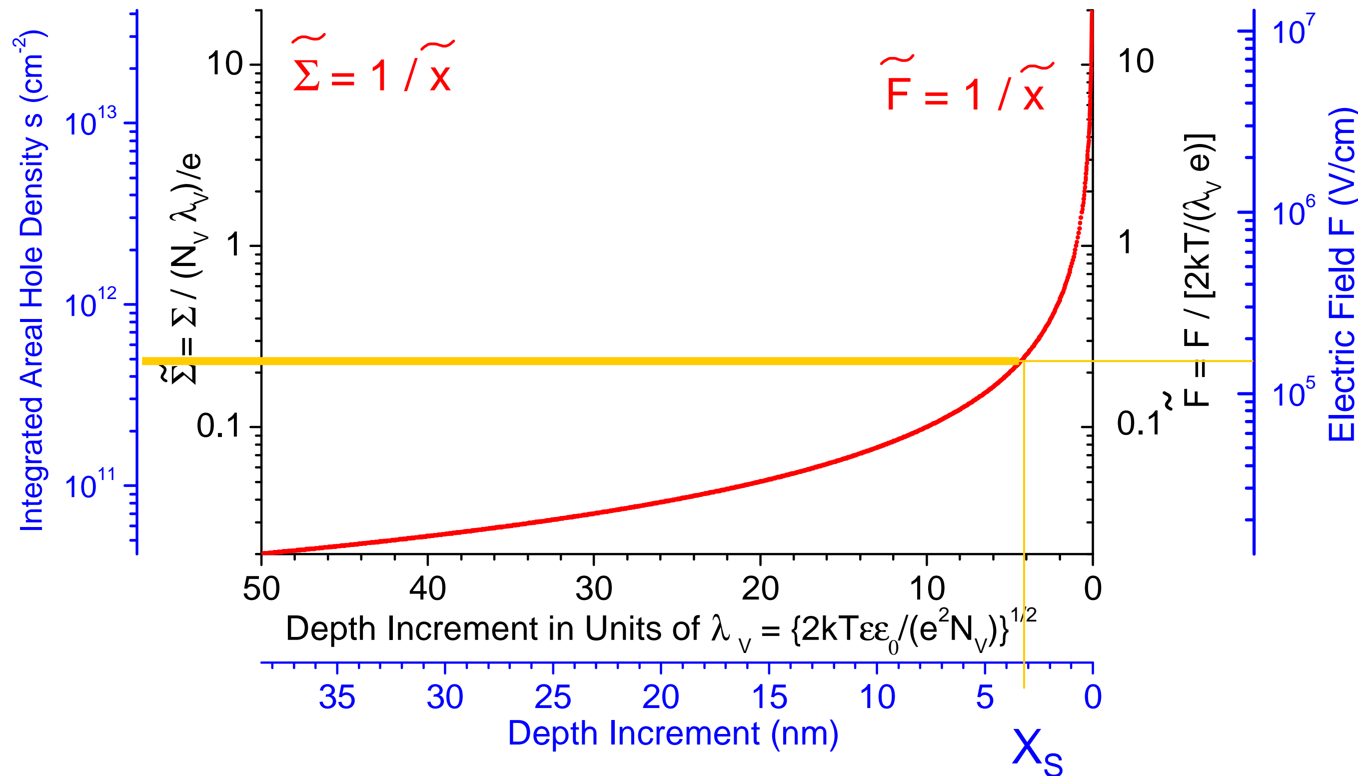
volume charge or hole density at the surface

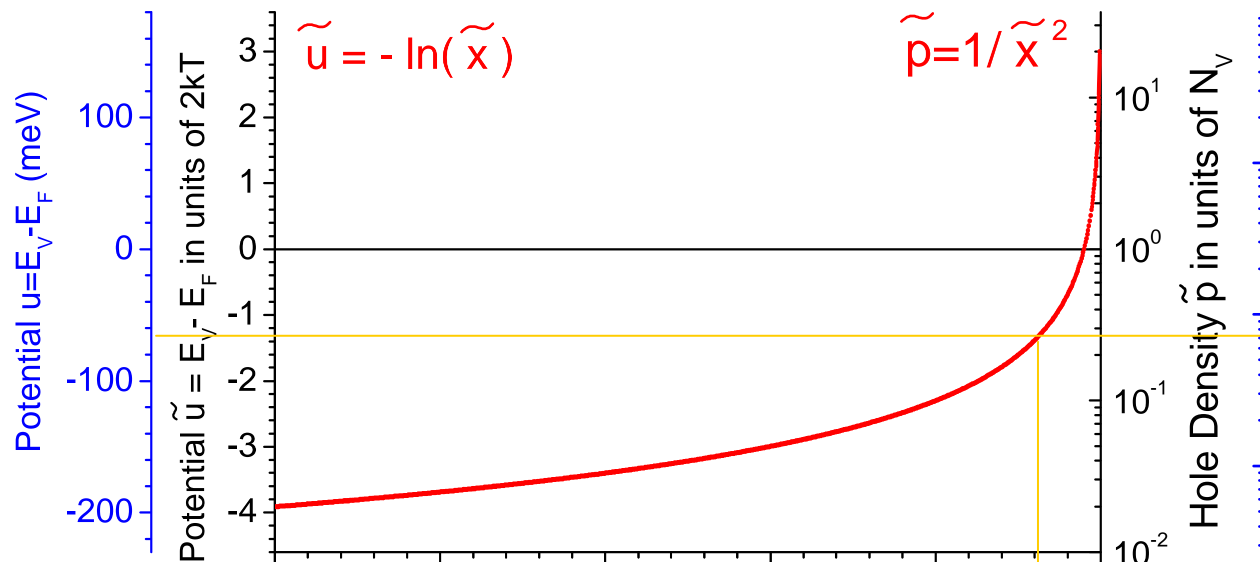


Example for Diamond at R.T.

$$\Sigma = e \cdot 5 \cdot 10^{11}\,\mathrm{cm}^{-2}$$

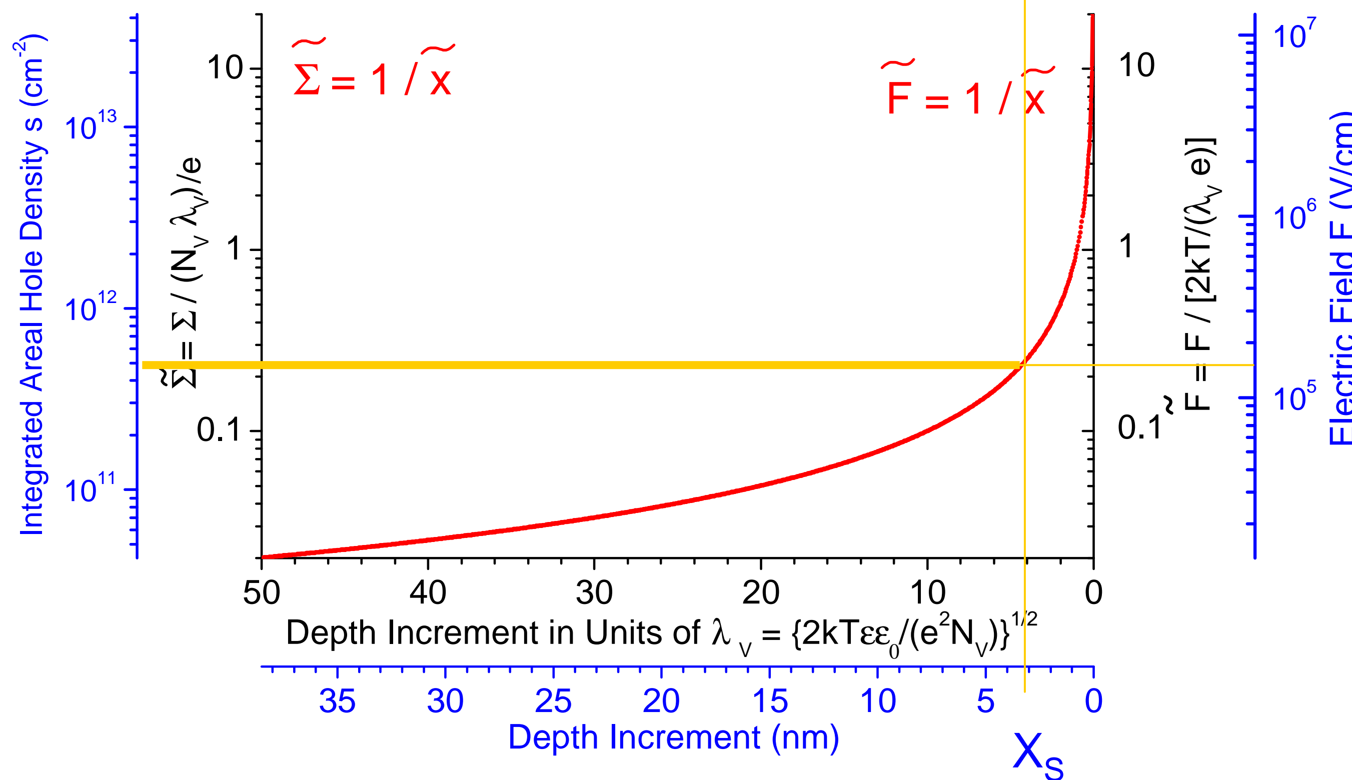






Example for Diamond at R.T.

$$\Sigma = e \cdot 5 \cdot 10^{11} \mathrm{cm}^{-2}$$



surface field

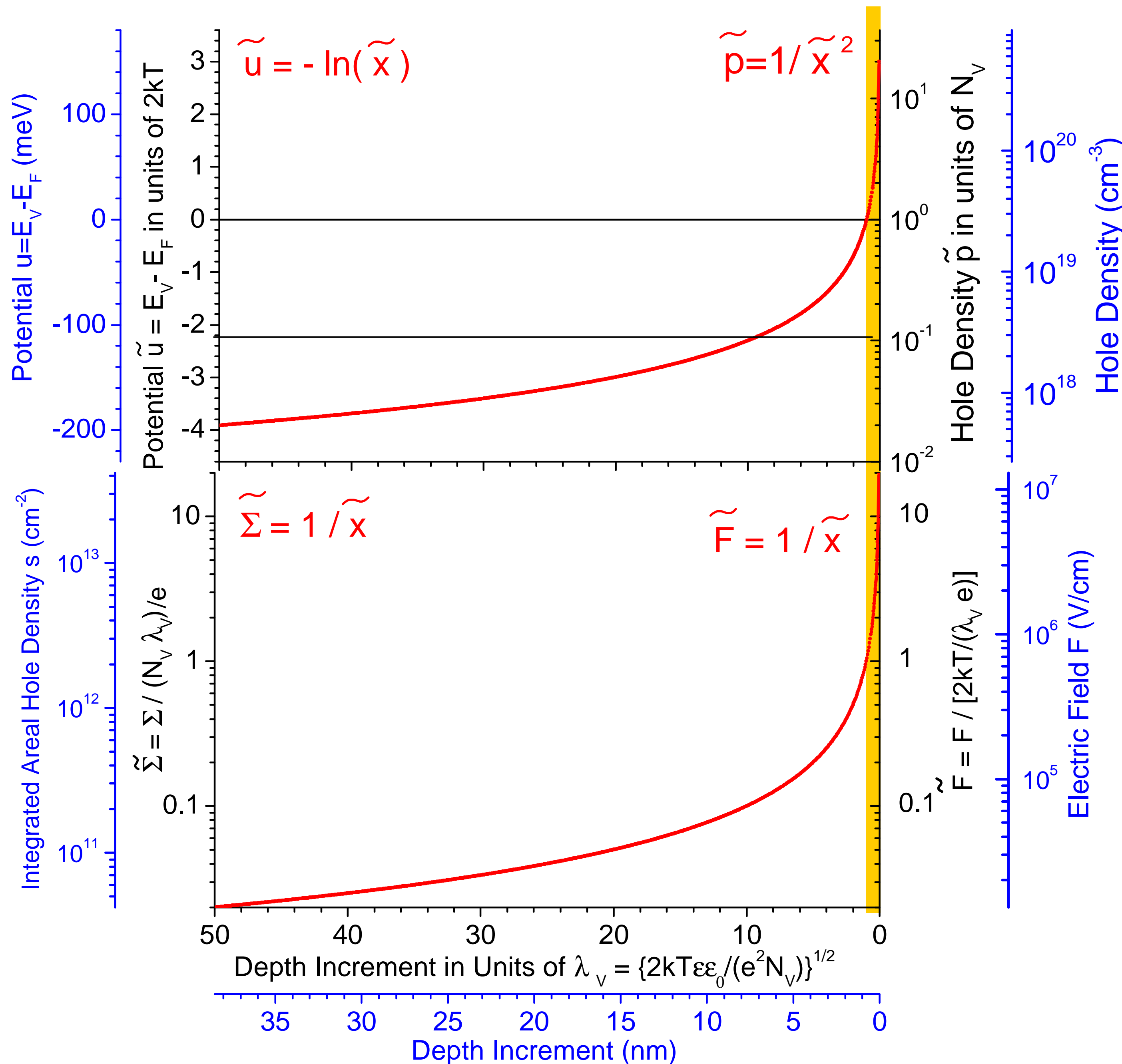
$$F_S = 1.5 \cdot 10^5 \ \mathrm{V/cm}$$

surface potential

$$u_S = -65 \ \mathrm{meV}$$

volume charge density at the surface

$$\rho_S = 7 \cdot 10^{18} \frac{e}{\mathrm{cm}^3}$$



Decay Lengths

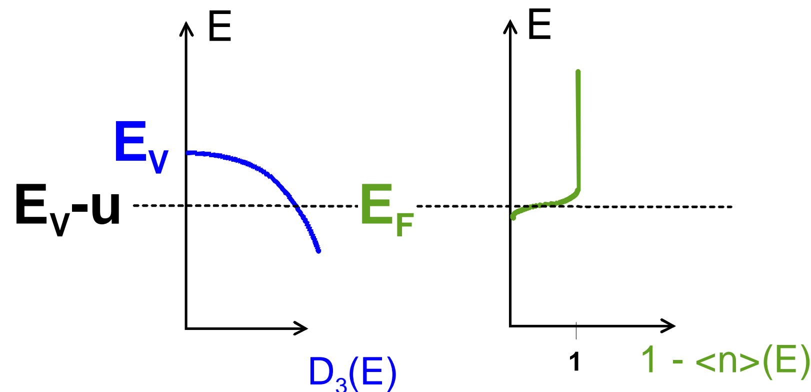
Note:
Steepness of profiles depends on total charge accumulated!

- **$C_2 - \lambda_V < x < C_2$ describes the degenerate case (beyond the approximation of the exponential space charge function).**

The Degenerate Regime

If the Fermi level penetrates the valence or conduction band, the exponential approximation for the space charge function $\rho(u) = eN_V \cdot \exp\left(\frac{u}{kT}\right)$ is no longer valid!

→ Re-evaluation of charge carrier density vs. Fermi level position neccessary for u>0 :



$$D_3(E) = 4\pi\left(2m_h^*/h^2\right)^{3/2}\sqrt{(E_V - E)}$$

with the effective hole mass m_v^*

$$1 - \langle n \rangle(E) = \frac{1}{1+\exp\left(\frac{E_F - E}{kT}\right)} \approx \Theta\left(E - (E_V - u)\right)$$

low T

for the hole occupation function.

$$\tilde{\rho}(u) \approx e4\pi\left(2m_h^*/h^2\right)^{3/2}\int_{E_V-u}^{E_V}\sqrt{(E_V - E)}\,dE$$

$$= \frac{8\pi e}{3}\left(2m_h^*/h^2\right)^{3/2}\cdot u^{3/2}$$

$$= \frac{4}{3\sqrt{\pi}}eN_V\cdot\left[\frac{u}{kT}\right]^{3/2}$$

Add eN_V for continuity at u=0:

$$\rho(u) = eN_V\left(1 + \frac{4}{3\sqrt{\pi}}\cdot\left[\frac{u}{kT}\right]^{3/2}\right)$$

Space charge function for u>0.

The Degenerate Regime

$$\rho(u) = eN_V\left(1 + \frac{4}{3\sqrt{\pi}} \cdot \left[\frac{u}{kT}\right]^{3/2}\right)$$

$$\rightarrow \quad u' = \sqrt{\left| 2\frac{e}{\varepsilon\varepsilon_0} \cdot \left(\int \rho(u)\,du + \tilde{C}_1\right)\right|} = \sqrt{2\frac{e^2 N_V}{\varepsilon\varepsilon_0}} \cdot \sqrt{\int\left(1 + \frac{4}{3\sqrt{\pi}(kT)^{3/2}} u^{3/2}\right) du + C_1}$$

$$= \frac{kT}{\lambda_V/2}\sqrt{\left(\frac{u}{kT}\right) + \frac{8}{15\sqrt{\pi}}\left(\frac{u}{kT}\right)^{5/2} + C_1} \qquad *$$

C_1 from field continuity for u=0:

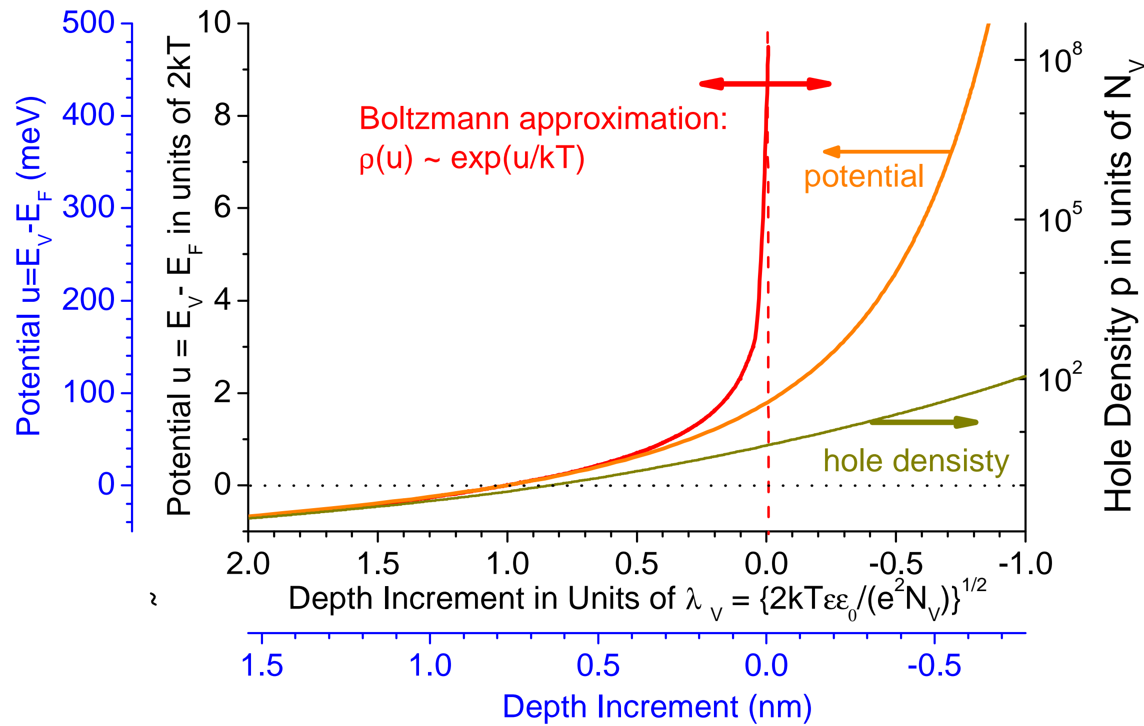
$$\lim_{u\to -0} u'(u) = \frac{kT}{\lambda_V/2} \overset{!}{=} \lim_{u\to +0} u'(u) \quad \rightarrow \quad C_1 = 1$$

Follow recipe from above for finding inverse potential profile:

$$x(u) = x(0) + \frac{\lambda_V}{2}\int_0^{u/(kT)} \frac{1}{\sqrt{1 + t + \frac{8}{15\sqrt{\pi}} t^{5/2}}}\,dt$$

Find by numeric intergration, then combine with * to find field profile, then add to universal plots !

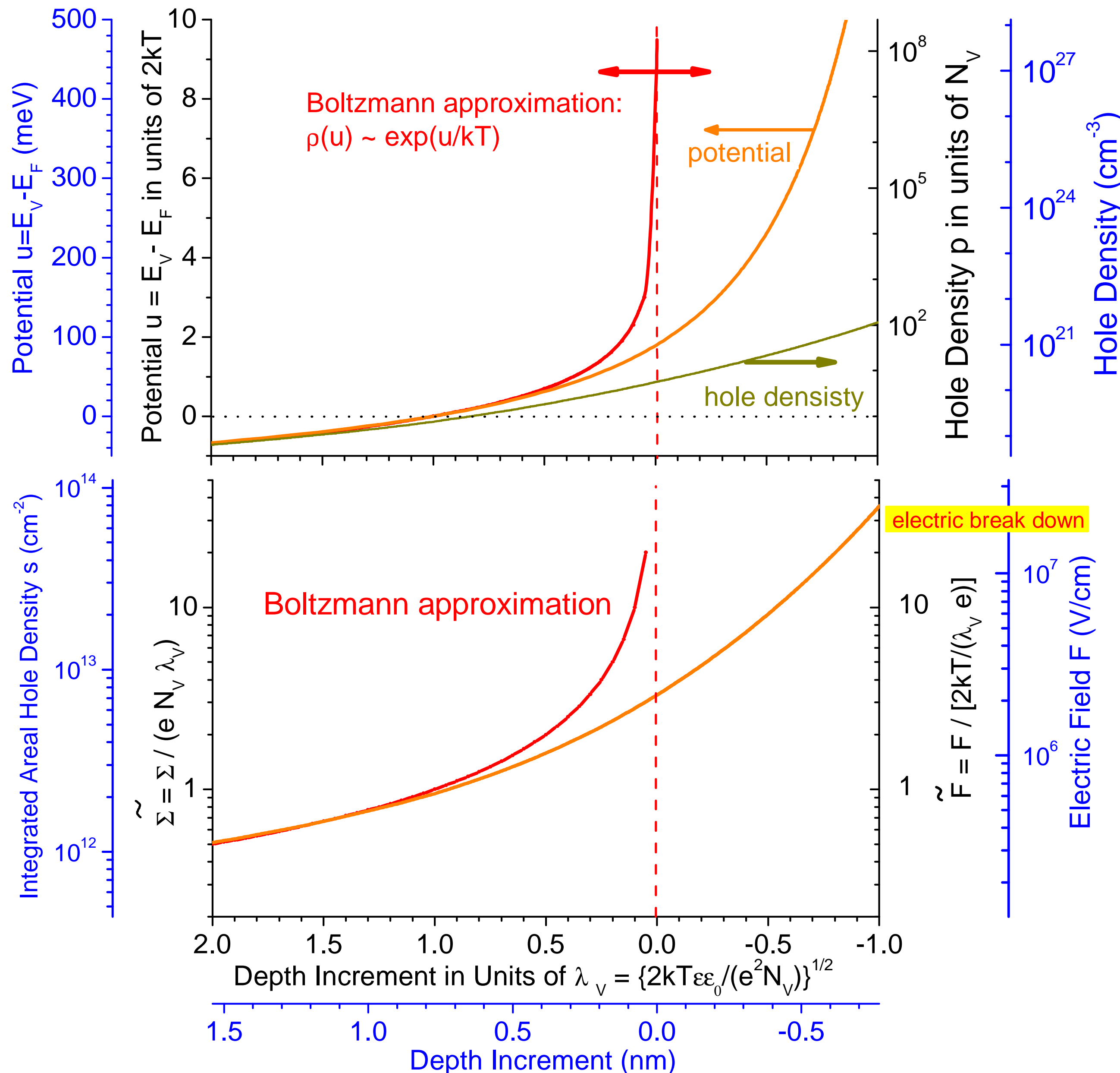
The Degenerate Regime



Profiles weaker (singularity removed)

Blue scales again: diamond at room temperature

The Degenerate Regime



Profiles weaker (singularity removed)

Total areal charge density limited by electic break down at about $\sim 10^{14}$ e cm^{-2}

Charge carrier density limited to about $\sim 10^{22}$ cm^{-3}

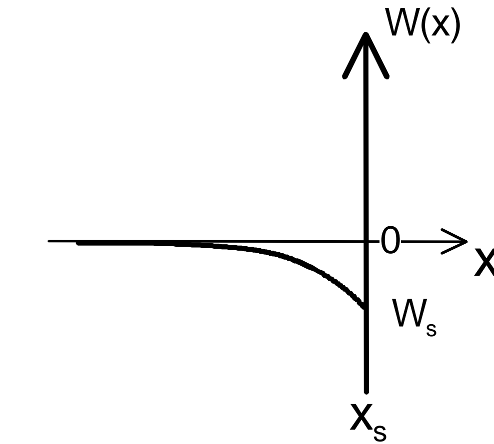
Potential limited at about $u=E_F-E_V\sim 0.5$eV

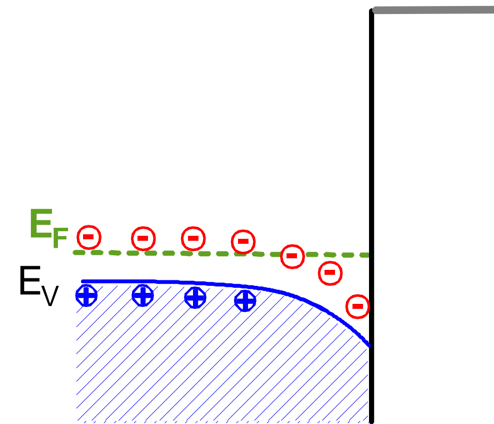
Note typical atomic densities:

1.8×10^{23} cm^{-3} for diamond
5.0×10^{22} cm^{-3} for Si

Case II:

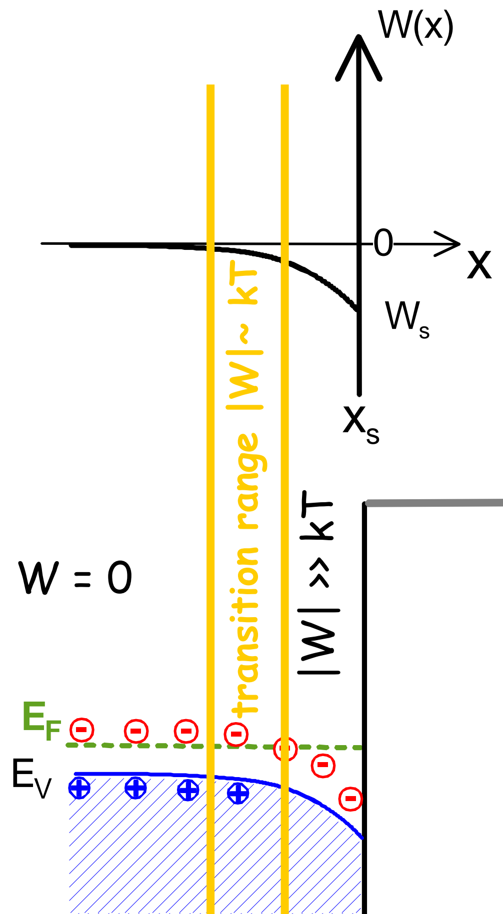
Depletion





(Hole) depletion of a doped semiconductor

The Schottky Approximation



N_A cceptors per cm^3, approx. all ionized

+

same concentration of holes: $\mathbf{p \approx N_A}$ (impurity exhaustion)

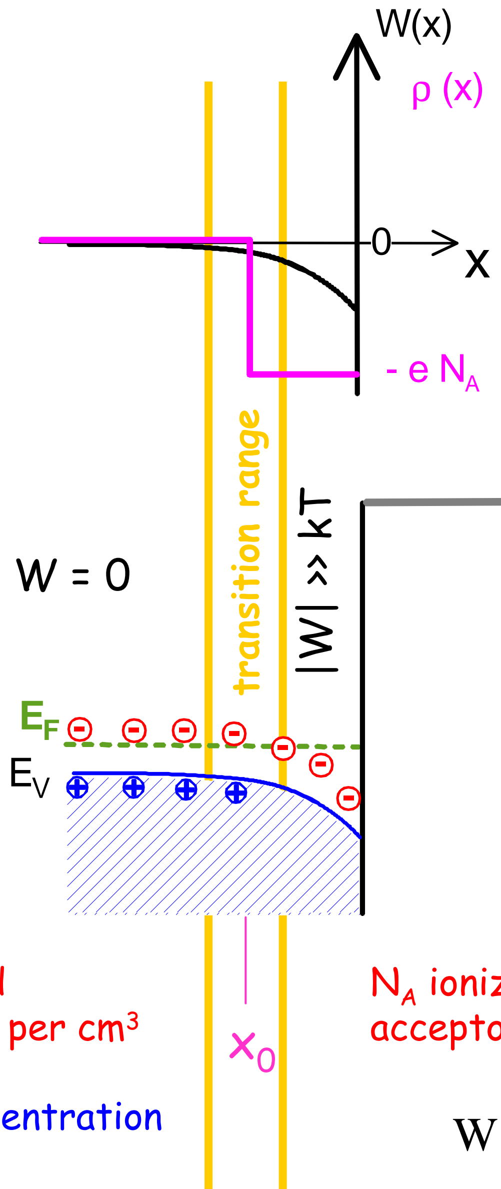
N_A ionized acceptors per cm^3

+

$$p = N_A \cdot \exp\left(\frac{-|W|}{kT}\right) \approx 0$$

Space charge now due to fixed impurities, not to mobile carriers!

The Schottky Approximation



N_A ionized acceptors per cm³
+
same concentration of holes

N_A ionized acceptors per cm³

Space charge function*:

$$\rho(W) = -eN_A \cdot \underbrace{\Theta(-W)}$$

Heavyside step function: 1 for positive argument, 0 else

*by neglecting the (normally narrow) transition range:

Poisson's Equation:

$$W'' = \frac{e}{\varepsilon\varepsilon_0}\rho(W) = -\frac{e^2 N_A}{\varepsilon\varepsilon_0}$$

in the depletion layer

→

$$W' = \pm\sqrt{2\frac{e}{\varepsilon\varepsilon_0}\cdot\left(\int \rho(W)\,dW + C_1\right)} = \pm\sqrt{2\frac{e^2 N_A}{\varepsilon\varepsilon_0}\cdot(W + C_1)}$$

Semi-infinite Geometry (Bulk → - ∞)

$$W' = \pm\sqrt{2\frac{e}{\varepsilon\varepsilon_0}\cdot\left(\int\rho(W)\,dW + C_1\right)} = \pm\sqrt{2\frac{e^2 N_A}{\varepsilon\varepsilon_0}\cdot(W + C_1)}$$

→ $C_1 = 0$ and $W' = e\cdot F = -\sqrt{2\frac{e^2 N_A}{\varepsilon\varepsilon_0}}\cdot\sqrt{|W|}$

Potential / field relation: $\Sigma_{-\infty,\,x(W)} = -\sqrt{2\varepsilon\varepsilon_0 N_A}\cdot\sqrt{|W|}$

Semi-infinite Geometry (Bulk → - ∞)

$$W' = \pm\sqrt{2\frac{e}{\varepsilon\varepsilon_0}\cdot\left(\int\rho(W)\,dW + C_1\right)} = \pm\sqrt{2\frac{e^2 N_A}{\varepsilon\varepsilon_0}\cdot(W + C_1)}$$

→ $C_1 = 0$ and $$W' = e\cdot F = -\sqrt{2\frac{e^2 N_A}{\varepsilon\varepsilon_0}}\cdot\sqrt{|W|}$$

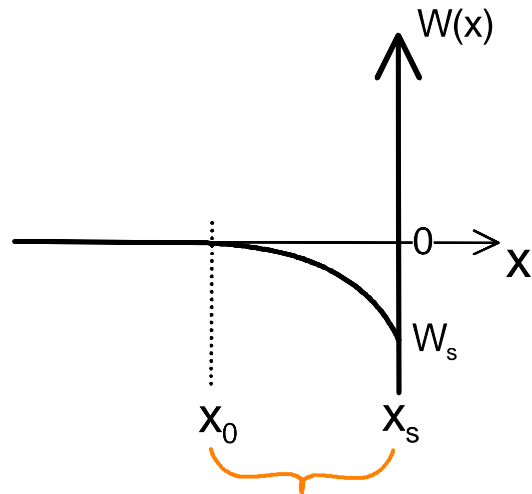
Potential / field relation: $$\Sigma_{-\infty,\,x(W)} = -\sqrt{2\varepsilon\varepsilon_0 N_A}\cdot\sqrt{|W|}$$

Potential: $$W(x) = -\frac{e^2 N_A}{2\varepsilon\varepsilon_0}(x - x_0)^2\cdot\Theta(x - x_0)$$

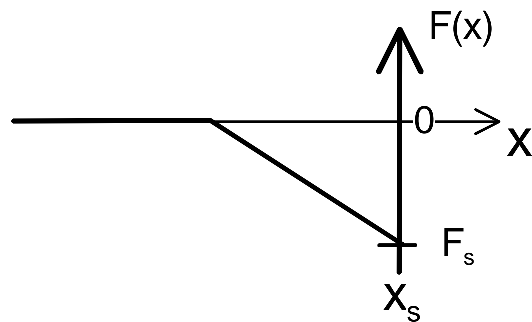
Electric Field: $$F(x) = W'(x)/e = -\frac{e\,N_A}{\varepsilon\varepsilon_0}(x - x_0)\cdot\Theta(x - x_0)$$

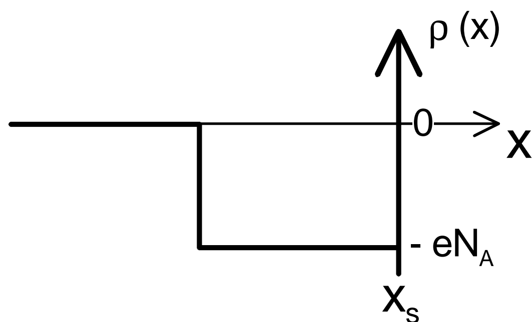
Space charge density: $$\rho(x) = -e\,N_A \cdot\Theta(x - x_0)$$

Depletion Width and Surface Potential



depletion range R



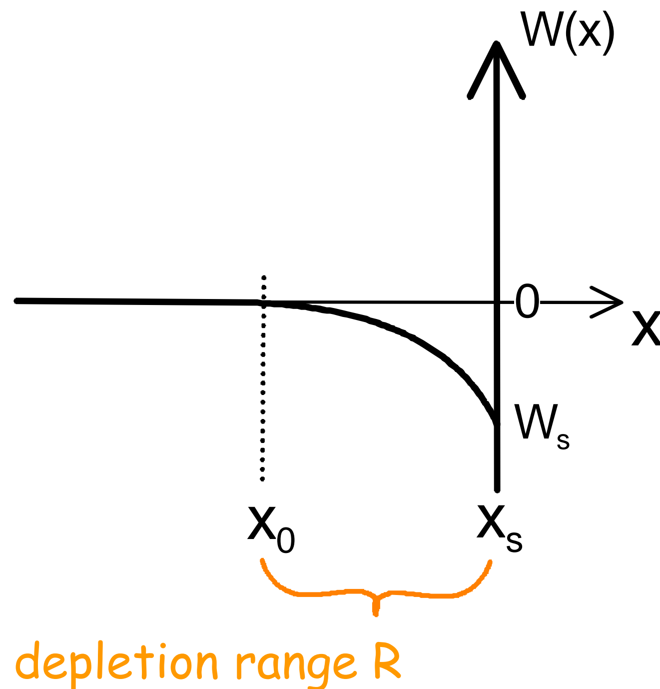


Charge exchange with overlayer system determines width R of depletion range:

$$R = \sqrt{\frac{2\varepsilon\varepsilon_0}{e^2 N_A}} \cdot \sqrt{|W_S|}$$

$$\Sigma = eN_A \cdot R = \sqrt{2\varepsilon\varepsilon_0 N_A} \cdot \sqrt{|W_S|}$$

Depletion Width and Surface Potential



Charge exchange with overlayer system determines width R of depletion range:

$$R = \sqrt{\frac{2\varepsilon\varepsilon_0}{e^2 N_A}} \cdot \sqrt{|W_S|}$$

$$\Sigma = -eN_A \cdot R = -\sqrt{2\varepsilon\varepsilon_0 N_A} \cdot \sqrt{|W_S|}$$

Depletion range and total (areal) charge density scale with the **square root of the surface potential !**

Example: p -type Si (ε=11.8; N_A=10^{16}cm^{-3}) for $|W_S|$=E_G/2=0.55eV: R= 360 nm
p^+ -type Si (ε=11.8; N_A=10^{19}cm^{-3}) for $|W_S|$=E_G/2=0.55eV: R= 11 nm

Note: all independent of temperature (Schottky approximation!)

Universal Representation of Hole Depletion Profiles

Potential:

$$\frac{W}{2kT} = -\frac{1}{2}\left[\frac{x-x_0}{\lambda_A}\right]^2 \cdot \Theta(x-x_0)$$

Electric Field:

$$\frac{F}{2kT/(e\lambda_A)} = -\left[\frac{x-x_0}{\lambda_A}\right] \cdot \Theta(x-x_0)$$

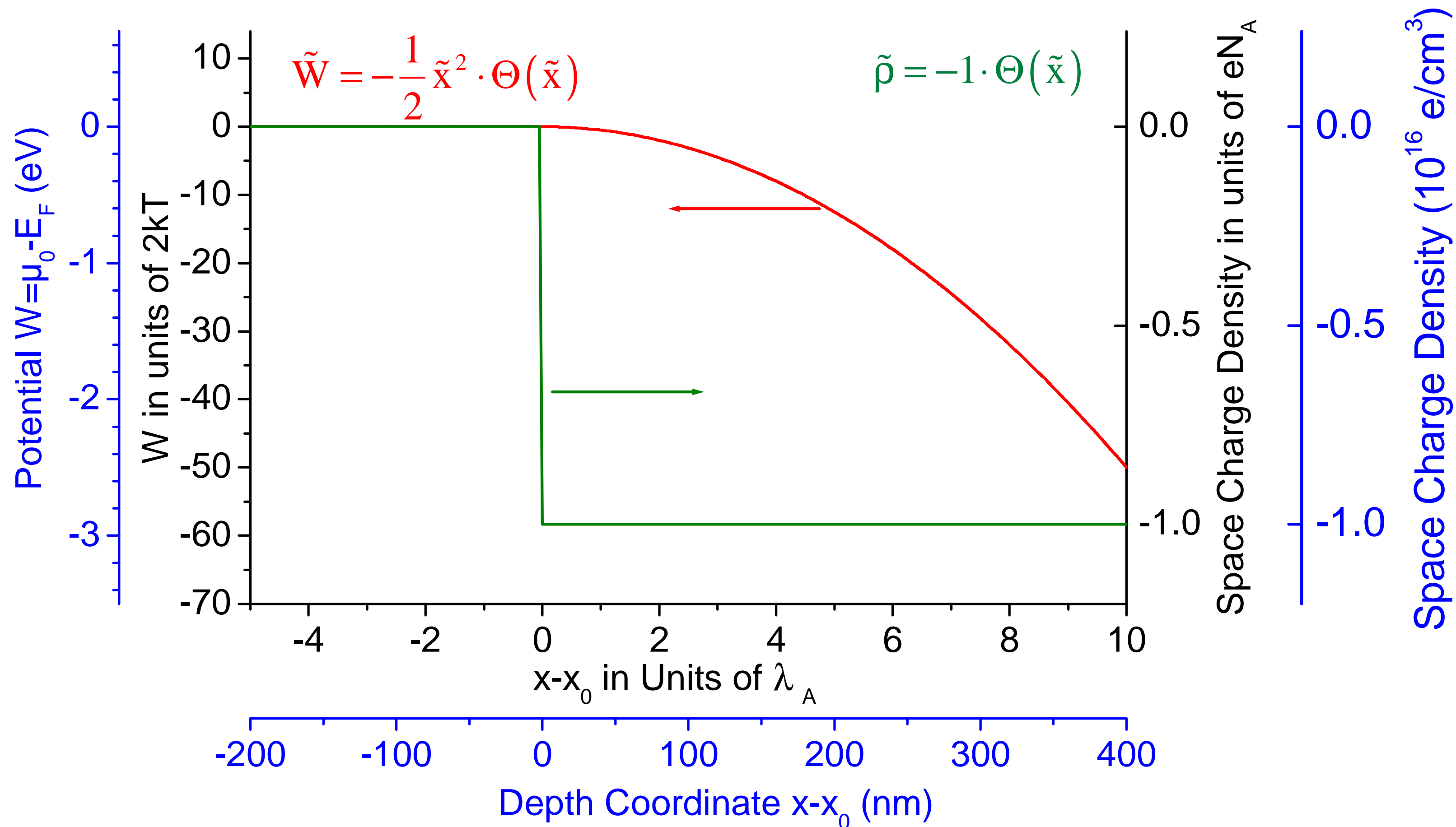
Space charge Density:

$$\frac{\rho}{eN_A} = -1 \cdot \Theta(x-x_0)$$

with scaling length $\lambda_A = \sqrt{2kT\varepsilon\varepsilon_0/e^2/N_A}$ and start of the depletion zone x_0

* Note the following useful rule which is accurate within 5%: $\Sigma/e = 1000\sqrt{\varepsilon \;\; N/cm^{-3} \;\; W/eV} \;\; cm^{-2}$

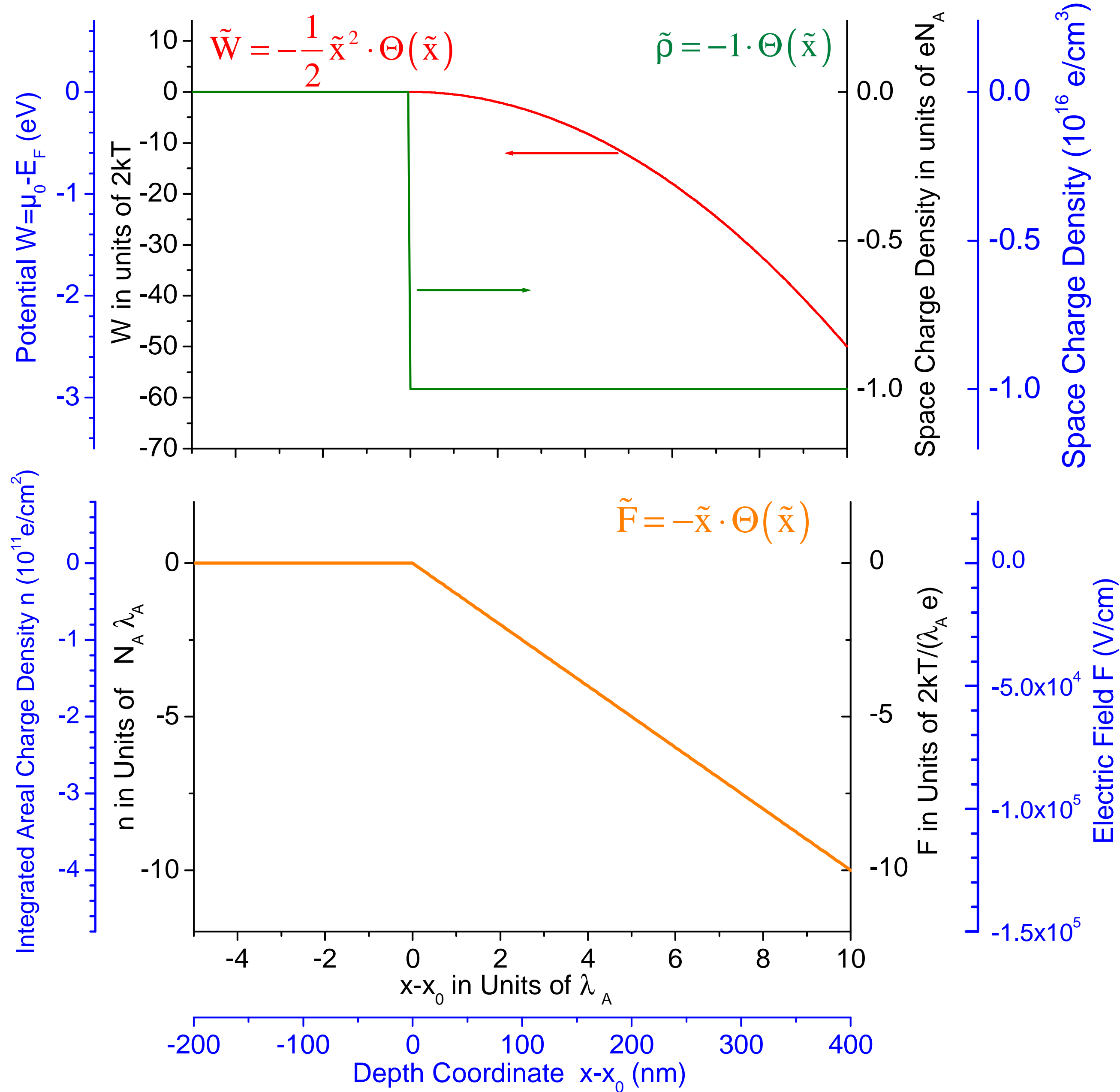
Universal Plots of Hole Depletion Profiles



➢ Displays any depletion profile, just choose surface coordinate !

blue scales: for diamond at R.T and $N_A=10^{16}cm^{-3}$ ⟶ $\lambda_A = \sqrt{2kT\varepsilon\varepsilon_0 / e^2 / N_A} = 40\ \mathrm{nm}$

Universal Plots of Hole Depletion Profiles



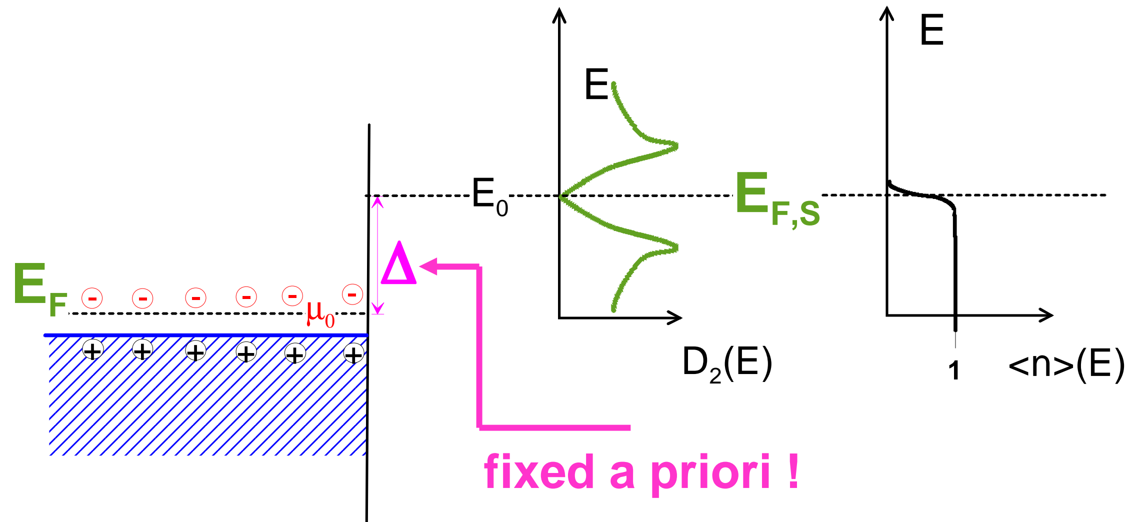
Depletion by Surface States or Surface Defects

Surface states: two-dimensional (Bloch type) electronic states, characteristic of the 2d-periodic potential of lattice + surface: 2d-bands; ~ 2 states per surface unit mesh ~ 10^{14} to 10^{15} cm^{-2}

Surface defects: one (zero) -dimensional el. states at line (point) defects on the surface (~ 10^{10} to 10^{12} cm^{-2})

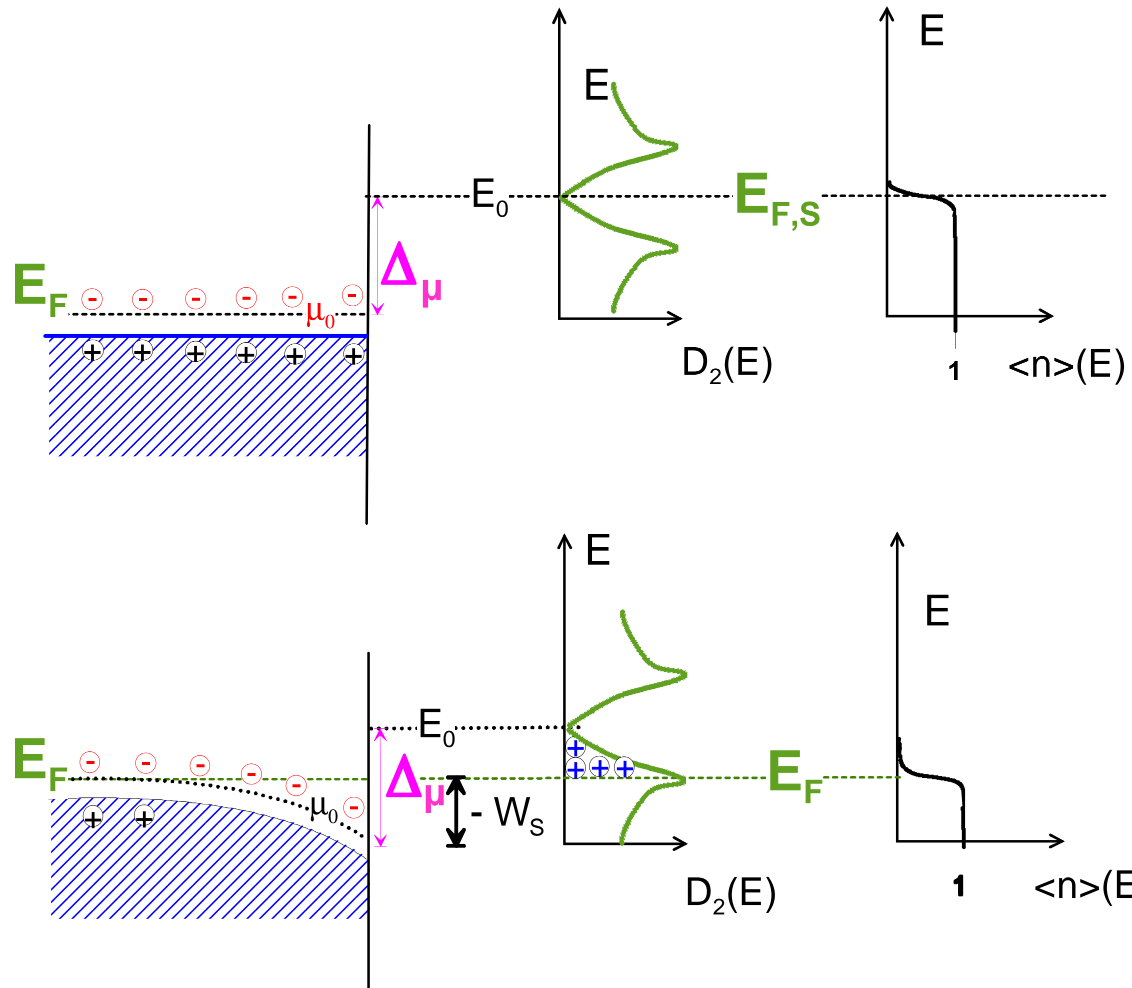
- Characteristic 2d density of states [$cm^{-2}eV^{-1}$],
- linked to the bulk band structure by quantum mechanics
- with a characteristic charge neutrality level
- capable of exchanging electrons with the bulk

Establishing 'Chemical Equilibrium'



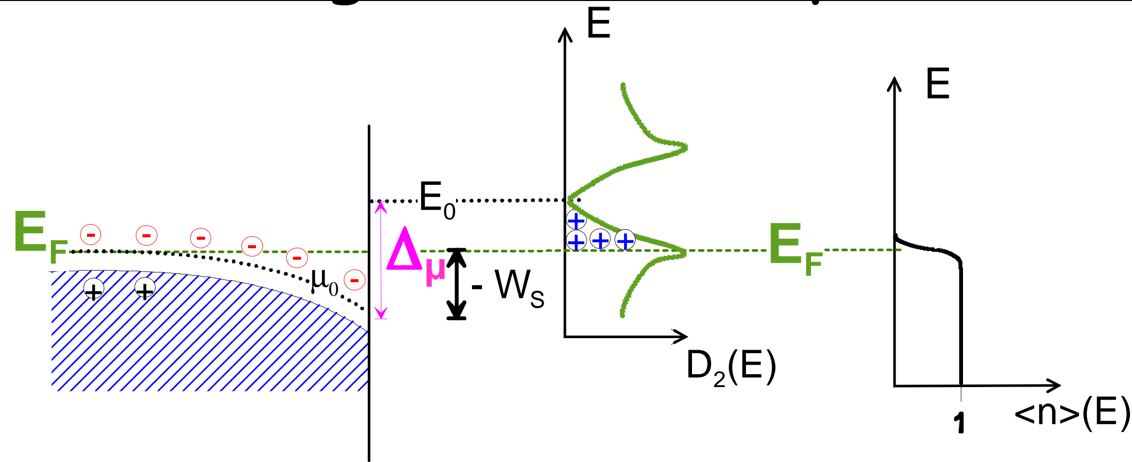
W_S in equilibrium is determined by common a Fermi level + charge neutrality!

Establishing ‚Chemical Equilibrium'



W_S in equilibrium is determined by common a Fermi level + charge neutrality!

Establishing ‚Chemical Equilibrium'



Charge balance

$$\Sigma(W_S) = -eN_A \cdot R = -\sqrt{2\varepsilon\varepsilon_0 N_A} \cdot \sqrt{|W_S|}$$

$$\sigma(W_S) = -e\left\{\int_{-\infty}^{\infty} \frac{D_2(E)}{1+\exp\left(\frac{E-(E_0-\Delta-W_S)}{kT}\right)} dE - \int_{-\infty}^{\infty} \frac{D_2(E)}{1+\exp\left(\frac{E-E_0}{kT}\right)} dE\right\}$$

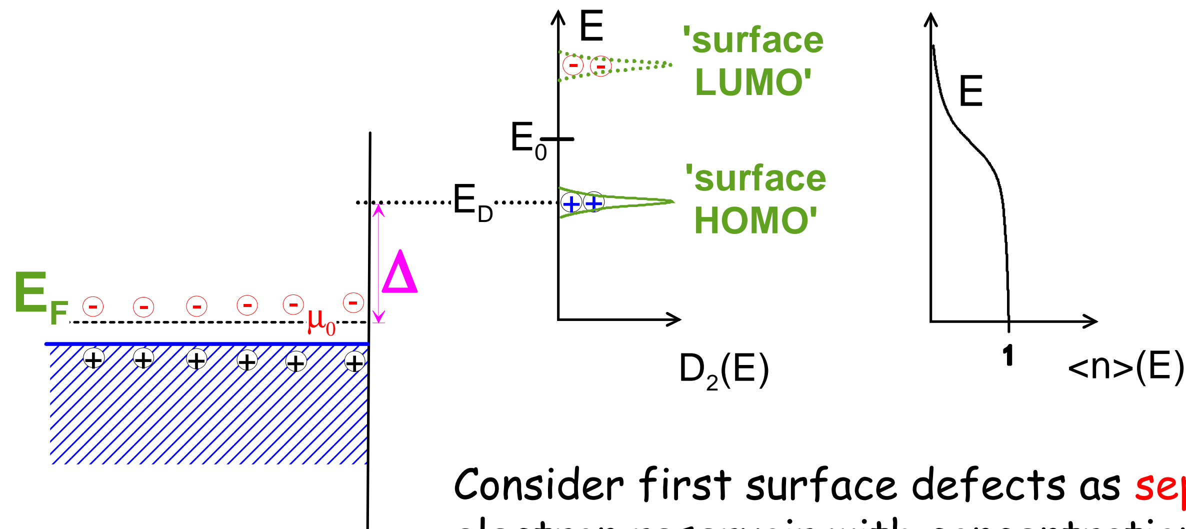
$$\approx \quad e \int_{E_0-\Delta+|W_S|}^{E_0} D_2(E)\, dE$$

low T

decreasing from zero !

positive and decreasing towards zero !

Special Case: Single Discrete Defect Level



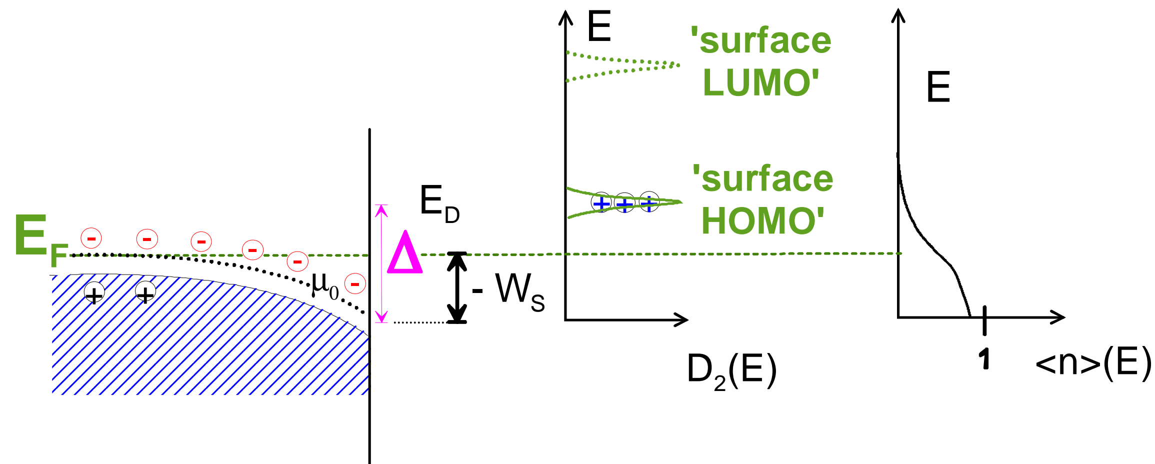
Consider first surface defects as separate electron reservoir with concentration n_D [cm^{-2}] of ‚donor-like', i.e. occupied, states at enery level E_D:

$$D_2(E) = n_D \cdot \delta\left(E - E_D\right)$$

Note:

- Charge neutrality level E_0 of the defects between (surface) HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest unoccupied Molecular Orbital) !
- $\Delta = E_D - \mu_0$ now with respect to defect level .

Special Case: Single Discrete Defect Level



Charge balance

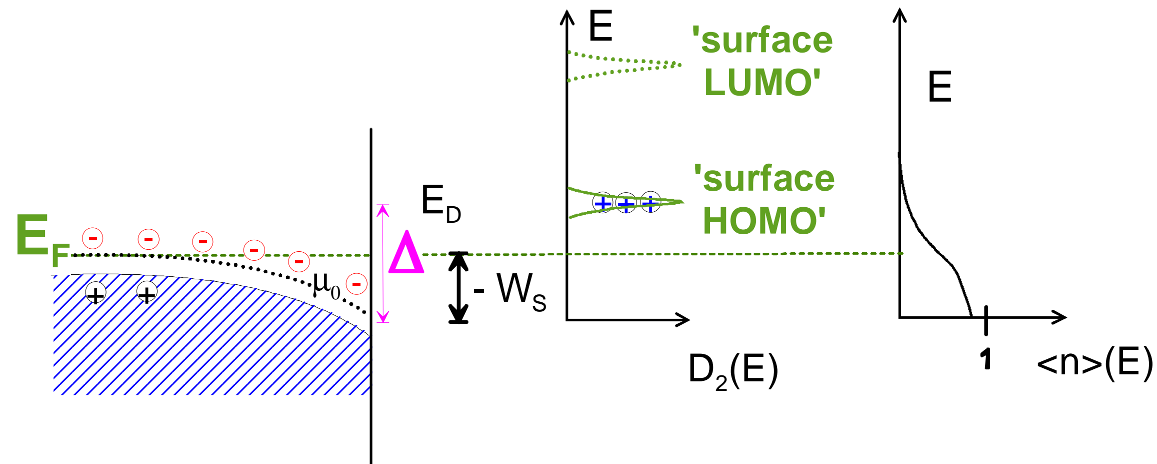
$$\left|\Sigma(W_S)\right| = \sqrt{2\varepsilon\varepsilon_0 N_A} \cdot \sqrt{|W_S|}$$

$$\left|\sigma(W_S)\right| = \frac{e\,n_D}{1+\exp\left(\frac{(|W_S|-\Delta)}{kT}\right)}$$

missing holes in the depletion zone !

holes in the surface defect level

Special Case: Single Discrete Defect Level



Charge balance

$$\left|\Sigma(W_S)\right| = \sqrt{2\varepsilon\varepsilon_0 N_A} \cdot \sqrt{\left|W_S\right|}$$

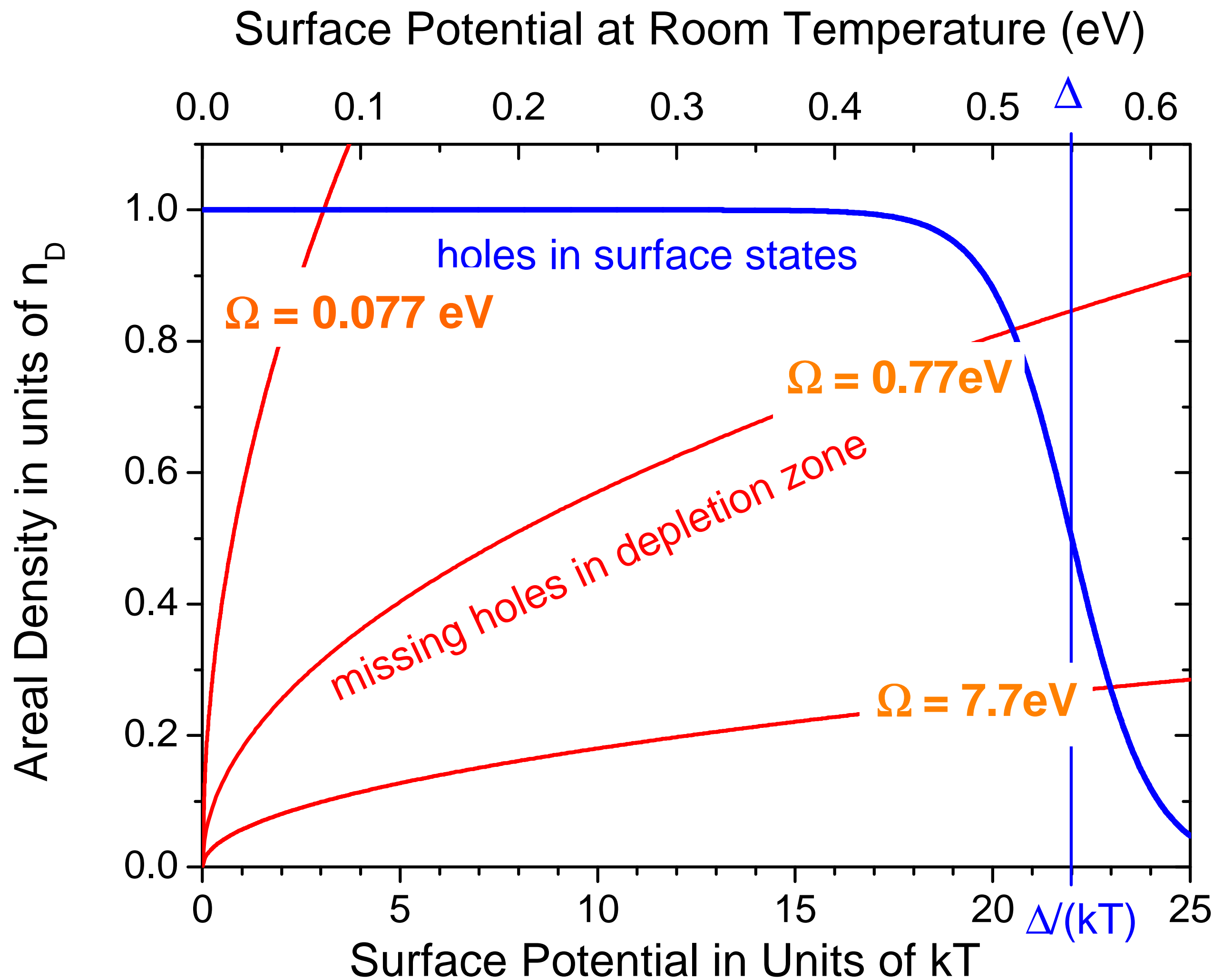
$$\left|\sigma(W_S)\right| = \frac{e\,n_D}{1+\exp\left(\frac{(|W_S|-\Delta)}{kT}\right)}$$

$$\frac{\left|\Sigma(W_S)\right|}{e\,n_D} = \frac{\left|\sigma(W_S)\right|}{e\,n_D} = \sqrt{\frac{|W_S|}{\frac{e^2 n_D^{\,2}}{\underbrace{2\varepsilon\varepsilon_0 N_A}}}} = \frac{1}{1+\exp\left(\frac{|W_S|-\Delta}{kT}\right)}$$

Ω^2 = upper limit for surface potential corresponding to $\Sigma = -en_D$
i.e. surface HOMO completely unoccupied.

→ Implicit equation for W_S. Solve graphically or by iteration!

Special Case: Single Discrete Defect Level

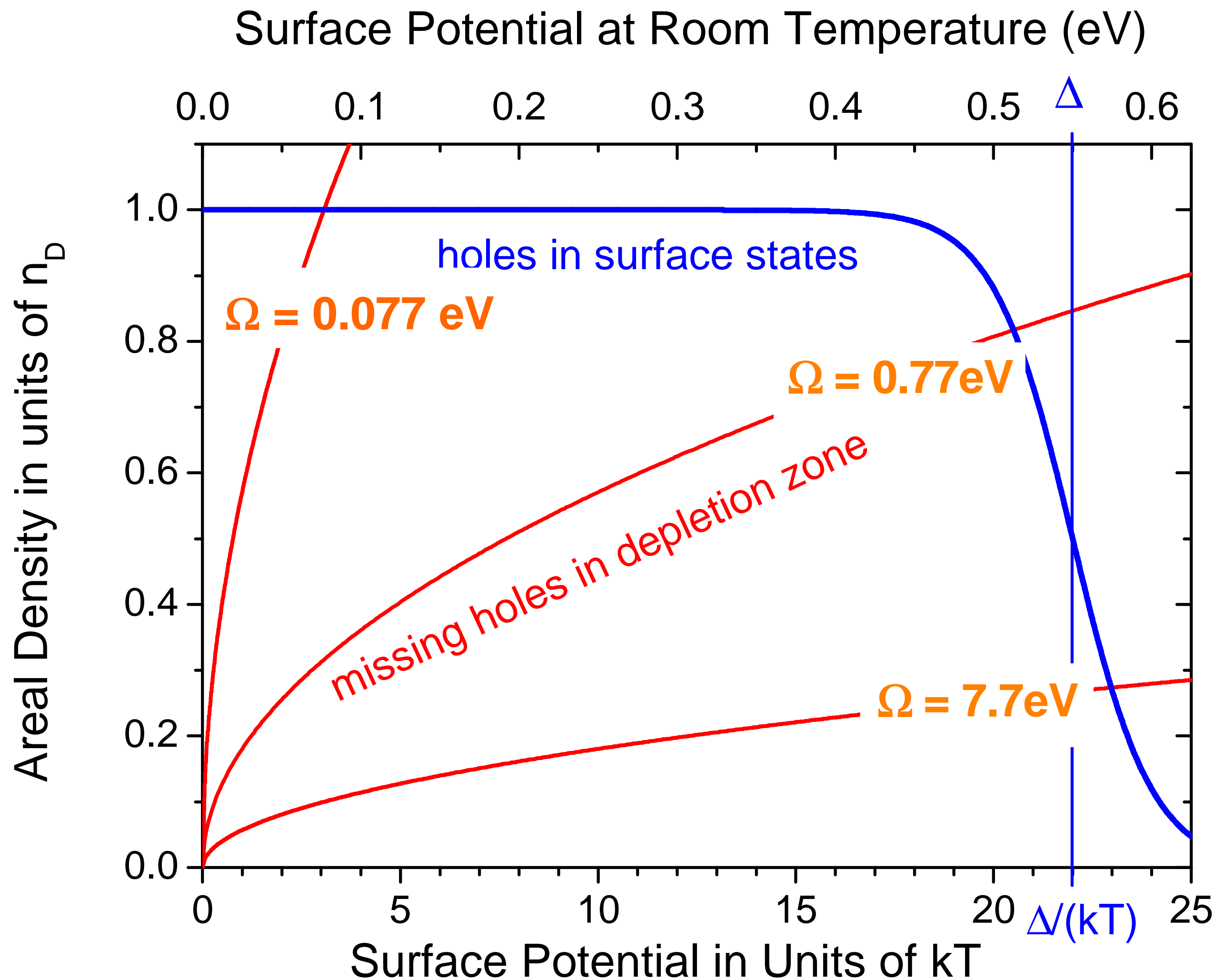


Note:

- $\Omega = \frac{e^2 n_D{}^2}{2\varepsilon\varepsilon_0 N_A}$ reflects the balance between surface and bulk states
- For high defect density: $|W_S| = \Delta$ 'pinning' of the surface Fermi level at E_D
- For low defect density: all defects filled with holes and $n_D = \sqrt{2\varepsilon\varepsilon_0 N_A / e^2} \cdot \sqrt{|W_S|}$
- For vanishing defect density $W_s = 0$:
- flat band conditions

Special Case: Single Discrete Defect Level

$$\Omega = \frac{e^2 n_D^2}{2\varepsilon\varepsilon_0 N_A}$$



Examples:

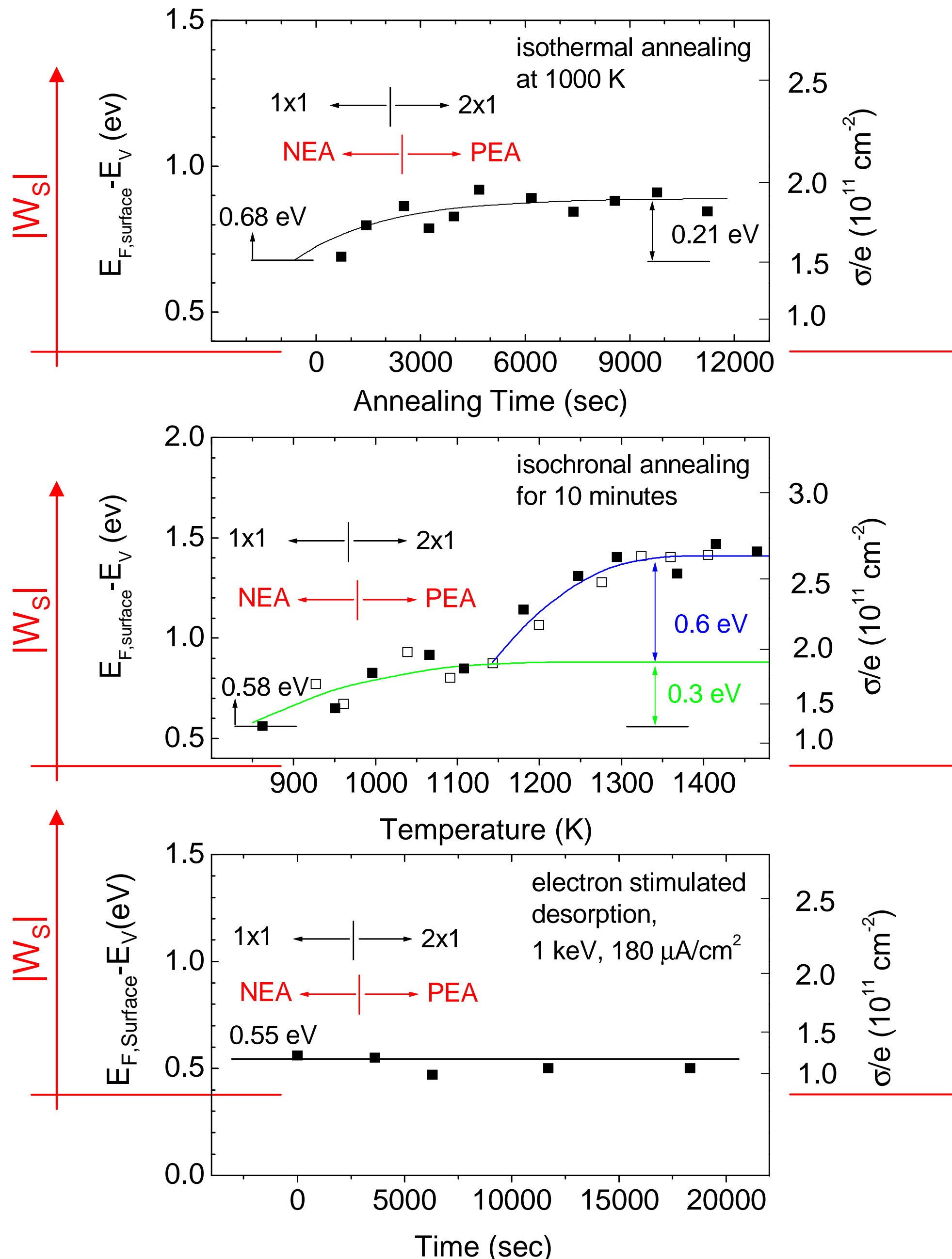
Si (ε=11.8, E_G=1.1 eV)
at R.T. with E_D
at mid gap position:

p-type $N_A = 10^{16}\,cm^{-3}$
with $n_D = 10^{12}\,cm^{-2}$
→ $\Omega = 7.7\,eV$

p-type $N_A = 10^{17}\,cm^{-3}$
with $n_D = 10^{12}\,cm^{-2}$
→ $\Omega = 0.77\,eV$

p-type $N_A = 10^{16}\,cm^{-3}$
with $n_D = 10^{11}\,cm^{-2}$
→ $\Omega = 0.077\,eV$

Application: Defect Density from Band Bending Analysis



With surface Fermi level position from photoelectron spectroscopy:

$$\left|W_S\right| = E_F - \mu_0 = E_F - E_V - 0.36\text{eV}$$

p-type diamond with $N_A = 2\cdot 10^{16}\,\text{cm}^{-3}$

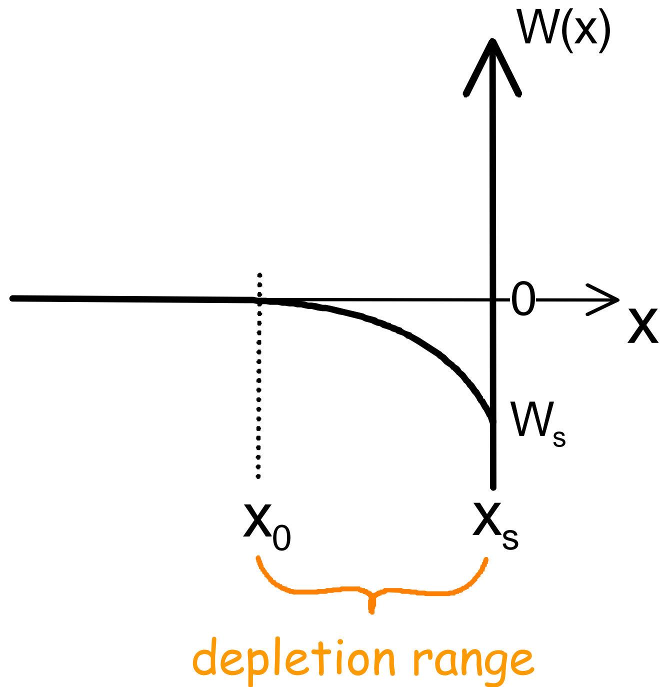
$$\sigma / e = \sqrt{2\varepsilon\varepsilon_0 N_A / e^2} \cdot \sqrt{\left|W_S\right|} \approx n_D$$

no pinning

- $n_D = 10^{11}\text{cm}^{-2}$ (N_A given) for the hydrogen terminated diamond (111) surface

- Pinning position = Defect energy $E_D = E_V + 1.4\text{eV}$

Special Case: Total Depletion of Nano-Grains



depletion range

When the depletion range exceeds the grain radius, no mobile charge carriers are left in a grain!

Consider a Si grain with Radius **R**, dopant concentration $\mathbf{N_A}$ and defect level at mid gap position, i.e. $\Delta = 0.55\,\mathrm{eV}$.

What is the critical surface/interface defect density n_C leading to total grain depletion?

$$R \cdot N_A = n_C \Big/ \left(1 + e^{\frac{|W_S| - \Delta}{kT}}\right)$$

and

$$W_S = R^2 \cdot \frac{e^2 N_A}{2\varepsilon\varepsilon_0}$$

$$\rightarrow \quad n_C = R \cdot N_A \cdot \left[1 + \exp\left(\frac{\frac{e^2 N_A}{2\varepsilon\varepsilon_0} R^2 - \Delta}{kT}\right)\right] \approx R \cdot N_A$$

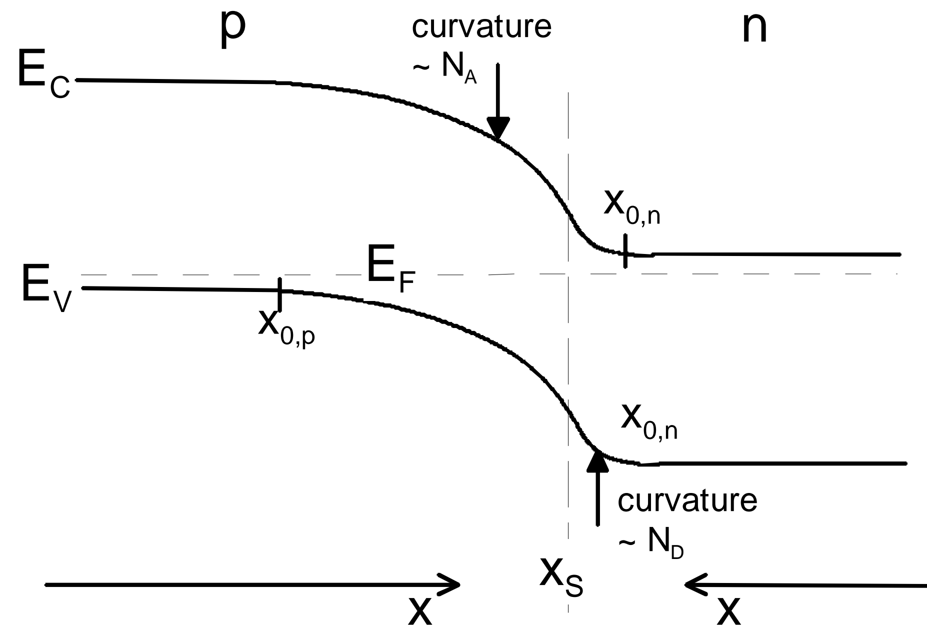
Total Depletion of Si Nano-Grains

Critical defect densities n_C for complete depletion

Grain Diameter 2R (nm)	10	50	200
p-type: $N_A = 10^{16}$ cm^{-3}	5×10^{9} cm^{-2}	2.5×10^{10} cm^{-2}	1×10^{11} cm^{-2}
$N_A = 3 \times 10^{17}$ cm^{-3}	1.5×10^{11} cm^{-2}	7.5×10^{11} cm^{-2}	$> 10^{18}$ cm^{-2}
p^+-type: $N_A = 10^{19}$ cm^{-3}	5×10^{12} cm^{-2}	$> 10^{18}$ cm^{-2}	$> 10^{18}$ cm^{-2}

Note: surface atom density on Si ~ 7×10^{14} cm^{-2}
defect densities on best Si/SiO interfaces ~10^{10} cm^{-2}

Basic Devices: the pn-Junction



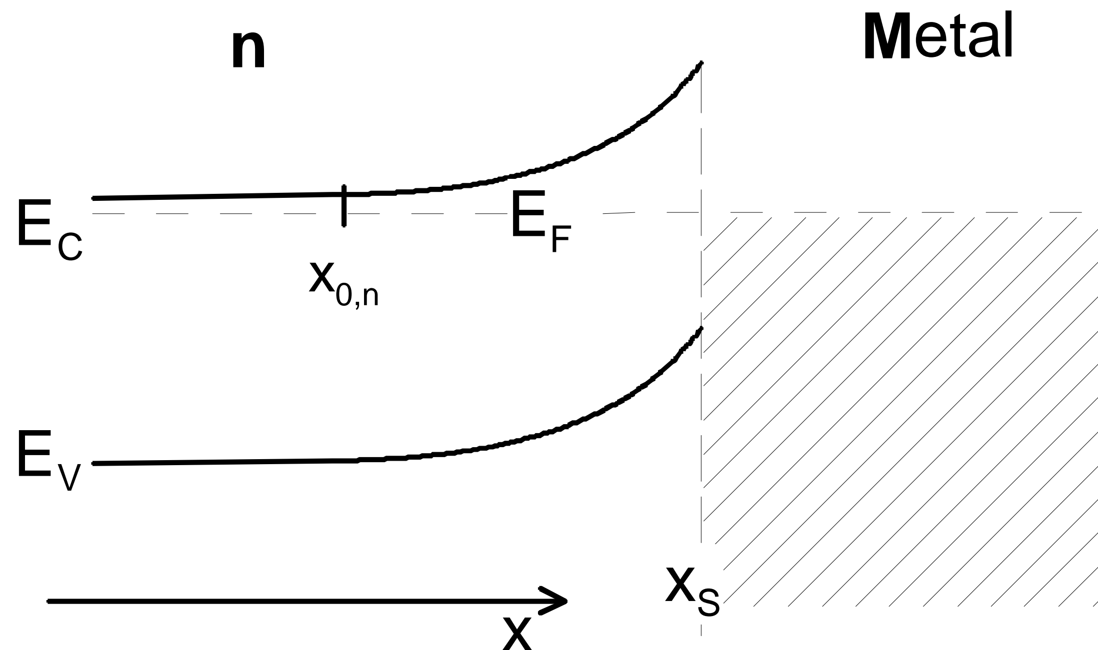
Two semi-infinite layers with dopant concentrations N_A and N_D and boundary conditions:

1.) $W_D = W_n - W_p = |W_n| + |W_n| = \phi_p - \phi_n \approx E_G$ is the so-called diffusion potential;

2.) $W_p'(x_S) = -W_n'(x_S)$, i.e. the electric field is continous.

Two parabola with in general different curvature have to be matched continously to add up to be (apporximately) the band gap energy!

Basic Devices: the Schottky-Junction

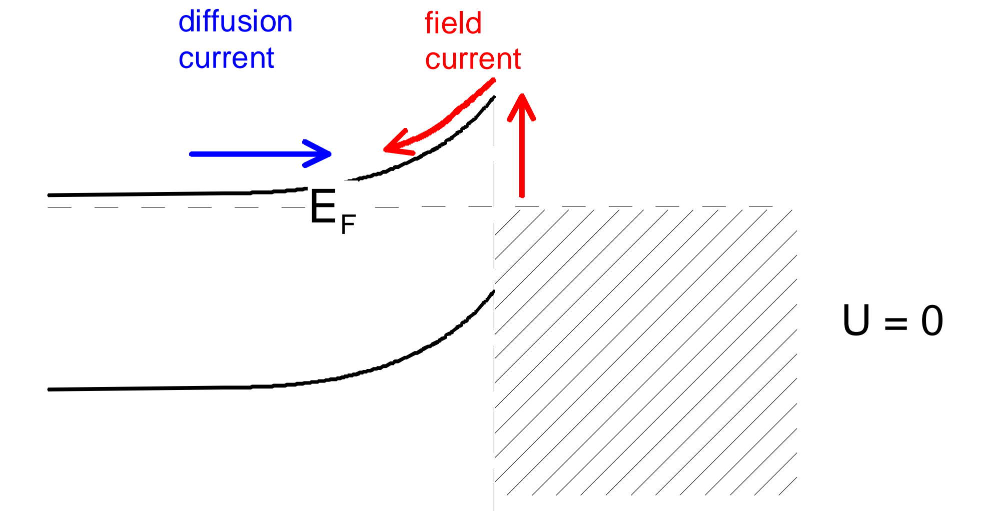


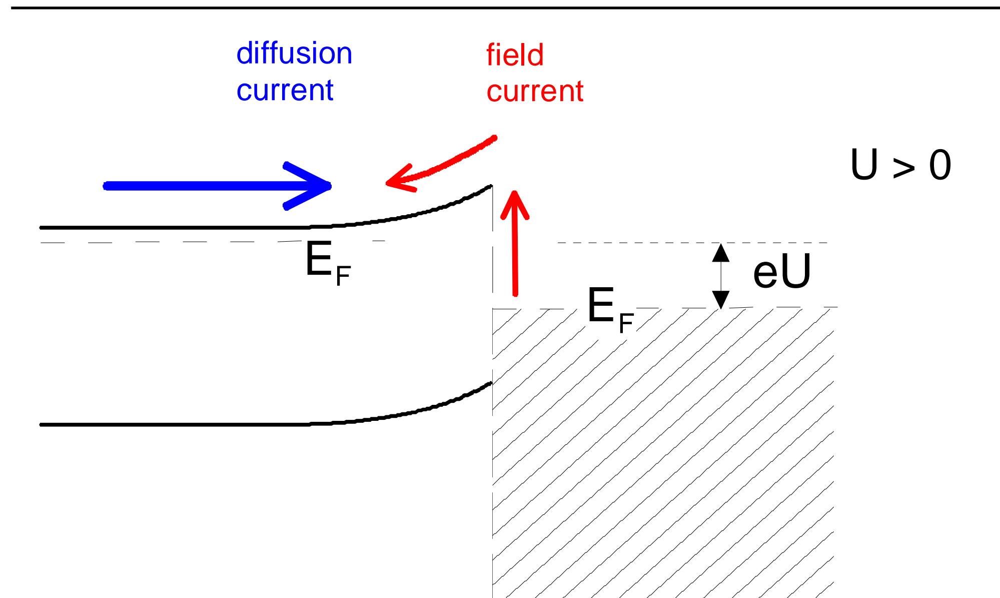
Infinite semiconductor layer with dopant concentration N_D and a metal sheet with boundary condition:

$B = \tilde{\phi}_M - \tilde{\phi}_n$ is the so-called Schottky barrier, the effective (dipoles!) work function difference.

→ One parabola, essentially half a p-n-junction.

I-V Characteristics: the Schottky-Junction





$$|j_F| = A^* \cdot T^2 \cdot \exp\left(-\frac{B}{k_B T}\right)$$

with the effective Richardson constant

$$A^* = \frac{4\pi e m^* k_B{}^2}{h^3}$$

$$(120\ \text{A cm}^{-2}\ \text{K}^{-2} \quad \text{for} \quad m^* = m \text{ and R.T.})$$

$$|j_D| = \tilde{j} \cdot \exp\left(-\frac{B - eU}{k_B T}\right)$$

$$= j_0 \exp\left(-\frac{B}{k_B T}\right) \cdot \exp\left(\frac{eU}{k_B T}\right)$$

For U=0: $|j_D|=|j_F|$, thus $j_0 = A^* \cdot T^2$

$$\rightarrow \quad j(U) = j_0 \left[\exp\left(\frac{eU}{k_B T}\right) - 1\right]$$

Note: identical for p-n-junction, with different meaning of j_0, however!

I-V Characteristics under Illumination: the Photovoltaic Effect

First order working principle:

Diffusion current unchanged, additional photo-induced field current $j_P(g) = -e \cdot g$ due to photoinduced electron hole pairs (in diode backwards direction!).

Areal elctron hole pair generation rate [$cm^{-2}s^{-1}$] :

$$g = \int_0^\infty j^0_{Photons}(\hbar\omega)\left(1-R(\hbar\omega)\right)\cdot\left(1-\exp(-\alpha(\hbar\omega)\cdot L\right)\,d(\hbar\omega)$$

Araeal spectral photon flux impinging on the photo junction

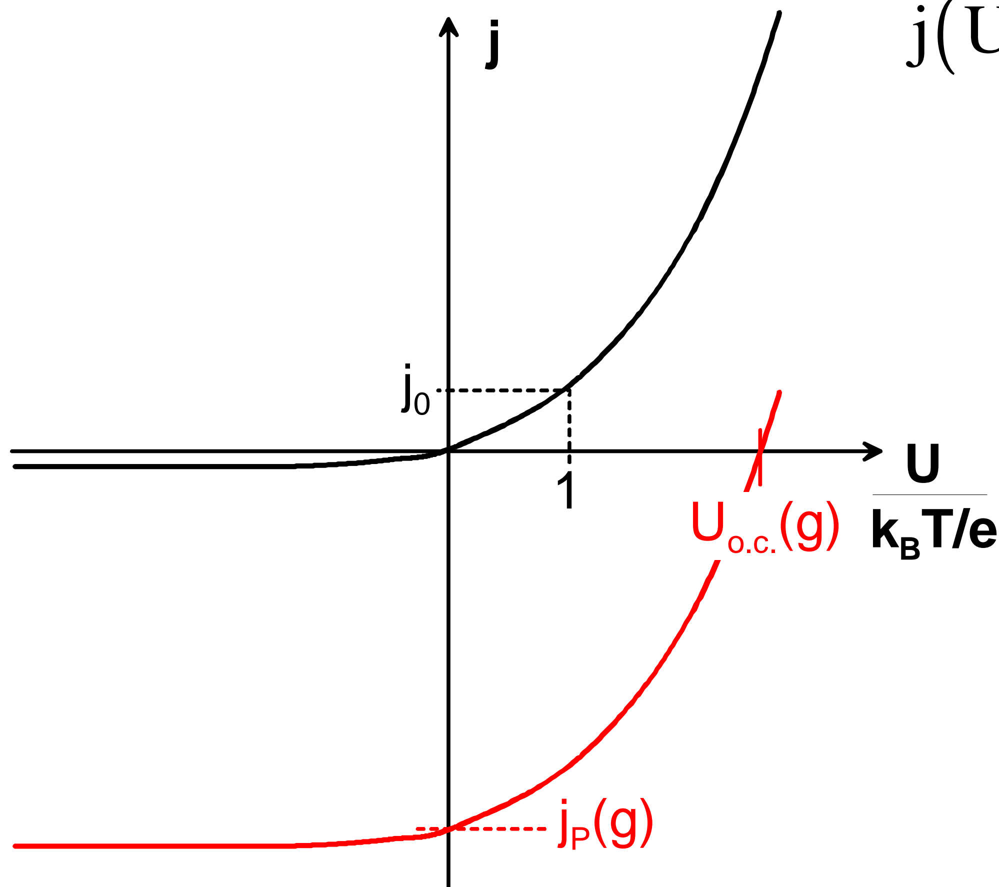
Reflection

Abssorption coefficient

Junction thickness or charge carrier diffusion length

$$j(U,g) = j_0\left[\exp\left(\frac{eU}{k_B T}\right)-1\right]-j_P(g)$$

I-V Characteristics under Illumination: the Photovoltaic Effect



$$j(U,g) = j_0\left[\exp\left(\frac{eU}{k_B T}\right) - 1\right] - j_P(g)$$

Note:

- open circuit voltage $U_{o.c.}$ scales logarithmically with light flux g!
- short circuit current j_P scales linearly wih light flux g.
- maximum achievable areal power is selected by appropriate load resistance and is lower than $U_{o,c,}\cdot j_P$ by the so-called fill factor! The more ‚rectangular' the I-V characteristic, the higher the fill factor.