Lecture Number 4: Charge Transport and Charge Carrier Statistics

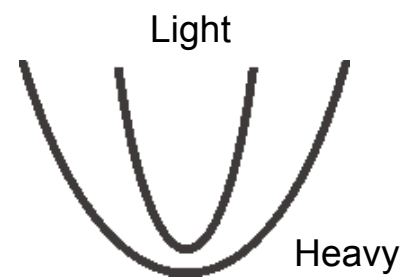
Chem 140a:

Photoelectrochemistry of Semiconductors

Review from Last Time

The quantum mechanics of wave packets gave us:

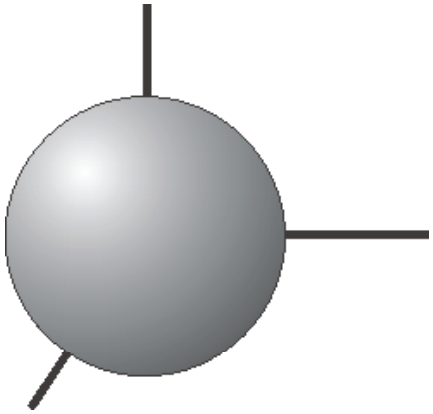
$$\frac{1}{m^*} = \frac{1}{\hbar^2}\left(\frac{d^2E}{dk^2}\right)$$



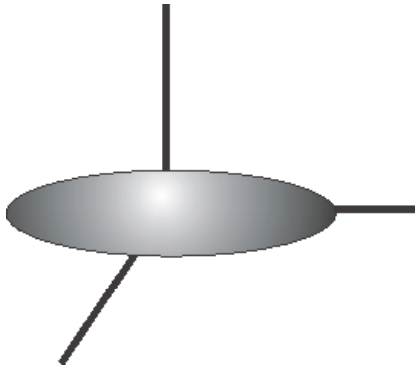
m* inversely proportional to curvature of E vs. k diagram

In a totally symmetric lattice, $k_x = k_y = k_z$, so there is one value of m*. In general, m* varies with crystallographic direction.

GaAs
$k_x = k_y = k_z$



Si
$k_x \neq k_y = k_z$



Review from Last time

Carrier Concentrations:

$$n = N_C \exp\left(-\left(E_C - E_F\right)/kT\right)$$

$$p = N_V \exp\left(-\left(E_F - E_V\right)/kT\right)$$

$$n_i^2 = np = N_C N_V \exp\left(-E_g/kT\right)$$

Intrinsic semiconductor:

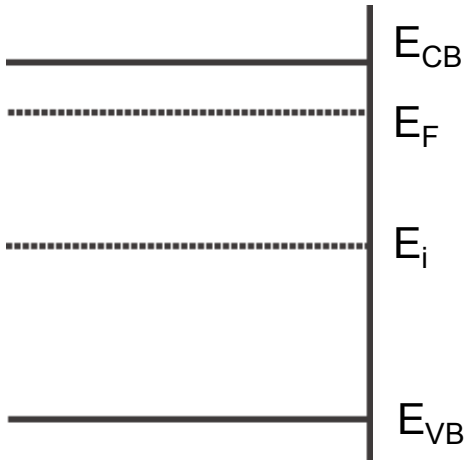
$$n = p = n_i \qquad E_F = E_i$$

$$E_i - E_V = \frac{E_g}{2} + \frac{kT}{2}\ln\left(\frac{N_V}{N_C}\right)$$

$$E_i - E_V = \frac{E_g}{2} + \frac{3kT}{4}\ln\left(\frac{m_h^*}{m_e^*}\right)$$

Doping Review

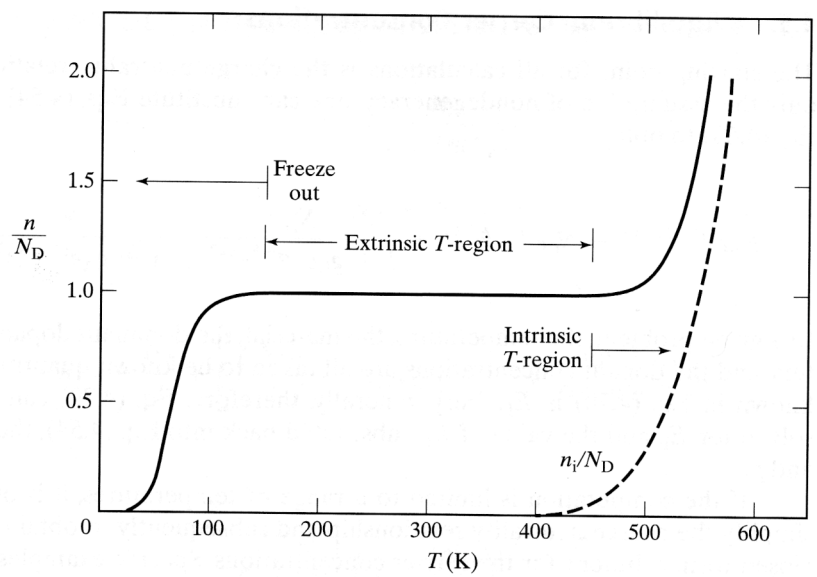
n-type Sample:



At room temperature:

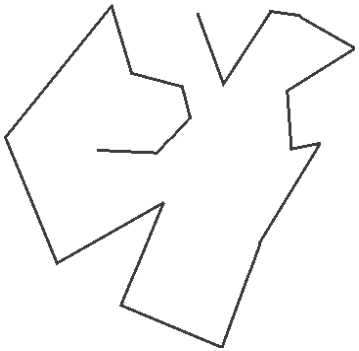
$$n = n_i + N_D^+ \approx N_D^+ \approx N_D$$

Temperature dependence:



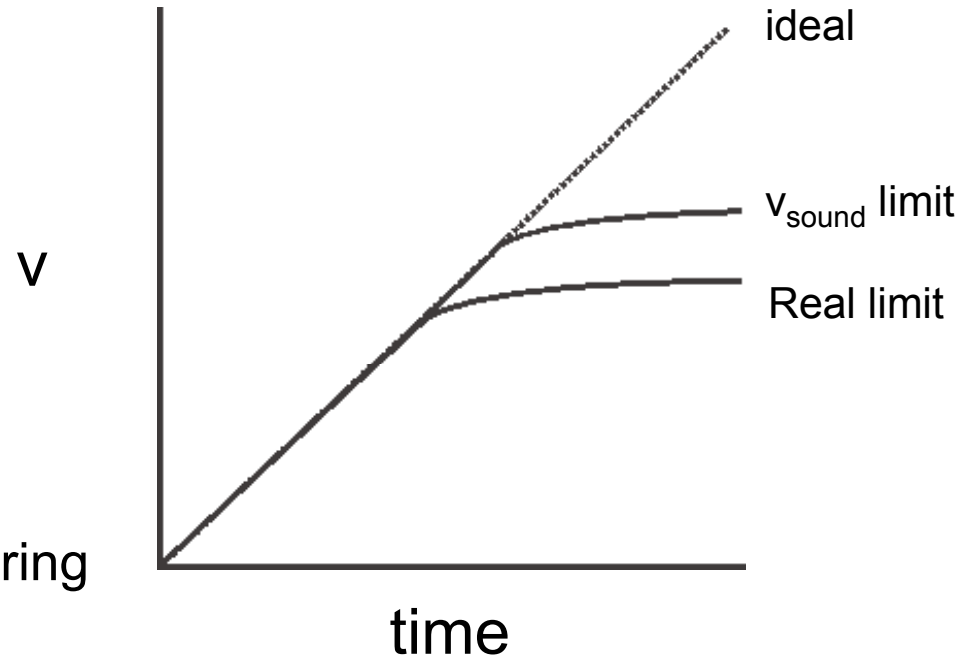
Charge Conduction

No Field - Random Brownian motion:



Constant Applied Field:

$$F = qE = m^* a$$



Real limit:

- Phonon scattering
- ionized impurity scattering
- neutral impurities
- carrier-carrier
- Piezo-electric (ZnO, TiO_2)

Charge Conduction

Due to scattering: mean free time, τ_m
mean free path, l_m

Average Drift Velocity: $$v_{avg,drift} = a\tau_m = \frac{qE}{m^*}\tau_m$$

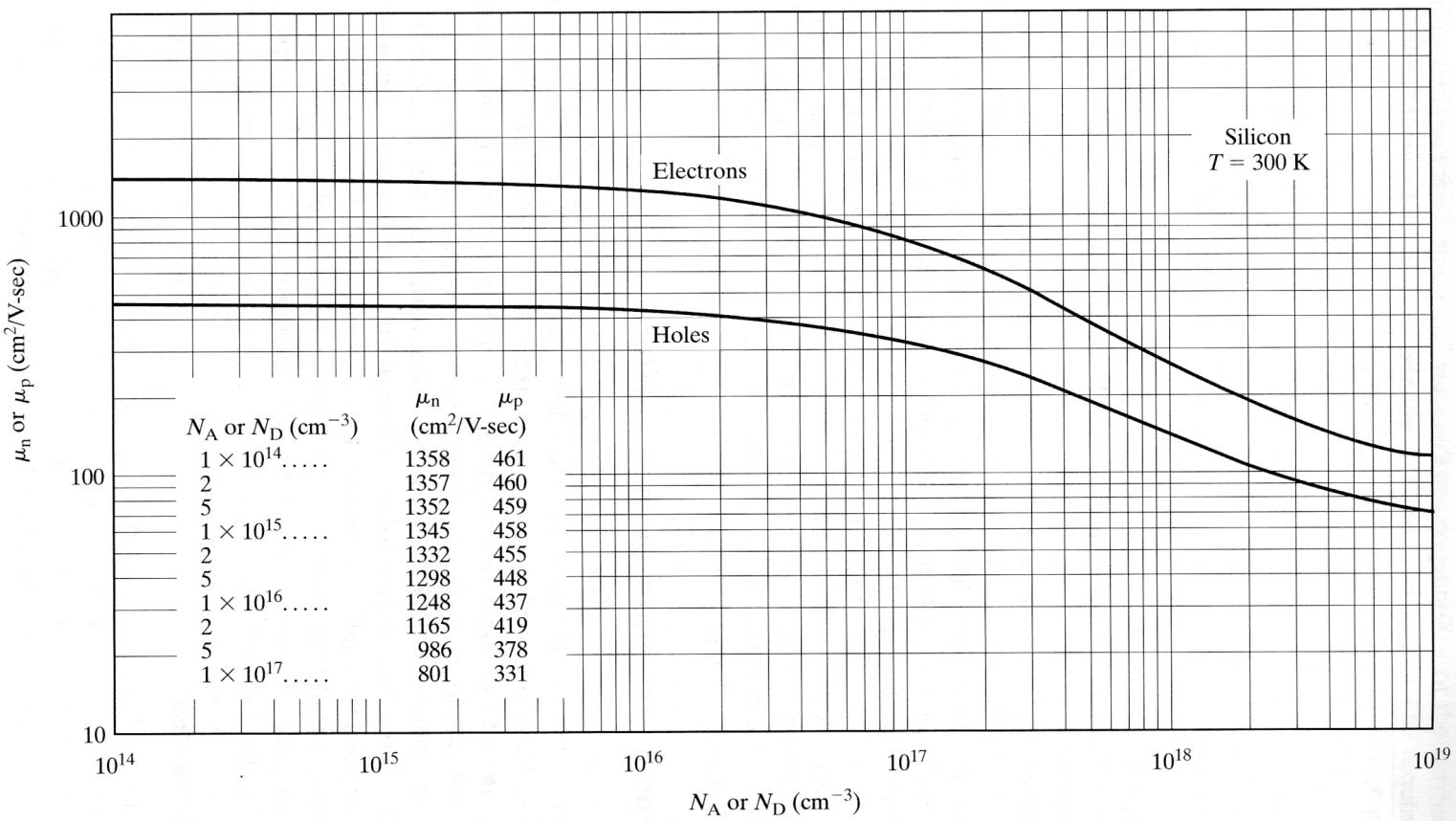
In vector form: $$\vec{v}_d = \frac{q\tau_m}{m^*}\vec{E} = \mu\vec{E}$$

Where we define the mobility, μ, as: $$\mu \equiv \frac{q\tau_m}{m^*}$$

There are separate mobilities for electrons and holes:

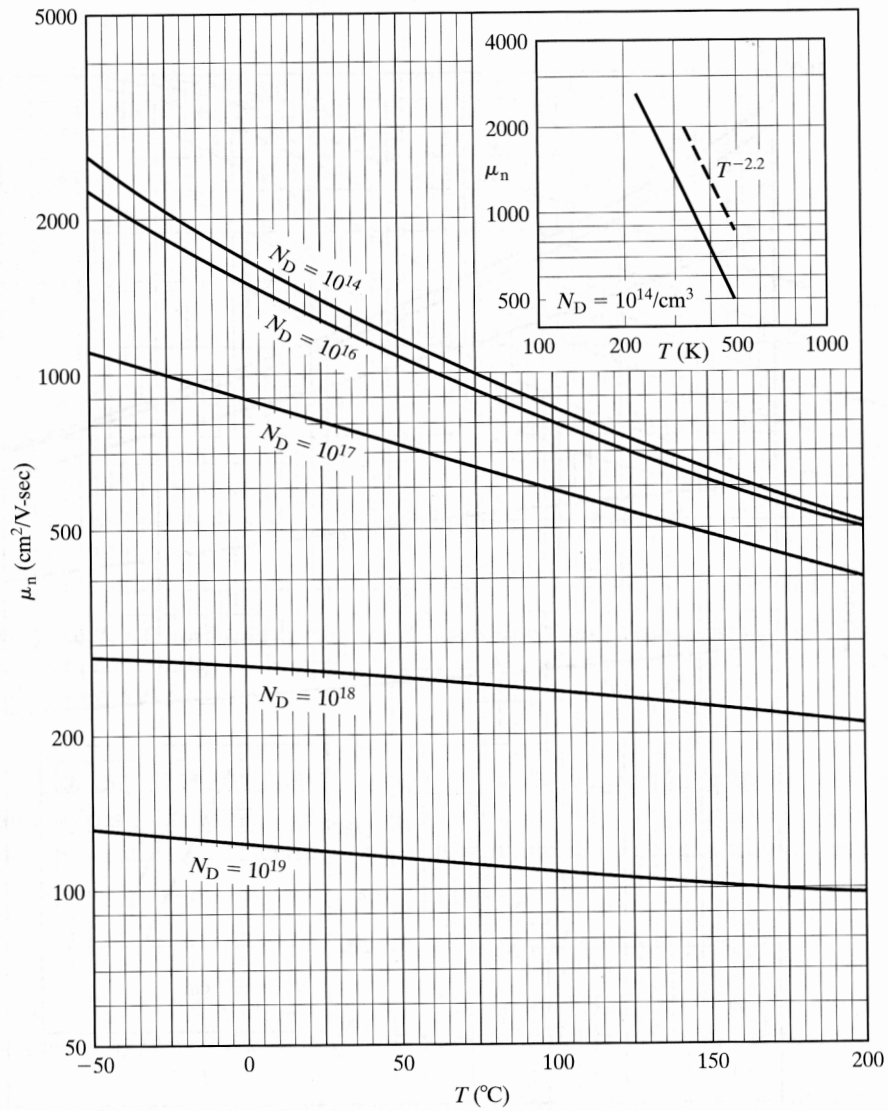
$$\mu_e = \frac{q\tau_{m,e}}{m_e^*} \qquad \mu_h = \frac{q\tau_{m,h}}{m_h^*}$$

Mobility and Doping



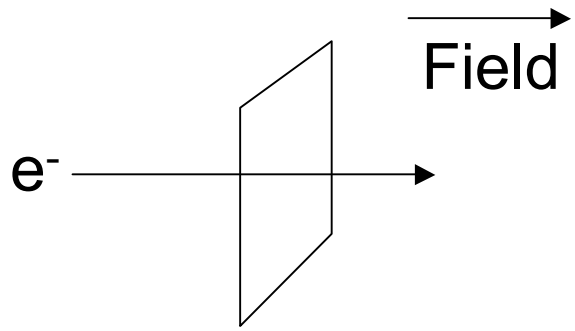
N_A or N_D (cm^{-3})	μ_n (cm^2/V-sec)	μ_p (cm^2/V-sec)
1×10^{14}.....	1358	461
2	1357	460
5	1352	459
1×10^{15}.....	1345	458
2	1332	455
5	1298	448
1×10^{16}.....	1248	437
2	1165	419
5	986	378
1×10^{17}.....	801	331

Mobility and Temperature



Drift Current

Flux:



$$flux = nv_d \qquad \left(cm^{-3}\right)\left(cm/s\right) = e^{-}/cm^{2} \cdot s$$

J = current density $\left(A/cm^{2}\right) = C/cm^{2} \cdot s$

$$\vec{J} = qn\vec{v}_d \qquad \vec{v}_d = \mu_n \vec{E}$$

$$\vec{J} = qn\mu_n \vec{E}$$

$\vec{J} = \sigma \vec{E}$ σ = conductivity $\sigma \equiv qn\mu_n$

Conductivity

Electrons: $\sigma_n = qn\mu_n \longrightarrow \sigma \propto n$

$\sigma_n = qn\mu_n \longrightarrow \sigma \propto \mu_n$

Holes: $\sigma_p = qp\mu_p$

Total: $\sigma = qn\mu_n + qp\mu_p$

n-type sample: $n = N_D >> p$

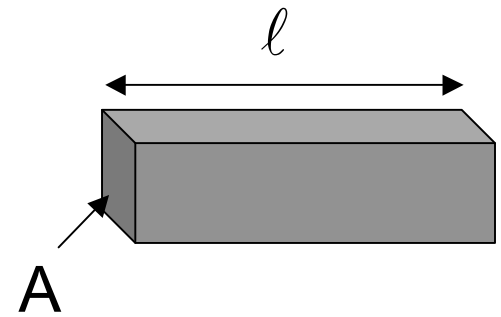
$$\sigma_n = qN_D\mu_n$$

Resistivity

Remember:

ρ = resisitivity
R = resistance

$$R = \frac{\rho \ell}{A}$$



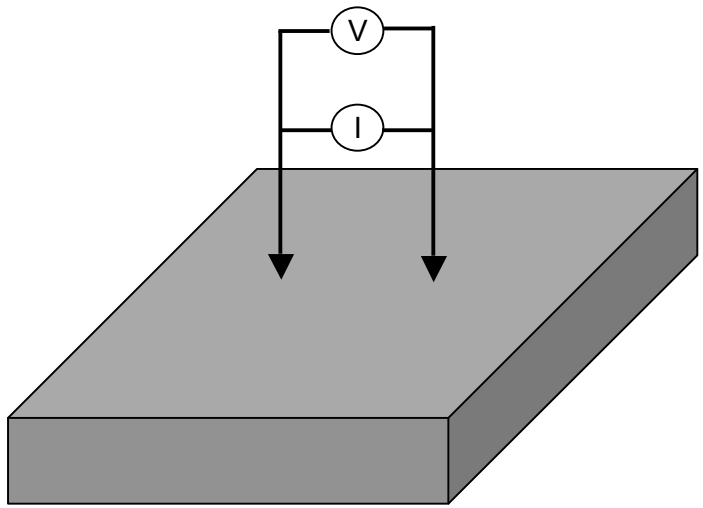
$$\rho \equiv \frac{1}{\sigma} = \frac{1}{q\left(\mu_n n + \mu_p p\right)}$$

For n-type Si:

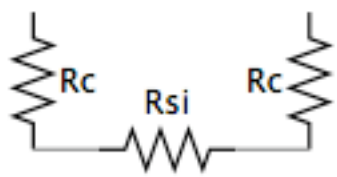
$$\rho = \frac{1}{q\mu_n N_D}$$

Measuring Resistivity

2-point probe:



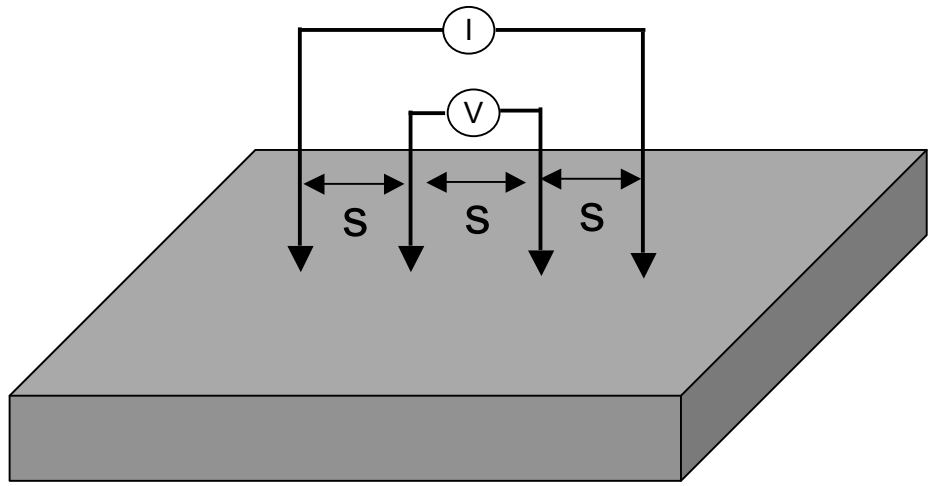
Equivalent Circuit:



Measured resistance includes contact resistance, which is large for metal contacts to Si, as we'll see later.

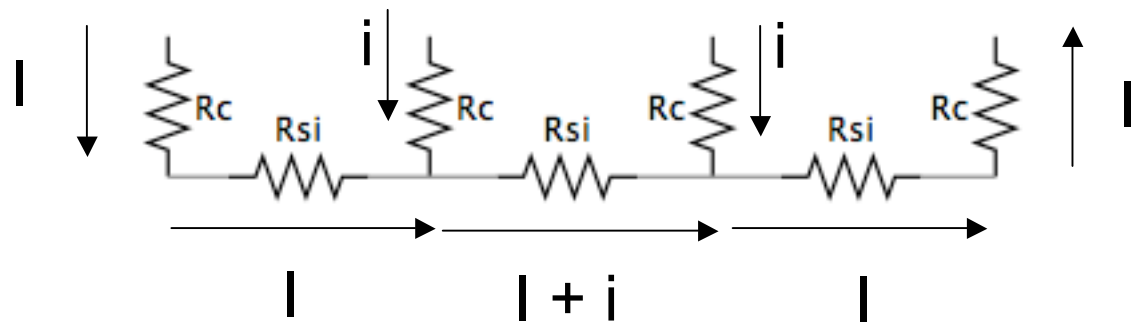
Measuring Resistivity

4-point probe:



Equivalent Circuit:

I >> i

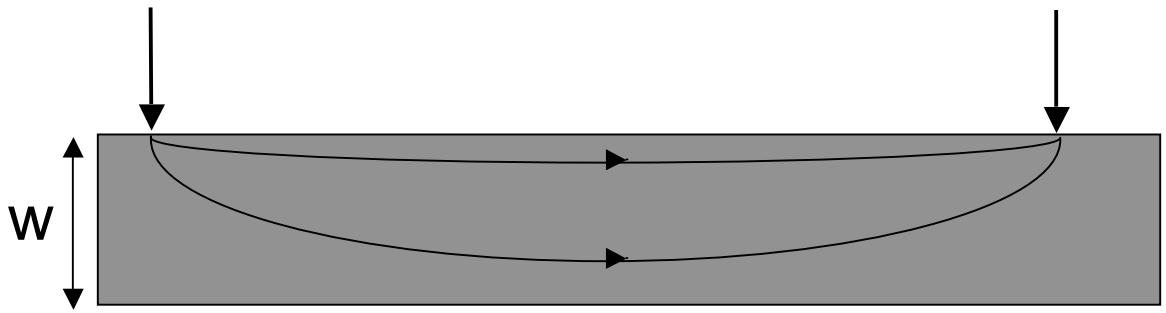


Measured Voltage: $V_{meas} = 2iR_C + (I+i)R_{Si} \approx 2iR_C + IR_{Si} \approx IR_{Si}$

4-point probe gets rid of the contact resistance.

Measuring Resistivity

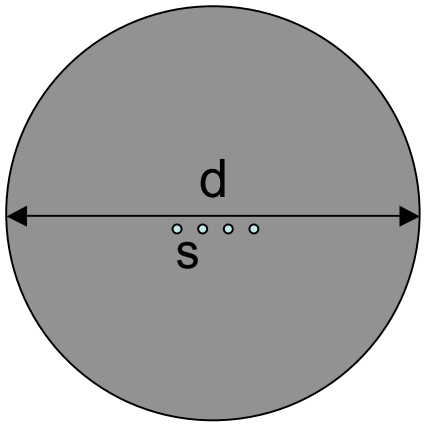
Actually measure sheet resistance, R_s (Sze, page 31)



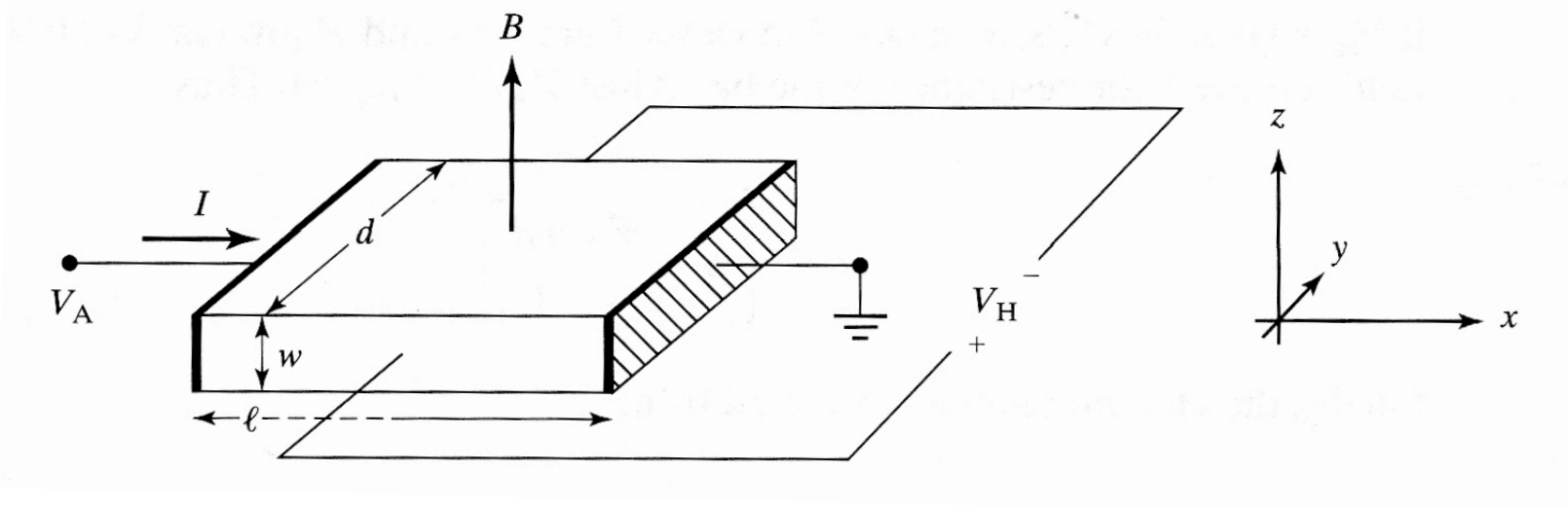
Different paths give different resistance, so total resistivity depends on the width, w, of the sample:

$$\rho = R_S w \qquad R_S = \frac{V}{I} CF \qquad R_S \propto \Omega/\square$$

CF=4.54 for d >> s



Hall Measurement



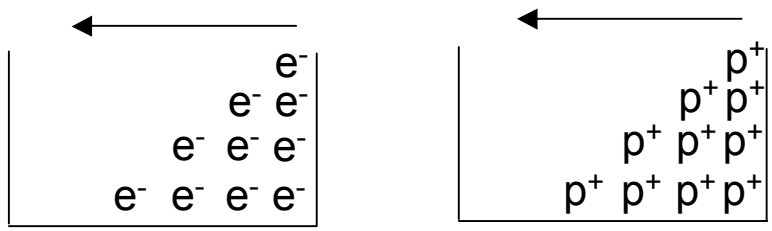
Carrier Concentrations: $R_H = \dfrac{V_H w}{BI}$ → $R_H = -\dfrac{1}{qn}$ $\quad n >> p$

→ $R_H = \dfrac{1}{qp}$ $\quad p >> n$

Mobility: $\rho = \dfrac{V_A}{I}\dfrac{wd}{\ell}$ $\quad \mu_H \equiv \dfrac{|R_H|}{\rho} \approx \mu_{drift}$

Diffusion Current

Even in the absence of fields, carriers move by diffusion:



$$J_{total} = J_{drift} + J_{diffusion}$$

(E-field) (conc. grad.)

Fick's First law of diffusion: $e^{-}\,flux = D_n\left(\frac{dn}{dx}\right)$

$$Current = q \cdot flux$$

$$J_{diffusion,e^{-}} = qD_n\left(\frac{dn}{dx}\right) = qD_n \nabla n$$

Current

Total current (electrons):

$$\vec{J}_e = q\left(\mu_n n\vec{E} + D_n \vec{\nabla} n\right)$$

Einstein Relationships:

$$D_n = \mu_n\left(\frac{kT}{q}\right) \qquad D_p = \mu_p\left(\frac{kT}{q}\right)$$

In the x-direction:

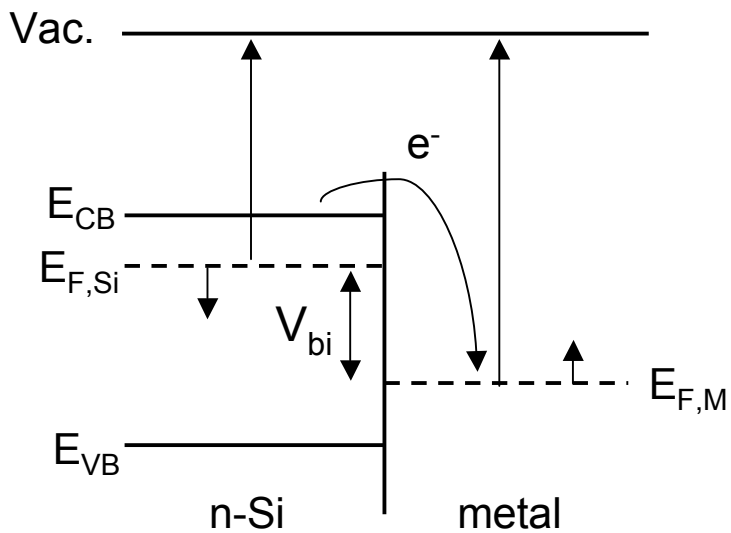
$$J_e = q\left(\mu_n n E_x + D_n \frac{dn}{dx}\right) = q\mu_n\left(nE_x + \frac{kT}{q}\frac{dn}{dx}\right)$$

Electrons and holes:

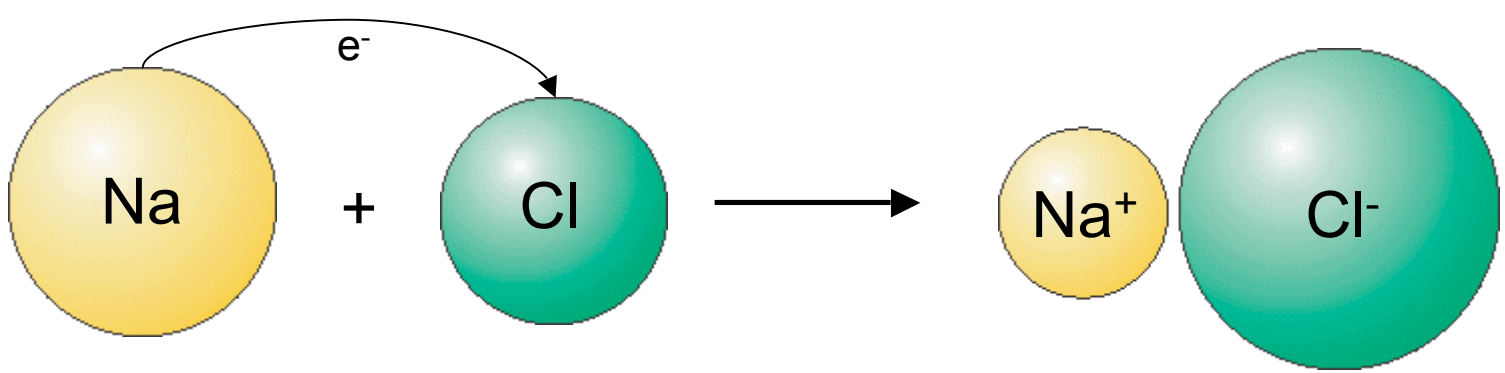
$$\vec{J} = q\left(\mu_n n\vec{E} + D_n \vec{\nabla} n - \mu_p p\vec{E} - D_p \vec{\nabla} p\right)$$

Semiconductor-Metal Junction

n-type Si/M before equilibration:

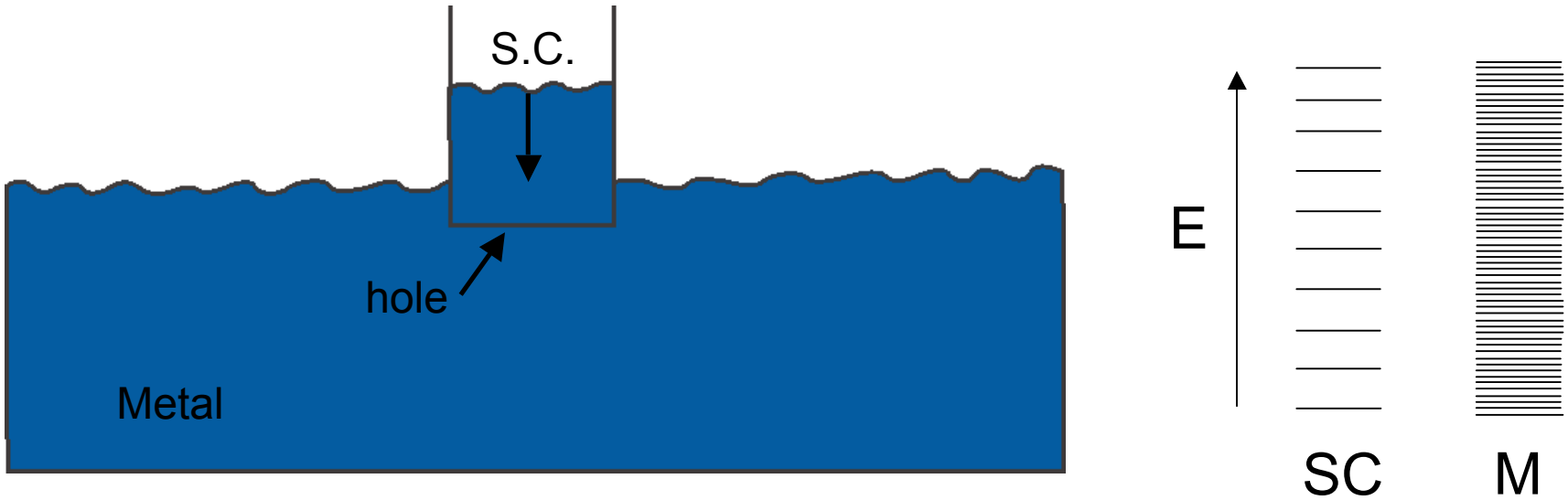


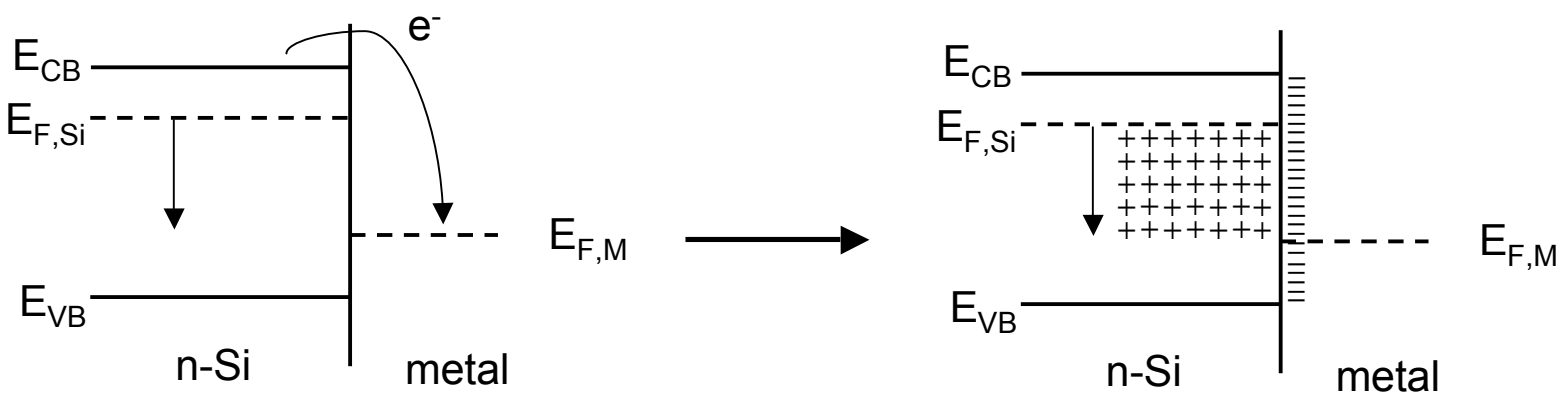
Electrons flow from Si to metal until E_F is the same everywhere. Analogous to reaction of Na with Cl



Charge Equilibration

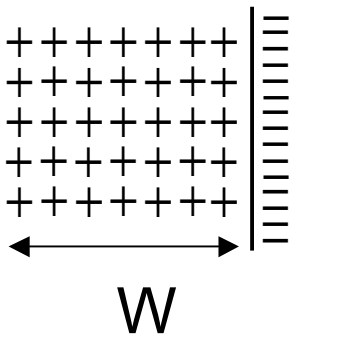
Much larger density of states for metal than semiconductor:

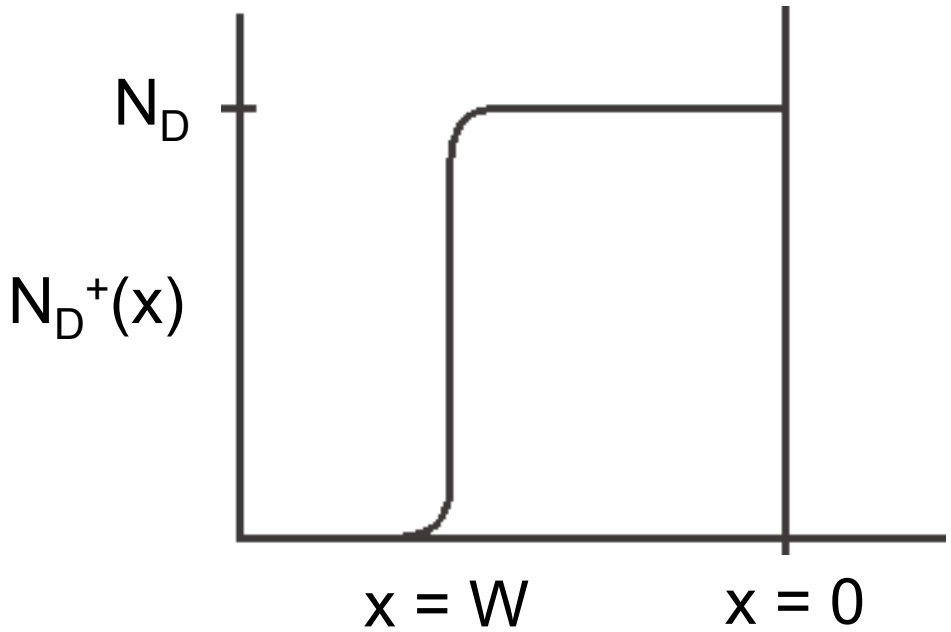




Depletion Region

Depletion Approximation: Only dopants can be ionized in the S.C., and they are completely ionized for a width W.

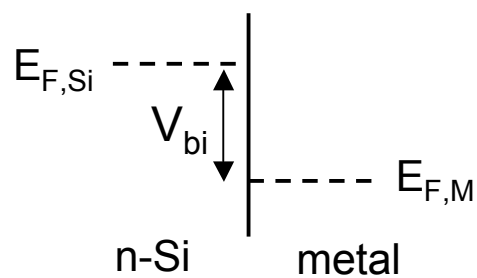




$$W = W(N_D, V_{bi})$$

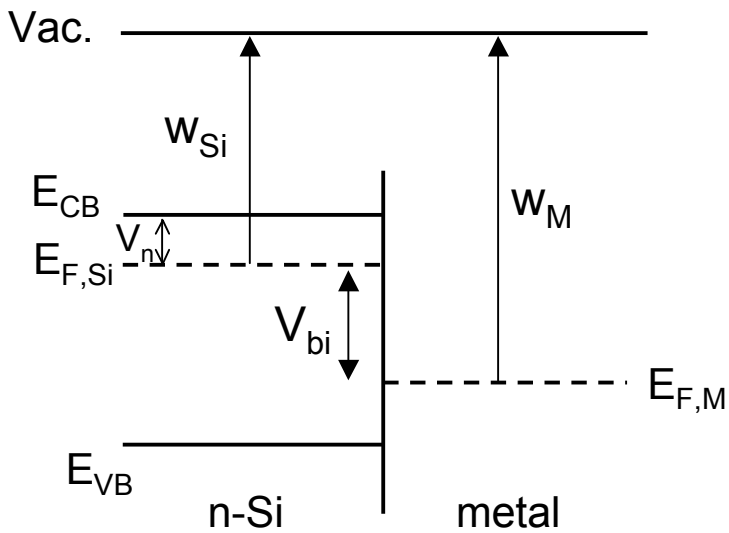
$$N_D \uparrow \longrightarrow W \downarrow$$

$$V_{bi} \uparrow \longrightarrow W \uparrow$$

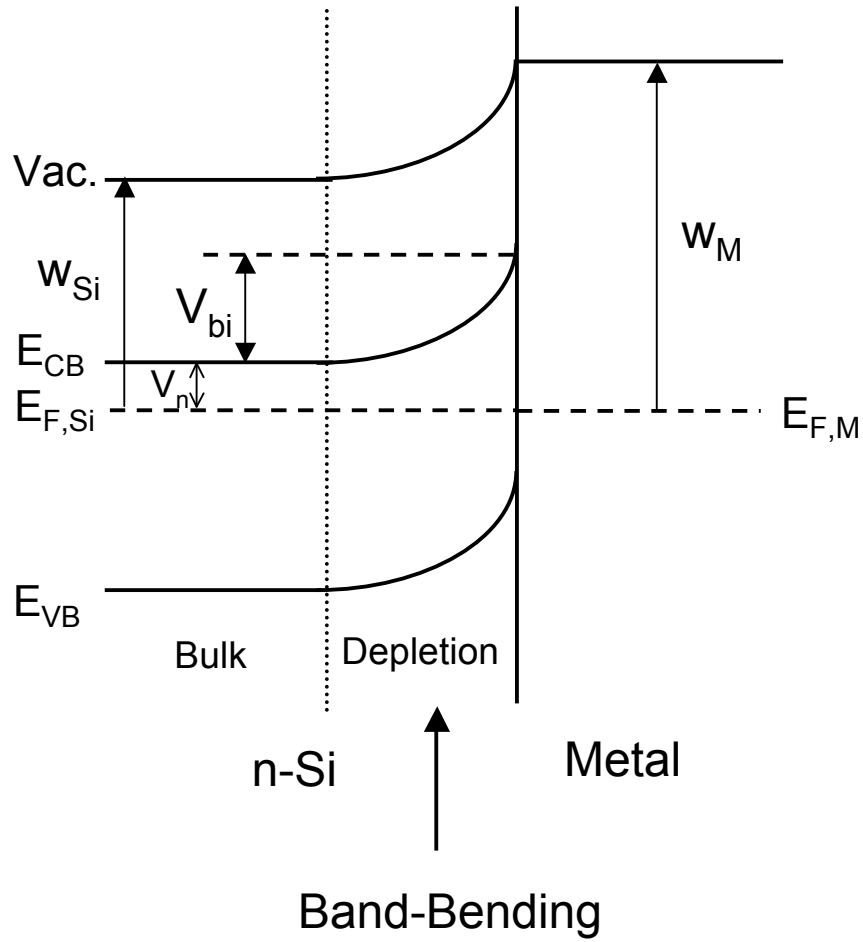


Band-Bending

Before equilibration:



After equilibration:



Band-Bending

Four important Equations:

1) $\mathscr{E}(x) = -\dfrac{d\psi(x)}{dx}$

$\mathscr{E}(x) = \text{Electic Field}$

$\psi(x) = \text{Electric Potential}$

2) $E(x) = -q\psi(x)$

$E(x) = \text{Electric Potential Energy}$

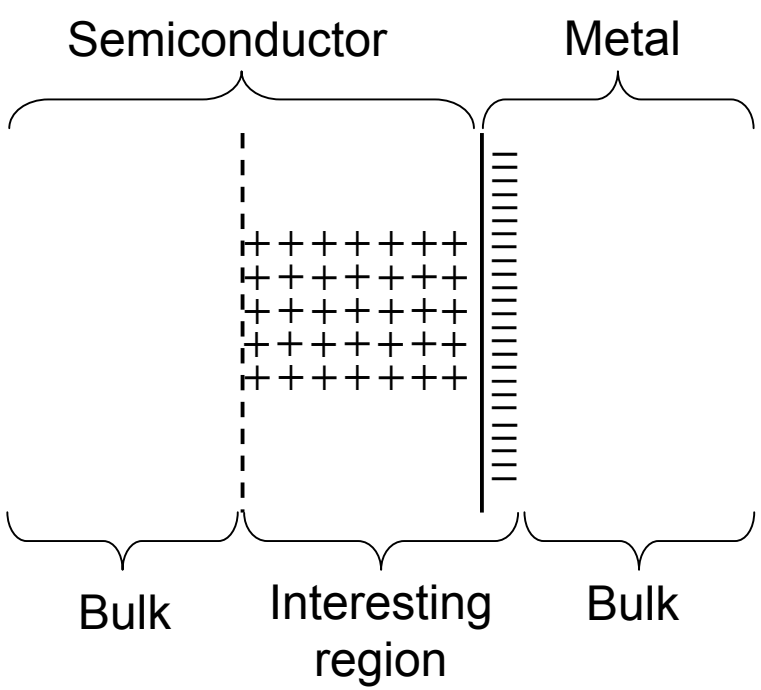
3) $\rho(x) = p(x) - n(x) - N_A(x) + N_D(x)$

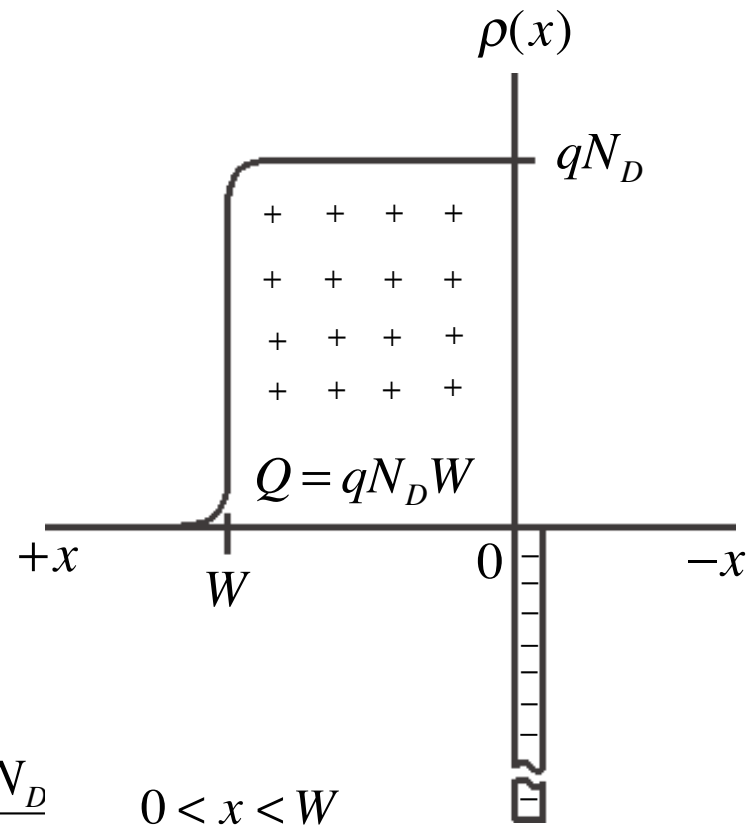
$\rho(x) = \text{charge density}$

4) $-\dfrac{d^2\psi(x)}{dx^2} = \dfrac{\rho(x)}{\kappa\varepsilon_0}$

Poisson's Equation

Charge Density





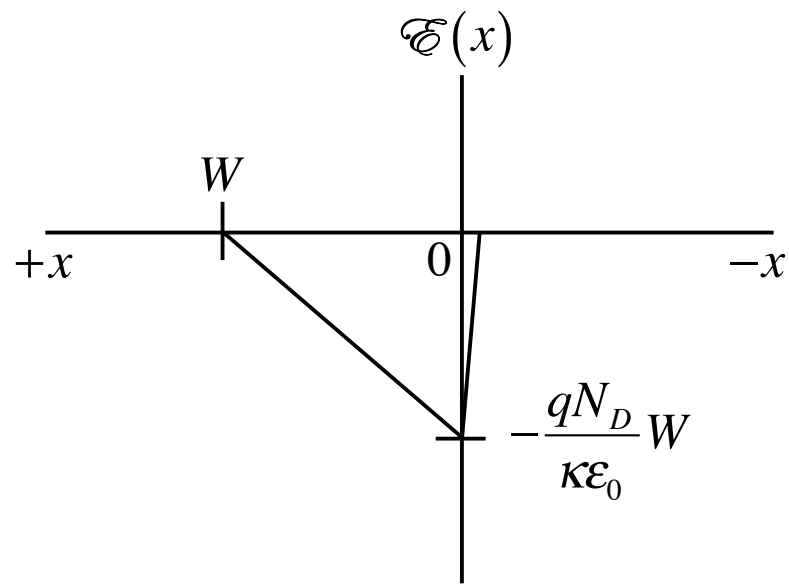
Poisson's Equation: $$-\frac{d^2\psi(x)}{dx^2} = \frac{\rho(x)}{\kappa\varepsilon_0} = \frac{qN_D}{\kappa\varepsilon_0} \qquad 0 < x < W$$

Integrating: $$\mathscr{E}(x) = -\frac{d\psi(x)}{dx} = \frac{qN_D}{\kappa\varepsilon_0}(x - W) \qquad \left(\text{Because } \mathscr{E}(W) = -\left.\frac{d\psi(x)}{dx}\right|_{x=W} = 0\right)$$

Electric Field

$$\mathscr{E}(x) = -\frac{d\psi(x)}{dx} = \frac{qN_D}{\kappa\varepsilon_0}(x - W) \qquad 0 < x < W$$

$$\mathscr{E}_{\max}(x = 0) = -\frac{qN_D}{\kappa\varepsilon_0}W$$



Integrate Electric Field:

$$\psi(x) = -\frac{qN_D}{2\kappa\varepsilon_0}(x - W)^2 \qquad 0 < x < W$$

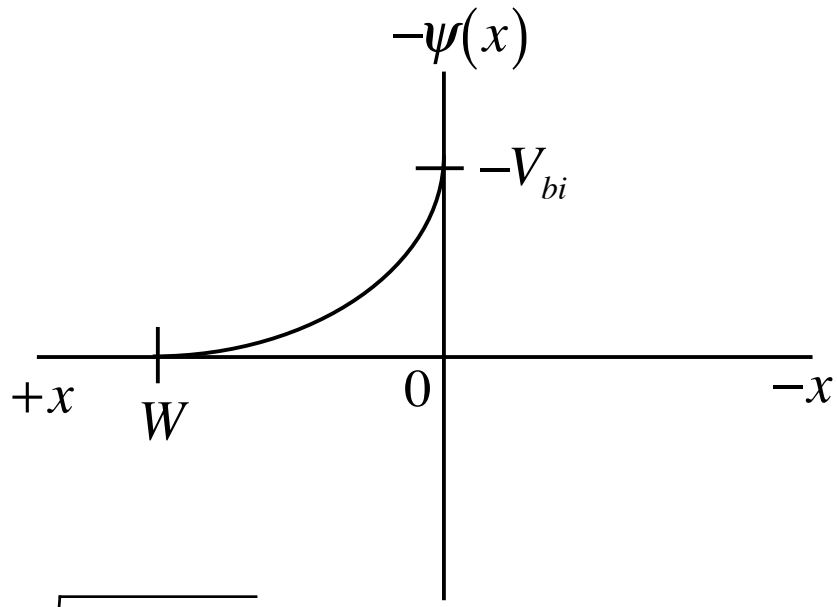
$$\left(\text{Because } \psi(x) = 0 \text{ for } x > W\right)$$

Electric Potential

$$\psi(x) = -\frac{qN_D}{2\kappa\varepsilon_0}(x - W)^2$$

$$\psi(0) = -V_{bi}$$

$$\left[qV_{bi} = \left(E_{F,SC} - E_{F,M}\right)\right]$$



Calculate Depletion Width:

$$-V_{bi} = -\frac{qN_D}{2\kappa\varepsilon_0}W^2 \longrightarrow W = \sqrt{\frac{2\kappa\varepsilon_0 V_{bi}}{qN_D}}$$

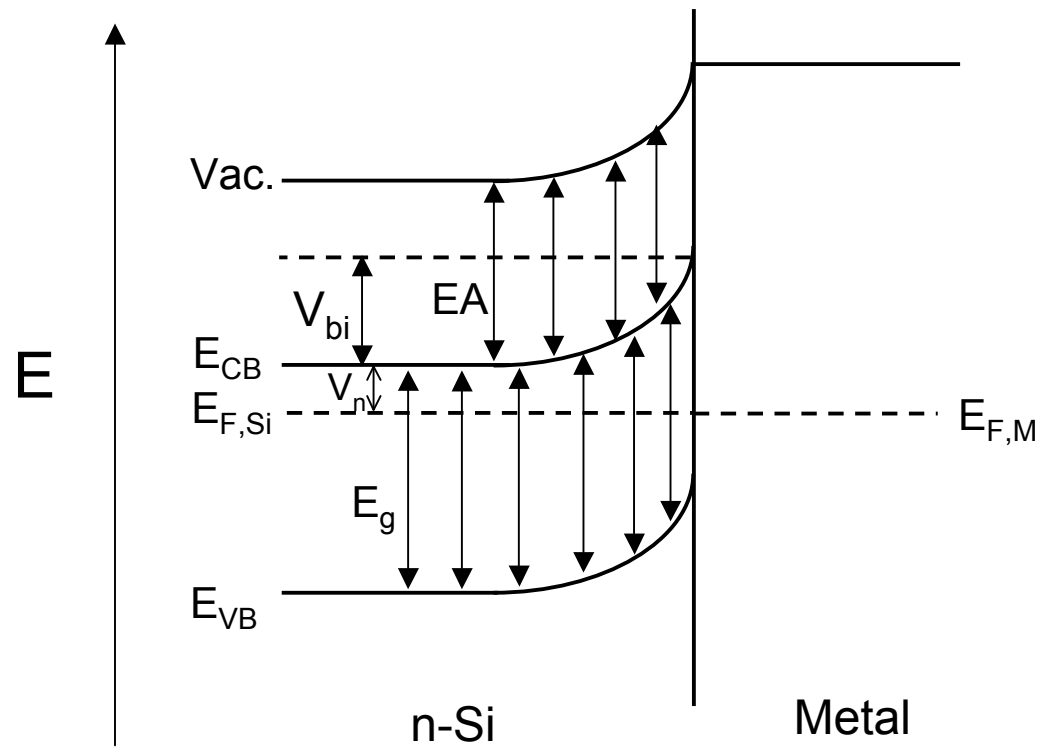
If we had started with: $\rho = q\left[N_D - n(x)\right]$

We would find: $W = \sqrt{\frac{2\kappa\varepsilon_0\left(V_{bi} - kt/q\right)}{qN_D}}$

Electric Potential Energy

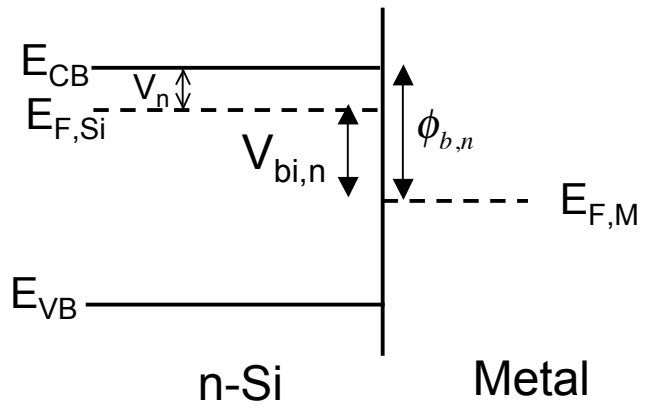
Electric potential energy is electric potential scaled by q.

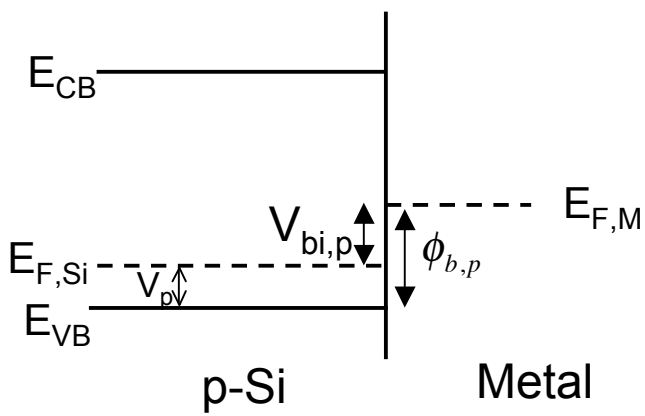
Band-bending is the same in CB, VB and Vac because E_g and electron affinity (EA) are the same everywhere



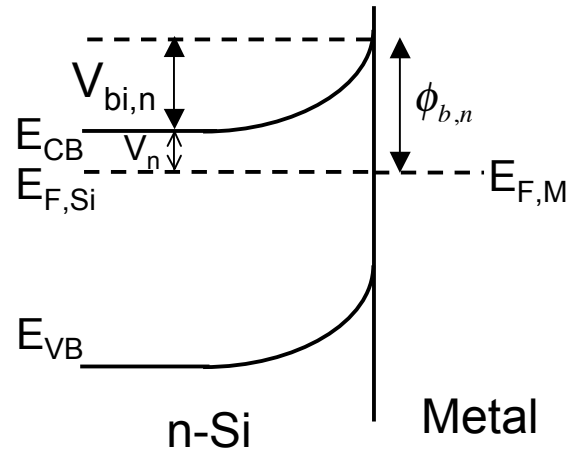
n-type vs. p-type

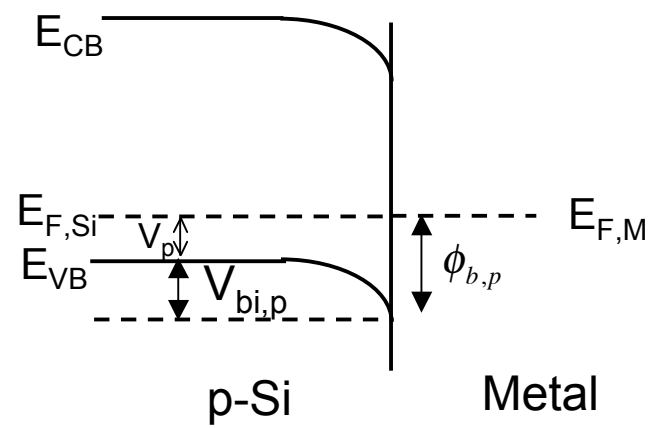
Before Equilibration:



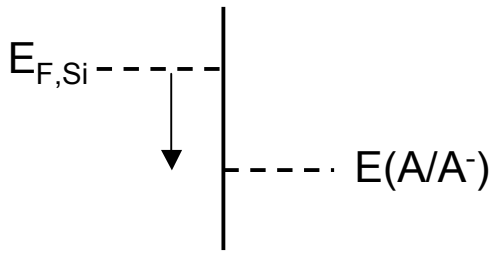


After Equilibration:





Solution vs. Metal Contact



D.O.S. is still much higher for a solution than for Si, so bucket in ocean analogy still holds. $E(A/A^-)$ doesn't move.

Semiconductor:

N_D: 10^{15}-10^{16} cm^{-3}

W: 0.1-0.01 μm

$Q=N_D W \longrightarrow Q_{max}=10^{11}\ e^-/cm^2$

Solution:

1.0 mM = 6 x 10^{17} molecules/cm^3

~2 nm solution depth has 10^{11} molecules/cm^2