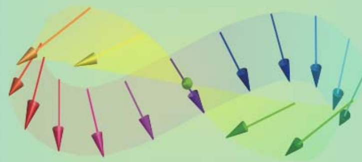
Introductory Nanotechnology

~ Basic Condensed Matter Physics ~



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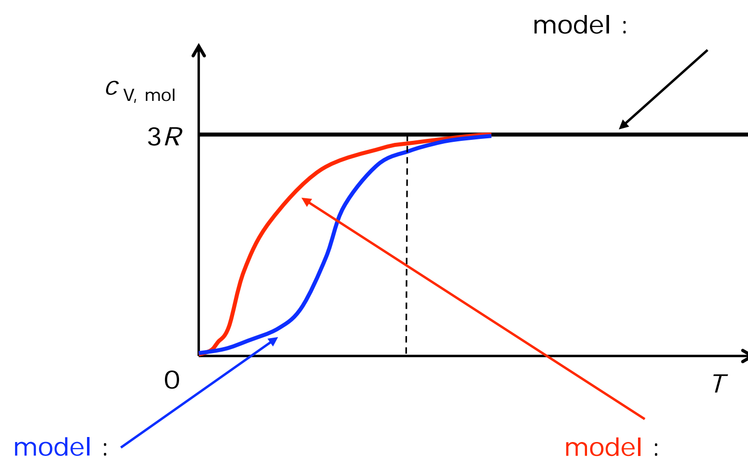
Quick Review over the Last Lecture



Contents of Introductory Nanotechnology

First half of the course :

Basic condensed matter physics

1. Why *solids* are *solid* ?
2. What is the *most common atom* on the earth ?
3. How does an electron travel in a material ?
4. How does lattices vibrate thermally ?
5. What is a *semi*-conductor ?
6. How does an electron tunnel through a barrier ?
7. Why does a magnet attract / retract ?
8. What happens at interfaces ?

Second half of the course :

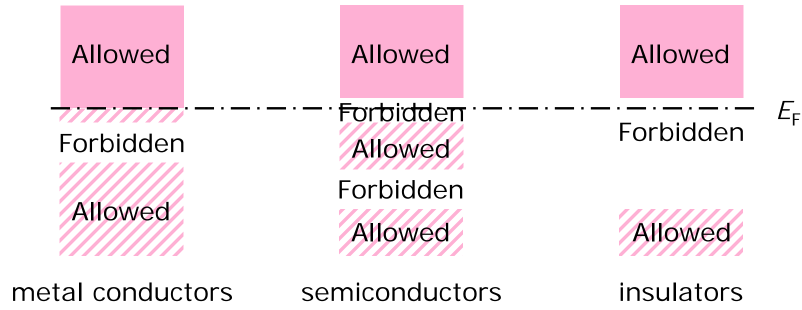
Introduction to nanotechnology (nano-fabrication / application)

What Is a *Semi*-Conductor ?

- Elemental / compound semiconductor
- Intrinsic / extrinsic semiconductors
- *n* / *p*-dope
- Temperature dependence
- Schottky junctions
- *pn* junctions

What is *semi*-conductor ?

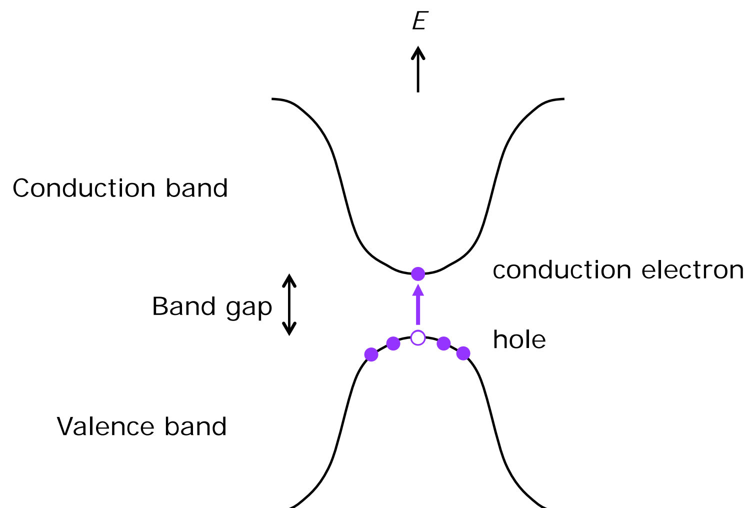
Band diagrams :



With very small energy,
electrons can overcome
the forbidden band.

Energy Band of a semiconductor

Schematic energy band diagram :



Elemental Semiconductors

In the periodic table,

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pd	Bi	Po	At	Rn
Fr	Ra																
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Carrier density : Cu (metal) ~ 10^{23} cm^{-3}

Ge (semiconductor) ~ 10^{13} cm^{-3}

Semimetal : conduction and valence bands are slightly overlaped.

As (semimetal) ~ 10^{20} cm^{-3}

Sb (semimetal) ~ 10^{19} cm^{-3}

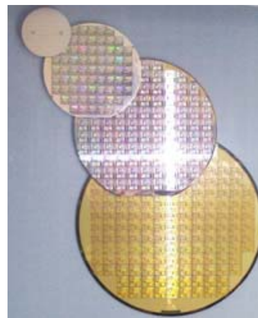
C (semimetal) ~ 10^{18} cm^{-3}

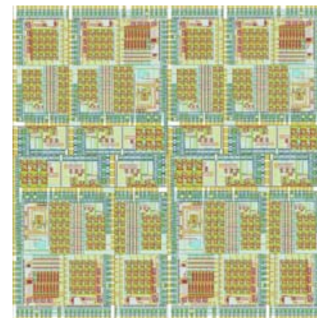
Bi (semimetal) ~ 10^{17} cm^{-3}

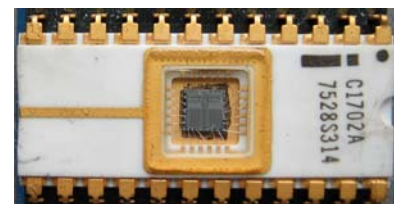
Fabrication of a Si-Based Integrated Circuit

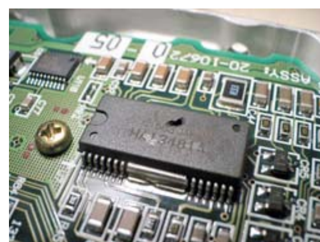
Czochralski method :

Si purity (%)









* http://www.wikipedia.org/

Compound Semiconductors

In the periodic table,

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

III-V compounds : GaAs, InAs, InSb, AlP, BP, ...

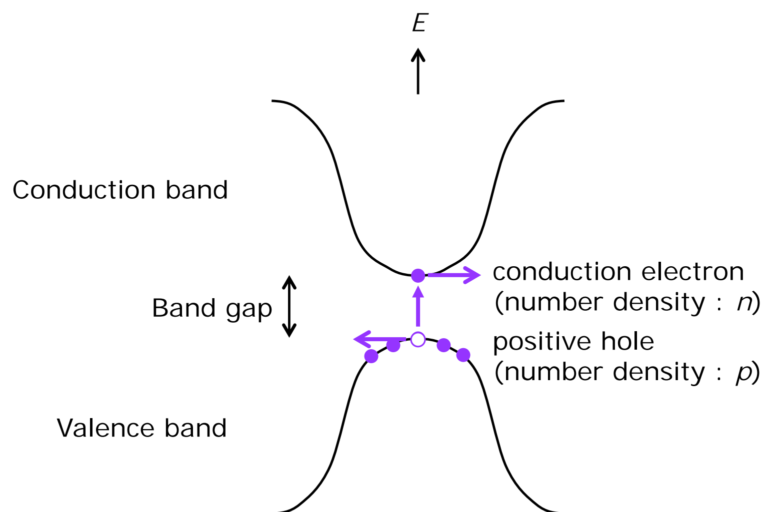
II-VI compounds : ZnO, CdS, CdTe, ...

IV-IV compounds : SiC, GeSi

IV-VI compounds : PbSe, PbTe, SnTe, ...

Shockley Model

Contributions for electrical transport :



→ Ambipolar conduction

→ Intrinsic semiconductor

$$\sigma = \sigma_e + \sigma_h = nq\mu_e + pq\mu_h = n_i q(\mu_e + \mu_h) \quad (n_i \equiv n = p)$$

* http://www.wikipedia.org/

Carrier Number Density of an Intrinsic Semiconductor

Carrier number density is defined as

$$n = \int f(E) g(E) dE$$

Here, the Fermi distribution function is $f(E) = \dfrac{1}{\exp\left[(E - E_F)/k_B T\right] + 1}$

For the carriers like free electrons with m^*, the density of states is

$$g(E) = 2\frac{1}{(2\pi)^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E}$$

For electrons with effective mass m_e^*, $g(E)$ in the conduction band is written with respect to the energy level E_C,

$$g_C(E) = 2\frac{1}{(2\pi)^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\sqrt{E - E_C}$$

For holes with effective mass m_p^*, $g(E)$ in the valence band is written with respect to the energy level $E_V = 0$,

$$g_V(E) = 2\frac{1}{(2\pi)^2}\left(\frac{2m_p^*}{\hbar^2}\right)^{3/2}\sqrt{-E}$$

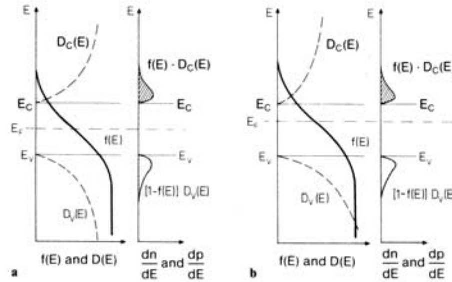


Fig. 12.5. **(a)** Fermi function $f(E)$, density of states $D(E)$ and electron (n) and hole (p) concentrations in the conduction and valence bands for the case of equal densities of states in the conduction and valence bands (schematic); **(b)** the same figure for the case of differing densities of states in the conduction and valence bands. The number of holes must again be equal to the number of electrons, and thus the Fermi level no longer lies in the middle of the gap between conduction and valence bands; its position then becomes temperature dependent

* H. Ibach and H. Lüth, *Solid-State Physics* (Springer, Berlin, 2003).

Carrier Number Density of an Intrinsic Semiconductor (Cont'd)

$f_p(E)$ for holes equals to the numbers of unoccupied states by electrons :

$$f_p(E) = 1 - f_e(E)$$

n is an integral in the conduction band from the bottom E_C to top E_{ct} :

$$n = \int_{E_C}^{E_{Ct}} f_e(E) g_e(E) dE = \int_{E_C}^{E_{Ct}} \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\sqrt{E - E_C}\,\frac{1}{\exp\left[(E - E_F)/k_B T\right] + 1}\,dE$$

p is an integral in the valence band from the bottom $-E_{Vb}$ to top 0 :

$$p = \int_{-E_{Vb}}^{0} f_p(E) g_p(E) dE = \int_{-E_{vb}}^{0} \frac{1}{2\pi^2}\left(\frac{2m_p^*}{\hbar^2}\right)^{3/2}\sqrt{-E}\left\{1 - \frac{1}{\exp\left[(E - E_F)/k_B T\right] + 1}\right\}dE$$

$$= \int_{-E_{vb}}^{0} \frac{1}{2\pi^2}\left(\frac{2m_p^*}{\hbar^2}\right)^{3/2}\sqrt{-E}\,\frac{1}{\exp\left[-(E - E_F)/k_B T\right] + 1}\,dE$$

Here, E_C ($= E_g = E_C - E_V$) $>> k_B T \rightarrow E - E_F \geq E_C/2$ for $E_C \leq E \leq E_{ct}$ ($E_F \sim E_C/2$)

$$f_e(E) \approx \exp\left[-(E - E_F)/k_B T\right]$$

Similarly, $E_C >> k_B T \rightarrow -(E - E_F) \geq E_C/2$ for $E_{Vb} \leq E \leq 0$

$$f_p(E) \approx \exp\left[(E - E_F)/k_B T\right]$$

Carrier Number Density of an Intrinsic Semiconductor (Cont'd)

For E - E_F > $3k_BT$, $f_e(E_F + 3k_BT) < 0.05$ and hence $E_{Ct} \rightarrow \infty$

Similarly, $f_p(E_F - 3k_BT) < 0.05$ and hence $E_{Vb} \rightarrow -\infty$

$$n = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \int_{E_C}^{\infty} \sqrt{E - E_C}\, \exp[-(E - E_F)/k_BT]\, dE$$

$$p = \frac{1}{2\pi^2}\left(\frac{2m_p^*}{\hbar^2}\right)^{3/2} \int_{-\infty}^{0} \sqrt{-E}\, \exp[(E - E_F)/k_BT]\, dE$$

As a result,

$$n = N_C \exp[-(E_C - E_F)/k_BT] \approx N_C f_e(E_C) \qquad \begin{cases} N_C \equiv N_{Ce} T^{3/2} \\ N_{Ce} \equiv 2\left(\dfrac{2\pi m_e^* k_B}{h^2}\right)^{3/2} \end{cases}$$

$$n = N_V \exp[-E_F/k_BT] \approx N_V f_p(0) \qquad \begin{cases} N_V \equiv N_{Vp} T^{3/2} \\ N_{Vp} \equiv 2\left(\dfrac{2\pi m_p^* k_B}{h^2}\right)^{3/2} \end{cases}$$

Fermi Level of an Intrinsic Semiconductor

For an intrinsic semiconductor, $n = p \equiv n_i$

$$N_C \exp[-(E_C - E_F)/k_BT] = N_V \exp[-E_F/k_BT]$$

$$\therefore E_F = \frac{1}{2}E_C + \frac{3}{4}k_BT \ln\left(\frac{m_p^*}{m_e^*}\right)$$

Assuming, $m_e^* = m_p^* = m^*$

$$E_F = \frac{1}{2}E_C = \frac{1}{2}E_g$$

np product is calculated to be

$$np = n_i^2 = N_C N_V \exp[-E_C/k_BT] = 4\left(\frac{2\pi k_BT}{h^2}\right)^3 \left(m_e^* m_p^*\right)^{3/2} \exp(-E_C/k_BT)$$

→ constant for small n_i

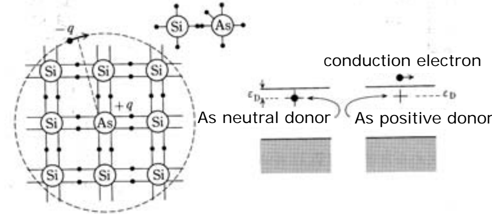
→ can be applied for an extrinsic (impurity) semiconductor

Extrinsic Semiconductors

Doping of an impurity into an intrinsic semiconductor :

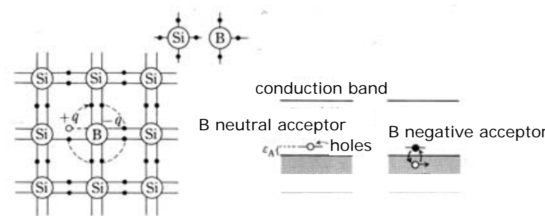
n-type extrinsic semiconductor :

e.g., Si (+ P, As, Sb : donor)



p-type extrinsic semiconductor :

e.g., Si (+ Ga, Al, B : acceptor)



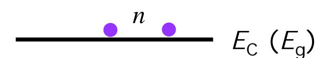
* M. Sakata, *Solid State Physics* (Baifukan, Tokyo, 1989).

Carrier Number Density of an Extrinsic Semiconductor

Numbers of holes in the valence band E_V should equal to

the sum of those of electrons in the conduction band E_C and in the acceptor level E_A :

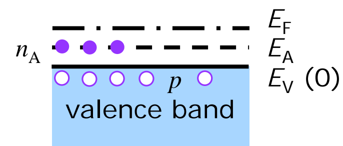
$$p = n + n_A$$



Similar to the intrinsic case,

$$p = N_V f_p(0) \approx N_V \exp\left(-\frac{E_F}{k_B T}\right)$$

$$n = N_C f_e(E_g) \approx N_C \exp\left(-\frac{E_g - E_F}{k_B T}\right)$$



Assuming numbers of neutral acceptors are N_A,

$$n_A = \frac{N_A}{1 + 2\exp\left(\frac{E_A - E_F}{k_B T}\right)}$$

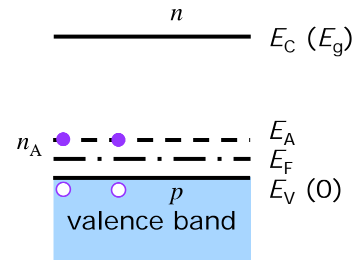
For E_A - E_F > $k_B T$, $n_A \approx N_A$

$$\therefore N_V \exp\left(-\frac{E_F}{k_B T}\right) \approx N_C \exp\left(-\frac{E_g - E_F}{k_B T}\right) + N_A$$

Carrier Number Density of an Extrinsic Semiconductor (Cont'd)

At low temperature, one can assume $p >> n$, $p \approx n_A$

As n_A is very small, $E_A > E_F$



$$n_A = \frac{N_A}{2}\exp\left(-\frac{E_A - E_F}{k_B T}\right)$$

$$\therefore N_V \exp\left(-\frac{E_F}{k_B T}\right) \approx \frac{N_A}{2}\exp\left(-\frac{E_A - E_F}{k_B T}\right)$$

$$\therefore \exp\left(-\frac{E_F}{k_B T}\right) \approx \sqrt{\frac{N_A}{2N_V}}\exp\left(-\frac{E_A}{2k_B T}\right)$$

$$\therefore E_F \approx \frac{k_B T}{2}\ln\frac{2N_V}{N_A} + \frac{E_A}{2}$$

By substituting $N_V \equiv N_{V_p} T^{3/2}$

$$\therefore E_F \approx \frac{k_B T}{2}\ln\left(\frac{2N_{V_p}}{N_A}T^{3/2}\right) + \frac{E_A}{2}$$

For $T \sim 0$, $E_F \approx \frac{E_A}{2}$

At high temperature, one can assume $n >> n_A$, $p \approx n$

Similar to the intrinsic case, for $m_e^* = m_p^*$, $E_F \approx \frac{E_g}{2}$

Temperature Dependence of an Extrinsic Semiconductor

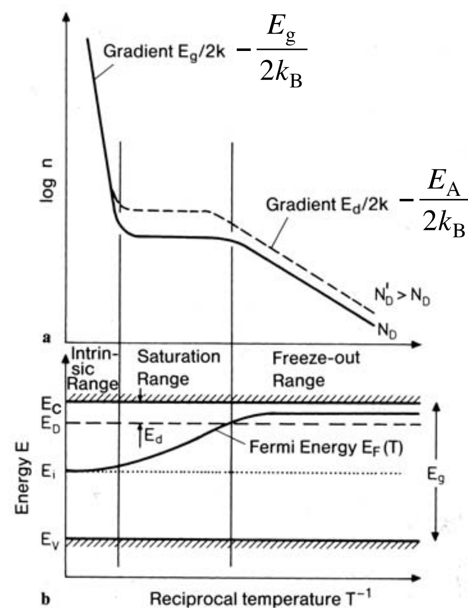


Fig. 12.10. **(a)** Qualitative temperature dependence of the concentration n of electrons in the conduction band of an n-type semiconductor for two different donor concentrations $N_D' > N_D$. The width of the forbidden band is E_g and E_d is the ionization energy of the donors; **(b)** qualitative temperature dependence of the Fermi energy $E_F(T)$ in the same semiconductor. E_C and E_V are the lower edge of the conduction band and the upper edge of the valence band, respectively. E_D is the position of the donor levels and E_i is the Fermi level of an intrinsic semiconductor

* H. Ibach and H. Lüth, *Solid-State Physics* (Springer, Berlin, 2003).

Semiconductor Junctions

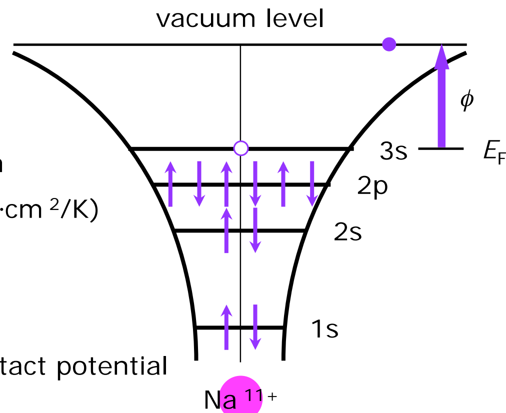
Work function ϕ :

Current density of thermoelectrons :

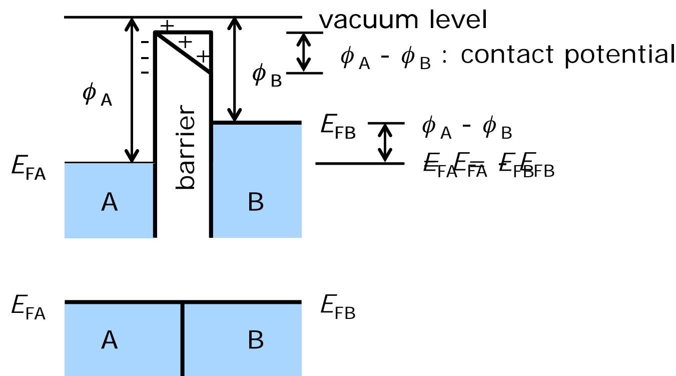
$$J = AT^2 \exp\left(-\frac{\phi}{k_B T}\right)$$

→ Richardson-Dushman equation

A : Richardson constant (~120 A·cm ^{2}/K)

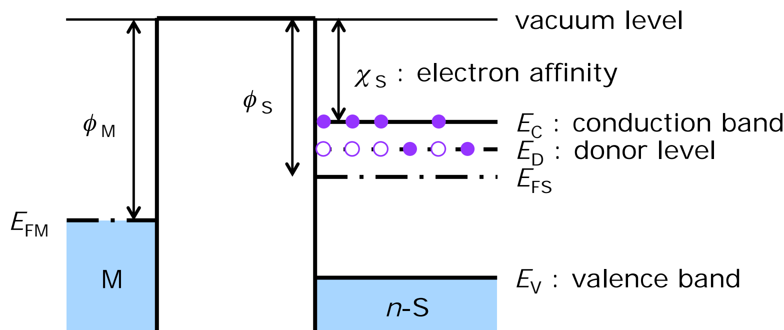


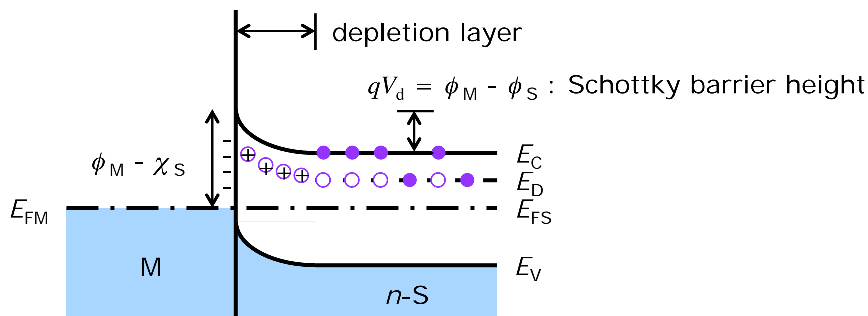
Metal - metal junction :



Metal - Semiconductor Junction - *n*-Type

Metal - *n*-type semiconductor junction :

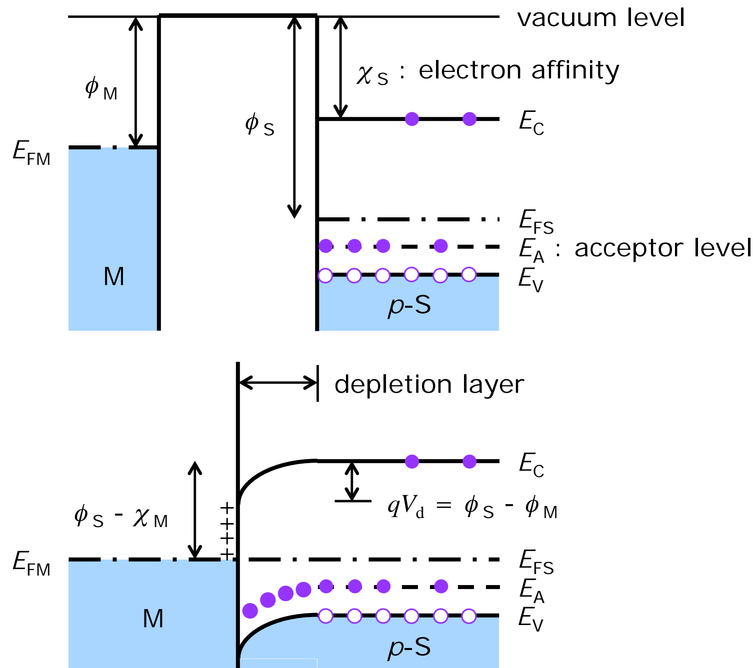




* http://www.dpg-physik.de/

Metal - Semiconductor Junction - *p*-Type

Metal - *p*-type semiconductor junction :



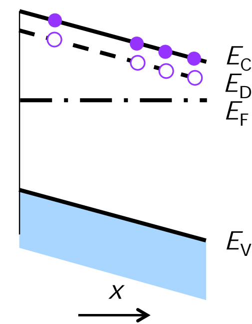
Einstein Relationship

At the equillibrium state,

Numbers of electrons diffuses towards -*x* direction are

$$-D_e \frac{dn}{dx} \qquad (\text{-}x \text{ direction})$$

(n : electron number density, D_e : diffusion coefficient)



Drift velocity of electrons with mobility μ_e under E is

$$v_d = -\mu_e E$$

Numbers of electrons travel towards +*x* direction under E are

$$nv_d = -\mu_e nE \qquad (+x \text{ direction})$$

As E is generated by the gradient of E_C, E is along -*x* and v_d is +*x*.

$$-\mu_e nE - D_e \frac{dn}{dx} = 0 \qquad (\text{equillibrium state})$$

Assuming $E_V = 0$, electron number density is defined as

$$n = N_e \exp\left(-\frac{E_C - E_F}{k_B T}\right)$$

Einstein Relationship (Cont'd)

Now, an electric field E produces voltage V_{CF} = V_C - V_F

$$E_C - E_F = -qV_{CF} = -q(V_C - V_F)$$

$$\therefore E = -\frac{dV_{CF}}{dx} = \frac{1}{q}\frac{d(E_C - E_F)}{dx}$$

Accordingly,

$$\frac{dn}{dx} = \frac{dn}{d(E_C - E_F)} \cdot \frac{d(E_C - E_F)}{dx} = -\frac{1}{k_B T} n \cdot qE$$

$$\therefore \mu_e nE = D_e \frac{nqE}{k_B T}$$

$$\therefore D_e = \mu_e \frac{k_B T}{q}$$ → Einstein relationship

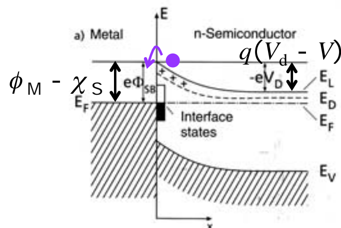
Therefore, a current density J_n can be calculated as

$$J_n = -\left(-q\mu_e nE - qD_e \frac{dn}{dx}\right) = qD_e\left(-\frac{qn}{k_B T} \cdot \frac{dV_x}{dx} + \frac{dn}{dx}\right)$$

$$\therefore J_n = B\left[\exp\left(-\frac{q(V_d - V)}{k_B T}\right) - \exp\left(-\frac{qV_d}{k_B T}\right)\right]$$

Rectification in a Schottky Junction

By applying a bias voltage V onto a metal - n-type semiconductor junction :



forward bias

$$J_{Foward} = J_{M \to S} - J_{S \to M} = B\left[\exp\left(-\frac{q(V_d - V)}{k_B T}\right) - \exp\left(-\frac{qV_d}{k_B T}\right)\right]$$

$$= J_0\left[\exp\left(\frac{qV}{k_B T}\right) - 1\right] \approx J_0 \exp\left(\frac{qV}{k_B T}\right) \quad (V : \text{large})$$

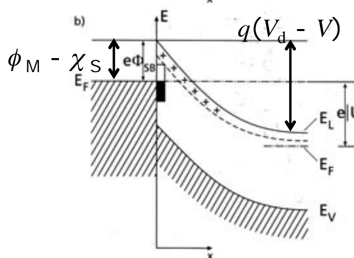
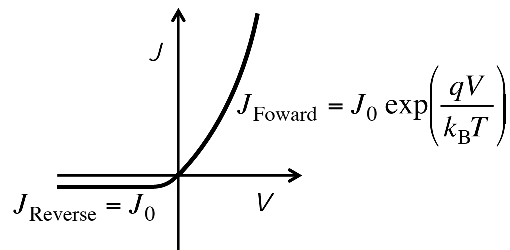


Fig. 12.22. Electronic band scheme of a metal/semiconductor (n-doped) junction; pinning of the Fermi-level E_F in interface states near the neutrality level causes the formation of a Schottky-barrier $e\phi_{SB}$ and a depletion space charge layer within the semiconductor. V_D is the "built-in" diffusion voltage. **(a)** In thermal equilibrium, **(b)** under external bias U



reverse bias

$$J_{Reverse} = J_{M \to S} - J_{S \to M} = B\left[\exp\left(-\frac{q(V_d + V)}{k_B T}\right) - \exp\left(-\frac{qV_d}{k_B T}\right)\right]$$

$$= J_0\left[\exp\left(-\frac{qV}{k_B T}\right) - 1\right] \approx J_0 \quad (V : \text{large})$$

* H. Ibach and H. Lüth, *Solid-State Physics* (Springer, Berlin, 2003).

pn Junction

Fabrication method :

- Annealing method :

  n-type : Spread P_2O_5 onto a Si substrate and anneal in forming gas.

  p-type : Spread B_2O_3 onto a Si substrate and anneal in forming gas.

- Epitaxy method ("epi" = on + "taxy" = arrangement) :

  Oriented overgrowth

  n-type : thermal deformation of SiH_4 (+ PCl_3) on a Si substrate

  p-type : thermal deformation of SiH_4 (+ BBr_3) on a Si substrate

pn Junction Interface

By connecting *p*- and *n*-type semiconductors,

p : Most of accepters become - ions

→ Holes are excited in E_V.

n : Most of donors become + ions

→ Electrons are excited in E_C.

Fermi level E_F needs to be connected.

→ Built-in potential : $qV_d = E_{fn} - E_{Fp}$

Electron currents balances

$p \rightarrow n = n \rightarrow p$

Majority carriers :

p : holes, *n* : electrons

Minority carriers :

p : electrons, *p* : holes

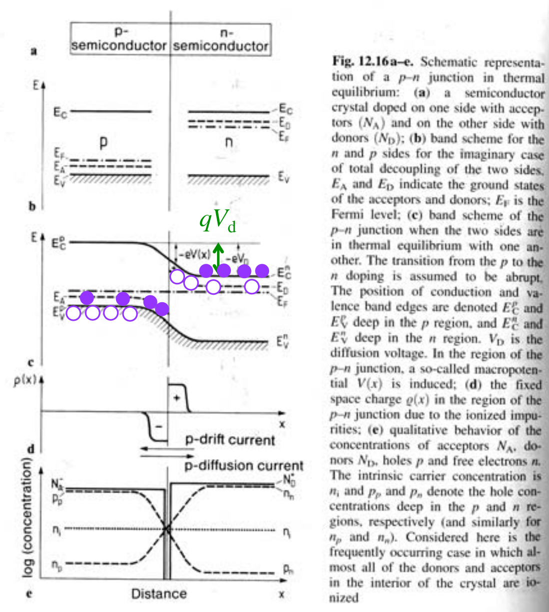
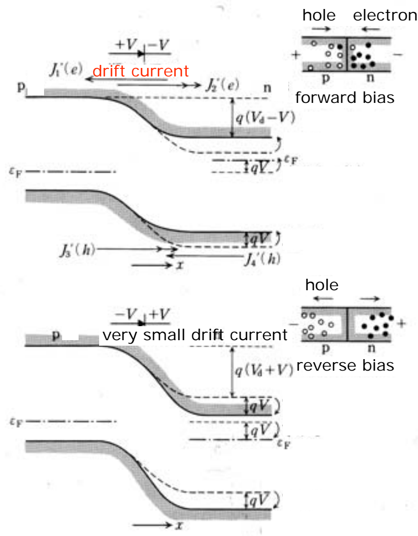


Fig. 12.16a–e. Schematic representation of a *p–n* junction in thermal equilibrium: **(a)** a semiconductor crystal doped on one side with acceptors (N_A) and on the other side with donors (N_D); **(b)** band scheme for the *n* and *p* sides for the imaginary case of total decoupling of the two sides. E_A and E_D indicate the ground states of the acceptors and donors; E_F is the Fermi level; **(c)** band scheme of the *p–n* junction when the two sides are in thermal equilibrium with one another. The transition from the *p* to the *n* doping is assumed to be abrupt. The position of conduction and valence band edges are denoted E_C^p and E_V^p deep in the *p* region, and E_C^n and E_V^n deep in the *n* region. V_D is the diffusion voltage. In the region of the *p–n* junction, a so-called macropotential $V(x)$ is induced; **(d)** the fixed space charge $\varrho(x)$ in the region of the *p–n* junction due to the ionized impurities; **(e)** qualitative behavior of the concentrations of acceptors N_A, donors N_D, holes *p* and free electrons *n*. The intrinsic carrier concentration is n_i and p_p and p_n denote the hole concentrations deep in the *p* and *n* regions, respectively (and similarly for n_p and n_n). Considered here is the frequently occurring case in which almost all of the donors and acceptors in the interior of the crystal are ionized

* H. Ibach and H. Lüth, *Solid-State Physics* (Springer, Berlin, 2003).

Rectification in a *pn* Junction

Under an electrical field ***E***,



Current rectification :

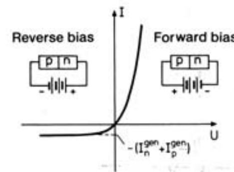


Fig. 12.18. Schematic representation of the current voltage (*I–U*) characteristic of a *p–n* junction, together with the corresponding circuit. The maximum current in the reverse direction is given by the sum of the generation currents for electrons and holes

* M. Sakata, *Solid State Physics* (Baifukan, Tokyo, 1989).
** H. Ibach and H. Lüth, *Solid-State Physics* (Springer, Berlin, 2003).