Quick Review over the Last Lecture

**Classic model:** Dulong-Petit empirical law

\[ c_V \sim 3R \]

**Einstein model:**

- \( E \): Einstein temperature
- \( c_V \sim 3R \) for \( E < T \)
- \( c_V \exp\left(-\frac{E}{T}\right) \) for \( E \ll T \)

**Debye model:**

- \( D \): Debye temperature
- \( c_V \sim 3R \) for \( D \ll T \)
- \( c_V \sim T^3 \) for \( D \ll T \)
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:

- Metal conductors: Allowed
- Semiconductors: Allowed
- Insulators: Forbidden

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

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Energy Band of a semiconductor

Schematic energy band diagram:

- Conduction band
- Valence band
- Band gap
- Conduction electron
- Hole

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Elemental Semiconductors

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<td>Te</td>
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</table>

Carrier density: Cu (metal) $\sim 10^{23}$ cm$^{-3}$

Ge (semiconductor) $\sim 10^{13}$ cm$^{-3}$

**Semimetal**: conduction and valence bands are slightly overlapped.

- As (semimetal) $\sim 10^{20}$ cm$^{-3}$
- Sb (semimetal) $\sim 10^{19}$ cm$^{-3}$
- C (semimetal) $\sim 10^{18}$ cm$^{-3}$
- Bi (semimetal) $\sim 10^{17}$ cm$^{-3}$

Fabrication of a Si-Based Integrated Circuit

Czochralski method:

Si purity (%)
Compound Semiconductors

In the periodic table,

<table>
<thead>
<tr>
<th>Period</th>
<th>Group III</th>
<th>Group IV</th>
<th>Group V</th>
<th>Group VI</th>
<th>Group VII</th>
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<tr>
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<td>H</td>
<td>He</td>
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<tr>
<td>2</td>
<td>Li, Be</td>
<td>B, C</td>
<td>N, O, F</td>
<td>Ne</td>
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<tr>
<td>3</td>
<td>Na, Mg</td>
<td>Al, Si</td>
<td>P, S, Cl</td>
<td>Ar</td>
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<tr>
<td>4</td>
<td>K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr</td>
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<tr>
<td>5</td>
<td>Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe</td>
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<tr>
<td>6</td>
<td>Cs, Ba</td>
<td>Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn</td>
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<tr>
<td>7</td>
<td>Fr, Ra</td>
<td>La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu</td>
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<tr>
<td>8</td>
<td>Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr</td>
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</tbody>
</table>

**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:

\[
\sigma = \sigma_c + \sigma_h = nq\mu_c + pq\mu_h = n_i q(\mu_c + \mu_h) \quad (n_i = n = p)
\]

*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

\[ f(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1} \]

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

\[ g(E) = \frac{2m^*}{(2\pi \hbar^2)^{3/2}} \sqrt[3]{E} \]

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

\[ g_C(E) = \frac{2m_e^*}{(2\pi \hbar^2)^{3/2}} \sqrt[3]{E - E_C} \]

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

\[ g_V(E) = \frac{2m_p^*}{(2\pi \hbar^2)^{3/2}} \sqrt[3]{-E} \]

\[ f_e(E) = 1 - f_e(E) \]

\[ f_p(E) = \exp\left(-\frac{(E - E_F)/k_B T}{1}\right) \]

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

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

Here, \( E_C = (E_g + E_C - E_F) >> k_B T \to E - E_F \approx E_C/2 \) for \( E_C \leq E \leq E_{Ct} \) \( (E_F \sim E_C/2) \)

\[ f_e(E) = \exp\left[-\frac{(E - E_F)/k_B T}{1}\right] \]

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

\[ f_p(E) = \exp\left[(E - E_F)/k_B T\right] \]
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 $E_C \to \infty$

Similarly, $f_p(E_F - 3k_BT) < 0.05$ and hence $E_v \to -\infty$

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

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

As a result,

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

$$p = N_V \exp\left[-E_F/k_BT\right] \approx N_V f_p(0) \quad \begin{cases} N_V = N_{Vp} T^{3/2} \\ N_{Vp} = 2 \left( \frac{2\pi m_p^* k_B}{\hbar^2} \right)^{3/2} \end{cases}$$

Fermi Level of an Intrinsic Semiconductor

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

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

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

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

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

$n_p$ product is calculated to be

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

→ 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)

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,

\[ p = N_V f_p(0) = N_V \exp \left( -\frac{E_F}{k_B T} \right) \]
\[ n = N_C f_c(E_g) = N_C \exp \left( -\frac{E_g - E_F}{k_B T} \right) \]

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 $E_A - E_F > k_B T$, $n_A = N_A$

\[ \therefore N_V \exp \left( -\frac{E_F}{k_B T} \right) \approx N_C \exp \left( -\frac{E_g - E_F}{k_B T} \right) + N_A \]
Carrier Number Density of an Extrinsic Semiconductor (Cont’d)

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

As $n_A$ is very small, $E_A > E_F$

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

$$\therefore N_v \exp\left(-\frac{E_F}{k_BT}\right) = \frac{N_A}{2} \exp\left(-\frac{E_A - E_F}{k_BT}\right)$$

$$\therefore \exp\left(-\frac{E_F}{k_BT}\right) = \frac{N_A}{2N_v} \exp\left(-\frac{E_A}{k_BT}\right)$$

$$\therefore E_F = \frac{k_BT}{2} \ln \frac{2N_v}{N_A} + \frac{E_A}{2}$$

By substituting $N_V = N_V p T^{3/2}$

$$\therefore E_F = \frac{k_BT}{2} \ln \left(\frac{2N_V p T^{3/2}}{N_A}\right) + \frac{E_A}{2}$$

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

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

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

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Temperature Dependence of an Extrinsic Semiconductor

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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. $E'_D$ and $E_D$ 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 $E_F$ is the Fermi level of an intrinsic semiconductor.

Semiconductor Junctions

Work function $\phi$:

Current density of thermoelectrons:

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

→ Richardson-Dushman equation

$A$ : Richardson constant ($\sim 120 \text{ A-cm}^2/\text{K}$)

Metal - metal junction:

Metal - $n$-type semiconductor junction:

$\chi_S$ : electron affinity

$\phi_M$ - $\phi_S$ : Schottky barrier height

* http://www.dpg-physik.de/
Metal - Semiconductor Junction - *p*-Type

Metal - *p*-type semiconductor junction:

- Vacuum level
- Electron affinity
- Accepter level
- Depletion layer

**Einstein Relationship**

At the equilibrium state,

Numbers of electrons diffuses towards -$x$ direction are

\[-D_e \frac{dn}{dx} \quad (-x \text{ direction})\]

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

Drift velocity of electrons with mobility $\mu_e$ under $E$ is

$\nu_d = -\mu_e E$

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

\[n\nu_d = -\mu_e nE \quad (+x \text{ direction})\]

As $E$ is generated by the gradient of $E_C$, $E$ is along -$x$ and $\nu_d$ is $+x$.

\[-\mu_e nE - D_e \frac{dn}{dx} = 0 \quad \text{(equilibrium state)}\]

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 $V_{CF} = V_C - V_F$

\[
E_C - E_F = -qV_{CF} = -q(V_C - V_F)
\]

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

Accordingly,

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

\[
\therefore \mu_e n E = D_e \frac{nqE}{k_B T}
\]

\[
\therefore D_e = \mu_e \frac{k_B T}{q} \rightarrow \text{Einstein relationship}
\]

Therefore, a current density $J_n$ can be calculated as

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

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

Rectification in a Schottky Junction

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

**pn Junction**

Fabrication method:

- **Annealing method**:
  - \(n\)-type: Spread \(\text{P}_2\text{O}_5\) onto a Si substrate and anneal in forming gas.
  - \(p\)-type: Spread \(\text{B}_2\text{O}_3\) onto a Si substrate and anneal in forming gas.

- **Epitaxy method** ("epi" = on + "taxy" = arrangement):
  - Oriented overgrowth
    - \(n\)-type: thermal deformation of \(\text{SiH}_4\) (+ \(\text{PCl}_3\)) on a Si substrate
    - \(p\)-type: thermal deformation of \(\text{SiH}_4\) (+ \(\text{BBr}_3\)) 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: \(qV_d = E_{in} - E_{ip}\)

Electron currents balances
\[ p \to n = n \to p \]

Majority carriers:
- \(p\): holes, \(n\): electrons

Minority carriers:
- \(p\): electrons, \(n\): holes

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Rectification in a \textit{pn} Junction

Under an electrical field $E$, 


**M. Sakata, \textit{Solid State Physics} (Baifukan, Tokyo, 1989).**

*Fig. 12.IB. Schematic representation of the current-voltage (I-U) characteristics of a \textit{pn} junction, together with the corresponding circuits. The maximum current in the reverse direction is given by the sum of the generation currents for electrons and holes.*