Outlines

1. Band gap and band edge
2. Equation of motion
3. Silicon and Germanium
4. Intrinsic carrier concentration
5. Impurity conductivity
6. Semimetals
7. Superlattices

Band gap and band edge

The properties of metal, semiconductor, and insulator can be understood through the following energy level diagram.

From energy band picture, a pure semiconductor at absolute zero temperature (T = 0K), will be an insulator. However, the band gap of semiconductor is relatively small compared with an insulator.

So thermal excitation, impurity doping or lattice defects etc can contribute to the electrical conductivity of the semiconductor.

<table>
<thead>
<tr>
<th>Type</th>
<th>Elemental semiconductors</th>
<th>Compound semiconductors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si [eV]</td>
<td>Ge [eV]</td>
<td>GaAs [eV]</td>
</tr>
<tr>
<td>Band Gap @ 0K</td>
<td>1.17</td>
<td>0.75</td>
</tr>
<tr>
<td>Band Gap @ 300K</td>
<td>1.12</td>
<td>0.67</td>
</tr>
<tr>
<td>Carrier concen. @300K</td>
<td>1.5x10^19</td>
<td>2.4x10^15</td>
</tr>
</tbody>
</table>

The charge carrier can be either electrons (n-type), or holes (p-type). For pure material, the creation of \( n \) carrier due to thermal excitation is always associated with the creation of \( p \) carrier. Therefore,

\[ n = p \]  \text{Intrinsic semiconductor}

When

\[ n \neq p \]  \text{Extrinsic semiconductor}  

Could be \( n \)-type or \( p \)-type.
Carrier concentration as a function of temperature

Calculated band structures of silicon and germanium

Direct band gap vs. Indirect band gap

In an indirect absorption, a phonon is created to satisfy the conservation of momentum/energy law.

\[ \hbar \omega = E_g + \hbar \Omega \quad \text{Conservation of energy} \]
\[ \hbar \vec{k} = h \vec{k}_c + h \vec{K} \quad \text{Conservation of momentum} \]

Since \( c \gg v_{\text{phonon}} \), so \( \vec{K} = 0 \), by similar argument, \( \hbar \Omega = 0 \)

\[ \hbar \omega \approx E_g \]
\[ \vec{k}_c \approx - \vec{K} \]

Equation of motion of an electron in an energy band

Since we can define \( \epsilon = \hbar \omega \)

\[ \frac{d \epsilon}{d \vec{k}} = \hbar \frac{d \omega}{d \vec{k}} = h \vec{v}_g \implies \frac{d \omega}{d \vec{k}} = \frac{1}{\hbar} \frac{d \epsilon}{d \vec{k}} \quad (0) \]

\[ d \epsilon = h \vec{v}_g d \vec{k} \]

From work-energy theorem, \( \delta \epsilon = -F \cdot ds = -eE \cdot v_g dt \)

\[ \hbar d \vec{k} = -eE \cdot dt \]
\[ \hbar \frac{d \vec{k}}{dt} = -eE = F \quad (1) \]
In an energy band at $T \neq 0$, when some electrons were excited into the conduction band, the vacant states left behind are called holes.

A hole $\equiv$ A completely filled valence band $-$ one electron.

When we have a completely filled band, the total momentum of the band is zero:

$$\sum_k \vec{k} = 0 \quad \text{(2)}$$

If all the states in a band are completely filled, then an electric field will have no effect on the valence band.

**Electron in a conduction band**

1. It has mass $\Rightarrow m_e$
2. It has momentum $\Rightarrow h \vec{k}_e$
3. It has energy $\Rightarrow \epsilon(k_e) = \frac{\hbar^2 k_e^2}{2m_e}$
4. It follows Newton law, $\bar{F} = \frac{h}{\hbar} \frac{d\vec{k}}{dt}$

**Hole in valence band**

1. $m_h = -m_e$ \quad \text{(3)}
2. $\vec{k}_h = -\vec{k}_e$ \quad \text{(4)}
3. $\epsilon(k_h) = -\epsilon(k_e)$ \quad \text{(5)}

Let’s comment on the expressions in red in previous page.

**Mass**

Since $\frac{d\vec{k}}{dt} = \frac{1}{\hbar} \frac{d^2\epsilon}{dk^2} = \frac{1}{\hbar} \frac{d\epsilon}{dk} \frac{d\epsilon}{dt} = \frac{1}{\hbar} \frac{d\epsilon}{dk} \frac{d\epsilon}{dt}$

$$F = \frac{\hbar}{\hbar^2} \frac{d\epsilon}{dk} \frac{d\epsilon}{dt}$$

Effective mass

$$\frac{1}{m_e} = \frac{1}{\hbar^2} \frac{d\epsilon}{dk}$$

From the band picture, electron at the top of valence band has a negative effective mass, so the effective mass of the hole in the valence band is positive.

$m_h = -m_e$

**Momentum**

$$\vec{k}_h = -\vec{k}_e$$

This can be understood as follow: Since we know that

$$\sum_k \vec{k} = 0 \quad \text{For a completely filled band}$$

So when we take out one $\vec{k}_e$ state out, then

$$\vec{k}_h = \sum_{all \vec{k} \ except \ \vec{k}_e} \vec{k} = -\vec{k}_e$$

**Energy**

The energy of the hole is opposite in sign to the energy of the missing electron, because it takes more work to remove an electron from a low orbital than from a high orbital.
**Intrinsic carrier concentration**

**Electron statistics**

From free electron gas model, we know that the density of states of the free electron is

$$D(e) = \frac{V}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \sqrt{e}$$

(6)

For free electron gas

The concentration of electrons in the conduction band can be calculated as follow:

$$n = \int_{E_c}^{\infty} D_e(e) f_e(e) \, de$$

$$= \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \int_{E_c}^{\infty} \sqrt{e-E_c} \frac{1}{e^{(\mu-e)/kT}+1} \, de$$

(8)

At low T, such that $(\epsilon - \mu) \gg k_B T$, above eq. becomes

$$n = \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \int_{E_c}^{\infty} \sqrt{e-E_c} e^{(\mu-e)/kT} \, de$$

$$n = 2 \left( \frac{m_e k_B T}{2\pi^2} \right)^{3/2} e^{(\mu-E_c)/kT}$$

(9)

**Define the effective density of electrons in the conduction band as**

$$N_e = 2 \left( \frac{m_e k_B T}{2\pi^2} \right)^{3/2}$$

$$n = N_e e^{(\mu-E_c)/k_B T}$$

(10)

$$\mu = E_c + k_B T \ln \left( \frac{n}{N_e} \right)$$

(11)

Since we know $f_k = 1 - f_e$

$$f_k(e) = 1 - \frac{1}{e^{(\mu-e)/kT}+1}$$

(15)

For $(\mu - e) \gg kT$ (low T)

$$p = \frac{1}{2\pi^2} \left( \frac{2m_h}{\hbar^2} \right)^{3/2} \int_{E_v}^{E_p} \sqrt{(E_p-e)} \, e^{(\mu-e)/kT} \, de$$

(16)

$$p = 2 \left( \frac{m_h k_B T}{2\pi^2} \right)^{3/2} e^{(\mu-E_v)/kT}$$

(17)

We can see that eq. (17) is very similar to eq. (9).
We define \( N_h \) as the effective density of holes in the valence band

\[
N_h = 2 \left( \frac{m_h k_BT}{2\pi \hbar^2} \right)^{3/2}
\]  
(18)

\[
p = N_h e^{(E_p-p)/k_BT}
\]  
(19)

Combine eq.(19) with eq. (10), we end up with

\[
p = 4 \left( \frac{k_BT}{2\pi \hbar^2} \right)^{3/2} (m_j m_h)^{3/2} e^{(-E_p/k_BT)}
\]  
(20)

This equation is true for both intrinsic and also extrinsic semiconductors.

For intrinsic semiconductors, the number of electron is the same as the number of holes, so eq. (20) becomes

\[
n_e = p_h = 2 \left( \frac{k_BT}{2\pi \hbar^2} \right)^{3/2} (m_j m_h)^{1/4} e^{(-E_e/k_BT)}
\]  
(21)

For intrinsic semiconductors, eq.(9) equals to eq.(17),

\[
2 \left( \frac{m_h k_BT}{2\pi \hbar^2} \right)^{3/2} e^{(-E_h/k_BT)} = 2 \left( \frac{m_e k_BT}{2\pi \hbar^2} \right)^{3/2} e^{(-E_e/k_BT)}
\]

\[
\exp \left[ \frac{2\mu}{kT} \right] = \left( \frac{m_h}{m_e} \right)^{3/2} \cdot \exp \left[ \frac{E_e + E_h}{kT} \right]
\]  
(22)

Take logarithmic on both sides

\[
\frac{2\mu}{kT} = \frac{3}{2} \ln \left( \frac{m_h}{m_e} \right) + \frac{(E_e + E_h)}{kT}
\]

After some re-arrangement, the above eq. becomes

\[
\mu = \frac{(E_e + E_h)}{2} \cdot \frac{3}{2} \cdot \frac{kT \ln \left( \frac{m_h}{m_e} \right)}{kT}
\]

Equation (23) is an important result. We can see that

1. If \( m_h = m_e \) \( \mu = \frac{(E_e + E_h)}{2} = E_F \)
2. If \( T = 0 \) \( \mu = \frac{(E_e + E_h)}{2} \)

The temperature dependence of the mobility \( \mu \) is quite small, so the change in conductivity is mainly comes from the concentration rather than the mobility.

In intrinsic semiconductor the mobility is mostly dominated by the scattering of charge carriers by phonon.

\[
\tau = \tau_{\text{phonon}}
\]

In extrinsic semiconductors, the scattering by impurity may become important!

\[
\frac{1}{\tau} = \frac{1}{\tau_{\text{pho}}} + \frac{1}{\tau_{\text{imp}}}
\]

(26)
We can use Bohr’s hydrogen model to find out the ionization energy of the dopant as follow:

For H atom, \( E_i = \frac{e^2 m_e}{2 \epsilon^2} = 13.6 \text{ eV} \)

For electron inside the crystal, the Coulomb potential is \( E_a = \frac{e^2 m_e}{2 \epsilon^2 h^2} \). Here, \( \epsilon \) is the dielectric constant

\[
E_a = \frac{e^2 m_e}{2 \epsilon^2 h^2} = 13.6 \left( \frac{1}{\epsilon^2} \frac{m_e}{m_e} \right) \text{ (eV)} \quad (27)
\]

For silicon, \( m_e^* \approx 0.2 m_e \) and \( \epsilon = 11.7 \)

\[
E_a \approx 13.6 \left( \frac{1}{(11.7)^2} \cdot 0.2 \right) = 20 \text{ meV}
\]

This hydrogen model also can be applied to the Bohr radius of the donor:

\[
\alpha_D = \frac{\hbar^2}{m_e} = \left( 0.53 \frac{e^2}{m_e} \right) \quad (28)
\]

For silicon crystal, \( \alpha_D \approx 30 \text{Å} \)

In table below, the donor ionization energies of common dopants P, As and Sb are shown.

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>As</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>45</td>
<td>46</td>
<td>36</td>
</tr>
<tr>
<td>E_D</td>
<td>12.0</td>
<td>10.7</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Acceptor states

When impurities with 3 valence electrons are doped in silicon, there is one electron missing to form the tetrahedral bonding. So we say that a hole is formed and is loosely bound to the trivalent impurity. However, it can easily accept an electron from the valence band and complete the 4-electron tetrahedral bonding and leave the valence band with one hole.

\[
\text{The situation here is very similar to the donor states. If the acceptor state is filled, the Fermi energy will be between } (E_v + E_a) \text{ and } E_v \text{ and the hole density in the acceptor band will be}
\]

\[
p = N_h e^{(E_v-E_a)/kT} \quad (31)
\]

(This is eq.(19) on page 25)

Now let \( N_a \) be the # of acceptor, and \( N_a^- \) be the # of electrons in the acceptor states,

\[
N_a^- = N_h e^{-(E_v+E_a)/kT} \quad \text{and} \quad N_a^- \approx p
\]

\[
p = \sqrt{(N_h N_a^-) e^{-(E_v+E_a)/kT}} \quad (32)
\]

From the law of mass action, eq. (20), we can see that the product of \( n \) and \( p \) is independent of the dopants.

\[
np = 4 \left( \frac{k_B T}{2 \pi \hbar^2} \right)^3 m_e m_h^{3/2} \exp(-E_g/k_B T)
\]

But \( n+p \) will change as a function of doping.
From the law of mass action, n-type doping can increase the electron concentration $n$, but it will reduce the hole concentration $p$ by the same factor.