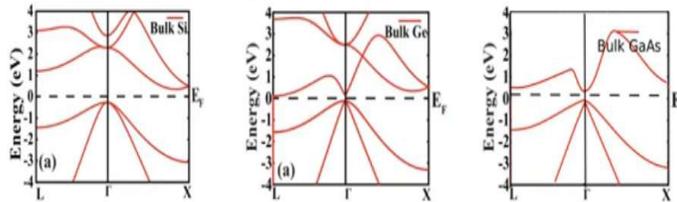


Electronic Properties of the Materials: Computational Approach
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Module No # 08
Lecture No # 39
Semiconductors: Part 3(Law of Mass Action)

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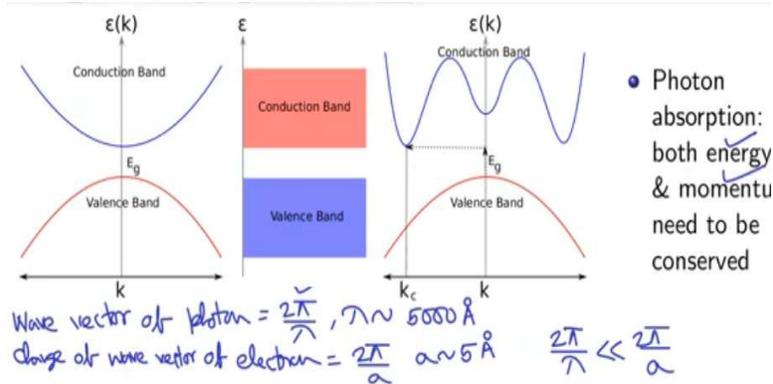
Direct & indirect bandgap semiconductor



Hello friends, we have learned about the band structure of silicon germanium and Gallia arsenide. There is an important difference between gallium arsenate and silicon or germanium. In gallium arsenate, both balance band maximum and conduction band minimum is located at the gamma point this is known as the direct band gap semiconductor. In silicon and germanium balance band maximum is at the gamma point while conduction band minimum is not at the gamma point.

In the case of silicon conduction band minimum is near the X point, and in the case of germanium conduction band minimum is near the L point. Silicon and germanium are called indirect band gap semiconductors.

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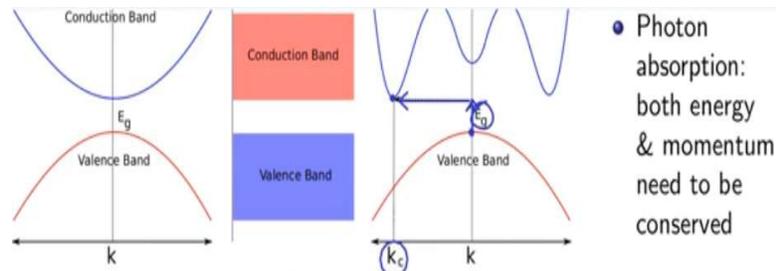
- Photon absorption in direct bandgap semiconductor (left):
 - ▶ Momentum conservation not an issue as: $k_{\text{photon}} \approx 0$
 - ▶ Energy conservation: $E_g = \hbar\omega_{\text{photon}}$

Consider an electron being excited from the valence band to the conduction band via photon absorption. In the process of photon absorption both energy and momentum need to be conserved. If we consider the absorption of visible light having a wavelength of λ , then the wave vector of photon is equal to $2\pi/\lambda$, where λ is of the order of 5000 angstroms. Now let us try to get some approximate estimate of the change in wave vector of the electron getting excited from the valence band back to the conduction band.

For example, consider this case an electron is getting excited from this point of the valence band to this point of the conduction band. In the process wave vector of the electron is changing by this much, thus the change of k of the wave vector of the electron is equal to $2\pi/a$. In this case, we find that this is approximately equal to the dimension of the first Brillouin zone, that is $2\pi/a$, where a is the lattice parameter, which is of the order of 5 angstrom.

Thus, the momentum of a photon $2\pi/\lambda$ is very small compared to the momentum change of an electron getting excited from the valence band to the conduction band. That is, $2\pi/\lambda$ is much smaller than $2\pi/a$. In case of a direct band in a gap semiconductor like gallium arsenide, the electron is getting excited from this point to this point. In this case, momentum conservation is not an issue because k_{photon} is negligible and energy conservation is $E_g = \hbar\omega$ is equal to \hbar times the frequency of the photon absorbed.

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- Photon absorption: both energy & momentum need to be conserved
- Note that, $k_{photon} = \frac{2\pi}{\lambda} \ll \frac{2\pi}{a}$, as $\lambda \sim 5000 \text{ \AA}$ & $a \sim 5 \text{ \AA}$
- Photon absorption in indirect bandgap semiconductor (right):
 - ▶ Momentum conservation: $k_{photon} \approx 0 \Rightarrow K_{phonon} = k_c$
 - ▶ Energy conservation: $\hbar\omega_{photon} = E_g + \hbar\Omega_{phonon}$
- Phonon energy $\hbar\Omega_{phonon} \approx 0.03 \text{ eV}$, small compared to bandgap
- Phonon wavevector K_{phonon} can be of the order of $\frac{2\pi}{a}$
- Indirect excitation: photons give energy, phonons give momentum

In the case of an indirect band gap semiconductor like silicon or germanium, an electron at this point in the valence band is getting excited to this point in the conduction band. The energy of the electron changes by E_g and the momentum of the electron changes by K_c . In this case, momentum conservation is not satisfied by momentum of the absorbed photon, which has negligible momentum compared to the momentum change of the excited electron.

In this case, a phonon is also involved. Phonons are quantized modes of lattice vibrations. They have a large point vector which is of the order of K_c as required to satisfy momentum conservation. Thus, momentum conservation is taken care of by phonon absorption. The energy conservation equation is this on the left hand side, we have the energy of the absorbed photon, which is equal to the band gap E_g plus energy of the absorbed phonon.

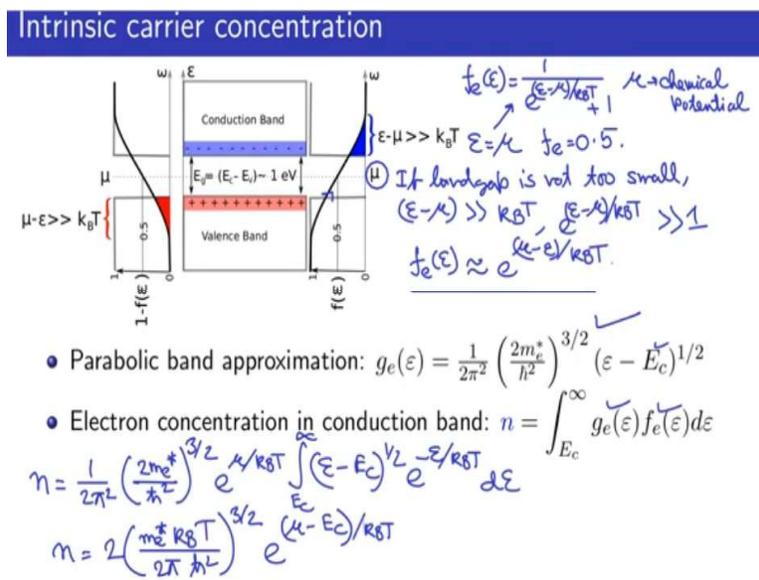
The phonon energy at room temperature is 30 millielectron volt which is very small compared to the band gap. In summary, in the case of an indirect band gap semiconductor, photons give required energy and phonons give required momentum for an electron to be excited from the valence band to the conduction band.

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Semiconductors at finite temperature

So far, I have discussed the band structure of semiconductors in detail at 0 Kelvin semiconductors are insulators because the balance band is completely full and conduction band is completely empty. At a finite temperature some electrons are going to be excited from the balance to the conduction band, making both of them partially occupied. As a result, such partially occupied bands take part in the electronic transport process.

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Let us find the number of electrons excited from the balance to the conduction band at some finite temperature T . Probability that an energy level of energy e is occupied at the conduction band is given by Fermi Dirac distribution. This is equal to $f_e(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}$, where μ is the chemical

potential k_B is the Boltzmann constant, and T is the temperature. This black thick line shows the Fermi distribution at a finite temperature.

How do we find the location of μ ? Note that if we put $e = \mu$ in this equation, then we get $f_e = 0.5$, thus at $e = \mu$ the Fermi function is 0.5. From this, we can easily locate the chemical potential μ . We note that if the band gap is not too small, then $\epsilon - \mu \gg k_B T$. In this case, the exponential term is very large compared to 1, that is exponential $e^{(\epsilon - \mu)/k_B T} \gg 1$

Thus, we can approximate the Fermi-Dirac distribution as $f_e(\epsilon) \approx e^{(\mu - \epsilon)/k_B T}$. We use the parabolic band approximation such that density of states is given by this expression, where m_e^* is the effective mass of an electron and E_c is the energy at the conduction band edge. Electron concentration in the conduction band at some finite temperature is given by the integral of the density of states times the Fermi function.

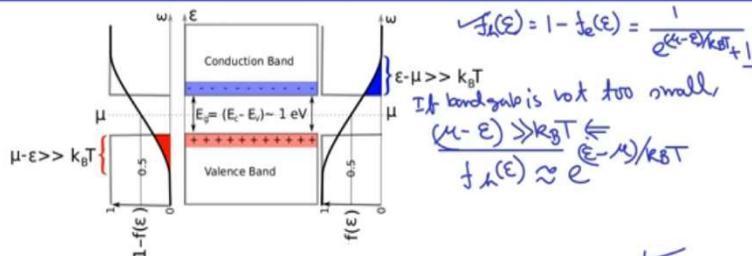
This integral is equal to the area under this blue shaded region. Putting the value of the density of states and Fermi function we get

$$n = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right) e^{\mu/k_B T} \int_{E_c}^{\infty} (\epsilon - E_c)^{1/2} e^{-\epsilon/k_B T} d\epsilon$$

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

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Intrinsic carrier concentration



- Parabolic band approximation: $g_h(\epsilon) = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} (E_v - \epsilon)^{1/2}$
 - Hole concentration in valence band: $p = \int_{-\infty}^{E_v} g_h(\epsilon) f_h(\epsilon) d\epsilon$
- $$p = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} e^{-\mu/k_B T} \int_{-\infty}^{E_v} (E_v - \epsilon)^{1/2} e^{\epsilon/k_B T} d\epsilon$$
- $$p = 2 \left(\frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-(E_v - \mu)/k_B T}$$

Now let us find the equilibrium concentration of holes in valence band. First, note that the whole distribution function is related to the electron distribution function by $f_h(\epsilon) = 1 - f_e(\epsilon) = \frac{1}{e^{(\mu-\epsilon)/k_B T} + 1}$. Now if band gap is not too small then $\mu - \epsilon \gg k_B T$ and we can approximate $f_h(\epsilon) \approx e^{(\epsilon-\mu)/k_B T}$. We can do this because under this condition, the exponential term becomes much larger than 1 and we can ignore the term 1.

We use the parabolic band approximation, such that the density of whole states is given by this expression, where m_h^* is the effective mass of holes and E_v is the energy at the valence band at the edge. The whole concentration in the valence band at some finite temperature is given by the integral of density of states times the Fermi function for holes. This integral is equal to the area under the red shaded region, putting the value of density of states and f_h .

$$p = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar} \right)^{3/2} e^{\mu/k_B T} \int_{-\infty}^{E_v} (E_v - \epsilon)^{1/2} e^{\epsilon/k_B T} d\epsilon$$

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

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Law of mass action

- $n = 2 \left(\frac{m_e^* k_B T}{2\pi\hbar^2} \right)^{3/2} e^{[(\mu - E_c)/k_B T]}$ $\begin{matrix} (\mu - E_c)/k_B T & (E_v - \mu)/k_B T \\ = e^{-(E_c - E_v)/k_B T} = e^{-E_g/k_B T} \end{matrix}$
- $p = 2 \left(\frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{3/2} e^{[(E_v - \mu)/k_B T]}$

- Law of mass action: $np = 4 \left(\frac{k_B T}{2\pi\hbar^2} \right)^3 (m_e^* m_h^*)^{3/2} e^{-E_g/k_B T}$

- The result holds in case of pure (intrinsic) semiconductors, as well as in presence of impurities
- As long as distance of Fermi level from the band edges is large compared to $k_B T$, the result holds good
- At 300 K, np is
 - ▶ $2.1 \times 10^{19} \text{ cm}^{-6}$ for Si (band gap 1.11 eV)
 - ▶ $2.9 \times 10^{26} \text{ cm}^{-6}$ for Ge (band gap 0.66 eV)
 - ▶ $6.6 \times 10^{12} \text{ cm}^{-6}$ for GaAs (band gap 1.42 eV)
- Clearly, np depends on band gap - note several orders of magnitude difference as band gap changes by a factor of ~ 2

So we got the expression for n and p . Let us multiply and find the expression for np . This is what we get from these 2 terms and if we multiply $e^{\mu - E_c}$ by $k_B T$ and $e^{E_v - \mu}$ by $k_B T$, then we get $e^{\mu - E_c - E_v}$ by $k_B T$, but $E_c - E_v$ is equal to the band gap that is, this term

is equal to $e^{-E_g/k_B T}$. Thus, we get an expression known as the law of mass action, which is independent of chemical potential μ .

We note that nowhere in the derivation we assume the semiconductor to be pure or intrinsic. Hence, the law of mass action works for pure as well as in pure semiconductors as long as the distance of the Fermi level from the band edges is large compared to $k_B T$ the result holds good. At 300 Kelvin n_p in Silicon is of the order of 10^{19} centimeters to the power -6. In germanium, n_p is of the order of 10^{26} centimeters to the power -6,

And in gallium arsenide n_p is of the order of 10^{12} centimeters to the power -6. Compared with the band gap values, clearly n_p depends on the band gap. The band gap is higher than the value of n_p . Note that n_p changes by several orders of magnitude as the band gap changes by a factor of 2.

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Intrinsic carrier concentration

- Law of mass action: $np = 4 \left(\frac{k_B T}{2\pi\hbar^2} \right)^3 (m_e^* m_h^*)^{3/2} e^{-E_g/k_B T}$
- In an intrinsic semiconductor, number of electrons is equal to number of holes: $n_i = p_i$
- $n_i = p_i = 2 \left(\frac{k_B T}{2\pi\hbar^2} \right)^{3/2} (m_e^* m_h^*)^{3/4} e^{-E_g/2k_B T}$

At room T
 $n_i \sim 10^{10} \text{ cm}^{-3}$ for Si (band gap 1.11 eV)
 $n_i \sim 10^{13} \text{ cm}^{-3}$ for Ge (band gap 0.66 eV)
 $n_i \sim 10^5 \text{ cm}^{-3}$ for GaAs (band gap 1.42 eV)

Slope = $-E_g/2k_B$

- Exponential T dependence of n_i is dominant, which explains several orders of magnitude change of carrier concentration due to change of band gap by a factor ~ 2

In an intrinsic semiconductor, the number of electrons is exactly equal to the number of holes because the thermal excitation of an electron leaves behind a hole in the balance tent. We can write $n_p = n_i^2 = p_i^2$, where the subscript I stands for intrinsic from law of mass action the intrinsic carrier concentration is given by this expression. Note that intrinsic carrier concentration depends on $T^{3/2}$ as well as exponential- $E_g/2k_B T$.

Obviously, exponential dependence dominates, and if you plot the log of n_i versus $1/T$, you get a straight line. Note that n_i values for silica Germania and gallium arsenide differ by several orders of magnitude. Now, intrinsic carrier concentration also has an exponential dependence on E_g the band gap. This explains the orders of magnitude change of carrier concentration due to the change of band gap by a factor of 2.

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Where is the Fermi level?

$$2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{(\mu - E_c)/k_B T} = 2 \left(\frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{(E_v - \mu)/k_B T}$$

$$\Rightarrow e^{(\mu - E_c + \mu - E_v)/k_B T} = \left(\frac{m_h^*}{m_e^*} \right)^{3/2}$$

$$\Rightarrow \frac{2\mu - (E_v + E_c)}{k_B T} = \frac{3}{2} \ln \left(\frac{m_h^*}{m_e^*} \right) \quad E_c - E_v = E_g \Rightarrow E_c = E_g + E_v$$

$$\Rightarrow 2\mu - (E_v + E_g + E_v) = \frac{3}{2} k_B T \ln \left(\frac{m_h^*}{m_e^*} \right)$$

$$\Rightarrow \boxed{\mu = E_v + \frac{1}{2} E_g + \frac{3}{4} k_B T \ln \left(\frac{m_h^*}{m_e^*} \right)} \quad T=0, \mu = E_v + \frac{1}{2} E_g$$

$m_h^* = m_e^*$

- Note that, if $m_h^* = m_e^*$, then $\mu = E_v + E_g/2$ for any T ✓
- Otherwise, μ depends on T ✓
 - ▶ If $m_h^* = 2m_e^*$, $\mu = E_v + \frac{1}{2} E_g + \frac{3}{4} k_B T \ln 2$ ✓
 - ▶ If $m_h^* = \frac{1}{2} m_e^*$, $\mu = E_v + \frac{1}{2} E_g - \frac{3}{4} k_B T \ln 2$ ✓
- Effective mass depends on curvature and $m_h^* = m_e^*$ when VB and CB has same curvature ✓

Since in an intrinsic semiconductor, electron and hole concentrations are equal, let me equate the 2 terms. Electron concentration is which is equal to the hole concentration. We can write

$$2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{(\mu - E_c)/k_B T} = 2 \left(\frac{m_h^* k_B T}{2\pi \hbar^2} \right)^{3/2} e^{(E_v - \mu)/k_B T}$$

$$\Rightarrow e^{(\mu - E_c + \mu - E_v)/k_B T} = \left(\frac{m_h^*}{m_e^*} \right)^{3/2}$$

$$\Rightarrow \frac{2\mu - (E_v - E_c)}{k_B T} = \frac{3}{2} \ln \left(\frac{m_h^*}{m_e^*} \right)$$

Now E_c is the energy at conduction band minimum- E_v , which is the energy at the valance band maximum. This is equal to the band gap, which implies that $E_c = E_g + E_v$ replacing this in this equation, we get

$$2\mu - (E_v - E_g + E_v) = \frac{3}{2} k_B T \ln \left(\frac{m_h^*}{m_e^*} \right)$$

$$\Rightarrow \mu = E_v + \frac{1}{2} E_g + \frac{3}{4} k_B T \ln \left(\frac{m_h^*}{m_e^*} \right)$$

Thus, at $T = 0$, $\mu = E_v + \frac{1}{2}E_g$. That is, μ lies in the middle of the band gap if the electron and hole has equal effective mass.

That is $m_n^* = m_p^*$ then the temperature dependent R is always equals to 0 then μ always stays in the middle of the band gap at any temperature. Otherwise if $m_n^* \neq m_p^*$ then μ depends on temperature. As a result, new shifts from the middle of the band gap at finite temperature as shown here. Remember that effective mass depends on curvature and the electron and whole electric mass will be equal only when the valence band and conduction band have the same curvature.

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Summary

- Law of mass action: $np = 4 \left(\frac{k_B T}{2\pi \hbar^2} \right)^3 (m_e^* m_h^*)^{3/2} e^{-E_g/k_B T}$
- Law of mass action: $np = n_i^2 = p_i^2$
- $n_i = p_i = 2 \left(\frac{k_B T}{2\pi \hbar^2} \right)^{3/2} (m_e^* m_h^*)^{3/4} e^{-E_g/2k_B T}$

- $\sigma = n_i e \mu_e + p_i e \mu_h$, μ depends on T by a modest power law
- Temperature dependence of conductivity dominated by temperature dependence of carrier concentration: $\sigma \propto e^{-E_g/2k_B T}$

Let me summarize the most important points discussed in this lecture, the law of mass action is a relation between the concentration of electrons and holes in a semiconductor under thermal equilibrium. Note that n is the electron concentration and E is the whole concentration. This expression is true for a pure or intrinsic as well as an interior or extrinsic semiconductor. In a semiconductor n times p is always equal to the square of the intrinsic carrier concentration.

This is the expression for intrinsic carrier concentration note that intrinsic concentration depends on T power 3 by 2, and it also has exponential temperature dependence. The exponential part dominates, and we get a straight line by plotting the log of n_i versus $1/T$. This is the expression for electrical conductivity. Note that σ depends on linear concentration as well as mobility now mobility depends on T by a modest power law.

As a result, the temperature dependence of conductivity is dominated by the temperature dependence of area concentration and if we plot $\log \Sigma$ versus $1/T$, we get a straight line like this. Thank you