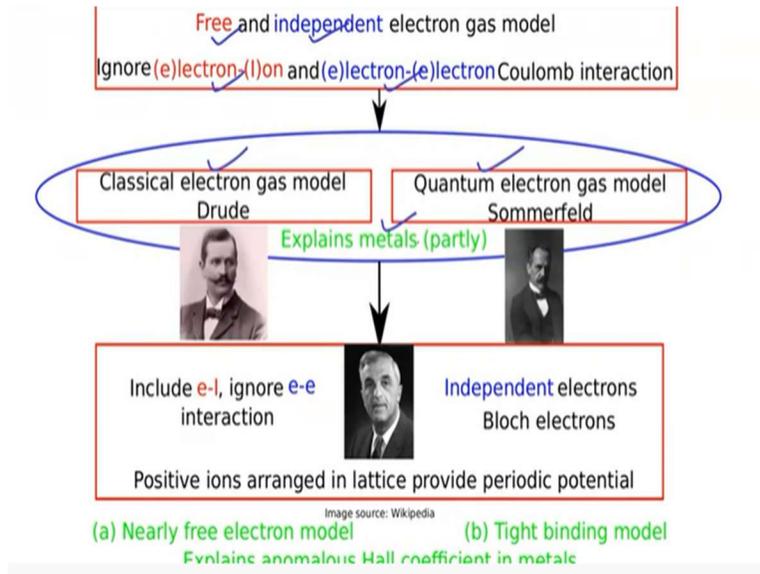


**Electronic Properties of the Materials: Computational Approach**  
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**Module No # 08**  
**Lecture No # 37**  
**Semiconductors: Part 1**

hello friends, so far I have many discussed metals although I have explained the origin of semiconductors and insulators I have not discussed them in detail in this lecture. I am going to start our discussion on semiconductors and insulators.

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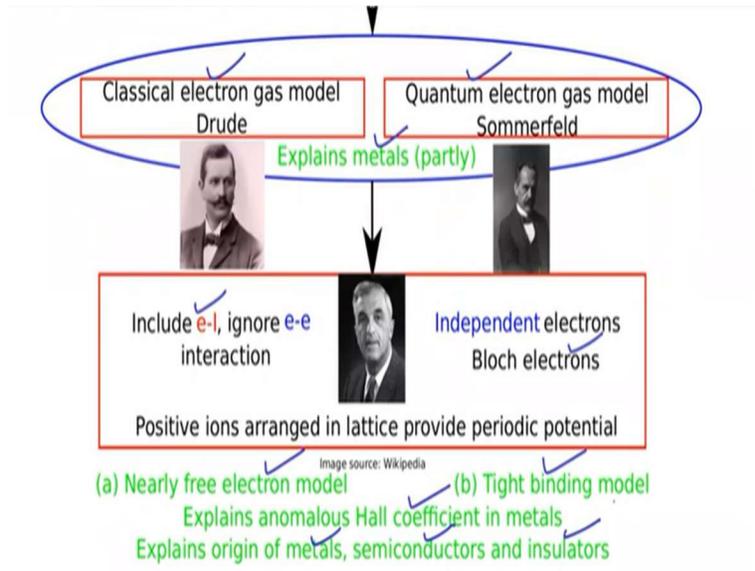


Before starting our discussion on semiconductors and insulators let me summarize what we have done, so far we started with a free and independent electron gas model. The model considers core electrons to remain attached to the nucleus, forming heavy immobile atomic cores by valence electrons forming an ocean of electrons moving around freely and taking part in the electronic transport process in solids.

The electron gas model ignores electron ion and electron Coulomb interaction this is known as the free and independent electron gas model. We discuss both the classical and Quantum model, although free and independent electron gas models can explain metals to some extent. There are

some failures most notable being anomalous all coefficient in metals, moreover free and independent electron gas model fails to explain the existence of semiconductors and insulators.

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Then we included electron ion interaction while solving the time-independent Schrodinger equation, and the ions are arranged in a lattice and provide some periodic potential to electrons such electrons are known as block electrons. We treated block electrons using 2 different models, a nearly free electron model and b tight binding model and found a satisfactory explanation for anomalous all coefficients in metals. We also got some idea about the origin of metals semiconductors and insulators. Now we are going to learn in detail about semiconductors and insulators.

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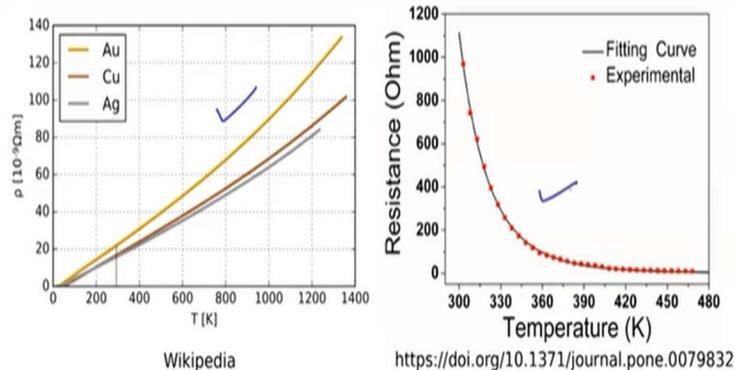
## Classification of materials based on electrical conductivity

Carrier concentration (cm <sup>-3</sup> )	Material	Conductivity (Ω <sup>-1</sup> cm <sup>-1</sup> ) <span style="font-size: small; color: blue;">Room temperature</span>
8.5 × 10 <sup>22</sup>	Metal Cu	5.9 × 10 <sup>5</sup>
1.5 × 10 <sup>10</sup> 2.4 × 10 <sup>13</sup>	Semiconductor Si Ge	1 × 10 <sup>1</sup> 2 × 10 <sup>1</sup>
Negligible	Insulator Diamond	2 × 10 <sup>-18</sup>

In terms of electrical conductivity, materials can be classified as metals, semiconductors, and insulators. At room temperature, metals have very high electrical conductivity, semiconductors have medium electrical conductivity, and insulators have very low electrical conductivity. Note that we are talking about electrical conductivity at room temperature because at very low temperatures, both semiconductors and insulators have very low conductivity.

Conductivity differs by several orders of magnitude because carrier concentration also differs by several orders of magnitude at room temperature.

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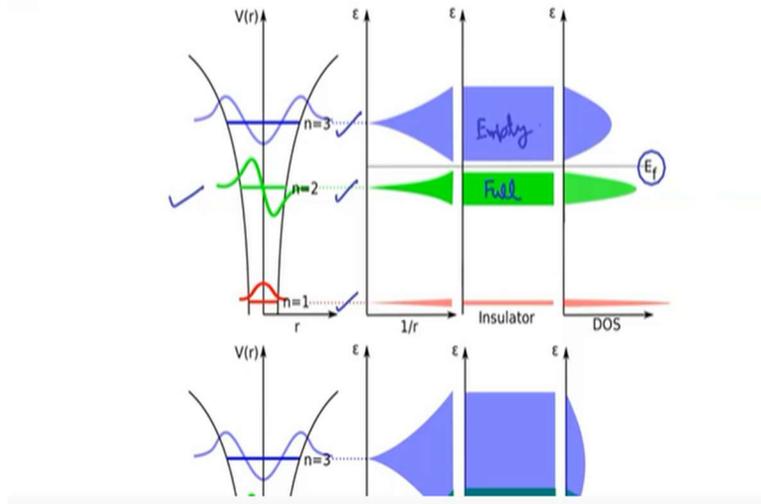


- Resistivity of metals increase with increasing temperature
- Resistivity of semiconductors decrease with increasing temperature

Not only do the resistivity in metals and semiconductors differ by several orders of the magnitude temperature dependence of resistivity also has the opposite trend. For example, the resistivity of metals increases with increasing temperature as shown in this plot. On the other hand resistivity of semiconductors decreases with increasing temperature as shown in this plot.

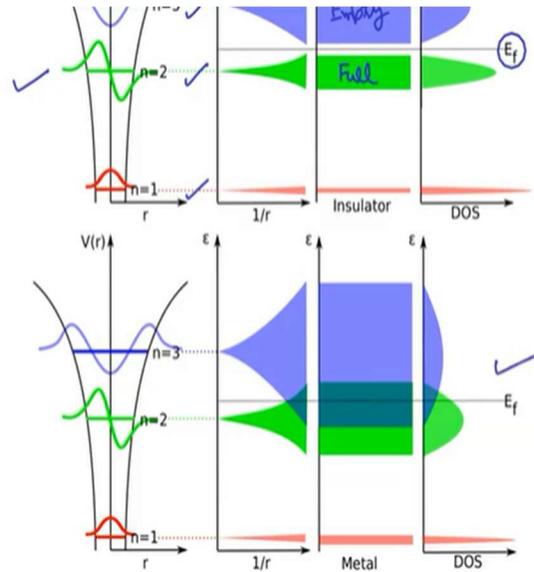
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### Band formation due to overlap of atomic orbitals



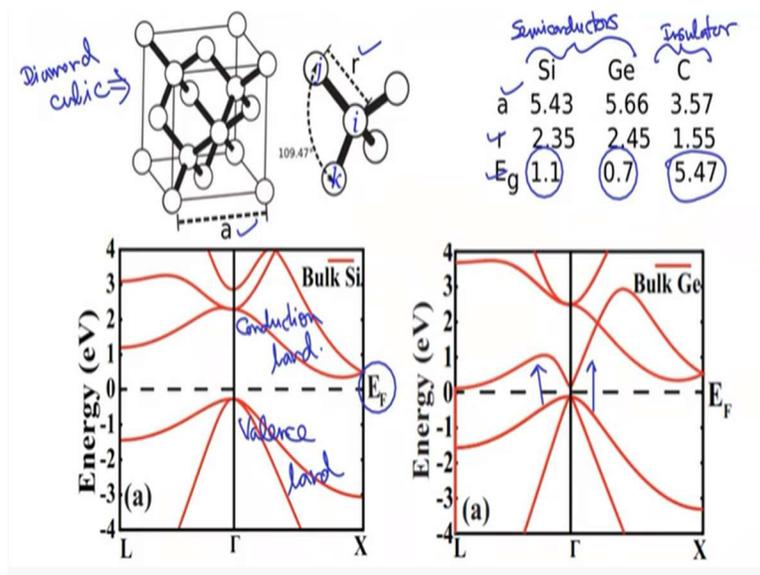
This is a simple cartoon showing the origin of metals and insulators starting from isolated atoms these are the atomic energy levels in an isolated atom. If you bring the isolated atoms close to each other energy bands start to form if the Fermi energy is here and the energy bands are not overlapping we get an insulator. Because the green band is full and the blue band is completely empty.

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On the other hand if 2 bands are overlapping, then both the bands are partially occupied leading to a metal.

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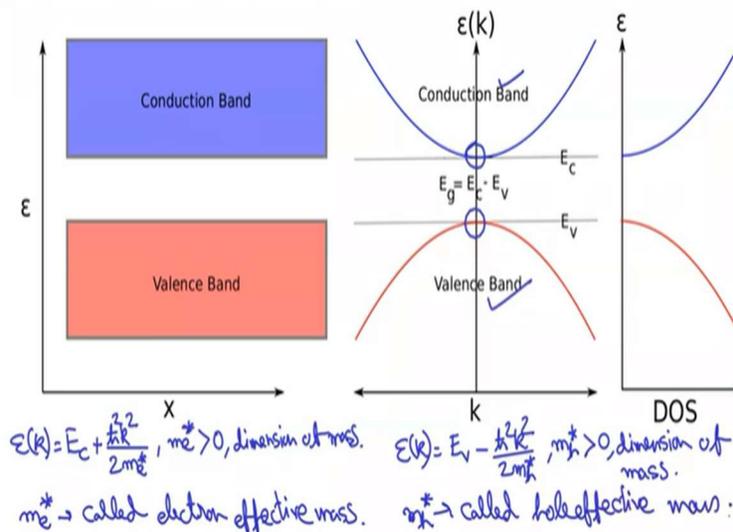


Let us now discuss the electronic band structure of 2 of the most famous semiconductors silicon and germanium. Both of them have a diamond cubic crystal structure,  $a$ ; is the lattice parameter  $R$  is the bond length and  $E_g$  is the band Gap. Note that at 0 Kelvin all the states below Fermi energy are occupied and all the states above Fermi energy are vacant. Thus at zero Kelvin semiconductors are insulators occupied levels are called valence band and vacant levels are called conduction band.

At that finite temperature, some electrons are excited from the valence to the conduction band. As a result, both valence and conduction bands are partially occupied such that electronic transport can take place. Note that electrons can be excited from the valence to conduction band, in the case of silicon and germanium because they have a small band gap of 1.1 electron volt and 0.7 electron volt.

Silicon and germanium are semiconductors however if you take diamond an allotrope of carbon, it has a band gap of 5.47 electron volts. Thus you need very high energy to excite an electron from the valence to the conduction band. As a result, diamond is an insulator the most important part of the band structure is the valence band maximum and conduction band minimum often the valence and conduction band edges are approximated by a parabola.

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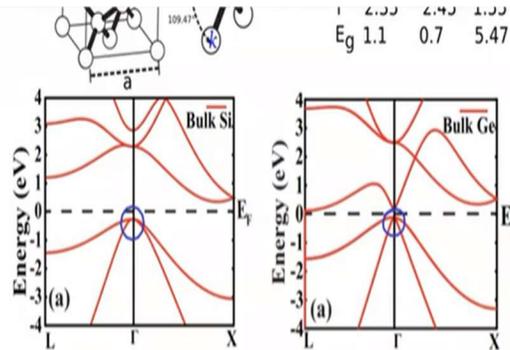
Let me explain what I mean by parabolic approximation, this is the conduction band and  $E_c$  is the energy at the conduction band minimum. We assume that energy increases quadratically in the conduction band, that energy is equal to energy at the conduction and minimum plus. As we go away from the conduction band minimum the energy is increasing quadratically as a function of  $k$ . here  $m_e^*$  is a number which is greater than 0 and it has a dimension of mass.

Similarly in the valence band  $E_v$  is the energy at valence band maximum and we assume that energy is decreasing quadratically. As we go away from the maximum point that energy is equal

to energy at the valence band maximum and it decreases quadratically as a function of  $K$  as we go away from the maximum point. Here image start is greater than 0 and it has a dimension of mass.

Since at the bottom of the conduction band, we have electron-like charged carriers  $m_e^*$  is called electron effective mass. Since we have hole-like charge carriers at the top of the valence band  $m_h^*$  is called the hole effective mass.

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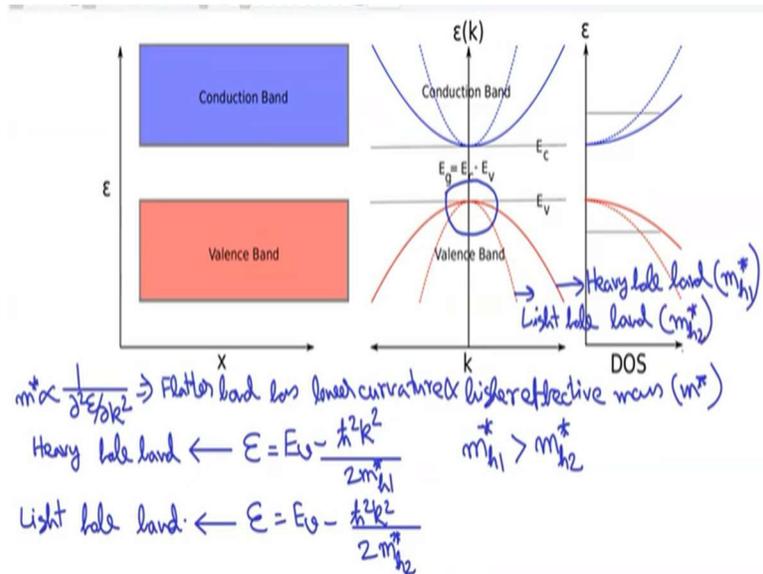


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- Two bands at the maximum point of valence band, one flatter than the other
- Curvatures of VBM and CBM are not same – how to model?

So I have told you about the parabolic approximation let us now revisit the electronic band structure of silicon and germanium. Note that the actual band structure is quite complicated for example there are 2 bands at the valence band edge of both silicon and germanium. One of the bands is flatter than the other moreover valence and conduction band also has a different curvature. How do we account for all such complications observed in actual band structures of a semiconductor? All the complications in the actual band structure are included in the term effective mass.

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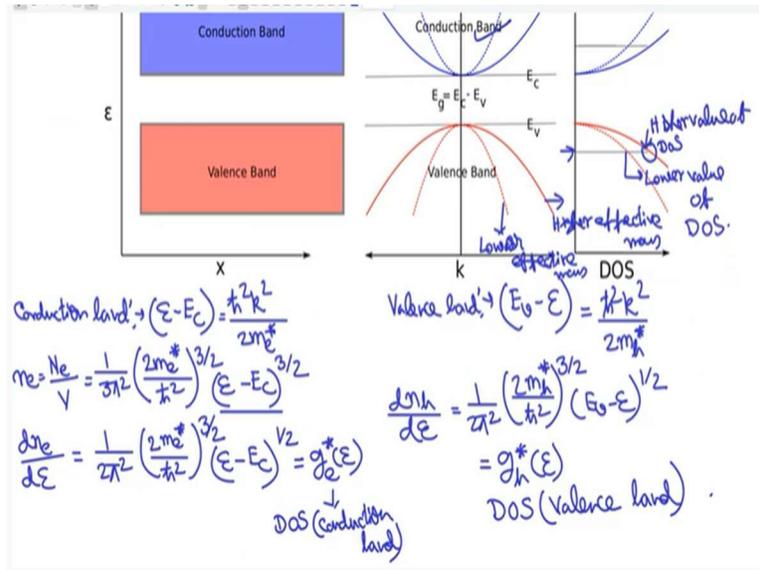


We know that effective mass  $m^*$  is inversely proportional to the curvature which implies that a flatter band has lower curvature and higher effective mass. For example, the band shown by the solid line has a higher effective mass and the band shown by the dotted line has a smaller effective mass. Thus; even if we have 2 degenerate bands at a  $k$  point we can model by using 2 different values of effective mass.

For example, take the case of degenerate valence bands as shown here, we can write,  $e = E_v - \hbar^2 k^2 / 2m_{h1}$  for one of them and  $e = E_v - \hbar^2 k^2 / 2m_{h2}$  for the other one. We get  $m_{h1}$  to be bigger than  $m_{h2}$  that means the effective mass of one band is higher than the effective mass of the other band. In that case, this is known as the heavy hole band and the other one is known as light hole band.

This is the heavy hole band having a higher value of the effective mass and this one is the light hole band having a smaller value of the effective mass. We already know that effective mass is related to the curvature of the band. As a result, a flatter band has a higher effective mass. Let us see how it is manifested in the density of states plots?

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Let us take the conduction band and write the energy dispersion relation  $e - E_C$  where  $E_C$  is the conduction band minimum =  $\hbar^2 k^2 / 2m_e^*$ . Now  $m_e^*$  is equal to the number of electrons per unit volume which is equal to  $1 / 3\pi^2$ . Let  $m_e^*$  be divided by  $\hbar^2$  to the power  $3/2$   $(E - E_C)^{3/2}$  this expression is very similar to the case of free electrons.

We are just writing  $e - E_C$  in place of  $e$  in this case. Now we calculate the first derivative of any with respect to energy which is equal to  $1 / 2\pi^2 \cdot 2m_e^* / \hbar^2$  divided by  $\hbar^2$  to the power  $3/2$   $(E - E_C)^{1/2}$  and this is equal to the density of states in the conduction band. Similarly for the valence band we can write the energy dispersion as  $E_V - e$  where  $E_V$  is the valence band maximum is equal to  $\hbar^2 k^2 / 2m_h^*$ .

And we can write the density of States as  $b_n \cdot h \cdot d = 1 / 2\pi^2 \cdot 2m_h^* / \hbar^2$  divided by  $\hbar^2$  to the power  $3/2$   $(E_v - e)^{1/2}$  this is equal to the density of states for the valence band. Thus if a band has a higher effective mass it has a higher density of states at given energy than compared to a band having a lower effective mass. For example, the band shown by the solid line has a higher effective mass. And if we take this energy, then this band has a higher density of states than compared to this band which has a lower effective mass and lower value of density of states.

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## More about effective mass

- An electron put in a periodic potential respond to applied field as if it has a mass of  $m^*$ 
  - ▶  $m^*$  can be greater than or less than free electron mass  $m$
  - ▶  $m^*$  can even be negative
- This is related to Bragg reflection due to the periodic potential
- Momentum of electron changes by,
  - ▶ Momentum transfer from external field
  - ▶ Momentum transfer from lattice (Bragg reflection)
- Near zone boundary, although  $k \uparrow$  by  $\Delta k$  due to applied field, Bragg reflection causes overall  $\downarrow$  of forward momentum  $\Rightarrow m^*$  is negative
- Mobility: magnitude of drift velocity per unit electric field  $\Rightarrow \mu = \frac{|v|}{E}$

We have found an important parameter effective mass, when an electron is put in a periodic potential it responds to applied field as if it has a mass of  $m^*$ .  $m^*$  can be greater than or less than the free electron mass  $m$ .  $m^*$  can even be negative this is related to Bragg reflection due to the periodic potential. Momentum of an electron changes due to 2 things, number one momentum transfer from the external field number 2 momentum transfer from the lattice, which happens due to the Bragg reflection.

For example consider an electron having wave vector near the zone boundary, although  $k$  increases by an amount  $\Delta k$  due to the applied field Bragg reflection causes an overall decrease of the forward momentum. Thus in this region,  $m^*$  turns out to be negative.

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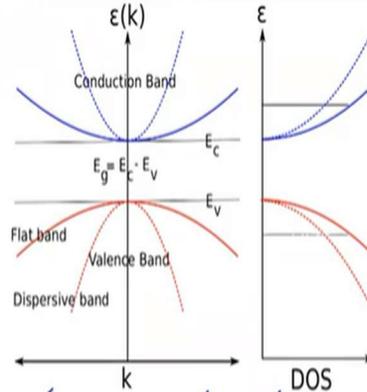
- ▶  $m^*$  can be greater than or less than free electron mass  $m$
- ▶  $m^*$  can even be negative
- This is related to Bragg reflection due to the periodic potential
- Momentum of electron changes by,
  - ▶ Momentum transfer from external field
  - ▶ Momentum transfer from lattice (Bragg reflection)
- Near zone boundary, although  $k \uparrow$  by  $\Delta k$  due to applied field, Bragg reflection causes overall  $\downarrow$  of forward momentum  $\Rightarrow m^*$  is negative
- Mobility: magnitude of drift velocity per unit electric field  $\Rightarrow \mu = \frac{|v|}{E}$
- Electrical conductivity  $\sigma = (n_e e \mu_e + n_h e \mu_h)$
- Since drift velocity  $v = \frac{qE\tau}{m} \Rightarrow \mu_e = \frac{e\tau_e}{m_e^*}$  and  $\mu_h = \frac{e\tau_h}{m_h^*}$
- Charge carriers travel faster if effective mass is smaller and vice versa

Let us try to understand the effect of  $m^*$  from a practical point of view in a semiconductor for that we need to know about mobility which is an important parameter in a semiconductor. Mobility is defined as the magnitude of drift velocity per unit electric field that is  $\mu$  equal to the magnitude of drift velocity divided by the electric field. Electrical conductivity is proportional to the mobility and electrical conductivity is a sum of electron and hole contribution.

$\sigma = n_e e \mu_e + n_h e \mu_h$  where  $n_e$  and  $n_h$  are electron and hole concentration and  $\mu_e$  and  $\mu_h$  are electron and hole mobility. Note that mobility is defined as positive for both electrons and holes although their drift velocity is opposite. Comparing with the drift velocity of free electron given by  $v = \frac{qE\tau}{m}$ . From this equation we can write  $\mu_e = \frac{e\tau_e}{m_e^*}$  and  $\mu_h = \frac{e\tau_h}{m_h^*}$ .

Thus mobility is inversely proportional to the effective mass, so we can conclude that charge carriers travel faster if the effective mass is smaller than vice versa.

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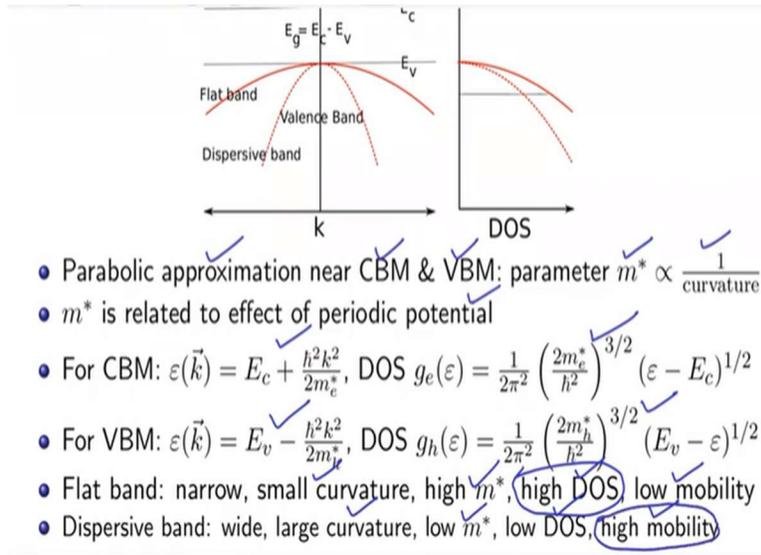


- Parabolic approximation near CBM & VBM: parameter  $m^* \propto \frac{1}{\text{curvature}}$
- $m^*$  is related to effect of periodic potential
- For CBM:  $\varepsilon(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_e^*}$ , DOS  $g_e(\varepsilon) = \frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} (\varepsilon - E_c)^{1/2}$

Let me summarize the most important concepts learned in this lecture. Conduction band minimum abbreviated as CBM and valence band maximum abbreviated as VBM are the 2 most important parts of the band structure as carriers in DBM and CBM take part in the electronic transport process. Often the band structure near VBM and CBM are approximated by parabolic approximation.

To apply parabolic approximation we need to know the parameter effective mass or  $m^*$ , which is inversely proportional to the curvature of VBM or CBM. We have seen that  $m^*$  is related to the effect of periodic potential this is the parabolic approximation near CBM and this is the expression for density of states of the conduction band.

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Similarly, this is the parabolic approximation corresponding to the VBM and this is the expression for the density of states of the valence band. Note that the density of states is proportional to the effective mass to the power 3 by 2 that is higher  $m^*$  implies a higher density of states. Just by looking at the band structure, we can say many things qualitatively. For example, narrow flat bands have small curvature as a result effective mass is high, which implies a high density of states and low mobility.

On the other hand, wide dispersive bands have large curvature as a result effective mass is low which implies a low density of states and high mobility. Note that we would like to have a semiconductor with a high density of states because a high density of states ensures high carrier concentration and high mobility.