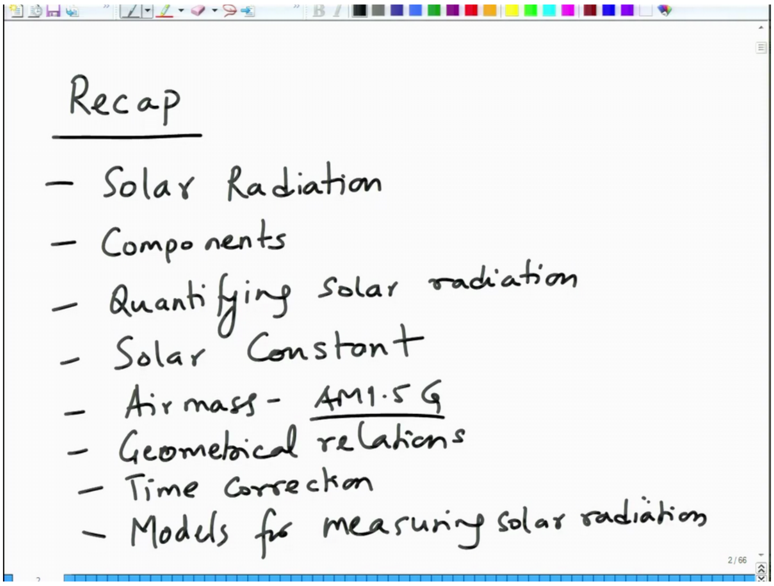
Solar Photovoltaics: Principles, Technologies and Materials
Prof. Ashish Garg
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture - 07
Introduction to Band Theory

(Refer Slide Time: 00:27)



Recap

- Solar Radiation
- Components
- Quantifying solar radiation
- Solar Constant
- Airmass - AM1.5 G
- Geometrical relations
- Time Correction
- Models for measuring solar radiation

So, welcome to this lecture number-7 of Solar Photovoltaics-Principles, Technologies and Materials. So, let us just recap the past few lectures. In the past few lectures, we talked about solar radiation.

Basically, what are the components of solar radiation, how do we quantify it, and then we looked at for quantification we require geometrical relation, we require first of all the energy that reaches the outside layer of the earth. So, we can say solar we define solar constant basically, leading to so extra terrestrial radiation falling on the surface of earth.

And then we defined air mass, which means whatever energy is coming on the outside, when it reaches earth surface, how much absorption does it go, and based on the absorption which is coming at, because sun ray does not always come at zenith, it always it is because the because the movement of sun the radiation undergoes different lengths of absorption in the atmosphere. As a result you need to define air mass. So, average air mass is 1.5 G, this is what is average intensity, when we characterize a solar cell for the char averaging for the whole day.

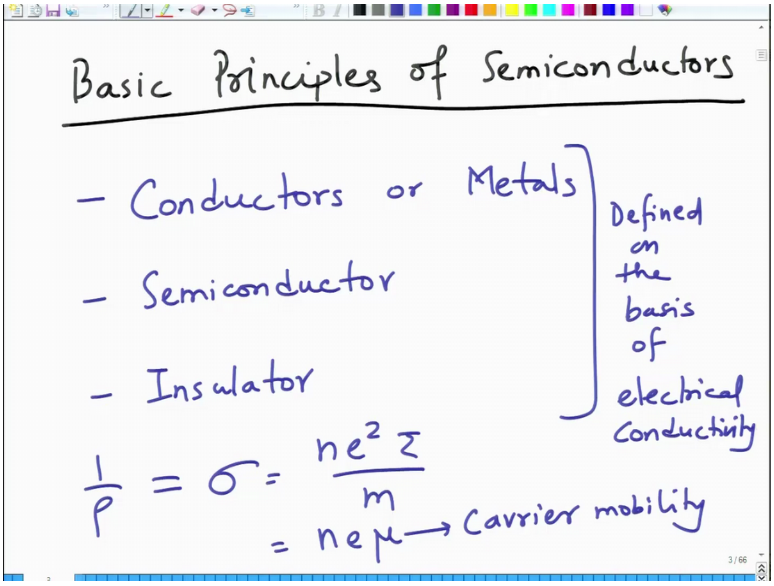
And then we looked at the geometrical relationships, so because solar panels are not horizontal on the surface, they are always at certain angle. And hence they make certain angle to the sun beam. And in order to calculate those angles, you need to know geometrical relations. So, we looked at things like zenith angle, solar altitude angle, solar azimuthal angle, and so on and so forth.

And then we also defined various time corrections. And time corrections together with geometrical relations give you rather accurate estimate of the angle at which angle and the time at which the radiation is coming, and falling on the surface. And then we looked at various model for measuring solar radiation.

So, all of this makes a complete sort of study of how do you measure the solar radiation falling on a surface at a given location at a given time of the year. So, all of this is required to, so it is not an very in great detail, because it is just 5 half an hour lecture what material.

However, if you wanted to go in to details, I had given you references such as principles of such as solar energy by Sukhatme and Nayak. Principle of solar energy engineering by Kalogirou, these are good books which go in to details of solar radiation measurement.

(Refer Slide Time: 03:40)



Basic Principles of Semiconductors

- Conductors or Metals
- Semiconductor
- Insulator

Defined on the basis of electrical conductivity

$$\frac{1}{\rho} = \sigma = \frac{ne^2\tau}{m}$$

$$= ne\mu \rightarrow \text{Carrier mobility}$$

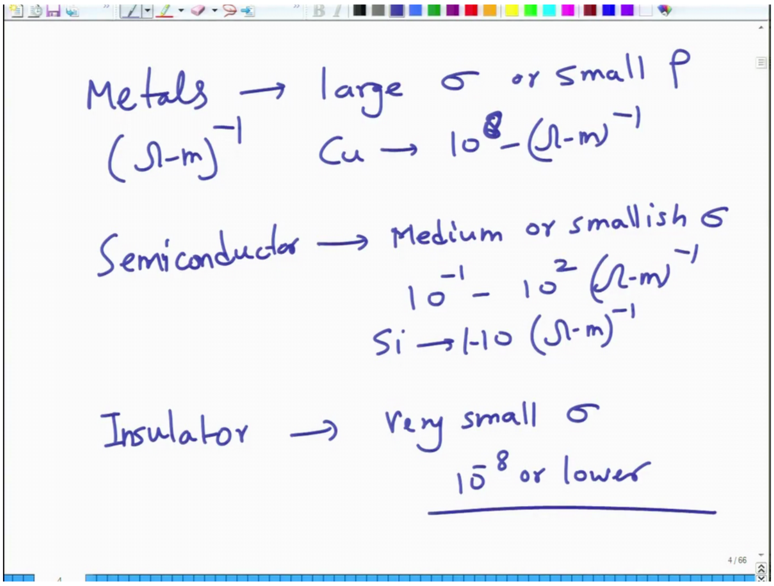
So, now we will get into learning the fundamentals of semiconductors, which are basically on the core of photovoltaics. So, we will leak look at some basic principles of semiconductors.

Now, the semiconductor as a name itself suggest is semiconductor, it is not completely conducting material, based on the electrical properties of material materials are defined three categories. So, the first type of materials is called as conductors or you can say metals, which of high electronic conductivity electrical conductivity. And then we have semiconductor, and then we have insulator ok.

And the property which defines these distinction is basically you can say defined on the basis of electrical conductivity, which is written as sigma is equal to n e square tau divided by m ok, where n is the carrier concentration, e is the electronic mass or carrier mass, tau is the relaxation time, and then m is the mass of the carrier. You can also write this equation as n e mu, where mu is the carrier sorry just spell it right carrier mobility ok. So, you can see that mu will be equal to e tau divided by m.

So, this equation gives you the conductivity, which is inverse of resistivity rho. So, essentially this is electronic conductivity, and based on the value of this conductivity we defined a material as a semiconductor or as a insulator or as a metal.

(Refer Slide Time: 06:10)



Metals → large σ or small ρ

$(\Omega\text{-m})^{-1}$ Cu → 10^{8} – $(\Omega\text{-m})^{-1}$

Semiconductor → Medium or smallish σ

10^{-1} – 10^{2} $(\Omega\text{-m})^{-1}$

Si → 1-10 $(\Omega\text{-m})^{-1}$

Insulator → very small σ

10^{-8} or lower

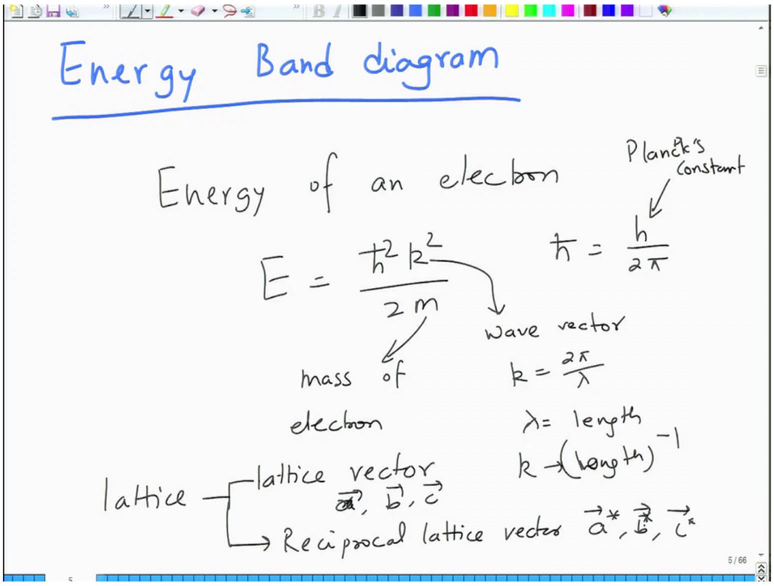
So, let me so the distinction between these three is it takes a value of about let us say, let me give you certain values so semiconductors would be so the metal should be the ones, they will have large sigma or you can say a small rho.

So, typically metal would have conductivity. So, metals conductivity is of the order of you can say ohm metre inverse. So, something like you know; something like copper would have conductivity of I can 10 to power 6 to 10 to the power 8 ohm metre inverse something like that ok, within the range you know minus 8 (Refer Time: 6:50) you can say the resistivity would be 10 to the power minus 8 inverse ohm meter.

Semiconductor on the other hand will have electrical conductivity of somewhere between suitable have medium or you can say smallish sigma. So, this would vary between anywhere from 10 to the power minus 1 to 10 to the power plus 3 or 3 ohm metre inverse.

So, silicon would have a value of about, so for example silicon will have a value of about 10 to the power 10 ohm metre 1 to 10 ohm metre inverse. If you look an insulator insulator will have very small conductivity. So, essentially you are looking at conductivity of the order of 10 to the power minus 8 or lower. So, in this category you will have most of the compounds materials oxides, nitride, carbides many oxides are insulating. So, they will all be in this category.

(Refer Slide Time: 08:27)



Energy Band diagram

Energy of an electron

$$E = \frac{\hbar^2 k^2}{2m}$$

wave vector

mass of electron

Planck's Constant

$$\hbar = \frac{h}{2\pi}$$

$$k = \frac{2\pi}{\lambda}$$

λ = length

$k \rightarrow (\text{length})^{-1}$

lattice → lattice vector $\vec{a}, \vec{b}, \vec{c}$

→ Reciprocal lattice vector $\vec{a}^*, \vec{b}^*, \vec{c}^*$

Now, we will come back to this later on, but first we would like to see what is that which makes tells you the difference between a metal, semiconductor, and insulator. And this is basically on the basis of energy band diagram.

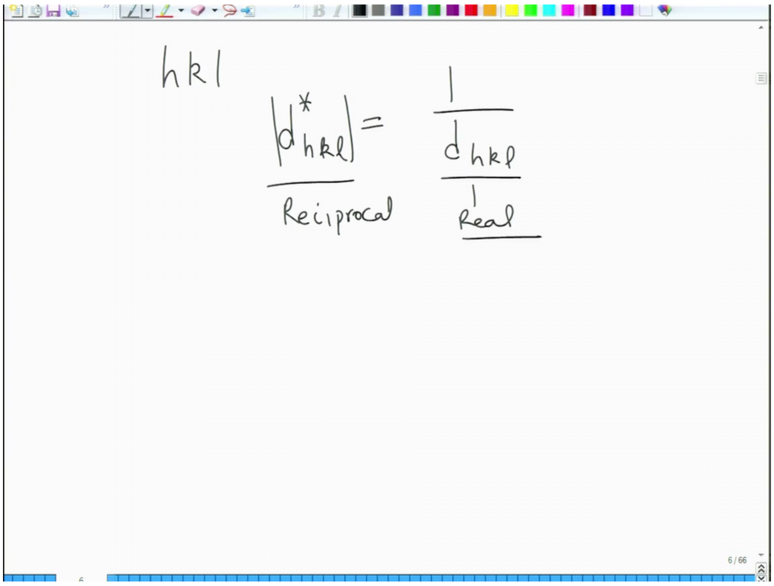
So, the energy band diagrams, because I mean we know the from the fundamentals of quantum mechanics that energy is quantized, and energy of a energy of a electron is can be written as so energy of an electron is written as E is equal to h square h cross square k square divided by 2 m, where h cross is equal to h divided by 2 pi, where h is plank's constant ok.

And k here is called as wave vector. Say k is essentially if you write k k is nothing but 2 pi divided by lambda. So, it is inverse it is inversely proportional to the wavelength. So, lambdas units is if lambda units are in length, then k's unit are in reciprocal of length, which means if lambda represents what we call as real space, k represent what we call as reciprocal space ok. And m is nothing but mass of electron here.

Now, in terms of lattice also we define what we call as lattice vector, which could be you know x a, b, c ok. But, lattice also has a reciprocal lattice vector, which is a star, b star, and c star. And the magnitude of this reciprocal lattice vector is inversely proportional to the magnitude of real lattice vector.

So, basically what you do is that you take a lattice point, and corresponding to that lattice point you have a reciprocal lattice points; and the reciprocal lattice and the distance from the origin to that reciprocal lattice point is nothing but inversely proportional to the to the real lattice vector ok.

(Refer Slide Time: 10:57)



hkl

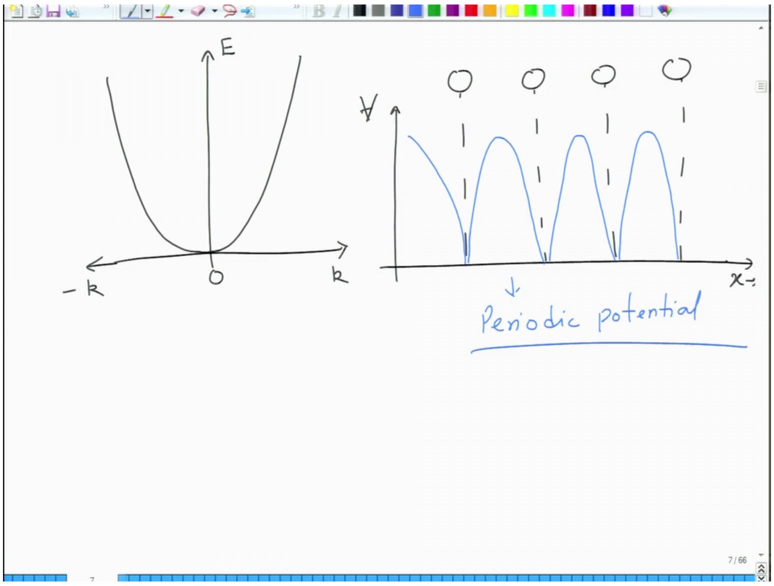
$$|d^*_{hkl}| = \frac{1}{d_{hkl}}$$

Reciprocal

Real

So, basically we say that for a given h k l, if you have d star h k l, which is the reciprocal lattice vector length that is equal to so this is reciprocal and this is real ok. This is the difference that you have.

(Refer Slide Time: 11:23)



Now, what happens is that when you plot this E versus k for a single electron it is like this. So, we have this is E, and this is what is k ok. So, it goes from so k can it is a wave vector, it can go to minus k also, it can take both the values plus and minus k, it makes a parabolic shape ok.

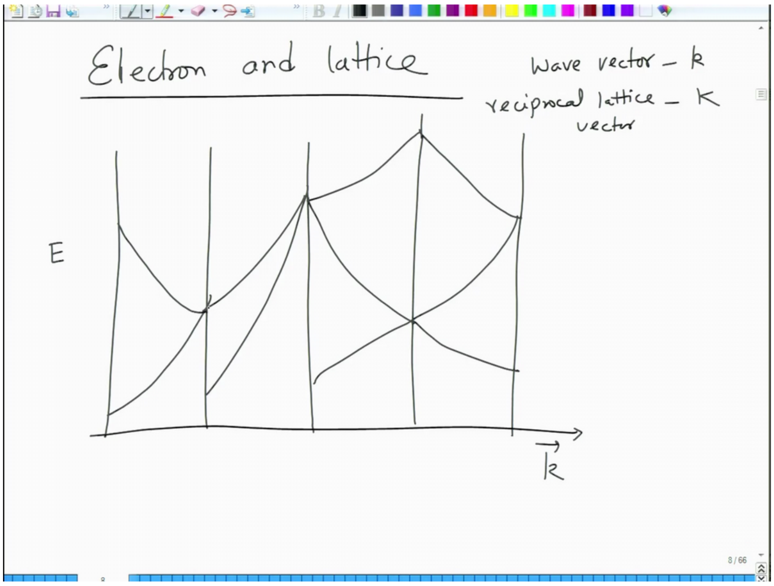
Now, there are various approximations of electron being confined, electron being present in a material. So, electron can be loosely bound, electron can be very strongly bound, so that that defines the value of potential that is present in the lattice.

So, we know that if you have a lattice like this ok. So, if you just take a one dimensional model of lattice, then you can see that if you plot the periodic potential, the potential in the lattice is basically the surface potential would be something like this here I plot it.

If I take this as the, so this is nothing but you can say the potential, I do not know potential can be written as v, and this can be taken as distance x. And here the potential varies as something like this. So, this is you can say it is nothing but periodic potential. So, you are going to have periodic potential in a periodic lattice ok. And if you do not have a periodic lattice, you will have a periodic potential which means the potential will not also have a periodicity.

Now, based on; now when you and this is the energy versus wave vector for a single electron in a material, you do not have single electron, you have multiple electrons. And you have these all the lattice sides will have this kind of periodic potential.

(Refer Slide Time: 13:44)



So, based on the interaction of electron with the lattice, when the electron interacts with the lattice, then when you plot E k for a given lattice. So, when you can say electron, and lattice when you take together. So, this is this has whole theory behind it, chronic, penny model, and so on and so forth.

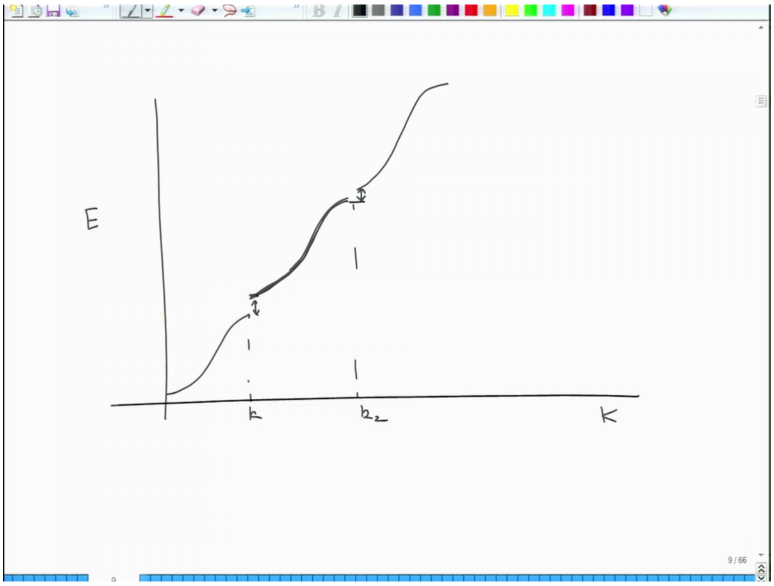
We do not have time to discuss all that, but when the electron is present in a lattice it undergoes interaction with the lattice. And based on that you can plot, the energy of electron as a function of, now this wave vector of electron that is a small k, and reciprocal lattice vector capital K, they are related to each other ok, because both of them reciprocal in space you can relate them to each other.

So, essentially what you do is that you plot the energy of electron in the reciprocal space. When you plot the reciprocal, when you plot this energy of electron in the reciprocal space, you will have and these vary from one plane of reciprocal lattice or one lattice one boundary of reciprocal lattice from another boundary or reciprocal lattice and so on and so forth. So, they represent variety of these kind of lines ok.

So, you can have a structures, you can have this kind of curves going all over the place and so on and so forth. So, I am not drawing in particular any particular diagram, but this is how lines you will observe. Now, these are the lines which are energy versus let us say k ok.

Now, as long as these lines are connected to each other, and they are continuous, so that electron will so suppose you have electron here, when it moves it always find the finds a continuity in the energy space. There is no discontinuity in the in the energy space, we can see that although there is a discontinuity here, but you find a electrons find a continuity here. Similarly, if you travels form this energy space, it always finds a continuity here. So, as long as electron is able to find a continuity in the energy space, it will always find energy state in which it can move into.

(Refer Slide Time: 16:09)

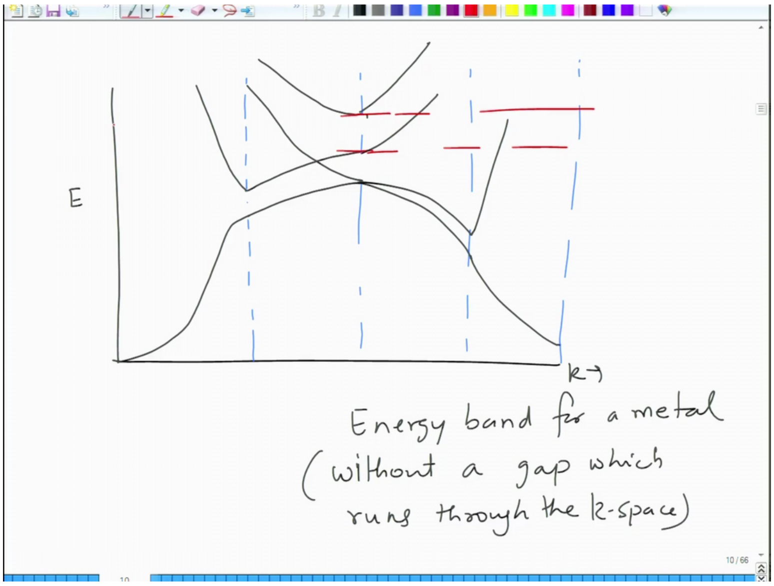


However, if they are systems for which you do not have continuity, if there are systems for which you have situations like, so if you plot E, K E versus K. And if you plot let us say you may have states in this fashion, let us say very simple diagram I will draw.

So, you may have states like if you have states like these, then so this lets say k 1, this is let us say k 2. So, if you look at without getting into this, if you look at this state, what you have here is you have a discontinuity at these k values. And if this discontinuity is can be, if this cannot be over combine by electron energy in a given system, then this is called sort of a energy gap.

So, the systems where you have these discontinuities in the energy states in the case space which have large enough, so that they cannot be crossed over by electrons; they are generally semiconducting or insulating in nature, they will have forbidding energy gap. Whereas, the systems in which energy states are continuous, they are generally called as a metal.

(Refer Slide Time: 17:26)



Energy band for a metal
(without a gap which
runs through the k-space)

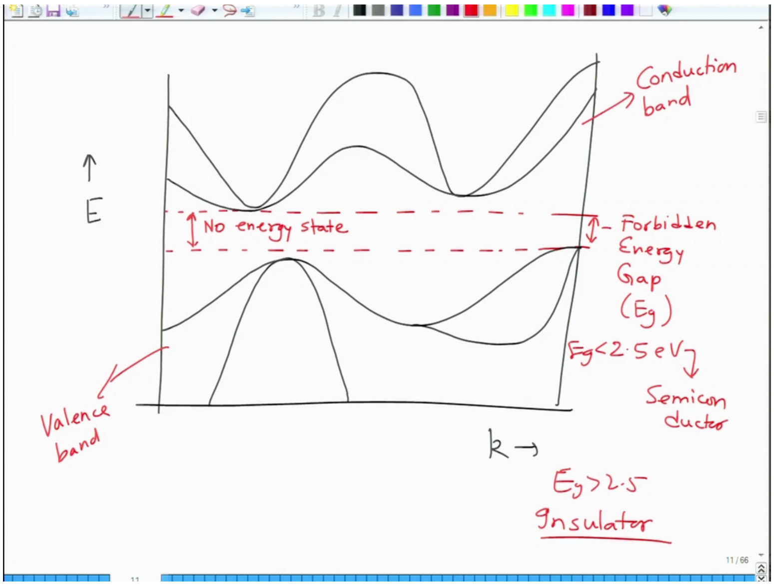
If you look at the band structure, so band structure is far more complicated than what I have drawn here. But, if you look at the band structure of a metal some, let us say so let us say this is for a given metal E. So, if I plot, so this is the first boundary of k space in the first line, let me just remove these things this is the first boundary ok.

Now, at this bound boundary, so let us say I have four of few of these regions ok. So, I can keep plotting. So, in this case closed from something like that or something like that, then let us say you have you have this energy state, then you have this energy state, this energy state continuous like this, this energy state continues like that, continues like this.

Now, you can see that although you can see that there are certain discontinuities in the energy space here, but there are certain energy states which are continuous across the energy spectrum, you have certain gaps here, you have a gap here, you have a gap here, but at the same time you always find a continuity. So, if this is this energy state is continuous, this energy state is continuous and this energy state is continuous, which provides a path between these energy states.

So, there is a connectivity in the energy states. There is no single gap which runs through the k space. So, this is sort of a energy band for a metal ok. So, this is k without a gap, which runs through the through the k space.

(Refer Slide Time: 19:44)



On the other hand if you look at semiconductor, what will happen in a semiconductor is something like this. And the same will be true for energy for the insulated also. So, for the semiconductor, you will have this E as a function of k. And this E could be something like this ok, then we have and so on and so forth.

Now, here what you see is that there are there is one region in which energy states are continuous, there is another region in which energy states are connected to each other, but there is one region where there is no energy state at all. So, you can see that, if I just connect this region, so within this region I have no energy state.

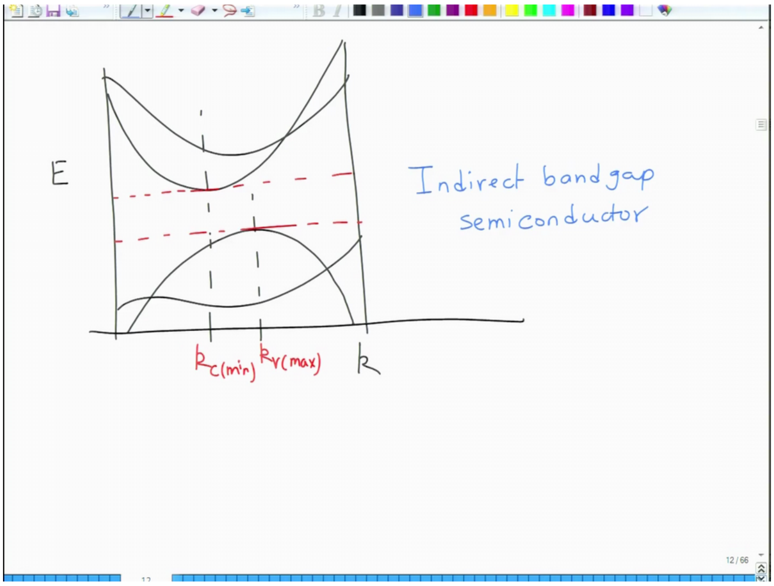
If you compare this with previous figure in the previous figure, you had no state. So, if you for example, if you say this is a gap, but some where you had a energy state, this is the energy state that is present. So, there is not a continuous region in the k space, when you do not have energy space, you always have some energy state present at certain at in the k space.

But, there is a diagram now here, where you do not have any energy state present anywhere. Now, this is what is so this is E k diagram energy versus wave vector diagram. And we see that there is a gap, and this gap is called as forbidden energy gap or the band gap. So, the lines which; the energy lines energy states which lie below this energy gap their called as, we depict them as valence band. In the lines which lie above this their called as the energy states which lie above this they are called as conduction band.

And depending upon the magnitude of this gap a material is semiconducting or insulating. So, if this energy gap is up to the free 2.5 eV. So, if Eg is then 2.5 e V, then we call it semiconductor. And if E g is greater than 2.5 e V, we call it insulator, and metals do not have a band gap ok, so metals do not have a band gap.

So, based on this configuration of E k diagram, we define so this is the distinction between a metal and semiconductor. In a metal, the energy states are continuous all across the energy all across the spectra. So, you can have variety of energy states all across the spectra, they cress cross in such a manner, so that you do not have a continuous gap across the k space. Whereas in case of semiconductors you have a gap in the k space well defined gap in the k space between the maxima and minima ok.

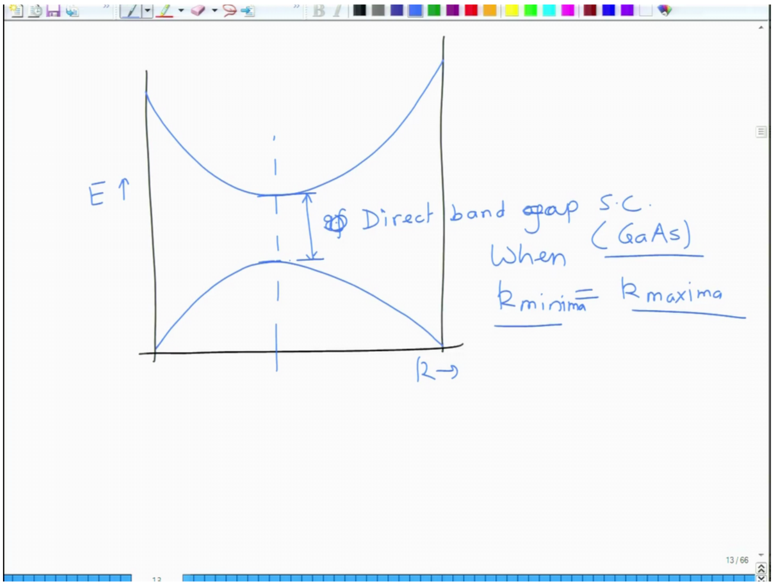
(Refer Slide Time: 23:21)



Now, depending upon the position of this maxima and minima; so now depending upon this maxima and minima I am now going to draw all the states. So, let us say we have a this is the valence band, conduction band, energy band, this is the valence band structure ok. So, valence band is something this is valence band, this is conduction band, and so on and so forth. So, this is E, this is k.

So, k is a reciprocal space. If the minima of conduction band, and a maximum of valence band do not coincide in the semi con in the k space; so, you can see they have a gap, and the gap is always with respect to maxima and minima ok. If the k you can say conduction band minima, and k with respect to valence band maxima and they do not coincide they are different, then this kind of semiconductor is called as indirect band gap semi conductor.

(Refer Slide Time: 24:43)

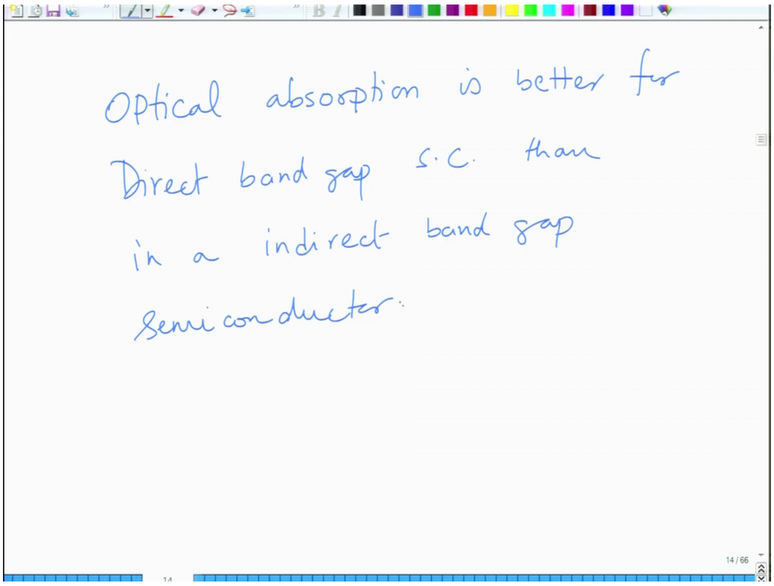


However, if you have a situation in which the energy bands are like this, so this is the minima, and your maxima also happens to be so this is the maxima. And if so this band gap is called as direct band gap semiconductor, when k minima is same as k maxima ok. There is no gap distance, there is no distance in these two k values. So, this is a this is k, this is the direct band gap semiconductor.

So, something like silicon is a indirect band gap semiconductor. And something like gallium arsenide is a direct band gap semiconductor. Now, this has profound implications in terms of optical properties, generally the light absorption is better in case of direct band gap semiconductor as compared to indirect band gap semiconductor, because light absorption you have a photon, and the photon causes a migration of electron to hole.

So, since there is no change in the k value. The absorption of light is much better in case of direct band gap semiconductor as compared to something like silicon, where k value is different. So, electron has to change its k value. So, when you excited account from valence to conduction band, it directly just does not go to valence band. It will have to change its k value corresponding to that energy level. So, you have some loss of energy here, and as a result the absorption is not very good.

(Refer Slide Time: 26:36)

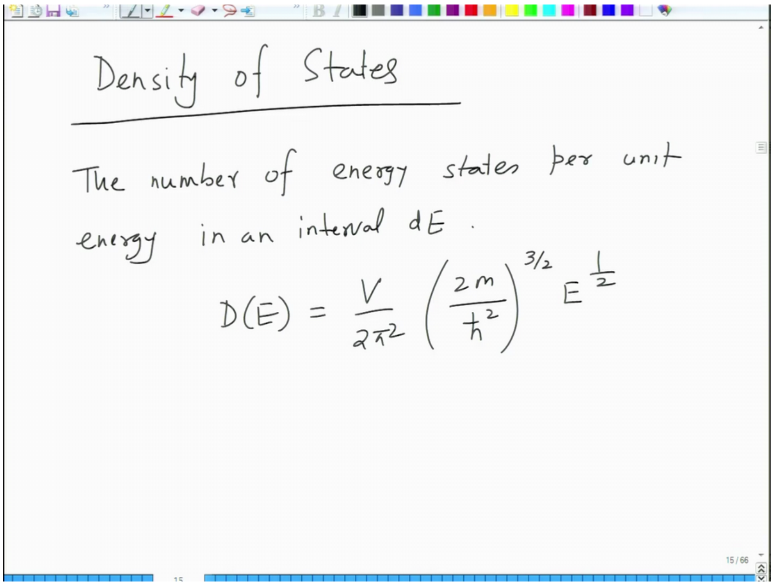


Optical absorption is better for
Direct band gap s.c. than
in a indirect band gap
semiconductor.

So, in general you can say that optical absorption is better for direct band gap semiconductor than in a ok. Now, there are lot of details in this which I have not touched upon. So, unfortunately those are not, I mean it is not possible to go through go through I mean in this short lecture series of short lectures.

There are something you need to to know along the way is something concepts of density of states, concepts of you know Fermi energy and so on and so forth. So, essentially let me just talk about the Fermi energy a little bit.

(Refer Slide Time: 27:43)



Density of States

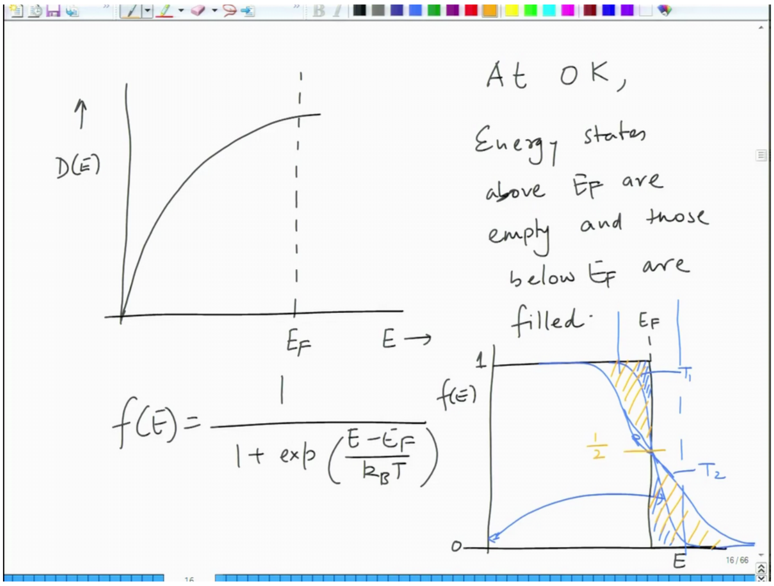
The number of energy states per unit energy in an interval dE.

$$D(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{\frac{1}{2}}$$

So, we can say what is you can begin with first density of states. So, when you have energy states in a given system, then we can define these energy states in the form of what we call as energy, density of states. Density of states, I can define as the number of energy states per unit energy in an interval d E ok. This is called as density of energy states, basically density of energy states ok.

So, how does the energy states are in a given interval. And this is we can write this as D E as V over 2 pi square. So, there is a whole analysis behind this, which I am not going to do here 2 m divided by h cross squared to the power 3 by 2 into e to the power half. So, you can do this analysis of density of states in one-dimension, two-dimension, three-dimension space.

(Refer Slide Time: 28:00)



At 0K,
Energy states above E_F are empty and those below E_F are filled.

$$f(E) = \frac{1}{1+\exp\left(\frac{E-E_F}{k_BT}\right)}$$

So, now density of states when you plot it as a function of energy, then it goes as you can see that it goes as E to the power half ok. So, D E over E to the power half. So, you can plot this as so you can see that if you have E is equal to 0, the D E will be equal to 0 as well. So, this goes as something like this right, so this is D E, and you will have E here.

Now, when the temperature increases, then what happens is that when the temperature increases, the density of states tend to show a behaviour around energy called as Fermi energy. So, this is let us say certain energy called as Fermi energy. Now, Fermi energy is generally defined by, so there something called as Fermi energy is an energy below which all the energy states are filled at 0 Kelvin ok.

So, you can say at 0 Kelvin ok. So, basically Fermi energy is defined by this Fermi director statistics, which is probability of energy occupation. So, f E is equal to 1 plus exponential of E minus E F divided by k B T. So, when you plot this Fermi data statistics, when you plot f E as a function of E at 0 Kelvin the plot is something like, this value is E F.

So, the probability of occupation is equal to 1 below E F at 0 above b F. Now, when you plot when you change the temperature, when you change the temperature this curve changes its behaviour in this fashion. So, it tends to go like this. So, this is at a temperature T 1. If you go to temperature T 2 goes like that, something like that T 2. So, it is drawn very well, but something like that ok.

So, basically what happens is that as you provide some thermal energy to the system, the electrons below E F, they get enough energy. So, this is the band in which they get thermal energy, this is the band they move around. So, when you will excited, so of course if you want to excite from energy levels which are far below E, you will have to provide a lot more thermal energy.

For conduction electron needs to be able to move into energy states above bit right, which means it must have some empty energy state surrounded, so that is not the problem in the semiconductor a. For conduction to occur, if you look at this E k diagram, electron has energy states available to move around right.

However, if you look at this situation where electron can move here, but if all these energy states are filled, where does it go? It has to go to energy states which are above. But, if it does not have enough energy to jump to the energy states, which means it cannot move around. So, you need to provide that that amount of energy.

So, essentially that is what we are saying in Fermi Dirac statistics that there is a reference energy E F below which all the energy levels are filled. So, this energy valence band maybe up to this part only, it may not coincide. So, it is just a hypothetical picture. So, when you provide some thermal energy, the energy levels the electrons which are ascending just in the vicinity of a E F, they get enough energy, so that they can go to an energy level which are available above E F.

And then there are lot many empty states around E F in which electrons can move around and conduct. As you keep increasing the temperature, more and more electron jump in, but it happens the whole thing happens in the vicinity of E F. So, the number of electrons which have left here or the number of electrons which have reached here.

Similarly, in this case number of electrons which have left in this fashion have reached here. So, this is this curve is basically around asymptotic round half ok. So, number of electrons which have moved, above E F are the same as the number of electrons, which have left below E F ok.

So, this we will continue in the next lecture ok.