# Properties of Materials (Nature and Properties of Materials: III)

**Professor Ashish Garg**

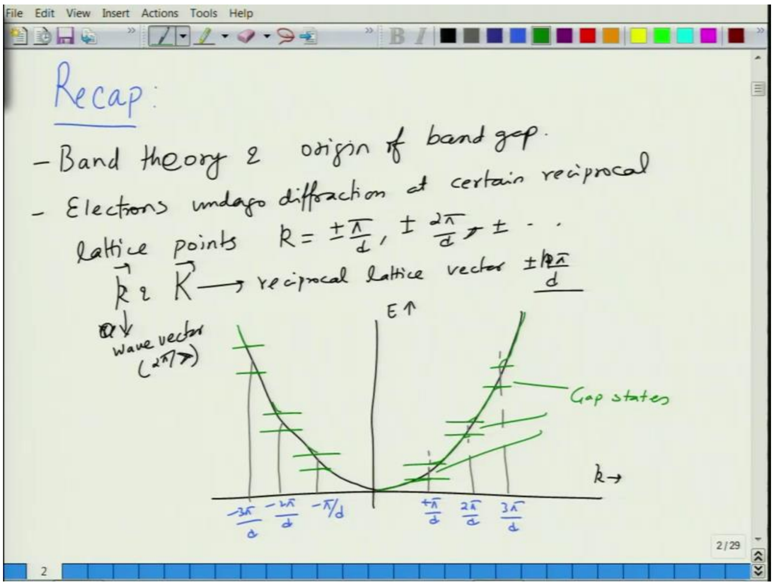
**Department of Material Science & Engineering**

**Indian Institute of Technology, Kanpur**

## Lecture 39 - Intrinsic Semiconductors

So, welcome again to the new lecture of the course, Properties of materials. So, let us just briefly recap what we did in the last lecture.

(Refer Slide Time: 0:22)



Recap:

- Band theory & origin of band gap.
- Electrons undergo diffraction at certain reciprocal lattice points $k = \pm\frac{\pi}{d}, \pm\frac{2\pi}{d}, \pm \cdots$

$\vec{k}$ & $\vec{K} \longrightarrow$ reciprocal lattice vector $\pm\frac{n\pi}{d}$

$\vec{k}$ ↓ wave vector $(2\pi/\lambda)$

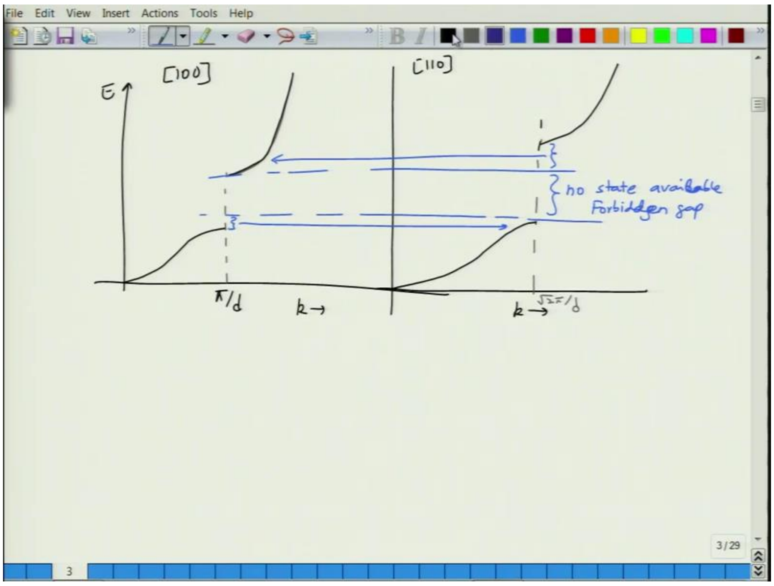
So, in the last class, we looked at basically the band theory and origin of band gap. So, essentially, band gap is so basically what happens is that, when electrons are in the travelling lattice, so when electrons are in the lattice, electrons undergo diffraction at certain reciprocal lattice points. So, let us say those are k plus minus pi by d, plus minus 2 pi by d, and so on and so forth. So, for this you will have to read a bit about the reciprocal lattice but basically reciprocal lattice space is the same reciprocal space or as we have wave vector.

So, basically k is the reciprocal you can say the wave vector, which is in reciprocal space, which is 2 pi by lambda and then capital K is the reciprocal lattice vector, which is of the order of, which is some 2 pi by some distance d. So, it could be plus or minus depending on the direction or let us say, n pi by d. So, you can see both of them are reciprocal of length, as a result they are called in they are called as reciprocal vectors.

So, this is wave vectors small k and capital K is the reciprocal lattice vector. We do not have time to get into this. The details of reciprocal lattice vector, basically when you have this energy band diagram, E k. So, instead of having continuous energy states, at certain point you have this diffraction by the lattice and these points are plus pi by d, 2 pi by d, 3 pi by d, minus pi by d, minus 2 pi by d, and minus 3 pi by d.

It is at these points the band structure changes. So, the band structure now is essentially like this. So, these states are basically you can say the forbidden gaps. So, these are the gap states. Same thing will happen here also. You will have, so these will be the gap states. Now, we also saw so, these are forbidden gaps in which there is no energy state available. So, electron either exists below this or above this but nothing is there present in the gap state.

(Refer Slide Time: 3:41)

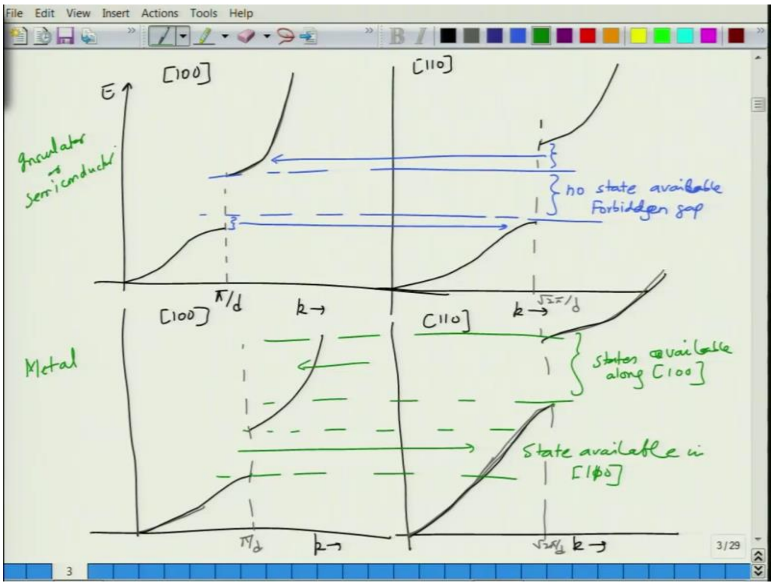


Now, what might happen in real crystals is that, let us say in real crystals as we say last time that, let us say along certain direction we have a gap state which is shown by this diagram let us say. So, in one direction, the gap state is like this. So, this is let us say at pi by d. so, this is let us say along 100 direction. This is E and this is k. Now, if you take the same thing along different direction, so this is again k vector and this is along 110 direction.

So, we can see that along 110 direction, if situation is something like but 110 k vector will be different. So, let us say the k vector now is a square root of 2 pi by d and at this point the curve follows like this. So, we can see that, although when the electron is traveling along 100 direction, at this k value encounters a gap but it can change its direction and find energy state in different direction up to this point.

So, effectively the gap is essentially this. Because corresponding to this region, there are states available here, corresponding to this region, there are states available here, so electron can always transition from one direction to another direction and find energy state. But in between there is a region where there is no state available. So, this is no state available. So, this is basically the forbidden gap. So, let us say, so this is basically across the, and if this continues across the k space along all the primary reciprocal lattice directions, then you will have a forbidden gap.

(Refer Slide Time: 5:45)

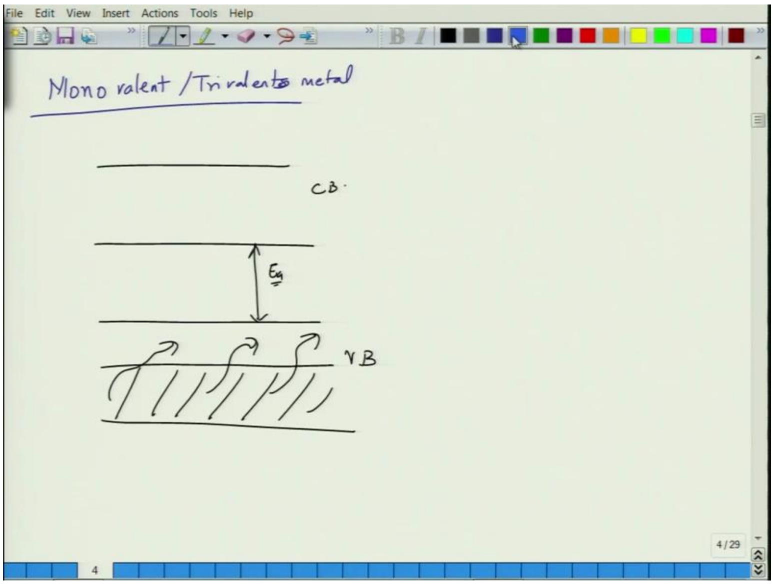


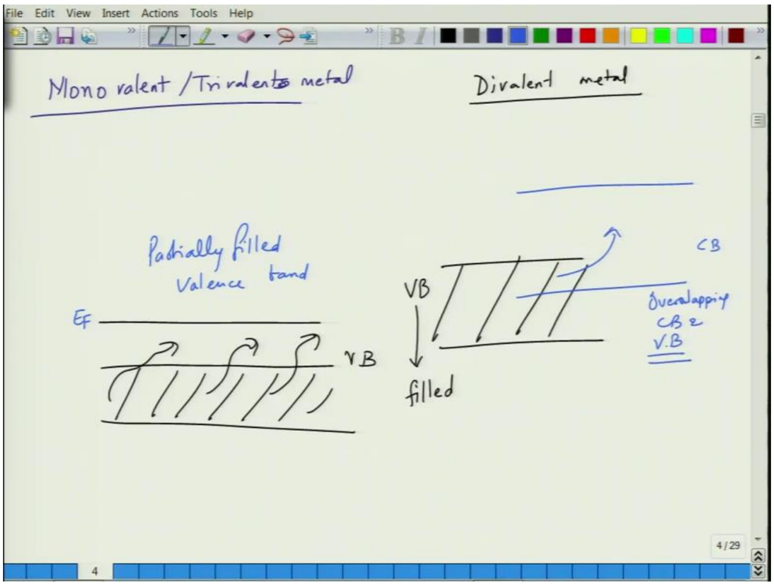
Suppose the situation was something like this, let us say I redraw this diagram in different way. This is k, this is k. So, this is again let us say 100 hypothetical situation. This is again 100. Let us say the situation was that we have, we had a situation like this.

And then for this direction at square root pi by d, this is pi by d. The situation at this point was that the energy gap went like this. I will use a black colour. Then we can see that for this region, for this gap region, I have states available in this region and for this gap region I have states available in this region. So, I can see you have states available here in 110 and here you can see the states available in 100.

So, basically, this material does not have, it has overlapping bands as a result, electron can transmit. So when it reaches here at this point, it sees a gap along this direction, but it can transition itself to 110 direction. And when it reaches at this point, it can transition itself to 100 direction, so there are no, there is not a continuous gap that exists in these materials. So, if you have a situation like this, then what we make is a metal and if you have a situation like this with the forbidden gap, then what we make insulator or semiconductor. So, we also saw that for monovalent and divalent....

(Refer Slide Time: 7:50)



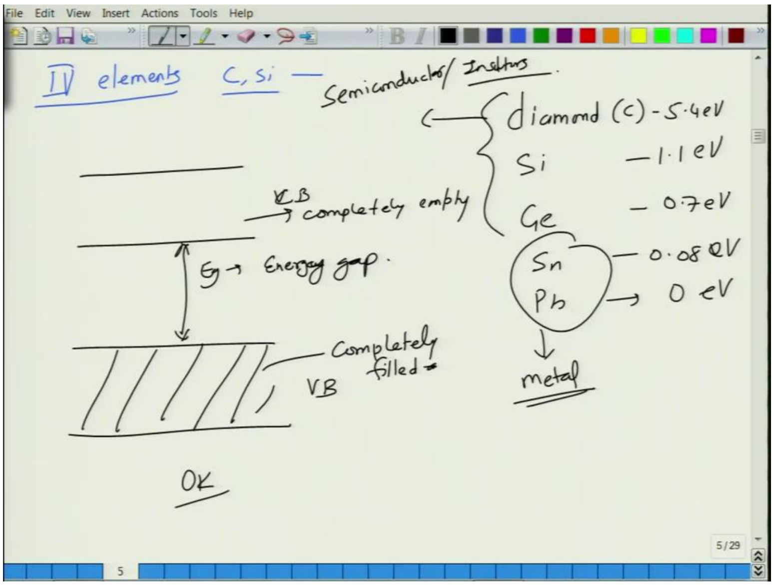


For monovalent and trivalent metals for which the electronic configuration is not complete, they have partially filled bands. As a result, for these kind of materials if you take this is valence band, this is conduction band. So, this is conduction band. This is valence band. But valence band is partially filled. So, it is up to let us say you can have a gap here also, let us say but there is overlap of states. So, and to avoid the confusion, let us now just draw the conduction band.

So, it is the valence band and this will be the basically you can say the Fermi level at this point, so this will be the Fermi level. So, this is you can say a partially filled valence band. In this in the case of divalent metals where you have outer shell filled, what will happen is that, valence band is filled. So, this is valence band which is filled but then the conduction band is partially overlapping.

So, this is conduction band so, electron can always transition from here to here. This is basically overlapping CB and conduction band and valence band. So, this is what happens in a divalent metal.

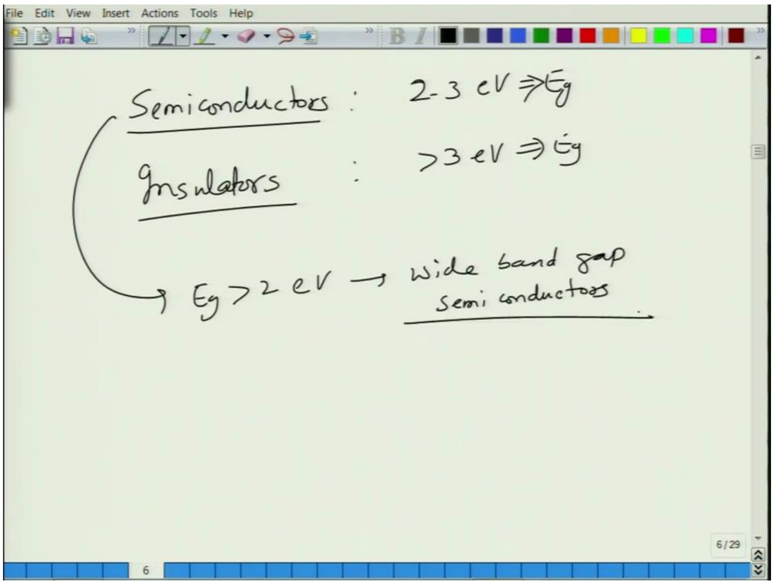
(Refer Slide Time: 9:26)



In fourth group, four elements such as carbon, silicon, etc what happens is that there is a gap. So, this valence band. So, this conduction band is separated with respect to valence band, valence band is completely filled. So, this is completely, we are taking at 0 k and this is completely empty. And these two are separated by energy gap E g which is called as energy gap.

So, in case of diamond, this magnitude is very large. So, in case of diamond, it is it is nearly, which is carbon which is 5.4 e V but in case of silicon this is 1.1 e V, if you come down germanium it is 0.7 e V and in case of tin it is 0.08 e V and in case of lead this gap is down to 0. So, lead and tin are metals because the gap is very small but diamond, silicon, germanium are, you can say semiconductors slash insulators.

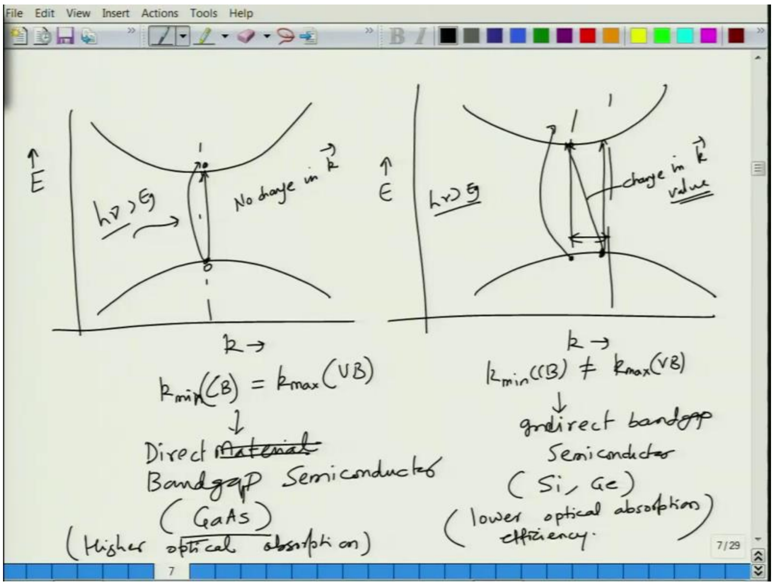
(Refer Slide Time: 10:55)



Semiconductors : 2-3 eV ⇒ $E_g$

Insulators : $> 3$ eV ⇒ $E_g$

$E_g > 2$ eV → wide band gap semiconductors



$k_{min}(CB) = k_{max}(VB)$
↓
Direct ~~Material~~ Bandgap Semiconductor
(GaAs)
(Higher optical absorption)

$k_{min}(CB) \neq k_{max}(VB)$
↓
Indirect bandgap Semiconductor
(Si, Ge)
(lower optical absorption efficiency.)

So, the way we define semiconductors and insulators are semiconductors are materials with band gap of 2 to 3 e V, E g. Insulators on the other hand greater than 3 e V is the E g for insulators. I mean it is the fussy boundary 3 e V. Some people say 2.5 e V, 2.6 e V and in case of semiconductors anything when E g is more than 2 e V we call them wide band gap semiconductors. Now let us go back to one more thing that we talked earlier. We said earlier that when you have conduction, in the E k space if the minimum of conduction band and the maximum of valence band they coincide each other.

So, when k minimum in conduction band is equal to k maximum for valence band then this is a direct band gap material. And in the context of semiconductor we call it direct, sorry direct, we call it direct band gap semiconductor. And if this conduction band minima and valence band minima they do not meet with each other, there is a difference between the k, so, k minimum conduction band is not equal to k maximum of valence band then it called as indirect band gap semiconductor. So, examples of this are, for example silicon, germanium, both are indirect band gap semiconductor.

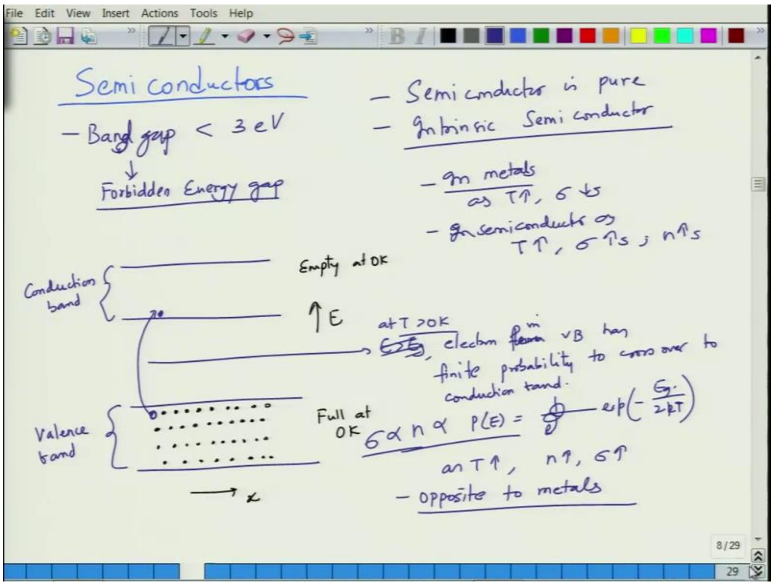
And if you take an example of gallium arsenide, this is a direct band gap semiconductor. There is a fundamental difference here because if electron has to transition from here to here, then it has to change its so, it cannot do so easily because there is a change in k value as well. Because if it wants to go from here to here then there is a change in k value. So, there is a change in k value. And k is basically you know, we saw that k is nothing but related to momentum. So, there is a change in momentum in this case.

Whereas in this case, the electron directly is able to transfer from here to here so, there is no change in k. So, as a result, indirect band gap semiconductors have lower optical absorption efficiency or lower absorption coefficient. And direct band semiconductor have higher optical absorption. There are other differences as well which we are not going to get into details of. But these are, this is a major difference between the two materials. Direct band gap semiconductors are those where k min and k max of conduction and valence band coincide. As a result, when electron has to transition, suppose you have a light coming at certain wave, certain energy.

If the h mu is more than E g then electron directly goes from here to here, creates a electron hole pair. So, there is no change in the k value so, as a result the materials of such nature absorb light easily. In the case of this kind of situation, the electron has to transfer from maxima of valence band to minima of conduction band. As a result, there is change in k value or if it has to go from here to here, then it has to use higher energy. So, basically, when h mu is greater than E g, absorption will acquire but either there will be change in k value or you will waste more energy. As a result, optical energy absorption efficiency is lower or optical absorption, light absorption is lower for the same band gap. Okay.

So, this is a fundamental difference between the two materials. So, this is a brief background on what is, what are the, what are semiconductors, what are insulators and what is the origin of bands in materials and stuff like that. We, of course, have not been able to gone into too much of details. But there is a bare minimum we can do for such introductory course.

(Refer Slide Time: 15:42)



Semi conductors

- Band gap < 3 eV

↓

Forbidden Energy gap

- Semiconductor is pure
- Intrinsic Semi conductor
- In metals as T↑, $\sigma$ ↓s
- In semiconducts as T↑, $\sigma$ ↑s ; n↑s

at T > 0K ~~E > Eg~~, electron ~~from~~ in VB has finite probability to cross over to conduction band.

$\sigma \propto n \propto P(E) = \cancel{\frac{1}{e}} \exp\left(-\frac{E_g}{2kT}\right)$

as T↑, n↑, $\sigma$↑

- opposite to metals

Now, let us concentrate mainly on semiconductors and why you want to do that? Because semiconductors are very important materials. They are used in lot of electronic applications, they are the backbone of electronic industry, microprocessor industry and as a result, we got to know about the properties of semiconductors. So, essentially, semiconductors are the materials which have a band gap, we can say less than 3 electron volt and this is basically we say it is a forbidden energy gap.

So, essentially, if you plot this energy band diagram of a semiconductor, so, this will be valence band and this will be conduction band. If you have electrons here so, at 0 k this will all be full.

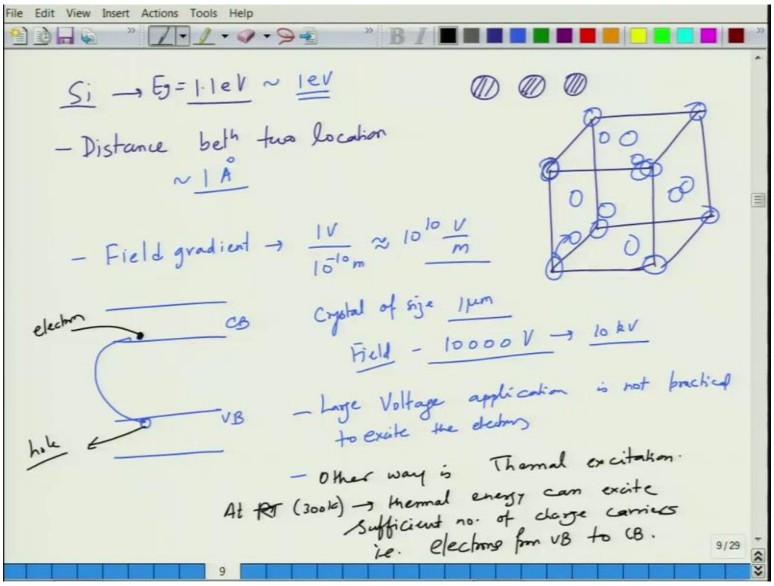
So, here energy is going up and this is distance x. So, this is fill at 0 k. This is empty at 0 k. The moment you increase the temperature, this electron has certain probability of crossing this energy gap. It goes to this conduction band and it leaves a hole here. So, this is basically when E is greater than E g, your electron from valence band has or we can say that at T greater than 0 k, electron from valence band, electron in valence band has finite probability to cross over to conduction band. And this probability is basically 1 over, sorry, exponential of minus of E g divided by 2 k T.

So, at a finite temperature depending upon the, depending upon the band, so, this is proportional to n so, n is proportional to P E. So, essentially, at the finite temperature for a finite band gap electron has finite probability of being found in the conduction band. As a result, even at very low temperatures you will have certain number of electrons in the conduction band which can be exited from valence to conduction band. So, essentially, there is a, there is a relation between the carrier concentration. So, let us say semiconductor is pure, it does not have impurities. In this case, we call it intrinsic semiconductor.

And most, in most cases we take example of silicon, in most cases we take example of silicon and for silicon we will see this as we, for a given temperature there is a finite probability. And this is related to conductivity. So, this is conductivity is proportional to n which is proportional to probability of finding electron. And basically, you can see that, from this you can see as the temperature increases, as temperature increases n increases and then sigma also goes up and this is basically opposite to what we see in metals.

This is one major difference between metals and semiconductors. So, in metals as temperature goes up, conductivity goes down. In semiconductors, as temperature increases, conductivity increases because n increases. So, essentially, now approximately we can also approximate this situation.

(Refer Slide Time: 20:19)



$Si \rightarrow E_g = 1.1 eV \sim 1 eV$

- Distance betn two location $\sim 1 \mathring{A}$

- Field gradient $\rightarrow \frac{1V}{10^{-10} m} \approx 10^{10} \frac{V}{m}$

Crystal of size 1μm

Field - 10000 V → 10 kV

- Large Voltage application is not practical to excite the electrons

- Other way is Thermal excitation.

At ~~RT~~ (300K) → thermal energy can excite sufficient no. of charge carriers i.e. electrons from VB to CB.

Let us take example of silicon. Silicon has a band gap of about 1.1 eV. So, this is the E g of silicon. And so basically this is approximately the energy difference between the an ion which is close to an electron which is or a place which is close to ion core and then a place which is away from the ionic core. So, let us say the distance between two such locations, so these are silicon atoms let us say, silicon has a diamond cubic structure by the way.

So, if you make a crystal structure of silicon, so silicon will have so you have silicon atoms here, here, here, here, here, here, here, here, here, here, here, here, here, here, and then four atoms of silicon in the two here and two there. So, these are all tetrahedricaly coordinated silicon atoms. So, diamond cubic structure so, distance between one location to another locations let us say is approximately 1 Armstrong.

So, this is the energy that is required to move the electron from one location to another location, which is about 1 Armstrong let us say. So, if you apply so, if you essentially what you are saying is that and if you approximate this as 1 eV, what you are saying is that, you require a field gradient of, so if we calculate the field gradient, it is 1 volt divided by 10 to power minus 10 metre or 10 to the power 10 volt per metre to move an electron from the top of valence band to conduction band.

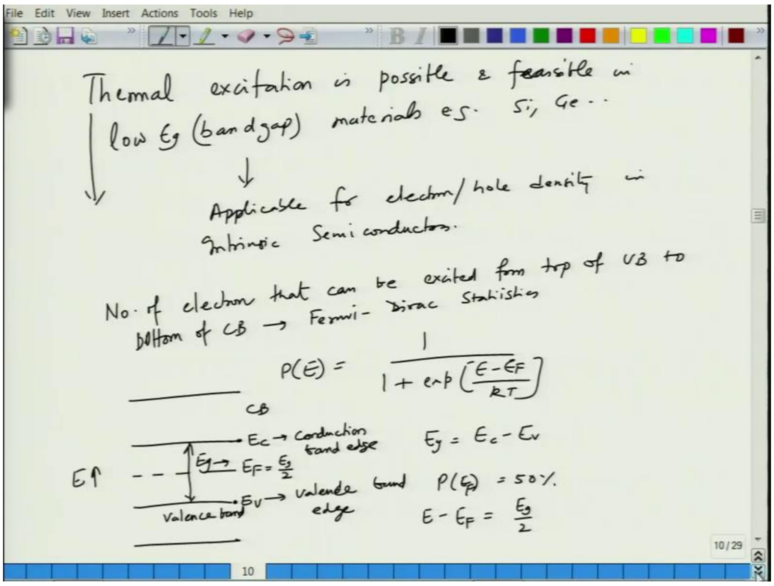
So, if you look at the valence and conduction band picture, you are going to move an electron from so, this is conduction band, this is valence band, you are going to move an electron from here to here. This will create electron here and empty state here which is called as hole in the language of semiconductors and this will take an energy of basically 10 to the power 10 volt per meter. So, it is a lot of field which is required to move.

And this filed is not possible so, even if you let us say, even if you let us say have a crystal of let us say crystal of size 1 micron. Even for 1 micron size you will require a field of 1,000 volt which is like 10 kV of field, which is a very large amount of field. So, basically applying a voltage is not the way to excite electrons. So, the only way by which you can excite the electron so, voltage application, large voltage application is not practical to excite the electrons.

So, what do you do? So, as we discussed earlier, the other way is thermal excitation. So, thermal excitation is essentially at room temperature. The thermal energy that is available so, at room temperature which is about 300 Kelvin, the thermal energy can excite sufficient number of charge carriers that is, electrons from VB to CB. And when you excite electron from VB to CB, you create electron here and what you create this is called as a hole, which is basically empty state.

So of course, when the gap is very large like diamond or some other materials, it is not possible to do, alumina but if it is like silicon or germanium, it is easier to do.

(Refer Slide Time: 24:49)



Thermal excitation is possible & feasible in low $E_g$ (bandgap) materials e.g. Si, Ge . .

↓

Applicable for electron/hole density in intrinsic Semiconductors.

No. of electron that can be excited from top of VB to bottom of CB → Fermi-Dirac Statistics

$$P(E) = \frac{1}{1 + \exp\left[\frac{E - E_F}{kT}\right]}$$

$E_g = E_c - E_v$

$P(E_F) = 50\%$

$E - E_F = \frac{E_g}{2}$

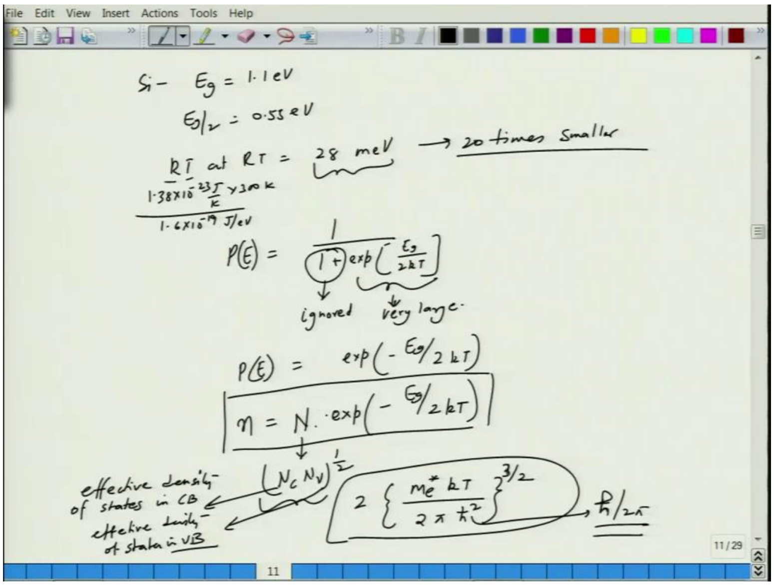
So, this is so thermal excitation is possible and feasible in low band gap materials such as example silicon, germanium and so on and so forth. So, in intrinsic semiconductors, so this is basically, so thermal excitation is the major process which happens, which is applicable for mainly for electron density, electron slash hole density in intrinsic semiconductors without any impurities being present.

So, number of electrons that can be excited so, we can say the number of electrons that can be excited from top of VB to bottom of CB, they can given as they can be so, for this we use what we say Fermi-Dirac statistics. So, we can say the P E, the probability of finding electron is 1 plus 1 over 1 plus exponential of E minus E F divided by k T. Now, for a semiconductor like this, the position of E F is always in between.

So, this is let us say, conduction band, the bottom of conduction band is always defined as energy E c which is conduction band edge. And this is valence band and the top of valence band is defined by energy E v which is valence band edge if you take this as E. And the distance between E c and E v in terms of energy is E g which is the energy gap. So, basically, E g is nothing but E c minus E v. And the Fermi level for a semiconductor lies midway which is at E g by 2 location.

So, Fermi energy lies always in the midway so, and we say that probability of finding electron at E F is 50 percent, even though let us say the, even though there are no energy states in this gap. So basically we are saying that E minus E F is equal to E g by 2, where E g is basically the, so the denominator here E minus E F that we can write as E minus E g, E minus E F as E g by 2.

(Refer Slide Time: 28:08)



Si - $E_g = 1.1\,eV$

$E_g/2 = 0.55\,eV$

$\underbrace{kT}$ at RT = $\underbrace{28\ meV}$ → 20 times smaller

$\frac{1.38\times10^{-23}\,\frac{J}{K}\times 300\,K}{1.6\times10^{-19}\,J/eV}$

$$P(E) = \frac{1}{\underbrace{1+}_{\text{ignored}}\underbrace{\exp\left(\frac{E_g}{2kT}\right)}_{\text{very large.}}}$$

$$P(E) = \exp(-E_g/2kT)$$

$$\boxed{n = N\cdot\exp(-E_g/2kT)}$$

$N \to (N_c N_v)^{\frac{1}{2}}$

effective density of states in CB

effective density of states in VB

$$\boxed{2\left\{\frac{m_e^*\,kT}{2\pi\hbar^2}\right\}^{3/2}} \to h/2\pi$$

And if you take for silicon, silicon has E g of 1.1 eV. So, E g by 2 will be 0.55 eV and if you take (0.), whereas k T at R T is nearly 28 m eV. If you can calculate so, just put the value of Boltzmann constant in temperature and room temperature is so basically 1.38 into 10 to minus 23 joule per Kelvin into 300 K divided by 1.6 into 10 to power minus 19 Joule per eV. So, this will turn out to 28 m eV, which is very large about 20 times smaller.

So, as a result, one can say that the factor so, you can say that P E was equal to 1 over 1 plus exponential of E minus so, this is E g by 2 k T. So, we can say that this factor 1 is basically ignored because this is very large. So, as a result, we can write this probability P E as exponential of minus of E g divided by 2 k T. And so, this is a very simplistic analysis.

So, as a result, the number of electrons that can be excited across the gap is equal to some constant N into exponential of minus of E g by 2 k T. N has a value which is basically N c into N v divided, to the power half and N c, N v have certain expression. So, we can write the value of let us say N c and N v. So, this can be written as so, this product of N c and N v can be written as 2 m e star k T divided by 2 pi h cross square to the power 3 by 2.

This is what basically it is. And so, essentially this is this you can say is the electron concentration. So, electron concentration is n, some constant which is basically effective number of you can say, you can say the number of electrons available for excitation from top of valence band to conduction band or you can say effective density of state N c and N v. So, N c is the effective density of states in and N v is effective density of states in VB.

So, we have not done the whole derivation but this is basically what it is. So, and product of N c, N v is given as 2 into m e star k T divided by 2 pi h cross square to the power 3 by 2. Where h cross is h divided by 2 pi. So, this is what we have done. This is the carrier concentration in intrinsic semiconductor as a function of band gap and temperature. And we can see as the temperature increases, the number of electron increase in the conduction band in intrinsic semiconductor.

We will do this analysis little bit effect of impurities and conductivity of some semiconductors in little lit more detail in the next lecture. Thank you.