Concepts of Chemistry for Engineering
Indian Institute of Technology, Bombay
Professor Arnab Dutta
Lecture 40
Density of states and doping in semiconductors

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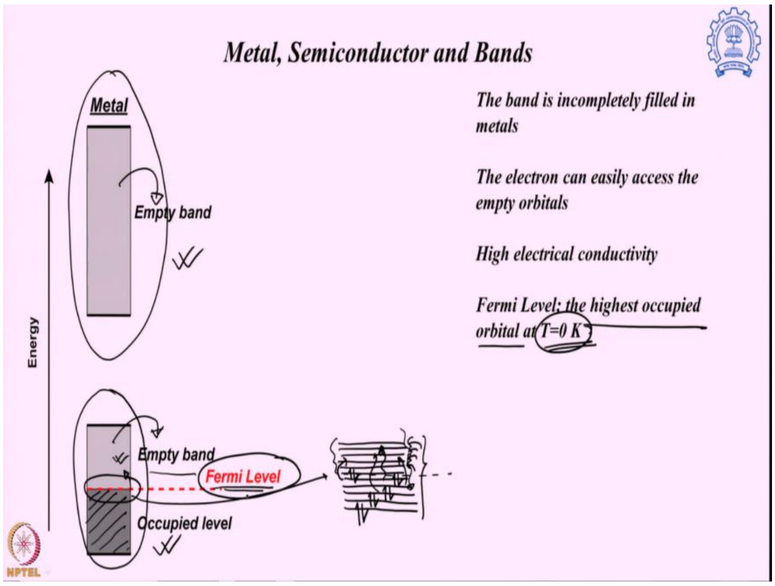

Metal, Semiconductor and Bands

The band is incompletely filled in metals

The electron can easily access the empty orbitals

High electrical conductivity

Fermi Level: the highest occupied orbital at T=0 K

So, welcome back to the second segment of the discussion on the semiconductor and metals band structure. So, in the previous section, we have discussed that the band structure is actually coming as an extension of molecular orbitals that are coming together and over there, we are actually showing you that this is the band structures possible for different systems. So, these are the bands coming say from the different set of orbitals s-band, p-band and even d electrons can give you the d bands. And we also discussed the difference of the band energies and the band gap that depends on how many atomic orbitals are actually participating in the bond formation and also, what is the initial energy gap between the different sets of orbitals.

Over here, I am showing you the band structure of the metal. So, in the metal as we know, we already have very less number of electrons present because it likes to leave the electron very easily. So, over here what we found that this is two different bands say one of them is lower energy band over here, one of them is a higher energy band over there and it has so, many electrons that it cannot even fill up the lower energy band. So, these dark colour over here show that up to that much is actually filled up and the light colour show they are actually empty.

So, there is no electron present over here. So, what happens, these electrons which are present in this occupied orbital, if I try to look very closely into this particular section where different sets of molecular orbitals are actually present so in the same band, that means the energy sets very close to each other, there are different electrons present, which is shown by these right numbers. And then it stops up to here, we have that many electrons.

Now, the next levels are empty, that no electrons are there. However, they are lying so close to these orbitals that the electron can easily jump over here without much effort because they are so closely lying. So, the energy of the orbitals are so close that it can trigger a movement of the electrons with very easy movement, there is not much energy required because they are very close to each other because they are belongs to the same band.

So, over there, and half-filled band always shows a very good conductivity because the field electron can travel to the empty part of the same band without much effort because the energy gaps are so close to each other. And that is the reason why do we see a very high electrical conductivity in metals because they always have a half-occupied band structures. So, where the occupied section of the electrons can travel very easily to the empty part. Then over here at different temperatures, the electrons will differ on their position.

Higher the temperature, they will start moving in the higher region, lower the temperature they will start moving in the lower segment. So, we want to make sure we know exactly where the electrons are at a particular temperature. And for that, this particular term is developed Fermi level. Fermi level is nothing but it is the highest occupied orbital at T equal to zero Kelvin. So, it is the lowest temperature possible.

Over there, if we want to measure where the electrons are, where we will find the electrons are at the maximum energy that will be called the Fermi level. And it has a huge impact because generally up to that much level, it should be filled up if you are not putting any kinetic energy with respect to the temperature to move the electron up. So, that is called the Fermi level and that is the scenario in metal where we have a half-filled set of bands where we will see a huge electrical conductivity because of the facile motion of the electron through the band.

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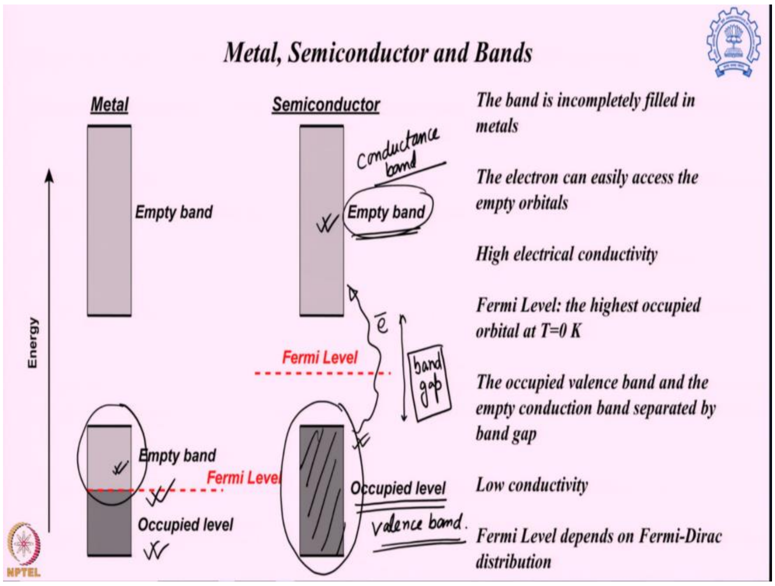

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High electrical conductivity

Fermi Level: the highest occupied orbital at T=0 K

The occupied valence band and the empty conduction band separated by band gap

Low conductivity

Fermi Level depends on Fermi-Dirac distribution

Now we come to the semiconductor. Semiconductor have more electrons and generally it has such electrons that the lower level is already filled up. So, there is not much any farther the electron can go because in this band, there is no such space left. All the available space are filled up by an electron. Are there any space available in this system? Yes, it is available in the high energy empty band.

So, over there if I can transfer some electron to there, only then I can see an electrical movement. However, for electrons going from this occupied lower level to unoccupied or empty higher level it has to cross this energy barrier which is nothing but the band gap we just discussed earlier and to cross this band gap it has to have some energy. So, that is why the electron movement is not as easy as it was in the metal where there are emptiness in the same band over here that is not present.

So, that is why in a semiconductor the actual conductivity is quite low because unless you cross some electrons from this occupied level to this Valence level, you cannot see an electrical conductivity and then generally in semiconductors these occupied levels are called the valence band whereas, this empty band or the higher energy band is known as the conductance band.

The logic behind this particular naming, valence band is it is actually formed from the valence electrons. So, that is why it is called the valence band and an electron if can go to this particular high energy band only then it can show conductivity. So, it is known as the conductance band. So, that is the basic difference between metal and semiconductor with respect to the bands in metal, it is actually having a half-filled band and in the case of semiconductor it has already filled band.

So, to create some conductivity, it has to cross this energy barrier to the empty band where it can find some empty orbitals and the electron can move there and show some conductivity whereas, for the metal, the empty orbitals are present in the same band. So, it is much easier to see and that is why an increase in conductivity is seen for the metals compared to the semiconductor.

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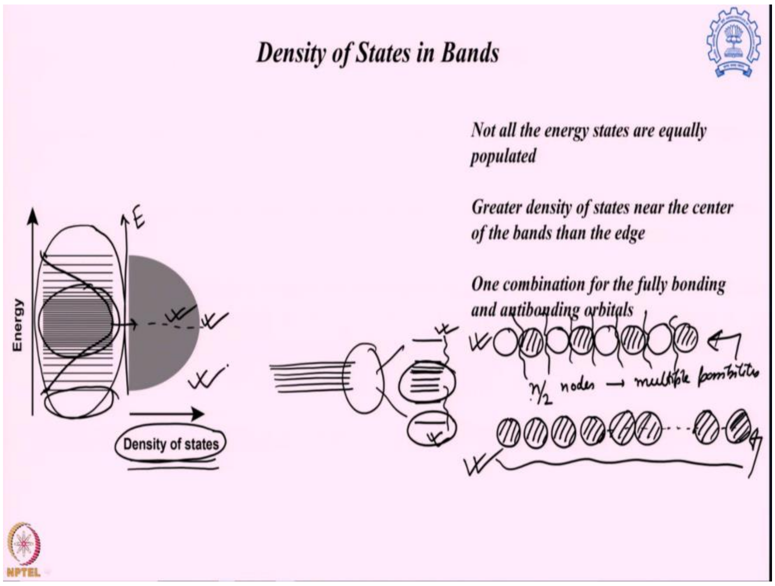

Density of States in Bands

Not all the energy states are equally populated

Greater density of states near the center of the bands than the edge

One combination for the fully bonding and antibonding orbitals

In the next section, we are going to discuss about how the energy bands are actually populated because we have different levels of orbitals. But are there same number of electrons present in each orbital? That is actually not true. And that is actually defined by this particular term known as density of states. So, what is the density of state? So, over here I am again showing you the band structure. So, previously, we have shown the band structure, a very equi-spaced molecular orbital.

But in reality, they are not always equi-spaced. They are actually if we look very closely, what we will find they are actually not equally distributed. At the middle of the band, they are quite highly populated. Whereas on the edge side, they are actually sparsely populated. Why? That is because, if I want to have this molecular orbital which is actually the lowest energy possible over here, I can produce it with only one combination when all the atomic orbitals are in the same phase.

Just to give you an example, say I am taking this s-orbitals again four of them, and there is only one particular way I can have all of them in the same phase. And if I increase it to n numbers and so on and so forth, there is only one possible way to have this particular symmetry present, where all of them are the same symmetry. Similarly, the other is the anti-bonding will be possible and each of them are in the opposite symmetry next to each other. So, every other atomic orbitals are in the opposite symmetry.

So, I can have anti-bonding interaction between each of them. Now, there is only one possible combination to do that, this one. One possible arrangement for this one, for the bonding one possible arrangement for the anti-bonding. Now, say I want to have n by 2 number of nodes and then I have multiple possibilities to do that. So, it is now a game of permutation and combination. So, that is why there will be much more different possibilities to do that which will share almost similar energy so that is why they will be densely packed almost at the centre of the band.

And now if I look into that how the energy is actually dispersed with number of electrons over there very less number of electrons, there is only one possibility over there is on one possibility and as I increase it slowly increased and maximum number will be exactly at the middle of the band and then it slowly goes down again. So, that is shown over here with this particular function, which is known as the density of states, where in the y axis it is showing energy, in the x axis is showing number of possible states.

And over here, you can see at the middle, I have the maximum numbers of possibility. So that is why just not the band, but this density of state is actually a true picture of how the electrons are actually arranged in a solid, not only with respect to the energy, but also with respect to the number because band structure do not give us the correct idea where most of the electrons are actually situated. So, that is why we are going to represent everything with respect to this density of state.

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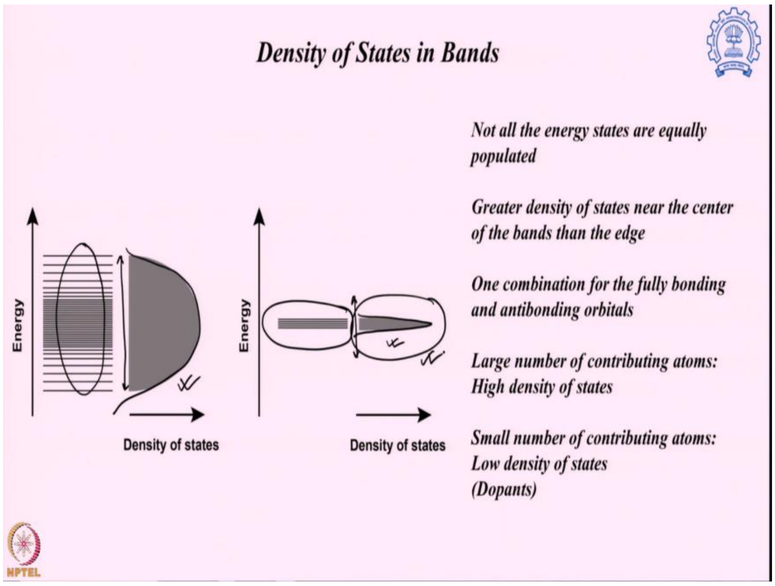

Density of States in Bands

Not all the energy states are equally populated

Greater density of states near the center of the bands than the edge

One combination for the fully bonding and antibonding orbitals

Large number of contributing atoms: High density of states

Small number of contributing atoms: Low density of states (Dopants)

So, how much this density of state will be spread with respect to the energy scale that depends how many atomic orbitals are actually combining. If you have a huge number, we will have a huge number of molecular orbital and we have a huge spread like this. However, if we are only contributing very small amount of atomic orbitals, their spread will be pretty low. So, it is nothing but we can say with respect to the previous one, it is much more narrowed down, it also have the same shape. But because the energy spread is quite low, it looks like this one.

It is quite narrow, but it is much more width when we have a huge number of atoms present. And that is very crucial, as we are coming into the later part of this section, that when we actually put some impurity in a huge amount of a semiconductor or any metal that is going to show these kind of band structures because it is going to remain in a very small amount that impurity in that original sample and that is known also as a dopant. We will look into the effect of that a little bit later.

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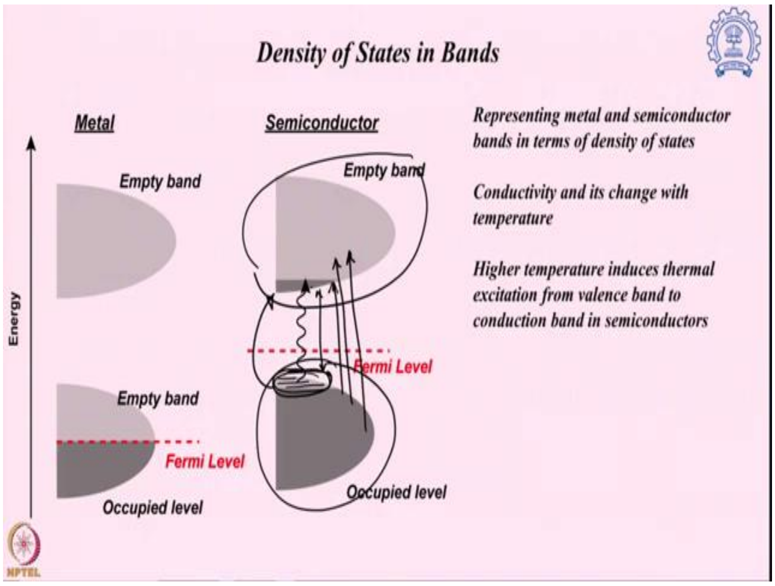
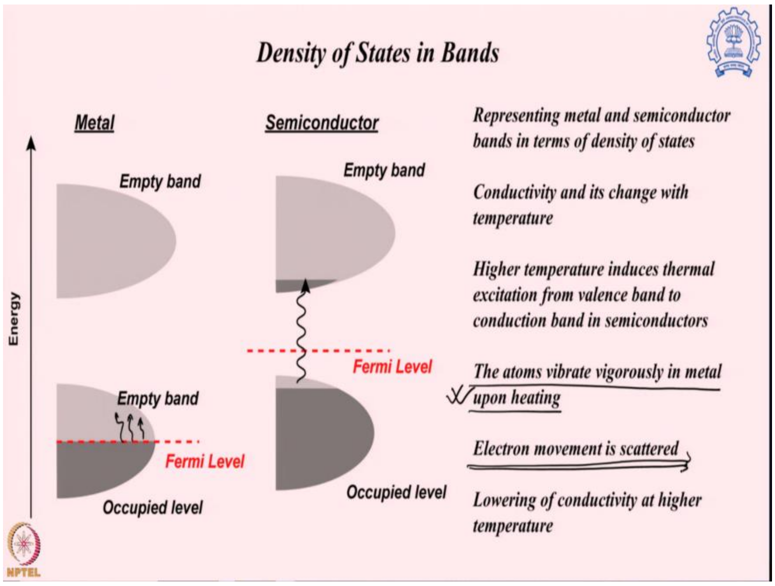


Density of States in Bands

Representing metal and semiconductor bands in terms of density of states

Conductivity and its change with temperature

Higher temperature induces thermal excitation from valence band to conduction band in semiconductors



Density of States in Bands

Representing metal and semiconductor bands in terms of density of states

Conductivity and its change with temperature

Higher temperature induces thermal excitation from valence band to conduction band in semiconductors

The atoms vibrate vigorously in metal upon heating

Electron movement is scattered

Lowering of conductivity at higher temperature

Now, over here, I have redrawn the metal and semiconductor bands with respect to the density of state. So, instead of just only band, now I have shown that with a specular density of state for both of them, and over here, I am showing you how far it is filled up and you can see in the metal it is filled up till only half and not only that, you have a huge number of electrons are actually available which can easily go to this empty band and show me the conductivity whereas in the semiconductor, it is something different.

In the semiconductor, what we are seeing that we have this particular empty band and over there we have this occupied band. And if we really want to have some electron density transferred, some of the chunk should go to the empty band and over here you can see not only this has very high energy with respect to the filled-up band, it also have very low population.

So, not too many electrons are present to go to there. However, only a little bit of electron movement is needed to see some conductivity. However, the how many electrons are moving there that will matter with respect to the magnitude of the conductivity.

So, this particular energy gap has to be covered and over there, this energy gap is covered with respect to the temperature because higher temperature produce enough kinetic energy to the electrons. So, they can jump from this occupied valence band to the empty conduction band. And that is why in semiconductor we have observed that with an increase in temperature, we see an increase in conductivity because as we are increasing the temperature more and more electron is going to move up to the conduction band and that is going to increase the conductivity. So, that was actually happening in semiconductor.

Now, what happens in the metals because in metals also, we expect that similar amount of electron movement should be happening as the temperature is increasing. And that should be the case however, what we have shown earlier that metal conductivity actually decreases with an increase in temperature. And that is a huge question.

Why? Because we have to understand in the metal most of the conductivity is happening over here in the same band structure and this band structure is formed due to the interaction between different atoms which are precisely positioned in a lattice in a metal but when we start increasing the temperature, we are increasing the vibration on the atoms. So, the atoms started vibration and then the atoms are going to move from their original position and with this position movement, the atoms are actually breaking the overall lattice structure.

And if the whole lattice structure breaks down, the bonding interactions are now affected and the electron movement is also affected because the electrons are actually moving through this bonding interaction through space. And as now the atoms can be present in multiple spaces compared to one precise space at low temperature, the electrons can move not only a particular direction but at any different directions as the temperature is increasing and that is known as a scattering of the electron movement.

So, it is not that the electrons stopped moving, but it is not moving in the direction it should be to show a very good conductivity. It is moving all around the place and they are cancelling each other's movement out, there is no such directional movement happening in the metals when we increase the temperature and that is why when we increase the temperature in metal, it actually decrease the overall conductivity that we have shown over here.

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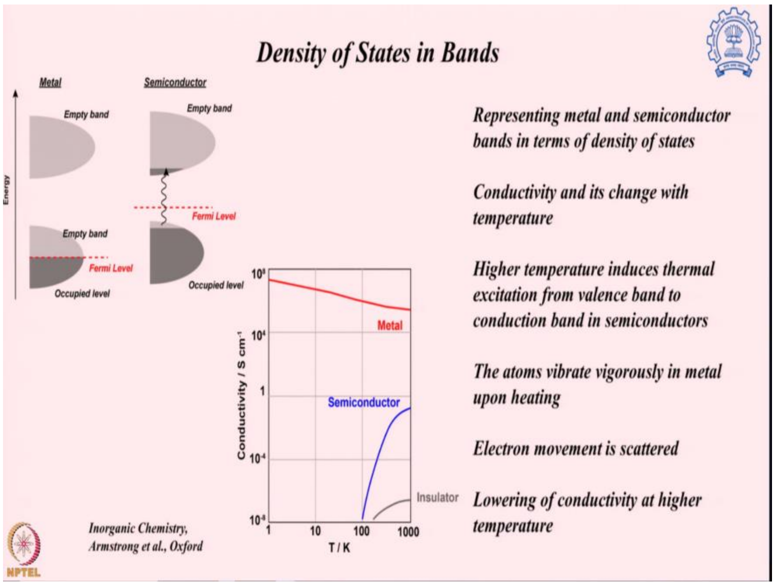

Density of States in Bands

Representing metal and semiconductor bands in terms of density of states

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Higher temperature induces thermal excitation from valence band to conduction band in semiconductors

The atoms vibrate vigorously in metal upon heating

Electron movement is scattered

Lowering of conductivity at higher temperature

Inorganic Chemistry, Armstrong et al., Oxford

And we have seen that the density of state is represented very nicely that the semiconductor are actually going to increase the conductivity whereas, metal is going to decrease the conductivity.

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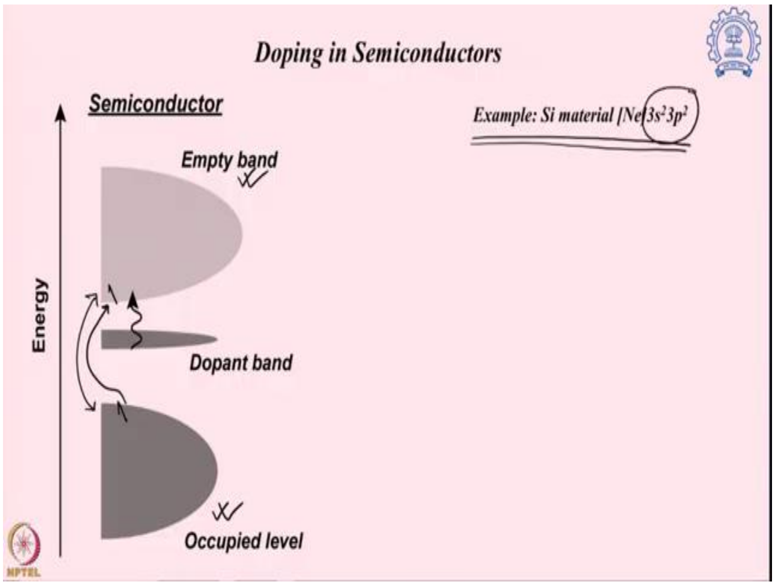
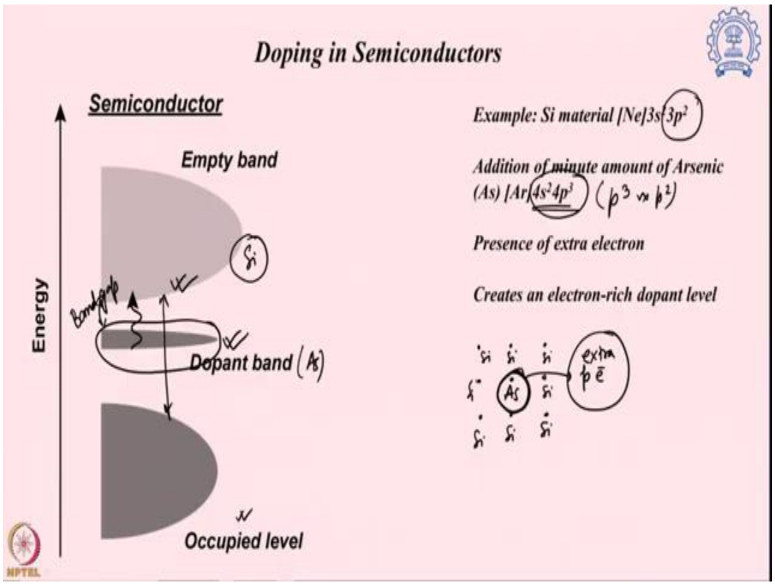


Doping in Semiconductors

Example: Si material [Ne]$3s^2 3p^2$



Doping in Semiconductors

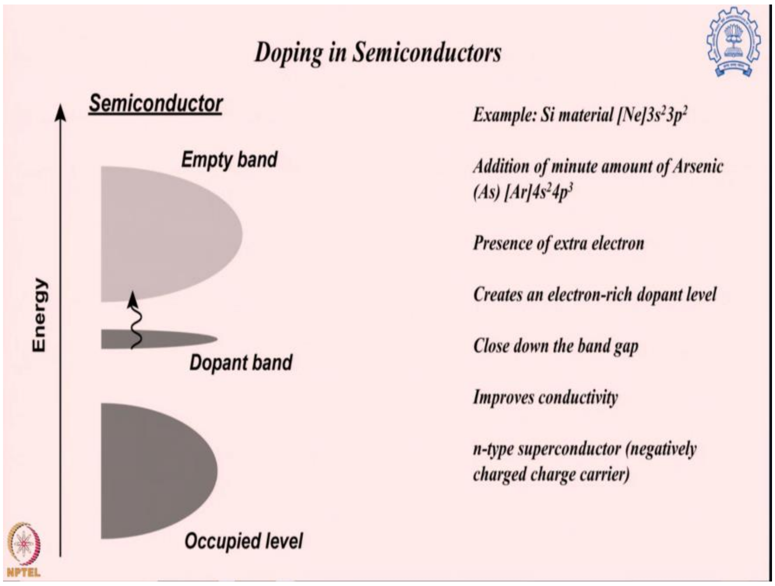
Semiconductor

Example: Si material [Ne]$3s^2 3p^2$

Addition of minute amount of Arsenic (As) [Ar]$4s^2 4p^3$ (p^3 vs p^2)

Presence of extra electron

Creates an electron-rich dopant level



Doping in Semiconductors

Semiconductor

Example: Si material [Ne]$3s^2 3p^2$

Addition of minute amount of Arsenic (As) [Ar]$4s^2 4p^3$

Presence of extra electron

Creates an electron-rich dopant level

Close down the band gap

Improves conductivity

n-type superconductor (negatively charged charge carrier)

Now, we come to another very important aspect the doping. So, as we just show that the semiconductors are actually can show some conductivity, but the issue is that there is an energy gap between the occupied level and the empty band and if we want to cross over this band, we have to give enough energy from that temperature so that the occupied electrons can come to the conduction band. How about there is another way possible, we can add some impurity over there to create an another energy band in between which can emphasize the electron movement in the system and which can improve the electron movement in the system.

So, for understanding that we take silica as a material, silica is the basic material which is creating the template which is actually giving me this occupied and this empty band and the silica has an electron distribution $3s^2 3p^2$. Now, we have added arsenic over here. Now, what happens when you have arsenic? Arsenic have an electronic configuration $4s^2 4p^3$. Now, it has one extra p electron p3 versus p2. So, it has a p3, it has a p2 in silica and where we are putting this arsenic, in the structure in the solid structure, where we have this array of silica is present over there in the beginning. In one of them, I am actually repressing the silica with an arsenic.

And that is going to bring a very similar structure because I am not adding a huge amount only a small amount. So, it is not going to deviate from the original structure a lot, but it is going to bring one extra p electron and this extra p electron because only a very small amount of arsenic is present, it is going to bring a very small amount of its own atomic orbitals and that is going to create this very narrow dopant band with this extra p electrons and these electrons are already present and this is going to be higher in energy compared to this occupied level of the silica. So, this is coming from this arsenic.

And now, you can see there are some electrons available near to the empty band based of silica which has much more lowered band gap previously it is having a huge energy gap now it is closed down because of the presence of this dopant and that is going to create a very good electron movement around the system and that is going to improve the conductivity of the system.

So, that is why a very minute amount of doping with arsenic in silica is going to improve the conductivity and over there this conductivity is improved because of presence of an extra electron which is known as the negatively charged system. So, the actual charge is carried over here by a negatively charged electrons. So, that is why this is known as the n type superconductor where we actually created a system where we dope that with a different material which has extra electron compared to the original material.

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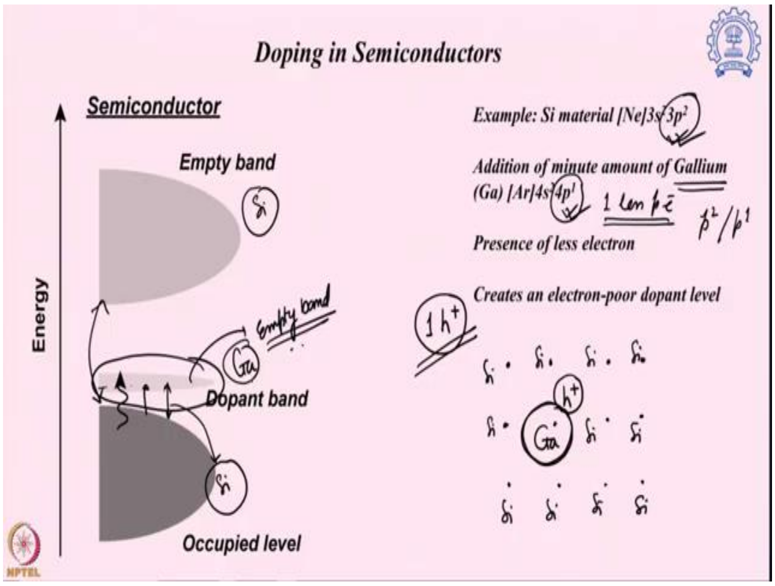


Doping in Semiconductors

Semiconductor

Example: Si material [Ne]$3s^2 3p^2$

Addition of minute amount of Gallium (Ga) [Ar]$4s^2 4p^1$

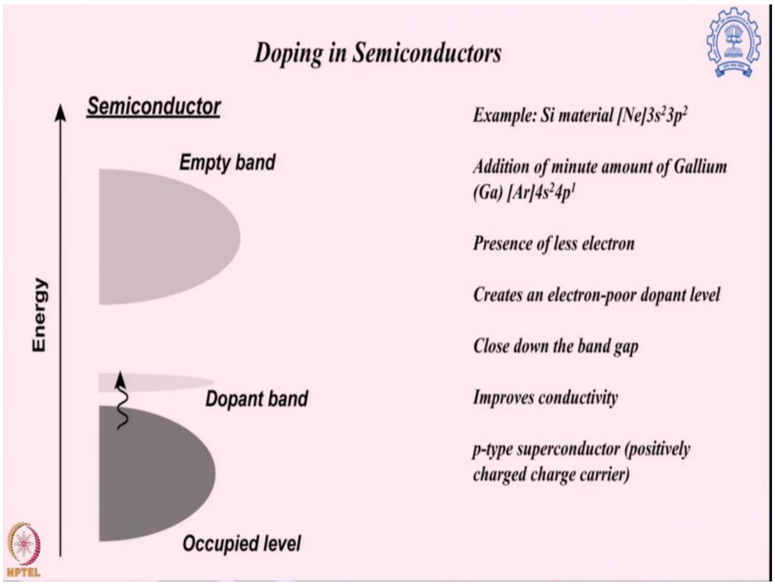
1 less p $\bar{e}$

p^2/p^1

Presence of less electron

Creates an electron-poor dopant level

1 h^+



Doping in Semiconductors

Semiconductor

Example: Si material [Ne]$3s^2 3p^2$

Addition of minute amount of Gallium (Ga) [Ar]$4s^2 4p^1$

Presence of less electron

Creates an electron-poor dopant level

Close down the band gap

Improves conductivity

p-type superconductor (positively charged charge carrier)

Now, go to the other different system. What happens instead of silica, if I take gallium, so, I start from the same silica system, but instead of arsenic now, I am putting gallium. So, in the periodic table gallium is in a different group than the silica it is in the previous group. So, it has one extra only one p electron, which is actually one less p electron. So, now, we are considering p2 versus p1 and what we are actually going to do, again we have an array of silica present and over there with all the silicas around this place, we will replace a few of the silicas with gallium and what is the effect of this presence of this gallium over here?

This gallium is going to bring one less p electron and that is going to create a hole in the system because where we expect two p electrons, now, we have only one p electron. So, you can say it is actually one less electron or you can say we have one extra hole. So, this hole formalism gives us a very similar result, but instead of one less electron we are considering we have one extra hole over here.

Now, this extra hole present over here will help us to create nothing but a unoccupied orbital system because the hole means lack of electron where the electron can go and that is shown over here that is the effect of the gallium which creates an empty band with this holes very near to the occupied level. So, previously this empty band belonged from silica it is way out, but this empty band coming out of gallium, now, it is very close. So, the band gap is much closer to the silicon based occupied system, the silicon-based valence band.

So, respect to that now, we do not need a huge temperature to transfer the electrons to this level from the silicon occupied level to the gallium filled level. So, we can easily transfer the electron from the silicon valence band to the conduction band, a narrow conduction band created over there by gallium and that also improves the electron movement.

However, over here electron movement was supported by the presence of an extra hole. So, we can say it is a positively charged carrier which is actually improving this electron movement. So, that is why this kind of system where we put such a dopant which actually has less electron compared to the actually the template system which is known as a p type semiconductor. So, now we would like to wrap up this full section of the band structure.

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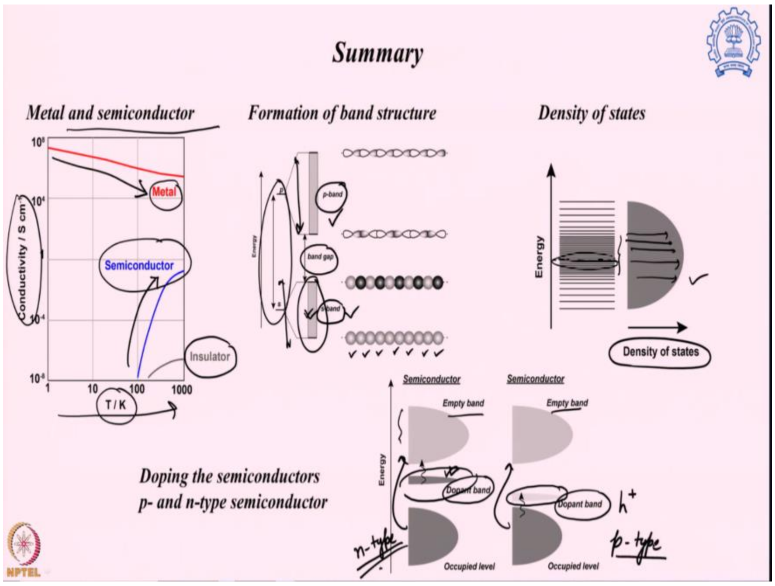

Summary

Metal and semiconductor

Formation of band structure

Density of states

Doping the semiconductors
p- and n-type semiconductor

So, over there, we have discussed four different system in details. The first system, how we differentiate between metal and semiconductor. The definition come how the conductivity varies with temperature. If the temperature increase brings the conductivity down, then it is a metal. If it brings the conductivity up it is semiconductor. So, it is the trend of conductivity change with respect to temperature defines whether it is a metal or semiconductor not that absolute values.

But if we really want to look into the absolute values, we can see the metal generally has higher conductivity compared to the semiconductor and then there is another particular kind of semiconductor which we say insulator which has so less conductivity even compared to the semiconductor there almost very negligible electron transfer. So, we say it is almost insulating. Then we understand how the electrons are actually behaving in a solid. So, what we found, it is nothing but an extension of molecular orbital theory.

In molecular orbital theory, we take particular atomic orbital and combine them together and over here what we have is different kinds of atomic orbitals contributed by each of the atoms present in the solid, we started from the one-dimensional system and we found we can create number of molecular orbitals, if we consider n number of atomic orbitals to start with, we will create n number of molecular orbitals which live very close to each other.

And that will create the band and this interaction, although we start from one-dimension, it happens in all the three-dimensions. So, that is why these bands are very well packed set of molecular orbitals. And depending on which orbitals are actually contributing to the system, so you can say is s-band, p-band in metal system you can also have d-bands and the difference between these bands are known as band gap, which is actually tuned by how many atoms are participating because that controls the width of this band and also what is the energy gap between these two orbitals in each of the atoms.

Then we look into one of the very important fact, density of state which says that, when we are creating these bands, we are not only creating very well packed atomic orbitals, but it also matters how many electrons will be present there. And that depends how many different ways we can combine them, because in certain places in the middle of the band, they are very much well-spaced.

And over there, they are so close packed that they are actually going to have similar combination with very different orientation but with very similar energy and that gives us a high number of possibilities of electrons orientation in those states. So, this is known as a density of state.

Now, coming back, this density of state we can use to define a metal and semiconductor and over there, we can also define how we can include a dopant system because otherwise, we have to cross this full band gap to give electrons from the occupied valence band to the empty conduction band of the semiconductors.

Now, if I put some dopants, it creates another hub of electron rich band, if I use a system which has one or two extra electrons compared to the material or we can create a low-lying empty band or conduction band which is coming from a dopant in such a way that it has less electron one or two less electron compared to the original material.

And we actually include only a very small amount of that because if you add a huge amount, it breaks down the overall symmetry of the system and this band structure which is totally dependent on what is the geometry and what is the arrangement of the material that will break down. So, we cannot use the same band structure again. So, you have to use a very small amount of dopant and that is how we can increase the electron conductivity in the semiconductors.

If I use an extra electron as a dopant. So, it will be n type semiconductor because it is the negatively charged system is carrying the charge. If I use a dopant with less electron, we can say it is the holes are actually carrying the charge and we call them the positive type or p type semiconductor. So, with respect to that, we will conclude our section on the band structure of solid and metals over here. Thank you.