Processing of Semiconducting Materials
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Lecture - 4
Doping in Semiconductors

Good morning. Let us start with the doping in semiconductors. We have discussed earlier that semiconductor differs from the metal or the insulator; in the sense that the band gap in semiconductor is very low, unlike in insulator, where the band gap is very high.

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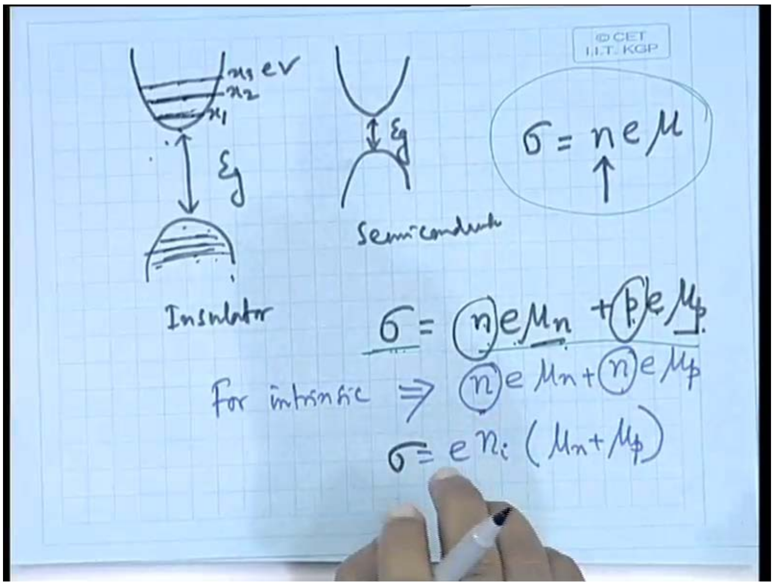

So, let us quickly remember those things that this is the band gap. And this value is high for, this is the E g the band gap it is high for insulator. And, for semiconductor it is very low. It is insulator and it is semiconductor right. In semiconductor the carrier transport is governed by both electrons and holes; unlike in metal where it is governed by only the electrons. There is no concept of hole in metals. So, if I write down the conductivity which is given by sigma, this is equals to n e mu. This is the normal expression or general expression for the conductivity, where n is the concentration of electrons, e the charge of electron and mu is the mobility of electron.

If we consider that it is a fully electron based system like metal, but for semiconductor it is not a fully electron based system. So, your new sigma will be the concentration of electron, the charge of electron, the mobility of electron plus the concentration of hole, the charge of hole and the mobility of holes right; remember that this mu n is the mobility of electron and mu p is the mobility of holes and e the charges are same for electrons and holes it is 1.6 Newton to the power minus 19 except the sign right and n is the concentration of electron, e is the concentration of holes. So, these electrons and holes are there in the semiconductor right.

Now, let us take an example that I have taken one silicon sample, and you know that the sample can be intrinsic can be extrinsic. Please remember that for intrinsic sample, the number of electrons and the number of holes are equal. So, I can write here you see, if the number of electrons and number of holes are equal, then this p becomes the number of electrons say. So, this n and this n because for intrinsic, remember for intrinsic, they are same. And if you replace that n by n suffix i, if you replace that concentration of electron or holes, because they are same by n i, i stands for the intrinsic, then you can write that it is equals to e n i mu n plus mu p.

So, for intrinsic n i is the concentration. And, if you consider that both electrons and holes are present n and p are there. For intrinsic semiconductor this the sigma becomes the conductivity becomes e n i mu n plus mu p right. Now, the question comes how the conductivity of semiconductor can be increased is there any process using which we can enhance the conductivity of electrons yes, there is a process using which you can increase the conductivity of the semiconductor and that process is known as the Doping process.

Doping process right, it is doping process that is not possible for other kinds of materials. It is a unique feature of semiconductor material and this doping is very interesting phenomena. At the end of the lecture, I shall show you that just if you replace 10 to the power 8 silicon atom by one arsenic or phosphorous atom remember 10 to the power 8 silicon atom by one phosphorous or arsenic atom, the conductivity will increase by several orders of magnitude. So, that is the unique feature of doping that you can change the conductivity of the semiconducting material by the controlled manner of doping in the material. So, why we dope the sample, to increase its conductivity, apart from that there is other advantage of doping that we shall discuss today itself right. Now, says you have a silicon sample.

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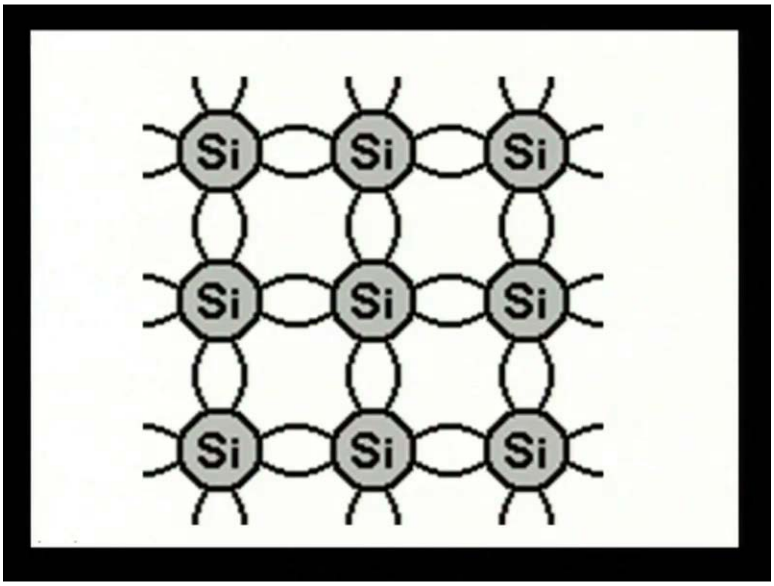

And, if you look at the picture, you see that this is the 2 dimensional diagram of silicon atomic arrangement inside the lattice. What is the valence of silicon? 4.

Student: 4.

So, you see that there are that the nearest neighbours are 4 for 1 silicon. If you consider this silicon then the nearest neighbours are 1 2 3 4. So, they have perfectly formed a covalent kind of bounding in silicon. So, that is why normally at 0 t you will not find any conductivity in silicon as well though it is a semiconducting material. Now, if you want to dope this silicon. What to do? What is the process? What is the physics of doping? How the doping is done? The process is silicon has 4 electrons in the valence band. So, if you add some element or an element having valence electron 5, then what will happen? 4 out of those 5 valence electron will share and remaining one will act as a free electron; thereby increasing the conductivity of the material.

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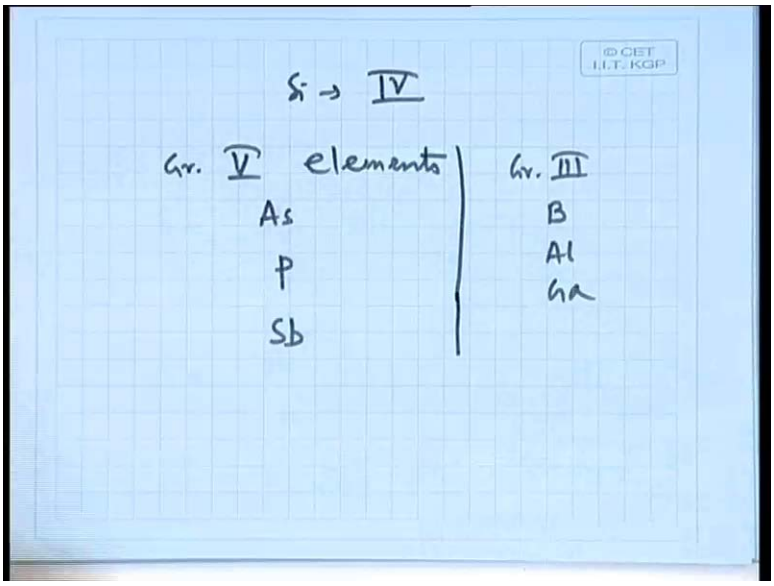

So, since silicon belongs to group 4. You need group 5 elements arsenic, phosphorous, antimony etcetera. They have all 5 electrons in their outermost cell. See this is the antimony.

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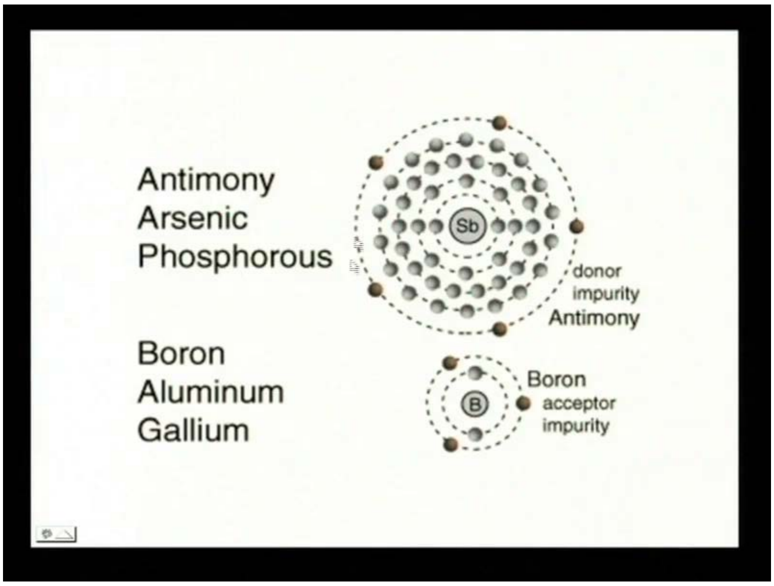

This antimony has how many electrons in the outermost cell? 1, 2, 3, 4 and 5. That is applicable for antimony, arsenic and phosphorous, but for boron, aluminium and gallium because they belong to group 3 of the periodic table boron, aluminium, gallium etcetera antimony is there S b. So, you see that for this boron, aluminium and gallium there are 3 electrons in the outermost cell right. So, this is the way using which you can dope silicon? Remember that now we are discussing the case of silicon either you use antimony or arsenic or phosphorous or you use gallium, aluminium or boron. That is applicable for silicon only why because silicon has 4 valence electrons.

So, either you have to dope it by 5 to get it n-type or you have to dope it by 3 to get it p-type that is not applicable for other materials. it is applicable for group 4 materials, in this technique you cannot dope gallium arsenide, in this technique you cannot dope indium phosphate or zinc oxide or gallium nitrate that is not possible, because the electrons are necessary for the increase in conductivity. And, you have to introduce controlled manner of doping.

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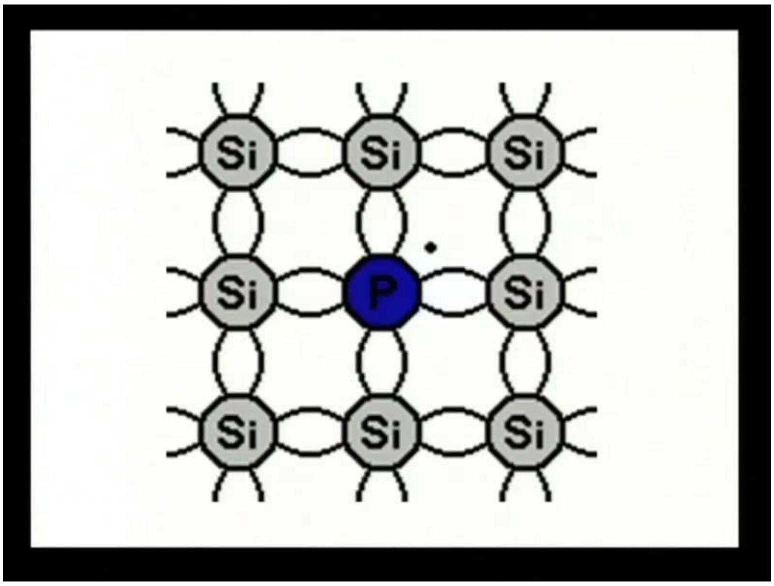

So, that free electrons are there, here in this slide you see that one silicon atom has been replaced by the phosphorous atom. So, 5 electrons of phosphorous only out of 5 electrons 4 electrons have formed 4. And, 1 electron this is the electron which is free in the crystal lattice, so this free electron will move throughout the crystal lattice, and if you impart electric field in it. Then you can increase the drift velocity of that electron in a particular direction because unless you give some electric field as I have shown you in my last lecture that they will move at random manner, only if you get an appreciable amount of current by the motion of those electrons. You have to apply an electric field.

And, if we apply an electric field these electrons will move in a proper direction. And, you will get a current out of it thereby increasing the conductivity.

Now, 1 Phosphorous atom gave you 1 electron if you dope 10 to the power 8, 10 to the power 5 or 10 to the power 18. Then, what will happen? You will get 10 to the power 18 numbers of electrons, 10 to the power 14 number of electrons, but one condition is there. The condition is the Phosphorous or Boron or Aluminium whatever be the do pant atom. Let us call those atoms as the dopant atoms because they are used for doping they must be ionised. Without ionisation that 5 th electron will not be available for not be available as a free electron.

So, you have to make it free from the Phosphorous for that you have to ionise. When it will be ionised? Then what will happen? The phosphorous atom will be positively charged ion it will be positively charged ion because the absence of electron means it is a positively charged. So, then it will be a positively charged ion; and the electron will be released to the crystal lattice. Not at all temperatures all the atoms will be ionised; it is not possible. So, at 0, so at 0 kelvins. At 0 kelvin, what will happen? Nothing will happen? Since, at that temperature, no ionisation will take place right. How the ionization energy is calculated? Who can tell? Any idea. You should tell. No, no. How it is calculated?

Basically from the hydrogen bohr's model. You have told the right thing, but you should generalise thing because this is not an atomic class. So, it is basically the material science class. So, I shall show you that by using the Bohr Theory of hydrogen atom in the ground state what he told that for taking n equals to 1. You can calculate the binding energy of the atom for particular crystal lattice. And, that means that is the ionisation energy. If you give that energy it will liberate itself from the bonding of the host lattice right.

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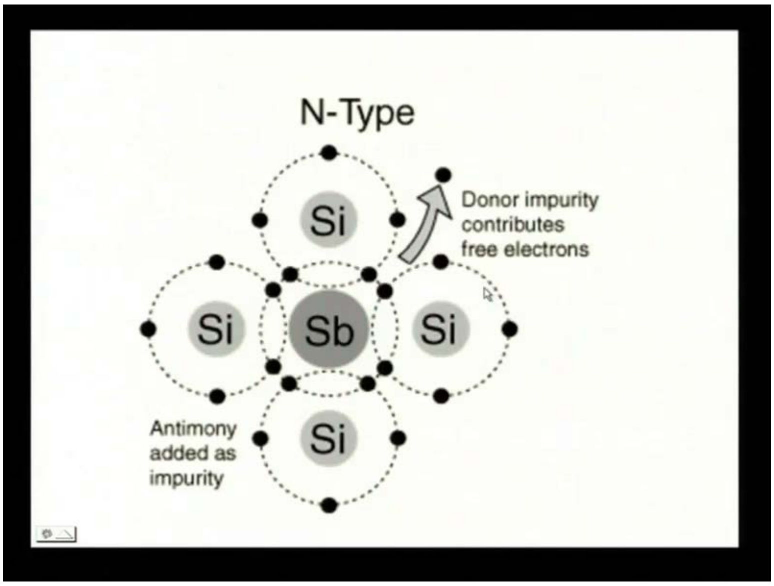

So, here who is the host lattice? Silicon is the host lattice, and dopant is phosphorous. Here the picture is more clear, the same picture. Here the picture is clearer you see that 1, 2, 3, 4, 5, 6, 7, 8 they form the bonding and the 5 th electrons is away. So, basically you need for 4 silicon atoms you need one antimony atom. For 4 silicon atoms you need one antimony atom or one phosphorous atom. Then after doping what will happen?

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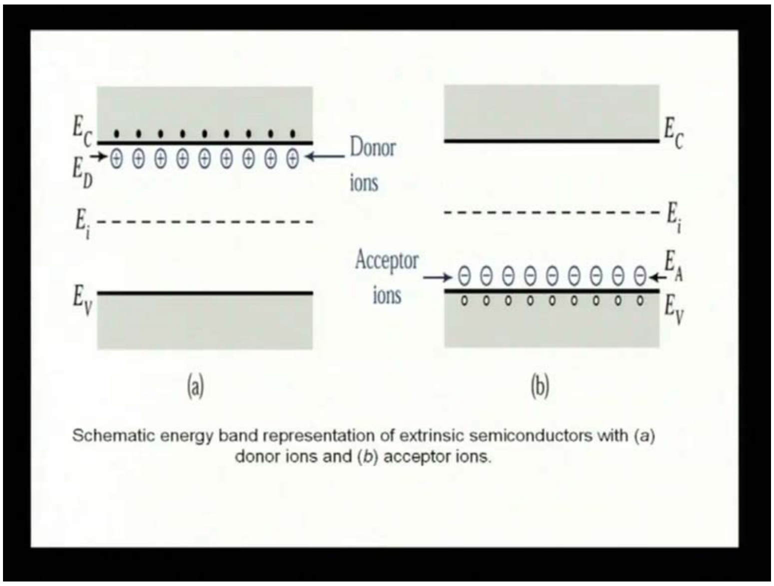

After doping you see that, here you confine this is the circles have been marked with positive sign. That means, they are positively charged ions. Remember that these are the phosphorous or arsenic or antimony. So, when they have liberated one electron to the crystal lattice they became ionised and positively charged obviously. So, this positively charged means it has liberated one Electron. Take the case here come here on the right side diagram. Here you sees that this is the negatively charged ion. So, they are boron or gallium or aluminium they are ready to accept. So, they are the acceptor atom ion in this case. And, these circles are basically the holes these circle basically the holes here yes.

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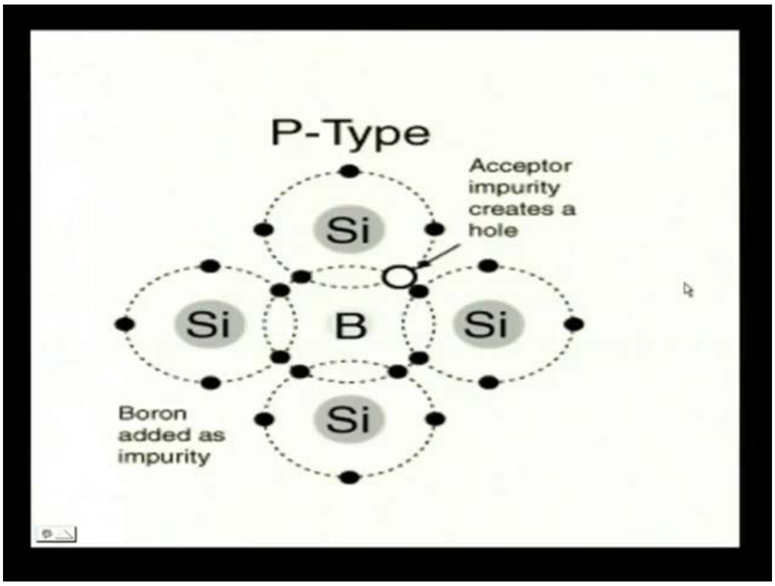

This picture will show you that phenomenon. You see that when silicon is doped with boron; boron has 3 electrons, silicon has 4 electrons. You have 7 electrons in this system. You need how many electrons?

Student: 8.

So, you see that there is a vacancy 1, 2, 3, 4, 5, 6, 7 electrons are there and one circle is there; open circle is there that is hole. So, electron from the adjacent atom will come to fill that hole electron from any adjacent atom will come to fill that hole; there one hole will be created then a neighbouring electron will come to occupy that hole. So, in that position one hole will be created. So, likewise there will be a movement of holes in p-type material.

So, we find that in n-type material the main carrier is the electrons. Remember that for n-type materials the majority carriers are the electrons, for p-type material the majority carriers are the holes. So, that is why in semiconductor both the electrons and holes take part in the conduction mechanism. Now, you come to that equation where I have shown you, what should be the conductivity in such case? You see that this is the conductivity sigma it is equals to n e mu n this mu n is the mobility of the electrons and this mu p is the mobility of the holes. This n and p are the concentration of electrons and holes respectively. So, now you cannot use this relation, where sigma is n e mu. After doping you have to use this relation, but we can make some approximation as well. How we can make the approximation?

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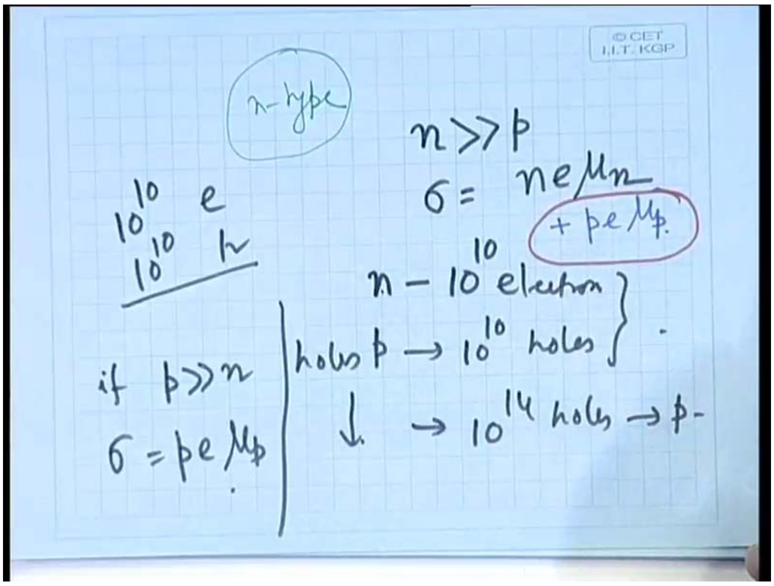

Suppose there is a material you have doped it n-type there is a material you have doped it n-type, this n-type material has both electrons and holes. You can tell me sir from where the holes are coming because one thing is sure that we have started with intrinsic materials. So, in intrinsic materials there are electrons as well as holes or say you have formed one p-n junction.

So, when you have formed one p-n junction then there will be both electrons and holes in that system. So, they will coexist. Basically we need almost in all electronic device we need the p-n junction be a diode, transistor, fet, mosfet, light emitting diode, laser diode, detectors. Basically those are junction device. Basically p-n junctions are there, but in different forms. We shall discuss those things also. So, in a p-n junction in a device both the electrons and holes are there, but if the number of electrons is very, very greater than the number of holes if the number of electrons is very, very greater than the number of holes then sigma can be written as n e mu n. We can avoid the 2 nd term consisting of plus p e mu p we can avoid or you can neglect this term this term we can neglect this term we can neglect. Why because? n is very greater than p.

So, we can neglect right. Suppose there is a material and you are adding conductivity for n-type that means, you are doping it say arsenic or phosphorous with arsenic or phosphorous. There is a material you are doping with arsenic or phosphorous. Then what will happen? Suppose there are 10 to the power 10 electrons were there and 10 to the power 10 holes are there.

So, as soon as you start doping. What will happen? The holes will be compensated. Remember the term compensation; the holes will be compensated that means, when there will be 10 to the power 8 electrons, so that 10 to the power 8 electrons will recombine with 10 to the power 8 holes. How many holes will be left? 10 to the power 2. Why 0? 10 to the power 10 holes were there yes. Now, if we add more 10 to the power 2 electrons then it will be 0. So, there will be no holes at all in the system. That is known as compensation.

You can change the conductivity even. You have you can start from p-type add on electrons. The holes will be compensated by the electrons it will be neutral or intrinsic and then it will change its conductivity. That means, if you can start from n say there are 10 to the power 10 electrons adding p that means holes. First these 10 to the power 10 holes will be there.

So, it will be neutral and then say 10 to the power 14 holes you if you add go on adding holes from n-type it will become p-type, from n-type it will become p-type. So, compensation in semiconductors is possible. Sometimes you find that you are adding the impurity of a particular type, but you are not getting the desired result. What should be there if you add on n or electrons? What will happen? You can expect that the conductivity will increase because you are doping with n-type, but your result does not show you the trend; that means, what will happen basically it is compensating. Some effect of compensation is taking place in the system in the material.

Then at one point of time you will see that the conductivity is changed to other type. If you started from p-type it will come to n-type or the vice versa. So, compensation is there. So, one thing is that we can increase the conductivity by doping, 2 nd things is that if both the materials are there both p and n-type. So, that conductivity will be given by both the electrons and holes. We have to calculate separately n e mu p e mu extra. And, if a particular type of material is say dominating in the system n if n is very greater than p then we can neglect this term or if p very greater than n. The sigma will be given by p e mu p that is also there.

So, depending on the number of electrons and holes you can approximate your equation or expression. This is known as the approximation. There are 10 to the power 14 electrons and 10 to the power 6 holes. You can tell that you can say that it is almost n-type. So, you can avoid the 2 nd term or say in a system there are 10 to the power 16 holes and 10 to the power 5 electrons; there also you can neglect the term containing electrons. So, majority carrier concepts are there, which one is the majority carrier? It is it hole or is it or is it electrons? If electrons are the majority carriers then it is known as the n-type material. If holes are the majority carriers it is known as the p-type material.

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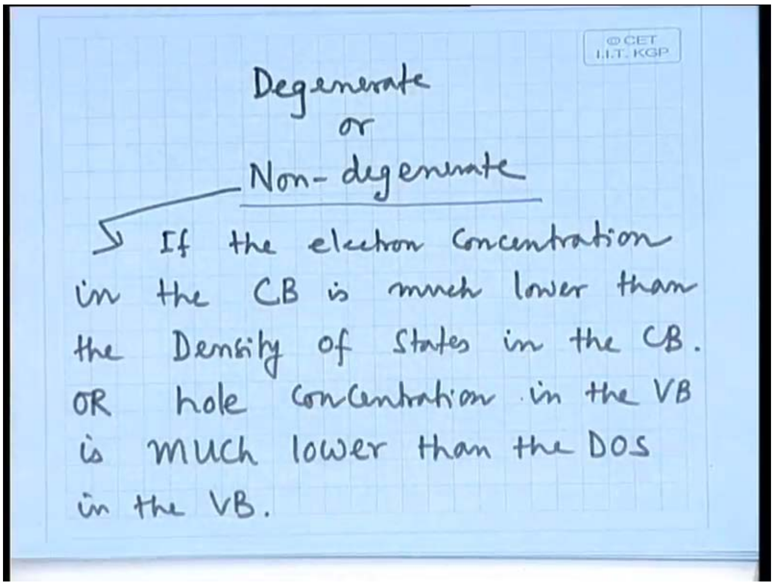

Then, another important thing is the degeneracy degenerate or non degenerate semiconductor.

Student: (( ))

Both are...

Student: (( ))

N-type is...

Student: (( ))

Electrically neutral means what is that? If you i do not know whether you are performing the experiment that when hot probe measurements are done carried out carried out or you say hall effect measurements are carried out. You will find that it is negative it is negative. Yes, that is positive. P type materials will show you positive and n type materials show you the negative. Now, another thing is that the degenerate and non-degenerate semiconductor. What are those? One is degenerate and another is non-degenerate. Degenerate non-degenerate is that in my last lecture we have introduced one concept of density of states. We shall use today also in my 2 nd lecture. Density of states is a concept where you can get the number of available states for electrons or holes in the material.

So, let us see that there are 2 bands. So, in this band how many numbers of states, levels are there? In this band how many levels or states are there, when you talk about levels or states it is basically the energy level. It is characterised by a particular energy x electron hold from the bottom of the conduction band. Why electron hold from the top of the valence band right. So, these states means say it is x1 from the bottom of the conduction band. Say this is x2 it is bottom of the conduction band, it is x3 it is bottom of the conduction band; all those are in electron hold. Basically those are energy states means here the energy the levels, where electrons can occupy in the conduction band or the holes can occupy in the valence band.

Similarly, there are states in the valence band also. So, number of states is known as the density of states. Number of states means how many states per units? How many levels are there? Levels means where the electrons or holes can be accommodated right, where the electrons and holes can be accommodated? And, you can measure it by electron volt, and they are very closely spaced. I have shown you that there is a finite gap in it, but since there are 10 to the power 18, 10 to the power 14, 10 to the power 17 states are there. So, you can imagine that they are they are very much close to each other. That is why they form a band; for all practical purpose they form a band very close to each other x plus delta x, e plus delta e likewise.

I am going to discuss the quantum mechanics because this is a general material science class. So, only the concept or the phenomena will be discussed. And, if someone is interested how those things happen then we can make some calculation, but not in this class. That is not possible also I can give you the reference etcetera. So, numbers of states are there and these numbers of states are different for different materials. It depends on the temperature and band gap of the material. It depends on the temperature and as well as the band gap of the material.

Now, what is non-degenerate semiconductor? Non-degenerate semiconductor is that where the Fermi level, non-degenerate semiconductor if the electron concentration in the conduction band is much lower than the density of states or hole concentration in the valence band is much lower than the density of states in the valence band right. Then we can say that the semiconductor is non-degenerate, non-degenerate.

Now, you can tell me that what is the value of the density of states what is the value of density of states? It is different in conduction band the value is say x and valence band the value is say y etcetera, but whatever be the value for a particular material. If the number of electrons in the conduction band is less than the density of states then you can say that it is non-degenerate semiconductor. And, that means the rooms are more than the guest in a hotel say the rooms are more than the guest in a hotel say then you can say that it is a non-degenerate case. And, if it is greater than the density of states if the if the number of electrons and holes are almost equal to or greater than, but chance of greater than is very is not possible because if there is no level electron cannot move there.

So, physically it is not correct to say that if it is greater than the density of states not that, but if it is comparable with the density of states. Then it is known as the degenerate semiconductor. We shall deduce some expression some relations of the current transport etcetera. The calculation of the electrons and holes in the conduction band or the valence band; these are valid for non-degenerate semiconductor remember; those are valid for non-degenerate semiconductor. For degenerate semiconductor, what happens? For degenerate semiconductors the band gap reduces.

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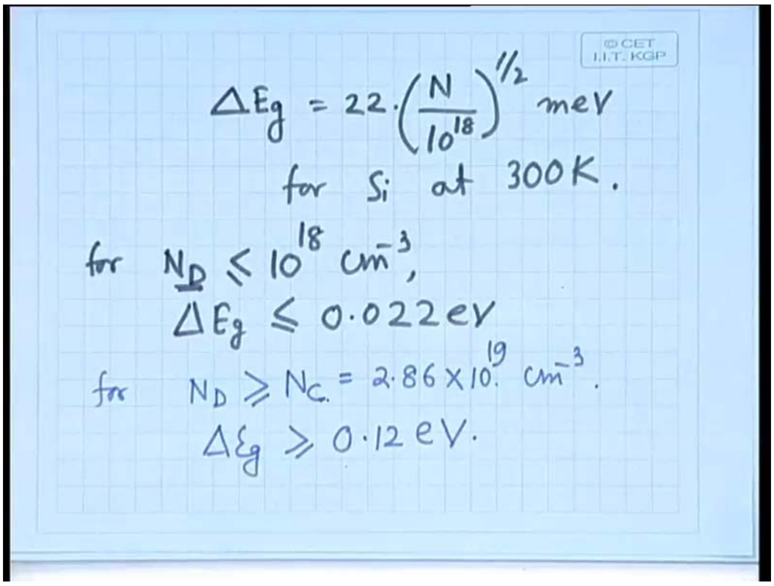

There is shrinkage of band gap. And, delta E g that means, reduction in band gap. It is given by 22 into N 10 to the power of 18 to the power half milli electron volt; it is for silicon at 300 k. This is the reduction in band gap, delta E g is the reduction in band gap and N is the number of electrons or holes in the respective band. And, I can show you that for ND less than equals to 10 to the power 18 centimetre cube inverse; delta E g is less than equals to 0.022 electron volts.

What is ND? ND is the Doping concentration that means, we have doped silicon with 10 to the power 18 dopant atoms. So, that 10 to the power 18 is the doping concentration 10 to the power 18 is the doping concentration. So, if it is less than equals to 10 to the power 18. Then we see that delta E g; that means, the reduction in band gap will be less than equals to 0.022 electron volt. And, it is almost 2 percent what is the band gap of silicon 1.12 electron volt. So, it is almost 2 percent of the original band gap of silicon at a room temperature.

So, it is not very high, but for ND greater than equals to NC; that means, the density of states the value is 2.86 into 10 to the power 19 centimetre cube inverse this delta Eg is greater than equals to 0.12 electron volt. 2 cases I have shown you. 1 is if it is less than 10 to the power 18 it is 0.22 electron volt this is non-degenerate, but if it becomes greater than or equals to 2.86 into 10 to the power 19. Then what will happen? It will be greater than equals to 0.12 electron volt. What it means? It is almost greater than 10 percent of the band gap 0.12 electron volt.

If the band gap is 1.12 electron volt then 0.12 electrons is almost 10 percent. So, it even if it greater; that means, it can be higher than 10 percent the band gap can is reduced. So, the original band gap can be reduced from 1.12 to 1 electron volt in this case or even less. So, there will be shrinkage of band gap. So, a material is characterised by is band gap, if band gap changes then a lot of phenomena will be there right. You are expecting that silicon will give this property, but it will not give because the band gap is change.

So, a lot of phenomena will be there and another thing is that generally the carriers; that means, the electrons or holes when move from the valance band to the conduction band these things we have discussed earlier that it moves from valance band to conduction band. Sometimes in degenerate semiconductors already there will be carriers in the conduction band already there will be carrier in the conduction band right because the doping is so high that internally they will move from the valence band to the conduction band. So, your starting material will show you some metallic type of conductivity because already there are 3 electrons in the conduction band.

So, till now some terminology we have learned 1 is that doping, 2 nd thing is intrinsic and extrinsic semiconductor, 3 rd one is n-type and p-type, and 4 Th one is degenerate and non-degenerate semiconductors. So, the knowledge of these things we shall we can use when we shall discuss about the crystal growth, and characterization, and the device application, because our ultimate aim is to study the application of semiconductor materials in device or electronic materials in various kind of device.

So, first say 10 lectures, we shall discuss the general type of thing. And, the other lectures after 10 lectures we shall actually go inside the subject, where we shall synthesise the material new and newer materials we can grow various kinds of materials their characteristics. Not that only the silicon or the gallium arsenide are the main semiconductor not that; obviously, sure they are the main semiconductors, but apart from silicon and gallium arsenide there are other several kinds of semiconductors for different kinds of application. So, it is there.

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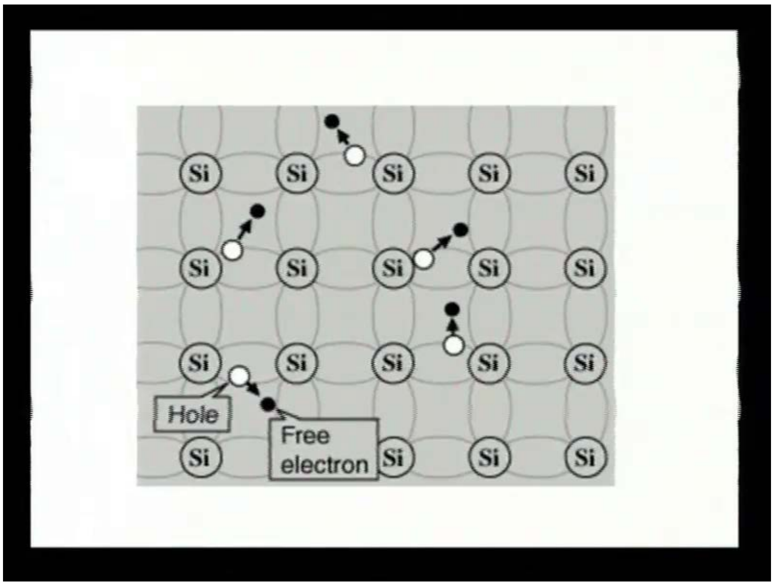

So, now let us consider here you see that after doping, what happens? These are the holes and these are the electrons. So, there will be free electrons.

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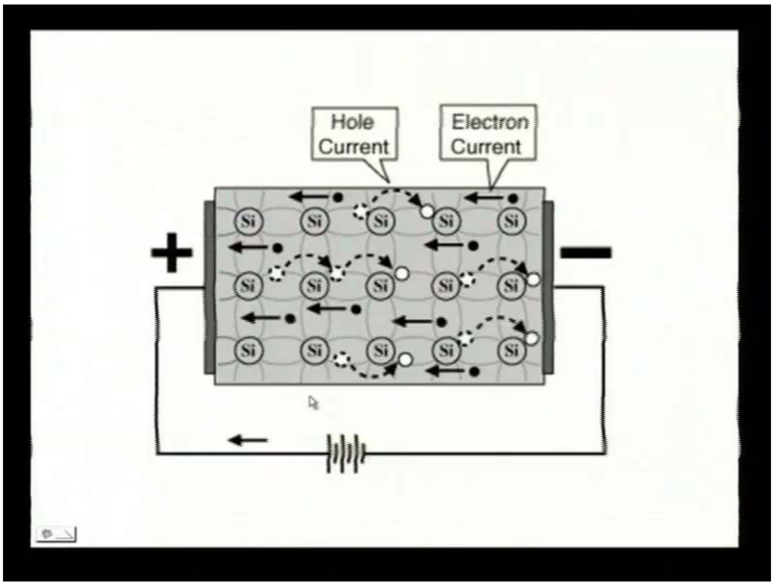

And, here if you apply a current or a say you apply a voltage; that means, electric field. Here see you have applied a voltage, and this is the positive terminal of the battery, this is the negative terminal of the battery. So, there will be a flow of current from where in the opposite direction, the electron moves in the opposite direction. So, that is very important thing that you see that the electrons move in this direction. So, the current will be from the positive polarity to negative polarity. Here see the electrons move from negative to positive because the electrons will move in the direction of the electron flow. And, so the conductional current will be opposite to the direction of the electron flow.

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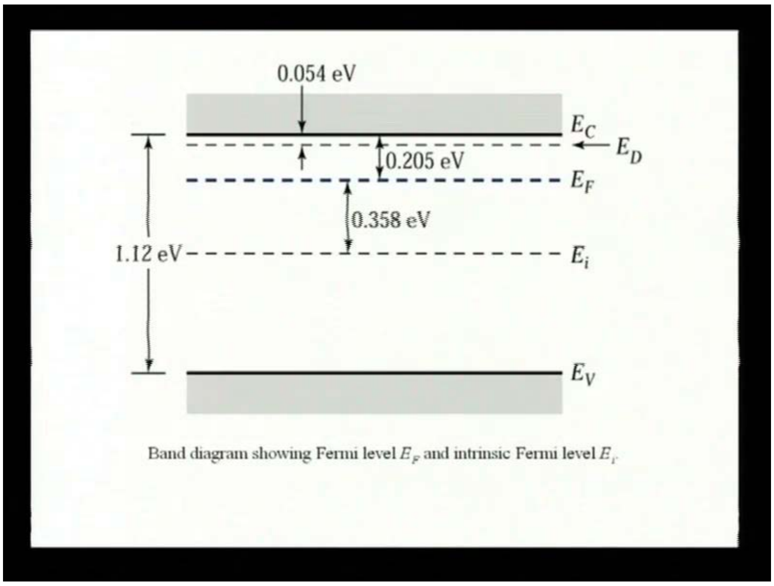

So, these things we have discussed. Now, another important thing is the intrinsic level E i, E i is the intrinsic level. What is intrinsic level? Intrinsic level is an imaginary electron state or imaginary level inside the band gap which is almost half away from the bottom of the conduction band or the top of the valence band. And, it is applicable for intrinsic materials only where the number of electrons and number of holes are equal.

So, intrinsic level is applicable for the intrinsic materials not for doped material remember; for doped material the level is denoted by the Fermi level. We shall discuss today the details of Fermi level in the next lecture. So, you see that this is the intrinsic level and this intrinsic level is basically the half way between supposed this is E c and this is E v.

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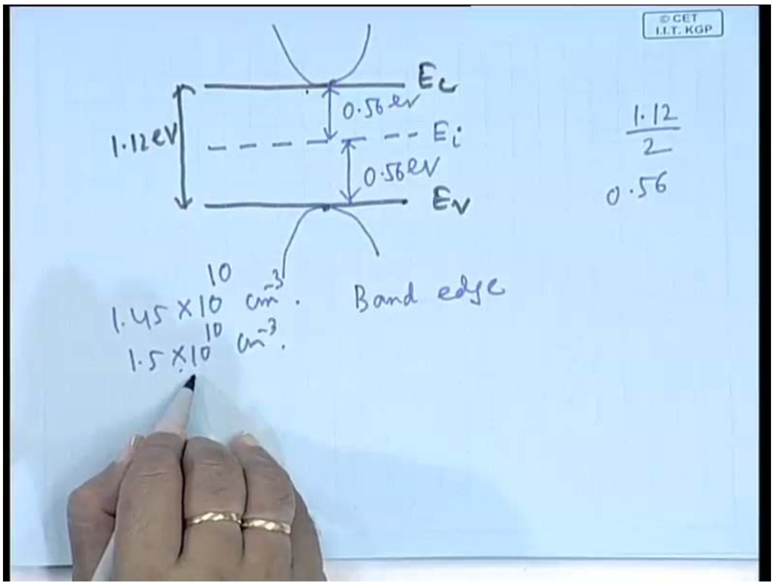

What is E c? E c is the bottom of the conduction band remember; that means, if you consider that the band is parabolic in nature. So, it is the bottom line. Similarly, E v is the top of the valence band and the difference is for silicon is 1.12 electron volt. So, that will give you the band gap. Now, if it is intrinsic silicon this is intrinsic silicon then what will happen there will be a level which is denoted by E i, which is denoted by E i, and this level is half way; that means, if you divide 1.12 by 2; 1.12 by 2 what will happen, what is the value? 0. 56.

So, it is 0.56 electron volt almost and it is 0.56 electron volt almost. Almost half way between the 2 band edges that are the band edge, Band Edge, Ec is the conduction band edge, and E v is the valence band edge. This is the band edge conduction band edge and this is the, this is conduction band edge this is valence band edge.

So, half way between the band edges there will be an intrinsic level and that is applicable for intrinsic materials. What is the intrinsic carrier concentration of silicon? Can you say? What is the intrinsic carrier concentration of silicon? It is 1.45 into 10 to the power 10 to the power how much? 10 centimetre cube inverse or in some books you will find that it is 1.5 into 10 to the power 10 intrinsic carrier concentration; that means, in the material 10 to the power 10 electrons and 10 to the power 10 holes are there 10 to the power 10 electrons and 10 to the power 10 holes are there that is the intrinsic carrier concentration it is different for different semiconductors. For germanium it is 10 to the power 13, for gallium arsenide it is 10 to the power 6. I shall show you the value in the next lecture.

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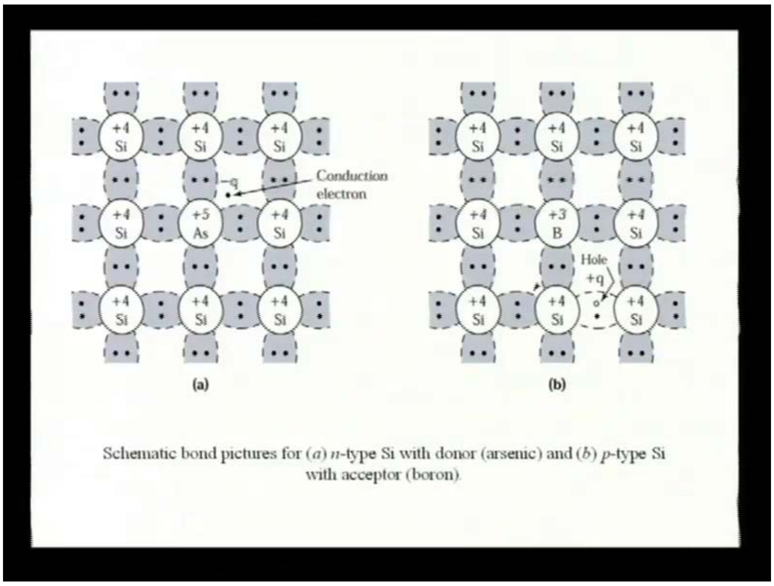

Schematic bond pictures for (a) n-type Si with donor (arsenic) and (b) p-type Si with acceptor (boron).

So, this is the schematic bond pictures for n-type silicon here we have used the arsenic as a donor and here the boron and already we have shown already we have seen that this is the free electron or this is the hole which is to be filled by the adjacent electron. So, when this electron moves here there will be a hole created here then this electron will move here to fill that hole. So, there will be a hole transport in the material for P-type semiconductor.

So, with this I conclude that there will be doping in the material. And, the doping basically changes the conductivity of the semiconductor it can cause other enhancement of the properties also as we shall show you in our next lecture. And, some of the terms we have introduced which we shall discuss in detail in the next lecture. So, there will be a break for some 2, 3 minutes then we shall assemble and we shall start.

Thank you.