# Electronic Materials, Devices and Fabrication

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## Lecture - 06
## Extrinsic Semiconductors

Last two classes, we looked at intrinsic semiconductors. So, intrinsic semiconductors or pure semiconductors are those where electrons and holes are generated in pairs.

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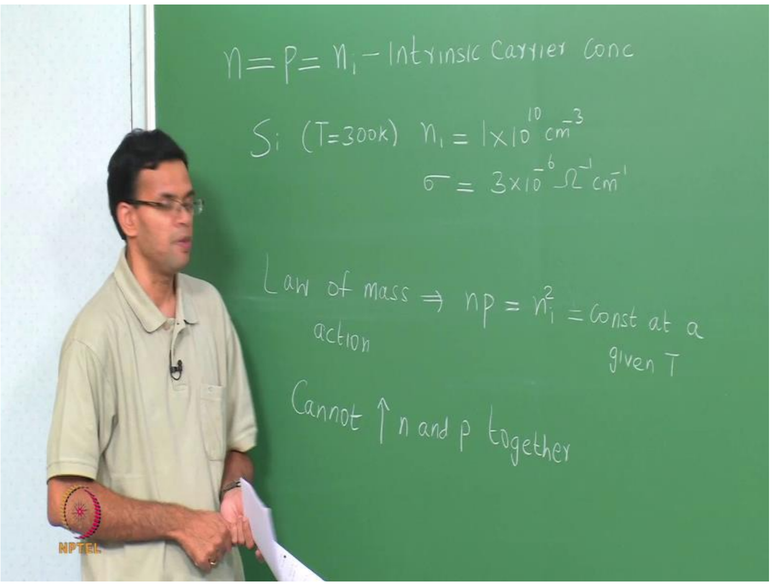

$n = p = n_i$ - Intrinsic Carrier Conc

Si (T=300K) $n_i = 1\times10^{10}\ cm^{-3}$

$\sigma = 3\times10^{-6}\ \Omega^{-1} cm^{-1}$

Law of mass action $\Rightarrow np = n_i^2$ = Const at a given T

Cannot ↑ n and p together

We saw that the electron concentration is the same as the whole concentration and we called it n i, for n i is the intrinsic carrier concentration. We also looked at some calculation for n i, in the case of the silicon at room temperature, we found that n i has a value of around 1 time 10 seconds to 10 per centimetre cube.

So, this number is really low when we look at the concentration of atoms, correspondingly the conductivity is also low. We got a value of 3 times 10 to the minus 6 ohm inverse and centimetre inverse. We also saw that in the case of an extrinsic semiconductors the carrier concentration n i is a function of temperature. So, the only way of increasing the conductivity if you are not allowed to change the material is by increasing temperature. Now, that is not practical, so what we need is a way to increase the concentration of electrons or holes while keeping the material at room temperature to do that we do doping and that is comes to extrinsic semiconductors.

We also saw this low of mass action which states the product of electron in whole concentration at equilibrium is equal to n i square. So, this is constant at a given temperature, what this means is we can either increase electron n or we can increase hole we cannot increase n, n p at the same time increase n n p together. Today, we will start looking at extrinsic semiconductors and I am going to start with the definition of extrinsic semiconductors.

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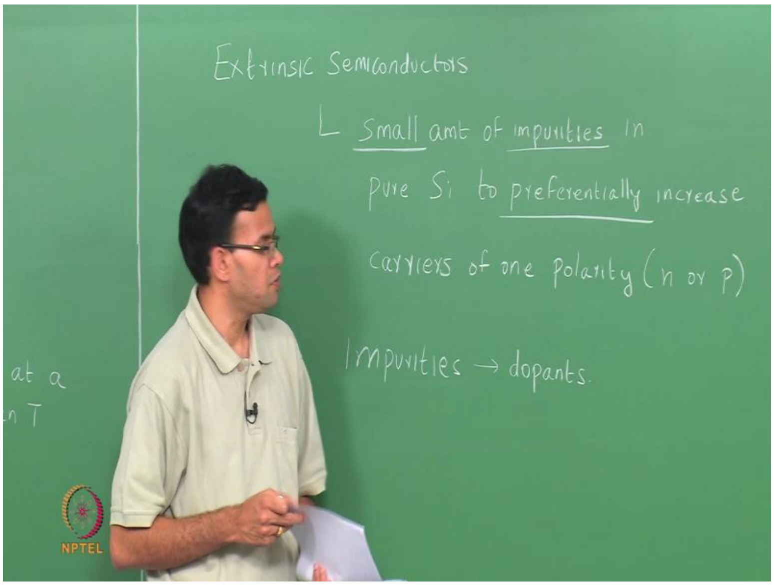

An extrinsic semiconductor we add small amount of impurities in your intrinsic material, since we are dealing mostly with silicon. I will say as small amount of impurities in pure silicon to preferentially increase carriers of one polarity and is either electrons or holes.

So, the preferential part comes from the low of mass action which says n into p is a constant at a given temperature. So, if we manage to increase n we will decrease p and vice versa there are two other operative terms, here one is small we will see how small the small the other word here is impurities. So, when we think of impurities the context of mythology we usually thing of impurities as small amounts of unwanted materials that is there because of any processing problem.

But, in the case of semiconductors, impurities are carefully controlled materials that are added to your pure semiconductor to change the conductivity. So, another word for impurities or a more appropriate word if you think about it is dopants. So, we can say that an extrinsic semiconductor is one where we add a small amount of dopant in order to preferentially generate electrons or holes, first we will start with n type doping.

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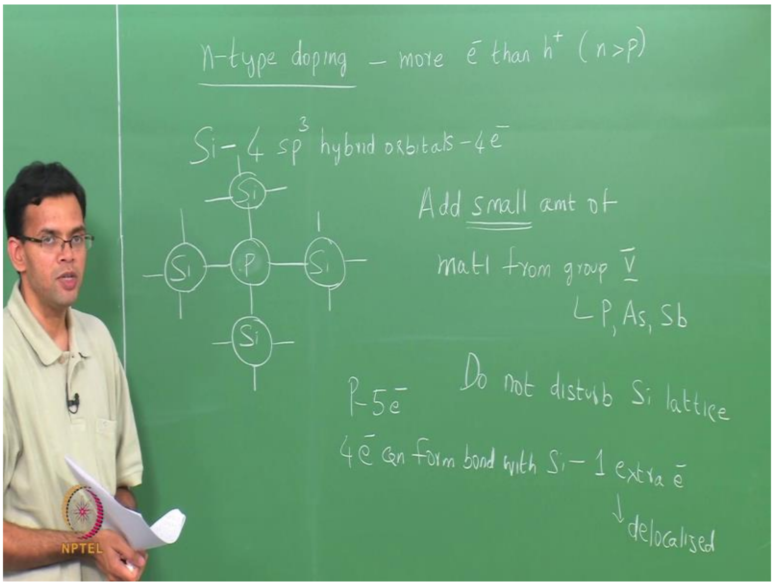

n-type doping – more $\bar{e}$ than $h^+$ $(n>p)$

Si – 4 $sp^3$ hybrid orbitals – 4$\bar{e}$

Add small amt of

matl from group $\overline{V}$

└ P, As, Sb

Do not distub Si lattice

P – 5$\bar{e}$

4$\bar{e}$ can form bond with Si – 1 extra $\bar{e}$

↓ delocalised

As the name implies, in the case of n type doping we preferentially increase the number of electros, so we have more electrons than holes rather they of stating as n will be greater than p. So, let us see how we can achieve this n type doping, let us go back to on model of silicon we said silicon has 4 electrons in the outer shell, 2 in the S and in 2 in the p which forms 4 S P 3 hybrid orbitals which gives you 4 electrons. Now, these orbitals are arranged in 3 dimensions in a diamond lattice, but just for the sake of illustration have you show them on 2 d lattice.

So, these are your silicon atoms, each silicon atoms have 4 bonds, remember this is 3 dimensional, but just for the sake of explanation I am giving at S to D it forms bonds with other silicon atoms and then the picture repeats. Now, let us say we add a small amount of a pentavalent material that is we add of material from group 5, examples of such material could be prosperous arsenic antimony again we only add a small amount. So, that the original silicon lattice is not disturbed, but what instead it does is the group 5 material goes and sites in the place of silicon we do not disturb the silicon lattice.

So, let us go back to this picture when, now instead of a silicon atom I have a prosperous atom I will just erase replace the silicon with prosperous. Once again, you see that prosperous has 5 electrons 4 of these electrons can easily form a bond with silicon and that leaves behind one extra electron. Now, this extra electron that is available can be delocalized and it can be made available for conduction with us by adding prosperous atoms.

So, for each prosperous atom we have created one extra electron in the system the question off course, then how much energy does this electron have? Is it easy to make a delocalized at room temperature? That is look at that calculating next, so what you are interested to find is the energy required, in order to take the extra electron from prosperous could be any other pentavalent impurity like arsenic or antimony to take their extra electron and delocalize it.

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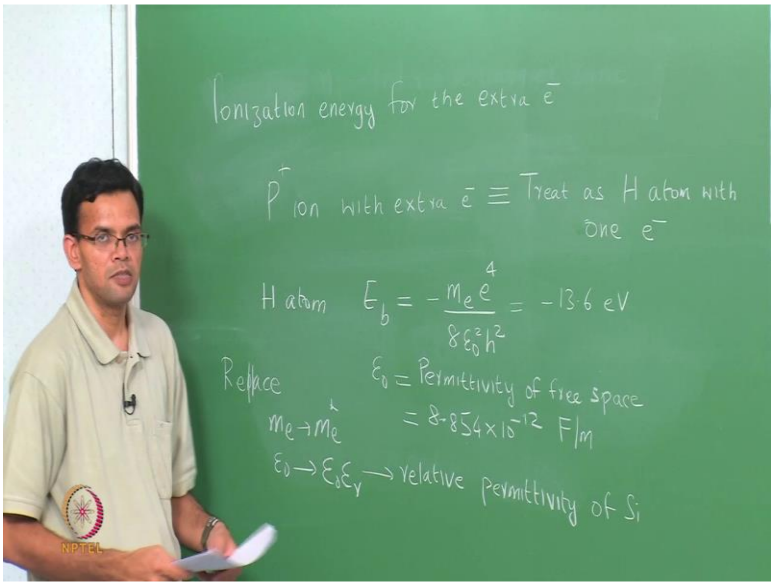

So, we need to find the ionization energy for the extra electron in the silicon lattice this extra electron is coming from the pentavalent impurity, so we can do a very precise energy calculation. To find this energy, we can also do a more easier back of the envelope calculation to do that we simply say that we have prosperous ion with one extra electron and we will treat this as a hydrogen atom with 1 electron with 1 electron. So, we get read of the complexity of the problem and then treated as hydrogen atom this will give us a simple calculation for the ionization energy of the extra electron.

If we have a hydrogen atom, the binding energy of an electron and hydrogen we can do the calculation by solving Schrodinger equation I will just write down. The expression is nothing but m e e to the 4 divided by 8 epsilon not square h square, m e is the rest mass of a electron, e is the electric charge epsilon not is the permittivity of free space. So, that is also a constant it is equal to 8.854 times 10 to the minus 12 farads per meter, so m e mass of the electron e to the 4 divided by 8 epsilon not square h square.

So, this is the binding energy of an electron in the hydrogen atom, if we solve this you get a value of minus 13.6 electron volts the negative tells you that is the binding energy slower than 0. We will take this expression and modify this for the prosperous atom within the silicon lattice, so we will replace m e by m e star which is the effective mass of the electron in silicon. We will replace epsilon not by epsilon, not epsilon r where epsilon r is the relative permittivity of silicon, so let us rewrite this explanation again.

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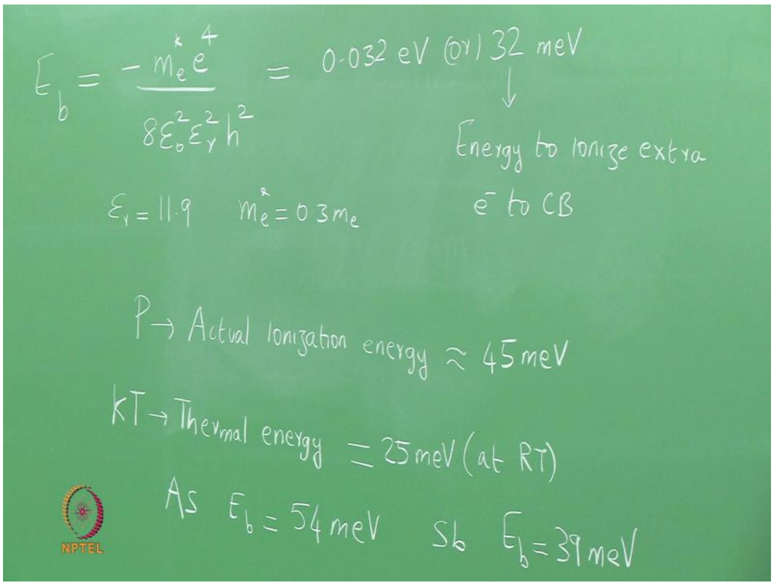

$$E_b = -\frac{m_e^* e^4}{8\varepsilon_0^2 \varepsilon_r^2 h^2} = 0.032 \text{ eV (or) } 32 \text{ meV}$$

↓

Energy to ionize extra $e^-$ to CB

$\varepsilon_r = 11.9$ $m_e^* = 0.3 m_e$

P → Actual Ionization energy ≈ 45 meV

kT → Thermal energy ≃ 25 meV (at RT)

As $E_b = 54$ meV Sb $E_b = 39$ meV

So, we want to calculate the binding energy of an electron, of an extra electron in the silicon atom because we added a group 5 impurity. To do the binding energy calculation we started with the binding energy for hydrogen and we replace it with the effective mass of the electron. So, it is m e star and we replace epsilon not by epsilon not square epsilon r square h square by epsilon r is the relative permittivity of silicon has a value of 11.9.

So, once again we can substitute the values m e star for silicon approximately point 3 m e epsilon r is 11.9, so we substitute the values this gives us answer 0.032 electron volts or if you write this in mille electron volts it is 32 mille electron volts. So, these energy 32 mille electron volts is the energy that is required in order to ionize that extra electron to the conduction band. The energy to ionize the extra electron and we did this calculation by simplifying this system and taking it to be a hydrogen atom.

If we do the actual calculation in the case of prosperous, the actual ionization energy is around 45 electron volts, I am sorry 45 mille electron volts which are very close to the value that we got by assuming a simple hydrogen atom. So, just for comparison if you looked at the value of K T which is the thermal energy at room temperature K T has a value of 25 mille electron volts. So, the ionization energy is very close to the thermal energy which means that at room temperature it is very easy, in order to ionize these electrons and take them to the conduction band and make available for conduction.

We will also show later on explicitly that all of these impurity atoms are ionized at room temperature when we do the calculation for electron and hole concentration as a function of temperature. But, for now just by looking at the ionization energies and the thermal energies we will say that all of these impurity atoms are ionized. So, the actual value for prosperous is around 45 mille e v, we said the other group 5 dopants like arsenic and antimony we look at ionization energies for these.

So, these are also very similar few have arsenic the ionization energies is around 54 mille e v and if we have antimony the ionization energies e b is around 39 mille e v, all of these numbers are very close to the thermal energy at room temperature. So, in all of these cases if you add them as dopants to the silicon the extra electron will be ionized, we can show these ionizations energies we can show these energy levels on a silicon band diagram.

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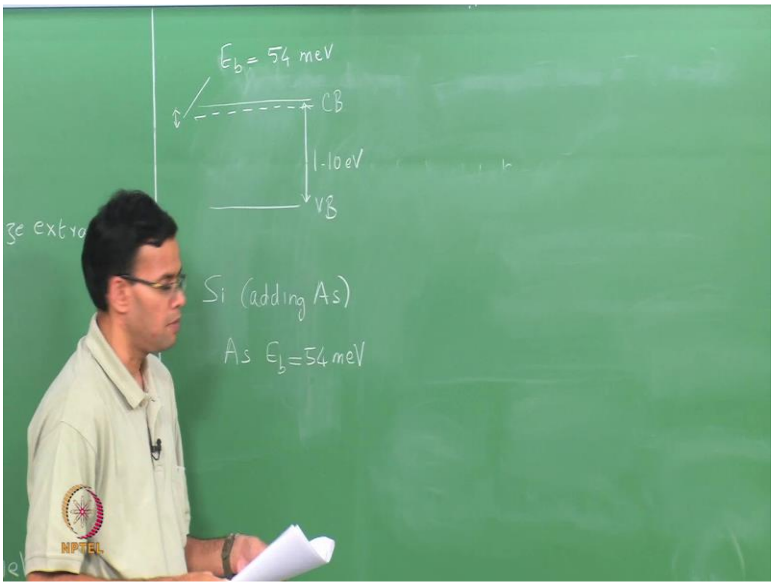

If you have a silicon band diagram, you have a valence band and a conduction band the distance between the valence band and the conduction band is the band gap. In case silicon the band gap is 1.10 electron volts at room temperature to this silicon we add some pentavalent impurities So, let us say we are adding arsenic, we already saw that arsenic has one extra electron and this one extra electron can easily ionized to the conduction band. But, the ionizations energy for arsenic is around 54 mille electron volts we add a small amount of arsenic, so that these are localized states.

They do not come into contact with each other and form a band and these states are located very close to the conduction band for write to depict this I will show the arsenic in terms of doted lines. The dotted lines just tells you it is a localized state, we have individual arsenic atoms within the solid and the difference between the arsenic levels. Now, the conduction band is nothing but e b just 54 mille e v if the concentration of these impurities the pentavalent impurities is written as N d.

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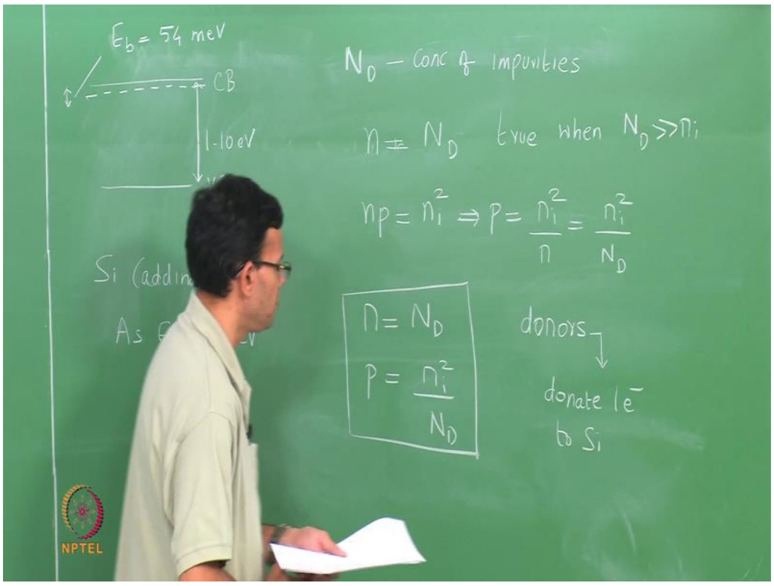

Each atom will give electron and room temperature all of these electrons are ionized which means the concentration of electrons n is the same as N d this is true when N d is much higher than the intrinsic carrier concentration. So, as long as N d is much higher than n i and all the atoms are ionized which is true in the case of silicon will find that n the same as N d. Now, to calculate p we use the low of mass action and say n p is n i square which implies p is n i square over n which is n i square over n d.

So, where to write these two together, the case of an n type material with N d being the concentration of the impurities n is the same as N d and p is n i square over N d and other name for a pentavalent impurity or an n type impurity is called donors. These are called donors because they have 1 extra electron which they donate, so they donate the one extra electron to silicon, next we will look at a p type impurity or a p type dopant.

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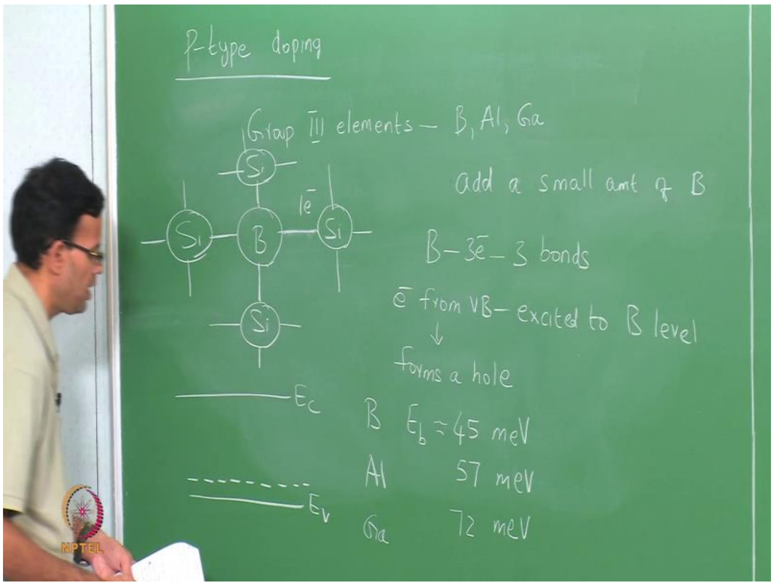

P-type doping

Group III elements – B, Al, Ga

add a small amt of B

B – 3e – 3 bonds

e from VB – excited to B level

↓

forms a hole

B $E_b \approx 45$ meV

Al 57 meV

Ga 72 meV

We look at p type doping the silicon atom is located in group 4 of the periodic table we said that donors which are n type dopants come from group 5. So, for p type doping, we look group 3 elements example of such elements include boron, aluminium, gallium. Soon, it can again use that ball and stick model for silicon to explain p type doping start with silicon has 4 bonds and I am only using a 2 D picture to illustrate actual molecule or actual soled is 3 dimension silicon, silicon each of the silicon has for the bonds.

So, they just propagate through your soled, so now you add a small amount of group 3 element, so let us say add a some amount of boron once again the boron atoms just replace the silicon silicon atoms in the lattice. The concentration is so small that it does not affect the lattice arrangement silicon and take the silicon atom and a replace it with boron, now a boron has 3 electrons, so you can easily form a bond or 3 bonds.

So, the boron confirm 3 bonds, but this silicon atom has one extra electron in order to form the bond with this silicon atom and electron from the valence band is excited to the boron level. So, that it can f a form the bond with silicon when in electron moves from the valence band you are left with the absence of an electron this forms a hole. We can do a similar calculation that we did for the entire impurities to look at the ionization energy that is the energy required to excide the electron from the valence band to the boron level.

If we do that, once again we will find that the energies are the order of mille electron volts if we do the actual calculation the case of boron the ionization energy e b is around 45 mille electron volts. If we have aluminium it is around, 57 if we have gallium it is around 72, once again these numbers are very close to the thermal energy at room temperature. So, once again we can say that all of the boron or all of the year atoms are ionized which means if you add n a boron atoms each boron atom will give you one hole. So, the concentration of holes at room temperature would be n a we can draw a similar band picture in the case of acceptors.

So, we will draw the band gap of silicon this is e c this e v, so this is your valence band, this is your conduction band in the case of n type, we said that they are localized levels very close to the conduction band. But, in the case of b type their localized levels very close to the valence band, so that an electron from the valence band can be excited to the boron or the acceptor level.

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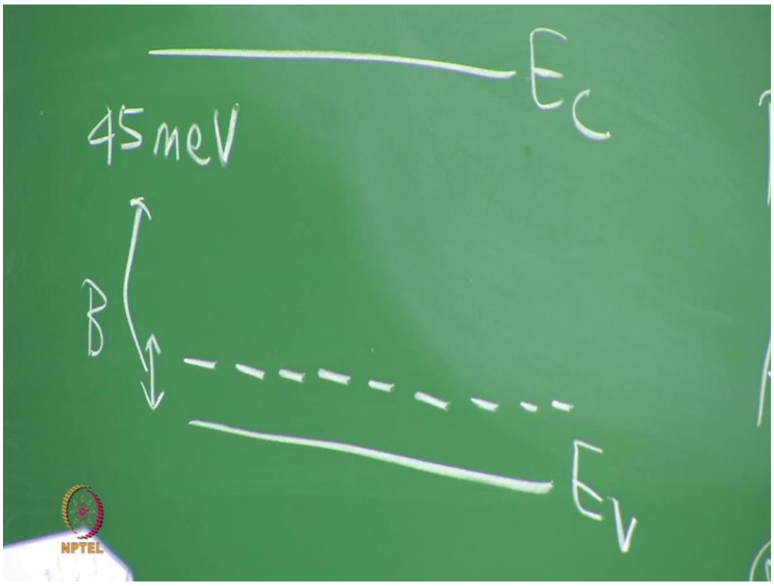

So, this is boron and the energy gap between them is around 45 mille electron volts.

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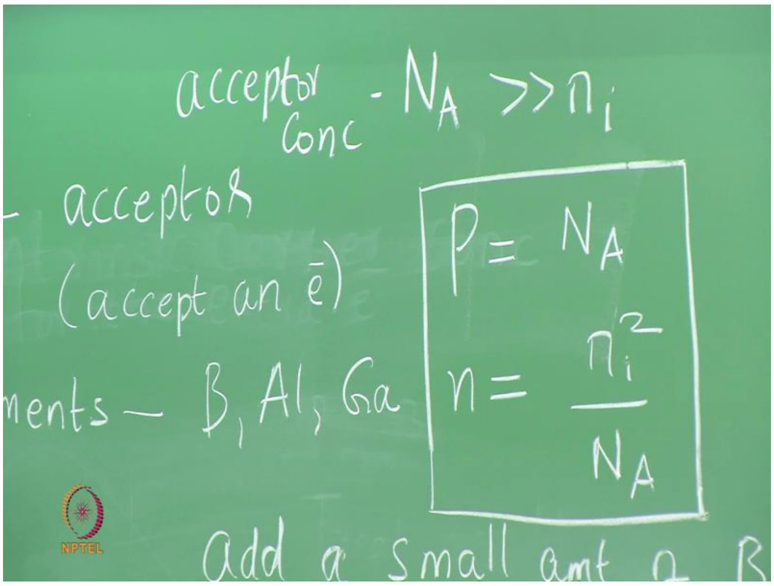

acceptor Conc - $N_A >> n_i$

- acceptor (accept an $\bar{e}$)

ments — B, Al, Ga

$$\boxed{\begin{aligned} p &= N_A \\ n &= \frac{n_i^2}{N_A} \end{aligned}}$$

Add a small amt o B

A p type dopant is called an acceptor, n type is called a donor because it donates one electron this accepts one electron. So, it is called an acceptor and just the same way with n type, if N A is your concentration of acceptor atoms and N A is much greater than n i. We will find that p is N A, n is n i square over N A, these are the same arguments that we used when we describe your n type dopants. So, let us actually put in some values now and try to calculate the electron in hole concentration and the conductivity, one of the reasons for doping is to increase the carrier concentration and to also increase the conductivity.

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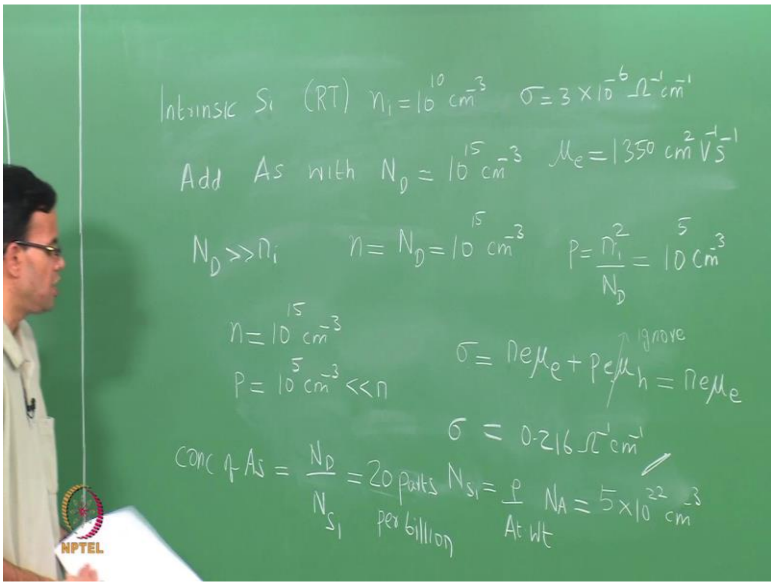

Intrinsic Si (RT) $n_i = 10^{10}\ cm^{-3}$ $\sigma = 3 \times 10^{-6}\ \Omega^{-1} cm^{-1}$

Add As with $N_D = 10^{15}\ cm^{-3}$ $\mu_e = 1350\ cm^2 V^{-1} s^{-1}$

$N_D >> n_i$ $n = N_D = 10^{15}\ cm^{-3}$ $p = \frac{n_i^2}{N_D} = 10^5\ cm^{-3}$

$n = 10^{15}\ cm^{-3}$

$p = 10^5\ cm^{-3} << n$

$\sigma = ne\mu_e + \overset{\text{ignore}}{\cancel{pe\mu_h}} = ne\mu_e$

$\sigma = 0.216\ \Omega^{-1} cm^{-1}$

conc of As $= \frac{N_D}{N_{Si}} = 20$ parts per billion $N_{Si} = \frac{\rho}{\text{At Wt}}$ $N_A = 5 \times 10^{22}\ cm^{-3}$

We saw earlier that if we have intrinsic silicon your carrier concentration at room temperature is 10 to the 10 and your conductivity sigma square 3 times 10 to the minus 6 ohm inverse and centimetre inverse. Let us take intrinsic silicon and add arsenic with a concentration of 10 to the 15 arsenic ohms per centimetre cube. So, N d is the concentration of arsenic, arsenic is a group 5 material, so it has one extra electron, so it is an n type dopant. We also see that N d is much greater than n i and the room temperature, all the arsenic are ionized.

So, the concentration of electrons n same as N d 10 to the 15 centimetre cube, the concentration of holes is n i square over N d, if you do the math n i is 10 to the 10 N d is 10 to the 15 . So, n i square is 10 to the 20 divided by N d which is 10 D to the 5, so we have a concentration of electrons which is 10 to the 15 concentration of holes which is just 10 to the 5. So, p is 10 orders of magnitude less than n, so it is much less than n, so by doping your silicon with arsenic which is an n type dopant.

You are preferentially increase the concentration of electrons to more than 10 orders of magnitude compare to holes were the equation for conductivity you seeing this earlier is n e mu e plus p e mu h. Now, n is so much larger than p we can ignore this term and then just write at as n e mu e mu e is the mobility for silicon. Later, we will look at the effect of dopant concentration on mobility we will see that dopants actually reduce the mobility, but for now we will just take the mobility of silicon.

So, mu e 1350 centimetre square volts per second, so we substitute n which is the same as n d e and mu e and if we evaluate the expression you get sigma to be equal to 0.216 ohm inverse centimetre inverse. So, we started out with in intrinsic silicon which has a conductivity of around 10 to the minus 6, we added 10 to the 15 arsenic atoms and we found that your conductivity as increased by more than 5 orders of magnitude. So, this is the reason why we use extrinsic conductors.

It is possible to increase the conductors by orders of magnitude, by adding these dopants whether they are n type dopants or p type dopants we say we added around 10 to the 15 arsenic atoms. So, what is that in terms of concentration to do? To know the concentration of arsenic we need to find out the number of silicon atoms by unit volume, so this let me say is concentration of silicon concentration of silicon.

Again, we have done this before is nothing but the density of silicon divided by the atomic weight times the number which is 5 times 10 to the 22 centimetre cube. So, if you looked at the concentration of arsenic is 10 to the 15 by 5 times 10 to the 22 which if you do is around 20 parts per billion parts per million is 10 to the minus 6 parts per billion is 10 to the minus 9.

So, by adding a really small amount of arsenic so much small that it is of the order of parts per billion were increase the conductivity by more than 5 orders of magnitude. So, also the reason why doping has be such a precise process because we have to make sure that we have the right concentration of dopant atoms. So, that we have the right concentration carriers and the conductivity that we desire we can do a similar analysis in the case of a p type impurity, so let me just write that down briefly.

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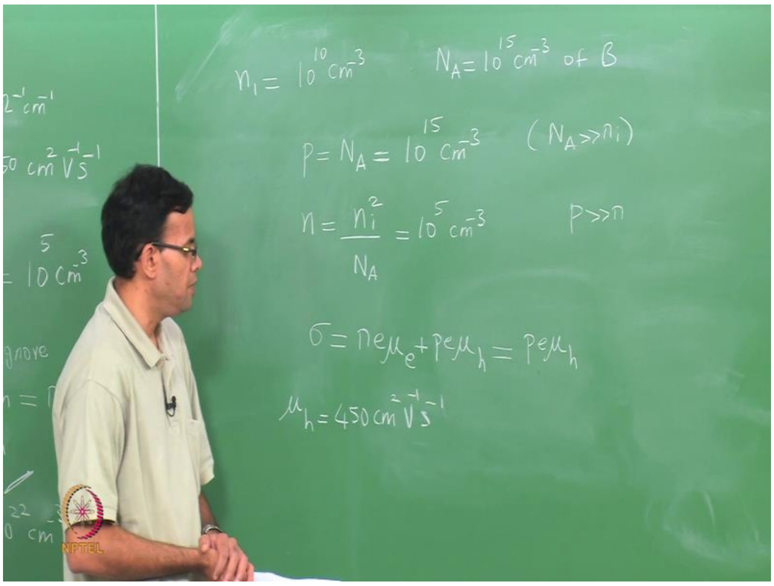

So, once again we start with intrinsic silicon n i is 10 to the 10 centimetre cube, but now instead of adding prosperous, let me add 10 to the 15 atoms of boron, boron is a group 3 element. So, when you add boron to silicon we basically increase the concentration of holes, once again at room temperature all of these holes are ionized or all of these atoms are ionized. So, the hole concentration is the same as N A in this is true again because N A is much greater than n i, we can once again calculate the electron concentration is n i square over N A which is 10 to the 5.

So, in the case of a p type impurity we find that p is much greater than n, so your conductivity equation which is n e mu e plus p e mu h will be just p e mu h. Once again, do the numbers the case of silicon mu h is around 45 centimetre square volts per second, so the conduct will be conductivity will be slightly lower than that of an n type dopant because of the difference in motilities.

But, it will still be 5 orders of magnitude higher than the conductivity of intrinsic silicon, we have looked at an n type dopant, we have looked at a p type dopant know. What will happen if we add both an n and a p type dopant together? So, we look at a situation where we have both the n type and the p type dopant this kind of doping is called compensation doping.

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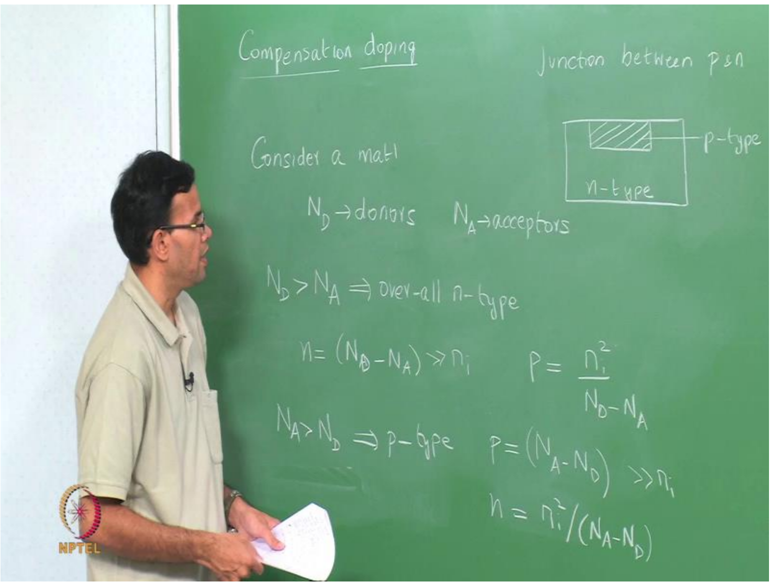

Compensation doping

Junction between p & n

Consider a mat'l

$N_D \rightarrow$ donors $N_A \rightarrow$ acceptors

$N_D > N_A \Rightarrow$ over-all n-type

$n = (N_D - N_A) \gg n_i$ $p = \frac{n_i^2}{N_D - N_A}$

$N_A > N_D \Rightarrow$ p-type $p = (N_A - N_D) \gg n_i$

$n = n_i^2/(N_A - N_D)$

The first question is why do you actually have to dope both materials, let me just give you a brief answer, so let us say we are trying to form a junction between p and n type materials. Usually, we need such junctions when we found devices we will talk about devices later, one way to form a junction is to start with the material that is completely n type and then dope a certain region of the material p type.

So, we will see later that they are certain ways of doing this, but in this particular region you have both n type impurities and both p type impurities and we do it in such a way the overall material is p type.

So, this type of doping with both kind of dopants is called compensation doping, so consider a material were N d is the concentration of donors, donors are you n type dopants and N A is a concentration of acceptors. You can have two scenarios, can have situation where N d is greater than N A, if we have situation where n d is greater than N A the material is set to be over all n type with n. The concentration of electrons nothing but N d minus N A, this will still be much greater than the intrinsic carrier concentration of holes is an n i square, so we have both donors and acceptors.

But, if the concentration of donors is more than acceptors material is set to be over all n type material, on the other hand if we have N A greater than N d it is a reverse case. So, over all it is a p type material, concentration of holes nothing but N A minus N d which is greater than n i and n, the n i square N A minus N d, let us just workout an example for this.

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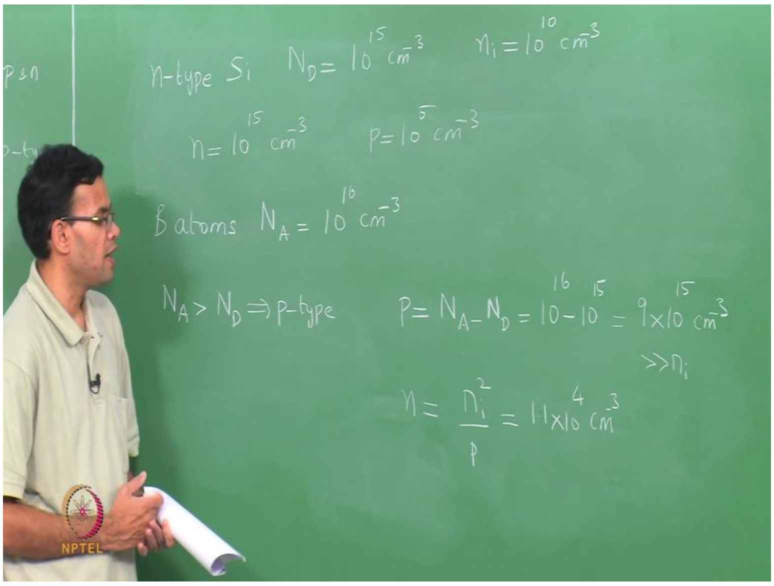

So, consider n type silicon with N d equal to 10 to the 15 a centimetre cubes, so this is an n type material, so n is 10 to the 15 n i for silicon is 10 to the 10. So, p 10 to the 5 centimetre cube, now you take this and we add arsenic we add boron atoms, so we add acceptors and the concentration acceptors N A is 10 to the 16. So, we originally started out with an n type material, now we have situation where the concentration of acceptors is more than that of donors. So, the material over all is p type the concentration of holes is nothing, but, n a minus N d which is 10 to the 16 minus 10 to the 15.

So, N A minus N d which is 9 times 10 to the 15 per centimetre cube and this is still greater than n i, since n i is only 10 to the 10 concentration of electrons is better. Now, n i square over p time 10 to the 4 centimetre cube, so thus we started out with an n type material, but by preferentially adding acceptors whose concentration is more and the concentration of donors you made this material into a p type material.

We will stop the class here for today, the next class we will look at the position of the Fermi energy in the case of an extrinsic semi conductor and we will also look at the behaviour of the co carrier concentration with temperature. We will try and explain how we can say that all the donors or all the acceptors are ionized at room temperature would we look at that in the next class.