Fundamentals of 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 semiconductor are those where electrons and holes are generated in pairs.

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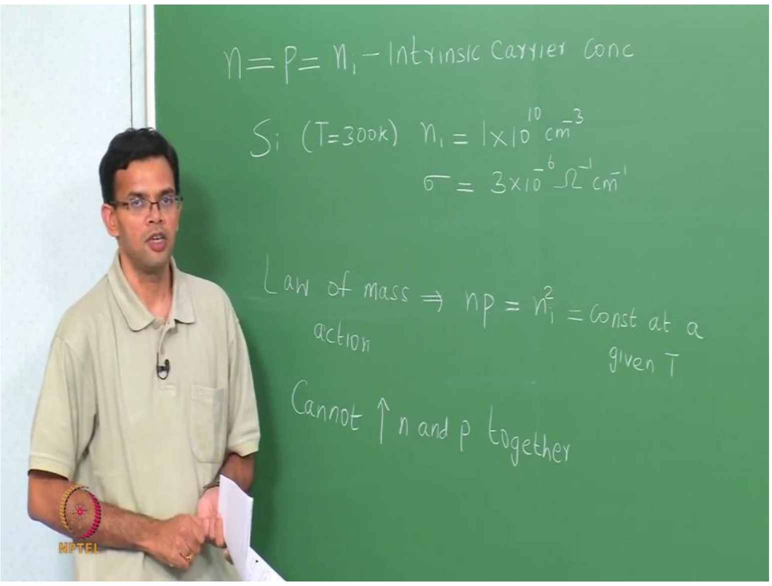

We saw that the electron concentration is the same as whole concentration and we called it n_i. If n_i is the intrinsic carrier concentration, we also looked at some calculations for n_i. In the case of silicon at room temperature, we found that n_i has a value of around 1×10^{10} cm^{-3}. So, this number is really low when we look at the concentration of atoms, correspondingly conductivity was also low. We got a value of 3×10^{-6} Ω^{-1} cm^{-1}. We also saw that in the case of an intrinsic semiconductor 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 law of mass action which states that the product of electron and hole concentration at equilibrium is equal to n_i^2. So, this is constant at a given temperature, what this means is we can either increase electron or we can increase hole, we cannot increase n and p at the same time, increase n and 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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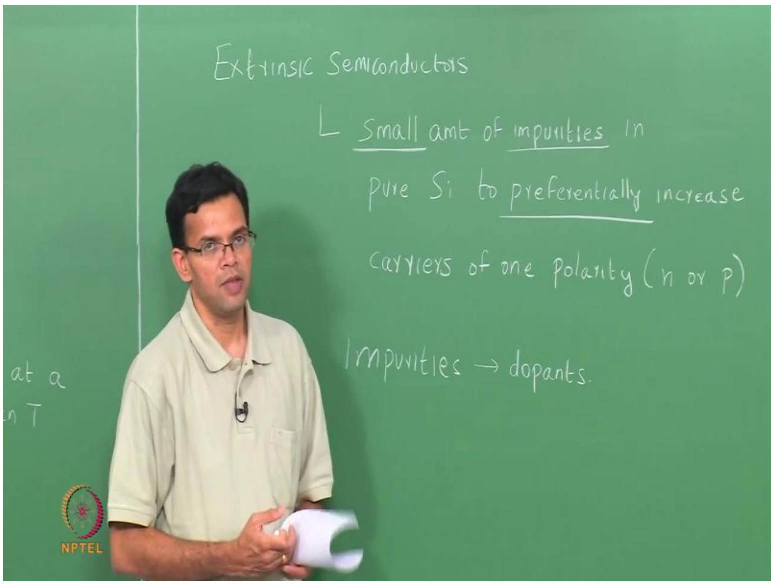

Extrinsic Semiconductors

Small amt of impurities in pure Si to preferentially increase carriers of one polarity (n or p)

Impurities → dopants.

Now, extrinsic semiconductor, we add small amount of impurities in your intrinsic material, since we are dealing mostly with silicon I will say a small amount of impurities in pure silicon to preferentially increase carriers of 1 polarity that is either electrons or holes. So, the preferential part comes from the law of mass action it 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 2 other operative terms here, one is small, we will see how small is small the other word here is impurities. So, when we think of impurities in the context of metallurgy, we usually think of impurities as small amounts of unwanted materials that is 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 in extrinsic semiconductor is a 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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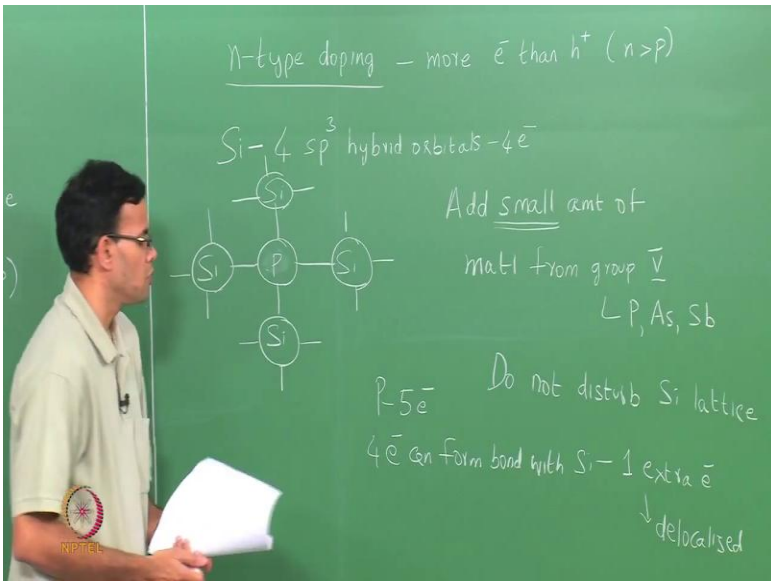

n-type doping – more $\bar{e}$ than h^+ ($n > p$)

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

Add small amt of
mat'l from group V
└ P, As, Sb

Do not disturb 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 electrons. So, we have more electrons than holes, another way of stating is n will be greater than p. So, let us see how we achieve this n-type doping. So, let us go back to a model of silicon, you said silicon has four electrons. In the outer shell, 2 in the s and then 2 in the p which forms 4 sp^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 I will show them on a 2 d lattice. So, these are your silicon atoms, each silicon atom has four bonds, remember this is 3 dimensional, but just for the sake of explanation I am giving it as 2 d, which 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 phosphorous, 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 sits in the place of silicon; we do not disturb the silicon lattice. So, let us go back to this picture where now instead of a silicon atom I have a phosphorous atom, I will just erase this replace the silicon with phosphorous. Now once again you see that phosphorous has 5 electrons, four of these electrons can easily form a bond with silicon and that lives behind one extra electron, now this extra electron that is available can be delocalized and can be made available for conduction. So, thus by adding phosphorous atoms for each phosphorous atom you have created one extra electron in the system. The question of course, is how much energy does this electron have and is it easy to make it delocalized at room temperature. Let us look at that calculation next.

So, what you are interested to find is the energy required in order to take the extra electron from phosphorous could be any other pentavalent impurity like arsenic or antimony to take their extra electron and delocalize it.

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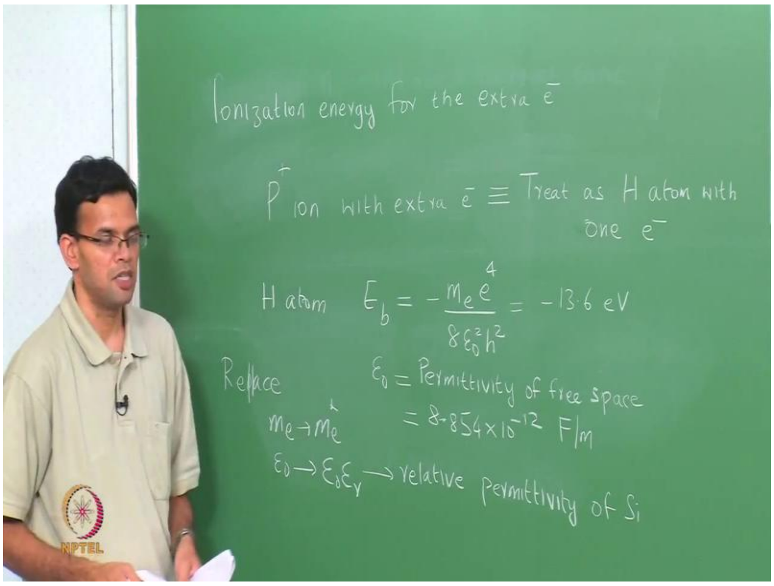

Ionization energy for the extra $\bar{e}$

P^+ ion with extra $\bar{e}$ ≡ Treat as H atom with one e^-

H atom $E_b = -\frac{m_e e^4}{8\varepsilon_0^2 h^2} = -13.6$ eV

Replace ε_0 = Permittivity of free space $= 8.854 \times 10^{-12}$ F/m

$m_e \to m_e^*$

$\varepsilon_0 \to \varepsilon_0 \varepsilon_r \to$ relative permittivity of Si

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, One we can do a very precise energy calculation to find this energy. We can also do easier back of the envelope calculation. To do that we simply say that we have phosphorous ion with one extra electron and we will treat this as a hydrogen atom with one electron. So, we get rid of the complexity of the problem and then treated as a hydrogen atom. This will give us a simple calculation for the ionization energy of the electron, if you 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 $\frac{m_e e^4}{8\varepsilon_0^2 h^2}$, m_e is the rest mass of the electron, e is the electric charge, ε_o is the permittivity of free space that is also a constant, it is equal to 8.854×10^{-12} F m^{-1}. So, m_e mass of the electron $\frac{e^4}{8\varepsilon_0^2 h^2}$. So, this is the binding energy of an electron in the hydrogen atom.

If you solve this to get a value of -13.6 ev, the negative energy tells you there is a binding energy slower than 0. We will take this expression and modify this for the phosphorous atom with in the silicon lattice. So, we will replace m_e by m_e^* which is the effective mass of the electron in silicon and we will replace ε_o by $\varepsilon_o\ \varepsilon_r$, where ε_r is the relative permittivity of silicon. So, let me rewrite this expression again.

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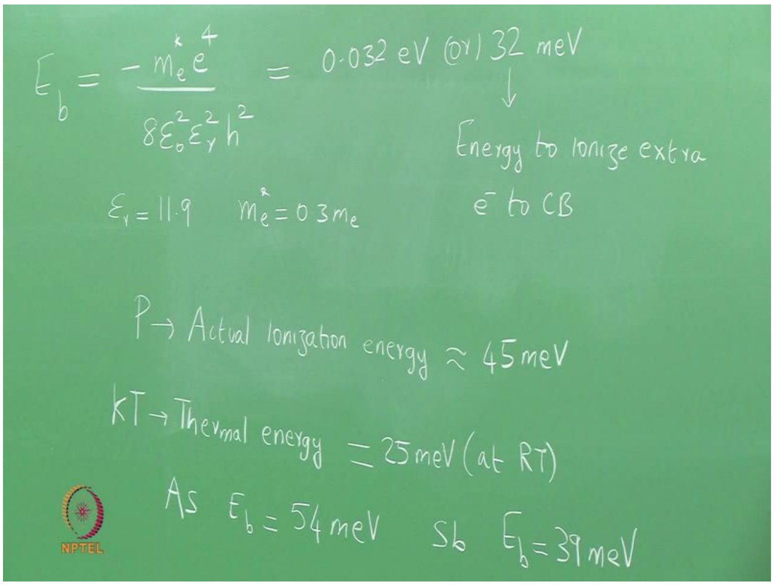

$$E_b = -\frac{m_e^* e^4}{8\varepsilon_o^2 \varepsilon_r^2 h^2} = 0.032\ \text{eV (or) } 32\ \text{meV}$$

↓

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^*, when we replace ε_o by $\varepsilon_o^2\ \varepsilon_r^2\ h^2$, where ε_r is the relative permittivity of silicon has a value of 11.9. So, once again we can substitute the values, m_e^* for silicon approximately 0.3 m_e, when ε_r is 11.9. So, we substitute the values this gives us answer 0.032 electron volts or if you write this in milli-electron volts that is 32 milli-electron volts. So, this energy 32 milli-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 you do the actual calculation. In the case of phosphorous, the actual ionization energy is around 45 milli-electron volts, which is very close to the value that we got by assuming a simple hydrogen atom. Just for comparison, if you look at the value of kT, which is a thermal energy at room temperature, kT has a value of 25 milli-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 ionization energies and the thermal energies we will say that all of these impurity atom are ionized. So, the actual value for the phosphorous is around 45 milli ev.

We said the other group 5 dopants like arsenic or antimony, if you look at ionization energies for these. These are also very similar, if you have arsenic the ionization energy is around 54 milli ev and if you have antimony, the ionization energy E_v is around 39 milli ev. All of these numbers are very close to the thermal energy at room temperature. In all of these cases, if you add them as dopants to the silicon the extra electron will be ionized. We can show these ionization's energies can show these energy levels on a silicon band diagram.

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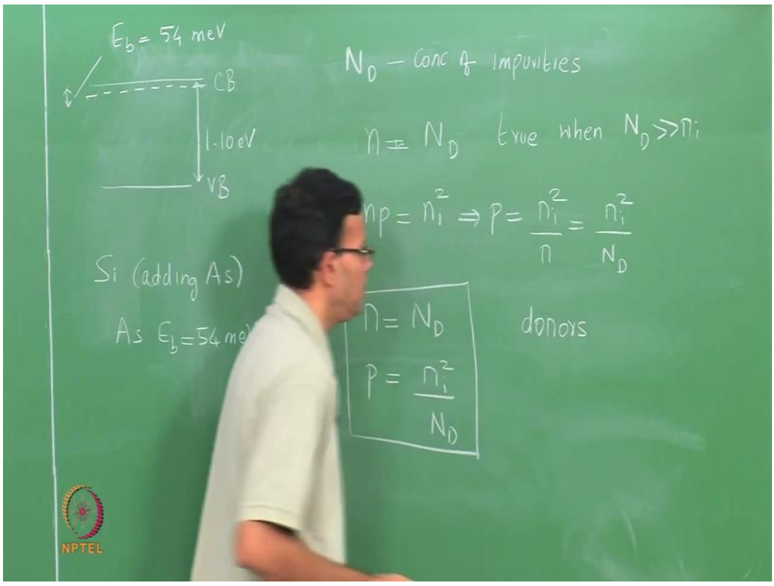

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If you have silicon band diagram, you have a valance band and a conduction band the distance between the valance band and the conduction band is the band gap. In case of silicon the band gap is 1.10 electron volts at room temperature; to this silicon we add some pentavalent impurities. So, let us say we are adding arsenic we already saw that arsenic has 1 extra electron and this 1 extra electron can easily ionize to the conduction band and the ionization energy for arsenic is around 54 milli-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. If I write to depict this, I will show the arsenic in terms of dotted lines.

The dotted line just tells you, it is a localized state. You have individual arsenic atoms within the solid and the difference between arsenic level and the conduction band is nothing but e b, which is 54 milli ev, if the concentration of these impurities the pentavalent impurities is written as N_D, each atom will give one electron and at 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 atom are ionized, which is true in the case of silicon will find that n is same as N_D. To calculate p, we use the law of mass action and say n p is n_i^2, which implies p is $\frac{n_i^2}{n}$. This is $\frac{n_i^2}{N_D}$, if I were to write these 2 together. In the case of n-type material with N_D being the concentration of the impurities, n is the same as N_D and p is $\frac{n_i^2}{N_D}$. Another name for a pentavalent impurity or an n-type impurity is called donors and these are called donors because they have 1 extra electron which they donate. So, they donate the 1 extra electron to silicon. Next we will look at a p-type impurity or a p-type dopant.

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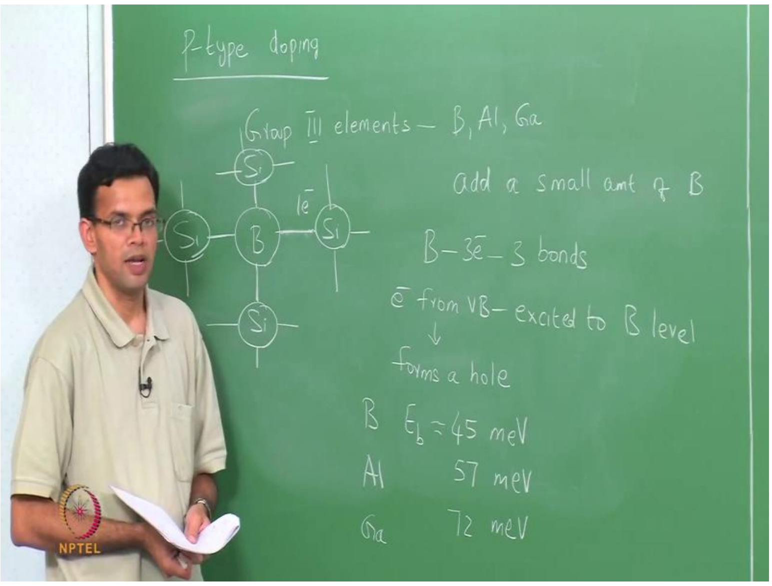

We look at p-type doping; the silicon atom is located in group four of the periodic table. We said that donors which are n-type dopants come from group 5. So, for p-type doping, we look at group 3 elements, examples of such elements include boron, aluminum, gallium and so on. Can I again use that ball and stick model for silicon to explain p-type doping? Start with silicon has 4 bonds and I am only using a 2D picture to illustrate actual molecule or actual solid is 3 dimensional. Silicon, silicon, each of the silicon has further bonds. So, they just propagate through your solid. So, now, you add a small amount of group 3 element.

So, let us say add a small amount of boron once again the boron atoms just replace the silicon atom in the lattice the concentration is so small that it does not affect the lattice arrangement of silicon. I will take this silicon atom and I replace it with boron now boron has 3 electrons. So, I can easily form a bond or 3 bonds. So, boron can form 3 bonds, but this silicon atom has one extra electron. In order to form the bond with this silicon atom, an electron from the valence band is excited to the boron level. So, that it can form the bond with silicon when an electron moves from the valence band your left with the absence of an electron this forms a hole. We can do a similar calculation that we did for the n-type impurities to look at the ionization energy that is the energy required to excite the electron from the valence band to the boron level if you do that once again, we will find that the energies are the order of milli-electron volts if you do the actual calculation. In the case of boron, the ionization energy E_b is around 45 milli-electron volts. If you have aluminum, it is around 57. If you 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 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.

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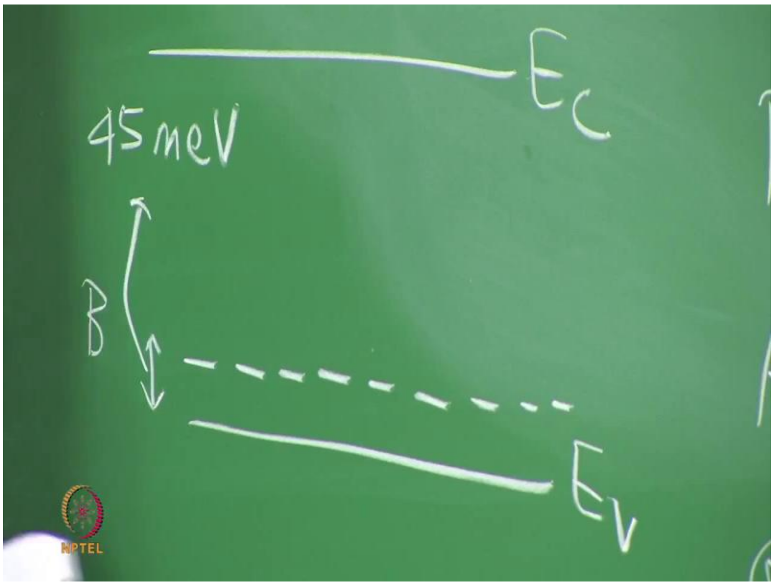

So, we will draw the band gap of silicon this is E_c this E_v. So, this is your valence band, this is your conduction band. In the case of n-type, we said that they are localized levels very close to the conduction band. In the case of p-type, they are localized levels very close to the valence band, so that an electron from the valence band can be excited to the boron or the acceptor level. So, this is boron and the energy gap between them is around 45 milli-electron volts, 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 will find that p is N_A, n is $\frac{n_i^2}{N_A}$.

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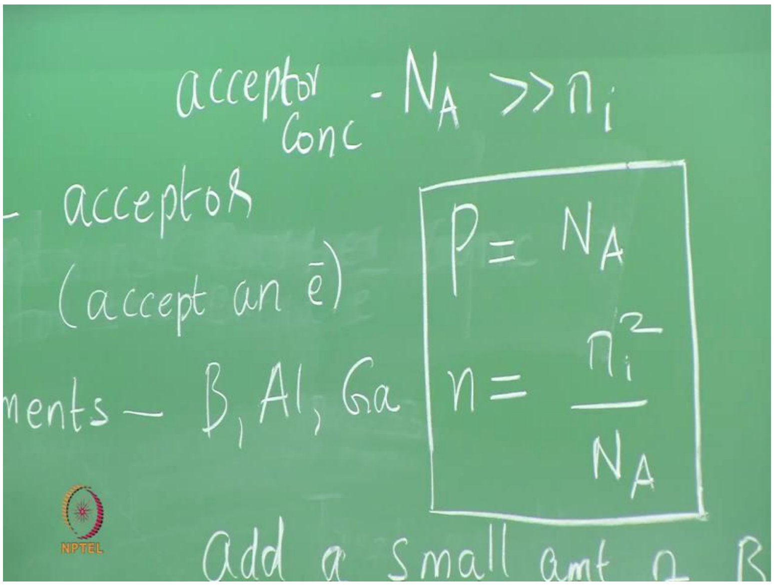

These are the same arguments that we used when we describe your n-type dopants. Let us actually put in some values now and try to calculate the electron and hole concentration and the conductivity. One of the reasons for doping is to increase the carrier concentration and to also increase the conductivity.

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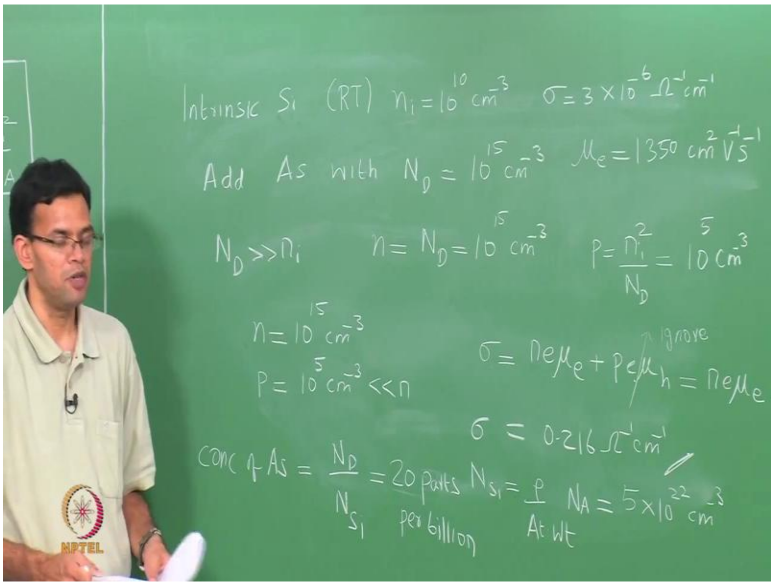

We saw earlier that, if you have intrinsic silicon your carrier concentration at room temperature is 10^{10} when your conductivity sigma is around $3 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$, let us take intrinsic silicon and add arsenic with a concentration of 10^{15} arsenic atoms cm^{-3}. So, N_D

is the concentration of arsenic, arsenic is the group 5 material. So, it has 1 extra electron. So, it is an n-type dopant, we also see that N_D is much greater than n_i and at room temperature all the arsenic atoms are ionized. So, the concentration of electrons n is same as N_D 10^{15} cm^{-3} the concentration of holes is $\frac{n_i^2}{N_D}$. If you do the math, n_i is 10^{10}, N_D is 10^{15}. So, n_i^2 is $\frac{10^{20}}{N_D}$, which is 10^5. So, we have a concentration of electrons which is 10^{15}, concentration of holes which is just 10^5. 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 have preferentially increased the concentration of electrons 2 more than 10 orders of magnitude compared to holes. Now, equation for conductivity you have seen this earlier is $n\ e\ \mu_e + p\ e\ \mu_h$ now n is. So, much larger than p we can ignore this term and then just write it as $n\ e\ \mu_e$, μ_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, μ_e is 1350 centimeter square holes per second. So, we substitute n, which is the same as N_{De} and μ_e and if we evaluate the expression you get σ to be equal to $0.216\ \Omega^{-1}\ cm^{-1}$.

So, we started out with intrinsic silicon which has a conductivity of around 10^{-6}. We added 10^{15} arsenic atoms and we found that your conductivity has increased by more than 5 orders of magnitude. So, this is the reason why we use extrinsic conductors it is possible to increase the conductor by orders of magnitude by adding these dopants whether they are n-type dopants or p-type dopants. We say we added around 10^{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 per 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 avogadro number which is $5 \times 10^{22}\ cm^{-3}$.

So, if you look at the concentration of arsenic is 10^{15} by 5 times 10^{22}, which if you do is around 20 parts per billion, parts per million is 10^{-6} parts per billion is 10^{-9}. By adding a really small amount of arsenic, so much small that it is of the order of parts per billion, we have increase the conductivity by more than 5 orders of magnitude. So, also the reason why doping has to be such a précised process because we have to make sure that we have the right concentration of dopant atoms. So, that we have the right concentration of carries and the conductivity that we deserve, we can do a similar analysis in the case of p-type impurity. So, let me just write that down briefly.

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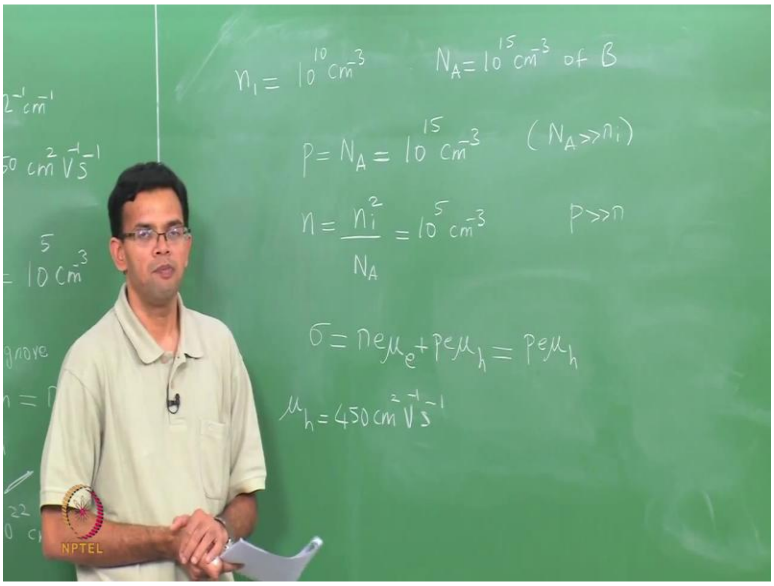

So, once again we start with intrinsic silicon n_i is 10^{10} cm^{-3}, but now instead of adding phosphorous let me add 10^{15} atoms of boron, boron is a group 3 element. So, when you add boron to silicon you basically increase the concentration of holes once again at room temperature all of these holes are ionized or all of these atoms are ionized. So, the hole concentration is the same as N_A and this is true again because N_A is much greater than n_i. We can once again calculate the electron concentration is $\frac{n_i^2}{N_A}$, which is 10^5. So, in the case of a p-type impurity, we find that p is much greater than n. So, your conductivity equation which is $n\ e\ \mu_e + p\ e\ \mu_h$ will be just $p\ e\ \mu_h$ and once again do the numbers the case of silicon μ_h is around $450\ cm^2\ v^{-1}\ s^{-1}$. So, the conduct will be conductivity will be slightly lower than that type of an n-type dopant because of the difference in mobilities, but it will still be 5 orders of magnitude higher than the conductivity of intrinsic silicon. So, we have looked at an n-type dopant. We have look at a p-type dopant, now what will happen if we add both an n and a p-type dopant together?

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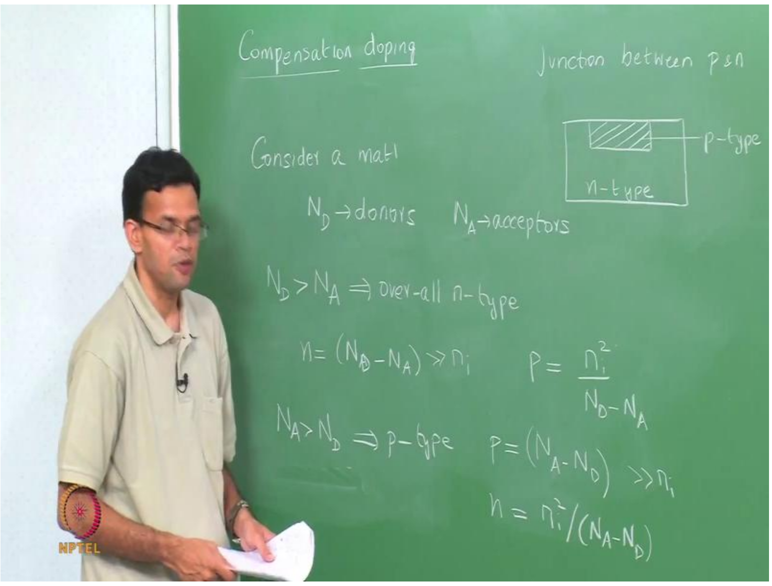

We will look at a situation, where we have both the n-type and the p-type dopant. This kind of doping is called compensation doping, the first question is why do you actually have to dope both materials, let me just give you a brief answer. So, let us say we are trying to form a junction between p and n-type materials, usually we need such type of junctions when we form 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 there are certain ways of doing, but in this particular region you have both n-type impurities and both p-type impurities and we do it in such a way that the overall material is p-type. So, this type of doping with both kinds of dopants is called compensation doping.

So, consider a material where N_D is the concentration of donors, donors are your n-type dopants and N_A is the concentration of acceptors. You can have 2 scenarios, can have a situation where N_D is greater than N_A, if you have a situation where N_D is greater than N_A, the material is said to be over all n-type with n the concentration of electrons nothing but N_D - N_A, this will be still much greater than the intrinsic carrier concentration, concentration of holes is an n_i^2. 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 you have n a greater than N_D is the reverse case. Over all it is a p-type material concentration of holes is nothing, but $N_A – N_D$ which is greater than n_i and n, the n_i^2 $N_A – N_D$. Let us just work out an example for this.

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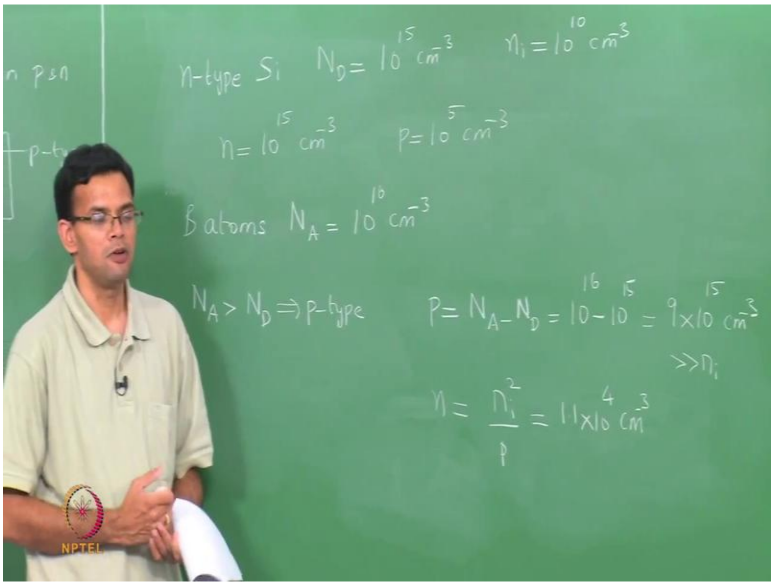

So, consider a n-type silicon with N_D equal to the 10^{15} cm^{-3}, so this n-type material. So, n is 10^{15} n_i, for silicon is to 10^{10}. So, p is 10^5 cm^{-3}, now you take this and we add arsenic we add boron atoms. So, we add acceptors and the concentration of acceptors, N_A is 10^{16}. So, we originally started out with an n-type material, now you have a 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 - N_D, which is $10^{16} – 10^{15}$. So, N_A - N_D which is 9×10^{15} cm^{-3} and this is still greater than n_i, since n_i is only 10^{10} concentration of electrons is now $\frac{n_i^2}{p}$, 1×10^4 cm^{-3} . So, thus we started out with an n-type material, but by preferentially adding acceptors whose concentration is more, when the concentration of donors, you have 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 semiconductor and we also look at the behavior of the 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. But, we would look at that in the next class.