Electronic Material Devices and Fabrication
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Lecture - 9
Extrinsic semiconductors - Fermi Level

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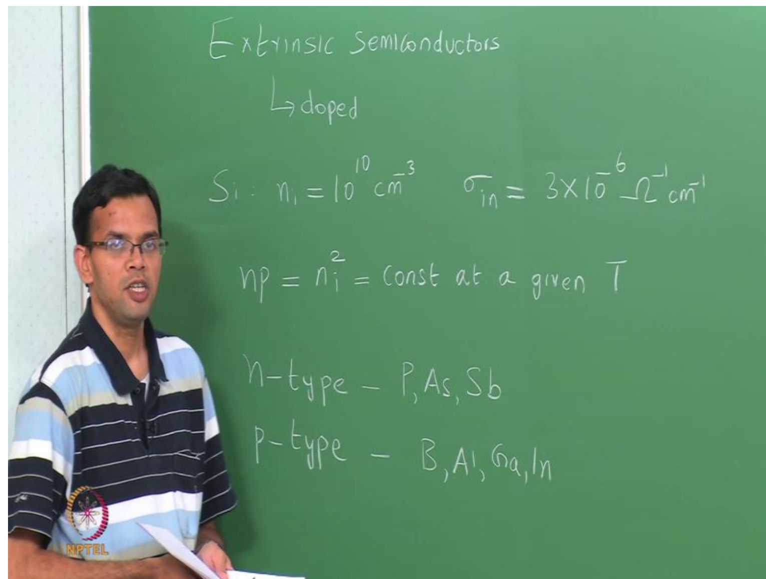

Let us start with a brief recap of last class. Last class we looked at extrinsic semiconductors, another name for these are doped semiconductors. Now, the reason why we want to dope was because we founded that we had an intrinsic or a pure semiconductor the carrier concentration at room temperature was very small correspondingly the conductivity was also small.

For example, in the case of Silicon we found that the room temperature carrier concentration, in a intrinsic semiconductor was only the 10 to the 10 per centimeter cube and the corresponding conductivity is very low was around 3 times 10 to the minus 6 ohm inward centimeters. So, we wanted to increase the conductivity, so we selectively added impurities or dopens to the silicon in order to make it extrinsic semiconductors.

We also saw, that in any semiconductor the law of mass action must always be satisfied. So, that np is equal to ni square which is a constant add a given temperature. This meant that could we either increase a concentration of electrons or increase the concentration wholes we cannot do both.

So, we also saw that there were 2 types of dopens: one was your n-type, the other was the p-type. We saw that in n-type dopants was found in the capes of silicon by adding group 5 elements, the typical elements that we add or phosphorus, arsenic, antimony.

All of these have 1 extra electron compare to the silicon atom which means, you have extra electron in the conduction band, so these are n-type. Similarly, we saw that we could from p-type by doping with group 3 Boron, Aluminum, Gallium and Indium. These form energy states there are close to the conduction band in the case of n-type or close to the valance band in the case of p-type. So, that these are ionized at room temperature. So, let us look some more today on the properties of extrinsic semiconductors so for only you talk about Silicon. So, what about other semiconductor materials and doping in them.

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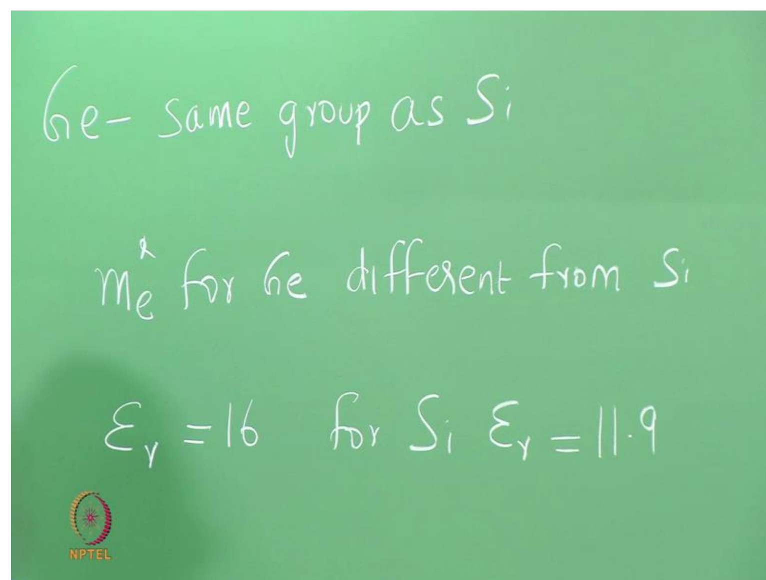

We look at Germanium lies in the same group a silicon which means, the all the elements that we used as dopens, for Silicon could also be used for Germanium. So, we can use your group 5 elements like phosphorus were arsenic as an n-type dopants could also use your group 3 elements like: Boron as p-type dopants.

Once again in the case of Germanium, we can calculate the ionization energy for these dopens we could use the Hydrogenic model. The only differences the effect 2 mass me star for Germanium will be different from that of Silicon and similarly, you relate to permittivity for c the values is around 16 value for Silicon epsilon r is a 11.9. But we can

use the same Hydrogenic model in order to calculate the ionization energies. So, let us look at some actual values in just to compare Silicon and Germanium.

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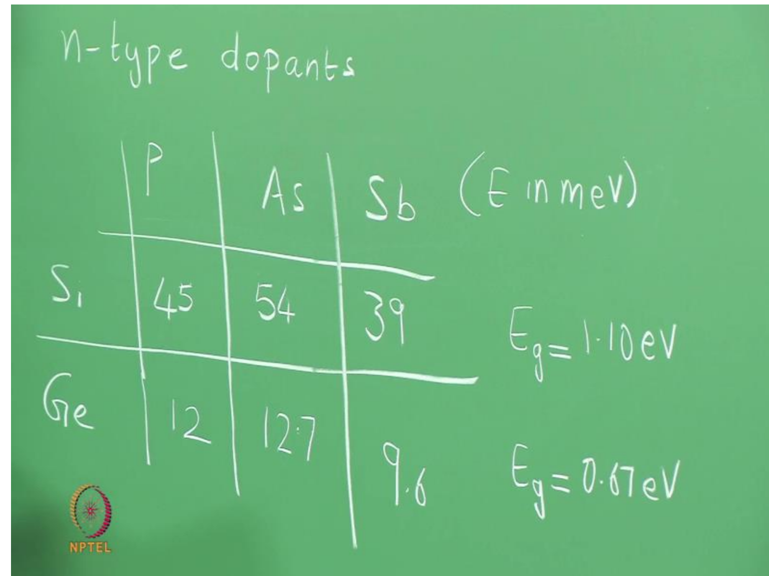

Now, its look at n-type Phosphorus, Arsenic, Antimony are a 3 dopens Silicon and Germanium. If we fill in the numbers in the case of Silicon we found that the ionization energy in milli electron Volts. So, energy is in milli electron Volts was around 45 54 39. Similarly, in the case of Germanium we will find that the ionization energies are very small.

So, this is around 12 12.7 9.6 if you remember the band gap of the Germanium is also smaller. So, at room temperature Eg first Silicon is around 1.10 electron Volts, Eg for Germanium is around 0.67 electron Volts. We can do the same thing with p-type impurities of p-type dopens.

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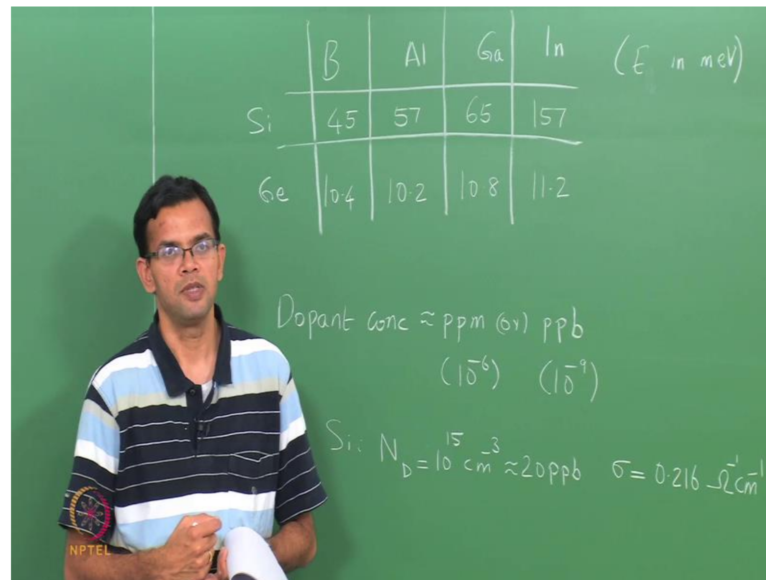

Boron, Aluminum, Gallium and Indium, so once again we write Silicon, Germanium 45 57 65 157 again we are writing Eg in milli we writing E energy in milli electron Volts; Remanium is around 10.4 10.2 10.8 11.2. So, what this means is whether we have silicon or we have germanium both line in the same group. So, you can dope both of them in a similar fashion if you want an n-type dopants we are going to add group 5 elements, if you want to p-type dopens you are going to add group 3 elements.

Usually the dopants concentration is very small we saw earlier the case of Silicon that your typical dopants concentration was around paths for million or paths for billions. So, paths for million is 10 to the minus 6, paths for billion was 10 to the minus 9 and even the small amount was enough to increase the conductivity by orders of the magnitude.

So, we saw for silicon if I had n-type dopants with 10 to the 15 atoms for centimeter cube, which was approximately 20 parts for billions, your conductivity sigma went up to around 0.2 ohm inverse centimeter inverse; 1 thing we have in look much is how we actually do the doping. So, later when we look at the fabrication part we will spend some more time on how we actually dope.

But if we think of a parallel to meteorology 1 where we can think of is in the case of

stainless steel or in the case of steel we do something call carburizing were, we increase the carbon content. So, typically what we do we have sample at high temperature you have a carbon source. So, that the carbon then just diffusers into the surface and in to the bulk of you steel. So, we can do something similar in the case of doping in semiconductors as well.

So, if you want to dope n-type you have a source of you n-type material this could be in the gas face, these could be ion implanted on to the surface we will see what ion implantation is later. So that, these can then defuse in to the surface and from the surface in to the bulk. If you want to do composition doping we saw compensation doping last class were you start with and n-type semiconductor and then you make it p-type by adding excess dopens of the other type.

In the similarly, in the case of compensation doping could take a small portion of your sample that is typically n-type add access of p-type. So, you could add excess of Boron and then make it a p-type semiconductor. These dopens are usually very stable at room temperature just to give you some numbers, let us take case of silicon.

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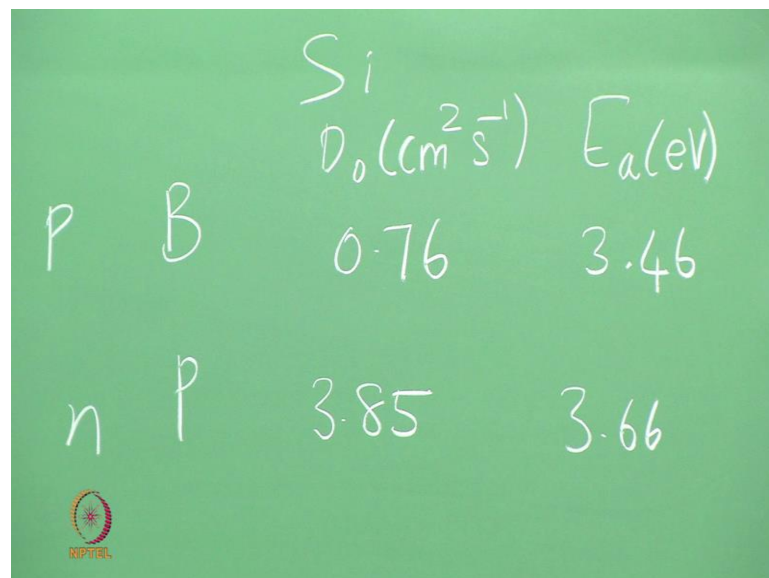

I have 2 dopens: 1 is Boron, 1 is Phosphorus, Boron is a p-type phosphorus is n-type we

can have we write down the values for the activation energy and the diffusion co coefficients for these dopens. So, if a write D0 and Ea; Ea is the activation energy for diffusion in D0 is a diffusion constant.

So, in the case of boron D0 has a value for on 0.76 activation energy is around 3 and half electron Volts, phosphorus 3.85 Ea is around 3.6 electron Volts what this means is in order to have Boron or Phosphorus diffusing in to a material we essentially need a high temperature process. The corollary of this is that, at room temperature your doping concentrations are inherently very stable in the case of silicon.

So far you seeing 2 semiconductors: Silicon and Germanium you have looked at some examples of dopens calculated the ionization energies. Since both Silicon and Germanium belong to the same group we essentially use the same elements. Things become a little more complicated when we look at other semiconductors. So, let us look first at Gallium arsenide.

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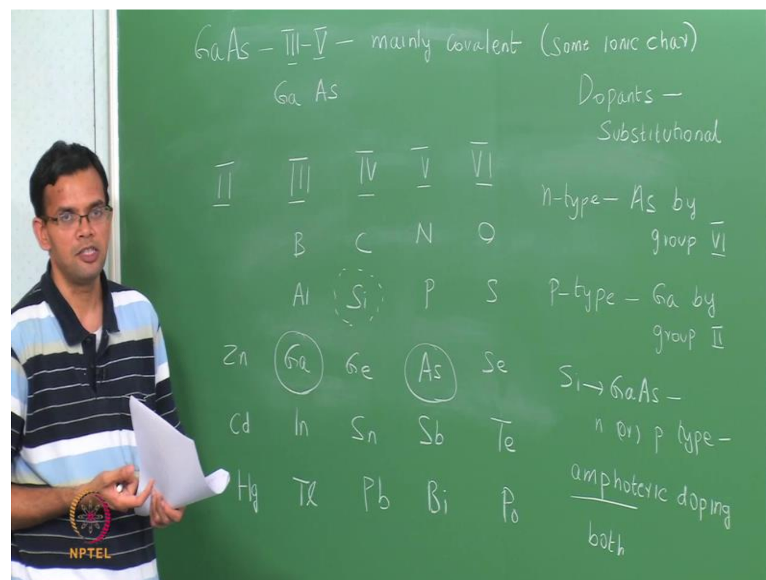

We saw earlier the Gallium Arsenide is an example of a 3 5 compound semiconductor. So, Gallium is from group 3, Arsenide is from group 5 the bonding in gallium arsenide is mainly covalent, but you also have some ionic character to the bond instead of gallium

arsenide if we have something like Zinc oxide which is 2 6 semiconductor there will be higher ionic character as compared to 3 5.

So, it is also possible to dope Gallium arsenide, but then now more possibilities in this case. To understand this let us, go back to the periodic table specially the portion around Gallium arsenide. So, let me write the periodic table we have done this earlier when we look at elemental and compound semiconductors.

So, group 2 3 4 5 and 6 Boron, Carbon, Nitrogen, Oxygen, Aluminum, Silicon, Phosphorus, Sulfur, Zinc, Gallium Germanium, Arsenide, Selenium, Cadmium, Indium, Tin, Antimony, Tellurium, Mercury, Thallium, Lead, Bismuth and Polonium. So, this is a just a portion of the periodic table around group 3 and 5. So, the semiconductor we have is Gallium Arsenide and you want to know what to know what sort of elements could be added as dopens to Gallium Arsenide to make it p or n-type.

So, when we think of dopens these are usually substitutional which means I going to replace either the Gallium or the Arsenic atom. So, let us say I want to make an n-type Gallium Arsenide. So, I would typically choose elements from group 6 because these elements have 1 more electron is compare to Arsenide. So, of an element from group 6 replaces Arsenic we will have 1 extra electron and new this extra electron is an shallow state.

If it is easily ionizible it can get ionize to the conduction band and be available for conduction. So, to form n-type going to replace to Arsenic by group 6 we can use the same argument if you want to make a p-type semiconductor. So, we replace Gallium by any of the group 2 s which has 1 less electron or you have 1 whole, so that will make a p-type. If you want to make some p-type we can replace Gallium by group 2.

The question is, what happens if you have a group 4 impurity that is say I have a Silicon now, Silicon is a impurity in Gallium Arsenide. So, the essentially 2 possibilities: the Silicon can replace the Gallium, the Silicon replace the Arsenic and depending on that we can either get and n-type or a p-type.

So, of the Silicon replaces the Gallium then Silicon has 1 more electron because; this is group 4, this is group 3. So, the extra electron is a available for conduction it will make it n-type. On the other hand, Silicon replaces Arsenic it has 1 less electron and it will make it p-type. So, Silicon added to Gallium Arsenide can be either n or p-type and this type of doping is called amphoteric doping.

This term am 4 essentially means both means, you have the same element ca act both as n-type or as an p-type dopants. The only issue here, it is really hard to control the position of Silicon it is very hard to get Silicon selectively dope into Gallium or selectively dope into Arsenide. So, if we have silicon has dopants it is very hard to control the type of the dopants and the concentration of dopens.

So, we saw that these are all the possible elements can be used to dope Gallium Arsenide the only other question is, where the energy levels located. So, let me just do that by drawing the band gap of Gallium Arsenide.

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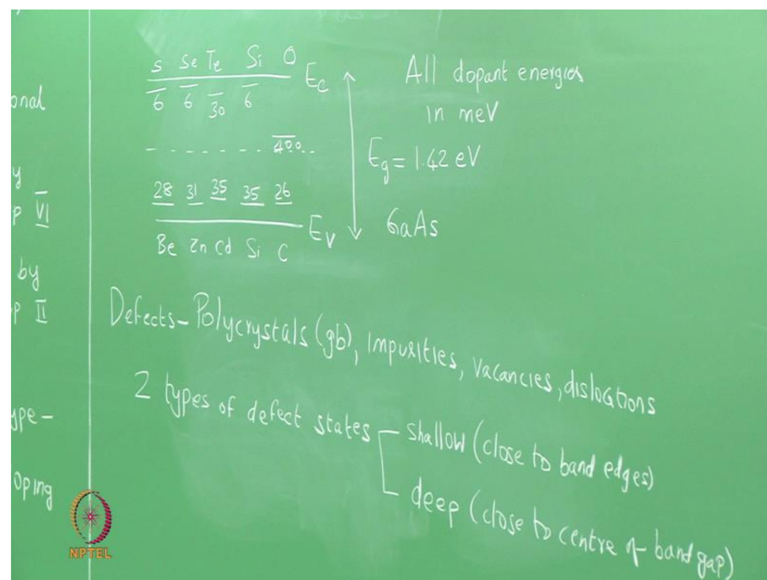

So, this is my conduction band that is my valence band the difference between the conduction band and the valence band is a band gap. The case of Gallium Arsenide the band gap is 1.42 electron Volts also mark the center of the gap. So, if you look at the

various elements the group 2 and the group 6 elements.

These will essentially form impurity states in the band gap of Gallium Arsenide in depending upon whether their n-type or p -type they will located either close to the conduction band edge or the valence band edge. So, if we look at the group 6 elements these are n-type. So, this 1 is Sulphur Selenium is also similar Tellurium is here again all the dopants energy's are milli electron Volts.

Which means, the diagram is not really it skill, but we will just show it semi qualitatively, so we have ruff idea. Silicon we said Silicon can go either to Gallium or to Arsenic. So, Silicon as an n-type is around 6 milli Ev, Oxygen on the other hand is around 400. Similarly, we can look at the group to elements, so we have Belilium is around 28, Zinc study 31, Cadmium is slightly hired 35 we can also have Silicon as a p-type that around 35 again Carbon is around 26.

So, if we have gallium arsenide depending upon the type of impurity we can either have n-type and p-type. Similarly, for other 3 5 semi conductors can once again have doping we choosing the appropriate group 2 or group 6 material. If we have 2 6 semiconductors something like: Zinc oxide, Cadmium sulphide or Cadmium Selenide similarly, we can choose appropriate dopens to get both n-type and p-type.

Most of what we have done here, so whether we have talking about Silicon or Germanium or Gallium or to Arsenic we typically want single crystals of the materials, whether we talk about intrinsic semiconductor or whether we talk about extrinsic semiconductor with dopens we want an ideals single crystal with no defects. This is because, whenever you have a polycrystal in material or if you have defects, so whenever you have polycrystal you always have grain boundaries.

Grain boundaries are a source of defects you could also have impurities; you can have vacancies, dislocations. All of these are defects in your crystal and whenever you have defects you always have defect states. So, there are 2 types of defect states: 1 shallow: shallow states are those that are located either close to the conduction band or close to valence band.

So, that close to the balance edges and because we are close to the band edges they can easily get eyenise at room temperature. So, shallow states mostly effect the conductivity can either increase or decrease the conductivity. The other types of defect states suppose to shallow stage are deep state. So, it deep states are located much closer to the middle of the band gap or they are located far away from the valence band and conduction band.

So, in this particular case you have Oxygen that is located approximately 400 milli electron Volts or 0.4 electron Volts below the conduction band. So, it deep states are located close to the center of the band gap deep states can essentially act as straps for electron and hole. So, they could modify the conductivity especially in the case of direct band gap semiconductors.

So, where we looking at optical properties deep states can also act as a strap for this electrons and holes and then decrease the efficiency of any optical recombination. We will see defects state later when we also look at conductivity in an extrinsic semiconductor. So, the next thing we going to do is look at how the Fermi level position changes in an extrinsic semiconductor.

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So, we want to find out the position of EF when you have dopens whether you have p or

n-type dopants. In the case of intrinsic semiconductor we have electron and whole concentration to be nearly the same. So, we wrote an expression for the Fermi level position Eg over 2 kT. So, this is for the case of intrinsic semiconductor were, n equal to P equal to ni and we found out that E Fi is very close to the center of the gap.

So, if Nc and Nv are exactly the same is exactly E Fi will be just Eg over 2 by if there not the same will be slightly shifted from the center of the gap, but for most cases is very close to the center. In the case of an extrinsic semiconductor n is no longer equal to P. In fact, if we have an n-type semiconductor we see that n is much larger than P we have a p- type semiconductor P is much larger than n.

So, in order to compensate for this difference in n np the Firmi level will also shift from the middle. 1 way to look at it or to calculate the shift is to use equation for the electron concentration. So, let me start with an n-type semi conductor with Nd being the concentration of the donors; the donors are completely ionized, so the electron concentration same as the donor concentration.

This we can write as Nc exponential minus Ec minus E Fn over kT. So, EFn refers to the Firmi level position in the n-type semiconductor. So, we can take this expression and then re arrange the terms a bet and what we will get E Fn minus E Fi is nothing, but kT ln of Nd over ni how we get this expression is that we start with this we can write the same equation for intrinsic as ni equal to Nc exponential minus Ec minus E Fi over kT.

So, we start with 1 and 2 and then we divide 1 2 and rearrange the terms, to get the expression for the Firmi level position extrinsic n-type semiconductor with respect to the Firmi level position in an intrinsic semiconductor can write a similar equation for a p-type material as well.

So, we had E Fp minus E Fi which is minus kT ln of Na over ni. So, this similar expression to this except that in an n-type we have the concentration of the donors in p-type we have concentration of accepters and there is a negative sign here. So, let us do some numbers to get a sense of where the Firmi level is located.

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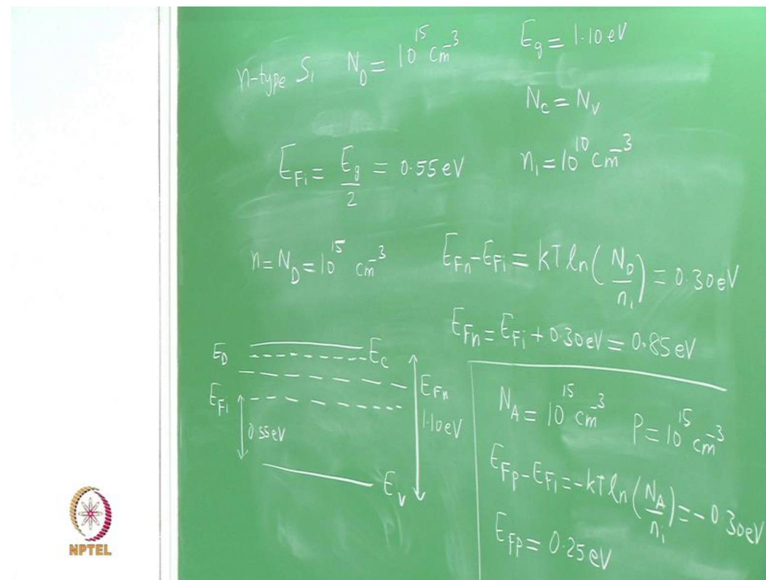

So, let us take n-type Silicon with Nd is around 10 to the 15 a centimeter cube. We know the band gap of Silicon Eg at room temperature 1.10 electron Volts for simplicity let us just say Nc is equal Nv. So, the intrinsic position of Fermi level E Fi will be just Eg over 2 we know this to be 0.55 electron Volts. Now, it room temperature you have all the donor atoms are ionized the n is equal to Nd equal to the 10 to the 15 for centimeter cube.

We will then use to formula that we just wrote down, so that E Fn minus E Fi is kT ln of Nd over ni. In the case of Silicon, ni is a 10 to the 10 so substituting the number this gives you value of around 0.30 electron Volts or another words E Fn is E Fi plus 0.30 electron Volts, which is 0.55 plus 0.3 0 85 adding and n type impurity. So or adding a donor shifts the Fermi level above the intrinsic level.

You want to show this in a band gap diagram, this is a valence band, this is the conduction band, this is the band gap. So, this is 1.10 electron Volts E Fi is located at the middle, so this is 0.55, so we've added and n-type impurity. So, this creates the donor levels Ed. So, these donor levels are very close to a conduction band at room temperature all of the donors are ionized and what we have is your Fermi level E Fn located above the intrinsic level, but below the donor level.

In the case of a p-type semiconductor, so let us do a situation where we have Na, so this a p-type we just block it off with 10 to the 15 instead of electrons you have wholes. So, your whole concentration is 10 to the 15 equation becomes E FP minus EFi is minus kT which is minus 0.30 electron Volts or E FP is 0.55 minus 0.30 0.25 eV.

So, in the case of p-type semiconductor you have the Firmi level located below the intrinsic level. So, a depending upon the type of extrinsic semiconductor you have can either have the Fermi level shift up, we have more electrons it shifts up towards the conduction bank if we have more wholes it shifts below towards a valence band.

So, all these calculations that we have done so far is for and extrinsic semiconductor at room temperature were, all the dopens are ionized whether there be donors or accepters. So, the next thing we going to do is to look at how the dopens constant or how the carrier concentration changes with temperature.

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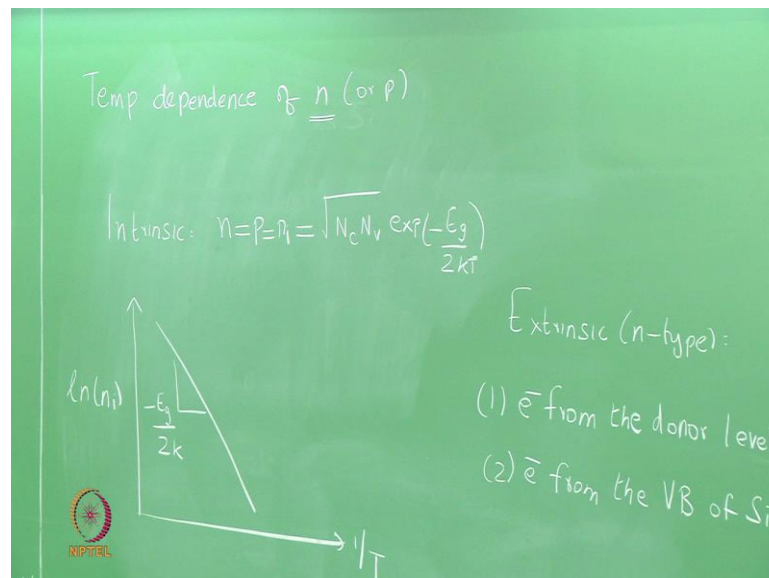

So, we want to look at the temperature dependence on the majority carrier concentration. So, it is temperature dependence of n if it is an n-type or p if it is a p-type for simplicity we are only going to look at the n type case. But whatever arguments we use for that, we can use the same for the p type semiconductor. How is this different we have an intrinsic

semiconductor? In an intrinsic semiconductor we have essentially no dopens.

So, a carrier concentration n equal to P equal to ni for square route of Nc Nv exponential minus Eg over to kT. So, if we want to look at the temperature dependence of n it is an exponential dependent on temperature. So, if you did a plot of the log of a carrier concentration over 1 over T it is approximately a straight line as long we assume that Nc and Nv are independent of temperature straight line which Eg over 2k.

This as far as intrinsic semiconductor goes, the case of an extrinsic semiconductor again that is an n-type you have essentially 2 sources for the electrons. We can get the electrons from the donor level, remember the donor atoms each have 1 more electrons than the silicon that is why it is an n-type.

So, we can get the electrons from the donor level and you can also, get the electrons from the valence band. So because you have the 2 sources you have a different behavior for the how the value of the n changes with temperature. You going to look at different regimes for that.

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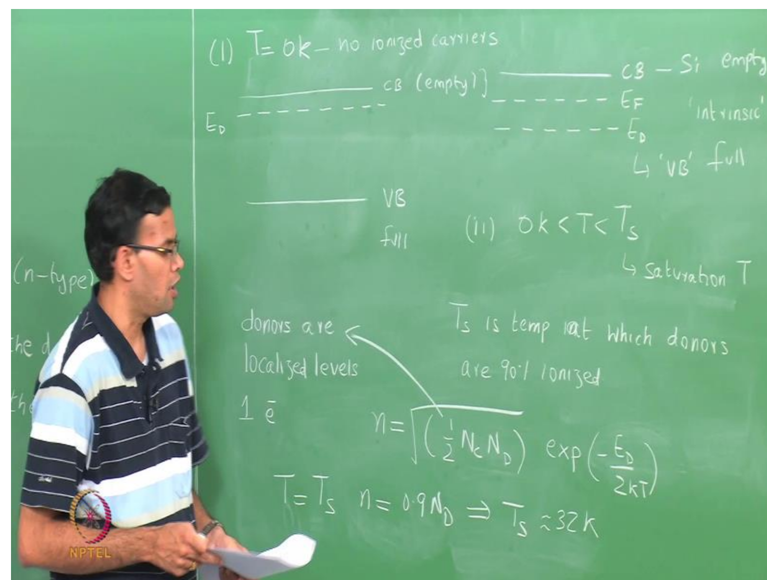

So, the first case let us look at the semiconductor at exactly 0 Kelvin. So, in this case you

have an n-type semiconductor at 0 Kelvin there are no ionized carrier you have valence band that is full and you have a conduction band that is empty. And you also, have donor level because it is n-type which is also full.

So, this is my conduction band this is my valence band so that is full, that is empty in these are my donor levels. The donor levels are located very close to the conduction band I am just exaggerating the difference to show the fact that there close to the conduction band. We can expand this portion of diagram so that, now I will draw the conduction band draw my donor level.

At temperature equal to 0 Kelvin and a temperature is very close you going to have negligible number of electrons coming from the valence band. So, we can ignore the valence band totally and think of this as an intrinsic semiconductor, so I will put intrinsic within bracket with the donor level acting as a valence band. And the conduction band being, the conduction band of silicon.

So, all I have done is just expand this portion here and take it to be an intrinsic semiconductor with donor level being the valence band and CB being the conduction band of the silicon. At 0 Kelvin you have a donor level that is completely full you have a conduction band that is empty and then you will have a Fermi level in between the conduction band and the donor level.

Now, if we start to increase a temperature from 0 Kelvin electrons going to get excited from the donor level to the conduction band. Once again you're temperature is low enough that you can ignore any contribution from the valence band of silicon. So, we do this still some temperature which we are going to call Ts or saturation temperature. So, temperature is above 0 Kelvin, but it below certain temperature call Ts we may define Ts as saturation temperature.

In this particular regimes you going to have electrons from the donor level getting ionized in to the conduction band. And this process is going to happen till all the donor atoms are ionized. So, saturation temperature is defined as the temperature in which the donors are 90 percent ionized.

Some books will give you definition of 99 percent ionized, but we will just use 90 percent here, at which donors are in order to calculate the value of Ts. We look at the expression for the electron concentration we will treat this material as an intrinsic material with the donor level being a valence band. This case n is 1 half Nc instead of Nv you will have Nd which your donor concentration exponential minus Ed over 2kT.

The 1 half term is here because, your donor levels are localize levels. So, they can only take 1 electron of a normal band can have 2 electrons of opposite spend. Because, your donors are localize levels they can take only 1 electron which why we have the term 1 half. So, a treating this as in intrinsic with Ec being conduction band and the donor being the balance band and at the saturation temperature n is 90 percent of Nd.

We can put this value here and try and solve this expression for Ts and if we do this we greater a value of Ts to be approximately 32 Kelvin. So, in this assumption we take Nc to be independent of temperature, if we take in the temperature dependence of Nc you will get a Ts of around 60 Kelvin. But either way the number is much below room temperature which is around 300 Kelvin what this means is a relatively low temperature.

In the case of silicon you have situation where the donors are completely ionized. So, we started at low temperature were we said that we will ignore all the electrons coming from valence band we found out that as we started going above 0 Kelvin, electrons are going to get ionized from the donor levels till we reach a saturation temperature when almost all the donors are ionized.

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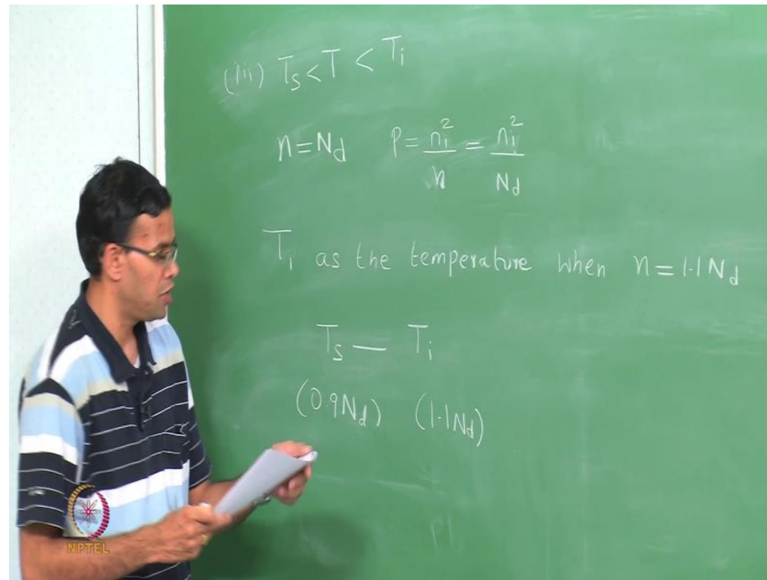

So, above the saturation temperature all the donor atoms are ionized. So, that n is nothing, but Nd and P would be ni square over n which is nothing, but ni square over Nd. Now, if we keep increasing temperature further there is a going to come a point when electrons are starting to get ionized from the valence band.

In this particular case in a semiconductor now behaves as an intrinsic semiconductor and we define the temperature as Ti. So, we define Ti as a temperature when n is equal to 1.1 Nd. So, you have extra carrier that are now coming from the valence band of the silicon and this makes it intrinsic semiconductor. So, we had 2 temperatures: Ts and Ti, so Ts was 0.9 Nd Ti is 1.1 Nd. So, we have a regime were the carrier concentration varies within 10 percent. If you want to calculate the value of Ti in the intrinsic temperature we can look at the numbers.

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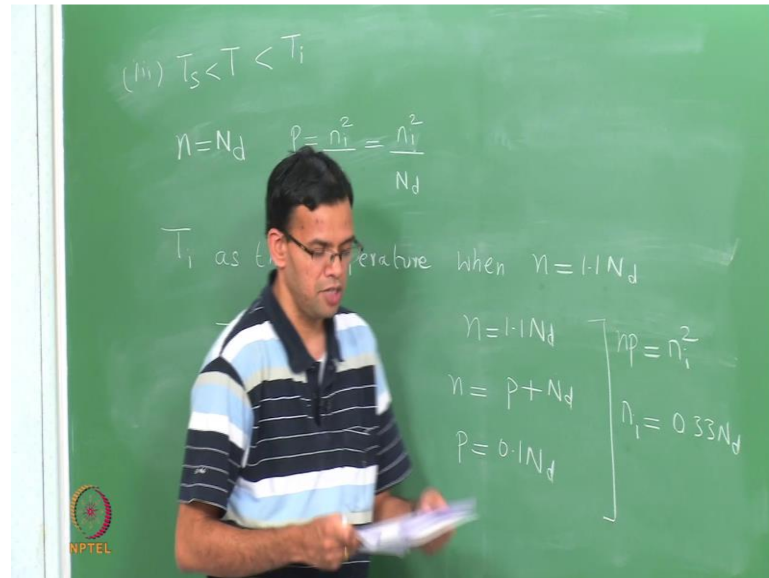

So, n 1.1 Nd and we are going to treat this as a intrinsic in any semiconductor the total charge should be balanced. So, n is equal to P plus Nd. So, that P is 0.1 we also know that np is ni square and then doing the math we get ni to be 0.33 Nd. So, n is 10 percent more than your donor concentration and at that temperature ni is approximately 0 33 Nd.

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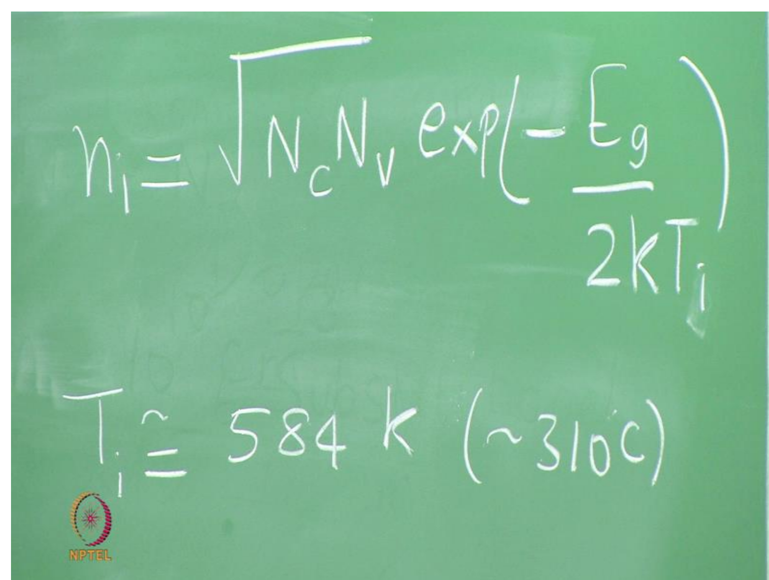

We can use this expression ni equal is square route of Nc Nv exponential minus Eg or 2kT, but the now the temperature will be Ti which is your intrinsic temperature. You can substitute in the values once again that we will assume that Nc and Nv are independent of temperature that gives you a Ti of approximately 584 Kelvin.

If you try to convert that into degrees is approximately 300 and 10 degrees above this temperature is semiconductor essentially behaves as an intrinsic temperature. So, in the case of silicon we have a regime starting from the saturation temperature which is around 50 Kelvin or 60 Kelvin to an intrinsic temperature there is around 580 Kelvin were, the carrier concentration is essentially a constant. And it is equal to the donor concentration the difference is only within 10 percent.

This means, the conductivity will also be very stable because the conductivity depends upon the carrier concentration. If we put these numbers together and did a plot of the log of the carrier concentration was is 1 over T, we can compare that to your intrinsic temperature. In the case of intrinsic we have already done this before.

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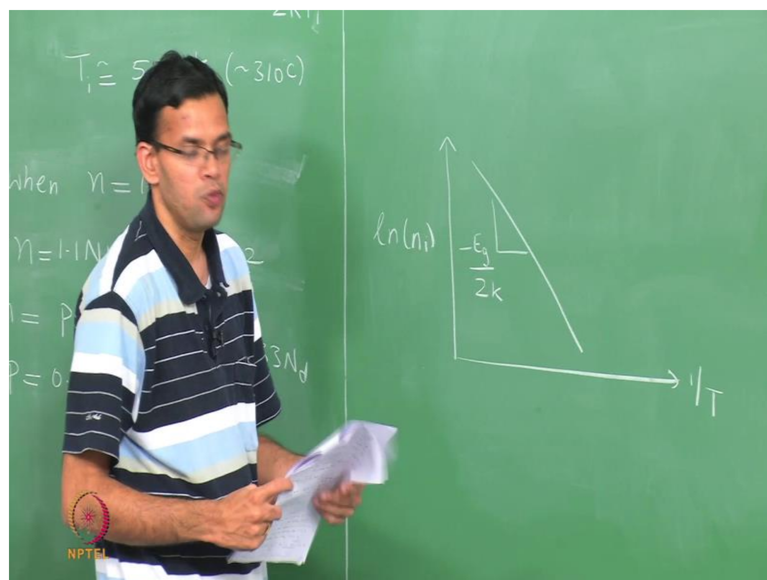

Log of n was is 1 over T is just a straight line with 1 slope, so this is intrinsic we can do the same for extrinsic.

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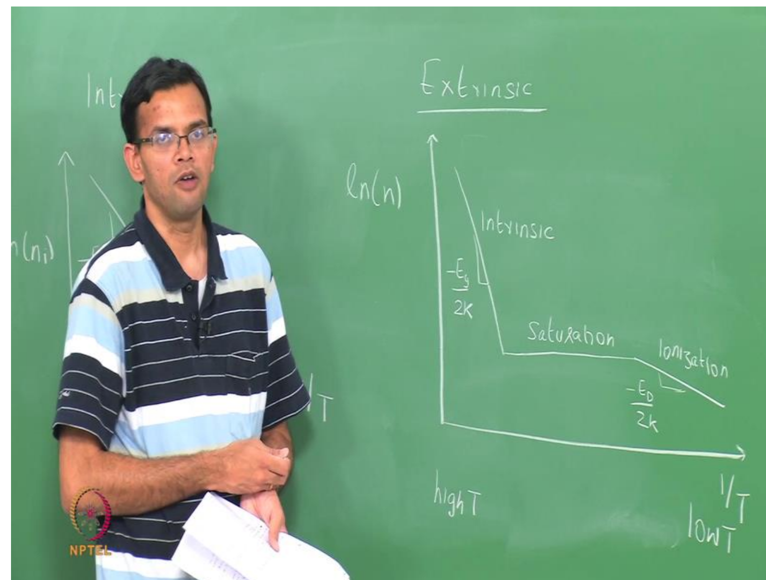

So, now instead 1 slope we will have 2 slopes we have 3 regimes. In this particular since case this is 1 over T this is low temperature this is high temperature. So, at low temperature you have electrons coming from your donor level, so you have a straight line with the slope, that is given by your donor ionization. Then, we have a situation where the donors or all ionized and a carrier concentration all most a constant.

At some high temperature we are going to get new carriers from the valence band the material behave like intrinsic, so this is minus Eg over 2k. So, we have 3 regimes and ionization regime, a saturation regime were the carrier concentration is all most a constant and in finally, an intrinsic regime were, the material start to behave like an intrinsic semiconductor. So, we will stop here for today in the next class, we will look at how the conductivity changes is a function of temperature and we also look at the effect of doping on the nobilities of electrons and wholes.