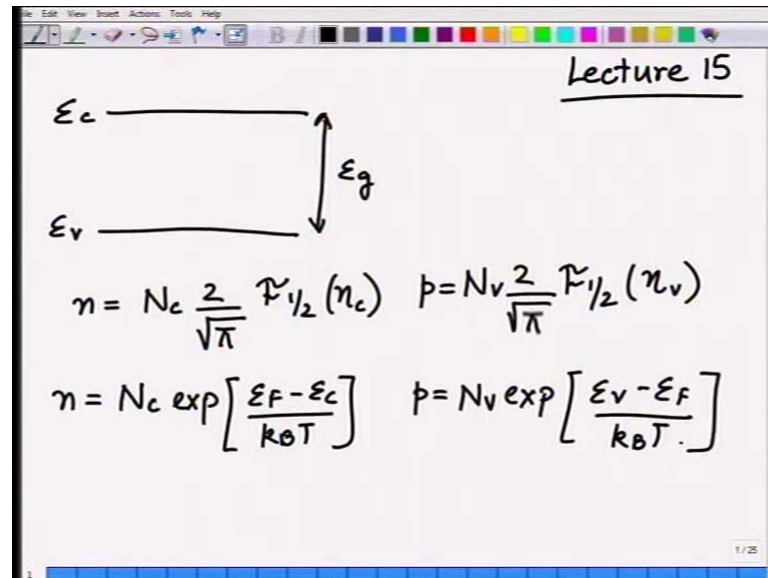


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**Lecture - 15**  
**Doping in semiconductors**

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Welcome to lecture number fifteen. So, we will continue from where we left of, but let us reconstruct where we left, what are the things we have learned so far. So, what we have learned so far, very quickly a summary of that is, that here we have conduction band and here is a valance band edge and conduction band edge, this is the band gap  $e_g$  of a semiconductor; if that is the case, then number of electrons per unit volume in conduction band is  $N_c$  times  $\frac{2}{\sqrt{\pi}}$  Fermi direct integral of this quantity  $\eta_c$  which we have defined.

Likewise,  $p$  is equal to  $N_v$  times  $\frac{2}{\sqrt{\pi}}$  Fermi direct integral of order half,  $\eta_v$  again  $\eta_v$  is defined. But if semiconductor is non degenerate meaning it by, if the Fermi energy lies between the  $3 k_B T$  away from either of the band edges in the band gap, then in that case we can also approximate  $n$  as  $N_c e^{(\epsilon_F - \epsilon_c) / (k_B T)}$ ,  $p$  as,  $k_B T$  Boltzmann constant,  $N_v e^{(\epsilon_v - \epsilon_F) / (k_B T)}$ .

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The image shows a whiteboard with the following handwritten equations:

$$n_i$$

$$n = n_i \exp\left[\frac{\epsilon_F - \epsilon_i}{k_B T}\right] \quad p = n_i \exp\left[\frac{\epsilon_i - \epsilon_F}{k_B T}\right]$$

$$\boxed{np} = (n_i)^2 = N_c N_v \exp\left[\frac{-\epsilon_g}{k_B T}\right]$$

$$\epsilon_i = \frac{\epsilon_v + \epsilon_c}{2} + \frac{3}{4} k_B T \ln \frac{m_h^*}{m_e^*}$$

intrinsic  $n = p = n_i \quad \epsilon_F = \epsilon_i$

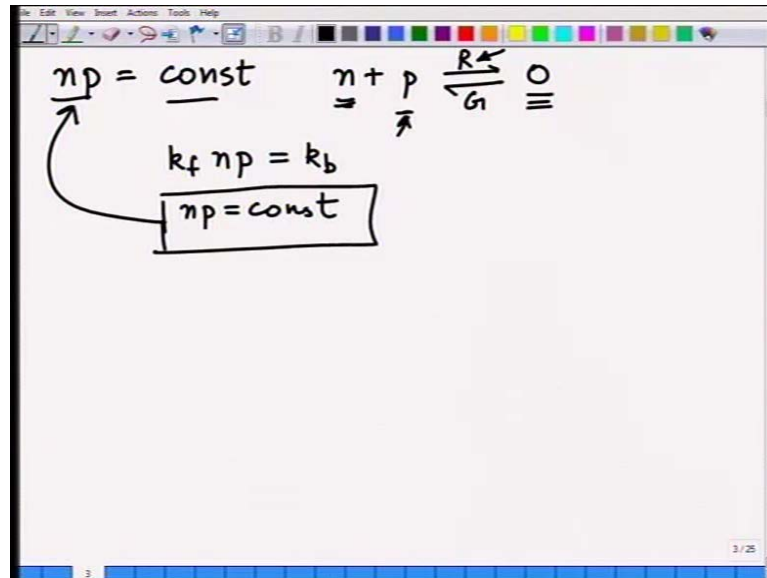
Then also we introduce the idea of intrinsic carrier concentration  $n_i$ ; that  $n_i$ , in terms of  $n_i$  we could have written the same relationship in general for whatever the, whether it is semiconductor is intrinsic or not, we can always write this is  $n$  is  $n_i e^{(\epsilon_F - \epsilon_i) / k_B T}$ ,  $p$  as equal to  $n_i e^{(\epsilon_i - \epsilon_F) / k_B T}$ . So, if we define this quantity  $n_i$  then we can write  $np$  in this form also.

Other thing we learned was, as long as semiconductor is non degenerate product  $np$  is always constant, and that is equal to  $n_i$  square; that is another thing we have learned. And, this quantity of course we have learnt, is equal to  $N_c N_v e^{-\epsilon_g / k_B T}$ , is another thing, another relationship we learnt. That product  $np$  is constant. This matter  $np$  equal to  $n_i$  square does not matter, it is always true. So, this is always true. This may be, it is worth looking at, let us come back to this in a minute, but before that let us finish everything else.

And then we also determined if semiconductor is intrinsic then whatever is the Fermi level that is called  $\epsilon_i$  and that is equal to  $\epsilon_v + \epsilon_c / 2 + 3/4 k_B T \ln(m_h^* / m_e^*)$ . So, these are few relationships we learnt. And, only thing is intrinsic semiconductor means and then we said intrinsic semiconductor means  $n$  equal to  $p$ , and that concentration, we gave it a name called  $n_i$  and Fermi energy whatever in that cases that is called  $\epsilon_i$ . So, you see and we then determined, went on to determine what the, what  $n_i$  value will be, and then we, I need a

plotting that as well. I want to spend few minutes talking about this product  $n p$  equal to  $n_i^2$ , which is constant.

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That means, let us think about this  $n p$  equal to constant, and that constant of course is  $n_i^2$ . Because in a special case when  $n$  is equal to  $p$ , when intrinsic case when  $n$  is  $n_i$  and  $p$  is  $n_i$ , then this constant will become  $n_i^2$ . Hence since its constant will always be true, therefore  $n p$  is  $n_i^2$ . But, any way, the point that  $n p$  is a constant, what does it mean? It means as follows.

This is always a continuous, you can think of in terms of a chemical reaction with which you are quite familiar; recall equilibrium constant of chemical reactions. So, if we write a reaction like thing for electrons and holes, then we could think of equilibrium situation and see what the law of mass action will be, for example. What I mean by that is, what is constantly happening, it is, so when I say that the certain number of electrons present in the conduction band, what does it mean?

It means that constantly in this material by some process some electrons are jumping from valance band over to conduction band; is a process by which carry has generated. That means, if every electron that jumps from valance band to conduction band, I get a electron and a hole pair. It creates electron in the conduction band, simultaneously from where it left in valance band it creates a hole. So, therefore I get a hole and electron pair, as usually, as a process what do we call as generation, process of generation.

Then what happens is somewhere electrons which are now in excited state, they want to return back. When they return back, what do they do? Electron and hole they recombine and annihilate each other; they leave nothing; that is process is called recombination. So, if I look at it as follows, if I look at this reaction as follows, that  $n + p \rightarrow \text{nothing}$ . In other words, if I think of it like this, I will write it here; if I think of like this that and I write a chemical reaction which is like this, where this process of  $n$  and  $p$  is recombination and this is a process of generation which I have shown pictorially there; up here I have shown pictorially.

So, now, what is it? From generation processes that I have nothing, or if you think I have a electron and a hole, I have electron sitting at valance band. But suddenly, what I did? That once electron jumps to the conduction band, that means, it goes here, here is the electron conduction band. It simultaneously leaves a hole in the valance band. That is the generation process. So, this left side going from right to left therefore is a generation process.

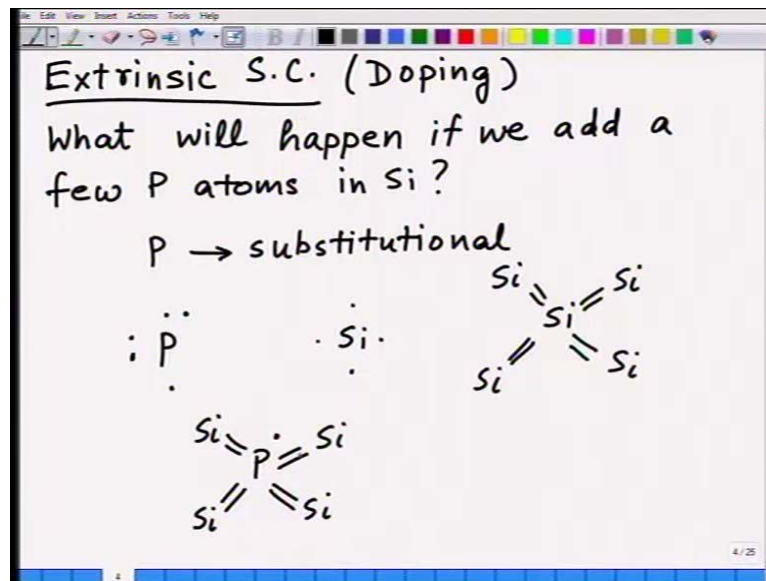
And, simultaneously at all times, this  $n$  which is in conduction band and this  $p$  which is in valance band, this electrons and holes on valance band, electrons in conduction band, they recombining, that process is  $R$ , going towards right; that recombine, recombination when happens, electron and hole pair is annihilated. That annihilation is shown in the right, in the reaction goes to right. So, you think, whatever the electron concentration here is and whatever is the hole concentration here, that is a result of a equilibrium between these 2 process of recombination and generation, and in a at some temperature.

If so, then you can see that, that this equilibrium will be established when the rate of forward reaction is same as rate of backward reaction. So, what would the rate of forward reaction will be? Rate of forward reaction will be something, rate of forward reaction will some constant  $k_f$ ; let us is name it a see,  $k_f$  is the constant of forward reaction multiplied by  $n p$ .

So, some, so, you think of rate of reaction as some constant times product  $n p$ , it will depend on how many electron or holes I have and accordingly the recombination will depend on that. That rate should become equal to rate of backward reaction. The backward reaction of course is just some constant, because remember  $0$  goes to  $n + p$ . So, it depends on the right hand side only. So, that is rate of backward reaction. What is that lead to? That says that  $n p$  is a constant.

So, you can see, this result is not a strike, not unusual result; in the sense that it follows exactly like what you have done for chemical equilibrium; that is exactly what you do. The rate of forward reaction becomes equal to rate of backward reaction, and then a chemical reaction is thought to be in thermal equilibrium. Exactly same analogy applies here of electron, equilibrium between electrons and holes. So, with that let us move forward. So, that is the, that is what we have been doing at a last time.

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Now, what I am going to do is move on to extrinsic semiconductors. I have talked about intrinsic semiconductors; now let us talk about extrinsic semiconductors. Extrinsic semiconductor that we are going to talk about; or, you think of that as doping, the doped semiconductor, you think of that as a doping. So, let us ask a question which is very typical question, what will happen if we add a few phosphorous atoms in silicon? What will happen? That is the question we ask, alright.

So, when we, first of all phosphorous atom goes on substitutional side- meaning thereby I have a lattice, silicon atom sitting on these lattice positions, when I add phosphorous essentially phosphorous is replacing some of this silicon atoms on their side, and phosphorous occupies the side which belongs otherwise to silicon, that is called substitutional side. And, thus phosphorous is a substitutional atom.

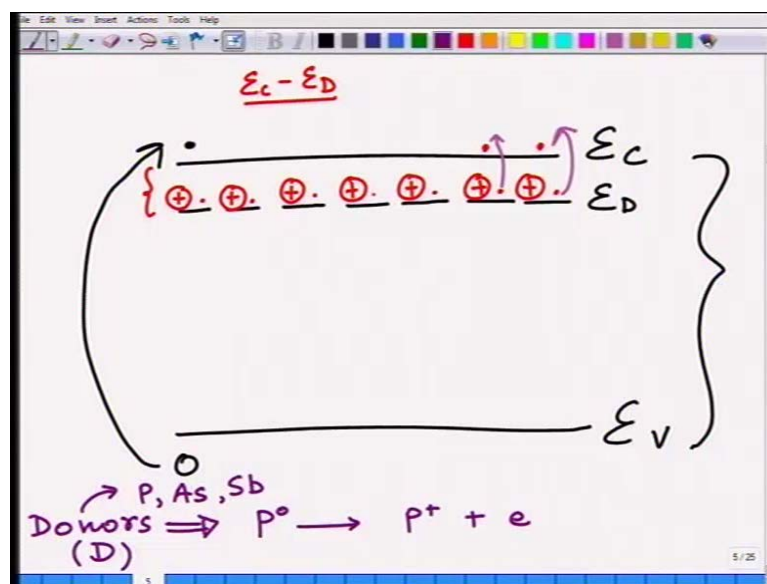
It is not necessary however; that all material, all atoms or impurities; consider phosphorous as impurities, small amount added in silicon. This small amount of impurity that we are adding in silicon is not necessary that it always goes to substitutional side; it is

possible that it goes to interstitial side for example, that is also possible; it is possible that we may not add impurity atoms at all except that there are some vacancies or interstitial of silicon atoms itself, all these defects could also be there and they could act like impurities, how? That we will see. So, our description is going to be more generalized, but phosphorous on substitutional atoms only forms an example, just an example.

So, what happens? This standard approach we take, that in the outer shell of phosphorous I have essentially 5 electrons; this 5 electrons are there. Whereas silicon has 4 electrons, and silicon undergoes this bonding with other, covalent bonding with other silicon atoms. Now, if we replace all these silicon with phosphorous, so if I have phosphorous here, then 4 of these electrons of phosphorous of course take part in bounding with this silicon atoms.

But then, I am left with 1 more electron, the fifth electron; I am still left with the fifth electron which in this picture is bound to phosphorous. In this picture, this phosphorous, this electron is bound to phosphorous, alright; now what happens? If this elect, if I raise the temperature for example, or you think like this that this fifth electron which is bound is being screened by other electrons and hence is very loosely bound, it is very loosely bound; that means it can easily be taken away from this phosphorous. So, that is essentially the picture which you want to see, say that 4 of the 4 electrons or phosphorous are go into bonding.

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The fifth extra electron, let us do it like this again, we have a  $e_c$ , we have  $e_v$ , that is a band edge. We know that if there was a impurity atom then you would have to break the, break this bond and then a electron from here would have jumped over to here and gone here, and leaving a hole behind here; that is a picture we have been talking about in intrinsic semiconductors.

Now when your phosphorous atom this fifth electron since it is being screened by rest of the electrons, so it is very weakly bound to phosphorous atom. I can think at this, in this picture I am showing that phosphorous is bound; that means, I can think of it like this- P plus as an entity which is phosphorous with 4 electrons. As, since phosphorous is neutral, when it has all the 5 electrons, so that is why I am showing 1 plus charge. Since the fifth electron is, I am going to show the fifth electron like this. So, this 4 electrons which is gone into bonding and that we calling as P plus, P plus with 4 in a, phosphorous of 4 electrons and the fifth electron is right here.

Now how much energy, question we ask is, how much energy we require for this electron to become free, this fifth electron to become free? Clearly, since it is being screened by electrons, it requires much less energy. The way we do it therefore is as follows. There we show, in this band gap there are no states; in this band gap we have shown here, in this band gap while there are no states.

Artificially we show a level like this which we call as the donor level; a donor level, donor level where the fifth electron sits. If I wish, I can talk about like this that here is in the, my picture then I will show something like this- a plus and a dot, a plus and a dot, a plus and a dot, a plus and a dot, plus dot, plus dot, etcetera, and a dot. What that means is, plus is indicating this phosphorus plus and the fifth electron. So, we think that there is a energy level like this we think, is a hypothetical energy level you think, in relative to  $e_c$ .

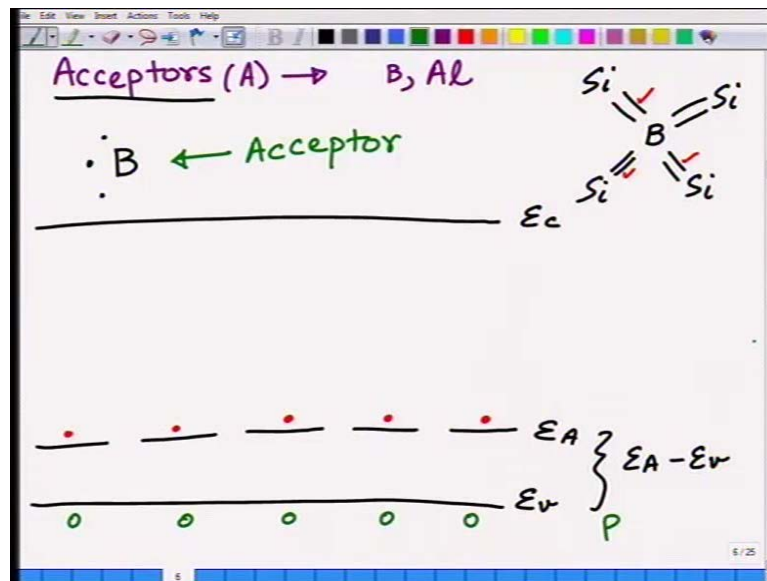
Then if I have a sufficient energy, sufficient energy meaning only energy which is the small,  $e_c$  minus  $e_D$ . If I add such a small energies in that case this fifth electron could simply jump and get here, get here in the conduction band. All these fifth electrons could therefore come and jump here; that means, I will be left with, what I have will, there will be a phosphorous which is neutral- means it is tied to, it has 5 electrons.

What is happening is then it is becoming P plus which is phosphorous of 4 electrons which have gone bonding, and the fifth electron which is very loosely bound it goes into

the conduction band, by having, room temperature is adequate enough that all these electrons can easily go to the conduction band. Once the conduction band, as you know conduction band means the electron are free to move about. They became like a, almost like a free electron. So, they can move around in that.

So, that is what is meant by, so clearly see if I add few atoms of phosphorous, I can therefore increase number of electrons in the conduction band because this fifth electron will be loosely bound and it can give electrons to the conduction band, alright. Now such dopens, such dopens are called donors because they are giving away electrons, they are donating electrons to the conduction band. So, they donate electrons to conduction band and hence we call them donors. In general we will give them a name D. And, in silicon for example, a list of such sub donors will be phosphorous, arsenic, phosphorous and arsenic and antimony would be some examples which are group 5 element because they are 5 electrons.

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Let us also talk about for example, accepters now. Let us talk about accepters. By analogy therefore accepters will be those which will accept electrons A. And example I will take is for example, Boron or Aluminum which are group 3 elements, which are group 3 elements. So, let us start talking about accepters.

Now think of Boron, that this Boron only has 3 electron in outer motion. See, if I take this silicon atom in bonding, again I show the same picture, and replace this central silicon atom by Boron, but Boron had only 3 electrons. So, how do I complete these, all

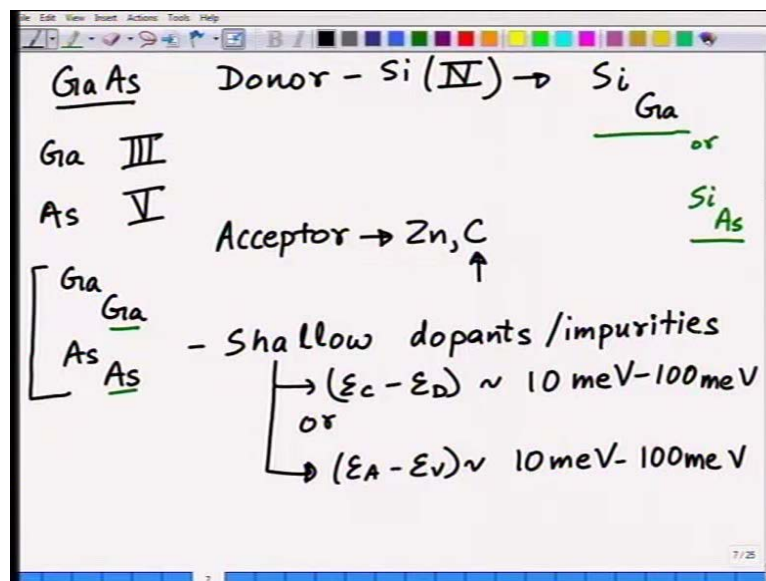


these. So, if this were like this then we are ok; that means, 3 electrons from Boron for example, a participating information A bond, but then I have not completely it I completed the core and bonding. I need this bond as well, how does that happen?

So, we conceptually imagine that this happens as follows. That again a picture like this where we have a conduction bandage, valance bandage. We think of see valance band having large number of electrons; we think that now Boron is going to borrow electron from conduction, from valance band because valance band is full of electrons; let us go to borrow electron from the valance band and complete it, complete the bonding.

When it does so, then essentially there is a hole left behind in the valance band. That we show as similarly a acceptor level, a acceptor level; and, this energy difference  $e_A$  minus  $e_v$  then indicates the amount of energy required for this electron to be taken from the valance band and Boron can complete its bonding leaving behind holes. So, essentially therefore once the electron goes here since this accepts the electrons from the valance band, it leaves holes behind here, it leaves holes behind here.

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So, you can see that like, just like phosphorous and silicon, Boron is capable of creating holes in the valance band and contribute to P in valance band. So, you can change the number of P that is number of holes per unit volume in valance band by including in material up board a group 3 element, alright. So, these and as a name it suggest that this should therefore we call acceptor because they accept electron and thereby creating a

hole in valance band. So, thus the picture we would like to have except, maybe I give you some more examples in this case.

So, for example if you are interested in gallium arsenide then I can name some donors in here; donors could be for example, silicon is a common donor in gallium arsenide. Now that is would be, this would be more interesting example. Now you see silicon has 4 electrons in outer most shell; if silicon goes, and look at gallium arsenide. So, let us consider this example also; it is very interesting example.

Gallium is a group 3 element, arsenic is a group 5 element, and silicon is group 4 element, and I am saying that silicon is a donor and gallium arsenide, what is that mean? That means, that silicon must have a preference to go on gallium arsenide; only then, if silicon is a preference to go on gallium arsenide, which let us integrate like this, that gallium is the side and silicon is sitting on it, imagine like this. In notation I will use is gallium sitting on gallium side, arsenic sitting on arsenic side; this subscript is indicating the side, and the atom on that side is also indicated there which is gallium on gallium side and arsenic on arsenic side.

Now suppose silicon is a substitutional impurity and 2 possibilities exists, silicon go on, could go on gallium side which means I will write it like this; or, silicon could go on arsenic side which means I will write it arsenic side and silicon sitting on that side. Clearly, if silicon goes on gallium side, since a group 4 element it would have extra electron and hence it can be a donor.

Whereas, if silicon goes on arsenic which is group 5 element then it could behave as acceptor; the thing of it is that silicon indeed in gallium arsenide goes on both this sides- gallium and arsenic sides, except it has preference to go on gallium side; and, more of silicon goes in gallium side than it goes on the arsenic side; and hence the net result is that silicon behaves as donor in gallium arsenide and is a pretty common donor in gallium arsenide.

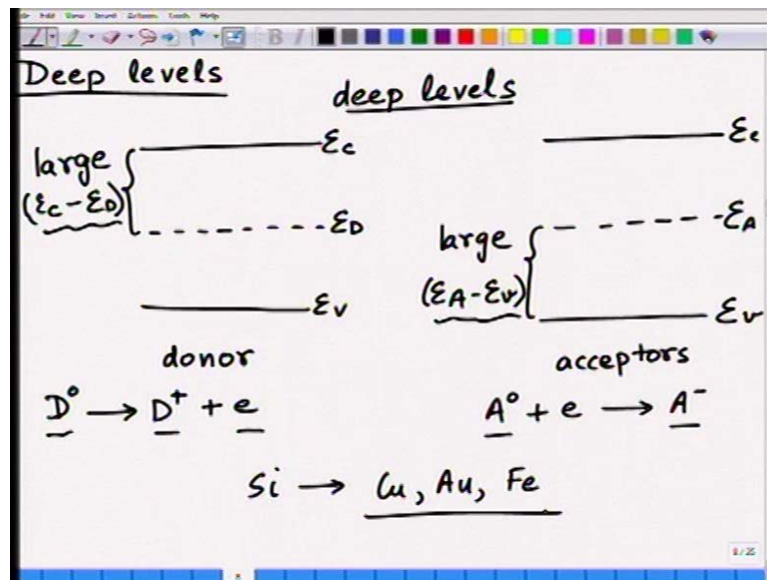
Similarly, acceptors in gallium arsenide, let me give some examples, could be zinc for example, a carbon is an acceptor which normally is present anywhere anyways in gallium arsenide. When you make gallium arsenide this behaves like an acceptor. Remember this is also group 4 element; you know this all also group 4 element carbon which means it has a preference to go on arsenic side, that is what it is behaving like an

acceptor. Zinc on the, hence is a group 2 element and hence clearly it can behave like an acceptor.

These are the few examples of your, for more examples you can look, look up in any book, in a text book or any data base now acceptors and donors for different materials. But what I want to say, a next thing is that all these materials I am talking about, all these dopants I am talking about are what we call is shallow donors, shallow dopants. Meaning thereby that if it is a donor then  $E_c - E_D$  is very small on order of 10 mille electron volts, something like that maybe 13 mille electron volt, maybe a 100 mille electron volts, but that is shallow.

And if it is acceptor then  $E_A - E_v$  is 10 mille electron volts or so, on that order; or, maybe even 100 mille electron volts in that range 10 to 100 if you wish, 10 to 100 mille electron volts is the order in which they are. So, these are we call as shallow dopants because room temperature  $kT$  energy is sufficient;  $kT$  at room temperature as I have said is about 13 mille electron volts, it is sufficient energy to promote this electrons either the conduction band or to accept the electrons from valance band. Electrons of valance band can easily jump to  $E_A$  level if this levels are shallow levels.

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So, if these are levels are shallow and shallow meaning that the energy difference is small. So, these we call as shallow dopants or shallow level impurities. There is a little difference between dopants and impurities; I suppose you can distinguish them by saying impurities are those which are got and added out of control; that means, you did not they

are not intentional they are just there, but you did not deliberately put them. Whereas dopants would be those where you deliberately add them to manipulate your  $n$  and  $p$ . So, that is what we will call as shallow levels.

Since I have introduced the name shallow levels, it is worthwhile to introduce also what is called as deep levels. So, the name suggest that these deep levels are also, deep levels are something where is energy will be large. So, if I have like this,  $E_c$  and  $E_v$ , then if the dopant level, let us say donor, donors lie, and accepters. If the donors lie somewhere deep large  $E_c$  minus  $E_D$  and  $E_D$  level, or acceptors are somewhere in the middle or even higher towards the  $E_c$ , a large, then these are called deep levels.

And clearly the deep levels because this energy difference is large. And, this energy difference is large then you can see that thermal energy may not be enough to completely ionize these defects into, either take, cannot ionize for the dopants and to promote the electron to conduction band or to accept the electrons from the valance band.

Notice that we have written here  $D$  as, when  $D$  has its electron bound to it, we are going to write it in 0 charge state; that means, charge state is that since like phosphorous has its 5 electrons then 0 charge states it ionizes, then it goes to  $D$  plus; that means, phosphorous plus with 4 electrons and a electron. Similarly, I could write here acceptor as, acceptor like a boron with 3 electrons has 0 charge on it because boron comes with 3 electrons. So, that is why, that is a native configuration. So, that is no net charge on it, boron when it has 3 electrons.

But, when it accepts electron because it wants 1 more electron to complete the bonding, but accepts 1 electron then it becomes ionize and it becomes  $A$  minus for example, it becomes  $A$  minus. So, that is what I mean that if deep levels, if the levels are deep then room temperature may not be sufficient for this acceptor to accept this electron because it require this much energy to accept the electrons and  $E_A$  minus  $E_v$  amount of energy. So, it may not be able to accept or very few maybe able to, and therefore very few of these dopants may ionize in that case.

Similarly, this energy difference  $E_c$  minus  $E_D$  may be large and therefore this dopants may not be able to ionize to deeper state there by giving the electron to conduction band, it may not happen or it happens, it happens in very small quantities. These are therefore deep levels. Deep levels are may, many. They have good, they have good use and they have bad use.

For example, if you add, if you add, in silicon if you add copper or gold or iron, all these form deep levels; what that means is that these are not going to, so, they are, they are life time killers; that part will be taught to you little bit in future, few lectures down the line, will be taught to you and we talk about what the, what the, how the statistics of recombination of these carrier says, how the carriers are generated, and how the carriers are recombining.

So far we are saying that recombination and generation rate are equal; that means, they are thermal equilibrium, then what is the condition? But when we individually start looking at recombination, and we individually start looking at generation process, then we will use this concept of time also. But the point I am trying to make is these deep level, because once a electron gets in there. Then since its energy required to ionize is so large, so it may not ionize easily, and hence it is called as a trap level; that means, it traps electron. It sits, once it gets it, it holds it; holds the electron. If so, then what it may happen is that it may happen that the carrier may not be available for conduction. So, that is the bad news.

The good news is, so good news is that if you have them, then they become the centers where the recombination may happen. The electron can come at this center and holes can come at this center and recombination can happen. Why that happens? That it has a large cross section that these aspects you will understand later when it is taught to you. However, these deep levels do have a use- good use and bad use. If you are making a silicon device for example, you will ensure that wherever you are making there is no scope of copper, gold, and iron, these kind of materials reaching there.

Similarly, so these are called deep levels because the energy level is large and they act as trap for electrons. Because they are traps, therefore they can have, they can suck up your electrons and not let it participate in conduction. On other hand, it may provide the level where it is suck up electrons and holes, and hence there for provide a level where this electron and holes physically can come together and recombine with each other. So, they have good role and bad role to play which you will learn little bit later. So, with this let me move on to the next topic.

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**Ionization of dopants**  $D^{n+} \rightarrow D^{(n+1)+} + e$

$$\frac{[D^{(n+1)+}]}{[D^{n+}]} = \exp\left[\frac{\epsilon_{Dn} - \epsilon_F}{k_B T}\right]$$

$\frac{n_{D^{(n+1)+}}}{n_{sites}} = \frac{n_{D^{n+}}}{n_{sites}}$

$n=0 \Rightarrow D^0 \rightarrow D^+ + e$   
 $[D^0] = \frac{\# \text{ D atoms in zero charge states}}{\# \text{ of sites D can go to}}$

Energy levels:  $\epsilon_c$ ,  $\epsilon_{Dn}$ ,  $\epsilon_v$

So, we have these dopants added, how do they ionize? Ionization of dopants. In general, what we can do is we can write some, there is a, we can, we could have derived this expression, but in this class we will not do that. Let us imagine like this. Suppose, you have a ionization reaction going like this. That I have any dopant, a donor dopant, let us call it D. D goes to, is exist right now in charge state, n plus. This n plus may be equal to 0 also. So, n may be 0 also, as I have written mine example earlier. And, what it happens is that it becomes D, one additional charge state was the charge state, plus electron.

Suppose this happens, or if this happens then without deriving I will give you an expression saying that number of, I just define the symbol in a second; the ratio of this, not x, but other D, I would write, exponential of. So, this energy  $e_v$ ,  $e_c$ , and  $e_{Dn}$  is this energy level;  $e_{Dn}$  is that energy level which is indicated there, then we say that fraction, you think of this is a fraction. We think of this, let me try to explain this like this, that this is number of D and plus 1, plus kind of stresses per volume, divided by number of sites for this D per unit volume, this what this quantity is.

Similarly, this quantity therefore will be equal to  $n_{D^{n+}} / n_{sites}$ , meaning thereby that this is the number or number of the, if this is the for consider, for example, phosphorous atoms. So, you think phosphorous is going on substitutional sides of silicon, then this is number of phosphorous atoms which are in.

In fact, let us choose this is example; suppose n is 0; n is equal to 0 here; this n charge which I am showing you 0 implying therefore imagine this  $D^0$ , a donor D is going to D

plus plus electron. Then this quantity  $D_0$  would indicate that this will be number of D atoms in 0 charge state divided by number of sites D can go per unit volume of course; of both per unit same bases, per unit volume, number of a sites for D atom.

For example, if it is in silicon, then its number of site possible for silicon atom, that is what it means number of silicon atoms per unit volume. Number of silicon set atoms sites per unit volume is the denominator and numerator is number of this phosphorous atom, D atoms per unit volume.

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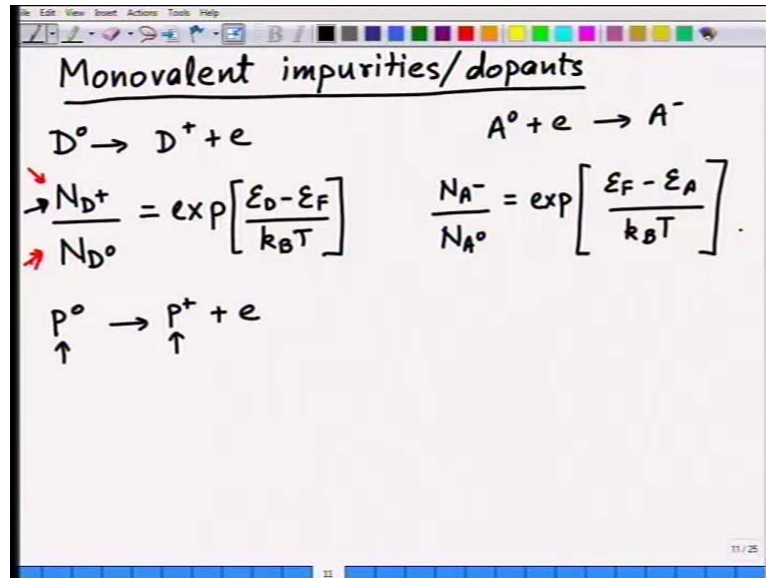
The image shows a whiteboard with handwritten notes. At the top, the word "Donor" is written in purple. Below it, a red box contains the equation: 
$$\frac{n_{D^{(n+1)+}}}{n_{D^{n+}}} = \exp\left[\frac{\epsilon_{Dn} - \epsilon_F}{k_B T}\right]$$
 Below this, the word "Acceptor" is written in purple. To its right is the chemical reaction: 
$$A^{n-} + e \rightarrow A^{(n+1)-}$$
 Below the reaction is another equation: 
$$\frac{n_{A^{(n+1)-}}}{n_{A^{n-}}} = \exp\left[\frac{\epsilon_F - \epsilon_{An}}{k_B T}\right]$$

So, in that sense, then if this number of sites are the same in both the cases for these defects, they both of silicon sites, in that case this ratio also indicates ratio of number of; so, I can write this whole expression also as number of  $D_{n+1}$  in plus site state number of  $D_n$  in plus state as being equal to same exponential which is  $e^{\epsilon_{Dn} - \epsilon_F}$  by  $k_B T$ . So, the number per unit volume, in this state and in this state, ratio of these 2 is given by this particular expression. Thus the ionization, how the ionization occurs, how much is ionizing, from, ratio between one state to other state.

Now let us continue. Now we will next go to acceptor behavior. So, similarly let us write down for acceptors also. If we have a acceptor reaction which is going on like this, let us say  $x$  of  $n-1$  charge state goes to, it accepts electron, it takes electron and becomes, goes to  $n$ , one more additional charge state, and plus 1 negative charge state. If so, then number of, by same token, number of this species,  $A_{n+1, -}$  per unit volume,

number of A this n minus ratio of this, then is simply given by exponential. These are the ratio in which the ionization occurs, alright.

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With this let me now restrict my attention to monovalent impurities or dopants, as earlier we considered, the same thing- dopants are intentional, impurities are unintentional. What do I mean by that? When I am writing this n minus, n plus, what I mean is, they are impurities. For example, sulphur which could go to s minus 1 state, it could, from s minus state it could go to s 2 minus state, it could go to second electron also and get 2 minus state also, these are multivalent impurities. And hence we have been using the symbol n, that means, sulphur 1 minus 1 state, accepting 1 more electron and becoming sulfur 2 negative, that kind of acceptor level also exists, which is why I have given you more general expression.

But, if we are talking about monovalent impurities, in that case what we mean is that exactly 1 ionization occurs; that means, we either have donor in 0, in neutral state and that becomes in plus state and gives a electron; whereas acceptor in neutral state accepts electron and gives you A minus state. This is monovalent, because it is a only one ionization level- from 0 to plus 1, or 0 to minus 1. In general from any charge state to another charge state different by only 1, and that is only reaction possible, no other reaction is possible; that is what is meant by monovalent impurity dopant.

If so, then we will restrict this, we will write down expression back again. For donors we had in the plus extra charge state divided by in the original charge state. So, we write this

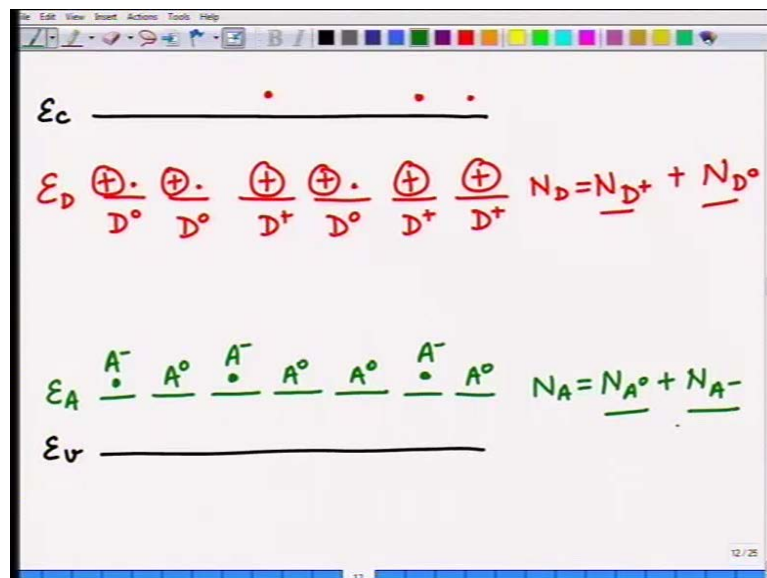


as D plus. So, we can write this as, now you use different symbol. I use capital N now which is more commonly used in this case,  $N_{D^+}$  divided by  $N_{D^0}$  charge state should be equal to  $e^{-\frac{E_D - E_F}{k_B T}}$ . So,  $N_{D^+} = N_{D^0} e^{-\frac{E_D - E_F}{k_B T}}$ .

And similarly, I am going to write here. And this small, I am using same small n, instead of small n I am started to write capital N which is number of D plus type of, D plus ionize atoms, for example, phosphorous if you thinking, number of phosphorous atoms which are ionized, which are given fifth electron. So, they only left with 4 electrons that is. So, a question asked is, that if this is phosphorous, then I would have given P plus and electron- some phosphorous returning its fifth electron and some electrons have been given away by phosphorous, and hence it is in P plus state.

So, and then question asked is what is the ratio of the two, how much are they, number of them per unit volume. And, that number is this capital N I am showing you, number of such, number of atoms in such state, impurity atoms in such state per unit volume. Therefore, similarly, using this expression I can write number of A in minus state divided by N of A in 0 charge state should be equal to  $e^{-\frac{E_A - E_F}{k_B T}}$ . Now let us make a picture of it and can see what it means.

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What it means is as this. So, I have, this is  $E_c$  and this is  $E_v$ . Let us say that I have certain acceptor level. So, let us show them the acceptor levels right here. And, I also have; and some of these acceptors which I have shown here, some ion 0 charge state; that

means, they are not occupied, and some have taken away their electron. They have taken; it is electron, some are having electrons; they have accepted electrons; meaning thereby they can indicate them as A minus, and this is state A minus, and this state A minus.

Whereas, the ones which have not accepted the electrons are in state A 0, A 0, A 0, A 0, and this is e A level; and total number of such states, number of acceptors I have added let us say is n of A; that is the total number of, I am showing here 1, 2, 3, 4, 5, 6, 7, acceptors states. So, I am thinking of N A has been 7. And, this quantity of course being equal to what is in 0 charge state, plus N A in minus charge state. These are 2 charge states that are existing. And we had already know what the ratio of these two are, how are they, what is the statistic of this ionization process.

Similarly, we think of these as the donor level. And, in the donor level I think of some sitting bound to electrons; some electrons are bound. Fifth electron in phosphorous for example, is bound; here is like this. And in some cases electron has been given away, electron has been given away. So, this is e D level, this is e D level, and I have total number of such in this example shown 1, 2, 3, 4, 5, 6, total number of donors like phosphorous atoms that I have added are 6 for example, and some of them have ionized; that means, they have N D plus meaning thereby here it is, this one is ionized, so this is N D plus; and this one is ionized, so this is N D plus, N D plus, because it has given its electron to the conduction band.

Whereas, and some of them have not given the electrons, they are still in 0 charge state; net charge state is 0; plus n with the electron there fifth electron. So, this is N D 0, this is N D 0, this is N D 0, or I should not say N D s. So, this is not N D 0, but D 0, this is D plus, and this is D 0, and this is D 0, and this is D plus, and this is D plus, the ones which have given away their electrons.

I hope that gives you idea of what these statistics are. Here is one statistics; that means, the one, the ratio in which these two are present are given by this ratio in which this and this are present are, is given by this expression. So, if so, our question becomes back again, alright. Let us manipulate this little bit more.

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$$\frac{N_{D^+}}{N_{D^0}} = \exp\left[\frac{E_D - E_F}{k_B T}\right] \quad N_D = N_{D^0} + N_{D^+}$$

$$\frac{N_{D^+}}{N_D - N_{D^+}} = \exp\left[\frac{E_D - E_F}{k_B T}\right]$$

$$\frac{N_D - N_{D^+}}{N_{D^+}} = \exp\left[\frac{E_F - E_D}{k_B T}\right]$$

$$\frac{N_D}{N_{D^+}} = 1 + \exp\left[\frac{E_F - E_D}{k_B T}\right] \Rightarrow \frac{N_{D^+}}{N_D} = \frac{1}{1 + \exp\left[\frac{E_F - E_D}{k_B T}\right]}$$

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$$\frac{N_{A^-}}{N_{A^0}} = \exp\left[\frac{E_F - E_A}{k_B T}\right] \quad N_A = N_{A^-} + N_{A^0}$$

$$\frac{N_{A^-}}{N_A - N_{A^-}} = \exp\left[\frac{E_F - E_A}{k_B T}\right]$$

$$\frac{N_{A^-}}{N_A} = \frac{1}{1 + \exp\left[\frac{E_A - E_F}{k_B T}\right]}$$

Let us just copy, let us copy; write down this statements one more time and continue on this for a few more minutes.  $N_{D^+}$  divided by  $N_{D^0}$  as equal to  $e$  to power  $e_D$  minus  $e_f$ , and  $N_{A^-}$ , this  $N_{A^-}$  divided by  $N_{A^0}$  as  $e$  to power  $e_f$  minus  $e_A$  by  $k_B T$ , alright. If so, also I know that  $N_D$  is equal to  $N_{D^0}$  plus  $N_{D^+}$ ; and,  $N_A$  is equal to, this is the total, this is the amount I know, I have added. This is the amount that I have actually added and I am asking a question, how are this split, what are I have added, how much have given it fifth electron here in this case, and how much has how many have not given the fifth electron.

Similarly, when I add so much acceptors- how many have accepted electrons which is this one, and how many have not accepted electrons which is this one, how many are these that is what we are asking. So, sum of the two therefore is 0, or is  $N_A$ . If so, then what we will do is that instead of this ratio we will use this expression, and we are going to write this as therefore  $N_D$ . So, I eliminate  $N_D$  in this, and instead write, will eliminate  $N_D$  in this. So, I am going to write this as  $N_D$  plus, divided by  $N_D$  minus,  $N_D$  plus as equal to,  $e^{-D}$  minus  $e^{-f}$  by  $k_B T$ , which I am going to write there for us.

Inverse of that;  $N_D$  minus  $N_D$  plus divided by  $N_D$  plus as  $e^{-D}$  minus  $e^{-f}$  by  $k_B T$ ; and, this I am going to write this as  $N_D$  divided by  $N_D$  plus, equal to  $1$  plus this quantity right here; and then, this going to, let us just carry out this. So, and then take inverse of this. If I take inverse of this, therefore I will write  $N_D$  plus by  $N_D$ ; therefore the total amount that I have added; what fraction of total amount has ionized, that is the question we are asking; should be therefore equal to  $1$  divided by  $1$  plus,  $e^{-D}$ .

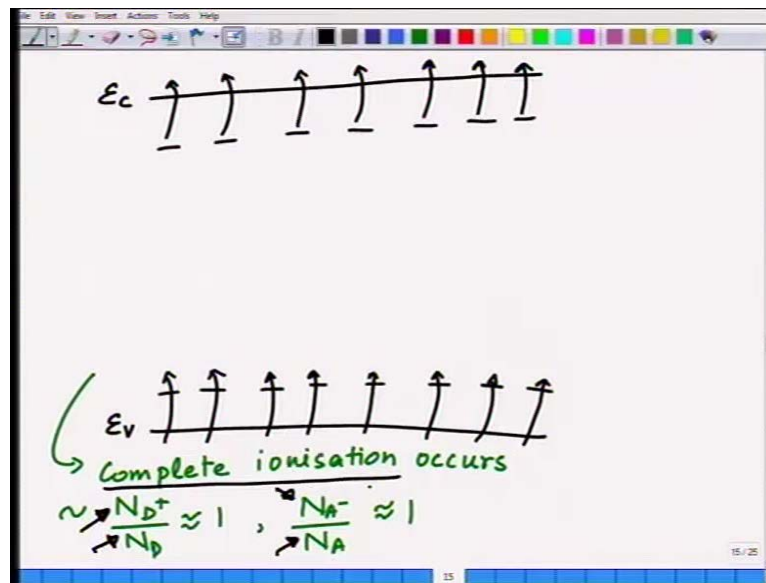
And by same token, similarly, you would get an expression where you write this as, sorry, when we write this, invert this, so in that case mistake here, an error here. When we invert this then we should have write it as, this as  $e^{-f}$  minus  $e^{-D}$  is what I should write here, as  $k_B$ . And, by same means, same way,  $N_A$ , following this  $N_A$  minus by  $N_A$  should be, this is  $A$  total  $N_A$  now; total  $N_A$  should be equal to  $1$  by  $1$  plus  $e^{-A}$  minus  $e^{-f}$  by  $k_B T$ , alright. So, this is fraction of total which I have added, how much of that has ionized; that is what therefore indicates.

Now, you would often, sometime see, now often in some books you will find a factor included here; for example, I am going to write with some blue pen that a factor, something like 2 or 4 added here; factor of 2 or 4 added in here. This factor you could add, but I do not want to get into this; about, I do not want to add. This has something to do with this pen available and this has also something to do with, this is degeneracy of the levels, this is something do with degeneracy; remember valance band, split of bands and a regular band was coming very close to each other, something to do with this fact which I will not include in this course.

Once I add this, they will include it there; then what I can do is, I can express this 4 as exponential or something quantity. Whatever that is, exponential I can take it inside this  $e$  in here and include it in  $e$ , and write this as a effective  $e^{-A}$ ; I can proceed this way and

therefore effectively I can remove what is in the front. So, as long as you imagine this, so I am not going to add this in here; I have decided to remove it; I will leave it at that. In some books if, when you read you will find a factor in front of it, but it is always possible to include that our factor also into the exponential. And then effectively, then values of  $e_A$  and this  $e_D$  will somewhat change; that is about it. So, I will not include in my lectures right here.

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Now, next question is that if I want, suppose temp now I mean saying that if the levels are shallow; this is  $E_c$ , this is  $E_v$ , if these levels are shallow, that means, we are saying the sufficient thermal energy that these electrons can jump in here, the electrons can jump in here, the electrons can jump in here also, the electrons can jump here at these levels which means whatever acceptor have added all of it becomes ionized, and whatever donors are added they become ionized because they give their electron to the conduction band.

What that means in the picture is when complete ionization occurs, complete ionizations occur, occurs then in that case approximately  $\frac{N_{D^+}}{N_D}$  is almost equal to 1, and  $\frac{N_{A^-}}{N_A}$  is almost equal to 1 is what we are saying. That means, whatever we added all that have ionized because everything, all the electrons went in near; all the acceptors accepted the electrons and they became. So, all the phosphorous atoms and silicon gave the fifth electrons away. So, they became ionized. So,  $\frac{N_{D^+}}{N_D}$  value is same thing as whatever we have added. Similarly, if we have added boron each boron

atom has accepted. So, therefore  $N_A$  minus is the same value as whatever we added; this is approximately equal to 1.

So, you imagine like this that they approx, this is the process, this is a condition where we call as complete ionization. In that case, we can, in the next lecture I will show you a problem, I will solve the problem of this complete ionization. Remember at the end of day in intrinsic case we have found, what value of  $n$  and  $p$  are? We know that  $n$  is equal to  $p$  as its value is  $n_i$ , and  $n_i$  we have calculated, and I will show you that.

Now, when I have done the doping I am again in thermal equilibrium, interested in knowing what the value of  $n$  and  $p$  are? What is the value of  $n$  in number of electrons in conduction band, what is the number of holes in the valance band; that is the number we are interested in. So, now, when we have doped it, we are going to do it for two cases. Now, one, first case is when temperature is high enough, and therefore complete ionization occurs. All the electrons are able to, from donor level they go to conduction band, the electrons in valance band are able to jump to the acceptor level.

In the next lecture I will start with that and show to you under complete ionization what the values of  $n$  and  $p$  are? Then what will we do is we will start moving to low temperatures and see how, when the ionization is, when the assumption of complete ionization is not appropriate; that means, ionization is incomplete then what happens to  $n$  and  $p$ . Those are the 2 questions which we will answer in next 2 lectures.

Thank you. .