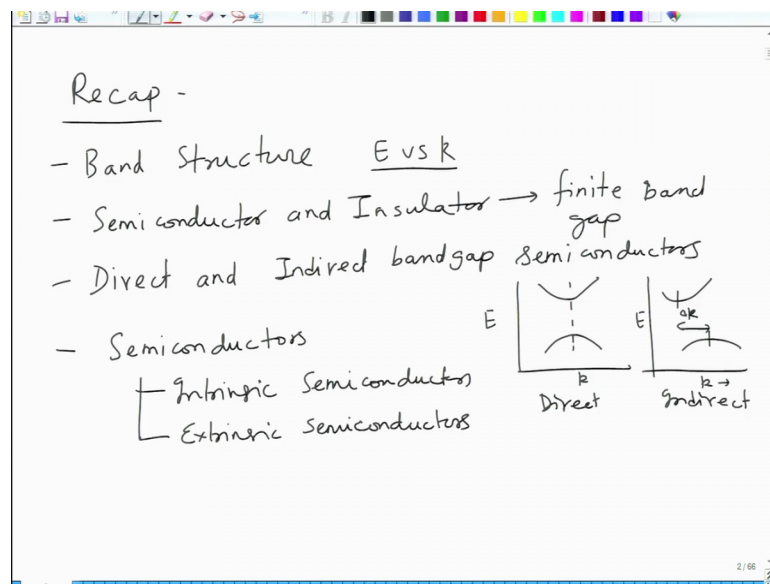


Solar Photovoltaics: Principles, Technologies and Materials
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Lecture – 09
Semiconductor Basics – II

So, welcome to lecture 9 of the course on Solar Photovoltaics Principles Technologies and Materials. So, let us just recap what we did in the last couple of lectures.

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So, we started our discussion on band structure very briefly, I mean without going into any details and basically what happens is that when you plot energy versus wave vector, there is a continuous gap and the E k diagram which is basically the band gap. And semiconductors and insulators have a finite band gap and if it is less than generally 2.2 eV and a half volt electron volt then it is semiconductor and for band gap higher than 2.5 eV we define the material normally as insulator.

Now, there was also something called as direct and indirect band gap semiconductor this direct and indirect band gap semiconductors, important to know at least we cannot get into details of this, but basically when the conduction band minima and the valence band minima and the E k space, when they coincide with when they coincide with each other, then it is a direct band gap semiconductor and when then when they do not coincide with

each other, when they shift. So, if you have a maxima here minima here maxima there. So, there is a shift in the k space then it is a indirect band gaps in here.

So, this is direct and this is indirect and this has influence on the way carriers are generated and carriers are recombined in semiconductors, we will get back to this later on. And then we moved on to what semiconducting materials are so, we defined intrinsic semiconductors and we define extrinsic semiconductors.

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The slide is titled "Intrinsic Semiconductors" and contains the following content:

- Equation: $n = p = n_i$
- Equation: $n_e = n_h = n_i$
- Equation: $n_e = N_c \cdot \exp\left\{-\frac{E_c - E_F}{kT}\right\}$
- Equation: $n_h = N_v \cdot \exp\left(-\frac{E_F - E_v}{kT}\right)$
- Diagram: An energy band diagram showing a conduction band (C.B.) with electrons (represented by dots) and a valence band (V.B.) with holes (represented by circles). A curved arrow indicates the transition of an electron from the valence band to the conduction band.
- Definitions:
 - N_c - Effective density of states in C.B.
 - N_v - Effective density of states in V.B.

So, moving forward on this discussion intrinsic semiconductors are the ones for which n is equal to p and this is mainly those semiconductor which are where carrier generation is because of thermal excitation.

So, you have conduction band you have valence band, and electrons from this are excited to the conduction band. So, this is conduction band this is valence band leaving rise to so, these are now holes giving behind the hole. So, these are electrons and these are holes so, these are mainly because of thermal excitation and as a result you have n is equal to p which is also called as n i some books also write as n e is equal to n h is equal to n i ok.

Now, the concentration is given as n e is equal to N c into exponential of sorry into exponential of minus of E c minus E F divided by k T and n h is N v into exponential minus of E F minus E v divided by k T where N c and N v are effective density of states in conduction band and this is effective density of states in valence band.

Now, we were talking about where the Fermi levels are Fermi levels will is it the middle of the band gap in case of intrinsic semiconductor whereas, it is closer to, it moves closer to conduction band edge in case of n type semiconductor it moves to valence band edge in case of p type semiconductor. So, let us move ahead with that discussion that we did last time.

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The slide contains the following equations and annotations:

Conduction band:
$$n_c = \int_{E_c}^{\infty} f(E) \cdot D(E) \cdot dE$$
Annotations: $f(E)$ is labeled "Probability of occupation", $D(E)$ is labeled "Density of states", and dE is labeled "Interval".

V.B. (Valence Band):
$$n_h = \int_{-\infty}^{E_v} (1 - f(E)) \cdot D(E) \cdot dE$$

Density of states formulas:

$$E > E_c: D(E) = \frac{1}{2\pi^2} \left(\frac{2 m_e^*}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2}$$

$$E \leq E_v: D(E) = \frac{1}{2\pi^2} \left(\frac{2 m_h^*}{\hbar^2} \right)^{3/2} (E_v - E)^{1/2}$$

So, the way these carrier concentrations are come about so, the carrier concentrations are basically calculated as so, from E_g to in E_c to infinity sorry next. So, this is E_c to infinity for conduction band. So, this is for conduction band so, this would be $f E D E$ into $d E$.

So, this is basically you can say probability of occupation $D E$ is density of states and this is over and interval $D E$. So, interval and we have integrated it from E_c to infinity to calculate the carrier concentration in the whole of conduction band for holes so, this is for n_e this is for for n_h for valence band it would be minus infinity to E_v ok. And in this case since we are looking at holes it would be one minus $f E D E$ into small $d E$ again it is probability of occupation of holes density of states and this is the interval $D E$ ok.

So, and we know what Fermi Dirac statistics is and g_s and the density of states to be precise is given as for conduction band at least is given as 1 over 2π square to m_e^* which is effective mass of electron we have not gone into effective mass of theory and all

that, but I will give you references from which you can read about effective mass E_c minus E_v to the power half.

And that for let me give you also the expression for holes just bear with me for a minute. And density of states for valence band is 1 over 2π square $2m_h^*$ divided by h cross square to the power $3/2$ into E_v minus E to the power half so, this is valid for E greater than or equal to E_c and this is for E less than or equal to E_v . So, now when you make the appropriate substitutions you may you will and if you do the integral and of course, you know the expression for Fermi Dirac statistics.

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$$n_e = N_c \cdot \exp\left(\frac{E_F - E_c}{kT}\right) = N_c \cdot \exp\left(-\frac{E_c - E_F}{kT}\right)$$

$$n_h = N_v \cdot \exp\left(\frac{E_v - E_F}{kT}\right) = N_v \cdot \exp\left(-\frac{E_F - E_v}{kT}\right)$$

$$n_e \cdot n_h = N_c \cdot N_v \cdot \exp\left(-\frac{E_c - E_v}{kT}\right)$$

$$E_c - E_v = E_g$$

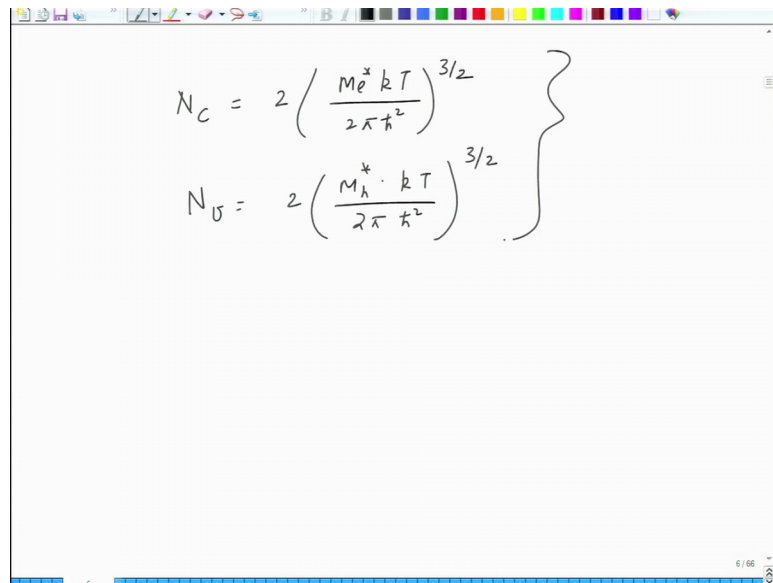
$$n_e \cdot n_h = n_i^2 = N_c \cdot N_v \cdot \exp\left(-\frac{E_g}{kT}\right)$$

$$n_i = (N_c N_v)^{\frac{1}{2}} \exp\left(-\frac{E_g}{2kT}\right)$$

You will get n as N_c into exponential of E_F minus E_c divided by kT and n_e and n_h as N_v into exponential exponential E_v minus E_F divided by kT , alternatively you can write is that exponential of minus of E_c minus E_F divided by kT . And this would be N_v exponential minus of E_F minus E_v divided by kT and when you multiply these two together n_e into n_h , it becomes N_c into N_v exponential of minus of E_c minus E_v divided by kT and E_c minus E_v is equal to E_g divided by 2 .

So, we get n_e into n_h which is equal to n_i square which is equal to N_c into N_v into exponential of minus of so, this is sorry E_c minus E_v is equal to E_g this is minus E_g divided by kT . And hence n_i becomes equal to $N_c N_v$ to the power half exponential of minus E_g divided by $2kT$ ok. What is now $N_c N_v$?

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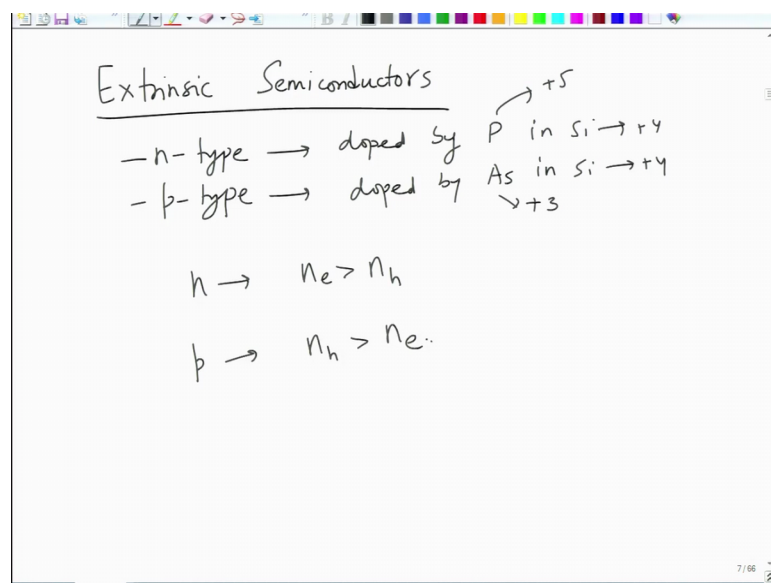


The image shows a whiteboard with two equations written in black ink. The first equation is $N_C = 2 \left(\frac{m_e^* k T}{2 \pi \hbar^2} \right)^{3/2}$. The second equation is $N_V = 2 \left(\frac{m_h^* \cdot k T}{2 \pi \hbar^2} \right)^{3/2}$. A large curly brace on the right side of the equations groups them together. The whiteboard has a toolbar at the top and a status bar at the bottom right showing '6 / 66'.

So, this N_C N_V is basically N_C N_V is N_C is 2 into $m_e^* k T$ divided by $2 \pi \hbar$ cross square to the power 3 by 2 and N_V is equal to $2 m_h^* k T$ divided by $2 \pi \hbar$ cross square to the power 3 by 2 , these are the expressions for N_C and N_V which we did not look at last time.

These are the expressions for basically, this is the expression for intrinsic carrier concentration, in a intrinsic semiconductor that is how you derive it.

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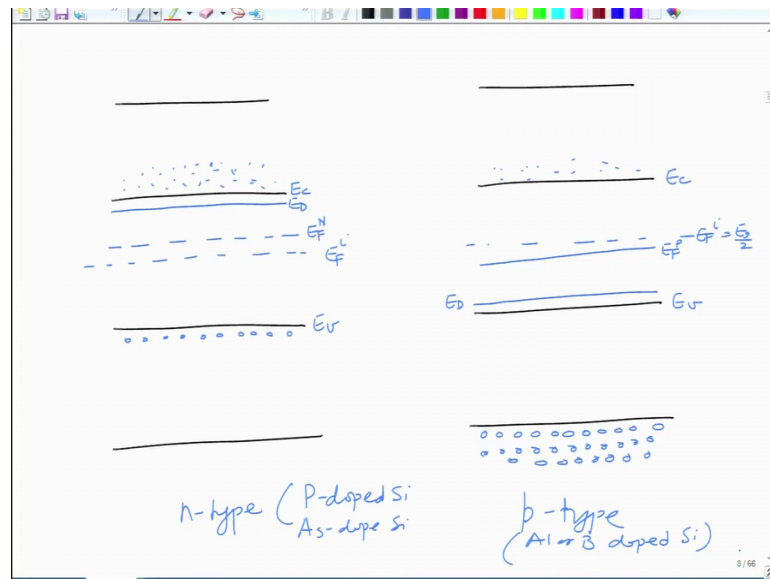


The image shows a whiteboard with handwritten notes. The title is 'Extrinsic Semiconductors'. Below it, there are two lines: '- n-type → doped by P in Si → +4' and '- p-type → doped by As in Si → +4'. To the right of these lines, there are arrows pointing to '+5' and '+3'. Below these lines, there are two more lines: 'n → $n_e > n_h$ ' and 'p → $n_h > n_e$ '. The whiteboard has a toolbar at the top and a status bar at the bottom right showing '7 / 66'.

Now, for extrinsic semiconductors we defined last time, extrinsic semiconductors we said there are two types one is n type and second is p type, n type is doped by so if it is in the context of silicon doped by phosphorus and silicon for example, silicon is the base material phosphorus is the dopant and this is doped by things like arsenic in silicon. So, this is plus 5 this is plus 3, silicon is plus 4 as a result they create extra electrons and extra holes.

So, basically since you have in these semiconductor so, n type we said you have n_e which is much larger than n_h and p type you have n_h which is much larger than n_e .

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So, if you look at the band diagram of n o p type semiconductor ok. So, for n type semiconductor there are high electron density and very few holes. So, this is n type and the Fermi level lies. So, this is let us say the E_F i the Fermi level of n type semiconductor lies little bit ahead, little bit above the E_F i and the donor level lies very close to so, this is E_c this is donor level.

In this case what happens is that there are more holes and fewer electrons ok. So, here this is E_v again the mid gap position is this, but the Fermi level lies here. So, this is E_F p this is E_F i; E_F i is equal to E_g by 2, but E_F p is little bit lower we will see the expressions of those in a little while this is E_c ok. And in this case the acceptor level lies here. So, we said last time that the donor and acceptor level are very close to E_c and E_v

so, that they are completely so that the atom sitting in them are completely donor acceptor and donor atoms are completely ionized.

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Ionization Energies	Si
<u>Donors</u> - E_{mp}	
Sb	0.0039 eV
P	0.045 eV
<u>Acceptors</u>	
B	0.045 eV
Al	0.057 eV

n-type $\leftarrow N_e \approx N_d \rightarrow$ donor concentration
 p-type $\leftarrow N_h \approx N_A \rightarrow$ Acceptor concentration.

So, ionization energies of these so, for donors we have impurities like antimony phosphorus which have if you put it in silicon for example, and the antimony has a value of 0.0039 sorry am I writing it 0.0039 E v. And for phosphorous this value is 0.045 E v for in this case in case of antimony in case of p type doping let me correct it, it should be boron or aluminum not arsenic, arsenic is plus 5.

So, it should be boron or phosphorus boron or aluminum phosphorous typically antimony, phosphorous antimony is used for n type doping and boron or aluminum or gallium or indium they are used for p type doping. So, let me correct myself there. So, this is p type.

So, this would be phosphorus dope silicon or antimony doped silicon in this case it would be aluminum, or boron doped silicon. And if you look at acceptors in case of acceptors the aluminum common impurities are boron and aluminum for boron the ionization energy is 0.045 electron volt. And for aluminum it is 0.057 E v.

So, you can see that these are very small energies as a result near complete ionization of these is obtained. And since these energies are very small all the extra electrons which they bring are able to get into the conduction of valence, into the conduction band all the

extra holes which are created they go they are created in the valence band. So, as a result since their energies are very small they are completely ionized we can write that n_e in n type is equal to N_d which is the donor concentration and n_h in p type is equal to n_a which is the acceptor concentration. So, this is for n type and this is for p type.

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The image shows a whiteboard with handwritten equations. At the top, the mass action law is written as $n_e \cdot n_h = n_i^2$. Below this, for n-type semiconductors, it is noted that $n_e = N_d$ and $n_h = \frac{n_i^2}{N_d}$. For p-type semiconductors, it is noted that $n_h = N_A$ and $n_e = \frac{n_i^2}{N_A}$. The whiteboard also features a toolbar at the top and a page number '10/66' in the bottom right corner.

$$n_e \cdot n_h = n_i^2$$

For n-type $n_e = N_d$
 $n_h = \frac{n_i^2}{N_d}$

For p-type $n_h = N_A$
 $n_e = \frac{n_i^2}{N_A}$

So, when we say that, but at the same time we also make sure mass conservation ensures that n_e and n_h is equal to n_i square ok. Which means for n type n_e is equal to N_d hence n_h is equal to $N_d n_i$ square divided by N_d . For p type n_h is equal to N_A as a result n_e is equal to n_i square divided by N_A . So, these are the concentration of carriers that we have alright.

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The image shows a whiteboard with handwritten mathematical equations. At the top, two equations are written: $n_i = n_e = N_c \cdot \exp\left(-\frac{E_c - E_f}{kT}\right)$ and $n_i = n_h = N_v \cdot \exp\left(-\frac{E_f - E_v}{kT}\right)$. A bracket on the right side of these two equations is labeled "For intrinsic S.C.". Below these, the Fermi level is given as $E_f = E_f^i$. Then, the equations are rearranged to solve for N_c and N_v : $N_c = n_i \exp\left(\frac{E_c - E_f^i}{kT}\right)$ and $N_v = n_i \exp\left(\frac{E_f^i - E_v}{kT}\right)$. Finally, it is noted that $n = p = n_i$, and the two expressions for N_c and N_v are set equal to each other: $N_c \cdot \exp\left(-\frac{E_c - E_f}{kT}\right) = N_v \cdot \exp\left(-\frac{E_f - E_v}{kT}\right)$. The whiteboard has a toolbar at the top and a status bar at the bottom right showing "11/66".

So, we can also write these expressions little bit differently so for example, we said that n_i is equal to we said that n_e is equal to N_c into exponential of minus E_c minus E_f by kT and n_h is equal to N_v into exponential of minus of E_f minus E_v divided by kT ok. We also know that this n_e this is equal to n_i for intrinsic semiconductors right ok. So, if you just turn the equation upside down and for intrinsic semiconductor E_f is equal to E_f^i then we can write expression for N_c as n_i exponential of E_c minus E_f^i divided by kT and N_v as n_i into exponential E_f^i minus E_v divided by kT ok.

So, now for intrinsic semiconductor since n is equal to p is equal to n_i . So, which means that N_c into exponential of minus of E_c minus E_f divided by kT is equal to N_v into exponential of minus of E_f minus E_v divided by kT ok.

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The image shows a whiteboard with handwritten mathematical equations. At the top, it says $E_F = E_F^i$. Below that, the first equation is $E_F^i = \frac{E_c + E_v}{2} + \frac{kT}{2} \ln\left(\frac{N_v}{N_c}\right)$. The second equation is $= \frac{E_c + E_v}{2} + \frac{3kT}{4} \ln\left(\frac{m_h^*}{m_e^*}\right)$. The whiteboard has a toolbar at the top and a status bar at the bottom right showing '12/68'.

If that is true then we can get the expression for and if E_F is defined as E_F^i , then we can write an expression for E_F^i ; E_F^i is equal to E_c plus E_v divided by 2 plus kT by 2 into $\ln N_v$ by N_c and this will turn out to E_c plus E_v divided by 2 plus $3kT$ by 4 \ln of m_h^* divided by m_e^* effective mass of hole electron.

So, if the effective mass of hole and electron were equal then E_F^i would be right at the mid gap position; however, if they were different then E_F will be different ok. And you can also see there is a strong there is a temperature dependence of E_F as well. So, as the temperature changes the Fermi level also goes its increases ok.

Now, another thing that you need to worry about a solid is since, now if you create electron and hole which means you have positive or negative charges, if you dope it with n type impurity you have n type impurities ionized atoms, if you have p type doping you have p type impurities; however, as a solid; solid must remain charged neutral.

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Charge neutrality

— A solid must always be charge neutral.

$$q(-n_e + n_h + N_d^+ - N_A^-) = 0$$

$$n_h = \frac{n_i^2}{n_e}$$

$$n_e = \frac{N_d - N_a}{2} + \left[\left(\frac{N_d - N_a}{2} \right)^2 + n_i^2 \right]^{\frac{1}{2}}$$

$$n_h = \frac{N_a - N_d}{2} + \left[\left(\frac{N_a - N_d}{2} \right)^2 + n_i^2 \right]^{\frac{1}{2}}$$

For n-type: $N_d \gg N_a$, $n_h = n_i^2 / N_d$, $n_e = N_d$

For p-type: $N_a \gg N_d \Rightarrow n_e = n_i^2 / N_a$, $n_h = N_a$

So, which means no matter what happens is that a solid must always be be charged neutral which means that for a given semiconductor q into n_e so, minus n_e is the negative charge plus holes n_h plus N_d plus which is the donor atoms minus the acceptor atoms which are negatively charged minus N_A minus that overall charge must be equal to 0 and we know that n_h is equal to n_i^2 divided by n_e .

So, if you substitute in the above equation you can get n_e is equal to $N_d - N_a$ divided by 2 plus $N_d - N_a$ divided by 2 square plus n_i^2 to the power half and n_h you can obtain as $n_i^2 / N_a - N_d$ divided by 2 plus $N_a - N_d$ to the power 2 to the power 2 plus n_i^2 to the power half.

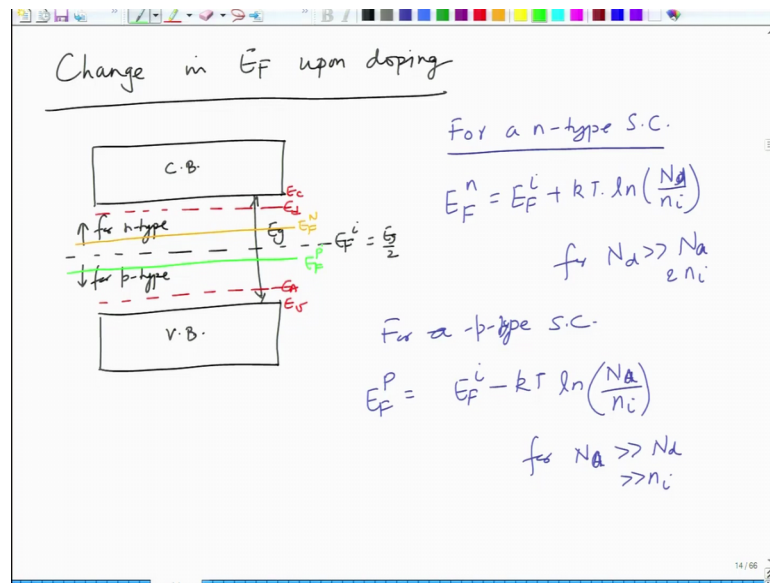
Now, if we make an approximation that for n type; if N_d is equal to is a lot greater than N_a which is true for n type semiconductor donor impurities are much larger than the acceptor impurities remember, you will always have some donor and acceptor impurities present in every semiconductor even in intrinsic 1, but the effect is almost effect almost cancels out each other. Because you cannot completely purify a semiconductor to 0 impurity nothing is completely pure on the based on the laws of thermodynamics.

So, as a result you always have some impurity some donor impurity some acceptor impurities. Now, if you intentionally dopar semiconductor to become n type which means N_d is a lot greater than n_a which means its predominantly p type. And if N_d is a lot greater than N_a , then if you plug this in the above equation we get p is equal to n_i is

square divided by N_d that is what we said previously also right. And for p type N_a is a lot greater than N_d which leads to so, sorry let me just not write as p let us write it as n h and in this case N_a will be equal to n_i square divided by N_a ok.

So, and of course, n_e will be equal to N_d and in this case n_h will be equal to N_a ok. So, these can also be derived.

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Now let us look at quantitatively the change in E_F upon doping so, we said that you have a conduction band you have a valence band ok. So, this is conduction band, this is valence band alright and this is your band gap E_g your intrinsic Fermi level is somewhere here. And the Fermi level moves up for n type moves down for p type and this is at $E_g/2$ for an intrinsic semiconductor alright. And for n type semiconductor you will have this as E_d and for p type you will have this as E_a this is conduction band edge and this is valence band edge ok.

Now, for a Fermi level of n type semiconductor we can define E_F^n is equal to E_F^i plus $kT \ln$ of N_d divided by n_i . And this is for N_d being a lot greater than N_a as well as n_i ok. And for a p type semiconductor the E_F^p on the other hand is equal to E_F^i minus $kT \ln$ of N_a divided by n_i for N_a being greater than N_d . So, it is getting a small a and it should be greater than n_i ok.

So, basically you can see from this expression that as you increase the donor concentration in the first equation, as we increase the donor concentration the term on the right increases right and it is multiplied by kT . So, when your impurity concentration, donor impurity concentration increases it when it is much larger than n_i , then E_F tends to move up. So, you add something on E_F i ok. For a p type semiconductor on the other hand since you have a minus term here as you add more and more to acceptor impurities the Fermi level tends to decrease or go lower with respect to the Fermi level of an intrinsic semiconductor ok.

So, this explained, so if you want if you have a p m type semiconductor your Fermi level will is likely to lie here. So, this is your $E_F n$ and if you have a p type semiconductor the Fermi level is likely to lie here so, this is $E_F p$ so, this is what we have done so far we have just in this lecture we have looked at the carrier statistics and effect of doping on Fermi level. And some things about the p and n type semiconductors, what we will do in the next class is we will so, this is let me just go through it.

So, we looked at the carrier statistics in intrinsic semiconductors. So, basically simple expression without going through complete derivation. So, this is how you get this n_i is equal to $N_c N_v$ to the power half exponential minus E_g by $2kT$. And then we looked at extrinsic semiconductors, the band diagram the ionization energies of donor, and acceptor impurities the relation between the carrier concentration and so, if I just draw these this is for n type and this is for p type ok. And then we looked at some other relations with respect to carrier concentration the Fermi position. And the Fermi position charge internally aspect which gives which ships ties to again carrier concentration expressions and the change in Fermi energy upon doping. So, we will continue with this carrier statistics and carrier mobility carrier motion and semiconductors in the next couple of lectures.

Thank you.