Fundamentals of electronic materials, devices and fabrication
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Lecture - 05
Intrinsic semiconductors - conductivity

Let us start with the brief recap of last class. Last class we looked at intrinsic semiconductors. These semiconductors are pure semiconductors and we calculated the concentration of electrons in the conduction band and holes in the valence band. We found that at any given temperatures, electrons and holes are created in pairs and in an intrinsic semiconductor n, which is the concentration of electrons is equal to the concentration of the holes and it is equal to a number n_i and n_i, we called as the intrinsic career concentration.

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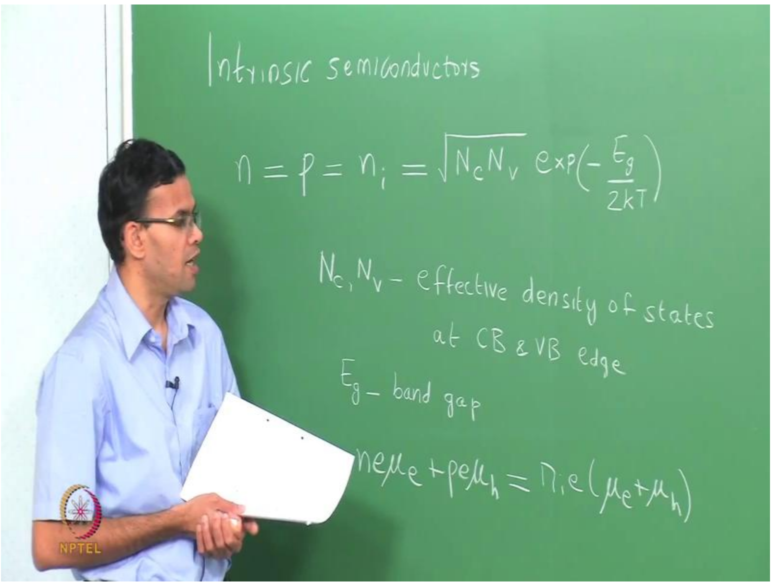

Intrinsic semiconductors

$$n = p = n_i = \sqrt{N_c N_v}\, exp\left(-\frac{E_g}{2kT}\right)$$

N_c, N_v - effective density of states at CB & VB edge

E_g - band gap

$$ne\mu_e + pe\mu_h = n_i e(\mu_e + \mu_h)$$

The expression for n_i, $\sqrt{N_c N_v}\, exp\left(\frac{-E_g}{2kT}\right)$, N_c and N_v, where the effective density of states at the conduction band edge and the valence band edge and E_g, is the band gap of the material. We also wrote down an expression for the conductivity, sigma as $n\ e\ \mu_e + p\ e\ \mu_h$, in the case of an intrinsic semiconductor. Where $n = p$ this simplifies into $\mu_e + \mu_h$, μ_e and μ_h are the mobilities of the electrons in the holes. They represent the ease with which the electrons can move through the conduction band or the holes can move through the valence band. Higher the value of n higher is the conductivity similarly; higher the value of μ_e and μ_e, higher is the conductivity. Today, we will start by calculating some of these values for the career, concentration, mobilities and conductivities and we will start with silicon.

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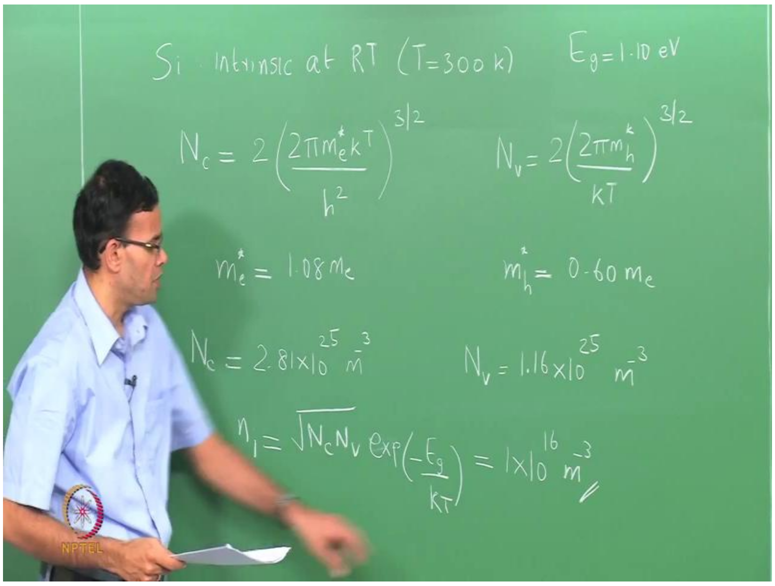

Si intrinsic at RT (T=300 k) $E_g = 1.10$ eV

$N_c = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2}$ $N_v = 2\left(\frac{2\pi m_h^*}{kT}\right)^{3/2}$

$m_e^* = 1.08\, m_e$ $m_h^* = 0.60\, m_e$

$N_c = 2.81\times10^{25}\, m^{-3}$ $N_v = 1.16\times10^{25}\, m^{-3}$

$n_i = \sqrt{N_c N_v}\, \exp\left(-\frac{E_g}{kT}\right) = 1\times10^{16}\, m^{-3}$

If we have intrinsic silicon at room temperature, temperature is 300 kelvin, the first thing we want to calculate is the effective density of states N_c and N_v. We looked at the expression for N_c and N_v in last class, N_c depends upon the effective mass of the electron. So, $2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{\frac{3}{2}}$, we can write a similar expression for the density of states in a valence band N_v whole power 3 over 2. In the case of silicon, m_e^* is 1.08 times m_e, where m_e is the rest mass of the electron, m_h star is 0.60 m_e. If you use these numbers, substitute them in here and also put in the values of the constants, N_c turns out to be $2.81 \text{ x } 10^{25}$ m^3 and then N_v is $1.16 \text{ x } 10^{25}$ m^{-3}. So, these 2 represent the effective density of states at the conduction band edge and the valence band edge.

Last class, we saw that most of the electrons in holes are concentrated near the valence band edges and the conduction band edge. So, we can go ahead and calculate the intrinsic career concentration times $exp\left(\frac{-E_g}{2kT}\right)$. At room temperature silicon has a band gap of around 1.1 ev so E_g is if, we plug in that, we get a value of N_i to be $1 \text{ x } 10^{16} m^{-3}$. This represents the intrinsic career concentration of silicon, we write this down here, n_i for silicon at room temperature

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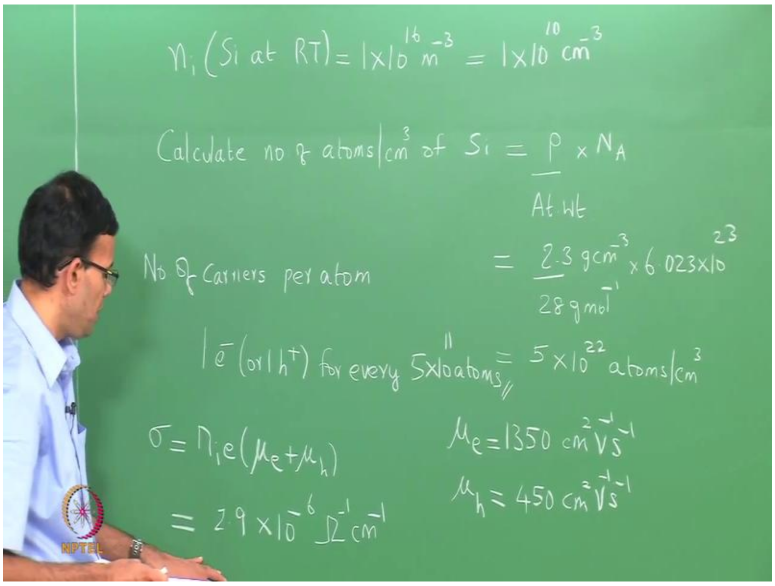

n_i (Si at RT) $= 1\times10^{16}\ m^{-3} = 1\times10^{10}\ cm^{-3}$

Calculate no of atoms/cm^3 of Si $= \frac{\rho}{\text{At Wt}} \times N_A$

No of carriers per atom $= \frac{2.3\ g\,cm^{-3}}{28\ g\,mol^{-1}} \times 6.023\times10^{23}$

$1\ e^-$ (or $1\ h^+$) for every 5×10^{11} atoms $= 5\times10^{22}$ atoms/cm^3

$\sigma = n_i e(\mu_e + \mu_h)$ $\quad \mu_e = 1350\ cm^2 V^{-1} s^{-1}$

$= 2.9\times10^{-6}\ \Omega^{-1} cm^{-1}$ $\quad \mu_h = 450\ cm^2 V^{-1} s^{-1}$

We can convert this to centimeter cube. So, this centimeter cube is around 1×10^{10} cm^{-3}. So, we have 10 billion careers that is electrons and holes in silicon at room temperature. Now, this looks like a really large number. Let us try and put that in context now. Let us calculate the number of atoms V^{-1} cm^{-3} of silicon.

This is nothing but the density of the material ρ divided by the atomic weight times Avogadro's number. We substitute the numbers, density of silicon is 2.3 g cm^{-3}, atomic weight is 28 g $mole^{-1}$ and Avogadro's number is 6.023×10^{23}. You substitute these values and evaluate, you get the number of silicon atoms per unit volume to be approximately 5×10^{22}. If you looked at the carrier concentration and said that was 10 billion, you can compare it to the number of atoms, which is 10^{22}. So, 10 orders of a magnitude more than 10 billion. So, if you look at it, the number of careers per atom, if you do the division you will find that you have 1 electron or 1 hole for every 10^{11} atoms and this turns out be really small. We can go ahead and calculate the conductivity using this equation, μ_e for silicon. We saw yesterday, was 1350 cm^2 v^{-1} s^{-1}, μ_h is 450. You can substitute for the value n_i which we have here e is nothing but the electric charge that is a constant, μ_e and μ_h are given here. If you substitute and evaluate you get a conductivity of 2.9×10^{-6} Ω^{-1} cm^{-1}. Let me write this down again.

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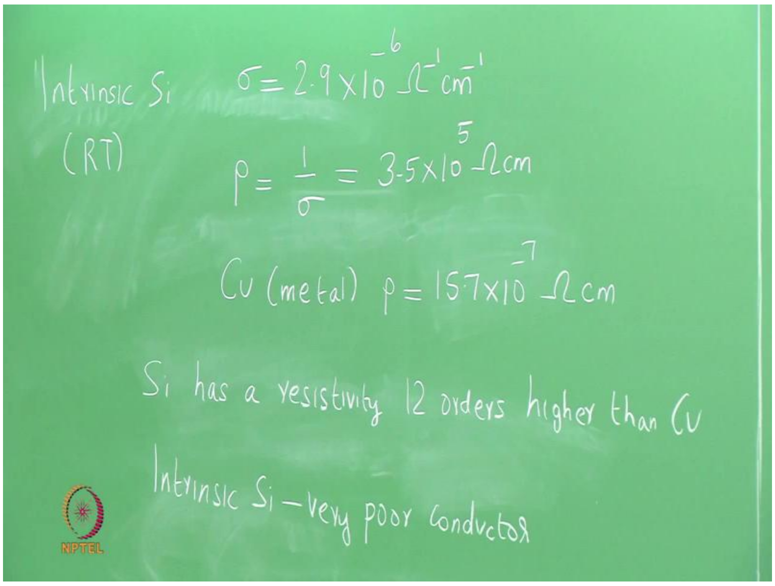

Intrinsic Si (RT) $\sigma = 2.9 \times 10^{-6}\ \Omega^{-1}\,cm^{-1}$

$\rho = \frac{1}{\sigma} = 3.5 \times 10^{5}\ \Omega\,cm$

Cu (metal) $\rho = 15.7 \times 10^{-7}\ \Omega\,cm$

Si has a resistivity 12 orders higher than Cu

Intrinsic Si – very poor conductor

If you have intrinsic silicon at room temperature, the conductivity sigma which we calculate is $2.9 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$, resistivity ρ is nothing, but 1 over the conductivity, the resistivity is $3.5 \times 10^{5}\ \Omega$ cm. So, it is just 1 over the conductivity just to compare. If you have copper, which is a metal the resistivity ρ approximately 15.7. We saw this in the first class when we wrote down resistivities for different elements. So, ρ is $15.7 \times 10^{-7}\ \Omega$ cm. So, comparing copper and silicon, silicon has a resistivity 12 orders higher than copper. So, this makes intrinsic silicon a very poor conductor and the reason for that is because we have a very low density of electrons in holes. So, you have a very low career density and this is related to the band gap of silicon. In the case of copper, which is a metal you have empty states that are there. So, both the valence band and the conduction band overlap. So, you have empty states that are available for conduction, if we have 10^{22} atoms then each atom can denote 1 electron. So, you have a high density of electrons which leads to a high conductivity.

Last class we also looked at the comparison of silicon with other semiconductors based on mobility.

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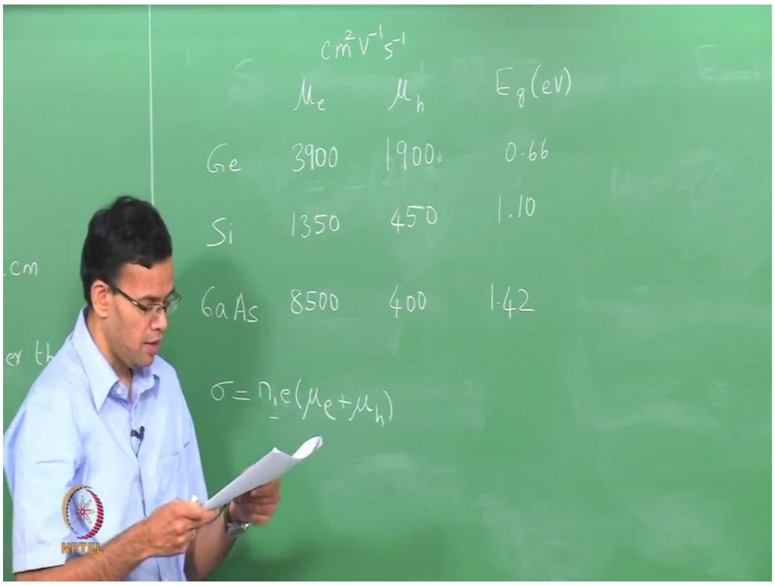

$cm^2 V^{-1} s^{-1}$

	μ_e	μ_h	$E_g(eV)$
Ge	3900	1900	0.66
Si	1350	450	1.10
GaAs	8500	400	1.42

$$\sigma = n_i e(\mu_e + \mu_h)$$

So, we had three semiconductors, we looked at germanium, silicon and gallium arsenide. Let me write down their mobility values, μ_e and μ_h the units will be in $cm^2\ v^{-1}\ s^{-1}$. Germanium is 3900, 1900 for your holes. Silicon is 1350 for the electrons and 450 for the holes and gallium arsenide has a very high mobility for electrons, it is around 8500, holes is around 400. So, the question was if you want to increase the conductivity then what materials will you choose based on mobility. The answer is you will choose gallium arsenide because gallium arsenide has the highest mobility and we know that sigma is directly related to the mobility, but it turns out that the overriding factor here is n_i, which is the concentration of electrons in holes, for that we also need the values for the band gap. So, let me write the values for the band gap, here E_g, this is in electron volts. So, germanium has a band gap of around 0.66 ev, this is at room temperature. Silicon is 1.10, gallium arsenide is 1.42. So, even though gallium arsenide has a higher mobility because it has a higher band gap, we find that the concentration of careers is lower because you have a lower concentration of careers, you will also have a lower conductivity. So, let us just do the math for gallium arsenide.

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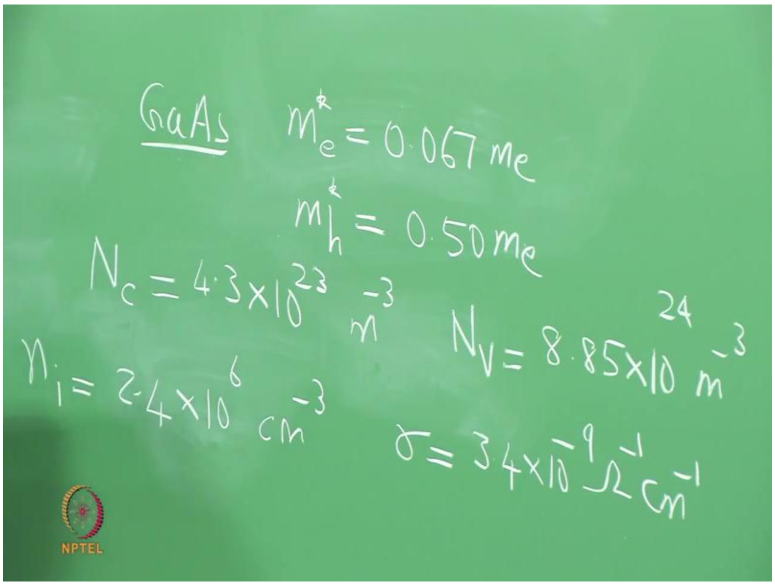

GaAs $m_e^* = 0.067\, m_e$

$m_h^* = 0.50\, m_e$

$N_c = 4.3 \times 10^{23}\, m^{-3}$ $N_V = 8.85 \times 10^{24}\, m^{-3}$

$n_i = 2.4 \times 10^{6}\, cm^{-3}$

$\sigma = 3.4 \times 10^{-9}\, \Omega^{-1}\, cm^{-1}$

Once again we need the masses, the effective masses of the electrons and holes. So, m_e^* for gallium arsenide is 0.067 m_e, m_h star is 0.50 m_e.

Now, you can calculate N_c using the same equation that we used for silicon, N_c is around 4.3 x 10^{23} m^{-3}, N_v is 8.85, from N_c N_v and the band gap which is 1.42, we can calculate the intrinsic career concentration is 2.4 x 10^6 cm^3, correspondingly the conductivity is lower, which is 3.4 x 10^{-9}. So, we find that in the case of gallium arsenide, intrinsic carrier concentration is lower, correspondingly the conductivity is lower. Just to complete this table, we will also do a similar calculation for germanium then we can come back and fill in the values for n_i in terms of cm^3 and also conductivity.

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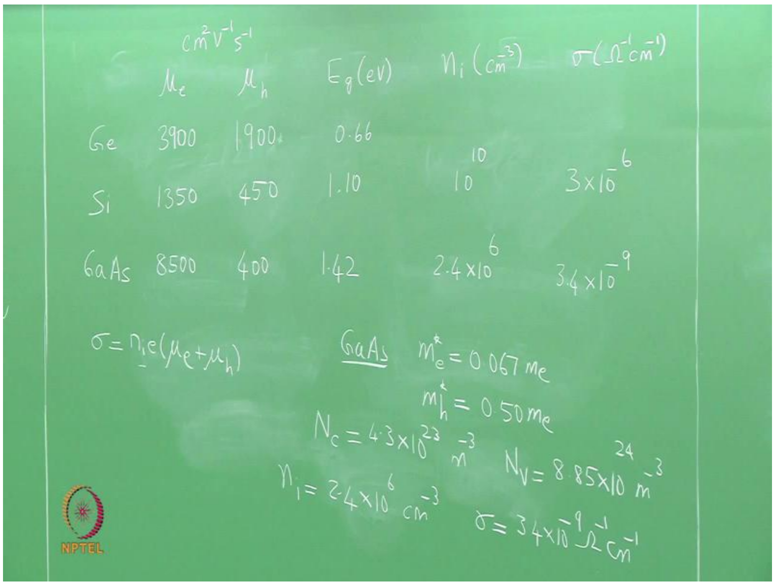

	μ_e ($cm^2V^{-1}s^{-1}$)	μ_h	$E_g(eV)$	$n_i\,(cm^{-3})$	$\sigma\,(\Omega^{-1}cm^{-1})$
Ge	3900	1900	0.66		
Si	1350	450	1.10	10^{10}	3×10^{-6}
GaAs	8500	400	1.42	2.4×10^{6}	3.4×10^{-9}

$\sigma = n_i e(\mu_e+\mu_h)$

GaAs $m_e^* = 0.067\,m_e$

$m_h^* = 0.50\,m_e$

$N_c = 4.3\times10^{23}\,m^{-3}$ $N_V = 8.85\times10^{24}\,m^{-3}$

$n_i = 2.4\times10^{6}\,cm^{-3}$

$\sigma = 3.4\times10^{-9}\,\Omega^{-1}cm^{-1}$

We already did this calculation for silicon. So, for silicon we had n_i to be 10^{10} and then we had the conductivity for silicon to be 3×10^{-6}. We just did the calculation for gallium arsenide. So, if you write the values for gallium arsenide n_i is 2.4×10^{6}, correspondingly conductivity is 3.4. So, let us do the calculation for germanium. So, then we can fill in these 2 values as well.

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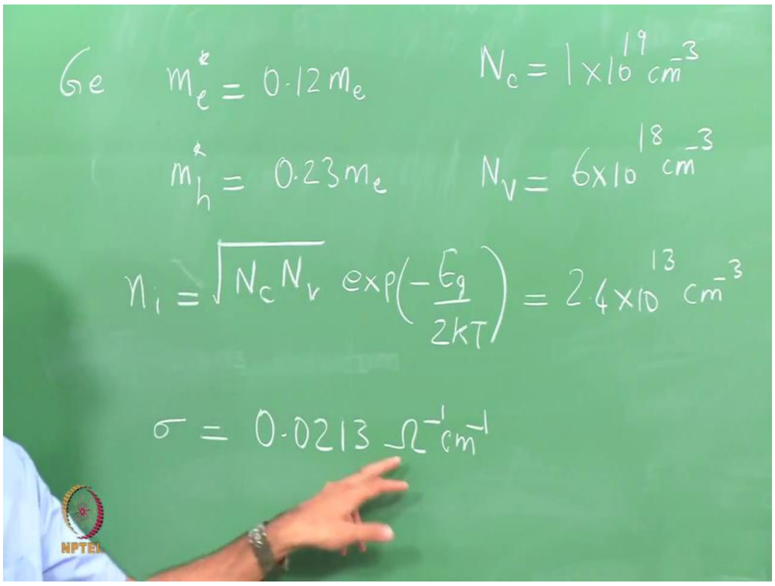

Ge $m_e^* = 0.12\,m_e$ $N_c = 1\times10^{19}\,cm^{-3}$

$m_h^* = 0.23\,m_e$ $N_V = 6\times10^{18}\,cm^{-3}$

$$n_i = \sqrt{N_c N_v}\,\exp\left(-\frac{E_g}{2kT}\right) = 2.4\times10^{13}\,cm^{-3}$$

$\sigma = 0.0213\,\Omega^{-1}cm^{-1}$

So, in the case of germanium, once again I need the effective masses m_e^* is 0.12 m_e, m_h^* is 0.23 m_e. So, once you know m_e^* and m_e^*, we can go ahead and calculate N_c and N_v. So, the formula is just the same you are just substituting different numbers, N_c is $1 \text{ x } 10^{19}$ cm^3, N_v is $6 \text{ x } 10^{18}$. So, the intrinsic career concentration, n_i is nothing but N_c N_v $exp\left(\frac{-E_g}{2kT}\right)$, which if you substitute the values give you an n_i of $2.4 \text{ x } 10^{13}$ cm^3. So, n_i is higher in the case of germanium. Similarly, you can calculate the conductivity; the conductivity works out to be 0.0213. We can now fill in this information back in the table where we started. So, let me go to the table and fill in the values for germanium. You already did for silicon and gallium arsenide. So, in case of germanium, the carrier concentration is $2.4 \text{ x } 10^{13}$ and the conductivity 0.0213.

So, we had three semiconductors germanium, silicon and gallium arsenide. We found that gallium arsenide has the highest mobility, germanium is also higher than silicon, but the main term that really dominates the conductivity is n_i, which is the career concentration and n_i depends upon the band gap. So, higher the band gaps lower the carrier concentration, correspondingly lower the conductivity. Based on this graph or based on this table, if you want to choose a material with the highest conductivity then the preference goes to germanium. In fact, the first transistor or the very first solid state transistor that was built in Bell labs is actually made of germanium.

One of the reasons, this silicon has now come to dominate the micro electronics industry is because we can actually control the conductivity and the electronic properties of silicon by doping. So, we will see doping next, more importantly silicon is much more abundant than germanium. So, silicon is the second most abundant element on earth. These are around 27% germanium, on the other hand, it is the fiftieth most abundant element. Its concentration is around 10^{-6}%. So, this is the reason why silicon has come to dominate the micro electronics industry. The next thing I like to do is, in last class we never calculated the position of the fermi energy. So, we will go ahead and calculate where the fermi energy is located in an intrinsic semiconductor.

Let us go ahead and draw the band picture.

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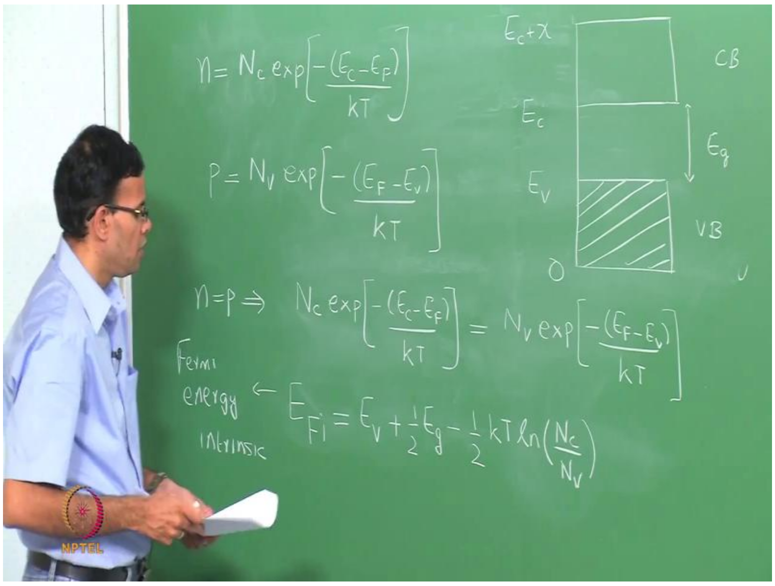

$$n = N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right]$$

$$p = N_v \exp\left[\frac{-(E_F - E_v)}{kT}\right]$$

$$n = p \Rightarrow N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right] = N_v \exp\left[\frac{-(E_F - E_v)}{kT}\right]$$

Fermi energy ← $E_{Fi} = E_v + \frac{1}{2}E_g - \frac{1}{2}kT\ln\left(\frac{N_c}{N_v}\right)$

Intrinsic

We have energy on the y-axis, we have a valence band, the bottom of the valence band is referenced as 0 and the top of the valence band is E_v. Then we have a conduction band, the bottom of the conduction band is referenced as E_c and the top of the conduction band $E_c + \chi$ and this distance between valence and conduction band is E_g. We also wrote down expressions for n and p, n it was $N_c\, exp\left(\frac{E_c - E_f}{kT}\right)$, where E_f is the fermi energy; p is $N_v\, exp\left(\frac{E_f - E_v}{kT}\right)$. So, in last class we went ahead and multiplied these two terms in order to eliminate E_f. To calculate the value of E_f that is where the fermi energy is located the semiconductor, let us just equate n and p. So, we have $N_c\, exp\left(\frac{E_c - E_f}{kT}\right)$ is equal to $N_v\, exp\left(\frac{E_f - E_v}{kT}\right)$. So, I have just equated n and p. So, we can take natural log on both sides and then rearrange this expression to give you the value of E_f, do that $E_f = E_v + \frac{1}{2}E_g - \frac{1}{2}kT \ln\frac{N_c}{N_v}$.

So, this you can get by just rearranging this expression, since we are looking at an intrinsic semiconductor this is usually denoted as E_{Fi}. So, that this is the fermi energy of an intrinsic semiconductor. So, let me rewrite this expression.

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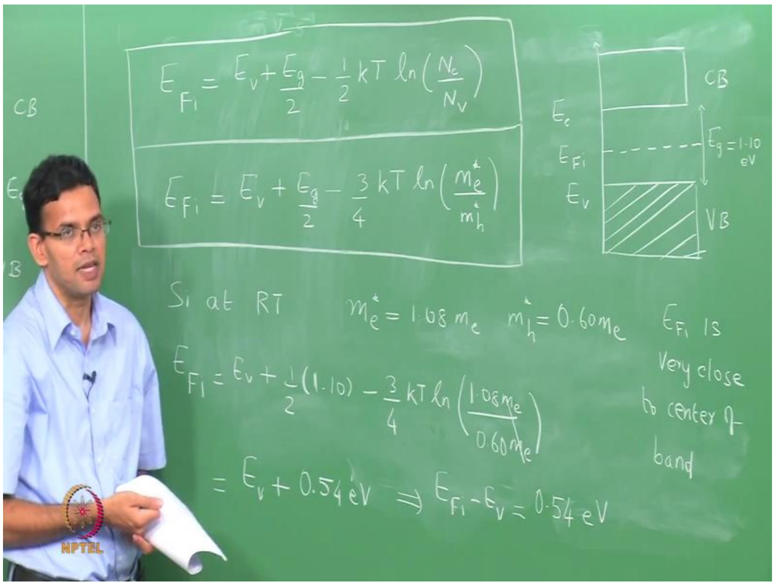

So, $E_{Fi} = E_v + \frac{1}{2}E_g - \frac{1}{2}kT \ln\frac{N_c}{N_v}$. Now, N_c and N_v are also related to the effective masses of the electrons in holes, you have seen that expression before.

Instead of N_c and N_v, we can substitute the effective mass and this expression will change as $E_{Fi} = E_v + \frac{1}{2}E_g - \frac{3}{4}kT \ln\frac{m_e^*}{m_h^*}$, So, now, you have essentially 2 equations to calculate E_{Fi}, E_{Fi} is the position of the fermi level in the intrinsic semiconductor. So, let us do the calculation for silicon at room temperature, we can either use N_c and N_v that we calculated earlier or you can use the effective masses. So, let me use the effective mass m_e^* was 1.08 m_e, m_h^* is 0.60 m_e.

Since I am using the effective mass, I will use the second equation from which you get E_{Fi}, this E_v, the band gap of silicon is $E_{Fi} = E_v + \frac{1}{2}(1.10) - \frac{3}{4}kT \ln\frac{1.08m_e}{0.60m_h}$. If you simply this expression, this gives you $E_v + 0.54$ or writing this another way is $E_{Fi} - E_v$ is 0.54. So, in the case of intrinsic silicon the fermi level is located approximately 0.54 electron holes above the valence band. So, if we try to redraw our picture for the energy band gap I will do that here, I have a valence band that is full, this is E_v have a conduction band that is E_c, E_g in the case of silicon is 1.1 and E_{Fi} is 0.54 above E_v, E_{Fi} which is the fermi energy is located very close to the center of the band. The actual center of the band from this value of E_g is 0.55 and the fermi energy is located at 0.54. So, E_{Fi} is very close to the center of the band.

If m_e^* and m_h^* are the same, if these 2 are the same, which means N_c and N_v will also be the same then E_{Fi} will be exactly at E_g over 2 or, if temperature were 0. So, if T were 0 then also E_{Fi} would be exactly at E_g over 2. It is because, effective masses are different and because the effective density of states is different. It is slightly shifted from the center of band gap. So, what does this value for E_{Fi} mean. In the case of a metal, we define fermi energy as a line that separates the highest fill states and the lowest empty state.

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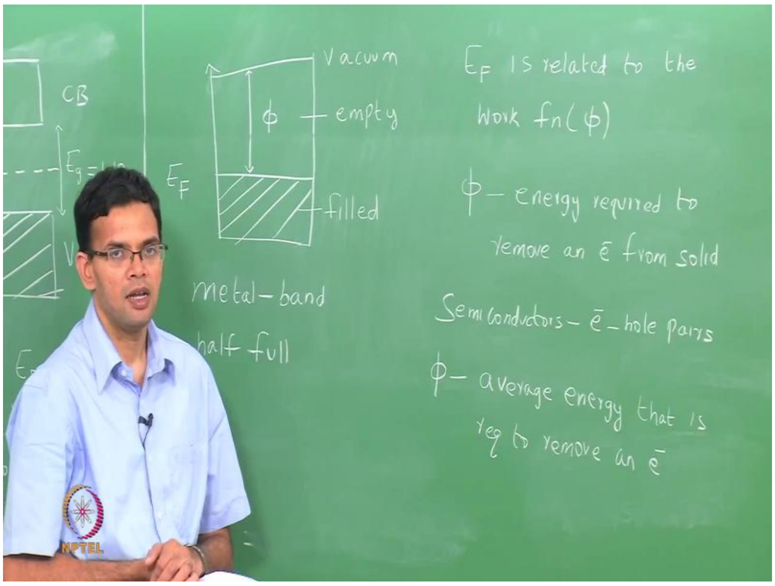

So, if you have a metal we draw a band picture for a metal, this is your band the case of a metal your band was half full. So, that you had filled states and you had empty states and the fermi energy is separated, the filled and the empty states. Now, In the case of a semiconductor, we have a valence band that is completely full; we have a conduction band that is completely empty. So, the question is where do we put the fermi energy? Now to look at it, there is another way of defining fermi energy, E_f is related to the work function. We will call the work function ψ now ψ represents the energy that is required in order to remove an electron from a solid. So, if you go back to this band picture and we take the top of the band to be vacuum level then ψ represents the energy to remove an electron from fermi level up to the vacuum level. In case of semiconductors, we don’t have electrons independently; we always have electron hole pairs. So, in such a case, ψ represents the average energy that is required to remove an electron. So, because we have electrons and holes, electrons in the conduction band and holes in the valence band because these are linked. We find that the fermi energy in the semiconductor is located within the band gap because it represents the average energy to remove the electron. If as I said earlier, the effective mass of the electrons in the holes were the same, the fermi energy will be located exactly at the middle of the gap, but because m_e^* and m_h^* are different it is slightly shifted in the case of silicon.

So, let us go back to an intrinsic semiconductor. We want to increase the conductivity of a material. In case of intrinsic semiconductor, we cannot change the carrier concentration at any given temperature right because the carrier concentration depends upon the band gap. What will do just to see the affect of temperature on n_i.

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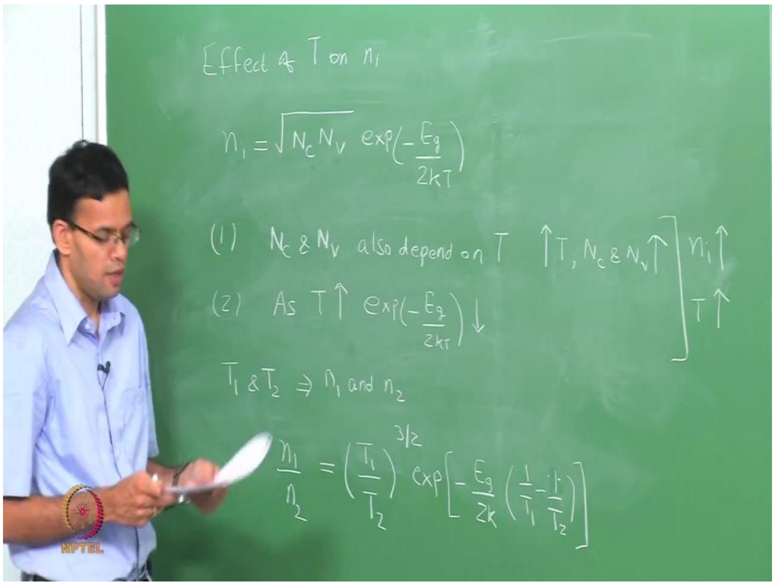

We will go back to this expression for the carrier concentration $N_c N_v\; exp\left(\frac{-E_f}{2kT}\right)$. Question is what happens when we increase the temperature, the temperature comes in 2 terms N_c and N_v also it depend on temperature. So, if we increase temperature N_c and N_v will also increase, but the dominant term where temperature plays a role is in the exponential term. So, as temperature increases $exp\left(\frac{-E_f}{2kT}\right)$ will drop because temperature is in the denominator. Both these affects, tends to increase the intrinsic career concentration. So, if you put these together n_i will increase as temperature increases, but the dominant term is the exponential term. So, consider the case of silicon, where we have 2 temperatures T_1 and T_2 and there are 2 intrinsic career concentrations n_1 and n_2. In this particular case, you can calculate the ratio of n_1 and n_2 by substituting them in this equation and also taking the temperature dependence of N_c and

N_v into account will give you $\left(\frac{T_1}{T_2}\right) exp\left(\frac{-E_g}{2kT}\right)$. So, all I did was substitute for n_1 and n_2 in this expression and then divide.

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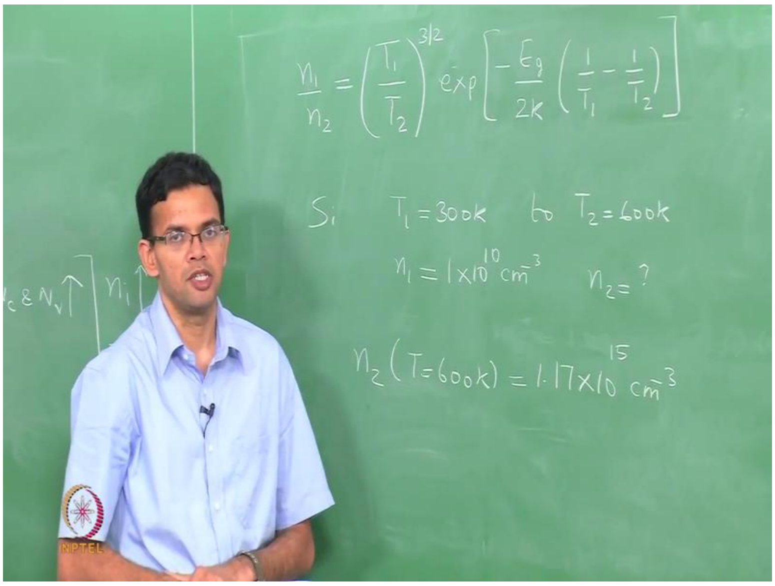

Let me just rewrite that expression n_1 over n_2, but T_1, if we have silicon and we increase the temperature from 300 kelvin to 600 kelvin. So, we double the temperature we want to know what the change in carrier concentration is at 300 kelvin, which is room temperature; n_1 has a value of 10^{10} cm^{-3}. You want to know what n_2 is. So, we can substitute in the values and evaluate this expression. So, we get n_2 which is the career concentration temperature equal to 600 is 1.17×10^{15} to the 15. So, by doubling the temperature from 300 to 600 kelvin, you have increased the carrier concentration from 10^{10} to 10^{15}, nearly 5 orders of magnitude. So, if you look at an intrinsic material or an intrinsic semiconductor, we only handle, changing the conductivity as long as we keep the material the same is temperature. To increase the conductivity we have to increase temperature. The problem though is most devices we now operate near room temperature or at room temperature. So, really we cannot increase the temperature beyond the normal operating temperature to increase conductivity it is for this reason that people go ahead and dope or add impurities to an intrinsic semiconductor, in order to form extrinsic semiconductors this increases the concentration of careers and thus increases the conductivity. So, with this we are done with intrinsic semiconductors.

In next class, we will start to look at extrinsic semiconductors. Before we do the transition, let me just briefly recap few points for intrinsic semiconductors that we will carry forward.

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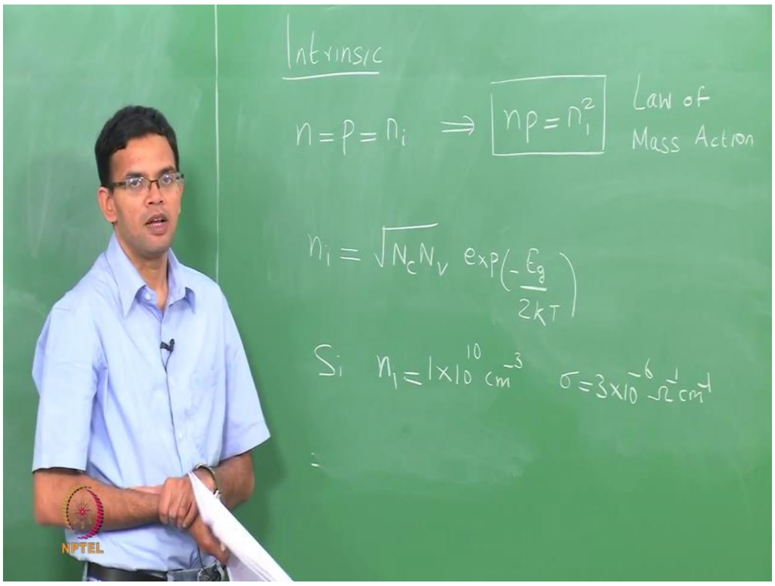

So, we saw that in case of an intrinsic semiconductor n = p. So, electron in hole concentration is the same which is equal to n_i. This generally can be written as $n\ p = n_i^2$. This is called the law of mass action, in the case of an intrinsic semiconductor, this relation $n\ p = n_i^2$ is very trivial because n = p, but later when we look at extrinsic semiconductors, we will find that this relation is true. So, you can increase n, but at the same time you will have to decrease p, if you increase p, you will have to decrease n, you cannot increase both of them at the same time. We also saw that the intrinsic carrier concentration is a function of temperature and it depends upon the band gap, where n_i is $\sqrt{N_c N_v}\ exp\left(\frac{-E_g}{2kT}\right)$,. We saw that silicon, the dominant material in the semiconductor industry has an n_i which is very small. So, only 10^{10} cm^{-3} which means the conductivity was also very small the value for conductivity was, the only way we could increase the conductivity.

If you still want to keep intrinsic, silicon was to increase the temperature, but increasing the temperature is not practical because the devices have to work at room temperature.

So, the next thing we will see is to how to increase the conductivity by doping and these are extrinsic semiconductors which we will start in next class.