Fundamentals of electronic materials, devices and fabrication
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Lecture - 04
Intrinsic semiconductors

Let us start with a brief review of last class. In last class, we looked at 2 important concepts.

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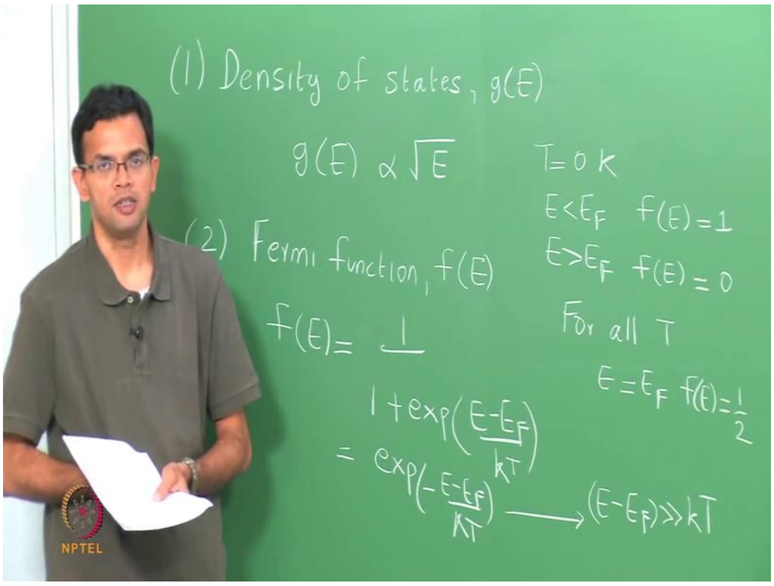

The first one is called the density of states; we denoted this as g(E). Density of states refers to the number of available states for electrons to occupy. We looked at a simple model, where we had a solid as a uniform three dimensional box with no potential. In such a case, we found that the density of states is directly proportional to the square root of the energy. So, thus as the energy goes up the total number of available states for the electrons to occupy also go up. We also looked at another concept, called the Fermi function, denoted by f(E). The fermi function tells you the probability of occupation of an energy state by an electron f(E) found is $\frac{1}{1+exp\left(\frac{E-E_f}{kT}\right)}$. We saw that temperature equal to zero Kelvin, if E is less than E_f, f (E) is 1, which means all the levels below the fermi energy are occupied. At E greater than E_f, f(E) is 0, which means above the fermi energy all the levels are unoccupied and we saw that for all temperatures at energy E equal to E_f,

$f(E)$ is half.

When the energy is much higher than kT, we can approximate the fermi function by a Boltzmann function. So, this becomes exponential minus $E - E_f$ over kT, which is the Boltzmann function and this is true. So, this is what we looked at last class. We will use these concepts of density of state and fermi function, in order to calculate the electron whole concentration in semiconductors and first we will start with intrinsic semiconductors.

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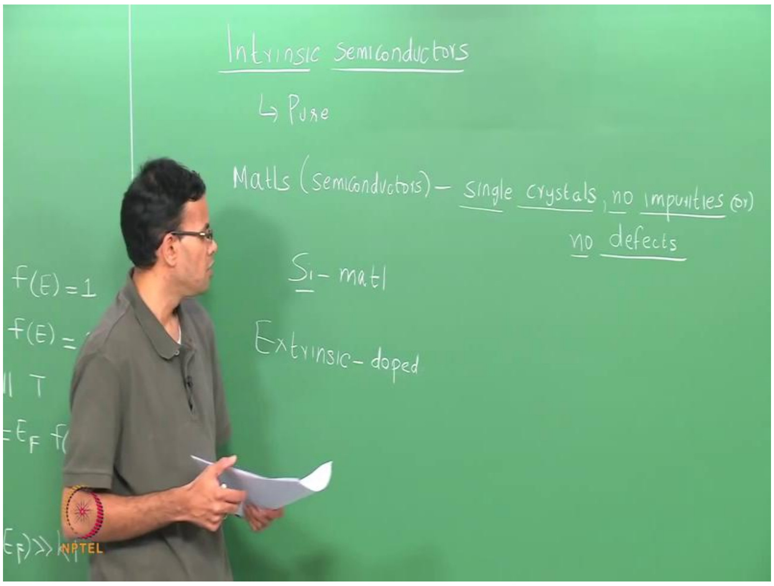

We will start with intrinsic semiconductors and other name for this is a pure semiconductor. We will use the concepts of the density of states and fermi function to calculate the carrier concentration that is the electron whole concentration. We will also define concepts of electron mobility and conductivity. Once we are done this for the intrinsic semiconductors, we will move on to extrinsic semiconductors.

So, what are intrinsic semiconductors? These are materials I will just say semiconductors within bracket that are single crystals and have no impurities or defects. We will see later why it is important that there should be no impurities or defects?

Most of what we do, we will reference using silicon as the material because silicon is the dominant material in today's micro electronics industry, but all the concepts that we developed can be equally applied to other semi conductors and later when we look at examples, we will also look at other materials to compare and contrast with silicon, but for the most part, we will deal with silicon. As opposed to intrinsic I mentioned earlier that you also have extrinsic semiconductors, these are doped semiconductors. If you look in terms of applications, extrinsic semiconductors are almost always used. Intrinsic semiconductors do find some applications, but not a whole lot. Mostly intrinsic semiconductors are used as optical sensors, in the case of photo luminescence experiments or as sensors for x-rays in electron microscopes. So, these are sensors which are called energy dispersive x-ray analysis. Usually, in those cases either intrinsic silicon or germanium is used cooled to around liquid nitrogen temperatures, but for most applications extrinsic semiconductors are preferred.

We will start with intrinsic first and once we develop these concepts we will go on to use them, to understand extrinsic semiconductors. So, let us start with intrinsic silicon.

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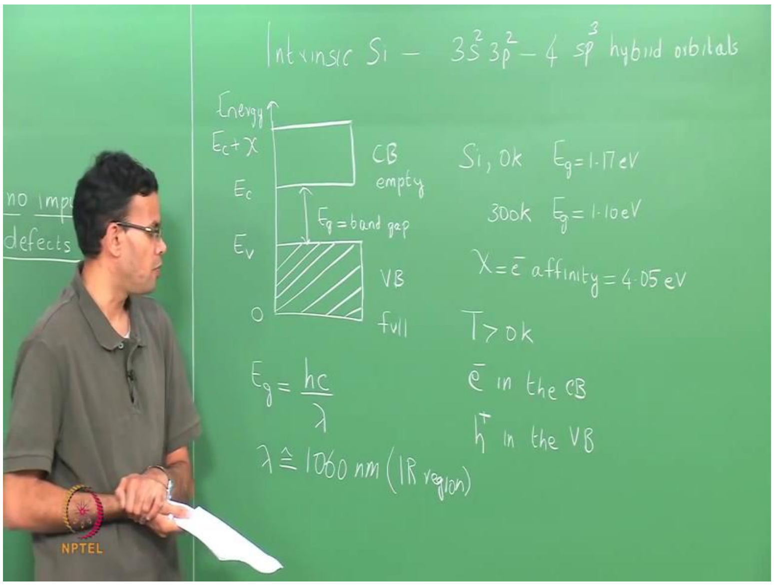

As we saw earlier, the electronic configuration of the outer shell of silicon is $3s^2$ $3p^2$. There are total of 4 electrons, the s and the p orbitals hybridize to give you 4 sp^3 hybrid orbitals and we later saw that these orbitals when they form a solid give you a valence band that is completely full and a conduction band that is completely empty. I will show this band diagram here. You have a valence band that is completely full you have a conduction band that is empty. The y-axis here refers to energy; usually the energy is referenced with respect to the bottom of the valence band. So, the bottom of valence band is given 0, E_v denotes the top of the valance band and E_c denotes the bottom of the conduction band. The difference between the top of the valence band and the bottom of the conduction band is the band gap. We call E_g in the case of silicon at 0 kelvin, E_g has a value of around 1.17 electron volts at room temperature. E_g slightly lower is around 1.10 electron volts.

The top of the conduction band is usually denoted as $E_c + \chi$, where χ is the electron affinity. For silicon χ has a value of around 4.05 electron volts. So, at 0 kelvin, you have a valence band that is completely full and a conduction band that is completely empty at any temperature above 0 kelvin. We saw earlier you will have thermal excitation of electrons, so that electrons from the valence band can move to the conduction band and living behind holes. So, at any temperature greater than 0 kelvin, you have electrons in the conduction band and holes, which is the absence of electrons in the valence band.

We also saw that apart from thermal excitation, we can also use light in order to excite carriers across the band gap. If E_g is the band gap of the material, the wavelength of light that is required in order to excite carriers is nothing, but hc/λ. We can do this calculation for silicon, where we find that λ is approximately 1000 nanometers and this lies in the IR region. As long as we shine light with a wavelength that is less than 1,000 nanometers, which means the energy will be higher than the band gap you can always excite carriers from the valence band to the conduction band. So, this explains, while silicon is opaque because visible light has a wavelength less than 1000 nanometers, the visible range is from 400 to 800 nanometers, which means silicon will be able to absorb the visible light and produce electrons and holes. Similarly, SiO_2 which is glass has band gap of approximately 10 electron volts.

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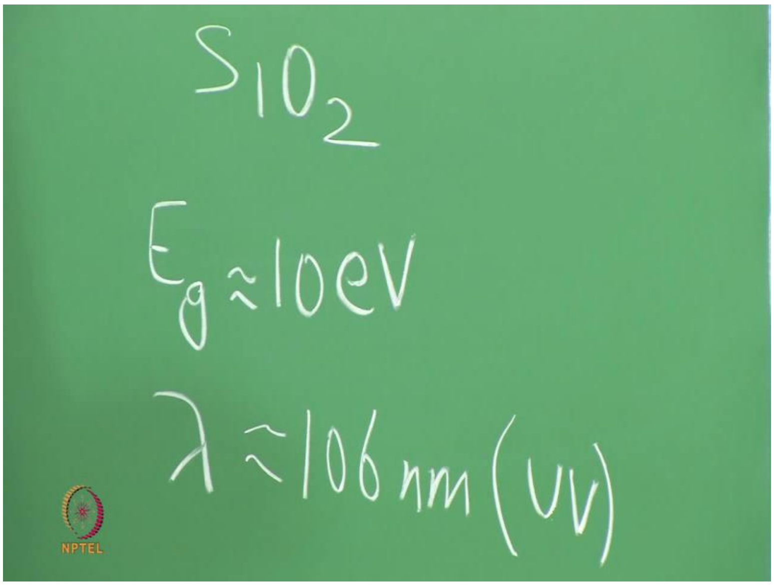

SiO_2

$E_g \approx 10 eV$

$\lambda \approx 106 nm$ (UV)

So, if we have SiO_2 has a band gap approximately 10 electron volts, which means the wavelength that is required to excite electrons from the valence band to the conduction band is approximately 106 nanometers. So, ten times less than that of silicon, this lies in the UV region which again explains why glass is transparent. So, coming back to silicon here is the picture we have at room temperature.

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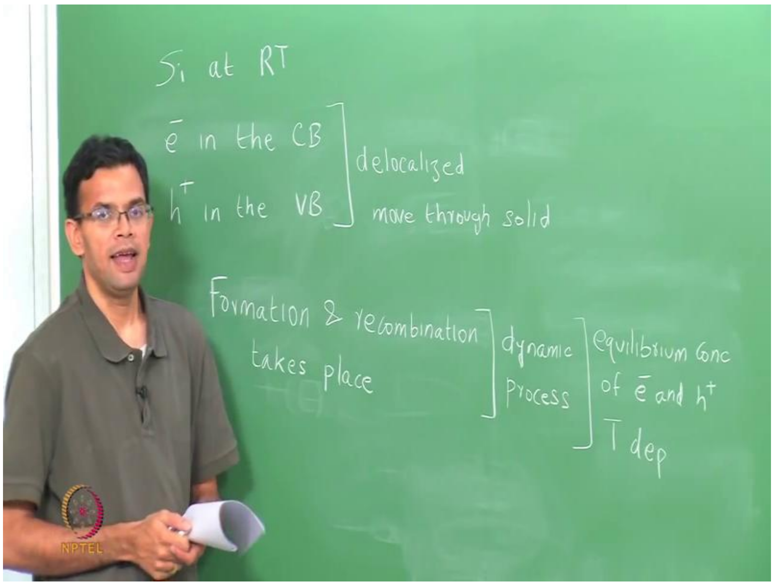

Si at RT

$\bar{e}$ in the CB
h^+ in the VB
delocalized
move through solid

Formation & recombination takes place
dynamic process
equilibrium conc of $\bar{e}$ and h^+
T dep

We have electrons in the conduction band, we have holes in the valence band and these electrons and holes are set to be delocalized that is they can move through the solid. The process of formation of the electrons and holes is a dynamic process that is electrons and holes are constantly being formed. At the same time electrons also fall back to the valence band and recombine with the holes, so that they are also getting eliminated. The formation and recombination takes place, so that we can say, this is a dynamic process. We have an equilibrium concentration of electrons and holes and this concentration depends upon the temperature, in say we have an equilibrium concentration of electrons and holes and this is temperature dependent. When we apply an electric field these electrons and holes can essentially move.

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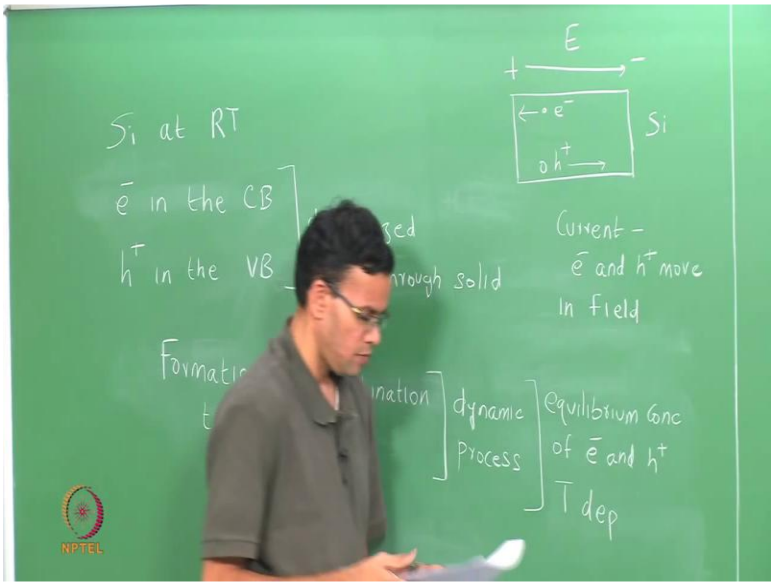

So, I will just show schematically a solid of silicon, you have electrons, you have holes, you apply an electric field. In the electric field, electrons will go in the direction opposite to the field, holes will go in the direction of the field and finally you will have a current. The current is because the electrons move in the conduction band and the holes move in the valence band. What are the factors on which the current depends on? Let us look at that next.

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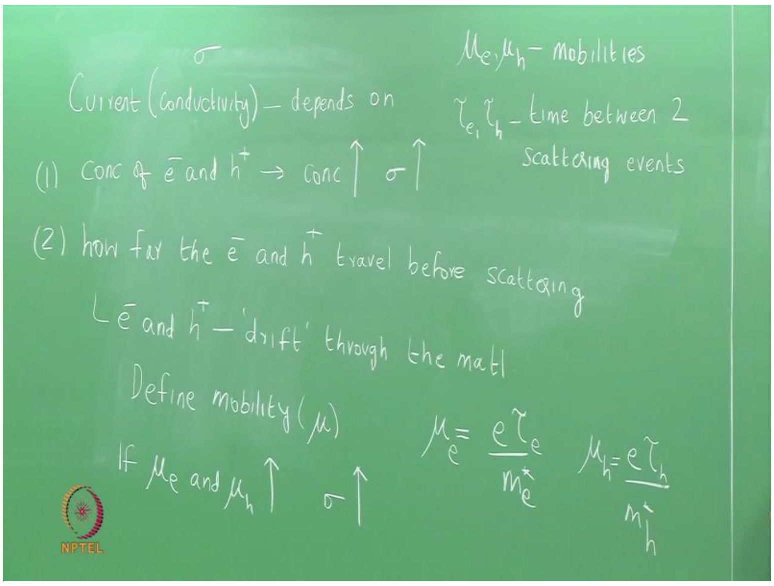

σ

Current (conductivity) – depends on

(1) Conc of $\bar{e}$ and h^+ → conc ↑ σ ↑

(2) how far the $\bar{e}$ and h^+ travel before scattering

$\llcorner$ $\bar{e}$ and h^+ – 'drift' through the mat'l

Define mobility (μ) $\mu_e = \frac{e\tau_e}{m_e^*}$ $\mu_h = \frac{e\tau_h}{m_h^*}$

If μ_e and μ_h ↑ σ ↑

μ_e, μ_h – mobilities

τ_e, τ_h – time between 2 scattering events

Current or if you want to think about it Conductivity, in the case of an intrinsic semiconductor depends upon two factors; the first one is the concentration of electrons and holes that are available. So, more the electrons and holes, higher is the conductivity concentration of electrons and holes we can denote conductivity by the symbol sigma and I will just say that if concentration increases, your sigma will also increase.

The next factor on which the conductivity depends on is how far these electrons and holes can travel before they get scattered by the lattice. So, remember you have electrons that are moving in the conduction band and you have holes that are moving in the valence band, but these are moving through a solid of silicon atoms. If you are looking at intrinsic silicon and all these atoms are vibrating which means these electrons and holes can interact with these atoms and gets scattered. In the case of a semi conductor these electrons and holes are set to drift through the material. To understand this, we define a quantity that we call the mobility, mobility is denoted by the symbol μ and the expression for μ, if you are looking at electrons you can say μ_e is nothing but τ_e over m_e^*. You can write a similar expression for holes μ_h. So, μ_e depends upon a factor, τ_e and the effective mass of the electron, τ_h depends on a factor, τ_h and the effective mass of the holes. So, μ_e and μ_h are the mobilities, the factors τ_e and τ_h refers to the time between two scattering events. So, if τ_e and τ_h are large which means time between two scattering events is large, the electrons can travel a large distance before scattering. In such a case, if these two are large your mobilities are also large and hence the conductivities is also higher. So, we can say if μ_e and μ_h increases and they would increase, if the scattering is less the conductivity increases. So, we saw that the conductivity depends on two terms, one is the concentration the other is the mobility. We can put these together to write an equation for the conductivity.

So, if σ is the conductivity, sigma is nothing but $n\ e\ \mu_e + p\ e\ \mu_h$. Now, this is a very important equation which relates the conductivity to the electron concentration and the mobility.

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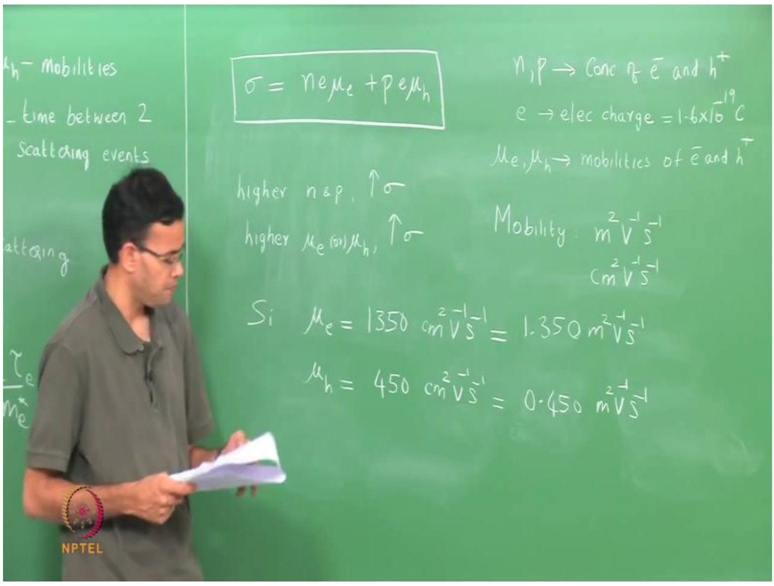

And this equation is true, whether you have an intrinsic semiconductor or an extrinsic semiconductor, n and p refers to the concentration of electrons in holes, which is the first factor that we saw earlier. e is the electric charge, which is 1.6×10^{-19} coulombs. So, that is content and μ_e and μ_h are the mobilities of electrons and holes. If you look at this expression, higher the concentration, so, higher n and p, your mobility is higher. Similarly, higher μ_e or μ_h, the conductivity is higher. The typical units for mobility are meter square volts per seconds. So, units for mobility can either use meter square per volt per second. You will also find that some books give values in centimeters square volts per second.

Let us take look at the mobility values for silicon. You have silicon μ_e, which is the mobility of the electron in the conduction band is around 1350 centimeters square volts per second. If you want to convert this to SI units, you just divide by 10^4. So, this is

0.1350 mu h, which refers to the mobility of the holes in the valence band slightly smaller. So, around 450 $cm^2 V^{-1} s^{-1}$ or you can divide this by 10^4, the top one should be 1.350, just rewrite that. So, these are the values of conductivity. In the case of silicon for both electrons and holes, we define mobility as the ability of the electron to move through the material before being scattered. We also saw that the mobility depends upon the scattering time. We will use this to do some calculations for the scattering time. So, consider the case of silicon, and we will only talk about electrons and use the similar calculations for the holes, consider the case of silicon, when μ_e is 1350.

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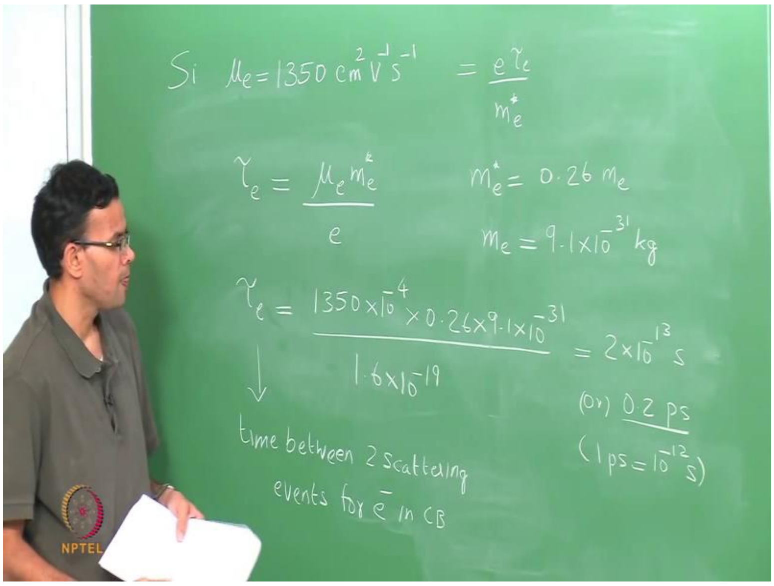

We also said earlier that, mu is related to the scattering time. The expression was $e\ \tau_e$ over m_e^*, just rearranging the terms gives you τ_e. So, all I did was take this term here and then bring e down. In the case of silicon, m_e^* is around 0.26 m_e, where m_e is the mass of an electron and m_e has a value, we can substitute the numbers here to get the value for τ_e. So, 1350 and multiply by 10^{-4}, convert to SI units. If you do the math, τ_e works out to be 2×10^{-13} seconds or 0.2 picoseconds, where 1 picosecond is 10^{-12} seconds. So, this time 0.2 picoseconds represents the time between two scattering events for an electron in silicon, that is moving through the conduction band. So, τ_e refers to the time between two scattering events and since you are talking about the electron this is for the electron in the conduction band, we will also like to calculate the distance the electron travels between these two scattering events or the distance electron travels in this time of 0.2 picoseconds.

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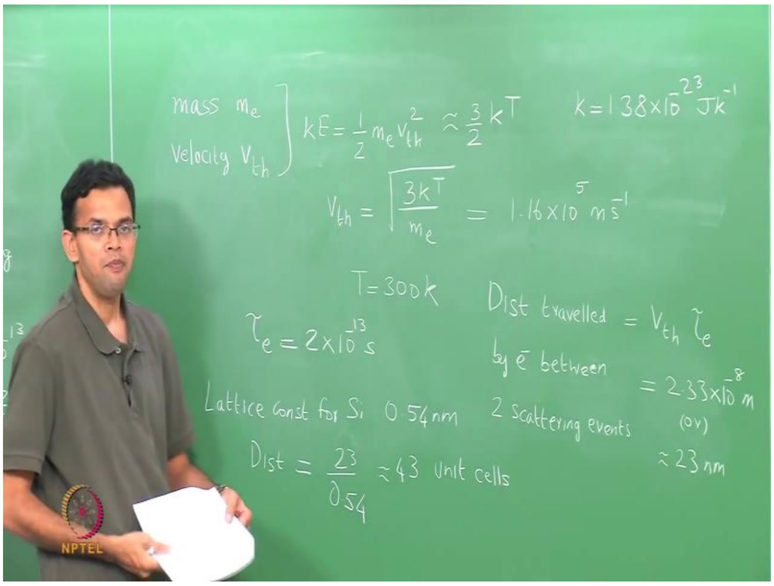

If we look at in electron with a mass given by m e and velocity that is given by v t h then the kinetic energy is nothing, but one half m v square. This is the kinetic energy of an electron. In case of most solids, we can say that the kinetic energy is approximately equal to the thermal energy, this is approximately equal to 3/2 kT, where k is the Boltzmann constant, k has the value 1.38 x 10^{-23} joules per kelvin. Equating this expression, we can find value for v thermal or the velocity of the electron which is nothing, but $\sqrt{\frac{3kT}{m_e}}$can again plug in all the numbers. We are doing this calculation at room temperature. So, temperature is 300 kelvin, if you do this v thermal works out to be 1.16 x 10^{5} m s^{-1} . So, we calculated v thermal to be 1 x 10^{5} per second. Earlier we saw that the time between two scattering events was 2 x 10^{-13} seconds or 0.2 picoseconds. So, the distance travelled by the electron between two scattering events is nothing but v thermal times tau, which if you do the math is around 2.33 x 10^{-8} m or approximately 23 nanometers. To put this into perspective, we can say that the lattice constant for silicon is 0.54 nanometers. So, the distance traveled in terms of lattice constant is 23/0.54, which if you see is approximately 43 unit cells. So, the time between two scattering events is really small, so the time is of the order of picoseconds, but because your electrons are of such a high velocity, the velocity is around 10^{5} s^{-1}. We find that the electron actually travels a substantial distance, it travels nearly 40 unit cells before it under goes another collision and then scattering. Mobility is usual a function of temperature. It also can be thought of as a material property as long as you do not add any impurities.

Later when we look at extrinsic semiconductors, we will find that increasing the concentration of the dopants, decreases the mobility. You can compare the mobility of silicon with some other semiconductors to see the values.

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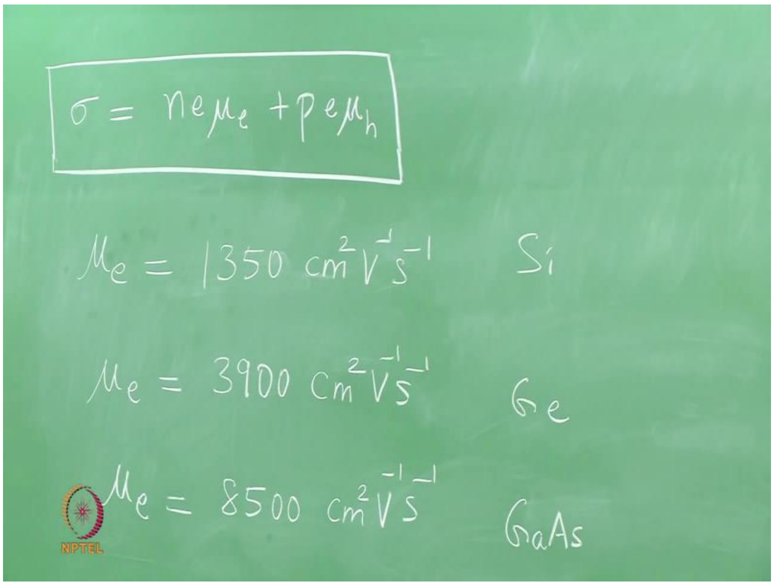

$$\boxed{\sigma = ne\mu_e + pe\mu_h}$$

$\mu_e = 1350\ cm^2 V^{-1} s^{-1}$ Si

$\mu_e = 3900\ cm^2 V^{-1} s^{-1}$ Ge

$\mu_e = 8500\ cm^2 V^{-1} s^{-1}$ GaAs

I will leave the expression for the sigma up here. We saw that the mobility of an electron in silicon was around $1350\ cm^2\ V^{-1}\ s^{-1}$, this is for silicon. If you had germanium, germanium has a slightly higher mobility, μ_e is 3900, that is the value for germanium. Gallium arsenide is even higher. If you want to improve the conductivity of a material and you are asked to choose materials in order to have higher conductivity. Just based upon the mobility values, the choice would be gallium arsenide because gallium arsenide has the highest value 8500, which is nearly 6 times or 7 times higher than that of silicon, but if you look at the expression for sigma, it not only depends upon the mobility, it also depends upon the concentration of electrons in holes. So, the next thing we will do is to calculate the electron in hole concentration as a function of temperature.

So, In last class, we looked at the concept of the density of states and the fermi energy putting those two concepts together you can say that the concentration of electrons in the conduction band is nothing but the integral over the entire width of the band of the density of states in the conduction band. I call that $g_{CB}(E)$ $f(E)\ dE$ to put this into words.

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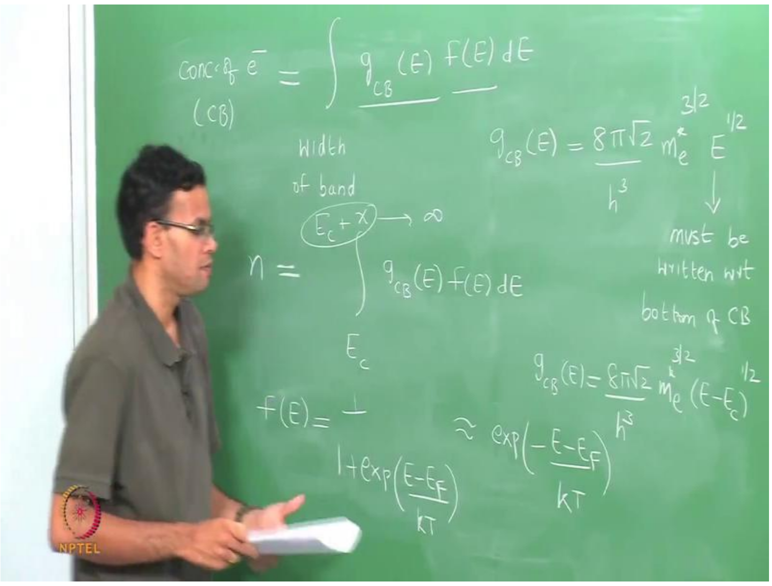

If you want to find the number of electrons in the conduction band at any given time temperature it is going to depend on the number of states that are available in the conduction band, which is g_{CB} (E), the density of states and the probability that those states are occupied by the electron, which is f(E). If you look at a conduction band, the width of the conduction band you saw earlier goes from E_c to $E_c + \chi$, where χ is the electron affinity. It goes from E_c, $E_c + \chi$. g_{CB}, which is the density of states times the fermi energy dE. Now, we want to calculate the density of states and silicon is a real crystal, but we can make use of the assumption of a solid with a uniform potential, which we did earlier for a solid with a uniform potential the density states, e is given by $\frac{8\pi\sqrt{2}\, m_e^*}{h^3}$, which is the effective mass of the electron in the conduction band times $E^{1/2}$. So, this expression we saw earlier for a solid with a uniform potential a 3D solid and we will use that expression to find the density of states for electron in the conduction band of silicon.

Since we are looking at only the conduction band, E here must be written with respect to the bottom of the conduction band. So, we will modify this expression g_{CB} and write it as $\frac{8\pi\sqrt{2}\, m_e^{*\frac{3}{2}}}{h^3}$, and instead of E, we will write it as $(E-E_c)^{1/2}$. So, that you are writing the energy with respect to the bottom of the conduction band f(E) is $\frac{1}{1+\exp\frac{(E-E_f)}{kT}}$. Usually, in the case of silicon and you will actually show explicitly, later on $E-E_f$ will be of the order of electron volts or a point greater than 0.5 electron volts, kT is usually of the order of mev. We can approximate the fermi function as a Boltzmann function and write this exp $\frac{(-E-E_f)}{kT}$. So, this expression approximates to this one. In the case of the silicon semi conductor our limits where the width of the band that goes from E_c to $E_c + \chi$ for ease of integration, we can replace the $E_c + \chi$ term with infinity this is also true because we will find that most of the electrons are located very close to the bottom of the conduction band. So, we can take the top of the conduction band to be infinity and we will not lose much in the model. So, we will replace $E_c + \chi$ with infinity. Let me then rewrite this expression again.

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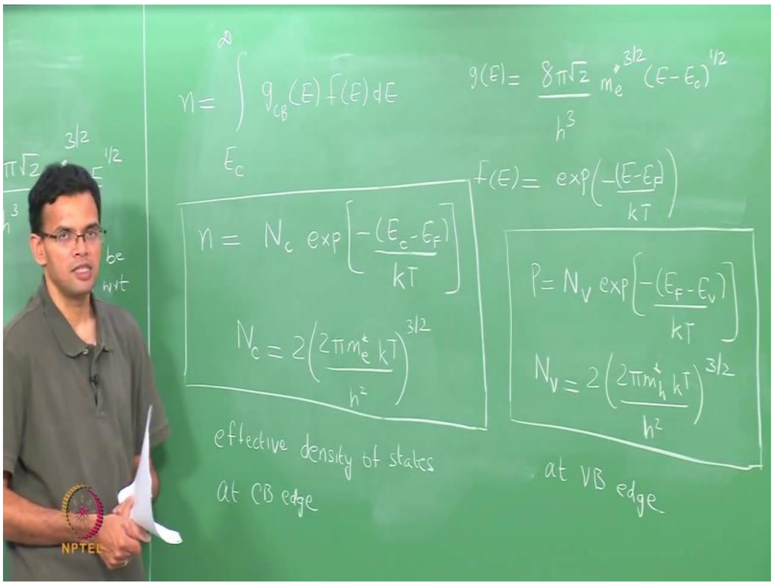

If you rewrite this n, which is the number of electrons in the conduction band goes from the base the conduction band E_c up to infinity, the density of states times the fermi function dE, where the density of states is given by this expression $m_e^{*3/2}$ $(E - E_c)^{1/2}$ and f(E) you will use the Boltzmann approximation and write it as exponential $\frac{E-E_c}{kT}$. We can substitute these two in this expression and do the integration, I will not show the integration explicitly, but write down the final result. When we do this, we get n is equal to N_c, which is constant at a given temperature times exp $\frac{(-E_c-E_f)}{kT}$, N_c is nothing but $2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2}$. This term N_c is called the effective density of states at the conduction band h. So, n depends upon the effective density of states at the conduction band, h times an exponential function.

Whatever derivation we did for electrons, we can equally do for holes in the valence band. I won’t do the derivation for holes, but I will just write down the expression for holes, p which is the concentration of holes in the valence band is N_v, which is a constant times exp $\frac{(-E_f-E_v)}{kT}$, N_v is $2\pi\, m_h^*$. So, instead of m_e it is $\left(\frac{m_h^* kT}{h^2}\right)^{3/2}$. This is the effective density of states at the valence band h. So, we have two expressions, one for electrons and one for holes. These expressions one for electrons and one for holes give you the concentration of electrons in the conduction band and holes in the valence band for a given semiconductor as a function of temperature.

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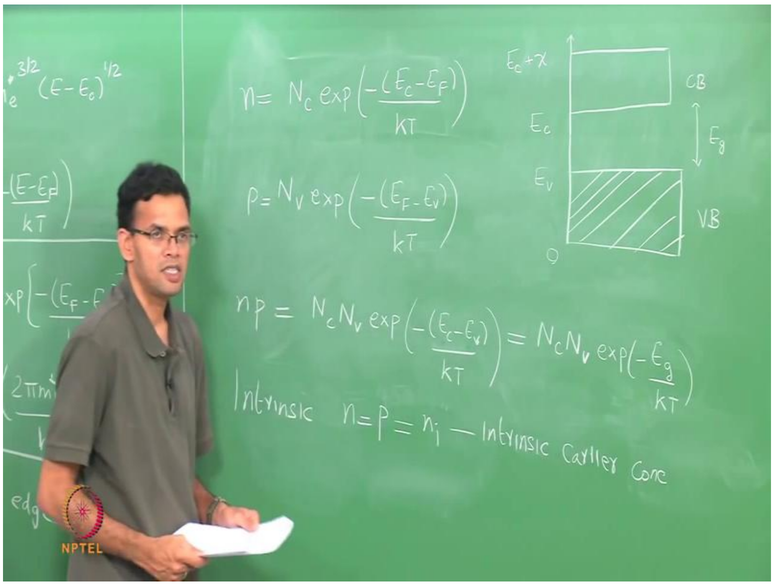

Let me just rewrite those two expressions, this N_c exponential and p is N_v exp $\frac{(-E_f-E_v)}{kT}$, we can mark the position of E_c and E_v in the band diagram. So, if you draw this, you have a valence band. The base of the valence band is set as zero, the top of the valence band is E_v, when you have a conduction band, the base of the conduction band is E_c, the top of the conduction band is $E_c + \chi$ and the difference between the valence band and the conduction band is the band gap. So, here is your expression, we know all these values N_c, N_v, E_c, E_v, we can calculate the concentration of electrons in holes. If you look at these expressions the fermi energy term E_f is in there, but I have not marked where the fermi energy is. So, if you do not know where e f is you will not be able to calculate n and p.

So, let us go ahead and eliminate E_f, where multiplying n and p together. If you do that, n p will be $N_c\ N_v \exp \frac{(-E_c-E_v)}{kT}$, all I have done is multiplied these two together, E_c - E_v. If you see from this band diagram, this whole thing is E_c, this is E_v. So, E_c - E_v is nothing, but the band gap.

This I can replace $N_c\ N_v \exp \frac{(-E_g)}{kT}$. In the case of an intrinsic semiconductor your electrons are created because they are excited from the valence band to the conduction band and whenever an electron is created a hole is also created. So, in the case of intrinsic semiconductors n, which is the concentration of electrons is equal to p, which is the concentration holes and this is usually denoted as n_i. n_i is called the intrinsic carrier concentration. So, for an intrinsic semiconductor $n = p = n_i$, if you make use of the fact that $n = p$.

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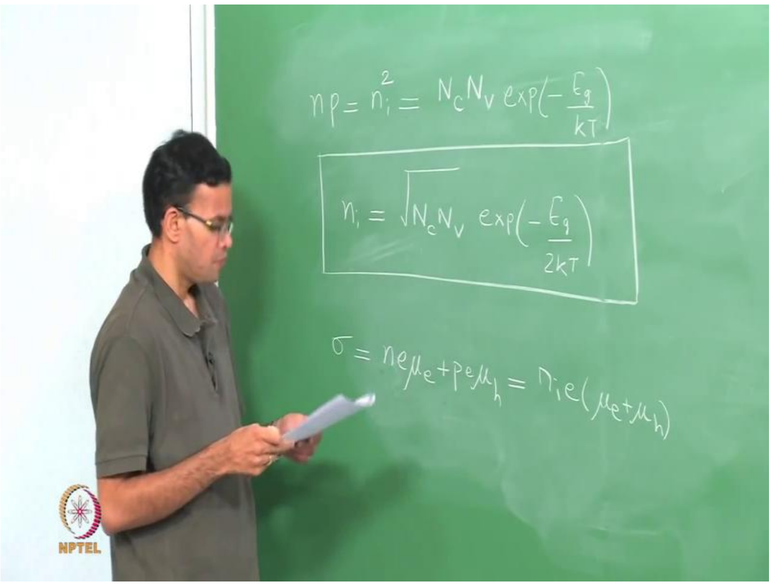

When we can rewrite the expression n p is nothing, but n_i^2 which is the square of the intrinsic carrier concentration that is equal $N_c\ N_v \exp \frac{(-E_g)}{kT}$ and then taking square root you get $n_i\ \sqrt{N_c N_v} \exp \frac{(-E_g)}{2kT}$, this is expression for the carrier concentration. So, the concentration of electrons and holes in an intrinsic semiconductor as a function of temperature, we saw that the conductivity equation is nothing, but $n\ e\ \mu_e + p\ e\ \mu_h$. In the case an intrinsic semiconductor $n = p = n_i$. So, we can take this term outside, it is n_i e μ_e over μ_h. So, the conductivity depends on the sum of the mobilities or both the electron and the whole in the case of an intrinsic semi conductor.

So, this is where we will stop for today. In the next class, we will start by calculating these values for the intrinsic carrier concentration and the conductivity for silicon, when we look at, how changing the material will change these values? Then we will proceed from there.