Fundamentals of electronic materials, devices and fabrication

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Lecture – 2
Introduction to semiconductors

Let us start with the brief recap of what we learned in the last class. So, last class, we said the based on resistivity, we can classify materials into three types - conductors or metals, semiconductors and insulators. We were trying to explain the vast difference in resistivity or conductivity between metals and semiconductors. So, metals are so much more conductive. In order to do that, we try to develop a simple band diagram where we have atomic orbitals that come together to form molecular orbitals and at really large values of n, where n is about Avogadro’s number, we found that these form bands.

In the case of metals, these bands are formed from s shells that are either incompletely filled or from s and p shells overlapping, so that we always have a band that is not completely full. So, we do have some empty states; these empty states basically help in conduction of electrons which is why metals are such good conductors. We also saw an example of energy versus a bond length diagram using lithium as the example. So, let me just redraw that again and from there, we will move onto semiconductors.

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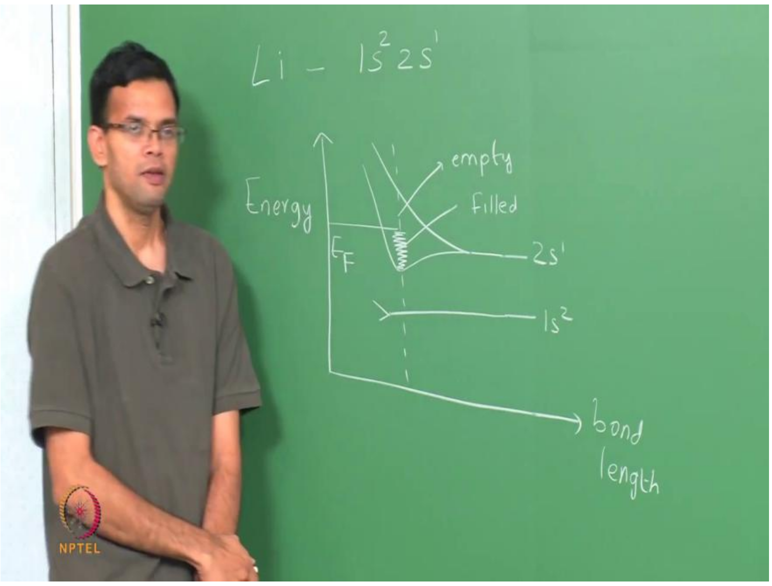

So, this is from last class, we looked at lithium which has an electronic configuration of

$1s^2$ and $2s^1$; $1s^2$ forms the inner shell and it is not involved in bonding; $2s^1$ is the outer shell. So, we can draw the energy versus bond length diagram. So, 1s shell is not involved in bonding; the 2s shells involve in bonding and basically forms a band. The s shell is half filled, so the band is also half filled; these are the filled states, these are the empty states and the gap between, and the highest filled state is called the Fermi energy. So, today we will move on to semiconductor materials, and see how we can draw a similar picture for semiconductors.

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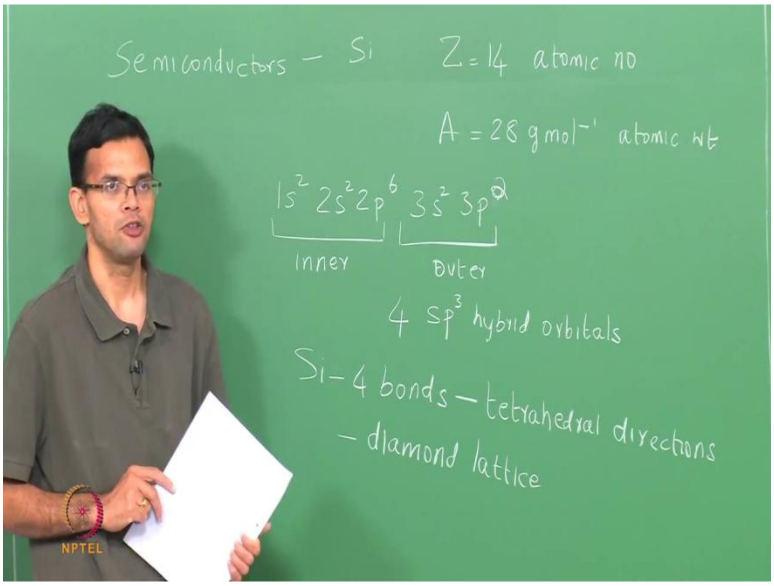

Semiconductors – Si $Z = 14$ atomic no

$A = 28\ g\,mol^{-1}$ atomic wt

$\underbrace{1s^2\,2s^2\,2p^6}_{\text{inner}}\ \underbrace{3s^2\,3p^2}_{\text{outer}}$

4 sp^3 hybrid orbitals

Si – 4 bonds – tetrahedral directions

– diamond lattice

When we talk about semiconductors, the dominant material there is silicon. Silicon has an atomic number of 14; it has an atomic weight of 28 grams per mole. Given the atomic number is 14, the electronic configuration for silicon is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. So, the 1s and 2s shells are the inner shells, and they are not involved in the bonding; the shells that are involved in bonding are 3s and 3p, these are the outer shells, should be $3p^0$. Rearrange in order to form sp^3 hybrid orbitals. So, you have two electrons in the s, two electrons in the p, they hybridize to form $4sp^3$ hybrid orbitals. Thus, each silicon atom can form four bonds, these bonds are directed in the tetrahedral directions, and essentially, what you have is a diamond lattice. So, let us look at where silicon is in the periodic table. We will concentrate in the group where silicon is.

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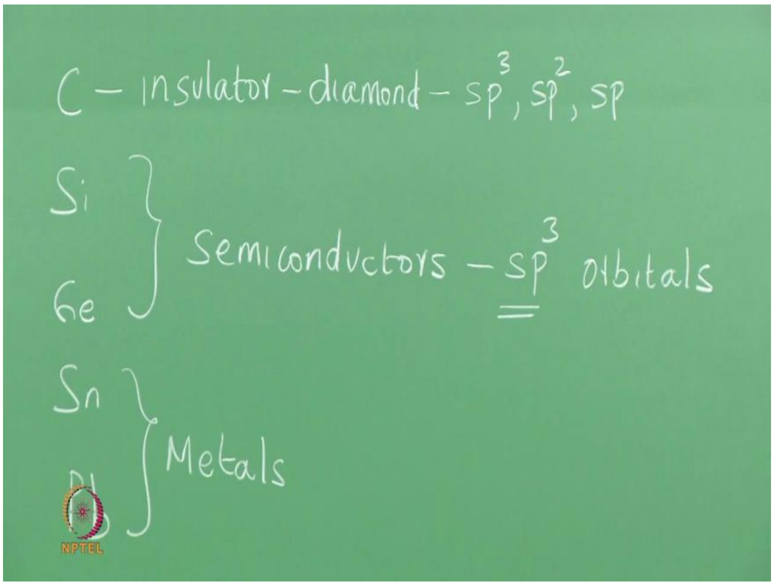

if you look at it the group has carbon, silicon, germanium, tin and lead, out of this five elements tin and lead are metals; carbon in the form of diamond is an insulator. And more importantly the s and the p electrons in carbon can form a variety of hybridizations. So, you can have sp^3, sp^2, s p hybridizations. Silicon and germanium are semiconductors, and they have sp^3 hybridization. So, instead of looking at atomic orbitals in silicon, we are looking at bonding using, this sp^3 orbitals. So, let us look at picture for bonding for silicon.

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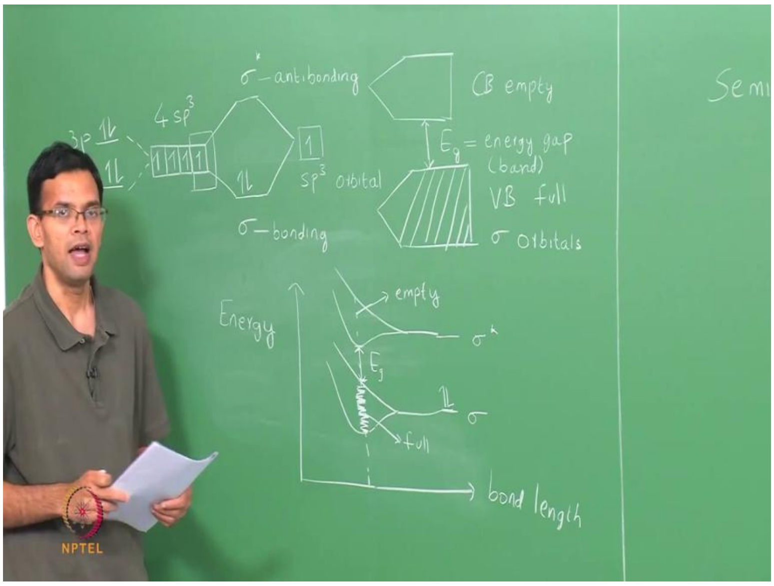

So, we start with the 3s and the 3p two electrons in them. We said that in silicon they hybridize to form sp^3 orbitals. So, you have $4sp^3$ hybrid orbitals and each of them are involved in a bond. We will consider one of these sp^3 hybrid orbitals; this can bond with another orbital to give you a bonding and an anti bonding orbital. This is the same picture that we had in the case of hydrogen. This forms σ, σ^* ; σ is your bonding orbital, σ^* is the anti bonding. And on the other side, you have another sp^3 hybrid orbital. So, you have two electrons, both electrons go to σ, and σ^* is empty. So, this is the picture we have when we have one silicon bond being formed.

Now, in a solid you are going to have large number of these silicon bonds. So, you are going to have large number of σ and σ^*. So, these will then interact with each other, and then they will give you a band. So, σ forms a band; in pictorially represent this as the valence band. So, the valence band is formed by the interaction of all the bonding orbitals, valence band is full. Same way, you have a conduction band that is formed by interaction of the σ^* and that is empty - conduction band. And, between the valence band and the conduction band there is a gap, this gap is called the energy gap. It is denoted by the symbol E_g, it is called the energy gap or sometimes the band gap. So, this is the picture of silicon we have from interaction of these molecular orbitals. So, we have a sigma and the σ^*, this just represents one bond. When we have a whole bunch of these bonds in a solid, they all interact with each other leading to broadening, and finally, we have an energy band which is the valence band as completely full. We have an energy band from σ^* that is completely empty and then you have a band gap between them. We can once again draw an energy versus bond length plot for silicon, but now instead of having the atomic orbitals you will have the σ and σ^*.

Let us do that. So, I have energy on the y-axis, bond length. There is some equilibrium spacing we have σ. So, here this σ represents the effect of one bond; in the solid, it forms a band. σ, there are two electrons here, which means you have this band is completely full. Now we also have a σ^* which is the anti bonding, this will also form a band, which is completely empty. And the space between these two bands is your band gap – E_g . So, this is the model for silicon, you can use the same model for germanium which lies in the same group. So, again it has s and p orbitals which hybridize to form sp^3 orbitals and so on. We can extend this model in the case of insulator as well, but in insulators for example, if you think of an insulator like sodium chloride, you have bonds being formed not by sodium and chlorine, but you have Na^+ Cl^- ions. So, it is the ions that are forming the bonds and the bands. So, it is a same picture, but depending upon the material, the details will change.

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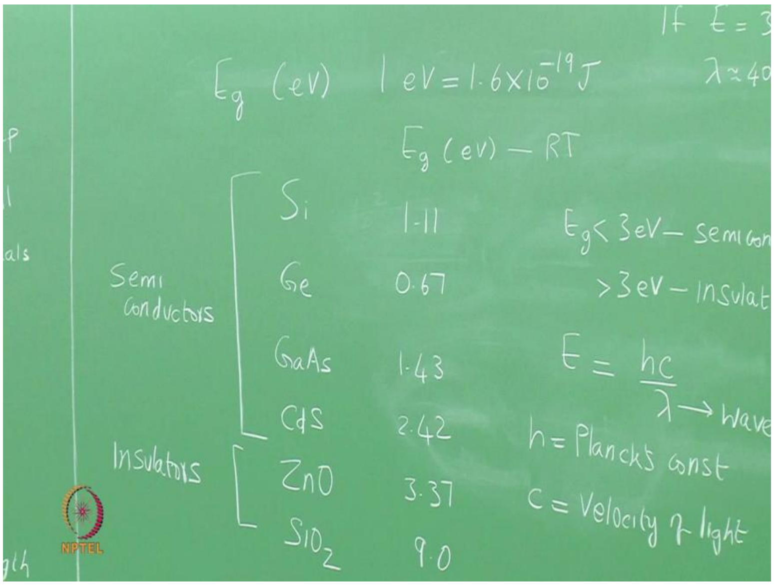

E_g (eV) 1 eV = 1.6×10^{-19} J

E_g (eV) — RT

		E_g (eV)
Semi conductors	Si	1.11
	Ge	0.67
	GaAs	1.43
	CdS	2.42
Insulators	ZnO	3.37
	SiO_2	9.0

If E = 3

$\lambda \approx 40$

$E_g < 3$ eV – semicon

> 3 eV – insulat

$E = \frac{hc}{\lambda}$

$\lambda \rightarrow$ wave

h = Planck's const

c = Velocity of light

What are some typical values for band gap? Let us write down some typical values for band gap E_g. The units for these are in electron volts; and as we saw yesterday electron volts is related to joules; one electron volt is nothing but $1.6 \text{ x } 10^{-19}$ joules. So, we have silicon E_g terms of ev all these values are at room temperature silicon has a value of 1.11, germanium is 0.67, gallium arsenide is 1.43, cadmium sulfide is 2.42 zinc oxide is 3.37, SiO_2 is 9. So, we have some different values of band gap. So, if you look at both semiconductors and insulators the difference between them is the difference in the band gap. So, typically if E_g is less than three electron volts we call a material as semiconductor, and if E_g is greater 3 electron volts we call the materials and insulator. Now, this is not very rigorous separation with 3 electron volts comes out because three electrons volts correspond to the end of the visible region.

For example, if you want to convert energy into wave length in the case of electromagnetic radiation E is nothing but hc/λ, where h is the Planck’s constant, c is the velocity of light, and λ is the wave length; write it here. If you use this if your energy is 3 electron volts, then λ is approximately 400 nanometers. So, any energy greater than 3 electron volts puts only ultraviolet region; energy less in 3 electron volts puts you in the visible region. So, this is used as a sort of marker for differentiating semiconductors and insulators, but as I mentioned earlier, it is not very strict. Based upon this, all this materials silicon, germanium, gallium arsenide, cadmium sulfide are semiconductors, zinc oxide is closed to this value of three, but it is on the higher side and silicon dioxide is much higher. So, these are considered to be insulators. So, we looked at some values for band gap of semiconductors.

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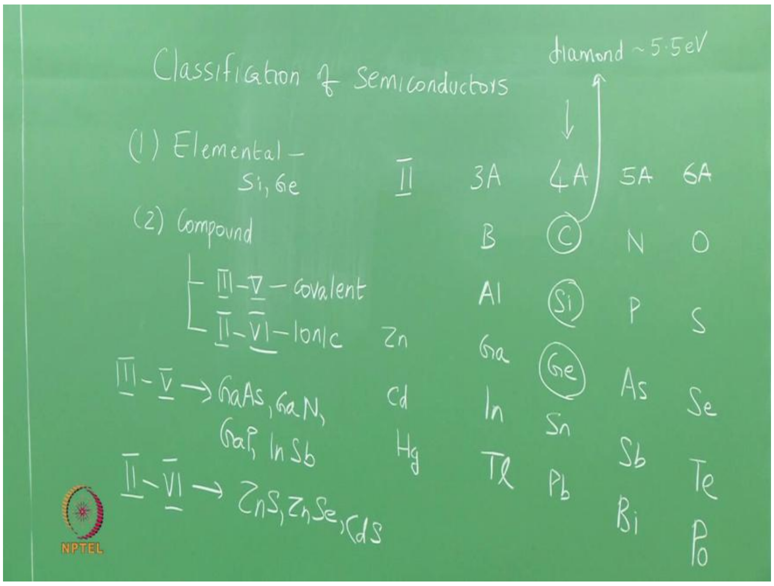

So, let us now look at some Classifications of semiconductors. So, there different ways of classifying semiconductors, so one particular method of classification is called elemental and compound semiconductors. So, this distinction is fairly straight forward. So, those semiconductors there are elements are essentially your elemental semiconductors, but you can also have compounds that have semiconductors that is, whose band gap lies less in 3 electron volts, these are compound semiconductors. There are lots of different types of compound semiconductors; you have III-V, you II-VI to understand them. Let us take a look at the periodic table. We won't look at entire periodic table, but focus ourselves in the area where we have the groups four, three and five.

If we do that to, group II, we have 3A, 4A. So, let me just write down the elements. So, I am writing the elements from group II, III, IV, V and VI; group V and then group VI. So, this is just a portion of the periodic table. Now if you look at it, group four has silicon and germanium, which are our classic elemental semiconductors. So, most prominent example silicon and germanium; carbon we said in the form of diamond is an insulator. So, diamond has a band gap of around 5.5 ev, so that carbon is really an insulator. You can also form semiconductors by using elements from 3 and 5, those are your three-fives, and you can also from 2 and 6 those are your two-sixes. So, some examples of III-V and II-VI can have gallium arsenide which is the most dominant compound semiconductor; gallium nitride, gallium phosphide, indium stibnite and so on. So, all of these are formed by putting elements from here and from here, so gallium arsenide, gallium phosphide, gallium nitride and so on. You can also have elements from 2 and 6 again some examples are zinc sulfide, zinc selenide, cadmium sulfide and cadmium selenide and so on.

If you look at the bonding character in this compound semiconductors III-V are mainly covalent, mainly have covalent bonding, they do have some ionic character in them the main bonding is covalent. In case of II-VI, the main bonding is ionic, so there is some covalent character in them. So, this is one way of classification where we have elemental and compound.

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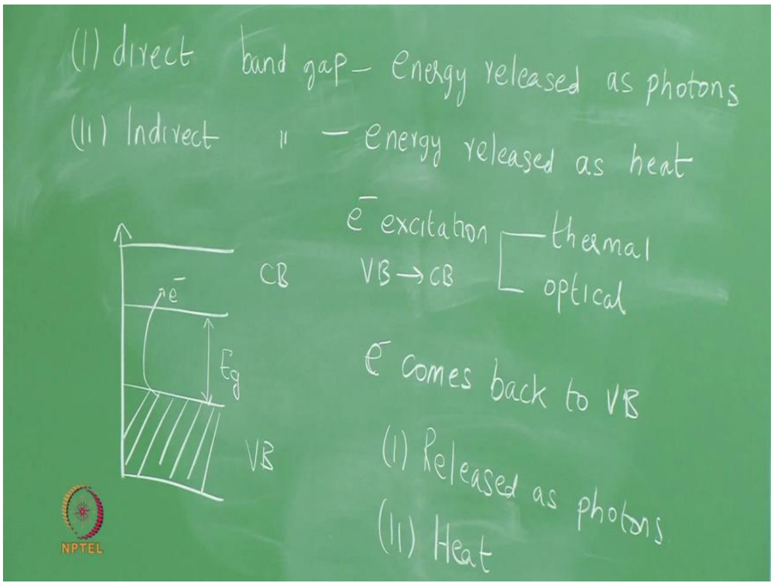

(I) direct band gap – Energy released as photons

(II) Indirect " – energy released as heat

e^- excitation $VB \rightarrow CB$ — thermal
optical

e^- comes back to VB

(I) Released as photons

(II) Heat

There is also another way classifying semiconductors. So, here we can classify semiconductor as direct and indirect band gap semiconductors. We have a direct band gap and indirect band gap. So, how do we understand the difference between these 2? So, let us go back to our model for semiconductors. We have a valence band that is completely full, we have a conduction band that is empty and we have a band gap in between them. So, you have electrons that are there in the valence band, these can be excited to the conduction band. This electron excitation can either occur because of thermal energy or because of optical energy. So, what happens when we have an electron in the conduction band? Now, this electron once to come back to the valence band, so that it losses whatever energy it is gained, and this energy loss can occur in 2 ways. So, when the electron comes back to valence band, it can release the energy in 2 ways; one can release it as photons or it can release it as heat. In the case of direct band gap semiconductors this energy release is dominantly in the form of photons. In the case of indirect band gap semiconductors, the energy released is dominantly as heat.

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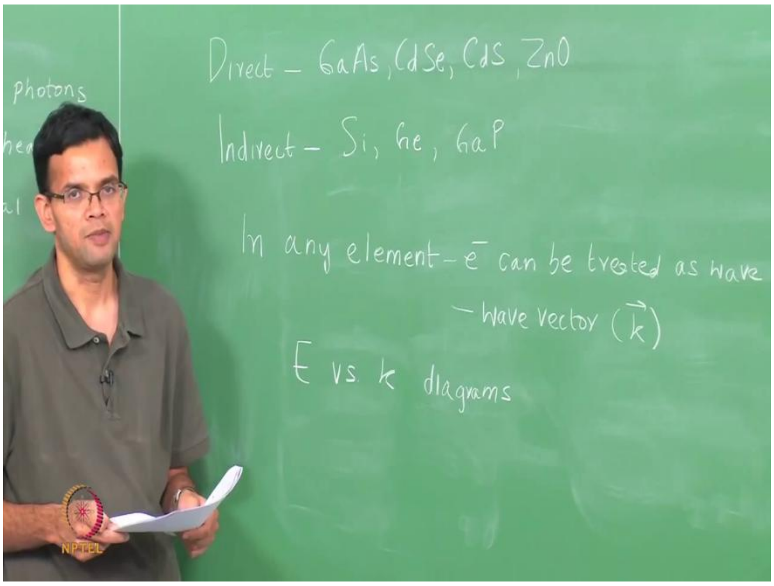

So, let us look at some examples of direct and indirect band gap semiconductors. In the case of direct, we have materials like gallium arsenide, cadmium selenide, cadmium sulfide. In the case of indirect band gap semiconductors, silicon and germanium which are our two elemental semiconductors are both indirect band gap semiconductors, another example gallium phosphide. Direct band gap semiconductors have applications in the case of optoelectronic devices; they can be used in LEDs, solar cells, photovoltaic and so on, so that is one of their advantages, they not only have application on the electronic side, they also have application on the optical side.

To understand the difference between direct and indirect band gap semiconductor some more, we can also look at the band structure. So, what I will do is give you a very simple picture of the band structure in the case of semiconductors. In any element, your electron in the solid can be treated as a wave. And when you have a wave, a wave always has something called as a wave vector, and the wave vector is denoted by k. So, thus for materials, you can construct what are known as e versus k diagrams. This is typically done for both the valence band and the conduction band. So, the difference between a direct band and an indirect gap semiconductor is a difference between how their e versus k diagrams look. So, let us look at an example of silicon which is an indirect band semiconductor, and then gallium arsenide which is the direct band semiconductor.

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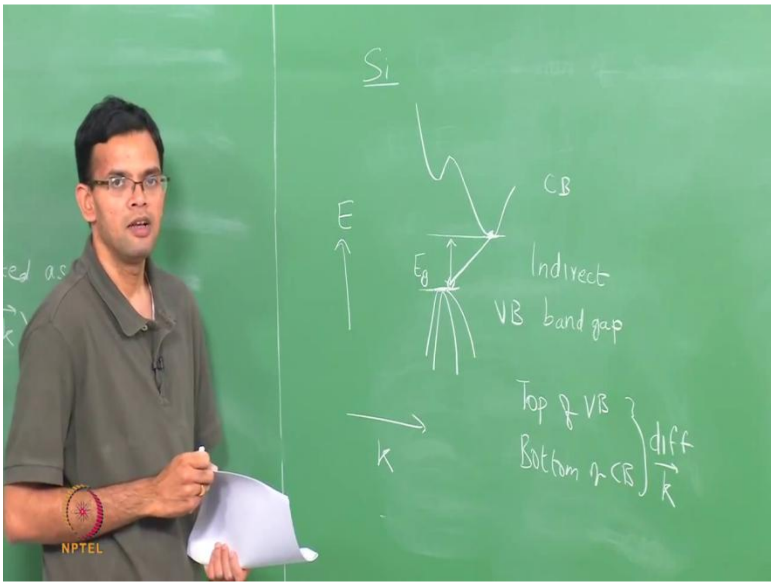

So, let us draw this e versus k for silicon. Again, I am only drawing simplified picture to explain the difference between direct and indirect. So, this is the conduction band; this is the valence band; there is a band gap between valence band and conduction band, and this is E_g. In this particular plot, E is on the y-axis and then k along the x-axis. So, in the case of silicon, the top of the valence band and the bottom of the conduction band are at different values of k; top of the valence band and the bottom of the conduction band have different values of k. This means that any electron transition from the conduction band to the valence band is accompanied by phonons which are essentially heat quanta, so that any transition in the case of silicon from the conduction to the valence band, the energy is released as heat. This makes it an indirect band gap semiconductor.

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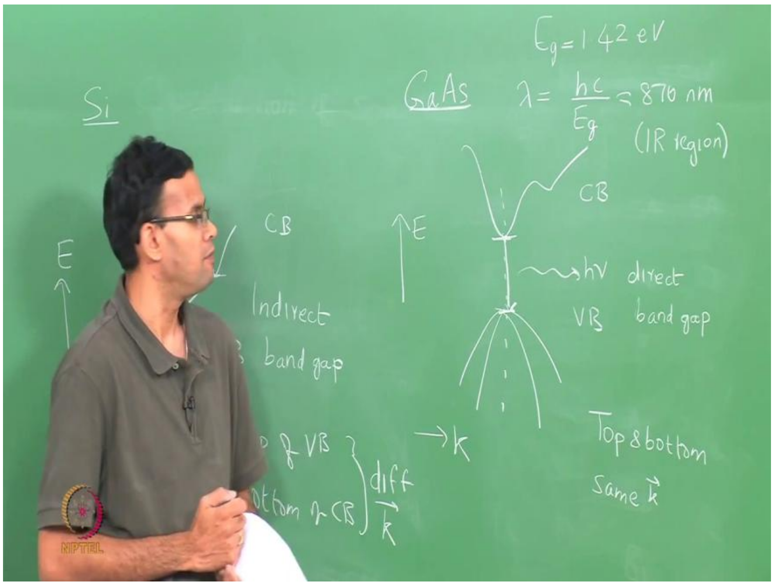

Let us look at gallium arsenide which is a direct gap semiconductor. So, once again this is the conduction band, this is the valence band, this is E, this is K. Here the top of the valence band and bottom of the conduction band have the same value of K. So any transition from the conduction band to the valence band can be accompanied by release of energy as a photon, and this makes it a direct band gap semiconductor. In the case of gallium arsenide, the band gap is 1.42 ev; this energy is released as a photon. So, the wave length of the photon using the same formula that we saw before is nothing but hc/λ which is approximately 870 nanometers, this lies in the IR region. If you had material like zinc oxide, its band gap is around 3.4 ev, and the wave length will lie in the UV region. So, if you have different material with different band gaps and all of these are direct then their optical transitions will have different wave lengths.

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So, let us go back to the picture of the semiconductor. You have a valence band that is full, and you have a conduction band that is empty. So, at any temperature, you can have electrons from the valence band being excited to the conduction band. When an electron goes from the valence band to the conduction band, you essentially have an absence or a loss of electrons. This represents the absence of an electron is called a hole.

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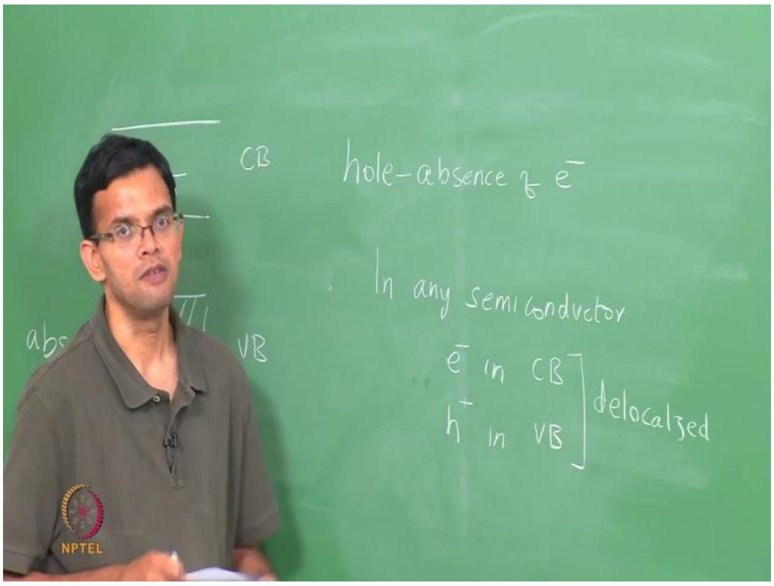

So, hole is nothing but a mathematical construct that we used to denote the absence of electrons in the valence band. So, in any semiconductor you will have electrons in the conduction band, and you have holes, holes are denoted h or h plus in the valence band. These electrons and holes are essentially free to move, so they are called delocalized. So, when you apply an electric field to a semiconductor, the electrons can move in the conduction band, the holes can move in the valence band, and this gives rise to current.

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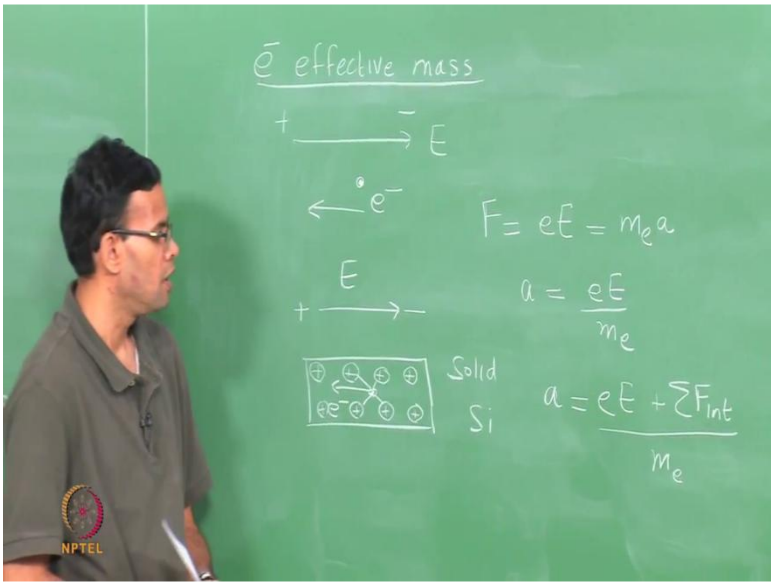

So, along with this concept of electrons and holes, you are also introduced a new concept called electron effective mass. You also have a whole effective mass, but the argument is very similar. Let us say you have a free electron or an electron in free space and you apply in electric field E, electric field usually goes from positive to negative. So, the electron travels in the direction opposite to the field. For such an electron, the force acting on it is nothing but the charge times the electric field, which equals to the mass of electron times the acceleration. So, the acceleration is equal to the electric field divided by the mass of the electron. Now, this is the picture for an electron that is in free space.

What about an electron in solid? Now, you have a solid you can take this to be silicon there is an electron here; once again you apply an electric field going from positive to negative. So, the electron will accelerate in the direction of the field. Now, if you try to write the acceleration of the electron, you have the term E, which is the same as before, so that is the effect of the external field, but you also have a solid where you have a lot of atoms. And an electron can feel the influence of all of these atoms. So, you not only have an external field, you also have an internal field. This we will write as sum of all the internal fields. So, F internal reflects the effect of all the atoms on the electron that is moving in a solid. So, the acceleration now is complicated because you also have to take into account the effect of the atoms. In order to simplify this picture, we replace this expression with this m e by another term which we call the effective mass. So, this F internal and m e are replaced by this term m_e^*; m_e^* is called the effective mass of the electron.

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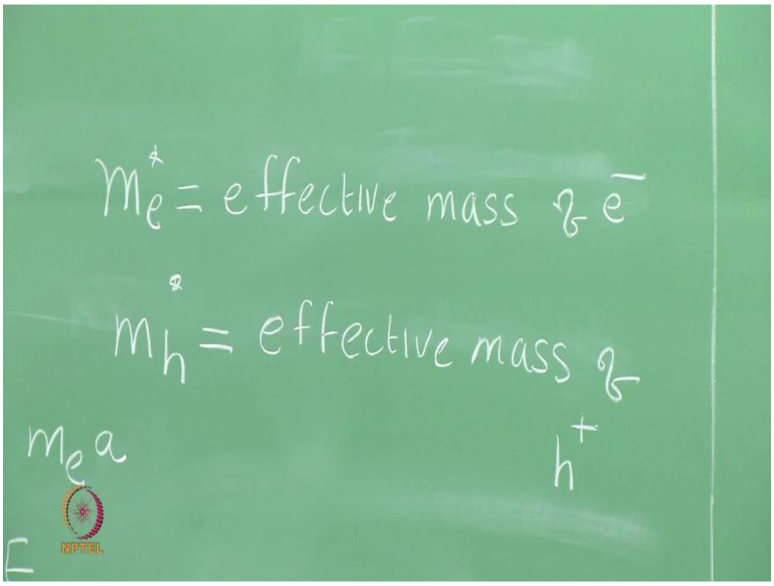

So, this represents the effect of all the atoms in the solid on the movement of the electron. It is important to note that there is no change in the actual mass of the electron; right we are not changing the mass, we only replacing the effect of the solid by using another term called m_e^*. What is true for electrons is also true for holes because a hole is nothing but an absence of an electron. So, we also have a term called m_h^* which we call effective mass of the hole. Now, the effective mass term will basically affect the conductivity of the material lower the value of m_e^* and m_h^*, higher is the conductivity. One way we can think about it is that if these values are lower than the influence of the lattice is less and so you have higher conductivity.

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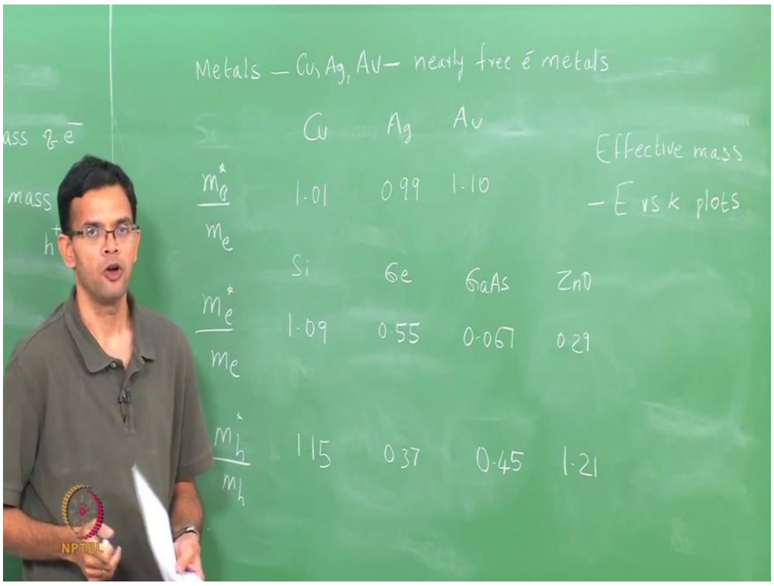

Let us look at some typical values for m_e^* and m_h^*. So, we will start with metals; if we look at metals like copper, silver and gold, so these metals are called nearly free electron metals. In this, we can describe the behavior of the electrons in them; typically, the valence electrons by nearly free electron models. This means that these electrons do not see the influence of the nucleus, they are delocalized and they are free to move through the entire metal. In such a case, we would expect m_e^* and m_h^* to be close to 1 that is what we get. Copper silver and gold m e star over m e silver is again 0.99, which is close to 1; copper is also close to 1, gold is similar.

Let us look at semiconductors. So, we will first look at the electron. So, we have silicon typical value is 1.09, germanium which is around 0.55, gallium arsenide 67, zinc oxide 0.29. You can also look at the effective mass of the holes, so this represents the effective the influence of all the atoms on the movement of the holes in the valence band. So, now, you have m_h^*, this is around 1.15 for silicon, 0.37 for germanium, 0.45 gallium arsenide, around 1.21 for zinc oxide. So, these values of the effective mass depend upon the band structure fine. So, the effective mass depends upon the E versus K plots that we saw earlier.

So, in the next class, we will look at the couple of concepts one of which is called density of states then we will also look at the concept called Fermi energy. We will use these to calculate the electron-hole concentrations in semiconductors and then proceed from there.