Electronic Materials, Devices and Fabrication

Dr. S. Parasuraman
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture - 2

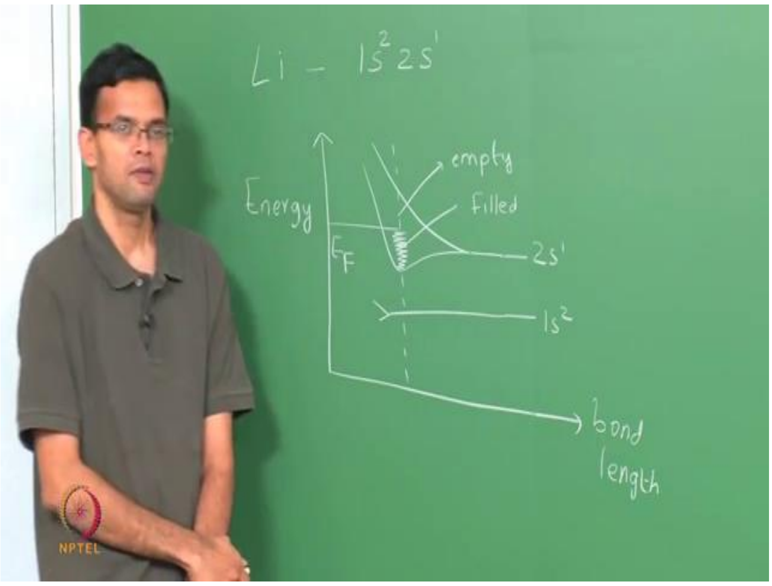
Introduction to Semiconductors

Let us start with brief recap of what we learnt in the last class. So, last class, we said the based on resistivity. We can classify materials into three type's, 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 orbital's, that come together to form a molecular orbital's 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.

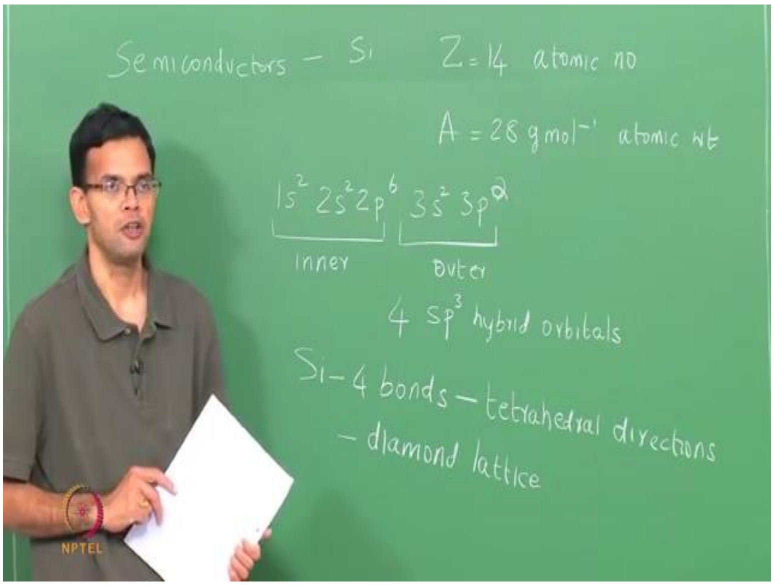
So, that we always have a band, that is not completely full. So, we do have some empty states, these empty states basically help in conduction of electrons, which is by metals are such good conductors. We also saw an example of an energy verses a bond length diagram, using lithium as a example. So, let me just re draw that again and from there, we will move on to semiconductors.

(Refer Slide Time: 01:41)



So, this is from last class, we looked at lithium, which has an electronic configuration of 1 S 2 and 2 S 1. 1 S 2 forms the inner shell and it is not involved in bonding. 2 S 1 is the outer shell. So, we can draw the energy verses bond length diagram, 1 S shell is not involved in bonding. The 2 S shell involves 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 bit and the highest filled state is called Fermi energy. So, today we will move on to semiconductor materials and see, how we can draw a similar picture for semiconductors.

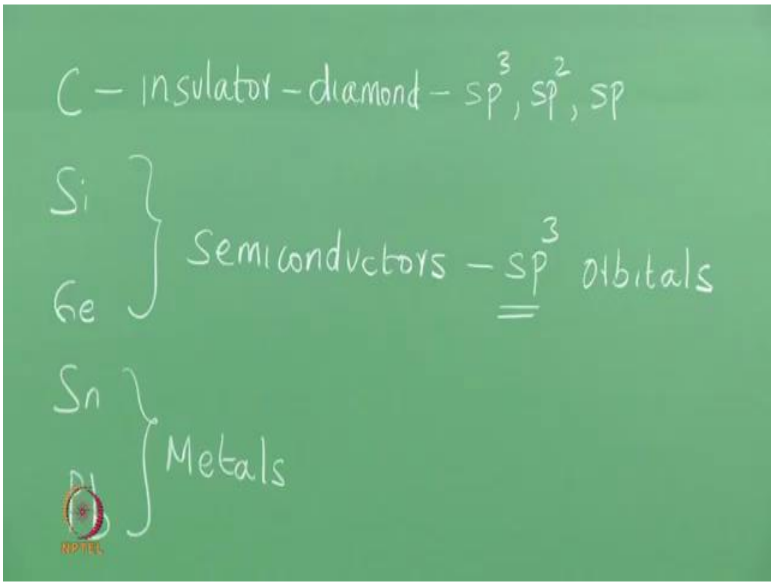
(Refer Slide Time: 03:13)



When we talk about semiconductors, the dominant material, there is silicon. Silicon has atomic number of 14. It as an atomic weight of 28 grams per mol, given the atomic number is 14. The electronic configuration for silicon is 1 S 2, 2 S 2, 2 P 6, 3 S 2, 3 P 6. So, the 1 S and 2 S shells are the inner shells. And they are not involved in bonding. The shells, there are involved in bonding are the 3 S and 3 P. These are the outer shells should be 3 P 0.

Rearrange in order to form S P 3 hybrid orbitals. So, you have two electrons in the S, two electrons in the P, they hybridized form 4 S P 3 hybrid orbitals. Thus, each silicon atom you form 4 bonds. These bonds are director in the tetrahedral directions and essentially, what you have is a diamond lattice.

(Refer Slide Time: 05:50)



C – insulator – diamond – sp^3, sp^2, sp

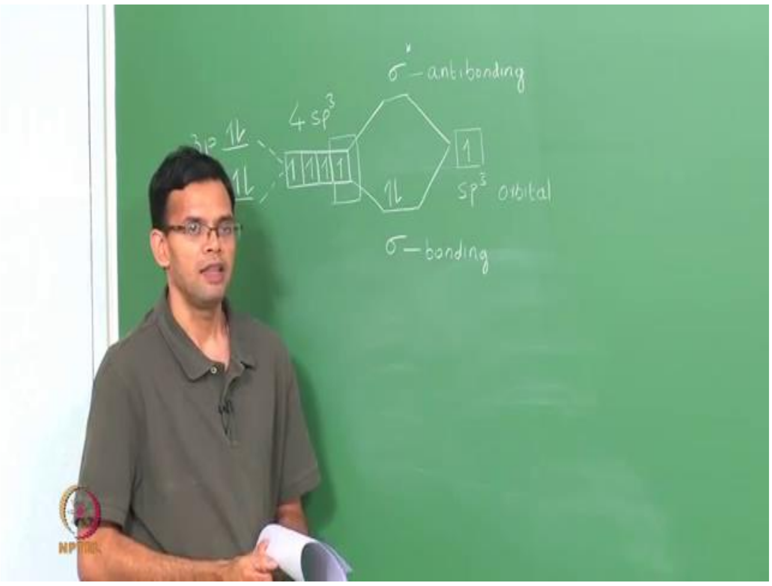
Si
Ge } Semiconductors – sp^3 orbitals

Sn
Pb } Metals

So, let us look at where silicon is in the periodic table. We will concentrate on the group, where silicon is, if you look at it, the group as carbon, silicon, germanium, tin and led. Out of these five elements, tin and led are metals. Carbon in the form of diamond is an insulator. And more importantly, the S and the P electrons in carbon in form a variety hybridizations.

So, you can have S P 3, S P 2, S P hybridizations. Silicon and germanium are semiconductors and they have S P 3 hybridization. So, instead of looking at atomic orbitals in silicon, we are looking at bonding, using these S P 3 orbitals. So, let us look at picture for bonding for silicon.

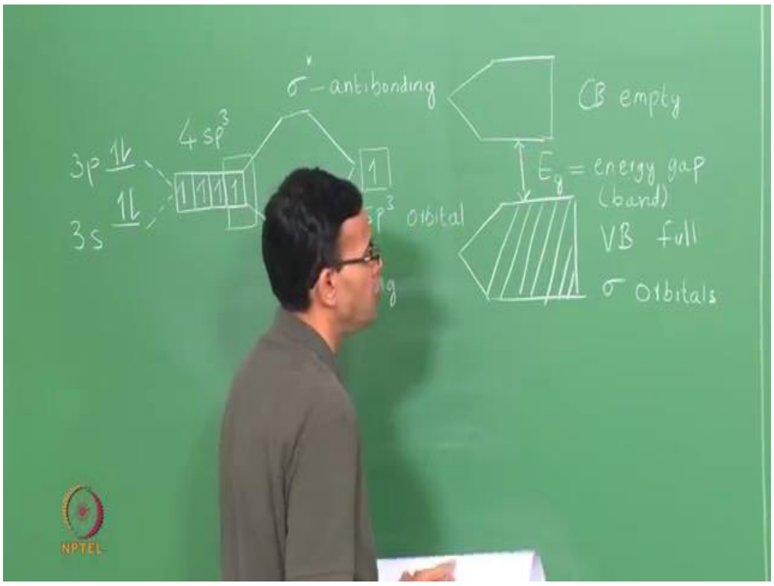
(Refer Slide Time: 07:15)



So, we start with the 3 S and the 3 P, two electrons in them. We said that in silicon, they hybridize to form S P 3 orbitals. So, you have 4 S P 3 hybrid orbitals and each of them are involved in a bond. We will consider one of these S P 3 hybrid orbitals. This can bond with another orbital to give you bonding and an anti bonding orbital’s. This is the same picture that we had in the case of hydrogen.

This forms sigma, sigma star, sigma is a bonding orbital’s, sigma star is the anti bonding. And on the other side, you have another S P 3 hybrid orbital. So, you have two electrons, both electrons go to sigma and sigma star is empty. So, this is the picture, we have, when we have one Silicon bond being found. Now, in a solid, you are going to have large number of the silicon bonds. So, you are going to have a large number of sigma and sigma star. So, these will then interact with each other, and then they will give you a band.

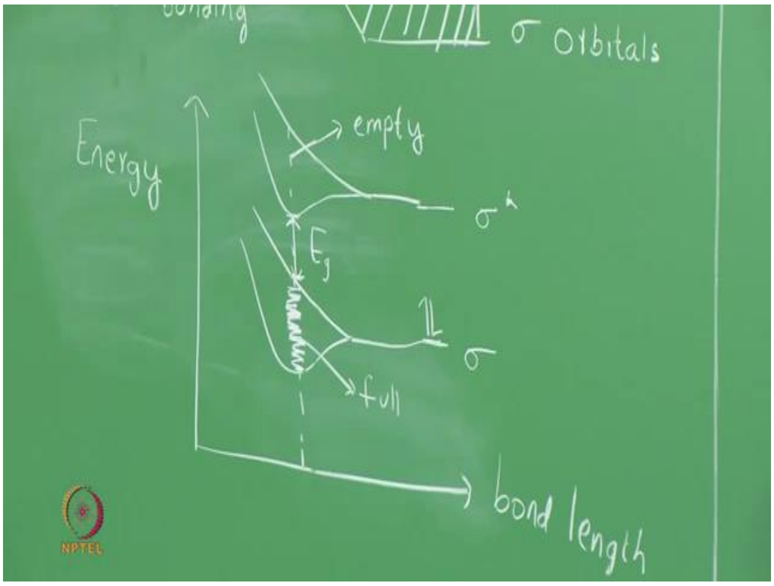
(Refer Slide Time: 09:03)



So, sigma forms a band in pictorially represent this as the valence band so the valance band is formed by the interaction of all the bonding orbitals. Valance band is full. Same way, you have a conduction band, it is formed by interaction of the sigma star in that is empty. Conduction band and between the valance band and the conduction band, there is a gap. This gap is called the energy gap. It is denoted by the symbol E g 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 a sigma star. This just represents one bond. When, we have a whole bunch of these bonds in a solid, they all interacts each other, leading to broadening. And finally, we have an energy band, which is the valance band is completely full. We have an energy band from sigma star. That is completely empty, and then you have a band gap between. We can once again draw an energy verses bond length plot for silicon. But, now instead of having the atomic orbitals, you will have the sigma and sigma star.

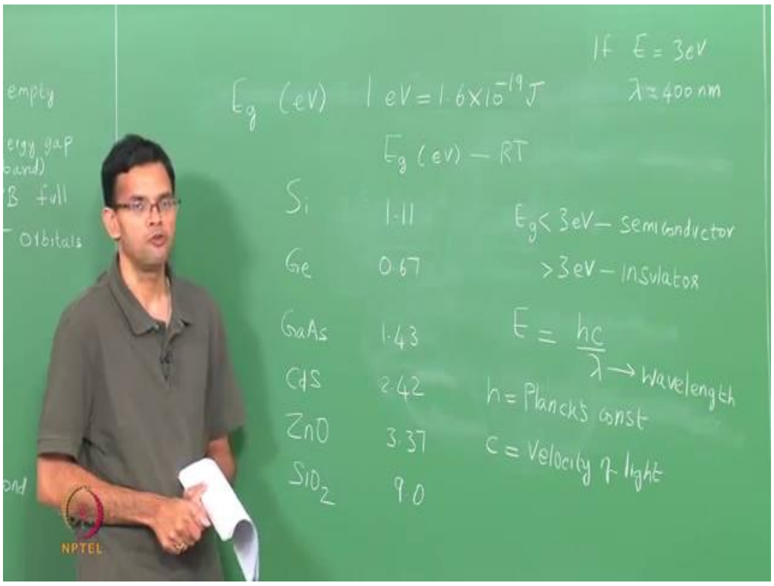
(Refer Slide Time: 10:52)



And is do that, so have energy on the y access bond length. There is some equilibrium spacing. We have sigma. So, here, this sigma represents the effect of one bond. In a solid, it forms a band. Sigma, there are two electrons here, it means, you have this band is completely full. Now, you also have sigma star, which is the anti bonding. This will also form a band, which is completely empty. And this space between these two bands is your band gap E g.

So, this is the model for silicon, you can use same model for the germanium, which lies in a same group. So, again, it has S and P orbitals, which hybridize to form S P 3 orbitals and so on. We can exchange this model in the case of insulator is well. But, in insulators, for example, if you think of an insulator, like a sodium chloride, you have bonds being formed, not by sodium and chlorine. But, you have N A plus and N C L minus ions. So, 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.

(Refer Slide Time: 13:05)



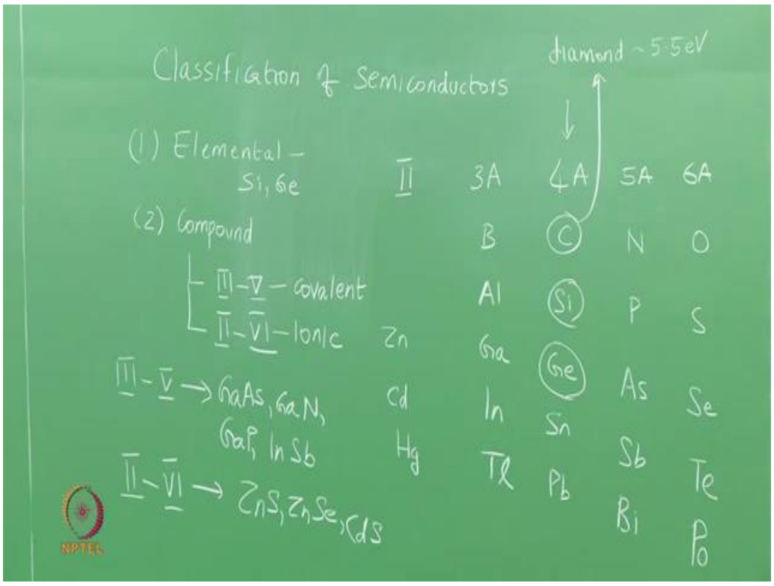
What are some typical values for band gap? Let us write downs some typical values for band gap E g. The unit is for this are in electron volts. And as we saw yesterday, the electron volt is related to joules. One electron volt is nothing but 1.6, 10 to the minus 19 joules. So, we have silicon E g terms of e v. 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, S I O 2 is 9.

So, we have some different values of band gap. So, if it looks 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 semiconductor. And if E g is greater in three electron volts, we call the material an insulator. Now, this is not a very regress separation.

The three electron volts comes out, because three electron volts corresponds 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, h c over lambda, where h is the Planck’s constant, c is the velocity of light and lambda is the wavelength. Write it here, if you use this, if you energy is three electron volts, then lambda is approximately 400 nanometers, E.

So, any energy is greater than three electron volts, puts you in the ultraviolet region. Energy less than three volts; put you in the visible region. So, this is used as a sod of marker. So, differentiating semiconductor and insulators, but as a mentioned earlier, it is not very strict. Based upon this, all these material, silicon, germanium, gallium arsenide, cadmium sulfide are semiconductors. Zinc oxide is closed to this value of 3. But, it is on the higher side and silicon dioxide is much higher. So, these are considered to be insulators. So, look at some values for band gap or semiconductors. So, let us long look at some classifications of semiconductors.

(Refer Slide Time: 17:13)



Classification of Semiconductors

(1) Elemental – Si, Ge

(2) Compound
- III – V – covalent
- II – VI – Ionic

III – V → GaAs, GaN, GaP, InSb

II – VI → ZnS, ZnSe, CdS

diamond ~5.5eV

II	3A	4A	5A	6A
	B	C	N	O
	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te
Hg	Tl	Pb	Bi	Po

So, there are different ways of classifying semiconductors. So, one particular method of classifications is called elemental and compound semiconductors. So, this distinction is fairly straightforward. So, those semi conductors are an elements are essentially, your elemental semiconductors. But, you can also have compounds, there have semiconductors. There is whose band gap lie less in three electron volts. These are compound semiconductors.

There are lot of different types of compound semiconductors. You have 3 5’s, you have 2 6’s. To understand them, let us take a look at the periodic table. We would not look at the entire periodic table, but focus our selves in the area, where we have the groups 4, 3 and

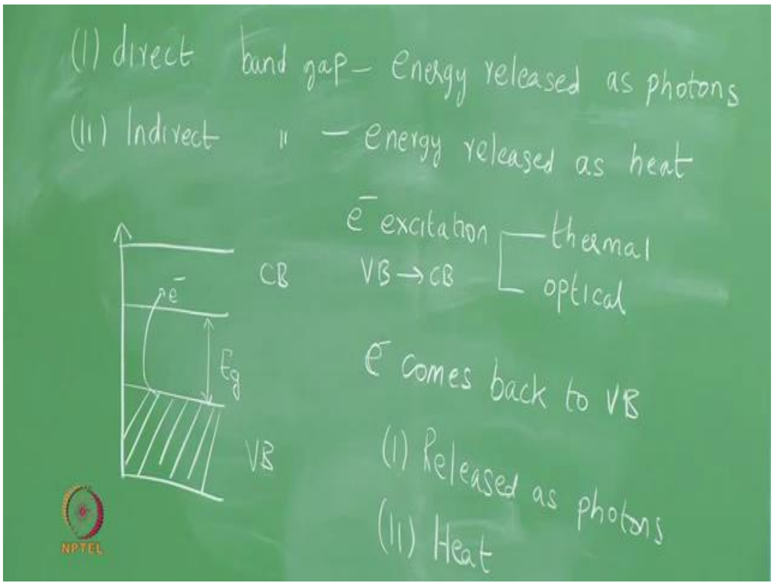
5. If we do that, the group 2, we have 3 A, 4 A. So, let me just write down the elements. So, I am writing the elements from group 2, 3, 4, 5 and 6, group 5, and then group 6. So, this is just a portion of the periodic table.

Now, if you look at it group 4 as silicon germanium, which are classic elemental semiconductors. So, most permanent example, silicon and germanium, carbon, beside in the form of diamond is an insulator. So, diamond as a band gap of around 5.5 e v. So, that carbon is really an insulator. You can also form semiconductors by using elements from 3 and 5. Those are your 3 5’s. You can also from 2 and 6. Those are your 2 6’s.

So, some examples of 3 5 and 2 6’s can have gallium arsenide is the most dominant compound semiconductor, gallium nitride, gallium phosphide in the end to bite and so on. So, all of these are form, we are 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, cadmium selenide and so on. If you look at the bonding character in the composer semi conductor, 3 5’s are mainly covalent, mainly have covalent bonding. They do have some ionic character in them, the main bonding is covalent. In case of 2 6, the main bonding is ionic. So, there is some covalent character in them. So, this is one way of classification, were we have elemental and compound. There is also another way of classifying semiconductors.

(Refer Slide Time: 22:06)



(I) direct band gap – Energy released as photons

(II) Indirect " – energy released as heat

e^- excitation – thermal, optical

VB → CB

e^- comes back to VB

(I) Released as photons

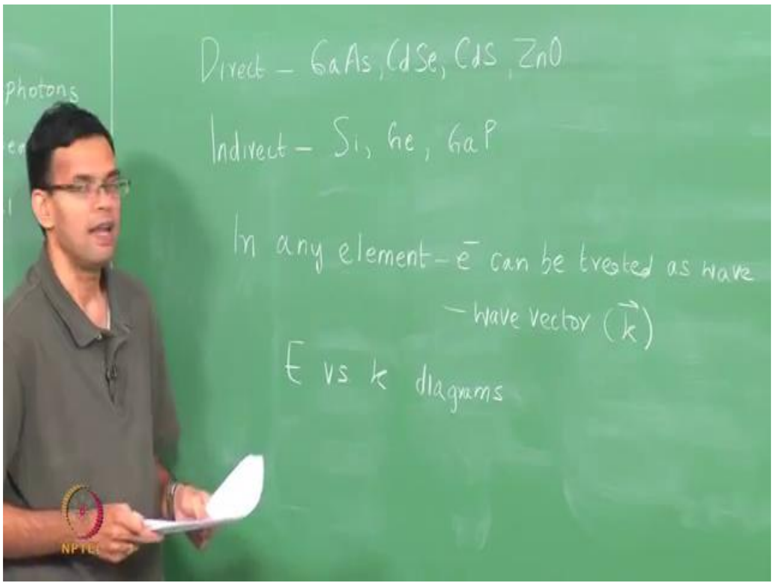
(II) Heat

So, here, we can classify semiconductors as direct and indirect band gap semiconductors. We have direct band gap and an indirect band gap. So, how do we understand the difference between these two? So, let us go back to 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 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 electrons in the conduction band. Now, this electron, once to come back to the valence band, so that, it losses, whatever energy regained. And this energy loss can occur in two ways. So, one the electron comes back to valence band, it can release the energy into two ways. One can release it as photons or you 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 release is dominantly as heat.

(Refer Slide Time: 25:02)



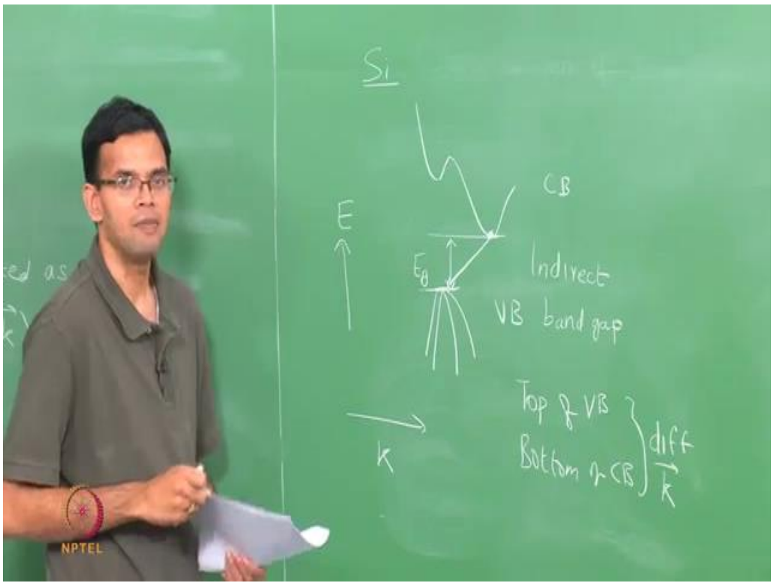
So, let us look at some examples of direct and indirect band gap semiconductors. In the case of direct, we have materials like gallium arsenide, cadmium selenide, cadmium sulfide. In the case of indirect band gap semiconductors, silicon and germanium, which are two elementals semiconductors or both indirect band gap semiconductors, in other example, gallium phosphide.

Direct band gap semiconductors have applications in the case of optoelectronics devices. They can be used in led’s, solar shells, photovoltaic and so on. So, that is one of their advantages in not only have application on the electronic side, we also have applications on the optical side. To understand the difference between direct and indirect band gap semiconductors 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, you are electronic in the solid; it can be treated as a wave. And when you have a wave, a wave, always have something called as a wave vector. And a wave vector is denoted by k. So, thus for materials, you can construct, what are known as E verses 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 band gap semiconductor is a difference between, how the E verses k diagrams look. So, let us look at an example of silicon, which is an indirect band gap semiconductor. And then gallium arsenide, which is a direct band gap semiconductor.

(Refer Slide Time: 27:40)

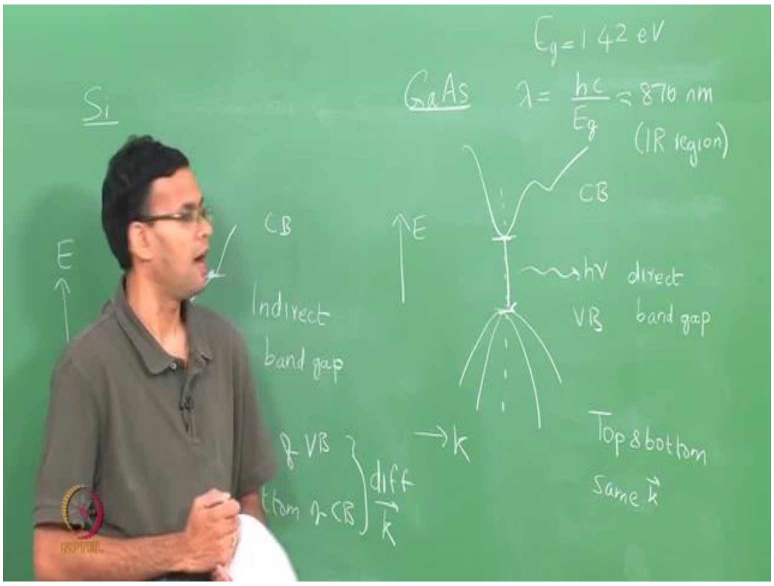


So, let us draw this E verses k for silicon. Again, I am only drawing a very simplified picture to explain the difference between direct and indirect. So, this is the conduction band. This is valence band. There is a band gap between the valence band and conduction band. This is E g. In this particular plot, E is on the y access, and then k along the x access.

So, in the case of silicon, the top the valence band and bottom of the conduction band have different values of k. Top of the valence band and bottom of the conduction band have different values of k. This means, 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. Let us look at gallium arsenide, which is a direct band gap semiconductor.

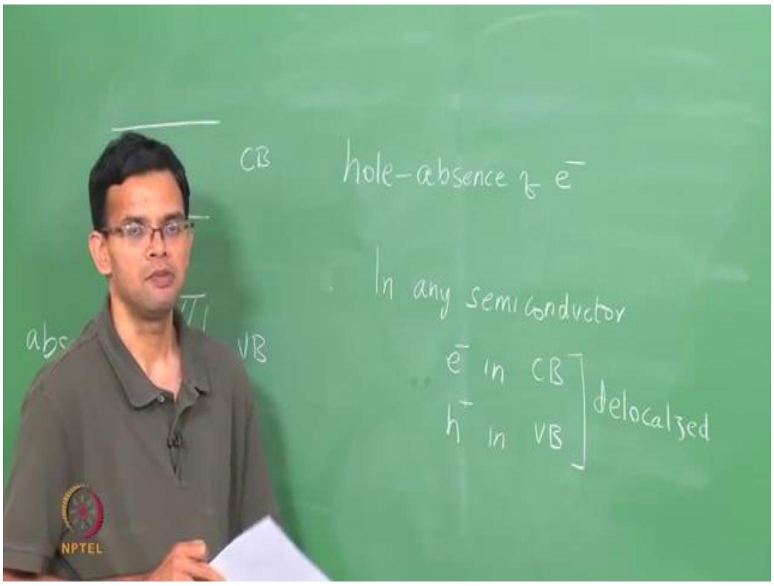
(Refer Slide Time: 29:24)



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 a 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 e v. This energy is released as a photon. So, the wave length of photon, using the same formula that we saw before is nothing but, h c over E g, which is proximately 870 nanometers. This lies in the I R region. If you had a material like zinc oxide, it is band gap is around 3.4 e v and the wave length will lie in the U V region. So, if you have different materials with different band gaps and all of these are direct. Then, their optical transitions will have different wave lengths.

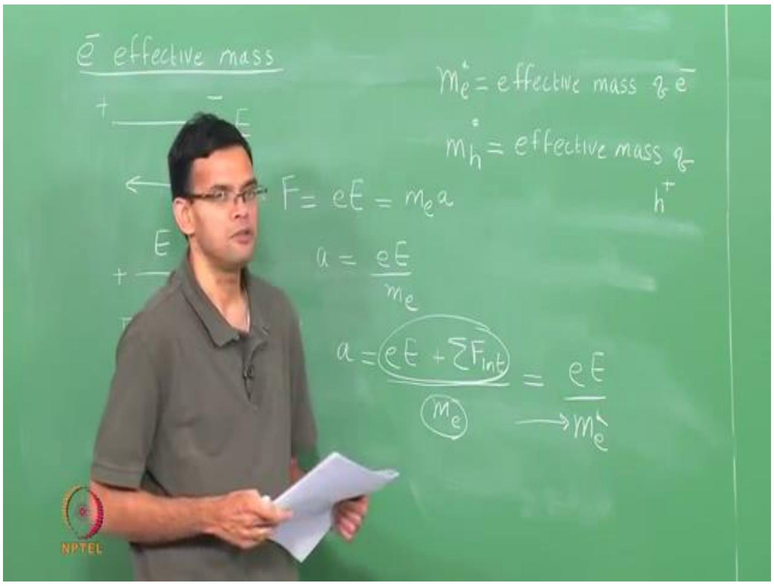
(Refer Slide Time: 31:38)



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

So, hole is nothing but, a mathematical construct that we use to donate the absence of electrons in the valence band. So, in any semi conductors, you have electrons in the conduction band and you have holes. Holes are donated by h or h plus in the valence band. These electrons in the holes are essentially free to move. So, they called delocalized. So, when you apply an electric field to a semiconductor, the electrons can move in conduction band. The holes can move in the valence band in this gives a raise to current.

(Refer Slide Time: 33:35)



So, along with this concept of electrons in holes, we also introduce 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 on 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 is equal to the mass of the electron times the acceleration. So, the acceleration is equal to 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 be the silicon. There is an electron here. Once, again you apply in electric field going from positive to negative.

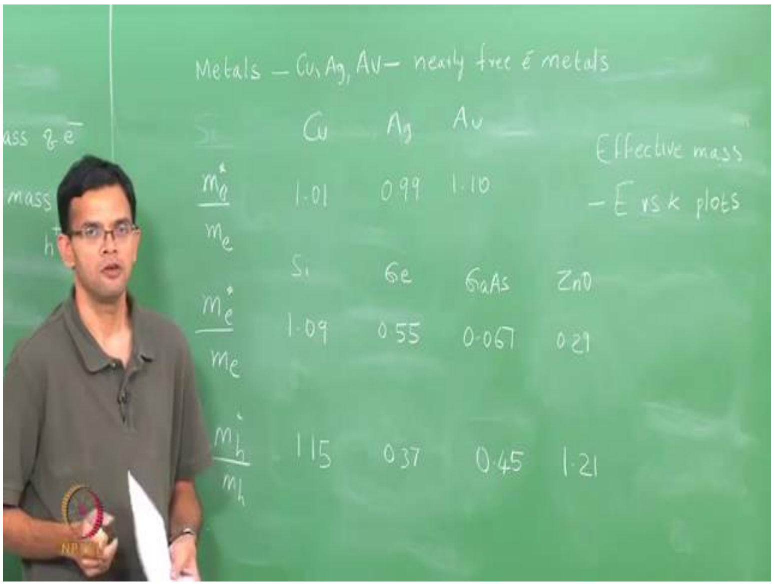
So, the electron will accelerate in the direction in the field. Now, if you try to write the acceleration of electron, you have the term e E, which is the same as before. So, that is the effect of the external field. But, you also have a solid, where you have a lot of atoms. And an electron can feel the influence of all of these atoms. So, in not only have an external field you also have an internal field. This we will write a sum of all the internal field. So, F internal you flex 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 it account the effect of the atoms. In order 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 replace by this term m e star, m e star is called the effective mass of the electron. So, this represents the effect of all the atoms in the solid on the movement of the electron.

It is important note, that there is no change in the actual mass of the electron. We are not changing the mass, we only replacing the effect of the solid by using in other term, called m e star. What is true for electrons is also true for holes, because the hole is nothing but, absence of an electron. So, we also have a term call m h star, which we call effective mass of the hole.

Now, the effective mass term will basically effect the conductivity of a material, lower the value of m e star and m h star higher is the conductivity. One way, we can think about it is that, if these values are lower than the influence of the latos is less. And so you have higher conductivity. Let us look at some typical values for m e star and m h star.

(Refer Slide Time: 38:10)



Metals – Cu, Ag, Au – nearly free $\bar{e}$ metals

	Cu	Ag	Au
$\frac{m_e^*}{m_e}$	1.01	0.99	1.10

Effective mass
– E vs k plots

	Si	Ge	GaAs	ZnO
$\frac{m_e^*}{m_e}$	1.09	0.55	0.067	0.21
$\frac{m_h^*}{m_h}$	1.15	0.37	0.45	1.21

So, we will start with metals. 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 electrons in them. Typically, valence electrons by nearly free electron model, this means that, these electrons do not see the influence of the nucleus. They are delocalized and that free to move to the entire metal.

In such a case, we would expect m e star and m h star to close to one. 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, you have silicon, typical value is 1.09, germanium 0.55, gallium arsenide 67, zinc oxide 0.29.

You can also look at the effective mass of the holes. So, this represents the influence of all the atoms on the movement of the hole in the valence band. So, now, you have m h star, m h, this is around 1.15. For silicon, it is around 0.37, for germanium, 0.45, gallium arsenide, 1.21, for zinc oxide. So, these values of the effective mass depend upon the band structure. So, the effective mass depends upon the E versus k plots; that we saw earlier. So, in the next class, we look at couple of concepts, one of which is called density of states. Then, will also look at a concept called form energy. We will use these to calculate the electron hole concentration in semiconductors, and then proceed from that.