Properties of Materials (Nature and Properties of Materials: III)
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Lecture 38 - Band Theory

So, welcome again to the new lecture of the course, Properties of materials. So, let us just briefly recap what we did in the last lecture.

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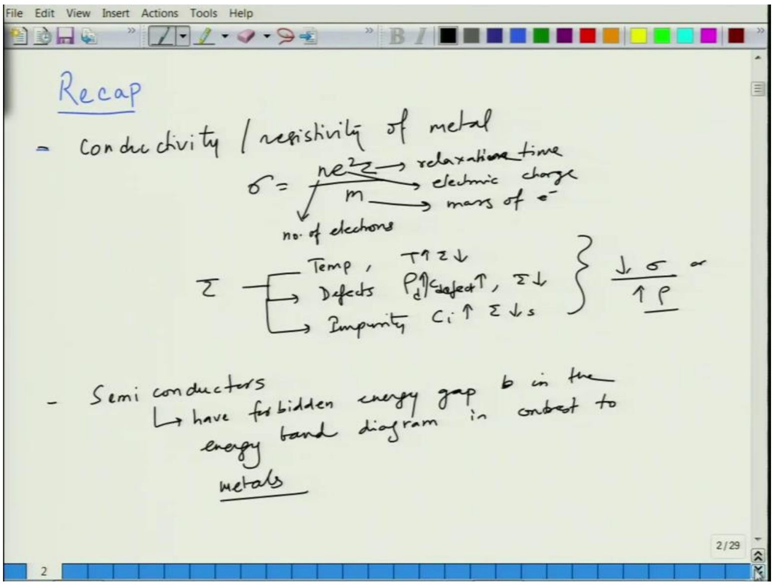

Recap

- conductivity / resistivity of metal

$$\sigma = \frac{ne^2\tau}{m}$$

$\tau \rightarrow$ relaxation time

$e \rightarrow$ electronic charge

$m \rightarrow$ mass of e^-

$n \rightarrow$ no. of electrons

$\tau \rightarrow$ Temp, $T\uparrow\ \tau\downarrow$

$\rightarrow$ Defects $\rho_d\uparrow\ C_{defect}\uparrow,\ \tau\downarrow$

$\rightarrow$ Impurity $C_i\uparrow\ \tau\downarrow$s

$\}\ \downarrow\sigma$ or $\uparrow\rho$

- Semiconductors

↳ have forbidden energy gap in the energy band diagram in contrast to metals

So, in the last lecture, we talked about conductivity or resistivity of metals and we said this sigma is equal to n e square tau divided by m, where tau is relaxation time, n is number of electrons, number of conduction electrons, e is electronic charge and m is basically mass of electron. Now, out of these for a solid you can basically vary tau effectively. Tau depends upon things like temperature. So, increasing temperature decreases tau. So, T increases, tau decreases.

Defects, so defects defect concentration let us say, C defect increases, tau decreases. Or you can say rho, the dislocation density rho d, rho d increases, tau decreases. And then you can have impurity. So, C i increases, tau decreases. So, basically, all of these will decrease conductivity or increase resistivity. This is what we discussed in the last lecture. And then we introduced the concept of semiconductors.

And we have just said that semiconductors have forbidden energy gap in the energy band diagram in contrast to metals.

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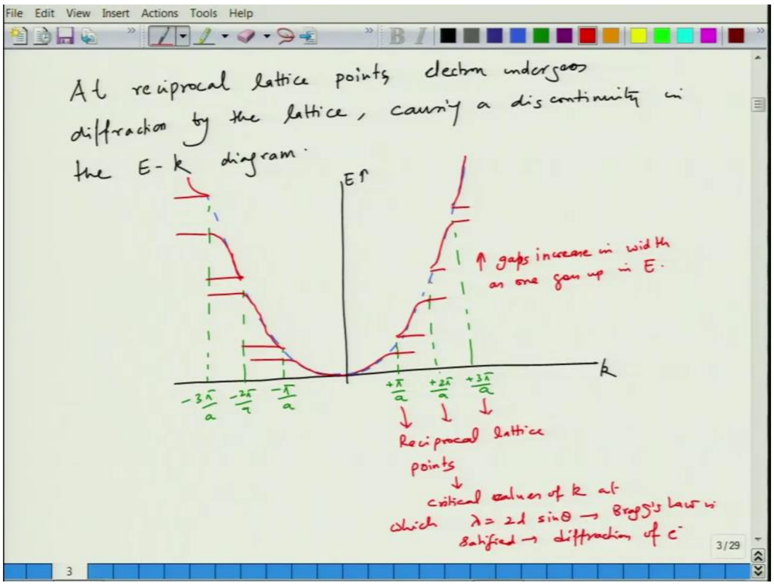

At reciprocal lattice points electron undergoes diffraction by the lattice, causing a discontinuity in the E-k diagram.

↑ gaps increase in width as one goes up in E.

Reciprocal lattice points → critical values of k at which $\lambda = 2d \sin\theta$ → Bragg's law is satisfied → diffraction of e^-

So, essentially, what we said was that at lattice points, in the reciprocal space at reciprocal lattice points electron undergoes diffraction by the lattice, causing a discontinuity in the E k diagram. So, for a single one-dimensional solid, this will be something like this. So, you were initially having a plot like this. I will just remove this line. So, this is E, this is k and at the reciprocal lattice points, you will have a diffraction.

So, reciprocal lattice points are k is the reciprocal wave vector. So, it is basically a vector in the reciprocal space. So, this is plus pi by a, plus 2 pi by a, plus 3 pi by a, and so on and so forth, minus pi by a, minus 2 pi by a, minus 3 pi by a. So, what happens in upon diffraction, we cannot go into details of diffraction theory unfortunately. For this I will recommend you to go through certain books and then it has a behaviour like this. Something like that.

So, you will have these discontinuities. So, these discontinuities are basically you can say, these are the gaps states. And these gaps increase in size, as you can see the gaps increase in size, increase in width let us say, as one goes up in energy. So, as you increase the energy, the gaps become larger and larger. So, if this is the case, then we can say that this is, essentially we can say that energy bands are separated by energy gap at a critical value of k.

So, these are the, you can say reciprocal lattice points or you can say critical values of k at which lambda is equal to 2 d sin theta, the Bragg's law is satisfied leading to electron diffraction. This is what we can do essentially, and this is also direction dependent by the way in crystals.

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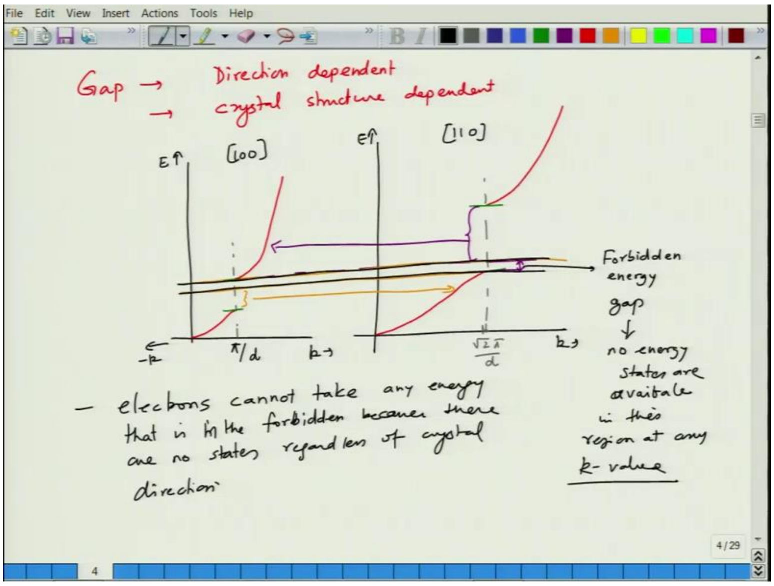

Gap → Direction dependent
→ crystal structure dependent

- electrons cannot take any energy that is in the forbidden because there are no states regardless of crystal direction

Forbidden energy gap
↓
no energy states are available in this region at any k-value

So, this gap is also basically, you can say direction dependent and crystal structure dependent because you know that the value of d depends upon the crystal structure and the type of material you have. As a result, the positions will change. So, for example, for a given crystal, for a given crystal, let us say, we have 100 direction. For 100 direction, it may be something like if you just plot the positive part of k, so this is E k, on this it will be minus k. So, let us just plot the one side of it.

So, this diagram is something like this. So, we are not plotting the state above. So, this is let us say, cubic crystal. This will be at pi by d. If you look at the same for, so this is k, E. If you look at for now 110 direction, for 110 direction, it may be different. For 110 the effective gap is at different so, the reciprocal lattice point for this is at slightly higher k value. This is at root 2 pi by d.

But in this case what happens is that, the gap is something like, so let us say let me just, if you let us say, it is something like this. So, this is for 110. So, you have certain gap state at 100 and certain gap state at 110. We can see that the effective gap because you can see that, all these things are connected in a crystal. So, the effective gap is essentially the difference between lowest point here and the above, because the crystal has gap although at this k state which is a larger gap.

But you can see that, in the crystal while there is a gap along 110 direction, there are energy states available along 100 direction. So, basically, the gap state here if electron cannot move in this direction, it will move along in the energy states available in this direction. But between these two, there is a common area, there is a common region where the states are, there are no states in that. So, you can see that there is no state between this and that.

So, for this region also, there is a state available here. So, this gap will not be so, this is effectively not a gap state because although it does not, the electron will not be able to travel alone 100 direction. It can switch to 110, energy states available along 110 direction. Similarly, although there is a gap in the 110 direction, in this region at this k value, electron can always shift to lower k values and travel at different energy states in 110, 100 direction.

However, having said that this region in between is a region which is, where there are no states available. So, this will be you can say, the forbidden energy gap. So, basically, no energy states are available in this region at any k value. So, this is what basically causes forbidden energy gap in semiconductors. And this forbidden gap is basically you can say electron cannot so, basically you can say, electrons cannot take, electron cannot take any energy that is in the forbidden gap because there are no states for it to reside.

So, this is basically regardless of crystal direction. So, this basically is the reason for energy gap. So, there is far more detailed physics behind it which we do not have time to get into details of.

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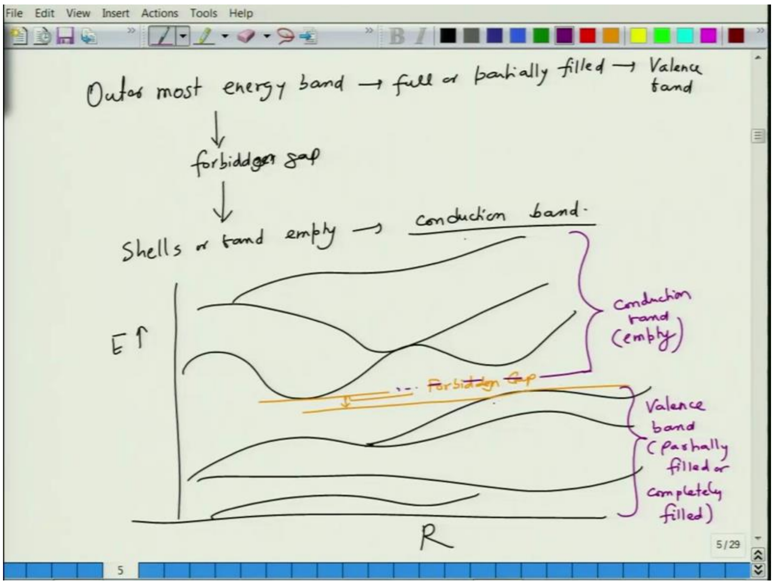
Outer most energy band → full or partially filled → Valence band
↓
forbidden gap
↓
Shells or band empty → conduction band.

But nevertheless, basically you can say that, if you have a situation when bands are so, we define these bands as the outermost energy band, which is full or partially filled. This is called as you can say, valance band and after the forbidden gap, so and then comes a forbidden gap. And after forbidden gap there is a, there are shells or bands which are empty, these are called as conduction bands. So, I mean if you look at in global picture, in a global picture, you may have gap states. The energy states may be like this.

For a given material let us say this is E, this is k. So, you can have energy states like this and then you can have energy states like these and so on and so forth. This is the hypothetical representation so, would can see that there is a clear gap here between these two points and these gap is the forbidden gap. So, this is basically so these bands, the bands below this will be you can say, these are valance bands and the band above this will be the conduction band.

So, these are we are saying partially filled or completely filled and this will be let us say empty. Now another thing is that you can see that minima in the conduction band, there is a maxima of energy states in the energy bands and the valence band. Depending upon whether these minima's are directly on top of each other or they are separate in k space, this will make a separate story.

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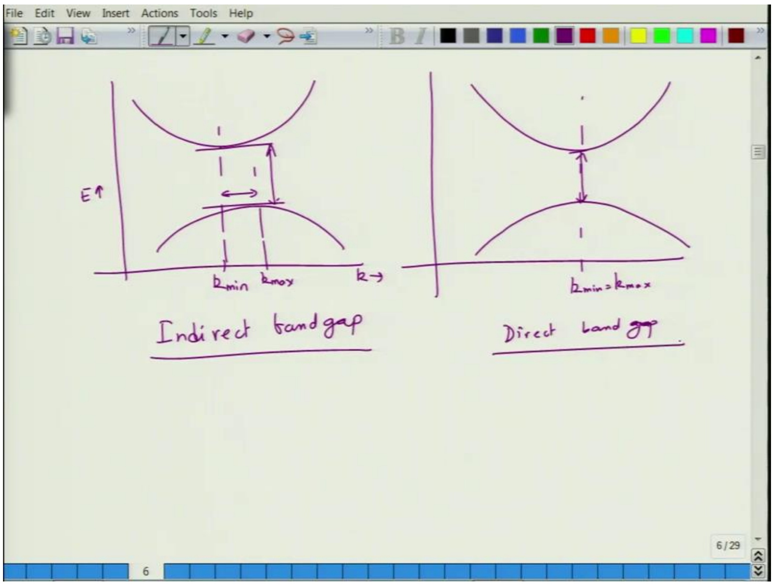

So now, I am drawing an exaggerated picture. So, if these k values are different, so this is k min, this is k max, you can see there is a separation in k space. So, when this is the case, there is energy gap here. This will make what we call as indirect band gap. I have not added the term semiconductor here. I will come to that little later. But indirect band gap material.

And if you have minima and maxima matching in the k space, so basically k min is equal to k max, then this is a direct band material. I will come to semiconductor and insulator little later. So, this is the so, basically diffraction of electron from the lattice is the reason lattice points at reciprocal lattice points is the reason you have band gap. However, a forbidden band gap will be there when electron cannot take any energy value across the k space in any direction in the crystal. If it manages to find something, then it is basically a metal.

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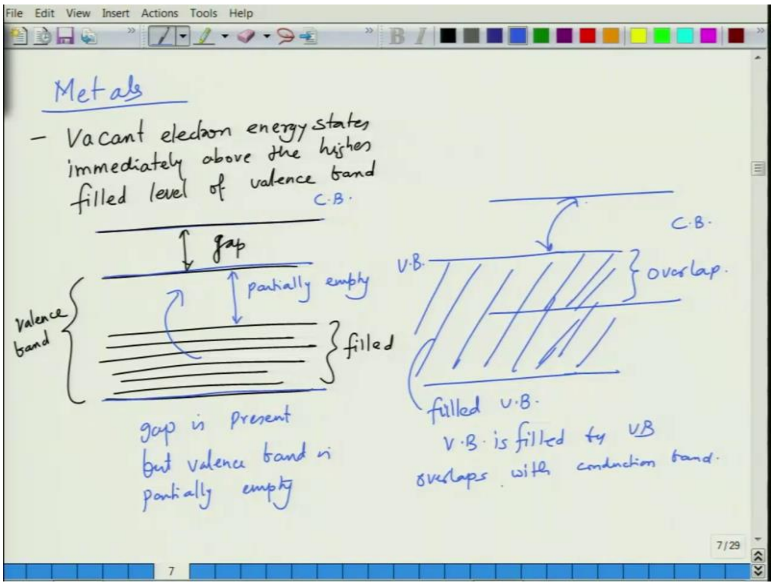

Metals

- Vacant electron energy states immediately above the highes filled level of valence band

gap is present but valence band is partially empty

filled V.B.

V.B. is filled by VB overlaps with conduction band.

So, essentially for a metal, now let us see the difference between the two. For a metal, we see we have vacant electron energy states immediately above the highest filled level of valance band. So, this is basically the situation, you have valance band. This is the valance band. You may have forbidden gap here, so this will be gap let us say, but the valance band is partially filled. So, it is filled up to this point.

So, you can say this is filled. So, let me just draw the boundary separately. This is valance band. This is conduction band. So, conduction band may be somewhere up. This conduction band. But the valance band itself is partially empty. So, this is one representation of metal. Other representation of metal could be, you have one band gap which is completely filled. So, this is valance band which is completely filled. But the conduction band may be overlapping.

So, this is conduction band. This is valance band. But you have overlap between the two. So, although, sorry, let me just draw it differently. So, you can see that this there is a bit of overlap. So, this is the overlap. So, it can also see the states here available states. So, essentially in this case, electron when they acquire velocity, they move into extra available states which are empty states or in the second case, the valance band is completely full.

So, this is full filled valance band but there is overlap with the conduction band which allow the electron to go to states available in the conduction band because there is no forbidden gap. So, here you have a gap but valance so, gap is present but valance band is partially empty. So, states are available for conduction. Here valance band is filled but valance band overlaps with conduction band. So, this is what happens in this case.

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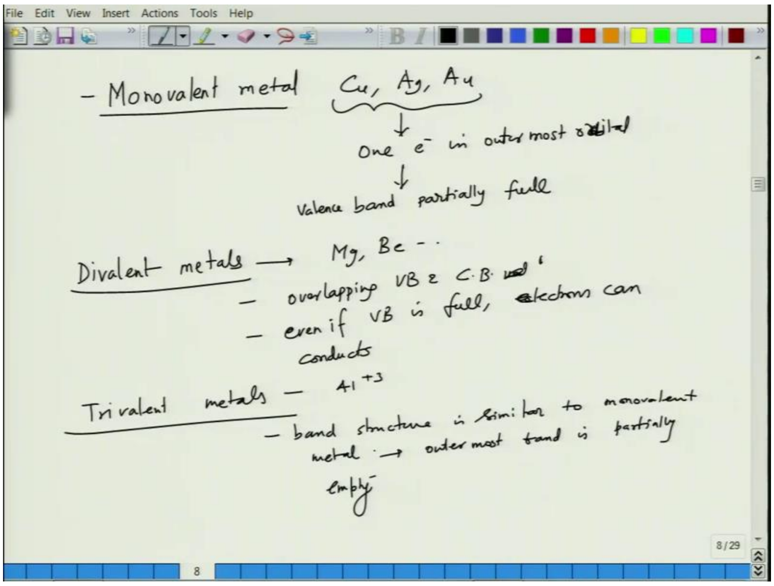

- Monovalent metal Cu, Ag, Au
↓
One e^- in outermost orbital
↓
Valence band partially full

Divalent metals → Mg, Be ..
- overlapping VB & C.B.
- even if VB is full, electrons can conducts

Trivalent metals – Al^{+3}
- band structure is similar to monovalent metal → outermost band is partially empty

Now, if you now compare this with semiconductor, so basically you can say that, let us first do the metals part first. So, in case of monovalent metals such as copper, silver, gold, they all of them have one electron in outermost orbital. As a result, so basically, you can say that, band valance band is partially full. Whereas, if you look at divalent metals, divalent metals such as magnesium, beryllium etcetera, they have overlapping valance band and conduction band. So, as a result, even if valance band is full, electron can conduct because they have empty states available in overlapping conduction band. On the other hand, if you look at trivalent metals such as aluminium which is plus 3.

So, in case of aluminium the band structure is similar to monovalent metals. So, basically, you can say that outer most band is partially empty.

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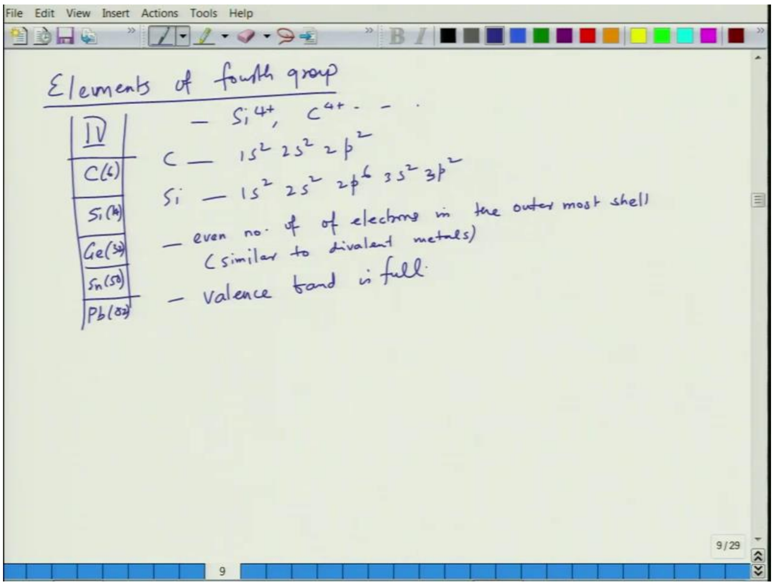


Elements of fourth group

IV
C(6)
Si(14)
Ge(32)
Sn(50)
Pb(82)

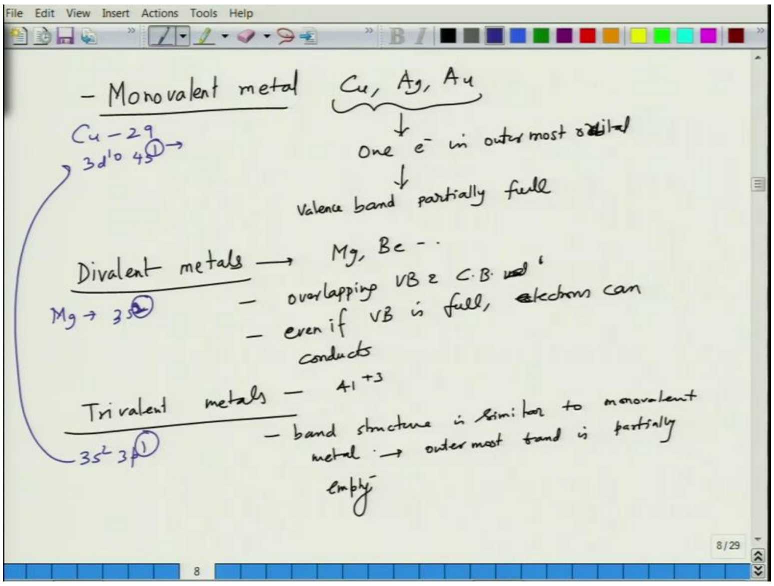
— Si^{4+}, C^{4+} . . .

C — $1s^2\ 2s^2\ 2p^2$

Si — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

— even no. of of electrons in the outer most shell (similar to divalent metals)

— valence band is full.



— Monovalent metal Cu, Ag, Au

↓

One e^- in outer most orbital

↓

Valence band partially full

Cu – 29

$3d^{10}\ 4s^{①}$ →

Divalent metals → Mg, Be . .

— overlapping VB & C.B.

— even if VB is full, electrons can conducts

Mg → $3s^{②}$

Trivalent metals — Al^{+3}

— band structure is similar to monovalent metal → outer most band is partially empty

$3s^2\ 3p^{①}$

Now in case of fourth group element, so, in case of, if you look at the elements which are in, if you look at the elements of fourth group, fourth group elements have basically, you have, in the fourth group we have, if you look at the column in the periodic table you have carbon, 6 atomic number, then you silicon which is 14, then we have germanium which is 32, then we have Tin which is 50.

And of course, you have lead below it which is 82. So, if you look at the situation there, in this case what is happens is that, outer most orbital is so you have this silicon plus 4, 4 plus, carbon 4 plus and so on and so forth. So, in these cases the electronic configuration if you look at, this is silicon would be since carbon is 6, so it is 1 S 2, 2 S 2, 2 P 2. Silicon would be 14, this is carbon, silicon would be 1 S 2, 2 S 2, 2 P 6 and then 3 S 2, 3 P 2. So, this is how the electronic configuration will be. So, what basically you have here is the outer most orbitals you can see there are even numbers. So, even numbers of electrons in the, so this is same as basically similar to divalent metals. So, let us just go back for a brief second here.

So, if you look at for example copper, the copper has atomic number of 29 and the electronic configuration of copper is 3 d 10, 4 S 1. So, you have only 1 electron, which means bands are partially full. So, if you look for divalent for example magnesium, magnesium has a structure of 3 S 2, so you can see that this is even number. If you look at aluminium, aluminium will be 13 which is 3 S 2 and 3 P 1. So, you can see that these are similar but this is same.

So, in this case of silicon, in case of carbon there are even number of electrons in the outermost shell and as a result, valance band is full. But there is another difference, valance band was full in those cases as well. So, these would be in case of…..

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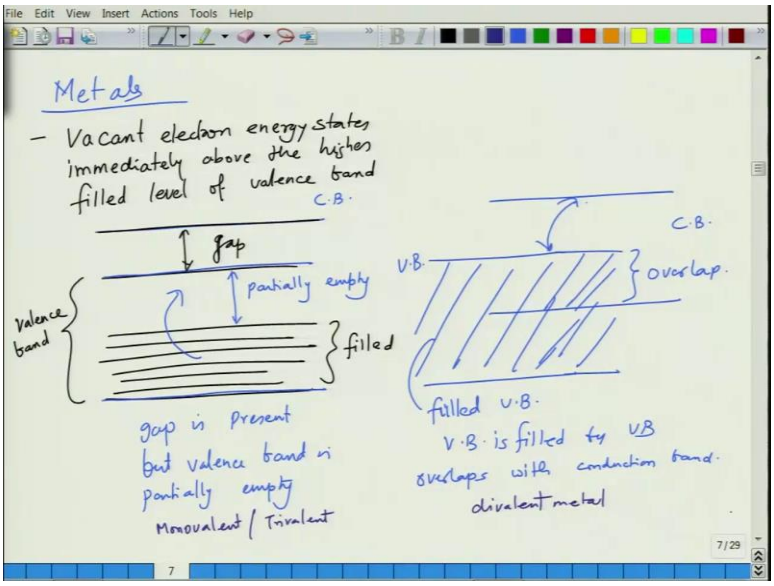

Metals

- Vacant electron energy states immediately above the highes filled level of valence band

gap is present but valence band is partially empty

Monovalent / Trivalent

filled V.B.

V.B. is filled by VB overlaps with conduction band.

divalent metal

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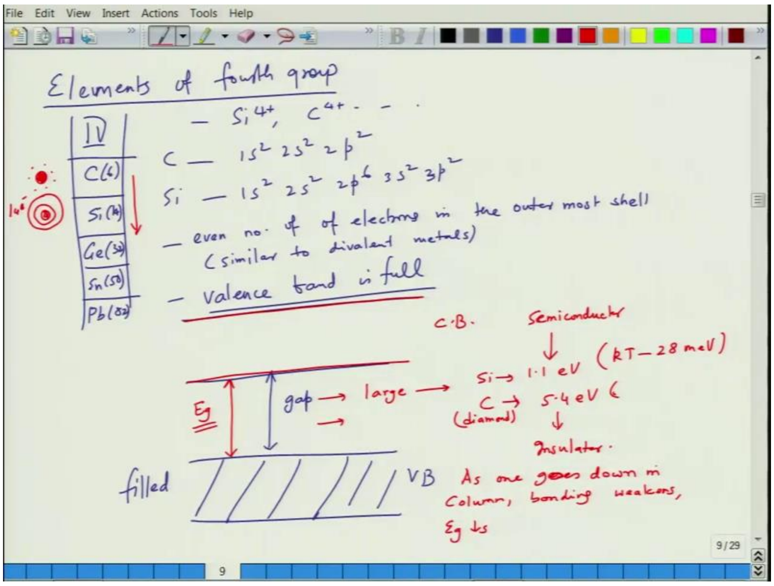

Elements of fourth group

- Si^{4+}, C^{4+} - - .

C — $1s^2 2s^2 2p^2$

Si — $1s^2 2s^2 2p^6 3s^2 3p^2$

- even no. of of electrons in the outer most shell (similar to divalent metals)

- valence band is full

Semiconductor ↓

Si → 1.1 eV (kT – 28 meV)

C → 5.4 eV (diamond) ↓ Insulator.

As one goes down in Column, bonding weakens, Eg ↓s

In this case for example divalent metal, this would be a monovalent and trivalent. So, in this case, even though valence band is full, there is no overlap with the conduction band. What we have here is this is valence band. This is completely filled. So, we are talking at 0 k of course.

The conduction band, there is a gap between conduction band and valance band here, this is gap, forbidden gap, let me draw a different line here. This is conduction band and there is a gap between these two and this gap is basically large. So, for silicon it varies. It is about 1.1 eV, 1.1 eV is lot of energy because k T is equal to only 28 m eV milli electron volt. So, you can see that this is 1100 milli electron volts.

So, you will need a lot of energy in terms of thermal energy for electrons to be able to migrate, that is why silicon is also not metallic and in case of carbon which is diamond, this gap is nearly a 5.4 eV makes it very large. So, this makes silicon as semiconductor because its gap is not very large but carbon is in the diamond form is insulator. So, this basically because the carbon is covalently bonded, is hybridised and so and so forth, because the bonding carbon has larger gap as compared to, and we can see that so, in the carbon case, the atoms are the electrons, they are not too many electrons. As a result, when you come down in the, in this case when you come down, so you have in this case situation like this.

This is the nucleus, around this you have only 6 electrons. In this case, there are so, you will have 14 electrons total of 14 electrons. So, as you come down in the column, the separation increases between the atoms, as a result the bonding becomes weaker. So, when the bonding becomes weaker, the energy gap also comes down.

So, for as you go down in column, as one goes down in column, bonding weakens. This weakens because atoms are more fatherly apart because there are more electrons between them. So, there is electrostatic repulsion between the electron clouds as well so, bonding weakens. As a result, the band gap goes down and this gap is called as E g, energy gap. So, this is forbidden gap or energy gap in metals. So, this basically is the reason why….

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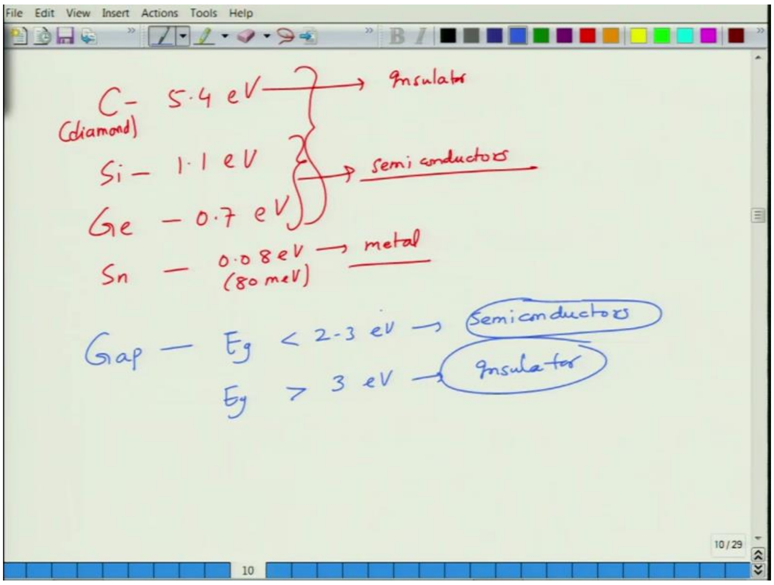

Essentially, you can say that in case of carbon it is, that is diamond, we saw that this gap is 5.4 eV. In case of silicon it is 1.1 eV, in case of germanium it goes down to 0.7 eV. Germanium is even lower and in case of tin it goes down to 0.08 eV. So, that is why tin is basically a metal 0.08 eV is nothing but 80 milli electron volt. Whereas in this case, these are all, so this is insulator because 5 is very large. These are semiconductors. So, basically, this is where now the distinction comes. So, when the gap is so, when E g is less than 2 to 3 e V, then the materials are called as semiconductors. When E g is larger than 3 e V, they are called as insulators. So, basically between 2 and 3 you will call them wide band gap semiconductors. Less than 2, you will call them semiconductors.

So, because semiconductors as we will see the electron concentrate, and there is a reason why we call them semiconductor. Because you make them conduct by other means. Insulators, it is very difficult to make them conduct because their energy gap is simply too high. And semiconductors they do not, the gap is high but it not high enough to make them completely insulating, we can try methods to make then conducting by various means.

We will stop here. we have discussed in this lecture the reason of band gap, how the continuous gap is necessary across the k space to create a band gap and then what is the reason, and the energy states below the gap are called as conduction band and the bands above the gap are called, sorry, valance band and conduction band, so valance band is below the energy gap and conduction band is above the energy gap. So, at 0 K, for a perfect semiconductor all the states below energy gap are filled and above is empty. We will discuss this further in the next two lectures. Thank you.