Lecture - 07
Energy Band Diagrams & Classification of Semiconductors

Welcome everyone to our second class of the second week. In today's class we will learn about energy momentum diagram and also the classification of semiconductors based on different parameters. So energy momentum diagram plays a very important role in describing some of the physical and overall behavior of the material.

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An E-k diagram shows characteristics of a particular semiconductor material. It shows the relationship between the energy and momentum of available quantum mechanical states for electron in the material. In the basic E-k diagram, it shows that x axis can be either momentum like p or the wave number k since p is equal to h bar k as we have learnt earlier and y axis is energy.

So in the E-k diagram, y axis is energy and the x axis is either it is momentum or the wave vector k. The band gap which is difference between the top of the valence band and the bottom of the conduction band that can also be shown in this E-k diagram. If you remember in the last class, very briefly, we have first started with how the band gap originates in materials.

So we have learned that the free electron theory or more precisely the quantum free electron theory was not enough to explain why some materials are conductor, why some of them are insulator and why some of them are semiconductor. But in nearly free electron theory, where we assume the exact potential of a solid, we have seen that the solution of the Schrodinger equation has to be modified.

And in a periodic potential, the solution of the Schrodinger equation is given by Bloch wave functions where there is a traveling part in the wave function, which was modulated by a periodic function and that periodic function has the periodicity of the crystal lattice. Now later on Kronig and Penney who have simplified this model and instead of a gradually varying potential, they have considered a one dimensional rectangular potential.
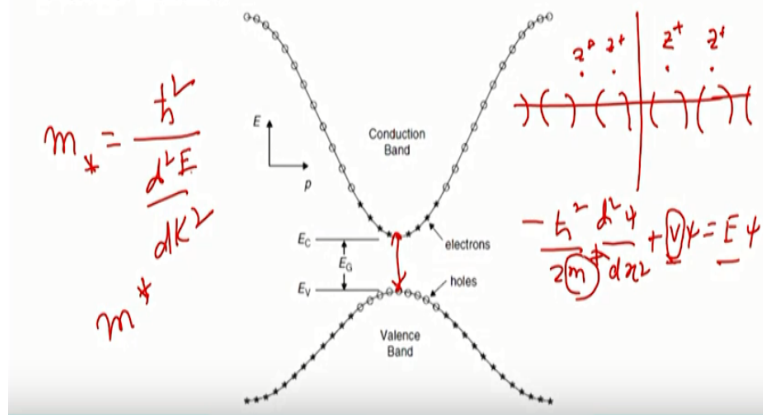
And considering that approach, they were successfully explained many of these properties of the material. And we have also seen how that expansion leads to the understanding of the origin of band gap and based on the band gap, we can classify the materials either as a conductor, where we have seen the valence band and conduction band virtually overlaps.

And the insulator where there is a big gap between the valence band and conduction band and semi conductor, which is intermediate between conductor and insulator. Now we like to understand this band gap phenomena or you have to understand the origin of this band gap in terms of the energy momentum diagram. We can also classify the semiconductor on the basis of this shape of the E-k diagram. That we will also see. So how the E-k diagram looks like?

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Energy – Momentum Diagrams

- The effective mass of electrons and holes in the material is given by the curvature of each of the bands.

$$m_* = \frac{\hbar^2}{\frac{d^2 E}{dK^2}}$$

m^*

$$-\frac{\hbar^2}{2m^*}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

E

p

Conduction Band

E_C

E_G

E_V

electrons

holes

Valence Band

So a typical E-k diagram looks like this following figure where you see this is the conduction band the top one and the bottom one is the balance band. And the bottom of the conduction band and the top of the valence band if you take the spatial distance between these two, that gives the band gap or forbidden energy gap. And we have learned previously that in this band gap, there is no solution of the Schrodinger equation exist.

Now when in semiconductor especially when a electron is excited from the valence band to the conduction band, that usually happens by band breaking. When the electron jumps from the valence band to the conduction band, there is a vacancy created in the valence band and that vacancy acts like a positive charge because it is an absence of a negative charge and this vacancy is called hole.

So in semiconductor there are two different kind of charge carrier participate in charge conduction namely electrons and holes. The effective mass of the electrons or hole in the material is given by the curvature of each of this band. So previously we have discussed that this energy momentum diagram is very insightful for explaining some of the properties of the material especially the semiconductor.

Now we have also learnt that in a real crystal, the situation is much more complicated than the particle in a box problem. Here the electron moves in a periodic potential and it experience lot of interactive ports from the neighboring electron and from the

crystal lattice sites, etc, etc. Because of that solution of the Schrodinger equation is very difficult. Let us take a look on that.

So if I like to draw the potential distribution in a real crystal, so it is somewhat like this roughly where we have a positive charge ion cores here which I can call as z+ and this potential has a very complicated form. Now let us considering this kind of potential, I like to solve the Schrodinger equation and what is one dimensional Schrodinger equation looks like?

This is we have done it earlier also where V is the potential and E is the energy. Now the potential V has now a very complicated form. Now if I wanted to solve this Schrodinger equation analytically, then I need to put the exact value of the potential V and then solving this differential equations will become much more complex. Another way of looking this problem is that, keeping the potential as simple as possible, but incorporate the effect of this potential in the mass.

When I say that what I mean that I can still solve this equations keeping the V as simple as possible, but we can take the effect of this periodic potential or whatever the form of potential into its mass. How can you do that and in that case, obviously the mass is not the electron rest mass. Then the mass is something different and that mass is called the effective mass.

Obviously, the effective mass is different from the rest mass of the electron. Effective mass, which is often denoted by m subscript star or you can also put the star on the superscript that is defined by deduce Planck's constant whole square by d 2 E d K 2. So it is defined by the curvature of the E-k diagram. Now look that energy momentum diagram, this curve is an energy momentum diagram.

This curve contains all the information about the potential. So if I take the curvature of this curve or if I do a differentiation of E with respect to k, so that curvature information contains all the necessary information about the potential. So from the curvature, which is reflected in the effective mass, I can incorporate all the information of the potential inside the effective mass.

So let us if we write m star also we can write like this way effective mass. So instead of writing the rest mass as m, if we replace the rest mass by the effective mass m star, so I can still solve the Schrodinger equation where all the effect of the complexity of the potential has been incorporated in the rest mass and potential remains as simple as possible like previous case.

Then it has become much easier to solve this differential equations. So Schrodinger equation become much more easy to solve if we incorporate the effect of this complicated potential in the effective mass. So effective mass plays an important role and it is obviously different from the rest mass and as you can see, it is given by the double derivative of E with respect to a.

What is dE dK represents? dE dK is the tangent or the slope of this curve. But when I do the second derivative, it either tells a maximum or minimum depending on the shape of the curve. So it can be positive or it can be negative. So that means effective mass can be positive or negative. Further the rest masst cannot be negative. So there is a significant difference between the concept of effective mass and the rest mass.

Now if I substitute this rest mass in the Schrodinger equation then solving the Schrodinger equation for this kind of periodic potential becomes more easy. For a real solid, the energy momentum diagram or the E-k diagram is not as simple like the previous parabola. There are lot of interactions prevailing in a solid. It can be Van der Waals interaction, it can be electromagnetic interaction.

And because of the electron interaction, electron lattice side interactions the E-k diagram become very complex.

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Energy – Momentum Diagrams

- There is a more complex form of E-k diagram that shows the relationship for different directions of k relative to the crystal lattice.
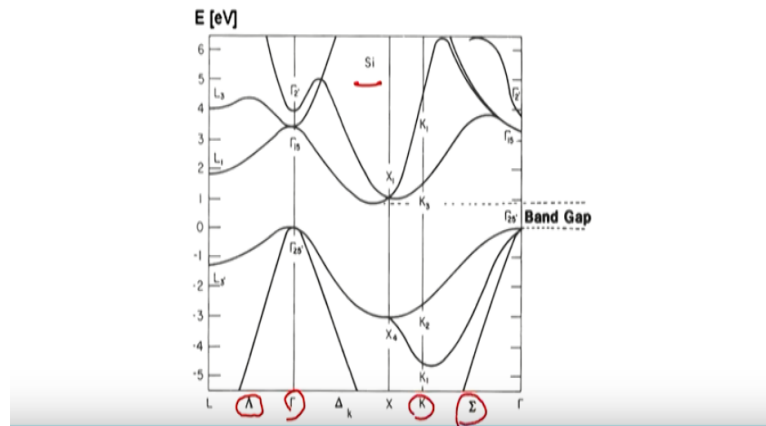
In a real solid, for example silicon the E-k diagram looks like this, where in the x axis you see lot of the Greek alphabet is there like tao, K, epsilon like this.

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Energy – Momentum Diagrams

- Here, the Greek letters (Γ, Δ, K, etc.) on the x-axis indicate different directions of k relative to the crystal axes.

- In addition to showing the effective mass at different band extrema, this also shows that the effective mass varies depending on the direction of conduction relative to the crystal orientation.
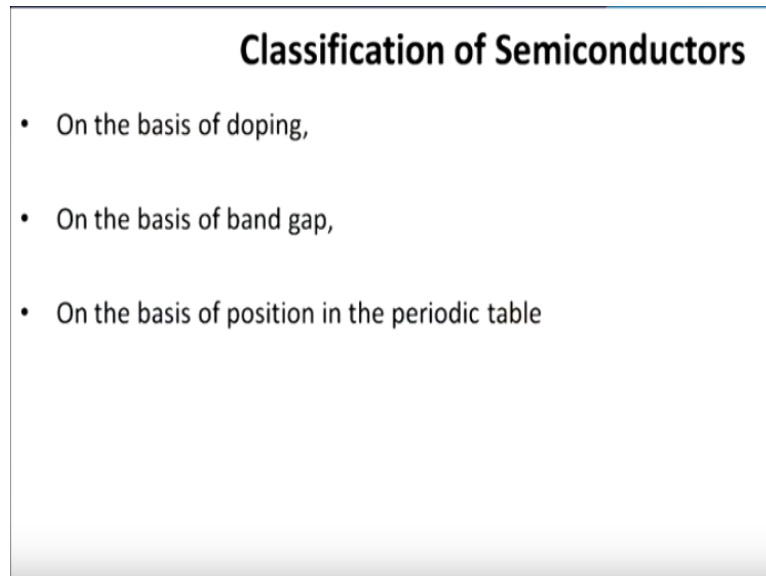
And this Greek letters on the x axis, they indicate different directions of the k relative to the crystal axes. So if you consider a three dimensional crystal axes, there can be three different directions. So according to the different directions, k have the relative orientation, they have the different values the wave vector. So this Greek letters like K, sigma, Nabla operator, etc. It is not a Nabla operator here it is delta.

So these all represent the different directions of the k along that crystal axes. In addition to showing the effective mass at different band extrema, this also shows the

effective mass varies depending on the direction of conduction relative to the crystal orientation. Next thing what we will learn now is the classification of semiconductors.

Now a semiconductor as we have learned previously its band gap lies between that of a conductor and insulator. Semiconductor materials can be broadly classified on three different categories.

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Classification of Semiconductors

- On the basis of doping,

- On the basis of band gap,

- On the basis of position in the periodic table

On basis of the doping, second basis of the band gap, and third basis of its position in the periodic table. Now the basis of the doping that is very important. Because based on the doping I can change the conductivity of a semiconductor and since the conduction plays an important role in fabricating optoelectronic device so doping plays a very important role in semiconductor.

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Semiconductors on the basis of doping
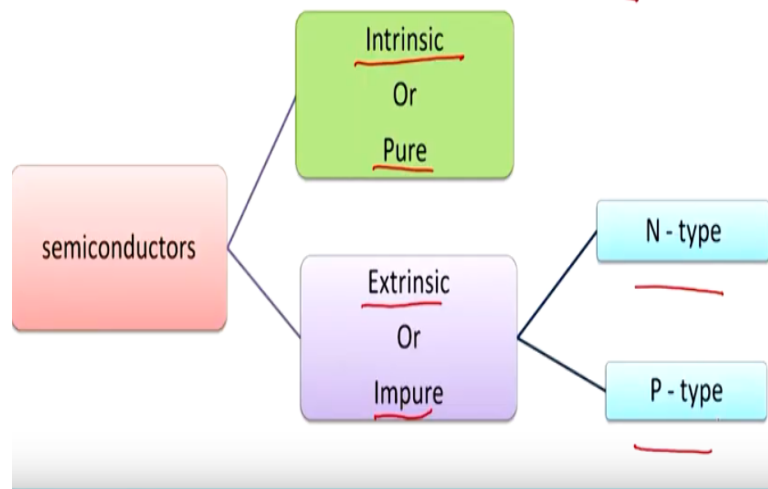
So a semiconductor material as you can see they can be broadly classified intrinsic or pure and extrinsic or impure. This is based on the doping. Doping is an external impurity. So when the semiconductor material do not or does not have any intent of any external impurity, then you call it as an intrinsic or pure semiconductor.

When the semiconductor material has some external impurities, either it can be negative impurity or it can be positive type of impurity, then it is called extrinsic semiconductor or impure semiconductor. Now this extrinsic semiconductor, they can be classified into two different class. One N-type material where the negative charge, the concentration of negative charge is higher than the concentration of the positive charge.

And the P-type materials where the concentration of positive charge is higher than the negative charge. So what is doping?
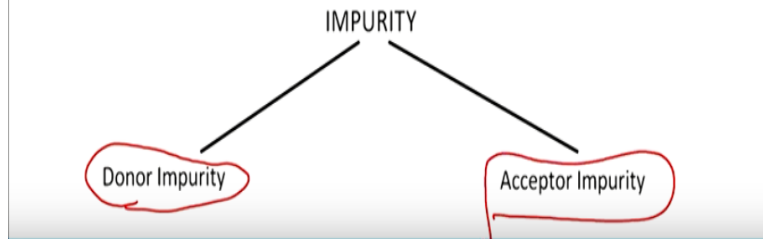
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Doping

- **Doping :-** The conductivity of semiconductor can be increased by adding some impurity atoms.

  Conductivity of the resulting semiconductor will depend upon the type and amount of impurity added.

  Added impurity can be of two types for intrinsic semiconductor:-

  IMPURITY

  Donor Impurity   Acceptor Impurity

The doping is the conductivity of the semiconductor can be increased by adding some impurity atoms. The act of adding this impurity atoms is called the doping. Conductivity of the resulting semiconductor will depend upon the type and amount of impurity added. So in which semiconductor what kind of impurity I am adding and what amount I am adding so that will depend or that will determine the conductivity of that particular semiconductor.

Added impurity can be of two different types for intrinsic semiconductor. One can be donor impurity which donates an electric charge or extra electron charge to the material and acceptor impurity which grabs a negative electron charge from the intrinsic material.

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Doping

- **Donor Impurities:-** If a pentavalent atom is added as impurity to an intrinsic semiconductor then this kind of impurity is known as donor impurity.
  Example:-arsenic, antimony, bismuth etc.

- Four of the five valence electrons of impurity atom form covalent bonds with the valence electrons of pure semiconductor i.e. Germanium or Silicon.

- The fifth valence electrons of impurity atom is not covalently bonded but it is not completely detached from the arsenic atom itself.

- A finite amount of energy is required to detach it is known as ionization energy of impurity atom. In Germanium ionization energy of all impurity atoms is found approximately 0.01eV.

Now donor impurities if a pentavalent atom is added as impurity to an intrinsic semiconductor, then this kind of impurity is known as donor impurity. So in the case of donor impurity, we add a pentavalent atom to the intrinsic semiconductor. So what is a pentavalent atom? A pentavalent atom as the name suggest penta stands for 5 and valence is the valency.

So these are the atoms which has 5 balance electrons in its outer orbit. For example, arsenic, antimony and bismuth. All these materials have high valence electron in its outer cell. Now when these materials like arsenic or antimony is added to an intrinsic semiconductor, let us say for example silicon or germanium then we call a donor impurity has been added to the material.

Four of the five valence electrons of the impurity atom form covenant bonds with the valence electron of the pure semiconductor, that is germanium or silicon. So you see that if this is the silicon atom, which has four valence electron in its outer orbit, now to get the nearest stable atomic orbital structure, what it needs is to share four more electrons so that it has eight electrons in its outer orbit.

Now if I add a pentavalent impurity ion, so this has four electrons in the outer orbits and one as extra electron that is total of five electrons. So these four electrons can make bond with the neighboring silicon atoms with the four electrons of the silicon atom, which gives a stable electronic structure, but the fifth electron that is now free, and that is now available for the conduction.

So since it add an extra electron or it donates an extra electron, this kind of impurity are called donor impurity. The fifth valence electron of the impurity atom is not covalently bonded, but it is not completely detached from the arsenic atom itself. A finite amount of energy is required to detach it known as the ionization energy of the impurity atom.

In germanium ionization energy of all impurity atom is found approximately as 0.01 eV.

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Doping

- So even at room temperature fifth valence electron in impurities like arsenic, antimony, bismuth is detached completely and moves freely in germanium crystal.

- More is the added impurity greater will be the free electrons.

- As the impurity atom donates free electron to the crystal conductivity, it is called DONOR ATOM.

So even at room temperature fifth valence electron in impurities like arsenic, antimony, bismuth is detached completely and most freely in germanium crystal. So since the amount of the energy required to detach an electron that is very small in the case of germanium 0.01eV and we know that the thermal excitations or the thermal energy which is Boltzmann constant times that temperature T, k BT so that is much higher then this amount of ionization energy which is 0.01eV in germanium.

So the room temperature can easily detach that electron from the germanium and fifth electron can easily move in the germanium crystal. More is the added impurity, greater the free electrons. As the impurity atom donates the electron to the crystal conductivity, it is called donor atom. On the other hand, we have accepted impurities. So it is obvious if donor atom donates an electron so accepted atom will grab an electron. What kind of impurity can do the job? It is a trivalent atom.

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Doping

- **Acceptor Impurities:-** If a trivalent atom is added as impurity to an intrinsic semiconductor then this kind of impurity is known as acceptor impurity. Example:- Boron and Aluminium etc.

- Three valence electrons of impurity atom form covalent bonds with the three valence electrons of pure semiconductor i.e. Germanium or Silicon.

- There is a deficiency of one electron and this deficiency is called a hole.

- Fourth electron of germanium also tries to form covalent bond and it does so by taking the advantage of any thermal motion that fortunately brings an electron from neighboring Ge atom.

If a trivalent atom is added as impurity to an intrinsic semiconductor, then this kind of impurity is known as acceptor impurity; for example, boron and aluminum. So they have three electron in the outer orbit. So the trivalent, tri stands for three and valent is the valency. So this kind of impurity has three valence electron in the outer orbit. Three valence electron of this impurity atom form covalent bonds with the three valence electron of pure semiconductor, that is germanium or silicon.

So there is a deficiency of one electron and this deficiency is called a hole. So there are three atoms or three electrons in the outer orbits of this accepted impurity and those three form covalent bond with the intrinsic semiconductors. But one electron is less. So how can that one electron gap will be filled? That is filled by breaking the bond of the intrinsic semiconductor.

And when the bond breaks, there will be a vacancy of one electron and that vacancy is called the hole. There is a deficiency or a vacancy of one electron and that deficiency is called a hole. Fourth electron of germanium also tries to form covalent bond and it does so by taking the advantage of any thermal motion that fortunately brings an electron from the neighboring germanium atom.

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Doping

- Due to this a hole is created in the adjacent atom that moves about in a random way due to thermal effects.

- For such a stealing action in which other electrons jump into the holes , some energy is required and is approx. equal to the ionisation energy of donor levels in the same material.

- Impurity atoms that contribute holes in this manner are termed as acceptors because they accept electrons from germanium atom.

Due to this a hole is created in the adjacent atom that moves in a random way due to that thermal effects. For such a stealing action in which other electron jumps into the holes, some energy is required and it is approximately equal to the ionization energy of the donor levels in that same material. Impurity atoms that contribute holes in this matters are termed acceptors material because they accept or grab electrons.

For this particular case it is germanium atom. So in the donor impurity they donates the electron. So there are more free electrons are available in the crystal lattice for conduction of the current and in acceptor impurity they accept or grab the electrons. So there are more number of deficiency of electrons or more number of positive holes are available in this material when we put the acceptor impurity inside the intrinsic material.

So once we have an understanding of what is a doping, so based on this concept we can classify the semiconductor in two different class as we have said earlier.

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One is called intrinsic or pure semiconductor another is called extrinsic or impure semiconductor. An intrinsic semiconductor is a pure semiconductor free from impurity that is there is no external doping or there is no external impurity is there. And that is by definition is an intrinsic semiconductor. So pure silicon and germanium in their natural form are intrinsic semiconductor.

Unless until I dope silicon or germanium to make any useful device so that is they are in the intrinsic form. Band gap of silicon and germanium are respectively 0.7 eV and 1.1 eV. Alternatively an intrinsic semiconductor may be defined as one in which the conduction electron is equal to number of holes. Hence there is not an current conduction occurs in them even after increasing the temperature.

So in general the material is neutral. So number of the negative charge carrier should be equal to the number of positive charge carrier. So that is why in a normal condition, the thermal motion is not able to make enough amount of free electron to have a reasonable amount of conductivity in this intrinsic semiconductor.

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Semiconductors on the basis of doping

- SILICON is a chemical element with symbol Si and atomic no. 14.
- It is a tetravalent metalloid more reactive than germanium.
- It was first prepared and characterized in pure form in 1823 and was given the name silicium which was taken from Latin word silex which means hard stone or flint.
- In making earth's crust silicon is the second most abundant material after oxygen.

Silicon is a chemical element with the symbol Si. And as we have said repeatedly, this is the heart of the electronics devices. And its atomic number is 14. We have learned how to put the 14 electrons in the different energy levels. So our basic chemistry we have learned that we have sequentially put the electrons and we can write it at different orbitals like this way 1s 2, 2s 2, 2p 6, 3s 2, 3p 4. So 2 + 2 4, 16, 12.

And then to make it 14 I would have to put outer orbit 2. So that will be 14. So in outer orbit how much electrons are there? 3s 2, 3p 2. So that is 2 + 2 4 electrons. So the outer orbit of a silicon atom consist of a four electrons. It is a tetravalent atom because tetra means four, since its outer orbit has four electrons and metalloid more reactive than germanium.

It was first prepared and characterized in pure form in 1823 and was given the name silicium which was taken from the Latin word silex which means hard stone or flint. In making earth crust silicon is the second most abundant material after oxygen. So silicon is the second most abundant material in the earth crust.

So that is why getting the silicon although it is very difficult and processing the silicon is quite costly, silicon has became the one of the important material of fabricating different optoelectronic devices.

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Semiconductors on the basis of doping

- Silicon is a semiconductor , it has a negative temperature coefficient , since the no. of free charge carrier increase with temperature.

- Single crystal silicon in its pure form is used to construct many of the electronic devices. In 1954cthe first silicon transistor was introduced and quickly silicon became the semiconducting material of choice.

It is a semiconductor which has a negative temperature coefficient. What do you mean by the negative temperature coefficient? Here the number of the free charge carriers increase with temperature; so total number of charge carriers that increase with temperature. Single crystal silicon in its pure form is used to construct many of the electronic devices.

In 1954, the first silicon transistor was introduced and quickly silicon became the semiconductor material of the choice. This is the diagram of how an intrinsic silicon looks like.

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Figure 1   2-D Crystal Lattice of Silicon
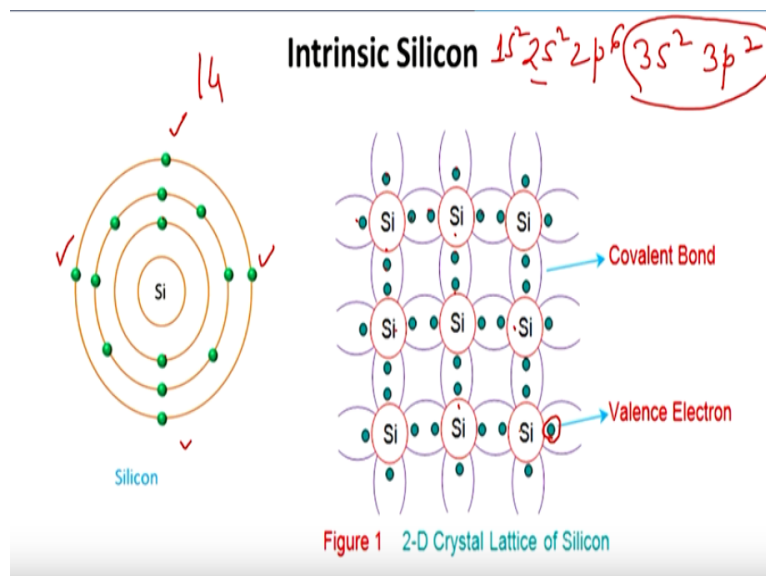
So you remember, we said that silicon has 14 electrons and we have put the 14 electrons once again If I write it 1s 2, 2s 2, 2p 6 because p orbital can accommodate

maximum six electron, 3s 2, 3p 2. So s orbital that has two electron right, the one and two. Then 2s 2, 2p 6, right? So then we are putting that 2s 2, 2p 6. Then finally the outermost orbital has four electron. So 1, 2, 3, 4.

This is for the one silicon atom. Now remember in a crystal lattice there are so many silicon atoms. So once I put all the silicon atoms together so then it looks like that. So each silicon atom has four valence electron which it can share with the neighboring silicon atoms. Now the neighboring silicon atoms which is this, it is also four valence electron like this.

Now it is much easier for this silicon atom to share one more electron from the neighboring silicon atom and make a covalent bond. So that is why they are making a covalent bond here. So similarly, so this silicon atom is making a covalent bond with this neighboring silicon atom. So it can mix, let us consider the central silicon atom here.

So it can make one covalent atom covalent bond with the here, one with here, one with here and one with here. So how what is the number of electrons in its outer orbit now? 2 + 2 + 2 + 2, 8. That is that nearest stable atomic structures. So the covalent bond exist in the case of silicon. And this electron which is in its outer orbit they are called valence electron.

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Semiconductors on the basis of doping

- GERMANIUM is a metalloid with symbol Ge and atomic no. 32.

- It is a lustrous, hard, grayish white metalloid in the carbon group chemically similar to its group neighbor Silicon.

- In 1869 Mendeleev predicted its existence but credit of its discovery goes to Clemens Winkler who named the element after his country Germany's name as Germanium.

- The energy band gap in germanium is of the order of 0.7 eV. Historically the first decade of semiconductor electronics was based entirely on Ge. Today however its production for use in semiconductor electronics is a small fraction (2%).

Another important semiconductor material which is also used very often in semiconductor industry is germanium. Germanium is also a metalloid whose symbol is Ge and its atomic number is 32. It is a lustrous, hard, grayish white metalloid in the carbon group chemically similar to its neighbor silicon. In 1869 Mendeleev predicted its existence.

But credit of its discovery goes to Clemens Winkler who named the element after his country Germany's name as Germanium. The energy band gap in germanium is of the order of 0.7 eV. Historically, the first decade of semiconductor element was based entirely on germanium. This is a very interesting fact. Initially silicon was not of the choice.

Initially lot of the semiconductor device was started fabricating from germanium and later on silicon picked up. Today however its production for use in the semiconductor electronics is **very** very small fraction 2%.

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Semiconductors on the basis of doping

- Today Silicon has replaced it as it is too reactive to be found naturally on earth in free (native) state. Ge ranks near fiftieth in relative abundance of the elements in earth's crust. Presently Ge major end uses are in fiber optics , infrared optics and in solar cell application .

Today silicon has replaced as it is too reactive to be found naturally on earth, native state. Germanium ranks 50s in relative abundance of the element in earth crust. And presently germanium major end use are in fiber optics, infrared optics and in solar cell applications. So especially for solar cell application in the space we use germanium based solar cells because that provides higher efficiency.

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Intrinsic Germanium
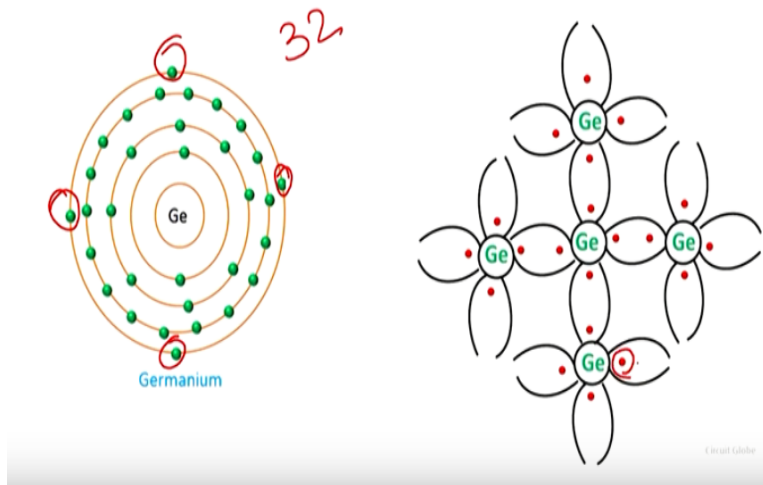
An intrinsic semiconductor looks like this. Again you look that out of this 32 electrons, germanium has 32 electrons. Out of this 32 electrons in outer orbit we have 1, 2, 3, 4 four electrons. And again like the same thing like a silicon crystal, this four germanium electrons in its outer orbit, they make covalent bond with the neighboring germanium atoms.

So there are two plus two plus two plus two eight atoms in the out orbit or outer orbit. So that got the eight electrons that means the stable atomic structures. So again, the covenant bond here also exist and this electron you call it as a valence electron.

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Semiconductors on the basis of doping

- **EXTRINSIC SEMICONDUCTOR:** Those semiconductors to which some suitable i.e pentavalent or tetravalent impurity or doping agents are added to increase its conductivity is called extrinsic semiconductor.

- Pentavalent doping agents (Bi, Sb ,As ,P)are donor atoms and Trivalent doping agents (Ga ,In ,Al ,B) are acceptor atoms.

- Extrinsic semiconductor is of two types:-
  N-Type semiconductor , P-Type semiconductor

In opposed to the intrinsic semiconductor as the name suggests, extrinsic semiconductor is those semiconductors to which some suitable pentavalent or

tetravalent impurity or doping agents are added to increase its conductivity that is called extrinsic semiconductor. As we mentioned that intrinsic semiconductor in its pure state has very negligible conductivity.

So that is why we need to put some doping or external material, so that the effective number of the charge carriers increase in this material. Now when we put some external material inside the pure intrinsic material, then those semiconductors are called extrinsic semiconductor. Relevant doping agent like bismuth, antimony, arsenic and phosphorus they are donor atoms.

And gallium, indium, aluminum and boron they are called trivalent atoms and they are considered as an acceptor impurities. Extrinsic semiconductor can be classified of two types, one is called N-type semiconductor and another is called P-type semiconductor.

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Extrinsic Semiconductors

- **N TYPE-SEMICONDUCTOR:-** when a pentavalent impurity atom (Sb,P) is added to Ge or Si crystal .

- It replaces a Ge or Si atom in the crystal lattice four of five valence electrons of the impurity atom from covalent bonds with one each valence electron of four Ge or Si atoms surrounded it and the fifth valence electron become free to move with in the crystal.

- This free electron act as a charge carrier thus by adding pentavalent impurity to Ge or Si the no. of free electron increases.

- Diffused impurities with 5 valence electrons are called
  DONOR ATOMS.

So an N-type semiconductor when a pentavalent impurity atom, like antimony or phosphorous is added to germanium or silicon crystal it replace a germanium or silicon atom in the crystal lattice four of five valence electron of the impurity atom from covenant bonds with each valence electron of the four germanium or silicon atom surrounded it and the fifth valence electron become free to move within the crystal. We will come to this picture.

So four valence electron of the silicon or germanium make covalent bond with this four valence electron of the antimony or phosphorous. So but these are pentavalent impurity. So one more extra electron is there. So that one more extra electron is now available for the conduction. This free electron acts as a charge carrier and thus by adding impurity which are pentavalent to germanium or silicon the number of the free electrons increase. Diffused impurities with five valence electrons are called donor atoms.

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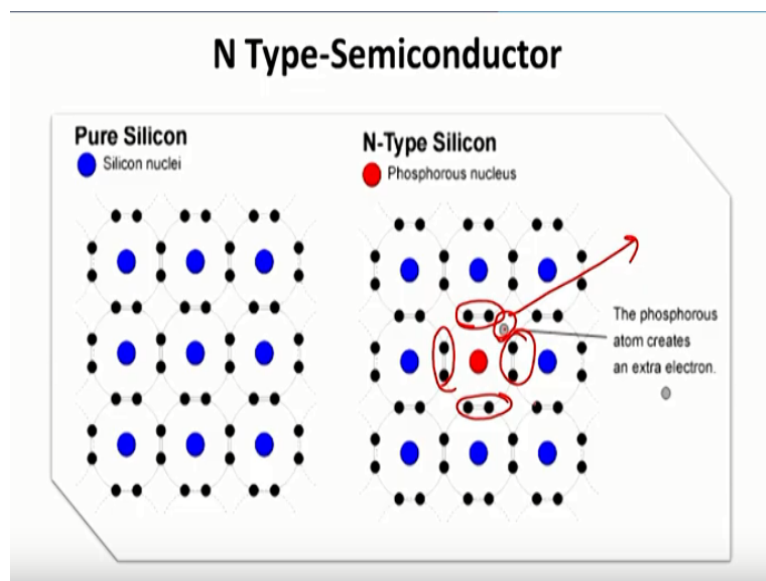
So for example, you look this is the pure silicon and the blue color core is the silicon nuclei and electrons are orbiting around the nucleus and we are putting a phosphorous as a pentavalent impurity in this N-type semiconductor. So the phosphorous atoms what they will do? So the phosphorous atoms has four electrons. So this four electrons, they will share with the neighboring silicon atoms.

So they will make covenant bonds and that is stable, but phosphorous in the outer orbit has five valence electron. So one electron is free and that free electron is available for the conduction. So all the other two electrons they are covalently shared with the neighboring phosphorous atom. When I put an impurity so what happens like you know, so this four electrons of the phosphorous they can make a covalent bond with the silicon.

But one electron this is extra and that can wander around the crystal. So now if I put let us say 10 to the power 12 phosphorous atoms, so I can generate such number of

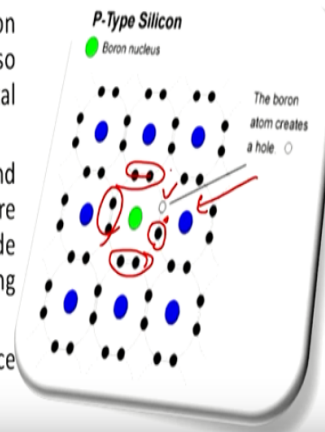electrons in this material. So those electrons are now free to conduct the electricity. Okay, and what is then the P-type semiconductor?

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When a trivalent impurity, for example boron or aluminum is added to a germanium or silicon crystal it also replace one of germanium or silicon atom in the crystal lattice. All its three valence electron form covalent bond with each valence electron of the three and remaining one state is empty, which is called hole and this hole moves around the crystal.

Germanium or silicon atom so when we put the trivalent impurity like aluminum or boron, so the three electrons of this impurity they forms the bond with the silicon or germanium atoms but one is still empty. So that one electron that comes by breaking the bond and that breaking the bond is actually gives a positive charge because it is an absence of electron and that we call as a hole.

Thus a diffuse impurity with three valence electron are sometimes also called the acceptor impurity or acceptor atom. Look at this example here. Again in this case, we are putting in the silicon atom, the boron. So what will happen? Boron will replace one of the silicon atoms and three of them will form the covalent bond with the silicon atoms.

But there is one electron, but boron do not have more electrons to make the sharing bond. So what can be done? One bond can break from the nearest silicon atom and it
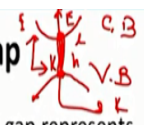
can come and share the electron here and once the bond breaks, so that means there is a vacancy has been created here and that vacancy moves here and that vacancy we call it as a hole.

So if I put let us say 10 to the power 12 boron atoms in this case here, that number of vacancy or holes will be created in the pure silicon. So here the positive charge will prevail. That was the story of the semiconductor based on the doping like we can put either a pentavalent impurity which gives us more number of negative charge carrying the material or we can put trivalent impurity which gives more number of effective positive charge inside the material.

And finally, what is the role of putting those doping material, to increase the conductivity. So based on that we have divided the material on intrinsic and extrinsic and later on extrinsic material based on the number of prevalent charge carriers we can divide into N-type or P-type material.

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Similarly, the semiconductor can also be divided based on its band gap. Based on the band gap or more precisely how the shape of the band gap looks, the semiconductor material can be divided into two distinct class. One is called direct band gap semiconductor another is called indirect band gap semiconductor. Let us look at this. Direct and indirect band gap semiconductors.

The band gap represents the minimum energy difference between the top of the valence band and the bottom of the conduction band. In a direct band gap semiconductor, the top of the valence band and bottom of the conduction band occur at the same values of the momentum. So if I draw, this is my valence band and this is my conduction band.

So what we are saying here, the top of the valence band, this is the valence band and this is your conduction band, right. So the top of the valence band and the bottom of the conduction band they lies along the same line. This is my E-k diagram. This is E this is k or you can also put it like this. This is E this is k. In a direct band gap semiconductor a direct recombination take place with the release of the energy equal to the energy difference between the recombining particle.

So let us say an electron which is now in the valence band that got excited to the conduction band, when it relax it comes back. So the electron is now going here, so there is an electron here. So once the electron goes there will be vacancy created in the valence band and you call that vacancy as a hole. So I have created an electron and hole together okay.

So now after some time when the electron jumps back, so this electron and hole will recombine and the recombination will take place when the electron and hole will combine. How much energy will be released? The amount of energy will be released that is equal to the amount of this band gap because there is no spatial separation between the top of the valence band and the bottom of the conduction band.

And this kind of direct band gap semiconductor it is worthwhile to mention that the choice for fabricating the optoelectronic devices like light emitting diode. The most thoroughly investigated and studied direct band gap semiconductor material is gallium arsenide GaAs.

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Direct and Indirect Band Gap Semiconductor

- A indirect band-gap semiconductor is one in which the maximum energy level of the valence band are misaligned with the minimum energy level of the conduction band with respect to momentum.

- Due to a relative difference in the momentum, first, the momentum is conserved by release of energy and only after both the momenta align themselves, a recombination occurs accompanied with the release of energy.

- The probability of a radiative recombination, is much less in comparison to that in case of direct band gap semiconductor semiconductors.

On the other hand an indirect band gap semiconductor is one in which the maximum energy level of the valence band are misaligned with the minimum energy level of the conduction band with respect to the momentum. Here like you know, unlike the previous case, let us say this is my E-k diagram. If the top of the valence band is here the bottom of the conduction band will be here.

So the top of the valence band and the bottom of the conduction band they do not lie along the same vertical axis. They have been replaced along the x axis. So that is why it has been told here in which the maximum energy level of the valence band are misaligned with the minimum energy level of the conduction band with respect to the momentum. This axis is the momentum axis.

So along the x axis or momentum axis that maximum energy or top of the valence band and the minimum energy or the bottom of the conduction band has been displaced. Due to a relative difference in the momentum first the momentum is conserved by release of energy and only after momentum align themselves a recombination occurs accompanied by the release of energy.

So electron cannot directly jumps back from here to here because that will violate the momentum conservation principle. First it has to drop from here to here. So that it aligns its momentum space and it comes back from here and then it jumps. So there is a momentum conservation has to be fulfilled here and then there is an energy jump happening.

So the amount released energy that is not exactly equal to the difference between this two extreme point, the top of the valence band and the bottom of the conduction band. But there is first a electron which jumps to a virtual state which stays in between and from that virtual state then the electron jumps to the top of the valence band. The probability of the radiative recombination is much less in comparison to that in the case of direct band gap semiconductor.

Now what is the radiative recombination? When an electron and hole recombine and give light that we call as a radiative recombination. And if the electron and hole recombine and if they do not give light, but give something other form of energy let us thermal energy, then we call it as a non-radiative recombination. It is obvious like you know, the radiative recombination chance is much less in the case of a indirect band gap semiconductor.

Because electron has to first jump to this virtual state or to this defect states and from there it has to jump to the bottom of the conduction valence band. So mostly sometimes we called this kind of emission happens by the phonon emission. So the except the photon there can be also the phonon plays a role here. Phonon is the quantum of the lattice vibration.

Later on we will learn that the photon, just like photon is the quantum of the electromagnetic radiation quantization phonon is the quantization of the lattice vibration. And that phonon also plays a very important role in constructing these semi-conducting devices.

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Direct and Indirect Band Gap Semiconductor

- The two well-known intrinsic semiconductors, Silicon and Germanium are both Indirect Band Gap semiconductors.
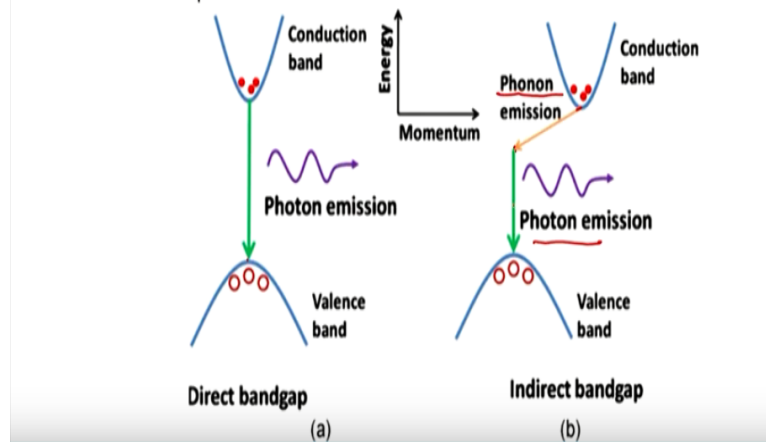
So the two well known intrinsic semiconductor silicon and germanium are both indirect band gap semiconductors. So it is very important to remember that silicon and germanium are not direct band gap semiconductor, but they are indirect band gap semiconductor. So for a direct band gap semiconductor as we said, look this is the conduction band and this is the valence band.

So the electrons are here, these are the holes. So electrons excited from the valence band to the conduction band go and stay here and that the vacancy is called the hole. And when the electron jumps back after sometimes, so this electron can be combined with the hole and the amount of energy which will be released because of the combination that emits in terms of the photon emission.

And these types of emission is called radiative recombinations. Whereas in the case of an indirect semiconductor or indirect band gap semiconductor, we can look that the conduction band is here, valence band is here. So they are displaced along the k axis. They are displaced along the momentum axis. Now the photon emission can happen along the same value of the momentum.

So first the electron jumps from here to here and that includes a phonon emission which is a quantum of lattice vibration followed by photon emission which is the quantum of electromagnetic light vibration or electromagnetic vibration. So obviously, if the light emission, if this part we call as a radiative recombination, the

radiative recombination not happened directly or the probability of radiative recombination in this particular case is less than the direct band gap semiconductor.

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On the basis of position in periodic table

- The atoms in a semiconductor are materials from either group IV of the periodic table or from a combination from group II and group IV (called II-VI) semiconductors.

- There may be semiconducting materials from group IB, IIB or either a recombination of III-V group and also can be formed by combination of IV-VI group.

- Elements which are highlighted in the periodic table are the key elements for elementary semiconductors and compound semiconductors.

Similarly, on the basis of the positions in the periodic table, we can also distinguish the semiconductor. For example, the atoms in a semiconductor are materials from either group IV of the periodic table or from a combination of group II and group IV called II-VI material.

There may be semiconducting materials from group IB, IIB or either a recombination of III and V group and also can be found by combination of IV and VI group. Elements which are highlighted in the periodic table are the key elements for elementary semiconductors and compound semiconductors.

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Let us look at this periodic table. So what we have highlighted like aluminum, silicon, phosphorous, selenium, arsenic, germanium, gallium, zinc, copper, cadmium, indium, tellurium. So these are the like you know I mean common example of the semiconducting material. Either individually or by combining together they make a semiconductor.

Like you know we can make like you know aluminum, phosphorus, aluminum then we can make like you know gallium and we can take arsenic we can make gallium arsenide alright. So that is why like we can make different we can mix copper and S. So different kind of semiconductor we can make by a combination, permutation combination of all these material.

So what we learnt right you know based on the three different factors. One on doping, another on the positions of the band gap and another on the periodic table or the element compositions we can distinguish the semiconductor in three different categories. One is the direct band gap semiconductor another is the indirect band gap semiconductor that was based on the positions of the band gap.

In a direct band gap semiconductor what happens? The positions of the valence band maxima and the positions of the conduction bad minima they lies along the same k axis or they lies at the same value of k. Whereas in an indirect band gap semiconductor, they are displaced along the k axis. Indirect band gap semiconductor example as silicon and germanium.

Whereas direct band gap semiconductor example is gallium arsenide. Similarly, based on the doping or the external impurity atoms we can divide the semiconductor either a intrinsic or pure semiconductor, where there is no external doping like pure silicon or pure germanium or we can put the doping inside the material and we call it as an extensive semiconductor or impure semiconductor.

And for example we can put either a pentavalent impurity and if we put a pentavalent impurity then the number of the electrons increase. So we call them as a donor impurity and this type of semiconductor are called N-type semiconductor or we can put a trivalent impurity like aluminum or boron and if we put that then there will be a absence of the electron or an excess of hole in that semiconductor and this kind of impurity is called acceptor impurity.

And this kind of semiconductor material is called P-type semiconductor material. And then finally what you have learned that the semiconducting material can also be compromised by the different permutation combinations of the periodic table element distributions. So based on that also we can find out or we can make different semiconducting materials. Thank you.