Semiconductor Optoelectronics
Prof. M. R. Shenoy
Department of Physics
Indian Institute of Technology, Delhi

Lecture - 10
Semiconductor Materials

Today we will discuss about semiconductor materials in this talk our focus will be on semiconductor optoelectronic material as the course being on semiconductor optoelectronics.

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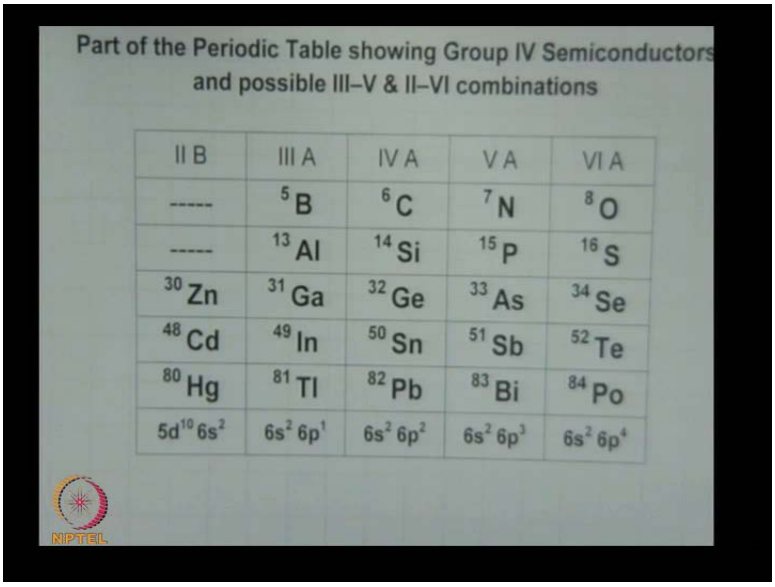

What I have put here is part of the periodic table the part of the periodic (( )) that shows group two, three, four, five and six elements of group two part of it. There are 2 a, 2 b and so on, but do not worry about a, b, c and so on, right now group two, three, four, five and six.

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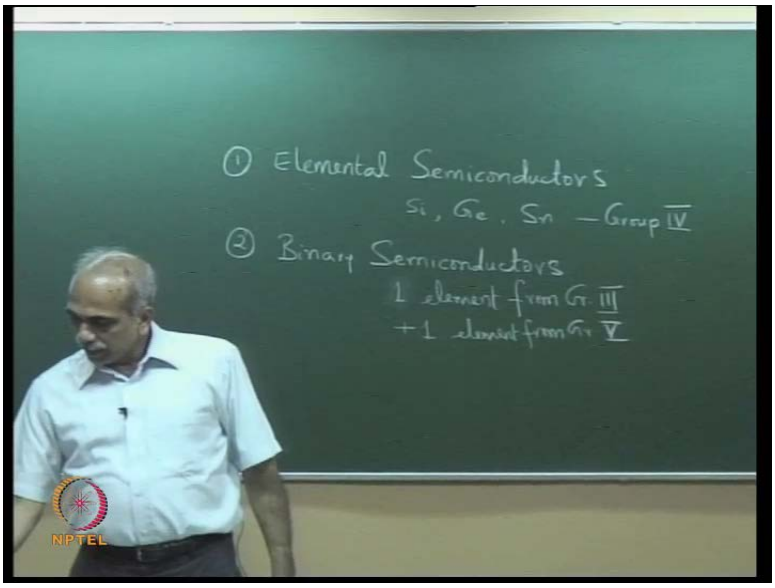

The elemental semiconductors the common elemental semiconductors comprise of group four elements, so elemental semiconductors. First the most common elements are Silicon, Germanium and also Tin, all group four elements as an element these are semiconductors, which means the basic definition of semiconductor (( )) Silicon, Germanium and Tin. We also have binary semiconductors or compound semiconductors; Binary semiconductors. These are usually either two elements two elements sorry, these are with one element from group three, one element from group three plus 1, element a compound formed by one element from group three and one element from group five group five.

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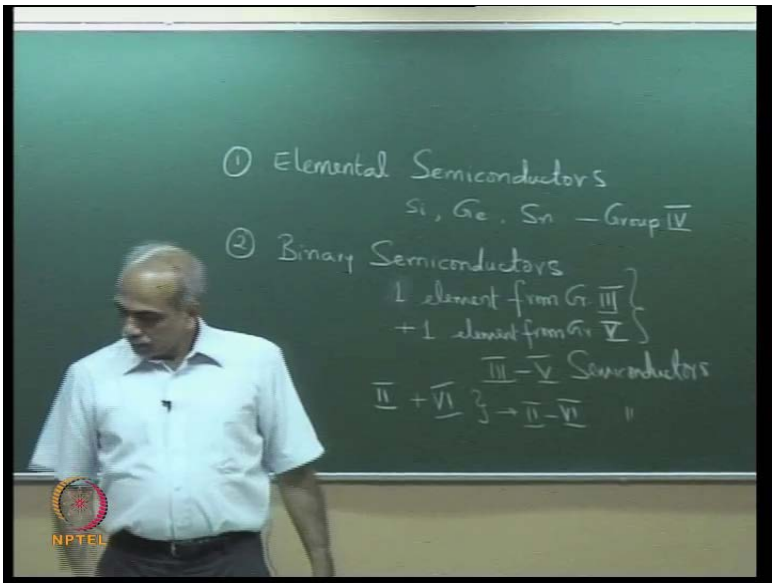

For example, if you see the table here the elemental semiconductors are here in group four Silicon, Germanium, Tin, the Binary semiconductors are 1 element from group three and 1 element from group five. The most commonly used elements are compounds are Gallium arsenide one from three and one from five Gallium arsenide. You also have a Aluminium phosphide, Indium phosphide all possibilities are there one from group three one one from group five. So, these are also sometimes called as three five semiconductors three five semiconductors.

Stable compounds of one element from group three and one from four, you could also have one element from group six, one element from group two and one element from group six forming what are called two six compounds two six semiconductors. For example, mercury here and one from six Cadmium Telluride is a widely used semiconductor, Zinc Selenide or Cadmium Selenide or Mercury Selenide, Mercury Telluride are all group two six semiconductors.

So, you may have three five semiconductors or two six semiconductors, what I have shown in the last row here in this, last row of this table is the electronic configuration in the outermost shell of the element. For example, here mercury is there, mercurys outermost shell has 5 d 10 and 6 s 2 it is group two because in the outermost shell there are 2 electrons. This is group three for example, this is Thallium 6 s 2, 6 p 1, all elements

in this group three have a configuration in the outermost shell like 6 x 2, 6 p 1 for Thallium, for Indium it is 5 s 2, 5 p 1.

If you go to Gallium it is 4 s 2, 4 p 1 and if you go to Aluminium it is 3 s 2, 3 p 1. Obviously if you come to Boron it is 2 s 2, 2 p 1. Boron has 5 atomic number is 5, which means there are 5 electrons the electronic configuration is 1 s2, 2 s 2, 2 p 1 exactly like this in the last column for all of these you can see that it is 6 s 2, 6 p 2 for Lead, but if you go to Tin, Germanium it the shell number reduces, but they have s 2 p 2 configuration, which means that there are 4 electrons in the outermost valence shell.

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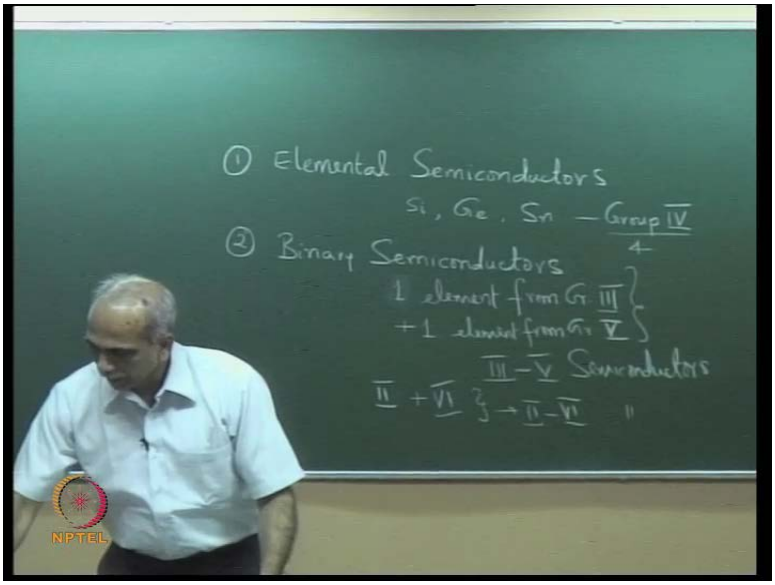

In group four there are four electrons in outermost valence shell and therefore, they form covalent bond sharing four electrons with an adjacent Atom to make an Octet, that is eight electron shell, which completes the Octet. If you take one from three and one from five, there are three electrons in the outermost shell here and five electrons in the outermost shell here and therefore, you again have Octet complete three and five. Similarly, in two six we have two and six making it an Octet.

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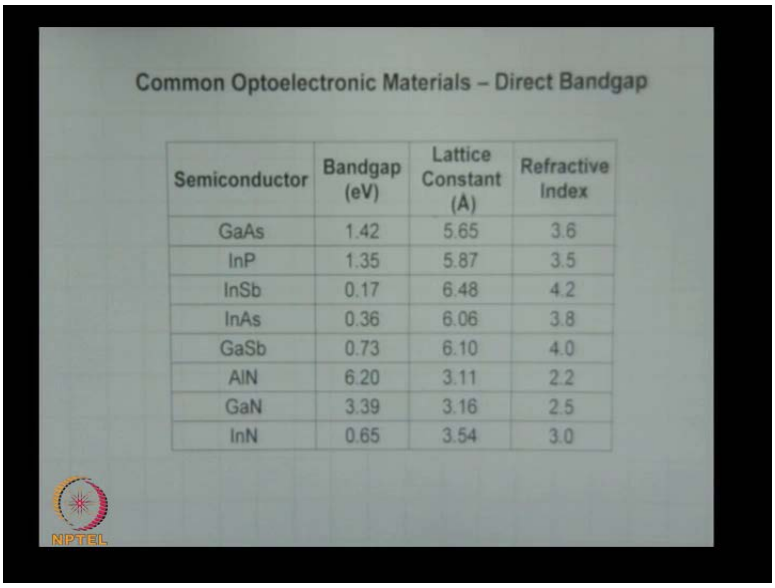

So, the outer shell has an Octet which means it is a complete shell, makes stable compound. So, these are Binary semiconductors, typical some of the Binary semiconductors and their Band gap. I display here I hope you are able to read this Gallium arsenide bandgap is 1.42 e v and Lattice constant is 5.65 Angstrom, Refractive index is given approximate Refractive index near the cut off your length or near the bandgap your length is also listed.

So, you can see some of the common binary compounds which are used Gallium Arsenide, Indium Phosphide, Indium Antimonide, Indium Arsenide, Aluminium Nitride these are the wide bandgap semiconductors, Gallium Nitride has a bandgap here of 3.39 electron volts. This is nowadays this is very important substrain Gallium Nitride to get blue LEDs and blue lasers it is the Gallium Nitride substrain, which is used Indium Gallium Nitride.

So, Indium Nitride what you see is also the numbers are listed to see that some of them have Lattice constant 3. Something, these the last three have Lattice constants 3.1, 3.1, 3.5 Angstroms as the lattice constant, but if you see the other common binary compounds like Gallium Arsenide, Indium Phosphide they have 5.6, 5.8 as the lattice constant this has some important implications which we will discuss shortly, so these are all direct bandgap materials the compounds that I listed here are all direct bandgap materials.

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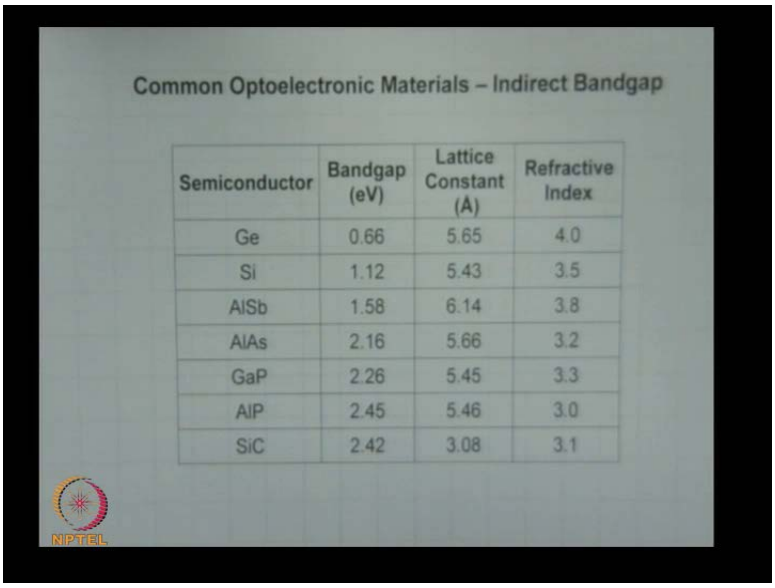

I have a second list here you can find these numbers in books and references, a common indirect bandgap of optoelectronic materials here Germanium, Silicon, Aluminium Antimonide, Aluminium Arsenide, Gallium Phosphide, Aluminium Phosphide and Silicon Carbide. Silicon Carbide is also today an important material used for humidity detectors. You see its bandgap is very large 2.42 electron volts and Lattice constant is about 3 Angstroms. All of them are high refractive indices as you can see unlike the normal glass most of them have refractive indices 3 to 4, these are all indirect bandgap materials, some of the common direct bandgap and indirect bandgap materials.

Now, the choice of semiconductor for any application depends on the bandgap, so this is the direct bandgap material. Now, when we have so many semiconductors how does one choose the required semiconductor? This is determine by the bandgap wavelength or the cut off wavelength, in optoelectronics most of the material properties, which are essential for the device functioning is Emission and Absorption, so it is the bandgap which determines what is the wavelength it can Emit and Absorb.

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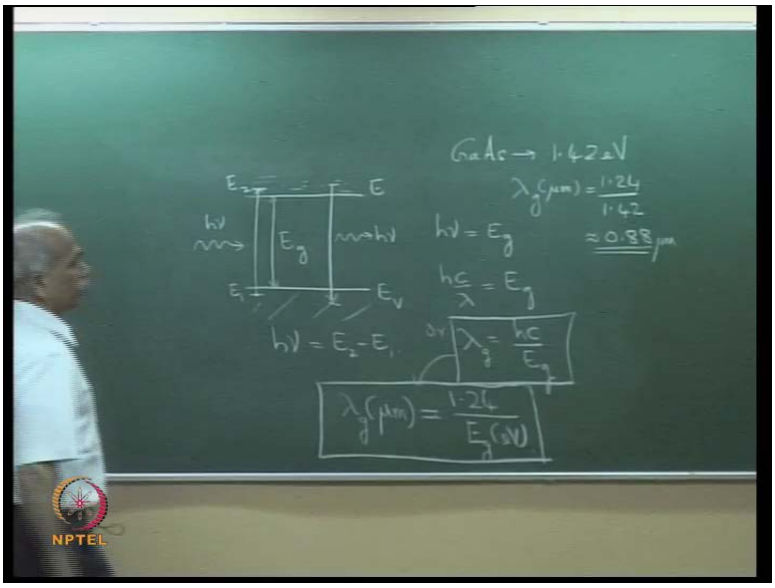

So we have E v, E c and this is the E g. If a photon is incident, photon of energy h nu is incident on the semiconductor, so this is the semiconductor which has electrons and vacant state or some electrons there. Incident photon can be observed provided, if I call this as energy E1 and E2 then h nu must be equal to E2 minus E1, if an electron sitting at energy level E1 makes an upward transition to an energy level E2, then E2 minus E1 is equal to h nu. Therefore, the smallest energy photon which can be absorbed by an electron transition, by an inter band transition, is h nu equal to E g that is the frequency or energy corresponding to the smallest smallest energy corresponding to the photon which could be absorbed.

Similarly, if there are electrons large number of electrons here, they could make the make downward transition and the difference in the energy will be emitted in the form of photon, so this emits energy in form of photon and the smallest energy smallest energy photon will correspond to h nu is equal to E g. So, if we write this h c by Lambda is equal to E g or Lambda is equal to h c h c by e g and this is called the bandgap wavelength lambda g is equal to h c by E g, h is the plant constant, c is the velocity of light in vacuum, which are constants so you can substitute values to this.

If you substitute the values you find that lambda g in micrometers is given by approximately equal to 1.24 divided by E g in electron volt, this is a very useful formula. The Bandgap wavelength in micrometer is approximately equal to 1.24 divided by E g in

e v. If I give you a material and say alright Gallium Arsenide has a Bandgap, Gallium Arsenide has Bandgap equal to 1.42 e v, what is lambda g the bandgap wavelength?

That is the smallest energy photon that can be observed is this, but in practice we handle sources with wave length we normally do not talk in terms of energy, but in terms of wavelength and therefore, lambda g in micrometer is equal to 1.24 divided by 1.42, which is approximately 0.88 micro meter, so a quick estimate is given by this formula 1.24 divided by 1.42 approximately 0.88 e v. Indium Phosphide has a bandgap of 1.35, Gallium nitride has a bandgap of 3.39 or 3.4.

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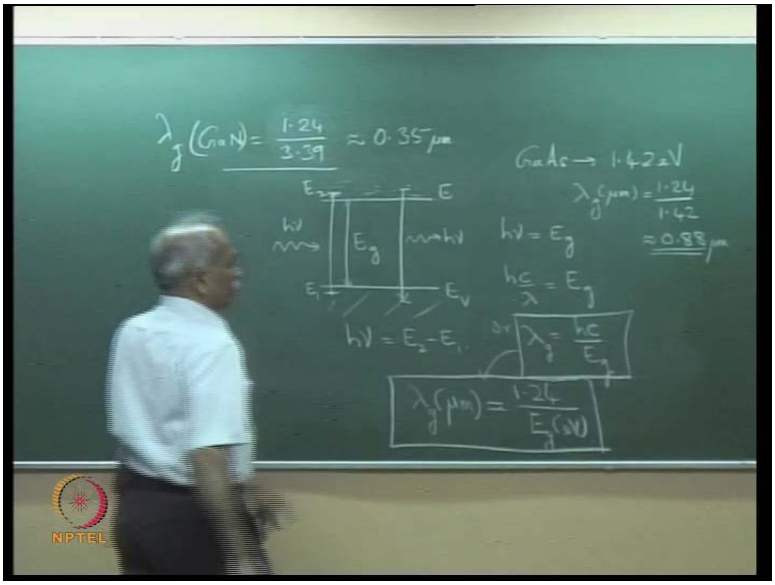

So, which photons what energy photons it can absorb or emit you can immediately find out Gallium Nitride do not need a calculator, Gallium Nitride is equal to lambda g for Gallium Nitride lambda g for Gallium Nitride is 3.4 divided by 1.24 oh sorry that is E g, so Gallium Nitride is 1.24 divided by 3.4 or 3.39 you can find out approximately. This is approximately equal to how much is this?

Approximately .35 or something .36 micrometers please check, but this is a very useful too instead of substituting h which is 6.6 into 10 to the power minus 34 c and then E g you have to convert into joules, because 6.64 into 10 to the power of minus 34 is joules second h and therefore, you have to convert E g to joules, but this is a very useful formula for engineers for a quick estimate of bandgap.

So, depending on the application you have to choose the compounds semiconductors, but we have a limited number of semiconductors useful semiconductors and therefore, if you want to continuously vary the Bandgap wave length or if you want to have materials with continuously variable Bandgap, then we go for the third type of materials that are called Ternary compounds.

So, first we have seen elemental semiconductors very limited choice, then we have Binary semiconductors, when we have Binary semiconductors the choice becomes larger because you can have any 1 compound 1 element from group three and 1 element from group four group five and therefore your choice becomes wider, so you have more number of a useful materials however you do not have continuously variable Bandgap materials and therefore, the third type of material are called Ternary compounds.

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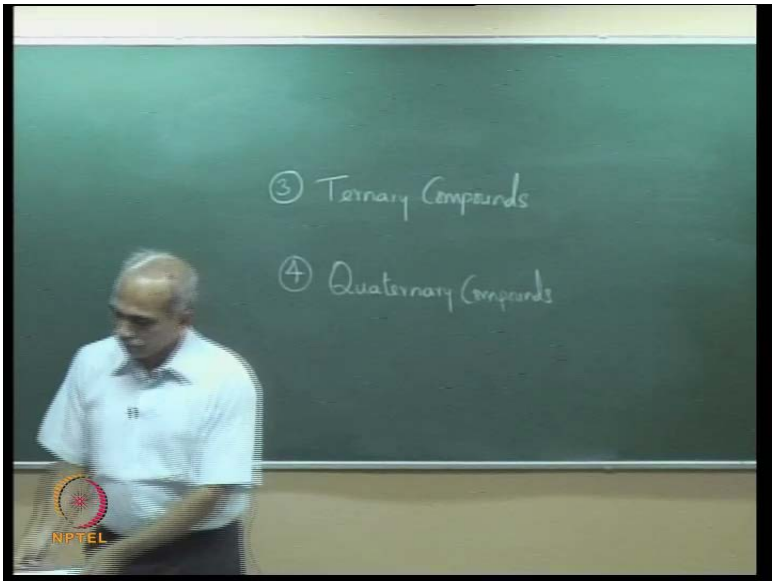

So, Ternary compounds ternary compound and Quaternary compound ternary and quaternary compound, so let me put back the table of elements here, in Ternary compound as name indicates there are 3 elements and in Quaternary compound there are 4 element, in Ternary compound we have 2 elements from group three and 1 from group five.

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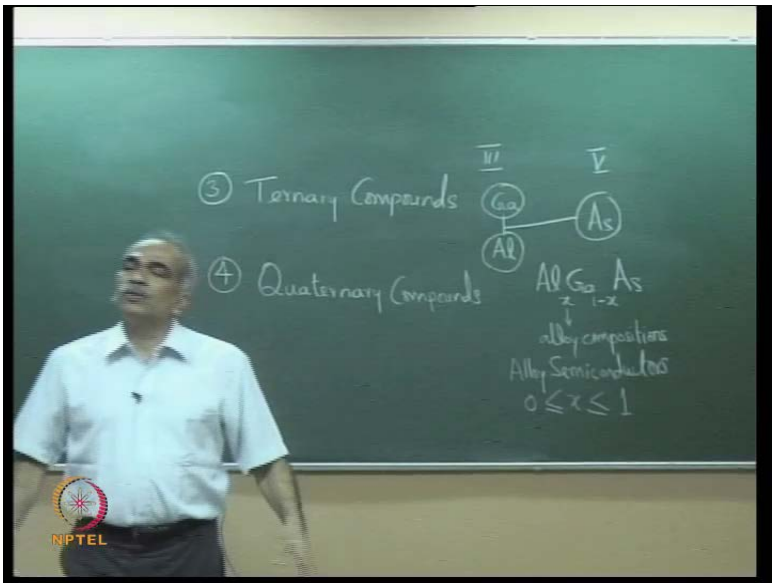

For example, Gallium, Aluminium and Arsenite, so from group three we have Aluminium, Gallium and Arsenite, so Gallium, Aluminium, Arsenite or you can have 1 element from group three, so this is from group three, there are still three five compounds still three five compounds, but instead of one element we have two elements, so how do we represent this? We represent this as ALx Gallium 1 minus x and Arsenite, where x is the alloy composition these Ternary compounds are also called Alloy semiconductors. alloy semiconductors

What kind of values are used? Generally x can lie anywhere between, so x lies between 0 less than or equal to 1, usually x lies between .1 to .5, but in principle it could lie anywhere in this region. What does that mean? If you put x equal to 0, x equal to 0, 1 minus 0 is 1, so we simply have Gallium Arsenite, if we put x equal to 0 the material is Gallium Arsenite, if you put x equal to 1 that means the Gallium is 0, we have the Binary compound Aluminium Arsenite.

So, this is an alloy where x fraction of Gallium Atoms are replaced by Aluminium Atoms, x fraction of Gallium Atoms are replaced by Aluminium Atoms at the fabrication state at the formation state, so these are called Alloy semiconductors. Now, the importance of this can be seen in Quaternary compound I come back to let us discuss the importance shortly I come to Quaternary compounds you can immediately draw an

extension that it must be having 2 elements from group three and 2 elements from group five indeed you have Gallium Indium Gallium Arsenite Phosphide.

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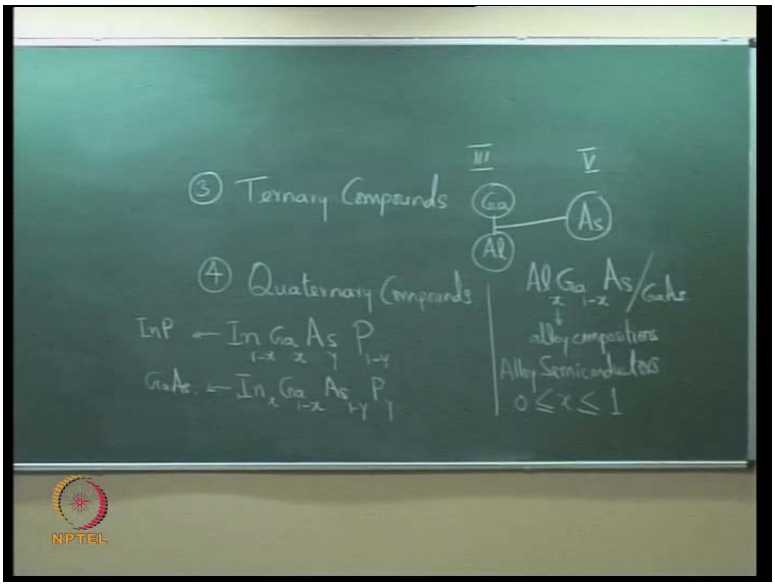

This is a very widely used material in optoelectronics and optical communication, most of you are laser layout for optical communication are fabricated by this material Indium Gallium Arsenite, I could have this as Indium and Gallium from group three, see the table Indium and Gallium are from group three and Arsenite and Phosphide Arsenite and Phosphide are from group five, so even the Quaternary compound is from a three five compound, but this could be written in this fraction or it could also be, see what is the difference between this Gallium 1 minus x and 1 minus y and P y.

I mentioned that in the formation of Aluminium Gallium Arsenite x fraction, x could be 0.1, 0.2, 0.3 typical typical numbers are 0.1, 0.2, 0.3, somewhere in that range 0.1 to 0.4 are typical numbers, but in principle you can have any combination x fraction of Aluminium Gallium Atoms are replaced by Aluminium Atoms, our starting material was Gallium Arsenite.

Gallium Arsenite is the substrate and you have replaced x fraction of Gallium by Aluminium, so this indicates that Gallium Arsenide was the substrate. So, the complete material system is very often indicated like this Aluminium Gallium Arsenite, oblige Gallium Arsenide, which means the starting substate is Gallium Arsenite, usually you

start with substate which is a binary compound and then you get the Alloys Aluminium Gallium Arsenite.

What is the difference between this two here? What is the substrate and here what is the substrate? The substrate in this case is Indium Phosphide, we started with Indium Phosphide x fraction of indium is replaced by Gallium and y fraction of Phosphorus is replaced by Arsenite. Whereas, in this case the starting substrate was Gallium Arsenite, so the x and y 1 minus x 1 minus y tells you which is the starting material. If x equal to y equal to .5 then it is difficult to tell which is the starting material, so normally x and y remain small, this is a Quaternary compound. And so Ternary and Quaternary compounds are in general three five semiconductors it could be two six also.

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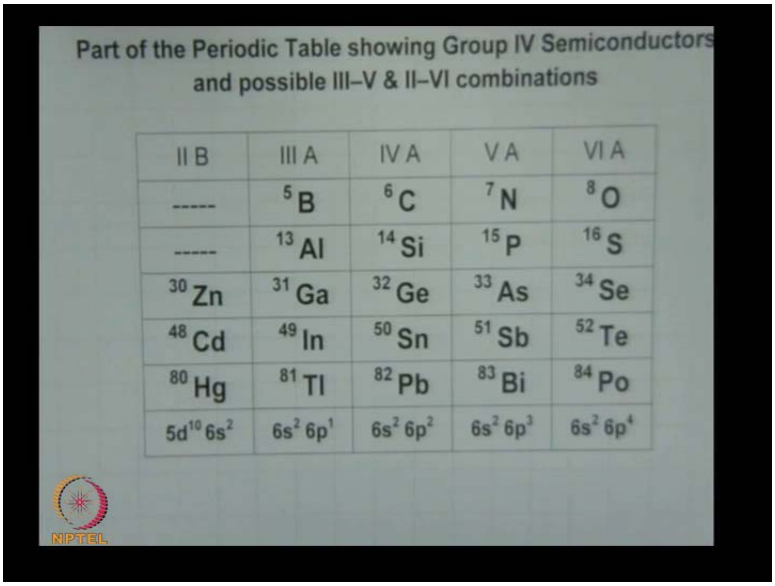

We can have two elements from two elements from group two and 1 from group six, in fact Zinc, Cadmium, Chloride or Mercury, Cadmium, Telluride is a widely used compound, Mercury, Cadmium Telluride. So, that is a two six compound this also a Ternary compound. Similarly, you could have Quaternary compound, which are also two six, you can have either three, five or two six, these are all stable compounds, stable semiconductor, but the question is why do we go for Ternary and Quaternary compounds or why go for alloy semiconductors? The Binary are compound semiconductors and the Ternary and Quaternary are in general called Alloy semiconductors, why Ternary and Quaternary compound?

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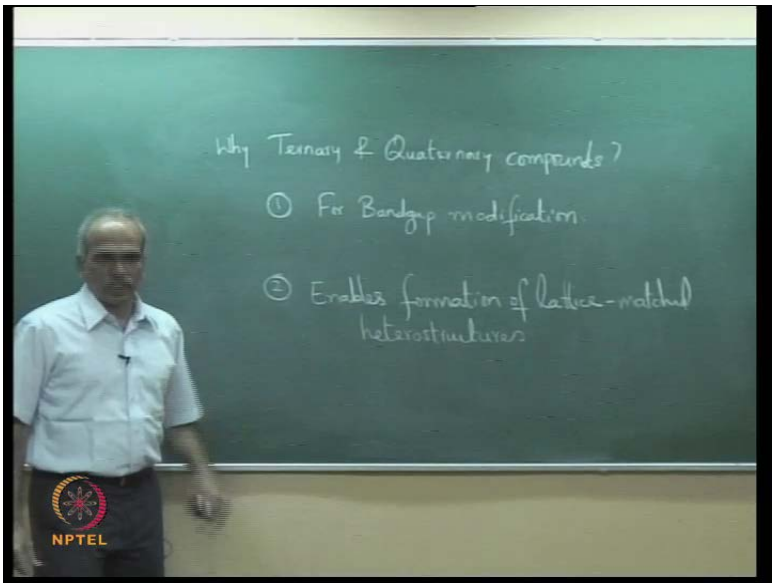

There are two important reason, let me write the answer first that for bandgap modification and second one enables formation of or growth of, formation of this is the most important lattice matched lattice matched hetero structures, lattice matched hetero structure it enables the formation or growth of lattice matched hetero structure. We will discuss the second point in the next class, hetero structures, growth of hetero structures, design considerations and lattice matching issue. Lattice matching is basically lattice constant of the compounds, which are used to form hetero structures have to be the same lattice matched. We will discuss this later first let us see for bandgap modification. As I mentioned by changing the composition of let me rub this point we will discuss that in detail for bandgap modification. Let us take an example and discuss what is for this bandgap modification.

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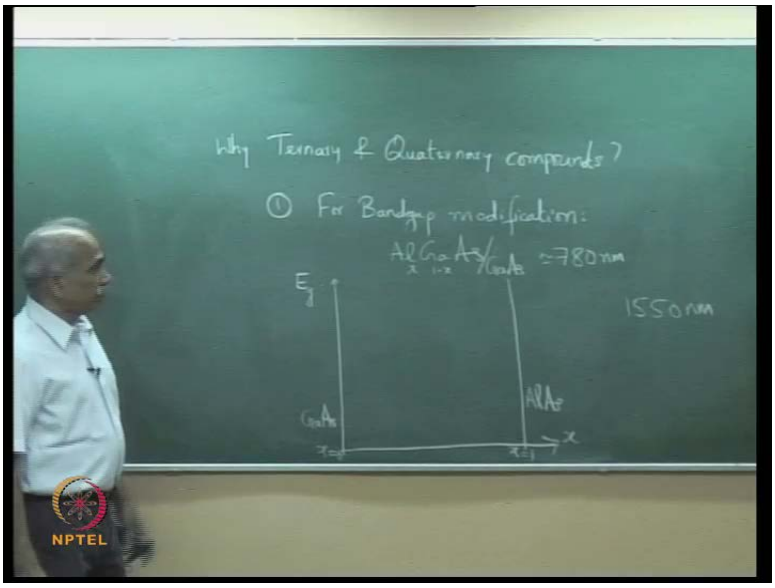

If we take the example of Aluminium, Gallium, Arsenide which is widely used material most of the laser diverse which are used in commercial products laser printers, laser pointers, all music system, c d system, all use Gallium Arsenide Aluminium Gallium Arsenide laser diode, usually emitting at 780 nanometer near in (( )). This is in fact the most widely studied material l x, 1 minus x Arsenite and Gallium Arsenite.

So most of the commercial (( )) other than optical communication as you know that optical communication takes place in the window of 1550 nanometer not 780 nanometer and therefore the material used is Indium, Gallium Arsenide, phosphide, the Quaternary material, most of the devices are either based on Indium Gallium Arsenide Phosphide or Indium, Gallium, Arsenite.

So, there are number of combinations which are possible, but remember that it is around 1550 nanometer low loss window of optical fibers and there are most of the commercial devices use 780 nanometer around, 780 nanometer and the material used in Aluminium Gallium Arsenide and Gallium Arsenite.

So, depending on x as I said if you see the bandgap the bandgap variation, so what I am plotting is x variation of x versus the material, so this is E g at x equal to 0 which means we are at x equal to 0 it is Gallium Arsenide, so Gallium Arsenide and at x equal to 1 we have Aluminium Arsenite, Gallium Arsenite all right? So, we have to bring in at another concept, that almost all semiconductors have a direct bandgap, indirect bandgap, I am

explaining the first point for bandgap modification if we plot the e k diagram or bandgap diagram for Gallium Arsenite the bandgap diagram looks something like this is E.

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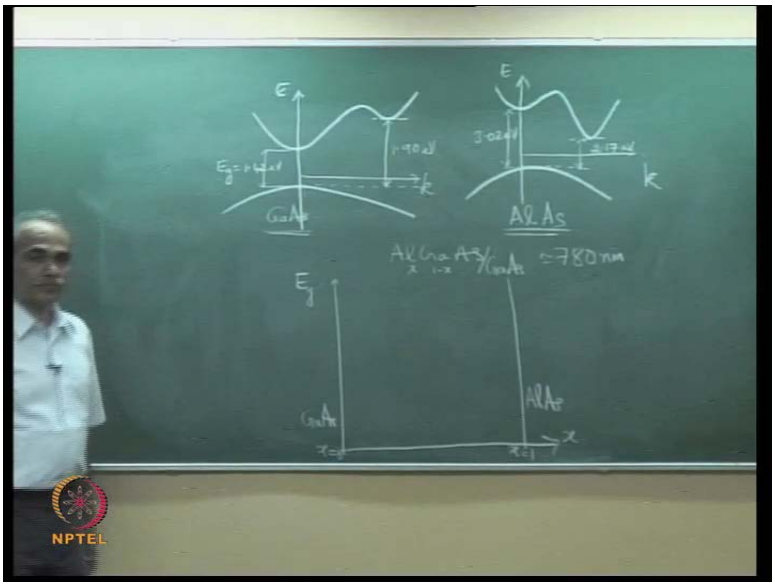

The bandgap here is this is direct bandgap and this E g is equal to 1.42 e v at 300 k, usually the numbers are put at room temperature at 300 k, 1.42 electron volts there is also a gap here corresponding to a stable minima here and this is the indirect gap and this is 1.90 e v this is for Gallium Arsenite. Almost all materials have a direct gap and a indirect gap, the indirect gap could be here at the gamma point and the direct gap could be else, the direct gap means the larger gap alright let me plot Aluminium Arsenite and then it will become clear in Aluminium Arsenite, this is again E versus k for Aluminium Arsenide, qualitative diagrams. Aluminium Arsenite has an indirect gap here this difference here is 2.17 e v and this difference here is 3.02 e v.

Please see this carefully the point is whether I take Gallium Arsenite or Aluminium Arsenite at k is equal to 0 there is a gap there is a bandgap and here also there is a bandgap there is a minima here, minima means that refers to stable states within this minima there are stable state, it means if an electron excited an electron comes here it could come down and be stable here.

So, this is a stable point, but this gap is larger than this gap this is an indirect gap this is the direct gap, a material is called indirect bandgap semiconductor or direct bandgap semiconductor depending on which one of them is minimum. The smaller of the bandgap

determines whether the material is direct bandgap semiconductor or indirect bandgap semiconductor, so Aluminium Arsenite is an indirect bandgap semiconductor because the smaller gap between the maxima of the valence band and the minima of the conduction band is smaller here which is indirect, because that does not occur at k equal to 0, that is occurring at the minima and the maxima and minima are at different k values.

So, it is a indirect bandgap semiconductor, in the case of Gallium Arsenite also you have an indirect gap, but the indirect gap is larger compared to the direct gap and we say Gallium Arsenite is a direct bandgap semiconductor. x equal to 0 we are here, x equal to 1 this will be the bandgap, so yes not necessary the question is will there be a local minima always, no not necessary here you will have a local maxima which is local minima for at k equal to 0 there is a gamma point, but this need not be there there are materials where there are nothing here, means it simply passes likes.

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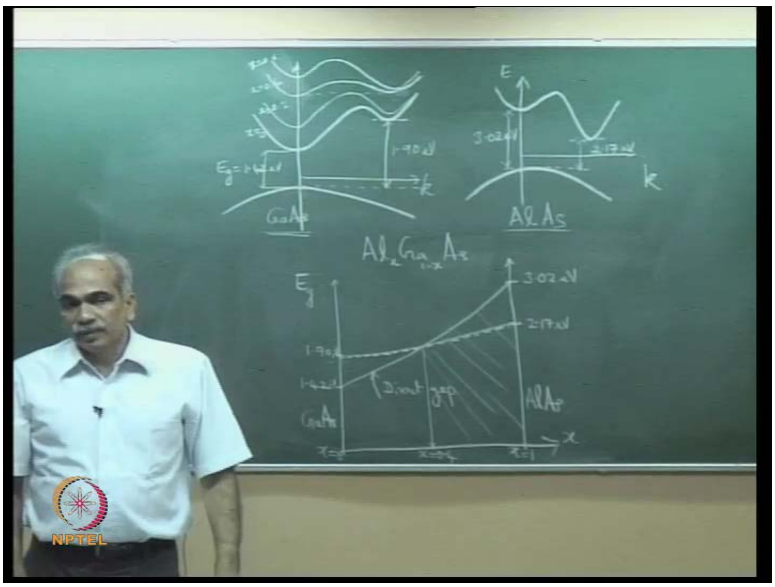

As you increase x this diagram changes, so this gap the new bandgap does this, this is for x equal to 0 and this is for x is equal to 0.2. For example as you increase x further, let us say 0.4 then let me increase this axis as you increased 0.4. They are almost coming at the same height, here this is for x is equal to point qualitatively explaining what is changing, when you change x please see, when you change x you are changing the environment in the crystal, because you are replacing Gallium Atoms by Aluminium Atoms the

electrostatic field. The distribution there changes and accordingly the allowed values of electrons change, which means the e k diagram changes with the composition of x.

So as x increases this is the situation, the direct gap has increased, the indirect gap has also increased and they have become equal. After sometime when x is equal to points I am going out of the board, x is equal to .6 this does this, what does that mean so this is x is equal to 0.6, which means now the indirect gap is smaller in compare to the direct gap and this material has now become indirect bandgap semiconductor.

It was a direct bandgap semiconductor as you increased x, it became an indirect bandgap semiconductor, so we have at Gallium Arsenite at x equal to 0 has a direct gap at 1.42 e v there was an indirect gap which is 1.90 e v, either I could have plotted this first and give an explanation or I gave the explanation. Now, I plot Aluminium Arsenite has the smallest gap 2.17 indirect bandgap. So, 2.17 its slightly over here, so 2.17 e v and a direct gap which is 3.02, so 3.02 e v qualitatively sure so the direct gap here is going from 1.42 to 3.02 e v this is the direct gap, the indirect gap is increasing, but slowly and at this value of x here around x is equal to 0.4 approximately around 0.4, so this is the p c. So, let me differentiate it by also having a broken line.

What am I plotting? I am plotting the direct gap and indirect gap for the material Aluminium Gallium Arsenide for different compositions x, so at any x you just go up and see what is the direct bandgap what is the indirect, which one is smaller? In this case direct is smaller, if you take an x here 0.8 then indirect is smaller, direct is larger, which implies that this material is indirect bandgap semiconductor.

In this half or this portion the material has become indirect bandgap because the smaller gap is indirect gap the direct gap is larger now and therefore the material is indirect bandgap. However, from x is equal to 0 to x equal to 0.4 it is a direct bandgap material and the bandgap can be varied with x by changing the composition x I can continuously vary the bandgap of the material.

And that is the importance of the Aluminium Gallium Arsenide Alloy 1 minus x. Is this clear, so material has a direct gap, indirect gap as the composition changes the e k diagram changes I have qualitatively shown, how it is changing? It is increasing both of them are increasing here, but later this becomes this gap that is minima to maxima this difference is smaller compare to this difference. Therefore the material is indirect

bandgap semiconductor, so in the range 0 to x equal to 0.4 Aluminium Gallium, Arsenite is a direct bandgap semiconductor, where the Bandgap can be continuously varied we will continue from here in the next class.

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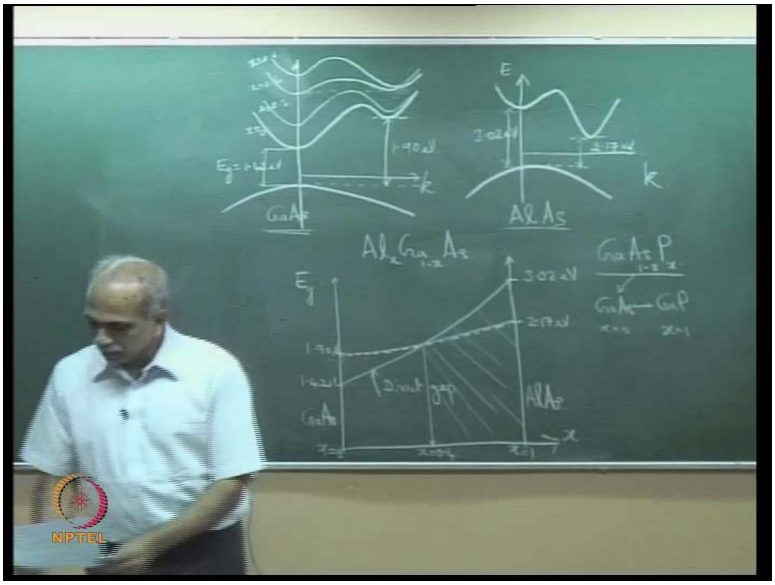

We have a quiz today, the other important material are also the composition is Bandgap is varied is Gallium Arsenide Phosphide, so Gallium Arsenide is 1 minus x and P is equal to x, instead of Aluminium Arsenide, so the starting point at x equal to 0 is Gallium Arsenide and at x equal to 1. We have Gallium Phosphide, so this is at x equal to 0, x equal to 1 this another important material, which is used to make all the visible l e d s are made by Gallium Arsenide Phosphide, which is also code up with nitrogen for certain reasons we will discuss that when we come to LEDs, but the principle and methodology of bandgap modification remains the same.

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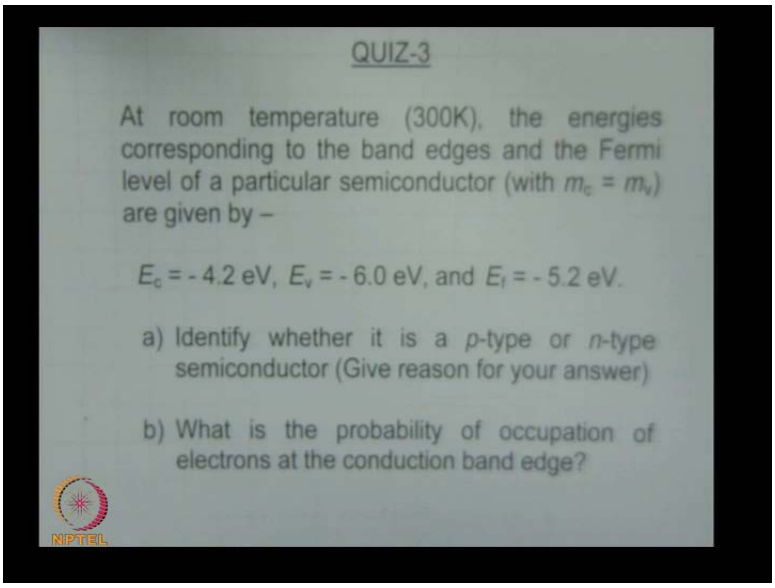

Normally it should not take more than 3 minutes, maximum time is 5 minutes and as you know every quiz is for 1 mark, at room temperature let me read the quiz at room temperature. The energies corresponding to the band edges and the Fermi level of a particular semiconductor with m c equal to m V are given by E c is equal to minus 4.2 e v, E V is equal to minus 6.0 e V, and E f is equal to minus 5.2 e V. A question a, identify whether it is a p-type or n-type semiconductor give reason for your answer just one line reason no detail explanations; b, what is the probability of occupation of electrons at the conduction band edge? All the energy values have a negative sign in front. We will discuss why?