

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


Lecture-10
Semiconductor Materials

Ok today we will discuss about semiconductor material, in this class our focus will be on semiconductor optoelectronic materials as supposed being on semiconductor optoelectronics, what I have put here is a part of the periodic table.

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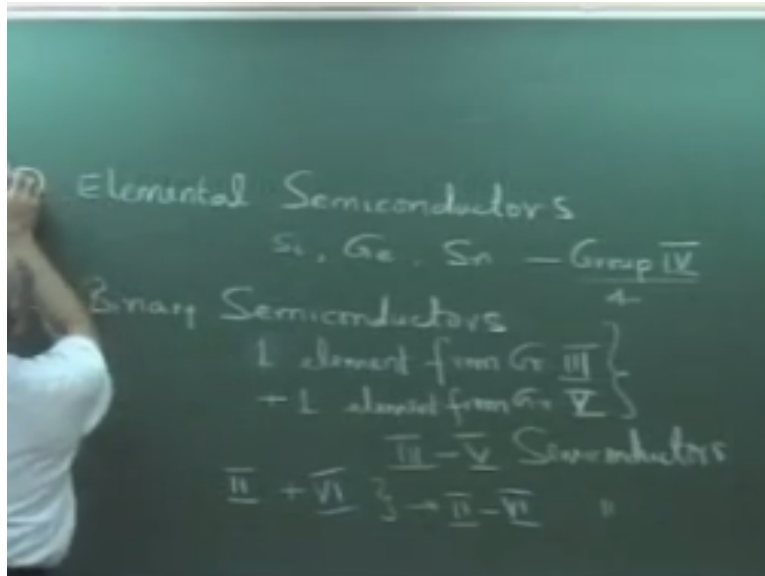
and possible III-V & II-VI combinations

II B	III A	IV A	V A	VI A
-----	⁵ B	⁶ C	⁷ N	⁸ O
-----	¹³ Al	¹⁴ Si	¹⁵ P	¹⁶ S
³⁰ Zn	³¹ Ga	³² Ge	³³ As	³⁴ Se
⁴⁸ Cd	⁴⁹ In	⁵⁰ Sn	⁵¹ Sb	⁵² Te
⁸⁰ Hg	⁸¹ Tl	⁸² Pb	⁸³ Bi	⁸⁴ Po
$5d^{10} 6s^2$	$6s^2 6p^1$	$6s^2 6p^2$	$6s^2 6p^3$	$6s^2 6p^4$



The part of the periodic table that shows group II, III, IV, V and VI elements of group 2 part of it, there are IIA, IIB and so on, but do not worry about A,B,C and so on right now group II, III, IV, V and VI. The elemental semiconductor the common elemental semiconductors combines of group IV elements.

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So elemental semiconductors first the most common elements are silicon, germanium, and tin. All group IV elements as an element these are semiconductors which means the basic definition of semiconductor code score, silicon, germanium and tin. We also have binary semiconductor or compound semiconductor, binary semiconductors. These are usually either two elements 2 elements.

These are one element from group III+one element or compound formed by 1 element from group III and 1 element from group V. For example if you see the table here the elementary semiconductors are here group I Silicon, Germanium, Tin. The binary semiconductors are 1 element from group III and 1 element from group V. The most commonly used elements are compounds are gallium arsenide 1 from III.

And 1 from V gallium arsenide, we also have a aluminium phosphate, indium phosphide, all possibilities are there, one from group B and 1 from group V. So these are also sometimes called as III, V semiconductors III, V semiconductors. Stable compound are one element from group III and 1 from IV. You could also have one element from group VI, 1 element from group II and 1 element from group VI forming what are called II, VI compounds.

II, VI semiconductors, for example Mercury here and one from VI cadmium to right is a widely used semiconductor, zinc Selenide, or cadmium Selenide or Mercury Selenide mercury telluride are all group II, VI semiconductor, you may have III, V semiconductors or II, VI semiconductor, that are show me in the last row in this last row of this table is the electronic configuration in the outermost shell of the element.

For example here mercury is there, Mercury is outermost shell has $5d^{10}$ and $6s^2$ it is group II because in the outermost shell there are two electrons. This is group III for example this is thallium $6s^2 6p^1$. All elements in this group III are the configuration in the outermost shell like $6s^2 6p^1$ for thallium for Indian it is $5s^2, 5p^1$, if you go to gallium it is $4s^2 4p^1$ and if you aluminium it is $3s^2 3p^1$ and obviously if you come to boron it is $2s^2 sp^1$.


Boron has 5 atomic number is 5 which means there are 5 electrons, the electronic configuration is $1s^2, 2s^2, 2p^1$ exactly like this, in the last column for of these you can see that it is $6s^2 6p^2$ for lead, but if you go to Tin germanium it the shell number reduces but they have S^2p configuration with means there are 4 electrons in the outermost valence shell. In group IV there are 4 electrons in outermost valence shell.

And therefore they form covalent bonds sharing 4 electrons with an adjacent atom to make an octet, that is 8 electron shell which completes the octet. If you take 1 from 3 and 1 from 5 there are 3 electrons in the outermost shell here and 5 electrons in the outermost shell here and therefore used again have the octet complete 3 and 5. Similarly in II, VI we have II and VI making it or not. So the outer shell as an octet it means it is a complete shell makes stable components.

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Common Optoelectronic Materials – Direct Bandgap

Semiconductor	Bandgap (eV)	Lattice Constant (Å)	Refractive Index
GaAs	1.42	5.65	3.6
InP	1.35	5.87	3.5
InSb	0.17	6.48	4.2
InAs	0.36	6.06	3.8
GaSb	0.73	6.10	4.0
AlN	6.20	3.11	2.2
GaN	3.39	3.16	2.5
InN	0.65	3.54	3.0



So these are binary semiconductor, typical some of the binary semiconductors and their band gaps I display here I hope you are able to read this gallium arsenide band gap is 1.42eV and lattice constant is 5.65 Armstrong the fact index given approximate refractive index near the

band gap wavelength or near the band gap wavelength 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 band gap semiconductor, gallium nitride has a band gap here of 3.39 electron volts. This is nowadays this is a very important substrate gallium nitride to get blue LED laser, blue laser it is the gallium nitride substrate which is used indium gallium nitride, so indium nitrite.

What you see is also the numbers are listed to see that some of them have lattice constant 3 point something. These the last 3 have lattice constant 3.1, 3.1, 3.5 Armstrong as the lattice constant. But if you see the other common binary compound 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.

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Common Optoelectronic Materials – Indirect Bandgap

Semiconductor	Bandgap (eV)	Lattice Constant (Å)	Refractive Index
Ge	0.66	5.65	4.0
Si	1.12	5.43	3.5
AlSb	1.58	6.14	3.8
AlAs	2.16	5.66	3.2
GaP	2.26	5.45	3.3
AlP	2.45	5.46	3.0
SiC	2.42	3.08	3.1



So these are all direct band gap material, the compounds that I listed here are all direct band gap material. I have a second list here you can find these numbers in books and references a indirect band gap optoelectronic materials here germanium, silicon, aluminium, antimonide, aluminium arsenate, gallium phosphide, aluminium phosphide and silicon carbide, silicon carbide is also today an important material used for UV detector.

You see band gap is very large 2.42 electron volts and lattice constant is about 3 Armstrong, all of them are high defective integer as you can see unlike the normal glass most of them

have refractive indices 3-4. These are all indirect band gap materials, some of the common direct band gap and indirect band gap materials. Now the choice of semiconductor for any applications depends on the band gap.

That is the direct band gap material, now and we have semiconductors how does one choose the required semiconductor, this is determined by the band gap 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 this is the band gap which determines what is the wavelength that you can emit and absorb.

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So we have E_v , E_c and this is the E_g if the photon of energies $h\nu$ is incident on the semiconductor, so this is a semiconductor which has electrons and vacant states for some electrons there, incident photon can be observed provided if I call this as energy E_1 and E_2 then $h\nu$ must to equal $E_2 - E_1$. If an electron sitting at energy level E_1 makes an upward transition to an energy level E_2 .

Then $E_2 - E_1 = h\nu$ and therefore the smallest energy photon which can be observed by an electron transition by inter band transition is $h\nu = E_g$, that is the frequency or energy corresponding to the smallest, smallest energy corresponding to the photon which could be observed. Similarly if there are electrons large number of electrons here we could meet the make a downward transition.

And the difference in energy will be emitted in the form of photon, this emits energy in the form of photon and the smallest energy photon will correspond to $h\nu = h$. So if you write this as $h c/\lambda = E_g$ or $\lambda = hc/E_g$ and this is called band gap wavelength $\lambda_g = hc/E_g$, h is the Planck constant, c is the velocity of light in vacuum which are constants. So you can substitute values to this.

If you substitute the values then you find that λ_g in micrometre is given by approximately equal to $1.24/E_g$ in electron hole, this is a very useful formula in the band gap wavelength in micrometre is approximately equal to $1.24/E_g$ in eV. If I give you a material and say alright gallium arsenide has a band gap, gallium arsenide band gap equal to 1.42 eV what is λ_g , the band gap wavelength.

That is the smallest energy photon that can be observed is this but in practice we handle sources with wavelength. We normally do not talk in terms of energy but in terms of wavelength and therefore λ_g in micrometre is equal to $1.24/1.42$ which is approximately 0.88 micrometer, so a quick estimate is given by this form $1.24/1.42$ approximately 0.88 eV, indium phosphide as a band gap of 1.35.

Gallium nitride has a band gap of 3.39 or 3.4, so which photons what energy photons it can absorb for an it you can imitate you find out gallium nitride, you do not need a calculator gallium nitride is equal to λ_g for gallium nitride, so λ_g for gallium nitride is $3.4/1.24$ I am sorry that is E_g gallium nitride $1.24/3.4$ or 3.39 you can find out approximately this is approximately equal to how much is this approximately 0.35 or something 0.36 micrometer.

Please check but this is very useful to register of a substituting h which is 6.6×10^{-34} C and then E_g convert into joules because 6.64×10^{-34} is joule 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 band gap. So depending on the application you have to choose the compound semiconductor.

But we have a limited number of semiconductor useful semiconductors and therefore if you want to continuously vary the band gap wavelength or if you want to have materials with continuously variable band gap then we go for third type of materials 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 one compound 1 element from group III and one element from group IV group V and therefore your choice becomes wider. So you have more number of useful materials however you do not have continuously variable band gap material and therefore the third type of material are called ternary compounds, ternary compounds and quaternary compounds.

So let me put that the table of elements here, in ternary compound as name indicates there are 3 elements and in quaternary compound there are 4 elements. In ternary compound we have 2 elements from group III and 1 from group V for example gallium, aluminum, and arsenide. So from group III we have aluminum, gallium and arsenide. So gallium, aluminum and arsenide or you can have one element from group III.

So this is from group III, we are still III, V compounds still III compounds but instead of one element we have two elements. So how do we represent this we represent this as a Al_x gallium $1-x$ and arsenide, where x is the alloy composition, these ternary compounds are also called a large semiconductors, what kind of values are used generally x can lie anywhere between, so x lies between 0 less than or equal to.

Usually x lies between 0.1 to 0.5 but in principle it could lie anywhere in this, but that means if you put $x=0$ $x=1$ is 1, so we simply have gallium arsenide if we put $x=0$ the material is gallium arsenide. If you put $x=0$ that means gallium is 0 we have the binary compounds aluminium phosphide. So this is an alloy where x fraction of gallium atoms are replaced by aluminium atoms extraction of gallium atoms are replaced by aluminium atoms at the fabrication states at the formation states.

So these are called alloy semiconductor. 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 two elements from group III and 2 elements from group V indeed you have gallium, indium gallium arsenide phosphide.

This is a very widely used material in optoelectronics and optical communication most of you are laser diodes for optical communication are fabricated by this material indium gallium arsenide. I could have this as indium and gallium from group III see the table indium and gallium are from group III and arsenic and phosphide arsenic and phosphide are from group V.

So even in the quaternary compound is from III, compounds that this could be written in this fashion or it could also be see what is the difference between gallium $1-x$ and $1-y$ and ty . I mentioned that formation of aluminium gallium arsenide x fraction x could be 0.1, 0.2, 0.3 typical number are 0.1, 0.2, 0.3 somewhere in the 0.1 to 0.4 are the 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 arsenide, gallium arsenide is the first states and you have replaced extraction of gallium by aluminium. So this indicates that gallium arsenide was the substrate. So this is the complete material system is very often indicated like this gallium arsenide or gallium arsenide which means the starting first state is gallium arsenide.

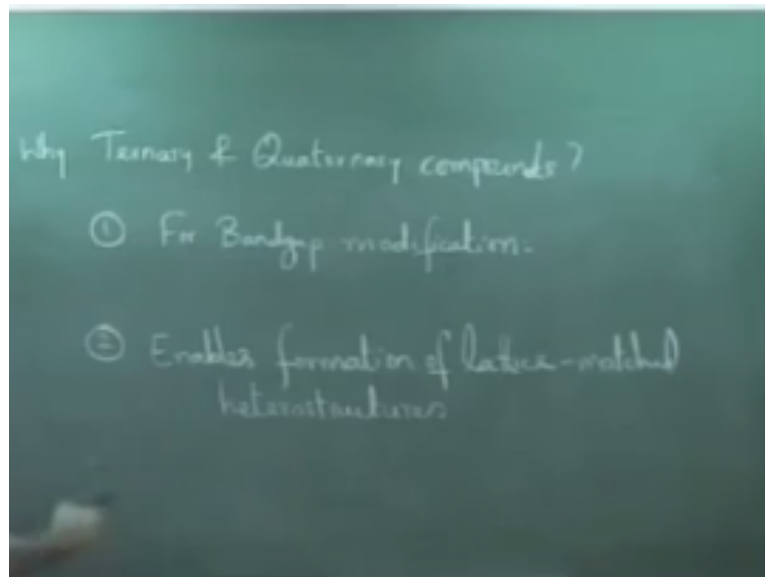
Usually you start in the first states the binary compounds and then you get the alloys aluminium gallium arsenide, what is the difference between these two here what is the substrate and here what is the substrate. The substrate in this case is indium phosphide is started with indium phosphide extraction of indium is replaced by gallium and why fraction of phosphorus is replaced by arsenide.

Whereas in this case the starting substrate was gallium arsenide, so x and y $1-x$ and $1-y$ tells you which is the starting material, if $x=y=0.5$ then it is difficult to tell which is the starting material. So normal X and Y remain small. This is the quaternary compound and so, ternary and quaternary compounds are in general III, V semiconductors it could be III, VI also. We can have two elements from two elements from group II and 1 from group VI.

If that is zinc cadmium telluride or mercury cadmium telluride is a widely used compound, mercury cadmium telluride so that is the II, VI compound this also a ternary compound similarly you could have quaternary compound which are also II, VI, so you can have either

III, V or II, VI. These are all stable compounds stable semiconductors. So the question is why do we go for ternary and quaternary compounds or why go for alloy semiconductor.

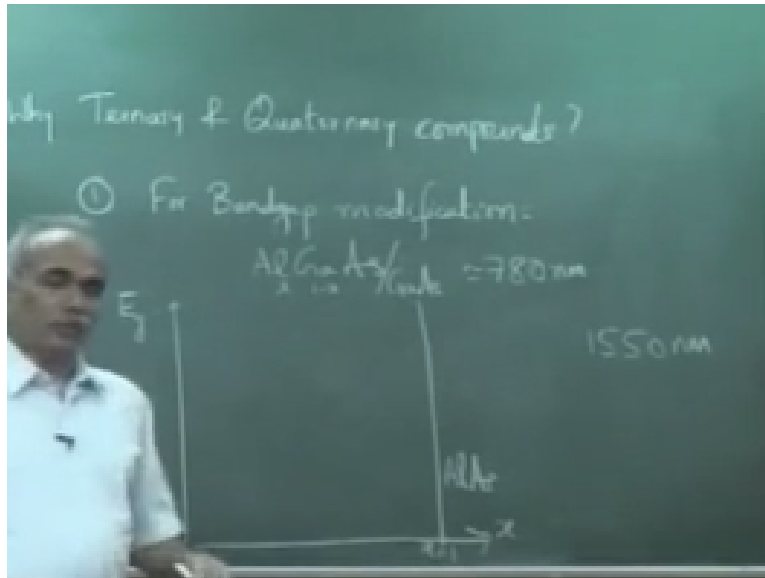
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The binary or compound semiconductors and the ternary and quaternary are in general called alloy semiconductors or why ternary and quaternary compounds recount the two important reasons let me the answer first that for band gap modification and second one enables formation or global formation for this is the most important lattice match heterostructure, it enables the formation or growth of lattice matched heterostructure.

We will discuss the second point in the next class, heterostructure growth of heterostructure, design consideration and lattice matching. Lattice matching is basically lattice constant of the compounds which are used to form heterostructure have to be the same lattice matched. We will discuss this later, first let us see for band gap modification. As I mentioned by changing the composition of the let me from this point we will discuss that in detail for bankers module a stick and example and discuss what is this for band gap modification.

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If I take the example of aluminium gallium arsenide which is widely used material most of the laser diode which are used in commercial products laser printers laser pointers all music system CD systems or used gallium arsenide aluminium user diode usual emitting at 780 nanometre, this will impact the most widely study material $\text{Al}_x\text{1-x}$ arsenide and gallium phosphide.

So most of the commercial is other than the optical communication, as you know that optical communication takes place in the window of 1550 nm not 780 nm and therefore the material used is indium gallium arsenide phosphide the quaternary material most of the devices are either based on indium gallium arsenide or indium gallium arsenide. So there are number of combinations which are possible.

But remember that it is around 1550 nm role of window of optical fibre and where is most of the commercial devices used 780 nm around 780 nm and the material used is aluminium gallium arsenide and gallium arsenide. So depending on x as I said if you see the band gap the band gap variation, so what I am plotting is x variation of x versus the material this is energy E_g and $x=0$ which means we are at $x=0$ are it is gallium arsenide so gallium arsenide.

So $x=1$ we have aluminium phosphide, gallium arsenide alright, so we have to bring in at another concept at almost all semiconductors have a direct band gap and indirect band, I am explaining the first point for band gap modification. If we got the E-k diagram or band gap diagram for gallium arsenide the band gap diagram look something like this.

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This is E the band gap here is this si direct band gap and this $E_g=1.42$ at 300 k usually the number set output are at room temperature at 300k 1.42 eV, there is also a gap here corresponding to a stable minima here and this is the indirect gap and this is 1.90eV, this is for gallium arsenide, almost all materials have a direct gap and an indirect gap.. So the indirect gap could be here at the gamma point.

And the direct gap could be the director gap is means the larger gap all right let me plot aluminium and then it will become fair, in aluminium oxide this is again E verse k or aluminium arsenide this was qualitative diagram, aluminium arsenide has an indirect gap here, this difference here is 2.17eV and this difference here is 3.02eV, please see this carefully the point is whether I take gallium arsenide or aluminium arsenate.

And $k=0$ there is a gap there is band gap and here also there is a band gap, there is a minima here, minima means that refers to stable states within this minima there are states it means if an electronic cited comes here it could come down and be stable hear this is a stable point. So but this gap is larger than this gap, this is an indirect gap, this is the direct gap. The material is for indirect band gap semiconductor or direct band gap semiconductor depending on which one of them is minimum.

The smaller of the band gap determines whether the material is direct band gap semiconductor or indirect band gap semiconductor. So aluminium arsenide is an indirect band gap semiconductor because the smaller gap between the maximum of the valence band and minima of the conduction band is smaller here which is indirect because that does not aware it could be 0, that is occurring at the minima and maxima and minima are at different K value.

So this is the indirect band gaps, in the case of gallium arsenide also you have an indirect gap, but the indirect gap is larger compared to the direct gap and we say gallium arsenide is a direct band gap semiconductor, $x=0$ we are here $x=1$ this will be the band gap, so yeah here, no 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 $k=0$ that is the gama point but this need not be there

the raw materials where there is nothing inside simply pass up like this. As you increase x changes this diagram changes, so this gap new band gap this is for $x=0$ and this is for $x=0.2$. For example as you increase x for there let us say 0.4.

Then let me increase this axis as we increase to 0.4, they are almost coming at the same height here, this is for x is equal to and quantitatively 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 alluminum atom that electrostatic field and the distribution there changes.

And accordingly the allowed values of electrons in which means the we need to change the diagram changes with the composition of x . So as x increases this is the situation the direct gap has increased the indirect gap has increased and they have become equal after some time when x is equal to point I am going out of the volt $x=0.6$, this what that means this is $x=0.6$ which means now the indirect gas is small compared to the direct gap.

And this material has now become indirect band gap semiconductor, it was a direct band gap semiconductor as you increase x it became an indirect band gap semiconductor. So we have a gallium arsenide at $x=0$ as a direct gas at 1.42 E, there was an indirect gap which is 1.90 Ev I have plotted this first and give an explanation or I give the explanation and now. Aluminium arsenide has the smallest gas 2.17 indirect band gap.

So 2.17 is slightly over here, so 2.17 EV and a direct gap which is 3.02, so 3.02, so the direct gap here is going from 1.42 to 3.02, this is the director gap, the indirect gap is increasing but slowly and at this value of x here around $x=0.4$ approximately around 0.4 that this is the please see so let me differentiated 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 we just drop and see what is the direct band gap what is the indirect which one is smaller. In this case direct is smaller. If you take a x here 0.8 smaller then indirect is smaller, director is larger which implies that this material is indirect band gap semiconductor. In this half or this portion the material has become indirect band gap. Because the smaller the direct gap is indirect gap.

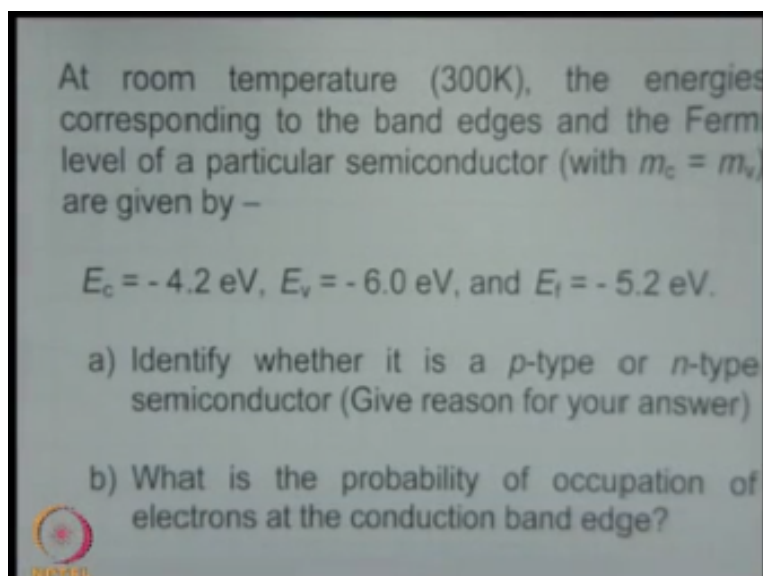
The direct gap is larger now and therefore the material is indirect band gap. However from $x=0$ to $x=0.4$ it is a direct band gap material and the band gap can be varied with x by changing the composition x I can continuously vary the band gap of the material and that is the importance of aluminium gallium arsenide along. $1-x$ is this clear so material has a direct gap, indirect.

As the composition changes the E-k diagram changes changing it is increasing both of them are increasing here this become this gap that is minima to maximum is difference is small compared to this difference and therefore the material is indirect band gap semiconductor. So in the range $0 < x < 0.4$ aluminium gallium arsenide is the direct band gap semiconductor where the band gap can be continuously vary.

And continue come here in the class we have a quiz today the other important material there also the composition is band gap is varying is gallium arsenide phosphide. So gallium arsenide is $1-x$ and $p=x$ this is of aluminium arsenate, so the starting point at $x=0$ is gallium arsenide and at $x=1$ we have gallium phosphide. So this is $x=0$ $x=1$, this another the important material which is used to make call the visible LED.

The red LED are made by gallium arsenide phosphide which is also coded of the nitrogen and reasons we will discuss that when we come to LEDs, but the principal and methodology of band gap modification remains the same. Normally it should not take more than 3 minutes and maximum time is 5 minutes and as you know every quiz is for one hour.

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At room temperature (300K), the energies corresponding to the band edges and the Fermi level of a particular semiconductor (with $m_c = m_v$) are given by –

$E_c = - 4.2 \text{ eV}$, $E_v = - 6.0 \text{ eV}$, and $E_f = - 5.2 \text{ eV}$.

a) Identify whether it is a p -type or n -type semiconductor (Give reason for your answer)

b) What is the probability of occupation of electrons at the conduction band edge?

At room temperature I mean at room temperature the energy is corresponding to the band edges and the Fermi level of a particular semiconductor the $m_c = M_v$ are given by $E_c = -4.2 \text{ eV}$, $E_v = -6.0 \text{ eV}$ and $E_f = -5.2 \text{ eV}$. A question A identify whether it is a b-type and n-type semiconductor. Give reason for your answer just one line reason, no detailed explanations. B what is the probability of occupation of electrons at the conduction band h , all the energy values have a negative sign in front we will discuss why, will stop here.