

Processing of Semiconducting Materials
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Lecture - 17
Band Gap Engineering - I

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Problem - 2

The energy of vacancy formation in the germanium crystal is about 2.2 eV. Calculate the fractional concentration of vacancies in Ge at 938 °C, just below its melting temperature. What is the vacancy concentration given that the atomic mass (M) and density (ρ) of Ge are 72.64 g/mole and 5.32 g/cm³, respectively? Neglect the change in the density with temperature which is small.



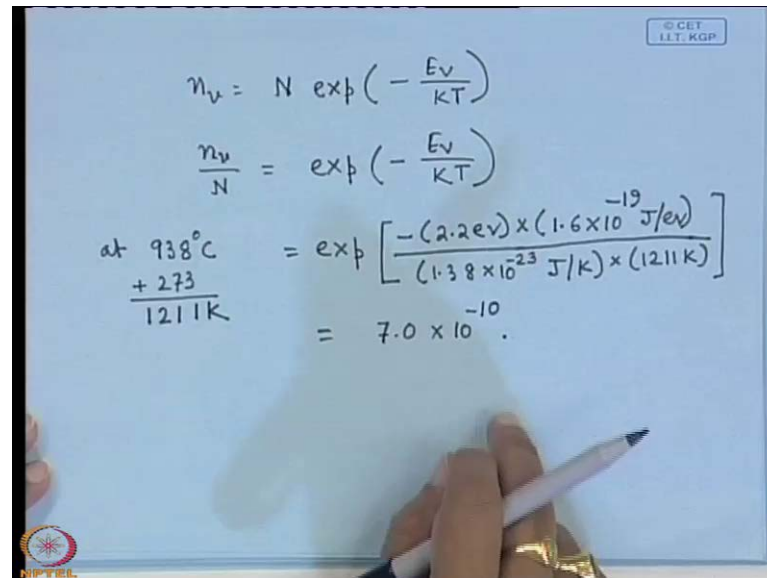
Now, before we start band gap engineering, let us conclude our discussion on the defect, because that is another problem you see that problem two is there and why we are interested in problem two. We can compare the concentration of vacancy type of defects in metal as well as in a covalent crystal, so you would like to compare this thing.

So, let us take another example, these examples is related to a covalent crystal germanium, the energy of vacancy formation in the germanium crystal is about 2.2 electron volts. Calculate the fractional concentration of vacancies in germanium at 938 degree centigrade just below its melting temperature, what is the vacancy concentration given. The atomic mass and density of germanium are 72.64 gram per mole and 5.32 gram per centimeter cube respectively; neglect the change in the density with temperature which is small.

So, here also like the previous example, you have to calculate the fractional concentration of vacancies at 938 degree centigrade. Then we have to calculate the actual vacancy concentration, here you see the number of atoms is not given rather atomic mass

is given and density is given. Then you calculate then you calculate what should be the vacancy concentration in germanium, because for aluminum we have seen that it is how much 1 into 10 to the power 19 here you see what is the value for germanium.

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The image shows a handwritten derivation on a blue background. At the top right, there is a small logo that says "© CET IIT KGP". The derivation starts with the equation $n_v = N \exp\left(-\frac{E_v}{kT}\right)$. Below this, it is rearranged to $\frac{n_v}{N} = \exp\left(-\frac{E_v}{kT}\right)$. Then, it specifies "at 938°C" and shows the conversion to Kelvin: $\frac{+273}{1211K}$. The equation is then written as $= \exp\left[\frac{-(2.2\text{eV}) \times (1.6 \times 10^{-19} \text{ J/eV})}{(1.38 \times 10^{-23} \text{ J/K}) \times (1211 \text{ K})}\right]$. Finally, the result is given as $= 7.0 \times 10^{-10}$. A hand holding a pen is visible at the bottom of the frame.

n_v is given by $N \exp\left(-\frac{E_v}{kT}\right)$ first is the fractional concentration of vacancy n_v by N it is equals to $\exp\left(-\frac{E_v}{kT}\right)$, now at 938 degree centigrade; that means, plus 273 1211 Kelvin. So, at 1211 Kelvin what is the fractional of concentration, it will be $\exp\left(-\frac{2.2 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV}}{(1.38 \times 10^{-23} \text{ J/K}) \times (1211 \text{ K})}\right)$. If you simplify it you will get 7 into 10 to the power minus 10 which is 7 into 10 to the power minus 10, what was the value for aluminum. It is not at melting point it is 10 to the power minus 4 here it is 10 to the power minus 10.

So, that means orders of magnitude less minus 4 and minus 10, so orders of magnitude less not 1 or 2 or 3 not 4 or 5 times, 8 times, 10 times it is orders of magnitude less in case of germanium. Now, what is the germanium, what is the number of germanium atoms in the crystal, how you can calculate, how you can calculate? You calculate, yes you calculate 4.44, 4.40.

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Handwritten calculation on a blue background:

No. of Ge atoms per unit volume

$$N = \frac{\rho N_A}{M} = \frac{(5.32 \text{ g/cm}^3) \times (6.02 \times 10^{23} \text{ /mole})}{72.64 \text{ g/mole}}$$

$$= 4.4 \times 10^{22} \text{ cm}^{-3}$$

Actual vacancy concentration at 1211 K:

$$n_v \Big|_{1211\text{K}} = (4.4 \times 10^{22} \text{ cm}^{-3}) \times (7 \times 10^{-10})$$

$$= 3.1 \times 10^{13} \text{ cm}^{-3}$$

So, basically we have calculated the number of germanium atoms per unit volume it is given by N equals to ρN_A by M atomic mass, what is the ρ ? ρ is 7 5.32 gram per centimeter cube and what is N_A 6.02 into 10 to the power 23 per mole per mole and divided by M is 72.64 gram per mole. So, that means, it is 4.4 into 10 to the power 22 centimeter cube inverse. Now, if you calculate the actual vacancy concentration in germanium near it is melting point.

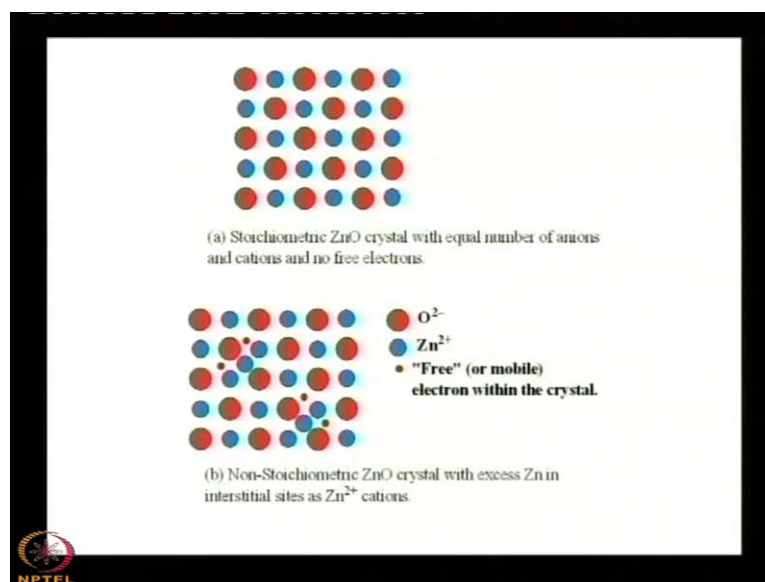
So, you have to calculate n_v at 1,211 Kelvin that is equals to 4.4 into 10 to the power 22 centimeter cube inverse multiplied by how much 7 into 10 to the power minus10, and what is its value? Its value is 3.1 into 10 to the power 13 centimeter cube inverse. Now, if you take the ratio, ratio between the number of germanium atoms and the number of vacancy, what you find that means 4.4 into 10 to the power 22 divided by 3.1 into 10 to the power 13. So, what you find that is 1 in 10 to the power 9 one vacancy in 10 to the power 9 atom one vacancy in aluminum what we find 1 in 6,000.

So, which is high aluminum obviously, it is mostly because of the thermal expansion of melting point at higher temperature metal expands more covalent crystal expansion is less. Another important parameter is that you see how much energy was required to create a vacancy in case of aluminum; it is 0.7 electron volt and here 2.2 it is almost three times higher.

So, that means creating a vacancy in covalent crystal is more and more energy is required

three times more energy has required in case of germanium if you compare with a metallic bonded crystal like aluminum. So, that is very important example to prove the point that a covalent crystal needs more energy to create a vacancy than a metal another application or of defect is the nonstoichiometry crystal say zinc oxide.

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Let us take one example of zinc oxide, let us take one example of zinc oxide you see that here the red balls are oxygen and blue balls are zinc. So, zinc oxide it is a stoichiometry zinc oxide crystal it is perfectly all right, equal number of oxygen and equal number of zinc that means equal number of anion and equal number of cations are there in the crystal matrix. Now, if you find that there is some excess amount of zinc in the crystal excess amount of zinc, how it happens. If the crystal has some deficiency in oxygen suppose there are n number of zinc.

So, how much number of oxygen must be there, N number of oxygen will be there then only it will be a stoichiometry crystal, but if you have n number of zinc and n minus m number of oxygen then there will be excess amount of zinc in the crystal. Now, when there will be an excess amount of zinc in the crystal zinc is a cation.

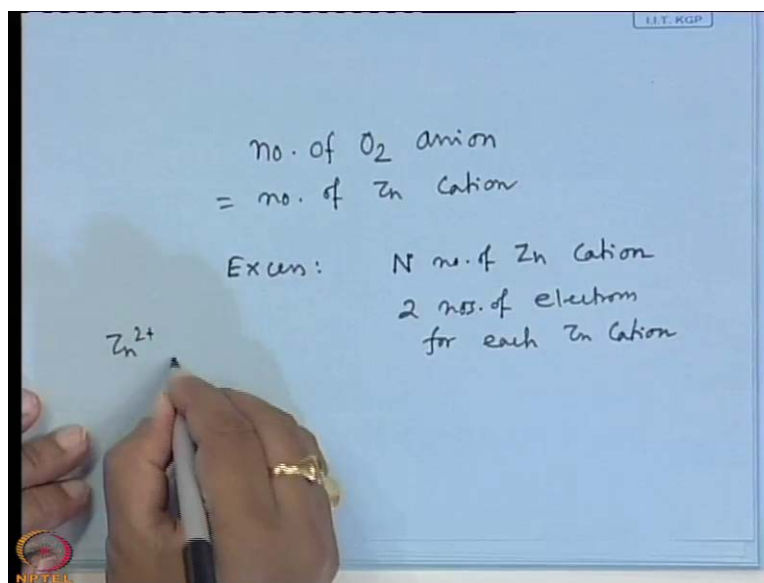
So, you see that this zinc cation is there in the interstitial position you see this blue ball is a zinc cation, which is in the interstitial position. It has donated two free electrons in the crystal because zinc is plus 2 zinc is plus 2 that means it has excess two electrons, when it is becoming a cation on ionization zinc has two electrons. Zinc ion is there that two

electrons cannot be taken up by oxygen why, because oxygen is in the form of anion, since it is in the form of anion it is not in a position to take up the electrons. So, you will have free electrons in the system you see these zinc has given this two free electron this zinc cat ion has given these two free electron, then there will be several zinc cations and multiplied by 2 will be the free electrons in the crystal.

So, the crystal has a whole will be n type in nature excess electrons will be there, so it will be n type in nature that is why as grown zinc oxide is always n type in nature. It is not intrinsic type, it is always n type and during our discussion on the semiconductors. We have seen that some semiconducting crystals are p type in nature as grown, as grown means during preparation without addition of any kind of doping or impurity here we have not used any kind of doping or impurity even then it is p type, it is n type in nature.

Similarly, lead telluride p b t it is p type in nature, see it is because of the non stoichiometry and it is a defect obviously it a defect that it is non stoichiometry because of the non stoichiometry. It is obviously the defect and this has given you the advantage that without doping it is n type in nature, but how the crystal remains electrically neutral, how the crystal remains electrically neutral. So, basically you see that there are n numbers of oxygen cat ion and n number of oxygen and zinc, sorry oxygen anion and zinc cat ion and two electrons are there for the excess zinc cation.

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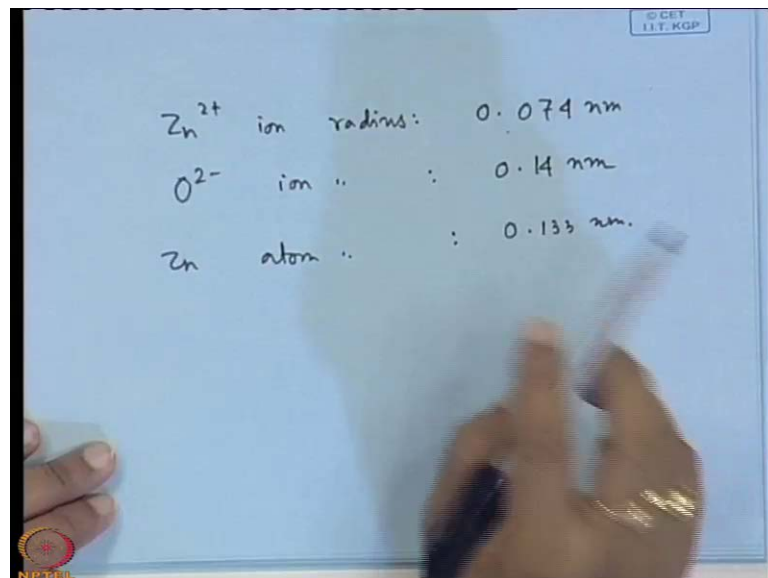


That means number of oxygen anion equals to number of zinc cation excess say N

number of zinc cation and 2 numbers of electrons for each zinc cation. That is why it is electrically neutral number of oxygen and number of zinc is same and excess number of zinc is there for each excess number of zinc cation there are two electrons. So, that is why it is electrically neutral in nature the crystal as a whole is electrically neutral but it is n type in it is conductivity because of the non stoichiometry. This non stoichiometry is very important in some cases, it has very important advantage and it has some important disadvantage, now what is the disadvantage. Advantage is that you get free electrons disadvantage is that you cannot; no you cannot make it p type.

It is very difficult to make it p type because as you go on doping it will be compensated by the electrons since there are many electrons in the system it will be compensated by the electrons if the number of oxygen is more than the zinc. Then, there will be anion type of defect, but that will not give rise to your n type conductivity n that will not give raise to n type conductivity may be it will be p type conductivity but, that is not thermodynamically favorable. So, it will never happen, in some cases it happens like led telluride, but in zinc oxide you cannot grow p type using just excess amount of oxygen that is not possible, why it is not possible?

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The possibility is rare, it is because of this thing that zinc ion its radius is zinc ion radius is 0.074 nanometer oxygen ion radius is 0.14 nanometer, zinc atom radius is 0.133 nanometer. So, that means what will happen, why I am citing this value? Oxygen will

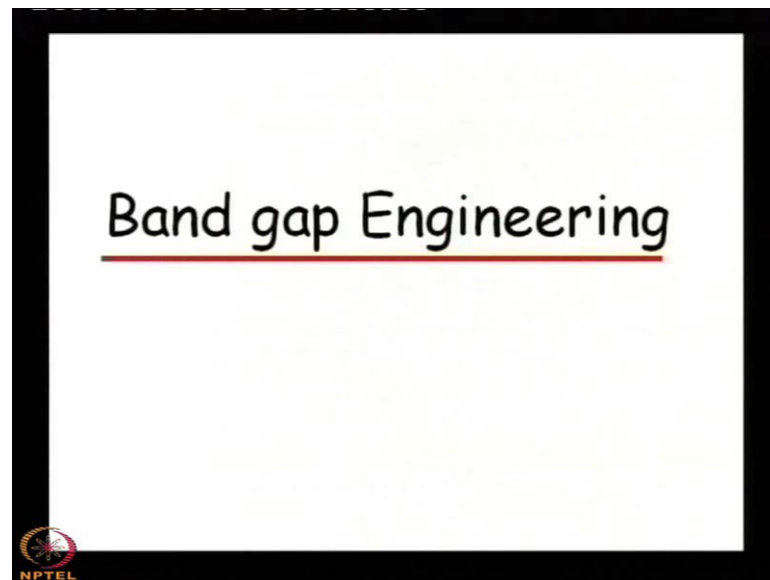
never be able to occupy the interstitial position; oxygen will never be able to occupy the interstitial position, so that is why p type conductivity by adding excess oxygen is not thermodynamically favorable, so there are constants.

Again, they will pushing it is not a railway compartment, it is not a railway compartment it has some thermodynamic consideration as well. Obviously, it will it can push, but how far how many oxygen's will be there not many because you see that it is 0.14 nanometer and it is 0.074 nanometer. So, only if there is excess zinc, it the zinc ion can only zinc ion can only be able to occupy the interstitial even not the zinc atom. You see that the zinc atom, it is 0.133 nanometer it is almost equal with the oxygen ion not even zinc atom will occupy the interstitial position. The interstitial position will be occupied by the zinc ion only and when there when we talk about zinc ion two excess electrons it is donating in the crystal lattice.

So, that is why oxygen doping is not favorable you cannot say that because of excess of oxygen, it will be p type not favorable because of the atomic dimension because of the dimension. So, these are the two very important examples say using which you can say that the defect sometimes give you some favorable advantage.

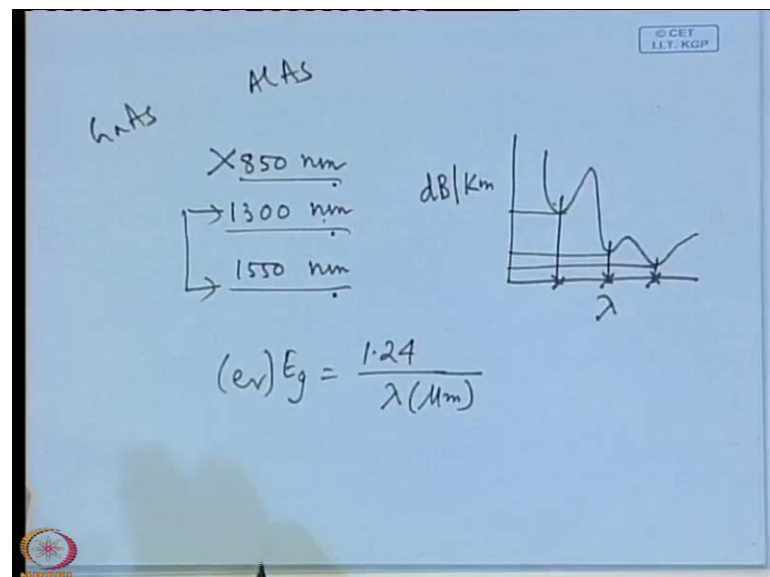
Obviously, we have seen that in case of say silicon obviously silicon that defect intentional defect is nothing but the doping with the phosphorus or boron it becomes n type or p type. So, that is also a defect sometimes in defect, you see how the steel is prepared from iron from normal iron. So, that is also a defect in the crystal, that is also a defect in the crystal it increases the strength and other property many times.

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Now, we come to our next example of next topic of Band Gap Engineering. This band gap engineering, you see that in some applications we have seen that a particular type of band gap value is required. We have talked about the fiber optic communication there we have seen that two windows are there in fiber optic communication, can you remember?

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The value of the windows, one is 850, 1300 and 1550 all in nanometer final talk about window what is window. Basically, Window is nothing but where the loss is less, dispersant is less; low loss dispersant less fiber at this three wave length of light low loss

dispersant less condition can be achieved using these three sources of light. You know that for fiber optic communication, what happens actually, how the information is sent from one place to another place, how it is happened? It is by the total internal reflection of light that means ultimately you have to send light through the fiber. You know that for any material the loss is a function of its wave length, say for silica glass fiber, fiber is made of different material, one is the silica glass fiber for silica glass fiber.

We have seen that at this through wave length the loss is minimum, how the loss is measured, what is the unit of loss? It is in decibel per kilometer and it is wave length we have seen that this type of a curve that means one is 850, this is 1300, and this is 1550. That means, the loss is minimum, it is decibel per kilometer and if you take this wave lengths you cannot name any single material using which you can get such kind of emission.

Emission means, either you have to use a light emitting diode or a laser diode for sending the light through the fiber either you need a light emitting diode or a laser diode. When we talk about the window that means the emission from the light emitting diode or the laser diode must be either 850 or 1300 or 1550 nanometer.

Remember that the present generation fiber optic communication, present generation does not use this 850 we use only 1300 and 1550 nanometer. Now, we have discussed many semiconductors various kind of semiconductors and you know their band gaps some of narrow some of wide then silicon, germanium, indium, phosphide 3, 5 semiconductors 2, 6 semiconductors many types of semiconductors we have discussed. You find that no semiconductor will be able to give you this kind of emission because it depends on $1.24 \text{ by } \lambda$. So, that means, the band gap must be $1.24 \text{ by } \lambda$ in micron then it will be in e v electron E g in e v.

So, if you put this 1300 or 1550 here you will get some value which is not available for any kind of semiconductors, what we have discussed till date, then what is the way out. The way out is that you have to grow new materials with these band gap you have to grow new materials with these band gap that is known as the band gap engineering. That is known as the band gap engineering, when 2 or 3 or 4 materials are mixed to form a new material to tune the band gap that is the band gap engineering.

Then, there are some constants also one constant is that these types of semiconductors

are all epitaxial layers because device is made out of epitaxial layers only device cannot be made from bulk crystal. You will find that device are always made of epitaxial crystal that means some 1 micron, 2 micron, 3 micron single crystal layer then where those layers are grown those layers are grown on substrate. So, you need a substrate and there must be matching of the lattice constant between the substrate and the grown layer that means lattice matching must be there.

So, that means even if you can mix three, four semiconductors to form one semiconductor, but as you mix say if you mix gallium arsenide with aluminum arsenide, so what will happen? Gallium arsenide is formed, but care must be taken that material must have the lattice constant same as that of the substrate on which you would like to grow the gallium arsenide. So, that is a constant you cannot use any kind of substrate for any kind of material one constant is that then another constant is the growth parameter that must follow the phase diagram because not all the materials can be mixed together to form a new material. It can be immiscible also it depends on the thermodynamic phase diagram.

So, that is another constant that you cannot mix chair with table is it possible, but you can mix water with sugar, can you mix chair in water? Totally immiscible so that is also there that means those phase diagram constant is there.

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$A_xB_{1-x}C$: x atoms of element A and (1-x) atoms of element B randomly mixed in the group III sublattice and all the group V lattice sites are occupied by element C: $Al_xGa_{1-x}As$

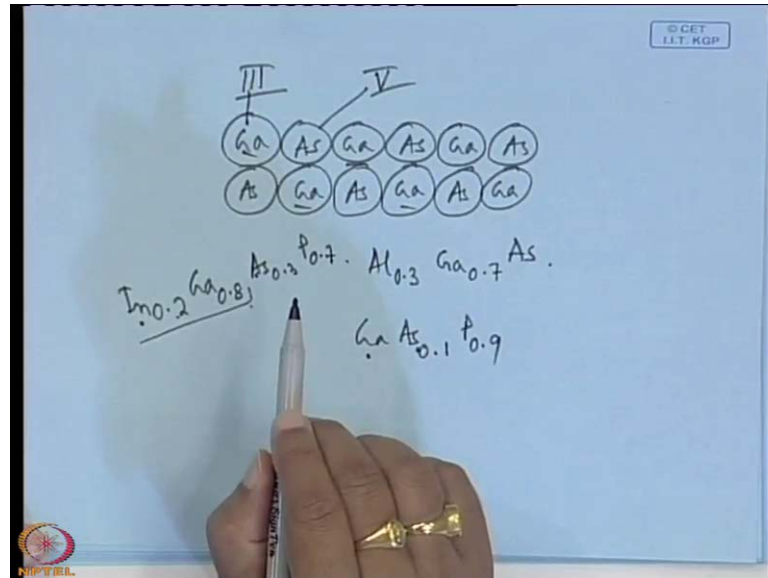
$AB_{1-x}C_x$: all group III sublattice sites are occupied by element A and mixing or alloying takes place in the group V sublattice between x atoms of element C and (1-x) atoms of element B: $GaAs_{1-x}P_x$



You see that one type of material can be $A_xB_{1-x}C$, $A_xB_{1-x}C$, if we

take 3, 5 semiconductor. Then we can say that X atoms of element A and 1 minus x atoms of element B randomly mixed in the group three sub lattice and all the group 5 sub lattice are occupied by element C.

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So, three elements are there A, B, C and when we talk about sub lattice means say this is gallium, this is arsenic, this is gallium, this is arsenic, this is gallium, this is arsenic and this is arsenic, this is gallium etcetera. So, that means you find that there are two sub lattice, one sub lattice is group 3 this one, that one this one that one etcetera and another is group 5 sub lattice. Here, in this example you see that A and B are 3 group 3 elements, that means, x atoms of A and 1 minus x atoms are B are there in the group 3 sub lattice, but all group 5 sub lattice are occupied by element C. Then, it is one material which can be found by band gap engineering and one example is aluminum, gallium arsenide.

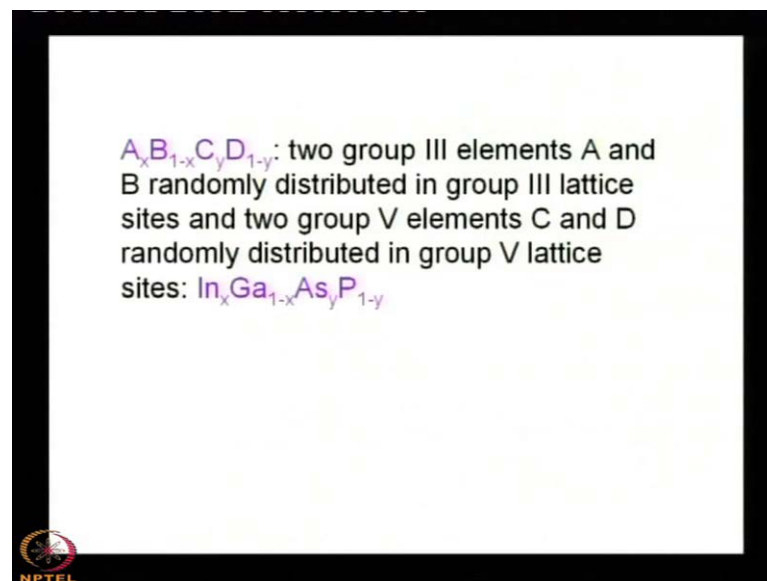
You see that aluminum is also a group 3 element, gallium is also a group 3 element if x number of aluminum's atoms are there, then 1 minus x atom number of aluminum gallium atoms will be there. Those are basically from group 3 sub lattices and arsenic will occupy the group 5 sub lattice. So, this is one example another can be A B minus B 1 minus x C x that means here A from group 3 of the periodic table and B and C are from group 5.

So, that means two elements from group 5 bar from the which will occupy the sub lattice of group 5 of both B and C if x number of C atoms are there, then 1 minus x atoms of at

number of the atoms will be there. The example is gallium, arsenide, phosphide here you see that gallium occupies the group 3 sub lattice and arsenic and phosphorus are group 5. They will occupy the group 5 sub lattice, so this is another example of the band gap engineer materials, what is the meaning of atoms. No obviously, it is basically the mole fraction it is basically the mole fraction, so it must be say 0 to 1 that means, the value of x must be from 0 to 1.

Let us take one example aluminum say 0.3 gallium 0.7 and arsenic that means 30 percent of aluminum atom and 70 percent of gallium atom then only there will be 100 percent of group 3 sub lattice out of out of 100 percent. Group 3 sub lattice arsenic will occupy 30 percent positions and the remaining 70 percent positions will be occupied by gallium, so that is the concept. Similarly, say gallium arsenide say 0.1 phosphorus 0.9 it means all the 100 percent position of group 3 sub lattice will be occupied by gallium, 10 percent of the group 5 sub lattice will be occupied by arsenic and the remaining 90 percent of the sub lattice will be occupied by phosphorus, so that is the thing.

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It can be other type of thing, say it is quaternary that means four elements are involve here you see four elements are involved to group 3 elements A and B and 2 group 5 elements C and D. So, they are randomly distributed and here you see that A and B from group 3 and C and D from group 5, so indium, gallium, arsenide, phosphide, indium, gallium, arsenide, phosphide. That means say indium 0.2, gallium 0.8, arsenic 0.8,

phosphorus 0.7 here you see that out of all the group 3 sides 20 percent will be occupied by indium and remaining 80 percent will be occupied by gallium.

Similarly, 30 percent of group 5 position will occupied by arsenic and 70 percent of group 5 70 percent of phosphorus will be 70 percent of group 5 positions will occupied by phosphorus. Now the implication, sir can we mix the 135 and 126 for p-type doping one element from second group.

It is not related to doping, doping it is not related it is basically because if you dope the material the band gap does not change. I am talking about the band gap engineering, where I want to make the new materials to tune the band gap for a particular application band gap does not change during doping. If you dope silicon with P or n type the band gap of silicon does not change. Similarly, if you dope say cadmium telluride or gallium arsenide or indium phosphide, band gap will not be changed then number of electron or whole concentration will be different during doping.

So, I am not talking about doping it is not related to doping it is related to band gap engineering where new materials are formed to tune the band gap for a particular application, say for your fiber optic communication you need 1300 nanometer or 1550 nanometer sources. So, you have to make new material with such composition show that its band gap will be match to it, but the thing is eh we are doping chlorine and silicon sides of silicon it at session is the relic band I dope. Boron can be take the interstitial position then after it goes.

It is the interstitial position as well does not mix up these two things it is the regular lattice side. I am not talking about any vacancy or interstitial if we takes up the interstitial or vacancy not there it is occupying the group 3 or group 5 sub lattice because in silicon the whole crystal is neither 3 nor 5. It is the silicon crystal and the boron is occupying either the vacancy position or the interstitial position here. It is not the case here, you have two sub lattices one is 3 and another is 5 and out of this three two sub lattice, you are making. So, those two types of elements will share the positions it is not the vacancy positions or the interstitial positions it is a regular lattice side position.

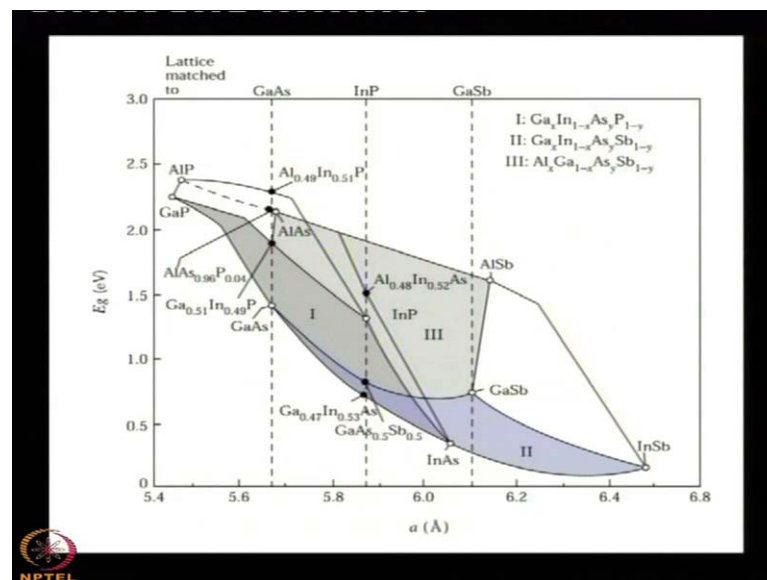
I am not talking about any vacancy or interstitial band gap engineering is not occupation of vacancy or interstitial is not related to the interstitial or vacancy. It is completely new material and the whole crystal lattice or the crystal structure will be utilized not the

interstitial or vacancy positions, so do not mix up these two things. Can we make the quaternary by using one second group one-third group one fifth group and one sixth groups? You can do any kind of permutation combination provided that it is miscible in nature, it is miscible in nature and you can grow the crystal. Otherwise, theoretically you can do anything, but our ultimate aim is to grow the crystal for a particular application.

It is not very easy thing because you see that till today, we have discussed this thing till today blue light emitting diode or blue laser material for blue laser or blue light emitting diode is not readily available. People use silicon carbide; people use nitride semiconductors, but it not very easy you cannot name any organization India which can provide you with blue led or blue laser because nitride semiconductors growth is not very easy thing.

Another thing is because of the wide band gap the doping is very difficult to make for any wide band gap semiconductors because of the non stoichiometry. The compensation of the dope end items theoretically you can make anything, now if you see those structures.

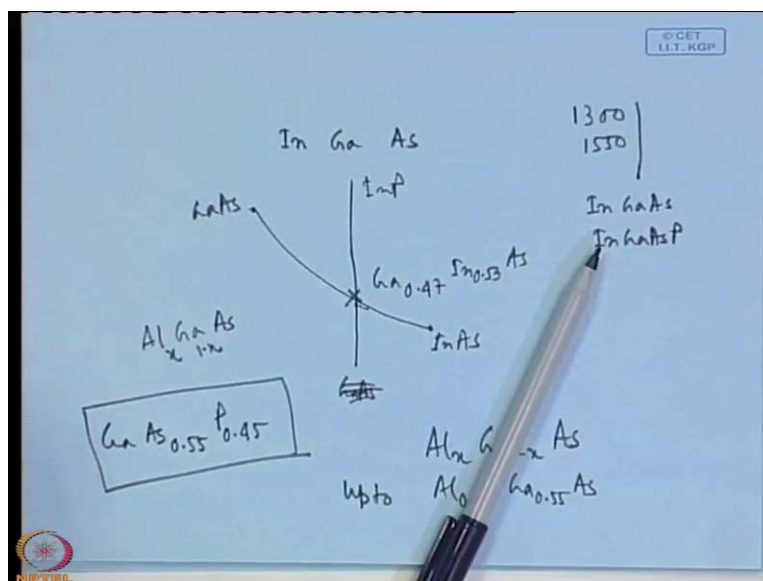
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You see that this is the constraint of the lattice mismatch here in the x axis I have shown you the lattice constant and in the y axis the band gap, it is a plot. Now, say one example of growth of say indium, gallium and arsenide, why I am talking about indium, gallium arsenide, it is because it is a material for fiber optic sources for 1300 and 1550

nanometer.

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If you want to grow 1300 nanometer or 1550 nanometer fiber optic sources then you have to use this material indium, gallium arsenide or indium, gallium arsenide and phosphide, these are two very important materials. That means, one this material gallium indium arsenide, phosphide, it is a quaternary and one constant is that you have to grow in lattice matching substrate, what substrate?

We have shown you three substrates gallium arsenide, indium phosphide and gallium antimonide, these three substrates are shown you with the dotted line that means gallium arsenide lattice constant are fixed, its lattice constant is fixed. So, this is the lattice constant for gallium arsenide, it is say 5.64 etcetera Armstrong this line throughout this line the lattice constant of gallium arsenide is constant. Similarly, indium phosphide lattice constraint is 5 not 87, it is 5.85, so it 5.87 this line.

Now, when we talk about indium, gallium arsenide, phosphide, you see that this is indium arsenide and where gallium arsenide is, it is gallium arsenide it is phosphide gallium phosphide. That means indium, gallium arsenide phosphide means it is a variation from indium arsenide to gallium phosphide. It is variation from indium arsenide to gallium phosphide wide range of variation you can make the band gap of gallium phosphide is 2.26, the band gap of indium arsenide is 0.47. So, from 0.47 to 2.26 huge variation, theoretically is possible by changing the composition of x and y, but what you find?

You find that you can grow this material at two positions at this position with some composition and at this position with some composition why because at two points only it is lattice match to indium phosphide and gallium arsenide; that means, at this position you take this position this position this is the position for indium phosphide then indium, gallium, arsenide, phosphide must be this thing otherwise the lattice matching will not be there at this point the lattice constant of the epitaxial layer will be same with the substrate.

Similarly, at this point it will be same with the gallium arsenide lattice constant because you cannot choose any material, say you if you take this point here also you see it is the position between indium arsenide and gallium, but why you cannot take this point? You cannot take this point because no substrate is available so that is a constant that you have to choose proper substrate. Similarly, gallium indium gallium arsenide you see that here also you can vary the indium arsenide to gallium arsenide this is the gallium arsenide point. That means if I draw it looks like this, it is indium arsenide point, it is gallium arsenide you see that only at one composition it is lattice match to gallium arsenide this point.

That composition is gallium 0.47, indium 0.53 and arsenic that means only 47 percent gallium and 53 percent indium with arsenic if you grow it is lattice constant will be same with that of the, sorry it is indium phosphide, indium phosphide. So, different type of material you can grow, but problem is the perfect lattice matching with the substrate because normally in the market indium phosphide and gallium arsenide substrates are readily available. You have indium antimonide or gallium antimonide, but those are not very readily available.

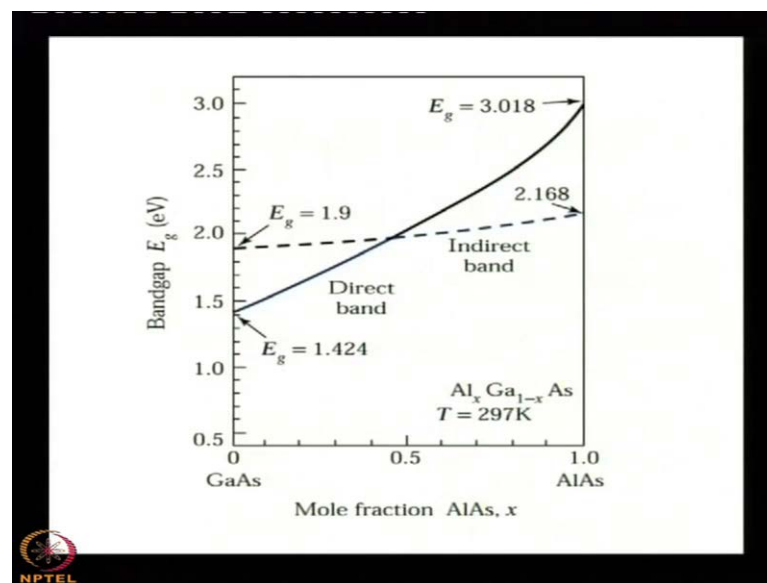
Let us take another example of aluminum gallium arsenide. Here to gallium phosphide 6.62 and gallium antimonide or these two the no substrate is available, which one gallium phosphide substrate is available, but it is not matching with gallium arsenide. Now, it will match because the lattice constants are different, there is a vertical lines actually if you take the gallium phosphide substrate it will match with gallium phosphide only or two some extent.

You see aluminum phosphide is very near, but if you use indium antimonide substrate is it is lattice constant is very high. It is almost 6.5 or 6.6 type of thing here gallium

phosphide it is 5.5 or even less than that, so why difference is there. Another example is very important, example is the gallium arsenide and aluminum arsenide if you take aluminum gallium arsenide, what you find? The lattice constant of gallium arsenide and aluminum arsenide is almost same it is almost same that means you can grow any composition of gallium aluminum arsenide on gallium arsenide substrate, since the lattice constant of gallium arsenide and aluminum arsenide is same.

So, you can grow any composition of aluminum gallium arsenide on gallium arsenide substrate because aluminum arsenide substrate is not available, substrate is gallium arsenide and since the lattice constant is very close. So, you can grow theoretically any composition of aluminum gallium arsenide that means aluminum x gallium $1 - x$ arsenic.

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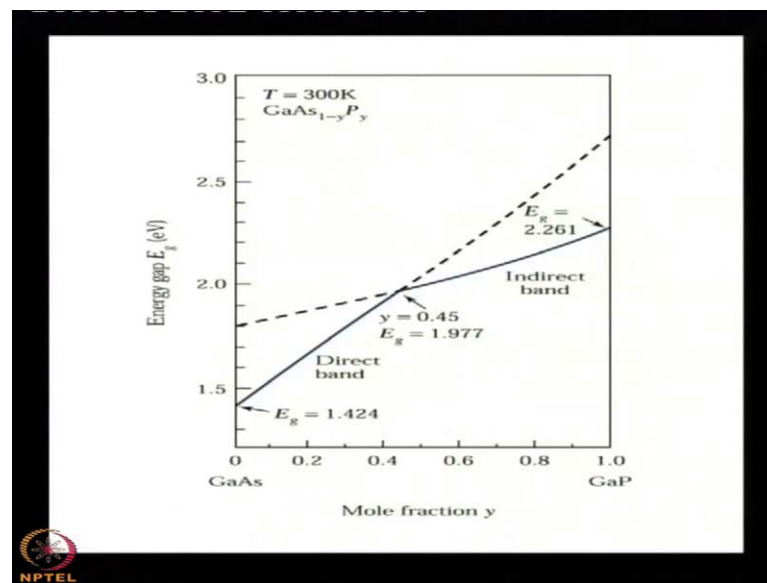
Theoretically, you can grow, but there is one problem the problem is this thing, this curve is plotted in this curve we have plotted band gap against the mole fraction of aluminum arsenide x that means this is gallium arsenide, this is aluminum arsenide. So, you see that at 0.45 it becomes indirect band gap semiconductor. So, aluminum gallium arsenide after 0.45 of concentration x when x is 0.45 that means when aluminum is 0.45, up to 0.45 it is direct band gap.

So, as you cross point as you cross 0.45, it becomes indirect band gap semiconductor, so what is the problem? Problem is that you can grow above 0.45 then it will not solve your

purpose for light emitting diode or laser because it becomes indirect band gap semiconductor. You need the conservation of momentum that means some defect labels or trapping labels must be there it must be introduced.

So, that is why this diagram will give you that you can grow theoretically, but this diagram sets you the limit that after 0.45 of aluminum. That means aluminum up to 0.45 gallium 0.55 arsenic up to this composition it is direct above this composition it is indirect, so it is useless for you.

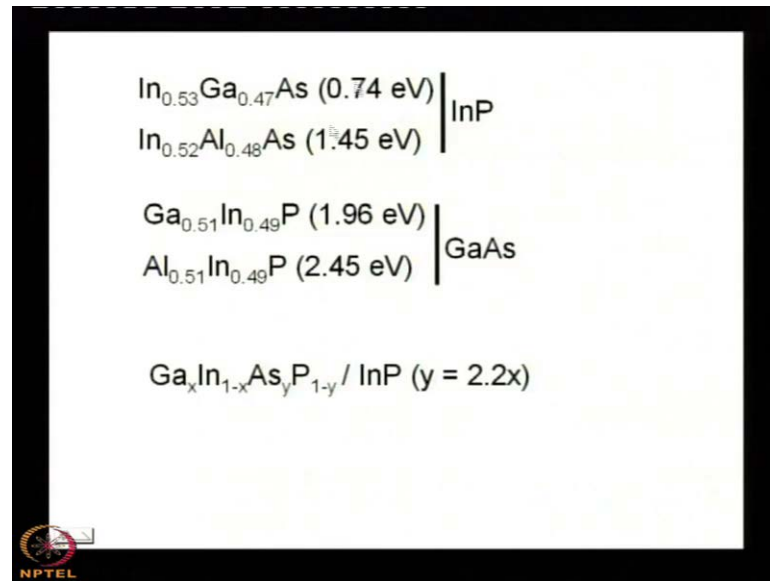
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Similarly, these are examples of say gallium arsenide phosphide, gallium arsenide, phosphide you see that gallium arsenide here also up to 0.45, it is direct then above 0.45, it becomes indirect band gap semiconductor. So, why 0.45 means gallium arsenic is 0.55 and phosphorus is 0.45 then it becomes indirect band gap semiconductor. Now, we talk about band gap engineering obviously, it is basically the fabrication or the growth of a compound semiconductor on a particular substrate, but there the limitations are the substrate.

Another limitation is the transition from the direct band gap to indirect band gap in many cases not all the cases, but in many cases and we find that for a particular atomic composition only it is lattice match to either gallium phosphide or indium phosphide or gallium arsenide type of substrate.

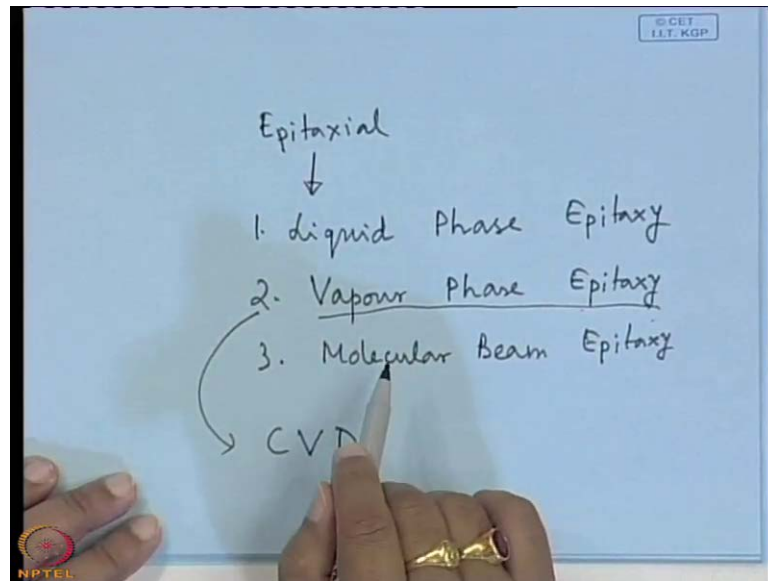
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So, that is constant and you see that these are the materials which are lattice match to this substrate that means if you talk about indium gallium arsenide it is lattice match to indium phosphide. Then indium aluminum arsenide it is lattice match to indium phosphide, gallium indium phosphide with this composition only it is lattice match to gallium arsenide, aluminum indium phosphide for this composition it is lattice match to gallium arsenide. Then gallium indium arsenide phosphide is lattice match to indium phosphide for y equals to $2.2x$ only for this value it is lattice match to indium phosphide.

So, that means you cannot grow any composition theoretically it is possible, but practically there is a limitation and you find that on the parentheses I have used the band gap. I have written the band gap it is 0.74 electron volt then indium aluminum arsenide is 1.45 electron volt, gallium indium phosphide with this composition is 1.96 electron volt, aluminum indium phosphide with this composition it is 2.45 electron volt. These are the band gap which will give you the different kinds of application, so these are the substrate and these are the materials. Now, how we will grow these materials, how we will grow these materials?

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This material can be grown you see that using some epitaxial technique, using some epitaxial technique only you can grow these material. Remember that you cannot grow this material using bulk crystal growth, bulk crystal growth is not possible for this material, because such kind of variation you cannot make, not only variation band gap engineering also incorporates the doping concentration, doping level of your choice. Say, you need 10 to the power 15 or you need 1.7 into 10 to the power 18 or you need say 2.3 into 10 to the power 18, it is possible using an epitaxial growth technique.

That kind of precise doping concentration and precise thickness is not possible in case of bulk crystal. It is an epitaxial growth technique and epitaxy means a single crystal layer, very thin layer of some nanometers, some angstroms 100 angstroms, 200 angstroms, 400 angstroms. So, how the epitaxial layers are grown there are epitaxial techniques of epitaxial machines one is known as the liquid phase epitaxy, number two is vapour phase epitaxy and number 3 is molecular beam epitaxy. These are the main three epitaxial techniques, using which you can grow different kinds of materials for band gap engineering.

Now, this vapour phase epitaxy is sometimes known as chemical vapour deposition or CVD. Vapour phase epitaxy is sometimes known as chemical vapour deposition, but chemical vapour deposition does not ensure that it will be a single crystal growth. It can be poly crystal in a dimorphous type of growth also.

So, that is why when we talk about epitaxy that means it is surely it is a single crystal layer otherwise VPE and CVD are the same meaning. The equipments are also almost same and there are different kinds of CVD techniques using which you can grow different materials. So, in the next classes, we shall discuss about the epitaxial growth techniques of material, what are the epitaxial growth techniques, how the material can be grown, how the machine look likes. What are the advantages and disadvantages of different kinds of epitaxial growth techniques, what are the advantages of LPE liquid phase epitaxy over VPE, what are the disadvantages of MBE over VPE or advantage of MBE over VPE?

Those things we shall take care in our next round of discussion, but remember that this band gap engineering is very importance so far as the electronic material its processing and device application is constant, because in some applications you will find that say solar cell. In solar cells or we have discussed about say for sensors or say DVD or CD type of application that means memory storage application, you need a particular wave length of light blue wave length wave length of light.

Then, you need to some band gap engineering, otherwise you cannot get that kind of a material not only is the material its doping level, its thickness, its compositional purity everything is involved in those material. So, in that sense the band gap material band gap engineering of material is very important advancement in case of electronic materials.