High Speed Devices and Circuits

Prof. K. N. Bhat

Department of Electrical Engineering

Indian Institute of Technology, Madras

Lecture – 7
Dopant and Impurities in GaAs and InP

We went through the details and discussed the crystal structure of gallium arsenide. In fact, what we discussed for gallium arsenide holds good also for indium phosphide that also has got zinc blend structure. Most of these three-five compounds have got zinc blend structure. So, wherever gallium was supposed to be sitting, we will have indium; wherever arsenic was supposed to be sitting we have phosphorus. So, general three-five elements are sitting there to form the zinc blend structure.

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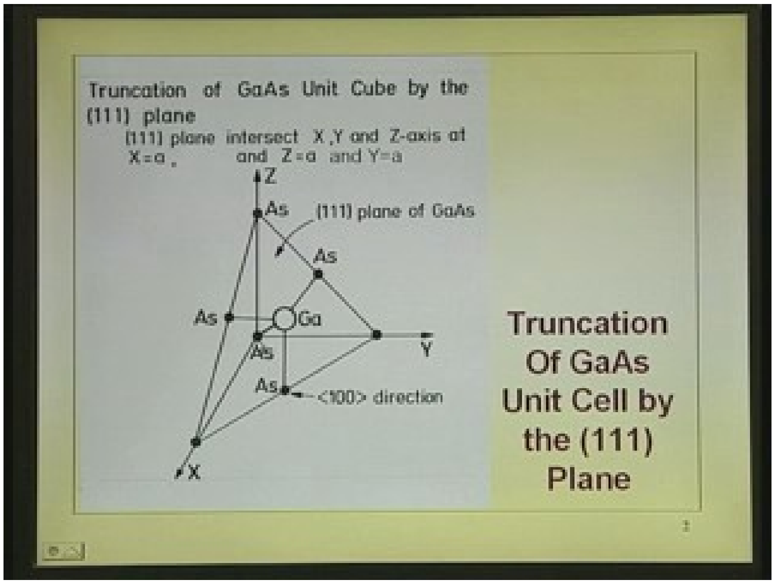

Truncation of GaAs Unit Cube by the (111) plane

(111) plane intersect X ,Y and Z-axis at X=a , and Z=a and Y=a

Truncation Of GaAs Unit Cell by the (111) Plane

Now, we saw the (1 1 1) plane again projecting it to you, to see that you have got on the (1 1 1) plane. All these are arsenic atoms and this gallium atom is below that because that is at a by 4, a by 4, a by 4 from this corner so, that is below that. This arsenic atom is even below that. So, which means as you go along the (1 1 1) plane, we have arsenic gallium arsenic gallium.

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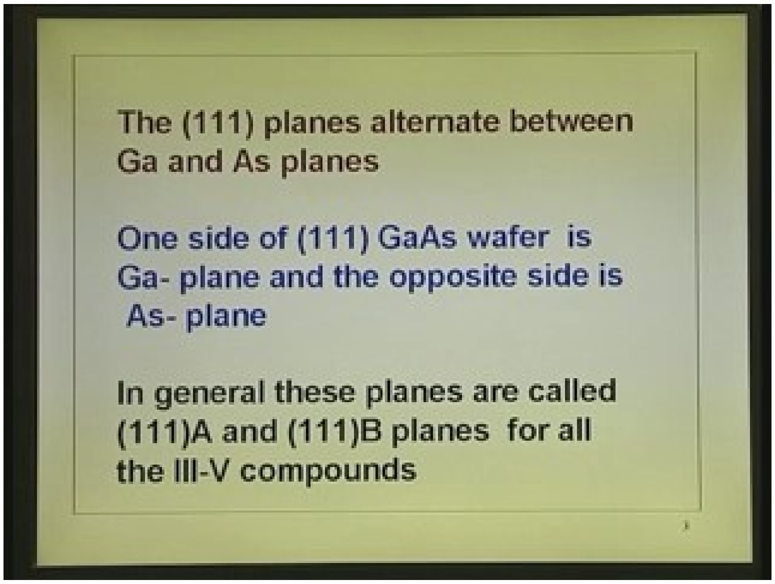

The (111) planes alternate between Ga and As planes

One side of (111) GaAs wafer is Ga- plane and the opposite side is As- plane

In general these planes are called (111)A and (111)B planes for all the III-V compounds

So, if you look at the entire wafer on one side of the (1 1 1) plane or (1 1 1) gallium arsenide wafer. If you take a gallium arsenide wafer, you have gallium plane on one side go on alternating at the other extreme end of the arsenic plane, because you can never remain arsenic on both sides. It starts with gallium ends with arsenic on the other surface. So, general even for indium phosphide starts with indium other end of the (1 1 1) plane is phosphorus. So, sometimes to keep the general term these three five semiconductors when you take (1 1 1) oriented wafer you call it as (1 1 1) A, top plane for one surface (1 1 1) A and (1 1 1) B. These two have distinct characteristics. They have distinct characteristics because, the (1 1 1) A, the A phase. Let me take the example of gallium arsenide has got gallium atoms which are having three valence electrons which are forming three bonds down; they are attached to the crystal with the three bonds going down. So, out of the three valence electrons all the three occupying down. There is no electron available on the surface. The implication of that is if there are no free electrons available, because all the three are busy forming the bonds with the crystal, because there are no free electrons available that surface is less reactive means it will oxidize slowly. It will etch also slowly because for any chemical reaction there must be electrons.

In the absence of that, all those reactions are slow. So x-rate is slow, oxidation rate is slow in that (1 1 1) gallium plane or (1 1 1) A plane. If you go to (1 1 1) B plane in the case of gallium arsenide it is (1 1 1) arsenic plane. That plane has also got the out of five; three of them will be bonding into the crystal. If you look into the crystal structure we will see it will be bonding into the wafer or crystal from bottom three bonds, three electrons, but there are other two electrons which are there on the surface. At least one will be free for chemical reaction. So, the arsenic phase will be quick to react chemically it will be quick to oxidize compared to the gallium plane or (1 1 1) A plane. So, these are the two differences. This property also reflects on the ability to polish the two surfaces, mechanical polishing or chemical polishing whatever you want to do, in a polished surface of a wafer it is easy to polish (1 1 1) B plane. That is arsenic plane because it is more highly reactive. Whereas, the A plane A phase difficult to polish. So, if you ask a vendor I want (1 1 1) gallium arsenide wafer with gallium surface polished, you will not get it. But if you say (1 1 1) arsenic phase polished, you will very easily get it, because it is easy to polish. These are some of the results, consequences of some of the peculiarities of the compound semi-conductor.

In silicon, it does not matter when you take silicon if top phase or bottom phase three are bonding there one is available for you for chemical reaction. So, whether you take top or bottom it oxidizes the same way you can polish both in the same way. These are some of the differences between the crucial or major differences apart from the crystal structure the reactivity of the surfaces. Now, let us take a look at further having seen these structures and differences, you also saw that the cleavage plane of three five compounds particularly gallium arsenide and indium phosphide etc., are (1 1 0) planes. That also, we explained why. Let us go further down. Having seen the crystal structure, we would like to see how to make devices and to make devices you must have the ability to dope them. You should be able to make PN functions you must be able to make P-type material.

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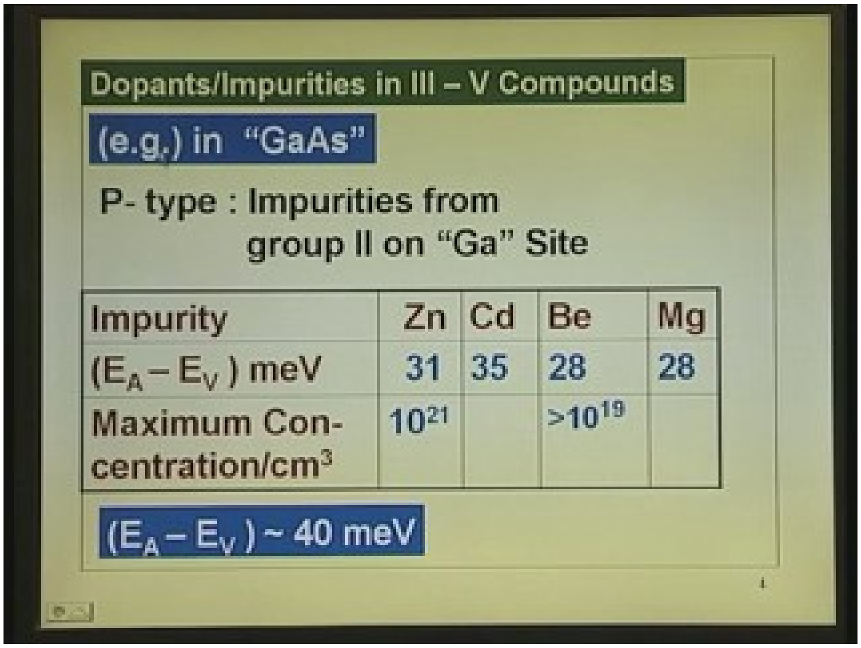

Dopants/Impurities in III – V Compounds

(e.g.) in "GaAs"

P- type : Impurities from group II on "Ga" Site

Impurity	Zn	Cd	Be	Mg
$(E_A - E_V)$ meV	31	35	28	28
Maximum Concentration/cm^3	10^{21}		$>10^{19}$	

$(E_A - E_V) \sim 40$ meV

It is not enough if you have a gallium arsenide crystal, we must be able to make P-type gallium arsenide N- type gallium arsenide. So, dopants or impurities in three five compounds: I will take the example of gallium arsenide. What I discussed holds good for indium phosphide also because they go hand in hand, they competed with each other for microelectronics and also up to electronics. Now, in this gallium arsenide, gallium is from third group arsenic is from fifth group. Now, if you take impurities from the group two from the periodic table, impurities from group two are zinc, cadmium, beryllium, and magnesium. If you take any one of them, if they are occupying the gallium site what will happen. In the gallium site, it calls for three electrons, gallium of three valence electrons. It forms covalent bond with arsenic with five electrons from arsenic, three electrons from gallium, so totally eight to form the covalent bond. Now, if you put zinc and if it is occupying the gallium site, zinc is from second group it has only two electrons. So when it is sitting on the arsenic gallium site there is one deficient one electron. That is there is one vacancy, so it becomes .P-type material. Absence of electron you say it is a hole that is equivalent of having a plus charge that is actually P-type. Now numbers here are the numbers which will tell you where that acceptor level is with respect to the valence band. After all, you would like to see what the ionization energy is. For example, the vacancy, we can call it as a hole, is that hole has to move from the vacancy to the valence band. How is it possible? By transfer of electrons from the valence band to that point that vacancy can be occupied by transferring electron from the valence band to that point that will be negatively charged when it is ionized. So, energy required to ionize that acceptor level is the ionization energy. Now it can be easily ionized if it is close to the valence band. Now, this is our 31 milli electron volts. Gallium arsenide band gap is 1.43 electron volts. Out of that, 31 milli electrons are very small, very close to the valence band.

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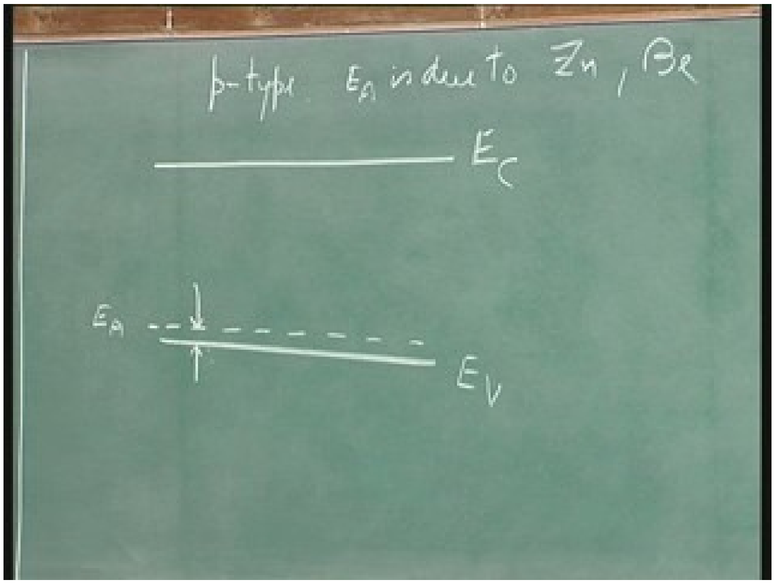

That is why E_A is the acceptor level, E_V is just for clarifying what I am implying E_C E_V that is the band gap. Now, what we are telling is you have this acceptor level or this when you introduce zinc or cadmium or beryllium that introduces a level. This is actually the ionization energy, energy required to transfer electrons from here to here, in other words to transfer the vacancy from here to here. That vacancy one electron moves from here you have a plus charge there that is that plus charge which is available for current transport. So, this is what we are talking of and this is the P-type. E_A is due to any one of the zinc, mostly it is zinc that is used and today people are using beryllium. In fact, if you see on this table you are given some of the concentrations which have been achieved.

For example, zinc can be introduced at the concentration of 10 to the power of 21 that means you can make P plus gallium arsenide, P plus means very heavily doped P-type material P plus gallium arsenide by introducing zinc to a level of 10 to the power of 21. Beryllium, it can go beyond 10 to the power of 19 but actually upper limit I do not have these two there is no numbers variable at the moment. Implying these can be used but, there are difficulties in realizing them using them, so mostly zinc and beryllium. In fact, if you open up literature the most popular P-type dopant in gallium arsenide and indium phosphide is zinc. Zinc doped gallium arsenide. It adds just a doping concentration. Now on an average that energy difference is about 40 milli electron volts which is almost similar to that of silicon. Silicon also if you introduce boron which is third group element, silicon is fourth group, so one less electron in boron it introduces a level similar to level at about 40 to 50 electron volts.

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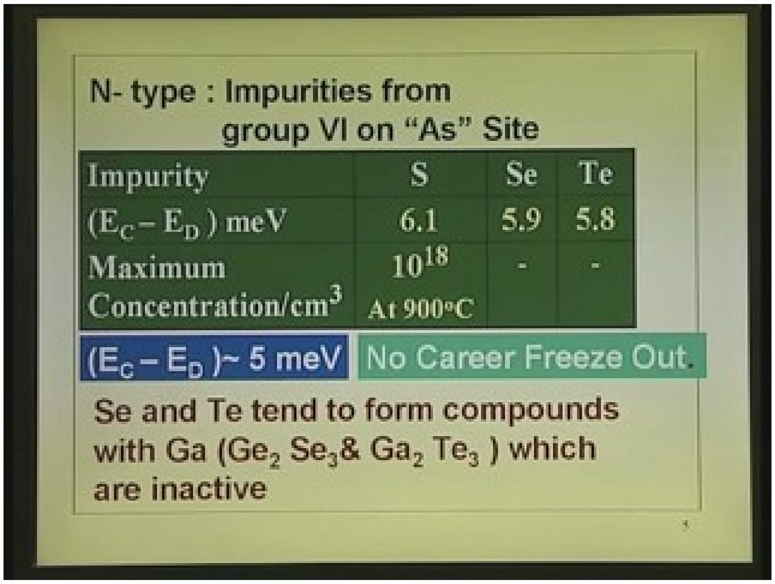

N- type : Impurities from group VI on "As" Site

Impurity	S	Se	Te
$(E_C - E_D)$ meV	6.1	5.9	5.8
Maximum Concentration/cm^3	10^{18} At 900°C	-	-

$(E_C - E_D) \sim 5$ meV

No Career Freeze Out.

Se and Te tend to form compounds with Ga (Ge_2Se_3& Ga_2Te_3) which are inactive

Let us take a look at the N- type impurities. N- type impurities introduces a level E_D donor level (Refer Slide Time: 13:41) E_C E_V that is supposed to donate an electron to the conduction band that means when it ionizes which should be possible even at room temperature. If he should be able to ionize a donor even at room temperature the implication is very small energy, the donor should donate electron to the conduction band.

That means, the donor level is located very close to conduction band if it should donate that is the meaning of that. So, we put it as what is the meaning of this plus? The meaning of the plus is when it has donated an electron it is like this (Refer Slide Time: 14:32) a donor atom with an electron attached to that and donor in the case of silicon is from the fifth group. So, the fifth electron donates because it requires only four to form the covalent bond. Now, if you take sixth group in the case of gallium arsenide, if it has six group elements, it has six valence electrons. If it is sitting on the arsenic site, there is one extra electron. Arsenic site requires 5 electrons you write it as 5 electrons, how? Instead of that if sixth group elements like sulphur, selenium, and tellurium all of them belong to sixth group. If they are occupying the arsenic site, then there is one extra electron which is very loosely attached because, all other five electrons will be forming the bond. So, those are the ones which formed the bond. So, the fifth one is available that will be donated to that. So this one (Refer Slide Time: 15:47) when it goes off once it is donated to the conduction band it is left to the positive charge. So, that is why we put that donor level as plus there implying it is ionized. What is ionization energy? Energy required over the electron to move from the donor level that is the E_D to the conduction band.

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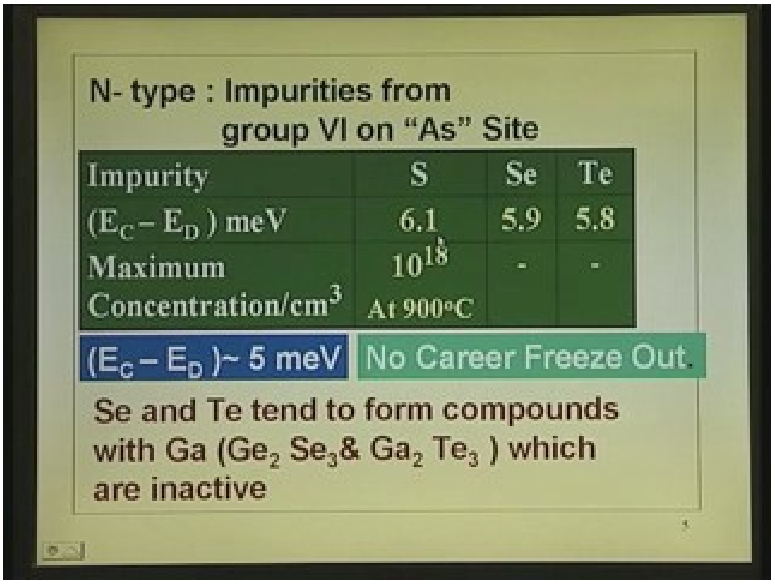

N- type : Impurities from group VI on "As" Site

Impurity	S	Se	Te
$(E_C - E_D)$ meV	6.1	5.9	5.8
Maximum Concentration/cm^3	10^{18} At 900°C	-	-

$(E_C - E_D)$~ 5 meV | No Career Freeze Out

Se and Te tend to form compounds with Ga (Ge_2 Se_3& Ga_2 Te_3) which are inactive

Now, noticed the difference. This is one of the things that we will note E_C minus E_D 6.1 mill electron volts. That is one of the major differences between donors in silicon and donors in gallium arsenide. In silicon, it is something like 40 to 50 milli electron volts gallium arsenide. These ionization energies of shallow donors are 6.1, 5.9, and 5.8 on an average 5 milli electron volts, very small. They are virtually very close to conduction band. What is the consequence of this? The consequence of that is you go down below room temperature there is no career freeze out. If you take silicon for example, it requires certain energy of 50 milli electron volts for donating the electrons. You go down below room temperature you would have calculated in some places that has to go down in temperature number of donors which are ionized that decreases. You go to much lower degree temperatures, less and less number of them is donated. What does it mean? That means, the electron concentration goes down it is frozen into the donor atom itself. It is not moving there, it is right here that is what we say imply when you say it is frozen. If you take gallium arsenide the energy is 6 milli electron volts or 5 milli electron volts then even if you go down liquid nitrogen temperature even if you go down to that temperature, the electron should remain there they are available for conduction, because very little energy is sufficient to release those electrons to the conduction band. So, even at much lower temperatures, you have these electrons which are available for conduction; whereas, in the case of silicon you go down to much lower temperature liquid nitrogen etc., the number of electrons which are available will be coming down drastically reduced.

So, the conductivity goes down and if it is delivering certain current at room temperature at lower temperature, the device will not be able to deliver much current, whereas; here it can work. You can immediately see what will be the benefit of this. The benefit of this is you can make use of gallium arsenide devices at lower temperature very confidently. If you recall what we discussed earlier you would like to operate some of the devices at lower temperatures to avoid scattering or to reduce the lattice scattering. So, if you go down to lower temperature if the electron concentration is reducing no point where is the question of scattering if the electrons are available for conduction. So, this is one of the advantages, you are cutting down lattice scattering by going to lower temperature. Now of course, you will have to be worrying what about ionized impurities scattering. They have got methods of separating the donor and acceptor to prevent the ionized impurity scattering that we will discuss when we go to high electron mobility transistor discussion.

So, main impurity that is used is sulphur. Selenium and tellurium are used you will see selenium doped or tellurium doped gallium arsenide, we try to avoid that because it forms some compounds. After all if you introduce tellurium it should remain as tellurium, so that it acts as the donor there. If it is making a compound like tellurium and gallium telluride like this, it is no longer a donor. It is an unwanted lump standing there in gallium arsenide, so no use. So that is why they are finding difficulty in that, but still when the doping concentration is low you can use that, but when it is higher you must use sulphur. There are better impurities. We will go and see those things afterwards after seeing what could be the reason for this low ionization energy.

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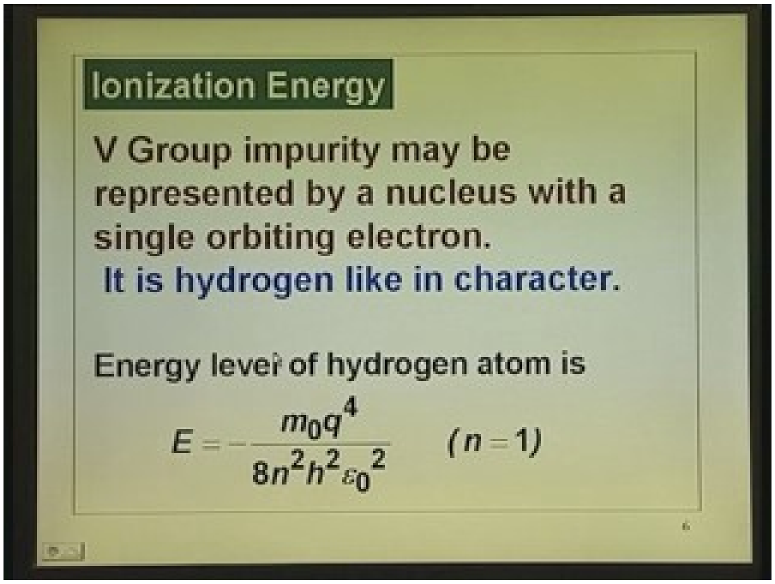

Ionization Energy

V Group impurity may be represented by a nucleus with a single orbiting electron.

It is hydrogen like in character.

Energy level of hydrogen atom is

$$E = -\frac{m_0 q^4}{8n^2 h^2 \varepsilon_0^2} \quad (n = 1)$$

Explanation for that because after all we would like to see why it is so low compared to silicon. If you recall when you discussed the silicon ionization energy, there is a simple model for this. The simple model is the fifth group impurity in silicon may be represented by a nucleus with a single orbiting electron. When you say it is in silicon, if you take gallium arsenide it is sixth group fitting on the arsenic side. So, what you are telling is the donor. A donor, shallow donor can be represented by means of a nucleus with a single orbiting electron like that.

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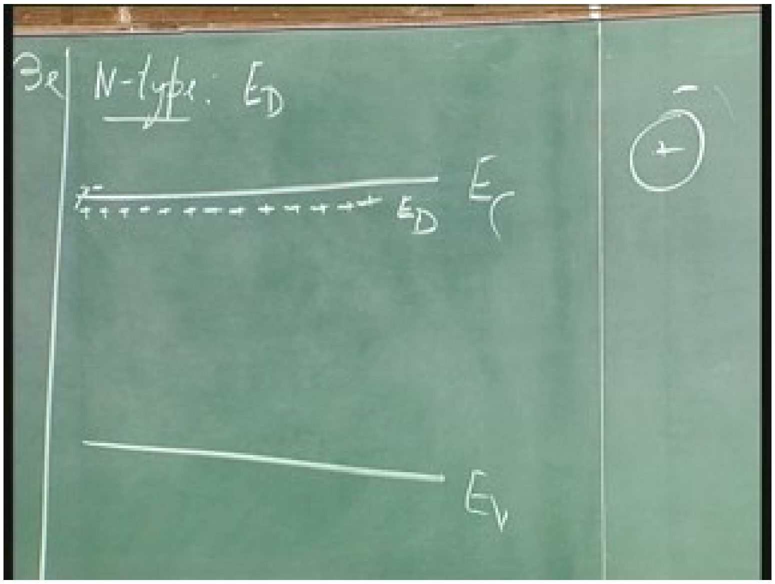

This is the one which is orbiting. This is equivalent to hydrogen atom, hydrogen like in character which has one electron which is orbiting. Now, there you find out what is the ionization energy of that electron. There what you mean is the energy required to remove it from the vacuum level that is calculated by this formula. Once you consider the hydrogen atom what is ionization energy of the electron that is the energy required to remove the electron away that is used by this (Refer Slide Time: 22:14) formula. This is almost dealt at the high school, let me not go into that where here m_0 is the mass of the electron. When you talk of hydrogen, we will talk of the free mass of the electron and q is of course the charge, n is 1 depending upon energy level when you talk of hydrogen atom of the electron that is n is 1 only 1 electron, h is Planck's constant, epsilon is permittivity of free space. So, when you use that, it so turns out that substitute for m_0h, n equal to 1 (Refer Slide Time: 23:05) epsilon$_0$ is 8.854 into 10 to the power of minus 14 farads per centimeter, m_0 is the mass you should have known what it is right now you can substitute that it is very small, h is Planck's constant, substituted all that this turns out to be 13.6 electron volts. Now, when you consider this silicon atom or gallium arsenide atom or for that matter indium phosphide atom with the donor or a donor in these materials when you consider, you consider this as just like hydrogen like atom.

So, if you want to compute the ionization energy of the donor what you do is you compute this quantity. Meanwhile of course when it goes to conduction band, it is available for free transport. It is freed from the donor, it is available. So, that is ionization energy.

Now what should we do to compute that n you can put it as 1 and m_0 you replace by the effect q mass, because the electron now is in a crystal. The way electron moves in a crystal is different from the way it would move in the free space. Because, an electron moves under the action of an external force plus it experiences the force within the lattice itself. Within the lattice itself, there are electrostatic forces acting on them internal forces. So, the way it moves is different, so people have simplified the whole thing so that we can apply Newton's laws of force, force is equal to mass into acceleration. That force is actually the applied force and the mass is the mass of the free space free electron if it is free space. So, for a given force it will accelerate decided by the mass. Now, if that electron is moving within a crystal where other forces also come if those forces are already aiding the movement for a given force there will be different acceleration. So, we can still apply the Newton's laws of force, the force is equal to mass into acceleration. The f is actually what you see outside is applied force, but the electron experiences a force which is a combined effect of external force and internal force. So, to accommodate that internal force still you use force is equal to mass into acceleration you use a different mass that is called effective mass. It will look as if the mass is different.

Normally, if the mass is m_0 when I apply a force f acceleration is force divided by mass. Now, when I apply the same force if the acceleration is more it appears as if mass is smaller. So, that is the effective mass that is because in addition to the applied force there is internal force that is coming. So acceleration is more still we can apply Newton's laws of force to use the effective mass concept. Now, what you should do here is replace the m_0 by effective mass you would have computed that and this epsilon_0 replace by epsilon_r epsilon_0 where, epsilon_r is the relative directive constant.

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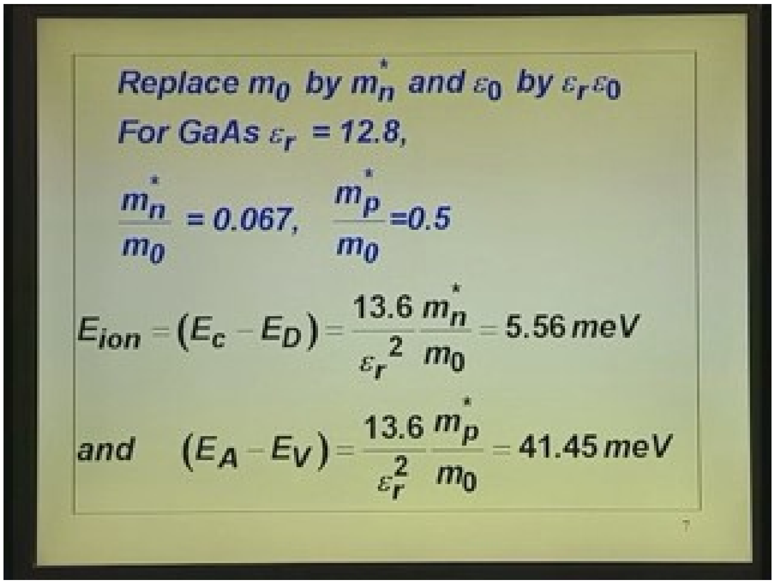

Replace m_0 by m_n^* and ε_0 by $\varepsilon_r \varepsilon_0$

For GaAs $\varepsilon_r = 12.8$,

$$\frac{m_n^*}{m_0} = 0.067, \quad \frac{m_p^*}{m_0} = 0.5$$

$$E_{ion} = (E_c - E_D) = \frac{13.6}{\varepsilon_r^2} \frac{m_n^*}{m_0} = 5.56\, meV$$

$$\text{and} \quad (E_A - E_V) = \frac{13.6}{\varepsilon_r^2} \frac{m_p^*}{m_0} = 41.45\, meV$$

That is what is put here. Epsilon$_r$ for gallium arsenide is 12.8 and m$_n$ star effective mass of electron divided by actual mass of electron is 0.067. You can see it looks as if it is much lighter which will tell you that if you apply a force the electrons will run virtually much faster than in the free space, because there are additional forces internally. A mass of hole that may not get into the physics of this, we borrow this result straight away. The effective mass of holes divided by the effective mass of an electron is 0.5. It is not as light as an electron. So, ionization energy now what you do is just I will go back once (Refer Slide Time: 28:08) replace m$_0$ by m$_n$ star. That means what I will do is whatever I get here is 13.6 divided by m$_0$ multiplied by m$_n$ star or what I do is 13.6 is there dividing by m$_0$ multiply by m$_n$ star. It is also to our convenience. I do not have to know the actual mass of an electron. All that I have to know is m$_n$ star by m$_0$. That ratio which is much smaller divided by in the place of epsilon$_0$ square the epsilon$_r$ also coming up so, that is there. So, this number when you evaluate is 5.56 volts milli electron volts.

So, the ionization energy comes out to be very small because the effective mass of electrons is very small. Whereas, the effective mass of holes if you see E$_A$ minus E$_V$ is much larger than that because that is m$_p$ star by m$_0$ is 0.5 for gallium arsenide m$_n$ star by m$_0$ is 0.067. So, depending upon how small is the effective mass you will get smaller this energy. This model is a very simplified model but it works out, it is amazing. A hydrogen-like model can be applied for such a complicated structure crystal. Now, you can see the whole lot of them. I hope this is clear enough. Exactly all that you do is 13.6 you multiply m_n star by m_0 divided by epsilon$_r$ square. The entire ionization energy depends upon that ratio of the effective mass to the actual mass.

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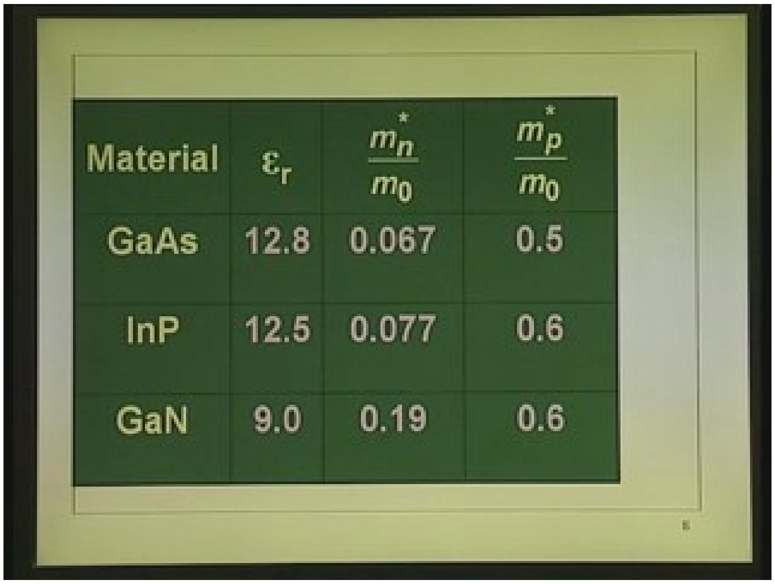

Material	ε_r	$\frac{m_n^*}{m_0}$	$\frac{m_p^*}{m_0}$
GaAs	12.8	0.067	0.5
InP	12.5	0.077	0.6
GaN	9.0	0.19	0.6

Using that if you sum up and see I have listed here gallium arsenide, indium phosphide, and gallium nitrate. Because these are the two, first two are the very popular ones. This is the one which is finding its way in the gallium nitrate. I have just added that also and they are almost comparable. What are not comparable, varying are effective mass of electron mass of electron 0.067 for gallium arsenide and 0.077 for indium phosphide. In fact, this also decides what the mobility is, mass is smaller the mobility is better. So, you can see from here that mobility of electrons in gallium arsenide will be higher than that of indium phosphide and that will higher than that of gallium nitrate. It is true 8500, 4500, and 2000 that way it goes. Now, m_p star by $m_{0,}$ almost 0.5 or 0.6 so, that is why this ionization energy when you take a silicon, gallium arsenide, indium phosphide they are almost same 40 to 50 milli electron volts. Whereas, if you take the ionization energy of donors, silicon it is about 0.5 because this is much larger than that of gallium arsenide etc., at least five to six times, so that when this is larger and in case of gallium arsenide and indium phosphide that is small. Let us model to see what actually the cause is for this. The cause is the lower effective mass which is decided by several physical phenomena happening between the crystals itself.

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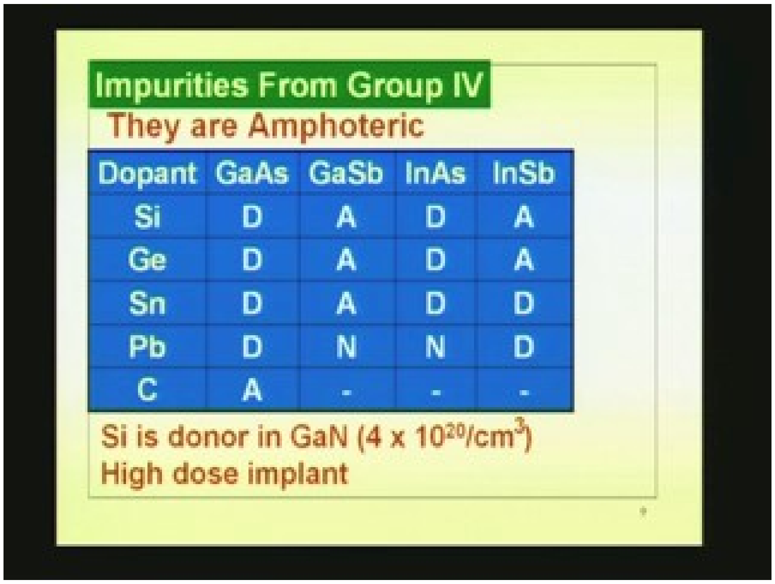

Impurities From Group IV

They are Amphoteric

Dopant	GaAs	GaSb	InAs	InSb
Si	D	A	D	A
Ge	D	A	D	A
Sn	D	A	D	D
Pb	D	N	N	D
C	A	-	-	-

Si is donor in GaN (4 x $10^{20}/cm^3$)

High dose implant

Now, we have discussed the donors from the fifth group sitting on the arsenic side acceptors from the second group of elements sitting on the gallium side forming acceptors elements on the sixth group site forming donors. What about the fourth group elements? They are amphoteric. Amphoteric meaning it can go either way. It is the greatest opportunist because it has got a chance. It can go and sit in the gallium site. If you give a chance it will go and sit in the arsenic side. What is the meaning of given a chance? If you say given a chance you give a vacancy there, it will go and occupy that position gallium. If you give a vacancy on the arsenic side it will go and occupy them. That is why it becomes amphoteric, either way it can go. If it occupies in a gallium site what does it behave? If silicon force group sitting in the gallium site behaves like a donor, one extra electron. They require three they have got fourth group element. If it is sitting on the arsenic site it is actually acceptor because one less electron, you need five electrons whereas silicon has only four. So, it can become either P- type or N- type but it so turns out. It has some sort of choice prefers to go act as donor and if the same setting if donor what you mean if silicon prefers to go to gallium site unless you create a special situation where arsenic vacancies are tremendously more. Normally, at room temperature itself, there will be vacancies. If you raise the temperature the vacancy concentration goes up. So, given any particular condition of a crystal growth there will be vacancies both gallium and arsenic and they are more or less comparable numbers it will go and occupy gallium site. I just deliberately put this table, just sort of theorized or observed certain patterns. See here silicon, germanium, tin, and lead all these belong to fourth group. All of them in gallium arsenide act as donors. When act as donors sometimes normal conditions unless you create additional vacancies in arsenic. When there are both arsenic and gallium vacancies present in comparable numbers it will become donor.

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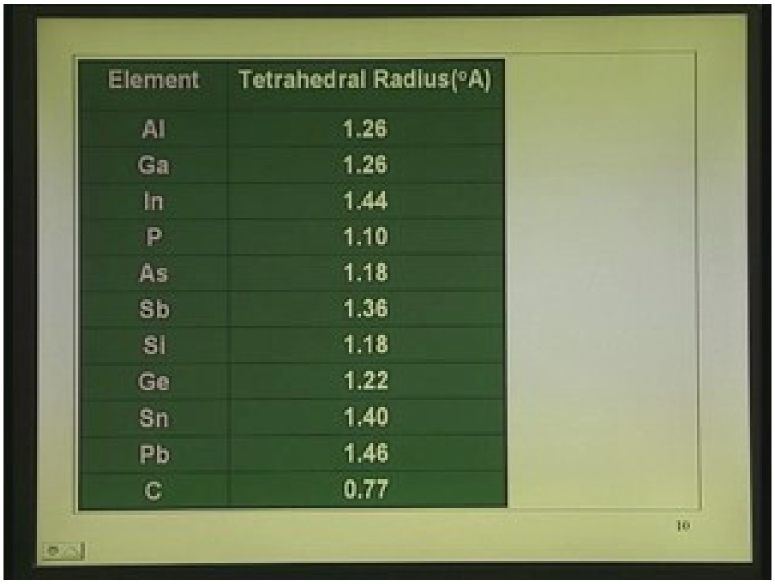

Element	Tetrahedral Radius(°A)
Al	1.26
Ga	1.26
In	1.44
P	1.10
As	1.18
Sb	1.36
Si	1.18
Ge	1.22
Sn	1.40
Pb	1.46
C	0.77

The reason, this is the table which I have put just for it is a hunch. It is just observation that I have made. I do not see it actually mentioned in books, but generally you can see radius of the gallium atom, tetrahedral radius of gallium atom is 1.26 angstroms, about arsenic that is 1.18 angstroms. So, in gallium arsenide if you have vacancy of gallium that vacancy site is slightly bigger. This is the physical phenomena which you can observe; whereas, vacancies that of arsenic is slightly smaller. So, if a foreign atom or if a guest is coming and sitting the guest atom will come and occupy where it is comfortable. It will be comfortable if the vacancy site is bigger. This is the law of the nature. So, observing that gallium vacancy is bigger than arsenic vacancy because gallium has bigger atom size that becomes donor. Now, you may ask you are flouting the rules there is one atom here called carbon it generally becomes acceptor.

Now, the carbon is small atom, tetrahedral radius you can see 0.77. So, it will go either way. It turns out that the gaze you can see is the law of the nature a small atom the bigger seats are there but tend to occupy which is a smaller one. It is just on the lighter sense. This is just on a lighter sense. So you can see the carbon is occupying that arsenic site and acts as an acceptor. It does not mean that it does not go to the gallium site it also goes but most of them tend to go and occupy that. There will be other criterion like electro negativity etc. But generally this is a basic. Now, let us take a look at what we say how far it is true? Take a look at gallium antimonite. Gallium 1.26, antimony 1.36, gallium is bigger. Now all these atoms will tend to go into the bigger vacancy that is antimony, all acceptors and n is neutral means it may be go either way, goes into both so that it is rather you do not see the effect of that. People are not being able to observe very clearly about Pb lead on gallium antimonite. Similarly, you can see indium arsenide. Which is bigger? From here itself we can see it is indium. Indium is 1.44 bigger, much bigger than gallium, and arsenic is 1.18. It goes and sits in the indium site. This is just a curiosity, just made this table to see whether something tangible is there and it seems to hold good like that and of course this one is neutral implying it goes either way. In fact, lead is quite big so that why it does not matter where it goes between the two of them that is indium arsenide; indium is 1.44 same as almost smaller than that. So, probably it tries to squeeze in both indium and indium arsenide generally, but what I am trying to tell is general law. Similarly, indium antimonite also generally follows similar rules, slightly flouting out the rules is there. It is just an observation.

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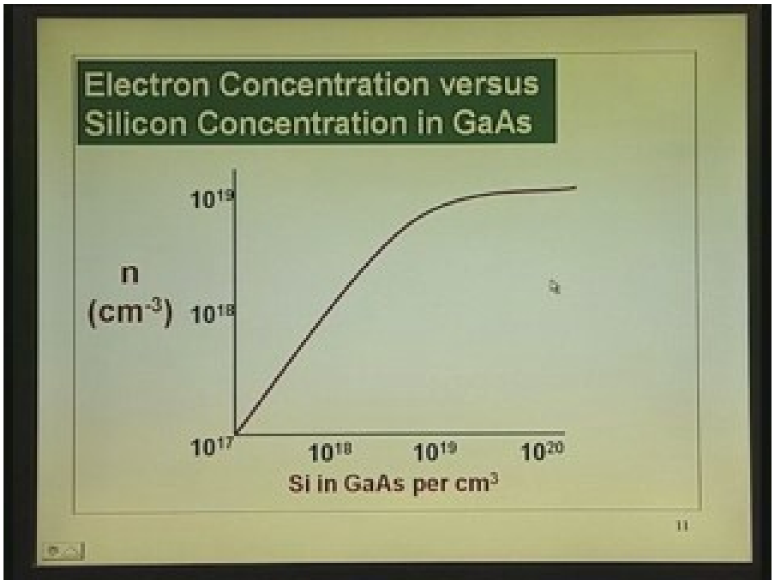

Electron Concentration versus Silicon Concentration in GaAs

So, now if you put silicon into gallium arsenide while growing gallium arsenide keep on adding silicon into that melt what happens is the carrier concentration becomes equal to silicon concentration. For example 10 to the power of 17 silicon atoms and gallium arsenide will go and occupy the gallium arsenide which is bigger than silicon. Silicon is 1.18 angstroms. So both are same or 10 to the power of 18 it is almost linear. For 10 to the power of 19 start deviating from it is not 10 to the power of 19 it is smaller than that. So as you go to higher and higher silicon concentration, the electron concentration does not increase linearly, it is sub linear. Reason as you go on dumping more and more silicon, they prefer to go to gallium site, but as you go beyond certain level they thought finding that there are arsenic sites also they can go into that. So, they are getting filled up the gallium vacancies starts getting into arsenic site. So what happens? From 10 to the power of 18 or 10 to the power of 19 around that as you go, if you go beyond this point, the additional silicon atoms do not go into gallium site. Many of them tend to go into arsenic site, so the electron concentration does not increase linearly, it becomes sub linear and beyond a certain point it saturates, because beyond that point it goes equally both into this gallium and arsenic site. So, if you introduce them equally you have one shallow donor, one acceptor; one donating one accepting. So, there is no continuity that is why the electron concentration saturates out beyond that point.

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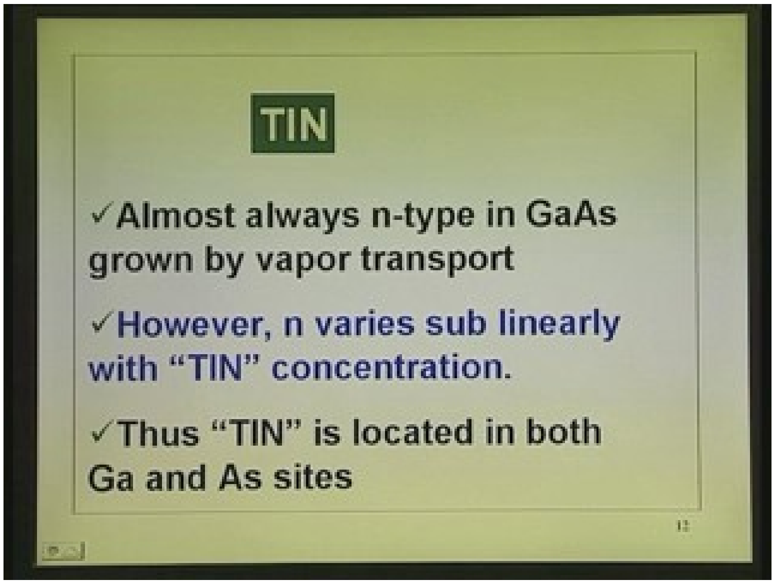

TIN

✓Almost always n-type in GaAs grown by vapor transport

✓However, n varies sub linearly with “TIN” concentration.

✓Thus “TIN” is located in both Ga and As sites

Now, just a few examples where you can see TIN follow the same rule. It can go either way and it contributes becomes n- type but there is a donor, the fourth group TIN sitting in the third group site, gallium site and it becomes nonlinear sometimes. That is exactly like in the case of silicon that is what we mean by that. So TIN also behaves sub linearly implying TIN is located in both gallium and arsenic site as you increase the concentration.

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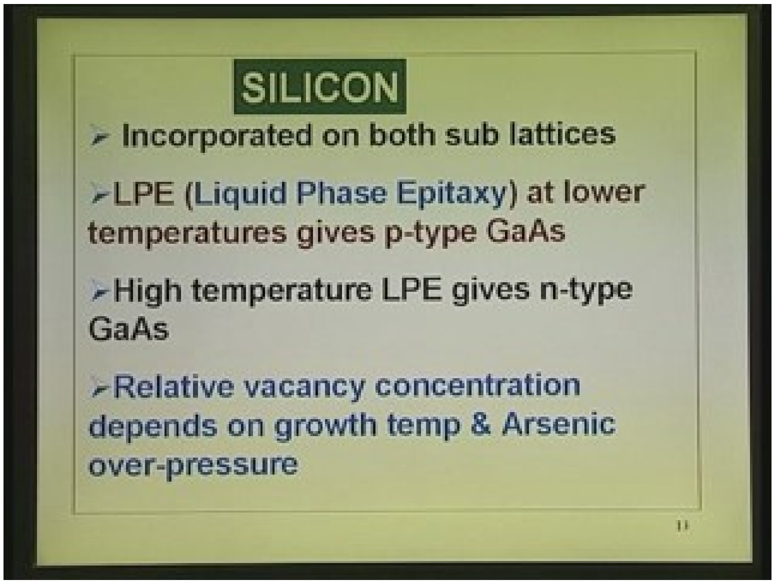

SILICON

- Incorporated on both sub lattices
- LPE (Liquid Phase Epitaxy) at lower temperatures gives p-type GaAs
- High temperature LPE gives n-type GaAs
- Relative vacancy concentration depends on growth temp & Arsenic over-pressure

Now, what I am trying to point out is going back to silicon, we said silicon prefers to go and occupy gallium site and become donor. Now, that is under normal circumstances, but when you grow the crystal by a method known as liquid phase epitaxy, then what happens is maybe I will have to draw the diagram, I will go through these statements first. See what happens? Liquid phase epitaxy LPE, take a gallium arsenide substrate and then I try to grow gallium arsenide layer on that with some silicon doping. Physical means even when it contaminates so with that when I do what happens is at lower temperature it gives p- type gallium arsenide.

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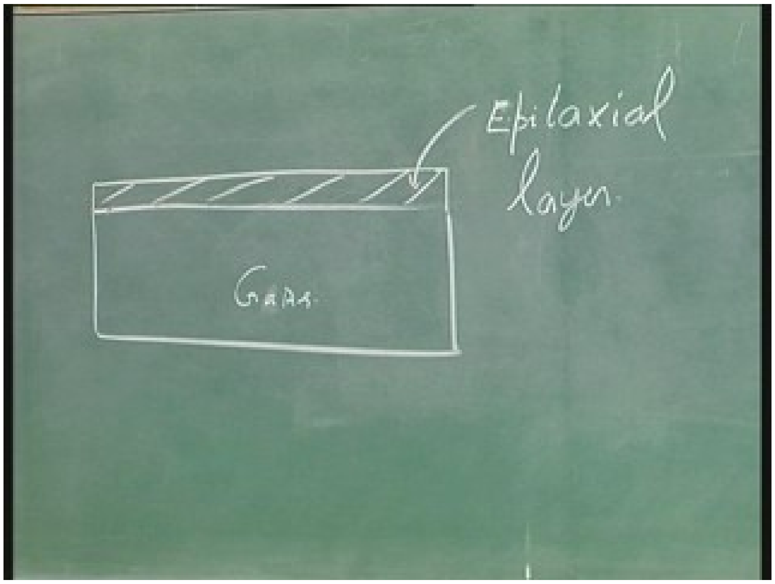

I have some gallium arsenide substrate. This may be undoped. It is a substrate which I am using. On that I want to grow another layer. This is a layer which I am growing, epitaxial layer. Maybe it is not visible as if it was not I will redraw that. That is epitaxial layer, epi is arranged upon. You arrange atoms on top of that. So, this can be done by different ways. In fact, we will have occasion to see in some detail immediately after this dopants etc. in the next one of the lectures. So, this layer when you grow what you can do is keep this gallium arsenide substrate in contact with the liquid of gallium arsenide. Let me draw that diagram for they are completeness sake here. Let me put it down here separately.

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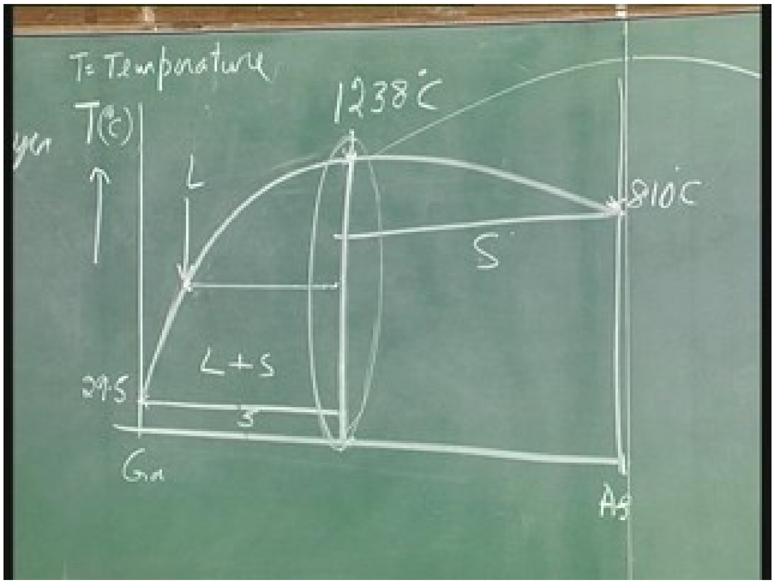

If you take a look at the gallium arsenide phase diagram, I am drawing into metallurgy now. If I take temperature, now if I take a look at that the phase diagram is like this. It tells you the phase of liquid gas or solid of the material that is existing at different temperature. So, if you draw this is a composition. Here, it is totally gallium, here it is totally arsenic. I can move into gallium arsenide, gallium rich gallium arsenide, and arsenic rich gallium arsenide and here stoichiometric gallium arsenide truly. Now, if you take a look at that, draw a line like this here, this is important because all those people who talk of gallium arsenide indium phosphide shall talk of this phase diagram. Now, what does it tell you? I have line here at 29.75 degree centigrade. What is that 29.5 degree centigrade? It is the melting point of gallium. That means in Chennai if you take gallium, it will liquid because it is never below 29 degree centigrade and even in this room may be cooler, but otherwise it will just like a mercury it will look like and if you take arsenic, its melting point is somewhere here 810 centigrade. In fact, it is volatile at that temperature. If you take gallium arsenide what is the melting point? Very easy to remember, silicon you know it is 1410 degree centigrade, gallium arsenide 1234, 1234 plus 4, 1238. Remembering is easy. What is the melting point of gallium arsenide? 1234 plus 4, that is 1238. See the phase diagram will give you the melting point here 1238 degree centigrade. So, this is a melting point here (Refer Slide Time: 48: 17) that is a melting point there, this is the melting point. In fact, draw those lines together like this crossly what is that line. This is liquid and this is solid. Liquid plus solid, this is solid and that is solid. You have liquid as line below that it will be liquid plus solid it will coexist and finally it will be solid here. Now, we will have as we move from here to here, we will have for example if you come down from here, freeze from here. This is solid actually. This whole thing in the phase diagram is solid telling you will get gallium arsenide. So, freeze from melting point you will get salt gallium arsenide stoichiometric. Now, in liquid phase epitaxy what to do is, you freeze somewhere here; take this gallium arsenide, keep it in contact with the liquid, slightly reduce the temperature. When you start reducing the temperature that is the liquid phase epitaxy, the composition from here will start freezing or crystallizing. The very interesting thing if I go across to Anna University, they will do the liquid phase epitaxy for gallium arsenide. We do not do it in IIT, Chennai. So, this is the method. You freeze it, you will get liquid plus solid, solid in contact with that, and the solid will set along, but long time it will take and the freezing solid has a composition decided by this (Refer Slide Time: 50:17). You just freeze here the composition of solid is decided by that and this has relevance to what we are talking of here. Why it becomes p- type? Why it becomes n- type? Now, if you expand this portion alone; this is not a single line. This is called congruent transformation from here to here that is just suddenly from liquid to solid; whereas, here liquid plus solid, here it is only solid totally. So, we have deviated from electrical engineering physics gone into metallurgy totally, but this is important to understand some of these things what are happening.

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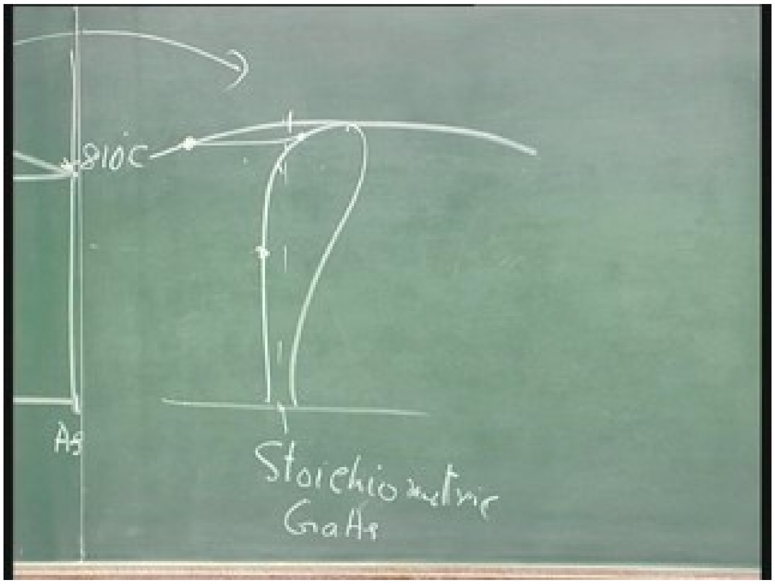

If you see that what happens is, you have that line, what we saw is something like that; this is that line and this is 0.5 gallium, 0.5 arsenic. This is stoichiometric gallium arsenide means 50% gallium, 50% arsenide that is how the stoichiometric is. If you come away from that, if I come down from this side what happens. This is 50% gallium, 50% arsenic, zero arsenic full gallium. If I come here, it is gallium rich, arsenic deficient. When you say gallium arsenide with gallium rich less arsenic what does it mean? That are arsenic vacancies. This is another way of telling gallium rich means arsenic vacancy. One is rich other one is poor automatically, arsenic vacancies present. So, if I freeze from here to here onto this point here. Freezing solid has got that composition that means I am coming down to this side and what is here, gallium rich that means arsenic vacancy is present and if arsenic vacancy is present, the silicon contaminated, unwanted silicon or silicon if you introduced along with that liquid if I introduced silicon that silicon will go and sit in arsenic vacancy, that is p- type. Go to higher temperature right up to this point then I am putting it to expand it here, freezing compound has got that composition. What is that composition? Is it arsenic rich or gallium rich, it is arsenic rich, because this is the 50% point that is arsenic rich that means gallium vacancy, less arsenic gallium vacancy? It means it goes and sits in the gallium vacancy. Now, you have provided forced a situation where either you have got arsenic vacancy or a gallium vacancy. If there is a gallium vacancy you get high temperature and n- type. So what we are trying to tell is relative vacancy concentration depends upon the growth temperature and arsenic over-pressure. So depending upon the relative vacancy concentration you can make p- type or n- type.

This is one of the approaches people used to make some of the p-n junctions by just the varying temperature. If you grow up to certain depth at that temperature, suddenly jack up the temperature quickly to that you will get n- type. So you can get a p-n junction. In fact light emitting diodes of that nature can be made we can get very high pure material with liquid phase epitaxy. So, this is one of the advantages and this tells you it is not necessary that silicon will go and make n- type only in gallium arsenide; it will also make p and n depending upon the opportunity. That is why I said it is an opportunist. If given opportunity it will grab it. Here you are giving an opportunity of gallium vacancies or arsenic vacancies you get p- type or n- type. So, this is the situation that you have got _______. So, that is actually as far as the impurities are concerned. So, today what we have done is we have talked about the p- type impurities and n- type impurities in gallium arsenide. Same impurities will be p- type and n- type in indium phosphide. In fact, even when you go to gallium nitrate you will see silicon can be used for doping gallium nitrate. So, impurities are same type and also we have seen I am summing up what we have said today, we have seen that ionization energy of donors is very small in the case of gallium arsenide and indium phosphide etc., but will not be as small in the case of gallium nitrate because effective mass is not so low. So because of this, it is very easy to use these materials at lower temperature because there is no career freeze out. This is one of the key things that one should remember that is n- type. What about P-type? We are not concerned about P-type or making F E T's etc., because, P-type is no use in switching over to gallium arsenide because gallium arsenide whole mobility is not better. So, we talk of only the devices which deal with the electron transport so that is why you talk of that type of impurities. In next lecture, we will just discuss some other impurities which have been a very popular for realizing semi-insulating gallium arsenide because semi-insulating gallium arsenide is important for making integrated circuits, that we will see in the next lecture.