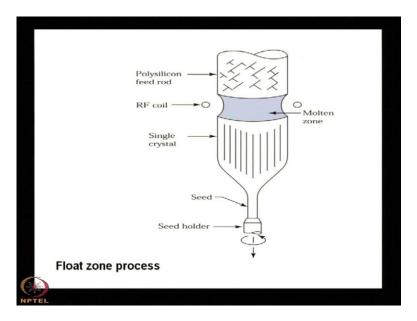
Processing of Semiconducting Materials Prof. Pallab Banerji Department of Metallurgy and Material science Indian Institute of Technology, Kharagpur

Lecture - 14 Ga As Crystal Growth

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You see that if the float zone process, the molten zone is travelled basically along the rod, and what should be the doping distribution in float zone process? Float zone process is very important in the sense that it can purify the crystal. It can purify the crystal, how it can purify the crystal? Since this is the molten state so that means as the crystal solidifies at it progress.

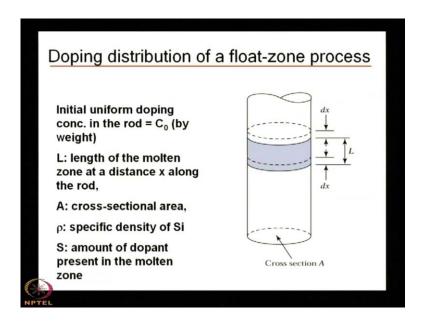
What will happen? There impurity concentration will be moved from this region to the top region, because here also there will be a rejection. Here also there will be rejection, so that means this end that is the retreating end, here the carrier concentration or the impurity distribution will be less compared to this end. Why? The same thing will happen. One-third will be rejected say if you dope with phosphorus. If you dope with phosphorous, one-third will be rejected.

So, here where is the melt? The melt is in the molten zone. So, they will they organize themselves in such a manner, that when it will solidify at this end, two-third will be in a molten zone, then as the molten zone travels, what will happen? At the end, some

amount will be full of impurity. Say this amount say this portion is of full of impurity, then you chop it off. You chop it off. You cut it through it. Again you take this polycrystalline rod or the singular crystalline silicon rod for purification. The same thing you do.

What will happen, some of the material will be lost, but during passes first pass, second pass, third pass it will be more and more pure, because the impurity will be finally will settle down at this end. So, that is why this float zone technique is very much important technology not only for the single crystal growth of silicon at the same time it will give you the purity. For any purification of the crystal, people use this kind of a float zone technique.

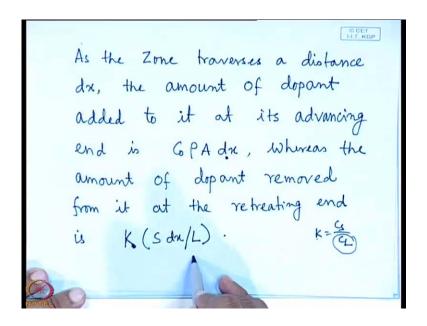
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In float zone, the doping distribution we can calculate. The doping distribution of a float zone process we can calculate. This portion is this zone; that means, this is the zone which is moved. Say by initial uniform doping concentration in the rod was C 0 by weight and L is the length of the molten zone at a distance x along the along the rod.

A is the cross sectional area, rho is the specific density of silicon and S is the amount of dopant present in the molten state, right? C 0 is the uniform doping concentration in the rod, L is the length of the molten zone at a distance x from the rod on the rod, A is the area of cross section, rho is the specific density of silicon and S is the amount of dopant present in the molten state.

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So, what we can write? We can write that, as the zone traverses a distance dx, the amount of dopant added to it at its advancing end is C 0 into rho into A into dx, where as the amount of dopant removed from it at the retreating end is k into S dx by L, right. As the zone traverses a distance dx, the amount of dopant added to it at its advancing end is C 0 rho A dx. What is A into dx?

Volume.

Volume, then rho is.

Density.

Rho density. So, volume value density is?

Mass.

Mass. So, C 0 is per gram. C 0 is the amount of say phosphorous per gram of silicon. C 0 is the amount of phosphorous say per gram of silicon. So, how much gram of silicon is there? rho into A dx. So, what is the concentration? Concentration is C 0 into rho into A into dx.

(())

Yes. Whereas, the amount of dopant of removed from it at the retreating end is K into S dx by L. S, what is S? S is the amount of dopant present in the molten state. Present in the molten state, you see that it is amount of dopant present in the molten state. It is the amount of dopant present in the molten state. And dx is the length, where this happens so; that means, dx by L multiplied by S is the amount of dopant present in this length, which when multiplied by K will give you the amount of dopant removed from it. What is K? K is the segregation coefficient; that means, CL by CL.

K is C S by C L. So, when you put K multiplied by C L, here C L is the concentration in the liquid state.

Student: Molten state.

Molten state. We have taken it as S, and since the length is dx, so, sdx by L. right?

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$$ds = C_0 PA dn - \frac{KS}{L} dn$$

$$= \left(C_0 PA - \frac{KS}{L}\right) dn$$
or,
$$\int_0^{\infty} dn = \int_0^{\infty} \frac{ds}{C_0 PA - \left(\frac{KS}{L}\right)}$$
when $S_0 = C_0 PAL$ is the amount of depent in the Zone when it was first formed at the front end of the rod.

So, now, we can write with this expression that ds is equals to C 0 rho A dx minus K S by L dx. That is equals to C 0 rho A minus K S by L into dx or integration 0 to x dx is equals to S 0 to S dx by C 0 rho A minus K S by L.

Where S 0 is equals to C 0 rho A L is the amount of dopant in the zone, when it was first formed at the front end of the rod. Yes. I have calculated ds, which is the difference between this two amount of dopant. One in the advance end, another one is retreating end, and then we make use of the integration to calculate for the whole rod.

And, for the x we have taken the limit as 0 to x and for dx we have taken the limit from S 0 to S. S is we know is the amount of dopant to present in the molten state, but what is S 0, S 0 we have written as C 0 into rho into A into L is the amount of dopant in the zone, when it was first formed at the front end of the rod. That is at the beginning that we assumed. So, with this limits we can make some more mathematics and you will find that the result will be like this. Should I work out the whole expression or I should give the result only? As you like.

Student: (()).

I have no problem, it is the choice is up to you.

Student: Expression (()).

Whole expression?

Student: Result.

Let me deduce. Absolutely there is no problem. So, the expression is this. Integration of dx. This is our final expression, on which we shall work out. On which we shall work out. Let us take this as equal to t, C 0 rho A minus K S by L equals to t.

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$$C_{0}PA - \frac{KS}{L} = t$$

So, let us write that this is equal to t. C O rho A minus K S by L equals to t or. dt (()). Or yes dt is equal to minus K. L by K. K ds K by L into ds. or x equals to minus. L by K. L by K (()). dt by t. dt by t. So, that is equal to minus L by K L n t. Then put the value of t. Minus L by K into L n. What is the value of t? rho 0 S 0 rho A minus K S by L then put the limit S and S 0. It is ok?

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$$= \frac{Kx}{L} = -\ln\left(\frac{c_0 PA - \frac{KS_0}{L}}{L}\right) + \ln\left(\frac{c_0 PA - \frac{KS_0}{L}}{C_0 PA - \frac{KS_0}{L}}\right)$$

$$= \ln\left(\frac{\frac{c_0 PA - \frac{KS_0}{L}}{c_0 PA - \frac{KS_0}{L}}\right)$$

$$= \ln\left(\frac{\frac{S_0}{L} - \frac{KS_0}{L}}{\frac{S_0}{L} - \frac{KS_0}{L}}\right)$$

$$= \ln\left(\frac{1 - \frac{K}{1 - \frac{KS_0}{L}}}{\frac{1 - \frac{KS_0}{L}}{L}}\right)$$

Or from this expression, or K x by L that is equals to minus of L n C 0 rho A minus K S by L plus L n C 0 rho a minus K S 0 by L, can I write? That is equals to L n C 0 rho A minus K S 0 by L by C 0 rho A minus K S by L. This is equals to L n S 0 by L minus K S 0 by L by S 0 by L minus K S 0 by L by S 0 by L minus K S 0 by L what I have done?

Student: (()).

No, we have assumed that S 0 equals to C 0 rho A L. So, I have put the value of C 0 rho A as S 0 by L can you remember that we have taken the value of C 0. You see that here S 0 was taken at C 0 rho A into L. So, what is the value of C 0 rho A? S 0. S 0 by L. So, I have put here S 0 by L C 0 rho A. That is equals to L n 1 minus K by 1 minus K into S by S 0, right?

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$$= \frac{1 - k \cdot \frac{s}{s_0}}{1 - k} = e^{-\frac{kx}{L}}.$$

$$K \cdot \frac{s}{s_0} = (1 - k)e^{-\frac{kx}{L}}$$

$$K \cdot \frac{s}{s_0} = 1 - (1 - k)e^{-\frac{kx}{L}}$$

$$K \cdot \frac{s}{s_0} = 1 - (1 - k)e^{-\frac{kx}{L}}$$

$$K \cdot \frac{s}{s_0} = \frac{s_0}{k} \left[1 - (1 - k)e^{-\frac{kx}{L}} \right].$$

$$K \cdot \frac{s}{s_0} = \frac{s_0}{k} \left[1 - (1 - k)e^{-\frac{kx}{L}} \right].$$

$$K \cdot \frac{s}{s_0} = \frac{s_0}{k} \left[1 - (1 - k)e^{-\frac{kx}{L}} \right].$$

Next stage is our, 1 minus K into S by S 0 by 1 minus K equals to e to the power minus K x by L. Why minus is there? e to the power minus? It is because here in the denominator it is S by S 0.

I have changed here to the numerator S by S 0. So, it becomes e to the power minus K x by L or 1 minus K into S by S 0, it is equals to 1 minus K e to the power minus K x by L or K into S by S 0. It is equals to 1 minus 1 minus K into x by L or S equals to S 0 by K multiplied by 1 minus 1 minus K e to the power minus K x by L.

So, now if you put the value of S 0, which is given by C 0 rho into A into L, you will get C 0 rho Aa L by K into 1 minus 1 minus K e to the power minus K x by L. So, this is the doping distribution of a float zone process. This is the doping distribution of a float zone process and you see that S is the amount of dopant present in the molten state. S is the amount of dopant present in the molten state and C 0 is that uniform doping concentration in the rod at the starting C 0. Rho is the specific gravity, A is the area of cross section, L is the length, K is the effective segregation constant. The other things you know.

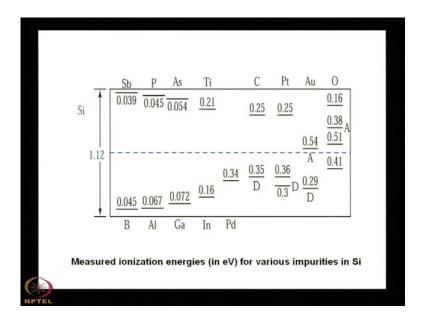
Now, this K, value of K you know that, K is C S by C L, right, but we have assumed that, when it is rejected to the melt there is a melt and almost two-third is being rejected to the melt. So, during rejection what happens? Does the impurity uniformly distribute throughout the melt or not? Does the impurity instantly diffuse through or distributed

throughout the melt or not? Because you see that there is a 60 kg melt or 100 kg of melt is there in the crushable.

So, if there is a 60 k g or 100 k g of melt and when it is rejected where it is rejected? It is rejected at the interface between the solid and liquid. If two-third is rejected, then at that point where the pull starts. Pulling is being made at the liquid solid interface and the rejection is going to be held in that interface only.

The rejection is also going to be held in that interface only, because the pulling is not through the whole mass of the molten state. It is from a single point, it is from a single point. So, the rejection is taken place in the single point only and instantly it cannot diffuse throughout the whole mass uniformly. So that means, there is a problem inside the molten state so far as the impurity distribution is concerned. That is why one term which is known as the effective distribution constant or effective segregation constant is used.

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This K is the effective distribution constant, taking into account that it is not uniformly being distributed throughout the mass of the mass of the molten state. So, that is a concept we have nothing to do with so far as the solving of the problem is constant. There we take simply C S by C L without going into those intricacies. And if you take the silicon as an example, you will find that different kind of kinds of doping has different levels. Say this is the antimony, phosphorous, arsenic or carbon platinum

etcetera. Oxygen is there and those are all, since this is the conduction band this is the valence band.

So, all will give rise to donor level. It will donate electrons and these are the ionization energy. 0.039, 0.45, 0.54 etcetera. Those are the ionization energies. Similarly for accepters, you see that boron, aluminum, gallium, indium etcetera, those are the ionization energies. So, different materials as different ionization energies, and another you see that this D, D stands for donor.

So that means, this carbon though it occupies 0.35 electron volt above the valence band, it acts as a donor for silicon. Similarly, platinum D, on the other hand you see that oxygen for 0.38, it act as a accepter. Unless otherwise it is written by A or D, it is basically near to the valence band, it is the accepter nearer to the conduction band, it is the donor. Unless otherwise mentioned.

And all this energies are in electron volt. So, if you analyze the band gap of the silicon, inside the band gap you will find different kinds of levels. And those levels are due to different kinds of doping concentrations of different elements and these are the elements. This is the mapping of the.

Student: (())

Of the band gap basically. All those levels are inside the band gap. Remember that within 1.1 2 electron volt all those levels will be there.

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Neutron Transmutation Doping

The whole wafer is irradiated with neutrons in an atomic reactor to dope phosphorus in silicon:

 30 Si₁₄ + neutron \rightarrow 31 Si₁₄ + γ -ray \rightarrow 31 P₁₅ + β -ray

³⁰Si captures thermal neutrons and is transmuted into ³¹Si which decays with a half-life of 2.62 hours by the emission of particles to ³¹P.

This assures homogeneous distribution of the phosphorus dopant resulting in uniform doping

Now, another type of doping I must introduce that is known as neutron transmutation doping. Diffusion type of doping you have acquainted with. Then there was ion implantation. Here this is the third type of doping, which is the used for silicon. It is known own as the neutron transmutation doping. In neutron transmutation doping, the whole wafer is irradiated with neutron thermal neutrons; obviously, in an atomic reactor to dope phosphorous in silicon. So, what is the methodology? Methodology is that, you take silicon you put the silicon wafer then you irradiate the silicon wafer with a thermal neutron.

So, what will happen? 30 will be 31 thirty will be thirty one why it will be 31?

Student: Mass 10.

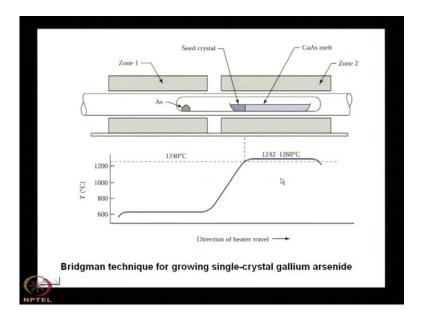
1 n 0 neutron. So, it will be 31 and this 31 basically is a radioactive form with half life of 2.62 hours. So, within 2.6 2 hours it will be transformed into phosphorous. 31 p 15 with the emission of a gamma ray and when phosphorous will be there, there will be an emission of beta ray. So, first with neutron bombardment irradiation, normal silicon will be converted to radioactive silicon and this radioactive silicon will be converted to phosphorous with a emission of a beta ray within 2.6 2 hours because the half life is 2.6 2 hours.

So what you find, that if you take the whole silicon wafer and irradiated with neutron. What is the penetration date of silicon and neutron? Its almost 100 millimeters it is very high. Neutron can penetrate throughout the length and breadth of silicon wafer. In our case what are is the what is the thing, it is almost 300 400 micron. So, you will find that the electro the silicon inside the wafer will be fully irradiated with neutron and that will be 30 silicon to 31 silicon. And then the whole 31 silicon will be converted to phosphorous; that means, you see the very uniform doping will be there in the silicon wafer.

The whole wafer will be uniformly doped. Homogenous distribution of a phosphorous dopant resulting in uniform doping. Where this is used, the whole wafer is used in some power electronic device, the whole wafer. If the whole wafer is used; that means, the doping distribution must be uniform. In normal IC technology we use only a piece of the material. So, if there is a degradation of, if there is some dislocation type of thing or if there is a problem in doping, you can avoid that portion.

But where the whole silicon is used, you cannot avoid any portion to remove from the host wafer. So, in that case the neutron transmutation doping is resorted to using which, the whole wafer can be uniformly doped with phosphorous.

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Then we come to the second issue of gallium arsenide crystal growth. Till now we were in the discussion of silicon crystal growth. In silicon crystal growth, we find that there are two types of methodologies used, techniques that are used. One is czochralski technique another is the.

Student: Float zone.

Float zone technique and there if you can compare those two techniques you will find that, in czochralski technique, generally a (()) is used in float zone no (()) is used. In czochralski technique the resistivity is less, in float zone technique the resistivity is high, but float zone technique crystals, crystals grown by float zone techniques, those are used in power electronics, discrete power device, not in IC technology. In IC technology it is the czochralski technique, which are used and almost 90 percent of the silicon wafer, which are used in the electronic industrial grown by the czochralski technique.

Then for gallium arsenide, one technique we shall introduce it is known as the Bridgman technique B r d g m a n Bridgman technique. In Bridgman technique we use two zone furnace. Two zone furnace you see there is it is zone 1 and it is zone 2. two zone furnace is used. If you take the profile of the furnace this is the profile of the furnace. In zone 1 the temperature is nearly 600 degree centigrade, in zone 2 it is 1242 to 1260 degree centigrade. So, what we use a two zone furnace.

In zone 1 the profile shows that, the temperature is less compared to the zone 2 profile. Then you take one quartz crucible, this is a quartz crucible, inside which there is a quartz boat. This is boat. On the boat you take gallium and inside the crucible at one end, where the temperature is low, you put some arsenic. It is sealed remember. This quartz tube is sealed. Inside the quartz tube, there is a crucible. It say the shape is boat like.

So, we take quartz tube inside which there is a quartz crucible boat. On the boat, there is a gallium and there is arsenic at one end of the quartz tube. Why this arsenic is there? You know that, what is the melting point of gallium. The melting point is gallium is 1238 degree centigrade 1238 degree centigrade. And at that temperature, the surface of the gallium arsenide will decompose into gallium and arsenic. Because the melting point of gallium is very very low, because it is liquid at room temperature and arsenic melting also low it is 600 almost, 610, 620 degree centigrade.

So, before reaching to the melting point of gallium arsenide, which is 1238 degree centigrade. You will find that, the surface is going to disassociate. There will be

decomposition into arsenic and gallium. So, there will be loss of arsenic. Why? The decomposition rate of arsenic is faster than the decomposition rate of Gallium. So, that is why arsenic is kept. So that, any loss of arsenic will be compensated by the over pressure of arsenic.

So, always gallium arsenide is grown using some overpressure of arsenic; that means, some saturate saturation of arsenic must be there in the environment. So, that any loss can be compensated by the arsenic, which is kept at one end of the quartz tube, so first you keep here gallium and you keep here arsenic, then what will happen? Arsenic wafer will be produced and here also gallium is there.

So, there will be gallium arsenide synthesis. First part is the synthesis, not the single crystal. Our aim is to grow the single crystal, but first you have to synthesis gallium arsenide polycrystalline material. So, either you can use this operates, you take a this operates, you take arsenic and gallium then you heat it. So, that gallium arsenide will be there or you can synthesis gallium arsenide in a separate operates and put it in the boat, either of the two. Either in the boat you can put gallium arsenide or you can put gallium and place arsenic little bit on the other side where the thermal profile is very, very low. Remember that, this arsenic is kept to create some overpressure of arsenic. So, that any dissociation of the arsenic from surface of the gallium arsenide, even if takes place, the crystal does not have any loss of arsenic. It is compensated by the arsenic overpressure. Right.

Then what is done? A seed crystal is placed here as usual and the heater is moved. This heater is moved. You see that there is the deduction of heater travel. So, as the heater is moved the this portion where the seed crystal and the melt is there will be a thermal gradient; that means, the because of the difference of the temperature it will solidify. It will freeze. And eventually as the heater progresses, the whole melt will be converted into single crystal of gallium arsenide.

So, it will depend on the temperature profile and that can be control very efficiently and conveniently using a computer. You can check how much crystal is grown. That can be done using some optical microscopy then you can take the weight inside. So, that the rate of can be calculated. If you see that the if the rate of growth is very high, you can less it easily. You can you can reduce it. Or if it is very low you can make some faster kind of

growth. Also you can check the dislocation inside the material. Everything it can be investigated during the growth process itself. So, accordingly you can change the parameter of kinds of growth. So, you will find that after the whole direction, after the whole melt is solidifies, there will be a single crystal of gallium arsenide. What will be the shape of this gallium arsenide single crystal?

Student: D type.

D type. It will be d shape because the boat is d shaped the boat is d shaped, because the melt will be converted to the crystal. Melt will be, because there is no pool remember. Here there is no pool. If there was a pool, then you can convert it into a circular shape. But there is no pool. Here only that heater travels. It is starts from this portion and it ends here. See eventually when all the melt solidifies you will find a d shape type of crystal.

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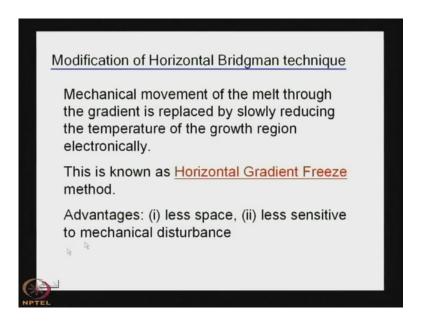
The growth chamber consists of a horizontal quartz tube at one end of which there is a quartz crucible containing GaAs melt kept at temperature (T_m) of 1238 °C.

Other end of the crucible is cooler (617 °C) and contains small quantity of As.

This As produces overpressure of As that controls the stoichiometry of the GaAs melt.

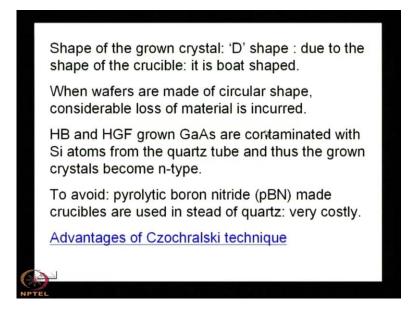
So we can summarize that, the growth chamber consists of a horizontal quartz tube. At one end of which, there is a quartz crucible containing gallium arsenide melt, kept at temperature of 1238 degree centigrade.

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Avoided and electronically the temperature is reduced. We have discussed this thing that the d shape of the grown crystal.

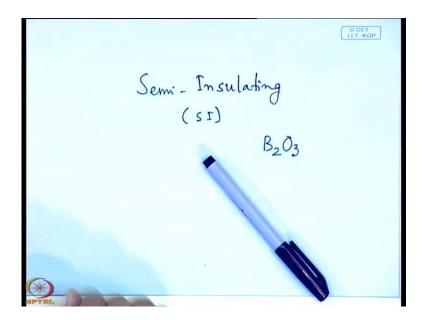
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So, when the wafers are made of circular shape considerable loss of material is incurred. Both in horizontal bridge band and horizontal gradient fridge grown gallium arsenide, both are contaminated with silicon atoms from the quartz tube. And thus the grown crystal become N type. That is another problem, because at this temperature, what was the temperature? We find we find 1238 degree centigrade. So, if you use silicon crucible,

so, silicon will be diffused from the crucible inside the gallium arsenide, but for gallium arsenide silicon an n-type dopant. So, your material will be n-type. So, you cannot go using this technique, the p-type martial or one very important type of compound semiconductor crystal is there. It is known as the semi insulating.

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Semi insulating. S I, semi insulating gallium arsenide. It can be n-type; it can be p type; it can be semi insulating type. Remember that for silicon or germanium, semi insulating type is not available. Semi insulating type means very high resistive sample without any doping. without any doping. So, what is the advantage? Advantage is that, for epitaxial crystal growth, you need a substrate. Suppose you are using an n-type substrate and you are growing a gallium arsenide layer on gallium arsenide substrate or aluminum gallium arsenide layer on gallium arsenide substrate, then, if you want to measure the electrical parameters; so, of the grown layer what will be there? There will be sufficient contribution from the substrate.

Because substrate is it is a itself is either n-type or p type. Your substrate is either n-type or p-type. So, for measurements of electrical characteristics of a grown layer, their substrate will contribute to the electrical parameters. Right.

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Liquid Encapsulated Czochralski (LEC) technique

When the partial pressure of one or both components are large, the melt surface must be protected either by incorporating an independent source of the vapour under dissociation (HB or HGF) or by other means.

In LEC, the surface is covered by B_2O_3 . It does not react with GaAs but reacts with silica crucible. So, graphite crucible or pBN crucible is used.

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Produce ingots of circular cross-section.

Rotation of the melt results in efficient mixing of the host and dopant: uniform doping.

In-situ synthesis of the compound.

High yield.

Large diameter.

Synthesis is possible. One thing I must mention here that normal czhochralski technique is not used for gallium arsenide growth. Normal czhochraslki is not used, why? Because of the degradation problem of arsenic from the melt. Right. Then what is used? One material is used which is known as B 2 O 3, boron tri oxide. Boron trioxide is a liquid type of thing, at that temperature which does not react with gallium arsenide. It is it acts as a gap on the gallium arsenide melt.

So, if this is gallium arsenide melt, you cap it with B 2 O 3. It will not react with gallium arsenide. B 2 O 3 is not a reactive in that sense. So, what will it do, it will prevent the loss of arsenic from the surface of the melt gallium arsenide. Right. That is why it is known as the liquid encapsulated czochralski. It is known as liquid encapsulated czochralski, L e c technique. When a partial pressure of one or both components are large; that means, gallium or arsenic, the melt surface must be protected either by incorporating an independent source of the vapor under dissociation. If you compare with horizontal bridge band or horizontal guardian fridge, you see that, it is independent source of wafer means, some arsenic is kept at one end of the quartz tube.

You remember. Or by other means. Other means means, you have to cap the surface of the melt. you have to cap the surface of the melt In liquid encapsulated czchralski, the surface is covered by V2O3. It does not react with gallium arsenide, but reacts with silica crucible. There is the another problem. It reacts with silica crucible. So, graphite crucible or pyrolytic boron nitrate crucible is used; that means, if you use B 2 O 3, you should not use the silica crucible. We have to use either graphite crucible or pyronitric baronial crucible. Otherwise what will happen, it will react with the silica. Right. So, in liquid encapsulated czhchralski what you find? That at the temperature of the at the melting point, the surface will have loss of arsenic. the surface we will have loss of arsenic To prevent that, you have to cover the surface with B 2 O 3. you have to cover the surface with B 2 O 3. In horizontal bridge band horizontal gradian fridge what we have seen? We have kept arsenic at one end of the tube to compensate the laws. Here we use a cover of B 2 O 3, remember that. That is why it is known as liquid encapsulated czchralski. You have encapsulated the melt using some liquid and that liquid is B 2 O 3. Only one care must be taken that, in B 2 O 3 you should use the silica crucible, you have to use either graphite or paralytic boron nitrate.

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Doping N-type: Si, Te, Se P-type: Zn, Cd Semi-insulating (SI) type: undoped, Cr & Fe

And, here as we as usual as doping can be made by a silicon tellurium or selenium for N-type and zinc and cadmium for P-type for semi insulating it is almost undoped, but in some cases iron or chromium is doped. For silicon we have used phosphorous or arsenic or antimony for N-type or boron or aluminum for P-type. Here we use zinc and cadmium for P-type and silicon tellurium or selenium for N-type. Right. And one more type I have introduce it is the semi insulating type, that is undoped in nature.