Semiconductor Optoelectronics

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Lecture-16
Fabrication of Heterostructure Devices

Okay, so this is the last lecture of a part 1 there we were recalling or reviewing the basic semiconductor device physics the objective of this talk is primarily to indicate to you what are the various methods which are used in the fabrication of devices. It is impossible to discuss the details of fabrication in one lecture. Because there are several inter cases however they just to indicate what methods are used and those of few are interested you can look at the references.

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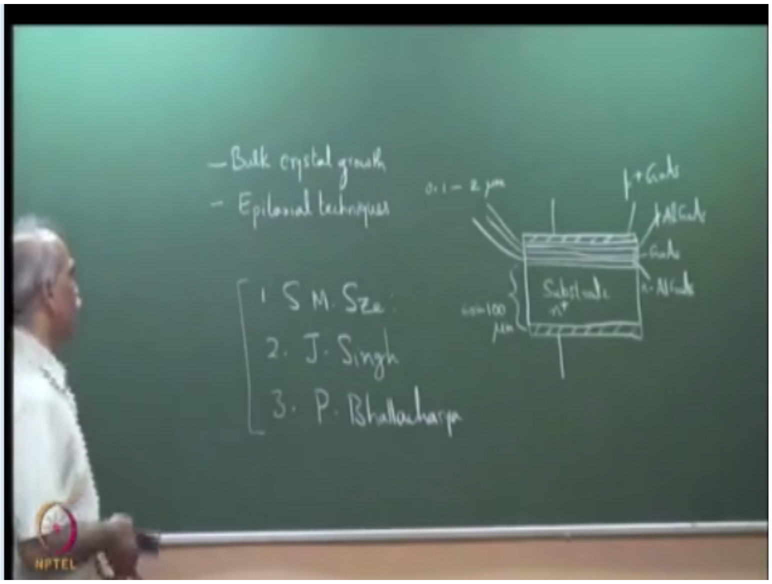

For beginners the good references will be 1 g physics and technology of semiconductor devices for beginners and also our reference just semiconductor of electronics by just**.** And you can also see semiconductor opto-electronics by Pallam Bhattacharya. So, these are some of the basic references however there are plenty of specialised books and articles which are evaluable on these grow processes.

And grow technology you would simply introduce you to the various growth processes. So, if I take a typical semiconductor opto-electronics device it has a substrate. So, a substrate a lower contact electrode it is a metal an upper contact electrode which is also a metal. What I am showing is a longitudinal cross section a cross section like this longitudinal cross section of a heterostructure device.

So, if you see a typical hetero structure device then the substrate would occupy most of the device. Because the thickness here is typically 60 t 100 micron is the substrate over that you have layer structures 1, 2, 3 there may be many more layers. And of course on top the contact electrodes 1 and contact electrode at the bottom, a typical device whose as shown a longitudinal cross section.

So, these devices could be for example in a double hetero structure LED is could be aluminium gallium arsenate for example. This could be gallium arsenate this could be again aluminium gallium arsenate and this is a p+ so, I start with an n+ substrate so, n+ substrate on which you deposit a n aluminium gallium arsenate a gallium arsenate p aluminium gallium arsenate, p+ gallium arsenate.

And these taking a simplest structure and on top again there is a metal contact. So, this is a simple double hetero structure LED or a laser diode, as you know now why we need n+ and metal n+ np+n metal. And then we have contact between n and n+ we have contact between p and p+ because these are all ohmic contacts. So, this would be a typical structure therefore what do we have we have a substrate which is a bulk crystal.

And followed by an top there are layers these layers could be typically anywhere the thickness could be anywhere from 0.1 to few microns may be 2, 3, 4 microns typical thickness of these layers. So, thickness of these layers is quite small compared to the thickness of the substrate therefore the substrate is grown by different techniques compared to the top layers here. They are grown by different techniques.

So, these are grown by bulk crystal growth techniques so, bulk crystal growth. And the top layers are grown by epitaxial techniques because the thickness of the layers which are grown here or very small compare to the bulk crystal. And these epitaxial techniques are generally used when the thickness is very small anywhere from a tens of Armstrong to a few micron.

Then these techniques would work otherwise you have to go for bulk crystal growth techniques. So, I will briefly discuss both bulk crystal grow techniques and epitaxial grow techniques. Some of them just to give you an idea however as I indicated that for details you may have to see several techniques or specialised papers depending on the detail that you are looking for. If you take bulk crystal growth here that is essentially from other point of view to grow the substrate here.

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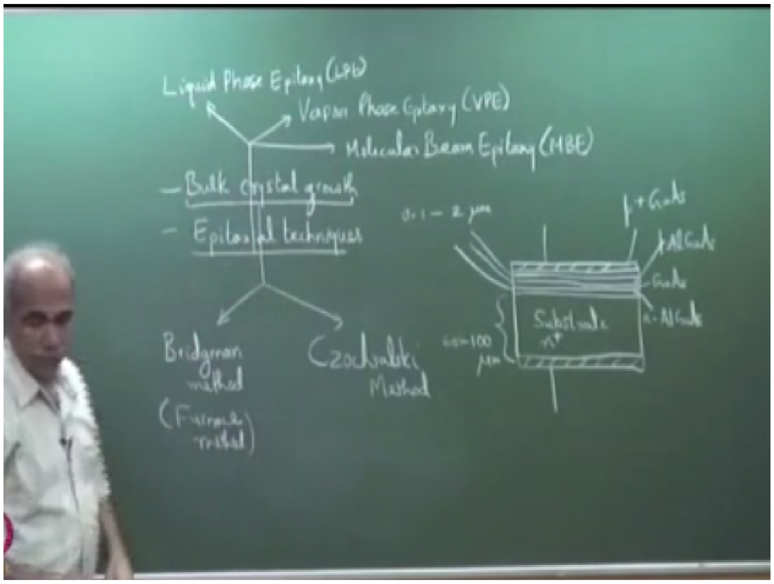

There are two important techniques which are used one is called the furnish method or Bridgeman method. There are several variation of these methods Bridgman technique or method or sometimes also called Furnace. And other one is very well known Czochralsk there are others and variations of these. But these are two are basically processes to have bulk crystal growth epitaxial techniques to have epitaxial layers.

There are three important techniques as I had indicated once are here liquid phase epitaxy vapour phase epitaxy. So, this is LPB vapour phase epitaxy VPB and molecular beam epitaxy or MBE each one has the advantages and features there molecular beam epitaxy. We will briefly discuss all these three techniques then we start first with the Czochralsk method here Czochralsk method.

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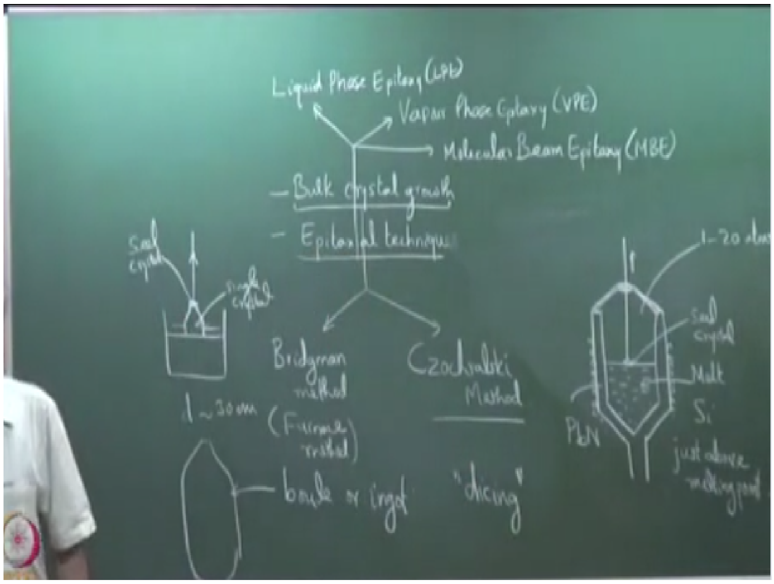

In this method you have a chamber a led nitride visible there are different structures, different variations. So, it is a there could be because sometimes this process is done it atmospheric pressure or sometimes it could be done it high, high pressure therefore in enclosed volumes shield volumes at control pressure. What is done is **is** one begins with a field crystal this is a molten melt, melt means molten starting solution here.

For example if you are growing a single crystal gallium arsenate so, let say this is you want to grow a single crystal gallium arsenate or silicon. Let us say silicon then you start with the silicon molten silicon here. And then that is a single crystal this molten silicon is this melt is the temperature of this melt is just above the melting temperature just above melting point. The melt here is just above melting point this is a crucible.

It is a led nitride usually led nitride crucible PbN and this is heated what I am showing now from the sides is the heating coils. And there is a crystal is starting this is a shield crystal as we draw all the parts everything the setup will come clear. And the shield crystal is slowly pulled up this as a temperature just above the melting point. Therefore as you slowly pull up the temperature here is much less than the melting point.

Therefore it crystallises the melt crystallises on the shield and as you pull up the crystal keeps on growing on the field. In fact as you pull up depending on the pulling rate the size of the crystal could be much larger. For example let me show you here and you could have crystal growing big crystals you started with a small speed, a speed crystal here.

And this is being pulled up so, this is a seed and the crystal is getting that is a melt is getting crystallized to form the single crystal. This is the single crystal this was the seed crystal so, to begin with the seed is in the melt. The melt has a temperature just above the melting point and you start the start very slowly pulling the seed crystal. So, the melt which is in contact with a seed when it comes up it crystallises.

And because it is in contact with the crystal seed it crystallises on the seed with exactly same lattice structure with the same directions. And therefore you have a single crystal and then as you if you control the pulling speed then this diameter can be vary that is the size of the single crystal could be varied. It is simple pulling through this but then one melt is control it is not in open sometimes this chamber may have atmosphere anywhere from 1 to 20 atmosphere.

Because there are several issues involve in terms of the vapour pressure of the material that you start the starting material, so if you this is called Czochralsk method to grow single crystals from a melt you can grow for example silicon crystals have at the diameter as large as 30 centimetres, so D or more is start with the small seed and grow a crystal which is as large as 30 centimetre in diameter.

So, this is one of the techniques to grow what are called if you see those boons so are ingot they are this is called ingot like a huge cylinder and then you cut these into slices to make the wafers out of this. So, you can grow large boons are ingot from this style using this technique Czochralsk technique of single crystal growth and this is diced or sliced in normally it is called dicing to make the substrates.

The wafers that you have the silicon wafers that you see are obtained by dicing this boons which are formed by the Czochralsk technique. The advantage of let me now discuss the Bridgman technique and then you see the advantage that using Czochralsk technique you can grow very thick very large boons are large single crystals whereas the Bridgman technique or Furnace technique is use do grow smaller crystals as the name indicates it has a Furness.

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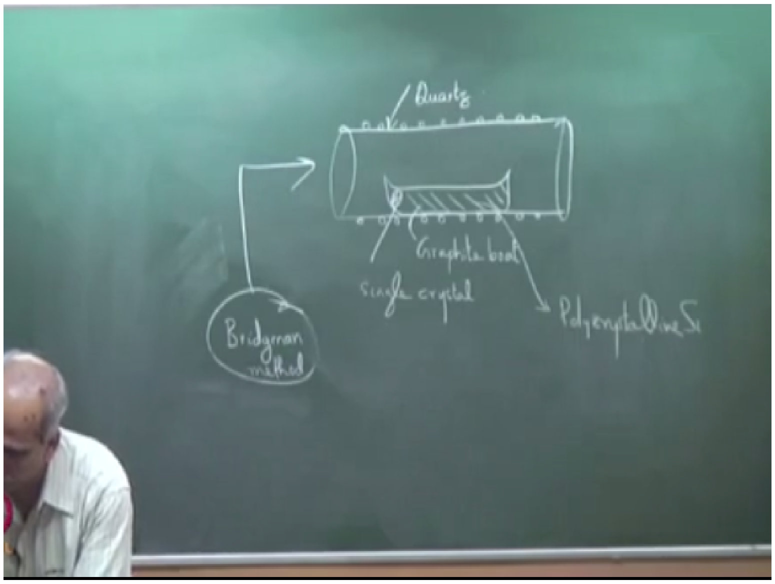

So, let me now discuss the Bridgeman technique here we have to discuss 5 techniques so, about 5 minutes each or 5 to 10 minutes maximum. So, in this technique this is the furnace usually these are graphite boards at this is a quartz, quartz cylinder heated with a this indicating the heating element or heating coil. What is done is at one end of the board a single crystal is placed single crystal.

And it is filled with the melt, the melt comprises of for example if it is silicon it is poly crystalline silicon. So, poly crystalline silicon how do we get poly crystalline silicon these the starting points the starting points which are poly crystalline silicon is obtained by chemical methods, chemical methods of okay let me show you any equations here.

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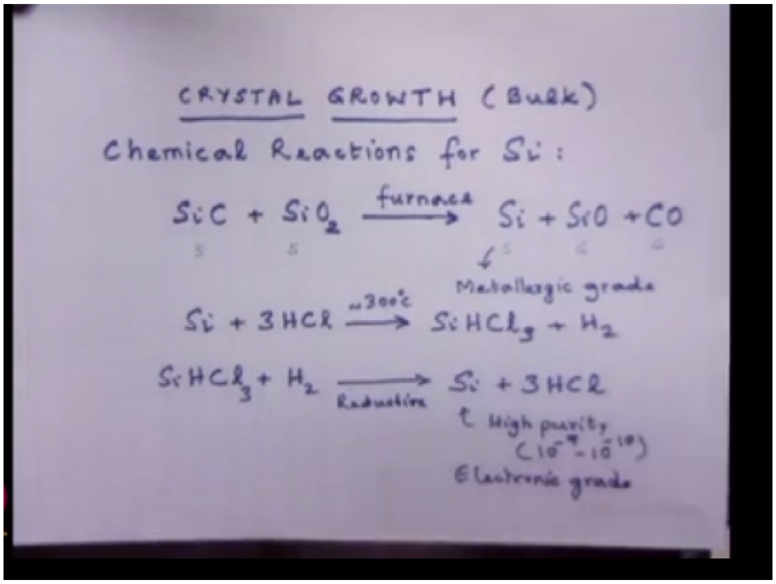

CRYSTAL GROWTH (Bulk)

Chemical Reactions for Si:

$$\underset{s}{SiC} + \underset{s}{SiO_2} \xrightarrow{\text{furnace}} \underset{s}{Si} + \underset{g}{SiO} + \underset{g}{CO}$$

Metallurgic grade

$$Si + 3HCl \xrightarrow{\sim 300^\circ C} SiHCl_3 + H_2$$

$$SiHCl_3 + H_2 \xrightarrow[\text{Reduction}]{} Si + 3HCl$$

High purity $(10^{-9} - 10^{-10})$

Electronic grade

How to get a polycrystalline silicon so, you start with a chemical reactions in a furnace silicon carbide and sio2 are the starting point. And in a furnace at high temperatures you can generate metallurgic grade of silicon sio2 is the gas and co is the gas which goes out. And what you get is metallurgic grade of silicon so, silicon carbide+silica starting point per silicon is silica. Silica is a plenty in a sand, so this is the first step of the crude process to get metallurgic grade of silicon.

Metallurgic grade is approximately 98% durative the metallurgic grade silicon then is it interacts with the hcl here. And you get trichlorosilane sihcl3 is trichlorosilane a compound trichlorosilane and hydrogen gas. This is reduced further in a hydrogen environment reduction in hydrogen environment gives you silicon+3hcl, hcl goes as a gas. This is the chemical reaction of heating and reducing reduction.

This is called reduction process so, what you get is high purity silicon which is electronic grade silicon high purity it is the impurities are one part per billion or less. So, 10 power-9-ten the numbers referred to the impurities concentration. So, this is electronic grade silicon so, you can get poly crystalline silicon by this technique and that is the starting point here. Both here and in the czochrabrake technique the melt comprises of chemically obtained silicon.

And then you have to grow single crystal growing single crystal means of single crystal does not mean 1 cubic lattice 1 shell. Single crystal means all over that structure all over that material you have a periodic structure of silicon. It is therefore you call it as a single crystal so, single crystal means everywhere there is crystalline structure poly crystalline means you have crystalline structure but there are domains.

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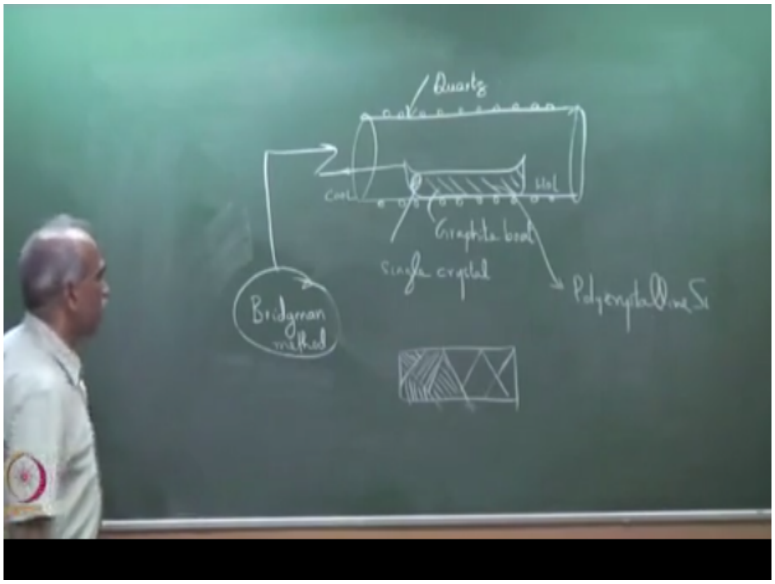

So you may a poly crystalline means you have a poly crystalline silicon it means there could be domains where there is crystal structures. Crystal structure is not uniformly present everywhere but in this a particular plane may be in this fashion and in another it could be like this. In another it could be like this so this is what I am showing is crystal planes. So, this is poly crystalline because crystalline structure is not over the entire silicon here over the entire structure.

Therefore it is poly crystalline single crystal means over the entire material or entire structure or entire piece you have one crystal set up that is the lattice structure is the same everywhere. So, that is obtained by one that is Czochralsk technique which I discuss. And the second one is the furnace method in the furnace method this boat is pulled and only giving you an idea. The techniques are quite involve.

So, the boat is pulled through a temperature gradient towards cooling. So, this end is cool and this here it is hot end. In fact everywhere this is at a maintained at a high temperature and then this is cooler temperature it is a lower temperature cool does not mean it directly it does not go to atmospheric temperature it is at a lower temperature. So, the boat is pulled through this what is the idea is as this passes to temperature below the melting point.

It starts crystallising because this end first meets temperature which are lower than the melting points. So, it starts paludification so, because there is a single crystal present the solidification takes crystalline form. Because there is a feed which is already present and therefore the entire thing if you pull this through the entire thing forms a single crystal. And this is called the furnace method or Bridgman method.

The idea behind formation of single crystals using bulk single crystals using the furnace method and the Bridgman method and the czochrabke method as I said for details please see references and specialist articles on this. So, from these single crystals we start we get the substrates are usually vapour or anywhere 100 micron thick depends on the material absorb.

Some materials are thicker substrates are used in some materials the substrate is likely thinner typically 60 to 100.

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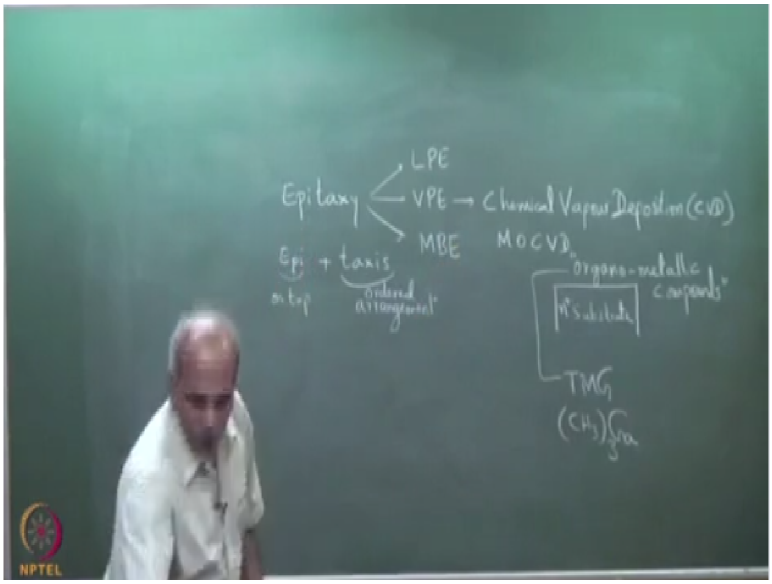

Once you have the single crystal substrate so, this is the substrate so, that two methods that I have described is to obtain the substrate. If you have to have doped substrates in the melt before the single crystal is form in the melt you include the dopants required dopants are included in the melt the starting melt. So, that you get for example I wrote n+ substrate how do we get n+ substrate for example if you add arsenic in silicon melt then you will have n+ substrate.

So, the dopants have to be added in the melt before the single crystal is formed if you want a doped substrate. So, we have a substrate now you want to have these methods epitaxial methods to grow on top. So, epitaxy apparently this is a combination of Epi+taxis this means upon or on top this is apparently greek word. So, on top or upon and taxis it seems ordered arrangement.

So, Epitaxial growth means growth on top ordered arrangement ordered growth on top ordered arrangement of atoms to form layers Epitaxial techniques. So, I have indicated the three techniques liquid phase epitaxy, vapour phase epitaxy this is also called CVD chemical vapour deposition. And if the chemicals involve organometallic compounds **you** so, this is CVD CVD is also vapour phase epitaxy.

And MOCVD in fact most of the gallium arsenate aluminium gallium arsenate are grown by MOCVD MOCVDs metal organic chemical vapour deposition. So, because if the chemicals which are being if the deposit if the chemicals involved in the CVD process if they have organo-metallic compounds then it is also called MOCVD metal organic vapour chemical vapour deposition organo-metallic what do I mean by I will give you an example.

For example tri methyl gallium TMG tri methyl gallium, so methyl group $(CH_3)_3$gallium tri methyl gallium, so this is methyl group is organic gallium is metal, so it is an organo-metallic compound tri methyl gallium this is not the starting for a gallium arsenate organo-metallic MOCVD and the last one is MBE. So, let me in the remaining part of this part let me discuss briefly the 3 techniques which are widely for epitaxial layers.

LPE this is the first technique liquid phase epitaxy as the name indicates the starting material is a liquid, liquid phase epitaxy.

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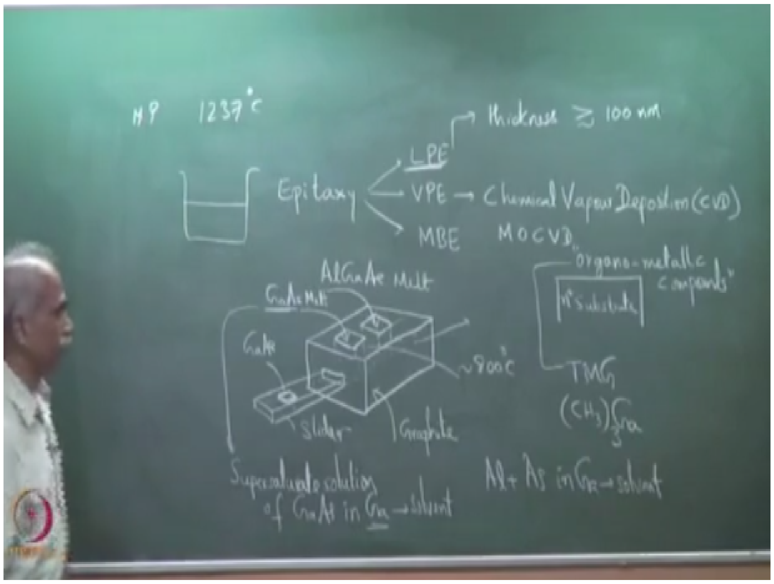

So this is done in a chamber you have let me draw this you will see nice figures in books and you will also see in internet there are several articles and which show videos. So, this is I am drawing it because as you see you will understand what it is there is a slot here. For example a rectangular slot through a graphite this is graphite it is a graphite container through which there is a slot. There are also on top there are like pill box 1, 2, 3.

This is these are boxes cylindrical boxes down pill box okay means you can pour some liquid into this. So, **so** these cylinders go down into this and on a slider there is a slider here my belief is that if I to this drawing in front of you. Then you can exactly understand what it is rather directly show you a diagram which is already existing. So, there is a slider so, this is a slider on which you place the substrate.

Let say gallium arsenate I did not describe how to get a gallium arsenate single crystals, I talked about silicon. Because that was the easiest gallium arsenate is more complicated a it actually has to be done in a shield close furnace. Because of the vapour pressure considerations but anyhow let me not going into that right now in this you put the melt so, gallium arsenate and aluminium gallium arsenate melt.

Now what is this gallium arsenate melt gallium arsenate melt is super saturated solution of gallium arsenate in gallium. Gallium is the solvent gallium arsenide in gallium dissolved in gallium. It is a super saturated solution of a gallium arsenide in gallium similarly here it is aluminium gallium arsenate it is aluminium and gallium here aluminium and arsenic aluminium of +arsenic in gallium.

So, gallium is the solvent molten this is melt means it is a molten solid, In this case metal aluminium arsenic gallium or all metal molten that is why melt super saturated and why super saturated you can imagine it is a basic crystallo graphic process you remember even in the schools we have making sugar crystals from sugar solution. You have super saturated sugar solution and you cool it.

And when you cool sugar crystals are formed because it was super saturated at a slightly elevated temperature you cool it then it cannot fold anymore those sugars and sugar crystallises. It is the same process which is used in this that you have super saturated belt and this is the gallium arsenide substrate arsenate. And you slight it so, that this comes exactly when it comes exactly under this pill box here. It just feds there it just holds on to that.

And then all of these are a some temperature let us say some temperature of I do not know i am saying let us say it is at generally this is the around 800 degree centigrade approximately around 800 degree centigrade the melting point of gallium arsenide is actually very high it is I think 1237 or 38 degree centigrade is the melting point of gallium arsenate however when it is in a solution it is in the liquid form even at around 800 degree centigrade.

Because the solution has the lower melting point compared to the pure solvent. Now this is approximately around 800 when this gallium arsenide is sitting under the pill box. The temperature of this please see this whole thing is in a oven when the temperature is reduced what happens is gallium arsenide crystalline gallium arsenide deposits on this. It is the same process of crystallisation of sugar.

But now there is a substrate gallium arsenide on which there are layers which are deposited gallium arsenide gets deposited. The time for which the temperature has been lower determines the thickness of the layer that is grown on gallium arsenide under this. Next if I want to grow aluminium gallium arsenide the slider is pushed for the to the next slot under this pill box. There is aluminium gallium arsenide melt.

And you again lower the temperature and aluminium gallium arsenide will get deposited on the substrate. So, you have gallium arsenate on which aluminium gallium arsenate deposited so, you if you need again gallium arsenide to be deposited or vice versa to make double hetero structures. You can have more chambers here so, there are there can be more chambers to deposit layers after layers what is the simplicity that you see here.

The arrangement is very, very simple only a simple graphite container with a slider and two pill boxes. You put the melt and the whole thing is in a furnace I will next describe you the other two you will see the complications in these. This is simplest and even today they are used when you need to deposit layers the thickness in LPE the thickness of layers. If you need thickness greater than r of the order of 1000 Armstrong that is 100 nano meter LPE can be used.

Why greater than this because the control on the thickness is not very good because you have to slide it to the next point. So, the control is not very good you cannot grow have control of 10 Armstrong, 5 Armstrong which you have in the other two techniques. So, if you do not need abstract junctions with precise control then LPE is the best technique. It is the simplest most cost effective and whenever you need to grow thicker layers LPE is the best idea.

And every device does not requires such abstract précis junctions to make quantum wells structures. You cannot make quantum well structures with LPE for example. Because you do not have so much of control but for many applications you do not need you need to use thicker layers. And LPE is still a commercial technique which is used to grow opto-electronic devices. this is LPE so, let me go old to the next vapour phase epitaxy.

I keep repeating please referred to literature for more details I have given you an idea what the technique is and details you can always go through other materials. Let me describe vapour phase epitaxy this is an interesting technique there are some let me give you some equations that describe deposition of gallium arsenide.

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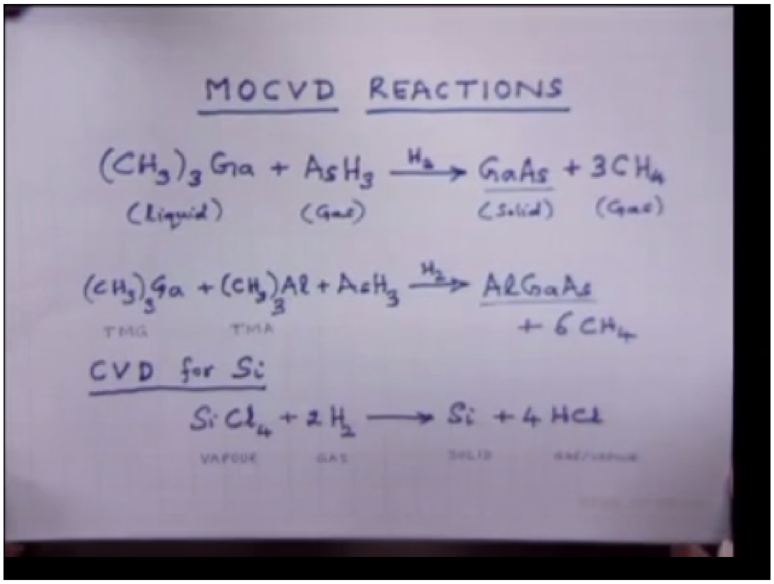

MOCVD REACTIONS

$(CH_3)_3Ga + AsH_3 \xrightarrow{H_2} GaAs + 3CH_4$

(Liquid) (Gas) (Solid) (Gas)

$(CH_3)_3Ga + (CH_3)_3Al + AsH_3 \xrightarrow{H_2} AlGaAs + 6CH_4$

TMG TMA

CVD for Si

$SiCl_4 + 2H_2 \longrightarrow Si + 4HCl$

VAPOUR GAS SOLID GAS/VAPOUR

Aluminium gallium arsenide layers using MOCVD reaction you have a reaction chamber.

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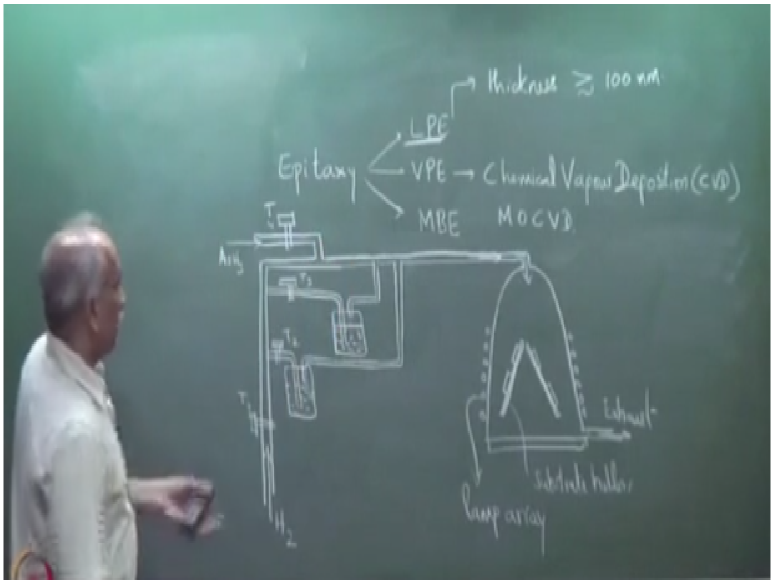

This is a reaction chamber in which there are substrate holders so, what I have shown is substrate holders these are substrate holders means on top of this there are substrate sitting 1, 2, so, these are substrates like I showed you in the LPE a gallium arsenide substrate will sit first. So, these are substrate city there is an exhaust here exhaust gas enters a mixture of gases required gases what are these gases I will show you in a minute enter from this

This is the reaction chamber so, mixture of gas enters from here and reaction takes place on the surface of the substrate inside the reaction chamber. This is chemical reaction which takes place on the surface of the substrate and layers get deposited. The remaining gas is exhausted now there could be there are different techniques use there could be lamp heating. So, these are heating lamps or there could be RF heating there are different heating techniques.

This is lamp array it is not coil now it is lamp array heater lamps or there could be RF heating, heating of this heating of the substrates. Now we have to see what is this mixture this mixture typically comprises of if I want to grow I will draw it then I will explain to you the reaction this is actually hydrogen gas is used h2 gas which is bubbling through these and the vapours are carried.

I could have probably drawn this and shown you directly the setup but it is okay so, we have so, let say this is there are everywhere there are mass flow controllers which are shown as tapes. So, the tapes which I am showing here or basically mass flow controllers let us say t1, t2, t3, t4 so, hydrogen gas from here and arsine from here arsine it is a highly poisonous gas. And if you need to add some dopants and let me erase this.

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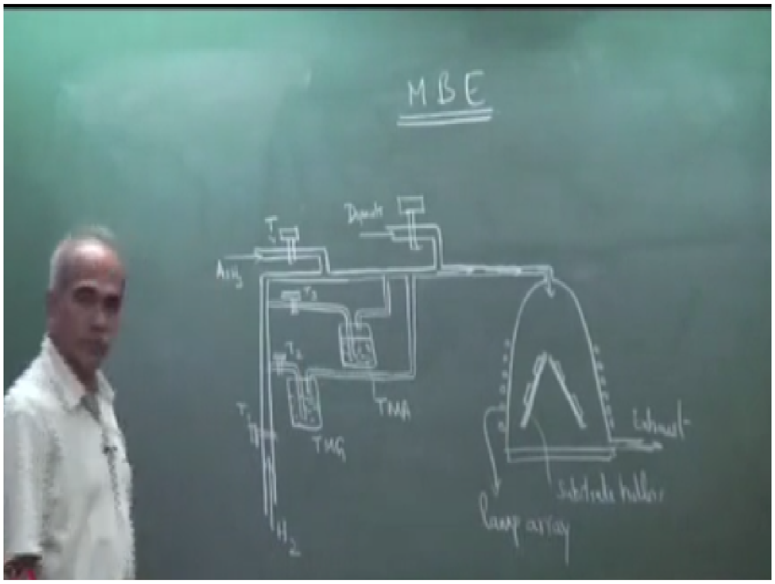

Dopants so, this is trimethyl gallium TMG trimethyl aluminium TMA trimethyl aluminium and arsine here. And hydrogen is the carrier gas so, this entire mixture is entering the vapour chamber the reaction chamber. So, see the reaction now let us look at the reaction trimethyl gallium+arsine here gives you gallium arsenide+hydrogen here is the carrier. The reaction is taking place inside the chamber.

So, gallium arsenide+methane gas trimethyl gallium+trimethyl aluminium+arsine gives you aluminium gallium arsenide+methane. This is the reaction the chemical reaction, chemical reaction taking place inside this chamber the CVD process is taking place here. It is a vapour phase epitaxy. Because the trimethyl gallium and trimethyl aluminium are carried by hydrogen gas in the form of vapours.

Hydrogen is bubbling through this so, these are mass flow controllers the rate at which the vapours have to go is controlled by the mass flow controllers t1, t2, t3. So, here is arsine coming and any dopant if you want to add you also add the dopant gas. So, the reaction is taking place on the surface of the substrate and the gallium arsenide which is formed here is directly deposited on the surface.

If you do not want in the next stage if you do not want gallium arsenide to be deposited you simply close this tape. And only you are bubbling this one if you want to deposit only aluminium arsenide but if you want to deposit only gallium arsenide close this tape t3. So, you can control by this technique the layers very precise the control is very good. Because the mass flow controllers can adjust the deposition rate on this is determined by the inflow of the mixture.

The reactant mixture and therefore the control is very precise, both in a MOCVD and the normal VPE. The reaction for CVD is also shown here it is called CVD because now there is no metal organic compound, so silicon tetra chloride+hydrogen gas is use silicon+hcl. It is called CVD basically they are al VPE MOCD is only meant the reactance have metal organic chemical vapours alright I go to the last technique that is MBE what this MBE can I erase this.

Anyhow please see some good material to know more details I come to the last technique MBE which is widely used to deposit quantum 2 make quantum well structures molecular beam epitaxy. The setup is quite involve but the control is extremely precise you can deposit mono layers of gallium arsenide or aluminium gallium arsenate molecular beam epitaxy which means there must be atomic beams which are coming to form molecules directly on top of the substrate.

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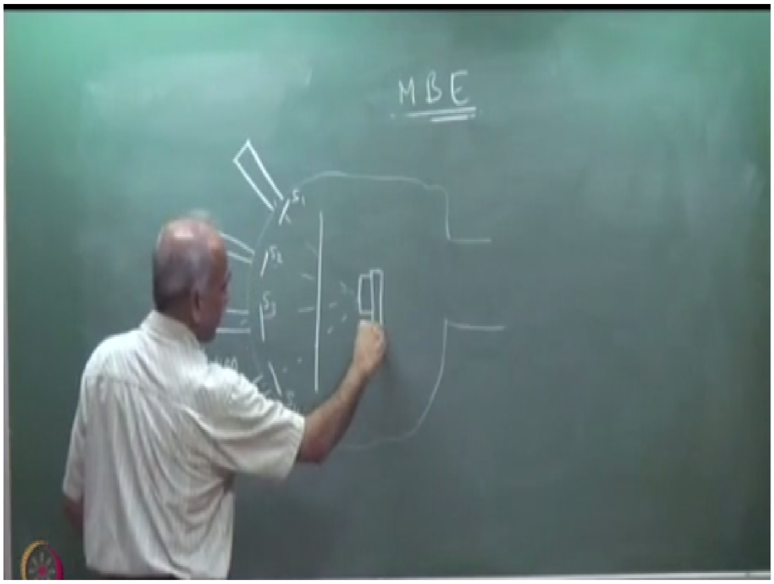

So, the chamber involves something like this let me draw it approximately I fairly like drawing that is why I want to draw this you have a fusion chambers a fusion furnaces or a fusion chambers several effusion chambers through which atomic gas through atomic beams come out so there are shutters for each chambers, so these are effusion chambers ultimately single effusion chamber or furnace effusion furnace.

So, atomic beams come from this what I have shown is shutters say s1, s2, s3,s4 shutters there is a main shutter and in front of this there is a substrate holder. There are quite a involved setups with gear wheels all those things I am not showing a all those arrangements here but so I have a chamber there is a raid gun here okay the diagram is more or less ready.

This is RHEED have you heard of RHEED reflection high energy electron diffraction gun RHEED gun. So, high energy electrons are electron beam is incident on this here and it is diffracted here there is a this is a fluorescent screen fluorescent fluorescence screen, this is for rotating mechanism it is actually rotating in a different way. So, on the substrate what I have shown is the substrate this is the substrate this is the loading chamber.

The double barrier ultra high vacuum lock okay now let me explain and then everything will come clear these are sources say gallium, aluminium, arsenic and some dopant if you want to put some dopant these are atomic sources. So, atomic sources it is atom by atom which is come, so atomic beam is incident on the substrate, the substrate is kept heated at a certain temperature the **ata** atoms which come there on the surface of the substrate.

So, atoms are arriving on the surface and because if this is gallium arsenate the atoms arranged themselves so that it forms it fits to the gallium arsenate latch. So, at a time it is growing one layer by layer that is why you call it to mono layer you are allowing gallium atomic gallium to come from here aluminium, arsenic if you do not aluminium you want to grow only gallium and arsenic you put this shutter closed this is a main shutter.

If you do not want any reaction to takes place or you are doing some setting then you close the main, so this is the main shutter molecular beam epitaxy please see this, this is at ultra high vacuum, ultra high vacuum of 10 power -10 to 10 power -11 torr it is ultra high vacuum chamber in which we have a substrate that is mounted this is the substrate holder you can rotate the substrate keeps on rotating atomic beams come from here gallium, aluminium, arsenic all these.

They are actually this atomic the effusion chamber has each one a crucible boron nitrate crucible usually boron nitrate crucibles in which you have aluminium you have placed pure metallic aluminium and it is heated and the atomic beam is coming out of these effusion guns are this chambers, effusion for this. So, there is independent beings are coming here the atoms rearrange themselves in the lattice on the surface of the substrate.

So, you can imagine the control that you have you are allowing the rate at which atoms are incident the rate at which atoms are incident is controlled by the temperature. So, ina controlled rate of gallium, aluminium, arsenate you can change the ratio Ga 1-x, Alx arsenic if you are going the turnery compound aluminium gallium arsenate AlxGa1-x arsenic you can control this x. So, that required composition of aluminium gallium arsenate can be obtain.

And the deposition is atomic mono layers mono layer by mono layer which means the control that you have is 1 atomic layer 1 atomic mono layer which means the control is of the order of 3 to 5 Armstrong. The layer thicknesses can be control correct to 1 mono layer which means you can make abrupt junctions you do not want gallium aluminium arsenate anymore you just block aluminium the next layers will be gallium arsenate gallium arsenide pure.

So, molecular beam epitaxy as it indicates as the name indicates there are beams atomic beams which come and does not call it as atomic beam epitaxy, because it is the layers which are grown are molecules. So, molecular beam uptake there are beams of atoms which come here and the layer is deposited quantum. So, this is the third technique you can read more details about this it is a very interesting techniques.

And most of the quantum well structures are grown by MBE technique, so I will stop here I hope I have given you an idea about the different techniques which are used plenty of details are required to understand each one of them further. So, we will stop here and go over to part 2.