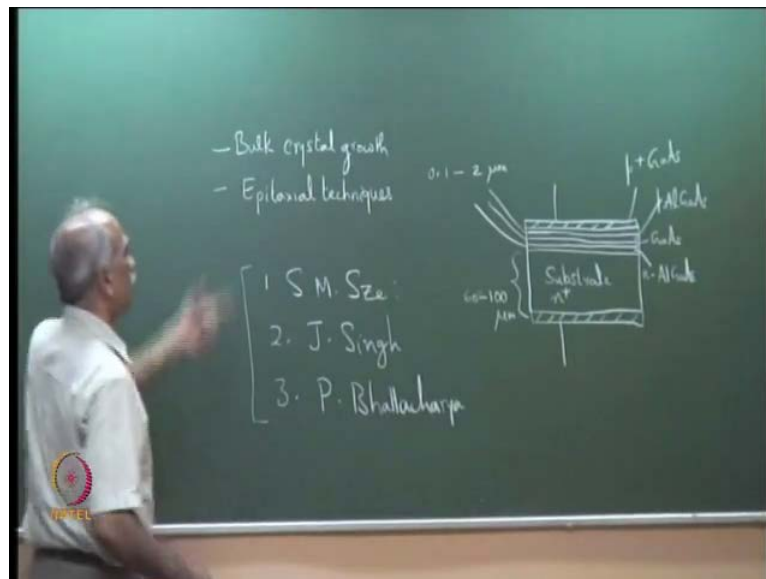


Semiconductor Optoelectronics
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Lecture - 16
Fabrication of Heterostructure Devices

So this is the last lecture of part one, 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 intricacies. However, it is just to indicate what methods are used and those of you are interested you can look at the references.

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For beginners the good references will be, one Sze Physics and technology of semiconductor devices for beginners, and also our reference Jaspreet Singh Semiconductor of electronics by Jaspreet Singh and you can also see Semiconductor of electronics by Pallab Bhattacharya. So, these are some of basic references. However, there are plenty of specialist books and articles which are available on these growth processes and growth technology.

We would simply introduce you to the various growth processes. So, if I take a typical semiconductor optoelectronic device, it has a substrate, so, a substrate, a lower contact electrode which is a metal and a 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 heterostructure device then the substrate would occupy most of the device because the thickness here is typically 60 to 100 60 to 100 micron is the substrate.

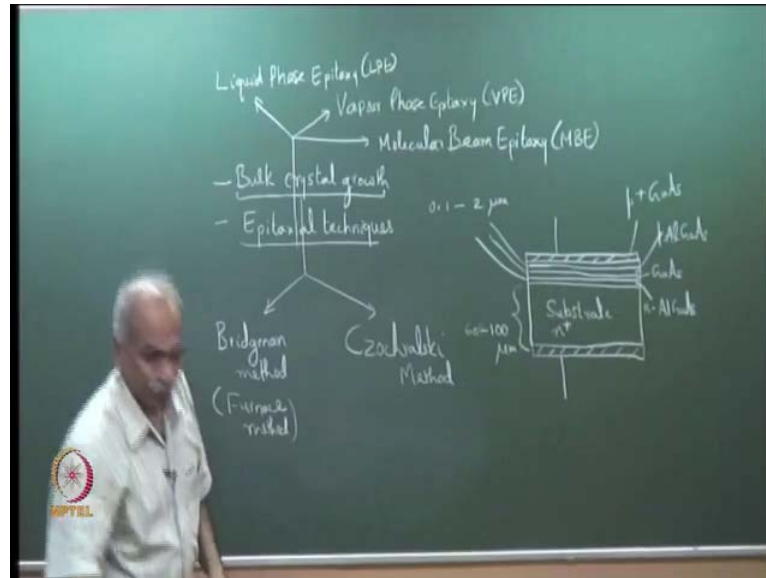
Over that you have layered structures 1 2 3 there may be many more layers and of course, on top the contact electrodes one and contact electrode at the bottom. A typical device, whose I have shown a longitudinal cross section. So, these devices could be for example in a double heterostructure LED this could be aluminum gallium arsenide for example, this could be gallium arsenide, this could be again aluminum gallium arsenide and this is a p plus. So, I start with an n plus substrate. So, n plus substrate on which you deposit a n aluminum gallium arsenide, a gallium arsenide, p aluminum gallium arsenide, p plus gallium arsenide and just taking a simplest structure and on top again there is a metal contact.

So, this is a simple double hetero structure LED (()) and you know why we need n plus and metal and n plus and p plus and metal and then we have contact between n and n plus, we have contact between p and p plus because these are all only 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 on 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, the thickness of these layers is quite small when 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 a epitaxial techniques, epitaxial techniques, because the thickness of the layers which are grown here are very small compared to the bulk crystal and these epitaxial techniques are generally used when the thickness is very small anywhere from if tens of amstrongs to a few microns, then these techniques to work otherwise, you have to go for bulk crystal growth techniques. So, I will briefly discuss both bulk crystal growth techniques and

epitaxial growth techniques. Some of them just to give you an idea however as I indicated that for details you may have to see several text or specific papers depending on the details that you are looking for.

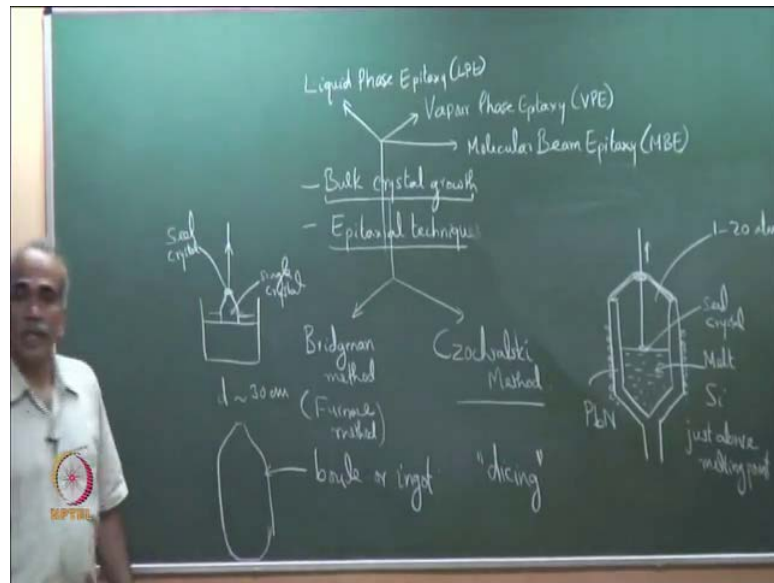
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If you take bulk crystal growth here that is essentially from our point of view grow the substrate here, there are two important techniques, which have used. One is called the furnace method or Bridgman method there are several variations of this method. Bridgeman technique or method or sometimes also called furnace and other one is very well known Czochralski.

There are others and variation of these, but these two are basic process is to have bulk crystal growth. Epitaxial techniques, to have epitaxial layers there are three important techniques as I have (()) liquid phase epitaxy, vapour phase epitaxy. So, this is LPE, vapour phase epitaxy VPE and molecular beam epitaxy or MBE. Each one has various advantages and features there, Molecular beam epitaxy. We will briefly discuss all these three techniques.

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Then we start first with Czochralski method here. Czochralski method, in this method you have a chamber a lead nitrate crucible. There are different structures, different variations. (()) there could be because sometimes this process is done at atmospheric pressure or sometimes could be done it high high pressure therefore we enclosed volumes, sealed volumes at controlled pressure. What is done is this begins with a seal crystal, this a molten melt, melt, molten starting solution here for example, if you have growing a single crystal gallium arsenide. So, let us say this is you want to grow a single crystal gallium arsenide or silicon or let us say silicon, then you start with the silicon molten silicon here and then there is a single crystal, this molten silicon is, this melt is the temperature of this melt is just above the melting temperature, just above the melting melt.

The melt here is just above the melting point, this is a crucible a lead nitrate usually lead nitrate crucible PBN and this is heated. What I am showing now from the sides is the heating coils and there is a crystal is acting, this is a seal crystal as we draw all the parts, everything in the setup will become clear and the seal crystal is slowly pulled up. This has 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 crystallizes the melt crystallizes on the seal and as you pull up the crystal keeps on growing on the seal.

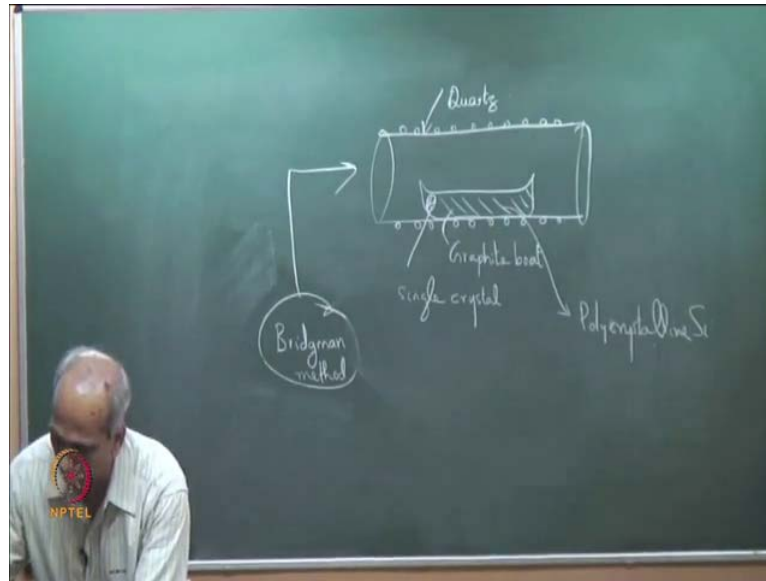
In fact as you pull up depending on the pulling rate, depending on the pulling rate the size of the crystal could be much larger. For example, let me show you here and you could have crystal growing big crystals you started with a small seal, a seal crystal here and this is being pulled up. So, this is the seal and the crystal is getting, that is the melt is crystallized to form the single crystal. So, this is the single crystal, this was the seal crystal. So, to begin with the seal is in the melt. The melt has a temperature just above the melting point and you start the, starts very slowly pulling the seal crystal.

So, the melt which is in the contact to the seal when it comes up, it crystallizes and because it is in contact with the crystal seal, it crystallizes on the seal 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 varied. That is the size of the single crystal could be varied. It is simple pulling through this, but the non (()) control, it is not in open. Sometimes, this chamber may have atmosphere anywhere from 1 to 20 atmosphere 1 to 20 atmosphere because there are several issues involved in terms of the vapor pressure of the material that you start, the starting material.

So, if you, this is called Czochralski method to grow single crystals from a melt. You can grow for example, silicon crystals have with diameter as large as 30 centimeters. So, d or more to start with a small seal and grow and grow a crystal which is as large as 30 centimeters in diameter. So, this is one of the techniques to grow what a, what are called, if you see those boule or ingots, they are, this is called boule or ingot, like a huge cylinder and then you cut these into slices to make the vapors out of this. So, you can grow large boules or ingots from this technique, using this techniques Czochralski technique of single crystal growth and this is diced or sliced and normally it is called dicing to make the substrates, the vapors that you have the silicon vapors that you see that are obtained by dicing this boules which are formed by the Czochralski technique.

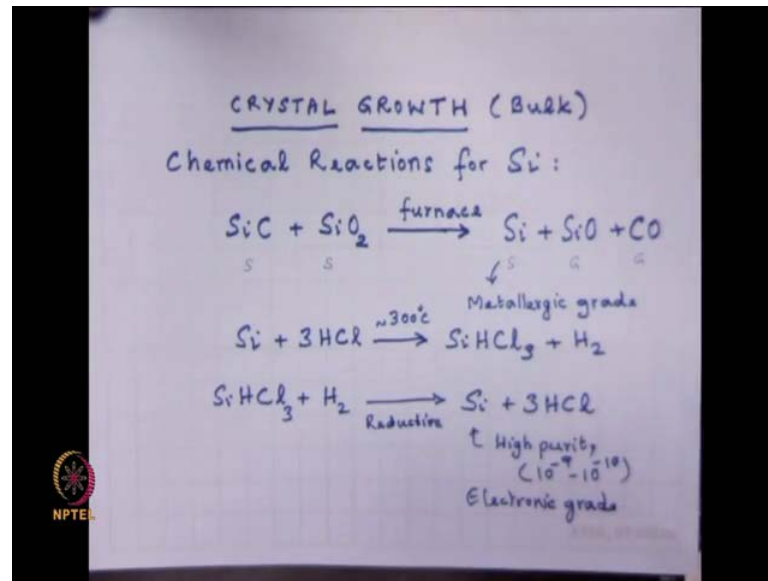
The advantage of the, let me now discuss the Bridgman technique and then you see the advantage that using Czochralski technique you can grow very thick and very large boules or large single crystals; whereas the Bridgman technique or furnace technique is used to grow smaller crystals.

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As the name indicates it has a furnace. So, let me now discuss the Bridgman technique we have to discuss five techniques, so about 5 minutes each, or 5 to 10 minutes maximum. So, in this technique, this is the formulas usually these are graphite boats, graphite boats and this is a quartz, quartz cylinder heated, this indicate the heating elements or heating coil. What is done is at one end of the boat is single crystal is placed, single crystal and it is filled with the melt. The melt comprises of poly 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 like poly crystalline silicon is obtained by chemical methods, chemical methods of.

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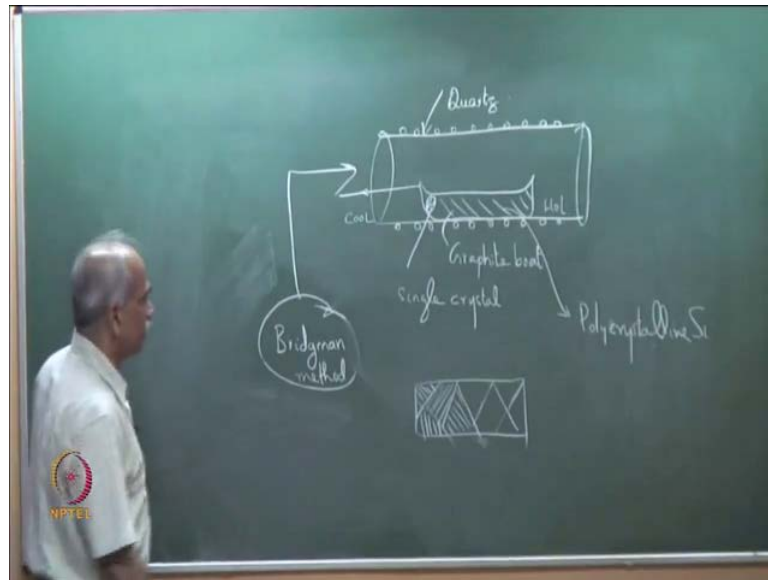
Let me show you one equation here. How to get poly crystalline silicon, so you start with the chemical reactions in a furnace silicon carbide and SiO₂ are the starting points and in a furnace at high temperatures you can generate metallurgic grade of silicon and SiO₂ is the gas and CO is the gas which goes out and what you get is metallurgic grade of silicon. So, silicon carbide plus silica, starting point of silicon is silica and silica is plenty in sand. So, this is the first step of the crude process to get metallurgic grade of silicon. Metallurgic grade is approximately 98 percent purity.

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 plus 3 HCl, 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 1 part per billion or less. So, 10 power minus 9 minus 10 the numbers that refer to the impurity concentration. So, this is electronic grade silicon.

So, you can get poly, poly crystalline silicon by this technique and that is the starting point here, both here and Czochralski technique, the melt comprises of chemically obtained silicon and then you have to grow single crystal. Growing single crystal means what? Single crystal does not mean 1 cubic lattice 1 cell, 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 a crystalline structure, poly crystalline means you have crystalline structure, but there are domains.

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So, you may have a poly crystalline means you have a poly crystalline silicon, it means there could be domains where there is crystal structures. Crystal structures 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 what I am showing is crystal planes.

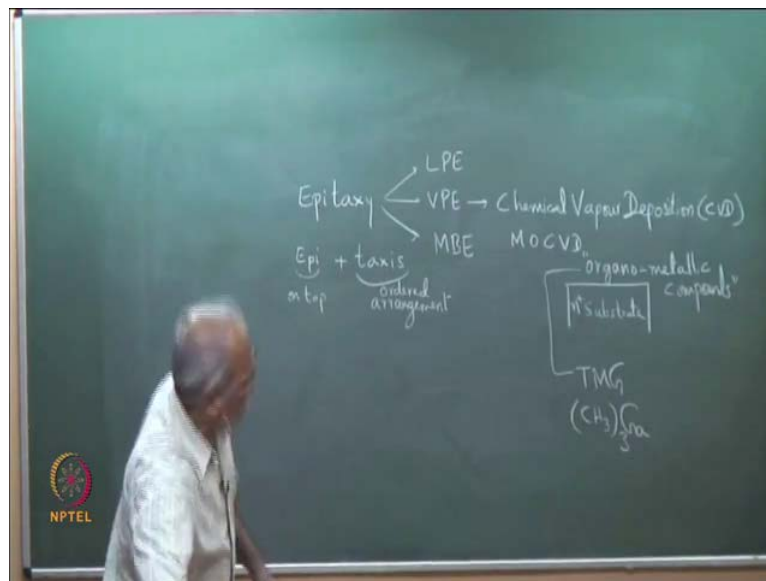
So, this is poly crystalline because crystalline structure is not over the entire silicon here, over the entire structure. Therefore, it is poly crystalline. Single crystal means over the entire material or entire structure or the entire piece you have 1 crystal set up, that is the lattice structure is the same everywhere. So, that is obtained by one that is the Czochralski technique which I discussed 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 involved to the boat is pulled through a temperature gradient towards cooling. So, this end is cooled end and this here, it is hot end.

In fact everywhere this is maintained at a high temperature and then this is cooler temperature, itself lower temperature cool does not mean it directly does not go to

atmospheric temperature. It is at lower temperature. So, the boat is pulled through this, what is the idea? Idea is at as this passes to temperature below the melting point, it starts crystallizing because this end first meets temperature which are lower than melting points. So, it starts solidification.

So, because there is a single crystal present the solidification takes crystalline form because there is a seed 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, the Bridgman method and the Czochralski method. As I said for details please see references and specialist articles from this. So, from these single crystals we start, we get the substrates. Substrates are usually diced vapors of anywhere 100 micron thick, depends on the material also, some materials are thicker, thicker substrates are used. In some materials the substrate is slightly thinner, typically 60 to 100.

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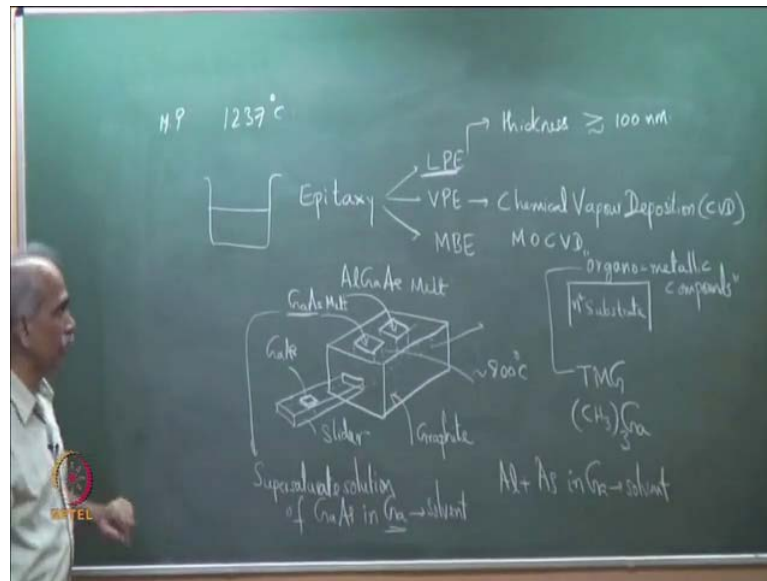
Once, you have single crystal substrate, so, this is the substrate. So, the two methods that are described is to obtain the substrate. If you have to have doped substrate in the melt before the single crystal is formed in the melt you include the dopants, required dopants are included in the melt, the starting melt, so, that you get for example, I wrote n plus substrate. How do we get n plus substrate? For example, you add arsenide in silicon melt

then you will have n plus 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, we want to have these methods, epitaxial methods to grow on top. So, epitaxy apparently this is a combination of epi plus taxis. This means upon or on top this is apparently Greek word.

So, on top or upon and taxis it seems ordered arrangement, arrangement, ordered arrangement. So, epitaxial growth means growth on top ordered arrangement, ordered growth on top, ordered arrangement of happens to forms layers, epitaxial, epitaxial techniques. So, I have indicated the three techniques liquid phase epitaxy, vapor phase epitaxy, this is also called CVD chemical vapor deposition and if the chemicals involved organo metallic compounds you. So, this is CVD. CVD is also vapor phase epitaxy and MOCVD in fact most of the gallium arsenide and aluminum gallium arsenide are grown by MOCVD. MOCVD is metal organic chemical vapor deposition.

Because if the chemicals which are being, if the deposit, if the chemicals involved in the CVD process, if they have organo metallic compounds, organo metallic, organo metallic compounds then it is also called as MOCVD metal organic vapor chemical vapor deposition. Organo metallic, what do I mean by? I will give you an example. For example, trimethylgallium TMG, trimethylgallium. So, methyl group C H 3 3 gallium. Trimethylgallium, this is methyl group is a organic, gallium is metal. So, it is an organo metallic compound trimethylgallium. This is one of the starting point for a gallium arsenide. Organo metallic, MOCVD and the last one is M B E.

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So, let me in the remaining part of this talk, let me discuss briefly the three techniques which are widely used or epitaxial layers. LPE this is the first epi, liquid phase epitaxy. As the name indicates the starting material is a liquid, liquid phase epitaxy. 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 slot here for example, a rectangular slot through graphite, this is graphite.

This is, it is a graphite container through which there is slot, there are also on top there are like till box 1 2 3 this is, these are boxes, cylindrical boxes drawn, till box which you can pour some liquid into this. So, these cylinders go down into this and on a slider, there is a slider here, my belief is that if I do this drawing in front of you then you can exactly understand what it is rather than directly show you a diagram which is already existing. So, there is a slider, it is a slider, this is a this is a slider on which you place the substrate let say gallium arsenide.

I did not describe a how to get gallium arsenide single crystal. I talked about the silicon because that was the easiest. Gallium arsenide is more complicated, it actually has to be done in a sealed close close furnace because there, because of the vapor pressure considerations, but anyhow let me not go into that right now. In this you put the melt. So, gallium arsenide and aluminum gallium arsenide melt. Now, what is this gallium

arsenide melt? Gallium arsenide melt melt, gallium arsenide melt is super saturated solution, super saturated solution, solution of gallium arsenide in gallium.

Gallium is the solvent, gallium is the solvent gallium arsenide in gallium dissolving gallium, it is a super saturated solution of gallium arsenide in gallium. Similarly, here it is for aluminum gallium arsenide, it is aluminum and gallium here, aluminum and arsenic or aluminum plus arsenic in gallium. So, gallium is the solvent, molten, this is melt. Melt means it is a molten solid. In this case metal, aluminum arsenide gallium are all metal, molten that is why melt. Super saturated and why super saturated? You can imagine it is a basic crystallographic 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 form anymore those sugars and sugar crystallizers.

It is the same process which is used in this that you have super saturated melt and this is the gallium arsenide substrate, arsenide and you slide it so that this comes exactly, when it comes exactly under this till box here, it just sets there. It just holds on to that and then all of these are at some temperature. Let us say some temperature of I do not know, I am saying let us say it is at, generally this is around 800 degree centigrade, 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 arsenide.

However, when it is in a solution, its, it is in the liquid form even at around 800 degree centigrade. Because a solution has a lower melting point compared to the pure salt. Now, this is approximately around 800 when this gallium arsenide is sitting under the till box, the temperature of this, we see the 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 crystallization 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 lowered determines the thickness of the layer that is grown on gallium arsenide under this.

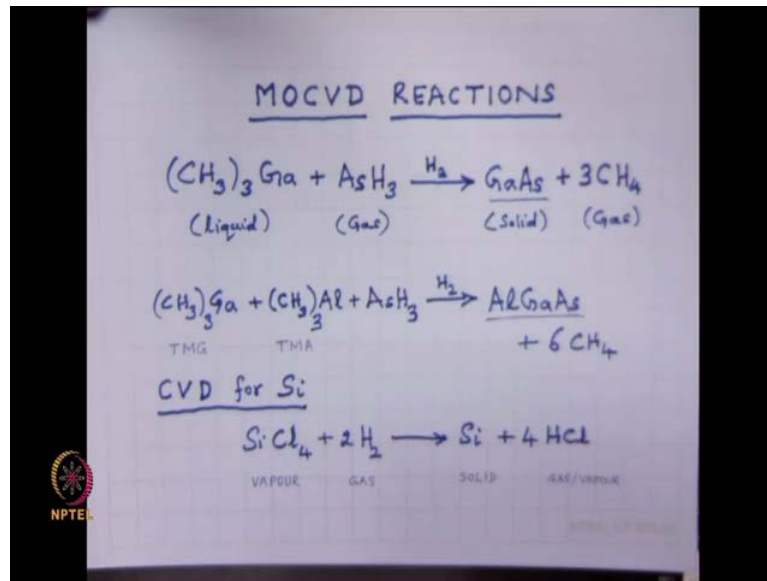
Next, if I want to grow aluminum gallium arsenide, the slider is pushed for the, to the next slot under this till box there is aluminum gallium arsenide melt and you again lower the temperature and aluminum gallium arsenide will get deposited on the substrate. So, you have gallium arsenide on which aluminum gallium arsenide deposited. So, you, if you need again gallium arsenide to be deposited or vice-versa to make double heterostructures you can have more chamber seal. 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 2 till boxes, you put the melt and 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 or of the order of 1000 Angstroms that is 100 nanometer 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 Angstrom 5 Angstrom which you have in the other two techniques.

If you do not need abrupt junctions with precise control then L P E is the best technique. It is the simplest, most cost effective and whenever you need to grow thicker layers LPE is the best and every device does not require such abrupt precise junctions to make quantum well 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 used to grow optoelectronic devices. This is LPE.

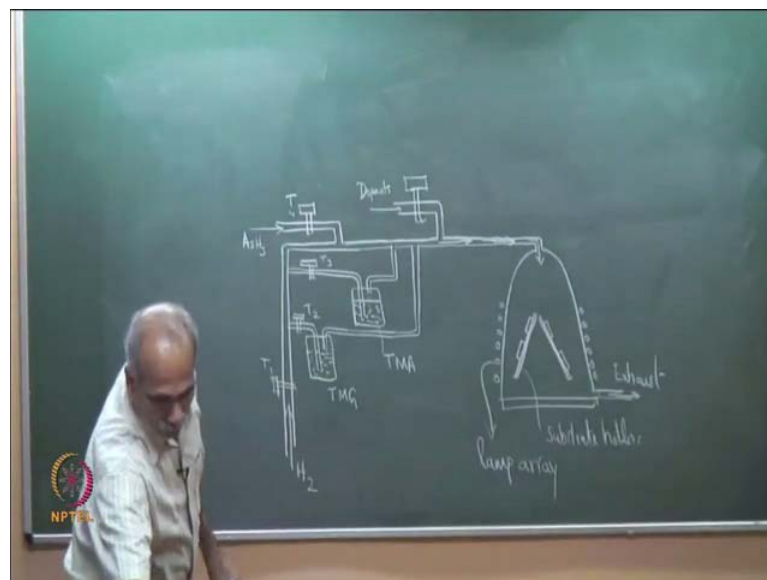
So, let me go over to the next vapor phase epitaxy. I keep repeating please refer to literature for more details. I have given you an idea what the technique is and details you can always go through other material. Let me describe vapor phase epitaxy, this is an interesting technique.

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There are some let me give you some equations that describe deposition of gallium arsenide, aluminum gallium arsenide layers using MOCVD reaction.

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You have a reaction chamber, 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 these there are substrate city 1 2. So, these are substrates like I showed you in the LPE 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 a 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 used, there could be lamp heating. So, these are heating lamps or there could be RF heating, there are different heating, this is lamp array, it is not coil now, it is lamp array.

Heated 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 vapors are carried. I could have preferably 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 taps.

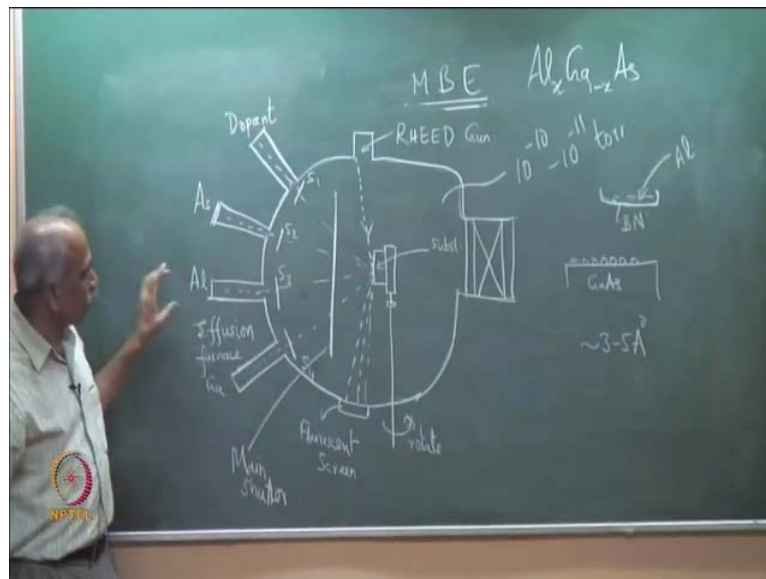
So, the taps which I am showing here are basically mass flow controller let us say T₁ T₂ T₃ T₄. So, hydrogen gas from here and arsine from here, arsine is a highly poisonous gas and if you need to add some dopants, let me erase this dopants. So, this is trimethyl gallium TMG trimethylaluminum TMA, trimethylaluminum and arsine here and hydrogen is the carrier gas. So, this entire mixture is entering the vapor chamber, the reaction chamber. So, see the reaction. Now, let us look at the reaction trimethylgallium plus arsine here gives you gallium arsenide plus hydrogen here is the carrier, the reaction is taking place inside the chamber; so gallium arsenide plus methane gas. Trimethylgallium plus trimethylaluminum plus arsine gives you aluminum gallium arsenide plus methane. This is the reaction, the chemical reaction.

Chemical reaction is taking place inside this chamber, the C V D process is taking place here. It is a vapor phase epitaxy because the trimethylgallium and trimethylaluminum are carried by hydrogen gas in the form of vapors, hydrogen is bubbling through this. So, these are mass flow controllers, the rate at which the vapors 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 tap and only you are bubbling this one if you want to deposit only aluminum arsenide, but if you want to deposit only gallium arsenide close this tap T 3. So, you can controlled by this technique the layers very precisely, 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 MOVCD 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 tetrachloride plus hydrogen gas gives you silicon plus HCl, it is called CVD basically they are all VPE. MOCVD is only when the reactants have metal organic chemical vapors. Alright, I go to the last technique that is MBE.

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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, to make quantum bell structures, molecular beam epitaxy. The setup is quite involved but the control is extremely precise, you can deposit mono layers of gallium arsenide or aluminum gallium arsenide. Molecular beam epitaxy which means there must be atomic beams which are coming to form molecules directly on top of the substrate. So, the

chamber involves something like this, let me draw it approximately. I purely like drawing that is I want to draw this. You have effusion chambers, effusion furnaces or effusion chambers.

Several effusion chambers, through which atomic gas to atomic beams come out. So, there are shutters for each chamber. So, these are effusion chambers. I think it is single effusion chamber or furnace, effusion furnace. So, atomic beams come from this, what I have shown is shutters say S 1 S 2 S 3 S 4 shutters. There is a main shutter and in front of this here is the substrate holder; there are 5 involved setups with gear wheels and all those things, I am not showing all those arrangements here, but I have a chamber, there is a RHEED gun here. 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 or electron beam is incident on this here and it is diffracted here there is a, this is a fluorescent screen, fluorescent fluorescent 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 loading chamber, the double barrier ultra high vacuum lock. Now, let me explain and then everything will become clear. These are sources say gallium, aluminum, 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 comes. So, atomic beam is incident on the substrate. The substrate is kept heated at a certain temperature, the atoms which come there on the surface of the substrate.

So, atoms are arriving on the surface and because this is gallium arsenide, the atoms arrange themselves so that it forms, it fits to the gallium arsenide legs. 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, aluminum, arsenic, if you do not want aluminum, you want to grow only gallium or arsenic you put this shutter closed. This is a main shutter, if we do not want any reaction to take place or you are doing some setting when you close the main. So, this is the main shutter. Molecular beam epitaxy, please see this.

This is at ultra high vacuum of 10^{-10} to 10^{-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, aluminum, arsenic all these. They are actually this atomic, the effusion chamber has, each one has a crucible boron nitride crucible usually boron nitride crucibles in which you have aluminum. You have placed pure metallic aluminum and it is heated and the atomic beam is coming out of these effusion guns or this chambers, effusion furnace.

So, there is independent beams are coming here, the atoms rearranged 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 the atoms are incident, the rate at which atoms are incident here is controlled by the temperature. So, in a controlled rate of gallium, aluminum, arsenic you can change the ratio $G_{Al} \times Al^x \times As^{1-x}$, if you are going the ternary compound aluminum gallium arsenide $Al^x Ga^{1-x} As$.

You can control this x so that required composition of aluminum gallium arsenide can be obtained 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 controlled, correct to 1 mono layer which means you make abrupt junctions. You do not want gallium or aluminum arsenide anymore you just block aluminum, the next layer will be gallium arsenide gallium arsenide pure.

So, molecular beam epitaxy as it indicates, as the name indicates there are beams, atomic beams which drawn. 1 dozen call it as atomic beam epitaxy because it is the layers which are grown or molecules. So, molecular beam, there are beams of atoms which come here and the layer is deposited on top. So, this is the third technique, you can read more details about these. It is a very interesting technique and most of the quantum well structure are grown by MBE technique. So, I will stop here. I hope I 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 two.