

## **3.1 Epitaxial growth**

Epitaxy means the growth of a single crystal film on top of a crystalline substrate. For most thin film applications (hard and soft coatings, optical coatings, protective coatings) it is of little importance. However, for semiconductor thin film technology it is crucial. Epitaxy is a greek word composed of two parts, namely epi and on and taxy which means on and ordered arrangement respectively. Thus epitaxy refers to ordered arrangement on some materials; oriented growth of epilayers on a single crystalline substrate, so that the two atomic planes in contact have planar unit cells that match each other. Epitaxy is a term applied to the process of growing a monocrystalline film on a substrate. Epitaxy is termed as homoepitaxy when a crystal is grown epitaxially on a substrate of the same material, as in silicon film grown on silicon substrate. It is termed as heteroepitaxy when a crystal is grown on a foreign substrate, as in a silicon film grown on sapphire or gallium arsenide grown on a silicon substrate.

Epitaxial growth techniques have largely superseded the bulk growth for electronic circuit fabrication because the devices to be fabricated needs only few micron dimensions. The use of epitaxial growth, therefore reduces the growth time, wafering cost and eliminates the wastages caused during growth, cutting, polishing etc. The major advantage of the epitaxy is the uniformity in the composition, controlled growth parameters and better understanding of the growth itself.

### **3.1.1 Different Epitaxial techniques**

Several epitaxial techniques have been used for the growth of epilayers of III-V, II-VI compound semiconductors and other materials. The , prominent among these techniques are Liquid Phase Epitaxy (LPE), Vapour Phase Epitaxy (VPE), Molecular Beam Epitaxy (MBE), Chemical Beam Epitaxy (CBE) and Atomic Layer Epitaxy (ALE) etc.

### **3.1.2 Advantages**

- Better structural & Electrical properties
- Growth is carried out at low temperature- decrease in concentration of both chemical and crystalline defects. Also, the Melt is subjected to less chemical contamination from surrounding
- The ability to control material thickness and carrier concentration
- Possibility to grow p-n junction & other multilayer structures
- Superior electrical properties due to the lower defect density

## 3.2 Liquid Phase Epitaxy

The liquid phase epitaxial (LPE) growth apparatus simply allows a growth solution of the desired composition to be placed in contact with the substrate for a certain time under controlled temperature conditions. In this technique, supersaturation necessary for deposition is achieved by reducing the temperature. The relationship between the temperature and solubility as predicted by the phase diagram has to be utilized in understanding the growth process. Besides thermodynamic consideration, there are other factors such as diffusion of constituents in the solution, nucleation and the mechanism of growth at the surface and convection as the result of temperature and compositional gradients that affect the LPE process

Liquid phase epitaxy means the growth of thin films from metallic solution on an oriented crystalline substrate. The solvent element can either be a constituent of the growing solid e.g. In or Ga, or it can be some other low melting metals like Sn, Bi or Pb, which is incorporated into the solid only as a dopant. The solvent contains a small quantity of solute e.g. As in Ga for epitaxial growth of GaAs layers which is transported towards the liquid-solid interface. The process is best controlled if this transport occurs only by diffusion, i.e. the driving force in the solution is a concentration gradient of the solute. The growth boats are commonly designed such that essentially, only diffusion perpendicular to the interface occurs; convection and surface tension related transport are suppressed. The temperature gradient is minimized by utilizing larger dimension of the substrate compared to the height and radius of curvature. Applying these constraints, the LPE process can be treated as an one-dimensional diffusion process in which the growth rate is found to be diffusion limited.

### 3.2.1 Apparatus

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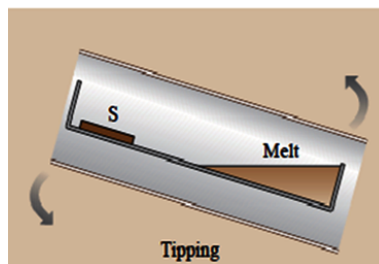


Figure 3.1: Schematic diagram of LPE tipping growth apparatus

There are three principal LPE growth techniques: tipping, dipping and sliding. In the **tipping** technique, the substrate is held tightly at the upper end of a graphite boat and the growth solution is placed at the other end. Initially the substrate wafer is well clear of the solution and the furnace is heated to form solution. The solution is brought into contact with the substrate by tipping the substrate. The furnace is then slowly cooled and an epitaxial layer is grown on the substrate. The solution remains in contact with the substrate for the defined temperature interval and growth is terminated by tipping the furnace back to its original

position. The solution remaining on the film surface is removed by wiping and dissolving in a suitable solvent. The original tipping furnace is shown in Figure 3.1.

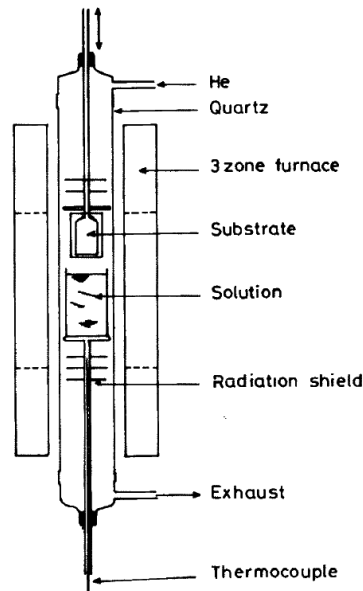


Figure 3.2: LPE growth apparatus employing the dipping technique

The **dipping** technique uses a vertical furnace as shown in Figure 3.2. The solution is contained in a graphite or alumina crucible at the lower end of the furnace. The substrate fixed in a movable holder is initially positioned above the solution. At the desired temperature, growth is initiated by immersing the substrate in the solution and it is terminated by withdrawal of the substrate from the solution.

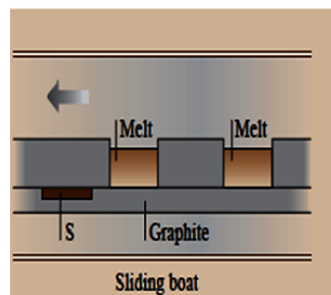


Figure 3.3: Horizontal slider LPE system

The apparatus used for the tipping and dipping techniques is very simple and easy to operate. However, growth of multiple layers by these techniques would require considerably more complex apparatus. The third LPE technique, the **sliding technique**, uses a multibin graphite boat to grow multiple epitaxial layers. Figure 3.3 shows a LPE system with sliding technique. The principal components of this apparatus are a massive split graphite barrel with a graphite slider, a fused silica growth tube to provide a protective atmosphere and a horizontal resistance furnace. The graphite barrel has the desired number of solution chambers depending on the number of layers to be grown, and the slider has two slots for the precursor seed substrate and the growth substrate. The substrate is brought into contact with the solutions by motion of

the barrel over the slider. This operation can easily be automated. The fused silica tube is usually within a heat pipe thermal liner in the furnace to ensure uniform temperature. Alternatively, a multizone furnace without a heat pipe can also be used. Growth is usually carried out in an atmosphere of hydrogen.

### 3.3 Molecular Beam Epitaxy

Molecular beam epitaxy is a process of depositing epitaxial thin films from molecular or atomic beams on a heated substrate under ultra-high vacuum (UHV) conditions. Figure 3.4 shows a schematic diagram of a typical MBE system. The beams are thermally generated in Knudsen-type effusion cells which contain the constituent elements or compounds of the desired epitaxial films. The temperature of the cells are accurately controlled to give the thermal beams of appropriate intensity. The beam fluxes emerging from these non-equilibrium effusion cells are generally determined experimentally in most cases using movable nude ionization gauge placed in the substrate position. The cells are made from non-reactive, refractory materials which can withstand high temperatures and they do not contribute to the molecular beams. Pyrolytic Boron Nitride (PBN) or high purity graphite are used as the cell materials. The cell consists of an inner crucible and an outside tube which is wound with Ta or Mo wires for resistive heating. A chemically stable W-Re thermocouple facilitates precise control of the cell temperature which is very essential for achieving constant growth rates since small temperature fluctuations of the order of  $\pm 1^{\circ}\text{C}$  can result in  $\pm 2$  to 4% fluctuations in molecular beam intensity. The various cells are all placed and angled in such a way that their beams converge on the substrate for epitaxial growth. Individual shutters provided for each cell and the cell temperature can be computer controlled to achieve high reproducibility and little human interventions. The cells are individually surrounded by a liquid nitrogen shroud to prevent cross heating and cross contamination.

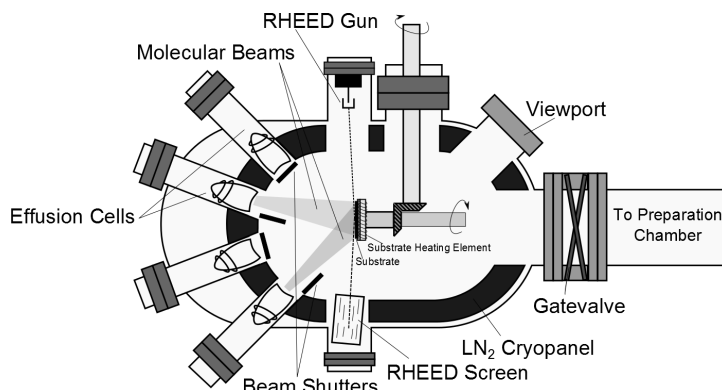


Figure 3.4: Schematic of MBE system

The MBE technique has a number of advantages over other techniques. The most important aspect of MBE is the deposition rate (typically less than 3,000 nm per hour) that allows the films to grow epitaxial. These deposition rates require proportionally better vacuum to achieve the same impurity levels as other deposition techniques. A particular advantage is that it permits growth of crystalline layers at temperatures where solid-state diffusion is negligible. Since chemical decomposition is not required for growth, deposition species need require only enough energy to migrate along the substrate surface to crystalline bonding site. The impurity dopant incorporation during molecular beam epitaxial growth is possible by having an additional source of the dopant. As a result, MBE has rapidly established itself as a versatile technique for growing elemental and compound semiconductor films. Thus using MBE, it is possible to produce multilayered structures including superlattices with layer thickness as low as  $10\text{\AA}$  for DH lasers and wave-guide applications.

However, there are few limitations in the epitaxial growth of compound semiconductors by MBE technique. The ultra high vacuum apparatus is very expensive. Frequent shutdowns are required to replenish the source materials and opening the UHV apparatus. A major problem is the difficulty in growing phosphorus-containing materials. Phosphorous is found to be bounce around the system ultimately collected in vacuum pumps.

### 3.4 Vapour Phase Epitaxy

The principles of VPE can be described in the following steps:

1. Transport of reactants to the substrate region
2. Transfer of reactants to substrate surface
3. Adsorption of reactants on substrate
4. Surface processes such as reaction and kinetics
5. Desorption of products
6. Transfer of products to main gas stream
7. Exhausting of gases away from reaction chamber

The steps 2 and 6 involve transfer of reactants to and fro from the crystal surface and are called mass transport process. The steps 3,4 and 5 represent chemical reactions on the crystal surface. The Schematic

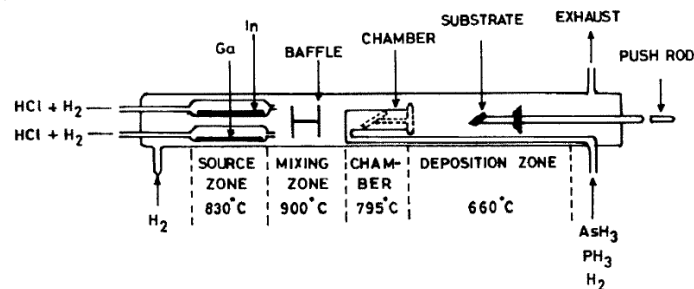


Figure 3.5: Schematic diagram of vapour phase epitaxial growth process

diagram of vapour phase epitaxial growth process is shown in figure 3.5. Vapour Phase Epitaxy (VPE) is one of the commonly used techniques for the growth of III-V compound semiconductors. In this technique, growth is carried out by vapourizing the source material for III-V compounds; inorganic or organic materials which react with the other materials to form the compound semiconductors on the substrate. Growth is controlled by the partial pressures of the each of the components of the source materials. Two different forms of the vapour phase epitaxial growth are:

- chloride vapour phase epitaxy
- hydride vapour phase epitaxy

The main practical difference between the two systems is just the input gas supply. The two processes can be outlined in the table below:

The chloride VPE involves group V transport using trichloride (e.g.  $AsCl_3$ ) and group III transport by the formation of chloride (e.g.  $GaCl$ ). Crystal growth is carried out in a hot walled reactor and the chemical reactions are reversible making it possible to etch as well as grow. Inherent advantages of trichloride VPE over other vapour phase growth methods arise from the fact that  $AsCl_3$  and  $PCl_3$  can be distilled into very pure liquids.



Hydride VPE is an epitaxial growth technique often employed to produce semiconductors such as GaN, GaAs, InP and their related compounds, in which hydrogen chloride is reacted at elevated temperature with the group-III metals to produce gaseous metal chlorides, which then react with ammonia to produce the group-III nitrides. Both the source reactions and the deposition reactions are done inside a hot walled quartz reactor. The reactions occur under near equilibrium conditions, and since they are reversible, controlled in-situ etching is possible.