

# Thin Film Growth/Deposition

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Almost all of these techniques do not depend upon the surface. Films can be deposited on almost anything from steel to plastic. Epitaxy means “arranges upon”. If an underlying crystalline material is available and any of these deposition techniques is used than usually a pretty good quality crystal “grows”. In this case its called “epitaxy” or “epitaxial deposition”. Otherwise an amorphous or poly-crystalline layer would get “deposited”.

## 1 Liquid Phase Growth/Deposition Techniques

Most important of these is the *LPE* (Liquid Phase Epitaxy). Suppose I have a homogeneous mixture of *GaAs* and *Ga* in liquid phase. Then the simple thermodynamics tells us that as we lower the temperature *GaAs* would condense earlier than the solution itself. This simple fact is used to crystallize *GaAs* over a substrate. Its a thermal equilibrium technique. For example a quartz slider holding the wafer is moved under a boat containing liquid mixture of *GaAs* and *Ga* and than tube is cooled to get the thin film deposited.

## 2 Vapour Phase Growth/Deposition Techniques

There are number of vapour phase thin film deposition/growth techniques available. Most important of these are Chemical Vapor Deposition *CVD* (which is also known as Vapor Phase Epitaxy (*VPE*)) and Physical Vapor Deposition (*PVD*) (which is also known as Vacuum Deposition) techniques. It should be noted that, even though, nowadays most popular *CVD* method is a low pressure (*LP – CVD*) technique still pressures in *PVD* schemes are much lower and hence *PVD* schemes are usually known as vacuum deposition techniques.

### 2.1 VPE or CVD Techniques

In this technique chemicals (sources) containing deposition constituents are transported in vapor phase to the substrate where they react to generate deposition constituents which then gets deposited over the substrate. Sometimes reactants are not available in the gaseous phase. In such cases a carrier gas (usualy hydrogen or argon) is bubbled through the liquid source which carries

the source vapor to the substrate (these techniques form a sub-class of CVD techniques and are called chemical transport processes). Chemical transport processes might be either hydride process or halide process or organo-metallic process (*MO – CVD*). For example for the deposition of epitaxial *Si*, one can either use a gaseous source of Silane *SiH<sub>4</sub>* which gets decomposed at the surface or one can use liquid source of Silicon-Tetra-Chloride *SiCl<sub>4</sub>* bubbled by hydrogen gas. Hydrogen carries the *SiCl<sub>4</sub>* vapor and reacts with it at the surface to generate *Si* and *HCl*. *SiCl<sub>4</sub>* process is actually preferred because it removes the metallic contaminants as well. Similarly, in halide process growth of *GaAs* one uses liquid *Ga* source and liquid *AsCl<sub>3</sub>* source and hydrogen as the carrier gas. *AsCl<sub>3</sub>* saturated hydrogen is made to flow over heated *Ga* region where *AsCl<sub>3</sub>* breaks into gaseous *As* and *HCl*. *HCl* reacts with *Ga* to generate gaseous *GaCl*. Both of these reacts at the surface of the wafer, which is little cooler, to crystallize *GaAs*. In hydride process gaseous Arsine *AsH<sub>3</sub>* or Phosphine *PH<sub>3</sub>* etc are used for group *V* element source. In *MO – CVD* alkyl metal liquid source is used for group *III* elements with hydrogen as the carrier gas. Gaseous *AsH<sub>3</sub>*/*PH<sub>3</sub>* etc is used for group *V* element.

The process can be broken down into many sub-steps - convection of gasses, diffusion of reactants across the boundary layer, adsorption of reactants on the surface, several steps of chemical reactions at the surface, desorption of products and then diffusion out and convection of the products. (By boundary layer we mean the stagnant layer due to viscosity. The velocity of gas just on the surface is zero and increases steadily as we move away. Distance between surface and uniform velocity region is called boundary layer.) Usually two of these that are diffusion across boundary layer and surface reaction are the two most important rate limiting steps. Diffusion rate is nearly independent of temperature while surface reaction rate goes as  $\exp(-1/T)$  (exact logarithmic dependence is determined by the exact elementary rate determining chemical step). Hence at higher temperatures rate limiting step should be the diffusion and the rate should be pretty much independent of temperature. While at low temperatures surface reaction would be the rate limiting step.

In *CVD* systems growth varies a little bit along the length of the tube due to two reasons. One is that the boundary layer thickness varies with distance and other is simply because of the consumption of the gasses with distance. First reason affects only diffusion limited processes but the second one affects both of these. For diffusion limited systems this is countered by tilting the substrates a little bit. This reduces the tube cross-section and increases the flow. For the surface reaction limited processes a simple temperature gradient is usually maintained to counter this problem. Following are most popular *CVD/PVE* techniques :-

- *AP – CVD* (Atmospheric Pressure *CVD*) (Cold-Wall, Hot-Wafer System) In this case deposition usually is limited by the diffusion of reactants through the boundary layer. This means that it is important to maintain a constant gas concentration across all the wafers that's why wafers need to be placed flat next to each other in the tube. In *AP – CVD* systems if one needs to deposit epitaxial layers then one needs to go for higher temperatures and hence it would be diffusion controlled. At lower temperatures rate would be surface reaction limited and film would be polycrystalline.
- *LP – CVD* (Low Pressure *CVD*) (Hot-Wall System) In this case deposition rate is limited

by the chemical reaction rate at the surface. This can be achieved, for example, by lowering the temperature. The deposition rate would be sensitive to temperature and hence one needs good temperature control. But reaction rates are not sensitive to the concentration (partial pressure) of the gases over the wafer assuming that the surface reaction controls the rate and hence diffusion always makes sufficient number of gas molecules available at all spatial location even though this number might not be uniform. Also if the pressure is kept same as that with *AP-CVD* and temperature is lowered to get into surface reaction rate limited regime, the deposition rate would be much smaller. Also the quality of film would deteriorate. Hence the total pressure of the gases is reduced keeping the partial pressure of reactants to be same (less dilutant gases used). This speeds up the diffusion rate since there are much less collisions and hence diffusivity goes up. Hence one can obtain surface reaction limited regime upto much higher temperatures. There is always a limit to what extent one can reduce the total pressure without reducing the partial pressures. Hence the usual pressures are not too low ( $1\text{ torr} \approx 1/760\text{ Atmp}$ ). Wafers can now be stacked more closely in vertical direction. This would increase the throughput. There are some other benefits of operating at low pressures as well. For example probability of gas phase reaction reduces and only surface reaction becomes most probable. Hence particulate deposition does not happen. Consumption of dilutant gases reduces. Autodoping problem reduces. These are the reasons why *LP-CVD* is the most common technique these days. In *LP-CVD* systems, if rate is determined by surface reaction then rate would also be dependent upon crystal plane. One that has more atoms would be faster. Also  $\text{SiH}_4$  should be faster than the  $\text{SiCl}_4$  because of molecular weights.

- *PE-CVD* (Plasma Enhanced *CVD*) This is used mainly when sufficient deposition rates are needed at low temperatures.
- *HDP-CVD* (High Density Plasma *CVD*)

## 2.2 PVD or Vacuum Deposition Techniques

- Evaporation (VTE)
- Sputtering

## 3 Molecular Beam Epitaxy (MBE)

### Further Resources

- Author's Home Page
- Other Articles