PH3EC2 Vapour Growth and Epitaxial Growth

Lecture 1: Vapour Growth Techniques

Lecturer: Dr. Shinoj V K

1.1 Vapour growth

The growth of single crystal materials from the vapour phase. Deposition from the Vapour Phase is the most preferred techniques for the fabrication of thin layer of metal, insulator and semiconductor materials.The crystal often have perfectly flat external surfaces and less imperfections that cannot be duplicated by other means.

1.1.1 Challenges

- Large number of variables involved tends to make it difficult process.

- Lower density of molecules in the crystal growth leads to lower growth rate

- The temperature required for the process is high (in the vicinity of sublimation point)

1.1.2 Advantages

- Convenient for large large scale operation

- Coat irregular-shaped substrates including growth on inner surfaces

- Offer maximum control of material properties such as thickness and composition

- Does not involve contacting of growing surface with liquid/ solid phase

The thin film technology using vapour growth technique can be broadly divided in to:

1. Physical Vapour Deposition

2. Chemical Vapour Deposition

1.2 Physical Vapour deposition

Physical Vapor deposition (PVD) is a class of vacuum deposition method which can be used to produce thin films. PVD uses physical process such as heating or sputtering to produce vapor of material which is then deposited on the object which requires coating. Traditional Vacuum evaporation technique involved either direct evaporation of source material onto substrate or reactive evaporation where the evaporated material reacts with a component intentionally added to the vapour phase to produce desired deposit. The schematic of PVD system is shown in figure 1.1.
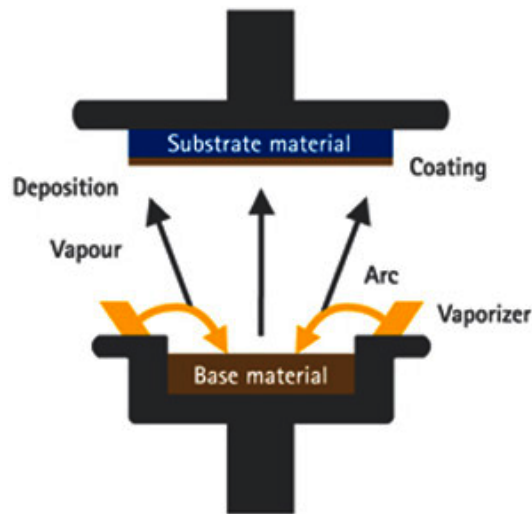
Figure 1.1: *Schematic of PVD system*

The PVD techniques involve three fundamental steps:

- Vaporization of materal from a solid source assisted by high temperature vacuum or gaseous plasma.

- Transportation of vapor in vacuum to substrate surface

- Condensation onto substrate to generate thin films

The two most common PVD processes are thermal evaporation and sputtering. Thermal evaporation relies on vaporization of source material by heating where as sputtering is a plasma assisted technique. Sputtering methods provide superior control over composition and is also capable of coating larger areas.

1.3 Chemical Vapour deposition (CVD)

CVD is a chemical process to produce high quality solid materials. The precursor gases are delivered into the reaction chamber at approximately ambient temperature. As they pass over or come into contact with heated substrate, they react and decompose to form a solid phase which are deposited onto substrate.

1.3.1 Advantages

- No vacuum or pumping facilities are needed

- Deposition rates are generally higher

- Controlled doping of impurities to deposit is possible

- Epitaxial layers are possible

- *In situ* chemical vapour cleaning of substrate/ system

1.3.1.1 Drawbacks

- Reactive gases are dangerous which needs special handling procedure

- Uniformity of deposit is hard to control

- During deposition, masking becomes difficult —item deposition take place on substrate as well as on the walls of container.

1.4 Chemical Vapour Transport

It is a process where a condensed phase, typically a solid, is volatilised in the presence of gaseous reactant (transport agent) and deposited elsewhere in the form of crystal. The various parameters optimized for successful CVT are growth temperature, transport direction, rate of mass transport and free energy of reaction. Transport is governed by two processes - Convection and diffusion.

1.4.1 Definition of CVT reactions

CVT reactions are those in which a solid or liquid substance 'A' reacts with a gaseous transporting agent 'B' at a temperature T_1 to form vapour phase reaction products (AB), which in turn, undergo reverse reaction at a different place in the system at a temperature T_2, resulting reformation of crystalline substance 'A'.

i $A_{(s,l)} + jB_{(g)} \rightleftharpoons k\ AB_{(g)})$
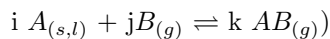
Here the substance is transported chemically. In addition to reversible heterogeneous reaction, a concentration gradient must be established.

1.4.2 Fundamentals of CVT

The principle of chemical vapour transport reactions in a cylindrical closed tube in a temperature gradient is represented in figure 1.2.
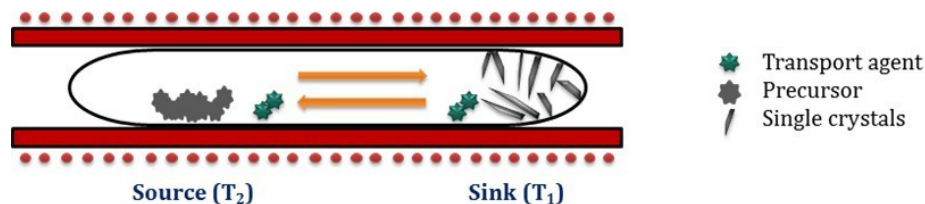

Figure 1.2: *CVT in cylindrical closed tube*

$$A_{(s,l)} + B_{(g)} \rightleftharpoons AB_{(g)}) \tag{1.1}$$

$$n_{AB} = (Dqt/lRT)(P_{AB(1)} - P_{AB(2)}) \tag{1.2}$$

Where n_{AB} is the number of moles of AB transported

D is the diffusion coefficient

q is the tube cross section

l is the length of the diffusion path

t is the duration of experiment

R is the gas constant

T is the absolute temperature of diffusion path

$P_{AB(1)}$ and $P_{AB(2)}$ ate partial pressure of AB at temperatures T_1 and T_2, respectively.

If the solid material **A** reacts with a gas **B** with the formation of a gaseous material **AB** and if the reaction is reversible, then a chemical vapour transport may take place at the suitable temperatures. If the observed reaction is endothermic, then the solid material A will be consumed at a higher temperature T_1, with the formation of gaseous product AB, while after the migration of AB to the new location with a lower temperature T_2, the reverse reaction take place and A is deposited from the gas phase with release of B. For exothermic reaction transport of solid phase take place from low temperature to high temperature.

1.4.3   Criteria for choice of transport reaction

The essential factors determining choice of transport reactions:

1. Aside from transported solid material, only gases participate in the reaction. Then only all components are mobile throughout the gas phase

2. Reaction must be reversible. This is true at higher temperature only.

3. The equilibrium position of transport reaction must be extreme. i.e it should not lie too far to reactant side or to the gaseous product side. Otherwise the concentration gradient becomes too small.

4. The transport efficiency is maximum if the concentration gradient ($\triangle P_{AB}$) is a maximum.

1.4.4   Specifications of the technique

The chemical vapour transport is carried out in sealed cylindrical tube made of pyrex glass or quartz. The substance and transporting agent are sealed off under vacuum. If the transporting agents are gaseous under room temperature, the tube loading with reactants is flushed for sufficient length of time with particular gas and then sealed off. The values of the free energy of the reaction must be near zero and the equilibrium constant near unity, so that the reverse reaction can also take place to an appreciable extent. The transport of the vapour can take place by diffusion between the source and deposition zones when a narrow tube is used and when the total pressure in the system is small. Transport takes place by convection at high pressures in wider tubes, and in tubes inclined against the horizontal. The crystallization chamber should not be too small in order to avoid inter-growth between the crystals. Distribution of the temperature in the deposition zone must be uniform in order to avoid reevaporation of crystals from warmer parts during the experiment.

1.4.5 Temperature variation methods for growth

The main drawback of of simple CVT method is gaseous solvent traces incorporated as impurity and high supersaturation. This will leads to uncontrolled primary nucleation and many small sized crystals. In Chemical vapour transport there are three methods which one can adopt for growing large size crystals.

1.4.5.1 Stationary temperature profile (STP)

In the STP procedure, the source temperature (T_s) and growth temperature (T_d) are fixed at particular values after keeping the reverse temperature profile for initial few hours in order to clean the crystallization zone. As T_s and T_d are kept at constant values, the supersaturation,σ, is maintained unchanged during the growth. Though this procedure can be adopted for getting single crystals of many compounds, this technique is not suitable for getting large crystals.

1.4.5.2 Linearly time varying temperature profile (LTVTP)

Here the source temperature is linearly increased with time while the growth temperature is kept constant. So as supersaturation increases from negative values (i.e. $T_s < T_d$) to positive values primary nucleation is possible. Though T_s continues to increase, σ drops due to diminishing of the vaporized mass which is consumed in producing the crystal. Then for a certain length of time, depending on the particular vapourization kinetics of the charge, σ remains sufficiently low so that the first crystal can be further grown by secondary nucleation. This LTVTP procedure was adopted for growing crystals much larger than those by STP procedures. Also the quality of crystal is superior in comparison with those by STP procedures.

1.4.5.3 Oscillating temperature profile (OTP)

In the OTP technique, either source temperature (T_s) or, deposition temperature (T_s) or, both, are made to oscillate, so that a growing crystal alternatively meets positive and negative supersaturations* in such a way that the amount of mass transported per T- cycle from source to the crystal will be positive. The supersaturation is the function of $[T_s(t) - T_d]$ is periodically made positive (growth condition) and negative (dissociation condition).

$$\sigma_{eff} = a(T_s^{OTP} - T_d)^n = a(\Delta T_{eff})^n \tag{1.3}$$

where 'a' and 'n' are empirical constants. T_s^{OTP} is the oscillatory source temperature. ΔT_{eff} can be arbitrarily reduced by suitably shaping the T-cycle via frequency and amplitude. If the frequency and amplitude of the said oscillations are properly chosen, the periodic inversion of the supersaturation will favour the growth of relatively larger and more perfect crystals.

The OTP procedure enables the good control over secondary nucleation though primary nucleation possess quite a problem. As LTVTP gives good control over primary nucleation a combined LTVTP plus OTP procedure is best suitable for the CVT growth.

1.4.6 Advantages of Chemical Vapour Transport

1. Growth temperature is much smaller than the melting point of the material.

2. Crystals of the material with an appreciable dissociation of their melting point can be easily grown.

3. Allotropic crystalline forms can be grown

4. Good control of stoichiometry is possible.

5. Growth of epitaxial layer is possible.

6. *lnsitu* chemical vapour cleaning of the substrate or system is possible

1.4.7   Limitations of Chemical Vapour Transport

1. Thermodynamics and kinetics are complex and poorly understood

2. Deposition on substrate as well as on the walls of the container.

3. Reactive gases are dangerous in some cases and they need special handling procedure.

*In order for crystallization to take place a solution must be "supersaturated". Supersaturation refers to a state in which the liquid (solvent) contains more dissolved solids (solute) than can ordinarily be accomodated at that temperature.