

Module 2 :

“Diffusive” heat and mass transfer

Lecture 9:

Mass Transfer with Chemical

Reaction

Case Study: Low Pressure Chemical

Vapor Deposition (LPCVD)

VAPOR DEPOSITION

Vapor deposition can be referred to any process in which materials in a vapor state are condensed through condensation, chemical reaction, or conversion to form a solid material. These processes are widely used to form coatings to alter the mechanical, electrical, thermal, optical, corrosion resistance, and wear properties of the substrates. They are also used to form free-standing bodies, films, and fibers and to infiltrate fabric to form composite materials. Vapor deposition processes usually take place within a vacuum chamber. The two main categories of vapor deposition processes are

1. Physical vapor deposition (PVD)

In PVD processes, the object is subjected to plasma bombardment. In CVD processes, thermal energy heats the gases in the coating chamber and drives the deposition reaction.

2. Chemical Vapor Deposition (CVD)

CVD is a widely used technique for depositing thin films of a large variety of materials. Applications of CVD range from the fabrication of microelectronic devices to the deposition of protective coatings. In a typical CVD process, reactant gases (often diluted in a carrier gas) at room temperature enter the reaction chamber. The gas mixture is heated as it approaches the deposition surface, heated radiatively or placed upon a heated substrate. Depending on the

process and operating conditions, the reactant gases may undergo homogeneous chemical reactions in the vapor phase before striking the surface. There is a great variety of chemical vapor deposition processes such as:

- (i) Atmospheric Pressure Chemical Vapor Deposition (APCVD)
- (ii) Low Pressure Chemical Vapor Deposition (LPCVD)
- (iii) Plasma assisted (enhanced) Chemical Vapor Deposition (PACVD)
- (iv) Photochemical Vapor Deposition (PCVD)
- (v) Laser Chemical Vapor Deposition (LCVD)
- (vi) Metal-organic Chemical Vapor Deposition (MOCVD)

Low Pressure Chemical Vapor Deposition (LPCVD)

The process carried out at low pressure in a chamber can be explained as follows:

1. Transport of reactants to the deposition region.
2. Transport of reactants from the main gas stream through the boundary layer to the wafer
3. Adsorption of reactants on the wafer surface.
4. Surface reactions, including: chemical decomposition or reaction, surface migration to attachment sites (kinks and ledges); site incorporation; and other surface reactions (emission

and redeposition for example).

5. Desorption of byproducts.
6. Transport of byproducts through boundary layer.
7. Transport of byproducts away from the deposition region.

In LPCVD, deposition rate is limited by reaction rate (controlled by temperature and pressure) and arrival rate (controlled by pressure since gas throughput is related to pressure by $Q=CP$). Fig (9.1) shown below illustrates the process of deposition of material by LPCVD.

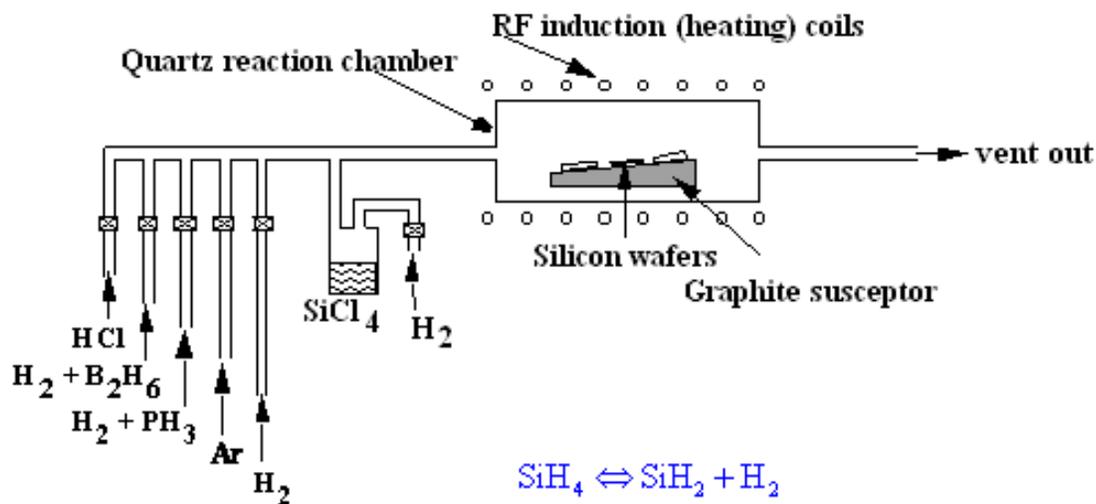
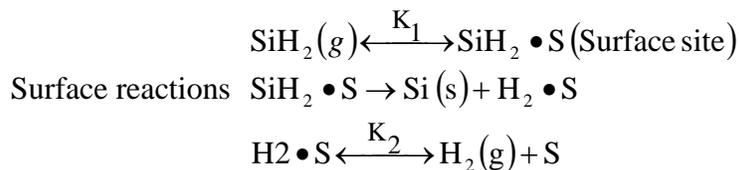


Fig.9.1. Material deposition in a Low Pressure Chemical Vapor Deposition process

Low pressure chemical vapor deposition (LPCVD) has some unique advantages such as excellent uniformity and high purity; therefore it can be used for a variety of materials: NPTEL, IIT Kharagpur, Prof. Saikat Chakraborty, Department of Chemical Engineering

- Polysilicon for gate contacts
- Thick oxides used for isolation between metal interconnects
- Doped oxides useful for global planarization
- Nitrides and other dielectrics for isolation or capacitors (higher K materials for larger capacitance)
- Metals for seed layers for vias and interconnect lines (not typically used for the entire metal line due to slow deposition rate)

To understand the mechanism of the process, consider the example of deposition of Si using SiH_4 (Silane) as precursor gas diluted in H_2 . The overall gas phase reaction is given by

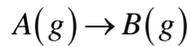


Langmuir–Hinshelwood Kinetics

By combining the surface-reaction rate laws with the Langmuir expressions for surface coverages, we can obtain Langmuir-Hinshelwood (LH) kinetics for surface catalyzed reactions.

A kinetic scheme for an overall gas phase reaction can be expressed as

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where A is the gas phase reactant and B is the gas phase product. If the surface reaction is unimolecular, then for the overall reaction $A(g) \rightarrow B(g)$ is given by

$$-r_A = \frac{kK_A c_A}{1 + K_A c_A + K_B c_B} \quad (9.2)$$

The equation (9.2) for LH model can be expressed in terms of partial pressure p_i , therefore

$$-r_A = \frac{kK_A p_A}{1 + K_A p_A + K_B p_B} \quad (9.3)$$

So assuming Langmuir–Hinshelwood Kinetics for reaction (9.1), the rate law is

$$r_{Si}'' = \frac{k_1 P_{SiH_2}}{1 + K_1 P_{H_2} + K_2 P_{SiH_2}} \quad (9.4)$$

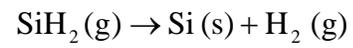
where K_1 and K_2 are adsorption constants. The values of K_1 and K_2 tend to decrease as temperature increases.

At high temperature (T), $K_1 P_{H_2} + K_2 P_{SiH_2} \ll 1$. Equation (9.4) then becomes

$$r_{Si}'' = k_1 P_{SiH_2} = k C_{SiH_2} \quad (9.5)$$

Diffusion and Reaction between Wafers

Deposition step overall reaction is given by



In terms of diffusing gaseous components, consider a reaction

