Introduction

• CVD is a chemical process used to produce high-purity, high-performance solid materials.

• This technique is suitable for the manufacture of coatings, powders, fibers and monolithic components.

• This technique is often used in many thin film applications.

• By varying the experimental conditions—substrate material, substrate temperature, composition of the reaction gas mixture, total pressure gas flows, etc.—materials with different properties can be grown.
Chemical vapour deposition may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapour phase. It belongs to the class of vapour-transfer processes which is atomistic in nature, that is the deposition species are atoms or molecules or a combination of these.

Schematic of a simple thermal CVD reactor
1. Diffusion in of reactants through boundary layer
2. Adsorption of reactants on substrate
3. Chemical reaction takes place
4. Desorption of adsorbed species
5. Diffusion out of by-products

Sequence of events during deposition
Classified by operating pressure:

- Atmospheric pressure CVD (APCVD) – CVD at atmospheric pressure.
- Low-pressure CVD (LPCVD) – CVD at sub-atmospheric pressures.
- Ultrahigh vacuum CVD (UHVCVD) – CVD at very low pressure, below $10^{-6}$ Pa ($\sim 10^{-8}$ torr).

Classified by physical characteristics of vapour:

- Aerosol assisted CVD (AACVD) – CVD in which the precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically.
- Direct liquid injection CVD (DLICVD) – CVD in which the precursors are in liquid form (liquid or solid dissolved in a convenient solvent). Liquid solutions are injected in a vaporization chamber towards injectors. The precursor vapours are then transported to the substrate as in classical CVD.
Plasma methods:

- Microwave plasma-assisted CVD (MPCVD)
- Plasma-Enhanced CVD (PECVD) – CVD that utilizes plasma to enhance chemical reaction rates of the precursors.
- Remote plasma-enhanced CVD (RPECVD) – Similar to PECVD except that the wafer substrate is not directly in the plasma discharge region.
- Atomic-layer CVD (ALCVD)
- Combustion Chemical Vapour Deposition (CCVD)
- Hot filament CVD (HFCVD)
- Hybrid Physical-Chemical Vapour Deposition (HPCVD)
- Metalorganic chemical vapor deposition (MOCVD)
- Rapid thermal CVD (RTCVD)
- Vapour-phase epitaxy
- Photo-initiated CVD (PICVD)
Historical perspective

- 1960: Introduction of the terms CVD and PVD to distinguish “chemical vapour deposition” from “physical vapour deposition.”


- 1960: CVD TiC coating on cemented carbide tools introduced and development of CVD tungsten.


- 1968: Start of industrial use of CVD coated cemented carbides.


- 1990s: Rapid expansion of metallo-organic CVD (MOCVD) for ceramic and metal deposition.

- 1990s: Development of cluster tools combining CVD, PVD and other processing steps in a single tool for semiconductor fabrication. Major development of CVD in optics and optoelectronics.
Classification of CVD reactions

Thermal decomposition (pyrolysis) reactions

$$AX(g) \rightarrow A(s) + X(g)$$

$$CH_4(g) \rightarrow C(s) + 2 \, H_2(g)$$

$$SiH_4(g) \rightarrow Si(s) + 2 \, H_2(g)$$

$$B_2H_6(g) \rightarrow B(s) + 3 \, H_2(g)$$

$$Ni(CO)_4(g) \rightarrow Ni(s) + 4 \, CO(g)$$

$$Si(CH_3)Cl_3(g) \rightarrow SiC(s) + 3 \, HCl(g)$$
Hydrogen reduction reactions

\[2 \text{AX}(g) + \text{H}_2(g) \rightarrow 2 \text{A}(s) + 2 \text{HX}(g)\]

\[\text{WF}_6(g) + 3 \text{H}_2(g) \rightarrow \text{W}(s) + 6 \text{HF}(g)\]

\[2 \text{BCl}_3(g) + 3 \text{H}_2(g) \rightarrow 2 \text{B}(s) + 6 \text{HCl}(g)\]

\[\text{SiCl}_4(g) + 2 \text{H}_2(g) \rightarrow \text{Si}(s) + 4 \text{HCl}(g)\]

Co-reduction reactions

\[\text{TiCl}_4(g) + 2\text{BCl}_3(g) + 5\text{H}_2(g) \rightarrow \text{TiB}_2(s) + 10\text{HCl}(g)\]
Metal reduction of halides

\[
\text{TiI}_4(g) + 2\text{Zn}(s) \rightarrow \text{Ti}(s) + 2\text{ZnI}_2(g) \\
\text{TiCl}_4(g) + 2\text{Mg}(s) \rightarrow \text{Ti}(s) + 2\text{MgCl}_2(g)
\]

Oxidation and hydrolysis reactions

\[
\text{SiH}_4(g) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) + 2\text{H}_2(g) \\
\text{SiCl}_4(g) + 2\text{CO}_2(g) + 2\text{H}_2(g) \rightarrow \text{SiO}_2(s) + 4\text{HCl}(g) + 2\text{CO}(g)
\]

Carbidization and nitridation

\[
\text{TiCl}_4(g) + \text{CH}_4(g) \rightarrow \text{TiC}(s) + 4\text{HCl}(g) \\
3\text{SiCl}_4(g) + 4\text{NH}_3(g) \rightarrow \text{Si}_3\text{N}_4(s) + 12\text{HCl}(g)
\]
1. The reaction gas dispensing system.

2. The reactor, including components for defining the gas flows.

3. The exhaust system containing a total pressure controller, vacuum pump, scrubber and/or reactant recycle system.
Applications

- In semiconductor and microelectronic industries
- In metallurgical coating industries
- Optical fibers for telecommunications
- Wear resistant coatings, corrosion resistant coatings, heat-resistant coatings etc.
- Preparation of high temperature materials
THANK YOU