

“ज्ञान, विज्ञान आणि सुसंस्कार यांसाठी शिक्षण प्रसार” – श्रीमच्छ्री श्री. जगदीश गुरुजी

Shri Swami Vivekanand Shikshan Sanstha, Kolhapur.



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Chemical vapour deposition

By

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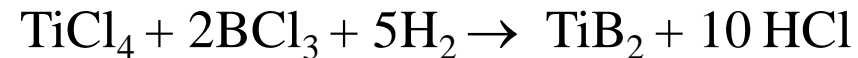
DEPARTMENT OF PHYSICS

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Introduction:

- “Chemical vapour deposition (CVD) is a process where one or more volatile precursors are transported via the vapour phase to the reaction chamber, where they decompose on a heated substrate”
- Many materials may be deposited using CVD and related techniques. Metals, oxides, sulfides, nitrides, phosphides, arsenides, carbides, borides, silicides...

Example: Preparation of TiB_2 , melting point 3325°C . May be deposited by CVD at 1000°C :



- CVD was first used for hard coatings (cutting tools etc.)

Microelectronics, 3D-structures

Glass (SnO_2 , TiN , SiO_2 , TiO_2)

Solar cells, catalysis, membranes, waveguides, mirrors, “synthetic gold” (TiN_x)

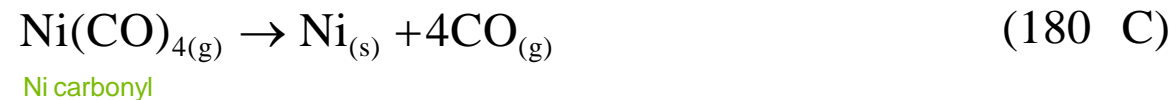
Classification of CVD

- According to the activation process it is classified as:
 1. Thermal CVD: heat energy for activation of the required gas and gas-solid phase reactions.
 - a. atmospheric pressure CVD- APCVD
 - b. low pressure CVD-LPCVD
 - c. metal organic CVD-MOCVD
 2. Plasma enhanced CVD- plasma activation of the chemical species.
 - a. plasma enhanced CVD- PECVD

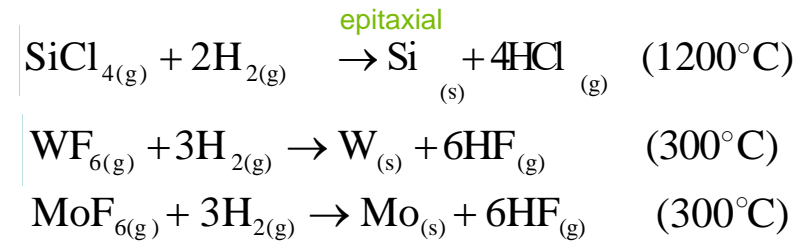
CVD reaction type:

- Pyrolysis
- Reduction
- Oxidation
- Compound formation
- Disproportionation
- Reversible transfer

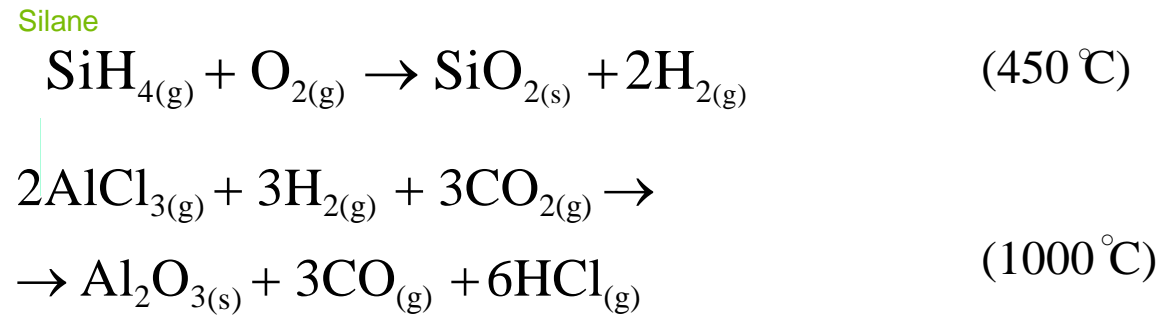
1. Pyrolysis: Thermochemical decomposition of organic material at elevated temperature in the absence of oxygen.



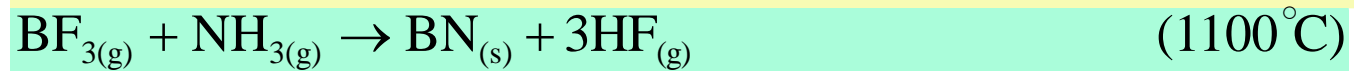
2. Reduction: any process in which electrons are added to an atom or ion (as by removing oxygen or adding hydrogen); always occurs accompanied by oxidation of the reducing agent



3. Oxidation: is any electrochemical process which involves the formal oxidation state of an atom or atoms (within a molecule) being increased by the removal of electrons (loss of electron). E.g. iron(II) can be oxidized to iron(III):

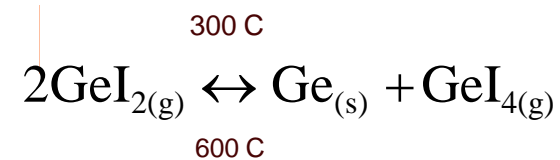


4. Compound formation: a variety of carbide, nitride films and coatings can be readily produced by CVD techniques. The requirement is that both compound element are exist in volatile form and be reactive in gasses form.



5. Disproportion : Disproportionation reactions are possible when a nonvolatile metal can form volatile compounds having different degrees of stability, depending on the temperature. This happens when the metal is two valance state.

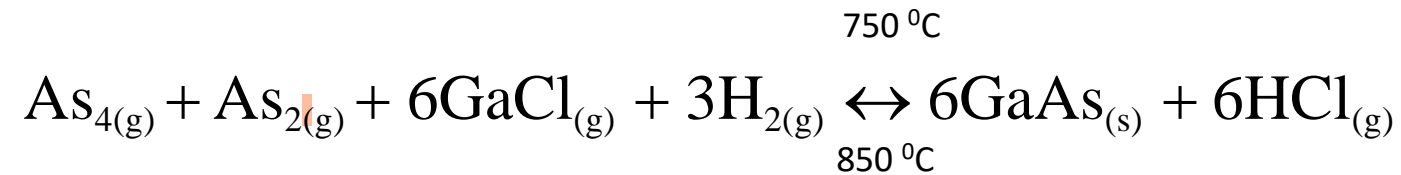
So it a chemical reaction in which a single substance acts as both oxidizing and reducing agent, resulting in the production of dissimilar substances



Al, B, Ga, In, Si, Ti, Zr, Be, Cr can be deposited this way

5. Reversible transfer: Chemical transfer or transport processes are characterized by a reversal in the reaction equilibrium at source and deposition regions maintained at different temperatures within a single reactor.

An important example is the deposition of single-crystal (epitaxial) GaAs films by the chloride process according to the reaction



Instrumentation of CVD:

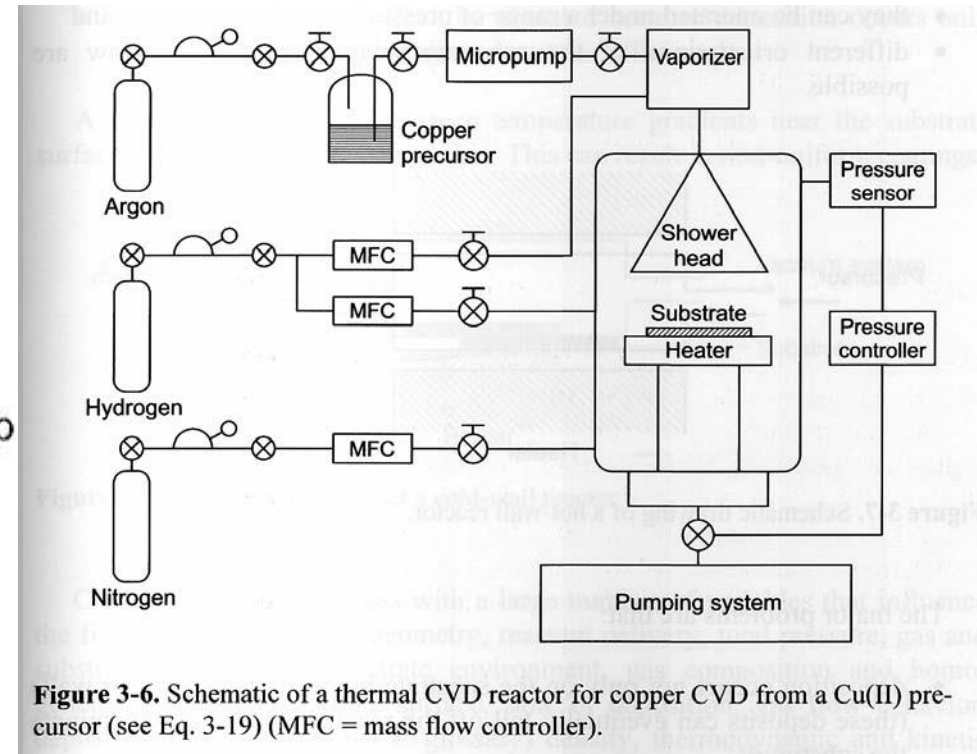
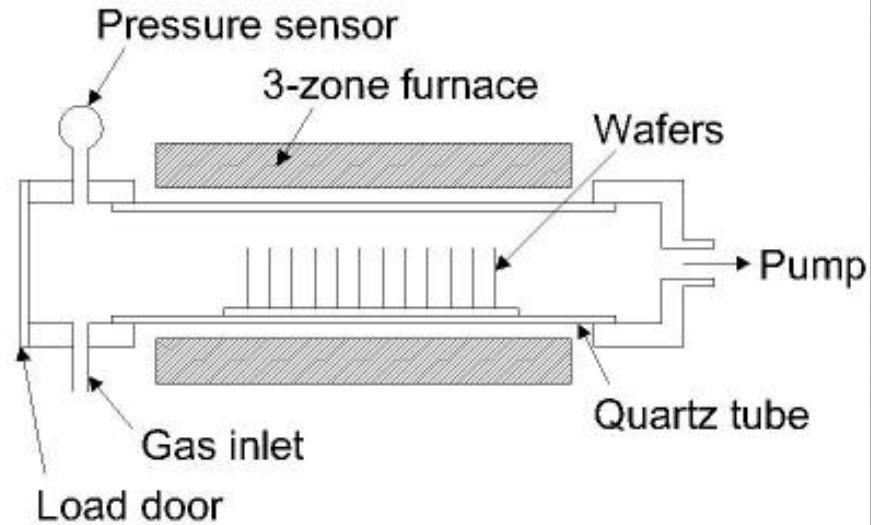


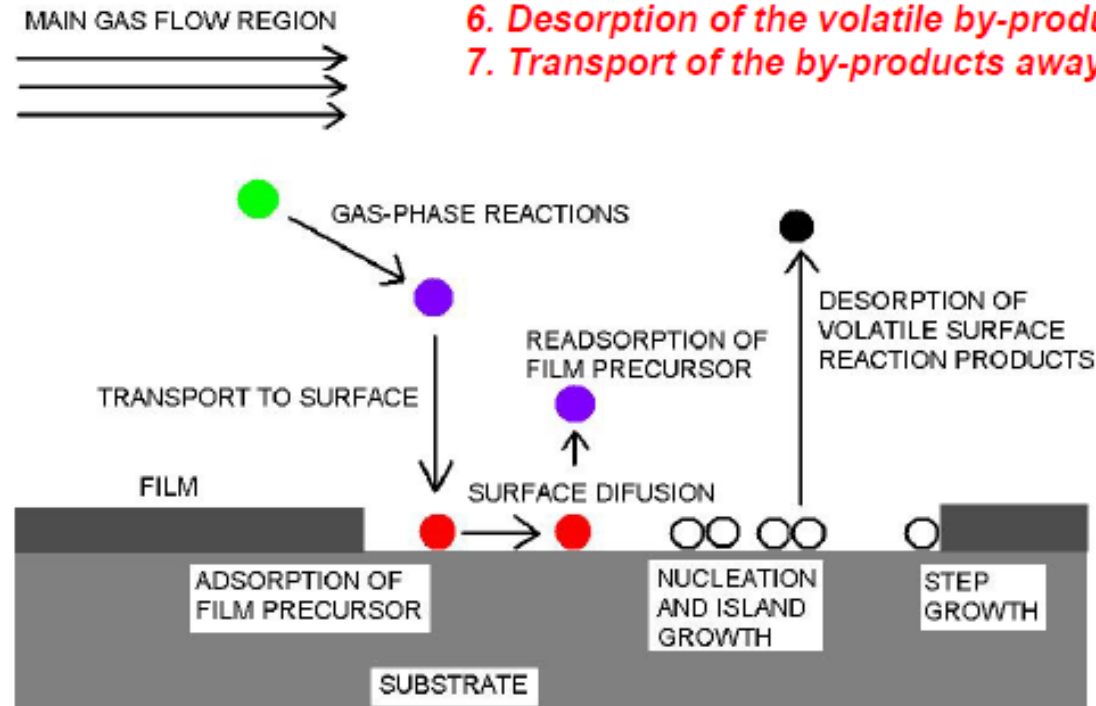
Figure 3-6. Schematic of a thermal CVD reactor for copper CVD from a Cu(II) precursor (see Eq. 3-19) (MFC = mass flow controller).

1. Carrier gas inlet with pressure control: with the help of carrier gas precursor will be inserted into reaction chamber.
2. Deposition (reaction) chamber: temperature controlled deposition chamber.
3. Proper exhaust: output gas is to be exhausted in the environment.

CVD – Chemical Vapor Deposition

The fundamental sequential steps of CVD process:

1. *Transport of reactants to the reaction zone.*
2. *Chemical reactions in the gas phase.*
3. *Transport of reactants and their products to the substrate.*
4. *Adsorption and diffusion on the substrate surface.*
5. *Heterogeneous reactions catalyzed by the surface leading to film formation.*
6. *Desorption of the volatile by-products of surface reactions.*
7. *Transport of the by-products away from the reaction zone.*



The ideal precursor

- Liquid rather than solid or gaseous
- Good volatility
- Good thermal stability in the delivery system, during evaporation and transport
- Decompose cleanly and controllably on the substrate without incorporation
- Give stable by-products which are readily removed from the reaction zone
- Readily available in consistent quality and quantity at low cost
- Non-toxic and non-pyrophoric

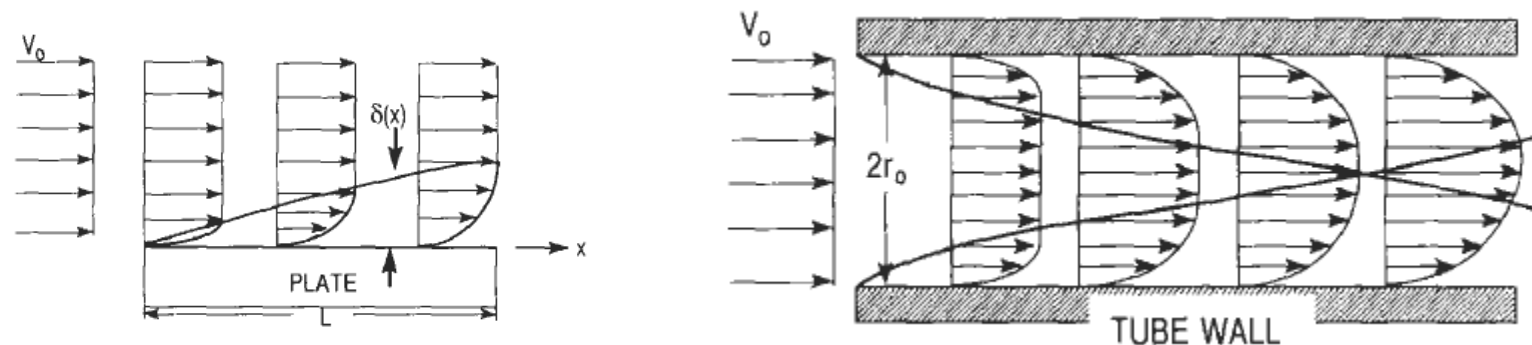
Gas Transport:

It is process by which volatile precursor or species flow from one part of the reactor to another. It is important to know because;

- Film thickness and uniformity highly dependent on the delivery of equal amount of reactant to all substrate surface.
- Deposition growth rate also dependent on the optimized flow rate
- Efficient utilization of process gases.

1. Viscous flow: The viscous flow region is operative when gas transport occurs at pressure of roughly 0.01 atm and above in a reactor.

- flow velocity has uniform value v_0 , but only prior to impinging to leading edge of the plate, however flow progresses velocity of gradients, which form because the gas clings to the plate.



2. Diffusion: The diffusion is the phenomenon occurs in gases and liquids as well as in solids. If two different gases are initially separated and then allowed to mix, each will move from regions of higher to lower concentration. This process is known as diffusion.

According to Kinetic theory of gasses

Diffusion (D) $\sim T^{3/2}/P$ depends on temperature on pressure.

$$D = D_0 \frac{P_0}{P} \left(\frac{T}{T_0} \right)^n,$$

Where,

D_0 - value of D measured at standard temperature T_0 (273 k)

P_0 - pressure (1 atm) depends on gas combination in question.

Generally the value of D_0 at temperatures of interest span is in the range 0.1-10 cm^2/sec and many orders of magnitude higher in case of diffused solids.

3. **Convection:** convection is a bulk gas flow process that can be distinguished from both diffusion and viscous flow.

- diffusion involves statistical motion of atoms and molecules driven by concentration gradient.
- Convection arises from the response to gravitational, centrifugal, electric, and magnetic forces.

Reactor: There are two type of reactor

1. hot wall reactor
2. cold wall reactor.

Hot wall reactor

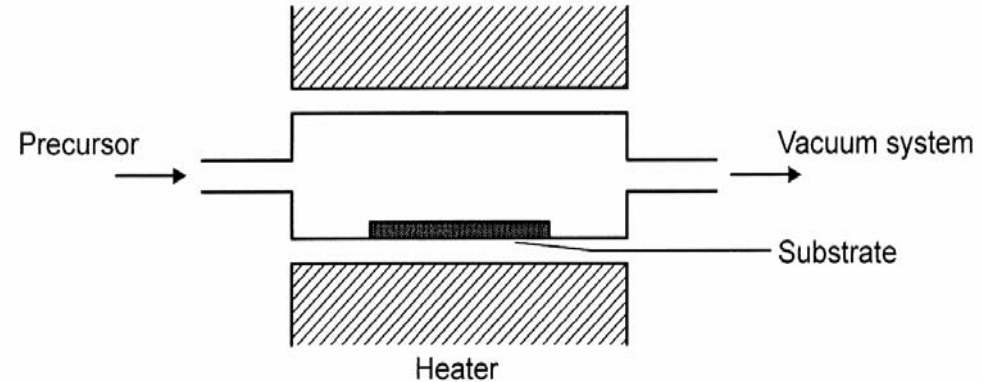


Figure 3-7. Schematic drawing of a hot-wall reactor.

Advantages:

- Simple to operate
- May accommodate several substrate.
- Uniform substrate temperature
- May be operated at a range of temperatures and pressures
- Different orientations of substrate

Disadvantages:

- Deposition occur not only at the substrate, but also on edges of reactor walls.
- The consumption of precursor is large and difficult to control. May result in feed-rate-limited deposition
- Gas-phase reactions may occur

Cold wall reactor

Substrate is at a higher temperature than the reactor walls. Often used in industry

Advantages:

- Pressure and temperature can be controlled
- Plasmas can be used
- No deposition on reactor walls
- Gas-phase reactions are suppressed
- Higher deposition rates may be reached (higher precursor efficiency)

Disadvantages:

- Steep temperature gradients near the substrate surface may lead to convection
- Less flexibility on substrate orientation and usually only one substrate at a time.

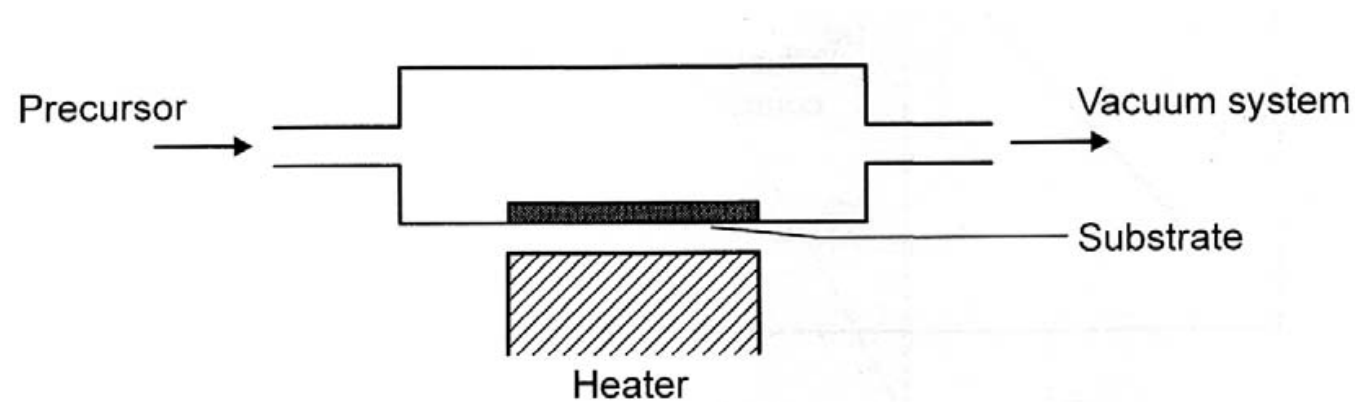


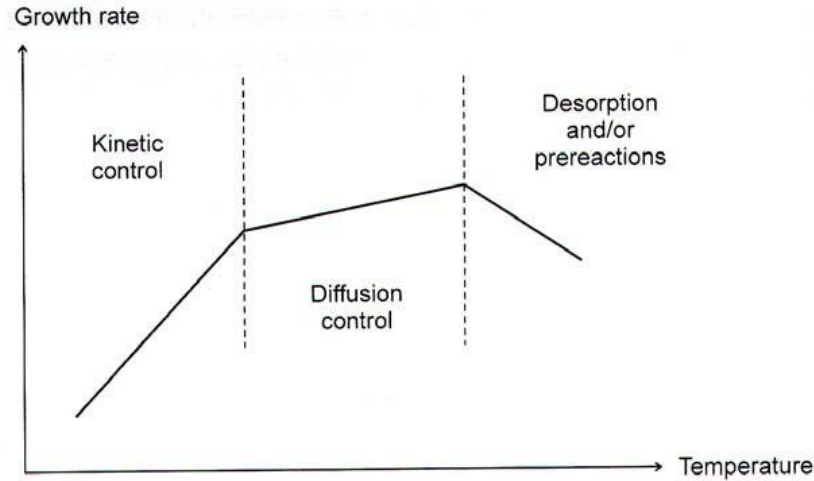
Figure 3-8. Schematic drawing of a cold-wall reactor.

Growth kinetics:

Growth kinetics in CVD depends on several parameters;

1. Transport of reactants through the boundary layer to the substrate
 2. Adsorption of reactants at the substrate
 3. Atomic and molecular surface diffusion, chemical reactions, and incorporation into the lattice.
 4. Transport of the byproduct away from the substrate through boundary layer
-
- **The growth rate uniformity** is part of growth kinetics, which depends on;
 1. The gas has a constant velocity component along the axis tube.
 2. The whole system is at constant temperature.
 3. The reactor extends a large distance in the z direction so that the problem reduces to one of two dimension.

- **Temperature dependence;** growth kinetics is temperature dependent and which separates into three regimes.

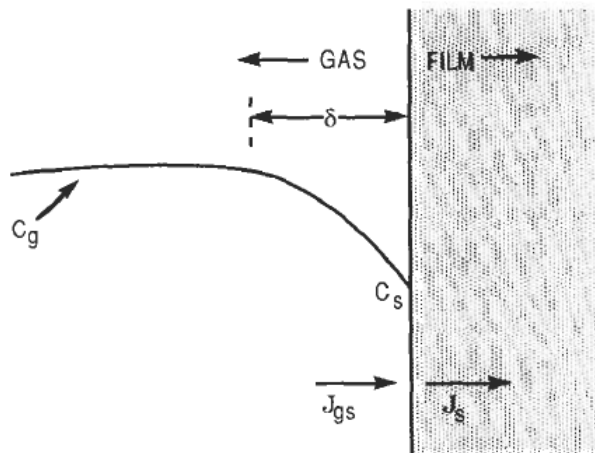


Three regimes:

- Surface reaction (kinetically) limited.
- Diffusion (or mass transport) limited.
- Increased desorption rate of precursors.

Figure 3-9. Dependence of the film growth rate on the substrate temperature.

According to Groves model of kinetics of film growth is temperature dependent



- A drop in concentration of reactant from C_g in bulk gas to C_s at the interface and it increases with the temperature hence growth rate limits even the bulk gas concentration is enough to deposit.

CVD Processes and system:

1. Low temperature systems:

in case of fabrication of Si bipolar and MOS integrated circuit there is important need to deposit thin film of SiO_2 , phosphosilicate and borophosphosilicate glasses and silicon nitride films for different purposes but it has upper temperature limit to tolerate is 450 °C because aluminum metallization used for device contacts and interconnection begins to react with Si beyond this temperature.

several type of atmospheric pressure CVD reactors are designed for such type of insulating film deposition.

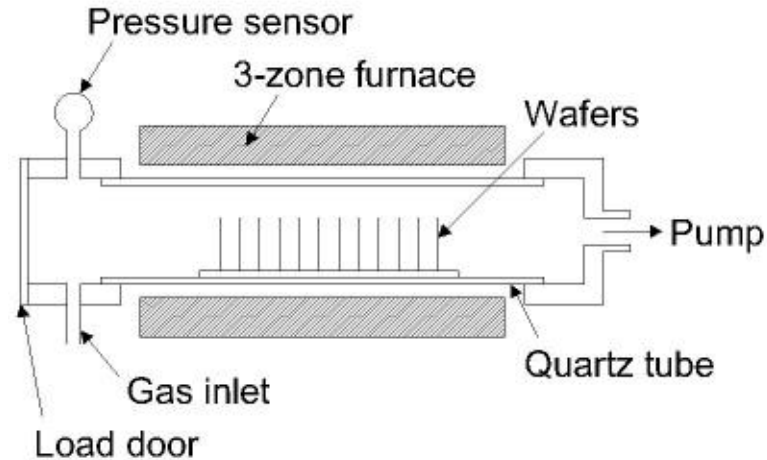
2. High temperature systems:

there is need to reduce the semiconductor processing temperature but the growth of high quality epitaxial thin films can be achieved at high temperature CVD methods.

- This is true of Si as well deposition of some type of compound semiconductors.
- High temperature ATM pressure system is extensively employed for metallurgical coating operation.
- cold wall reactor systems are extensively used for epitaxial Si films

Low pressure CVD: (LPCVD)

- Historically it is first employed to deposit polysilicon films with greater control over stoichiometry and contamination problem.



- Gas pressure range- 0.5 to 1 torr.
- To compensate for the low pressure, the input reactant gas concentration has to increase relative to the atmospheric reactor case.
- Diffusivity is 1000 times higher than the APCVD.

Advantages: high deposition rate, improved film thickness uniformity, better step coverage, lower particle density etc are the important advantages relative to atmospheric CVD processing.

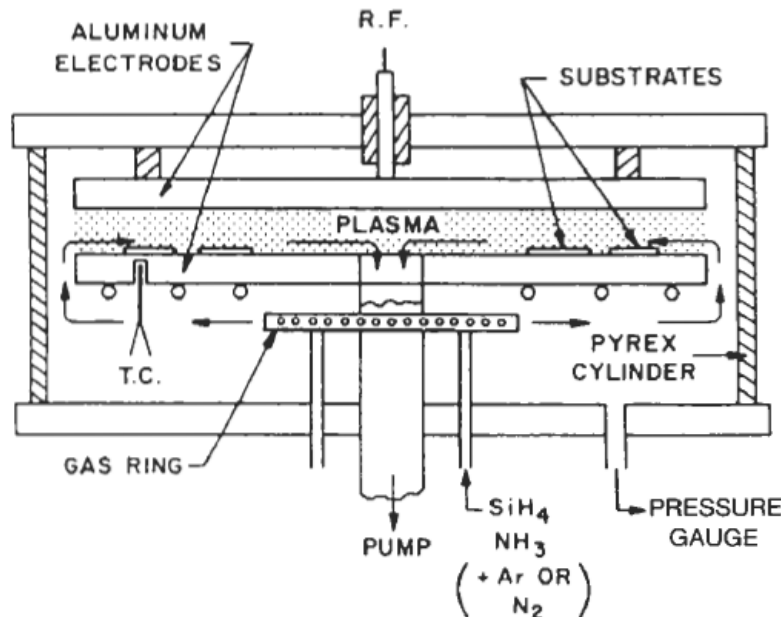
Plasma enhanced CVD: (PECVD)

- Wherein glow discharge plasma is sustained within the chambers where the simultaneous CVD reactions occurs. It is same as LPCVD.
- Radio frequency range – 100kHz to 40 MHz

gas pressure – 50mtorr to 5 torr

at this condition electron and positive ion density number ranges between 10^9 to $10^{12}/\text{cm}^3$ and average electron energy range from 1 to 10eV. This energetic discharge is sufficient to decompose gas molecules into variety of component species.

- So the net effect of interaction cause chemical reactions to occurs at much lower temperature than convectional CVD.



- The major commercial application of this technique is to deposit a silicon nitrate films.
- The deposition is takes place at low pressure and growth rate is around 300 Å/min.
- Some elements e.g. carbon, boron, in addition to metals, oxides, nitrides and silicides has been deposited by using this technique.

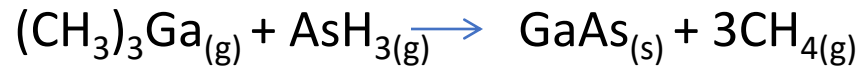
Different materials
deposited by PECVD

Table 4-4. PECVD Reactants and Products, Deposition Temperatures, and Rates

Deposit	T (K)	Rate (cm/sec)	Reactants
a-Si	573	10^{-8} – 10^{-7}	SiH_4 ; SiF_4 - H_2 ; $\text{Si}(x)$ - H_2
c-Si	673	10^{-8} – 10^{-7}	SiH_4 - H_2 ; SiF_4 - H_2 ; $\text{Si}(x)$ - H_2
a-Ge	673	10^{-8} – 10^{-7}	GeH_4
c-Ge	673	10^{-8} – 10^{-7}	GeH_4 - H_2 ; $\text{Ge}(x)$ - H_2
a-B	673	10^{-8} – 10^{-7}	B_2H_6 ; BCl_3 - H_2 ; BBr_3
a-P, c-P	293–473	10^{-5}	$\text{P}(x)$ - H_2
As	< 373	10^{-6}	AsH_3 ; $\text{As}(x)$ - H_2
Se, Te, Sb, Bi	373	10^{-7} – 10^{-6}	Me-H_2
Mo			$\text{Mo}(\text{CO})_6$
Ni			$\text{Ni}(\text{CO})_4$
C (graphite)	1073–1273	10^{-5}	$\text{C}(x)$ - H_2 ; $\text{C}(x)$ - N_2
CdS	373–573	10^{-6}	$\text{Cd-H}_2\text{S}$
Oxides			
SiO_2	523	10^{-8} – 10^{-6}	$\text{Si}(\text{OC}_2\text{H}_5)_4$; SiH_4 - O_2 , N_2O
GeO_2	523	10^{-8} – 10^{-6}	$\text{Ge}(\text{OC}_2\text{H}_5)_4$; GeH_4 - O_2 , N_2O
$\text{SiO}_2/\text{GeO}_2$	1273	3×10^{-4}	SiCl_4 - GeCl_4 + O_2
Al_2O_3	523–773	10^{-8} – 10^{-7}	AlCl_3 - O_2
TiO_2	473–673	10^{-8}	TiCl_4 - O_2 ; metallorganics
B_2O_3			$\text{B}(\text{OC}_2\text{H}_5)_3$ - O_2
Nitrides			
$\text{Si}_3\text{N}_4(\text{H})$	573–773	10^{-8} – 10^{-7}	SiH_4 - N_2 , NH_3
AlN	1273	10^{-6}	AlCl_3 - N_2
GaN	873	10^{-8} – 10^{-7}	GaCl_3 - N_2
TiN	523–1273	10^{-8} – 5×10^{-6}	TiCl_4 - H_2 + N_2
BN	673–973		B_2H_6 - NH_3
P_3N_5	633–673	5×10^{-6}	$\text{P}(x)$ - N_2 ; PH_3 - N_2
Carbides			
SiC	473–773	10^{-8}	SiH_4 - C_mH_m
TiC	673–873	5×10^{-8} – 10^{-6}	TiCl_4 - CH_4 + H_2
B_2C	673	10^{-8} – 10^{-7}	B_2H_6 - CH_4

Metal organic CVD: (MOCVD)

- It differs from the conventional CVD on the basis of chemical nature of the precursor gases.
- As a name metal organic trimethyl gallium (TMGa), Trimethyl-indium(TMIn) etc are used. They are reacted with group V hydrides.



Advantage:

- The great advantage of this type of precursor is that they are volatile at moderately low temperature.

Disadvantage: carbon contamination

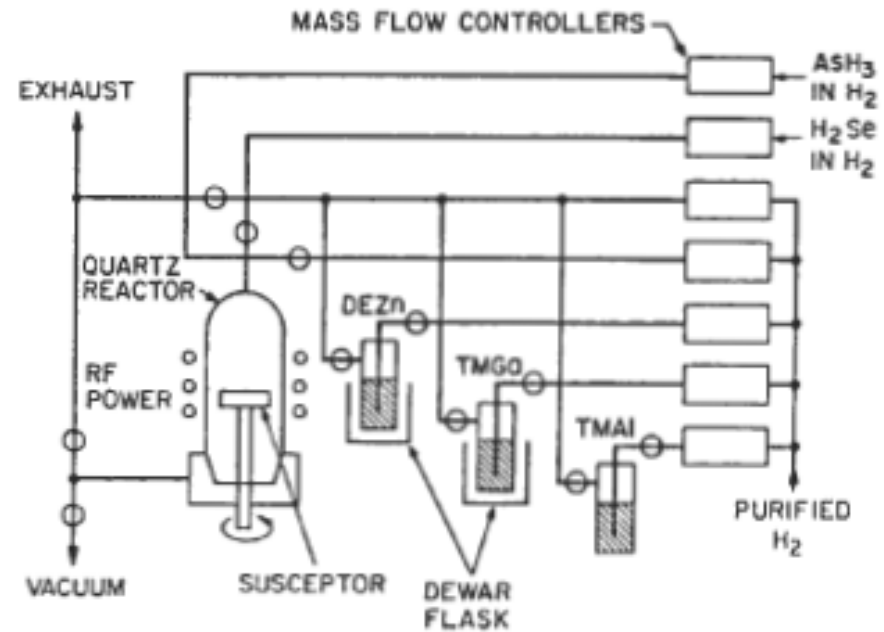


Table 4-5. Organo Metallic Precursors and Semiconductor Films Grown by MOCVD

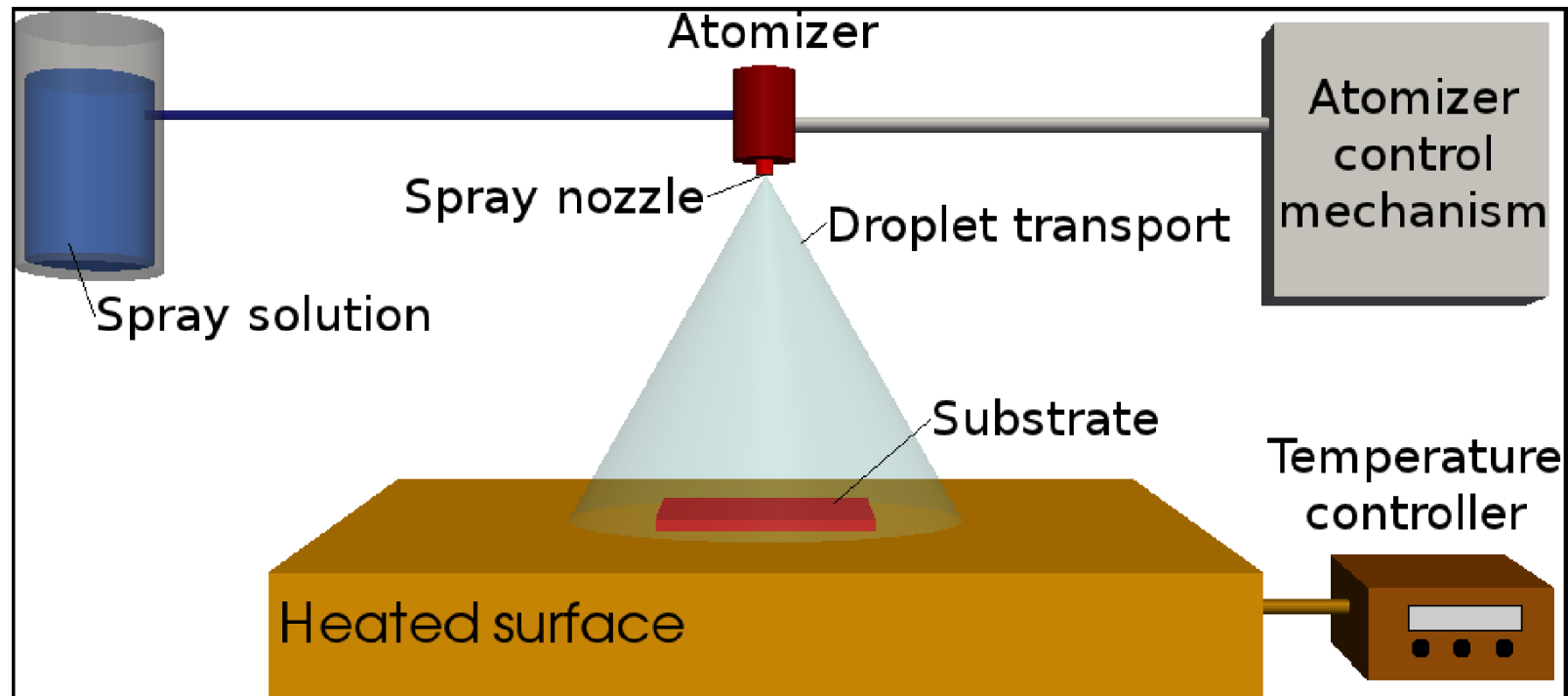
Compound	Reactants	Vapor Pressure* of OM precursor		Growth Temperature (°C)
		<i>a</i>	<i>b</i>	
AlAs	TMAI + AsH ₃	8.224	2135	700
AlN	TMAI + NH ₃			1250
GaAs	TMGa + AsH ₃	8.50	1824	650-750
GaN	TMGa + NH ₃			800
GaP	TMGa + PH ₃			750
GaSb	TEGa + TMSb	9.17	2532	500-550
		7.73	1709	
InAs	TEIn + AsH ₃			650-700
InP	TEIn + PH ₃			725
ZnS	DEZn + H ₂ S	8.28	2190	
ZnSe	DEZn + H ₂ Se			
CdS	DMCd + H ₂ S	7.76	1850	
HgCdTe	Hg + DMCd + DMTe	7.97	1865	
CdTe	DMCd + DMTe			

*log $P(\text{torr}) = a - b/T \text{ K}$
Adapted from Ref. 31.

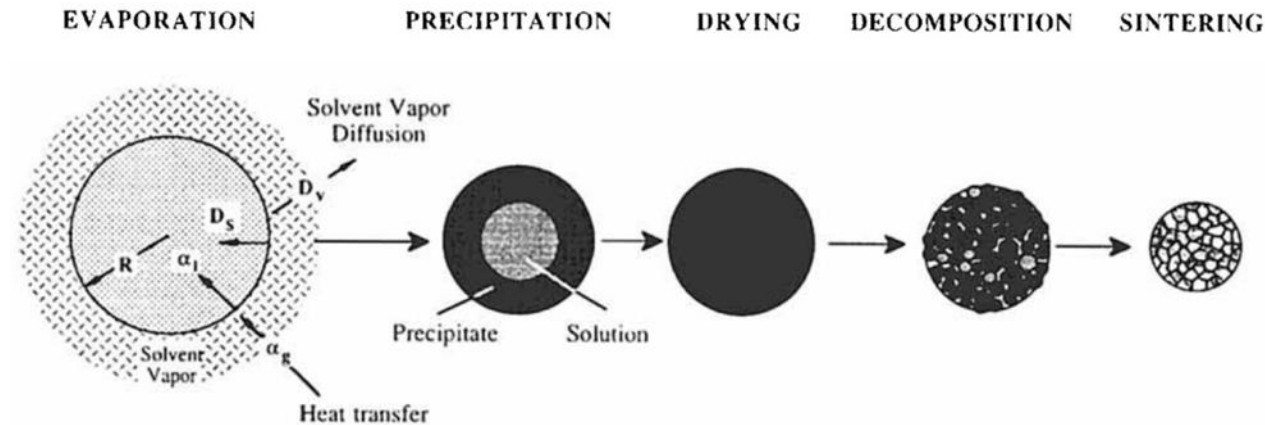
Different materials deposited by MOCVD

Introduction

- Spray deposition is fundamentally work on two major principle atomization or aerogel formation.
- **atomization** – is the production of droplets which are dispersion into the gas.
- **aerosol** – defined as a suspension of solid or liquid particles in a gas.



Fundamental steps involved in spray deposition technique:



- **evaporation** – evaporation of solvent from the surface, diffusion of solvent vapour away from droplet, change in droplet temperature, diffusion of solute toward the center of the droplet, change in droplet size .
- **precipitation/drying** – involves volume precipitation or surface precipitation of the solute, followed by the evaporation of the solvent through the nanoporous crust
- **thermal decomposition or pyrolysis** – forms a nanoporous structure
- **sintering** – involves the adhesion/solidification of the crystallites

fundamentals – precipitation control

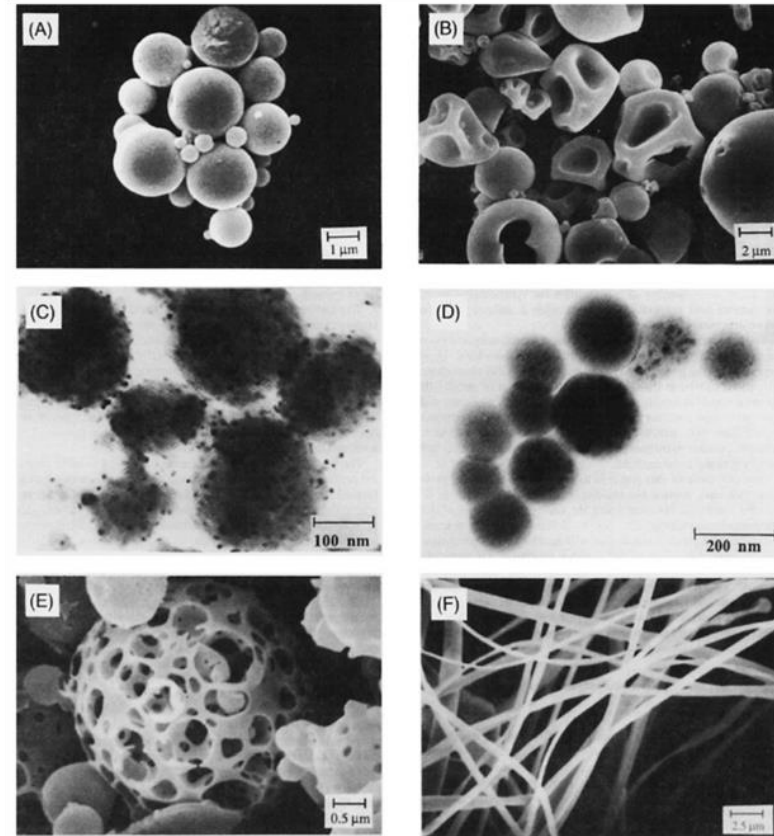
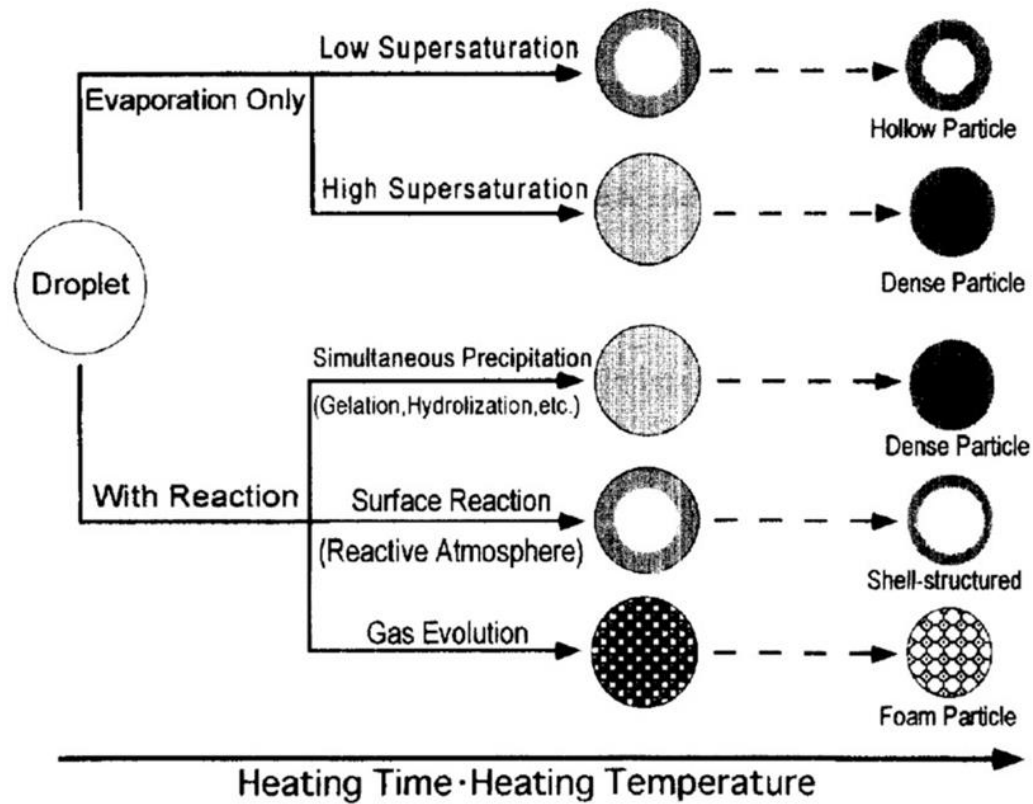


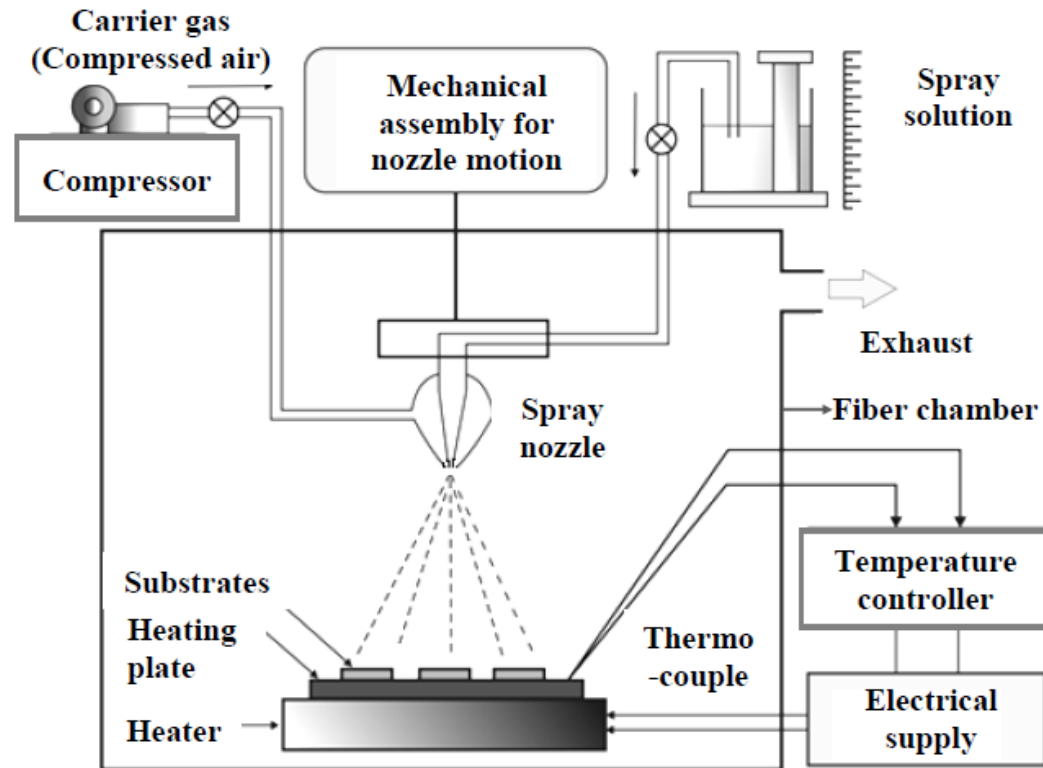
Fig. 3. Various morphologies of particles produced by SP processes: (A) solid ZrO_2 particles derived from 0.1M ZHC solution, (B) irregular ZrO_2 particles derived from 1M ZAC solution, (C) Al_2O_3 /platinum nanocomposite particles derived from 0.5M $Al_2(SO_4)_3$ - H_2PtCl_6 solution, (D) Al_2O_3 /platinum nanocomposite particles derived from 0.5M $Al(OBu)_3$ - H_2PtCl_6 solution, (E) catalyst particles derived from 0.1M NH_4VO_3 - H_3PO_4 -citric acid solution, and (F) Y_2O_3 -stabilized ZrO_2 discontinuous fiber derived from ZAC-6 wt%-PVOH-surfactant solution.

precipitation behavior can be controlled by the solubility of the starting materials or by introducing a precipitation reaction into the droplet

Types of Spray deposition technique:

- According to the way how we are doing atomization or aerogel formation spray technique are classified into
 1. Spray pyrolysis technique
 2. Electrospray deposition technique
 3. Electrospin deposition technique
 4. Spray painting.

Spray pyrolysis technique:



1. Spray nozzle
2. Mechanical assembly for spray nozzle motion
3. Spray solution container
4. Compressor
5. Heater with temperature controller
6. chamber

Spray pyrolysis is the process in which spray nozzle atomizes and sprayed the precursor solution in small droplets on a preheated substrate, wherein the evaporation of solvent solution, thermal decomposition or pyrrolysis takes place and forms uniform thin film.

Factors affecting in spray pyrolysis technique

- **Atomization of precursor solution:** forms a fine and uniform droplets is the significant step in spray pyrolysis technique. The atomizer forms the droplets with different size, different atomization rate and different velocity. It depends on a) pressure of the carrier gas
 - b) density of spraying solution and
 - c) viscosity of the spraying solution.
- **Aerogel transport:** the precursor solution is atomized at the nozzle and fine droplet or aerogel is formed which is transported from nozzle to substrate. During transportation following forces affects
 - a) **gravitational-** pull the droplets downward, droplet size increase gravitation force increases
 - b) **stokes force-** friction force on droplet in air, droplet size increases stokes force also increases.
 - c) **thermophoretic force:** this is caused due to thermal gradient, this force repels the droplets from the hot surface.

- **Decomposition of the precursor:** After arrival of the droplets in the vicinity of substrate several processes takes place such
 - residual solvent evaporation,
 - spreading of the droplets over the substrate surface,
 - decomposition of salt due to thermal energy occur

Following factors play major roll in decomposition;

- a) substrate temperature,
- b) carrier gas flow rate,
- c) distance between nozzle to substrate,
- d) viscosity of the solution,
- e) solution concentration
- f) spraying rate.
- g) chemical composition of the carrier gas
- f) environment in the chamber

Steps involved in spray pyrolysis technique:

- Aerosol formation of the droplets at the tip of the nozzle
- Solvent evaporation starts due to the temperature gradient. It forms precipitate during their passage through the temperature gradient from nozzle (low temperature) to substrate (high temperature).
- Pyrolytic decomposition of the precipitate occurs due to the temperature gradient before the precipitate reaches the substrate.
- Pyrolyzed precipitate reaches the substrate. Nucleation and growth of film starts on the surface of substrate.
- With deposition time, film thickness increases.

Advantages:

- Cost effective
- Large area deposition
- Relatively uniform film formation
- No extreme high temperatures required during processing
- Easier to dope films with virtually any elements in any proportion, by merely adding the source of dopant in the spray solution.
- Synthesis of layered films and films with composition gradients throughout the thickness is possible by varying the composition of the spray solution.

Dis- advantages:

- Contamination issue: sometimes byproduct does not decompose completely and trapped inside the film.
- Spray pyrolysis is very effective for oxide film formation but not suitable for metal thin film deposition.