

# HYDRO THERMAL GROWTH



## Hydrothermal Synthesis Autoclave Reactor



# HYDRO THRMAL GROWTH

- The first report of the hydrothermal growth of crystals was by German geologist Karl Emil 1845: he grew microscopic quartz crystals in a pressure cooker.

- In 1848, [Robert Bunsen](#) reported growing crystals of barium and strontium carbonate at 200 °C and at pressures of 15 atmospheres, using sealed glass tubes and aqueous ammonium chloride as a solvent.
- Giorgio Spezia published reports on the growth of macroscopic crystals. He used solutions of [sodium silicate](#), natural crystals as seeds and supply, and a silver-lined vessel. By heating the supply end of his vessel to 320-350 °C, and the other end to 165-180 °C, he obtained about 15 mm of new growth over a 200-day period.

# TYPES OF CRYSTALS GROWN

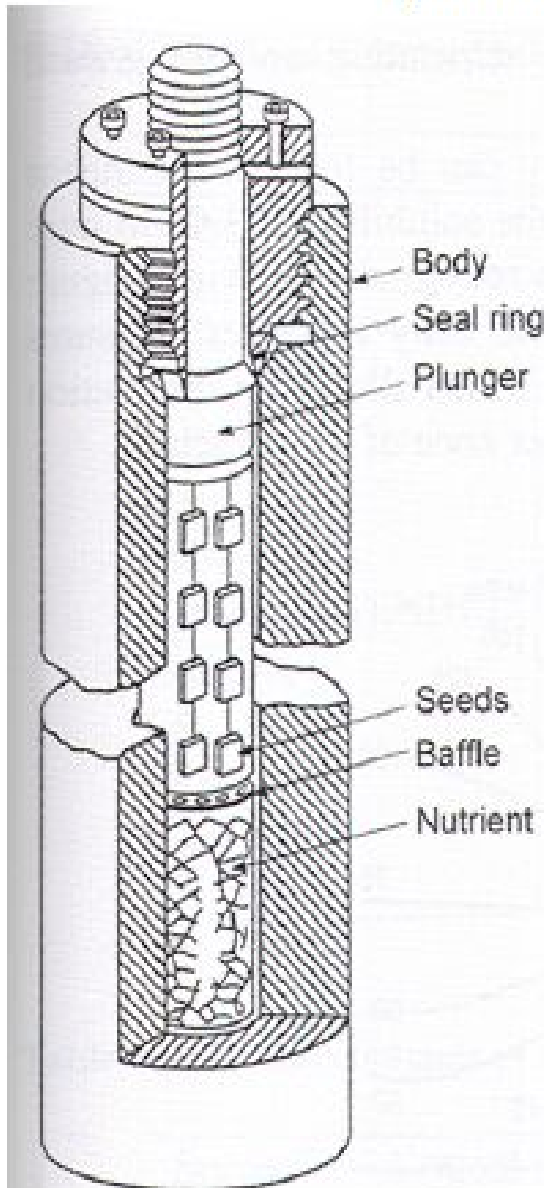
- A large number of compounds belonging to practically all classes have been synthesized under hydrothermal conditions: elements, simple and complex oxides, tungstates, carbonates, silicates, germanates etc.

- Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure.
- The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water.
- A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal

Synthetic quartz crystals produced in the autoclave shown in hydrothermal quartz plant in 1959



## Synthesis in a temperature gradient.



Nutrient (polycrystalline powder of starting material) is placed in the bottom. A perforated disk (baffle) separates the dissolution and growth zones (better thermal gradient), and reduces particle flow (secondary nucleation). Seed crystals with given orientation is placed in the growth zone.

$T_1$  The temperature in the growth zone is lower than in the dissolution zone. Convection transport the hot liquid up to the growth zone.

Typical requirements:  
 $T_2$  Some weight percent solubility  
0.001 – 0.1 w% difference in solubility over 10°C

Figure 4-40. Scheme of an autoclave for hydrothermal single crystal growth.

# Experimental set up

- The crystallization vessels used are [autoclaves](#). These are usually thick-walled steel cylinders with a hermetic seal which must withstand high temperatures and pressures for prolonged periods of time.
- Furthermore, the autoclave material must be inert with respect to the [solvent](#). Many designs have been developed for seals, the most famous being the [Bridgman seal](#).



- In most cases, [steel](#)-corroding solutions are used in hydrothermal experiments. To prevent [corrosion](#) of the internal cavity of the autoclave, protective inserts are generally used.
- These may have the same shape as the autoclave and fit in the internal cavity (contact-type insert), or be a "floating" type insert which occupies only part of the autoclave interior.
- Inserts may be made of carbon-free [iron](#), [copper](#), [silver](#), [gold](#), [platinum](#), [titanium](#), [glass](#) (or [quartz](#)), or [Teflon](#), depending on the temperature and solution used

# AUTOCLAVE SELECTION

## Low pressure autoclaves

- Made out of glass (pyrex glass vessels or quartz tubes) • For temperature to about 300C and pressure limited to 10 atmosphere.
- Advantages
- • Good visibility of growth process • resistance to acid solutions

## • **Medium pressure autoclaves**

- For pressure upto 500 atmospheres and temperature near 400C
- Steel (ordinary low carbon) vessels with flat plate enclosures
- Provided with safety pressure seals
- Easily assembled and requires minimum mechanical precision

## **High pressure autoclaves**

- • For pressure upto 3000 atmospheres and temperature upto 450C
- Robust steel enclosure
- Removable liner permits no corrosions as in complex vessels

## **High pressure-modified Bridgman autoclaves**

- For pressure upto 3700 atmospheres and temperature upto 500C
- The initial seal that closes the vessel is made by mechanical tightening

## WORKING

- The finely divided particles of material to be grown are taken in the bottom of vessel and suitably oriented single crystal seed plates are suspended in the upper growth region. A dilute alkaline solution is then poured into the remaining 60 to 80% of free space of vessel.
- The vessel is then placed inside a furnace that has been designed to heat the lower dissolving section isothermally hotter than the upper growth region which is also maintained isothermal. Under these condition the alkaline solution expands and is compressed; the pressure inside reaches very high.

- Under these high temperatures and pressures the materials in the lower compartment of the autoclave dissolve in the alkaline solution to become saturated solution. This saturated solution rises due to the convection caused by the temperature difference between the upper and lower compartments of the autoclave.
- When the solution reaches the upper compartment of the autoclave, it becomes supersaturated because of the lower temperature of the compartment, and according to the degree of the temperature difference it is crystallized on the seed crystal.

# PREPARATION OF QUARTZ

- Nutrient quartz is placed in the hotter bottom zone (dissolving zone) and frame holding the seed crystals are placed in the upper part (crystallizing zone) of the vessel. A dilute alkaline solution (1.0 M NaOH) is then poured into the remaining 80% of free space.
- The vessel is then closed and placed inside a furnace that gives desired temperature and temperature gradients. As the temperature of the vessel reaches operating conditions (4000C at dissolving zone and 3600C at crystallizing zone), the nutrient quartz begins to dissolve and saturate the solution.

- The top portion of the autoclave is cooler which causes the supersaturation of the solution. The seed crystal plates begins to grow as the supersaturated solution deposits solid phase. Convection currents caused by temperature gradient accomplish the continuous growth.
- The baffle arrangement (5% opened) allows transport of newly saturated solution to the growth zone and the depleted solution away. This continuous cycle of solution and deposition permits growth of larger crystals.

- **Advantages** of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can be grown by the hydrothermal method.
- The method is also particularly suitable for the growth of large good-quality crystals while maintaining control over their composition
- **Disadvantages** of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows

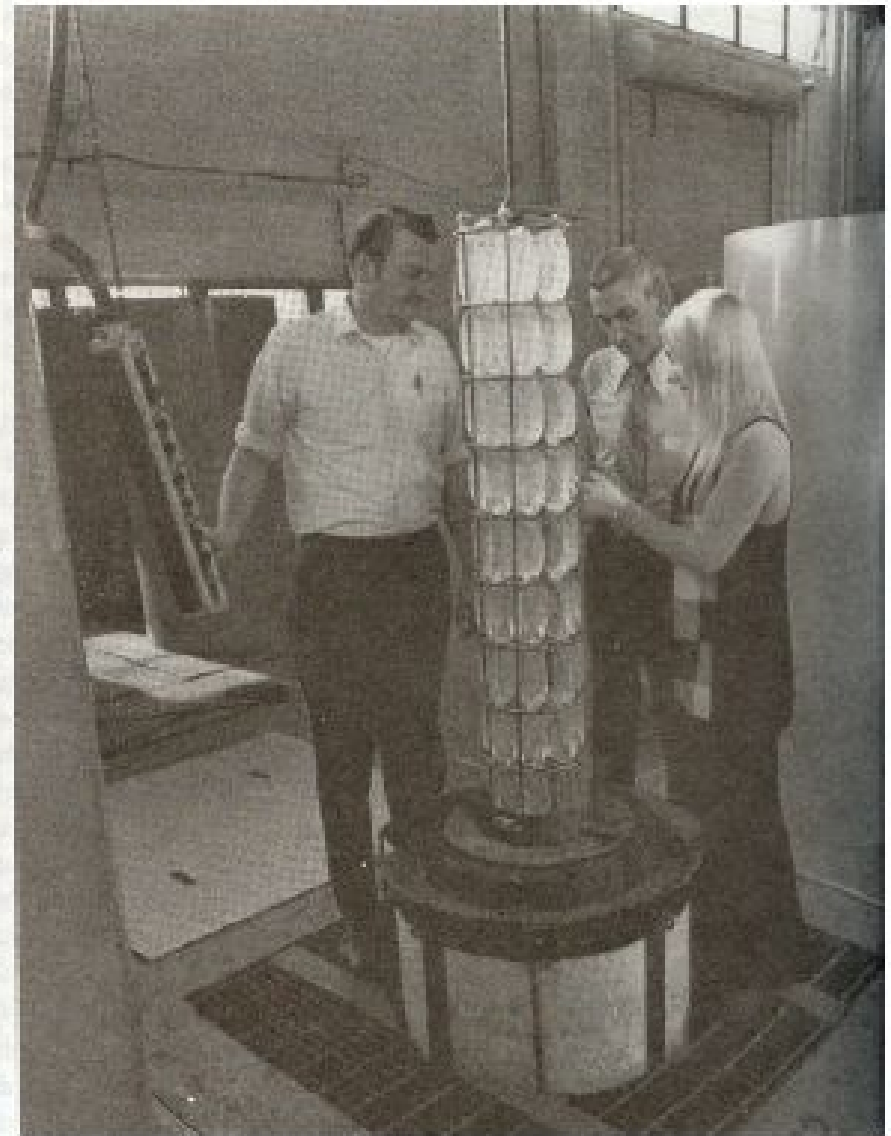


## Other solvents for solvothermal synthesis

**Table 4-3.** Examples for hydrothermal processes in non-aqueous environments.

<i>Solvent</i>	<i>Examples of synthesized compounds</i>
NH <sub>3</sub>	nitrides, imides, amides, CsOH, Cs <sub>2</sub> Se <sub>2</sub>
HF	MO <sub>3-x</sub> F <sub>x</sub> (M = Mo, W)
HCl, HBr	AuTe <sub>2</sub> Cl, AuSeCl, AuSeBr, Mo <sub>3</sub> S <sub>7</sub> Cl <sub>4</sub>
Br <sub>2</sub>	SbSBr, SbSeBr, BiSBr, BiSeBr, MoOBr <sub>3</sub>
S <sub>2</sub> Cl <sub>2</sub>	MoS <sub>2</sub> Cl <sub>3</sub> , Mo <sub>3</sub> S <sub>7</sub> Cl <sub>4</sub>
S <sub>2</sub> Br <sub>2</sub>	Mo <sub>3</sub> S <sub>7</sub> Br <sub>4</sub>
SeBr <sub>2</sub>	SbSeBr, BiSeBr
H <sub>2</sub> S + (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NHCl	β-Ag <sub>2</sub> S
C <sub>2</sub> H <sub>5</sub> OH	SbI <sub>3</sub> , BiI <sub>3</sub>
CS <sub>2</sub>	Monoclinic Se
CCl <sub>4</sub>	SeCl <sub>4</sub> , TeCl <sub>4</sub>
C <sub>6</sub> H <sub>6</sub>	Selenium
CH <sub>3</sub> NH <sub>2</sub>	CH <sub>3</sub> NHLi

## Quartz, autoclaves



## Synthetic hydrothermal crystals



**ZnO**

**Emerald  
(Beryl:  
 $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ )**



**Calcite**

## Morey autoclave

Everything is heated  
Up to ca. 400°C, 400 bar  
Simple to use  
Autogenous pressure

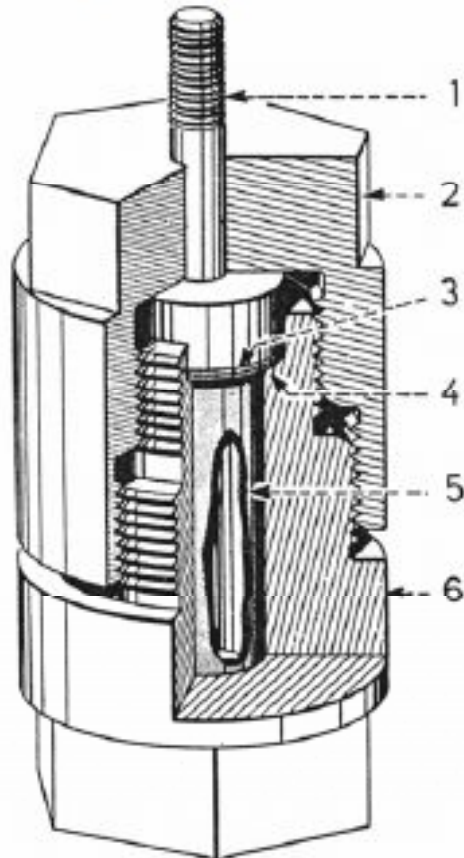


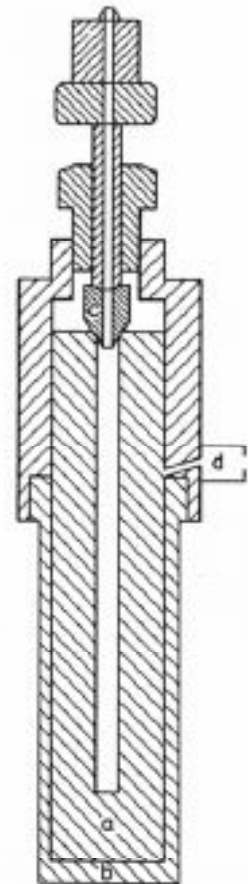
FIG. 9

## Autoclaves II

Two principles

### Tuttle “cold seal” autoclave

The upper part is outside the furnace (may be water cooled)  
Pressure is applied from an external source.  
Up to 1100°C, 5000bar

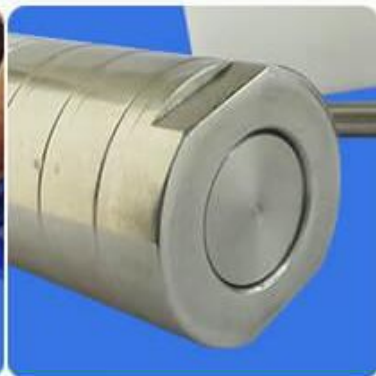


TZM-autoclave with inert gas flushing.  
(a) Autoclave body of TZM-  
(molybdenum) alloy; (b) protective mantle  
of Inconel 750 (nickel alloy); (c) conical  
seal; (d) inlet vent for inert gas.

# Hydrothermal Synthesis Autoclave Operating



- Pour reaction material into PTFE / PPL liner. Charging coefficient  $< 0.8$ .



- Reactor lower gasket's salient surface is downward.



- Put in PTFE / PPL liner and upper gasket.



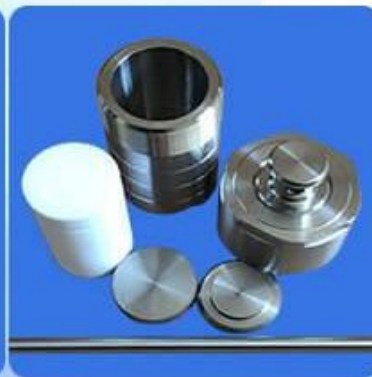
- Tightening reactor lid, use screw rod to tighten up until locking.



- Place reactor in heating apparatus to heat.
- Safe temperature: PTFE lined  $220^{\circ}\text{C}$ , PPL lined



- Ensure reactor inner temp.  $<$  reaction solvent boiling point.
- Then could use screw



- After reaction finish, please cooling strict according to standard rate of temperature fall.

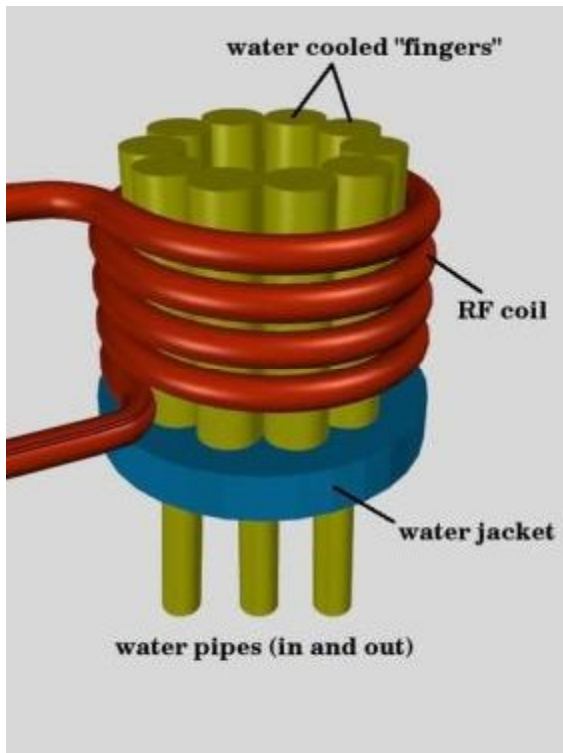


- Please clean reactor when every time reaction finish, avoid corrosion.



Skull melting





- Idea: MP too high for any crucible
- Make sample act as own crucible!
- Make large cylinder of desired material
- Interior heated by RF induction
- Cool exterior with flowing H<sub>2</sub>O in “fingers”



- Remove xtals from inside “skull”
- Very large samples! ~kgs
- Typical use: ZrO<sub>2</sub>





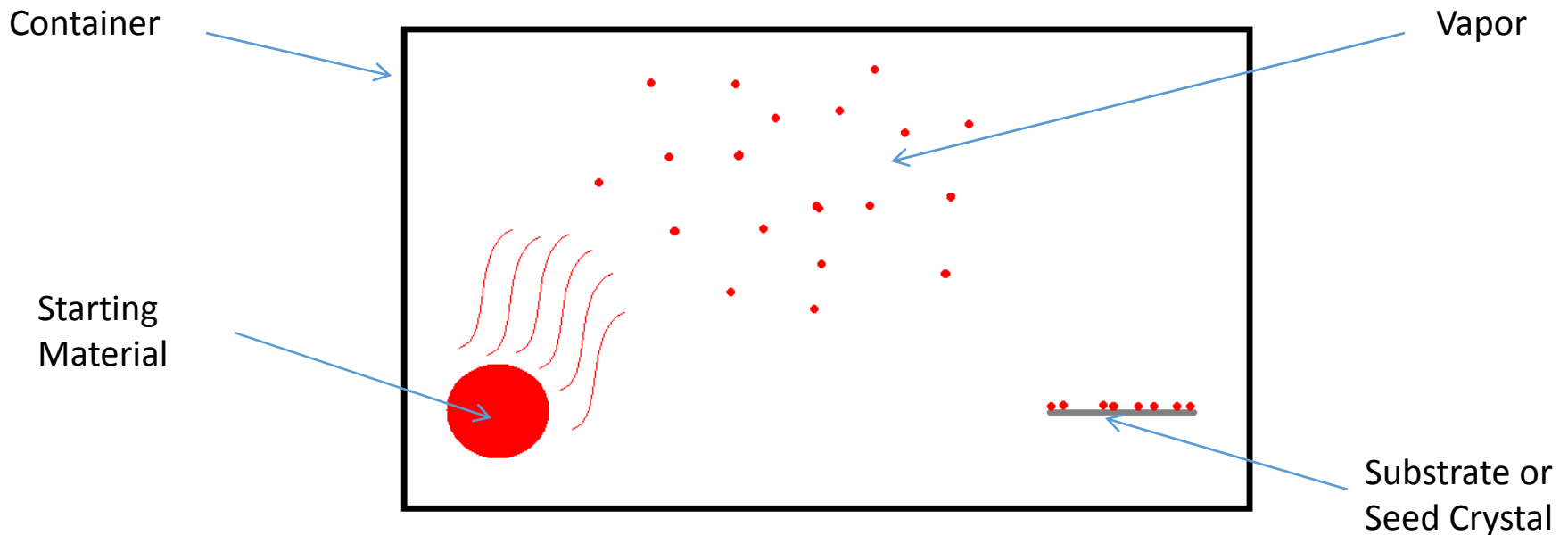
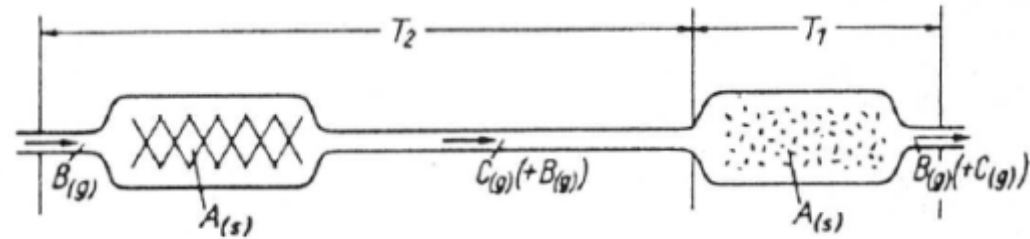






# Crystal Growth from Vapor Phase

- Sublimation
- Chemical Vapor Transport
- Pulsed Laser Deposition
- Metal-Organic Chemical Vapor Deposition



# Crystal Growth from Vapor Phase

- Useful for growing epitaxial thin films!
- Issues:
  - Need high vapor pressure / ability to evaporate
  - Need substrate/seed onto which to grow crystal?
  - Often quite slow
  - Will vapor react with container?
  - Need for specialized equipment

## Chemical Vapor Deposition (CVD)

CVD is used to produce high - purity, high -performance solid materials, usually in the form of a thin film on a substrate

In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit

Frequently, volatile byproducts are also produced, which are removed by gas flow through the reaction chamber

Microfabrication processes widely use CVD to deposit materials in various forms, including: monocrystalline, polycrystalline, amorphous, and epitaxial

These materials include: silicon, carbon fiber, carbon nanofibers, filaments, carbon nanotubes, SiO<sub>2</sub>, silicon-germanium, tungsten, silicon carbide, silicon nitride, titanium nitride, and various high - k dielectrics

The CVD process is also used to produce synthetic diamonds

# Types of chemical vapor deposition

A number of forms of CVD are in wide use and are frequently referenced in the literature

These processes differ in the means by which chemical reactions are initiated (e.g., activation process) and process conditions



These processes can be classified by operating pressure

*Atmospheric pressure CVD (APCVD)* - CVD processes at atmospheric pressure

*Low-pressure CVD (LPCVD)* - CVD processes at subatmospheric pressures

Reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity across the wafer

Most modern CVD processes are either LPCVD or UHVCVD

*Ultrahigh vacuum CVD (UHVCVD)* - CVD processes at a very low pressure, typically below  $10^{-6}$  Pa ( $\sim 10^{-8}$  torr)

Classified by physical characteristics of vapor

*Aerosol assisted CVD (AACVD)* - A CVD process in which the precursors are transported to the substrate by means of a liquid/gas aerosol, which can be generated ultrasonically.

This technique is suitable for use with nonvolatile precursors

*Direct liquid injection CVD (DLICVD)* - A CVD process 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 (typically car injectors).

The precursor vapors are then transported to the substrate as in classical CVD process

This technique is suitable for use on liquid or solid precursors  
High growth rates can be reached using this technique

*Microwave plasma-assisted CVD (MPCVD)*

*Plasma-Enhanced CVD (PECVD)* - CVD processes that utilize a plasma to enhance chemical reaction rates of the precursors

PECVD processing allows deposition at lower temperatures, which is often critical in the manufacture of semiconductors

*Remote plasma-enhanced CVD (RPECVD)* - Similar to PECVD except that the wafer substrate is not directly in the plasma discharge region

Removing the wafer from the plasma region allows processing temperatures down to room temperature

*Atomic layer CVD (ALCVD)* – Deposits successive layers of different substances to produce layered, crystalline films

*Hot wire CVD (HWCVD)* - Also known as Catalytic CVD (Cat-CVD) or hot filament CVD (HFCVD)

Uses a hot filament to chemically decompose the source gases