# Fundamental CVD Processes

- Convective and diffusive transport of reactants to the reaction zone

- Gas phase reactions

- Transport of reactants to the substrate surface.

- Chemical and physical adsorption

- Surface reactions leading to film formation

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- Desorption of volatile by-products

- Convective and diffusive transport of by-products away from the reaction zone
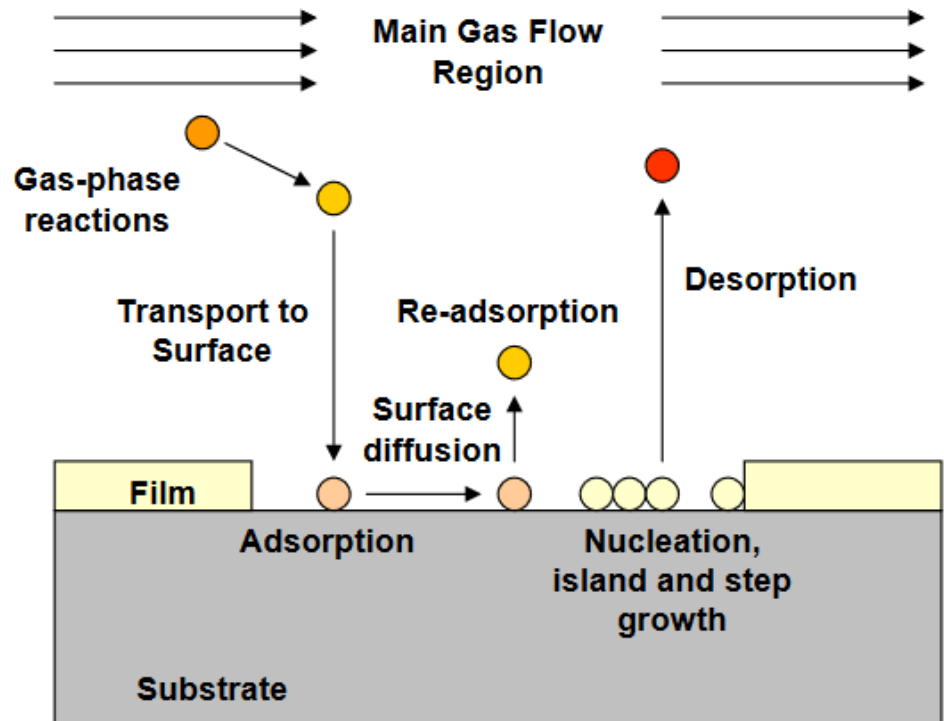
Types of CVD

APCVD (Atmospheric Pressure CVD), mass transport limited growth rate, leading to non-uniform film thickness.

LPCVD (Low Pressure CVD)
- Low deposition rate limited by surface reaction, so uniform film thickness (*many wafers stacked vertically facing each other*; in APCVD, wafers have to be laid horizontally side by side.
- Gas pressures around 1-1000mTorr (lower P => higher diffusivity of gas to substrate)
- Better film uniformity & step coverage and fewer defects
- Process temperature $\geq 500°$C

PECVD (Plasma Enhanced CVD)
- Plasma helps to break up gas molecules: high reactivity, able to process at lower temperature and lower pressure (good for electronics on plastics).
- Pressure higher than in sputter deposition: more collision in gas phase, less ion bombardment on substrate
- Can run in RF plasma mode: avoid charge buildup for insulators
- Film quality is poorer than LPCVD.
- Process temperature around 100 - 400°C.

MOCVD (Metal-organic CVD, also called OMVPE - organo metallic VPE), epitaxial growth for many optoelectronic devices with III-V compounds for solar cells, lasers, LEDs, photo-cathodes and quantum wells.

Choice of Chemical Reactions
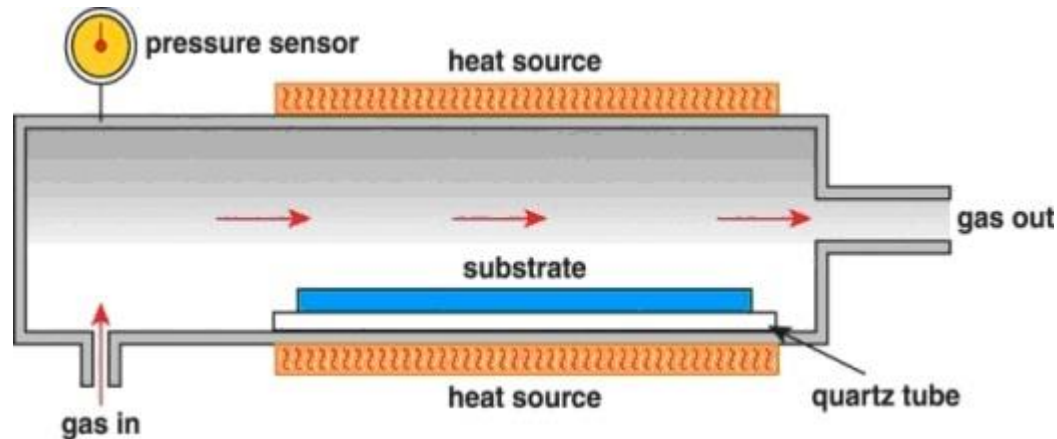
- The precursors have to be volatile (gaseous)
  - ✓ Ex: SiH (Silane) is a popular precursor to deposit Silicon

- The chemical reactions need to be thermodynamically predicted to result in a solid Film
  - ✓ This means that there should be an energy advantage for the desired reaction to occur, meaning the Gibbs Free Energy (GFE) has to decrease.
  - ✓ T and P can be adjusted for $\Delta G < 0$.

- The by-products need to be volatile (gaseous)

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

Impossible to meet all criteria

Industrially important precursors:
Hydrides: AiH_4, AsH_3
Metal alkyls: $AliBu_3$, $GaEt_3$
Metall halides: WF_6, $TiCl_4$

Multi element CVD

Two approaches:

Use two (or more) individual precursors. Must decompose individually on the substrate and react to give the desired product.

$GaMe_3 + AsH_3 \longrightarrow GaAs + 3CH_4$

Problems: Must have similar adsorption and decomposition properties and compatible volatilities. Stoichiometry difficulties.

Single source precursors contain all the elements in the desired stoichiometry. Bonds between the film-forming elements must be stronger than to the ligands in order to obtain clean decomposition. Single source precursor for GaAs:

$$\longrightarrow \quad GaAs + 4 C_2H_4 + 4 CH_2=CMe_2 + 4 H_2$$

Problems with single-source precursors are often related to increased molecular weight (low volatility) and to decomposition behaviour

Equipment

Substrate temperature 200-800°C, pressure 0.1 mbar – 1 bar
Vapour pressure of precursor should be > 0.01 bar at 25°C

Reactors

There are two kinds of reactors most frequently used in the CVD processes, *hot wall reactor* and *cold wall reactor*

Hot wall reactor

The reactor tube is surrounded by a tube furnace making the substrate, and the reactor wall to be the same temperature. A large number of substrates can be coated in this type of reactor
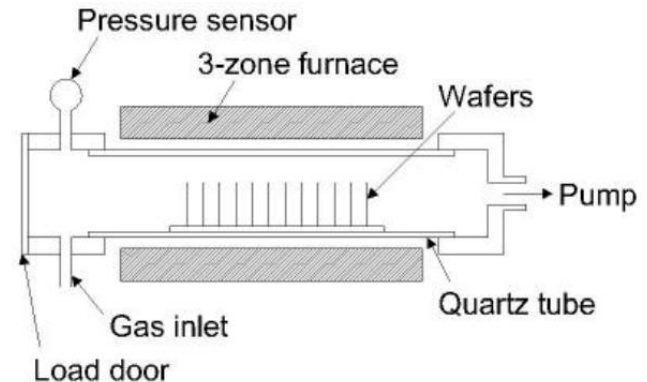
Hot wall reactor

Pressure sensor
3-zone furnace
Wafers
Pump
Quartz tube
Gas inlet
Load door

Advantages:
•Simple to operate
•May accommodate several substrates
•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 e.g. 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

In the cold wall reactor, only the susceptor where the substrates are placed isintentionally heated by RF induction, or high radiation lamps

This type of reactor is predominantly used for the deposition reaction which is endothermic, such as Si deposition from the halides. Since the substrates have a higher temperature than the reactor wall, the reaction will proceed most readily on the hot surface of the substrate

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
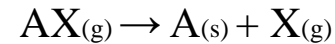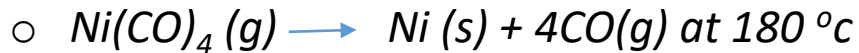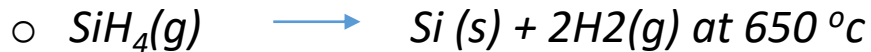
Cold wall reactor
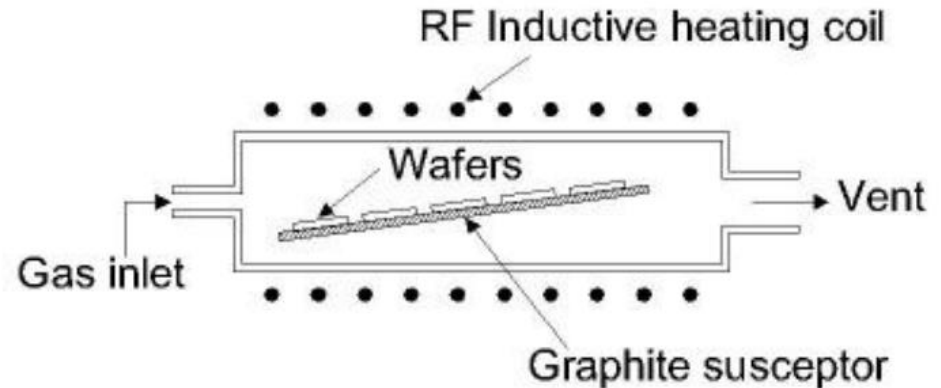
Disadvantages:
• Steep temperature gradients near the substrate surface may lead to convection
• Less flexibility on substrate orientation and usually only one substrate at a time
• Very frequently, the walls are water-cooled to further prevent deposition on the wall or reactions between walls and vapor
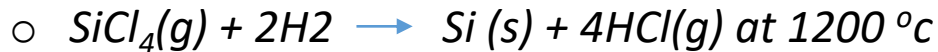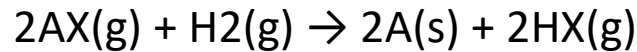
CVD Reaction Types - I

- ## Pyrolysis

✓ Thermal decomposition of gaseous species on hot substrates.

○ $SiH_4(g)$ ⟶ $Si (s) + 2H2(g)$ at $650\ ^oc$

○ $Ni(CO)_4 (g)$ ⟶ $Ni (s) + 4CO(g)$ at $180\ ^oc$

$$AX_{(g)} \rightarrow A_{(s)} + X_{(g)}$$

○ Also can deposit, Al, Ti, Pb, Mo, Fe, B, Zr, C, Si, Ge

- ## Reduction

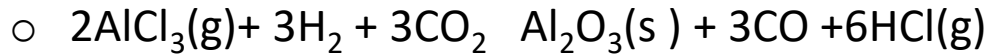Use hydrogen gas to reduce halides, carbonyl halides and oxyhalides

$$2AX(g) + H2(g) \rightarrow 2A(s) + 2HX(g)$$

○ $SiCl_4(g) + 2H2$ ⟶ $Si (s) + 4HCl(g)$ at $1200\ ^oc$

○ $WF_6(g) + 3H2$ ⟶ $W (s) + 6HF(g)$ at $300\ ^oc$

✓ Also can deposit, Al_2O_3, TiO_2, Ta_2O_5, SnO_2, ZnO

CVD Reaction Types - II

- ## Oxidation

✓ Using oxygen gas to produce oxides .

○ $SiH_4(g) + O_2 \longrightarrow SiO_2(s) + 2H_2(g)$ at $450\,^oc$

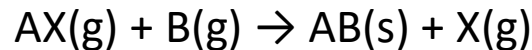○ $2AlCl_3(g) + 3H_2 + 3CO_2 \quad Al_2O_3(s) + 3CO + 6HCl(g)$

○ Also can deposit TiO2, Ta2O5, SnO2, ZnO

- ## Compound Formation

A variety of carbide, nitride and boride films can be formed

Displacement reactions. These reactions are also known as exchange reactions.

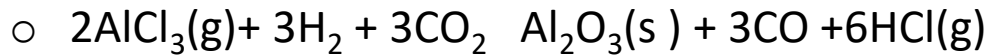In the molecule *AX*, *X* is replaced by another element *B*.

$$AX(g) + B(g) \rightarrow AB(s) + X(g)$$

○ $SiCl_4(g) + CH4 \longrightarrow SiC(s) + 4HCl(g)$

○ $BF_3(g) + NH3 \longrightarrow BN(s) + 4HF(g)$

✓ Also can deposit, Al_2O_3, TiO_2, Ta_2O_5, SnO_2, ZnO

CVD Reaction Types - II

- ## Oxidation

✓ Using oxygen gas to produce oxides .

○ $SiH_4(g) + O_2 \longrightarrow SiO_2 (s) + 2H_2(g)$ at 450 ᵒc

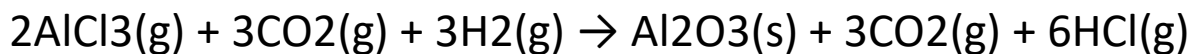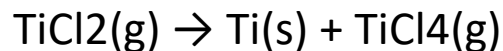○ $2AlCl_3(g)+ 3H_2 + 3CO_2 \; Al_2O_3(s) + 3CO + 6HCl(g)$

○ Also can deposit TiO2, Ta2O5, SnO2, ZnO

- ## Compound Formation

A variety of carbide, nitride and boride films can be formed
Disproportionation reactions. In these reactions, the oxidation number of an element both increases and decreases through the formation of two new species. Some typical examples are:

$$2GeI2(g) \rightarrow Ge(s) + GeI4(g)$$

$$TiCl2(g) \rightarrow Ti(s) + TiCl4(g)$$

$$2AlCl3(g) + 3CO2(g) + 3H2(g) \rightarrow Al2O3(s) + 3CO2(g) + 6HCl(g)$$

More about Gibbs Free Energy (GFE)

As we have seen in choice of chemical reactions

- GFE is a measure of the total available energy in a system.

- If the overall GFE of the reactants is greater than the overall GFE of the products, that reaction is thermodynamically favourable.

- The equations relating the GFEs also determine the reaction rates.

- All of these quantities are affected by temperature and pressure

Nucleation

In addition to being thermodynamically favorable, the barrier to nucleation (creating a nucleus increases surface energy) as to be overcome.
• Two types of nucleation exist:
– Homogenous
: Nuclei are formed in vapor form before being deposited and do not incorporate into the crystal structure of the film.
– Heterogeneous
: Nuclei are formed on the substrate and incorporate into the film structure more easily.

Gas Transport

•   This   is   the   flow   of   the   reactants   through   the   CVD   chamber.
• The goal is to deliver the gas uniformly to the substrate.
•   The   flow   needs   to   be   optimized   for   maximum   deposition   rate.
• Flow can be molecular (gas diffusion) or viscous (liquid flow).
• CVD takes place in the viscous regime. ($Kn < 1$)

• In the viscous regime:
– Low flow rates produce laminar flow (desired).
– High flow rates produce turbulent flow (avoided)

Film Deposition

• In a simplified model, as gas flows over the substrate film growth is determined by adsorption and reaction rates.

• However, in reality, the deposition rate is affected by:
– Distance from gas inlet
– Specifics of the reaction– Radial variance

• Tricks to improve film uniformity:
– Tilt substrate into flow
– Increase T along the substrate
– Single wafer processing

Deposition Rate
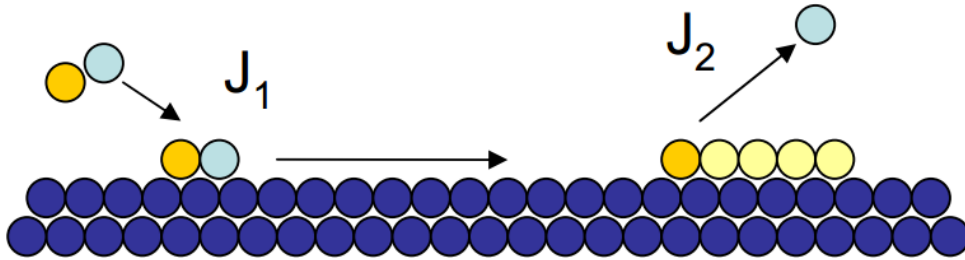
$$J_1 = h_G\left(C_g - C_s\right)$$

$$J_2 = k_S C_s$$

J_1: Flux to surface
J_2: Reaction flux
C_g: Gas concentration
C_s: Concentration on surface

h_g: Gas phase mass transport coefficient
k_s: Surface reaction rate

In steady state $J_1 = J_2$ ⟶

$$v = \cfrac{C_g}{\dfrac{1}{h_G} + \dfrac{1}{k_S}}$$

: deposition rate

Limiting Cases

- $h_G \gg k_S$: Reaction Limited Growth

- $k_S \gg h_G$: Transport Limited Growth

Reaction Limited Growth

- growth controlled by processes on surface
  – adsorption
  – decomposition
  – surface migration
  – chemical reaction
  – desorption of products

- k_S is highly temperature dependent (increases with T)
- common limit at lower temperatures
- often preferred, slow but epitaxial growth
- temperature and reactant choices are important
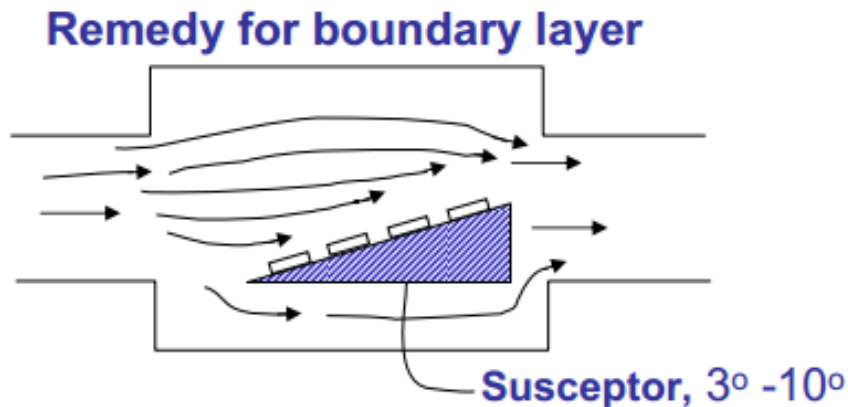
Mass Transport Limited Growth

- growth controlled by transfer to substrate
- h_G is not very temperature dependent
- common limit at higher temperatures
- non-uniform film growth
- gas dynamics and reactor design are important
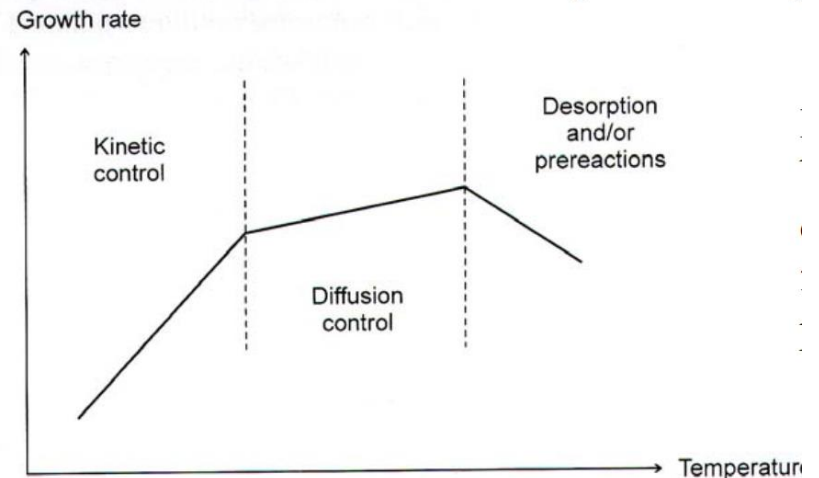
Transport limited growth :

$$v = \frac{h_g C_g}{N_f} \rightarrow \frac{3DC_g}{2LN_f}\sqrt{Re} = \frac{3\lambda \bar{v}_x C_g \sqrt{Re}}{4LN_f}$$

Most CVD is done in this limit where <u>gas dynamics,</u> <u>reactor design are important</u>.

Remedy for boundary layer

Susceptor, 3° -10°

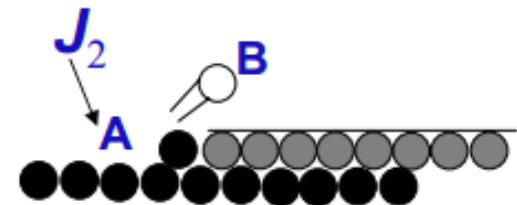More uniform u_g, C_g ⇒ uniform film growth rate , v

Reaction limited growth :

$$v = \frac{k_s C_g}{N_f} = \frac{C_g}{N_f} k_0 e^{-\frac{\Delta G}{kT}}$$

ΔG = free energy change in reaction

(ΔG ≅ ΔH for gas becasue gas reaction no ΔS)

J_2 B A

<u>Choice of reactants and temperature are critical</u>

CVD FILM GROWTH

GAS TRANSPORT-LIMITED

$$v = \frac{3\lambda \bar{v}_x C_g}{4 N_f L} \sqrt{\mathrm{Re}}$$

$$\bar{v}_x = \sqrt{\frac{2 k_B T}{\pi m}},$$

$$\lambda = \frac{k_B T}{\sqrt{2} \pi d^2 P_g},$$

$$\sqrt{\mathrm{Re}} \sim \sqrt{u_0}$$

$$\frac{C_g}{P_g} = \frac{1}{k_B T}$$

$$v \propto T^{1/2} \sqrt{u_0}$$

REACTION-RATE LIMITED

$$v = \frac{k_s C_g}{N_f} = \frac{C_g}{N_f} k_0 e^{-\frac{\Delta G}{kT}}$$

ΔG = free energy change in reaction

$$\Delta G = \Delta H - T\Delta S$$

($\Delta G \cong \Delta H$ for gas $\rightarrow$ no ΔS for

gas reaction)

$$v \sim e^{-\Delta H / kT}$$

CVD Reactor Types by process

• APCVD – Atmospheric Pressure CVD

• LPCVD – Low Pressure CVD

• MOCVD – Metalorganic CVD

• PHCVD – Photon (Laser) Induced CVD

• PECVD – Plasma Enhanced CVD

Thermal CVD processes

• Heat energy is supplied to activate the required gas and gas-solid phase reactions.

• There are many possible classifications to the thermal CVD processes:

– High or low temperature

– Atmospheric or low pressure

– Cold or hot wall

– Closed or open

Atmospheric Pressure CVD

• High Temperature APCVD

– Used to deposit epitaxial Si and compound films (cold wall reactors) or hard metallurgical coatings like TiC and TiN (hot wall reactors)

Low Temperature APCVD

– Many insulating film layers (SiO_2, BPSG glasses) need to be deposited at low temperatures

APCVD Issues

Wafer throughput is low due to low deposition rate.

• Film thickness uniformity can be an issue.

• Step coverage is not very good.

• Contamination is a problem and maintaining stochiometry can be hard.

• Large number of pinhole defects can occur

Low Pressure CVD

- Classify by gas pressure:
  – For 100 torr > P > 1 torr, we have reduced pressure CVD (RPCVD)
  – For 10 mtorr > P > 1 mtorr, we have LPCVD
  – At UHV (~10^{-7} torr), we have UHV/CVD.
- Higher gas concentrations to compensate for lower pressure.
- Higher diffusivity of gas to the substrate
- Often reaction rate limited growth
- Due to lower pressures, there are fewer defects.
- Better step coverage, better film uniformity.

Advantages of LPCVD
Faster growth
Less autodoping
Little diluent gas needed
Lower gas consumption
Fewer byproducts (particles)

Disadvantages:
Line of sight
shadowing

LPCVD Reactors

• Reaction rate limited growth enables close packed stacking of wafers in LPCVD chambers, resulting in high wafer throughput.

• Can be "hot wall" or "cold wall" reactors

• Most commercial LPCVD reactors are hot walled.

• Hot wall reactors have a more uniform temperature distribution but the surface of the reactor walls can also get coated. This limits the reactor to one species. Used more for polycrystalline films.

• In cold wall reactors, the reaction rate is reduced but film quality can be better controlled. Better for epitaxial films.

Metalorganic CVD (MOCVD)

Use organometallic source gasses.

• eg: $(CH_3)_3Ga$ . . . . tri-methyl Gallium

• Reactants are volatile at relatively low temperatures.

• Can grow high quality epitaxial films at nanometer scale.

• Both the reactants and the byproducts can be hazardous

Plasma Enhanced CVD Processes

Create a plasma (RF or DC) in the vicinity of the substrate.
• As in sputtering, the energetic ions impart their energy and momentum on the reactant gas molecules and atoms.
• The energy transfer breaks up the molecules and aids the chemical reactions.
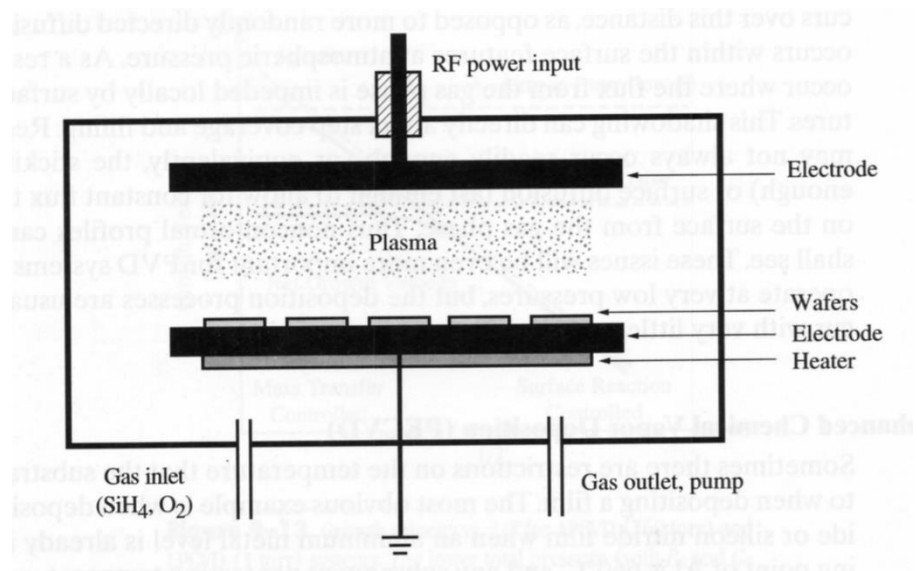
The "helping hand" of the plasma allows for lower temperatures and pressures and improves film quality. For example, TiC would not normally form below 1200 °C (from GFE consideration) but with PECVD, it is possible to deposit it at 700 °C.
• The lower temperatures are especially useful when depositing metal contact layers (eg. Al) between dielectric (insulating) layers (eg. SiO_2).
• The higher temperatures of plain LPCVD would melt the metal and the alternate layers would interact.
• The imparted momentum allows for better step coverage.
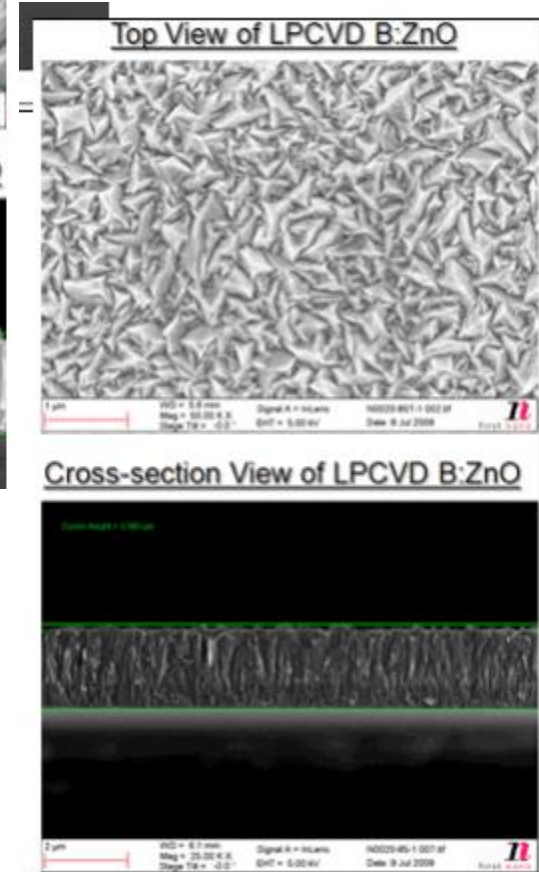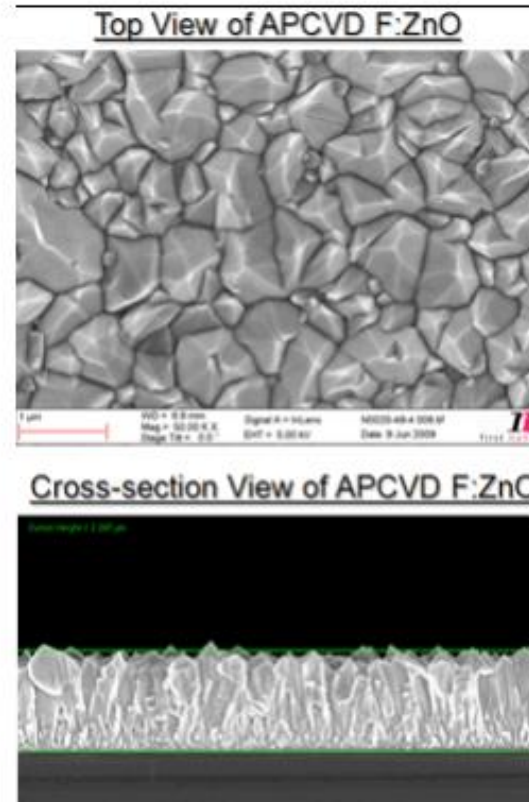
Structure of CVD Grown Films

The main parameters affecting film structure are substrate temperature and vapor supersaturation.

– Temperature determines growth rate.

– Supersaturation determines nucleation rate.

• Together they determine whether epitaxial or amorphous films, whiskers, platelets, polycrystals, etc. are produced.

• In general, single crystal growth is favored by low supersaturation and high substrate temperatures, and amorphous films are favored by the opposite situation.

Top View of APCVD F:ZnO

Cross-section View of APCVD F:ZnO

Top View of LPCVD B:ZnO

Cross-section View of LPCVD B:ZnO

Carbon Nanotubes

Carbon nanotubes are tubular structures of carbon, typically several nanometers in diameter and hundreds to thousands of nanometers in length.
• They can be single or multiwalled.
• Can have a wide range of electrical, mechanical and optical properties
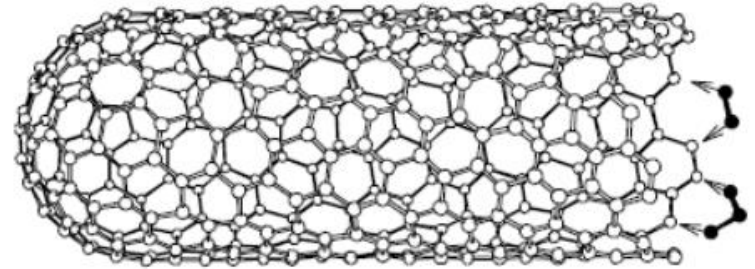
CVD Growth of Carbon Nanotubes

A hydrocarbon gas is passed over a catalyst in a high temperature oven.
• The catalyst (often transition-metal nanoparticles on alumina) allows the dissociation of the hydrocarbon.
• The carbon then dissolves and saturates the nanoparticles
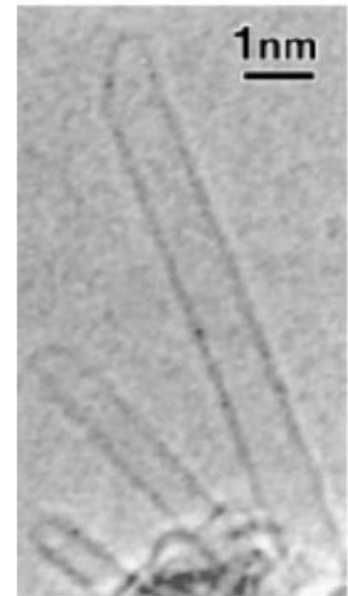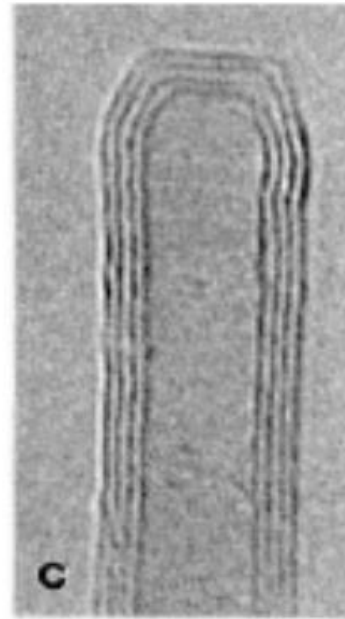
**CVD Growth of Carbon Nanotubes**

Upon precipitation from the catalyst, carbon atoms form nanotubes (energetically favored over graphite sheet formation).

• The chamber is cooled to room temperature and the tubes are collected.

• The choice of the hydrocarbon, the catalyst and the temperature determine the nature of the nanotubes.
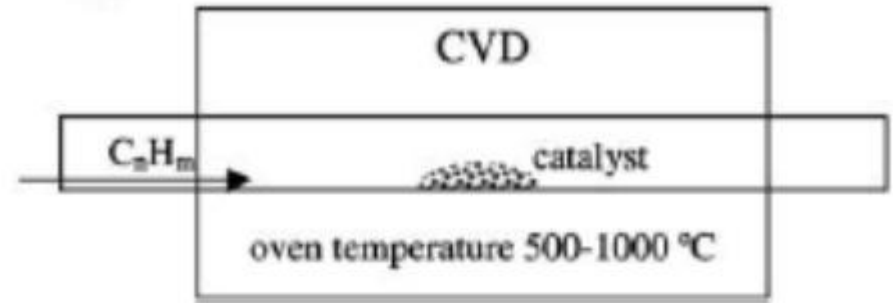
CNT Growth Details
• MWCNT
– Ethylene or acetylene as the hydrocarbon
– Temperature: 550 °C – 700 °C
– Nickel or Cobalt nanoparticles as catalyst
• SWCNT
– Methane as the hydrocarbon
– Temperature: 850 °C – 1000 °C
– Nickel, Cobalt or Iron nanoparticles as catalyst
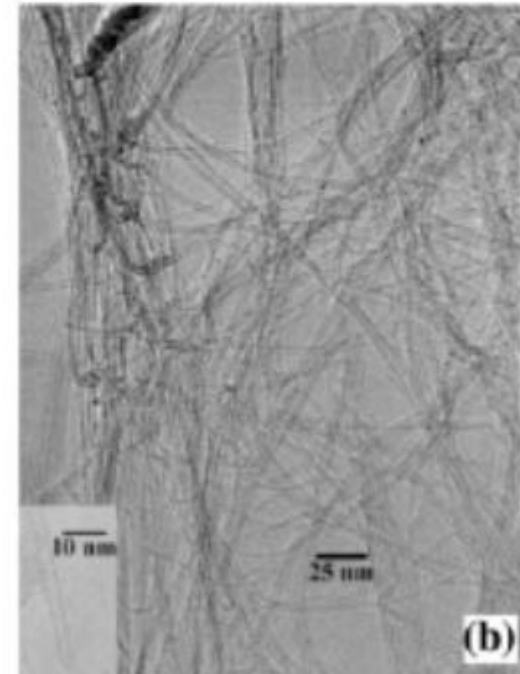
Graphene

Many variations of CVD can be utilized to synthesize graphene. Although many advancements have been made, the processes listed below are not commercially viable yet.

•Physical conditions

Physical conditions such as surrounding pressure, temperature, carrier gas, and chamber material play a big role in production of graphene. Most systems use LPCVD with pressures ranging from 1 to 1500 Pa .However, some still use APCVD. Low pressures are used more commonly as they help prevent unwanted reactions and produce more uniform thickness of deposition on the substrate.

On the other hand, temperatures used range from 800-1050 °C. High temperatures translate to an increase of the rate of reaction. Caution has to be exercised as high temperatures do pose higher danger levels in addition to greater energy costs.

- Hydrogen gas and inert gases such as argon are flowed into the system
- The use of catalyst is viable in changing the physical process of graphene production.
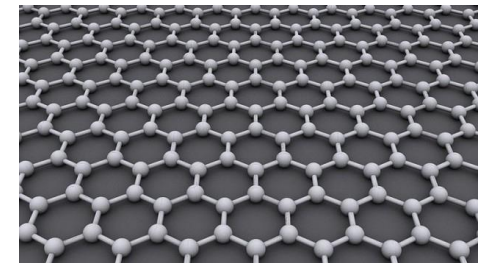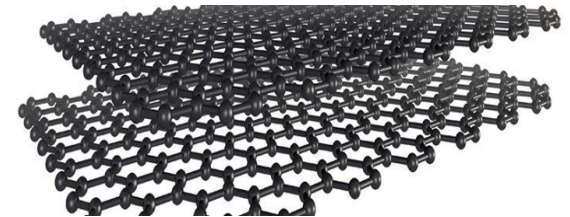
Fluid dynamics:

$$\delta(x) = \sqrt{\frac{\eta x}{\rho u_0}}$$

ρ = mass density, η = viscosity

$$\langle\delta\rangle = \frac{1}{L}\int_0^L \delta(x)\,dx = \frac{2}{3}L\sqrt{\frac{\eta}{\rho u_0 L}} \equiv \frac{2}{3}\frac{L}{\sqrt{Re}}$$

Reynolds #: $\quad Re = \rho\dfrac{u_0 L}{\eta}$

ease of

gas flow

So: $\quad h_g = \dfrac{D}{\langle\delta\rangle} \to \dfrac{3}{2}\dfrac{D}{L}\sqrt{Re}$