CNDL

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- 2.1.2. Nanostructured Polymer (Copolymer, DNA)
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1. Introduction

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3. Chemical Vapor Deposition

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    3.3. Atomic Layer Deposition

Reference:
Handbook of nanostructured materials and nanotechnology, volume 1, Chapter 4, Academic press (2000)

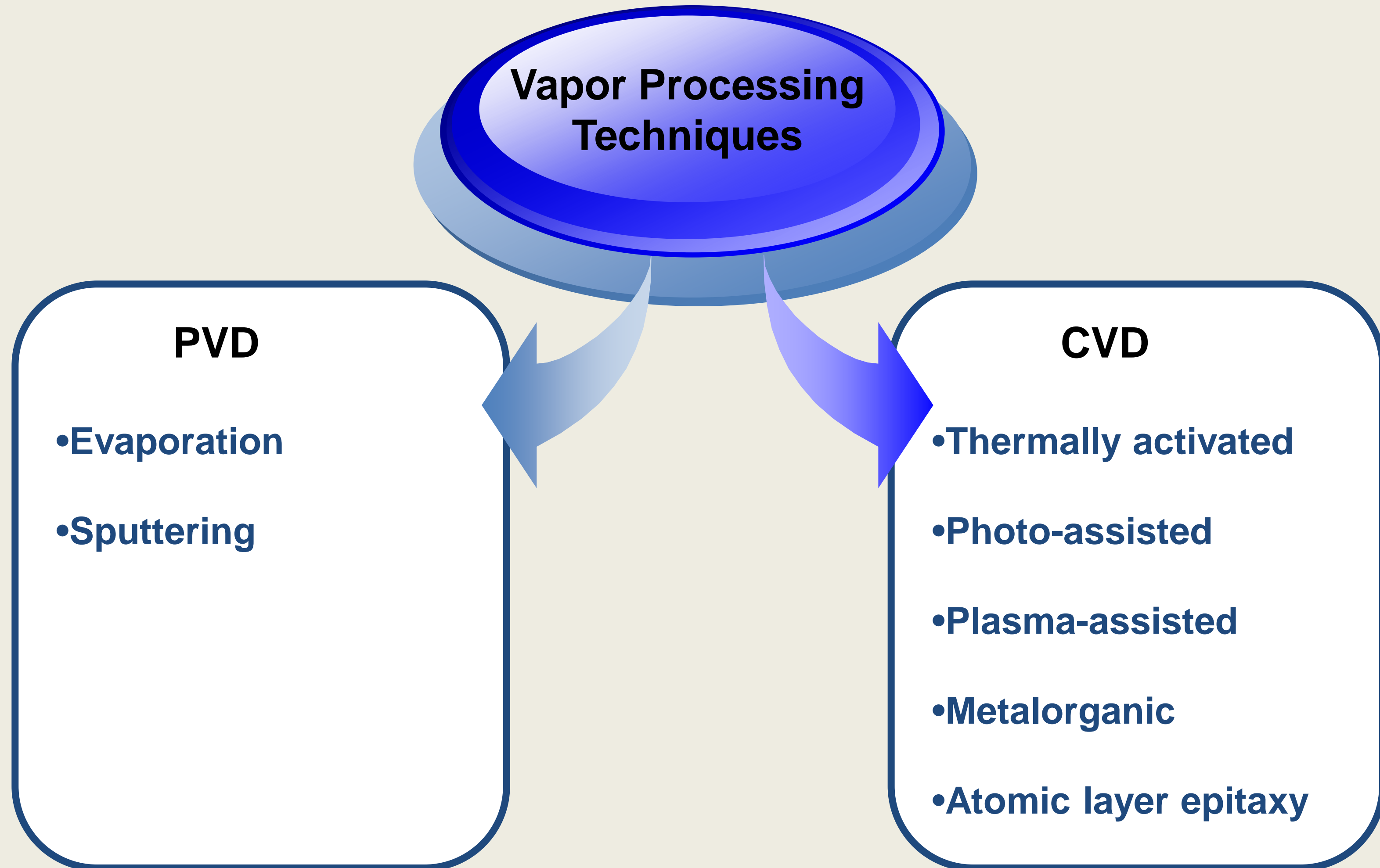
1.1. Nanophase Processing Technique

Processing route	Processing methods	Product materials
Solid-liquid	Mechanical milling	Powder
Liquid	Sol-gel Sonochemistry Hydrothermal Electrodeposition Gas atomization Laser beam melting Melt spinning	Powder/film Powder Powder Powder/film Powder Film Continuous ribbon
Vapor	Chemical vapor deposition Physical vapor deposition Aerosol processes Flame-assisted deposition	Powder/film Powder/film Powder/film Powder

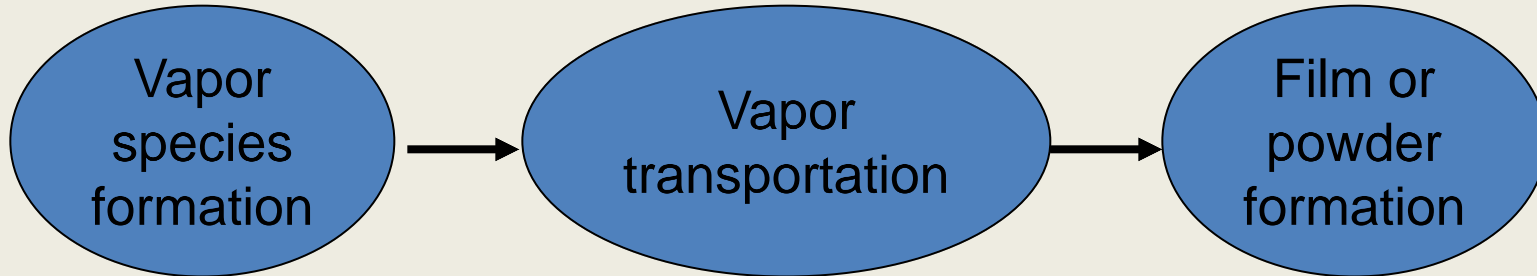
1.1. Nanophase Processing Technique

Processing route	Processing methods	Disadvantages
Solid-liquid	Mechanical milling	• Tedious and time consuming process (Mixing, frinding, calcination, sintering, etc) • Prone to contamination from milling media • Suffering from chemical and phase inhomogeneities • Expensive and limited to the processing of ultrafine powder
Liquid	Sol-gel Sonochemistry Hydrothermal Electrodeposition Gas atomization Laser beam melting Melt spinning	• Require a high number of processing steps (Pretreatment, mixing, chemical reactions, filtration, purification, drying, etc) • Tedious ad can cause contamination • Waste treatment is difficult

1.2. Classification of Vapor Processing Techniques



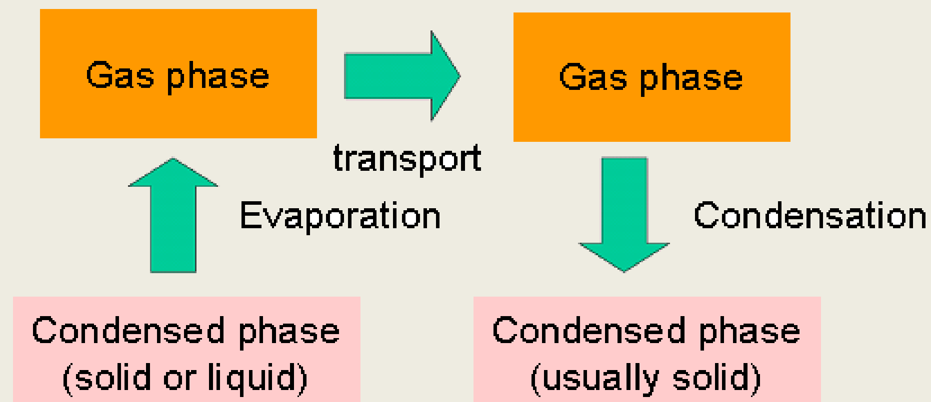
2.1. Process Principle



- evaporation
- sputtering (Ar+)
- ion plating (high v)

- collision
- ionization

- condensation
- nucleation
- growth
- ion bombardment



2.1. Process Principle

Evaporation rates

➢ Heinrich Hertz equation (empirical eqn.)

*P** is the equilibrium vapor pressure of the evaporant at T.
P is the ambient hydrostatic pressure acting upon the evaporant in the condensed phase.

Experimentally, that the evaporation rate was proportional to (*P** - *P*)
– Also, the evaporation rate could not be increased by supplying more heat unless the equilibrium vapor pressure was also increased by this action.
– maximum evaporation rate when is only achieved in a vacuum, where *P* = 0.

The net evaporation flux is the difference between the collision rates for the two fluxes

$$\frac{dN_e}{A_e dt} = (2\pi m k_B T)^{-1/2}(P^* - P)$$

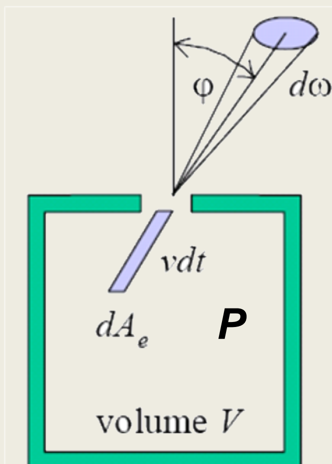
N_e : number of evaporating molecule
A_e : area
m : mass of the molecule
P : gas pressure
T : temperature
k_B : Boltzmann constant

2.1. Process Principle

Evaporation rates

- Solid angle $d\omega = \dfrac{dA}{r^2}, \quad \text{Max.}\,\omega = \dfrac{4\pi r^2}{r^2} = 4\pi$

➢ Knudsen Cell



The evaporant flux into a solid angle of dw from a source area of dA_e

$$d^4 N_e = N \frac{v\,dt \cos\varphi\, dA_e}{V} \frac{d\omega}{4\pi} \Phi(v^2)\, dv$$

Maxwell distribution of velocity

Fraction of molecules within striking distance in time dt

Fraction of molecules entering the solid angle dw is dw/4π

$$\frac{d\omega}{4\pi} = \frac{\text{Target solid angle, dw}}{\text{Maximum solid angle}}$$

After simple mathematical operation,
Total impingement rate is

$$\frac{d^2 N_e}{dA_e\, dt} = (2\pi m k_B T)^{-1/2} P$$

Mass evaporation rate through the orifice and the total mass of evaporated material are,

$$\Gamma = m \frac{d^2 N_e}{dA_e dt} = \left(\frac{m}{2\pi\, k_B T} \right)^{1/2} P$$

$$M_e = \int_0^t \int_0^{A_e} \Gamma\, dA_e\, dt$$

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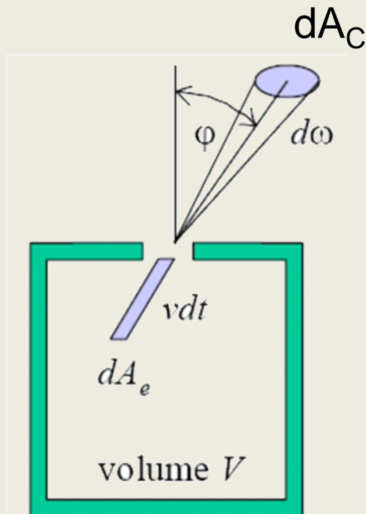
2.1. Process Principle

Condensation

The deposited evaporant mass per unit area of condensation surface is

Solid angle, dw, is

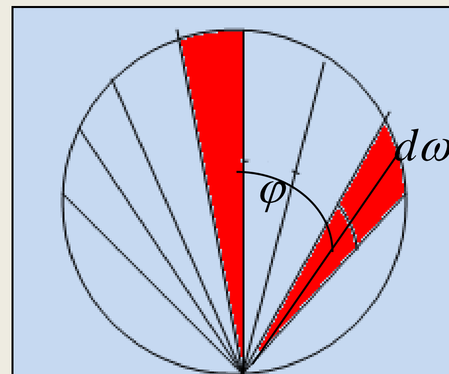
$$d\omega = \frac{dA_c \times \cos\psi}{r^2} \quad , \quad dA_c = \frac{r^2 d\omega}{\cos\psi}$$



$$dM_c = M_e \cos\varphi \frac{d\omega}{\pi} \leftarrow \left(\int \cos\varphi d\omega = \int_0^{2\pi} \int_0^{\pi/2} \cos\varphi \sin\varphi d\varphi d\phi = \pi \right)$$

By Lambert's cosine law

$$\rightarrow \frac{dM_c}{dA_c} = \frac{M_e}{\pi r^2} \cos\varphi \cos\psi$$



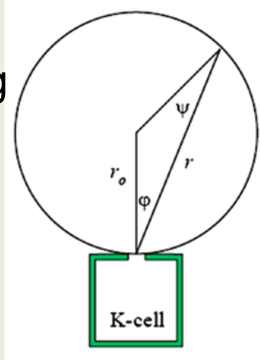
- Lambert's cosine law

  the radiant intensity observed from a "Lambertian" surface is directly proportional to the cosine of the angle

2.1. Process Principle

Condensation

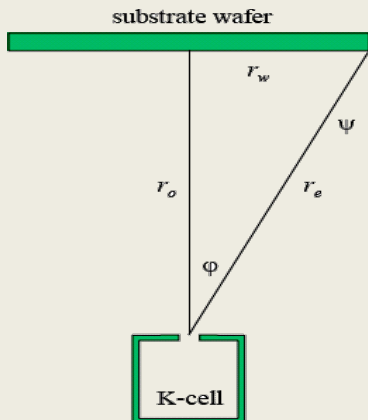
Uniform coating on sphere



$$\cos\varphi = \cos\psi = \frac{r}{2r_o}, \qquad \frac{dM_c}{dA_c} = \frac{M_e}{4\pi r^2}$$

Uniform coating

Uniformity of an evaporated film across a flat surface



Reduction factor for edge thickness:

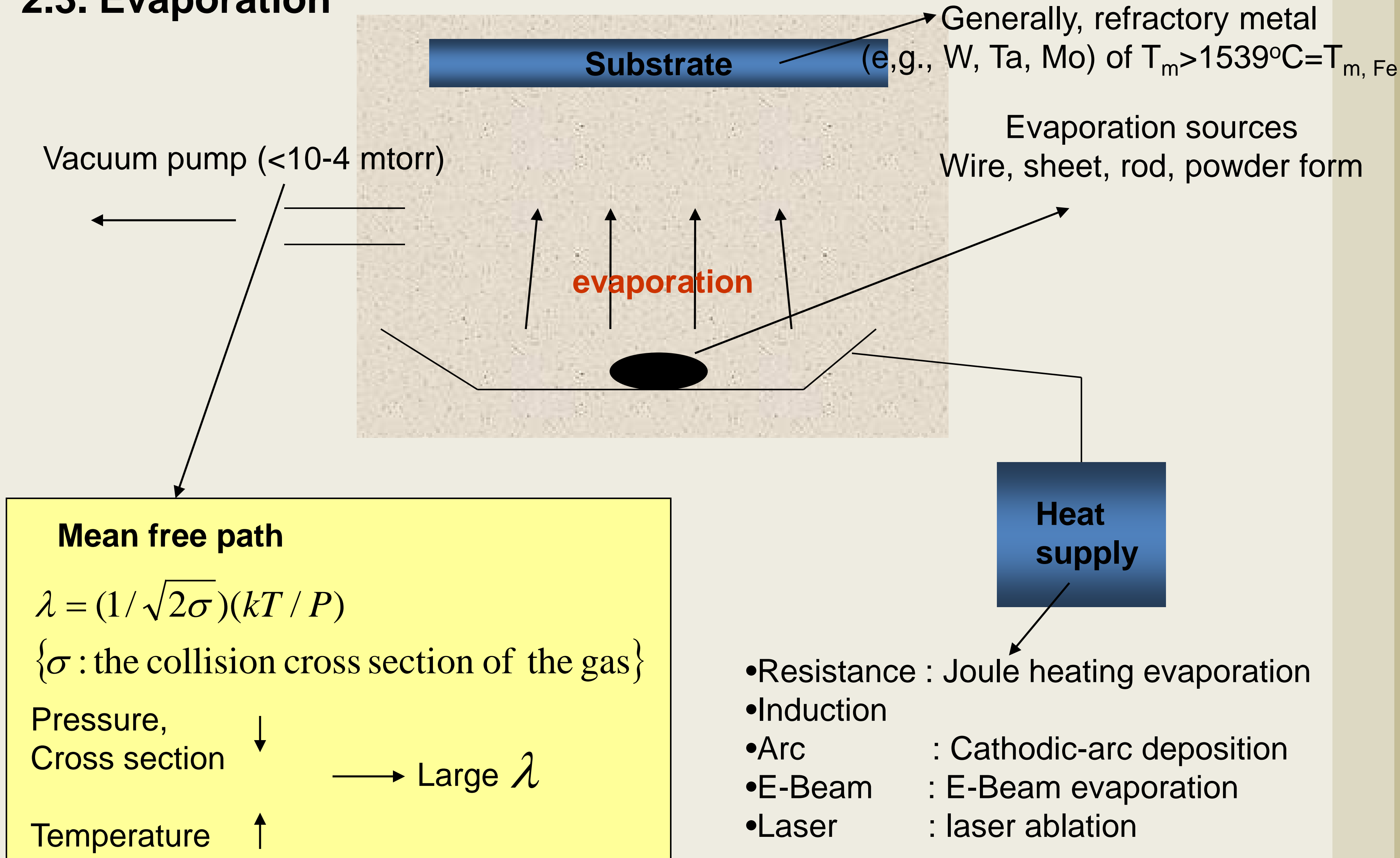
$$\frac{d_{edge}}{d_{center}} = \frac{r_0^2}{r_0^2 + r_w^2}\cos\varphi\cos\psi = \left[\frac{r_0^2}{r_0^2 + r_w^2}\right]^2$$

Ex) for a 3-inch diameter wafer suspended 18 inches above a Knudsen cell:
d_{edge}/d_{center} = 0.986, or a non-uniformity of 1.4 %

2.2. Advantages & Disadvantages

Advantages	Disadvantages
• ultrapure, fine film or powder can be produced • good structure control by care monitoring of the processing conditions • as-deposited materials are already nanocrystalline in nature and do not require any further work to reduce the particle size or heat treatment to burn out the precursor complexes	• deposition process needs to operate in the low vapor pressure range • the synthesis of multi-component materials is difficult, except for the laser ablation method • Line of sight deposition process, which causes difficulty in producing nanocrystalline films on complex-shaped components, and has poor surface coverage

2.3. Evaporation



2.3. Evaporation

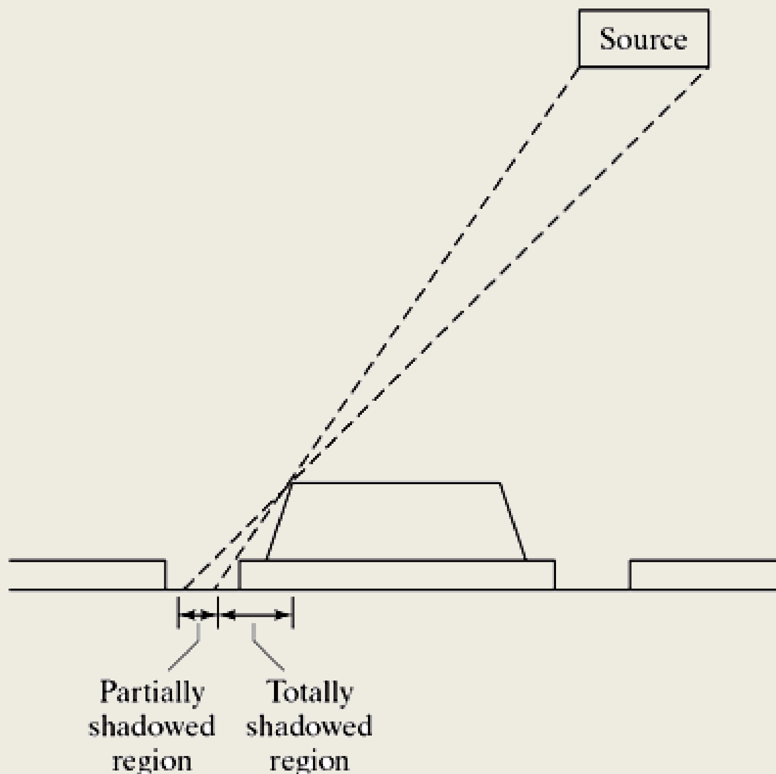
Feature of Evaporation Method

- The material to be vaporized can be in any form and purity
- The residual gases and vapors in the vacuum environment are easily monitored
- The rate of vaporization is high
- The line-of-sight trajectories and point sources allow the use of deposition onto defined areas
- The cost of thermally vaporizing a given quantity of material is much less than that of sputtering the same amount of material

- However, limitations of utilization of material, non-stoichiometric deposits

2.3. Evaporation

Shadowing or step coverage



- Shadowing and Step Coverage Problems Can Occur in Low Pressure Vacuum Deposition in which the Mean Free Path is Large

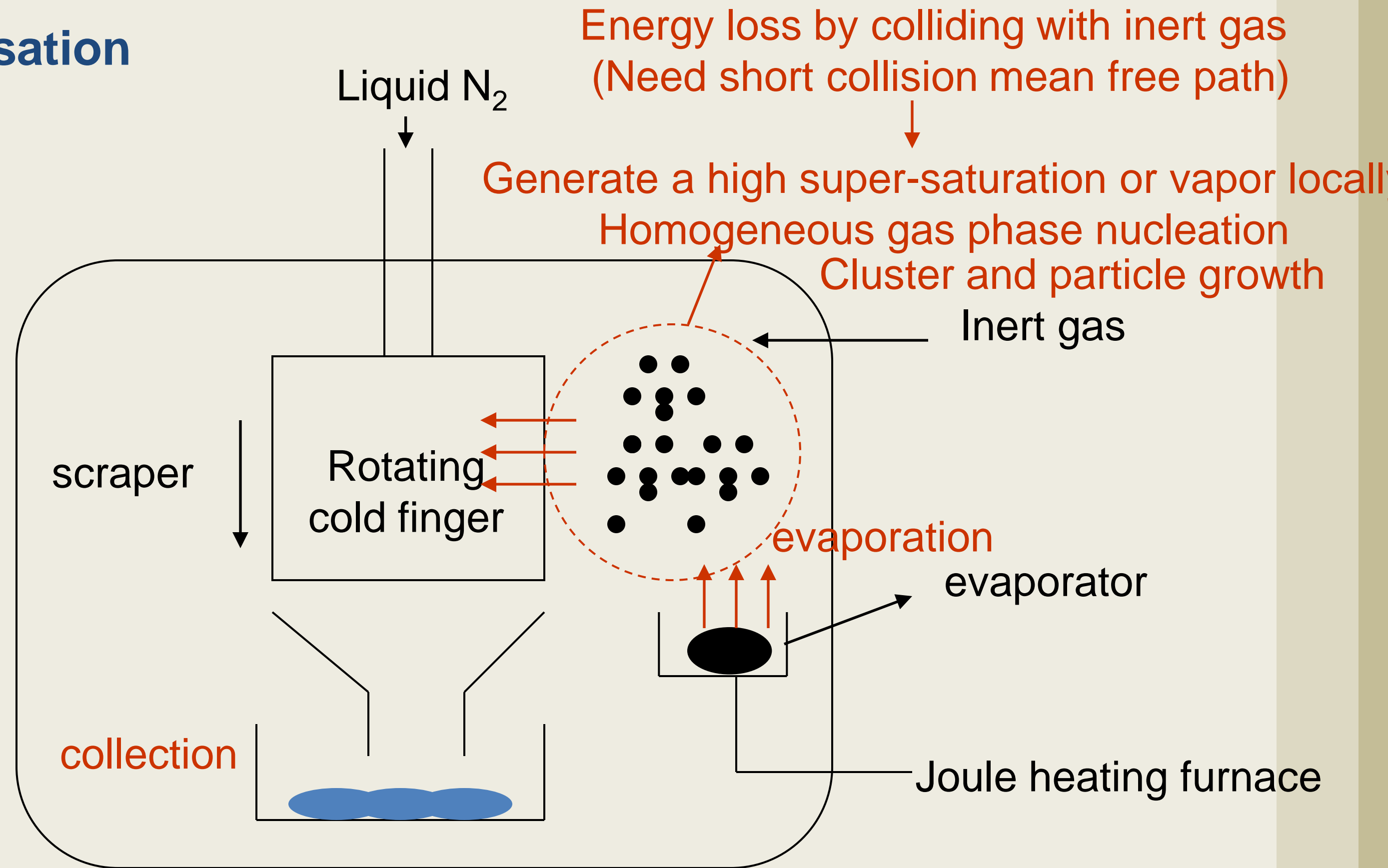
- When evaporation is performed in poor vacuum or close to atmospheric pressure, the resulting deposition is generally non-uniform and tends not to be a continuous or smooth film. Rather, the deposition will appear fuzzy or cloudy.

2.3. Evaporation

Inert-Gas Condensation

Transportation via natural gas convection

For small particle size, higher evaporation rate is required



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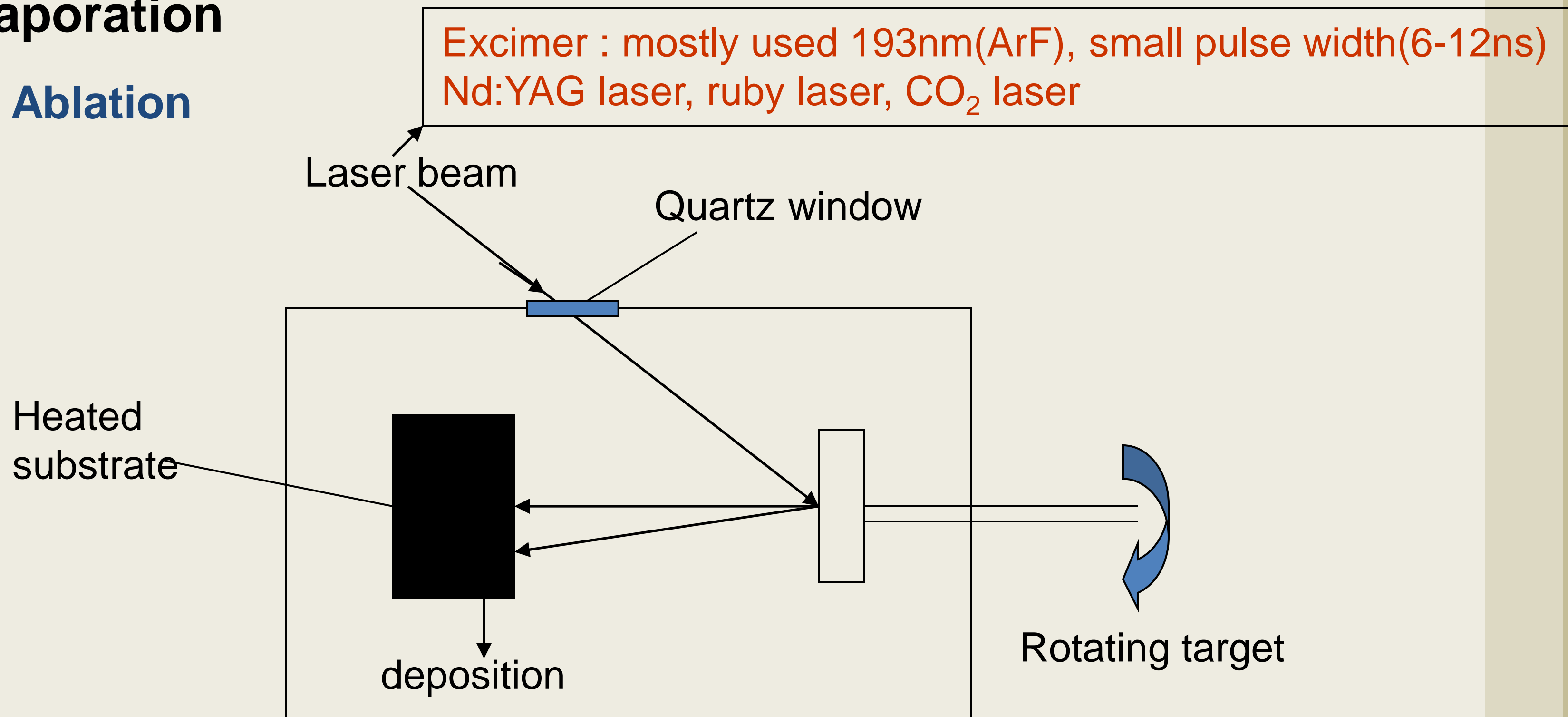
2.3. Evaporation

Laser Ablation

Excimer : mostly used 193nm(ArF), small pulse width(6-12ns)
Nd:YAG laser, ruby laser, CO_2 laser



- Producing multi-component materials
  with well-controlled stoichiometry by accurate transfer of the target composition to the coating
- High production cost

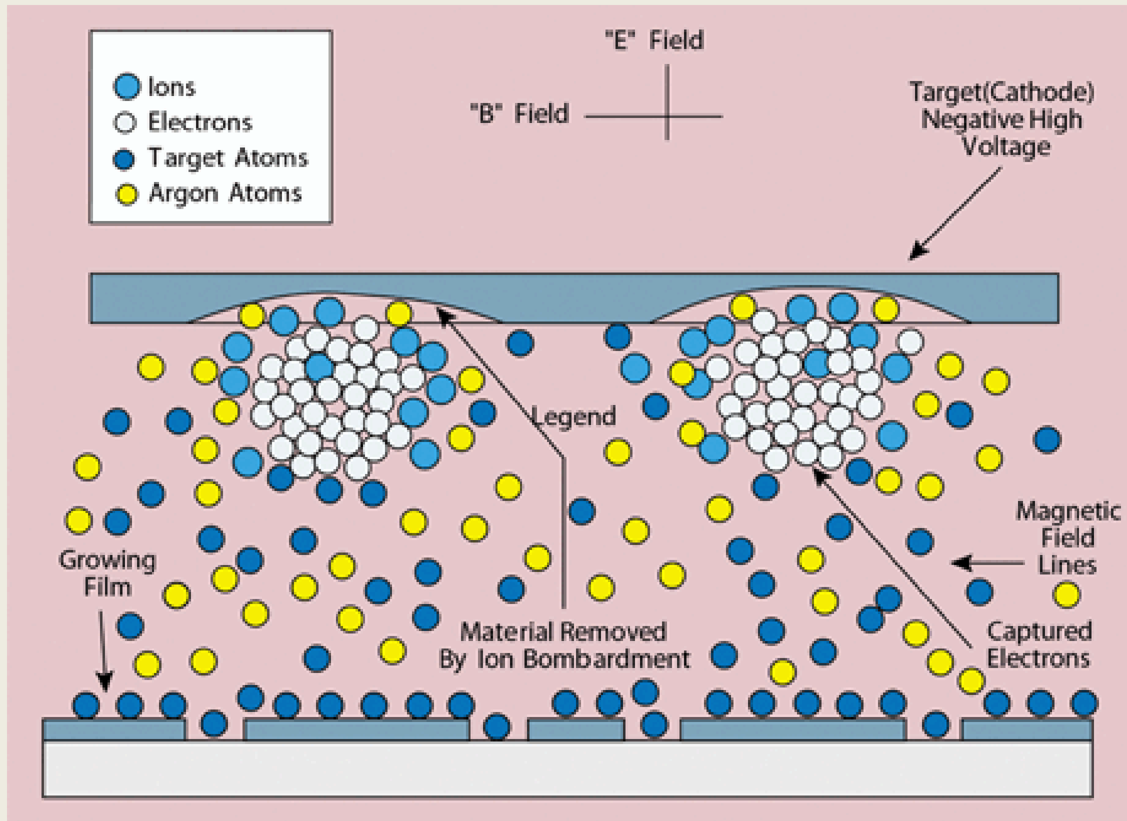
2.4. Sputtering

- Sputtering is a term used to describe the mechanism in which atoms are ejected from the surface of a material when that surface is struck by sufficiency energetic particles.
- Alternative to evaporation.
- First discovered in 1852, and developed as a thin film deposition technique by Langmuir in 1920.
- Metallic films: Al-alloys, Ti, TiW, TiN, Tantalum, Nickel, Cobalt, Gold, etc.

Advantages

- Use large-area-targets which gives uniform thickness over the wafer.
- Control the thickness by Dep. time and other parameters.
- Control film properties such as step coverage (negative bias), grain structure (wafer temp), etc.
- Sputter-cleaned the surface in vacuum prior to deposition.

2.4. Sputtering



Ref. www.vacgen.com/catalogue/section-16/intro.htm

Glow discharge to produce energetic particles (ions)

Momentum transfer from an indirect energetic projectile to a solid or molten target,

resulting in the ejection of surface atoms or molecules to produce the sputtered species

2.4. Sputtering

Application of Sputtering

- Thin film deposition:
  - Microelectronics
  - Decorative coating
  - Protective coating
- Etching of targets:
  - Microelectronics patterning
  - Depth profiling microanalysis
- Surface treatment:
  - Hardening
  - Corrosion treatment

2.4. Sputtering

Parameters influencing to sputtering yield

• The ejected atoms have much more energy and velocity than atoms that have been thermally evaporated

• Sputtering yield , **S**
- The number of atoms ejected per incident particle (ion)

•Energy of the incident particle
- threshold exists
- E↑→S↑

•Target temperature, T
- insensitive at below 600°C

•Mass of incident particle, M
- M↑→S↑ : more collisions will occur

•Angle of incidence,
angle↑→S↑

$$S \propto \frac{1}{\cos\theta}$$

•Heat of vaporization, H, of target materials
- H↓ →S↑

•Target crystallinity
- densely packed crystallographic place →S↑

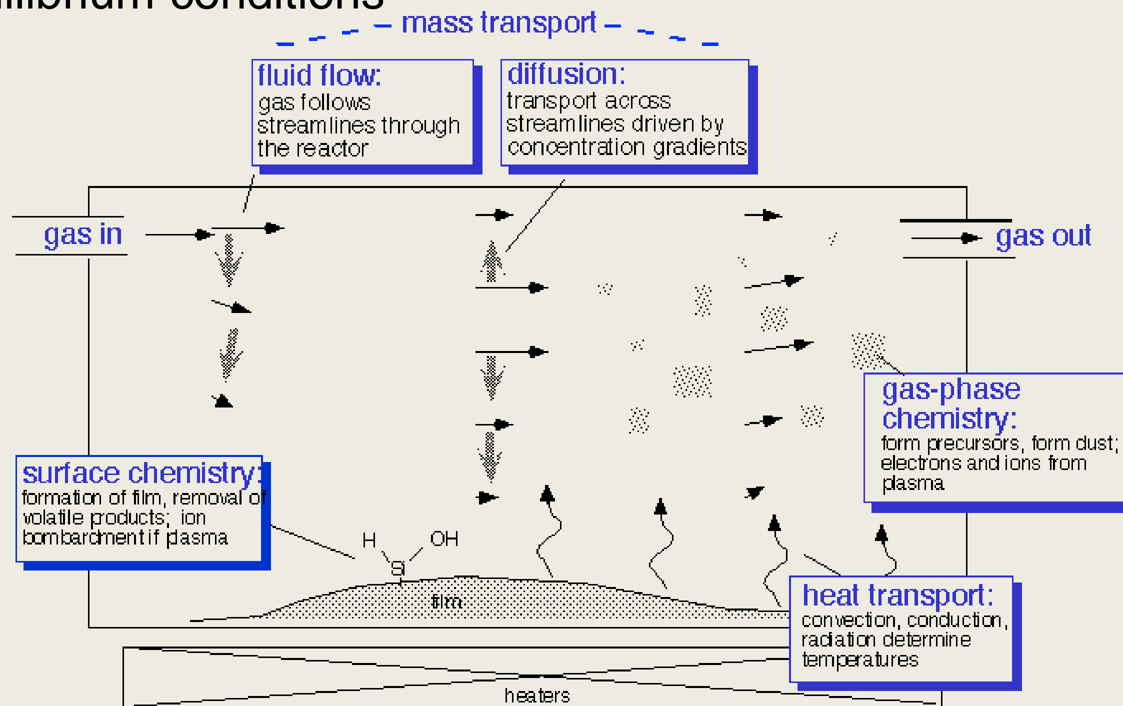
Momentum transfer

$$W = \frac{kV}{P_T d}$$

V: working voltage
i :discharge current
d: anode-cathode distance
P_T: gas pressure
k :proportionality constant

Chemical Vapor Deposition

- CVD is a more complex method than PVD
- Involves mass transport, heat transfer, and chemical reactions under non-equilibrium conditions



•However, the process modeling or simulation is mostly based on thermodynamic database, thermo-chemical equilibrium modeling and transport phenomena modeling, which assumed the CVD system is in equilibrium

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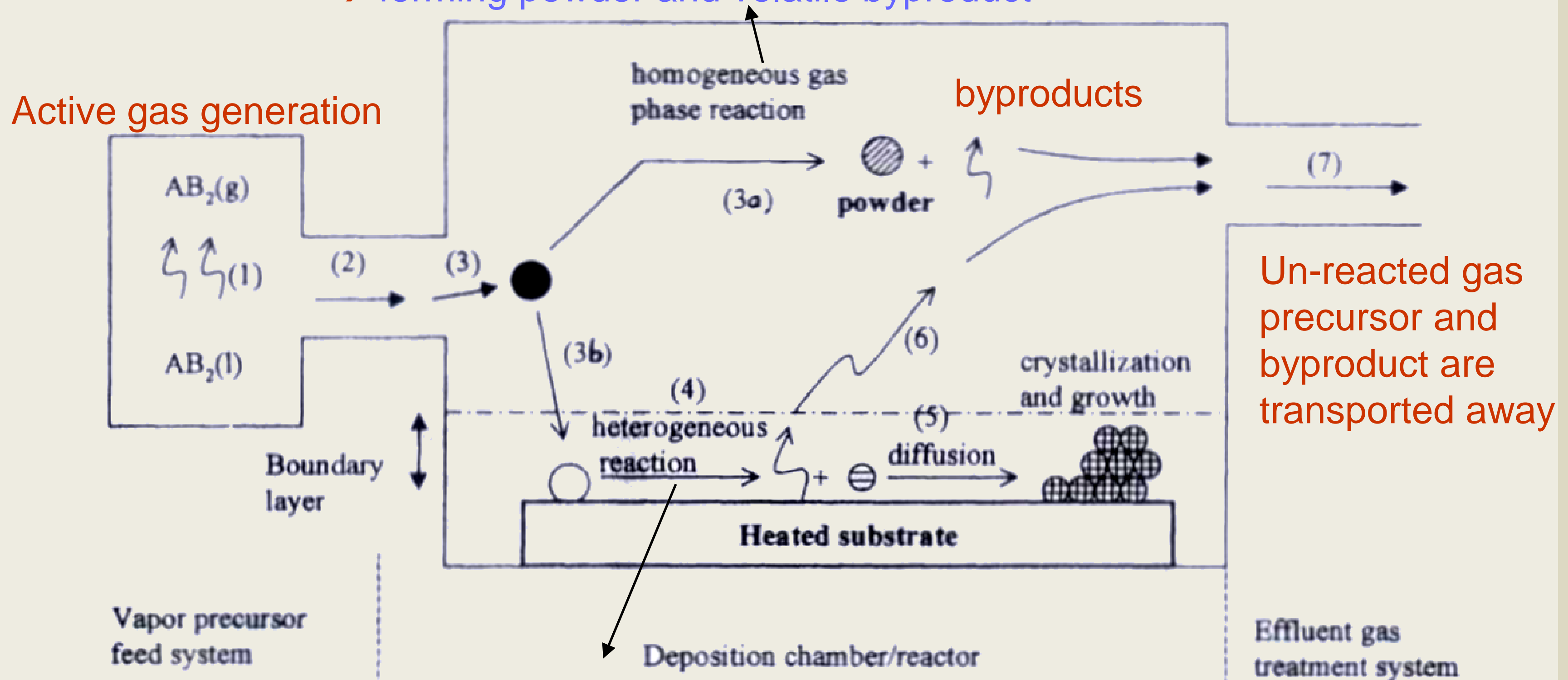
3.1. Process Principle

At high temp., decomposition and homogeneous gas phase reaction intermediate species → decomposition and/or chemical reaction→ → forming powder and volatile byproduct

Active gas generation



Un-reacted gas precursor and byproduct are transported away

At low temp., absorbed onto the substrate, heterogeneous reactions occur at the gas-solid interface

→ forming thin layer (films) and byproduct

3.1. Process Principle

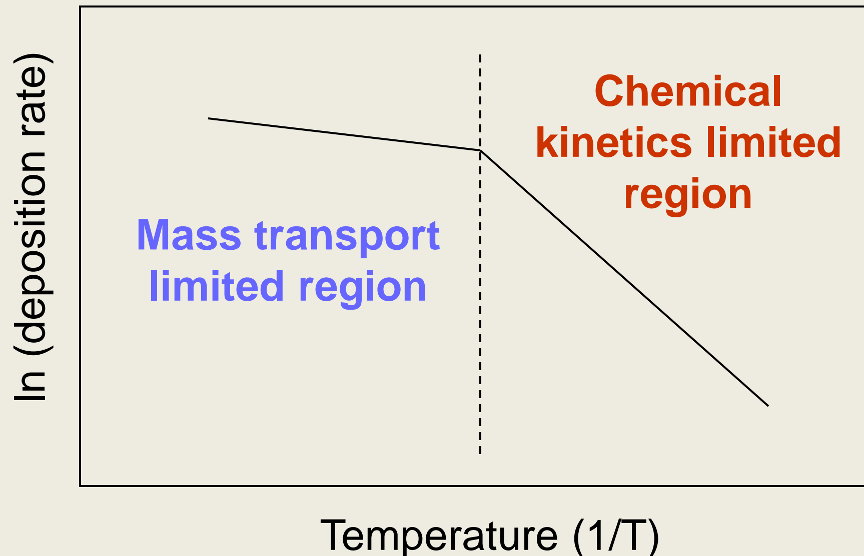
The effect of the temperature on the deposition rate

- Main CVD parameters : T, P, input gas ratio, and flow rate [temp. is the dominant parameter]

Mass transport limited region

-depend on the rate of diffusion of active gases due to enough high temperature

- so, efficient at low pressure condition



Chemical kinetics limited region

-depend on temperature

- The deposition increases rapidly in the chemical kinetics limited regions as temperature increase

Temp ↑

- **thermally activated reactions ↑**

↓

- growth rate ↑
- surface mobility of atomic species ↑
- surface diffusion ↑

3.1. Process Principle

Thermodynamic aspects I

$A + B = C_{solid} + D$

Where A and B are supplied gas, C is solid product (deposition)
Gas D diffuses away from the substrate during process

Molar Gibbs free energy change is $\Delta G_m = G_m^f - G_m^i$ $\quad \left(G_m = \sum X_n \mu_n\right)$

i is initial state

f is final equilibrium state

$$G_m^i = X_A^i \mu_A^i + X_B^i \mu_B^i, \quad G_m^i = X_A^f \mu_A^f + X_B^f \mu_B^f + X_C^f \mu_C^f + X_D^f \mu_D^f$$

$$\left(\mu_j = \mu_j^0 + RT \ln P_j\right)$$

As CVD reaction is proceed → P_C, P_D is increased → ΔG_m is increased → reaching equilibrium
P_A, P_B is decreased

Driving Force for Deposition in the CVD Process, Journal of Materials Science Letters, 13, 1437-1439 (1994)

3.1. Process Principle

Thermodynamic aspects I

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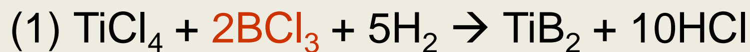
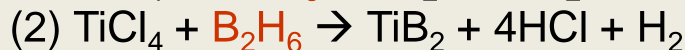
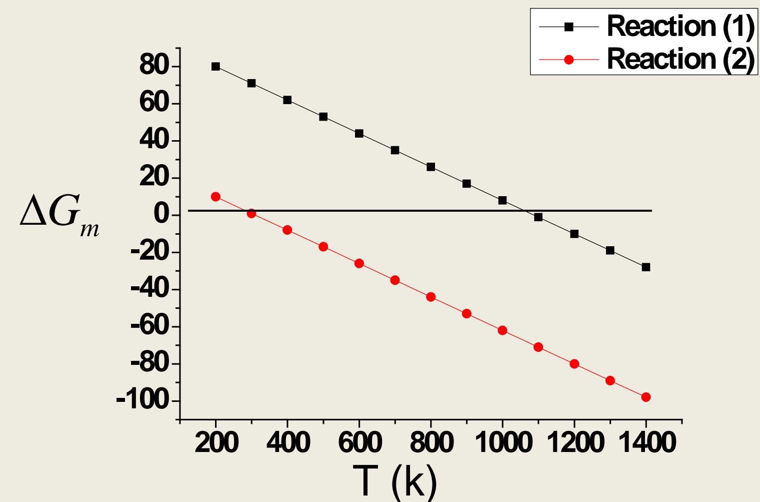
Example



(1) $TiCl_4 + 2BCl_3 + 5H_2 \rightarrow TiB_2 + 10HCl$

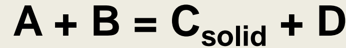


(2) $TiCl_4 + B_2H_6 \rightarrow TiB_2 + 4HCl + H_2$



3.1. Process Principle

Thermodynamic aspects II



$A + B = C_{solid} + D$

Where A and B are supplied gas, C is solid product (deposition)
Gas D diffuses away from the substrate during process

- In a point of view of product (C_{solid}) during CVD process,

Equilibrium vapor pressure of solid C →

Partial pressure of C in the gas phase

Chemical potential of solid product

$$\mu_{C_{solid}} = \mu_C^0 + RT \ln P_C^{\mathrm{v.p}}, \qquad \mu_{C_{gas}} = \mu_C^0 + RT \ln P_C^{\mathrm{gas}}$$

Chemical potential of gaseous state

$$\Delta\mu_C = -RT \ln \frac{P_C^{\mathrm{gas}}}{P_C^{\mathrm{v.p}}}, \qquad \alpha = \frac{P_C^{\mathrm{gas}}}{P_C^{\mathrm{v.p}}}$$

saturation ratio

In order for deposition to be possible, $P_C^{\mathrm{gas}} > P_C^{\mathrm{v.p}}$
So, the gas phase reaction on the growing surface is sufficiently fast → CVD is proceeded

Driving Force for Deposition in the CVD Process, Journal of Materials Science Letters, 13, 1437-1439 (1994)

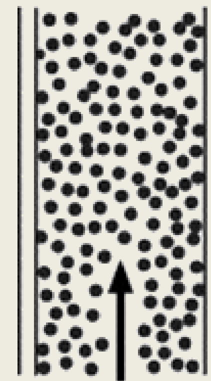
3.1. Process Principle

Efficient contact between the gas phase and the growing surface

- The simplest ones are **fixed bed and flat hearth**, whose particles do not move relative to each other

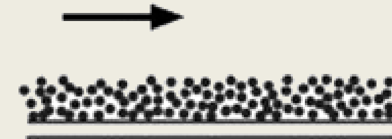
- If the gas flow rate is sufficiently low, the gas merely percolates through the void species between the stationary particles

- Often used for CVD processes devoted mainly to catalyst preparation and CNT synthesis



Fixed bed

Gas flows over powders



Flat hearth

Gas flows through powders

In both cases, particles do not move relative to each other

Principles and applications of CVD powder technology, Vahlas et al, Materials Science and Engineering R 53 (2006) 1–72

3.1. Process Principle

Efficient contact between the gas phase and the growing surface

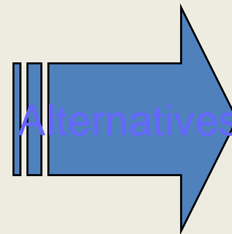
drawbacks of simple fixed bed and flat hearth

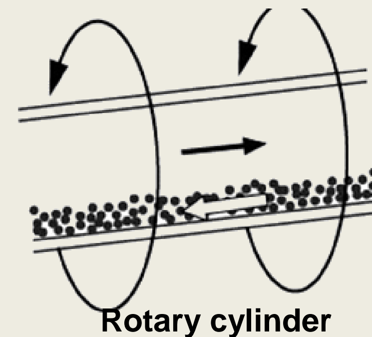
(i) - diffusion limitations in the case of chemical vapor infiltration
- inefficient contact between the gas reactants and the inner particles;

(ii) impossible to perform deposition on the entire surface of each particle due to contact points among them and with the reactor walls

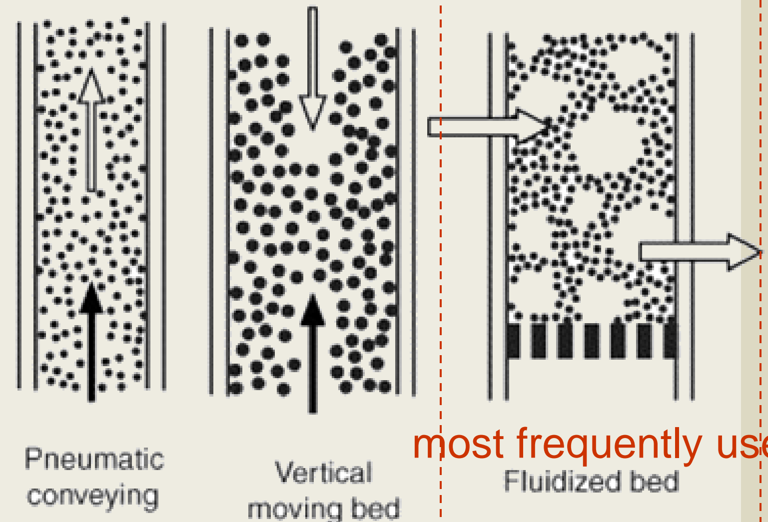
(iii) when high growth rates and/or high thickness is aimed, clogging phenomena can occur;

(iv) due to all above drawbacks, the scale-up of these processes is problematic.





each particle will present its entire surface to the gaseous reactants during the process



most frequently used

Principles and applications of CVD powder technology, Vahlas et al, Materials Science and Engineering R 53 (2006) 1–72

3.2. Advantages & Disadvantages

Advantages	Disadvantages
• Capability of producing highly dense and pure materials • Non line-of-sight process. Can be used to coat complex-shaped components uniformly	• Include the chemical and safety hazards • Toxic, corrosive, flammable, and/or explosive precursor gases • Difficult to deposit multi-component materials with well-controlled stoichiometry because different precursors have different vaporization rates

3.3. Atomic Layer Deposition

Definition of ALD

- ALD is a method of applying thin films to various substrates with atomic scale precision.
- Similar in chemistry to chemical vapor deposition (CVD), except that the ALD reaction breaks the CVD reaction into two half-reactions, keeping the precursor materials separated during the reaction.
- ALD film growth is self-limited and based on surface reactions, which makes achieving atomic scale deposition control possible.
- By keeping the precursors separated throughout the coating process, atomic layer thickness control of film grown can be obtained as fine as atomic/molecular scale per monolayer.
- Introduced in 1974 by Dr. Tuomo Suntola and co-workers in Finland to improve the quality of ZnS films used in electroluminescent displays.
- Recently, it turned out that ALD also produces outstanding dielectric layers and attracts semiconductor industries for making High-K dielectric materials.

Ref: "Atomic Layer Deposition," Wikipedia: The Free Encyclopedia, Wikimedia Foundation, 24 April 06.

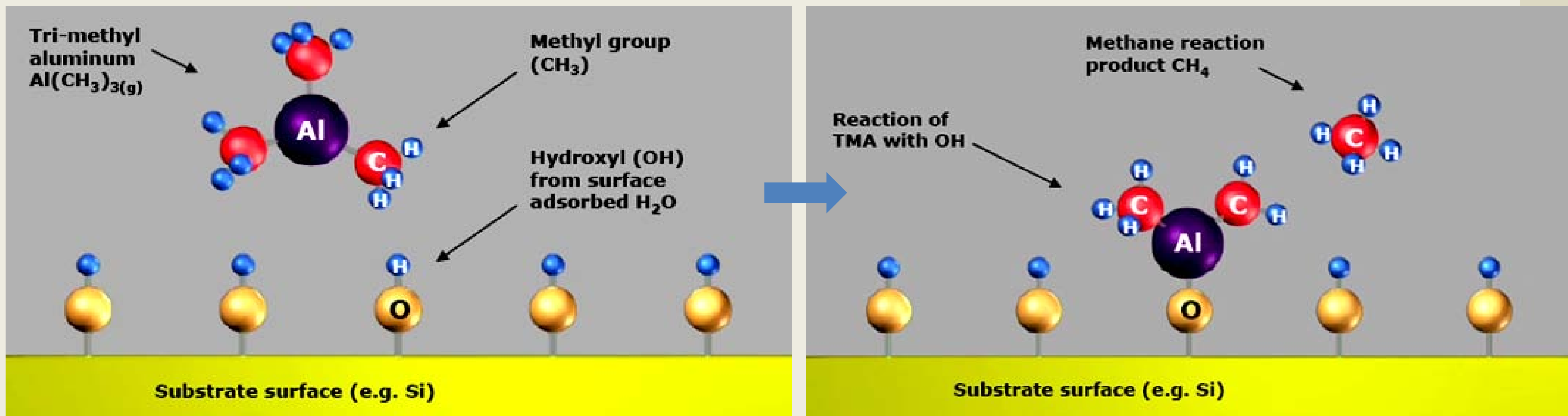
3.3. Atomic Layer Deposition

Definition of ALD

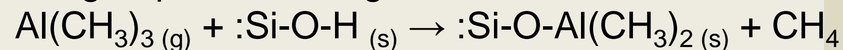
- Releases sequential precursor gas pulses to deposit a film one layer at a time on the substrate.
- The precursor gas is introduced into the process chamber and produces a monolayer of gas on the wafer surface. A second precursor of gas is then introduced into the chamber reacting with the first precursor to produce a monolayer of film on the wafer surface.
  Two fundamental mechanisms:
  - *Chemisorption saturation process*
  - *Sequential surface chemical reaction process*
- Example: ALD cycle for Al_2O_3 deposition
- Since each pair of gas pulses (one cycle) produces exactly one monolayer of film, the thickness of the resulting film may be precisely controlled by the number of deposition cycles.

3.3. Atomic Layer Deposition

Example: ALD cycle for Al_2O_3 deposition



Trimethyl Aluminum (TMA) reacts with the adsorbed -OH groups, Producing methane

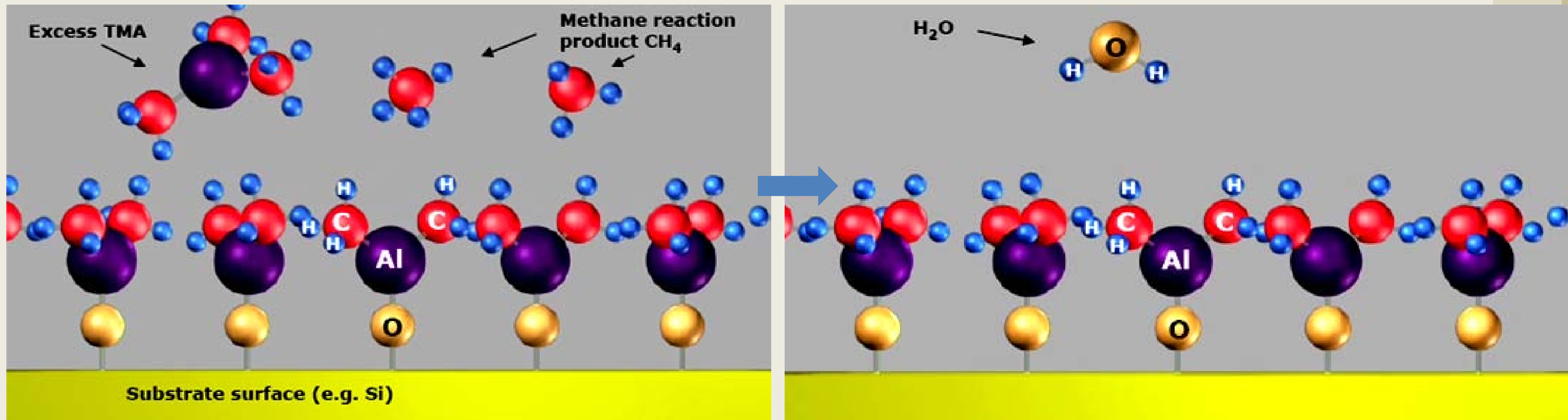


$Al(CH_3)_{3\,(g)}$ + :Si-O-H $_{(s)}$ → :Si-O-$Al(CH_3)_{2\,(s)}$ + CH_4

Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www.cambridgenanotech.com/>.

3.3. Atomic Layer Deposition

Example: ALD cycle for Al_2O_3 deposition



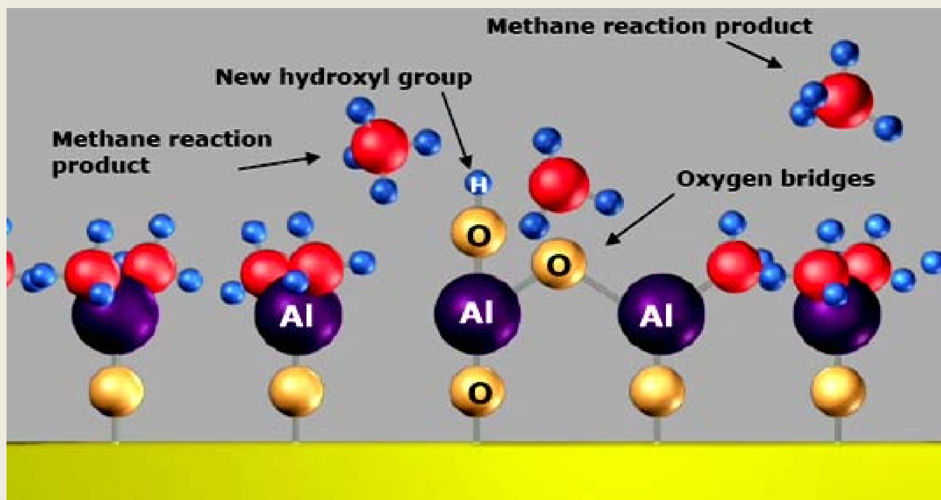
Trimethyl Aluminum (TMA) reacts with the adsorbed -OH groups, TMA does not react with itself, terminating the reaction to one later. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.

After the TMA and methane reaction product is pumped away, water vapor (H_2O) is pulsed into the reaction chamber.

Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www.cambridgenanotech.com/>.

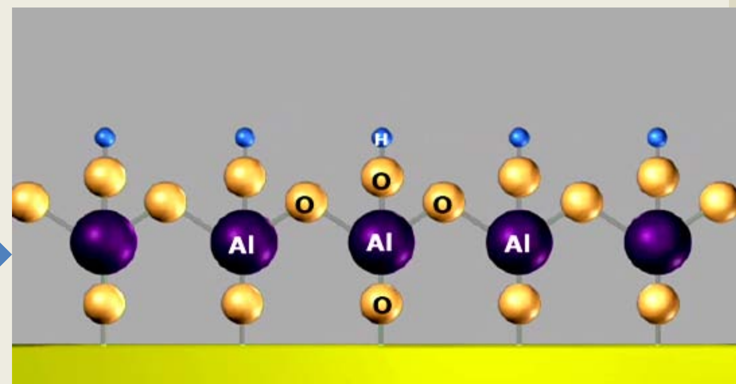
3.3. Atomic Layer Deposition

Example: ALD cycle for Al_2O_3 deposition

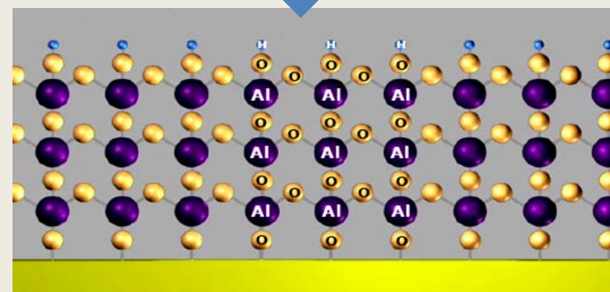


H_2O reacts with the dangling methyl groups on the new surface forming aluminum oxygen (Al-O) bridges and hydroxyl surface groups, waiting for a new TMA pulse. Again methane is the reaction product

$2H_2O_{(g)} + :Si\text{-}O\text{-}Al(CH_3)_{2\,(s)} \rightarrow :Si\text{-}O\text{-}Al(OH)_{2\,(s)} + 2CH_4$



The reaction product methane is pumped away, Excess H_2O vapor does not react with the hydroxyl surface groups, again causing perfect passivation to one atomic layer

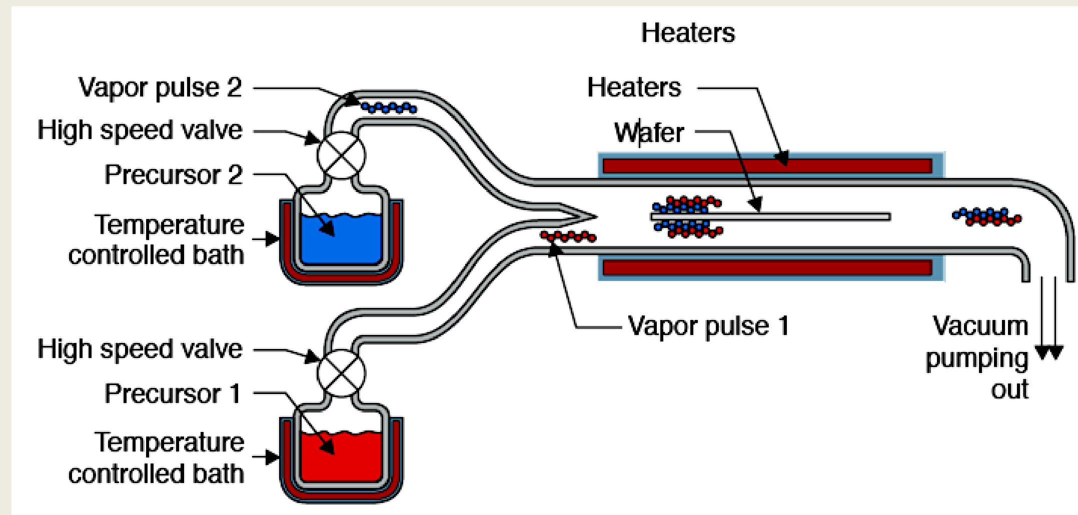


Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www.cambridgenanotech.com/>.

3.3. Atomic Layer Deposition

ALD reactors

- **Closed system chambers** (most common)
  - The reaction chamber walls are designed to effect the transport of the precursors.



Schematic of a closed ALD system

Ref: "Technology Backgrounder: Atomic Layer Deposition," IC Knowledge LLC, 24 April 06.