Introduction to CVD (Chemical Vapor Deposition) System / Process

2001. 6. 조 현상

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1. Classification and Characteristics of CVD equipment

(1) Classification by Process condition

Process condition	Classification	Characteristic
Pressure	High vacuum	Pull pumping when process progress
	LP (Low Pressure) CVD	Low vacuum (10E-3 ~ 10E0)
	AP (Atmosphere Pressure) CVD	ATM (10E2 ~)
Activation energy	Thermal CVD	Thermal reaction (relative high Heterogeneous reaction) Dense film, low deposition rate
	PE (Plasma Enhanced) CVD	Plasma Enhanced reaction (relative high Homogeneous reaction) Porous film. High deposition rate, Particle issue
	Photo CVD	Activated by Photo energy

(2) Other classifications

1) By wafer handling type

ⅰ) Batch process type

-. Furnace boat / Disk / Other cluster process systems

ⅱ) Single wafer process type

2) MOCVD (Metal Organic CVD)

ⅰ) Metal Organic precursor for variety of metal deposition.

ⅱ) Relative low temperature and good step coverage.

ⅲ) Complex source feed system (ex. LDS) for using liquid source.

3) ALD (Atomic Layer Deposition)

ⅰ) Using adhesion energy (wholly heterogeneous reaction).

ⅱ) Cyclic source feed and remove.

ⅲ) Excellent step coverage and uniformity control.

2. CVD process.

(1) Introduction

1) The formation of a non-volatile solid film on a substrate by reaction of vapor phase chemical (reactants) that contain the required constituents.

2) Material deposition process by using chemical vapor.

3) Vapor include gas and vaporized liquid.

4) Superior characteristics

ⅰ) High purity deposits can be achieved.

ⅱ) Great variety of chemical compositions can be deposited.

ⅲ) Good economy and process control are possible for many films.

ⅳ) Some films cannot be deposited with adequate film properties by other methods.

(2) CVD Process classification

1) Epitaxy

ⅰ) Denotation : Deposit a thin layer of single crystal material upon the surface of a single crystal substrate.

ⅱ) Relative high temperature to form crystal structure

ⅲ) Homoepitaxy : When the deposited material is same with substrate material

ⅲ) Heteroepitaxy : When the deposited material is different to substrate material

2) Deposition :

ⅰ) Denotation : Depositing amorphous or poly-crystal material.

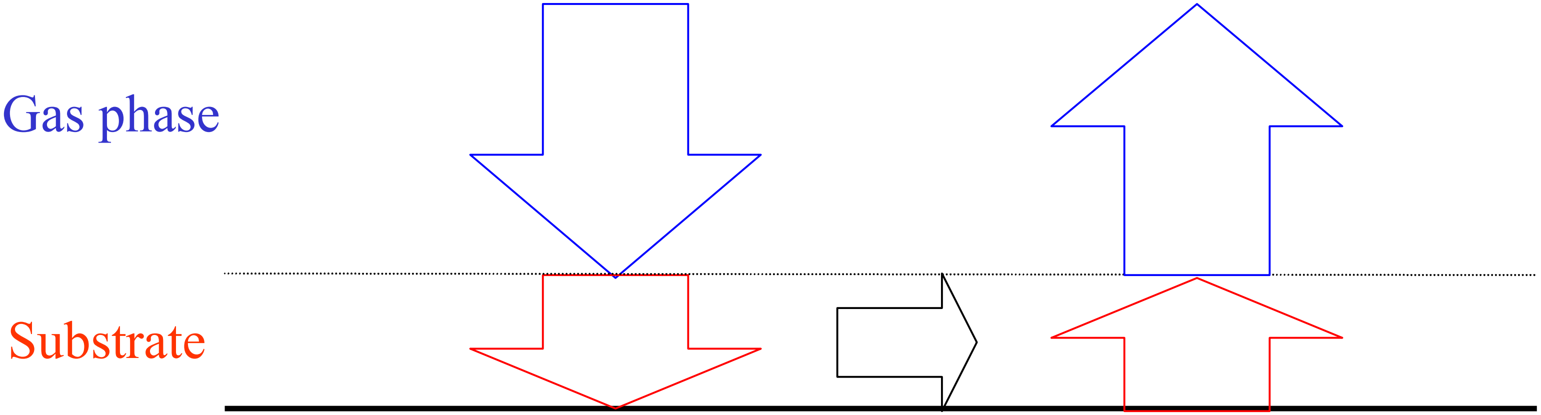
Substrate

(3) Source feed mechanism

1) Fundamental procedure of CVD source supply mechanism

ⅰ) Reactants are transported to the substrate surface

ⅴ) The products are transported away from the surface



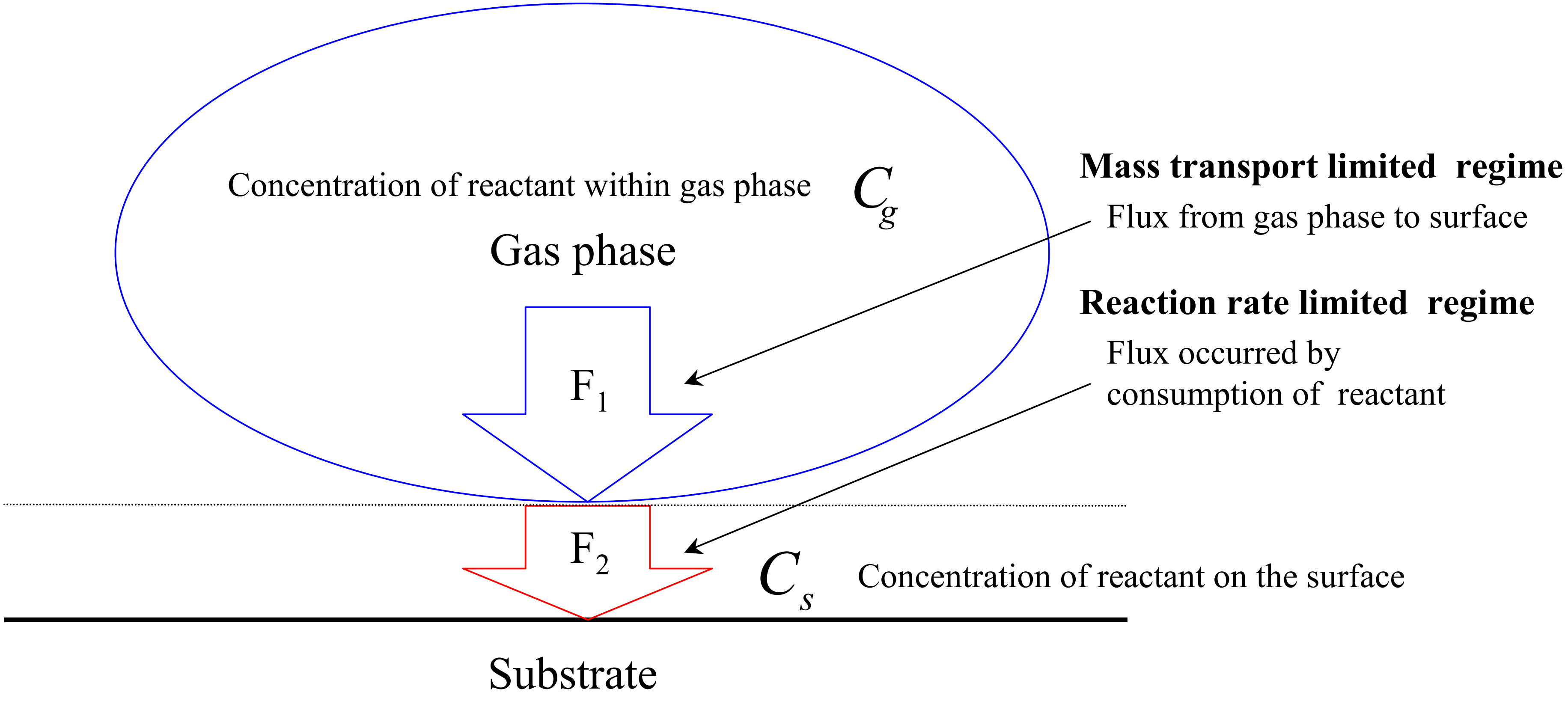
ⅱ) Reactants are absorbed on the substrate

ⅲ) Chemical reaction produce film formation and reaction products

ⅳ) Reaction products are desorbed from the surface

2) The Grove CVD source flux transfer model (For step 1 and 3) :

A. S. Grove developed this model at 1966 - ‘Mass transfer in Semiconductor technology’



Concentration of reactant within gas phase C_g

Gas phase

F_1

F_2

C_s Concentration of reactant on the surface

Substrate

Mass transport limited regime

Flux from gas phase to surface

Reaction rate limited regime

Flux occurred by
consumption of reactant

ⅰ) Mass Transport limited regime (Flux F_1)

-. Assumption :

F_1 is linearly proportional to the concentration difference between the reactant in the C_g (concentration of reactants in the bulk gas) and C_s (concentration of reactants on the surface)

-. The constant of proportionality : h_g - gas phase mass transfer coefficient

$$F_1 = h_g(C_g - C_s)$$

Where,

C_g : Concentration of reactants in the bulk gas

C_s : Concentration of reactant on the surface

h_g : gas phase mass transfer coefficient

ⅱ) Reaction rate limited regime (Flux F_2)

-. Assumption :

F_2 is linearly proportional to the surface concentration of the reactant.

-. The constant of proportionality : k_g - chemical surface reaction rate coefficient

$$F_2 = k_s C_s$$

Where,

C_s : Concentration of reactant on the surface

k_g : chemical surface reaction rate coefficent

ⅲ) Two CVD control region

-. At steady state, the fluxes $F_1=F_2$

$$F_1 = h_g(C_g - C_s) = k_s C_s = F_2$$

$$\therefore C_s = \frac{C_g}{1+\frac{k_s}{h_g}}$$

-. Surface-reaction control case : $h_g >> k_s$, $\mathbf{C_s \rightarrow C_g}$

$$\therefore C_s = \frac{C_g}{1+\cancel{\frac{k_s}{h_g}}} \quad \text{'0'}$$

-. Mass-transfer control case : $h_g << k_s$, $\mathbf{C_s \rightarrow 0}$

$$\therefore C_s = \frac{\cancel{C_g}}{1+\cancel{\frac{k_s}{h_g}}} \; \infty \quad \text{'0'}$$

ⅳ) Relation between growth rate and source supply mechanism

-. Growth rate of CVD deposited film

$$V = \frac{F}{N_1} = \frac{k_s h_g}{k_s + h_g} \frac{C_g}{N_1}$$

F from F_2=F and [C_s - C_g] relation is substituted for it.

Where,

N_1 : Number of atoms incorporated into a unit volume of the film (atoms/cm^3)

F : Flux of source to the film (atoms/cm^2s)

-. Let's define C_g with C_T and Y

$$C_g = C_T Y$$

Where,

C_T : Total number of molecules per cm^3

Y : Mole fraction of the reaction species

-. Expression for Film growth rate by exchange C_T and C_g

$$V = \frac{F}{N_1} = \frac{k_s h_g}{k_s + h_g} \frac{C_T}{N_1} Y$$

→ Growth rate should be proportional to the mole fraction of reactants in the gas phase

: Agreed with exp. Result when Y is small

: When $SiCl_4$, DCS etc. for poly dep., Cl affects the growth rate → reduce.

→ The Growth rate at constant Y is controlled by the smaller value of k_s and h_g in the limited condition.

∨) Growth rate related with CVD control region

-. By above equation we can suppose two limited condition

$$V = C_T k_s \frac{Y}{N_1}$$: at surface-reaction control $$k_s = k_0 e^{-\frac{E_a}{kT}}$$

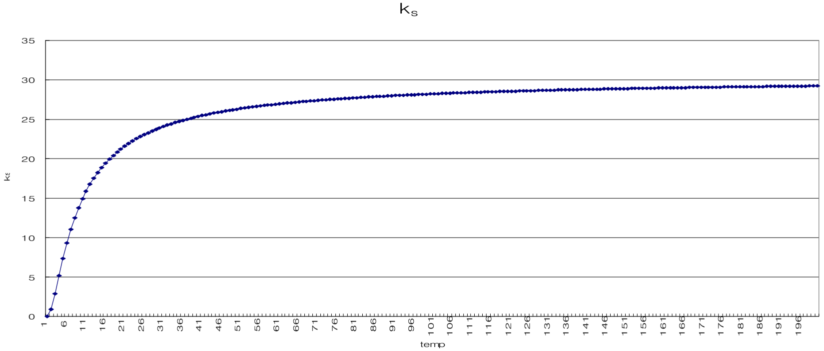
→ k_s describe the kinetics of the chemical reaction at substrate surface

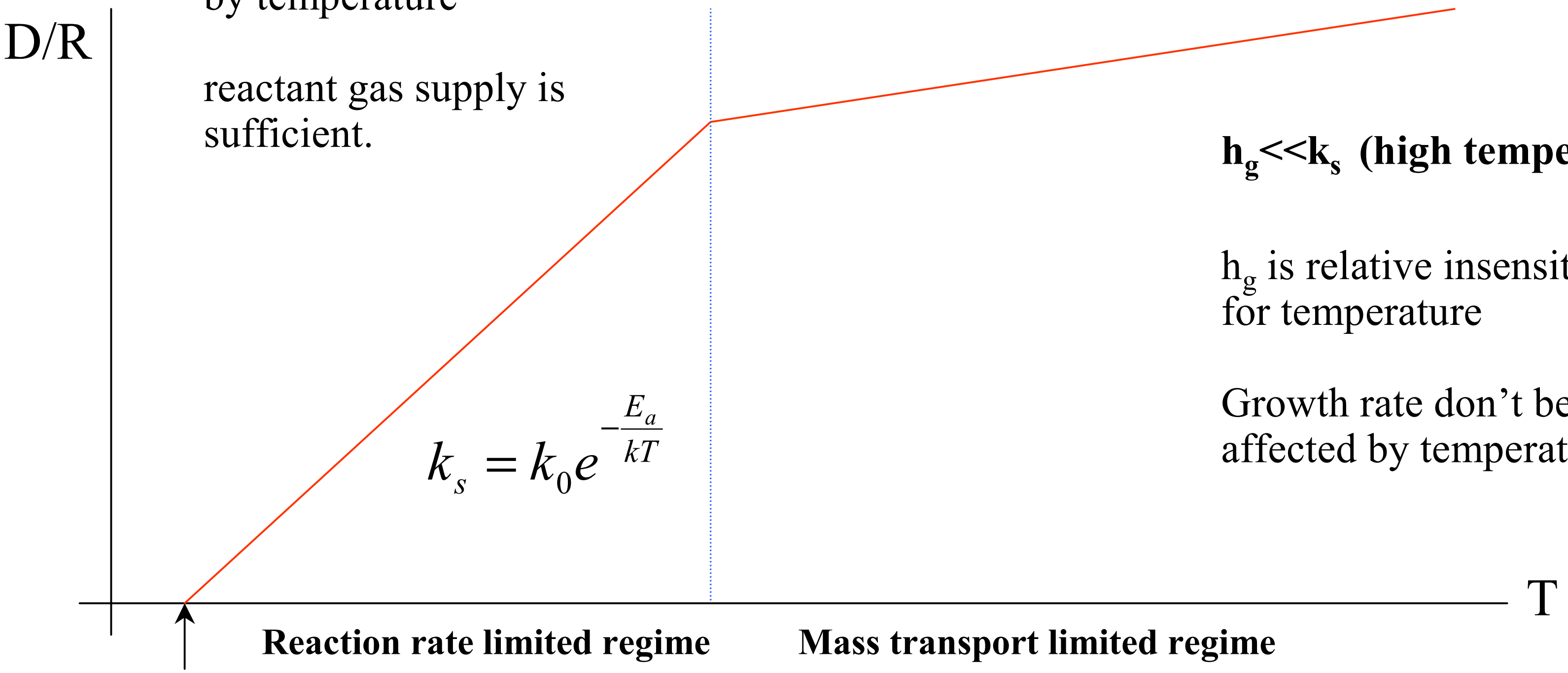
→ At the condition of thermal activated reaction, it can be represented by Arrhenius type equation.

$$V = C_T h_g \frac{Y}{N_1}$$: at mass-transfer control

→ hg is relatively temperature insensitive, and depends primarily on the gas flow fluid dynamics in the reactor

ⅵ) Activation energy with Arrhenius plot





h_g>>k_s (low temperature)

k_s is rapidly increased
by temperature

reactant gas supply is
sufficient.

$$k_s = k_0 e^{-\frac{E_a}{kT}}$$

h_g<<k_s (high temperature)

h_g is relative insensitive
for temperature

Growth rate don’t be
affected by temperature

Reaction rate limited regime

Mass transport limited regime

Incubation time

※ Arrhenius equation and activation energy

1) Reaction rate of reactor which depend on temperature is well predicted by Arrhenius equation.

2) This equation is formulated by J. Hood and named by Svante Arrhenius.

$$R(t) = R_0 e^{-\frac{E_a}{kT}}$$

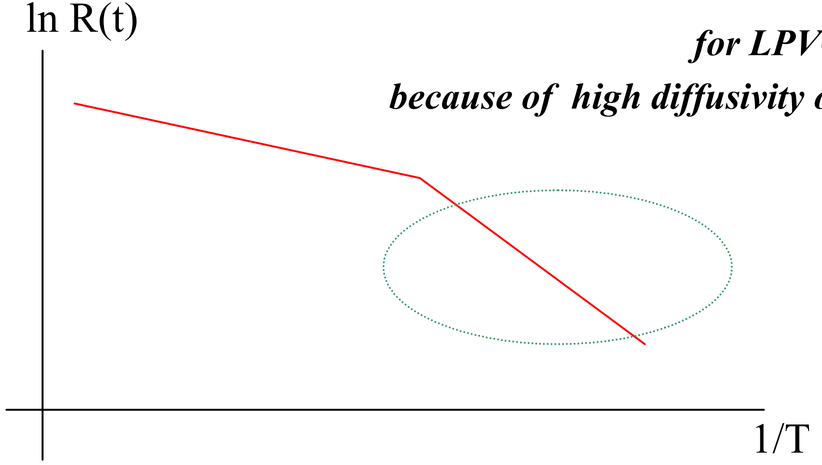
Where, E_a and R_0 is arrhenius parameter

R(t) : rate constant at temperature T (°K)

R_0 : frequency factor

E_a : activation energy (eV)

k :Boltzmanns constant (8.6E-5 eV/ °K)



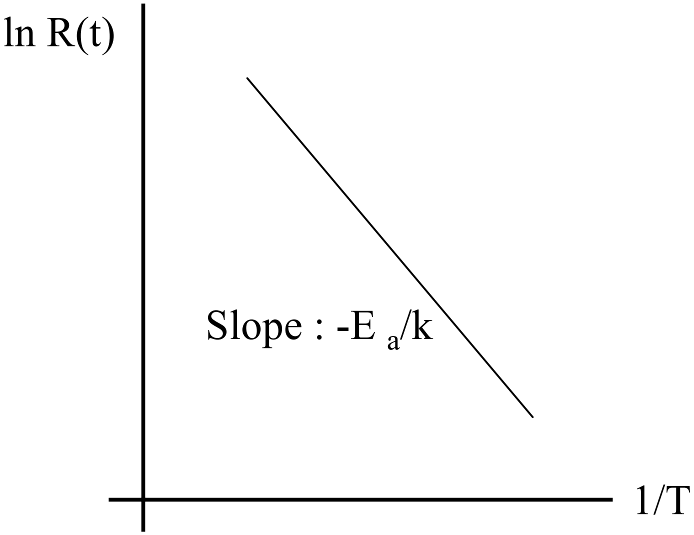
※ We use reaction-rate limited regime for LPVCD process because of high diffusivity of reactants

3) If the equipment is operated by thermal energy, it is possible to define arrhenius relation

4) Arrhenius equation and relation use reciprocal temperature axis (1/T) and log scale R(t) (ln R(t))

5) Determination of Arrhenius parameters (E_a and R_0)

ⅰ) by Graphic



If the line between ln R(t) and 1/T is straight,

This reaction obeys the Arrhenius relation

and proper thermal process

ⅱ) by analytical technique

$$R_1(t) = R_0 e^{-\frac{E_a}{kT_1}} \qquad R_2(t) = R_0 e^{-\frac{E_a}{kT_2}}$$

put, $R_0 = R_0$ and arrange for E_a

$$\therefore E_a = \frac{k \ln[\frac{R_2(t)}{R_1(t)}]}{\frac{1}{T_2} - \frac{1}{T_1}}$$

ⅵ) Limitation of Grove model

-. Neglect the flux of reaction products from surface to gas phase after reaction.

-. Assume the reaction rate flux depends linearly on the surface concentration.

(It is true only for low values of Y)

-. Neglect the effect of temperature gradient on the gas phase mass transfer.

-. The model predicts the two regions of the growth process.

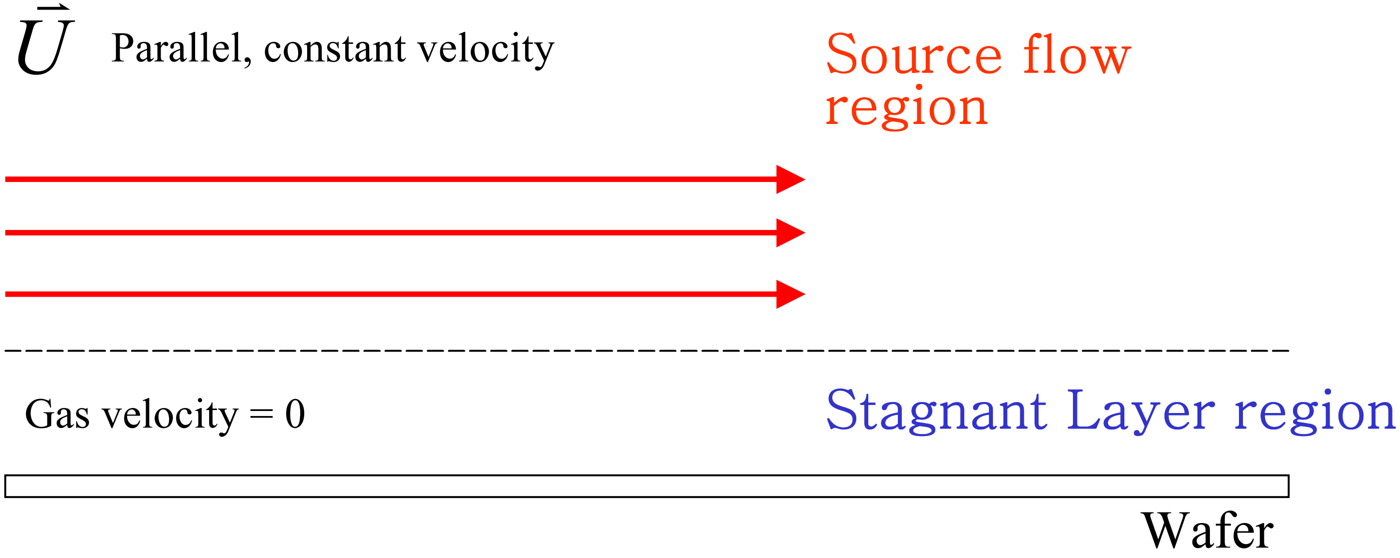
-. Provide a reasonable estimate to the values of k_s and h_g from the growth rate data.

-. It helps to understand of thermal CVD deposition mechanism.

3) Boundary Layer Model

ⅰ) Stagnant film model

-. Assume two gas region on the wafer surface



$\vec{U}$ Parallel, constant velocity

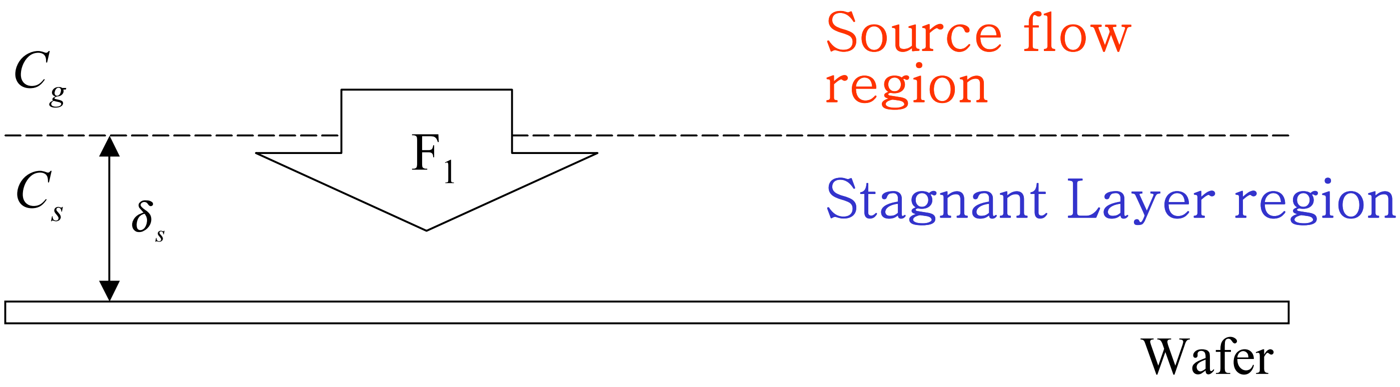
Source flow region

Gas velocity = 0

Stagnant Layer region

Wafer

-. Mass transfer mechanism with stagnant layer model



From gas phase mass transfer model and Fick's first law

$$F_1 = D_g \frac{(C_g - C_s)}{\delta_s}$$

Where,

F_1 : Mass flux

D_g : Diffusion coefficient (species dependant)

C_g : Concentration of reactant species in the source flow region

C_s : Concentration of reactant species in the stagnant film region

δ_s : Thickness of stagnant film layer

-. Fick’s first law

Representation of a mechanism of diffusion across a given plane is proportional to the concentration gradient across the plane

$$\vec{J} = -D\frac{\partial C(x,t)}{\partial x}$$

Where,

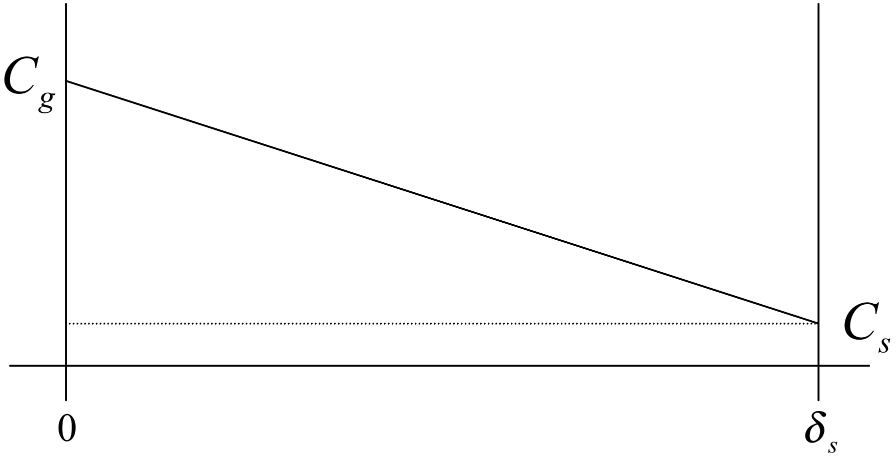
J [kg/m^{2}s] : Flux from high concentration region to low concentration region

D [m^2/s] : Diffusion constant for the material

C(x,t) [kg/m^3] : Concentration profile along time

x [m] : distance between two region

-. Concentration gradient



$$\frac{C_g - C_s}{\delta_s}$$

Where,

C_g : Concentration of reactant species in the source flow region

C_s : Concentration of reactant species in the stagnant film region

δ_s : Thickness of stagnant film layer

If δ_s is thinner, concentration gradient is steeper.

Therefore,

The driving force of reactant species for gas phase layer to wafer is increased.

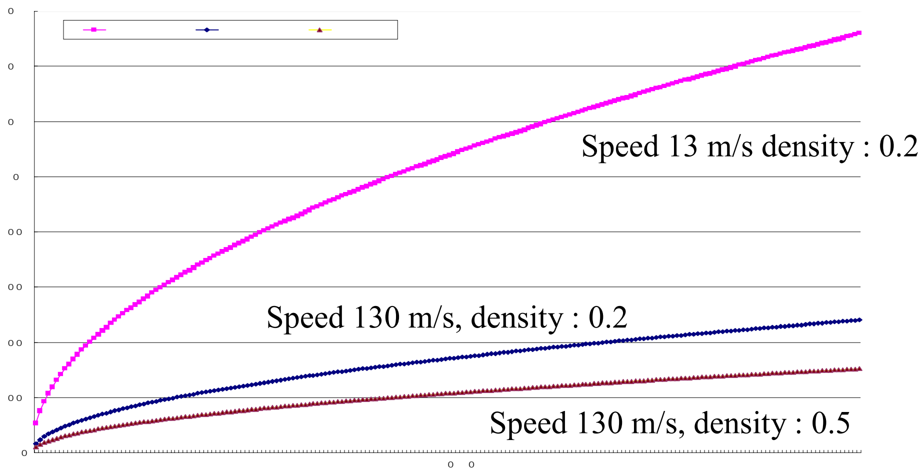
ⅱ) Parameters of the boundary layer

-. Boundary layer (adaptation of stagnant film model to real system) :
Transient region between solid surface (where the gas velocity is zero) and free gas stream (where gas velocity is constant, U) that occurred by **friction** between wafer surface and gas stream

-. Boundary layer thickness :
The height that the velocity of gas stream is 99% of the free stream

$$\delta \quad) = \sqrt{\frac{\mu}{\vec{U}}}$$

Where,
μ : viscosity of gas
d : gas density
U : distance along the wafer plate



-. Average layer thickness

$$\delta = \frac{}{}\int_0^L \delta\ \ x)dx \quad = \frac{}{} L\ \frac{\mu}{dUL})^{\frac{}{2}} \quad = \frac{}{3}\frac{L}{\sqrt{N_R}}$$

Where,

$${}_R = \frac{dUL}{\mu}$$: Reynolds number $$\frac{Inertial\_force(d \times \vec{U}^2 \times L^2)}{Viscous\_force(\mu \times \vec{U} \times L)}$$

※ Reynolds number :

ⅰ) Dimensionless, used in fluid dynamics which represent the ratio of the magnitude of ***inertial effects to viscous effect*** in fluid motion

ⅱ) Decision factor for flow type (Laminar / Turbulence)

-. $N_R > 3000$: Turbulence

-. $2000 > N_R > 3000$: Phase shift

-. $N_R < 2000$: Laminar flow

cf For tube

$${}_R = \frac{dUD}{\mu}$$

Where,

μ : viscosity of gas

d : gas density

U : distance along the wafer plate

D : diameter of tube

(4) Reaction characteristics

1) Reaction classification

ⅰ) Homogeneous reaction

-. Reaction in the gas phase.

→ Forming gas phase cluster and can generate particle.

→ Poor adhesion / low density / defect in the deposited film.

→ Consume reactants and can cause decrease in deposition rate.

ⅱ) Heterogeneous reaction

-. Reaction on the wafer wafer.

-. Desired reaction :

→ Reaction occur selectively on heated wafer.

→ Produce good quality film.

2) Deposition procedure

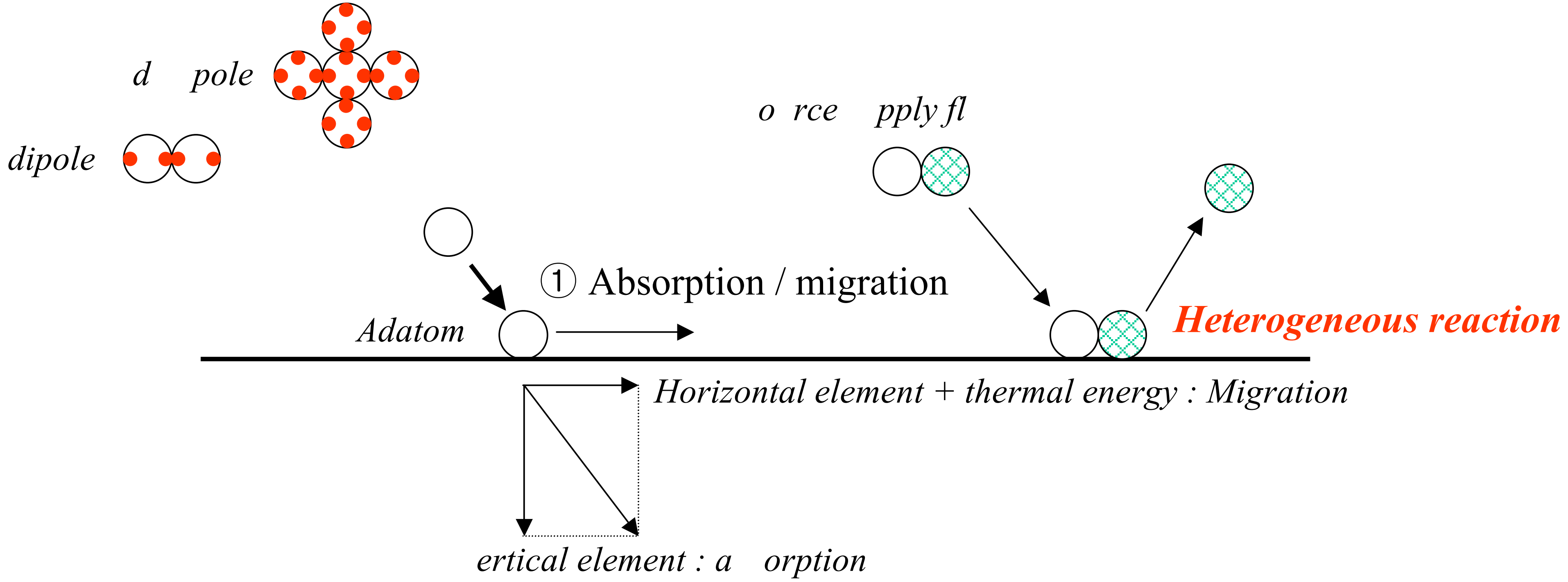
※ Two types of Absorption

-. **Physisorption** : absorption with electron exchange
(absorption energy : ~ 0.25 eV)

-. **Chemisorption** : absorption without electron exchange
(absorption energy : 8~10eV)

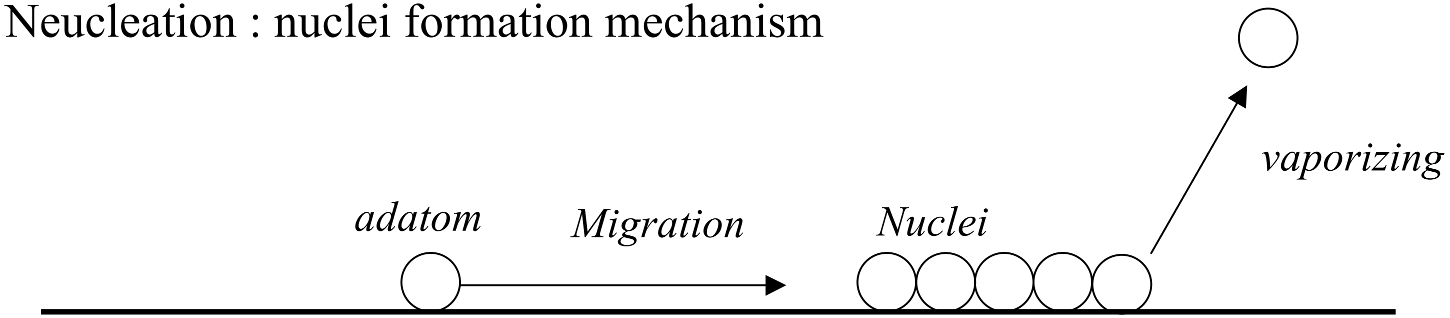
ⅰ) Adatom :

Homogeneous reaction



ⅱ) Critical radius and incubation time

② Neucleation : nuclei formation mechanism



※ Critical radius (by Gibbs free energy)

1) Theory of nucleation was developed by Gibbs.

2) Along the particle growth : New surface is create

⇒ Surface free energy is positive : to create surface, require added energy

⇒ Volume free energy is negative :

Precipitates grow → solute is removed from solution

→ overall material system return closer to equilibrium

3) Summation of above two free energy along radius of particle reveals critical radius C_R

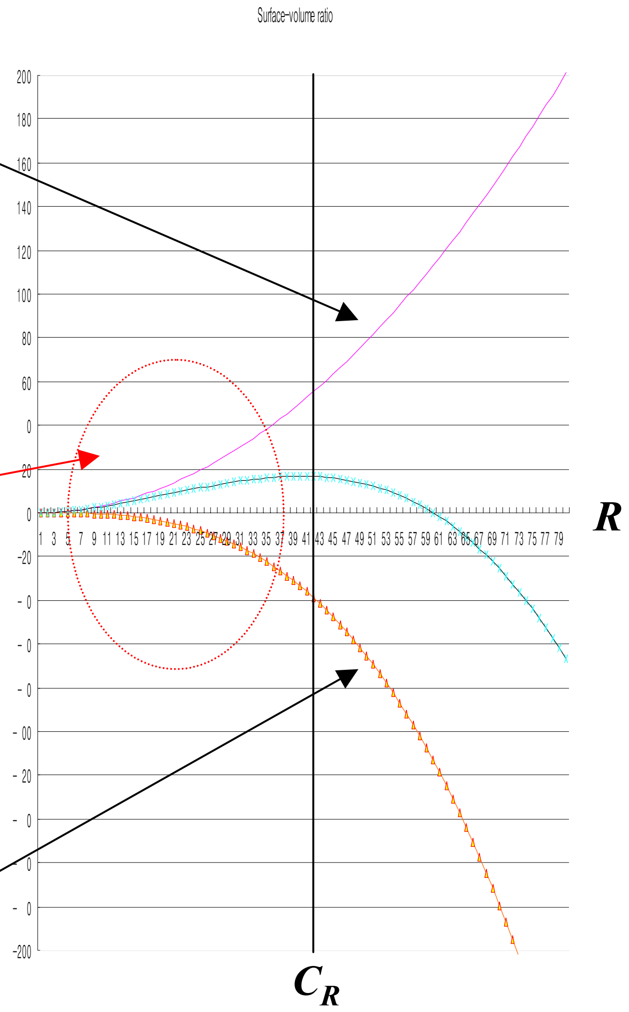
Surface free energy

$$S = 4\pi r^2$$

High surface to volume ratio

Volume free energy

$$V = \frac{4}{3}\pi r^3$$



System tend to decrease its free energy to go to stable state.

That means maximum free energy corresponds to the state of minimum stability of the particle.

Therefore, if the radius is less than ***C_R*** a particle can lower its free energy by decreasing its size.

This characteristic can be used for ***selective deposition*** since the time to reach C_R is different for each material and condition.

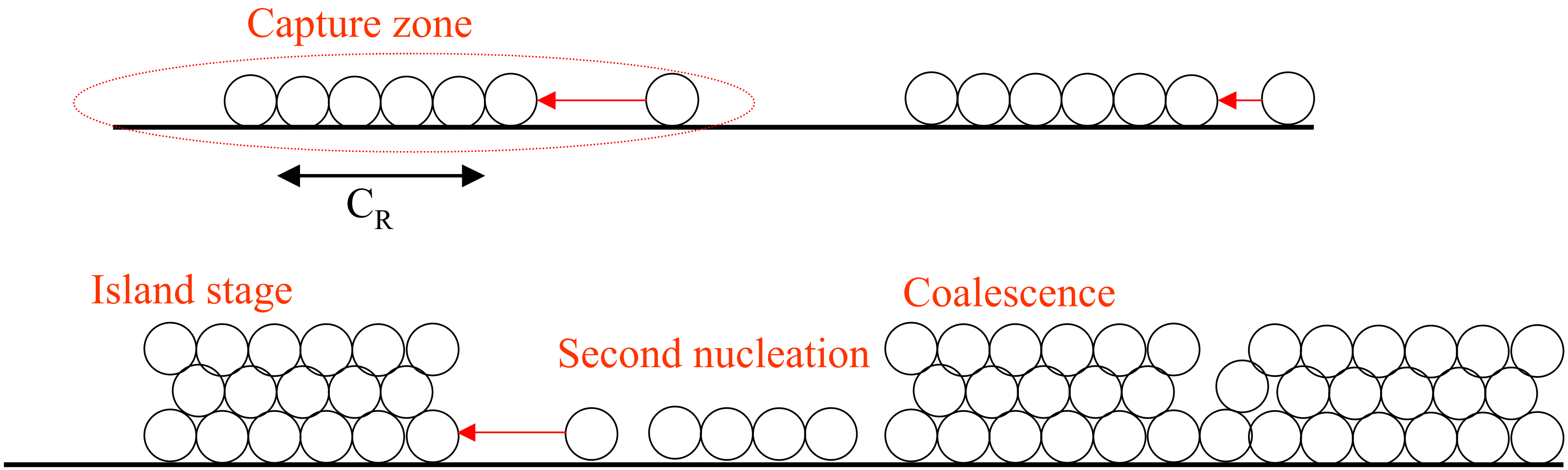
The time when all particle reach to C_R and can form film is ***incubation time***.

If source supply stop before the particle reach to C_R, the particle will be dissolved

It is another important characteristic of thermal CVD characteristic.

ⅲ) Film formation

③ **Growth** : Film formation by merge of nuclei



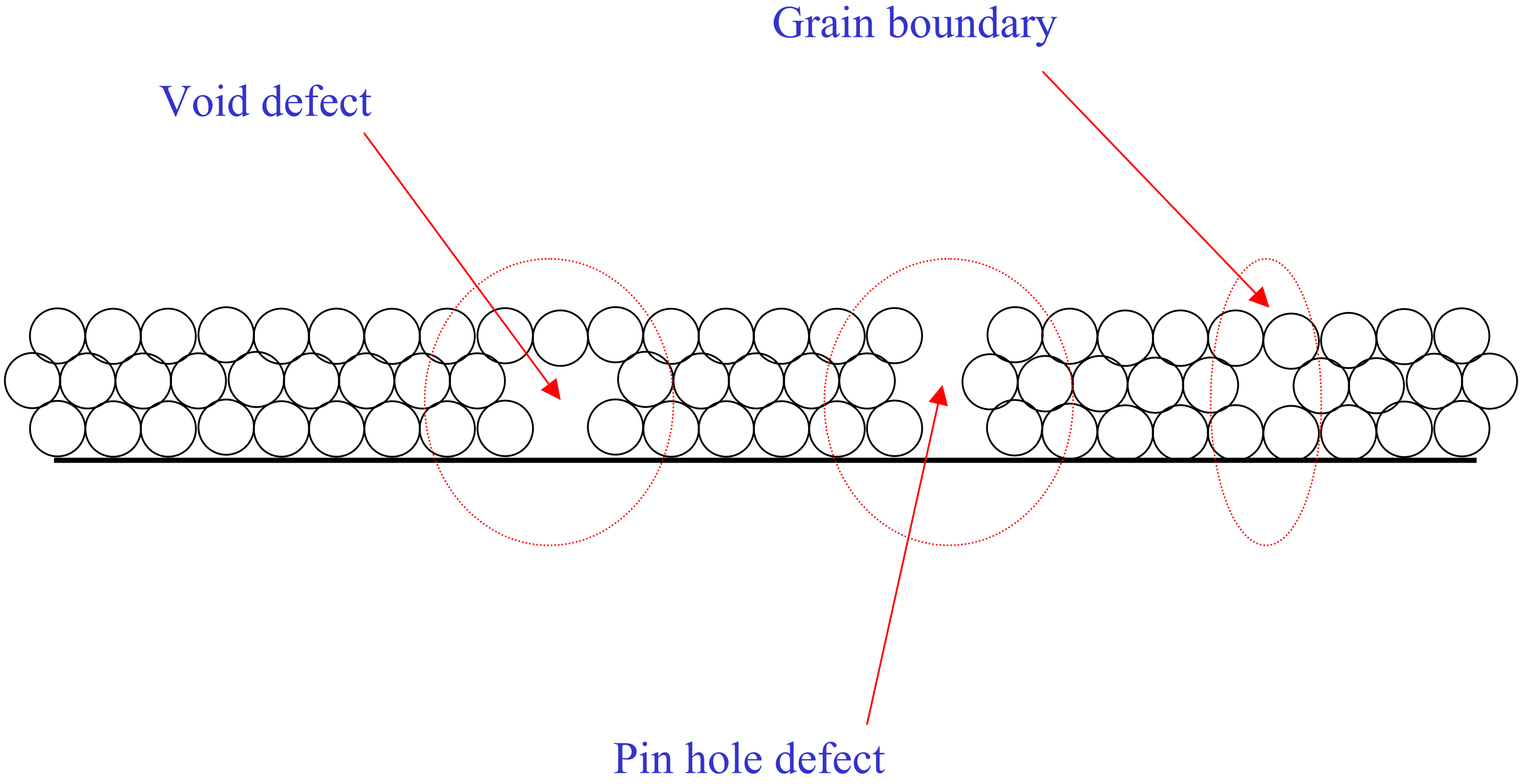
-. **Island stage** : 3 dimensional growth, can find crystal structure

-. **Coalescence** : Nuclei contact each other and form lager and rounded shape

-. **Second nucleation** : formed at exposed area generated by forming of coalescence which grow to vertical direction and attract adatoms.

ⅲ) Film formation

④ Film formation


Grain boundary

Void defect

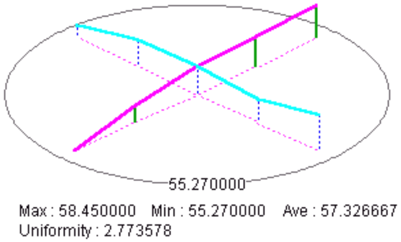
Pin hole defect

(5) Process result characteristics

1) Deposition rate : Deposit thickness per minute (in general, Å /min)

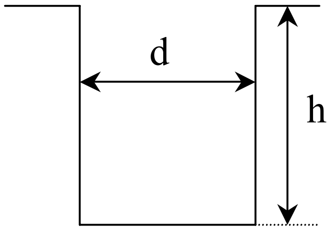
2) Uniformity : Process uniformity estimation factor

$$\frac{\max - \min}{average * 2} \times 100(\%)$$



3) Aspect ratio : Shape characteristic of via, contact

$$\frac{Horizontal\_length}{Vertical\_height} \times 100$$



4) Step Coverage : Performance that deposit inner side of via

$$\frac{t_{\min}}{t_{MAX}} \times 100(\%)$$