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진공 박막 공정 기술

CVD & ALD

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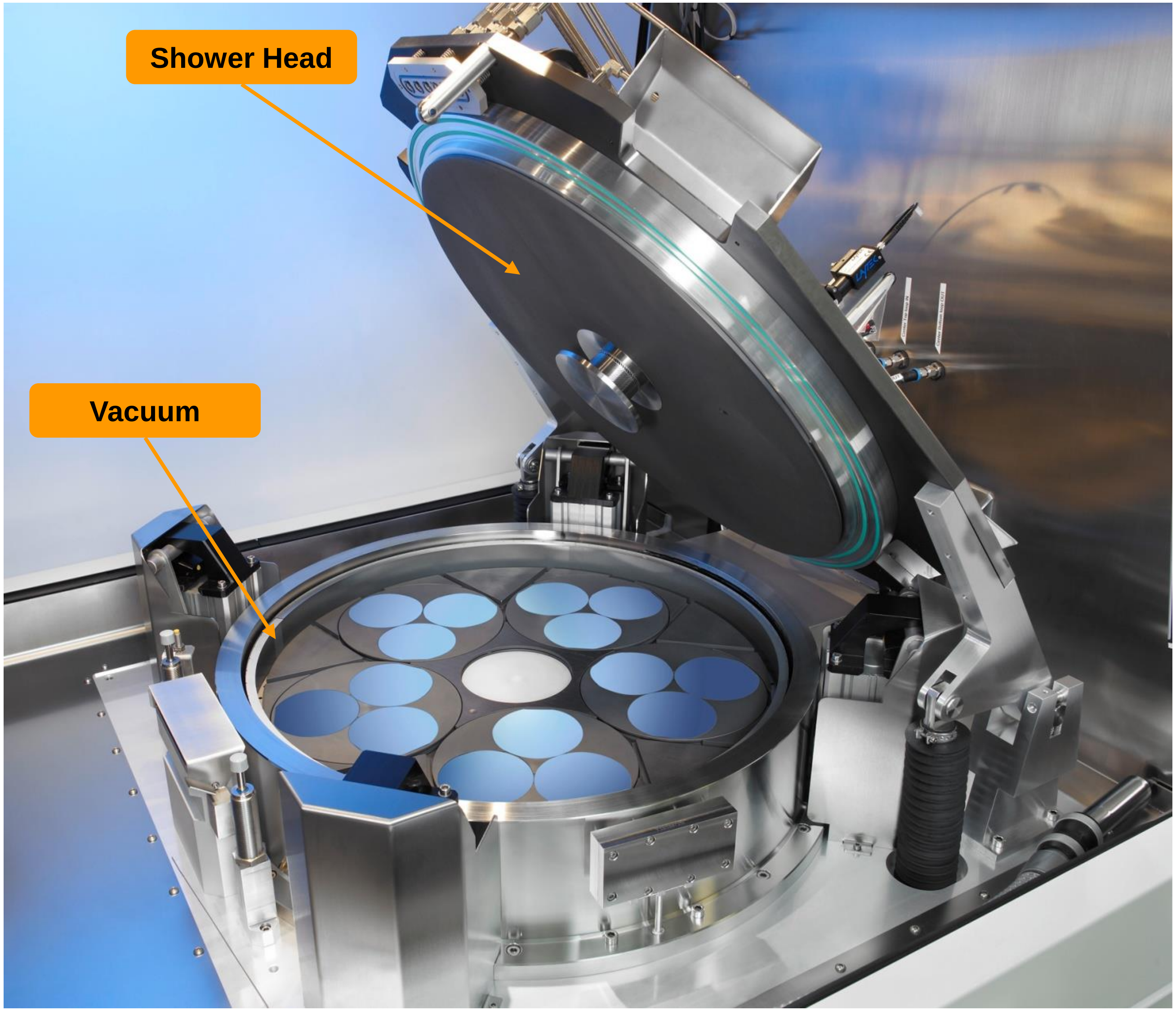
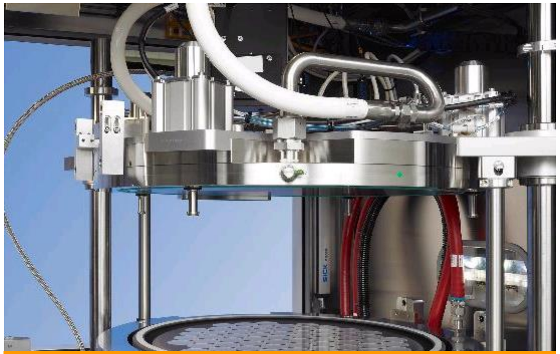
Introduction to Chemical Vapor Deposition (CVD)





Gas & Precursor Feeding System

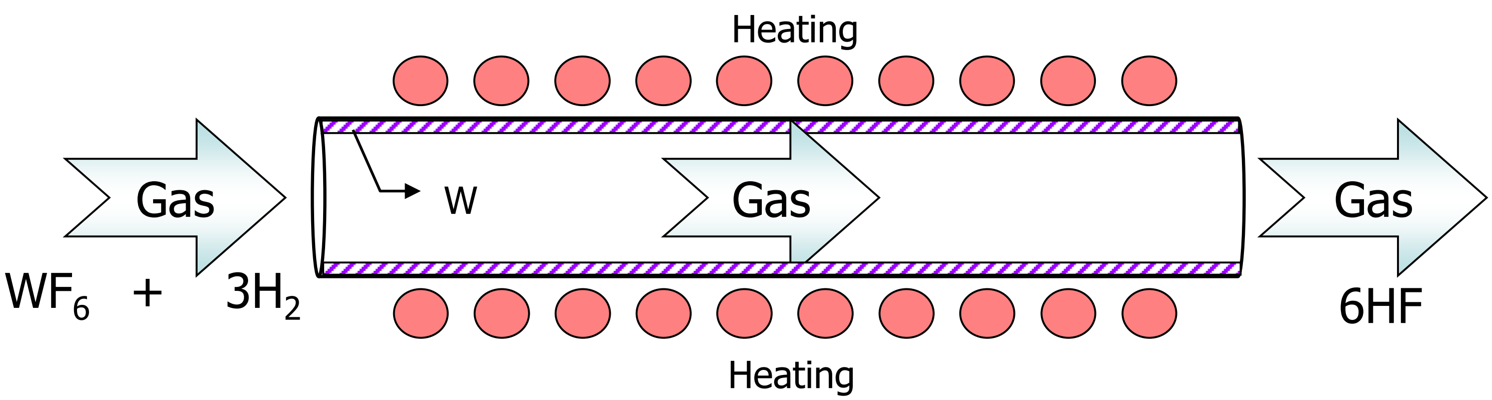
Energy Source (Thermal Energy)

Historical Sketch for CVD

- 1st CVD Material: Tungsten (W)
  - 백열등의 Carbon filament의 수명 향상을 위해 처음 적용

$$WF_6 + 3H_2 \xrightarrow{1000°C} W + 6HF$$

$$(WCl_3)$$



Current CVD Applications

- Semiconductor (Memory & Logic..)
- Display (LCD, LED, PDP..)
- Energy (Solar Cells)
- Fuel Cells (Protective Coating)
- Cutting Tools
- Automobile Engine Block & components (DLC)
- Rocket Engine Turbin
- Nuclear Reactor Components

Advantages & Disadvantages of CVD Process

Advantages

- **Good step coverage**
- **High Quality Epitaxial Film growth (LED & Semiconductor)**
- Various chemical compounds can deposit
- High mass production
- High deposition speed
- High Materials Usage

Disadvantages

- Needs high temperature (chemical reaction)

  (but it depends on the chemical reactions)
- Impurities (sometimes, it become advantage to hard coating applications)
- Environment pollution

Classification of CVD processes

- Energy Source
  - Thermal Energy : **Thermal CVD (CVD or TCVD)**
  - Extrinsic Energy: **Plasma enhanced CVD (PECVD)**
    - Catalytic enhanced CVD (CECVD)
    - UV enhanced CVD (UVCVD)
- Pressure
  - APCVD (Atmospheric CVD)
  - **LPCVD (Low Pressure CVD)**
- Precursor Type
  - Halide CVD
  - **Metal-organic CVD (MOCVD)**

But , don't worry! - Theories are very similar!

Introduction to Chemical Vapor Deposition (CVD)

Definition

- **Chemical Vapor Deposition (CVD)** is the process of chemically reacting **a volatile compounds of a materials (precursors)** to be deposited (**with other gases(reactant)**) to produce a nonvolatile solid that deposits atomistically on a suitably placed substrates.

1) Precursors (전구체)

- Halides precursors: $TiCl_4$, TaF_5, $CuCl_3$ …

- Metal organic precursors: $Al(CH_3)$, $Zn(C_2H_5)_2$, $Ru(EtCp)_2$, CH_4, C_2H_6, …

2) Reactants (반응물)

- for oxide CVD: H_2O, O_2, H_2O_2, O_3, O_2 plasma, N_2O, … and their plasma

- for nitride CVD: NH_3, N_2 and their plasma

- for sulfide CVD: H_2S, S and their plasma

- for metal CVD: typically H_2 or H_2 plasma

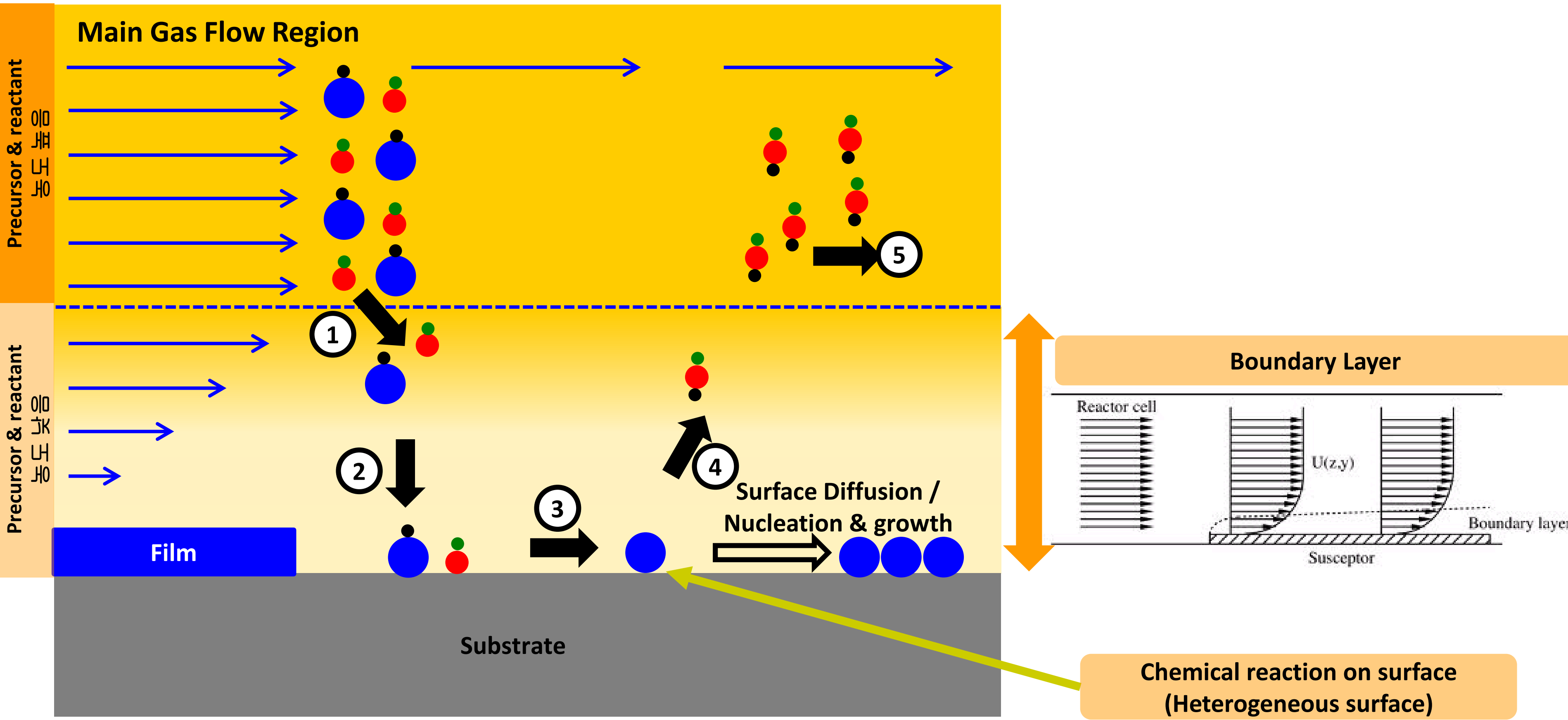
((NH_3 or pyridine can be used for noble metal CVD)

3) Substrates (기판)

Sequential CVD processes

Sequential reaction in CVD

(1) Diffusion-in → (2) Adsorption →(3) Chemical Reaction → (4) Desorption → (5)Diffusion Out



Reaction Types in CVD

- **Pyrolysis (Thermal Decomposition)**

  ex) $SiH_{4(g)} \rightarrow Si_{(s)} + 2H_{2(g)}$

  $Ni(CO)_{4(g)} \rightarrow Ni_{(s)} + 4CO_{(g)}$

- **Reduction**

  ex) $SiCl_{4(g)} + 2H_{2(g)} \rightarrow Si_{(s)} + 4HCl_{(g)}$

  $WF_{6(g)} + 3H_{2(g)} \rightarrow W_{(s)} + 6HF_{(g)}$

- **Oxidation**

  ex) $SiH_{4(g)} + O_{2(g)} \rightarrow SiO_{2(s)} + 2H_{2(g)}$

  $2Al(CH_3)_{3(g)} + 3H_2O_{(g)} \rightarrow Al_2O_{3(s)} + 6CH_{4(g)}$

- **Compound Formation (Nitride, Carbide, Sulfide)**

  ex) $SiCl_{4(g)} + CH_{4(g)} \rightarrow SiC_{(s)} + 4HCl_{(g)}$

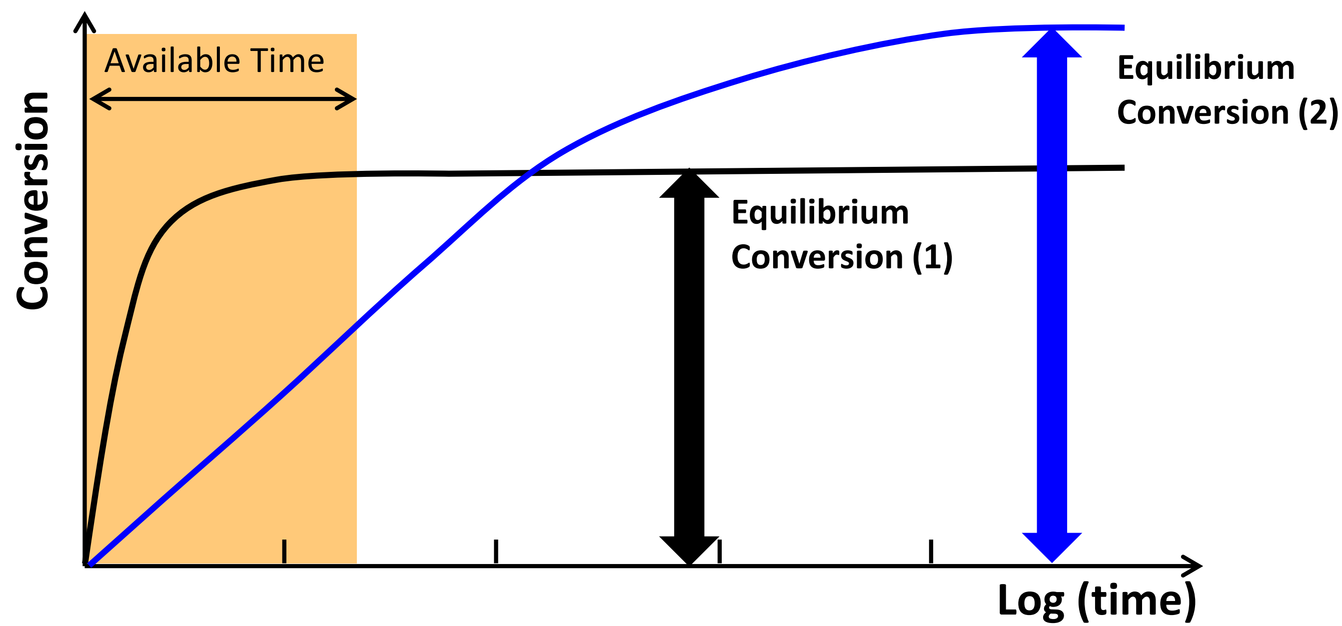
  $BF_{3(g)} + NH_{3(g)} \rightarrow BN_{(s)} + 4HF_{(g)}$

  $Zn(C_2H_5)_{2(g)} + H_2S_{(g)} \rightarrow ZnS_{(s)} + 2C_2H_{6(g)}$

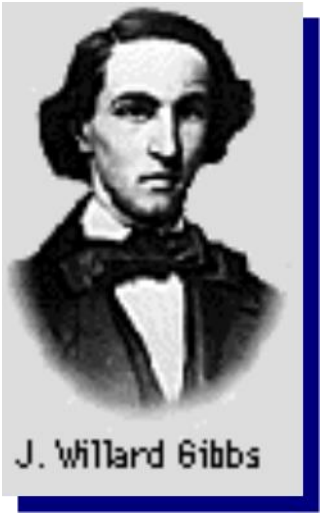
Theory & Mechanism

- **Thermodynamic & Kinetics**
  - Thermodynamics : 주어진 반응 조건(P, V, T)에서 반응 조건에서 반응이 최대로 진행된 상태(maximum yield)를 예측.
  - Reaction Kinetics : 다양한 elementary step에서의 반응 속도를 통해서, 전체 반응속도를 예측한다.

Q. Which reaction is favorable?



Gibbs Free Energy, G



$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$$

$$\Delta S_{univ} = \frac{-\Delta H_{sys}}{T} + \Delta S_{sys}$$

Multiply through by -T

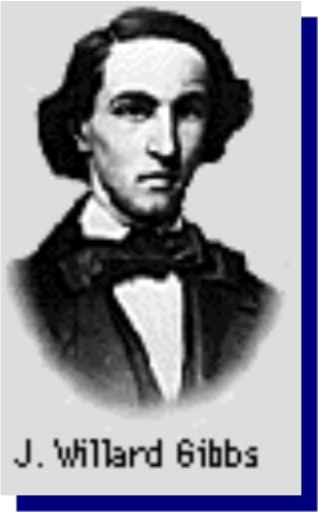
$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$

$-T\Delta S_{univ}$ = change in Gibbs free energy for the system = ΔG_{system}

Under standard conditions —

$$\Delta G^o_{sys} = \Delta H^o_{sys} - T\Delta S^o_{sys}$$

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



Gibbs **free energy** change = total energy change for system - energy lost in disordering the system

If reaction is

- exothermic (negative ΔH^o) (energy dispersed) and entropy increases (positive ΔS^o) (matter dispersed), then ΔG^o must be **NEGATIVE**
  : reaction is **spontaneous (and product-favored).**
- endothermic (positive ΔH^o) and entropy decreases (negative ΔS^o) then ΔG^o must be **POSITIVE**
  : reaction is **not spontaneous (and is reactant-favored).**

ΔH^o	ΔS^o	ΔG^o	Reaction
exo(–)	increase(+)	–	Prod-favored
endo(+)	decrease(-)	+	React-favored
exo(–)	decrease(-)	?	T dependent
endo(+)	increase(+)	?	T dependent

$$\Delta G^o_{rxn} = \Sigma\ \Delta G_f^o\ (\text{products}) - \Sigma\ \Delta G_f^o\ (\text{reactants})$$

(1) Thermodynamics of CVD Process

- Equilibrium Thermodynamics of Reactions

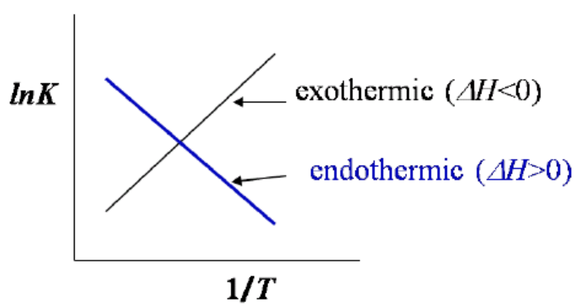
$$aA + bB = cC + dD \Rightarrow K = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \exp\left(\frac{-\Delta G^0}{RT}\right)$$

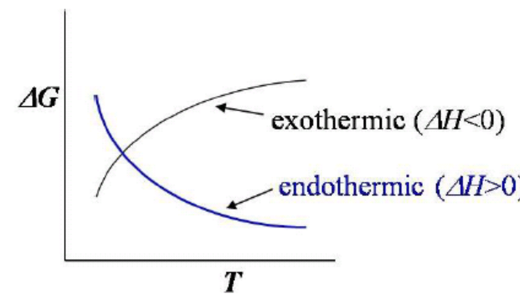
- Van't Hoff Equation

$$\frac{d\left(\Delta G^o/RT\right)}{dT} = -\frac{\Delta H^o}{RT^2} \xrightarrow{\Delta G^o/RT = \ln K} \frac{d\ln K}{dT} = \frac{\Delta H^o}{RT^2} \quad \text{or} \quad \frac{d\ln K}{d(1/T)} = -\frac{\Delta H^o}{R}$$

(assume : for a small T change, **Heat of sublimation이 constant**)

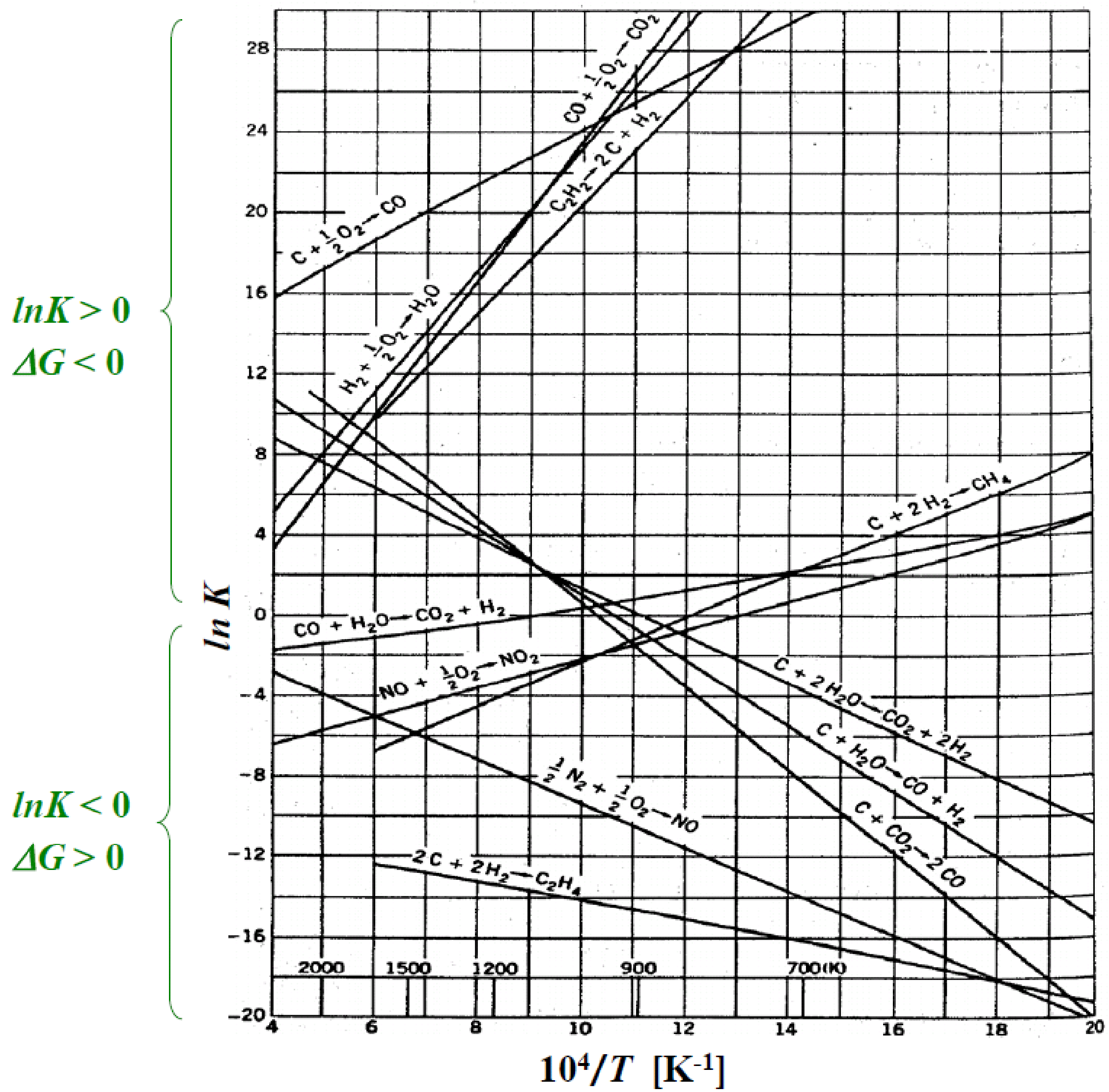
$$\therefore \ln\frac{K}{K_1} = -\frac{\Delta H^o}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)$$





Exothermic : 발열반응
Endothermic : 흡열반응

The variation of equilibrium constant K vs T



(2) Reaction Kinetics

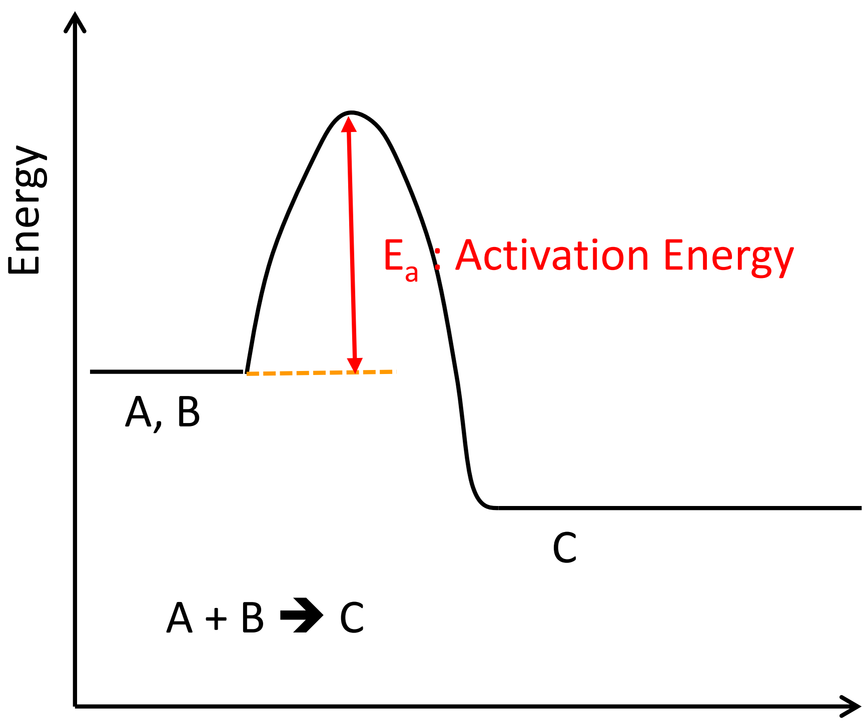
- Reaction Kinetics

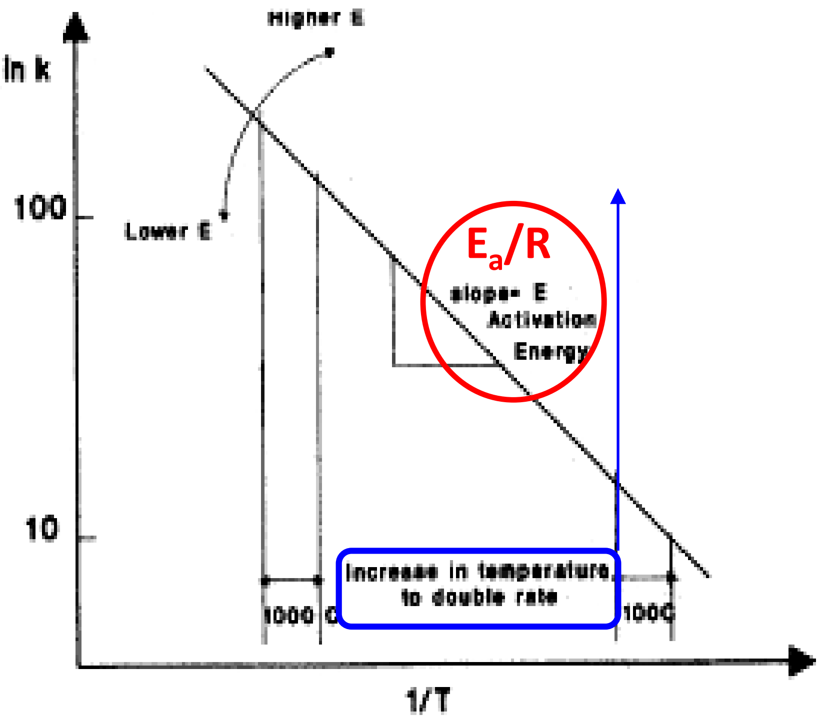
  - Rate of reaction : 단위시간에 소비된 반응물의 몰수 또는 생성된 생성물의 몰수

  - Rate constant : $k_s = \chi \exp(-\frac{E_a}{RT}) = k_o \exp(-\frac{E_a}{RT})$

    χ: collision frequency

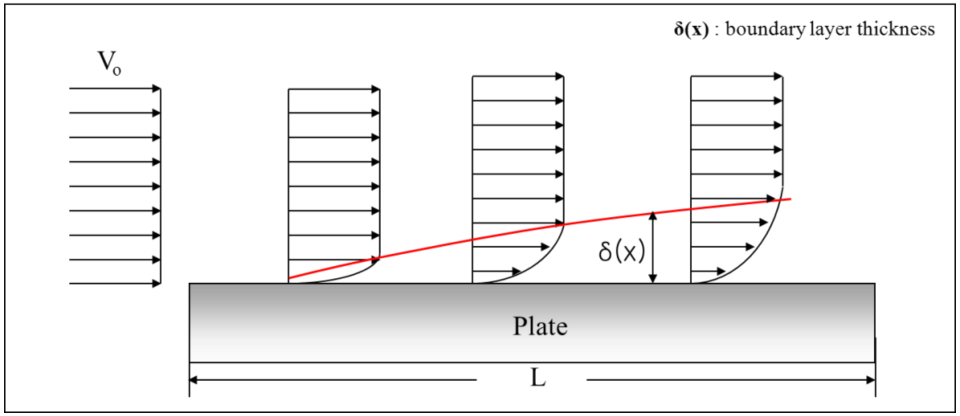
    E_a : activation energy





Boundary Layer

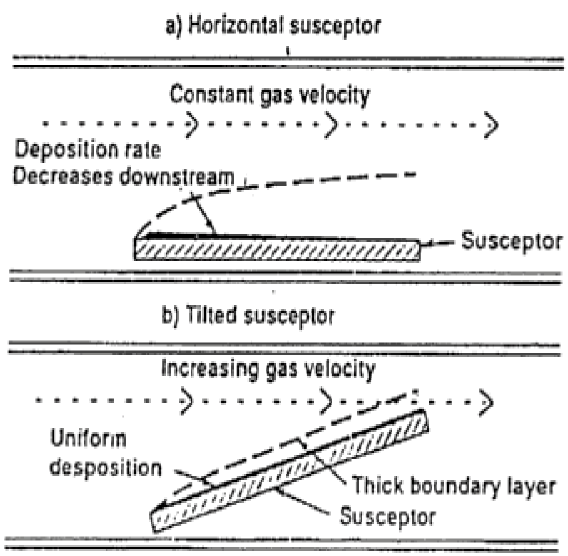
- Boundary layer
  - 기체의 속도가 0인 tube wall로부터 bulk velocity에 도달하는 지점까지를 boundary layer로 정의
  - 반응 기체가 이 boundary layer를 통해 기판 표면으로 Diffusion.
  - Boundary layer thickness ➔ 증착률에 영향을 미침.



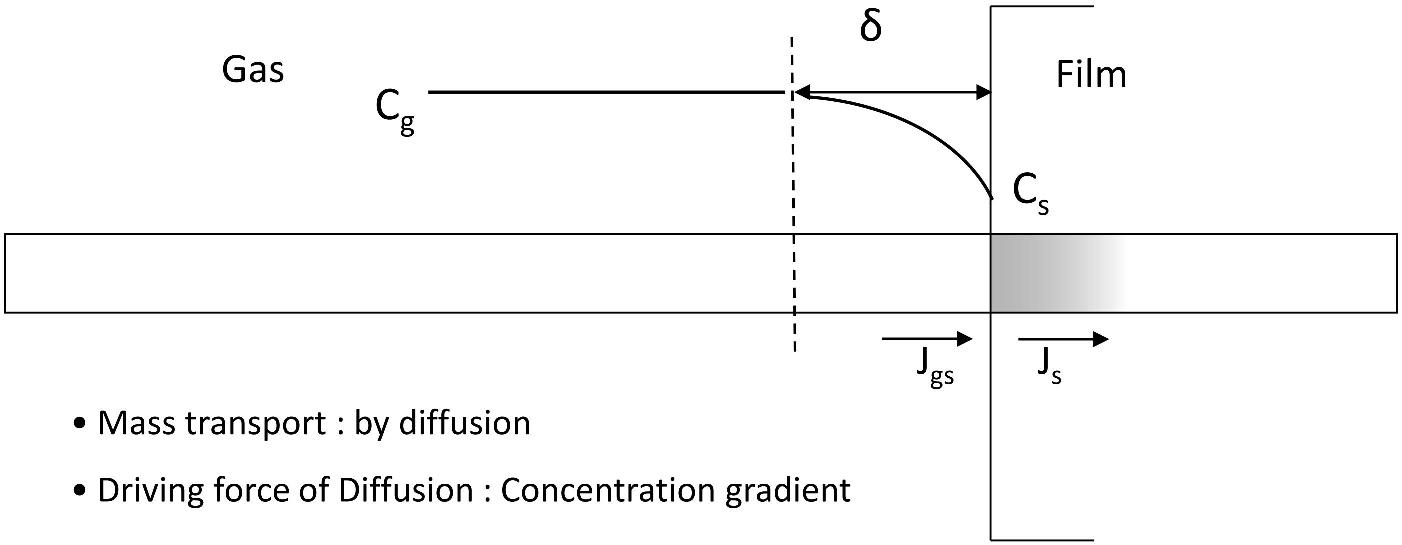
$$\delta = \sqrt{\frac{x}{R_e}}$$

$$R_e = \frac{\rho v D}{\eta}$$

δ : boundary layer thickness
x : distance along the susceptor
R_e : Reynolds number
ρ : density of gas
ν : velocity of gas
D : dimension of tube
η : viscosity of gas



Growth Rate (Effect of Temperature)



- Mass transport : by diffusion
- Driving force of Diffusion : Concentration gradient

Mass Flux ⟶ $$J_{gs} = h_g (C_g - C_s)$$ * h_g : mass transfer coefficient $\left(\frac{D}{\delta RT} = h_g \right)$

Reaction at the Surface ⟶ $$J_s = k_s C_s$$ * k_s : rate constant for surface reaction

Growth Rate

- Mass transport: $$J_{gs} = \frac{D}{\delta RT}(C_g - C_s) = h_g(C_g - C_s)$$
- Reaction at the surface: $$J_s = k_s C_s$$
- Steady state: $$J_{gs} = J_s$$

J_{gs} : mass transport flux
J_s : surface reaction flux
J : flux at steady state
D : diffusivity of gas
δ : boundary layer thickness
h_g : mass transport coefficient
k_s : rate constant for surface reaction
C_g : concentration of gas at bulk
C_s : concentration of gas at surface
G_R : growth rate
N_o : atomic density at surface

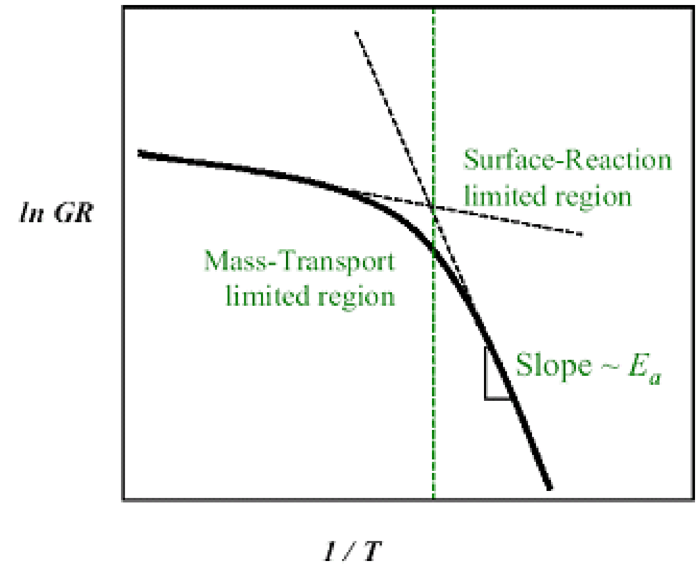
$$\therefore J = \frac{1}{(1/k_s)+(1/h_g)} C_g = \frac{k_s h_g}{(k_s + h_g)} C_g$$

$$\therefore G_R = \frac{J}{N_o} = \frac{C_g}{N_o} \frac{1}{(1/k_s)+(1/h_g)} = \frac{k_s h_g C_g}{(k_s + h_g) N_o}$$

Mass transport vs. Surface Reaction

- Arrhenius plot

$$G_R = \frac{J}{N_o} = \frac{C_g}{N_o}\frac{1}{(1/k_s)+(1/h_g)} = \frac{k_s h_g C_g}{(k_s+h_g)N_o}$$



- **Mass-transport limited reaction (E_a=1~10kcal/mole)**

$$G_R = \frac{h_g}{N_o}C_g \qquad h_g = \frac{D}{\delta RT}$$

  - G_R depends on reactant concentration gas flow & reactor design
  - Bad comformality
  - Case : $K_s >> h_g$

- **Surface-reaction limited reaction (E_a>10kcal/mole)**

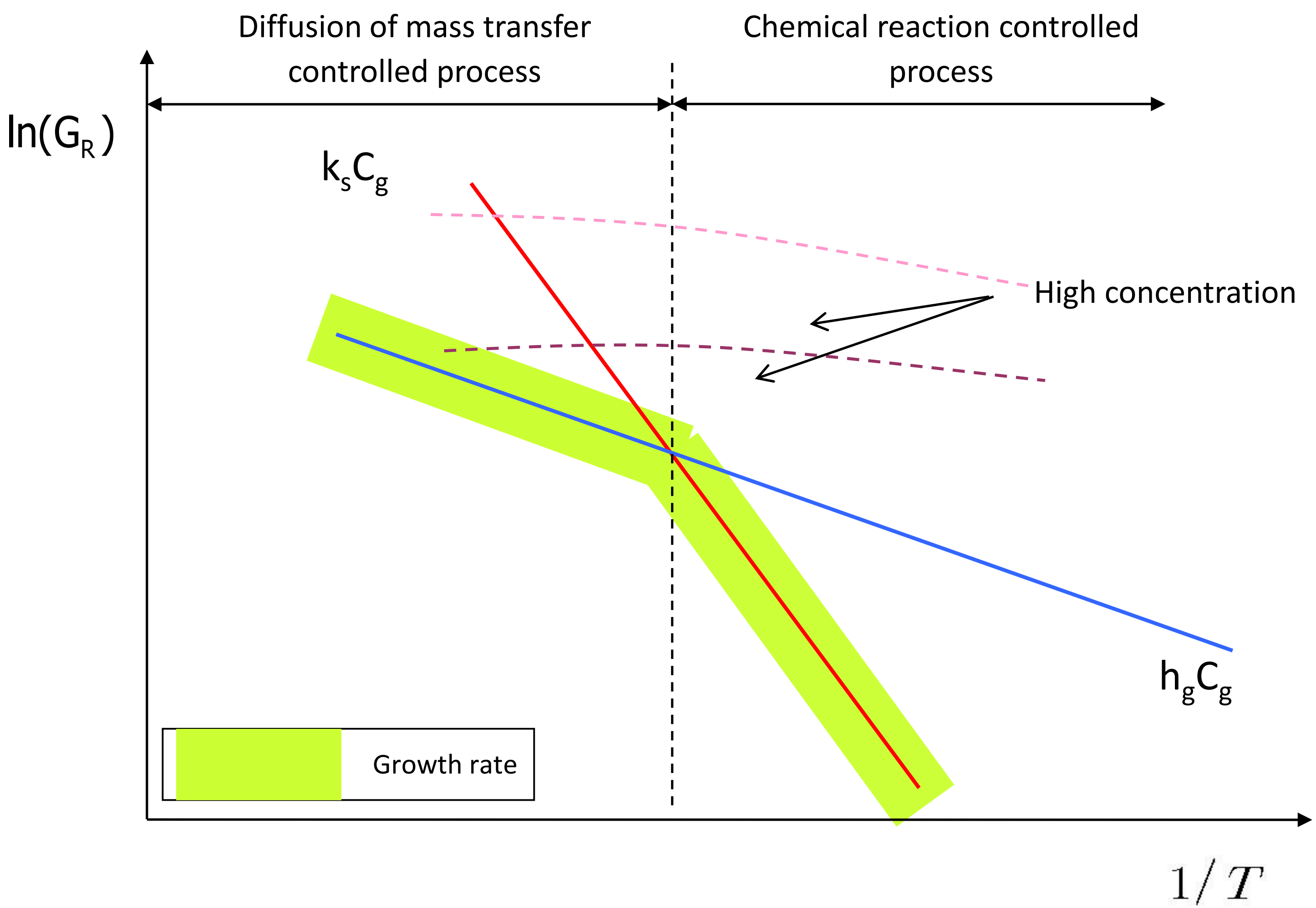
$$G_R = \frac{k_s}{N_o}C_g \qquad k_s = k_o \exp\left(-\frac{E_a}{RT}\right)$$

A : constant

E_a : activation energy

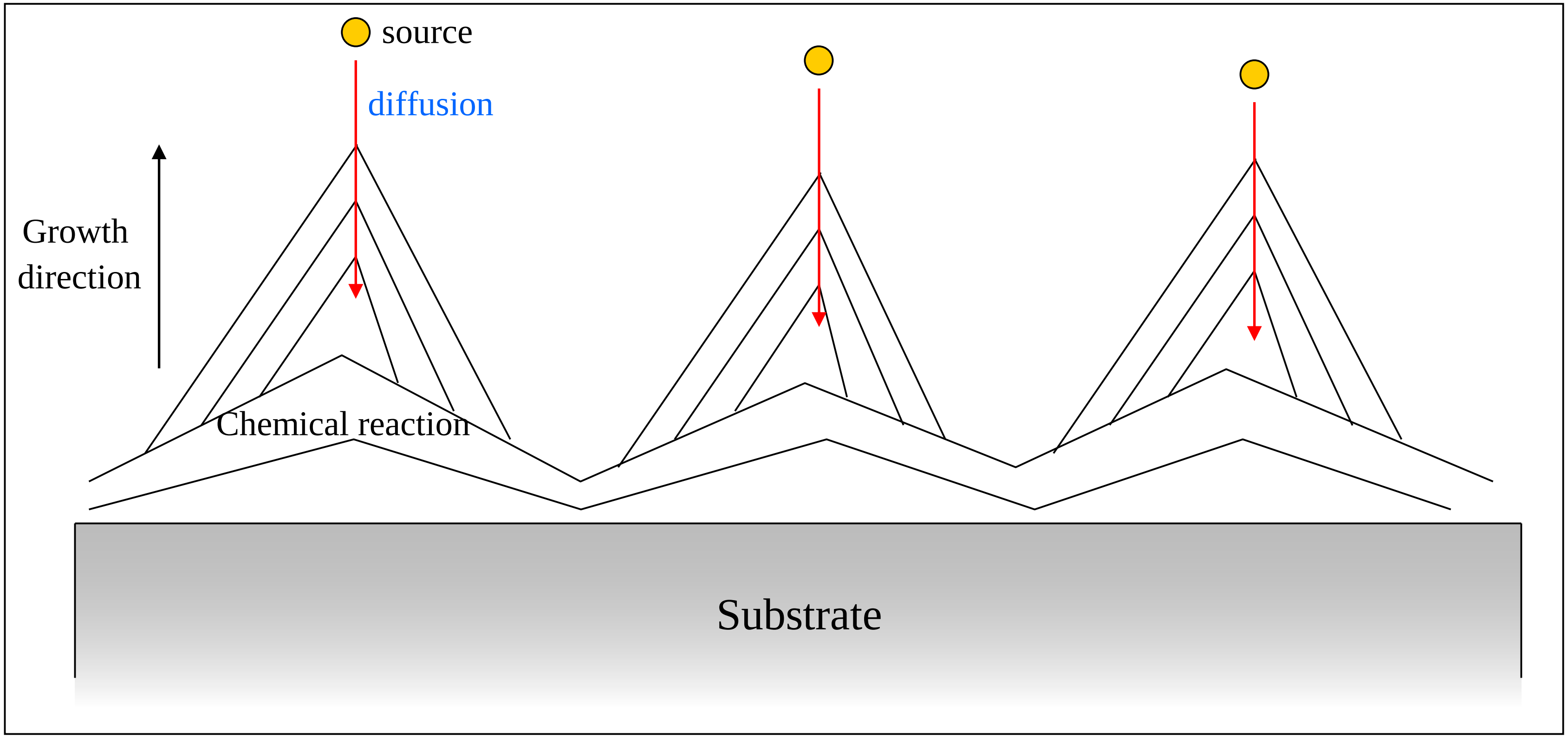
  - G_R depends on substrate temperature
  - Good comformality
  - Case : $K_s << h_g$

Mass transport vs. Surface Reaction



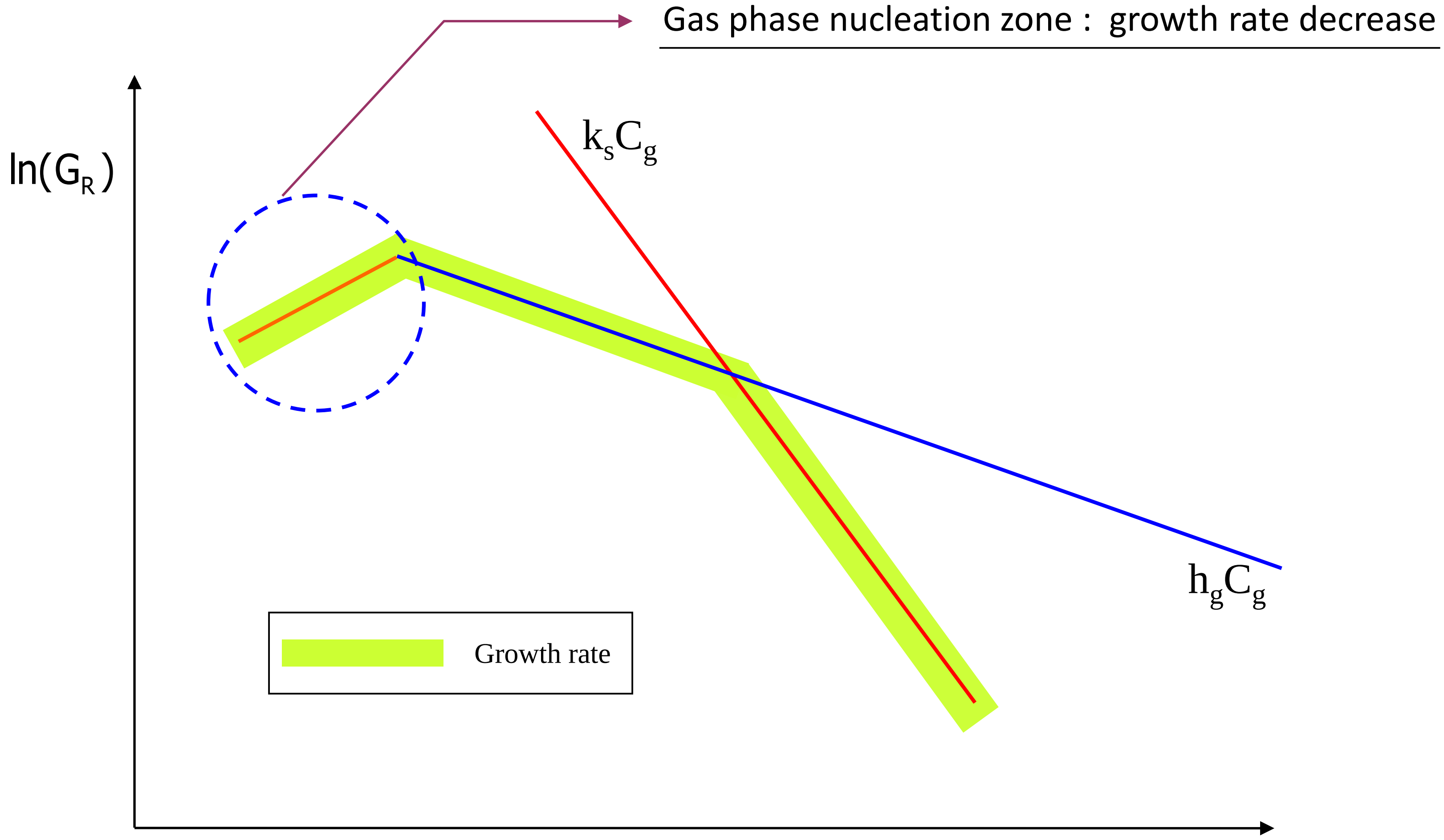
(1) Mass Transport limited Region (i)

Film grow towards the origin of source because the lack of source induces to react with each sources directly (fast chemical reaction on the surface).

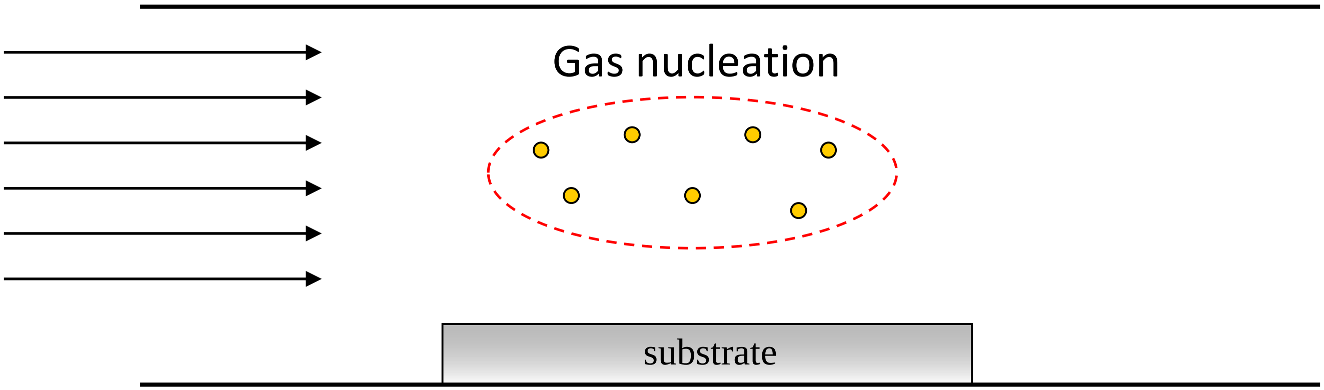


(1) Mass Transport limited Region (ii)

At too high temperatures



At too high temperatures



Gas nucleation (Homogeneous nucleation)	→	Grow up to the nano-powder

- Homogeneous nucleation

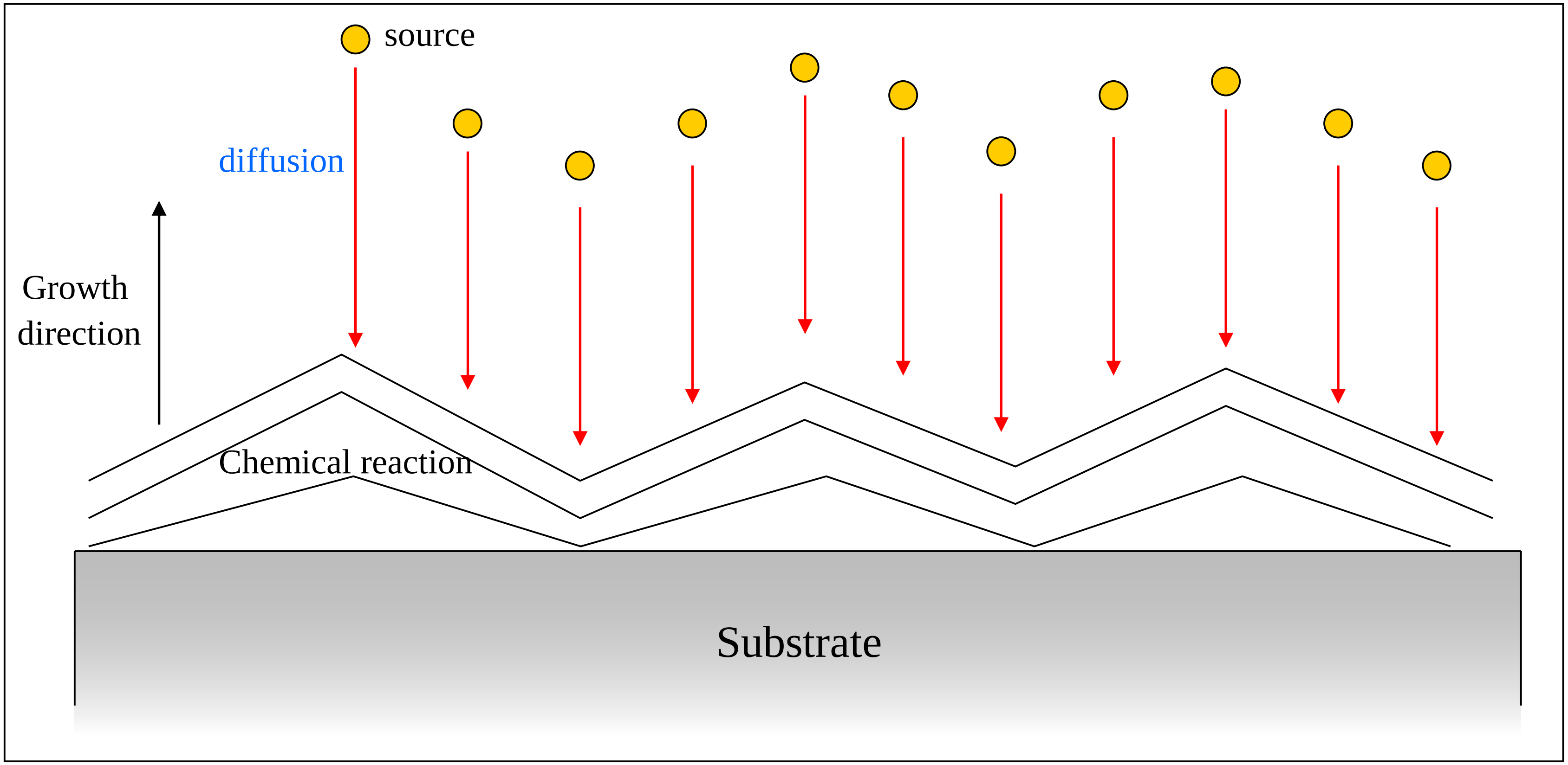
Gas nucleation → nano-power formation → decrease of reactant gas concentration

⇩

Decrease of growth rate at surface

(2) Surface Reaction Region

In spite of abundance of sources, growth rate of the film is very low. Because the film uniformly grows with lower surface energy.



Homogeneous & Heterogeneous Reaction

- Homogeneous reaction (주로 mass transport limited 영역)
  - 반응 기체들의 화학 반응이 기체 상에서 발생 (powder, particle 발생)
  - Adhesion이 나쁘고, defect도 존재
  - 고온/reactant의 높은 압력/기체의 반응성이 좋은 경우

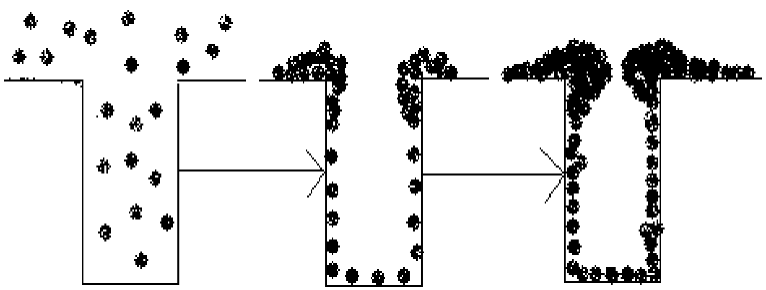
- Heterogeneous reaction (주로 Surface reaction limited 영역)
  - 반응 기체들의 화학 반응이 기판 표면에서 발생
  - Adhesion이 좋고 quality가 좋은 박막이 얻어짐

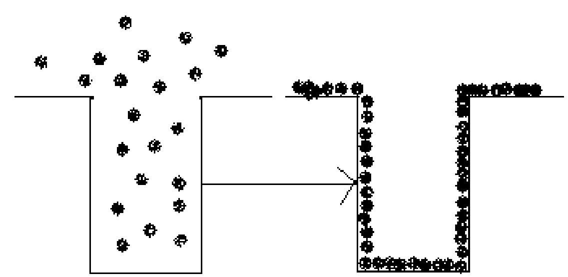
박막 증착을 위한 CVD는 Heterogeneous Reaction으로 이루어져야한다
➔ surface reaction limited region을 선호하는 이유
예외) nanopowder를 CVD process로 만드는 경우

Comparison

`	Mass transport limited	Surface reaction limited
Deposition rate	빠르다	느리다
Comformality	나쁘다	좋다
온도	고온	저온
온도 의존성	작다	크다

- Mass transport limited region에서의 hole의 증착
- Surface reaction limited region에서의 hole의 증착



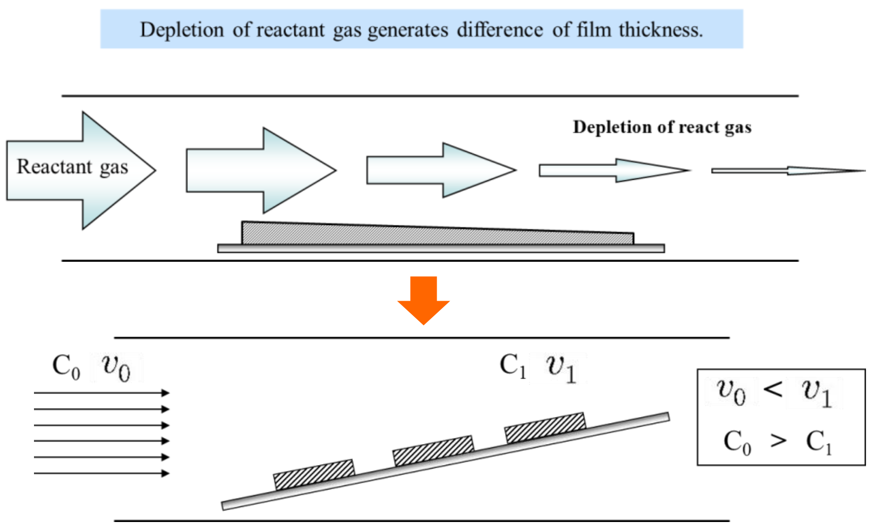


Thermal CVD Process (1)

- **Atmospheric Pressure CVD**

i) Merits

- Simple reactor
- High deposition rate



ii) Demerits

- Gas phase reaction (Homogeneous reaction)
- Poor step coverage
- Particulate contaminations

iii) Process

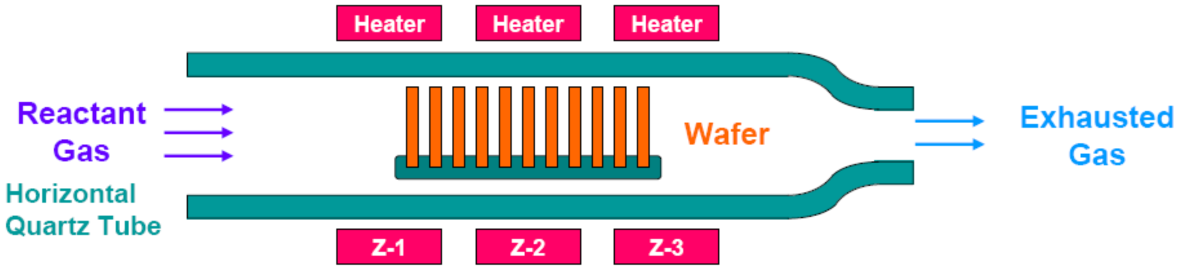
- High Pressure (760 Torr) ➔ Low gas velocity ➔ Large Boundary layer ➔ Slow diffusion
- 주로 mass transport controlled 영역 ➔ Homogeneous reaction이 일어날 수 있다
- 농도 구배의 문제로 박막의 두께 불균일
- 균일한 증착을 위해서는 특별한 형상의 반응로 필요

Thermal CVD Process (2)

■ Low Pressure CVD

i) Merit

1. Good uniformity.
2. Good step coverage
3. Low contamination rate



ii) Demerit

1. Low deposition rate
2. High operating temperature

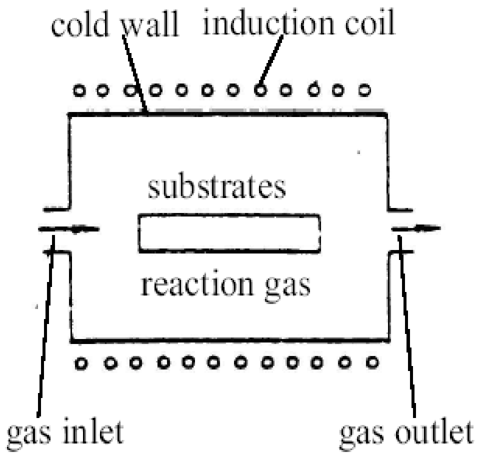
iii) LPCVD의 동작 범위

- Pressure : 0.25~2.0 Torr ➔ High gas velocity ➔ Small Boundary layer ➔ Fast diffusion
- 주로 surface reaction limited영역

Thermal CVD Process (3)

- Reactor 온도에 따른 분류
  - Cold wall CVD
    - 기판만을 가열 → chamber내 온도 불균일
    - Homogeneous reaction 억제
    - **기판에만 증착** – pinhole생성의 위험 없음
    - Low T – 반응물과 wall사이에 반응에 의한 source 의 오염 가능성 감소

    ➔ 소형장비, single wafer type CVD (반도체)

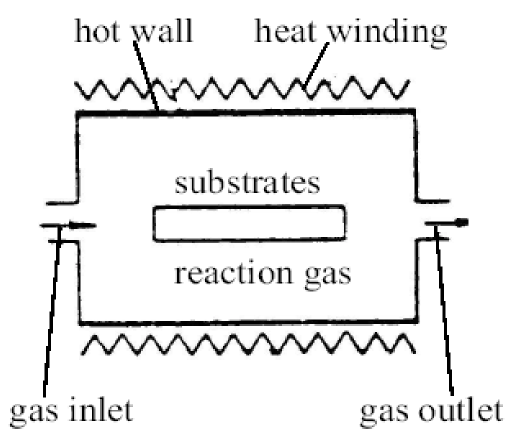


(b) Cold wall reactor

  - Hot Wall CVD
    - 기판과 chamber 모두 가열 → homogeneous reaction
    - Reactor wall내부에도 박막 증착.

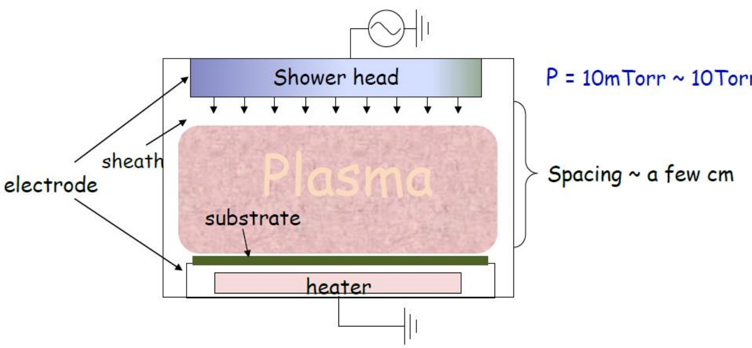
      ⇒pin-hole형성 가능성, source의 오염 가능성
    - 내부온도 균일.

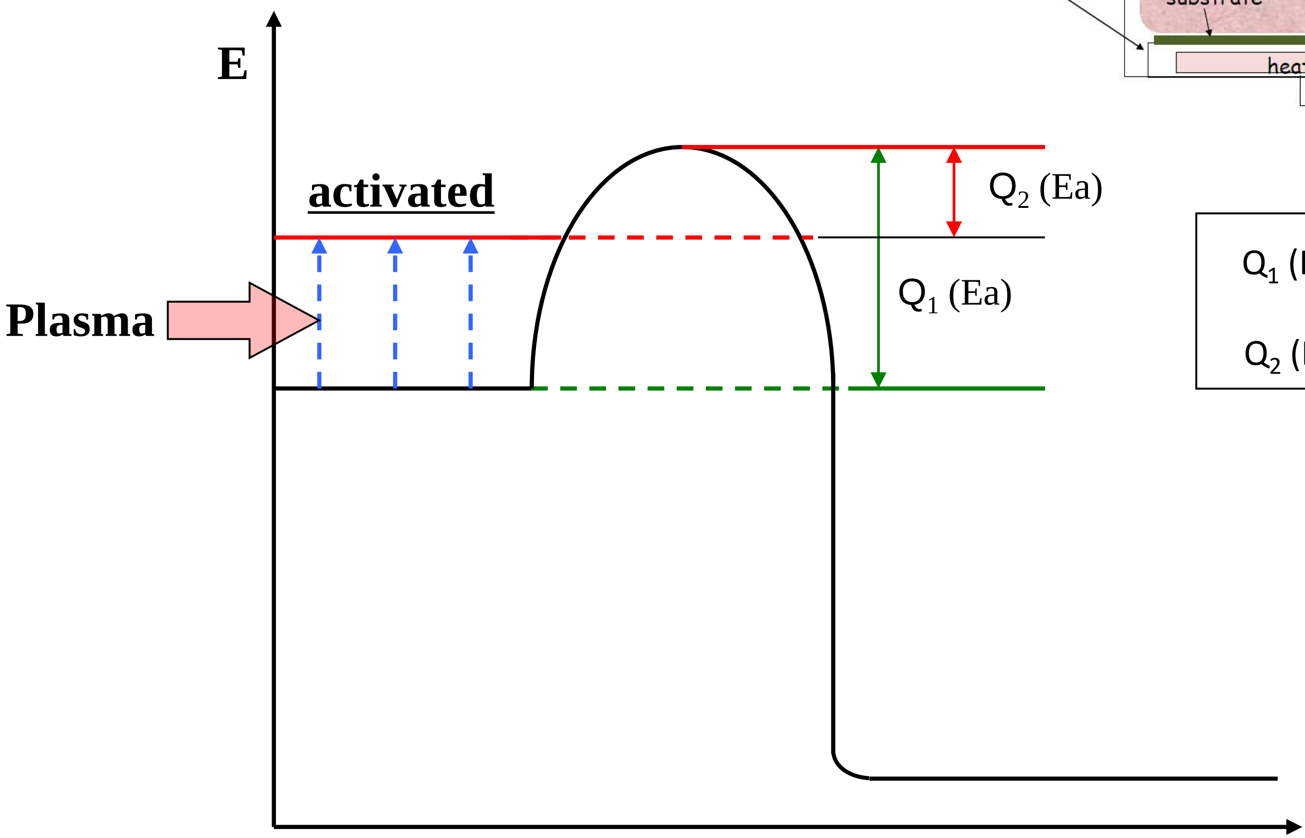
    ➔ 대형장비, 여러 장을 함께 증착시 (batch-type)



(a) Hot wall reactor

Plasma-Enhanced CVD (PECVD)





Q_1 (Ea) : non-PECVD process

Q_2 (Ea) : PECVD process

PECVD

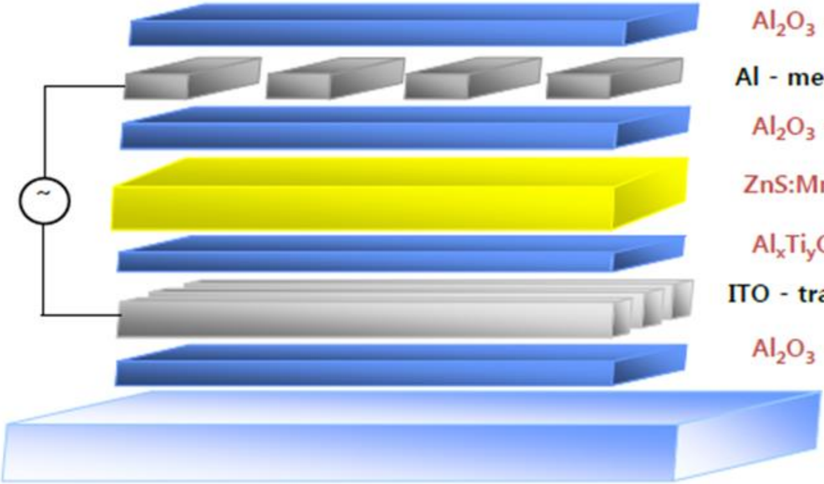
- Plasma 내에서 ion이나 radical 같은 reactive species를 형성
  - Activation energy 감소로 인한, 반응 온도를 낮추는 효과
- Deposition mechanism
  - Radical – highly reactive, high density
  - Ion - Breaking down weakly bonded reactive species, densification
- **장점**
  - 낮은 온도(ex) SiN, thermal CVD – 800~900℃ / PECVD – 약 350℃
  - 다성분계 박막 증착시, 각 성분 입자의 반응속도가 유사하다. (절대적이지 않음)
    - 각 성분 물질의 반응성이 일정하다.
- **단점**
  - 낮은 온도로 인해 부산물의 탈착이 이루어 지지 않는다
  - Ion bombardment에 의한 damage
  - Reactive species의 경우 homogeneous reaction
  - Poor step coverage (물질마다 다른 경향이 있을 수 있음)

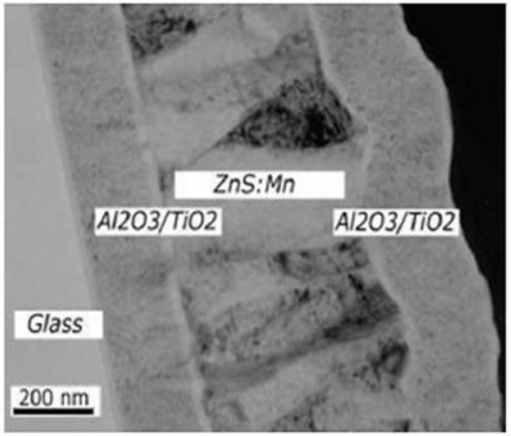
Summary - CVD

CVD의 분류		장점	단점
Thermal CVD	APCVD	간단한 구조 빠른 증착속도	불균일한 두께
	LPCVD	균일한 박막 우수한 step coverage	느린 증착속도
PECVD		저온 증착 빠른 증착속도	Poor step coverage Homogeneous reaction Ion 충돌에 의한 damage

Atomic Layer Deposition : Birth of ALD

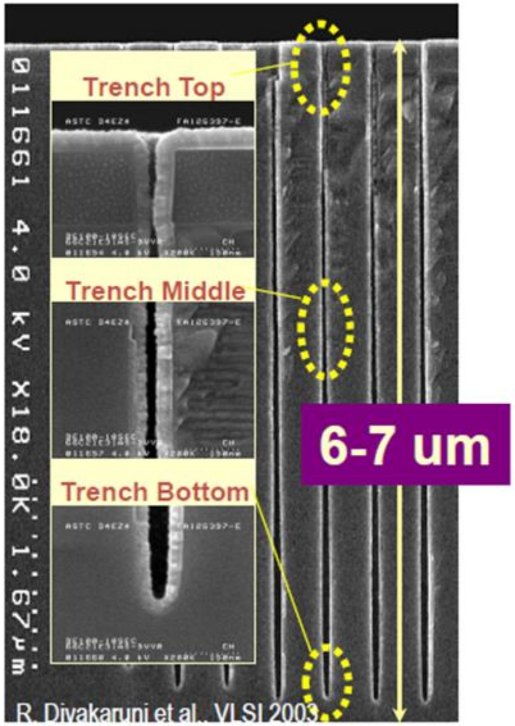
- ALE invented by Dr. T. Suntola in early 70'
- Originally adapted for films for EL devices
  - large-area, large-batch
  - multilayer processing (0.2 - 1 μm each)



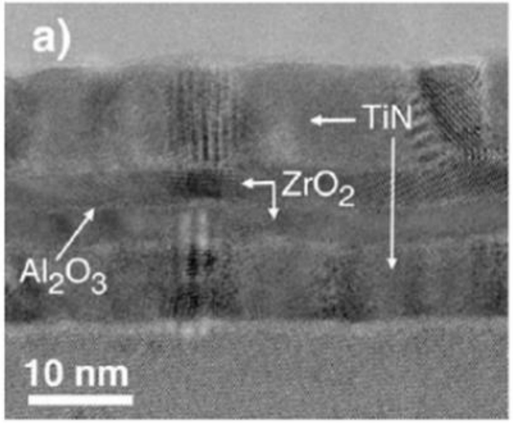


M. Ritala, ALD conference 2001

Atomic Layer Deposition : Revival



70:1 AR Trench Metal Fill

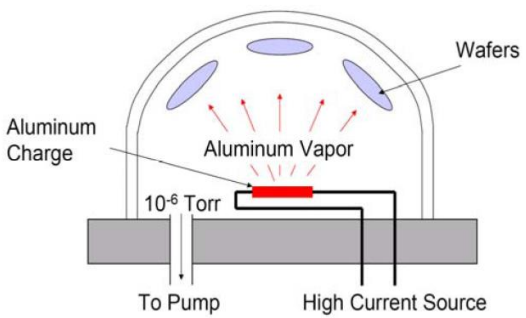


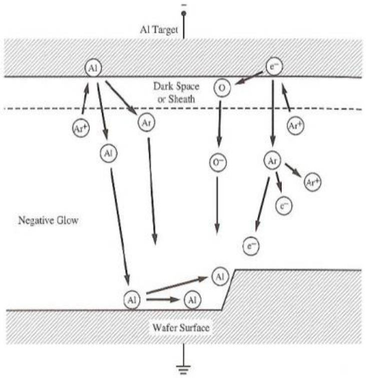
- For nanoscale 3D structure requires capability of deposition into high AR is specifically required: ALD is the only solution.
- High k based nanolaminates are standard materials for comtemporary DRAM devices

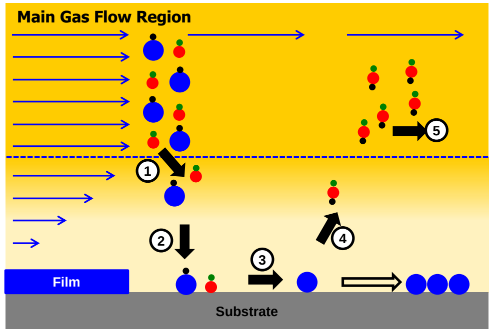
D.G. Park et al, IBM, ALD 2003 J.A. Kittl et al, Microelectronics Eng, 86, 1789 (2009)

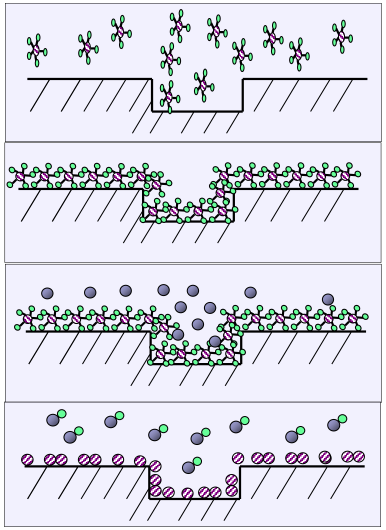
Atomic Layer Deposition (1)

Representative "thin Film Deposition Processes in Vacuum"









AX(g) + BY(g)(reactant) → AB(s) + XY(g) ↑

1. Complementary reaction

- Each reactant supplying sequentially without thermal decomposing
- To form films by repeating cycles

2. Self-limiting mechanism

- A precursor vapor distributes on non-uniform surface and saturating to a certain amount on surface
- Surface reaction btw. reactants

- Superior step coverage, Exact thickness control in nano-scale.
- Excellent large area uniformity, Easy to control multi-phase.

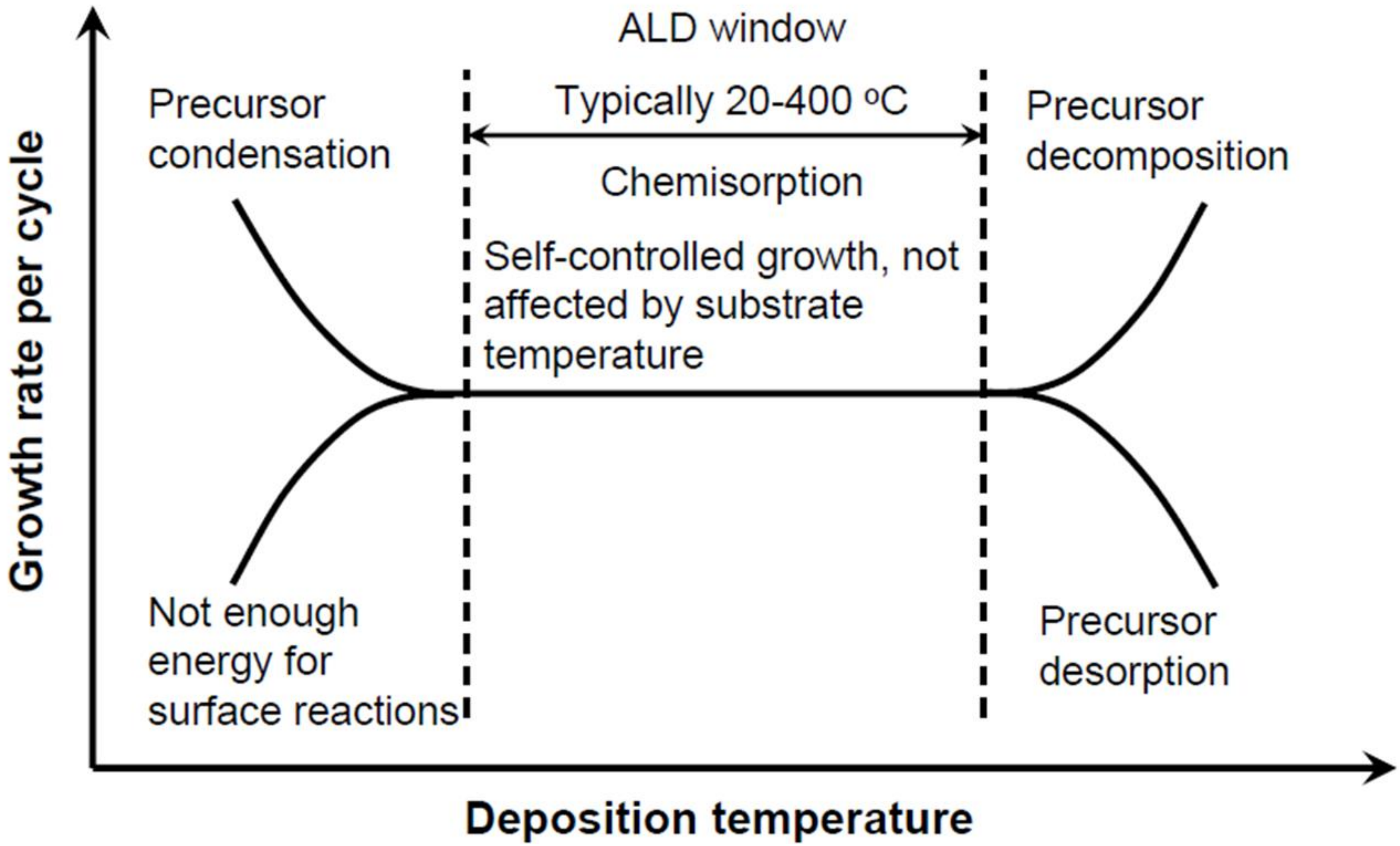
Atomic Layer Deposition (2)

- Thickness determined simply by number of cycles
- Precursors are saturatively chemisorbed
  ⇒stoichiometric films with large area uniformity and 3D conformality
- Uniform step coverage and pinhole-free films
- Nanolaminates and mixed oxides possible
- Low temperature deposition possible (RT-400 ºC)

⇕

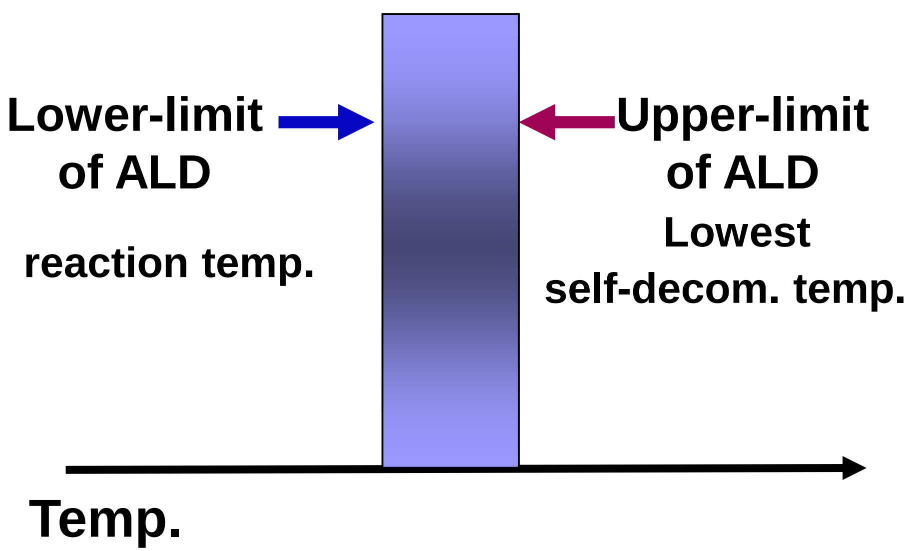
- Low Deposition Rate
  - —typical rate ≤ 0.1 nm/cycle
  - —1 second to 1 minute cycle time
  - —depending on temperature and properties of precursors and by-products etc
- Limitation of Materials
  - —controlled by availability of suitable ALD precursors
  - —thin film growth limited by activation energy

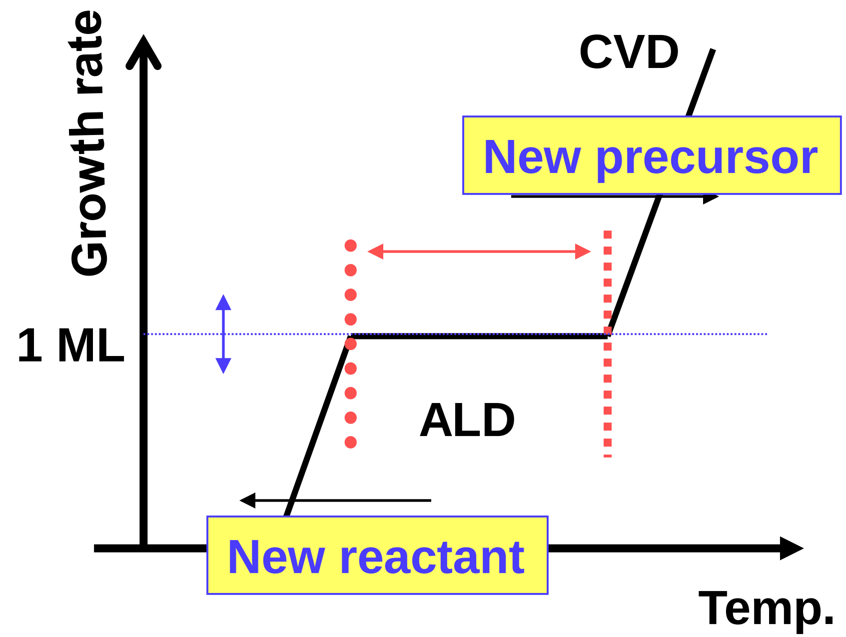
Atomic Layer Deposition (3)



ALD Window Zone

: Max deposition temperature; below thermal decomposition of precursors
Min deposition temperature; over possible reaction between sources

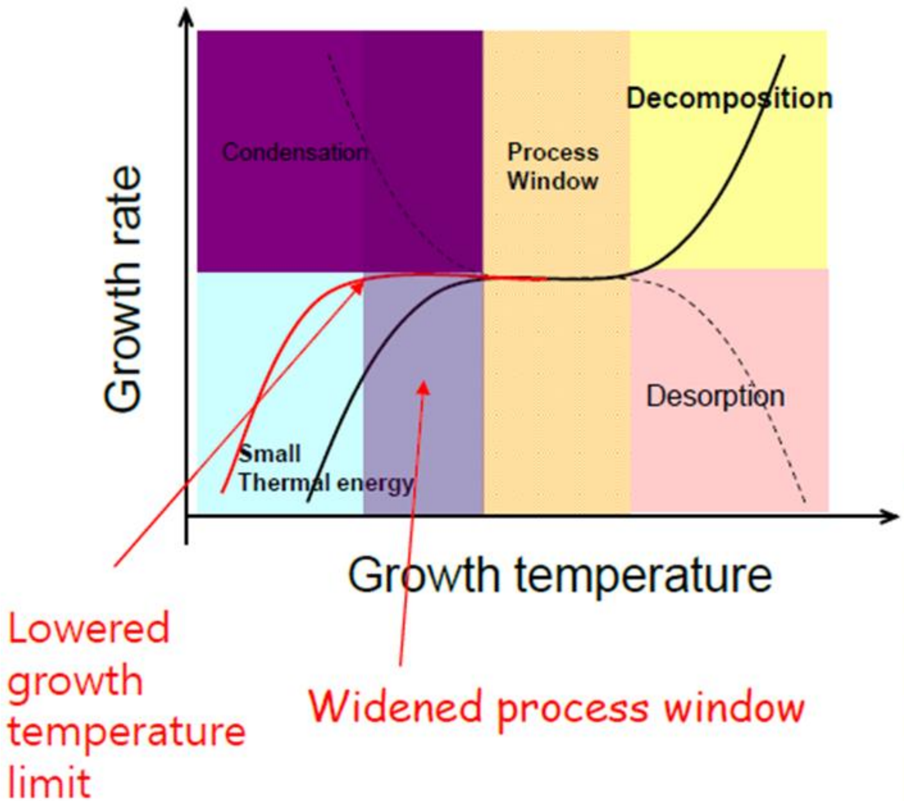




Atomic Layer Deposition (5)

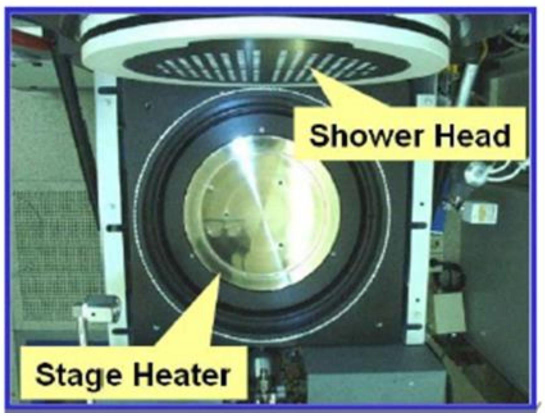
◆ **Higher reactivity of radicals**

– Large "process window"
– Low temperature deposition



- More versatile reactions

Metal precursor + H / N / O → Metals / Nitrides / Oxides



Atomic Layer Deposition (6)

Pros

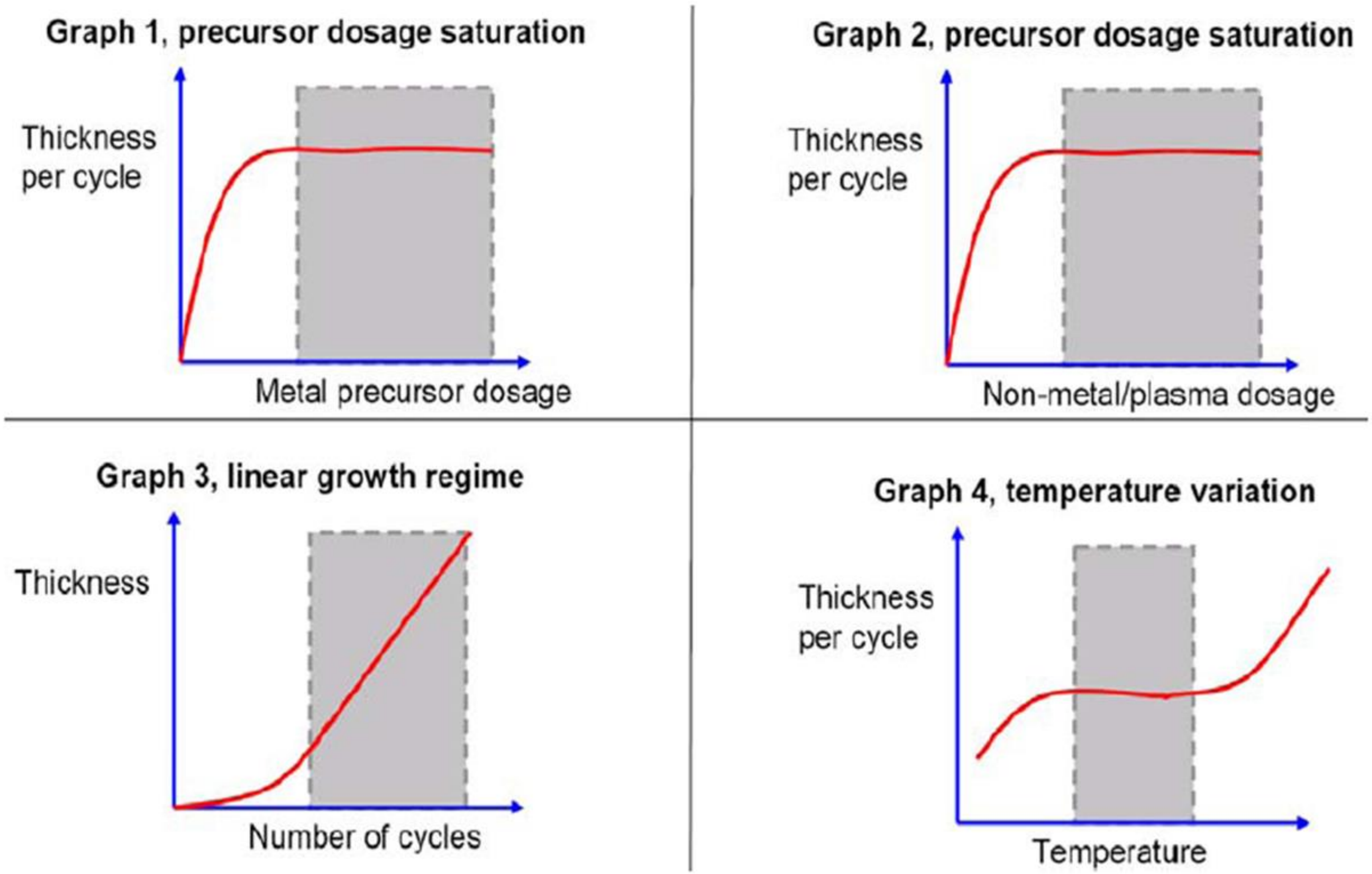
- Lower deposition temperature: metal deposition for BEOL
- Broader range of chemistry possible: metal ALD, SBT ALD
- Denser films: diffusion barrier
- Lower impurity: high k
- Higher throughput* (some cases)
- *In situ* plasma treatments
- Additional growth parameters: plasma power, configuration, bias..

Cons

- More complicated chamber design
- More complicated reaction chemistry
- Slower * (not always)
- Damage to films * (Not always)

	Metals/nitrides	Oxides
Reported materials	Ti, Ta, Al, Ru, Cu, Co, Ni.. TiN, TaN, RuTiN, $TiSi_xN_y$, $TaSi_xN_y$, W_2N, SiN_x,…	Al_2O_3, Ta_2O_5, Y_2O_3, ZrO_2, HfO_2, $SrTiO_3$, $SrTa_2O_6$ and $SrBi_2Ta_2O_9$,…

Atomic Layer Deposition (7)



Atomic Layer Deposition (8)

- Dosage optimizations (pulse times, precursor temperatures)
  - Under dosing ⇒ lower saturated growth rates and poor uniformity
  - Overdosing ⇒ precursor waste and possible CVD component
  - Normal ALD process is slightly overdosed to ensure good uniformity
- Optimization of wait times
  - Too short a wait time ⇒ excess precursor overlapping and thus introduces CVD component
  - Too long a wait time ⇒ a waste of time (increases cycle time) and may lead to undesired thermal desorption or decomposition
- Optimization of growth temperatures
  - Effects on properties of films (purity, crystallinity, conductivity and dielectric constant etc.)
- Growth rate linearity test-rate (thickness vs. # of cycles)
  - Slope, intercept and low cycle curvature provide hints about ALD mechanism

Atomic Layer Deposition (9)

	PVD	CVD	ALD
Reaction	Physical adsorption	Surface +vapor reaction	Surface reaction
Growth temperature	Low (RT)	High (> 600 °C) to middle (MO source <300 °C)	Low to middle (<500 °C)
Step coverage	Poor	Good	Excellent
Impurity	Very low (<1%)	A few %	Low (< 1%)
Thickness control	> 50 Å	> 10 Å	< a few Å
Particle	OK	poor	OK
Wafer uniformity	Good	Good	Excellent
Growth rate	Fast	Middle	Slow

- ALD could be best solution for some applications in device fabrications

Atomic Layer Deposition (10)

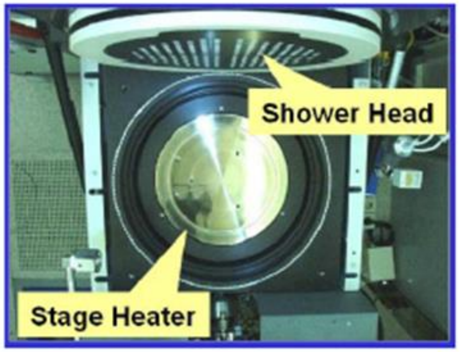
Tool configuration: Travelling wave type

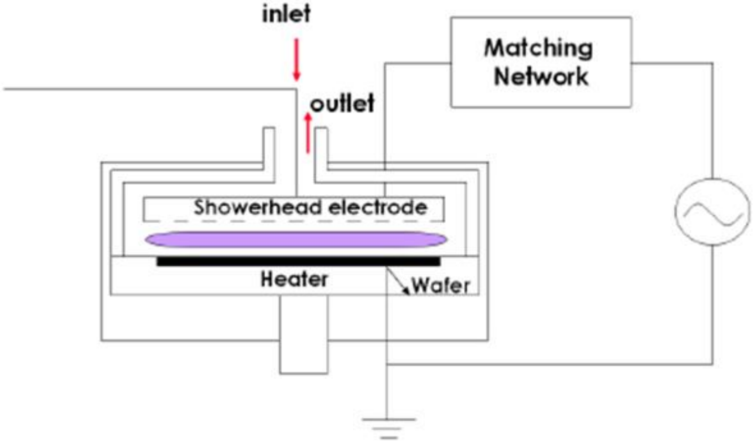
- The simplest type of reactor configuration: gas flows from side in laminar flow mode

Atomic Layer Deposition (11)

Tool configuration: Shower head type

CN1 Plus200

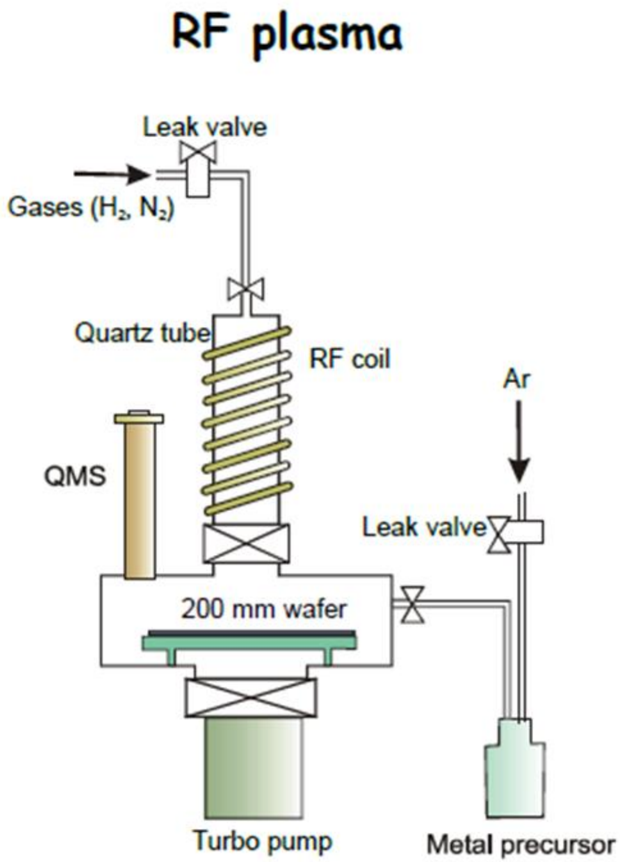




- Ideal for semiconductor device process with good uniformity
- Also good for direct PE-ALD: higher reaction rate, but possible damage due to ion and electron bombardment

Atomic Layer Deposition (12)

Tool configuration: Remote PEALD



- Use ICP plasma source: decrease potential damage issue, but with limited industrial use

Atomic Layer Deposition (13)

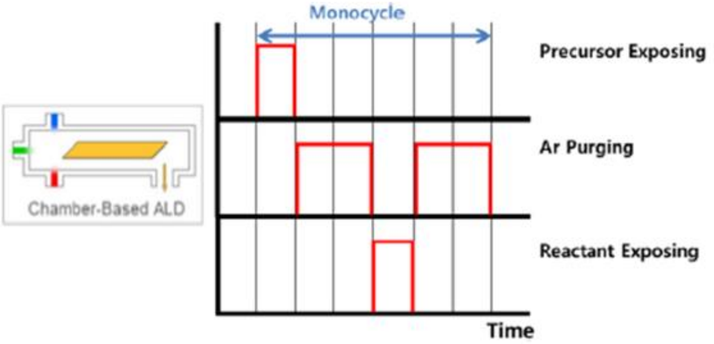
Tool configuration: batch type

Beneq 550

- Throughput enhancement by batchtype ALD: demonstrated up to 3000 wafers/hr (NCD)
- Large area tool available: up to Gen4 (1200x1200)

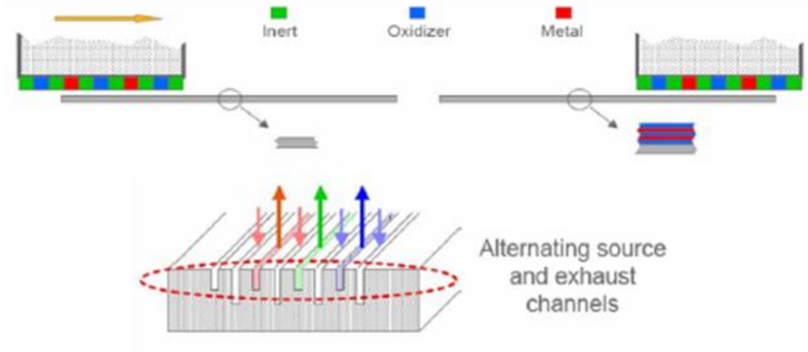
Atomic Layer Deposition (14)

Tool configuration: Spatial ALD



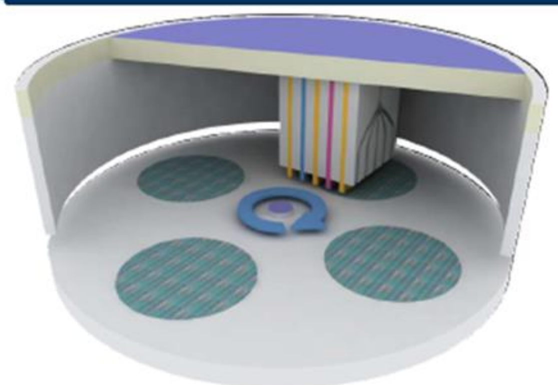
- Time sequential process

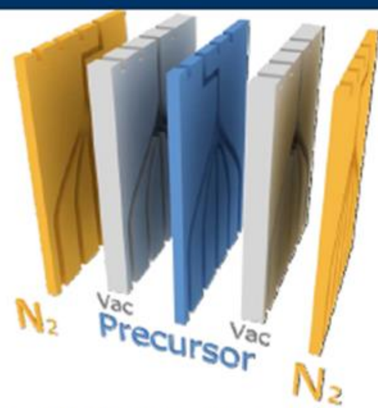
➔ Low throughput



- Enhanced throughput by space division
- Compatible with atmospheric process

Schematic for high throughput ALD

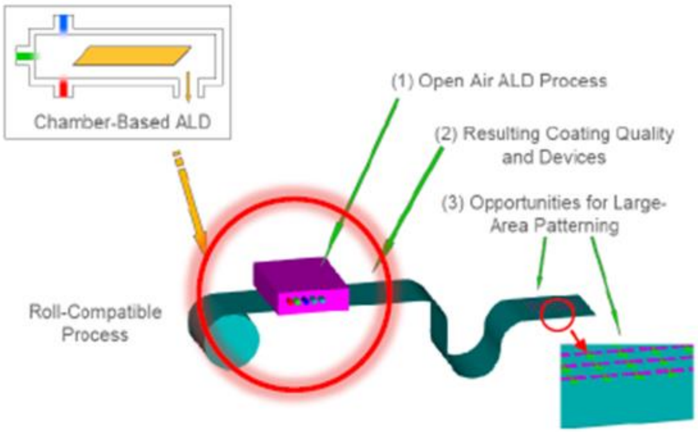




- Air barrier (N_2)

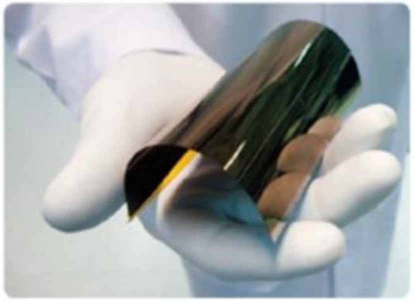
Atomic Layer Deposition (15)

- R2R ALD Process



Ref. Kodak, ALD 2008, Brugge

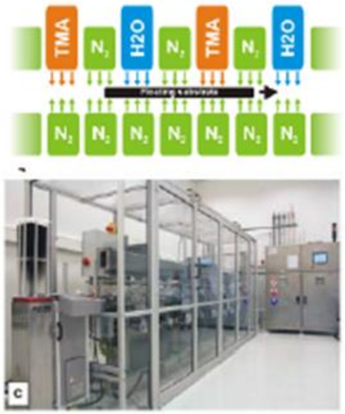
BENEQ



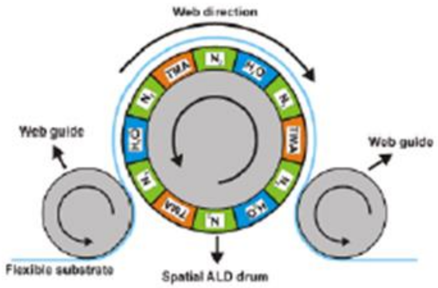
A polymer (PET) substrate coated by the TFS 200R.

Lotus Appl. Tech.

Levitech's atmospheric spatial ALD

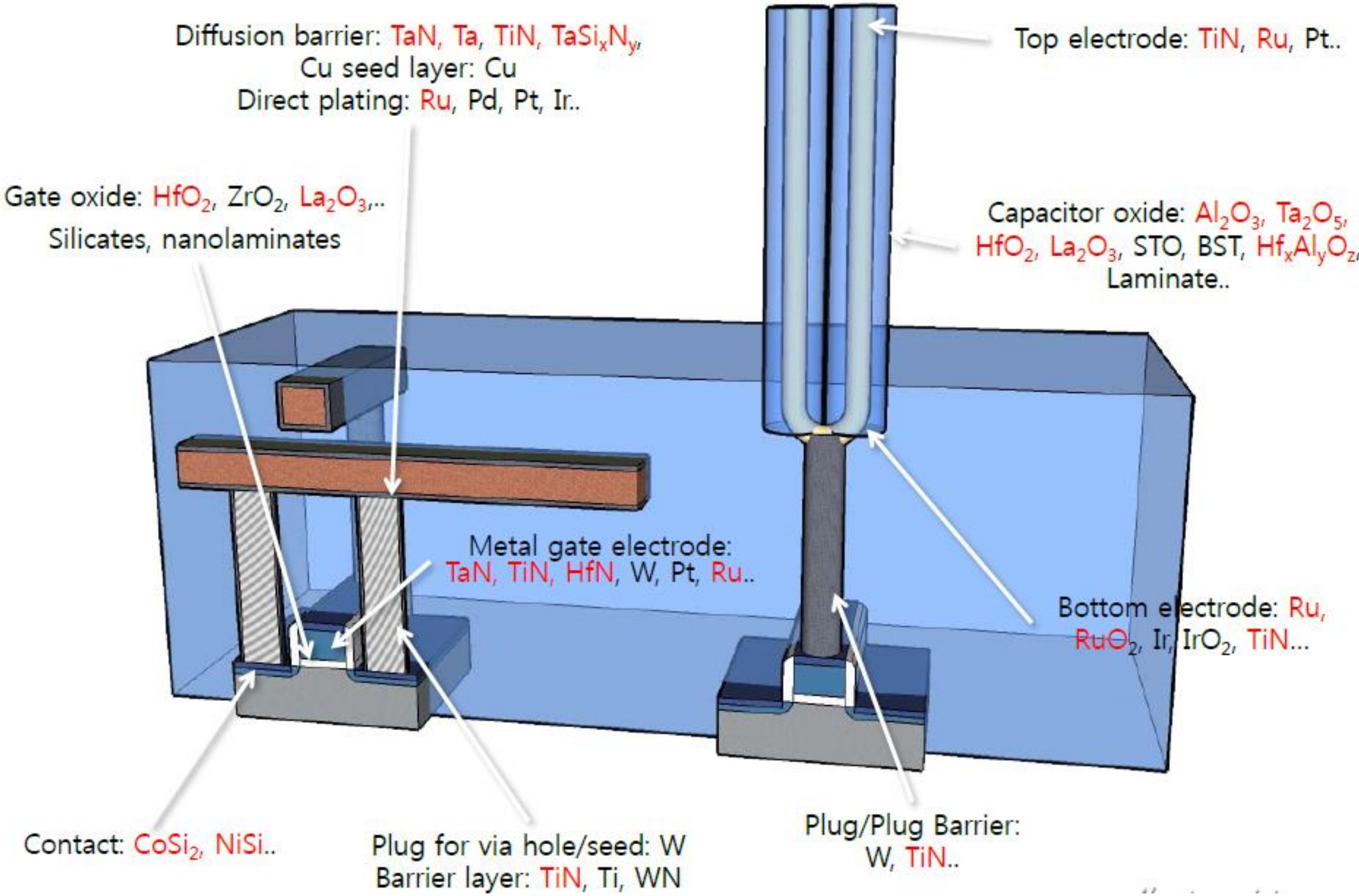


TNO's R2R atmospheric ALD



ALD Layers for Semiconductor Devices

- **Various ALD Materials (used, candidate, and promising group)**



ALD Layers for DRAM (1)

Basic Requirements and Issues

DRAM : 1Transistor (switch cell, mostly n-type) + 1 Capacitor (storage cell)

- *Writing the data within a short enough time (<50ns)*
- *Keeping the stored data stable*
- *Showing a high on/off current ($I_{on/Ioff}$) ratio (>10^8) and V_{th} (~0.7-0.8V)*

: DIBL Issue (short channel effect)

→ Reducing the on current and the operating speed.

Gate Insulator Scale down for the future:

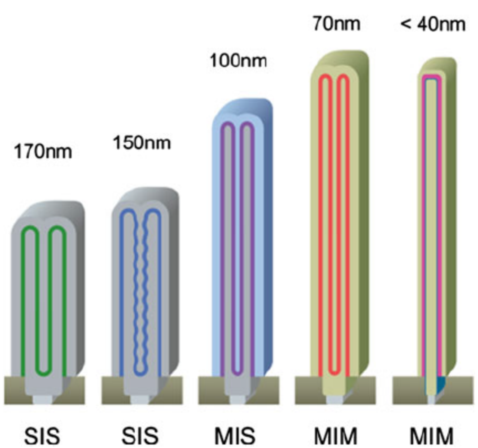
Non-uniform growth of gate SiO_2 on the various crystallographic planes

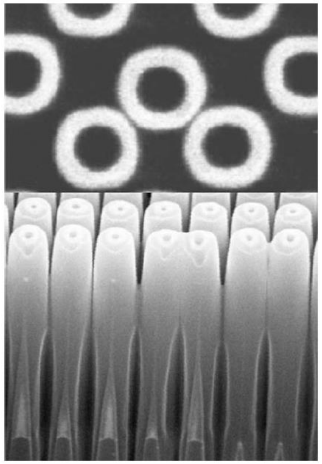
→ ALD gate dielectric layer for conformal formation on the select transistor

ALD Layers in DRAM Cells (2)

Capacitor: Basic Requirements and Issues

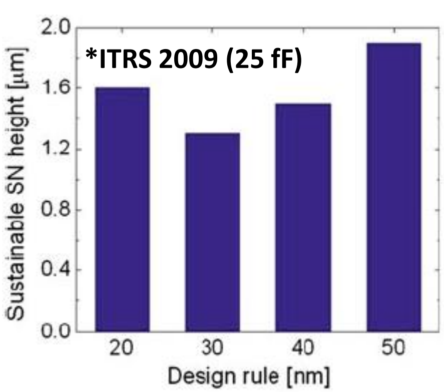
DRAM : 1Transistor (switch cell, mostly n-type) + 1 Capacitor (storage cell)

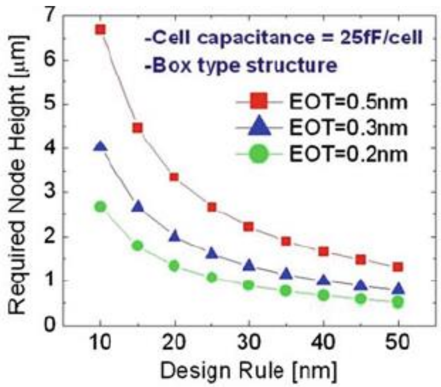




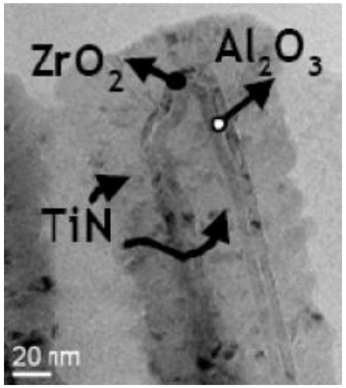
Feature size (Storage node shape)

Cylinder or hemispherical grains (>50nm)
A simple box type (<50nm)





Storage node height

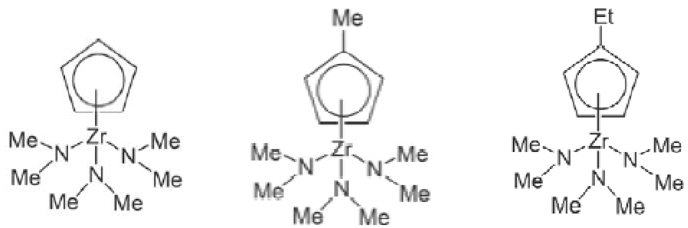


$ZrO_2/Al_2O_3/ZrO_2$ (ZAZ) dielectric film in a stacked Capacitor. With thickness 3.2nm Tox=0.99nm at 1V And 1fA/cell (Hynix)

ALD Layers in DRAM Cells (3)

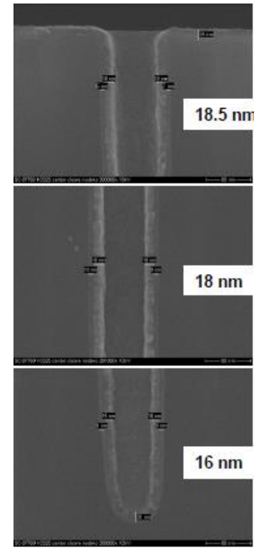
High-k dielectrics : ZrO_2 class

- Tetragonal ZrO_2 (k=40)



Mono-Cp-compounds produce high-k (tetragonal) polumorph easier

The other way is to use doping: (HfO_2:Y, ZrO_2:Sr)

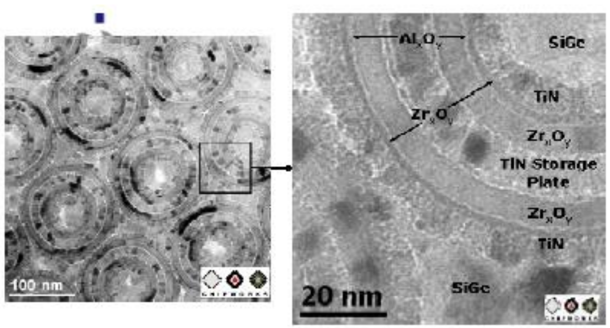


$Zr(CpEt)(NMe_2)_3/O_3$

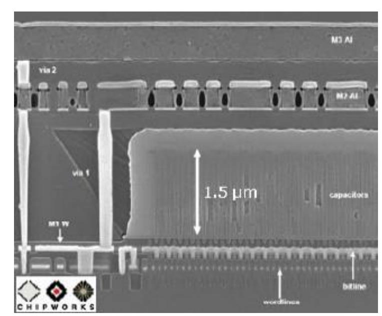
@ 275^{o}C.

AR = 1:60

Step coverage ~90%



TEM Plan-View Sectional Images
Of Samsung 48nm 1GB-DDR SDRAM

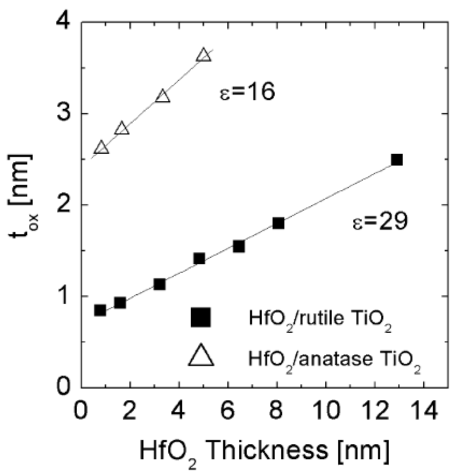


SEM Cross-Sectional Image of Samsung
48nm DDR3 SDRAM

Ref) Markku Leskela 10th MIICS Conference
“Industrial Applications of Atomic Layer Deposition”

ALD Layers in DRAM Cells (4)

High-k dielectrics : HfO_2, TiO_2, Ta_2O_5 etc



Top Electrode

T_{ox} (EOT) <0.3 nm
Dielectric constat
(as high as Possible)
Cap. Value ~25pF*
Step Coverage >95%

Bottom Electrode

Changes in the t_{ox} of HfO_2/rutile TiO_2 and HfO_2/anatase TiO_2 stacks as a function of the HfO_2 thickness

Ref) Seo M. et al. Chem. Mater 22 4419 (2010)

Also Ternary phase such STO etc……

Candidate Materials

1. Ta_2O_5

- Amorphous and orthorhombic
(relatively low k ~ 25)
- Hexagonal phase
(k ~ 65 along the c-axis)
- ALD films : low K on Si, TiN
high k on Ru

Post annealing, Leakage current issues

2. HfO_2

- Amorphous and monoclinic
(relatively low k ~ 20)
- Cubic or tetragonal phase
(k >30, high temperature stable phase)

3. TiO_2

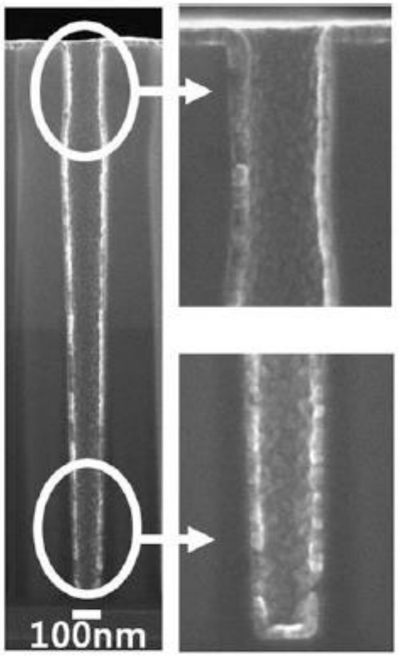
- Anatase phase (relatively low k ~ 40)
- Rutile phase
(k ~90, a-axis ; k ~ 170, c-axis)

Post annealing issue (>500 or 800°C)
Matched with Ru or Ir electrodes

*ALD for Semiconductors (Book)

ALD Layers in DRAM Cells (5)

Electrode for Capacitor : TiN, Ru, and RuO etc.



Vertical SEM image of Ru film grown on The SiO_2 contact hole with an aspect ratio of 17

Electrode Materials

1. TiN

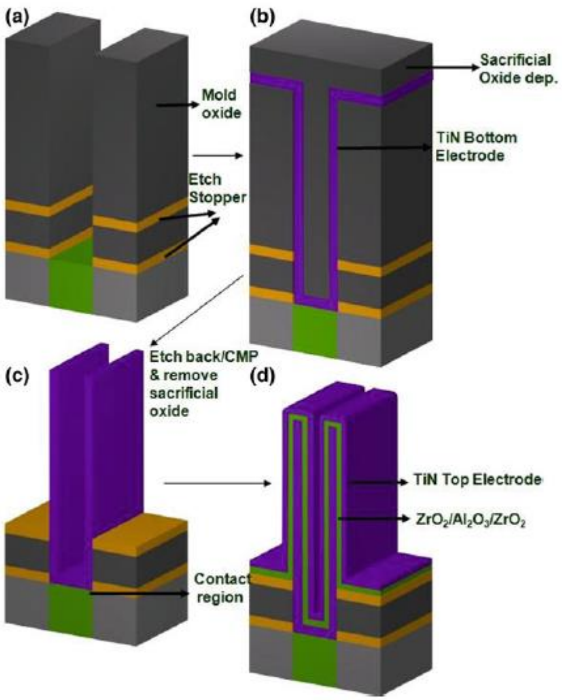
- Metallic (negligible depletion layer thickness)
- Lower oxidation potentials than Al2O3, HfO2, and ZrO2 as a top electrode.
- Issues: No reaction with the dielectric material
  Low contact resistance
  High work function for a low leakage current

2. Noble Metals

- Pt, Ir, and Ru
  a. Ru : WF ~ 4.8 eV, etchable under O2 plasma, ~ 13μΩcm
  cf. Pt (WF ~ 5.6) and Ir (WF ~ 5.3 eV)
  issue: incubation cycle on TiN and SiO_2, Rough/continuous surface
  b. $MeCpPtMe_3$, $Ir(acac)_3$ + Oxygen dissociation (catalytic effect)
  issue: Cost and Patterning

ALD Layers in DRAM Cells (6)

Sacrificial Layer : SiO_2 ALD



☐ Process Requirement for Sacrificial Layer

1. Extremely high aspect ratio
2. Potential oxidation of TiN Bottom electrode

☞ SiO_2 ALD at low temperature

Precursor: DIPAS, BTBAS etc.

Summary

증착법	PVD	CVD	ALD
Source	Target	Precursor	Precursor/Reactant
Mechanism	Thermal /Momentum	Thermal/ Plasma	Thermal/ Plasma
Deposition Rate	O	O	△
Step Coverage	Poor	Good	Excellent
Film adhesion	O	O	O
Uniformity (조성)	△	△	O
Uniformity (두께)	△	△	O
Applications	Semiconductor Display Hard coating Barriers	Semiconductor Display Hard coating Barriers	Semiconductor Solar Cells