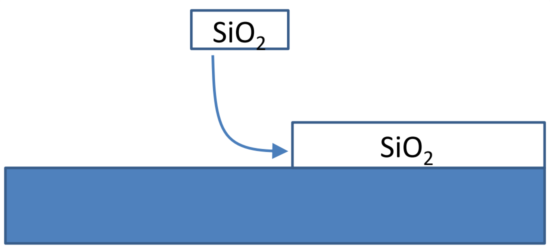
Lecture#10:

Film Deposition (2)

:Chemical Vapor Deposition (CVD)

Deposition (2): Chemical Vapor Deposition (CVD)

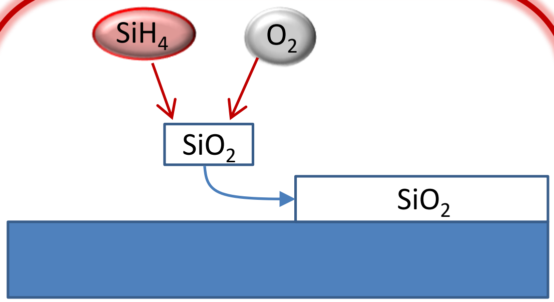
Physical vapor deposition (PVD)



Evaporation
Sputtering
Molecular beam Epitaxy (MBE)

- At low/moderate temperature
- Energetic particle
- Physical adhesion

Chemical vapor deposition (CVD)



Thermal oxidation
Atmospheric pressure CVD (APCVD)
Low pressure CVD (LPCVD)
Plasma enhanced CVD (PECVD)
Metal organic CVD (MOCVD)

- At high temperature
- Reactive substances
- Chemical reaction(Deposit)

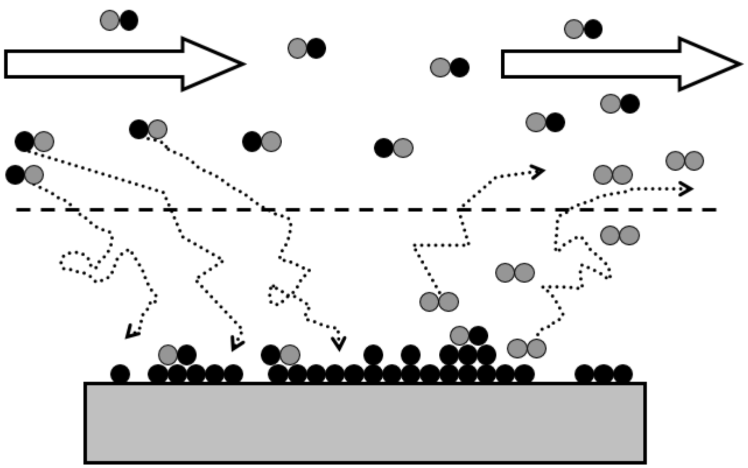
Chemical Vapor Deposition (CVD)

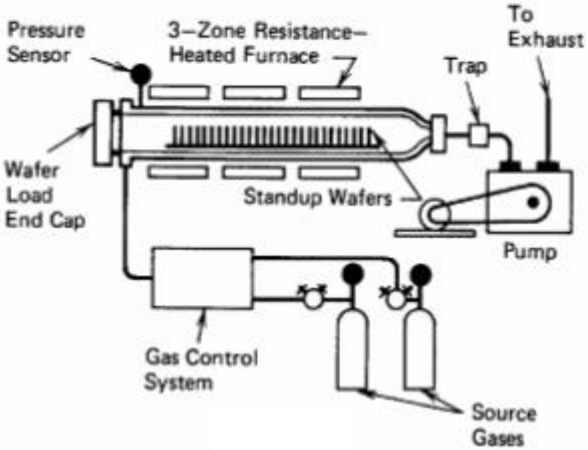
Deposition (2): Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD)

- Chemical vapor deposition forms thin film on the surface of a substrate by thermal decomposition and/or reaction of gaseous compounds.
- The desired material is deposited directly from the gas phase onto the surface of the substrate.

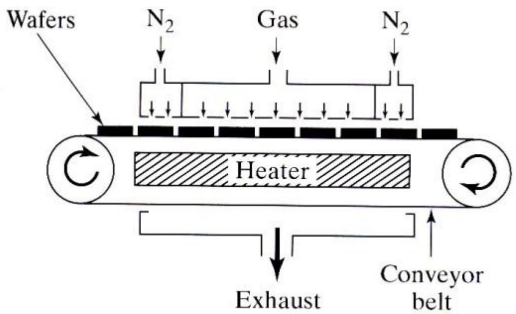
- Process pressure & Temp are higher than PVD
- Good step coverage





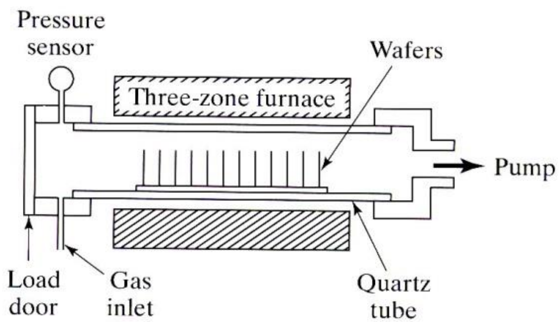
Atmospheric Pressure CVD (APCVD) & Low Pressure CVD (LPCVD)

; formation of thin films on substrate by thermal decomposition and reaction of gaseous compounds
→ poly Si, SiO_2, Si_3N_4



(a)

APCVD: - SiO_2 passivation layer
- Requirement of high gas flow rate



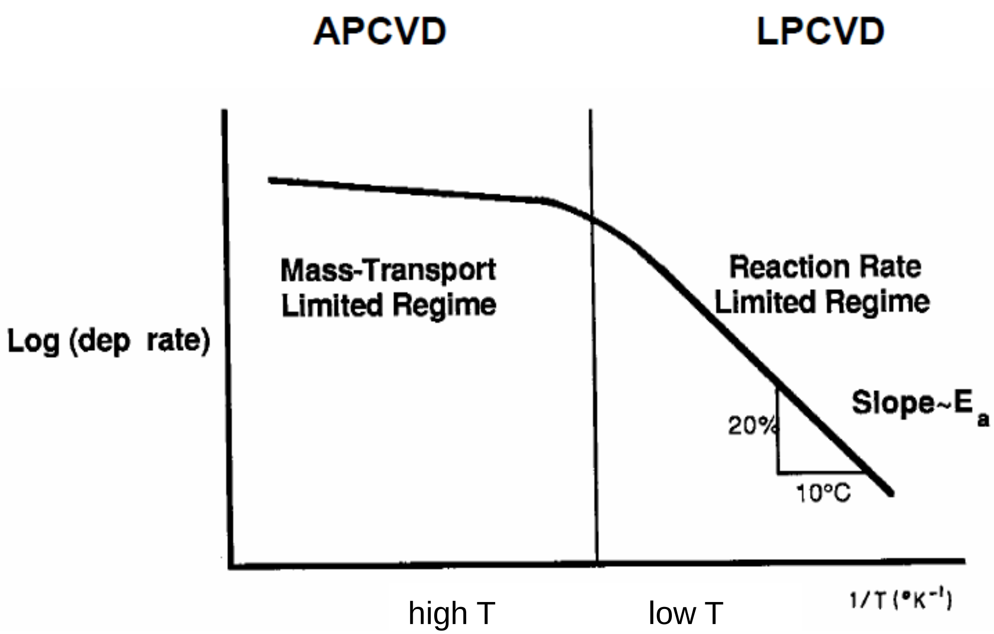
(b)

LPCVD: - Good uniformity
- Materials deposit on the surface of tube

Reactive Regime

Deposition (2): Chemical Vapor Deposition (CVD)

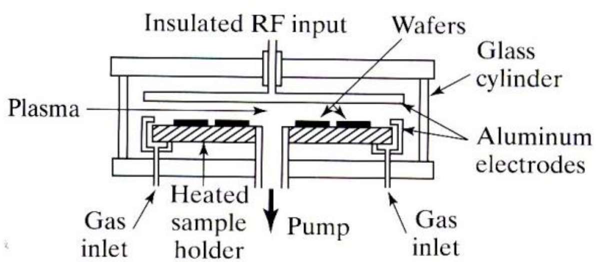
- **Temperature dependence of growth rate**



- When temperature is low, surface reaction rate is slow, and overabundance of reactants is available. Reaction is then surface reaction limited.

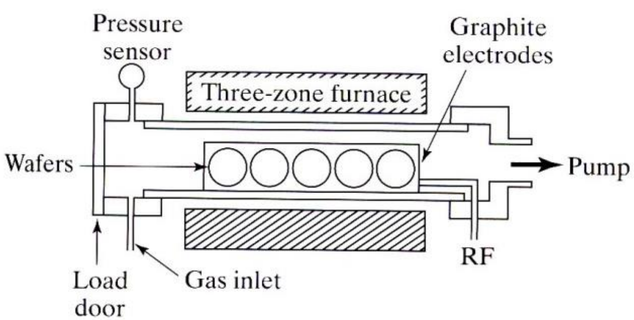
- Above a certain temperature all source gas molecules react immediately. The reaction is then in mass-transport limited regime (also known as diffusion limited and supply limited regime).

Plasma Enhanced CVD (PECVD) & Metalorganic CVD (MOCVD)



(c)

PECVD: - Source gases are decomposed by plasma system
- Process temperature is decreased compared with AP or LPCVD.



(d)

MOCVD: - Source is metalorganic compound
→ Generally, to get III-V or II-VI compound

GaAs : $AsH_3 + Ga(CH_3)_3 \rightarrow GaAs + 3CH_4$

Deposition of Dielectric Layer: SiO_2

Deposition (2): Chemical Vapor Deposition (CVD)

- **Comparison**

$$\text{APCVD: } SiH_4 + O_2 \rightarrow SiO_2 + 2H_2$$
$$\text{PECVD: } SiH_4 + 2N_2O \rightarrow SiO_2 + 2N_2 + 2H_2$$
$$\text{LPCVD: } SiH_2Cl_2 + 2N_2O \rightarrow SiO_2 + 2N_2 + 2HCl$$

Decomposing $Si(OC_2H_5)_4$
TEtraelthyl **O**rtho **S**ilicate

PROPERTIES OF CVD AND THERMAL SILICON DIOXIDE[1]

FILM TYPE:	THERMAL	PECVD	APCVD	LPCVD	TEOS
Deposition Temp. (°C):	800-1200	200	450	900	700
Step Coverage:	conformal	good	poor	conformal	conformal
Stress ($\times 10^9$ dynes/cm^2):	3C	3C-3T	3T	3T	1C
Dielectric Strength (10^6 V/cm):	3 - 6	8	10	10	
Etch Rate (Å /min): (100:1, H_2O:HF)		400	60	30	30

[Note] Decomposition of the vapor produced from a liquid source, TEOS, can also be used in an LPCVD system between 650 and 700 °C.

Deposition of Dielectric Layer: Si_3N_4

Deposition (2): Chemical Vapor Deposition (CVD)

Comparison

- APCVD: Silane with ammonia at 700 - 900 °C :

$$3SiH_4 + 4NH_3 \xrightarrow{700-900^\circ C} Si_3N_4 + 12H_2$$

- LPCVD: Dichlorosilane with ammonia at 700 - 800 °C :

$$3SiCl_2H_2 + 4NH_3 \xrightarrow{700-800^\circ C} Si_3N_4 + 6HCl + 6H_2$$

- Thermal growth of silicon nitride is possible, but not very practical; Silicon nitride will form when silicon is exposed to ammonia at temperature between 1000 and 1100 °C, but the growth rate is very low.

- PECVD: Silane with nitrogen to plasma nitride (SiN) :

$$2SiH_4 + N_2 \rightarrow 2SiNH + 3H_2$$

(at 250 ~ 300 °C)

Silane with ammonia :

$$SiH_4 + NH_3 \rightarrow SiNH + 3H_2$$

Plasma deposition does not produce stoichiometric silicon nitride films.

[Note] LPCVD films have high internal tensile stresses (10T), on the other hand, plasma deposited films have much lower tensile stresses (5T).

The resistivity and dielectric strength of the LPCVD nitride films are better than those of most plasma films.

Deposition (2): Chemical Vapor Deposition (CVD)

LPCVD

- > 580°C Polysilicon
- < 580°C Amorphous silicon

SiH_4 (vapor) → Si (Solid) + $2H_2$ (gas)
Typically, ramp temperature due to depletion of SiH_4

- Low pressure system (25 to 150 Pa) use either 100 % silane or 20 to 30 % silane diluted with nitrogen. A temperature between 600 - 650 °C results in deposition rate of 100 - 200 A/min.

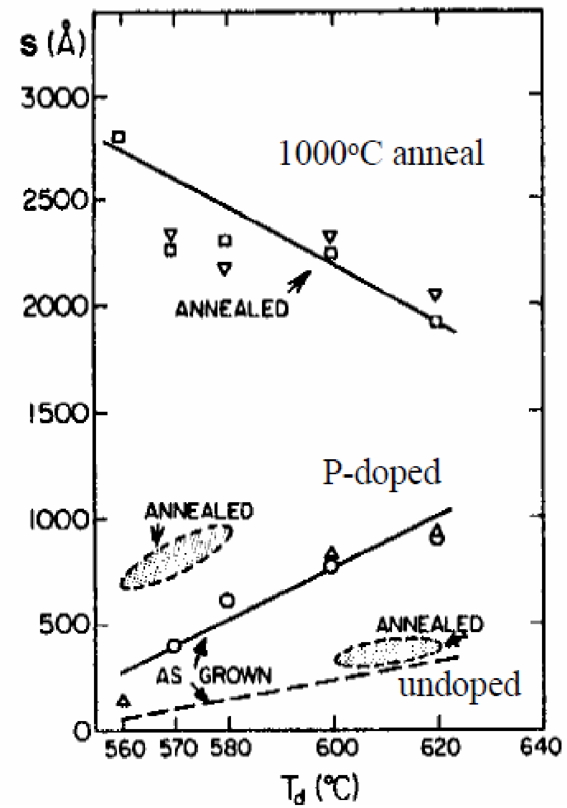


Fig. 15 Average crystallite size S for phosphorus-doped LPCVD silicon layers as-grown (o = interface, Δ = surface), and annealed at 1000°C (◊ = interface, ∇ = surface) as a function of deposition temperature, T_d. Undoped layers (dashed lines) are shown for comparison. From G. Harbeke, *et al.*, RCA Review, 44, 287 (June, 1983).

Deposition of Metal

Deposition (2): Chemical Vapor Deposition (CVD)

CVD for metal films

W: $WF_6 \rightarrow W + 3F_2$

$WF_6 + 3H_2 \rightarrow W + 6HF$

Mo: $2MoCl_5 + 5H_2 \rightarrow 2Mo + 10HCl$

Ta: $2TaCl_5 + 5H_2 \rightarrow 2Ta + 10HCl$

Ti: $2TiCl_5 + 5H_2 \rightarrow 2Ti + 10HCl$

- Many metals can be deposited by CVD processes. Molybdenum (Mo), tantalum (Ta), titanium (Ti), and tungsten (W) are all of interest in because of their low resistivity and their ability to from silicides with silicon.

Comparison

Material/method	Source gases	Temperature	Stability
LTO	$SiH_4 + O_2$	425 °C	Densifies
HTO	$SiCl_2H_2 + N_2O$	900 °C	Loses Cl
TEOS	TEOS + O_2	700 °C	Stable
PECVD OX	$SiH_4 + N_2O$	300 °C	Loses H
LPCVD poly	SiH_4	620 °C	Grain growth
LPCVD a-Si	SiH_4	570 °C	Crystallizes
LPCVD Si_3N_4	$SiH_2Cl_2 + NH_3$	800 °C	Stable
PECVD SiN_x	$SiH_4 + NH_3$	300 °C	Loses H
CVD-W	$WF_6 + SiH_4$	400 °C	Grain growth

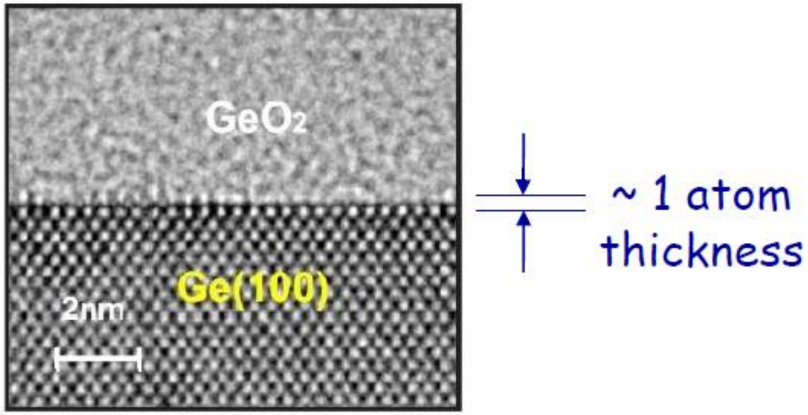
LTO = Low-Temperature Oxide; HTO = High-Temperature Oxide; TEOS = TetraEthylOxySilane, $Si(OC_2H_5)_4$.
The precursor name TEOS has become synonymous with the resulting oxide film; it should be obvious which meaning is used.

Atomic Layer Deposition (ALD)

Deposition (2): Chemical Vapor Deposition (CVD)

Definition and Features

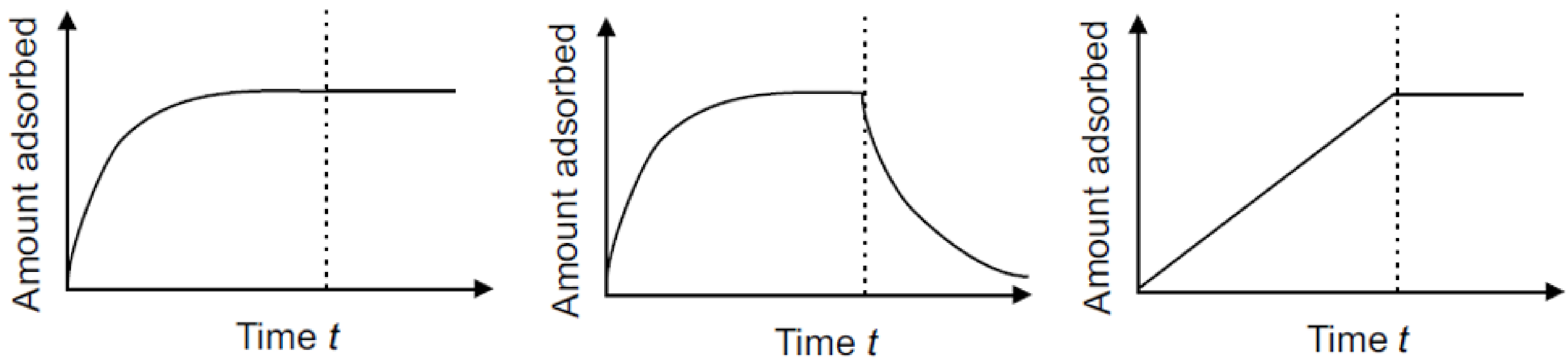
- Atomic layer deposition (ALD) is a method of applying thin films to various substrates with atomic scale precision.
- ALD film growth is self-limited and based on surface reactions, which makes achieving atomic scale deposition control possible.
- By keeping the precursors separate throughout the coating process, atomic layer thickness control of film grown can be obtained as fine as atomic/molecular scale per monolayer.
- Examples) GeO_2 over crystalline Ge for MOSFETs



Tanaka and Takagi, ECT Trans, 2011

Surface Saturation of ALD

- **Self-limitation**



Irreversible saturation ALD reactions

Surface saturates with a monolayer of precursor, strong chemisorption (=chemical bonds formed)

Reversible saturation

Physisorption only (weak bonds like van der Waals): once precursor flux is stopped, surface species will desorb.

Irreversible non-saturating

CVD regime:
more reactants in, more film is deposited (continuously)

ALD Process (1)

Key features

Chemisorption

- Suitable temperature for chemical bonding, no thermal decomposition
- Covalent bonding ⇨ excellent adhesion

Saturation

- Sufficient dosing of precursor material
- Self-terminating reactions ⇨ extremely precise dosing not required

Surface controlled reactions

- Film thickness is independent of substrate geometry ⇨ uniform film onto deep trenches and 3D structures

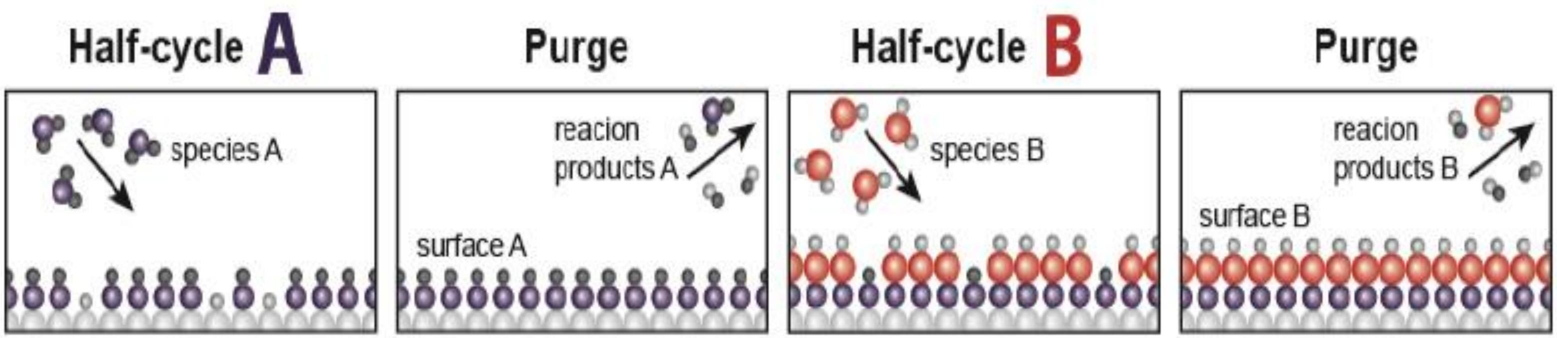
Sequential

- Digital growth
- Sufficient purging needed between pulses
- Good flow dynamics required to ensure rapid gas changes

ALD Process (2)

Deposition (2): Chemical Vapor Deposition (CVD)

- **Process flow**



- Reactants (precursors) are pulsed into reactor alternately and cycle-wise (ABAB..)
- Precursors react through saturative (self-limiting) surface reactions
- A sub-monolayer of material deposited per cycle

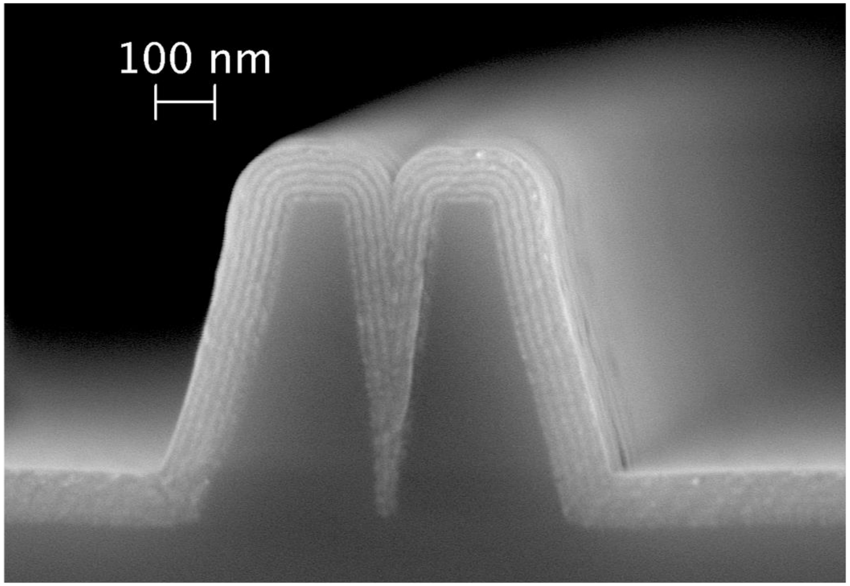
ALD Process (3)

Deposition (2): Chemical Vapor Deposition (CVD)

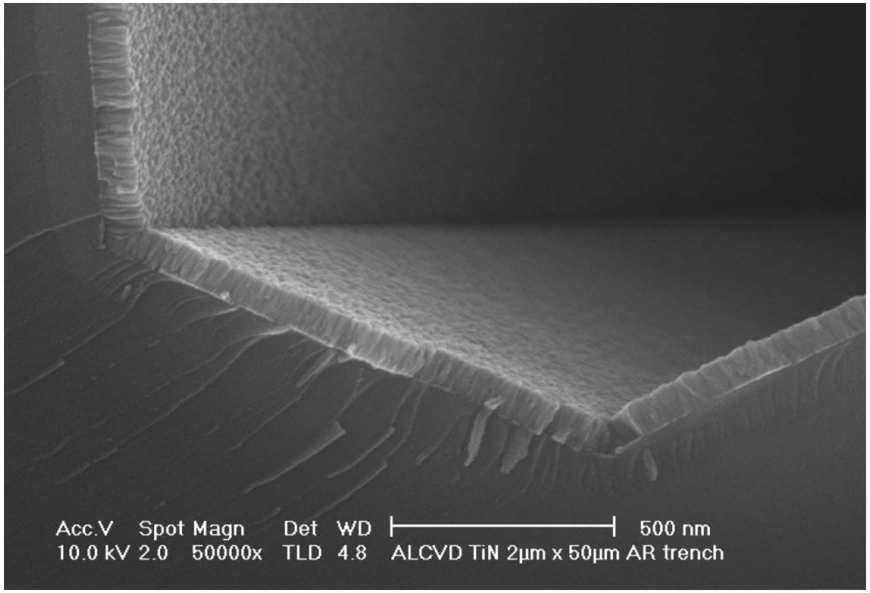
- Video: Process flow (ALD)

Deposition (2): Chemical Vapor Deposition (CVD)

- **Conformality**
  - Excellent conformality; all surfaces coated by diffusing gaseous precursors in the surface reaction limited mode.



Al_2O_3/TiO_2 nanolaminate

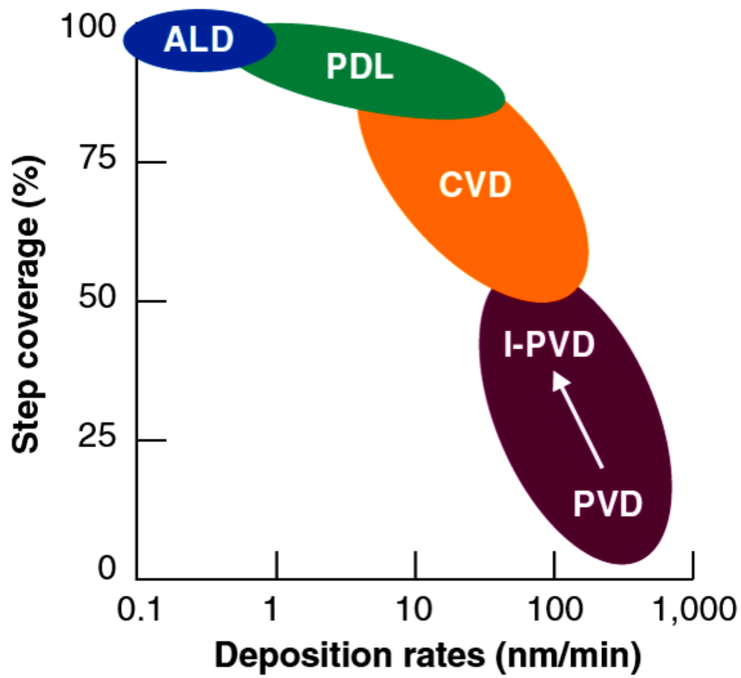


TiN barrier

Deposition Trends

Deposition (2): Chemical Vapor Deposition (CVD)

- **Various deposition technique**
  - 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



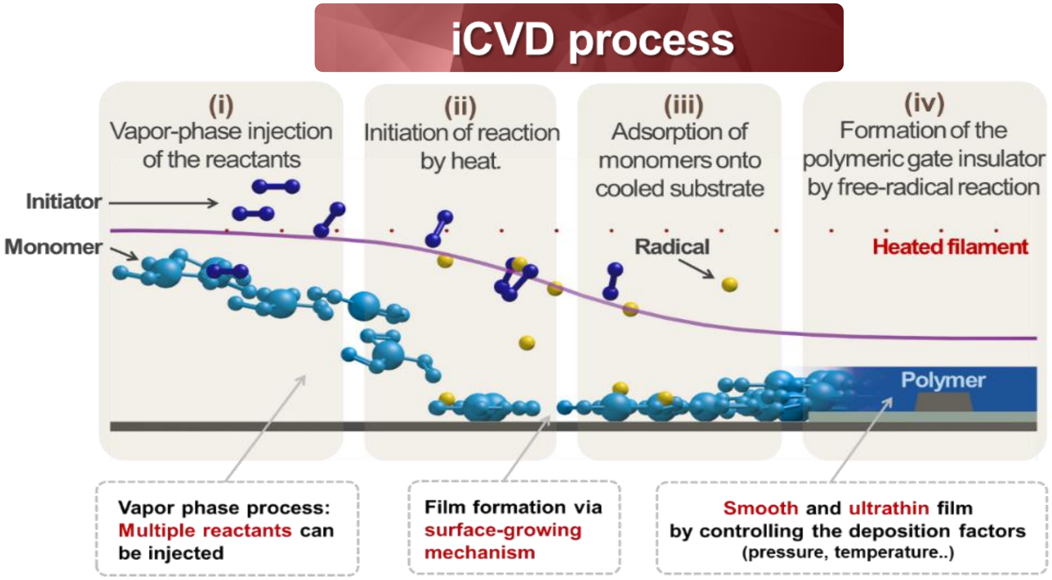
Step coverage and deposition rate Vs. deposition technique.

Ref: "Technology Backgrounder: Atomic Layer Deposition," IC Knowledge LLC, 24 April 06. <www.icknowledge.com/misc_technology/Atomic%20Layer%20Deposition%20Briefing.pdf>.

Overview

- Initiated chemical vapor deposition (iCVD) is a novel vapor-phase deposition method capable of producing ultrathin (sub-10 nm) and highly pure polymeric films.

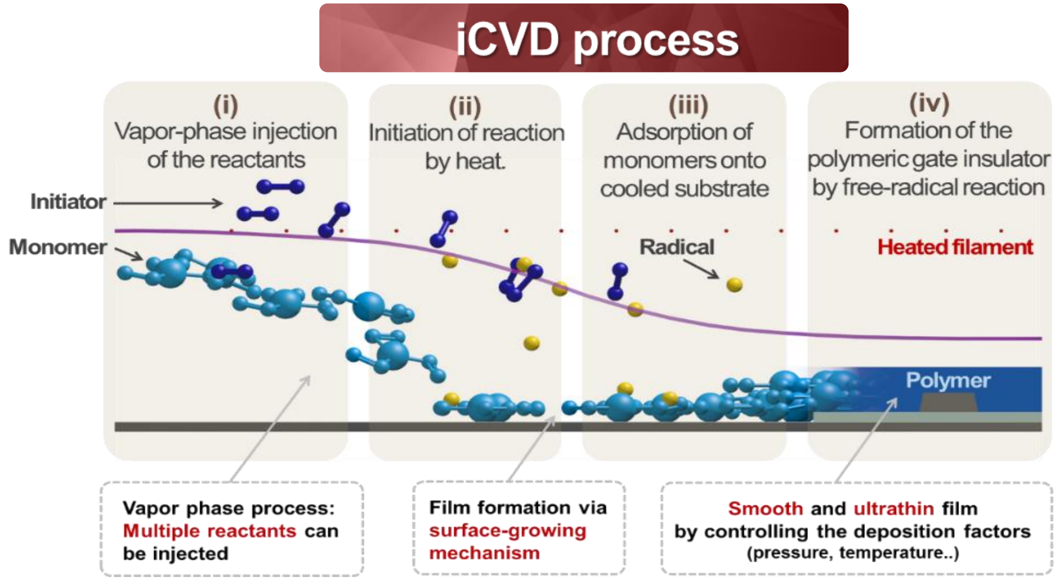
- In the iCVD chamber, an initiator is thermally decomposed into radicals, and these radicals react with monomers to form growing polymer chains.



Hanul Moon et al, Nature mater., 14, p.628-635 (2015)

Deposition (2): Chemical Vapor Deposition (CVD)

Features



Hanul Moon et al, Nature mater., 14, p.628-635 (2015)

- Polymerizaiton in vapor phase
- A surface-growing films
  - ✓ Superior step coverage
- Homogeneous mixing in vapor phase
  - ✓ Tunability of the composition

- **Solvent-free polymer film** growth
- Deposition of conformal film
  - ✓ **Conformal doping** at 3D structure device
- **Easy to synthesize a wide variety of polymer with desired functions.**
  - ✓ Containing dopants

Summary: PVD

Deposition (2): Chemical Vapor Deposition (CVD)

Evaporation

- Evaporation of a source under vacuum condition ($1 \sim 10^{-4}$ Pa)
- Thermal type & E-beam type
- Process parameters : pressure, temperature
- advantage : simple, popularly-used
- disadvantage : poor step coverage, shadowing,
  no metal compound and alloy deposition

Sputtering

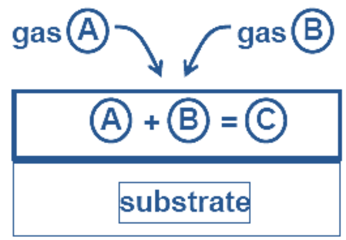
- Bombardment of a target with energetic atom (Ar^+)
- Process parameter : everything (power)
  * DC power : for conductive materials (Al, W, Ti)
  * RF power : for dielectric materials (SiO_2, AlO_2, ..)
- Advantage
  * metal compounds, alloy..
  * better step coverage than evaporation
- Disadvantage
  * Ion incorporation into the film

Summary: CVD

Deposition (2): Chemical Vapor Deposition (CVD)

CVDs

- Thermal decomposition & Reaction of gaseous compounds on the substrate



- * APCVD (250~450°C)
- * PECVD (substrate heating ~400°C)
- * LPCVD (300~1150°C)

- Advantage : uniformity, good step coverage
- Disadvantage : High temperature process
  - * Poly silicon(600~650°C), SiO_2(300~500°C), Si_3N_4(700~900°C)
    in situ, doping

ALD

- Advantage:
  - Uniformity, 3D conformality, precise thickness control.
  - Low temperature deposition possible.
- Disadvantage:
  - Deposition Rate slower than CVD.
  - Number of different material that can be deposited (fair compared to MBE).