NANYANG TECHNOLOGICAL UNIVERSITY

Course: EE3013 Semiconductor Devices and Processing

School: School of Electrical and Electronic Engineering

Deposition - Chemical Vapour Deposition

Thin Film Deposition Methods

Two main **deposition methods** are used today:

- **Physical Vapour Deposition (PVD)** (no chemical reaction involved)
  The vapour of thin film materials is created inside the chamber, and condensation occurs on wafer surface leading to the deposition of a solid thin film.
  E.g. Evaporation and sputter deposition are most commonly used for metals.

- **Chemical Vapour Deposition (CVD**) (involves chemical reaction)
  Reactant gases are introduced into the chamber, and chemical reactions occur on wafer surface leading to the deposition of a solid thin film.
  E.g. APCVD, LPCVD, and PECVD, which are most commonly used for dielectrics and Si.

Chemical Vapour Deposition: Introduction

- Chemical Vapour Deposition (CVD) is a thin film deposition technique based on chemical reactions, supplied through the use of gaseous compounds. The major difference between CVD and PVD is at the nucleation step; CVD has a chemical reaction at the substrate, whereas PVD does not.
- CVD techniques have been commonly used for **dielectric** and **polysilicon** depositions.
- **Dielectric** films such as SiO_2 and Si_3N_4, are used as isolation, mask, and passivation layers.
- **Polysilicon** film can be used as the conducting layer, semiconductor, or resistor by proper doping with different impurities.
- The deposited material structure can be amorphous, polycrystalline, or single-crystal.
- It operates at a temperature of 300 – 900°C. Deposition temperatures of below 300°C are currently under extensive studied by various research groups.

CVD Advantages and Disadvantages

(As compared to physical vapour deposition)

Advantages:

- High growth rates possible good reproducibility
- Can deposit materials which are hard to evaporate
- Can grow epitaxial (refers to the deposition of a crystalline layer on a crystalline substrate)
- Generally better film quality due to a more conformal step coverage

Disadvantages:

- High process temperature
- Complex processes, toxic, and corrosive gasses
- The film may not be pure (e.g., hydrogen incorporation)

Types of CVD Reactions

The possible types of CVD reactions are:

- **Pyrolysis (thermal decomposition)**: a compound dissociates (breaks bonds, or decomposes) with the application of heat, usually without oxygen
- **Reduction**: a chemical reaction occurs by reacting a molecule with hydrogen
- **Oxidation**: a chemical reaction of an atom or molecule with oxygen
- **Reduction-oxidation (redox)**: a combination of reactions 3 and 4 with the formation of two new compounds

In this lesson, we are focusing on pyrolysis (thermal decomposition) reaction.

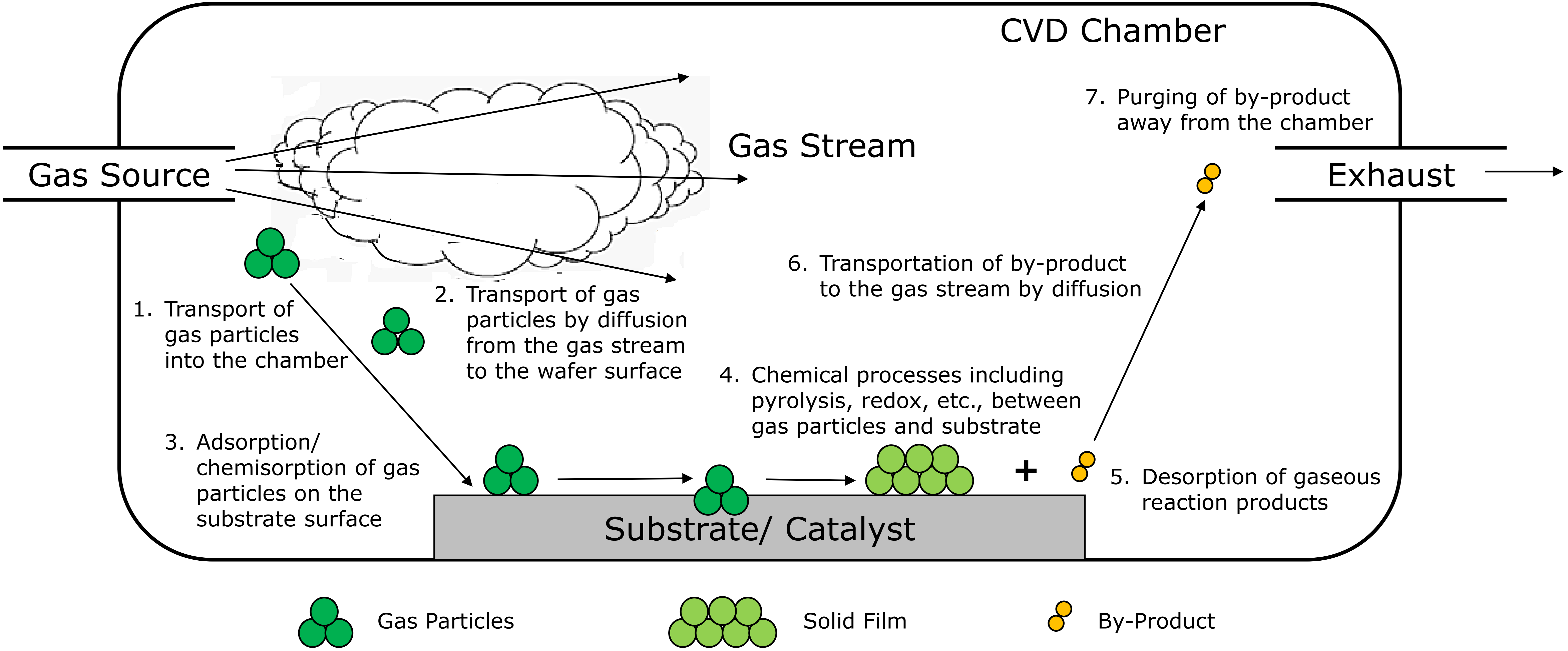
Steps Involved in a CVD Process

- The formation of a nonvolatile solid film on the substrate occurs due to the reaction of vapour-phase chemicals (reactants) that contain the required constituents:
  Example: (SiO_2 deposition): SiH_4 (gas) + O_2 (gas) → SiO_2 (solid film) + H_2 (gas)

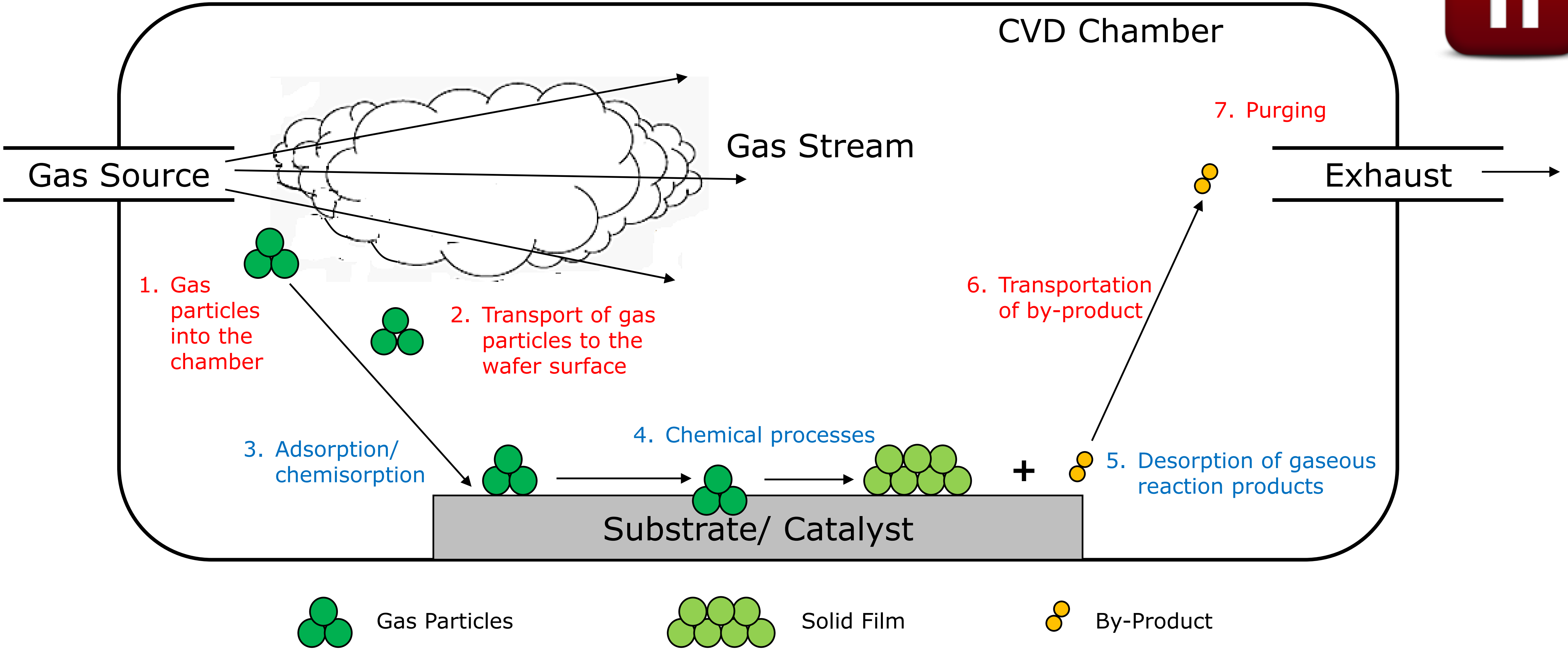
- Here are the reaction steps that occur in the CVD process:
  - Transport of reacting gaseous species to the substrate surface *(Steps 1 and 2)*
  - Adsorption or chemisorption of the species on the substrate surface *(Step 3)*
  - The heterogeneous surface reaction catalysed by the substrate surface *(Step 4)*
  - Desorption of gaseous reaction products *(Step 5)*
  - Transport of reaction products away from the substrate surface *(Steps 6 and 7)*

For Steps 1 – 7, refer to the next slide

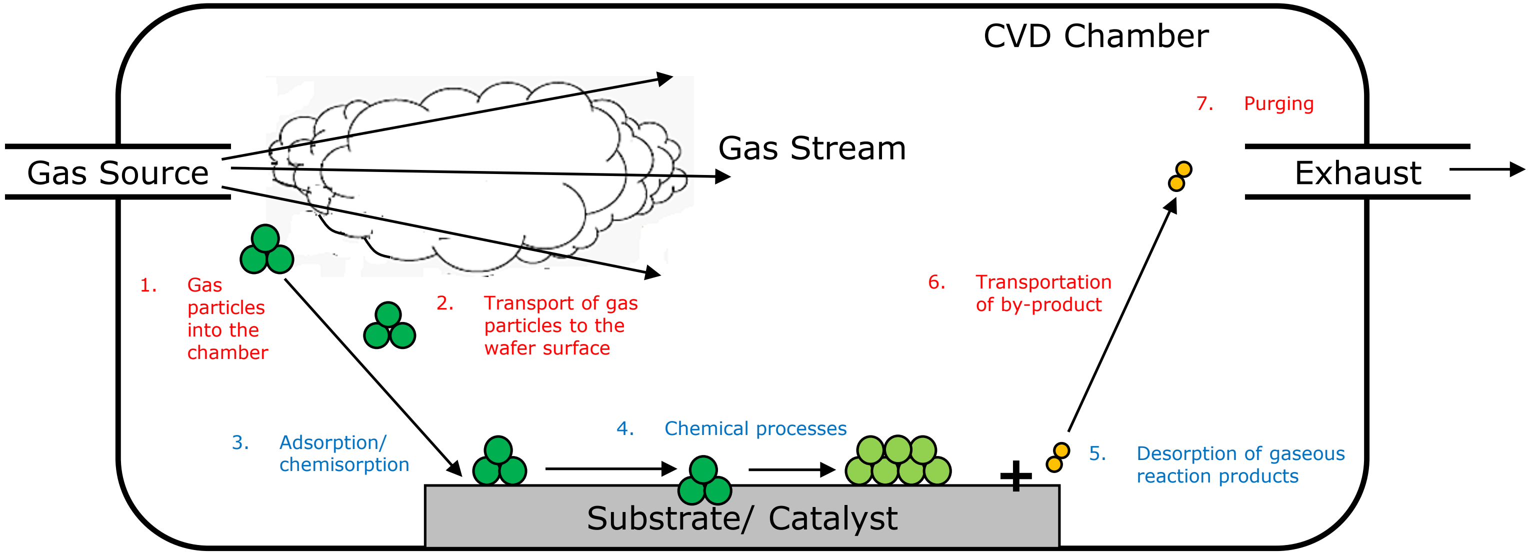
Steps Involved in a CVD Process



Steps Involved in a CVD Process



Steps Involved in a CVD Process



- Steps 1, 2, 6, and 7 are closely related and can be grouped together as "mass-transport" processes.
- Steps 3, 4, and 5 are closely related and can be grouped together as "surface-reaction" processes.
- Reaction rate may be limited by:
  - Gas transport to/ from surface
  - The surface chemical reaction rate
- Hence, both mass transport and surface reaction processes are important for film growth rate.

Deposition Rate: Mass Transport-Limited Region

Mass transport-limited:

As the name implied, the rate of gas particles diffusion (transportation) onto the substrate's surface is limited but the chemical reaction rate between gas particles and the substrate is fast. Therefore, the deposition rate is determined by the rate of gas particles diffusing (transporting) onto the substrate's surface.

In other words:

- Gas particles exhibit low transportation/ diffusion rate onto the substrate's surface
- High chemical reaction rate between gas particles and substrate's surface
- A chemical reaction occurs immediately as the gas particles are absorbed on the substrate
- Hence, the deposition rate is not determined by surface reaction rate but by the rate of gas particles transportation onto the substrate

Deposition Rate: Surface Reaction-Limited Region

Surface reaction-limited:

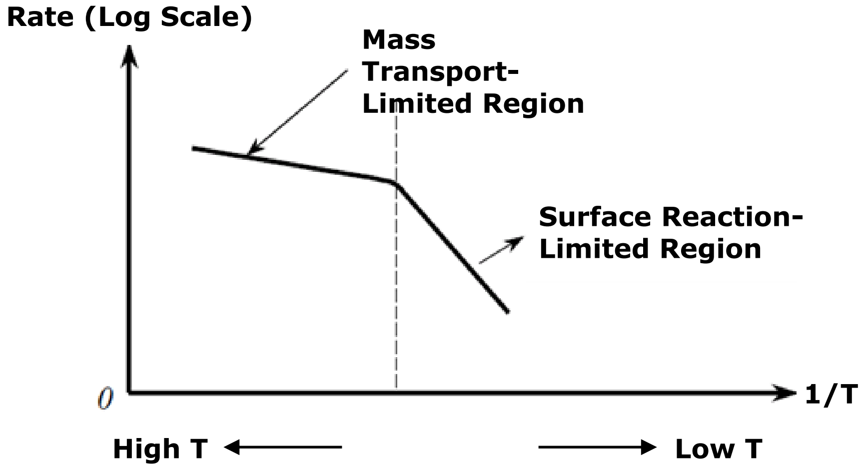
As the name implied, the chemical reaction rate between gas particles and the substrate is limited but the rate of gas particles diffusion (transportation) onto the substrate's surface is high. Therefore, the deposition rate is determined by the rate of chemical reaction between the gas particles and the substrate's surface.

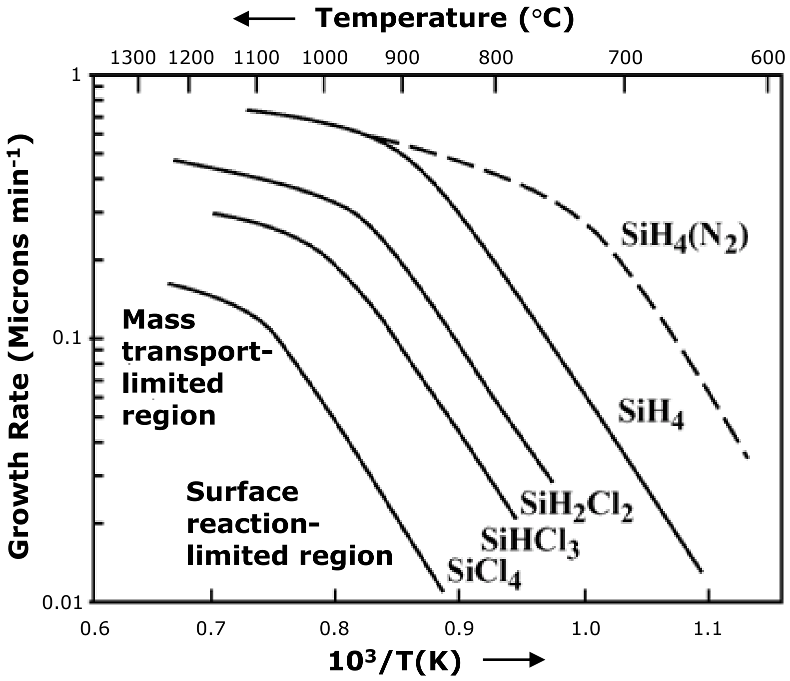
In other words:

- Gas particles exhibit high diffusion/ transportation rate onto the substrate's surface
- Low chemical reaction rate between gas particles and substrate's surface
- Hence, deposition rate is not determined by rate of gas particles transportation onto the substrate but by the rate of chemical reaction between gas particles and substrate

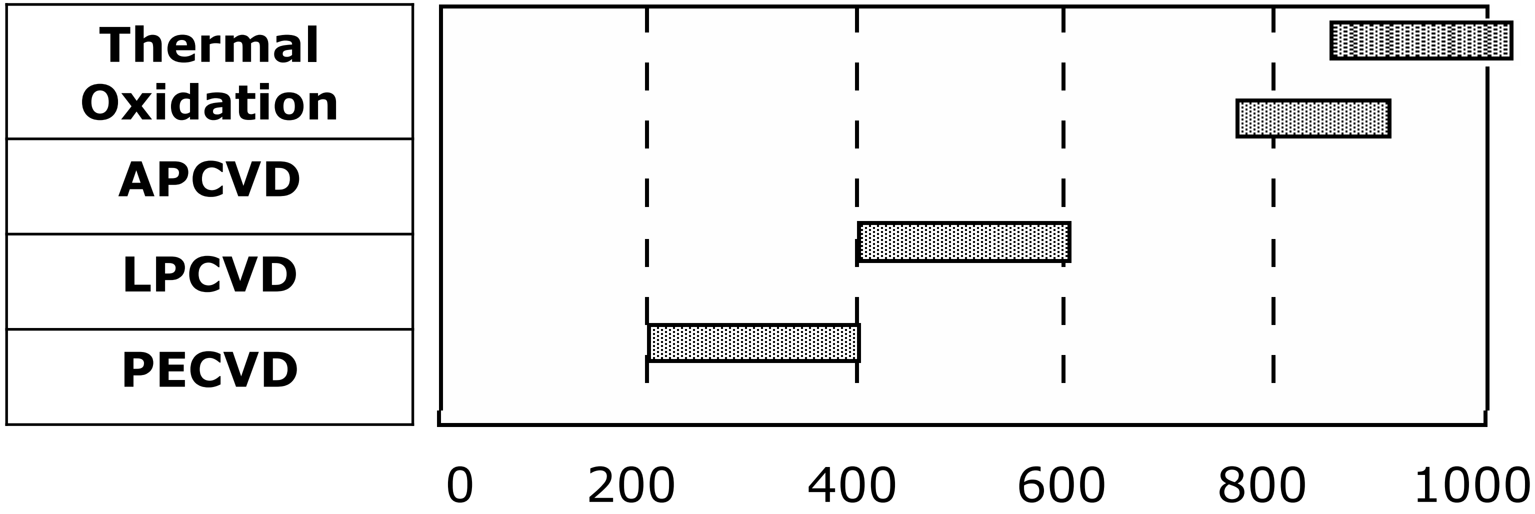
CVD Film Growth Rate

- The growth rate in CVD reaction depends on the temperature.
- The two figures below show the Arrhenius plot showing the log of the growth rate versus the inverse temperature.
- **Mass transport-limited region:** Occurs at high temperature (temperature is needed to decompose the gases and move the species easily to the substrate).
- **Surface reaction-limited region:** Occurs at low temperature but sensitive to temperature change. A small change in temperature can greatly affect the chemical reaction rate.





Arrhenius behaviour of a variety of silicon-containing growth species



APCVD: Atmospheric-Pressure Chemical Vapour Deposition

LPCVD: Low-Pressure Chemical Vapour Deposition

PECVD: Plasma-Enhanced Chemical Vapour Deposition

The figure shows typical operating temperatures for deposition of various kinds of Si-based films using various types of CVD techniques.

What are the differences in growing silicon oxide between thermal oxidation and CVD process?

Practice Question

When the speed of a CVD reaction cannot proceed more rapidly than the mass-transport rate at which the reactant gases are supplied, this situation is referred to as

a) Precursor-rate limited

b) Reaction-rate limited

c) Mass-transport limited

d) Decomposition-rate limited

Pause and try out this question

Types of Chemical Vapour Deposition

Types of CVD

APCVD (Atmospheric-Pressure CVD)

- Atmospheric pressure (760 Torr)
- Mass transport limited growth rate
- Process temperature >700 °C
- High film growth rate, poor step coverage

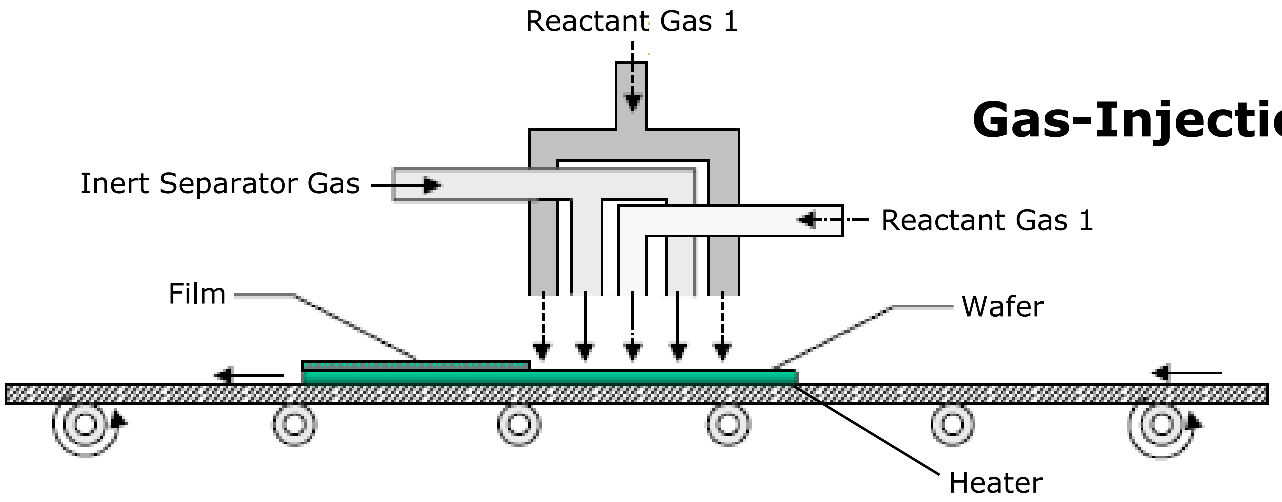
LPCVD (Low-Pressure CVD)

- Low pressure (around 1-1,000mTorr) is employed
- The surface reaction-limited growth rate
- Process temperature 400–600°C
- Lower growth rate than APCVD. Better film uniformity and step coverage, with fewer defects

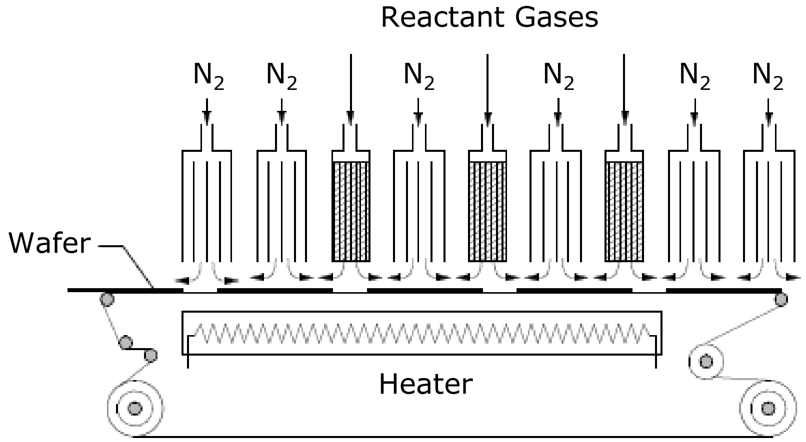
PECVD (Plasma-Enhanced CVD)

- Can run in RF plasma mode
- Plasma helps to break up gas molecules for surface reaction, able to process at a much lower temperature
- Process temperature around 200–400°C
- Film quality is poorer than LPCVD

Atmospheric-Pressure CVD



Gas-Injection Type

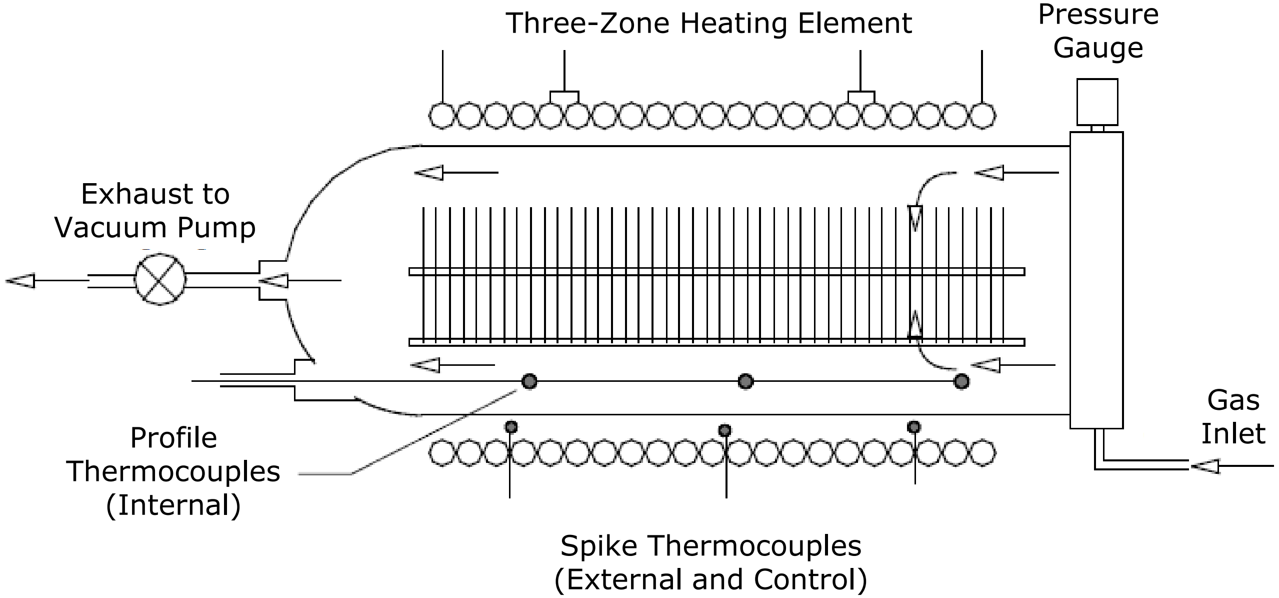


Plenum Type

Why does APCVD operate in mass transport limited regime?

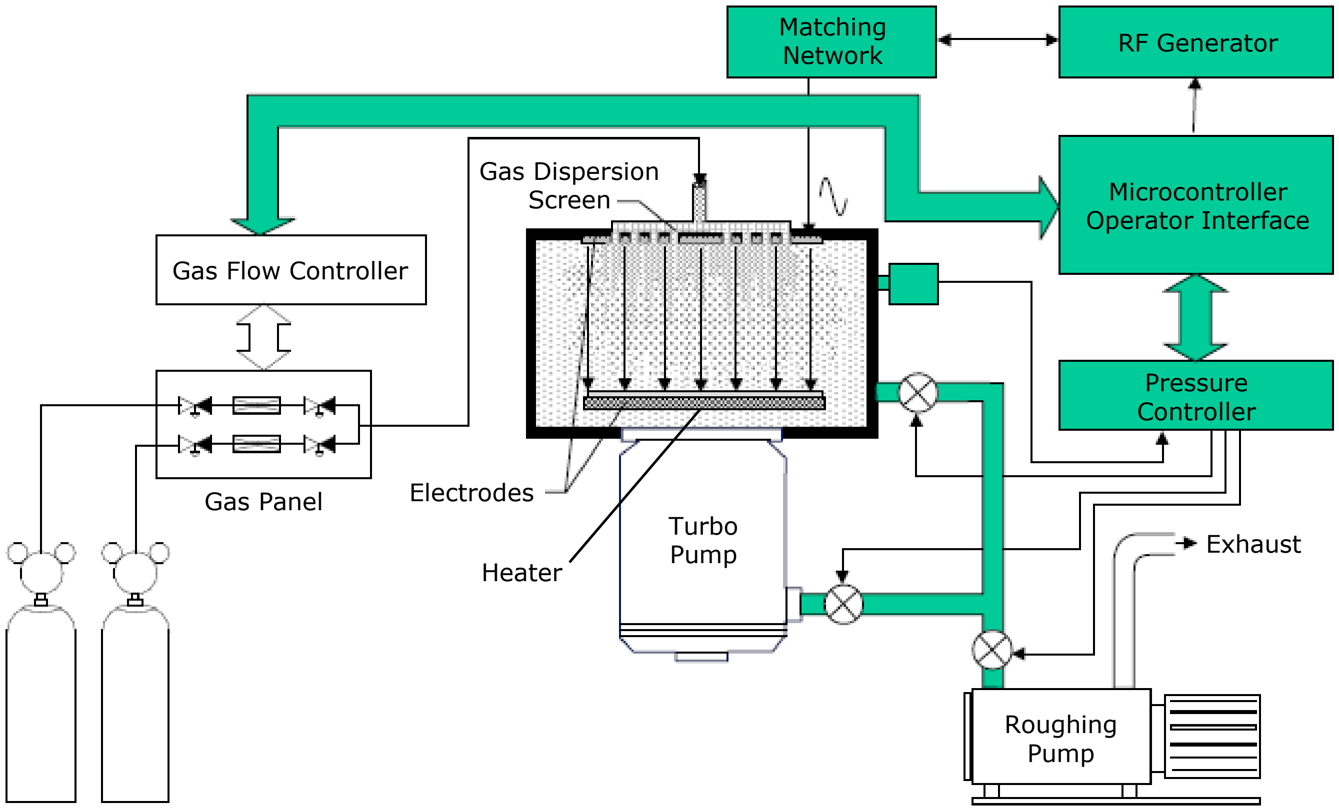
- There is a collision between the gases and the air molecules.
- High temperature needed to decompose the gases, especially at atmospheric pressure.

Low-Pressure CVD



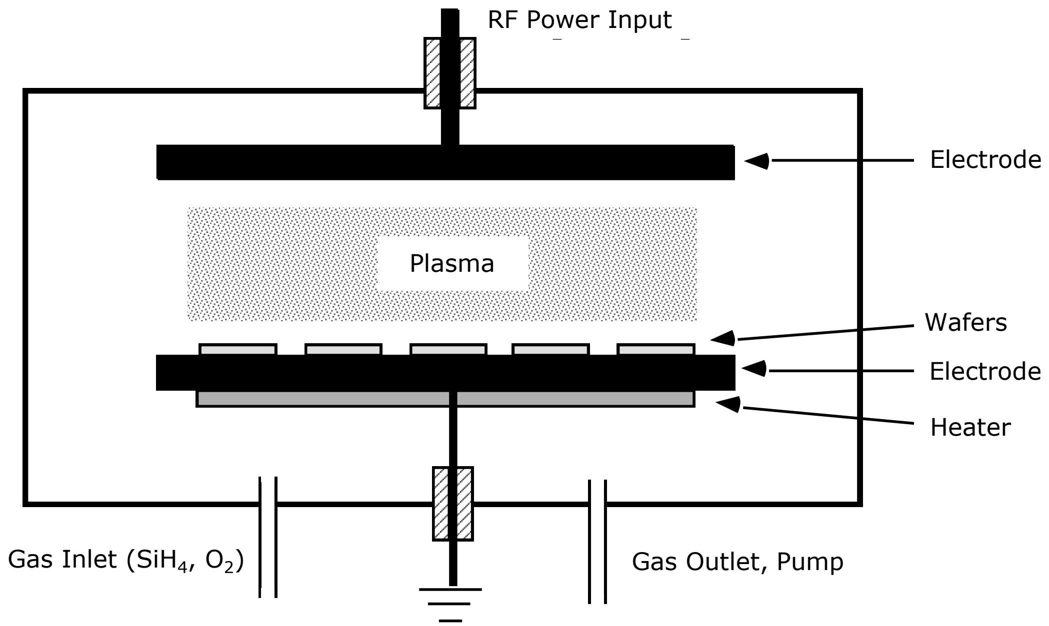
- Operated in surface reaction-limited mode. Why?
- Because of the low-pressure reaction condition (vacuum), the diffusivity of gas species is increased (increase in the transport of reactants to the substrate surface)
- As LPCVD operates in reaction limited regime, it is **VERY** sensitive to temperature. So, the temperature needs to be controlled closely (within +/- 1°C)

Plasma-Enhanced CVD



- A plasma-assisted CVD process
- Use RF-induced plasma to transfer energy into the reactant gases, forming radicals that is very reactive (RF: radio-frequency, typically 13.56MHz for PECVD)
- A pure chemical process
- Low-temperature process (<400^{o}C), as RF energy assists the breaking of gas molecules. This enables PECVD to provide chemical reaction which is equivalent to a high temperature but without actually heating up the substrate to a high temperature

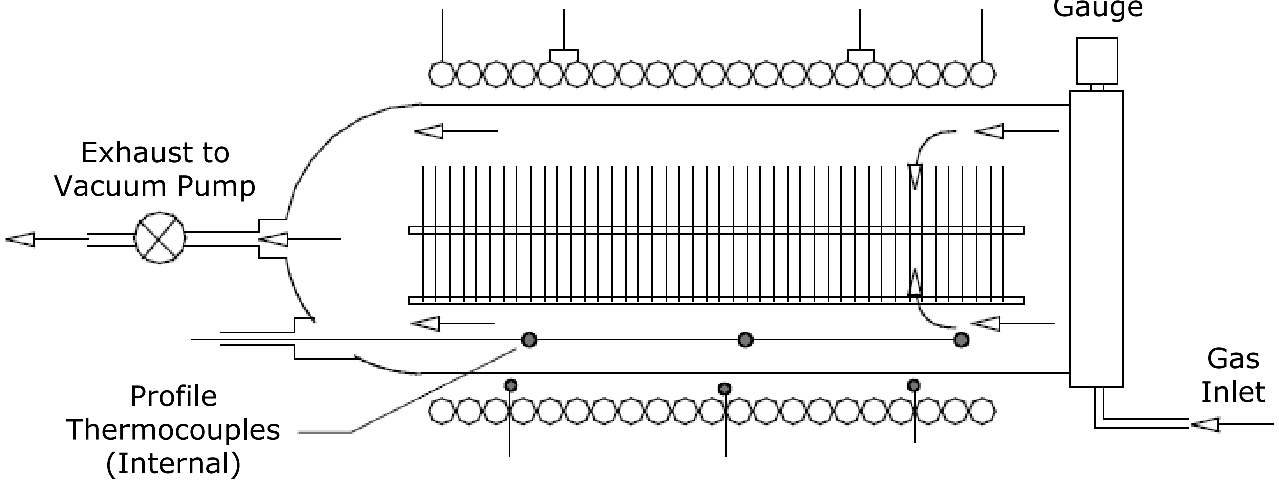
Plasma-Enhanced CVD



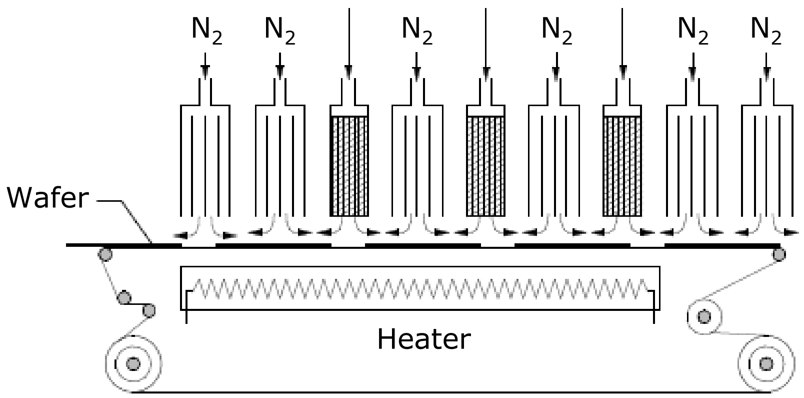
- Generally, the film quality is not as good as LP or APCVD films deposited at a much higher temperature.
- Energy supplied by plasma (i.e. ion bombardment of the film) increases film density, composition, and step coverage.

- Used for depositing the film on metals (Al, etc.) and other materials that cannot sustain high temperatures (APCVD/ LPCVD at such low temperatures gives increased porosity and poor step coverage).
- Surface reaction-limited deposition thus, substrate temperature control is important.
- Disadvantage: Plasma damage.

Explain why wafers can be stacked close and vertically in one process system while a horizontal stacking is preferred in the other system?



Vertically-Stacked Wafers

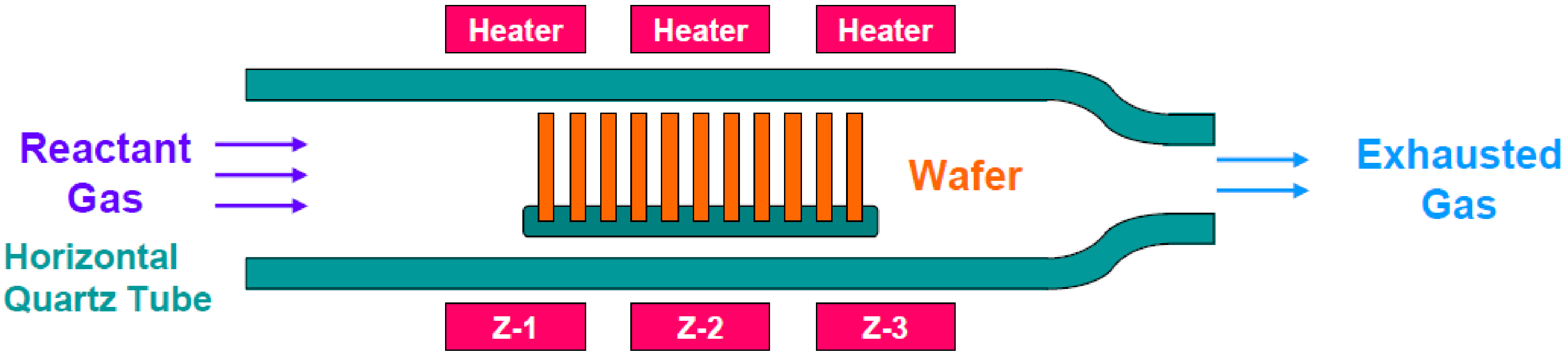


Horizontally-Stacked Wafers

Answer

- A direct application of these two possible rate-limiting processes is the way substrates are stacked in low-pressure CVD (LPCVD) vs atmospheric pressure CVD (APCVD) reactors,
- In an LPCVD reactor (~1 Torr), the diffusivity of the gas species is increased by a factor of 1000 over that at atmospheric pressure, resulting in one order of magnitude increase in the transport of reactants to the surface. The rate-limiting step becomes the surface reaction. LPCVD reactors enable wafers to be stacked vertically at very close spacing as the rate of arrivals of reactants is less important.
- On the other hand, APCVD operates in the mass-transport-limited regime. It must be designed such that all locations on the wafer and all wafers are supplied with an equal flux of reactant species. In this case, the wafers often are placed horizontally.

Deposition Methods in CVD: Low Pressure CVD



- Transport of reactants from the gas phase to the surface is not rate-limiting due to low-pressure op
- Eration (fewer air particles in the chamber), so wafers can be stacked vertically for high throughput (100-200 wafers per run)
- LPCVD operates in reaction limited regime, it is VERY sensitive to temperature. So temperature needs to be controlled closely (within +/- 1^{o}C)

Comparison Among the Types of CVD

Type	Advantage	Disadvantage	Usage	Pressure/ temp
APCVD	Simple and fast	Poor step coverage	Oxides	Atmospheric pressure > 700 °C
LPCVD	Excellent purity, conformity, and uniformity	Low deposition rate	Polysilicon nitride and oxide	10 – 1000 mTorr 400 – 600 °C
PECVD	Low deposition temperature	Plasma damage, more maintenance intensive, and requires RF generator	Low temperature oxides and passivation nitrides	1500 – 4000 mTorr 200 – 400 °C

Deposition by CVD Process

Deposition by CVD Process: SiO_2 (APCVD & LPCVD)

- **SiO_2 is useful as the dielectric material for capacitor and diffusion mask. For SiO2 deposition using APCVD & LPCVD techniques:**

  Pyrolytic decomposition of TEOS (Tetraethylorthosilicate) or silane-oxygen reaction process

- TEOS process T: $400 - 1100°C$

$$Si(OC_2H_5)_4 \xrightarrow{heat} SiO_2 + by - products$$

- Silicon tetrachloride $(SiCl_4)$ or silicon tetrabromide $(SiBr_4)$ with O_2 can produce SiO_2 film

$$SiCl_4 + 2CO_2 + 2H_2 \rightarrow SiO_2 + 2CO + 4HCl$$

- Silane (SiH_4) process at lower T $(about\ 500°C)$ possible

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$$

Deposition by CVD Process: SiO_2 (PECVD)

- Features with lower intrinsic stress than APCVD and LPCVD films (less likely to crack).
- Better step coverage than APCVD and LPCVD film
- Deposition temperature: 200 – 400°C
- Typical reactants for PECVD SiO_2:

$$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2$$

$$SiH_4 + 2N_2O \rightarrow SiO_2 + 2H_2 + 2N_2$$

$$SiH_4 + CO \rightarrow SiO_2 + CH_4$$

$$Si(OC_2H_5)_4 \rightarrow SiO_2 + by - products$$

CVD Si_3N_4

- The excellent barrier for sodium migration unlike SiO_2 thus, a good protection layer for finished Si devices
- Used for diffusion mask for capping GaAs to stop Ga escaping from GaAs surface at high temperature
- High-temperature process, 800 – 900°C, amorphous Si_3N_4 deposited
- The common reaction is: $2SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$

Lesson Summary - CVD

- CVD is a thin film deposition technique based on chemical reactions that are supplied through the use of gaseous compounds.
- CVD is usually used to deposit dielectric films, such as silicon oxide and silicon nitride films.
- CVD process can be summarised as transportation of gas reactants onto substrate, chemisorption and reaction of the gas reactants onto the substrate, transportation of by-product away from the substrate, and purging of the by-product from the chamber.
- CVD deposition rate is limited by the gas reactant transportation-limited regime and surface reaction-limited regime.
- To maximise the film deposition, various types of CVD techniques can be used, such as Atmospheric-Pressure CVD, Low-Pressure CVD, and Plasma-Enhanced CVD.

Practice Question 1

A common LPCVD method for depositing silicon dioxide is

a) Pyrolysis of TEOS
b) Photolysis of TEOS
c) Oxidizing SiH_4
d) Reduction of SiH_4

Pause and try out this question

Practice Question 2

Determine if the statements below are true or false.

Pause and try out this question

a) Low-pressure CVD reactors are reaction-rate limited, which means they can be vertically stacked at close spacing with a large number of wafers per run. True

b) In an atmospheric pressure CVD process, the reactor design is complicated and has low deposition rates. False

c) The ability to fill high aspect ratios is a characteristic of am acceptable thin film. True

d) The deposition temperature for PECVD is about the same as LPCVD. False

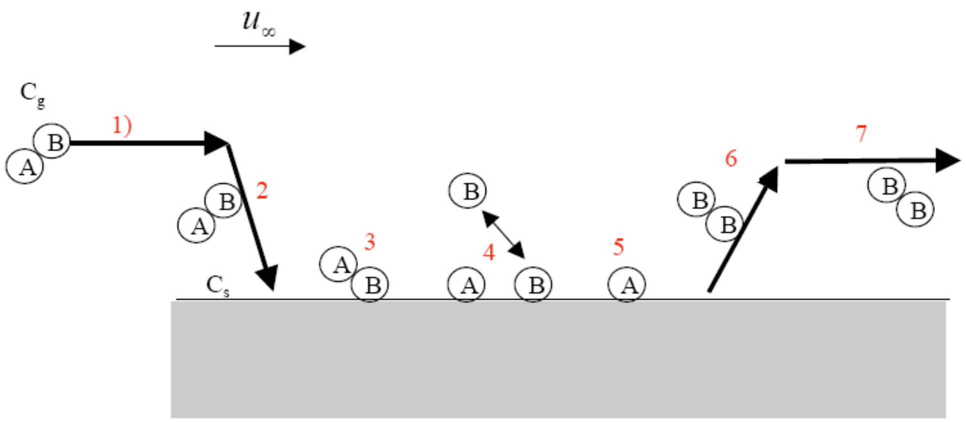
e) An advantage to sputtering is its ability to deposit alloys. True

Practice Question 3

Assume a CVD process based on the reaction: $2AB(g) \longleftrightarrow 2A(s) + B_2(g)$

Sketch and briefly describe the individual steps that control the reaction.

Pause and try out this question



1) Bulk transport governed by gas velocity
2) Diffusion across boundary layer
3) Adsorption involves sticking
4) Dissociation of AB due to temperature and possibly catalysed by interaction of A with surface. B may remain adsorbed or desorbed upon dissociation.
5) A(*s*) actually bonds with a site on substrate surface (film growth).
6) $B_2(g)$ diffuse across boundary layer.
7) Bulk transport of $B_2(g)$ under carrier gas velocity.

Practice Question 4

Pause and try out this question

a) What are the two commonly observed rate limiting mechanisms in chemical vapour deposition (CVD) systems? Under what conditions do they normally dominate the overall deposition rate?

b) In the CVD growth, under mass transfer limited conditions, is it more important to control the reactor temperature or the source gas composition in the gas stream to obtain reproducible results? Why?

c) Sketch (with labels) the typical CVD system that deposits film in the regime that is limited by mass transport. Explain the preferred wafer stacking configuration deployed in such a system.

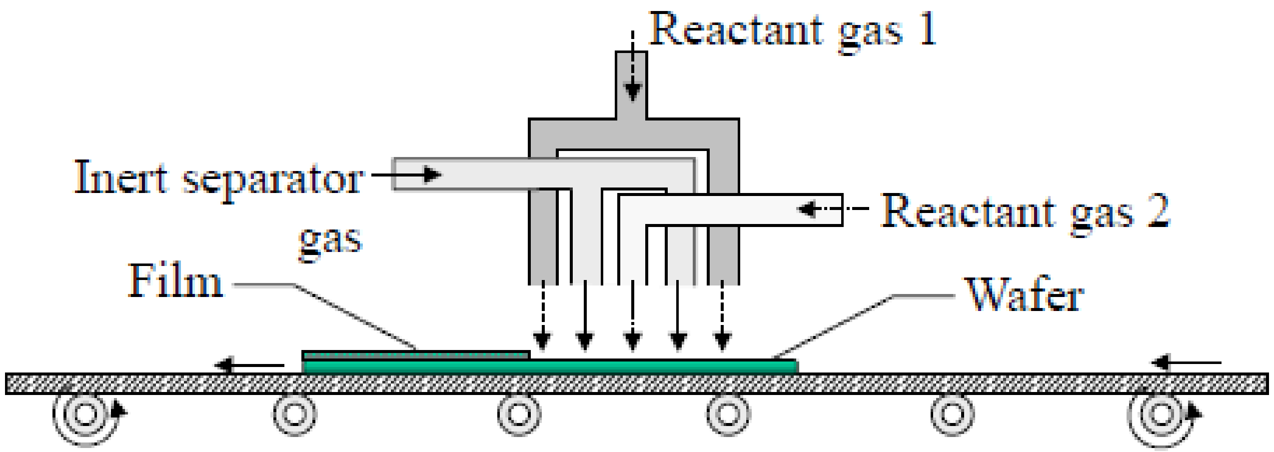
Practice Question 4

a) The two commonly observed rate limiting steps are mass transfer (diffusion through the stagnant boundary layer) and surface reaction(s). The former normally dominates at higher temperatures and higher total pressures, and the latter at lower temperatures and lower pressures.

b) Under mass transfer limited conditions, it is more important to control the source gas composition in the gas stream to obtain reproducible results. The mass transfer process is rather temperature insensitive (with a low activation energy), while the source gas composition in the gas stream strongly affects the deposition rate.

Pause and read carefully

c) APCVD system, Horizontal Stacking



Pause and read carefully

APCVD operates in the mass-transport-limited regime. It must be designed such that all locations on the wafer and all wafers are supplied with an equal flux of reactant species. In this case, the wafers often are placed horizontally

Practice Question 5

What is TEOS? State what film can be deposited using LPCVD TEOS. If TEOS is to be avoided, suggest alternative approach to deposit the same film by decomposition of gases. Write the reaction equation between these gases.

Pause and try out this question

TEOS is a tetraethylorthosilicate, which is an organic liquid precursor used to deposit silicon dioxide.

$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2$