Chemical Vapor Deposition

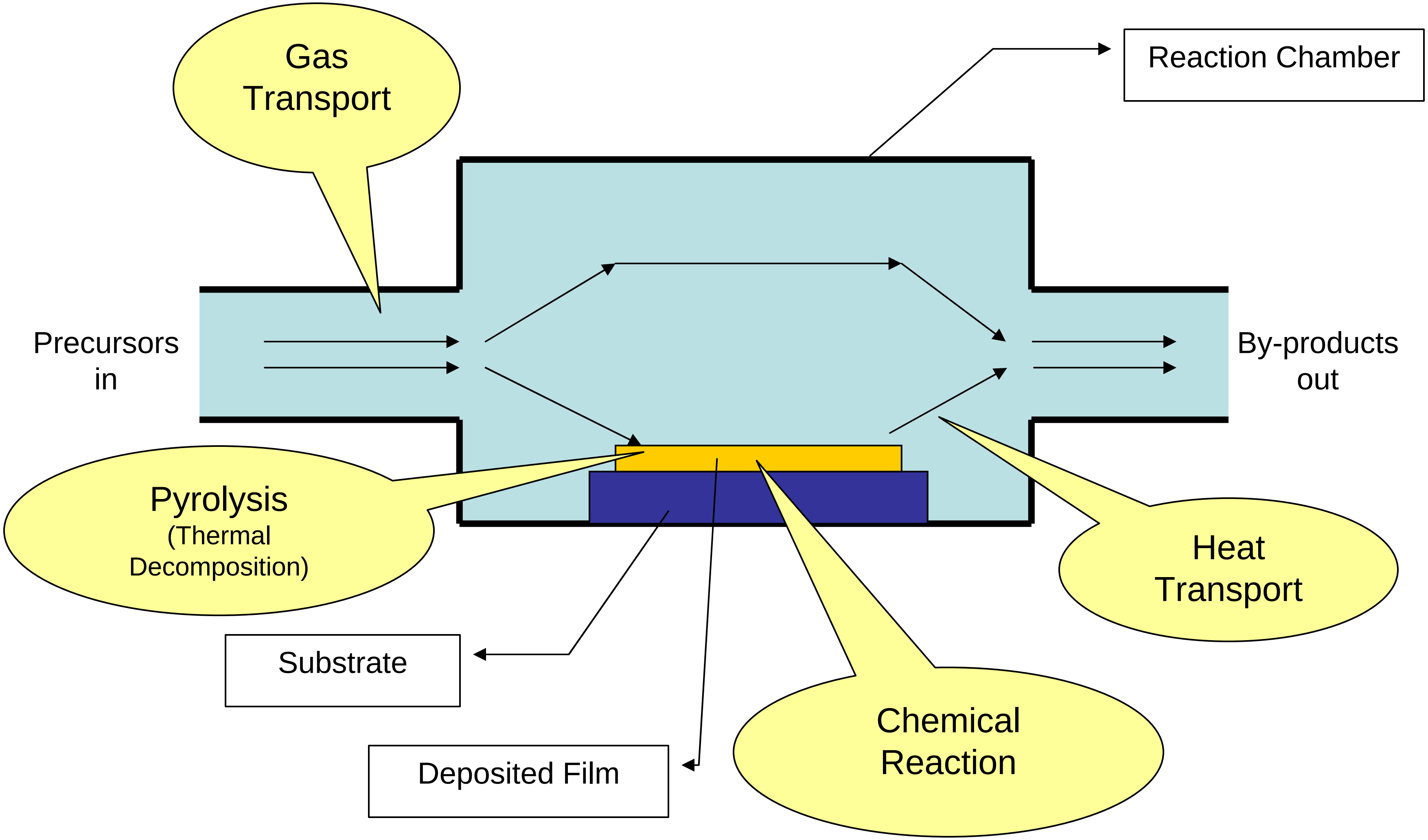
Physical Vapor Deposition (PVD)

- So far we have seen deposition techniques that physically transport material on to a substrate.
- The material to be deposited is somehow emitted from the source already in the form that we need for the thin film (ex.: evaporation, sputtering).
- No chemical reactions are assumed. In fact, they are generally unwanted.

Chemical Vapor Deposition (CVD)

- Deposition can also take place due to a chemical reaction between some reactants on the substrate.
- In this case reactant gases (precursors) are pumped in to a reaction chamber.
- Under the right conditions (T, P), they undergo a reaction at the substrate.
- One of the products of the reaction gets deposited on the substrate.
- The by-products are pumped out.

CVD Reactor and Processes



Gas Transport

Reaction Chamber

Precursors in

By-products out

Pyrolysis
(Thermal Decomposition)

Heat Transport

Substrate

Deposited Film

Chemical Reaction

CVD reactors

Control module

Four reaction chambers (similar to those for Si oxidation)

Control *T*, gas mixture, pressure, flow rate

Choice of Chemical Reactions

- The source gases and the chemical reactions need to be thermodynamically predicted to result in a solid film.
  - This means that there should be an energy advantage for the desired reaction to occur.
  - In thermodynamic terms the Gibbs Free Energy (GFE) has to decrease.
- The by-products need to be volatile (gaseous).

Some Typical Reactions

Pyrolysis $SiH_4(g) \rightarrow Si(s) + 2H_2(g)$ at 650 C

Also can deposit, Al, Ti, Pb, Mo, Fe, Ni, B, Zr, C, Si, Ge, SiO_2, Al_2O_3, MnO_2, BN, Si_3N_4, GaN, $Si_{1-x}Ge_x$

Reduction: $WF_6(g) + 3H_2 \rightarrow W(s) + 6HF(g)$

Also can deposit, Al, Ti, Sn, Ta, Mo, Fe, Nb, Si, Ge, SiO_2, TaB, TiB_2, Al_2O_3, $Si_{1-x}Ge_x$, BP, Nb_3Ge

Oxidation: $SiH_4(g) + O_2 \rightarrow SiO_2(s) + 2H_2(g)$ at 450 C

Also can deposit, Al_2O_3, TiO_2, Ta_2O_5, SnO_2, ZnO

Other reaction types: Nitridation, disproportionation, carbide formation

More on GFE

- GFE is a measure of the total available energy in a system.
- If the overall GFE of the reactants is greater than the overall GFE of the products, that reaction is thermodynamically favorable.
- The equations relating the GFEs also determine the reaction rates.
- All of these quantities are affected by temperature and pressure.

Nucleation

- In addition to being thermodynamically favorable, the barrier to nucleation (creating a nucleus increases surface energy) has to be overcome.
- Two types of nucleation exist:
  - Homogenous: Nuclei are formed in vapor form before being deposited and do not incorporate into the crystal structure of the film.
  - Heterogeneous: Nuclei are formed on the substrate and incorporate into the film structure more easily.

Gas Transport

- This is the flow of the reactants through the CVD chamber.
- The goal is to deliver the gas uniformly to the substrate.
- The flow needs to be optimized for maximum deposition rate.
- Flow can be molecular (gas diffusion) or viscous (liquid flow).
- CVD takes place in the viscous regime.
  - ($K_n < 1$)
- In the viscous regime:
  - Low flow rates produce laminar flow (desired).
  - High flow rates produce turbulent flow (avoided).

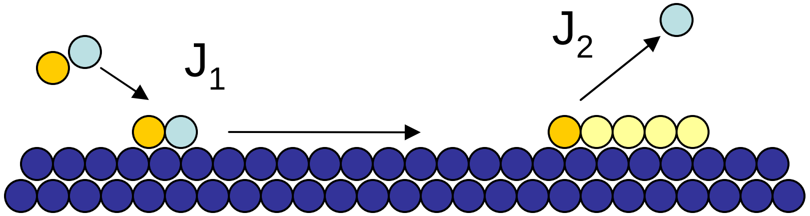
Boundary Layer

- While most flow in the chamber is laminar viscous flow, near the substrate surface the velocity of the gas has to go to zero.
- This creates a stagnant layer above the substrate.
- The thickness of this layer depends on the chamber conditions.
- The gas will move through the layer by diffusion.

Film Deposition

- In a simplified model, as gas flows over the substrate film growth is determined by adsorption and reaction rates.
- However, in reality, the deposition rate is affected by:
  - Distance from gas inlet
  - Specifics of the reaction
  - Radial variance
- Tricks to improve film uniformity:
  - Tilt substrate into flow
  - Increase T along the substrate
  - Single wafer processing

Deposition Rate



$$J_1 = h_G\left(C_g - C_s\right)$$

$$J_2 = k_S C_s$$

J_1: Flux to surface
J_2: Reaction flux
C_g: Gas concentration
C_s: Concentration on surface

h_g: Gas phase mass transport coefficient
k_s: Surface reaction rate

In steady state $J_1 = J_2$ $\longrightarrow$ $$\boxed{v = \frac{C_g}{\frac{1}{h_G} + \frac{1}{k_S}}}$$: deposition rate

Limiting Cases

$$\boxed{v = \frac{C_g}{\frac{1}{h_G} + \frac{1}{k_S}}}$$

Two limiting cases:

- $h_G >> k_S$: Reaction Limited Growth
- $k_S >> h_G$: Transport Limited Growth

Reaction Limited Growth

- growth controlled by processes on surface
  - adsorption
  - decomposition
  - surface migration
  - chemical reaction
  - desorption of products
- k_S is highly temperature dependent (increases with T)
- common limit at lower temperatures
- often preferred, slow but epitaxial growth
- temperature and reactant choices are important

Mass Transport Limited Growth

- growth controlled by transfer to substrate
- h_G is not very temperature dependent
- common limit at higher temperatures
- non-uniform film growth
- gas dynamics and reactor design are important

Summary

- Advantages:
  - high growth rates possible
  - can deposit materials which are hard to evaporate
  - good reproducibility
  - can grow epitaxial films
- Disadvantages
  - high temperatures
  - complex processes
  - toxic and corrosive gasses