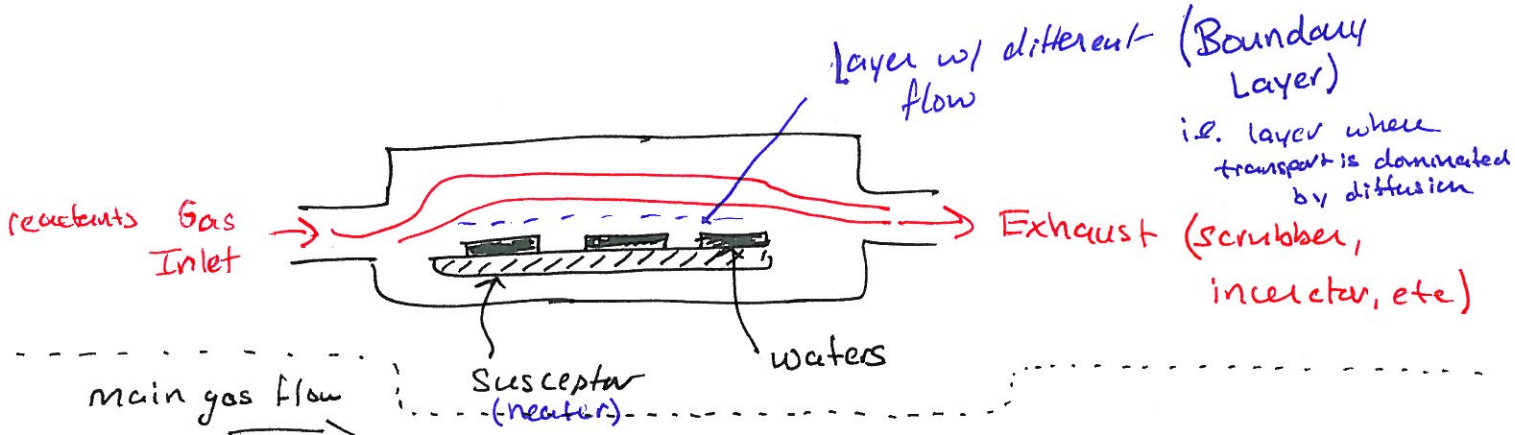
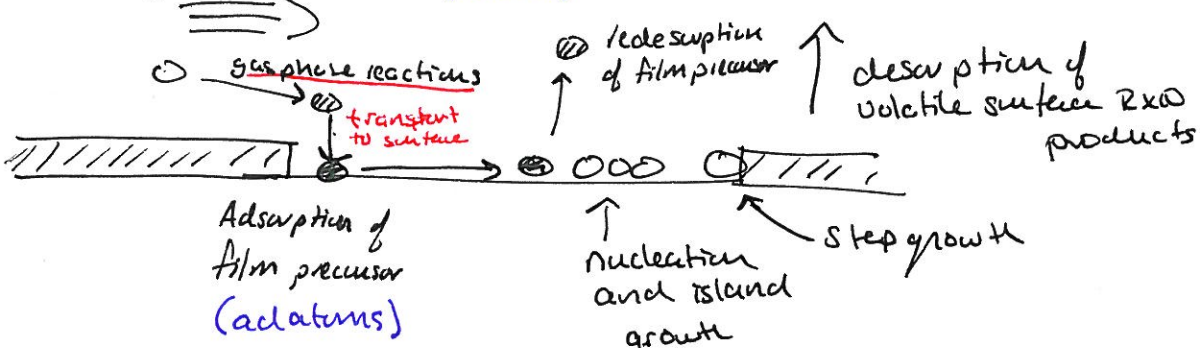
(13) Chemical Vapor deposition





Practical:

process must be ...

(1) fast (2) low-temperature (compatible w/ underlying substrate)
(big issue for thin film solar! would like to use cng ICSS)

(3) high precursor usage efficiency

(4) ~~[illegible]~~ ~~[illegible]~~ high-quality films (heterogeneous nucleation ← on film

vs.

homogeneous nucleation) → in vapor phase – leads to particulate defects

Grove's Model of CVD

$\boxed{\text{Growth-rate-limiting step}}$ => determines overall speed of the ~~pore~~ film growth

— typical kinetic analysis

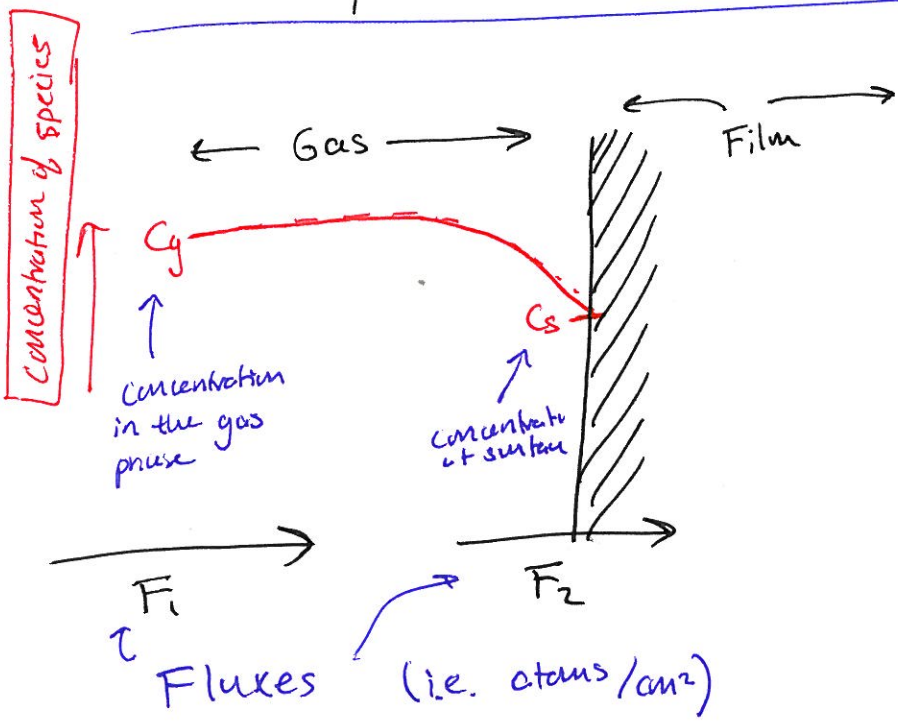
CVD processes typically grouped into ~~[illegible]~~ two catagories:

(1) ~~[illegible]~~ gas phase processes

(2) surface processes

Grove (1966) assumes:

$\boxed{\text{one surface}}$ or $\boxed{\text{one gas phase}}$ process rate limiting.



Schematic of process.

Groves model of CVD growth of Films

A. $$\boxed{F_1 = h_g (C_g - C_s)}$$

Flux

mass transfer coefficient

driving force
concentration difference

Note:

* this is similar to Ficks law of diffusion:

$$Flux = -D \frac{\partial C}{\partial x}$$, if you assume linear concentration gradient, and

$$\boxed{h_g = -D/\Delta x}$$ flux only due to diffusion

Move on this later!

B. $$\boxed{F_2 = k_s C_s}$$

concentration of species at the reactor surface

chemical surface rate constant {assume first order behavior → very often true for rate limiting step}

Note → should include F_3, Flux of species leaving surface, but ~~ignore~~ assume mass transfer coefficients of products higher.

Note: both A. and B. are linear approximations

Flux is ~~linearly~~ proportional to driving force

→ like ohms law, etc.

In Steady State:

$$F_1 = F_2 = F$$

Solve algebra:

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

$$C_s k_s + C_s h_g = h_g C_g$$

$$C_s (k_s + h_g) = h_g C_g$$

$$C_s = h_g C_g / k_s + h_g = \boxed{\frac{C_g}{\frac{k_s}{h_g} + 1}} = \underline{C_s}$$

Explore two limits:

if $\boxed{h_g \ll k_s} \rightarrow C_s \rightarrow \phi$

everything that hits the surface reacts

mass-transfer control

$\boxed{\text{if } h_g \gg k_s} \Rightarrow \boxed{C_s \rightarrow C_g}$

surface-reaction control

The growth rate of the film is thus given by:

$$G = F/N_1 \quad \text{(units of length/time = velocity)}$$

F = # of atoms $cm^{-2}\,s^{-1}$

N_1 = # of atoms cm^{-3} (e.g. $\frac{5\times10^{22}}{cm^{-3}}$ for Si)

$$G = F/N_1 = k_s C_s / N_1 \quad (\text{since } F = F_1 = F_2)$$

$$= \frac{k_s C_g}{N_1\left(1 + \frac{k_s}{h_g}\right)} = \boxed{\frac{k_s h_g}{k_s + h_g}\,\frac{C_g}{N_i}} = G \text{ (growth rate)}$$

Note: now equation only depends on the concentration of gas in the bulk and not at the surface.

If the reactants are diluted in a carrier gas (e.g. H_2, etc.) then the concentration is:

$$\boxed{C_g = C_T Y}$$

Molecules/cm^3 including carrier gas

mol fraction

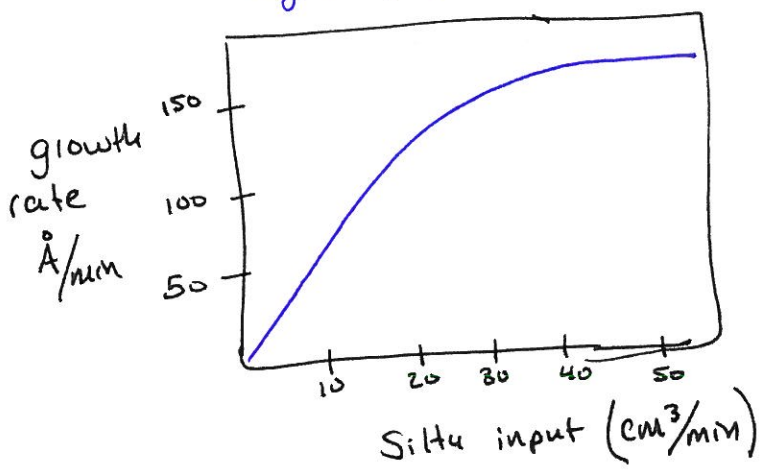
$$\boxed{G = \frac{k_s h_g}{k_s + h_g}\,\frac{C_T}{N_1}\,Y}$$

growth rate proportional to C_g or Y

LPCVD

mole fraction of reactant species in APCVD

C_g is proportional to flow rate in this case:



Why does growth rate saturate at higher flow rates?

→ reaction not always simple first-order

* Hydrogen bonded to surface sites restrict access of the SiH_4 molecules. It is a product of the reaction.

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again growth rate is controlled (at constant C_g or Y) by the relative size of k_s and h_g.

$k_s \ll h_g$ $\quad G = C_T k_s Y / N_1$ $\quad$ surface-reaction rate-limited case

$h_g \ll k_s$ $\quad G = C_T h_g Y / N_1$ $\quad$ mass transfer rate limited case

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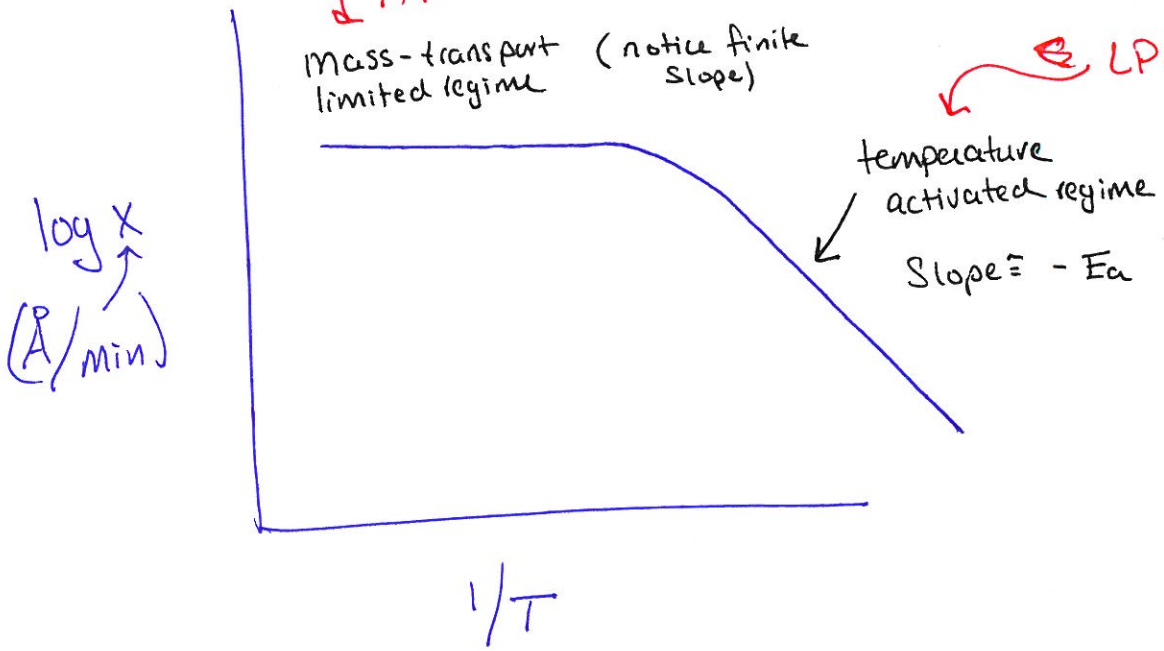
Chemical Reactions are typically thermally activated:

$$\boxed{k_s = k_0 \exp(-E_A / kT)}$$

k_0: prefactor, T-independent

E_A: activation energy

APCVD deposition of SiO_2



LPCVD eg Si_3N_4

easier to make sure temperature is uniform than mass flow!

does growth rate depend on pressure in the mass-transport limited regime?

→ yes $\boxed{D \propto T^{1.75}/P}$

(Diffusion mass transfer in fluid systems 2nd Ed. E.L. Cussler. Very good book!)

for constant P, increasing T increases the diffusion coefficient... more on this later.

Gas Flow also important.

Limitations of Grove's Model:

(1) neglects flux of products away from surface

(2) assumes 1st order RXN kinetics (only true for low γ values)

(3) neglects T gradients (e.g. that might exist due to cold walls and hot reactor surface)

Gas Flow and Gas-Phase Mass Transport

we approximated $\boxed{F_1 = h_g (C_g - C_s)}$ = what is h_g?

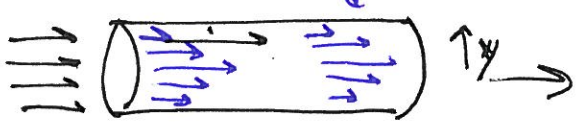
CVD / LPCVD

operate in the viscous regime, $\lambda \ll d_{reactor}$

$$\lambda\,(1\ \text{torr}) = 0.045\,\text{mm} = \boxed{45\ \mu m}$$

gas flow in a tube

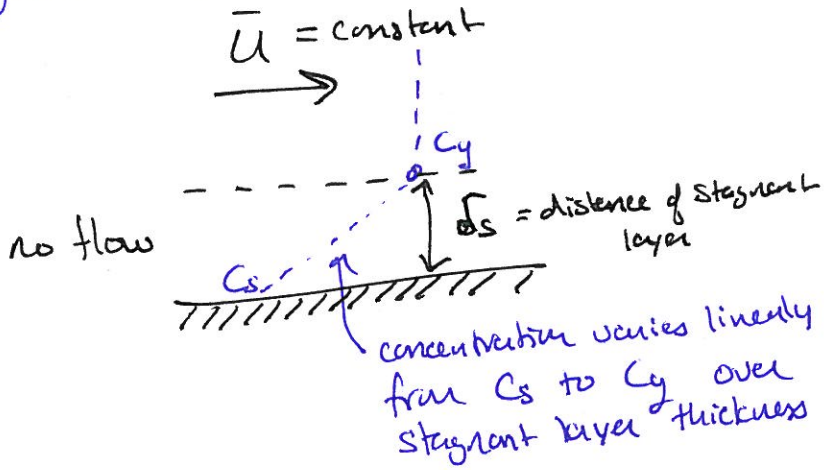
Poisseuille flow – $u \sim y^{1/2}$ parabolic.



$\partial u / \partial y$ develops due to drag on the cylinder walls

"plug" flow = gas velocity uniform throughout the region

The Stagnant layer model (simplest approximation)



$$\left[F = -D \frac{\partial C}{\partial y} = \frac{D\,(C_g - C_s)}{\delta_s} \quad \text{and} \quad h_g = D_g / \delta_s \right]$$

(sign arbitrary ~~depend~~ Flux goes toward surface)

useful, but limited...

δ_s arbitrary $\Rightarrow$ $u(y)$ is parabolic

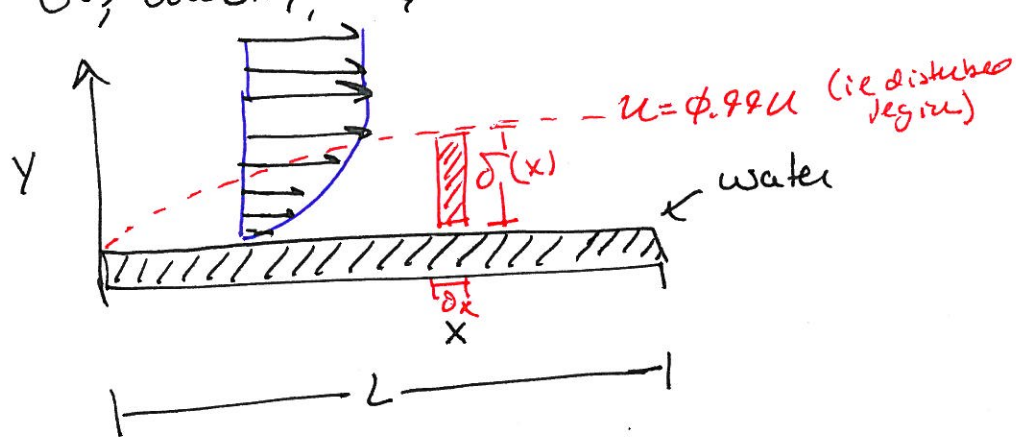
Boundary layer Theory

Fluid Mechanics → estimate h_g

1. Consider Fluid Flowing Parallel to a flat plate of length L.

2. extent of flowing fluid large (ie unbounded)

3. next to plate $U(x)$ velocity, $= \phi$



Velocity next to plate must be ϕ as:

(in presentation should use V for velocity

this is a macroscopic classical physics argument.

$$F_{friction} = \mu \frac{\partial u}{\partial y} \qquad \mu = \text{viscosity}$$

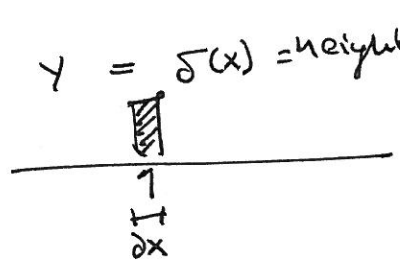
→ Solid not moving.
→ if liquid has finite velocity then
$\partial u / \partial y \to \infty$ $\quad F_{friction} \to \infty$

Boundary Condition of ϕ velocity at the reactor wall leads to velocity disturbance that grows as you move down the length of the reactor.

Newtons 2nd Law:

$$F = ma$$

gas flow $\rightarrow$



principle force acting is:

unit length in dimension perpendicular to the paper

Friction is force per unit area along the x-direction $\rightarrow$

$$F = \partial x \cdot F_{friction} = \mu \frac{\partial u}{\partial y} \cdot dx$$

$$\frac{\partial u}{\partial t} = \frac{\partial u}{\partial x}\frac{\partial x}{\partial t} = \underbrace{\frac{\partial u}{\partial x} u}_{a}$$

velocity $= \frac{\partial x}{\partial t}$

acceleration

change in velocity as f (time)

change in velocity over position

$$\text{Mass of element} = \underbrace{\boxed{\rho\, \delta(x)\, \partial x}}_{m}$$

$$F = ma$$

$$F_{Friction} = \mu \frac{\partial u}{\partial y} = \frac{ma}{\partial x} = \rho\, \delta(x)\, u \frac{\partial u}{\partial x}$$

velocity at δ(x)

velocity has gone from ϕ at x = 0 to V at δ(x)

travelled total distance x in Reactor

$$\sim \mu \frac{V}{\delta(x)} \cong \rho\, \delta(x)\, V \frac{V}{x}$$

dv

dy

replace differentials by differences (ie linear approximations)

$$\boxed{\delta(x) \cong \sqrt{\mu x / \rho u}}$$

Boundary layer grows w/ time

So $$\boxed{\delta(x) \cong \sqrt{\frac{\mu x}{\rho V}}}$$

x = distance into reactor

μ = viscosity

ρ = density of gas

V = velocity of un disturbed gas stream.

the average boundary layer thickness $\bar{\delta}$

$$\bar{\bar{\delta}} \equiv \frac{1}{L}\int_0^L \delta(x)\,dx = \boxed{\frac{2}{3} L \sqrt{\mu / \rho V L}}$$

now $\boxed{Re_L \equiv \frac{\rho V L}{\mu}}$ this is the Reynolds number

- dimensionless, ratio of inertial effects to viscous effects

For Pipe:

$Re < 2000$ laminar flow

$R > 2000$ Turbulent Flow

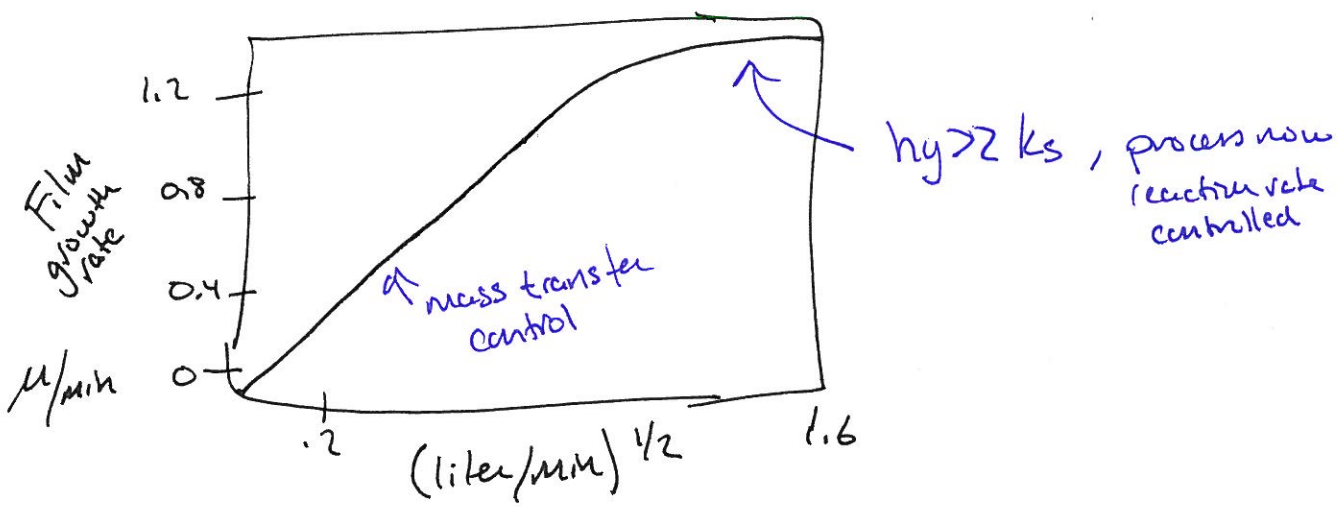
$$\bar{\delta} = \frac{2}{3} L / \sqrt{Re_L}$$

$$\boxed{h_g = \frac{D}{\bar{\delta}} = \frac{3}{2}\frac{D}{L}\sqrt{Re_L}}$$

we can plug in physical values for D, L and Re

use stagnant layer model to relate D to h_g

So in mass-transport limited regime... the film grow rate should go as $\sqrt{V}$ ...



CVD Reactor types

→ velocity increases w/ $\underline{\underline{x}}$

→ $\delta(x) \cong \sqrt{\frac{\mu x}{\rho V}}$.

→ so $\delta(x) \sim$ constant!

- then deposition rate constant across the wafer.
- must be optimized for specific CVD system.