Chemical Vapor Deposition (CVD)

Processes: gift of **SiO_2** - Expose Si to steam => uniform insulating layer…

clean and simple

or metal film growth : high vacuum, single element… **clean and simple**

… Contrast with **CVD:** toxic, corrosive gas flowing through valves,

T up to 1000°C, multiple, simultaneous chemical reactions,

gas dynamics, dead layers…

whose idea was it?

Insulator $Si0_x$,

wet growth

Figure removed for copyright reasons.

Figure 4-1 in Ohring, M. *The Materials Science of Thin Films*. 2nd ed.
Burlington, MA: Academic Press, 2001. ISBN: 0125249756.

Poly Si electrode:

0.3 - 0.4 µm CVD

Gate oxide:

500Å $Si0_x$,

dry growth

CVD is the single most widely used deposition method in IC manufacture

CVD reactors

Control module

Four reaction chambers (similar to those for Si oxidation)

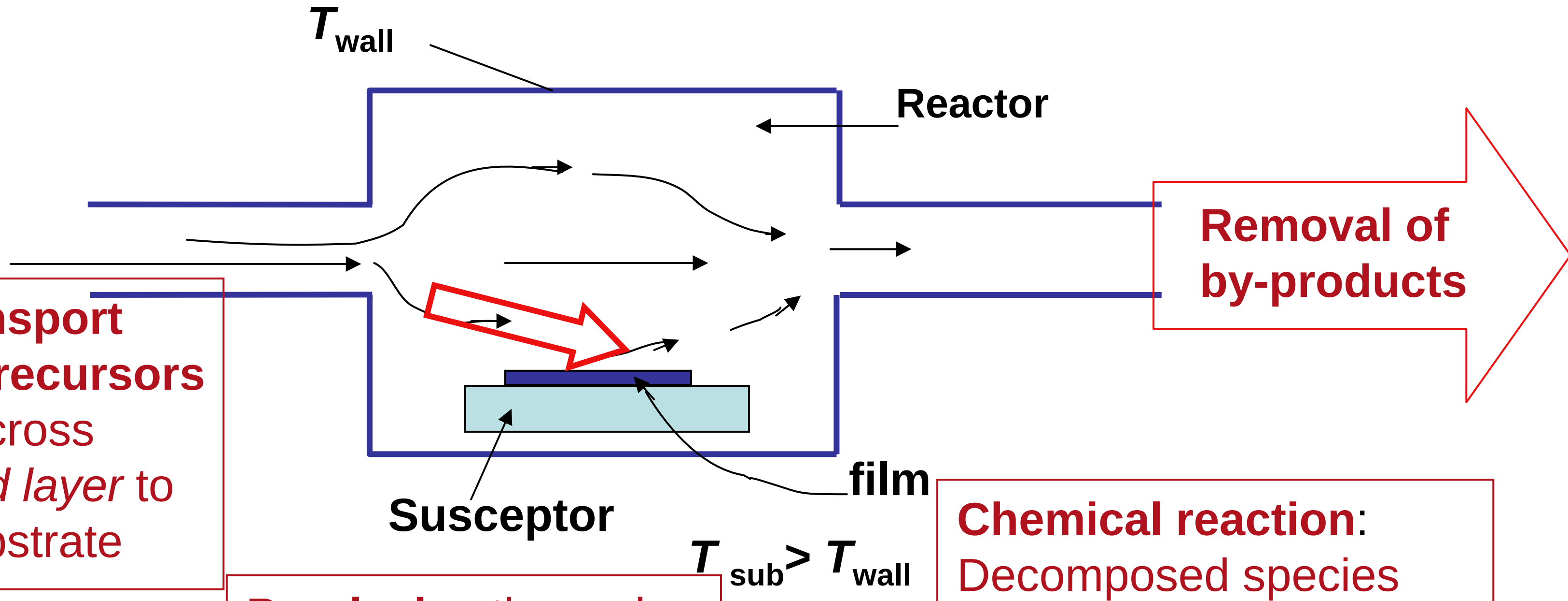
Control *T*, gas mixture, pressure, flow rate

CVD is film growth from vapor/gas phase

via chemical reactions in gas and on substrate:

e.g. $SiH_4 (g) \rightarrow Si (s) + 2H_2 (g)$

Do not want Si to nucleate *above* substrate (*homogeneous nucleation*), but ***on*** substrate surface (*heterogeneous nucleation*).



Transport of precursors across *dead layer* to substrate

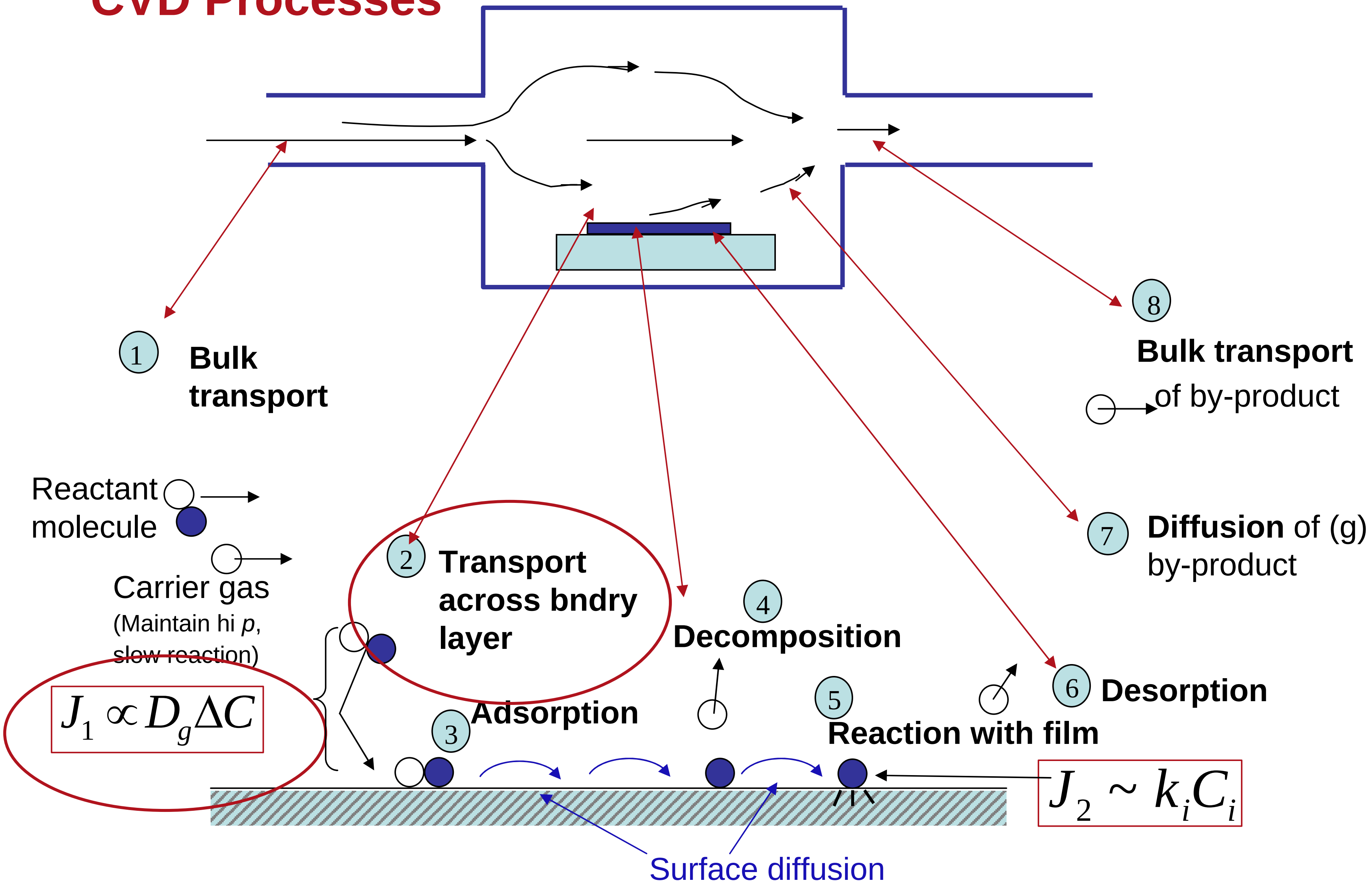
Removal of by-products

Pyrolysis: thermal decomposition at substrate

Chemical reaction: Decomposed species bond to substrate

More details…

CVD Processes



① **Bulk transport**

Reactant molecule

Carrier gas

(Maintain hi *p*, slow reaction)

$$J_1 \propto D_g \Delta C$$

② **Transport across bndry layer**

③ **Adsorption**

④ **Decomposition**

⑤ **Reaction with film**

⑥ **Desorption**

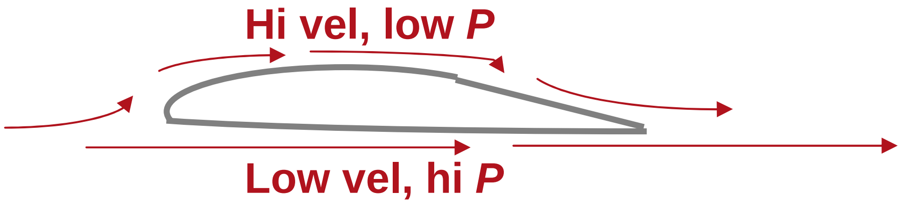
⑦ **Diffusion** of (g) by-product

⑧ **Bulk transport** of by-product

$$J_2 \sim k_i C_i$$

Surface diffusion

Gas transport



Laminar flow across plate:

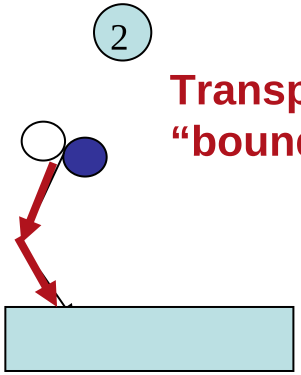
Hi vel, low p_y

Figure removed for copyright reasons.

Figure 4-7a in Ohring, 2001.

Low vel, hi p_y…
…shorter λ

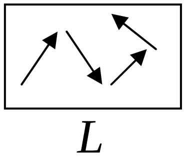
$$\boxed{\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 P}}$$



Transport across "boundary layer"

$$\boxed{J_1 \propto D_g \Delta C}$$

Knudsen $N_K \equiv \frac{\lambda}{L} < 1$



Viscous flow

Figure removed for copyright reasons.

Figure 4-7b in Ohring, 2001.

Dimension out of screen must also be considered

$$\boxed{D_{\text{gas}} \approx \frac{\lambda \bar{v}_x}{2}}$$

Laminar flow pipe.

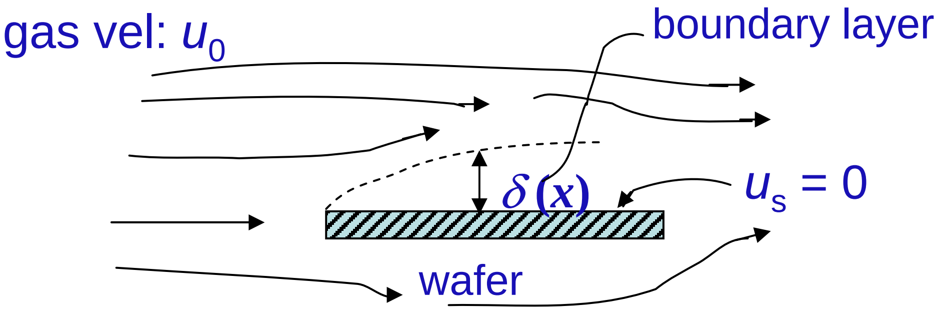
Conductance $\propto$ *A/L*

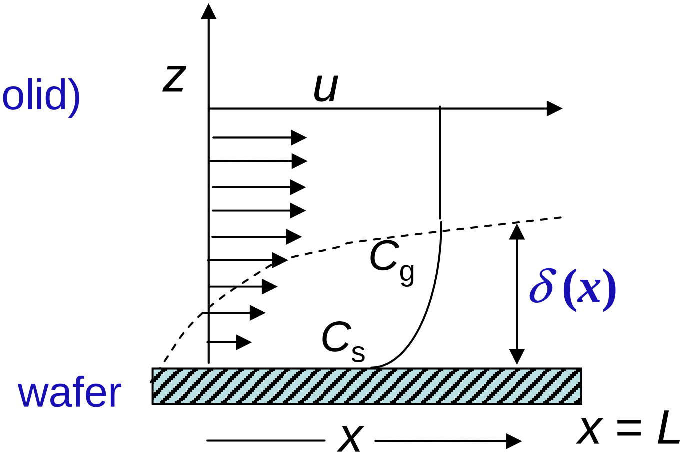
Revisit gas dynamics:

$$J_1 = -D\frac{dC}{dx} = -\frac{D}{\delta(x)}\left(C_g - C_s\right) \qquad J_1 = -h_g\underbrace{\left(C_g - C_s\right)}_{\text{Boundary layer}}$$

Layer thickness, $\delta(x)$

And we saw gas diffusivity $D = \dfrac{\lambda \bar{v}_x}{2}$ (unlike solid)





Fluid dynamics: $\boxed{\delta(x) = \sqrt{\dfrac{\eta x}{\rho u_0}}}$

ρ = mass density, η = viscosity

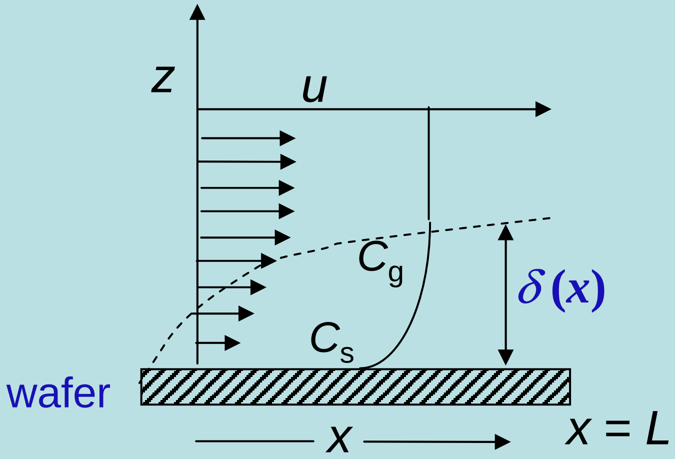
$$\boxed{\langle\delta\rangle = \frac{1}{L}\int_0^L \delta(x)\,dx = \frac{2}{3}L\sqrt{\frac{\eta}{\rho u_0 L}} \equiv \frac{2}{3}\frac{L}{\sqrt{\mathrm{Re}}}}$$

Reynolds #: $\mathrm{Re} = \rho\dfrac{u_0 L}{\eta}$

ease of gas flow

So: $\boxed{h_g = \dfrac{D}{\langle\delta\rangle} \rightarrow \dfrac{3}{2}\dfrac{D}{L}\sqrt{\mathrm{Re}}}$

Where $\delta(x)=\sqrt{\frac{\eta x}{\rho u_0}}$ does come from?



Diffusion Eq.:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} \Rightarrow \frac{\cancel{C}}{t} \approx D\frac{\cancel{C}}{\delta^2}$$

$$\delta = \sqrt{Dt}$$

Analogous to diffusion length

$$D(\mathrm{cm}^2/\mathrm{s}) = \frac{\eta}{\rho}$$

$$t = x / u_0$$

$$\eta = \frac{\sigma}{\&}\ (Nsm^{-2}),\quad \frac{\eta}{\rho}\left(\frac{m^2}{s}\right)$$

$$\boxed{\delta = \sqrt{\frac{\eta}{\rho}\frac{x}{u_0}}}$$

η= viscosity,

ρ = mass density

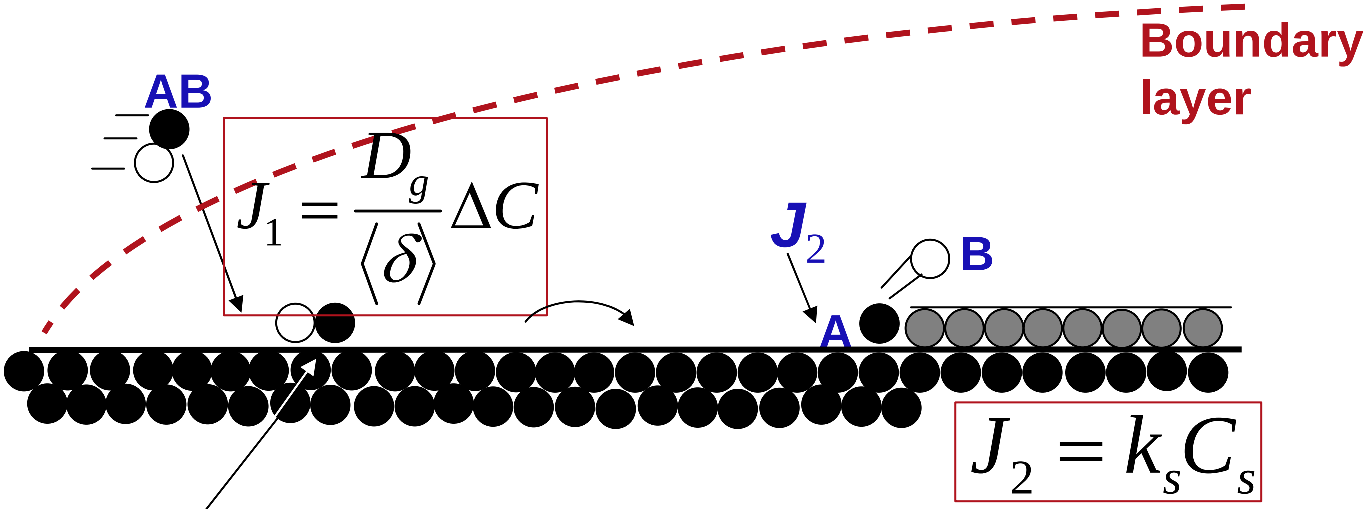
Reynolds #: $\mathrm{Re} = \rho\frac{u_0 L}{\eta}$

ease of

gas flow

Several processes in series

Simplify CVD to 2 steps:



$$J_1 = \frac{D_g}{\langle \delta \rangle} \Delta C$$

$$J_2 = k_s C_s$$

Reaction rate constant, k_s

…no sold-state diffusion here, reaction occurs at surface.

Sticking coefficient γ_{AB},

$$0 \leq \gamma_{AB} \leq 1$$

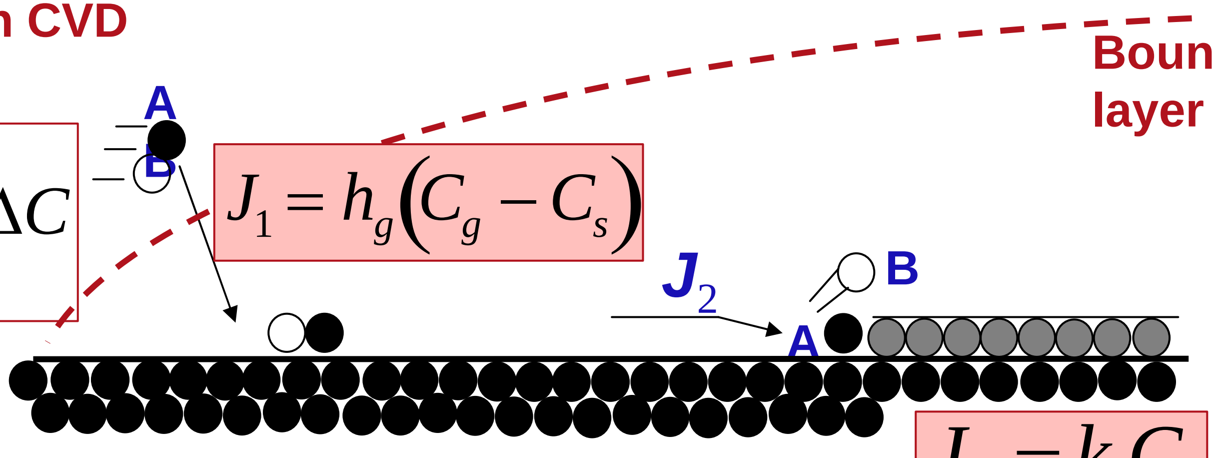
AB bounces off surface

Good adhesion

Let's analyze, solve for J_2…

Two main CVD process:

$$J_1 = \frac{D_g}{\langle \delta \rangle} \Delta C$$



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

$$J_2 = k_s C_s$$

In steady state: $J_1 = J_2$,

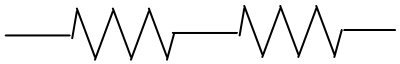
$h_g\,(C_g - C_s) = k_s C_s$

$$C_s = \frac{h_g}{h_g + k_s} C_g\,,$$

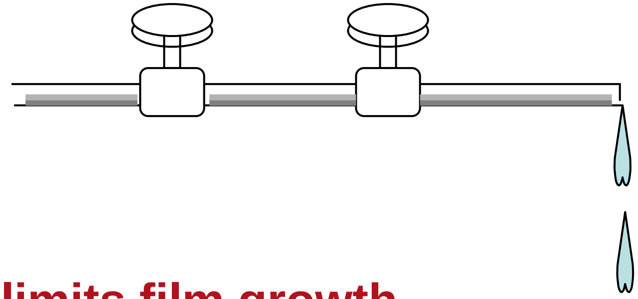
$$\boxed{J_2 = k_s C_s = \frac{h_g k_s}{h_g + k_s} C_g}$$

Electrical analogy: $J_1 = J_2$,

$R = R_1 + R_2$

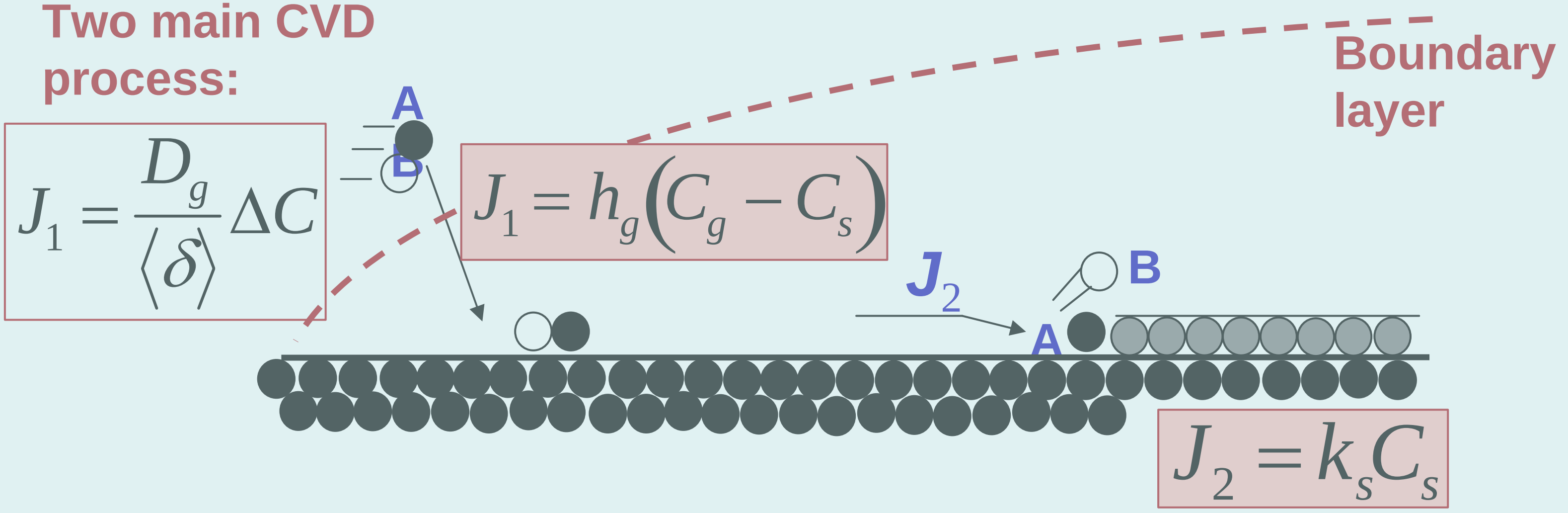


$G = 1/R = G_1 G_2 / (G_1 + G_2)$



Two processes in series; slowest one limits film growth

Two main CVD process:



$$J_1 = \frac{D_g}{\langle \delta \rangle} \Delta C$$

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

$$J_2 = k_s C_s$$

$$\boxed{J_2 = k_s C_s = \frac{h_g k_s}{h_g + k_s} C_g}$$

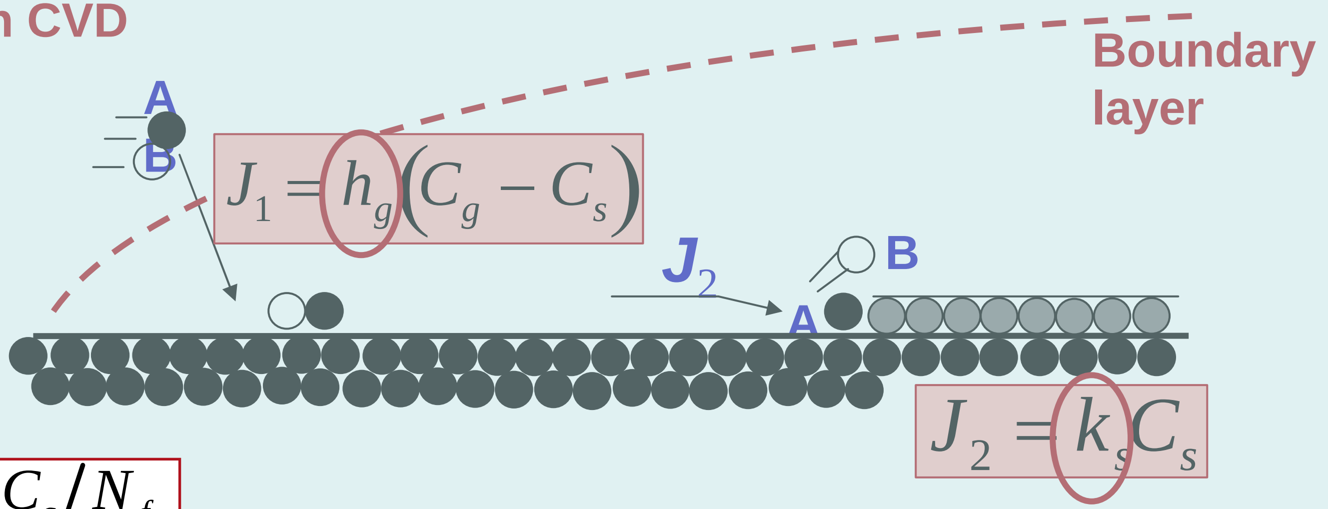
Film growth rate $\equiv v = J\left(\frac{\#}{\text{area} - t}\right)\frac{1}{N_f\left(\frac{\#}{\text{vol}}\right)},$

v (thickness/time)

$$\boxed{v = \frac{h_g k_s}{h_g + k_s} \frac{C_g}{N_f} = \frac{C_g / N_f}{\frac{1}{h_g} + \frac{1}{k_s}}}$$

Slower process controls growth

Two main CVD process:



Boundary layer

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

$$J_2 = k_s C_s$$

$$v = \frac{C_g / N_f}{\dfrac{1}{h_g} + \dfrac{1}{k_s}}$$

Examine these 2 limits of growth: h_g limited or k_s limited…

Transport limited growth,

$h_g << k_s$:

$$v = \frac{h_g C_g}{N_f} \rightarrow \frac{3DC_g}{2LN_f}\sqrt{\mathrm{Re}} = \frac{3\lambda \bar{v}_x C_g \sqrt{\mathrm{Re}}}{4LN_f}$$

ease of gas flow

Reaction limited growth,

$k_s << h_g$:

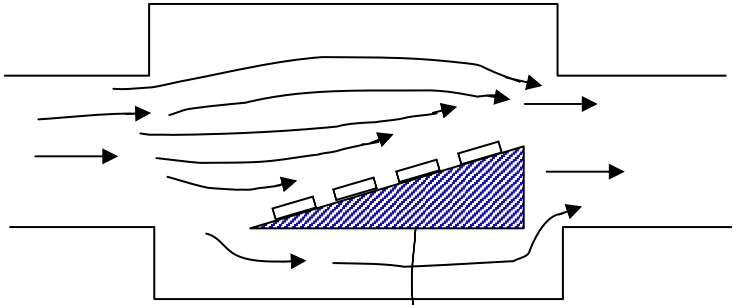
$$v = \frac{k_s C_g}{N_f} = \frac{C_g}{N_f} k_0 e^{-\frac{\Delta G}{kT}}$$

Transport limited growth :

$$v = \frac{h_g C_g}{N_f} \rightarrow \frac{3DC_g}{2LN_f}\sqrt{\mathrm{Re}} = \frac{3\lambda \bar{v}_x C_g \sqrt{\mathrm{Re}}}{4LN_f}$$

Most CVD is done in this limit where gas dynamics, reactor design are important.

Remedy for boundary layer



Susceptor, 3° -10°

More uniform u_g, $C_g \Rightarrow$ uniform film growth rate , v

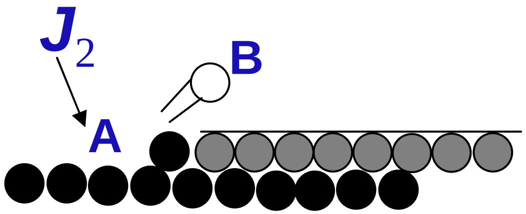
Reaction limited growth :

$$v = \frac{k_s C_g}{N_f} = \frac{C_g}{N_f} k_0 e^{-\frac{\Delta G}{kT}}$$

ΔG = free energy change in reaction

($\Delta G \cong \Delta H$ for gas

becasue gas reaction no ΔS)



Choice of reactants and temperature are critical

CVD FILM GROWTH

GAS TRANSPORT-LIMITED

$$\boxed{v = \frac{3\lambda \bar{v}_x C_g}{4 N_f L}\sqrt{\mathrm{Re}}}$$

$$\bar{v}_x = \sqrt{\frac{2k_B T}{\pi m}},$$

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 P_g},$$

$$\sqrt{\mathrm{Re}} \sim \sqrt{u_0}$$

$$\frac{C_g}{P_g} = \frac{1}{k_B T}$$

$$\boxed{v \propto T^{1/2}\sqrt{u_0}}$$

REACTION-RATE LIMITED

$$\boxed{v = \frac{k_s C_g}{N_f} = \frac{C_g}{N_f} k_0 e^{-\frac{\Delta G}{kT}}}$$

ΔG = free energy change in reaction

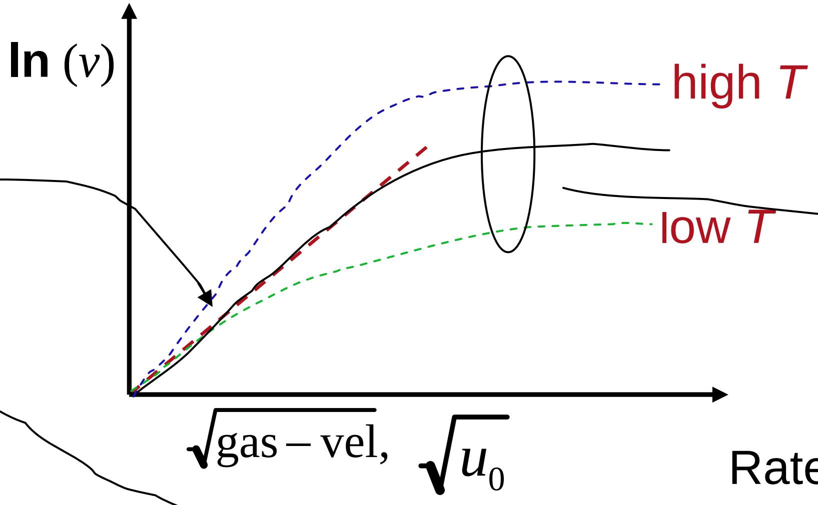
$\Delta G = \Delta H - T\Delta S$

($\Delta G \cong \Delta H$ for gas $\rightarrow$ no ΔS for gas reaction)

$$\boxed{v \sim e^{-\Delta H/kT}}$$

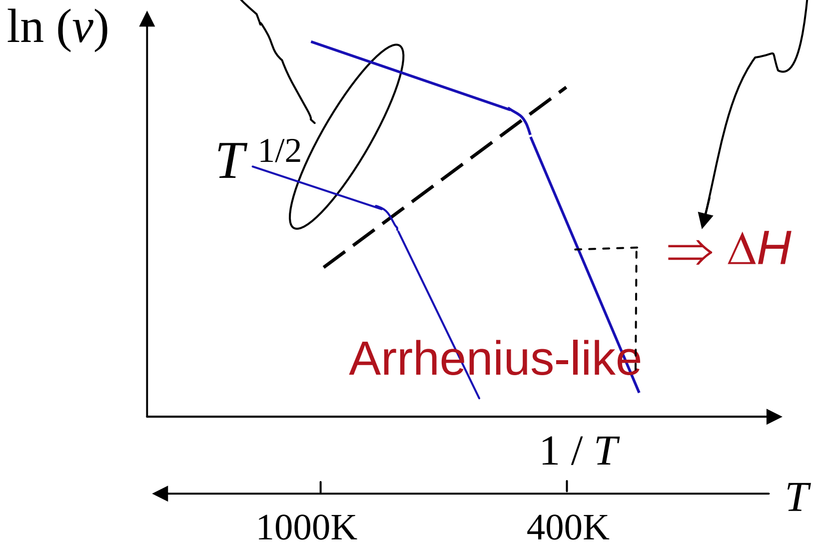
Transport limited

$$\boxed{v \propto T^{1/2}\sqrt{u_0}}$$



Reaction limited

Rate: $\boxed{v \sim e^{-\Delta H/kT}}$



Most CVD is transport-limited. Slow, layer-by-layer growth, epitaxy. Requires high *T*, low pressure, low gas viscosity. Chamber design, gas dynamics control process.

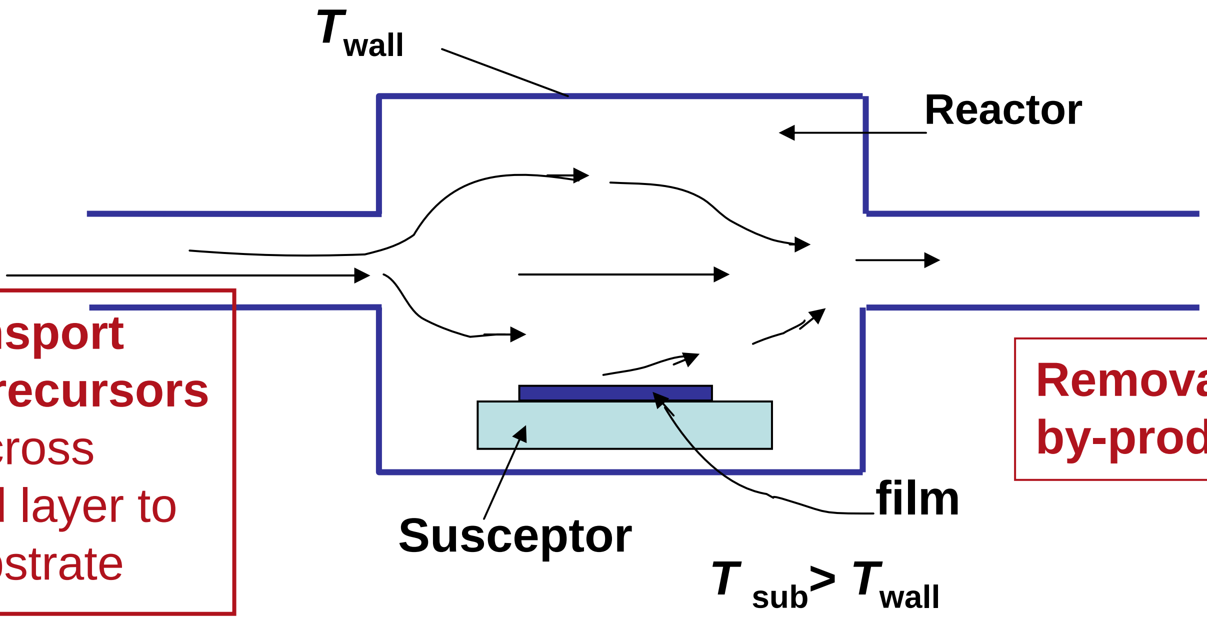
To reduce nucleation of products in gas phase, use low partial pressure (LPCVD).

Review CVD

We saw…

CVD is film growth from vapor/gas phase via chemical reactions in gas and at substrate:

e.g. SiH_4 (g) → Si (s) + $2H_2$ (g)



Transport of precursors across dead layer to substrate

Removal of by-products

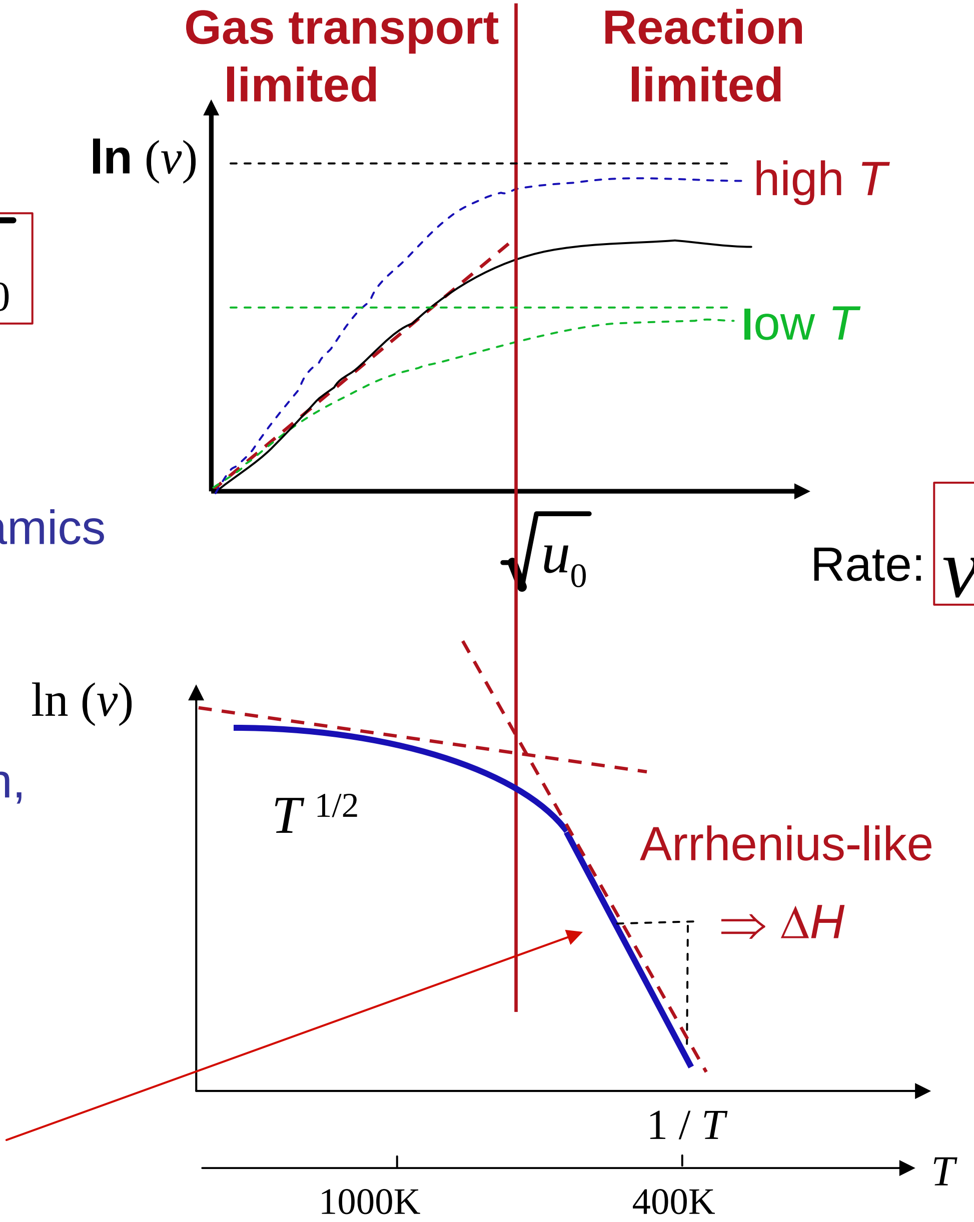
Pyrolysis:

thermal decomposition at substrate

Chemical reaction:

Decomposed species bond to substrate

$$\boxed{v \propto T^{1/2}\sqrt{u_0}}$$



Rate: $\boxed{v \sim e^{-\Delta H/kT}}$

Transport-limited CVD.
Chamber design, gas dynamics control film growth.
Non uniform film growth.

Slow, layer-by-layer growth, epitaxy, require high *T*, low pressure, $\lambda/L = N_K >> 1$.
That puts you in the
Reaction-limited regime

Some CVD reactions

Silane pyrolysis

(heat induced reaction)

$SiH_4\text{ (g)} \rightarrow Si\text{ (s)} + 2H_2\text{ (g)}$ (650°C)

This ⇒ poor Si at 1 atm, so use low pressure

Silane oxidation (450°C)

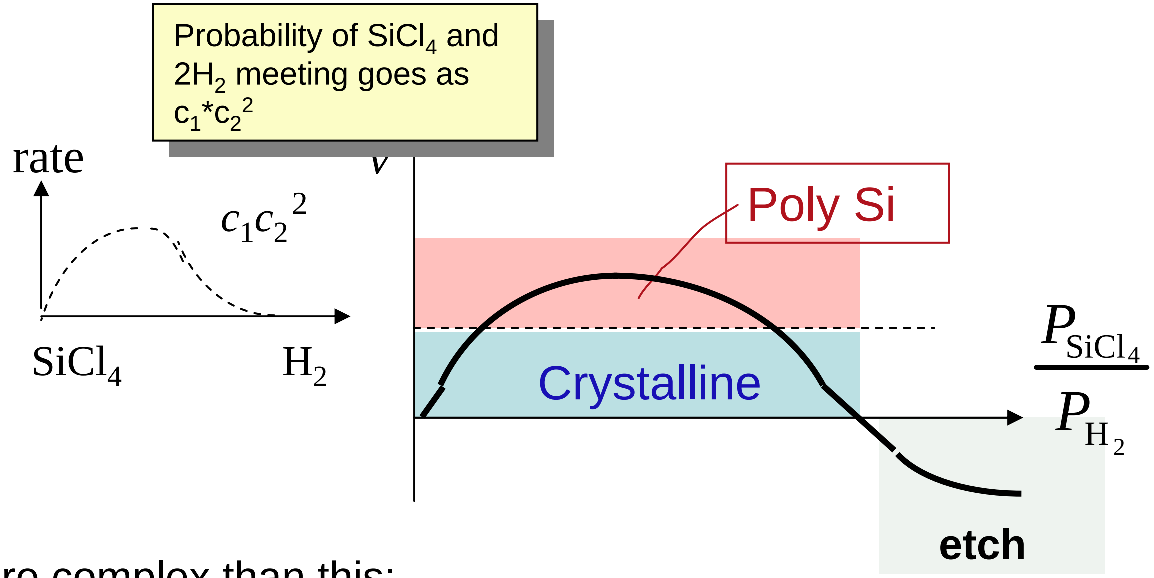
$SiH_4\text{ (g)} + O_2\text{(g)} \rightarrow SiO_2\text{ (s)} + 2H_2\text{ (g)}$

(by LPCVD for gate oxide)

Si - tetrachloride reduction

$SiCl_4\text{ (g)} + 2H_2\text{ (g)} \rightarrow$

$Si\text{ (s)} + 4HCl\text{ (g)}$ (1200°C)



Probability of $SiCl_4$ and $2H_2$ meeting goes as $c_1*c_2{}^2$

(Si-tetrachloride actually much more complex than this;

8 different compounds are formed, detected by RGA)

Some CVD reactions (cont.)

Doping

Phosphine

$2PH_3\ (g) \rightarrow 2P\ (s) + 3H_2\ (g)$

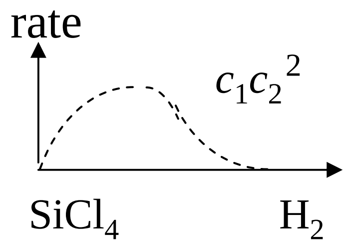
Diborane

$B_2H_6\ (g) \rightarrow 2B\ (s) + 3H_2\ (g)$

Si-nitride compound formation

$3\ SiCl_2H_2\ (g) + 4NH_3\ (g) \rightarrow Si_3N_4\ (s) + 6H_2(g) + 6HCl\ (g) \quad (750^\circ\ C)$

(dichloro-silane)



GaAs growth

Trimethyl Ga (TMG) reduction

$(CH_3)_3\,Ga + H_2 \rightarrow Ga\ (s) + 3CH_4$

Arsene →

$2AsH_3 \rightarrow 2As\ (s) + 3H_2$

Least abundant element on surface limits growth velocity

Or $As_4\ (g) + As_2\ (g) + 6\ GaCl\ (g) + 3\ H_2\ (g) \underset{850^\circ C}{\overset{750^\circ C}{\rightleftarrows}} 6\ GaAs\ (s) + 6\ HCl\ g$

How can you select process parameters to get desired product and growth characteristics?

Consider: $SiH_4\ (g) \rightarrow SiH_2\ (g) + H_2\ (g)$ **Three unknown pressures**

1) Total pressure = $\sum$ partial *P*s

$$P_{tot} = P_{SiH_4} + P_{H_2} + P_{SiH_2}$$

…still have **2 unknown *P*s**

2) Conservation of atoms $\frac{Si}{H}$ =>

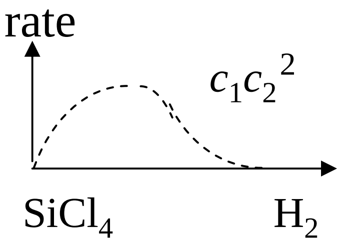
$$\frac{P_{SiH_2} + P_{SiH_4}}{4P_{SiH_4} + 2P_{SiH_2} + 2P_{H_2}} = const$$

…still have **1 unknown *P***

$P_{molecule} \propto N_{molecule}$

3) "Equilibrium constant", *K* (cf. Law of mass action)

$$K \equiv \frac{P_{H_2} \cdot P_{SiH_2}}{P_{SiH_4}} = K_0 e^{-\frac{\Delta G}{kT}}$$



And similarly for each reaction.

These 3 equations provide a *starting* place for growth parameters.

(Many equations for real systems; done on computer)

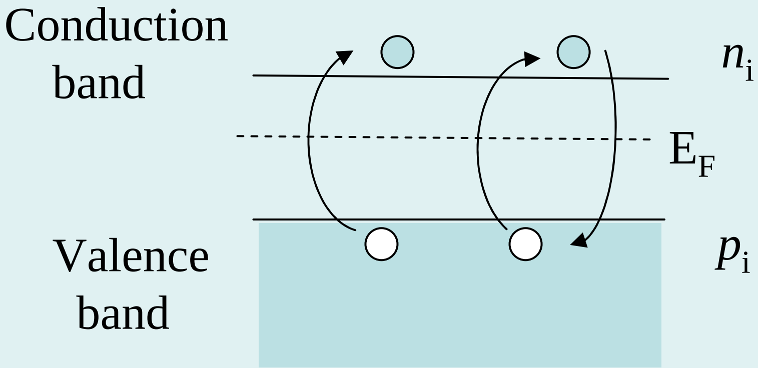
Do a run, analyze results, …tweak process.

Where does $K \equiv \frac{P_{H_2} \cdot P_{SiH_2}}{P_{SiH_4}} = K_0 e^{-\frac{\Delta G}{kT}}$ come from?

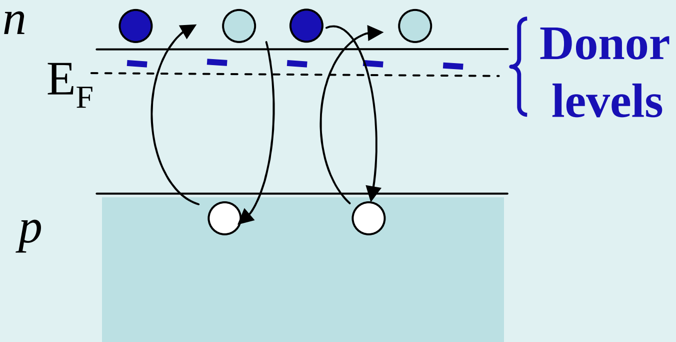
Consider "mass action" for dice…

Consider "*mass action*" for electrons and holes:

Intrinsic semiconductor

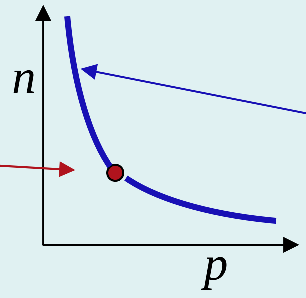


N-type semiconductor



Recombination probability set by energy gap and number of each species

$$\boxed{n_i^2 = n_i p_i}$$



$$\boxed{n_i^2 = np}$$

More free electrons
=> more recombination,
fewer holes **(E_g same)**

K indicates a **bias** *at equilibrium* in the reaction toward the products(different molecular species)

$$\boxed{K\,P_{SiH_4} = P_{H_2} \cdot P_{SiH_2}}$$

Exercise

Assume reaction: $AB \rightleftarrows A + B$ $P_{tot} = 1$ atm, $T = 1000$ K,

$K = 1.8 \times 10^9$ Torr $\times \exp(-2\ \text{eV} / k_B T) = 0.153$

Assume $P_A \approx P_B$ **find** $\boldsymbol{P_{AB}}$

Solution: $K = \dfrac{P_A P_B}{P_{AB}} = 0.153$

and $P_{tot} = P_A + P_B + P_{AB}$, $P_A \approx P_B$. $\therefore$ 760 Torr $= 2P_A + P_{AB}$

$P_A{}^2 = 0.153\, P_{AB} = 0.153\,(760 - 2\,P_A)$, quadratic → $P_A = 10.8$ Torr $= P_B$,

so **$P_{AB} = 738$ Torr**

$$P_A^2 + 0.306 P_A - 0.153 \times 760 = 0$$

Small value of *K*, 0.153 Torr, implies that at equilibrium,

the product of the right-hand side partial pressures

Is but 15% of the reactant (left-hand-side) partial pressure;

the reaction may not produce much in equilibrium. What if you change *T*?

Atmospheric Pressure CVD: APCVD

(little used today, but illustrative)

High *P*, small λ => slow mass transport, large reaction rates;

film growth limited by mass transfer, boundary layer;

(quality of APCVD Si from silane is poor, better for dielectrics).

Example:

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O \quad T = 240 - 450°C$$

Done in N_2 ambient (**low partial pressure** of active gas, reduces film growth rate)

add 4 - 12% PH_3 to make silica flow, planarize.

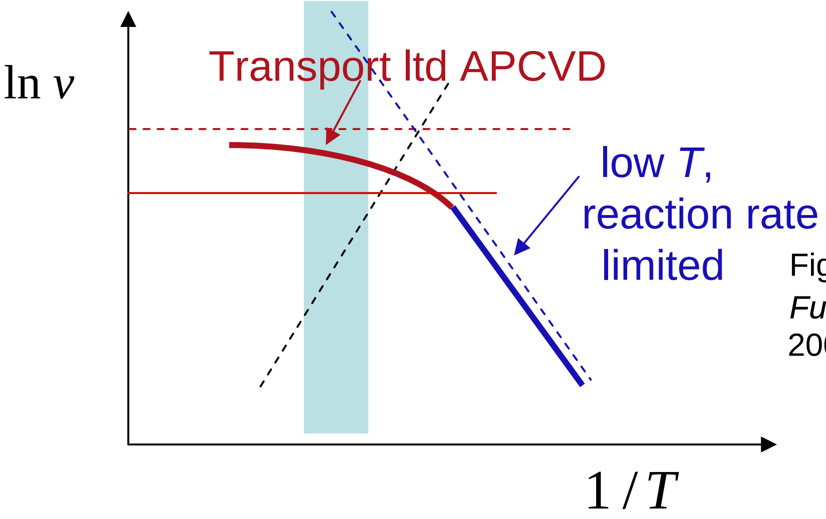


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Figure 9-4a in Plummer, J., M. Deal, and P. Griffin. *Silicon VLSI Technology: Fundamentals, Practice, and Modeling*. Upper Saddle River, NJ: Prentice Hall, 2000. ISBN: 0130850373.

Note induction heating of substrate; cold walls

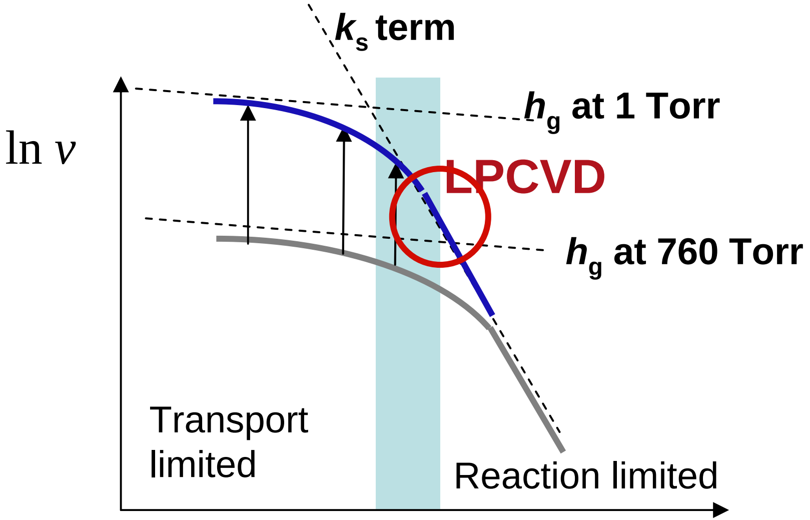
Low Pressure CVD (LPCVD) for dielectrics and semiconductors

Equilibrium not achieved at low *P* where (molecular flow, few collisions).

$$\frac{\lambda}{L} = K_n > 1$$

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 P}$$

lower *P* => higher D_g, h_g; this improves transport reduces boundary layer, extends reaction-controlled regime (which is where you operate)



Hot walls

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Figure 9-4b in Plummer et al., 2000.

Conversely: if you wanted to work in transport limit at low *T*, you must reduce gas flow

Low Pressure CVD (LPCVD) for dielectrics and semiconductors

If hot-wall reactor

⇒ uniform *T* distribution but surface of reactor gets coated. So system must be dedicated to 1 species to avoid contamination.

If cold-wall reactor

Reduce reaction rate, reduce deposition on surfaces. For epi Si.

All poly-Si is done by hot-walled LPCVD; good for low pin-hole SiO_2, conformality

Figure removed for copyright reasons.

Figure 9-4b in Plummer et al., 2000.

Low Pressure CVD (LPCVD) for dielectrics and semiconductors

In such non-equilibrium, large λ, reactant-starved cases, growth rate can be controlled by reaction kinetics

LPCVD is kinetically throttled; transport-rate controls film growth

Silane pyrolysis $SiH_4\,(g) \rightarrow Si(s) + 2H_2\,(g)$ $T = 575 - 650°C$

10 - 100 nm/min

(APCVD is at equilibrium; transport limited)

LPCVD

Requires no carrier gas

Fewer gas-phase reactions, fewer particulates

Eliminates boundary-layer problem

Lower p => larger D_g, extends reaction limited regime

Good conformal growth (unlike sputtering or other PVD methods which are more directional)

Strong T dependence to reaction growth rate.

Easier to control T with hot-walled furnace.

R.F. Plasma-enhanced CVD (PECVD) for dielectric

MOS metallization: avoid contact interaction betw. Al & Si, SiO_2, ∴ $T < 450°C$

At low *T*, surface diffusion is slow,

must supply kinetic energy for surface diffusion.

Plasma provides that energy…and enhances step coverage.

What is a plasma? Ionized noble gas, accelerated by AC (RF) or DC voltage, collides with active species in gas and at surface, importing E_{kin}

Metal CVD

Step coverage is important for electric contacts.

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

$\Delta G \approx 70$ kJ / mole (0.73 eV/atom)

below 400°C

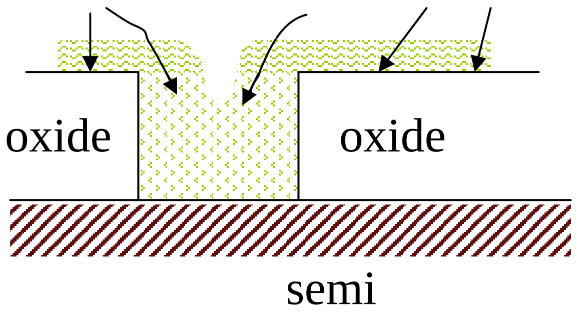

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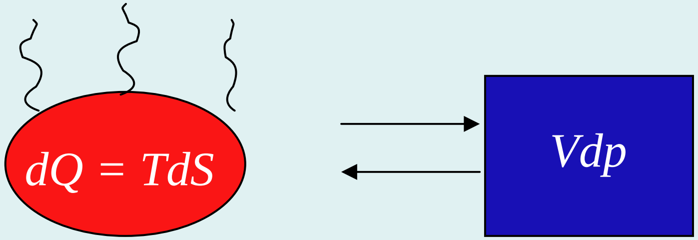
Table 4-1 in Ohring, 2001.

When a system undergoes a process in which only heat energy, dQ, and pV work occur at constant T, then $dG = Vdp$


$dQ = TdS$

Vdp

$$dG = Nk_BT\frac{dp}{p} \text{ or } RT\frac{dp}{p}$$

$$\int_A^B dG = RT\int_A^B d\ln(p) \Rightarrow G_B - G_A = RT\ln\left(p_B/p_A\right)$$

$$\boxed{\exp\left(-\frac{dG}{RT}\right) \propto \frac{p_B}{p_A}}$$

Define this ratio p_B/p_A, as K

For multiple reagents:

$$\boxed{K \equiv \frac{P_{H_2} \cdot P_{SiH_2}}{P_{SiH_4}} = K_0 e^{-\frac{\Delta G}{kT}}}$$

Entropy of mixing, $dS_{mix} = -RN_i \ln(N_i)$, leads to similar result