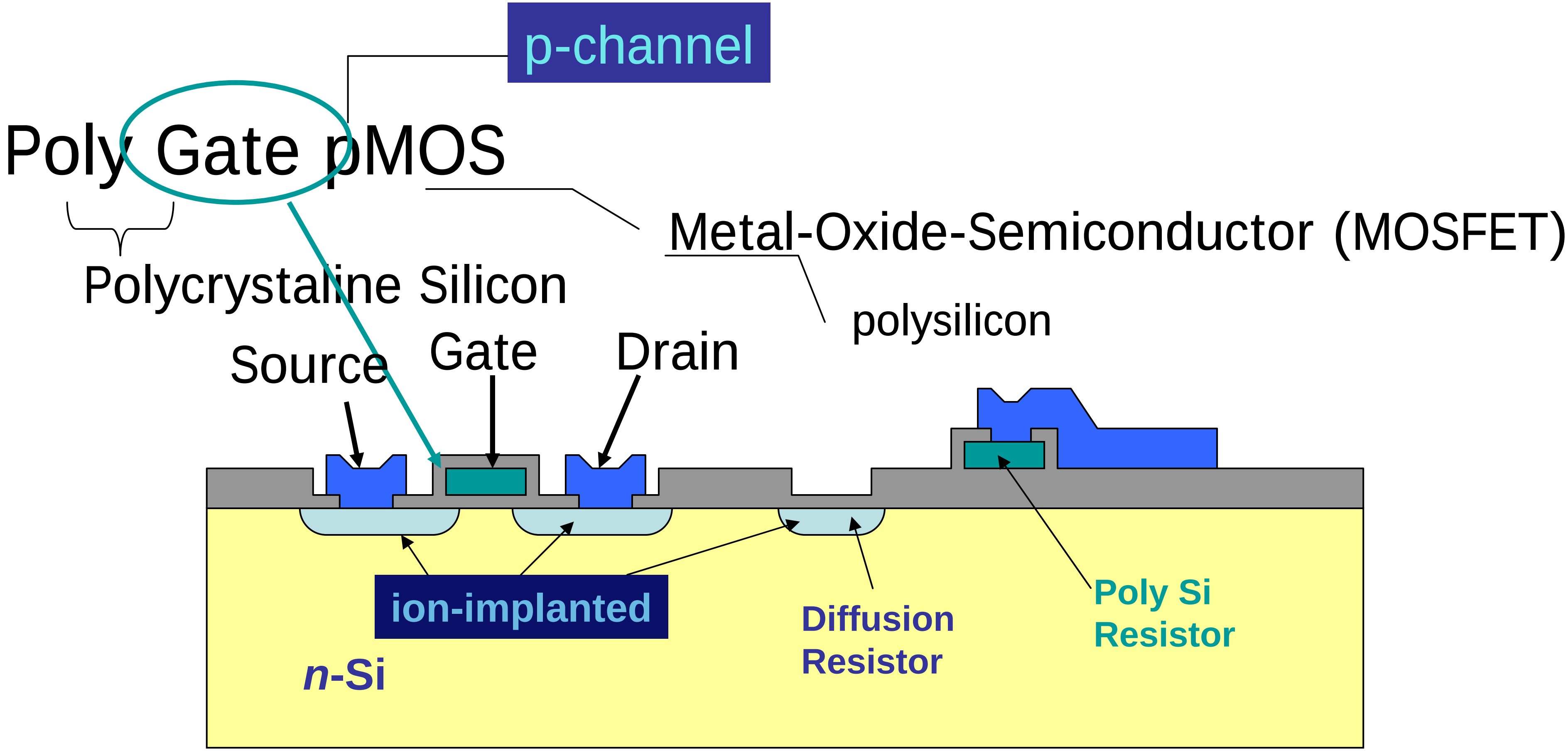
Vacuum Technology and film growth



Field oxide grown in steam, gate oxide made by CVD

***p*-regions ion-implanted, Al sputter deposited or evaporated**

Why cover vacuum science?

• Oxidation Sept. 14

Key advantage of Si: stable uniform oxide
How control its growth, thickness, quality

• Ion implantation and diffusion Sept. 28

How semiconductor surfaces are doped

• Chemical vapor deposition (CVD) Oct 12

Most widely used method for growth of high-grade semiconductor, metals, oxide films,

• Physical vapor deposition (PVD) Oct. 19, 26

Growth of quality films by sputter deposition or evaporation

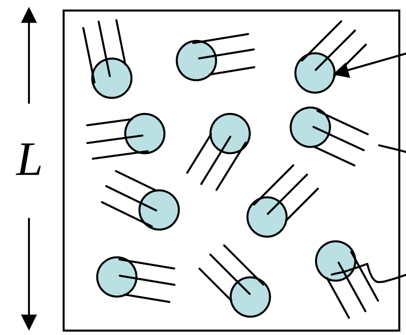
These processes done in vacuum or controlled environment.
Therefore, need to understand
vacuum technology,… gas kinetics.

Gas Kinetics and Vacuum Technology

How far does a molecule travel between collisions?

Consider a volume *V* of gas (e.g. N_2)

"Snap shot"

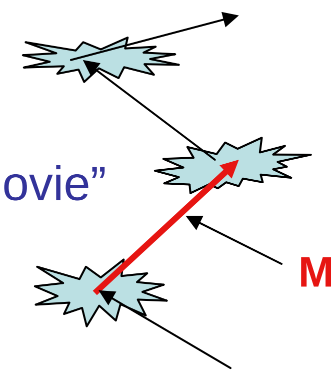


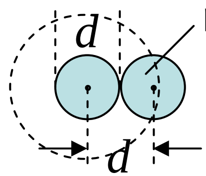
$m \approx 5 \times 10^{-26}$ kg

velocity

number *N*, $n = \dfrac{N}{V} = \dfrac{N}{L^3}$

"Movie"



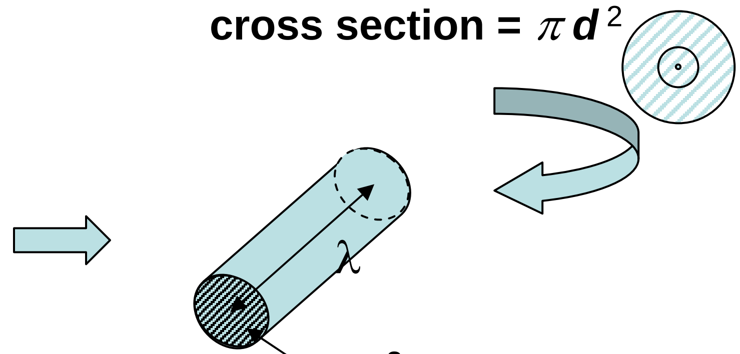


molecule

=>

impact parameter, scattering cross section = πd^2

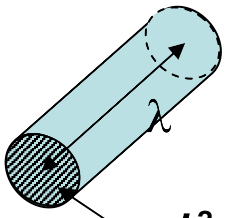
Mean free path $\equiv \lambda$



πd^2

Volume swept out by 1 molecule between collisions = $\lambda \pi d^2$

Volume swept out by 1 molecule between collisions = $\lambda\pi d^2$



Total volume of sample

$L^3 = V \approx N\lambda\pi d^2$

$$\boxed{\therefore \lambda \approx \frac{V}{N\pi d^2} = \frac{1}{n\pi d^2}}$$

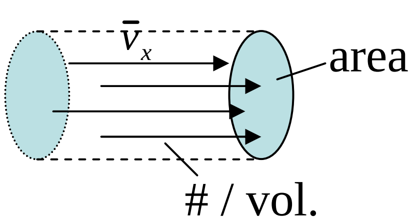
More accurately: $\lambda = \dfrac{\sqrt{2}}{2n\pi d^2}$

Use Ideal gas: $\boldsymbol{n = N/V = p/k_B T}$

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

p	λ (cm)
1 atm	10^{-5}
1 Torr	10^{-2}
1 mT	10

What is flux of atoms hitting surface per unit time?



$$J\,(\#\,/\,\text{area time}) = \frac{n\bar{v}_x}{2}$$

$$We\ need\ \bar{v}_x,\ \bar{v}$$

Do dimensional analysis on

$J = nv$

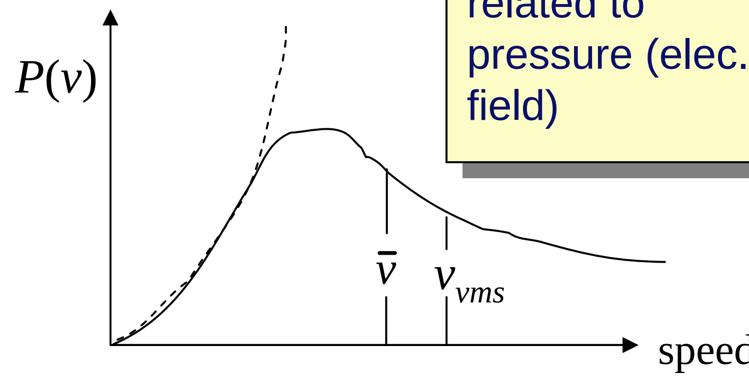
Show J analogous to current density,

related to pressure (elec. field)

Calculating gas velocities

Maxwell speed distribution:

$$P(v) = 4\pi\left[\frac{m}{2\pi kT}\right]^{3/2} v^2 \exp\left[-\frac{mv^2}{2kT}\right]$$



$$\bar{v} = \int vP(v)dv$$

$$\bar{v}_x = \sqrt{\frac{2kT}{\pi m}} \qquad \bar{v} = \sqrt{\frac{8kT}{\pi m}}\ , \quad \bar{v}_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

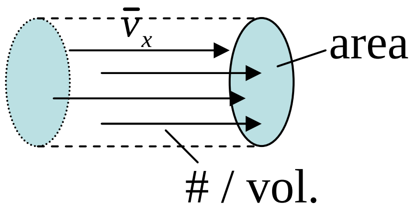
Generally: $\boxed{\frac{1}{2}mv^2 \approx \frac{3}{2}k_B T}$

$$\bar{v}_x = \bar{v}/2$$

$v_{\text{rms}} \approx 500$ m/s

T <=> molecular velocity

So flux of atoms hitting surface per unit time



$$J_x = \frac{n\bar{v}_x}{2} = \frac{n}{2}\sqrt{\frac{2kT}{\pi m}} \xrightarrow[\text{gas}]{\text{ideal}} \boxed{\frac{p}{\sqrt{2\pi mkT}} = J_x}$$

Compare: $\lambda = \dfrac{\sqrt{2}k_B T}{2\pi d^2 p}$

Dimensional analysis: (force/area = en/vol.): $p = \dfrac{E_{kin}}{Vol} = \boxed{n\dfrac{m\bar{v}^2}{2}} = Jm\bar{v}$

Pressure = (Molecular momentum) x flux, *J*

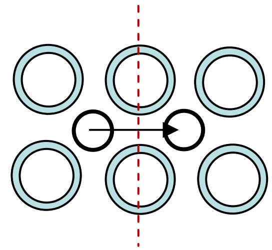
Numerically, $J_x = 3.5\times 10^{22}\dfrac{p(Torr)}{\sqrt{MT(g/mole\cdot K)}}\ (atoms/cm^2\,\sec)$

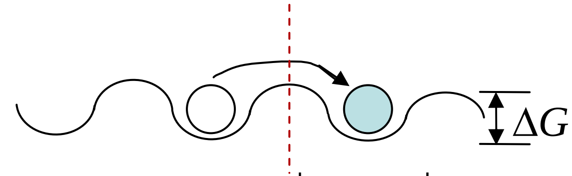
This gives a flux at 10^{-6} Torr of 1 monolayer (ML) arriving per sec

Why not per unit area?

Diffusivity

Recall diffusion in solids:





$$D = D_0 \exp\left[-\frac{\Delta G}{kT}\right]$$

Debye $\nu \approx 10^{13}$ s^{-1}

For gas, no energy barrier, just collisions.

$$J_{\text{gas}} = -D_{\text{gas}} \frac{dc}{dx} \cong -D \frac{n}{\lambda}$$

$$\downarrow$$

$$\frac{n v_x}{2}$$

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

(cm^2/s)

recall

$$\lambda = \frac{\sqrt{2}kT}{2\pi d^2 p}$$

$$\bar{v}_x \propto \sqrt{T}$$

$$\therefore D_{\text{gas}} \propto \frac{T^{3/2}}{p}$$

$$or \; D_{\text{gas}} \propto T^{1/2}$$

much weaker *T*-dep. than
in solid (which is exponential)

Figure removed for copyright reasons.

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

10^{-6} Torr => 1 monolayer/ sec

Review

Ideal gas: $pV = Nk_BT$,

$$\boxed{\therefore \lambda = \frac{\sqrt{2}k_BT}{2\pi d^2 p}}$$

$\approx$ 10 cm at p = 1 mT
100 m at 10^{-6} Torr

Generally: $\boxed{\frac{1}{2}mv^2 \approx \frac{3}{2}k_BT}$

$$J_x = \frac{n\bar{v}_x}{2} = \frac{n}{2}\sqrt{\frac{2kT}{\pi m}} \xrightarrow[\text{gas}]{\text{ideal}} \boxed{\frac{p}{\sqrt{2\pi mkT}} = J_x}$$

$$p = \frac{E_{kin}}{Vol} = n\frac{m\bar{v}^2}{2} = Jm\bar{v}$$

$$J_{gas} = D_{gas}\frac{dc}{dx} \cong D\frac{n}{\lambda}$$

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

(cm^2/s)

Weak temperature dependence
relative to solid state diffusion

Knudsen number

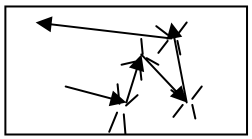
L = dimension of chamber or reactor

p	λ (cm)
1 atm	10^{-5}
1 Torr	10^{-2}
1 mT	10

Recall: $$\lambda = \frac{\sqrt{2}k_B T}{2\pi d^2 p}$$

Knudsen number, $N_0 = \lambda / L$

$\lambda/L < 1$

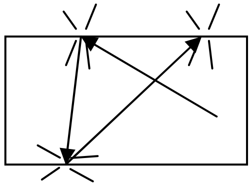


Flow is *viscous; p* > 1 mT

Pump power must be > viscosity;

Must transport large # of molecules

$\lambda/L > 1$



Molecular, ballistic flow*;*

p < 1 mT

Pump efficiency is critical;

Must attract and hold molecules

What does this imply for pumping?

Gas flow and pump speed

Gases are compressible, *unlike* liquids.

∴ express flow as <u>***number*** of molecules</u>/time, not ***volume****/t.*

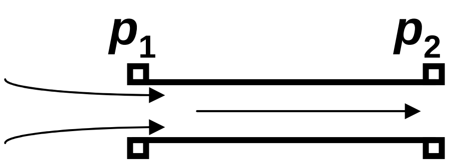
$$Q = \frac{dN}{dt} = \frac{1}{k_B T}\left(V\frac{dp}{dt} + p\frac{dV}{dt} \right)$$

Using ideal gas law

Conductance of

vacuum component:

dp/dt* = *v* ∇*p



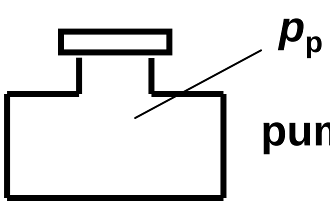
$$\Rightarrow Q = C\left(p - p_p\right)$$

Ohm: *I* = *V/R*

Units of conductance = 1/(sec-Pa*)*

C ∝ *area/length*

Pump *throughput, Q:*



$$Q \equiv pS$$

***S*=*Q*/*p* units**

#/(sec*Pa)

Pump speed units, *S* = *V*/($k_B T$ *t*)

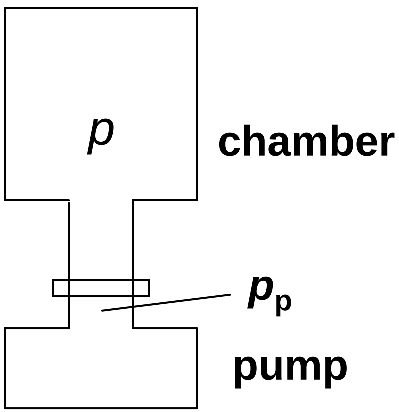
sccm or L/s

Std. cc/min Liters/sec

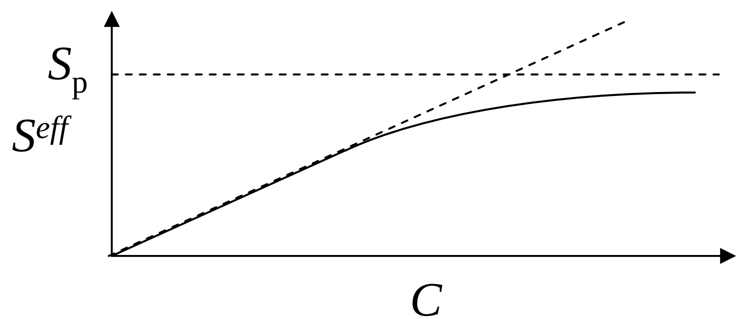
Gas flow and pump speed

Conductance of vacuum component: $\Rightarrow Q = C\left(p - p_p\right)$ (p_p is pressure nearer pump)

System throughput: $Q \equiv pS,^{eff}$ $\quad p = \dfrac{Q}{S^{eff}}$ $\quad \boxed{p_p = \dfrac{Q}{S_p}}$



$$Q = C\left(\frac{Q}{S^{eff}} - \frac{Q}{S_p}\right) \;\; \boxed{\Rightarrow S^{eff} = \frac{CS_p}{C + S_p} = \frac{1}{\dfrac{1}{C} + \dfrac{1}{S_p}}}$$



Like parallel resistors

Series conductances:

$1/C = 1/C_1 + 1/C_2$

S* = *Q*/*p* and *C* = *Q*/*dp

Effective pump speed, S^{eff}, never exceeds conductance of worst component or pump speed, S_p.

Vacuum technology: Generating low pressure

Two classes of vacuum pumps:

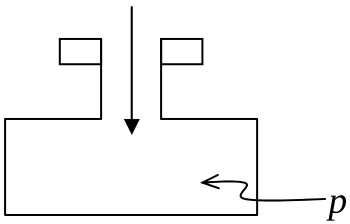
1) Molecules physically removed from chamber

a) mechanical pump

b) Turbo molecular pump

c) Oil diffusion pump

$$S = \frac{1}{kT}\frac{dV}{dt}$$



2) Molecules adsorbed on a surface,

or buried in a layer

a) Sputter/ion pump (with Ti sublimation)

b) Cryo pump

1) Molecules physically removed from chamber

a) Mechanical pump | **b) Oil diffusion pump** | **c) Turbo molecular pump**

1 atm

a) Mechanical pump

Oil contamination,
Vibrations.
But pumps from
1 atm to mT.
$S \approx 2 \times 10^4$ L/s

b) Oil diffusion pump

Hot Si oil vaporized,
jetted toward fore pump,
momentum transfer to gas,
which is pumped out.
$S = 12A$ L/s

c) Turbo molecular pump

Rotating (25 krpm) vanes
impart momentum to gas,
pres're incr's away from chamber,
gas pumped by backing pump.
No oil. $S = 10^3$ L/s

1 milliT

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copyright reasons.

Figure 2-9 in Ohring, 2001.

10^{-6} T

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Figure 2-8 in Ohring, 2001.

10^{-9} T

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Figure 2-7 in Ohring, 2001.

2) Molecules adsorbed on a surface, or buried in a layer

a) Sputter/ion pump (with Ti sublimation)

b) Cryo pump

1 atm

(760 Torr)

1 Torr

Gas is ionized
by hi-*V*,
ions spiral in *B* field,
embed in anode,
Coated by Ti.
No moving parts,
no oil.
S depends on
pump size and
S(H) >>*S*(O,N,H_2O)

Figure removed for copyright reasons.

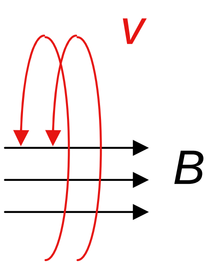
Figure 2-11 in Ohring, 2001.

Figure removed for copyright reasons.

Figure 2-10 in Ohring, 2001.

Very clean,
molecules condense
on cold (120 K) surfaces,
No moving parts. *S* ≈ 3*A* (cm^2)L/s

10^{-6} T



10^{-9} T

PUMP SUMMARY

Two classes of vacuum pumps:

1) Molecules physically removed from chamber

a) mechanical pump — Pumps from 1 atm; moving parts, oil

b) Turbo molecular pump — Clean, pumps lg. *M* well, from 1mT; low pump speed, moving parts

c) Oil diffusion pump — No moving parts; oil in vac

2) Molecules adsorbed on a surface, or buried in a layer

a) Sputter/ion pump (with Ti sublimation) — Clean, pumps reactants, no moving parts; pumps from 10^{-4} T down.

b) Cryo pump — Clean, no moving parts; pumps from 10^{-4} T down.

Most systems use different pumps for different pressure ranges…

Vacuum technology: Deposition chambers

Standard vacuum, $p \approx 10^{-5}$ -10^{-6} Torr
Glass or stainless steel,
usually diffusion pumped,
CVD, thermal evap. or sputter dep.
=> polycrystalline films

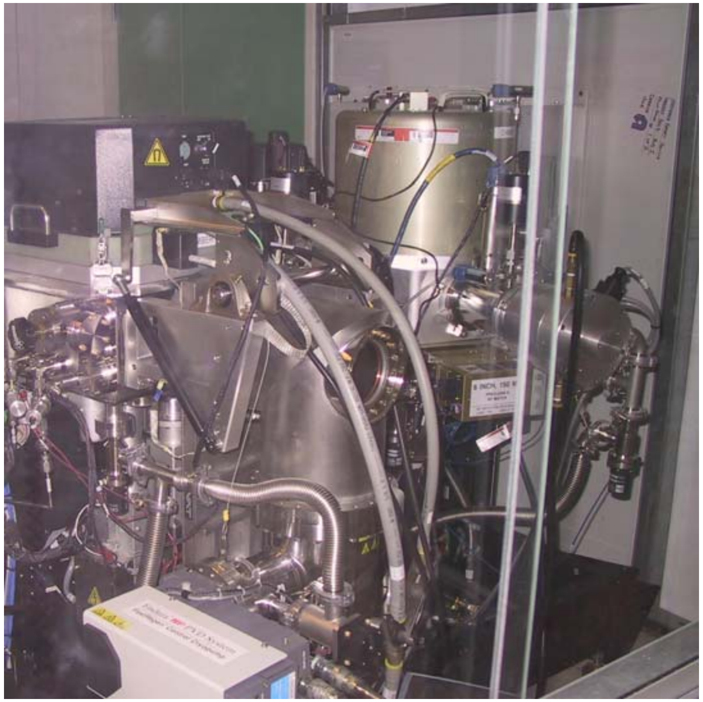
Ultrahigh vacuum, $p \approx 10^{-8}$ -10^{-11} Torr;
Stainless steel (bakeable);
Ion and/or turbo pumped
thermal evap. Sputter deposition
=> better quality films, epitaxial

Figure removed for copyright reasons.

Figure 2-12 in Ohring, 2001.

1. Get p < 1 mT; close valve

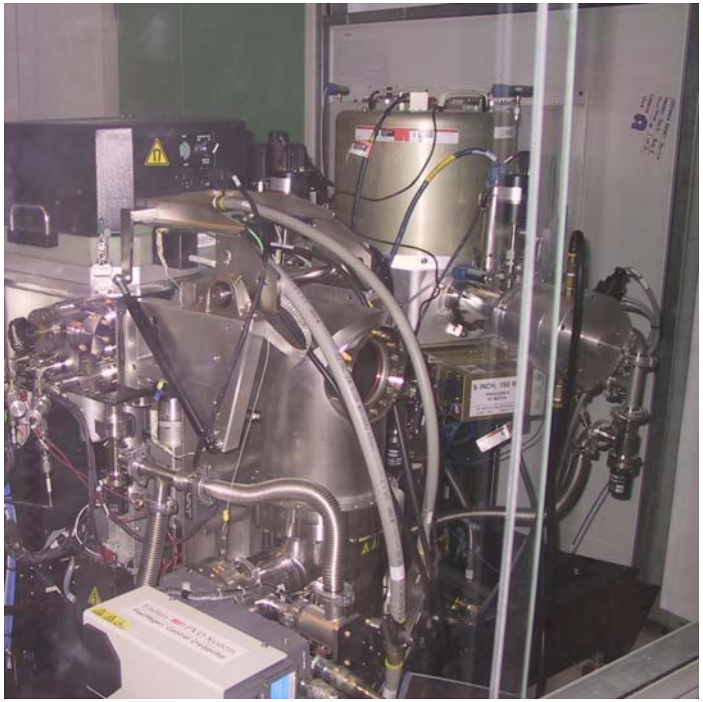
2. Open backing valve, Turn on diff'n pump



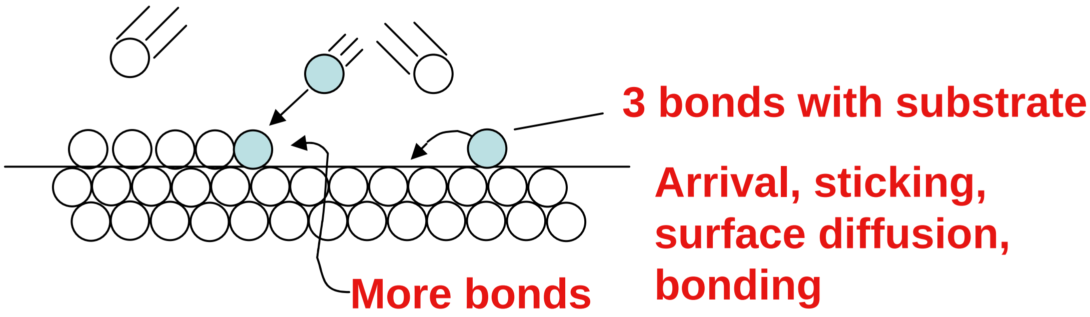
Vacuum technology: Deposition chambers

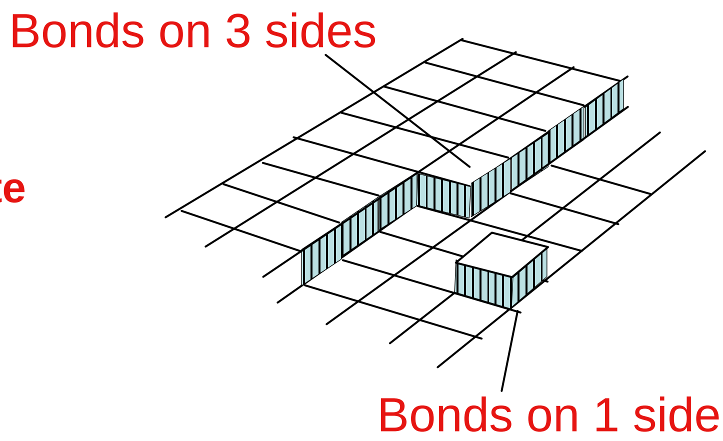
Ultrahigh vacuum, $p > 10^{-11}$ Torr;
Stainless steel (bakeable);
Ion and/or turbo pumped
thermal evap. Sputter deposition
=> better quality films, epitaxial

Baking a stainless-steel uhv system
(*T* up to 200 C for 10's of hrs)
desorbs water vapor, organics
from chamber walls;
these are ion-pumped out;
pressure drops as *T* returns to RT.



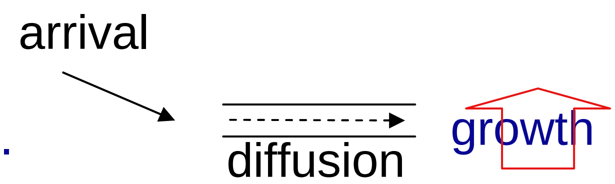
Thin film growth general





$$R \equiv \frac{\text{Rate of arrival}}{\text{Diffusion rate}}$$

Film growth competes with gas arrival.

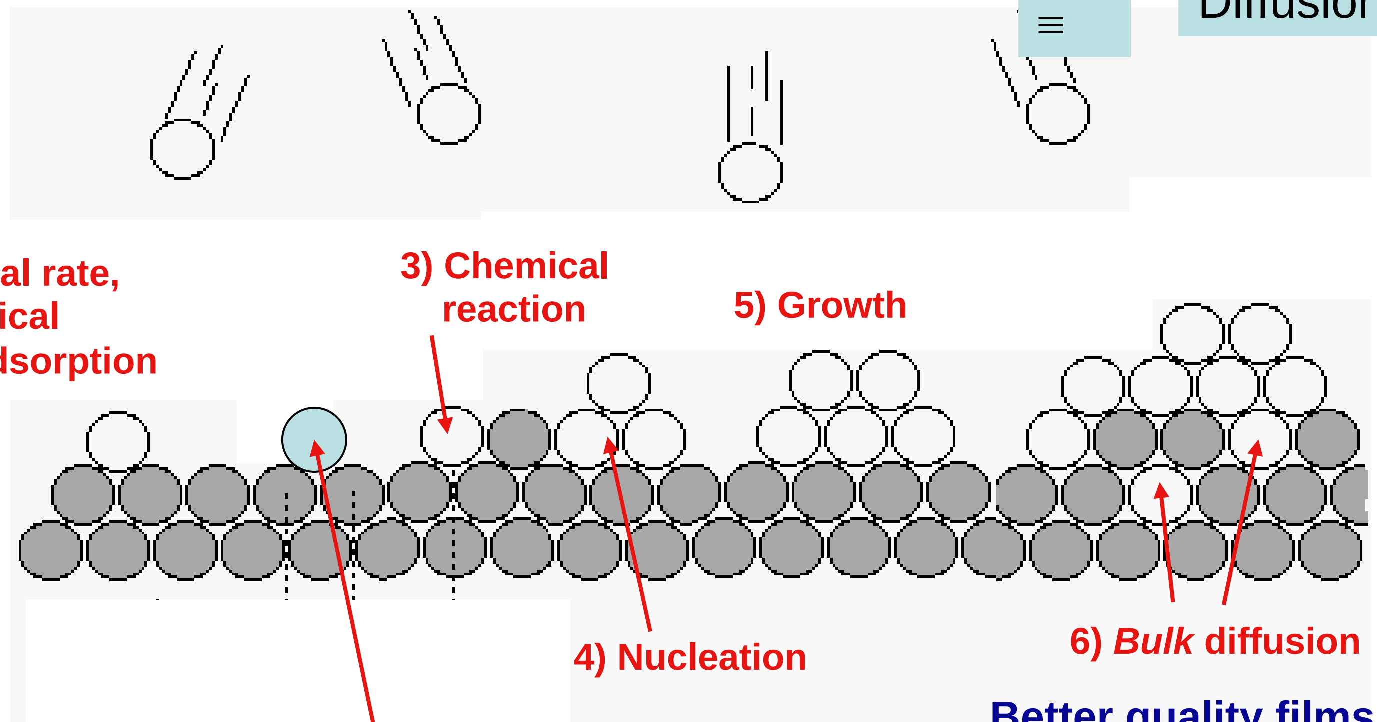


1) *R* > 1 ⇒ Non-equilibrium, fast growth, many misaligned islands form, leading to defective (high-surface-en), polycrystalline film, columnar grains, This 3-D growth is "*Volmer-Weber*" mode; Can ⇒ amorphous film.

2) *R* < 1 => Slower, more equilibrium, layer-by-layer growth, larger grains (raise surface temperature to ↑ mobility ⇒ ↑ g.s.). If film and substrate have same crystal structure, film may grow in perfect alignment with substrate ("epitaxy"). This 2-D growth is "*Frank-van der Merwe*" mode.

Thin film growth details (*R* < 1)

$$R \equiv \frac{\text{Rate of arrival}}{\text{Diffusion rate}}$$



Better quality films; layer-by-layer growth

If *R* > 1, processes 2) - 6) have reduced probability;
=> poor quality, rough films

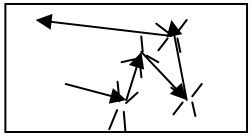
Knudsen number

p	λ (cm)
1 atm	10^{-5}
1 Torr	10^{-2}
1 mT	10

L = dimension of chamber or reactor

Knudsen number, $N_0 = \lambda/L$

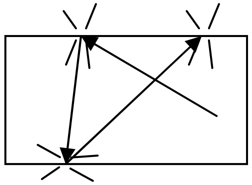
$\lambda/L < 1$



Flow is *viscous; p* > 1 mT

Deposited species “thermalized”;
Growth is from all directions,
good step coverage

$\lambda/L > 1$



Molecular, ballistic flow*;*
$p < 1$ mT

Deposited species arrives “hot”;
Growth ballistic, shadow effects,
poor step coverage

What does this imply for film growth?

Looking ahead…

Thin films made by a variety of means:

thermal vapor deposition (evaporation)
- for metals

sputter deposition
DC-magnetron- for metals
-RF for oxides

Physical vapor deposition (PVD)

chemical vapor deposition
- for metals, semiconductors

Chemical vapor deposition (CVD)