Vacuum Technology and Physics

(important to understand for upcoming segments on thin film deposit techniques)

Q. Why use vacuum?

- prevent reaction w/ air
- increase mean-free path: Directionality, diffusion (CVD) (LP)

→ overview of Practical Vacuum Pressure Ranges

Consider basic Vacuum Physics

- Concept of mean free path: critical vacuum parameter
- describes how often gas molecules "interact" or scatter

λ = mean free path

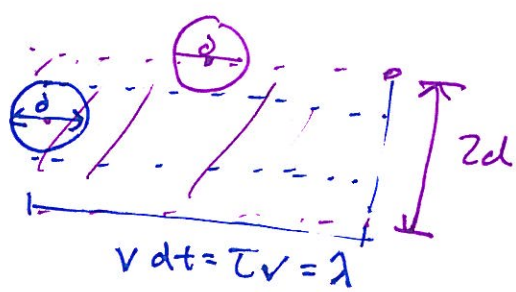
Consider molecule with:

d = diameter and v = velocity

- the molecule will move: $\boxed{v\,dt \text{ in time } dt}$

say $\boxed{\tau = dt}$ is the time between collisions.

What is probability of hitting another molecule?



Volume swept out by motion during time $dt = \tau$ is

$$V = \pi d^2 \cdot v\tau$$

$2d$ is diameter of interaction; d is the radius

Practical Vacuum Pressure Range

1 atm = 1.0135×10^5 Pa = 760 Torr

			techniques
low vac	$< 10^5$ Pa = 750 torr	→	LP CVD
Med vac	$< 3 \times 10^3$ Pa = 25 torr		mechanical Pumps Schlenk Line
hi-vac	$< 10^{-1}$ Pa = 7.5×10^{-4} torr	(~ 1m torr)	
Very-hi-vac	$< 10^{-4}$ Pa = 7.5×10^{-7} torr	→	thermal/electron evaporation
UHV	$< 10^{-7}$ Pa = 7.5×10^{-10} torr	→	MBE, Surface science

Since we set $dt = \tau$ (i.e. average collision time) then we know there must be one molecule in the interaction volume V.

We relate V to P, T etc. using the ideal gas law:

$$PV = nRT \quad \text{or} \quad \boxed{PV = N_{av} kT}$$

n moles of molecules

N_{av} # of molecules

$N_{av.} = n \cdot N_a$

$k = R/N_a$

So $\dfrac{N_{av}}{V} = P/kT =$ # of molecules per volume or $\dfrac{kT}{P} =$ avg. volume per molecule.

$$V = \pi d^2 \underbrace{v\tau}_{v\tau = \lambda} = \frac{kT}{P} \quad \text{so} \quad \lambda = \frac{kT}{\pi d^2 P}$$

but derivation w/ more rigor gives additionals $\frac{1}{\sqrt{2}}$

$$\lambda = \frac{kT}{\pi d^2 P \sqrt{2}} = \boxed{\frac{0.66}{P(\text{mPa})} \text{ cm}}$$

So for rough vacuum:

$1\ Pa = 7.5\ mtorr$ "roughing" (mechanical pump)

$\boxed{\lambda = 0.66\ cm}$ "Rule of thumb"

for $P = 10^{-8}\ Pa$ (MBE pressures)

$\lambda = \underline{660\ km}$ molecules flow in "beams" <u>never collide</u>

for $P = 10^{-4}\ Pa$ ($\sim 10^{-6}$ torr)

$\lambda = 66\ m$

typical thermal or ebeam evaporation pressures.

"line-of-sight"

Any vacuum process...

Should ask yourself "what is λ"?

Impingement Rate

Next year
See chapter 12 Pohan Silbey and Albert.

Pressure also determines # of molecules that hit a surface per time

MBE / Thermal Evaporator

← flux of species you want

Background → O_2, N_2, H_2O can react w/ growing film

← substrate

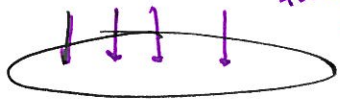
Distribution of velocities in a gas given by Maxwell - Boltzmann Distribution:

$$\frac{1}{n}\frac{\partial n}{\partial v} = f_v = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2kT}\right)$$

$$V_{av} = \frac{2}{\sqrt{\pi}}\sqrt{\frac{2kT}{m}} = \frac{\int_0^\infty v f_v \, dv}{\int_0^\infty f_v \, dv}$$

(expectation value of velocity)

What # of molecules pass this plane per unit time?



← plane perpendicular to x direction

in 1D

$$\frac{1}{n}\frac{dn_x}{dV_x} = \left(\frac{m}{2\pi kT}\right)^{1/2} V_x^2 \exp\left[\frac{-mV^2}{2kT}\right]$$

Mass

$n = \frac{\#\text{mol}}{\text{Volume}}$

how many molecules per velocity dV_x

$$\phi = \text{impingement Rate} = \int_0^\infty V_x \, dn_x$$

← add up impingement rates for all velocities (in one direction)

Rate not negative ☹

$V = \frac{cm}{s}$ $n = \frac{\#}{cm^3}$

$n \cdot v = \frac{\#}{cm^2 \cdot s} = \text{flux}$

V.4

$$\phi = \int_0^\infty v_x \, dn_x = n\sqrt{\frac{kT}{2\pi m}}$$

where $dn_x = n f_v \, dv$

per volume

velocity probability distribution

volume element

$$\phi = \int_0^\infty n f_v v_x \, dv$$ (average speed in one direction!)

as $n = \frac{P}{kT}$ (from $PV = RT = N_{av} kT$

molar volume

Avogadro's #

and $n = \frac{N_{av}}{V} = \frac{P}{kT}$)

$$\phi = \frac{P}{kT}\sqrt{\frac{kT}{2\pi m}}$$

$$\left[= P\sqrt{\frac{1}{2\pi m kT}} = P(2\pi m kT)^{1/2} = 2.64\times10^{20}\left(\frac{P}{\sqrt{MT}}\right)\right.$$ molecules · $cm^{-2}\,s^{-1}$

in Pa

Temp = T

M = molecular weight

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example: impingement rate and time required to form a monolayer.

at 300K molecular diameter $D_2 = 3.64\,A^\circ$

per unit area $\boxed{N_s = 7.54\times10^{14}\,cm^{-2}}$

at 1

$$t = \frac{N_s}{\phi} = \frac{N_s\sqrt{MT}}{2.64\times10^{20}}$$

# of monolayer

impingement rate

mechanical	$t = 0.28$ ms	at 1 Pa	(7.5 mtorr)
high vac/turbo diffusion	$= 2.8$ s	at 10^{-4} Pa	(7.5×10^{-7} torr)
UHV MBE system	$= 7.7$ hr	at 10^{-8} Pa	(7.5×10^{-11} torr)

7 weeks → intermediate...

(12) Thin films : Basics

(we will use these basics to discuss thin film deposition techniques → CVD, PVD, and ALD etc.)

→ metals, semiconductors or insulators

→ must have low defect density, for instance of pinhole

→ thin film properties can be very different than bulk

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* Film nucleation: in absence of epitaxial relationships,

→ film must nucleate: "critical" nuclei typically higher energy intermediate

Competing effects

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

ΔG_v: volume free energy change upon going from gas to condensate (bulk value)

γ: surface energy (surface tension) → because bonds are not satisfied at the surface.

ΔG_v can be positive or negative! depending on (P_v/P_s)

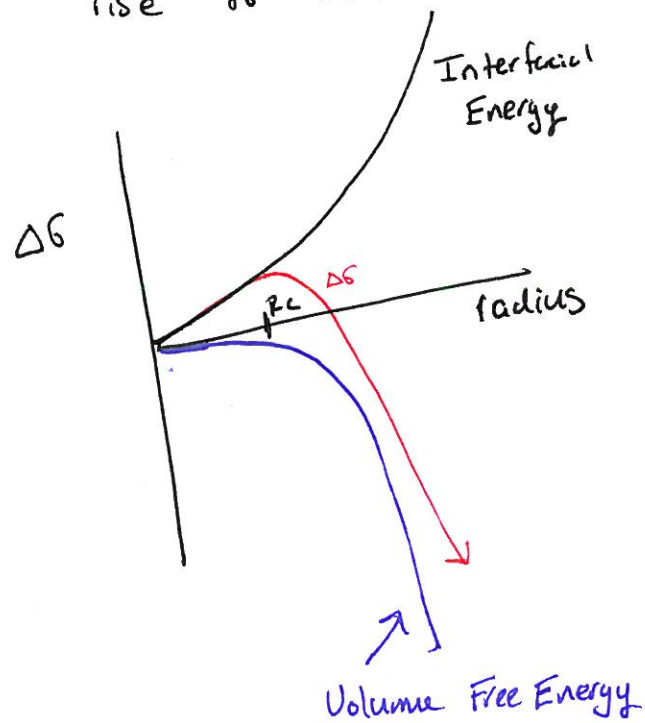
$$\Delta G_v = \frac{-kT}{\Omega} \ln\left(\frac{P_v}{P_s}\right)$$

P_v: Pressure of supersaturated vapor

P_s: equilibrium vapor pressure

Ω: atomic volume

Competition betwe Volume and surface energies gives rise to a critical energy for nucleation:

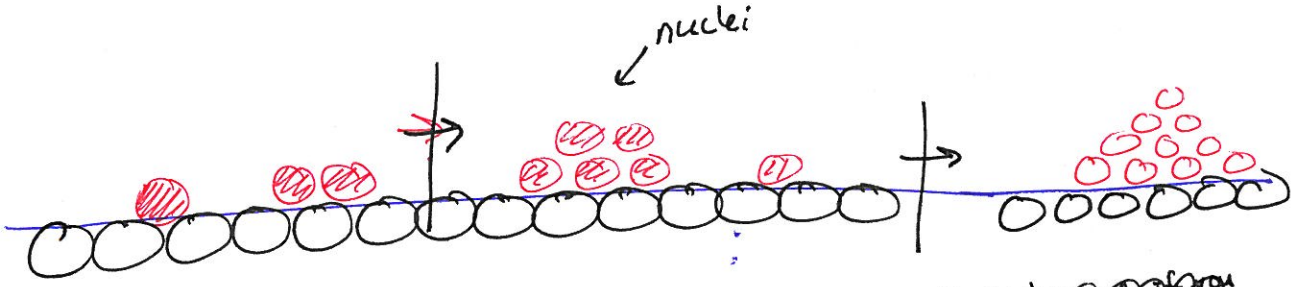


- idea of critical nucleus.
- explains supersaturation

Different Growth Modes

1. Island Growth (Volmer-Weber)

3D islands form; film atoms more strongly bound to each other than substrate, or surface diffusion slow.



- poly crystalline films
- poor lattice matching (or deposit on amorphous substrate, etc)

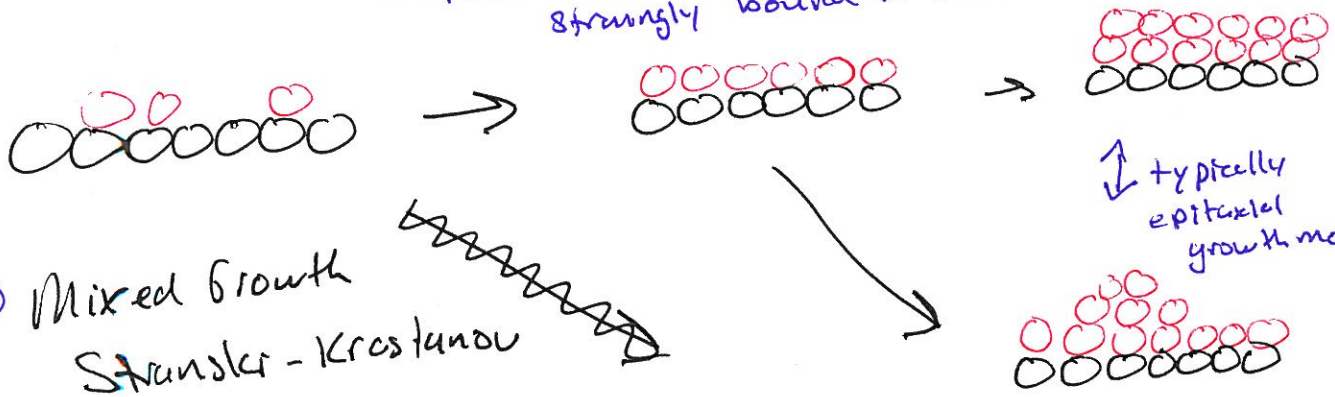
→ Typical of PVD, of metals, etc.

* ~~not good if you~~ ~~want films!~~

good if you want "quantum dots" and such.

② Layer-by-Layer Growth (Frank-van der Merwe)

- fast diffusion, or/and atom in film more strongly bound to substrate than each other



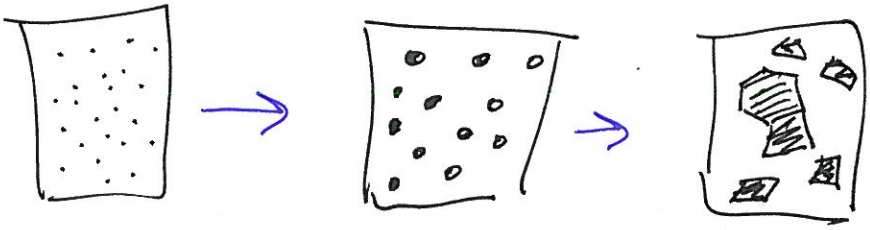
↕ typically epitaxial growth modes

③ Mixed Growth Stranski-Krastanov

- initially layer-by-layer then mixed growth.

Structure of thin films:

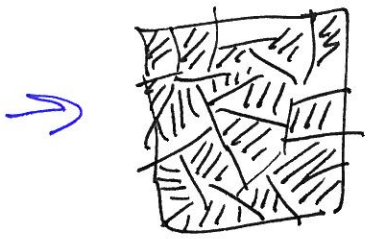
for most PVD process (non-epitaxial growth), e.g. metal deposition



Supersaturation ($P_v > P_s$) leads to nucleation of crystallites on the sample surface.

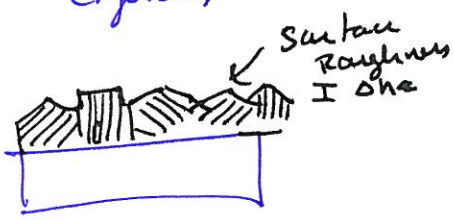
crystallites begin to grow

eventually coalescing



↕ grain size (average size of crystals)

leading to a poly crystalline film



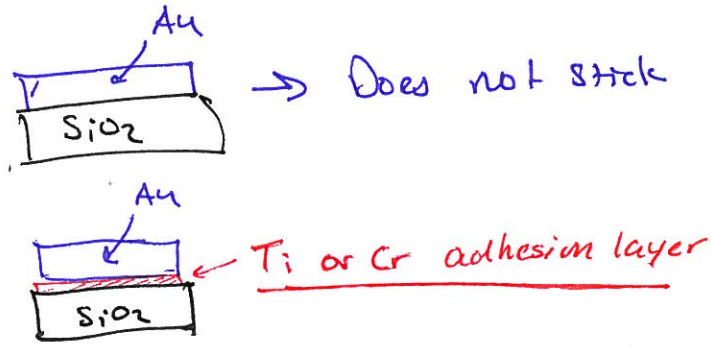
hotter T ↑ → ~~crystals~~ grain size increases as the mobility of atoms on the crystallite surfaces allows them to move about and minimize surface area.

→ amorphous materials
- → grain size = ∅! no crystalline structure (SiO_2) (Si_3N_4)
- → PVD metals → poly crystal ~~are~~ grain size 10-100 nm
- → epitaxy = single crystal
- → preferred orientation of film → "texture"

Mechanical Properties of Films

- adhesion - how well film sticks to underlying layer

Example: Metals on SiO_2



- Ti or Cr form strong M-O bonds to surface (chemisorbtion!)

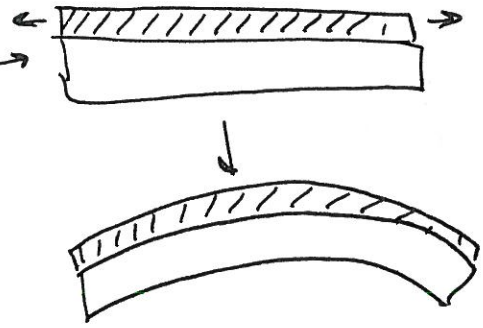
- Au does not form bonds to SiO_2 (noble metal) so does not adhere well.

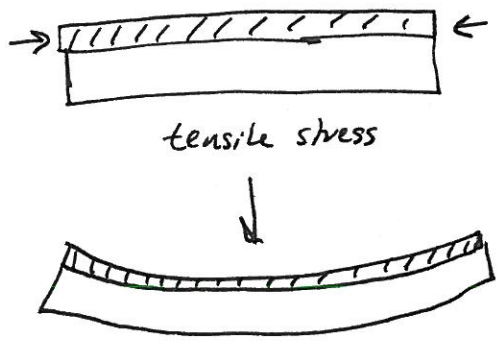
- Au does form metal bonds to Ti,

Ti or Cr are good adhesion layers.

Stress in thin Films

Compressive stress → film wants to expand





tensile stress

film wants to contract

drying after solution deposition can cause this... volume contraction

→ cv ~~g~~ crack the film to relive stress

~~→ Post cracks cause big problems for IC~~

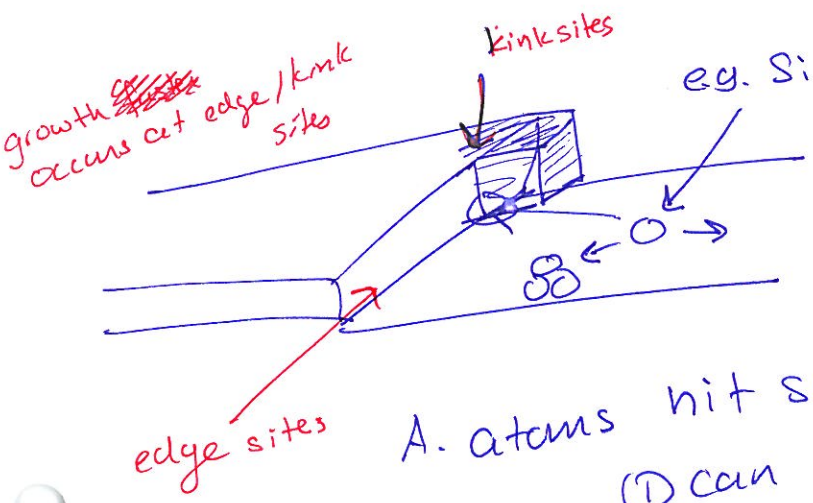
Cracks are big problems for IC manufacture.

Vapor Phase Epitaxy – Used to grow thin crystalline films

– Si on Si (Lower T, lower # of defects)

→ GaAs → III-V semiconductor

complex multilayered structures (e.g. ultra high efficiency solar cells)



A. atoms hit surface
① can stick
② reevaporate

B. If atoms stick
- can move
- can be buried
- can de absorb
- can attach to growing crystal
- can form island

C. Parameters to Control (minimum)

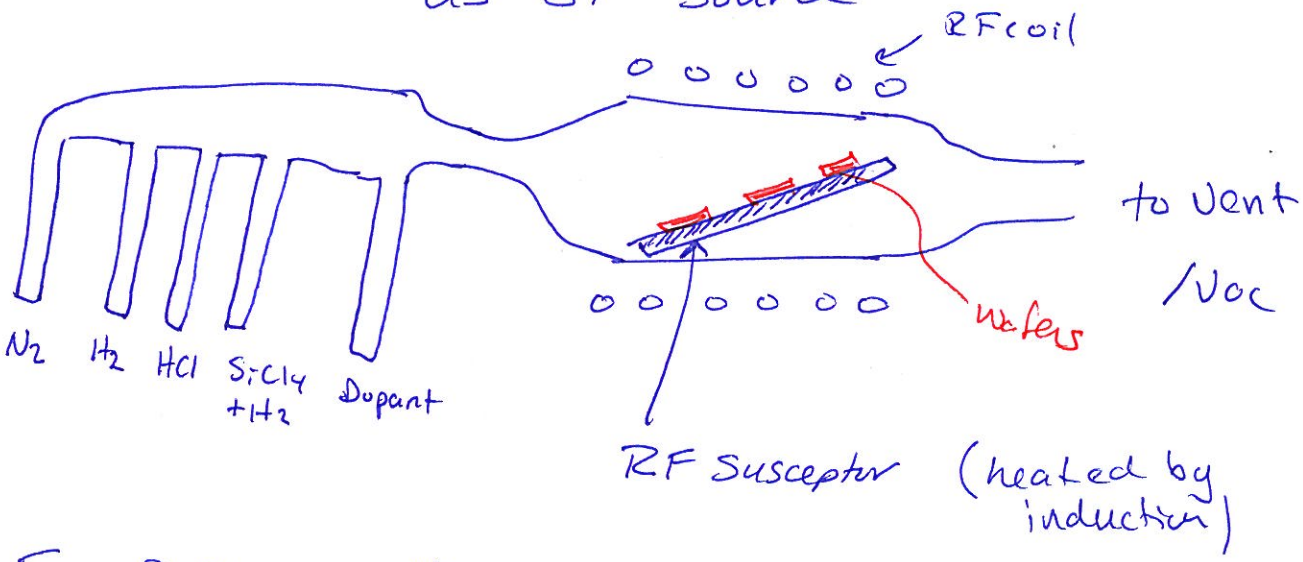
① Flux of atoms

② Surface Temperature

For Silicon

$SiCl_4$, $SiCl_2H_2$, $SiCl_3H$ or SiH_4

as Si Source

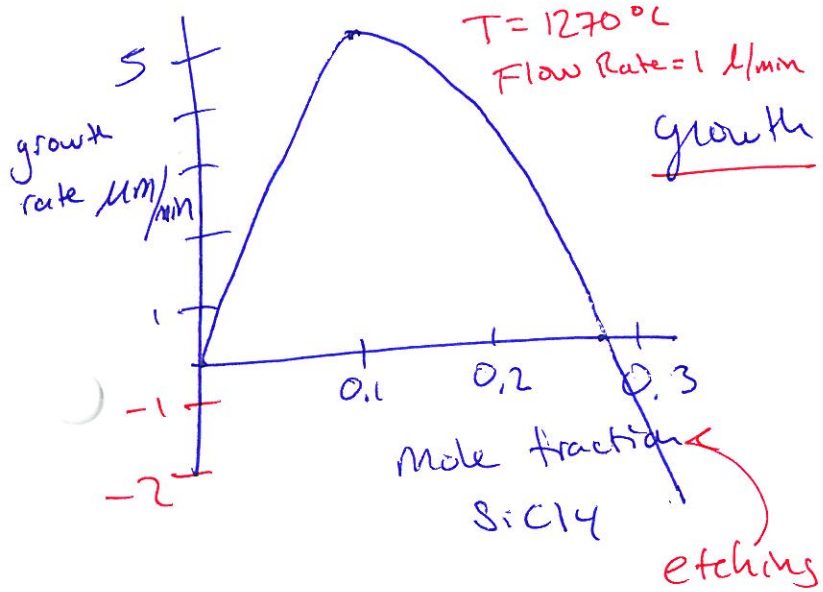


Ex. $SiCl_4$ growth

$$SiCl_4(g) + 2H_2(g) \rightleftharpoons Si(\text{solid}) + 4HCl(g)$$

$$SiCl_4(g) + S(\text{solid}) \rightleftharpoons 2SiCl_2(\text{gas})$$

$SiCl_4$ concentration too high → etching!



Doping

B_2H_6 → diborane p-type

PH_3, AsH_3 - n-type (very toxic gases)

Why use Si Epitaxial wafers?

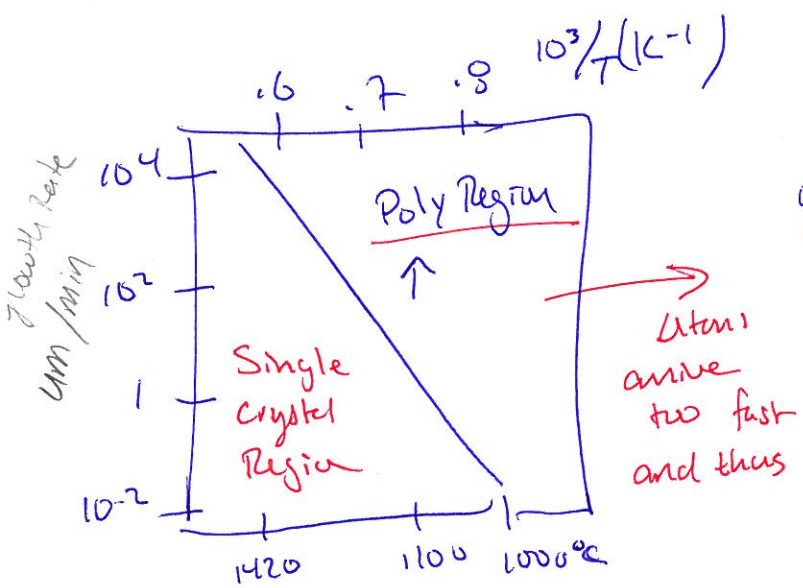
1) Prevent Latch-up (low-resistance path between supply voltage and ground) ⇒ high current
→ can burn up the sample

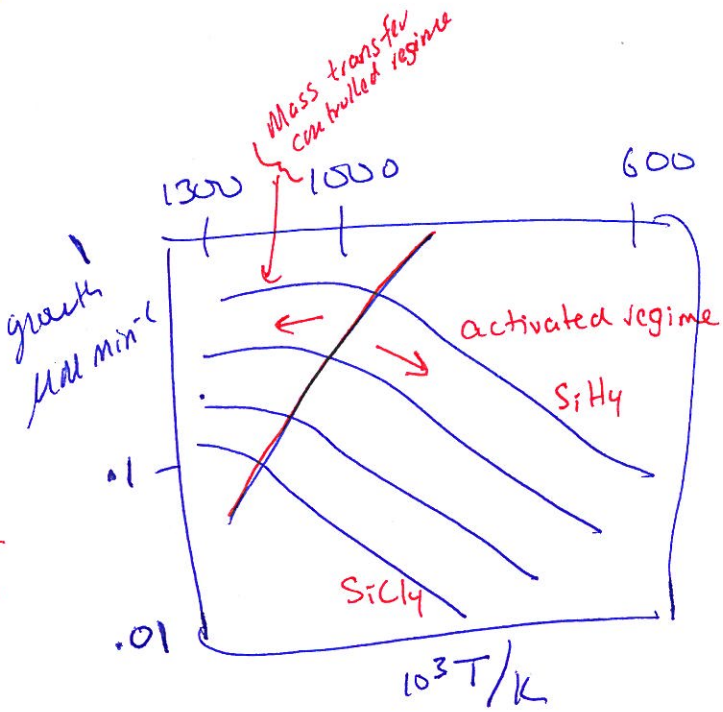
2) EPI layers cleaner
→ no SiOx precipitates
→ no defect clusters (as T ↓ defects ↓)
→ no polishing (mechanical) defects

Doping can be precisely controlled

3) (Wafers Cost more)

Growth Rates and Reaction Pathways





will derive later in terms of model of growth.

CVD of GaAs

- more complicated!

GaAs decomposes into Ga and As upon melting / Evaporation

direct vapor phase transport not possible!

A.

$$As_4 + 4GaCl_3 + 6H_2 \rightarrow 4GaAs + 12HCl$$

Arsine cracking $\rightarrow$ $4AsH_3 \rightarrow As_4 + 6H_2$

$6HCl + 2Ga \rightarrow 2GaCl_3 + 3H_2$

$\boxed{\text{Chloride Route}}$

Temp. 650 - 850 °C, need As overpressure to prevent decomposition of the growing layer

B. Metal-Organic CVD (preferred research + industrial III-V Epi growth route)

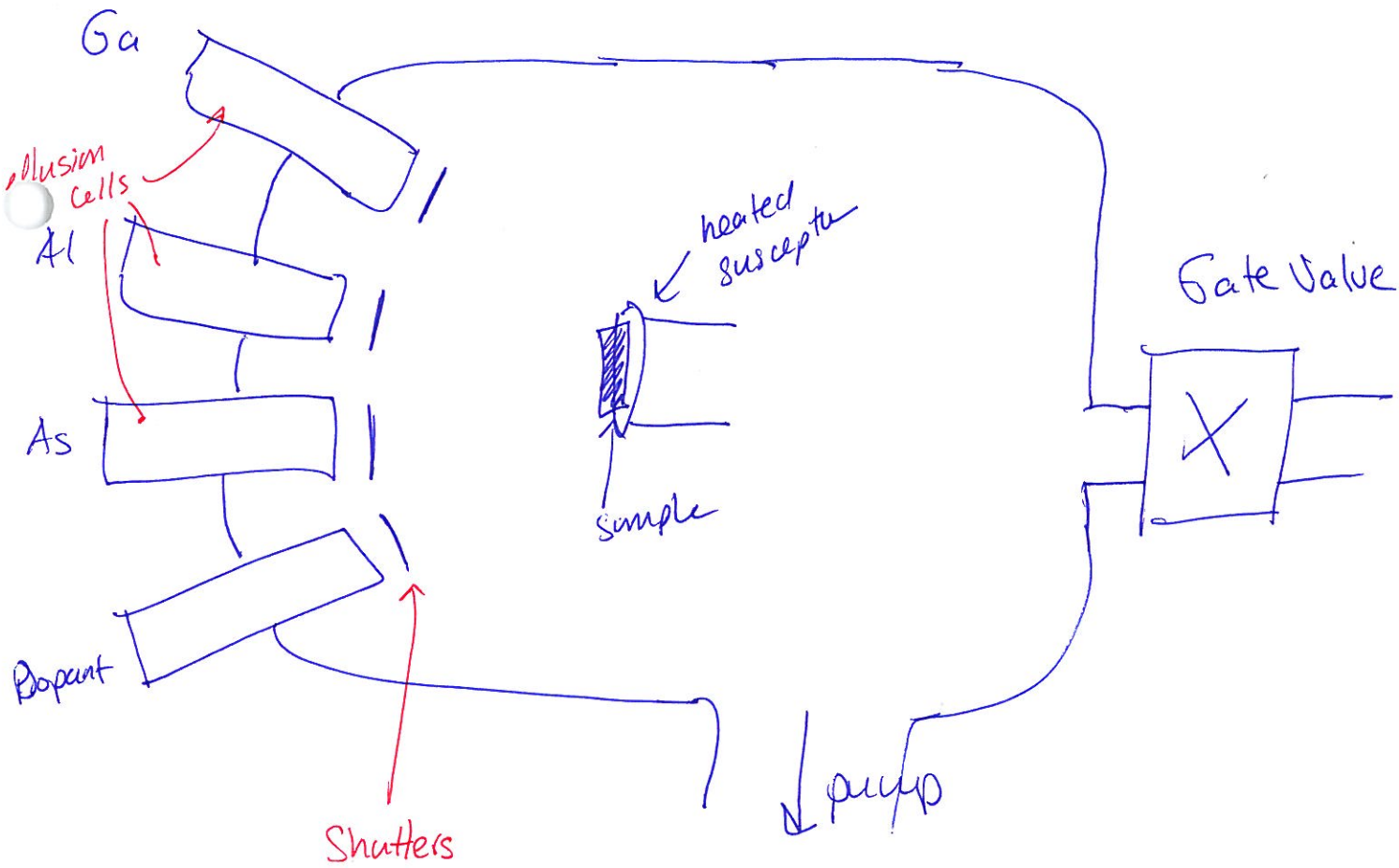
$$AsH_3 + Ga(CH_3)_3 \rightarrow GaAs + 3CH_4$$

MOCVD reactor similar to CVD reactor $\rightarrow$ RF susceptor, liquid-sources (bubblers), flow control, etc.

Molecular Beam Epitaxy (aka. million or mega ~~ba~~ buck evaporator)

- UHV (ultra high vac) ~10^{-10} torr (~10^{-8} Pa)
- can acheive single layer control → heterostructures and other complicated architectures
  ↑ atomic

MBE system Example GaAs



1. pump chamber to 10^{-10} torr
2. adjust effusion cell temperatures to get rates right
3. adjust substrate temperature