CVD

Chemical Vapor Deposition

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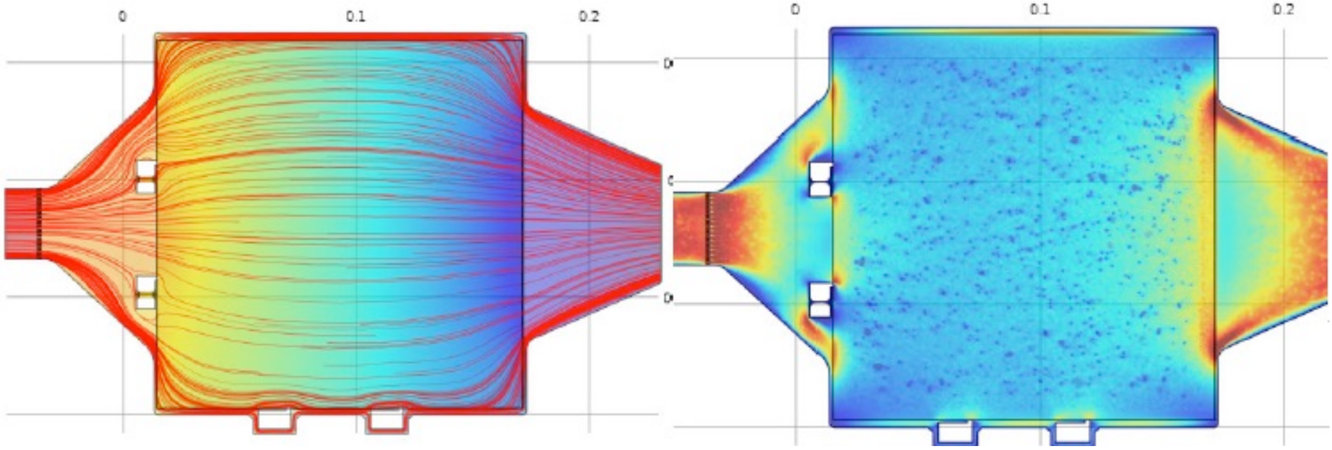
CVD & ALD

Chemical Vapor Deposition, CVD
Atomic Layer Deposition, ALD

Both depend on chemical reactions and reactor fluid dynamics must be considered.

PVD is in different pressure regime, no viscous flow.

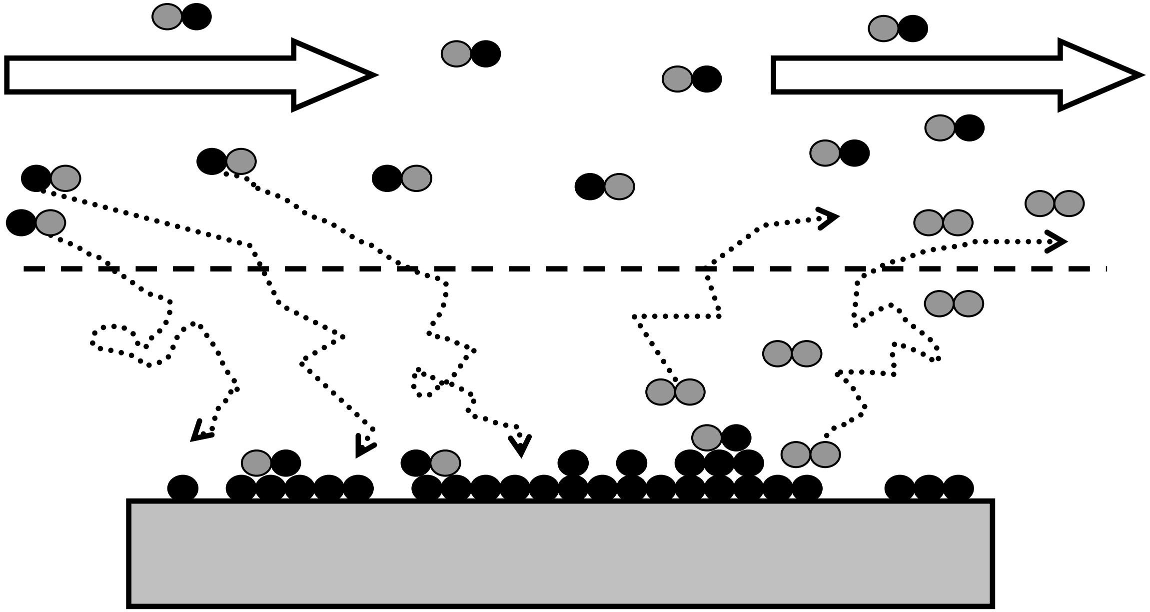


Thermal CVD reactions

Gaseous precursor + surface reaction
➔ solid film + gaseous byproducts

pyrolysis	$SiH_4\ (g) \rightarrow Si\ (s) + 2\ H_2\ (g)$
reduction	$SiCl_4\ (g) + 2\ H_2\ (g) \rightarrow$ $Si\ (s) + 4\ HCl\ (g)$
hydrolysis	$SiCl_4\ (g) + 2\ H_2\ (g) + O_2\ (g) \rightarrow$ $SiO_2\ (s) + 4\ HCl\ (g)$
compound formation	$3\ SiH_2Cl_2\ (g) + 4\ NH_3\ (g) \rightarrow$ $Si_3N_4\ (s) + 6\ H_2\ (g) + 6\ HCl\ (g)$

CVD basics



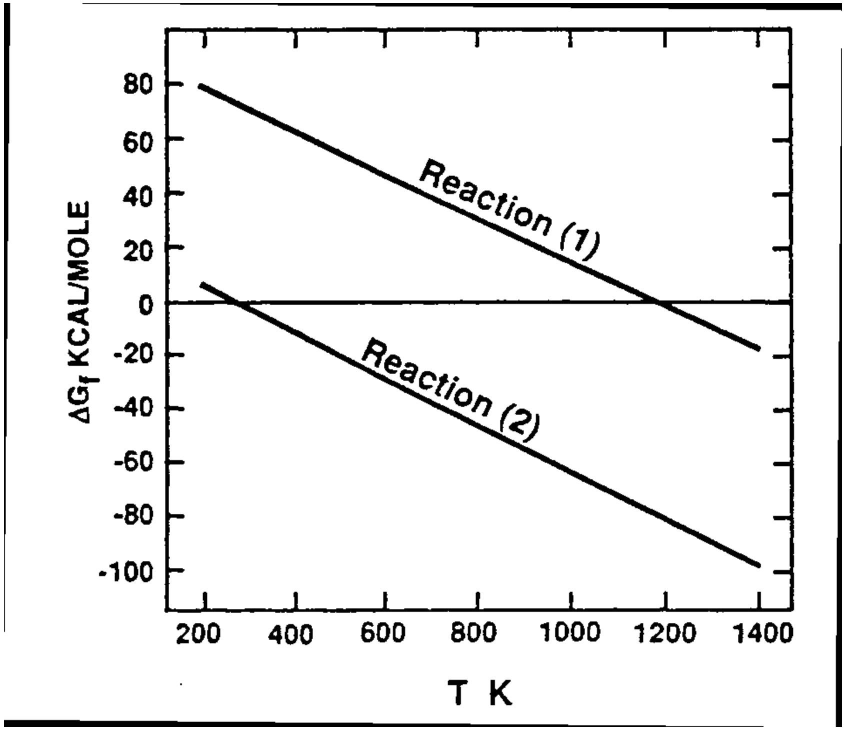
gas phase convection

diffusion through boundary layer

surface processes (adsorption, film deposition, desorption)

S. Franssila: Introduction to Microfabrication, 2nd ed, 2010

Thermodynamics of CVD



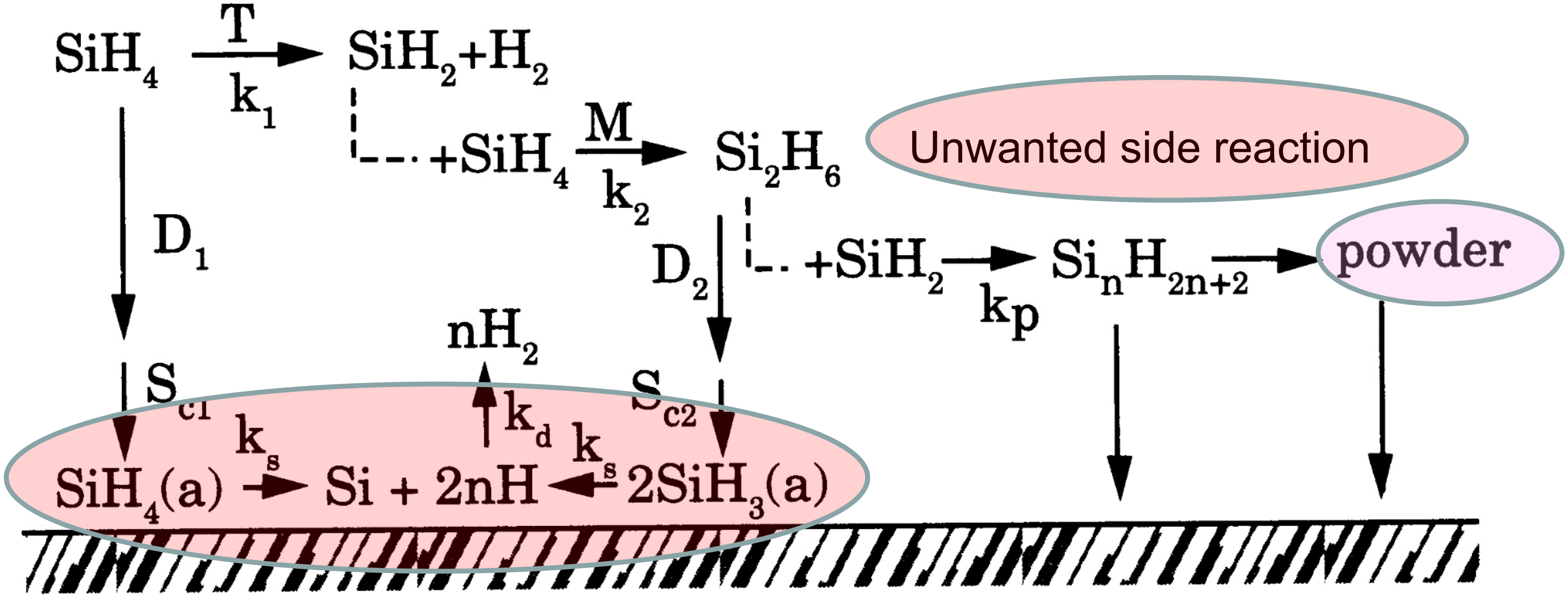
ΔG < 0 for reaction to take place

(1) $TiCl_4 + 2BCl_3 \longrightarrow TiB_2 + 10HCl$

(2) $TiCl_4 + B_2H_6 \longrightarrow TiB_2 + H_2 + 4HCl$

Pierson: Handbook of CVD, p. 22

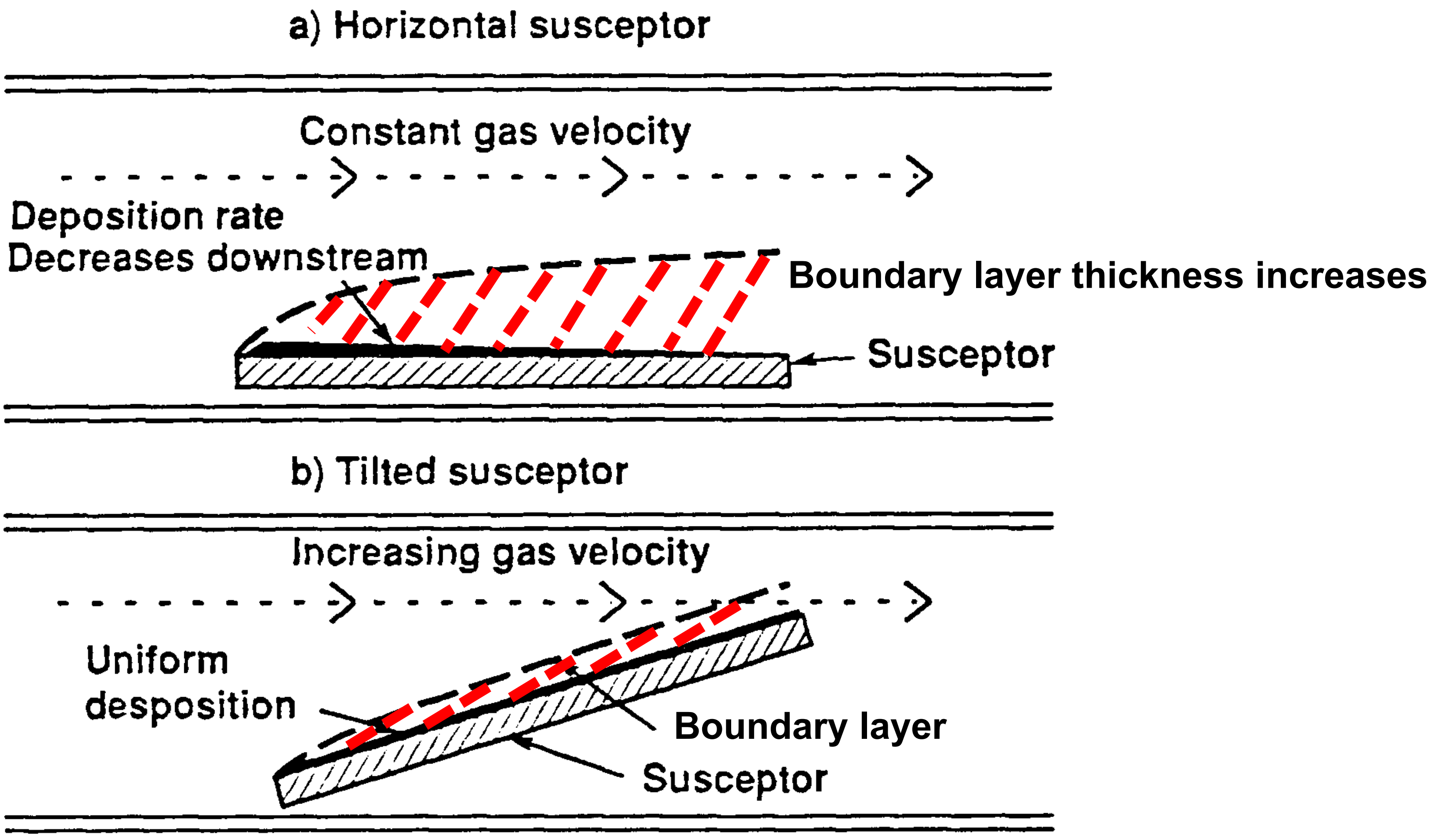
Silicon CVD from SiH_4



Wanted deposition reaction

Smith: Thin-film deposition

Boundary layer
= stagnant gas layer



Pierson: Handbook of CVD, p. 36

Boundary layer thickness, δ

$$\delta(x) = \sqrt{\frac{x}{\rho}\frac{\eta}{v}} = \sqrt{\frac{x}{Re}}$$

Re = Reynolds number

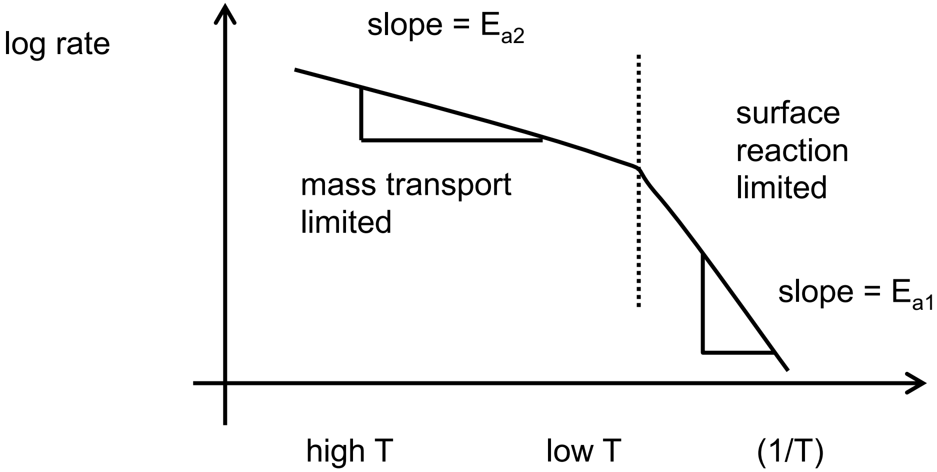
x= distance from entry point
v= velocity

$$\rho = \frac{M \bullet p}{R \bullet T}$$ density

where M = molecular weight and p = total pressure;

$$\eta = \eta_o\left(\frac{T}{T_o}\right)^m$$ viscosity

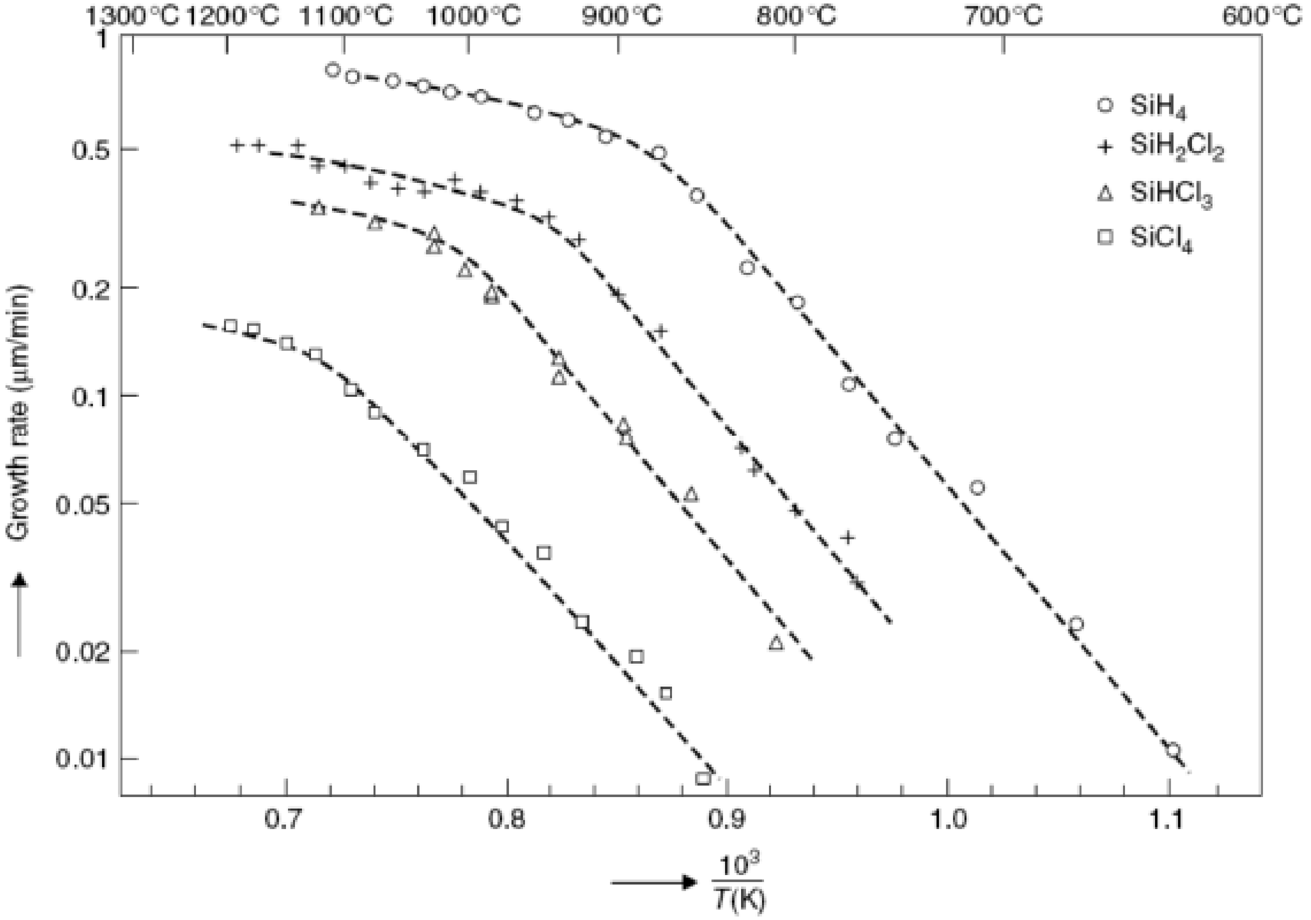
Surface limited vs. mass transport limited reactions



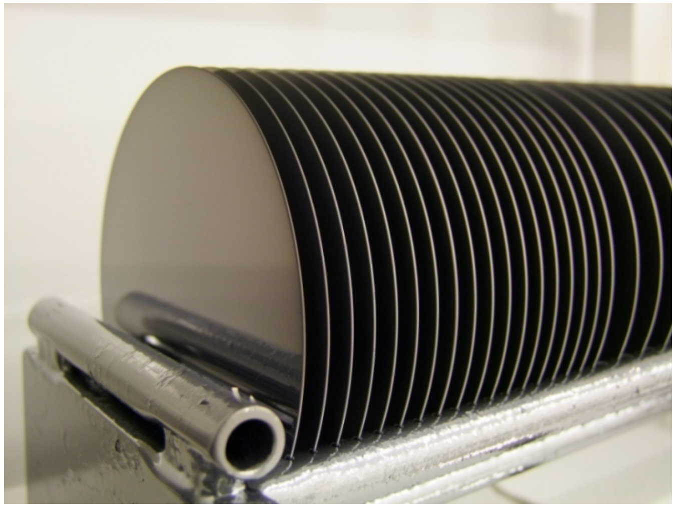
When temperature is low, surface reaction rate is slow, and overabundance of reactants is available. Reaction is then surface reaction limited.

Above a certain temperature all source gas molecules react immediately. The reaction is then in mass-transport limited regime (also known as diffusion limited and supply limited regime).

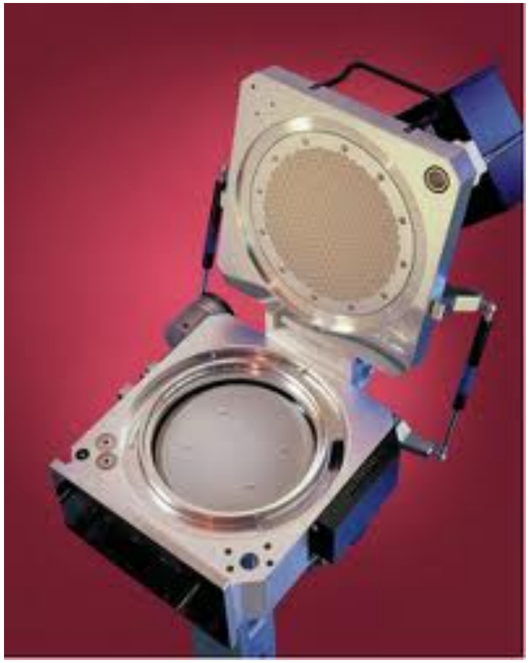
Si epitaxy: surface controlled vs. mass flow controlled



Surface limited vs. mass transport limited reactions (2)

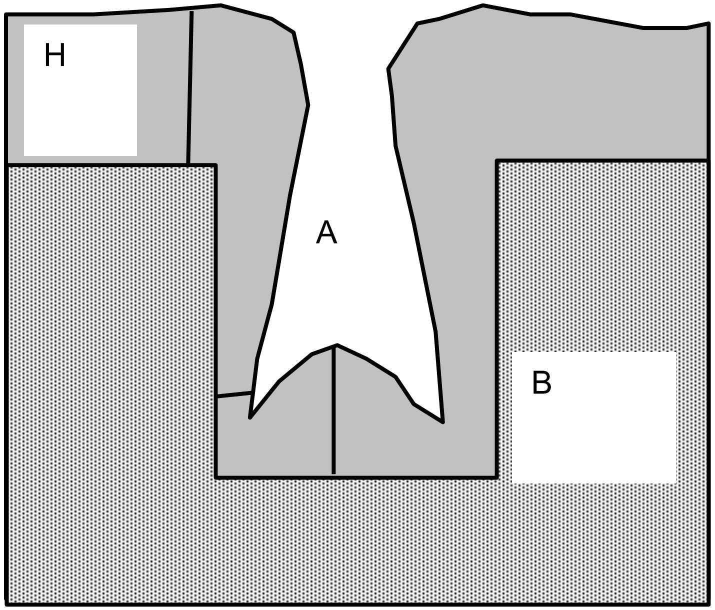


A batch reactor operating in surface reaction limited mode:
-slow reaction
-many wafers because flow patterns are not important



A mass transport limited reactor:
-single wafer
-simple flow patterns
-rotation reduces boundary layer
➔ high deposition rate

Step coverage



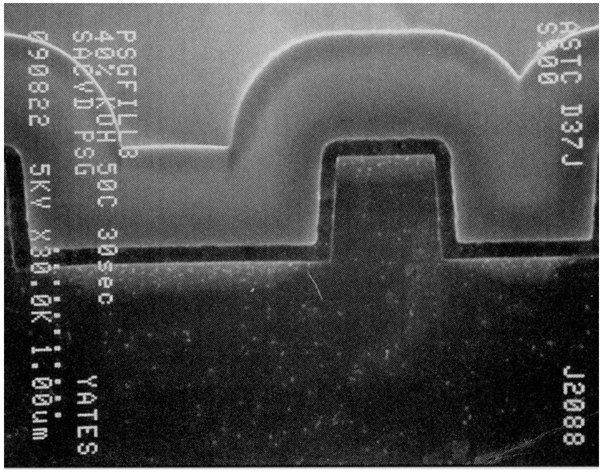
Ratio of film thickness on sidewall to horizontal = A:H

In sputtering, A:H ≈ 20-30%

100% step coverage is called ***conformal***

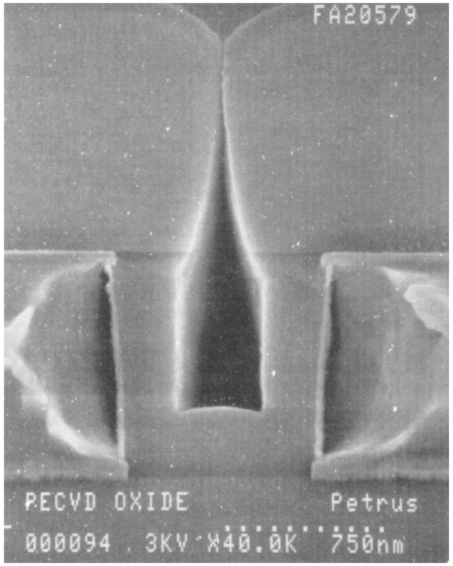
CVD oxide step coverage

Conformal,
near 100%
step coverage



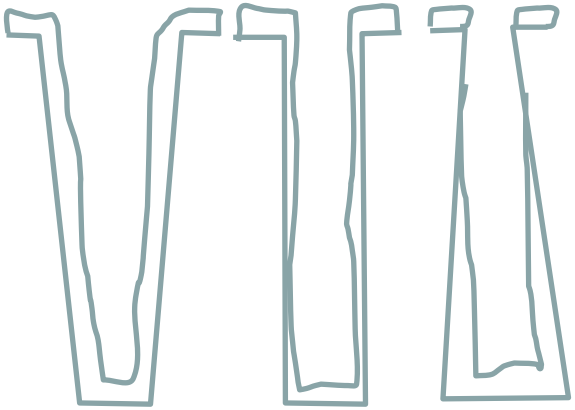
ALD
Thermal CVD

Satisfactory step
coverage, e.g.
50%



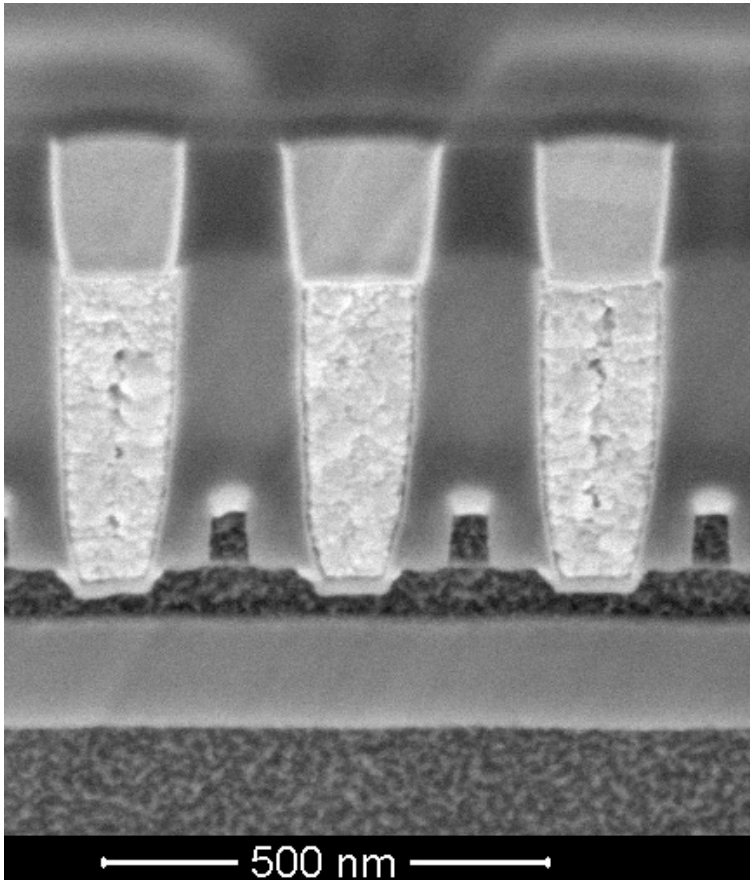
Sputtering
PECVD

Step coverage
depends on
sidewall angle



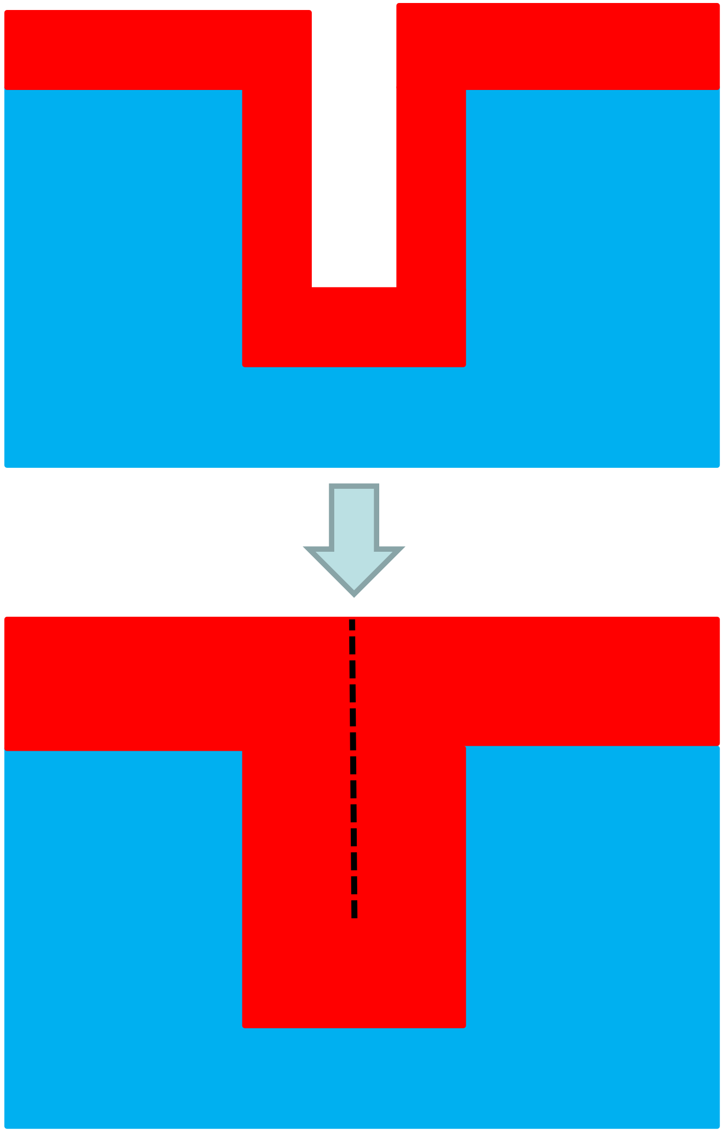
Easier if
positively sloped
sidewalls

Thermal CVD: good step coverage

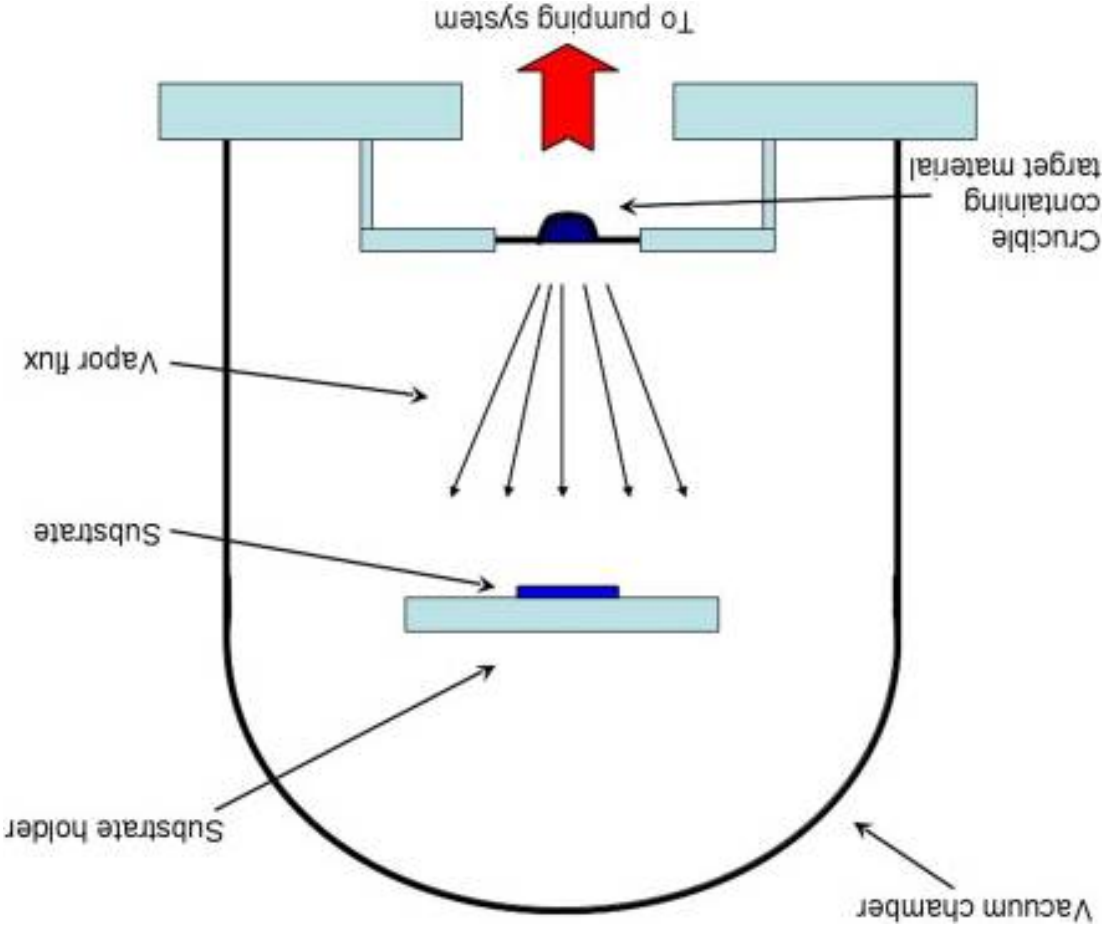


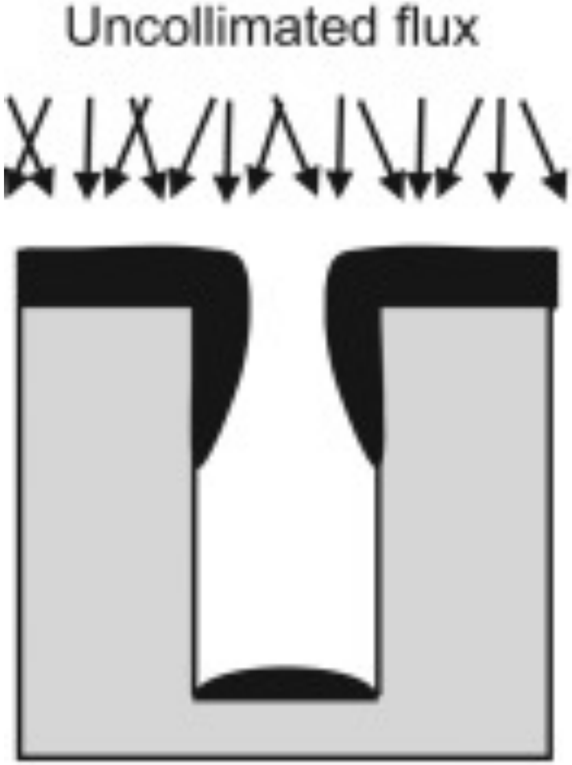
Tungsten:

WF_6 (g) $\rightarrow$ W(s) + $3H_2$ (g)

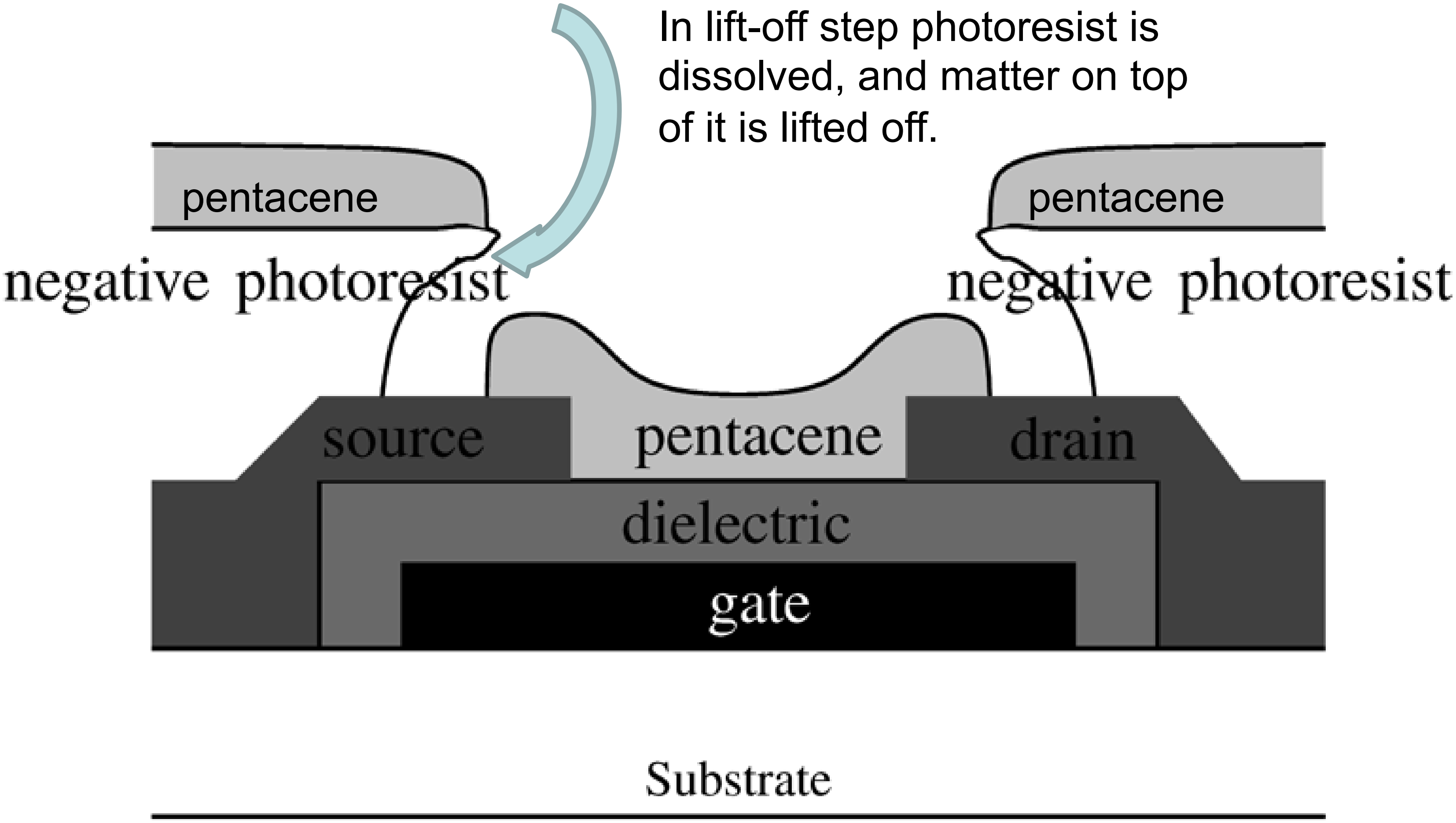


Evaporation: poor step coverage



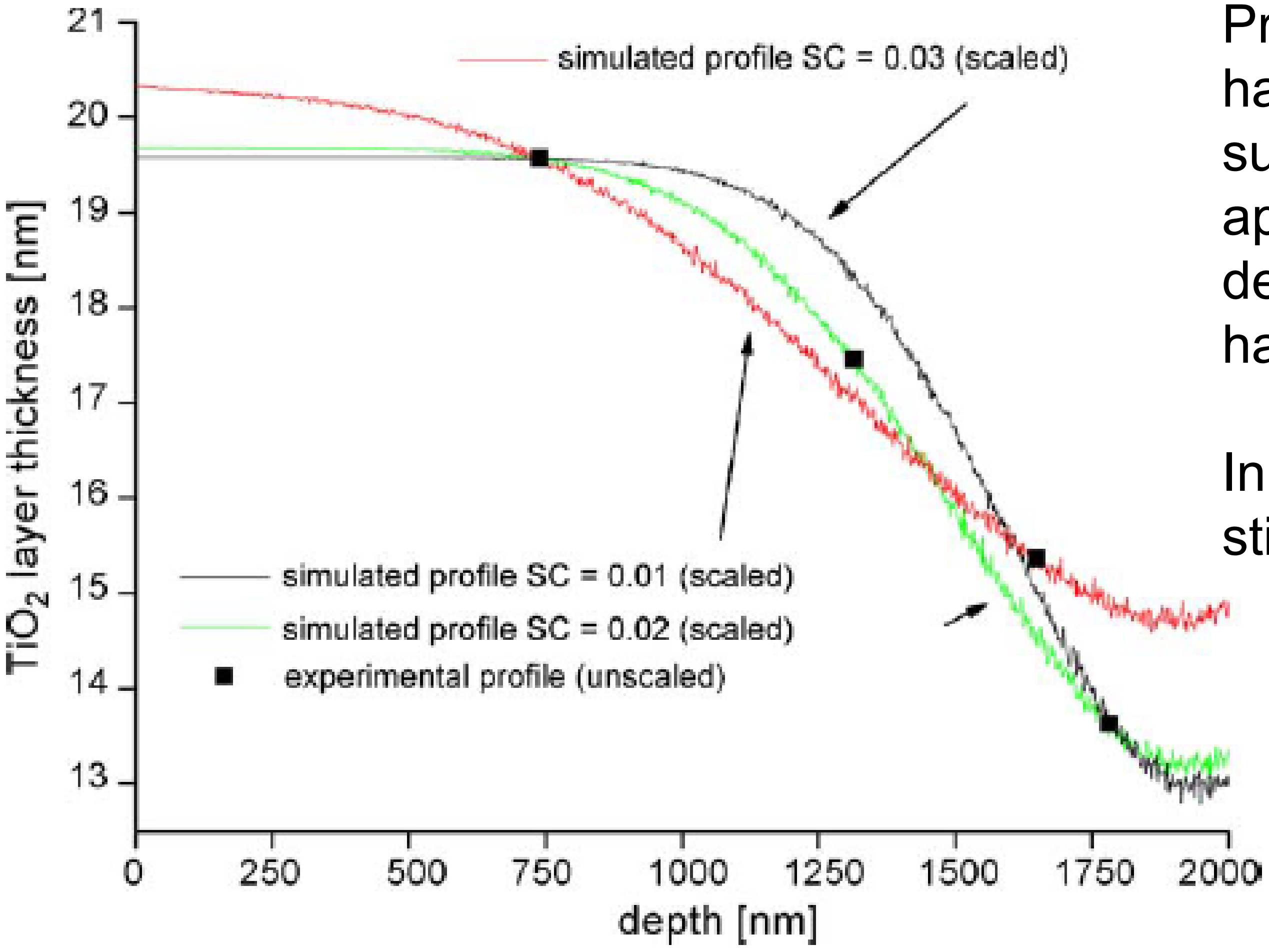


Evaporation good for lift-off


In lift-off step photoresist is dissolved, and matter on top of it is lifted off.

Goettling et al: JOURNAL OF DISPLAY TECHNOLOGY, VOL. 4, NO. 3, SEPTEMBER 2008

Sticking coefficient

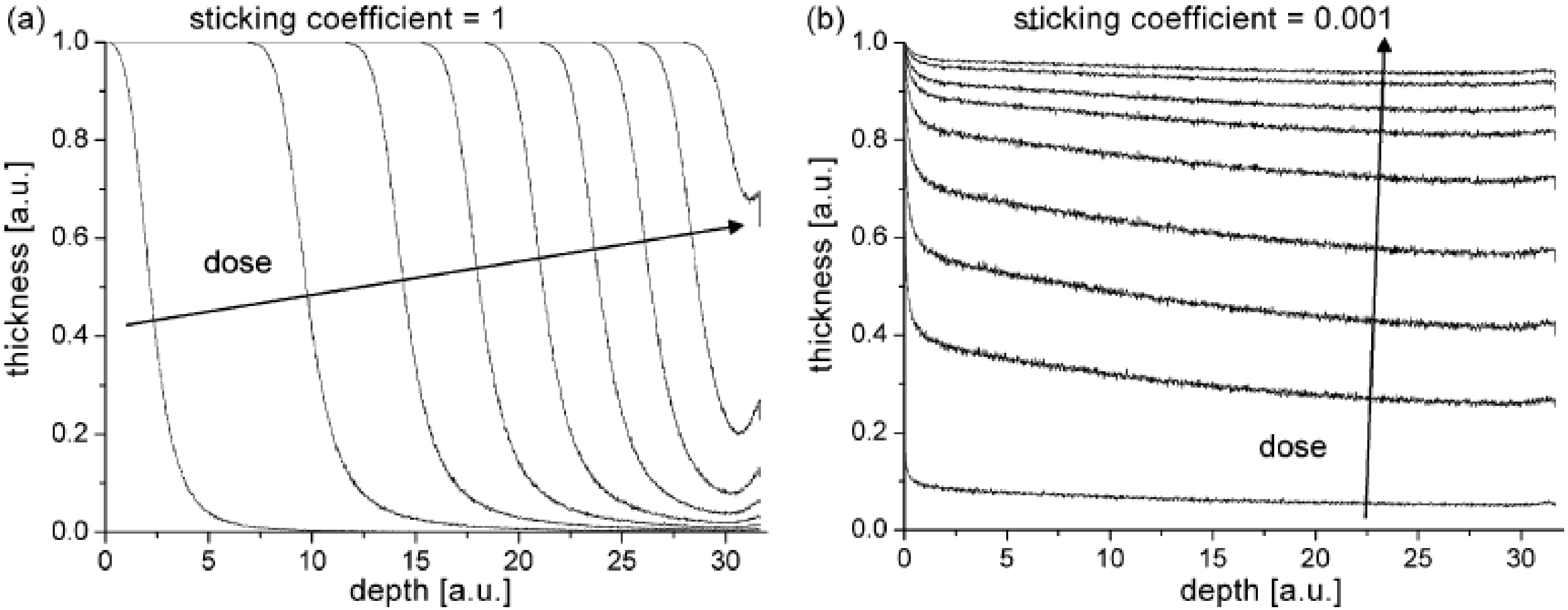


Precursor molecules have to stick to the surface for appreciable deposition can happen.

In this case only 1-2% stick (SC = 0.01-0.02)

Rose & Bartha: Applied Surface Science 255 (2009) 6620–6623

Sticking coefficient (2)

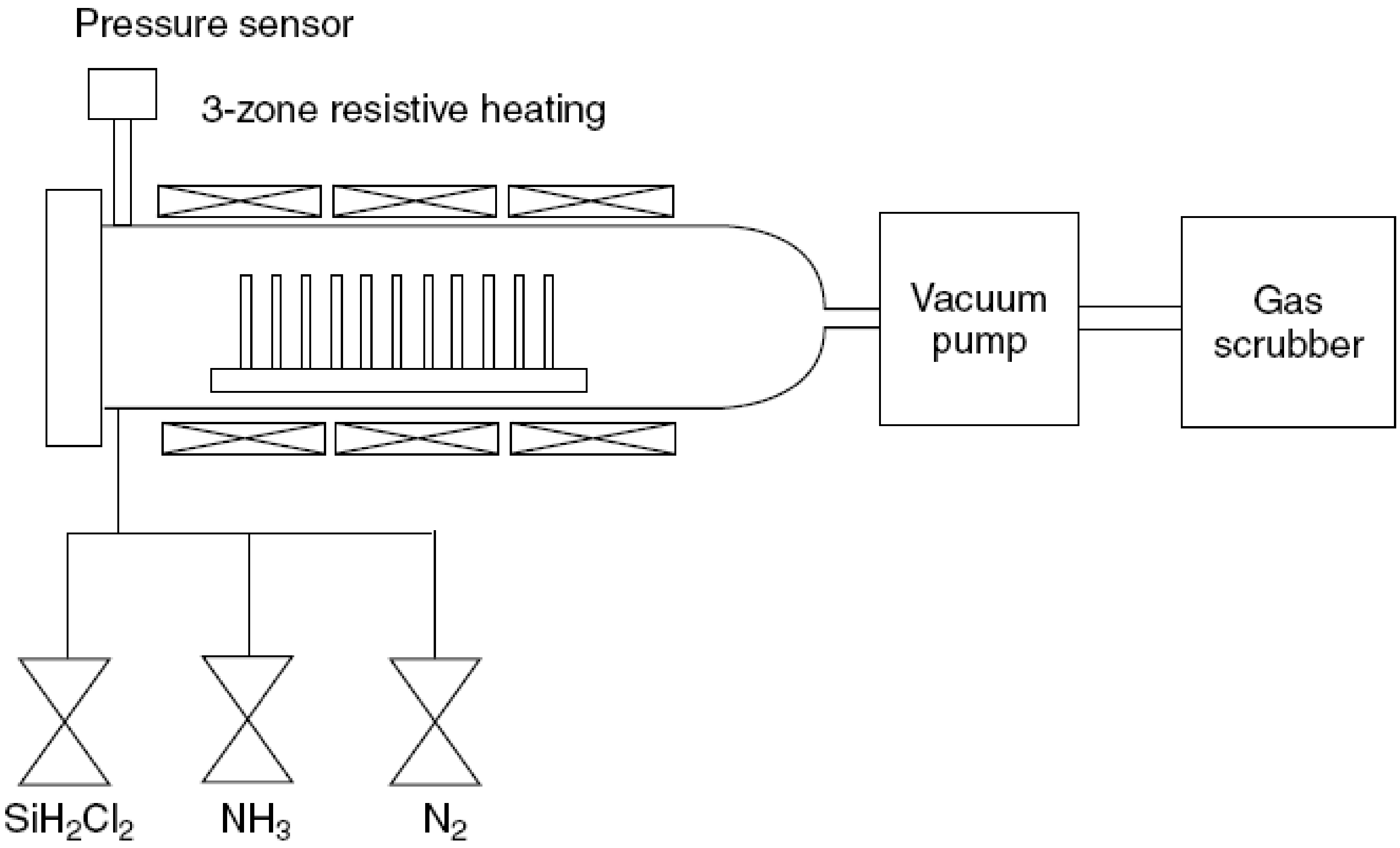


100% sticking may lead to deposition on top of a trench only

➔ Increase flow/dose

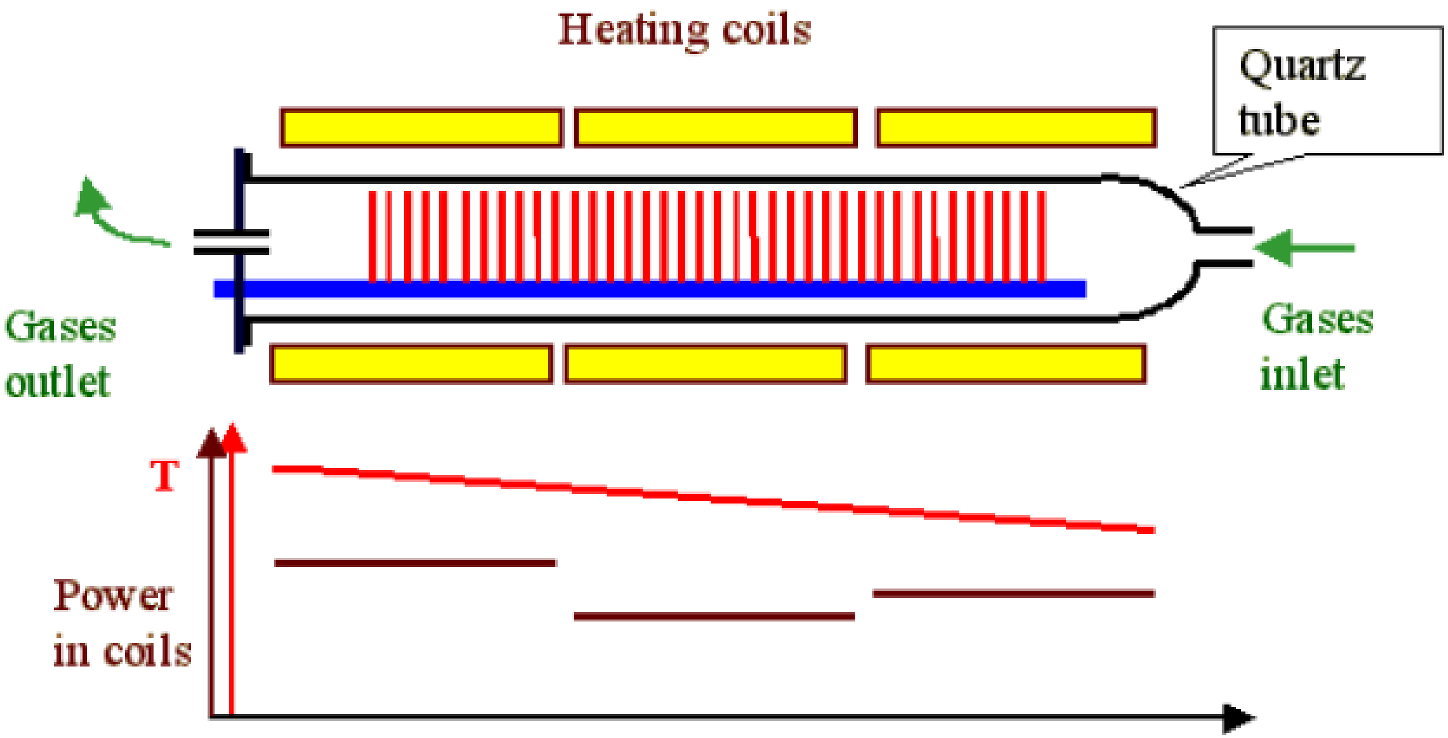
Low sticking coefficient will lead to more uniform film thickness on sidewall, but very poor step coverage.

Thermal CVD reactor: gaseous precursors, resistive heating



Franssila: Introduction to Microfabrication

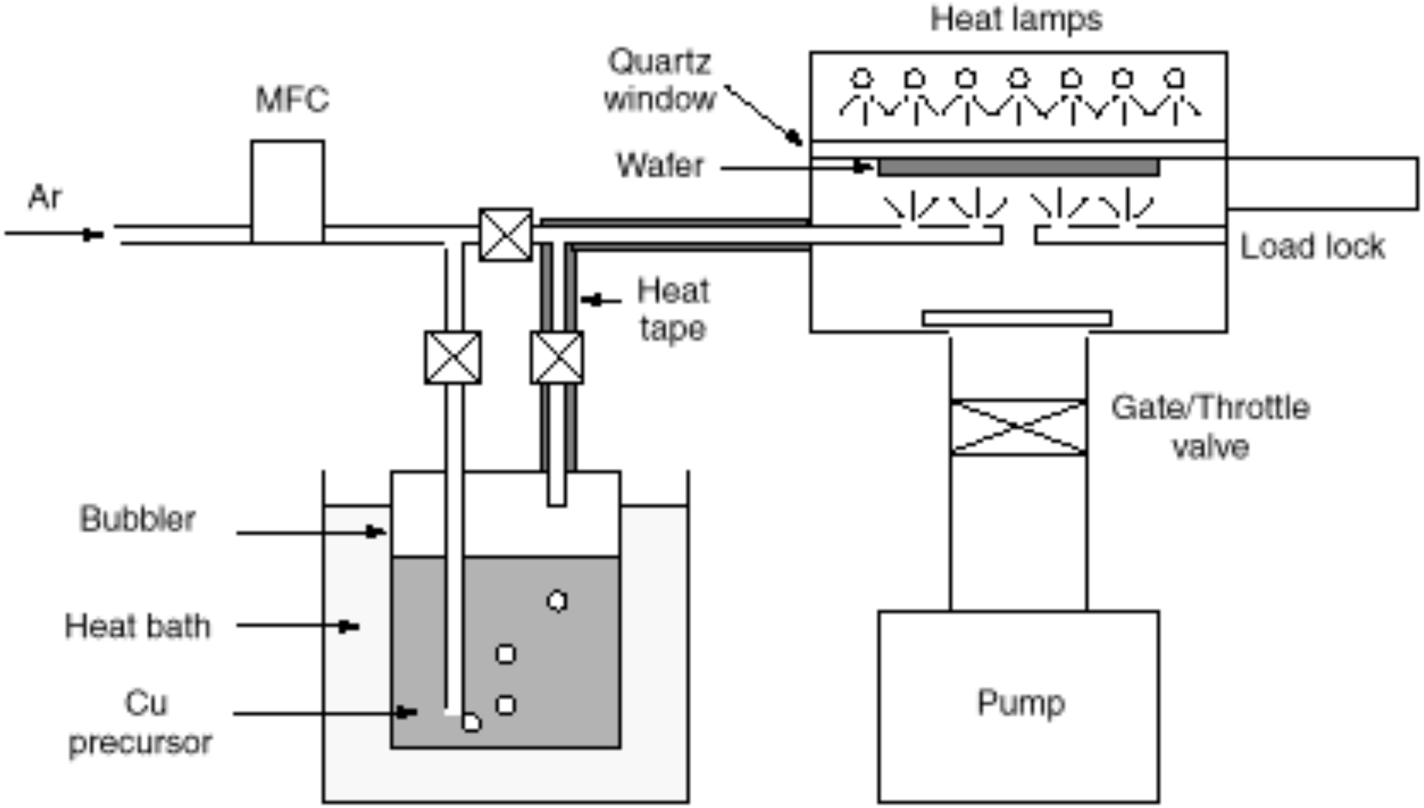
Ramped furnace



In the surface reaction limited regime
T is critical (+-1^{0}C). Ramping T compensates depletion.

Micronova cleanroom, CVD and thermal oxidation tubes

Thermal CVD reactor: liquid precursors, lamp heating



Changsup Ryu, PhD thesis, Stanford University, 1998

LRP= Limited Reaction Processing

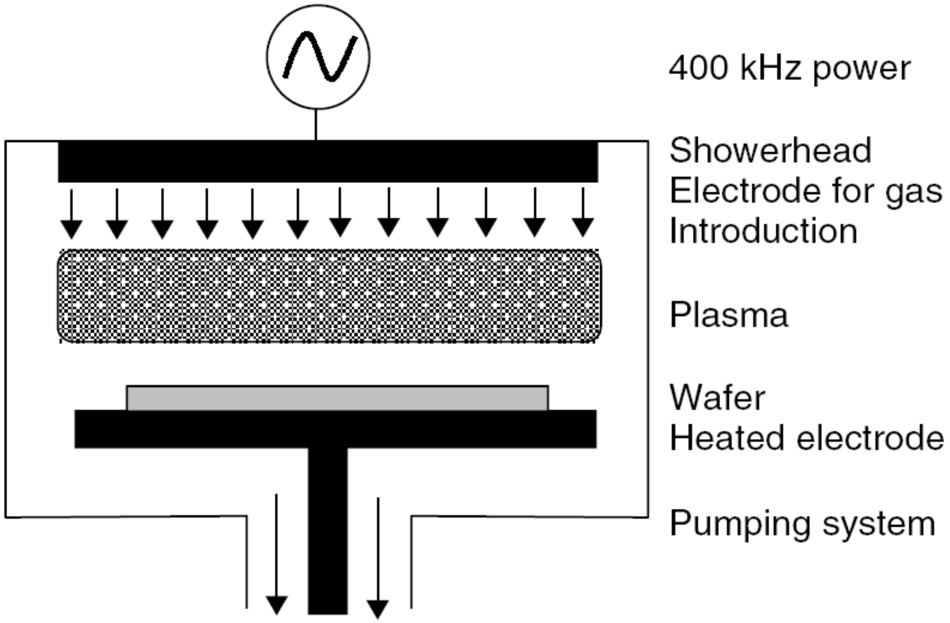
- Very fast and powerful lamp heating
- Introduce gases
- Flash the lamp ➔ T up ➔ reaction
- Pump away the gases
- Introduce new gases
- Flash the lamp ➔ T up ➔ reaction

...

PECVD: Plasma Enhanced CVD

- Plasma aids in chemical reactions
- Can be done at low temperatures
- Wide deposition parameter range
- High rates (1-10 nm/s) (thermal 10% of this)

PECVD @ 300°C: can be deposited on many materials



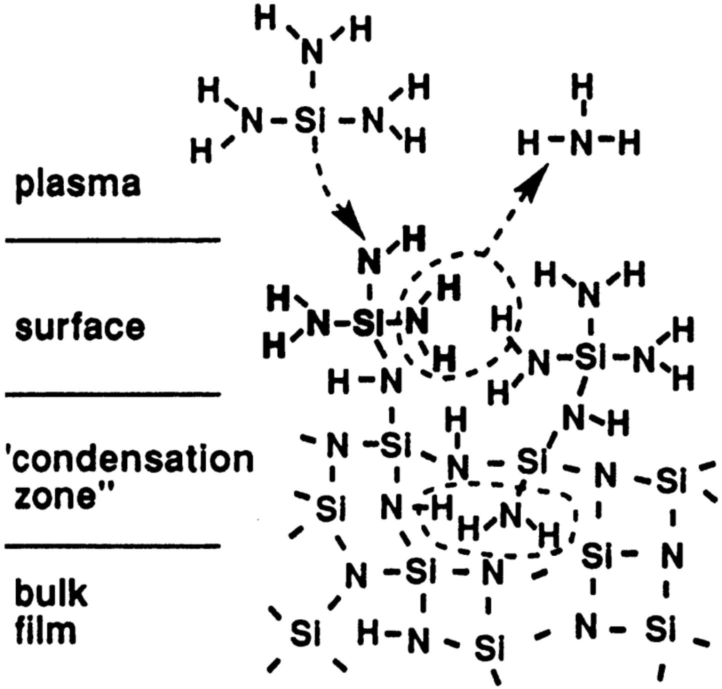
Oxide:

SiH_4 (g) + N_2O (g) ==> SiO_2 + N_2 + $2H_2$

Nitride:

3 SiH_2Cl_2 (g) + 4 NH_3 (g) ==> Si_3N_4 (s) + 6 H_2 (g) + 6 HCl (g)

SiN_x:H: thermal vs. plasma



Thermal CVD at 900°C

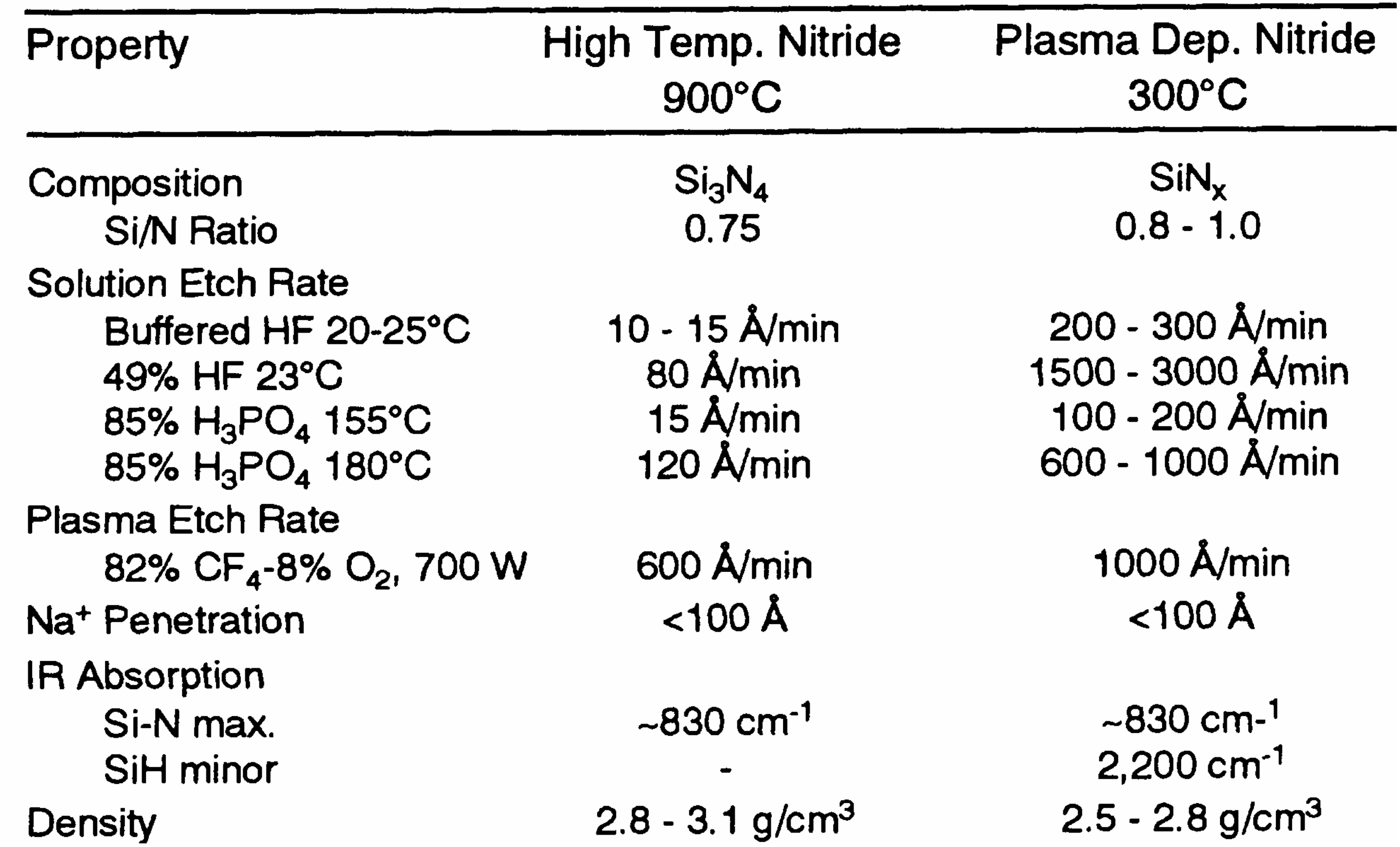
$$3\mathrm{Si(NH_2)_4} \xrightarrow{\text{heat}} \mathrm{Si_3N_4} + 8\mathrm{NH_3} \uparrow$$

PECVD at 300°C

$$\mathrm{SiH_4} + 4\mathrm{NH_3} \xrightarrow{\text{plasma}} \mathrm{Si(NH_2)_4} + 4\mathrm{H_2}$$

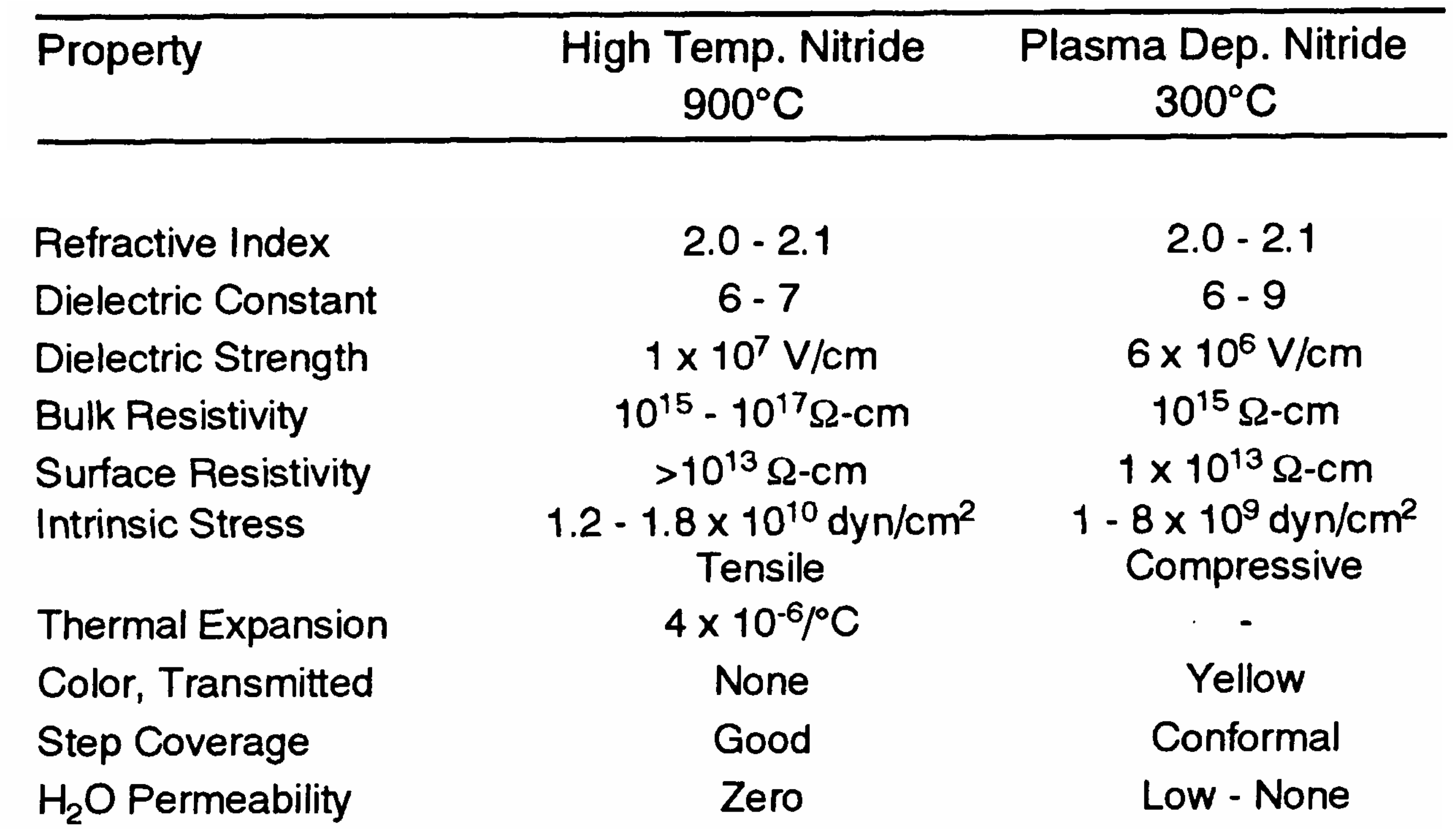
Smith: J.Electrochem.Soc. 137 (1990), p. 614

Nitride thermal vs. PECVD (1)



Property	High Temp. Nitride 900°C	Plasma Dep. Nitride 300°C
Composition	Si_3N_4	SiN_x
Si/N Ratio	0.75	0.8 - 1.0
Solution Etch Rate		
Buffered HF 20-25°C	10 - 15 Å/min	200 - 300 Å/min
49% HF 23°C	80 Å/min	1500 - 3000 Å/min
85% H_3PO_4 155°C	15 Å/min	100 - 200 Å/min
85% H_3PO_4 180°C	120 Å/min	600 - 1000 Å/min
Plasma Etch Rate		
82% CF_4-8% O_2, 700 W	600 Å/min	1000 Å/min
Na^+ Penetration	<100 Å	<100 Å
IR Absorption		
Si-N max.	~830 cm^{-1}	~830 cm-^{1}
SiH minor	-	2,200 cm^{-1}
Density	2.8 - 3.1 g/cm^3	2.5 - 2.8 g/cm^3

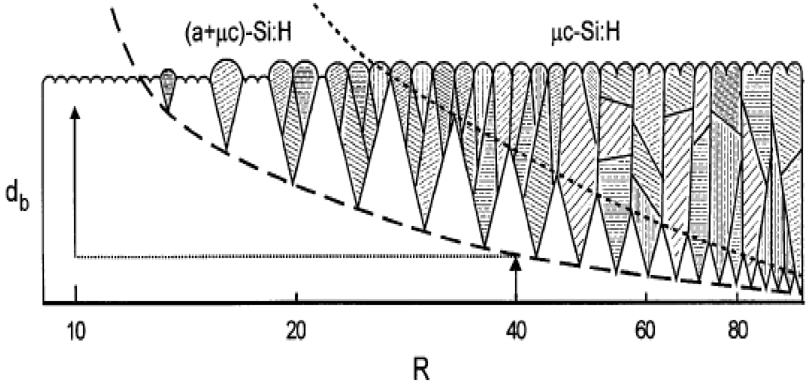
Nitride thermal vs. PECVD (2)



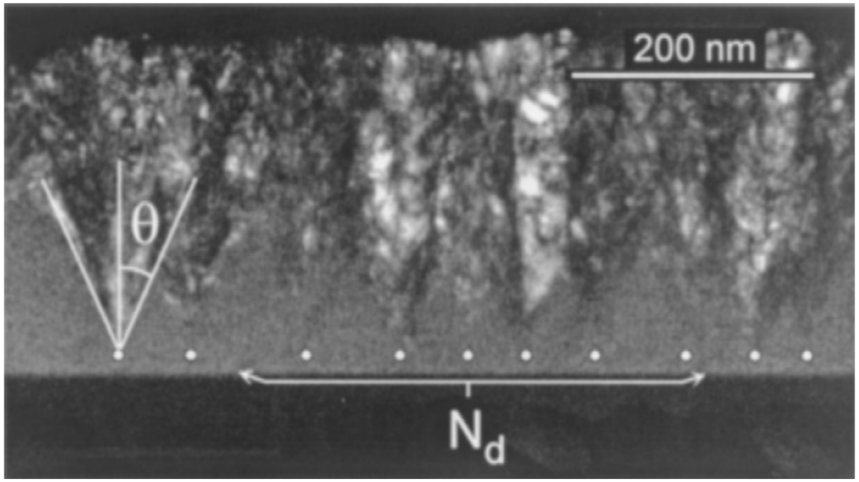
Property	High Temp. Nitride 900°C	Plasma Dep. Nitride 300°C
Refractive Index	2.0 - 2.1	2.0 - 2.1
Dielectric Constant	6 - 7	6 - 9
Dielectric Strength	1×10^7 V/cm	6×10^6 V/cm
Bulk Resistivity	$10^{15} - 10^{17}\Omega$-cm	$10^{15}\ \Omega$-cm
Surface Resistivity	$>10^{13}\ \Omega$-cm	$1 \times 10^{13}\ \Omega$-cm
Intrinsic Stress	$1.2 - 1.8 \times 10^{10}$ dyn/cm^2 Tensile	$1 - 8 \times 10^9$ dyn/cm^2 Compressive
Thermal Expansion	4×10^{-6}/°C	-
Color, Transmitted	None	Yellow
Step Coverage	Good	Conformal
H_2O Permeability	Zero	Low - None

Amorphous to microcrystalline (PECVD)

SiH_4 (g) + n H_2 (g) ➔ a-Si:H + xH_2 (g)

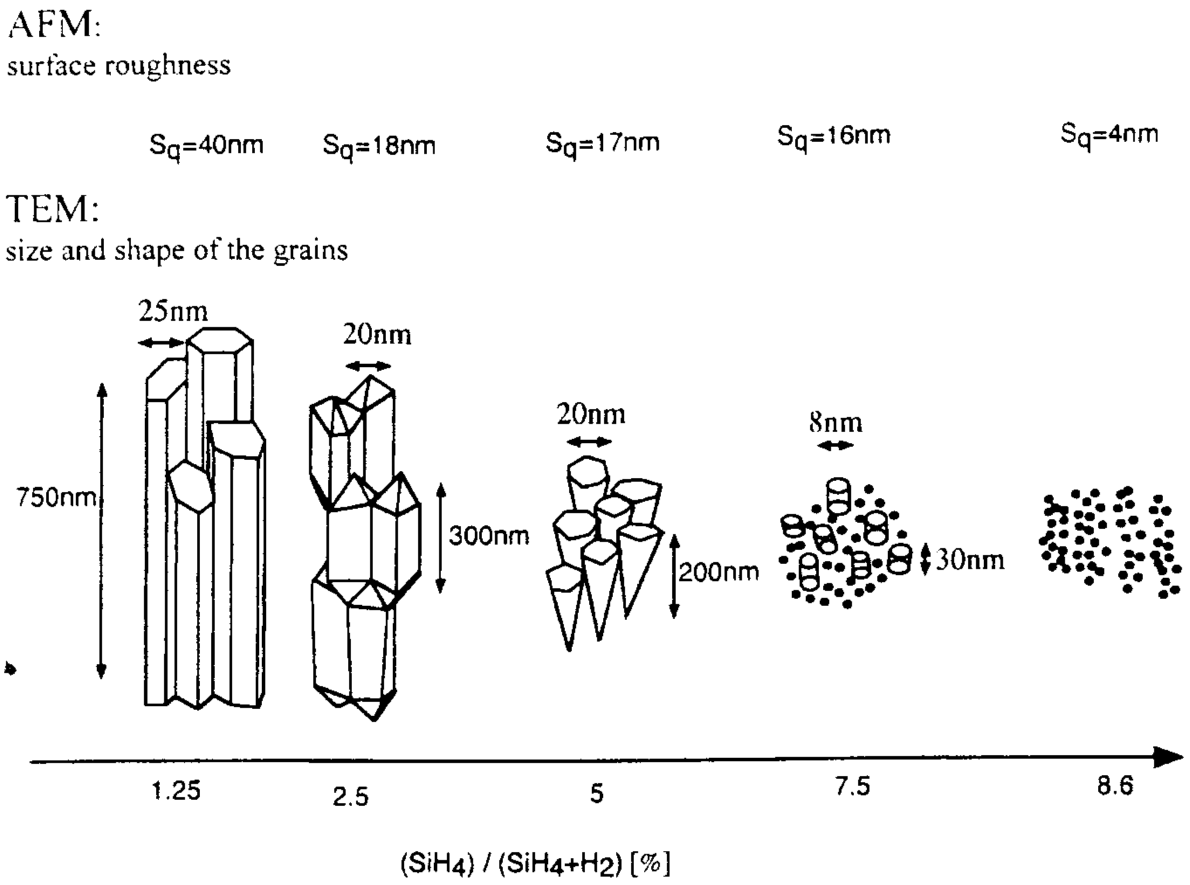


H_2-dilution ratio, R



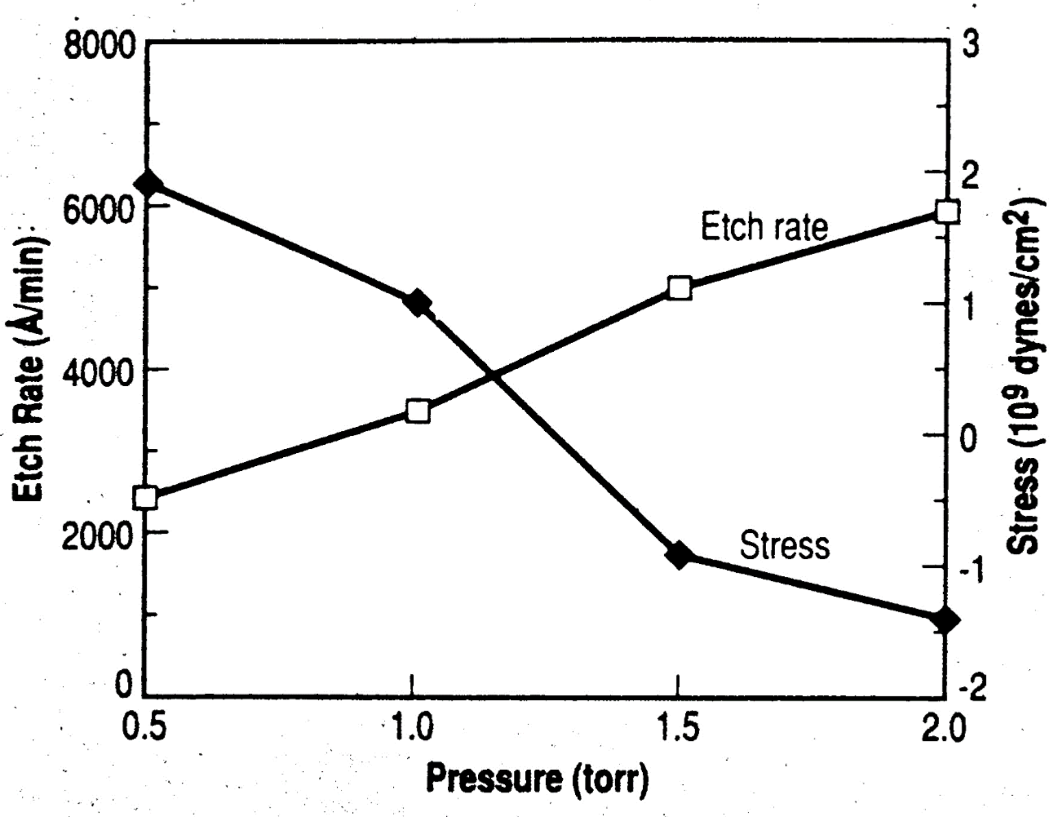
R.W. Collins et al. / Solar Energy Materials & Solar Cells 78 (2003) 143–180

Grain size & roughness



Vallat-Sauvain

Film quality: etch rate

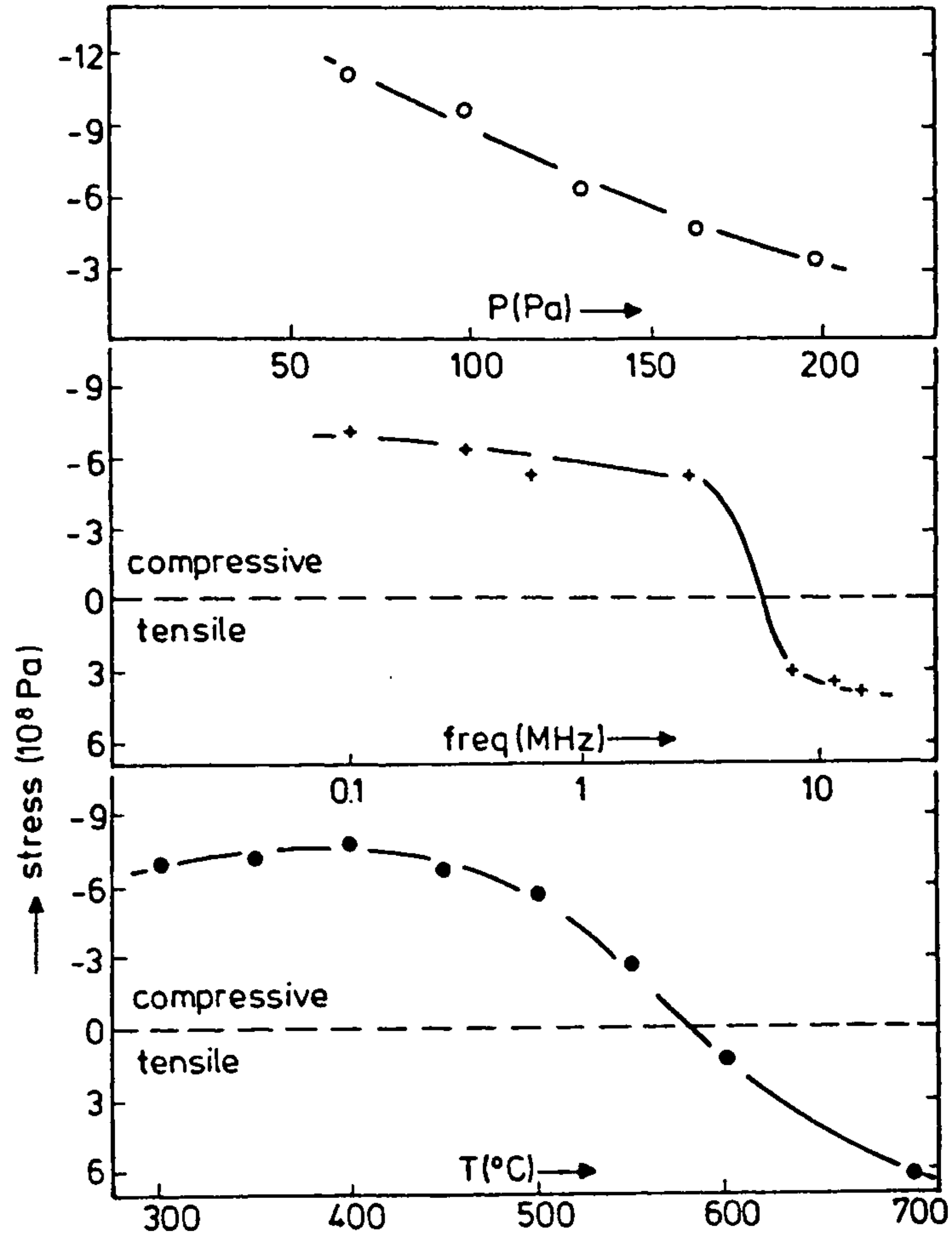


Low pressure equals more bombardment, and thus denser film, and compressive stress

With SiO_2, BHF etch rate is a film quality measure

(should be no more than 2X thermal oxide reference)

Hey et al: Solid State Technology April 1990, p. 139



Stress affects by:

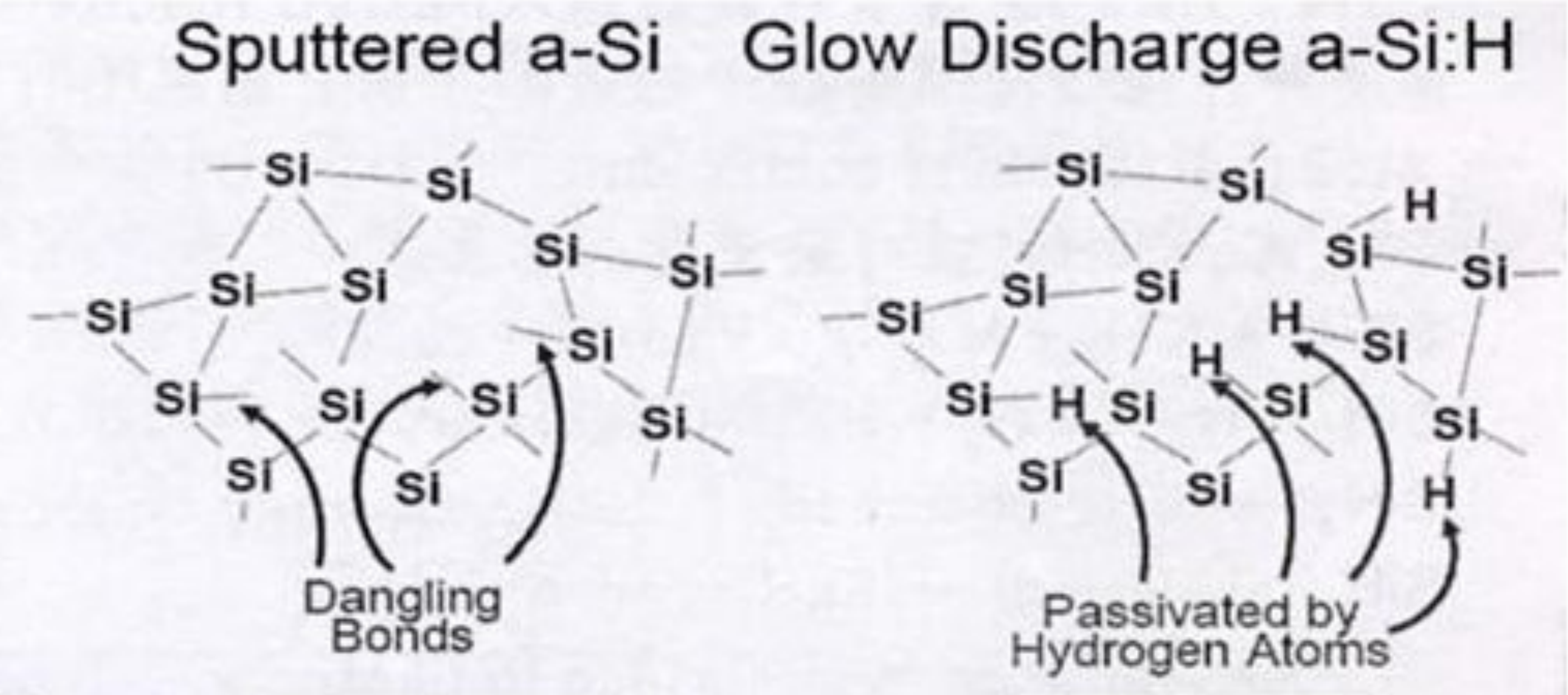
pressure

frequency

temperature

Hey et al: Solid State Technology April 1990, p. 139

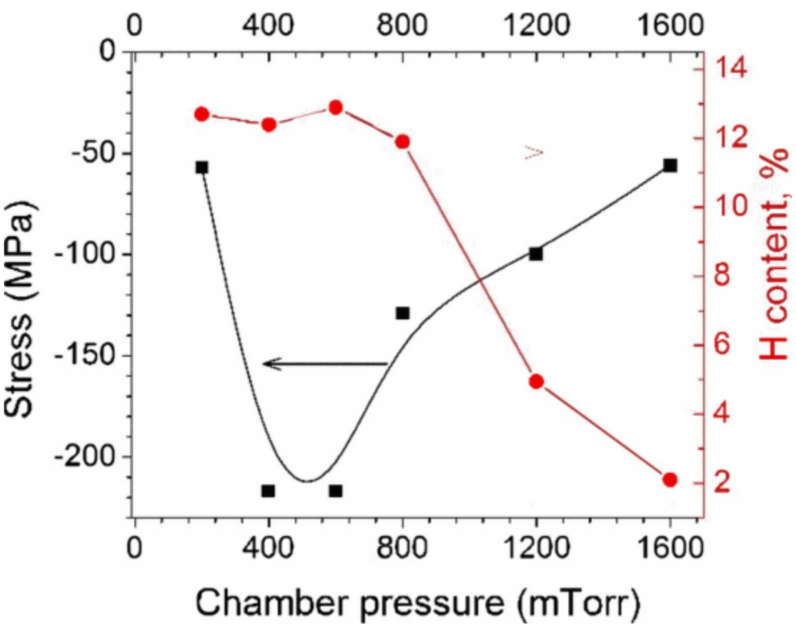
Hydrogen-passivation: good !

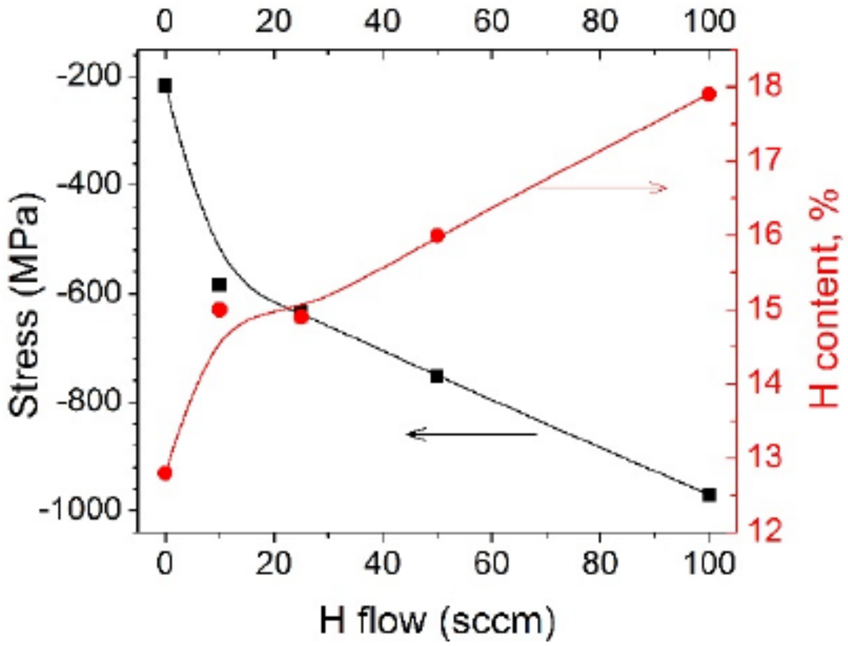


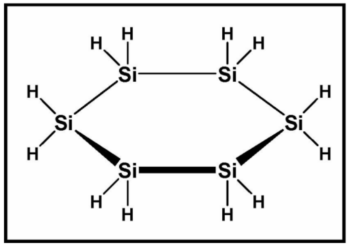
Only silicon (and traces of argon)

CVD and PECVD films have always hydrogen

Hydrogen in PECVD film







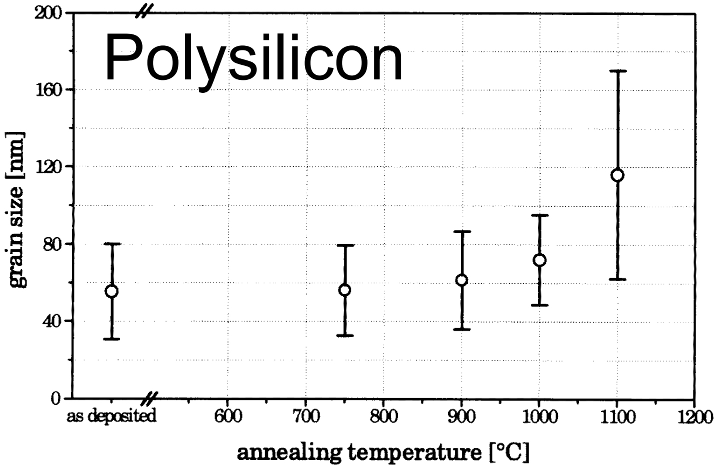
PECVD
at 200°C

10-30 at% hydrogen is usual;

3-5% is as small as it gets

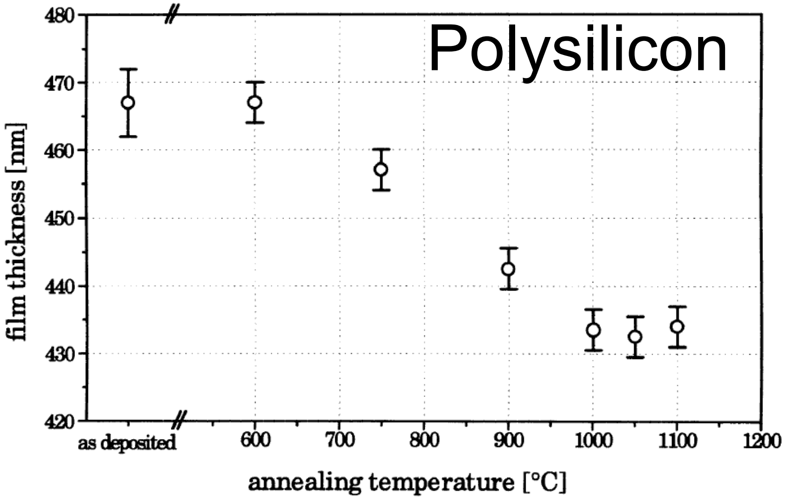
Study of intrinsic stress in hydrogenated amorphous silicon PECVD films with cyclohexasilane (CHS) as a precursor,
DOI: 10.1109/PVSC.2014.6925582

Annealing effects



Grain size increases

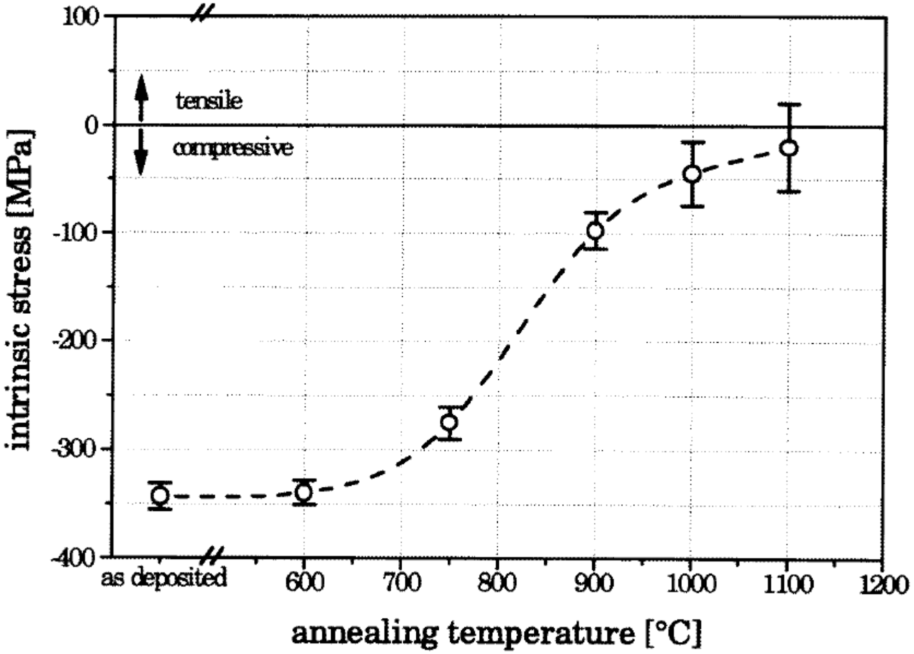
Thickness decreases



6% reduction

Maier-Schneider: J. Micromech. Microeng. **6** (1996) 436–446.

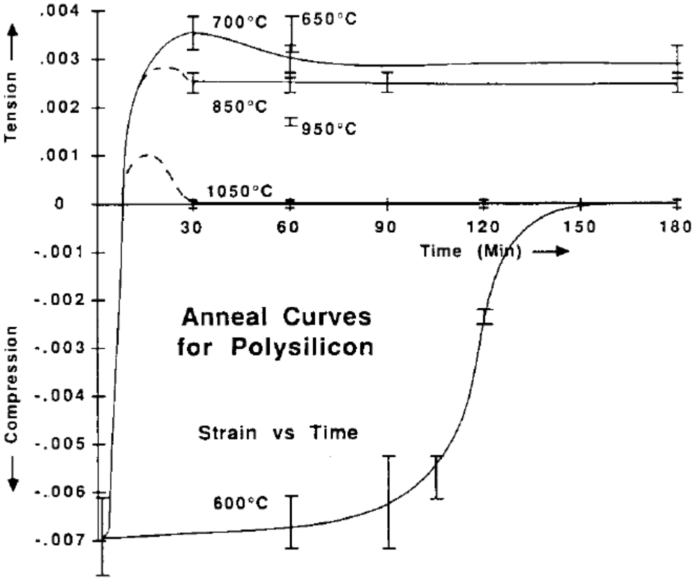
Annealing effects (2)



Stress modified

Maier-Schneider: J. Micromech. Microeng. **6** (1996) 436–446.

Stress might change from compressive to tensile !



Guckel et al: IEEE TRANSACTIONS ON ELECTRON DEVICES. VOL. **35.** NO. ***6,*** JUNE 1988