Aalto University
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CVD & ALD

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CVD & ALD

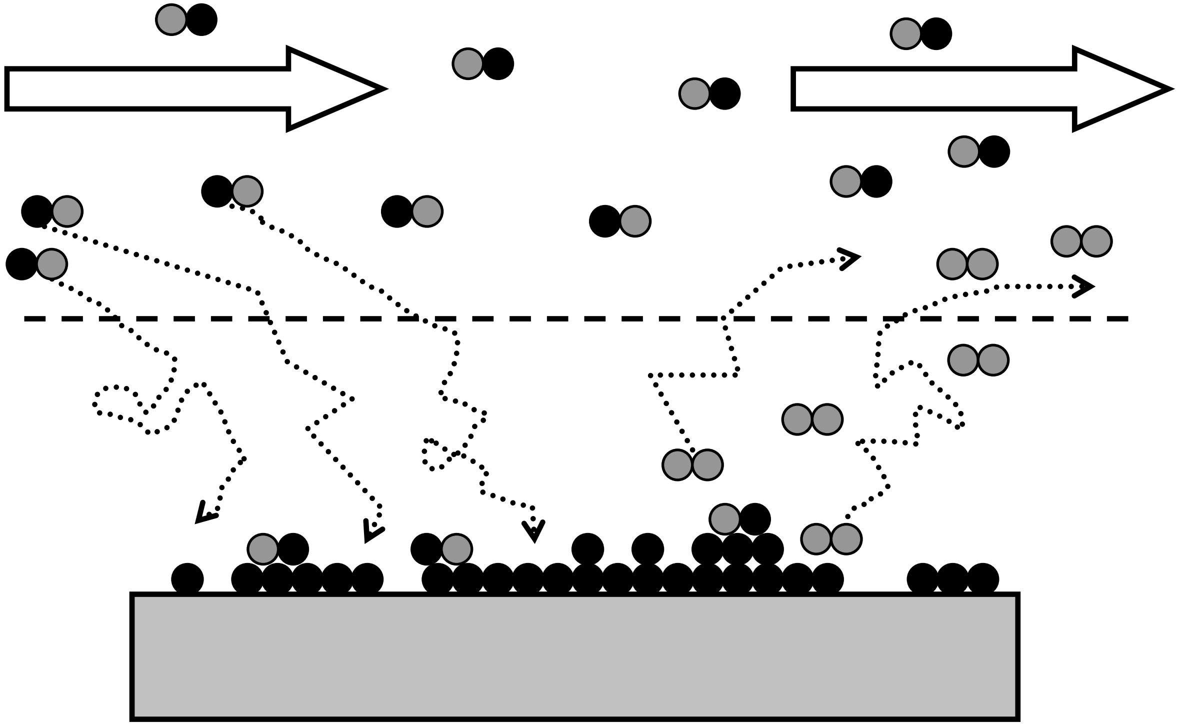
Chemical Vapor Deposition, CVD
Atomic Layer Deposition, ALD

Alternatives to PVD, but only partially.

Major uses:

-optical fiber fabrication
-films in microelectronics & MEMS
-optical coatings
-solar cells
-a-Si and poly-Si for flat panel displays

CVD schematically



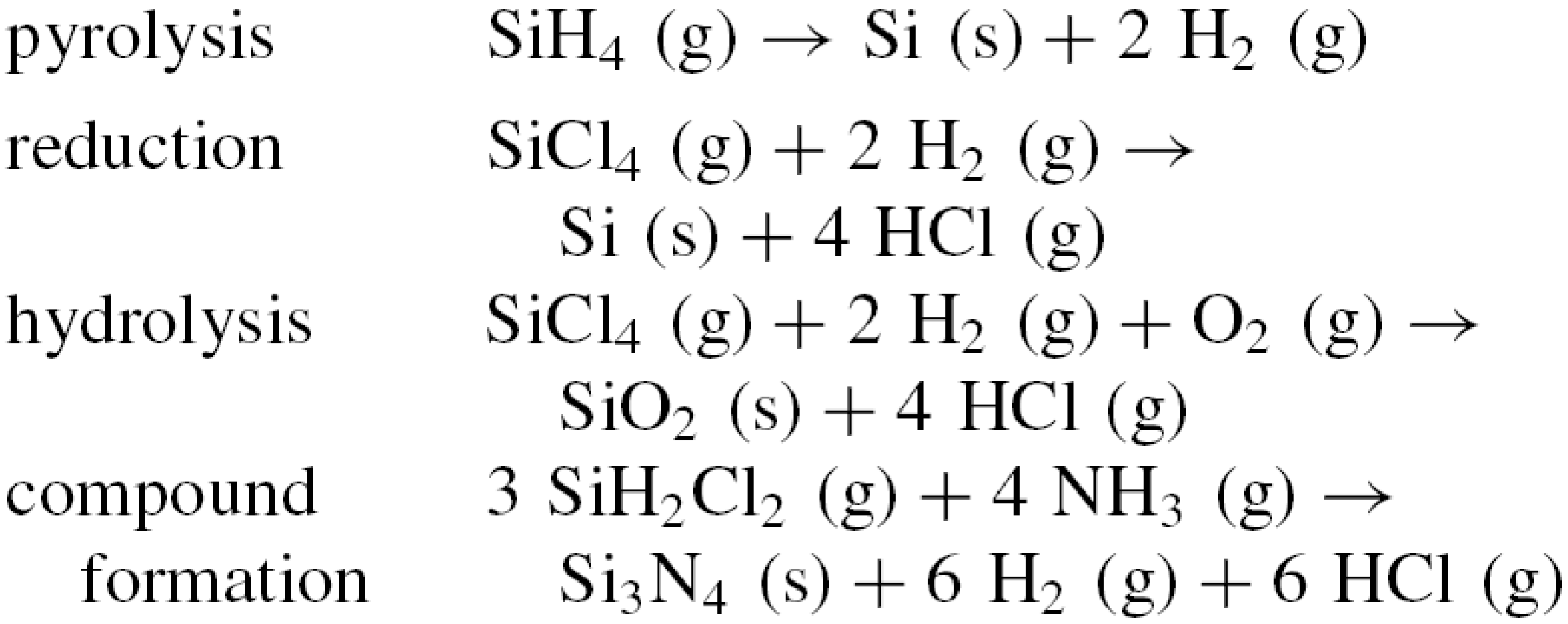
Gas phase convection

Diffusion through boundary layer

Surface processes:
- adsorption
- surface reaction
- byproduct desorption

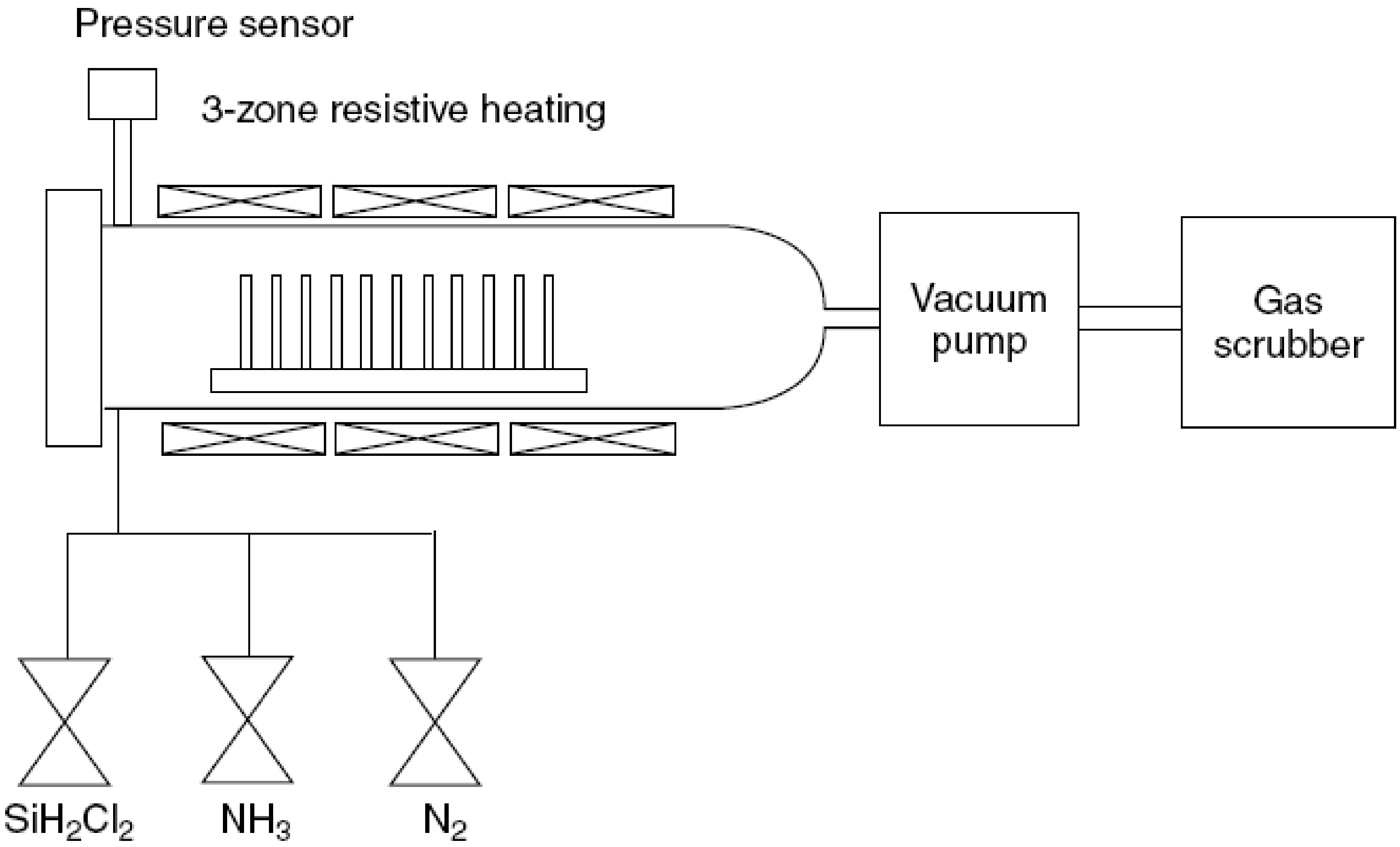
Thermal CVD reactions

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	$3\ SiH_2Cl_2\ (g) + 4\ NH_3\ (g) \rightarrow$ $Si_3N_4\ (s) + 6\ H_2\ (g) + 6\ HCl\ (g)$

Thermal CVD reactor: gaseous precursors, resistive heating



Franssila: Introduction to Microfabrication

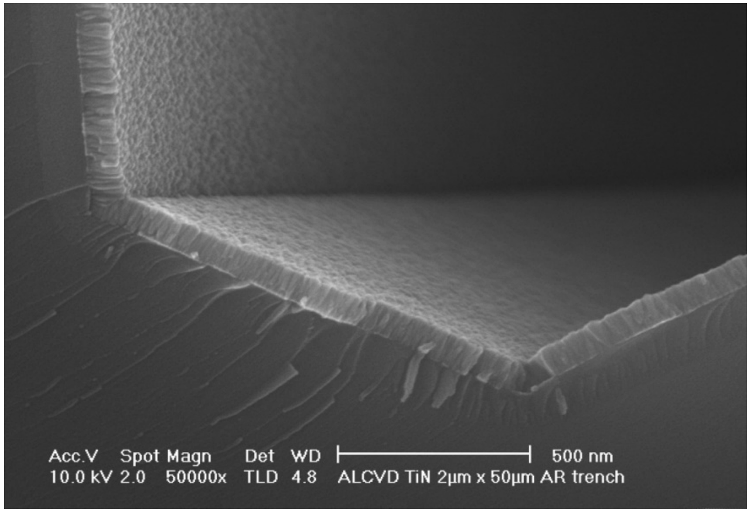

centrotherm

Surface controlled reaction

Slow reaction rate (e.g. due to low temperature). Lots of gas available, and only a fraction of it has chance to react.

Because all surfaces are at same temperature, same deposition rate everywhere. Because surface controlled ➔ good step coverage.

ALD is a prime surface controlled reaction, excellent conformality.



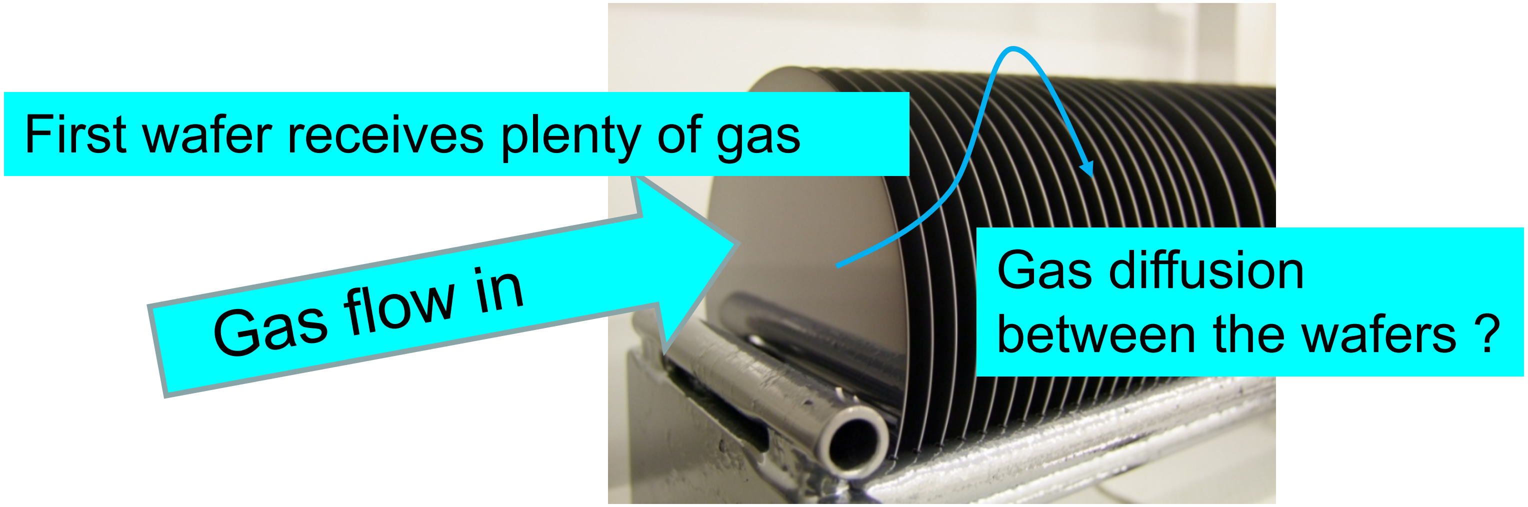
ALD TiN at the bottom of high aspect ratio groove.

Mass transport limited reaction

Reaction rate is very fast at high temperatures
(Arrhenius: rate is exponentially temperature-dependent).

All arriving gases react immediately ➔ need to ensure that gases arrive equally to all parts of reactor. If not, position dependent depo rate.

Reaction is in mass transport limited mode.

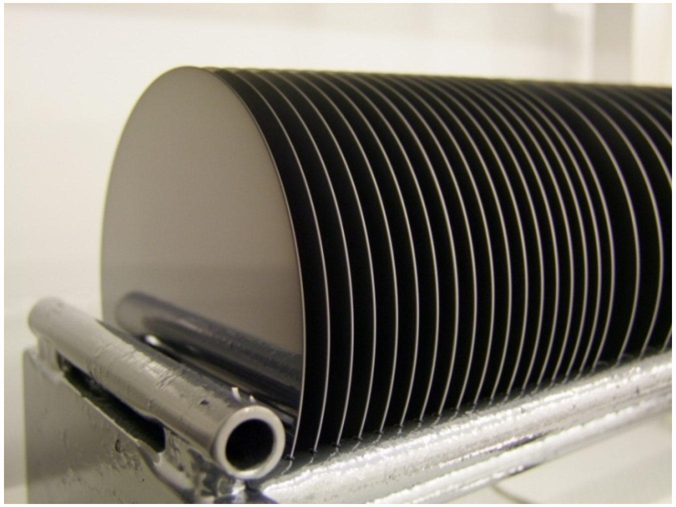


First wafer receives plenty of gas

Gas flow in

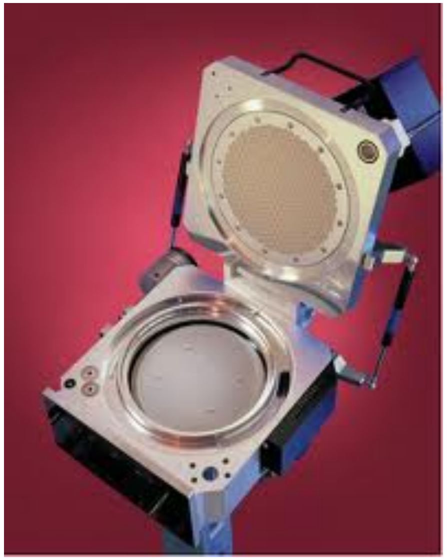
Gas diffusion between the wafers ?

Surface limited vs. mass transport limited reactions



Surface reaction limited mode:

- -slow reaction rate
- -time for gases to diffuse
- -always extra gas available
- -can pack wafers tightly



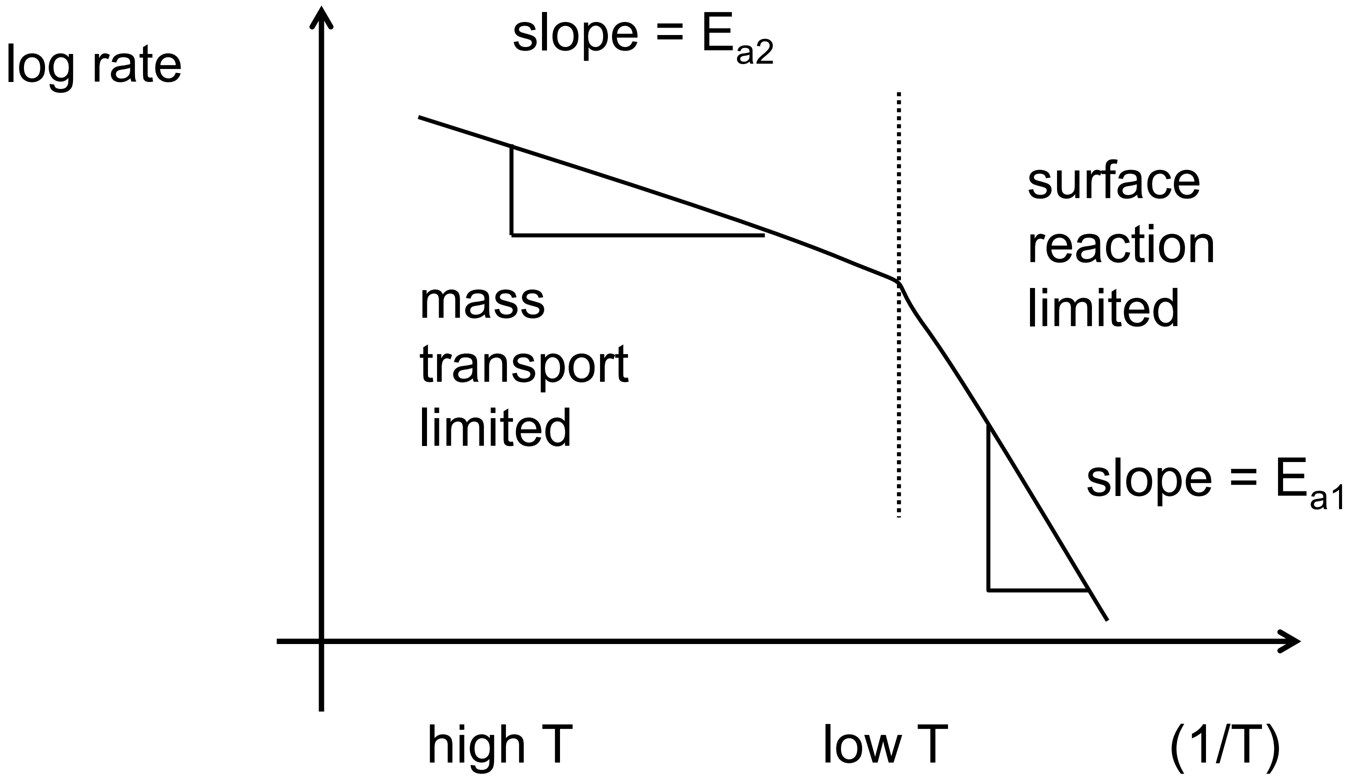
A mass transport limited reactor:

-all arriving gases react at once

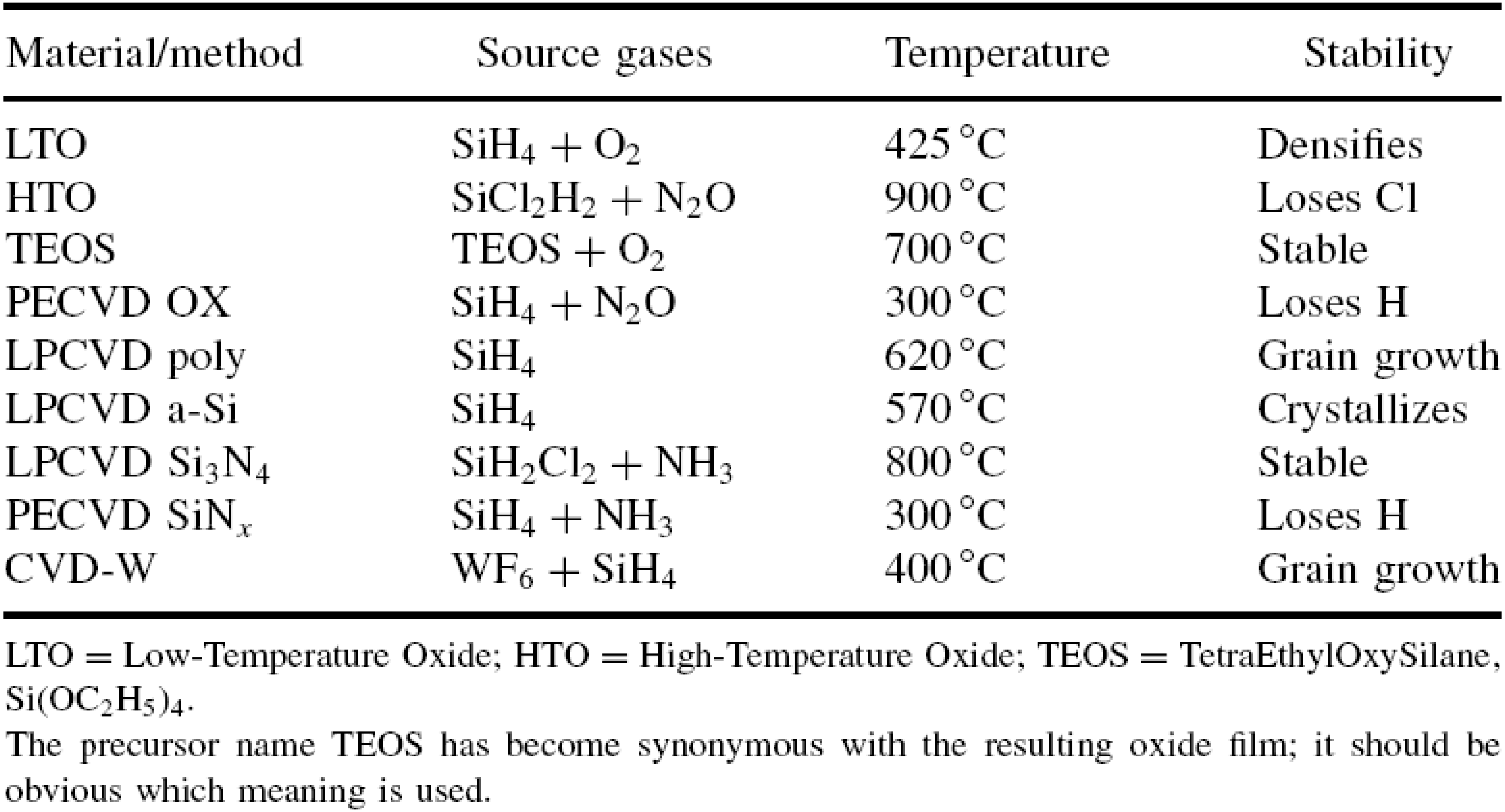
-therefore all wafers need to experience the same gas flow

-easier to design uniform flow for single wafer reactors

Surface limited vs. mass transport limited reactions



Common CVD reactions

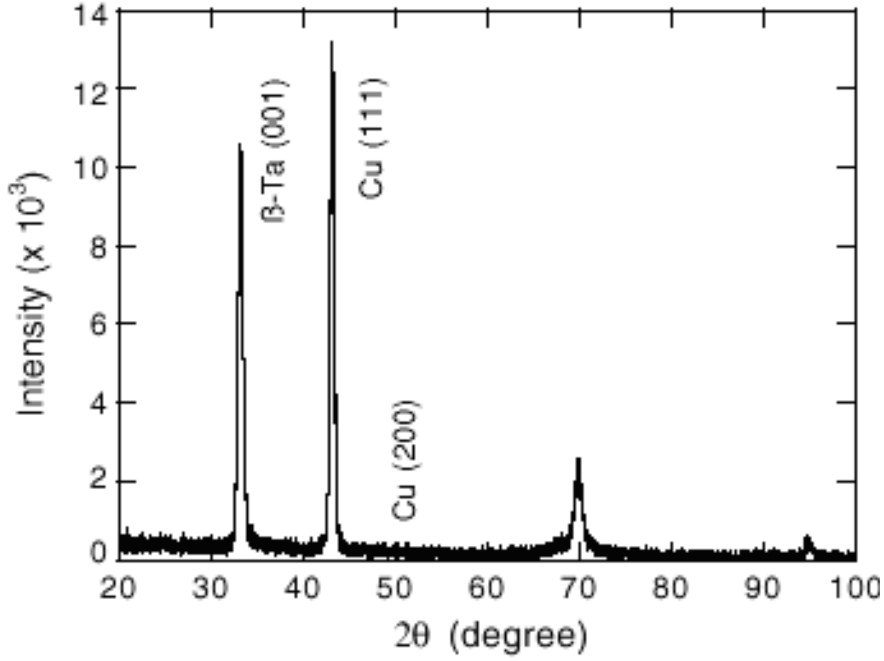


Material/method	Source gases	Temperature	Stability
LTO	$SiH_4 + O_2$	425 °C	Densifies
HTO	$SiCl_2H_2 + N_2O$	900 °C	Loses Cl
TEOS	$TEOS + O_2$	700 °C	Stable
PECVD OX	$SiH_4 + N_2O$	300 °C	Loses H
LPCVD poly	SiH_4	620 °C	Grain growth
LPCVD a-Si	SiH_4	570 °C	Crystallizes
LPCVD Si_3N_4	$SiH_2Cl_2 + NH_3$	800 °C	Stable
PECVD SiN_x	$SiH_4 + NH_3$	300 °C	Loses H
CVD-W	$WF_6 + SiH_4$	400 °C	Grain growth

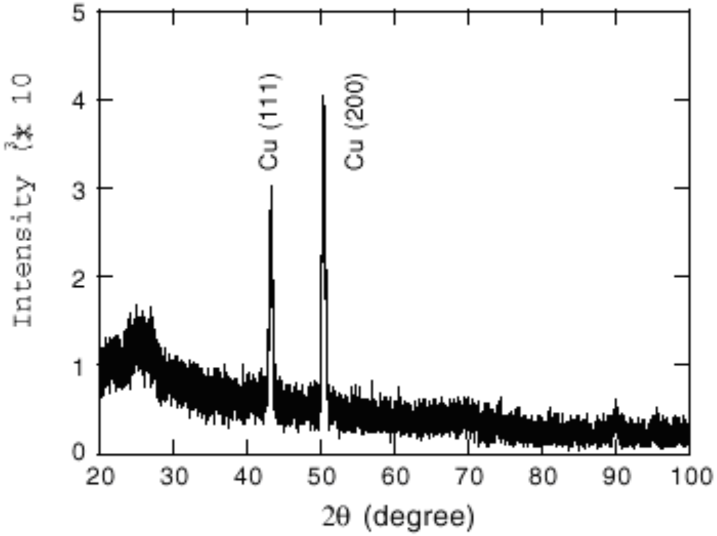
LTO = Low-Temperature Oxide; HTO = High-Temperature Oxide; TEOS = TetraEthylOxySilane, $Si(OC_2H_5)_4$.

The precursor name TEOS has become synonymous with the resulting oxide film; it should be obvious which meaning is used.

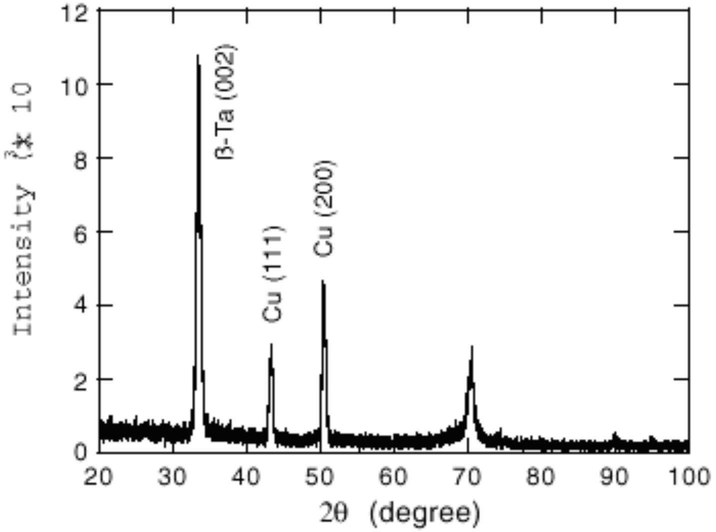
Copper: sputter vs. CVD



(a)



(b)

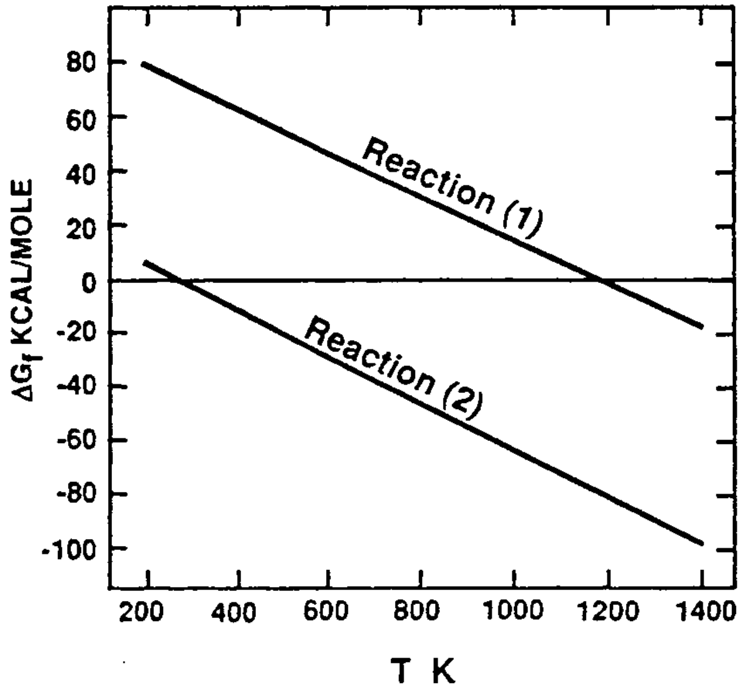


Sputtered Cu 0.5 μm on Ta (up)

CVD Cu 0.5 μm on Ta (bottom right)

CVD Cu 0.5 μm on TiN (top right)

Thermodynamics of CVD



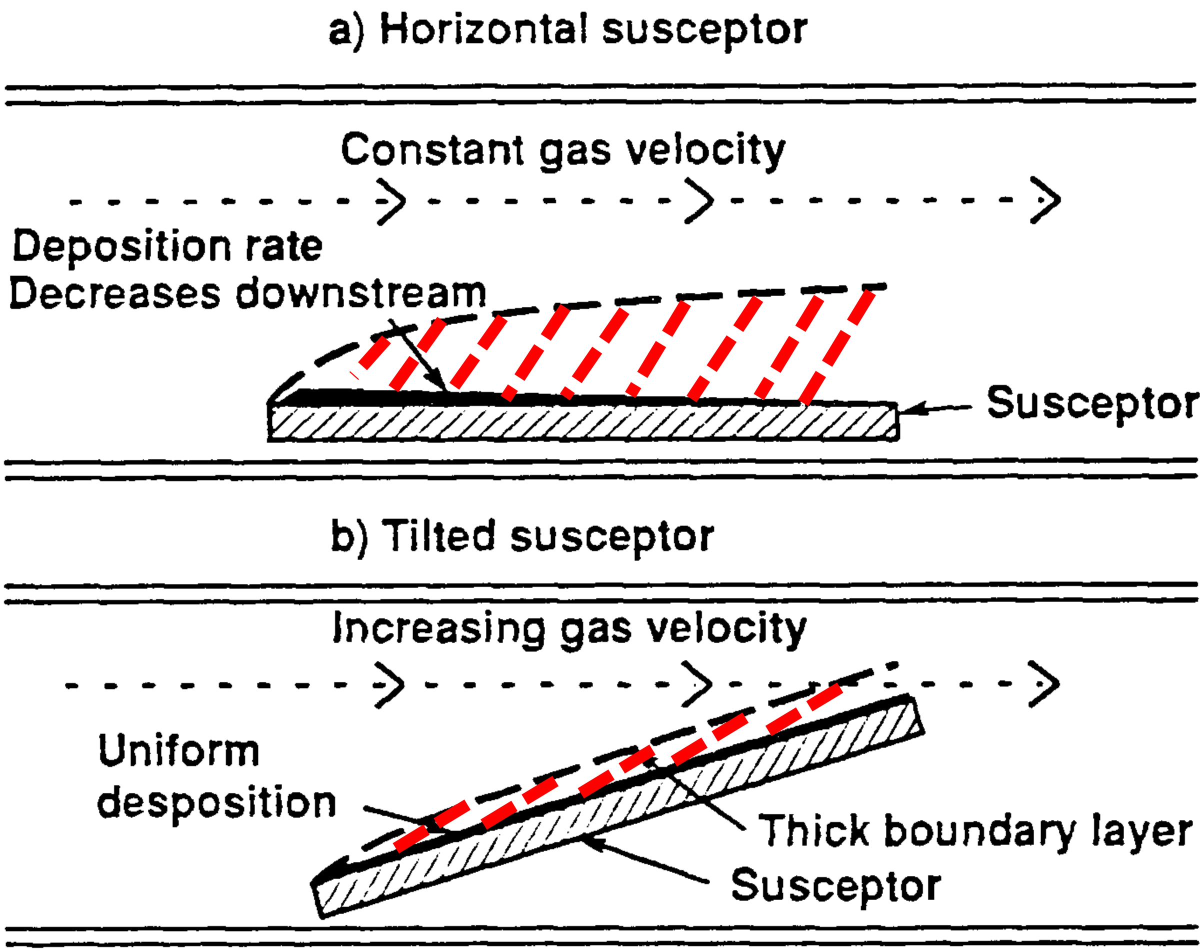
ΔG < 0 for reaction to take place

(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

Boundary layer
= stagnant gas layer



Pierson: Handbook of
CVD, p. 36

Rate modeling

$$J_{gas-to-surface} = -\frac{D}{\delta} C_{gas}$$

Diffusion of precursor gas from main flow to the surface.

$$\delta = \sqrt{\frac{\eta L}{v\rho}}$$

Boundary layer thickness δ.

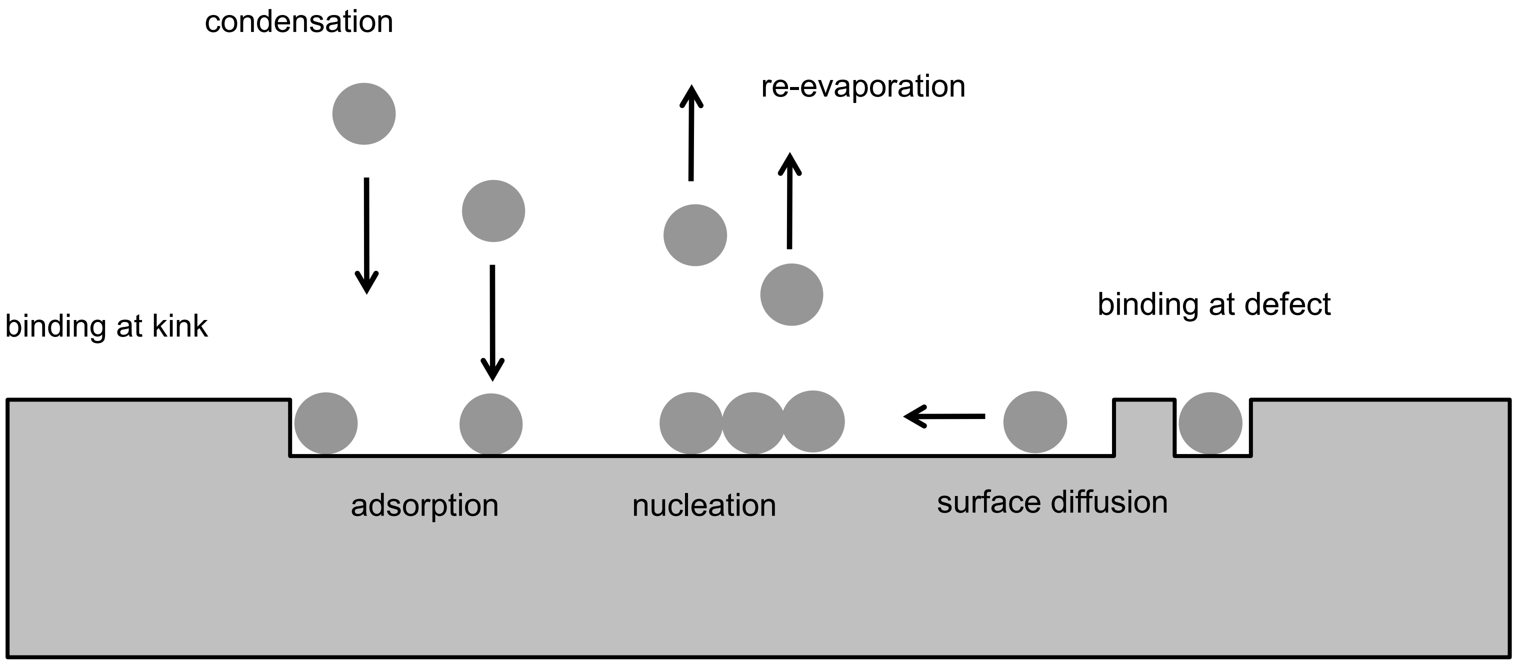
Raising temperature ➔ density slightly increases and velocity increases

$$D \propto \frac{T^{\frac{3}{2}}}{P}$$

But lowering pressure, e.g. by 1000X
➔Diffusivity D increases 1000-fold.

➔$J_{gas\text{-}to\text{-}surface}$ increases dramatically

Surface processes in deposition



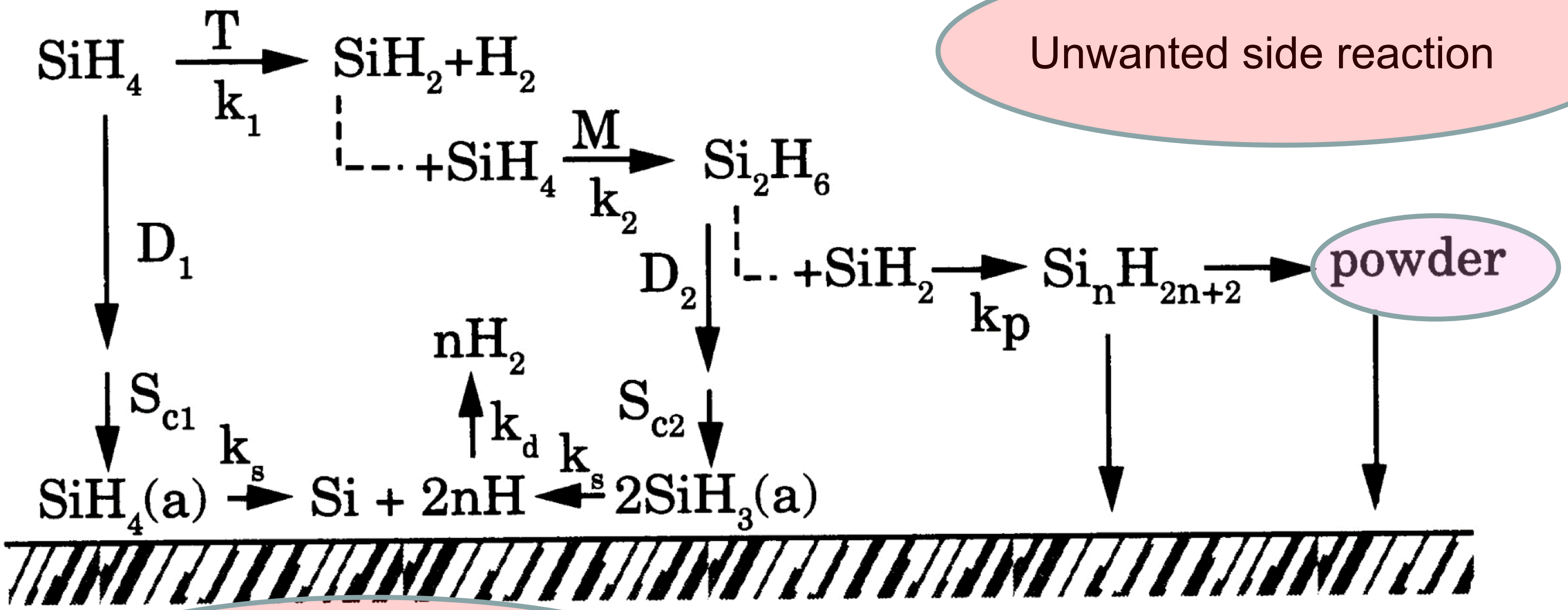
Adsorption processes

- SiH_4 (g) ➔ SiH_4 (ad) ➔ Si (c) + 2 H_2 (g)
- usual process: molecular adsorption

- Zn (g) + Se (a) ➔ ZnSe (c)
- separate vapors adsorb strongly to the other specie

- passivation protects surface from reaction
- hydrogen typical passivation agent

Silicon CVD from SiH_4



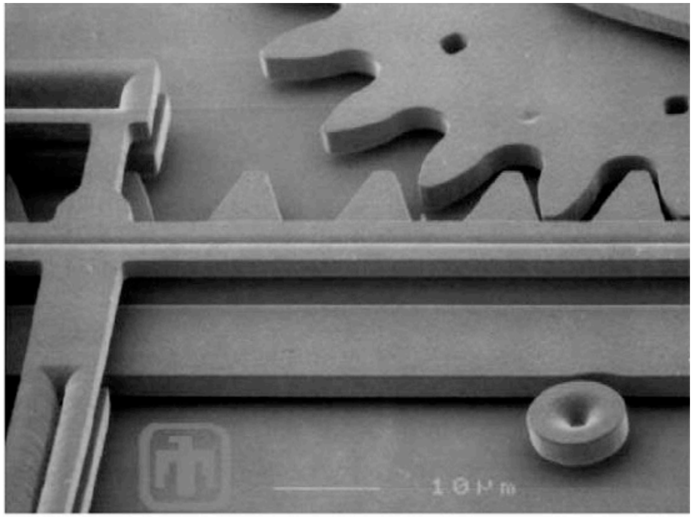
Unwanted side reaction

Wanted deposition reaction

Smith: Thin-film deposition

Polysilicon

- SiH_4 (g) ==> Si (s) + 2 H_2 (g)
- Deposited by CVD at 625^{o}C ➔ true poly
- Can be deposited at 575^{o}C ➔ amorphous
- Anneal after deposition: a-Si ➔ poly !
- Typical thickness 100 nm-2 µm



Structure and Properties of LPCVD Silicon Films

T. I. Kamins*

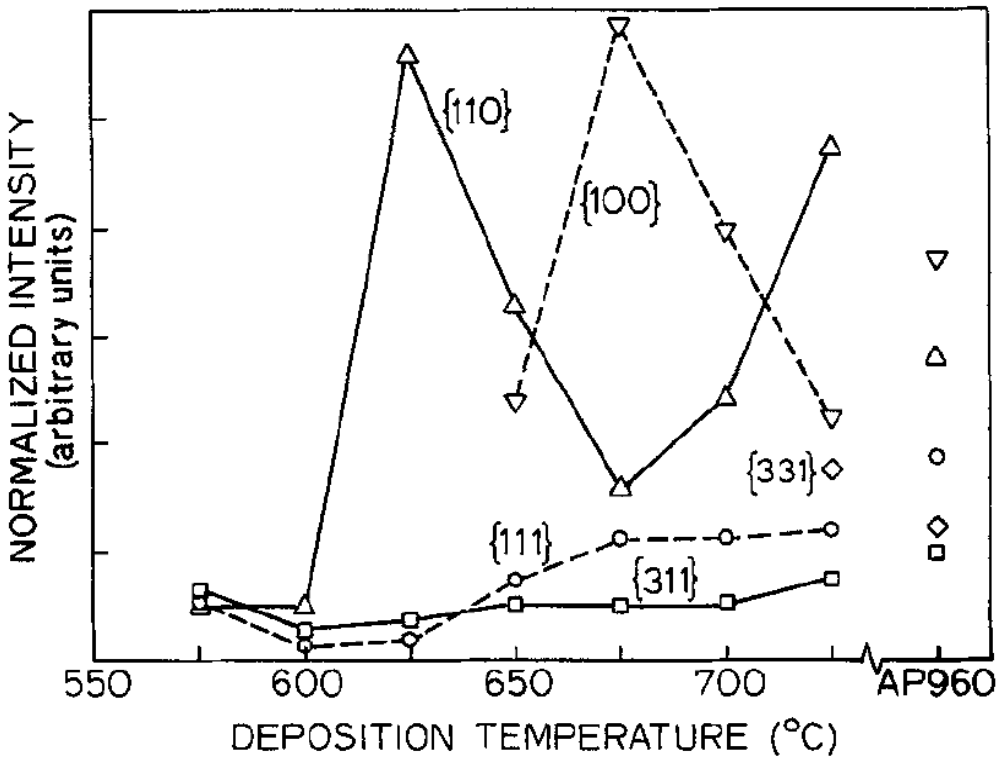


Fig. 1. X-ray texture as a function of deposition temperature for LPCVD silicon films and for an atmospheric pressure film.

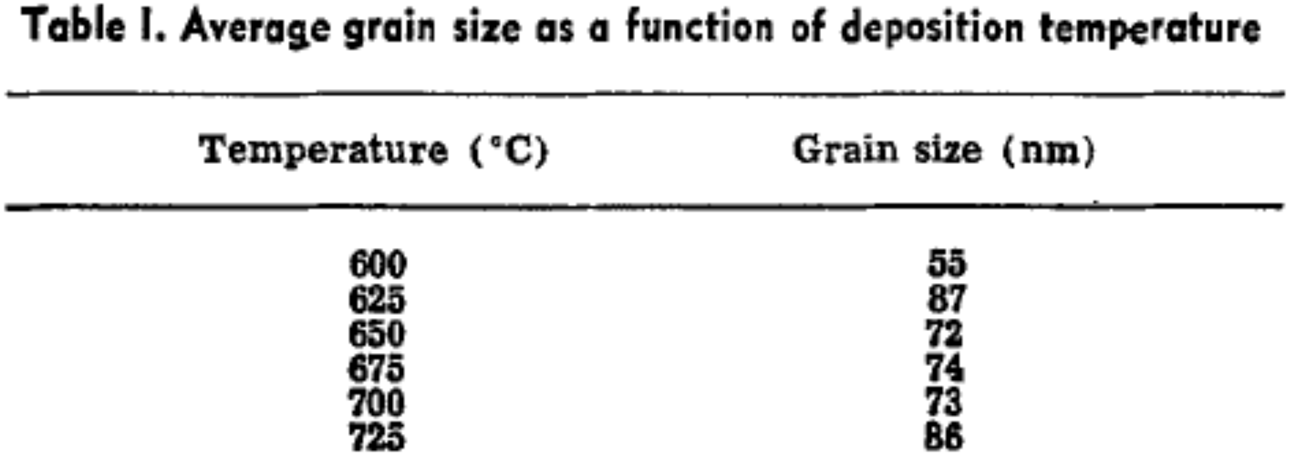
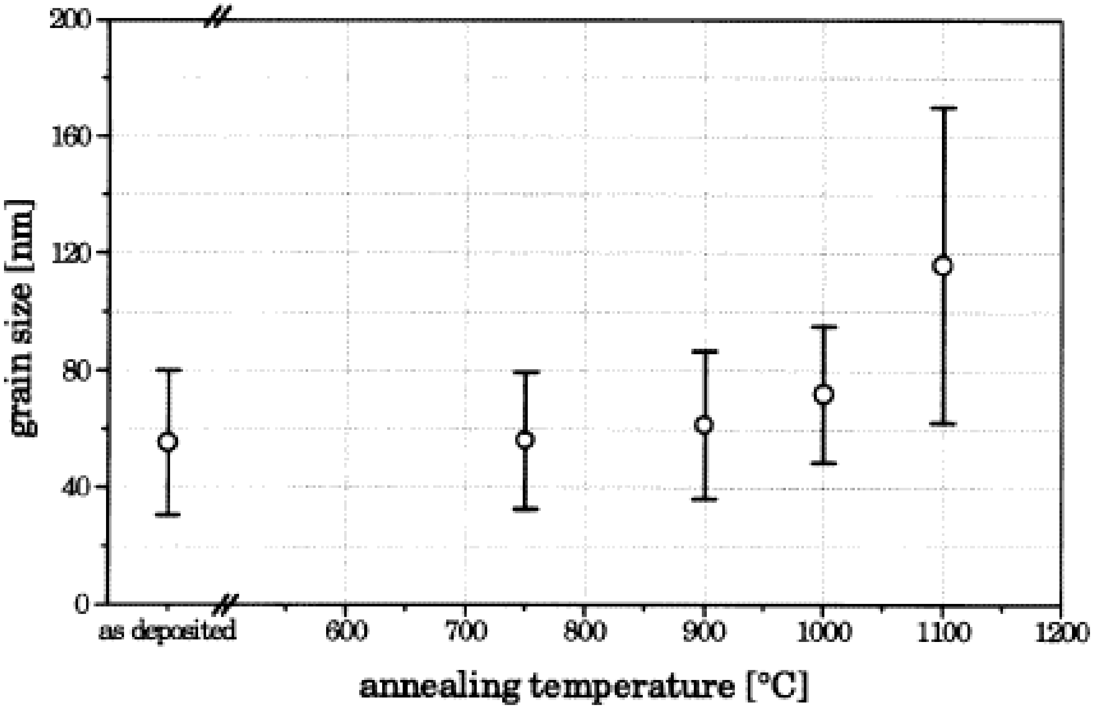


Table I. Average grain size as a function of deposition temperature

Temperature (°C)	Grain size (nm)
600	55
625	87
650	72
675	74
700	73
725	86

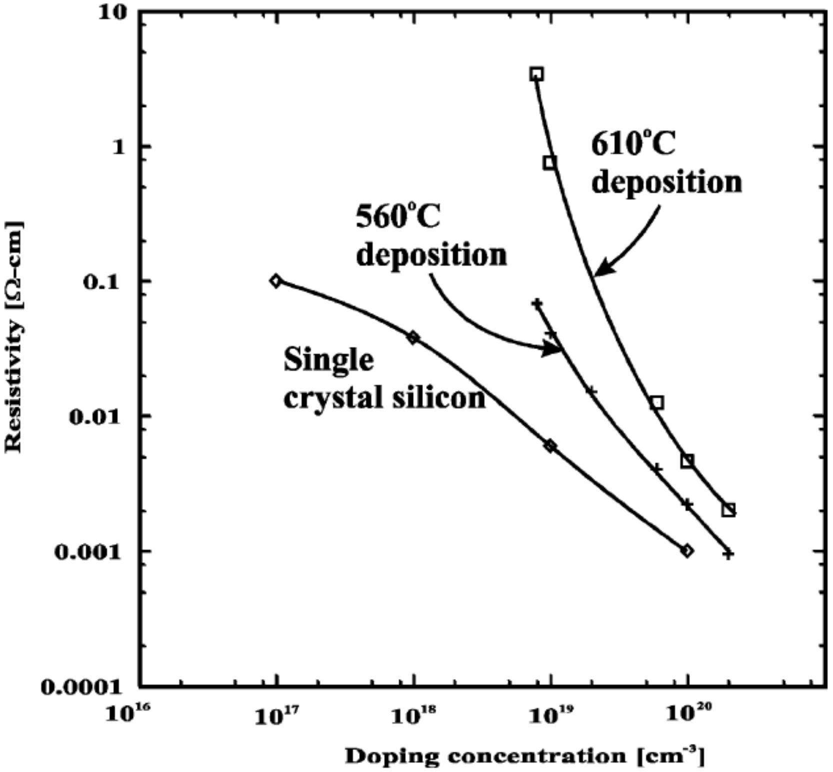
Deposition temperature affects grain size



Post-deposition anneal affects grain size

J. Micromech. Microeng. 6 (1996) 436–446

Poly vs. <Si>



Poly resistivity always higher !

Density: same 2.3 g/cm3

Young’s modulus: same 170 GPa

CTE: same 2.5 ppm/K

Thermal conductivity:

<Si>	156 W/K*m (at room temp)
poly	32 W/K*m

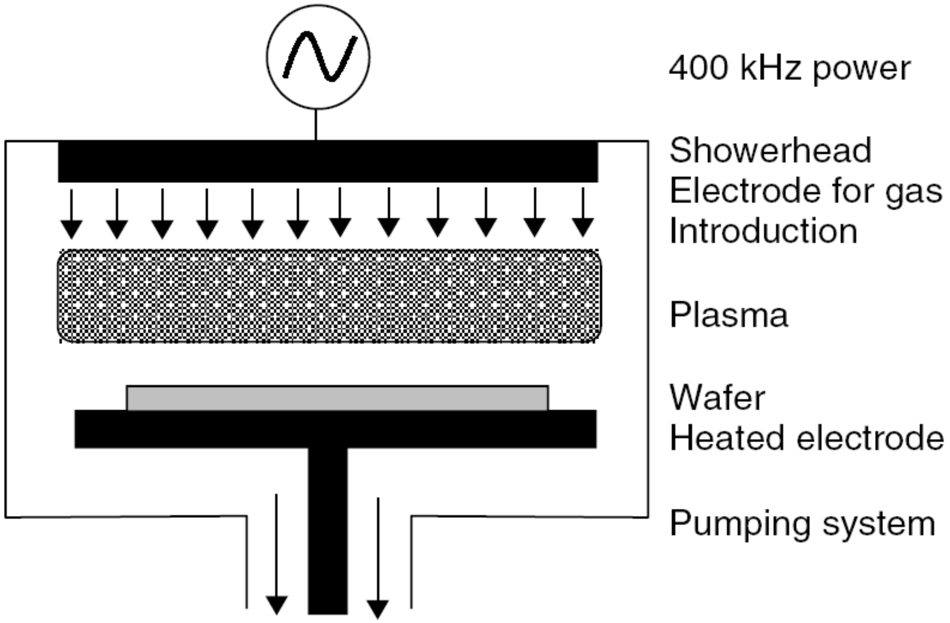
Carrier mobility:

<Si>	100 cm^2/Vs
poly	10 cm^2/Vs

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^{o}C: can be deposited on many materials



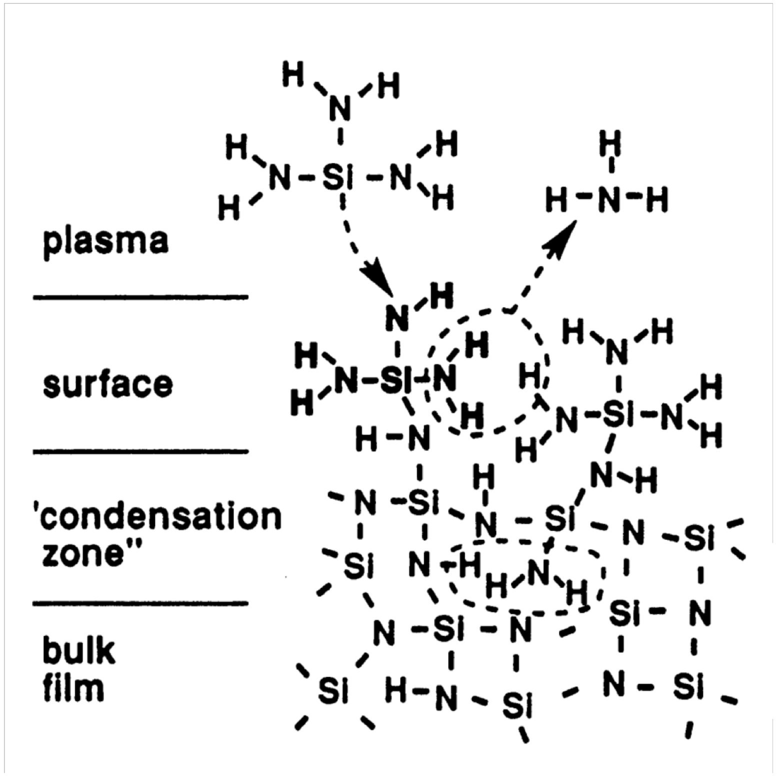
Oxide:

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

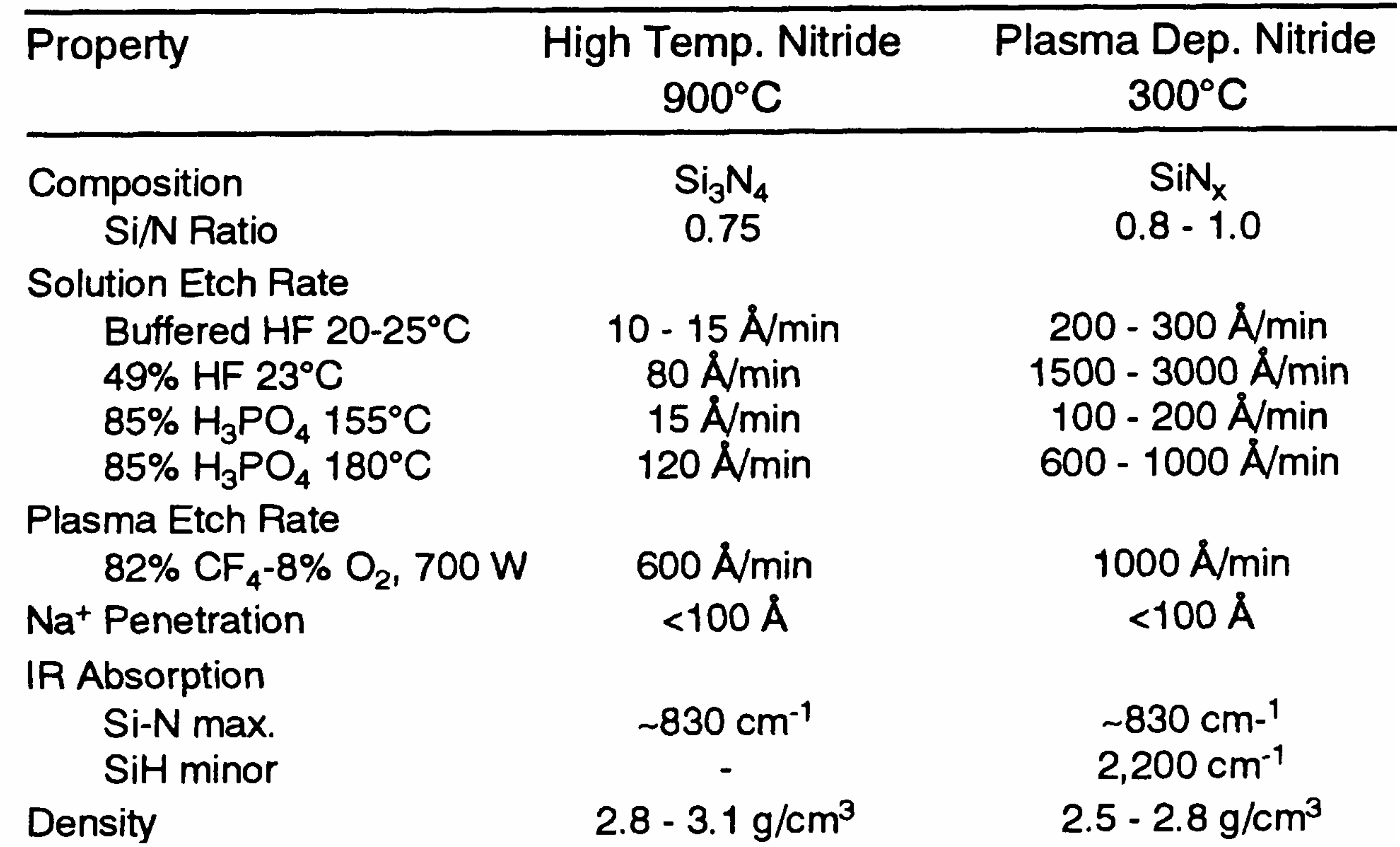
$$3\mathrm{Si(NH_2)_4} \xrightarrow{\text{heat}} \mathrm{Si_3N_4} + 8\mathrm{NH_3} \uparrow$$

PECVD at 300°C

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

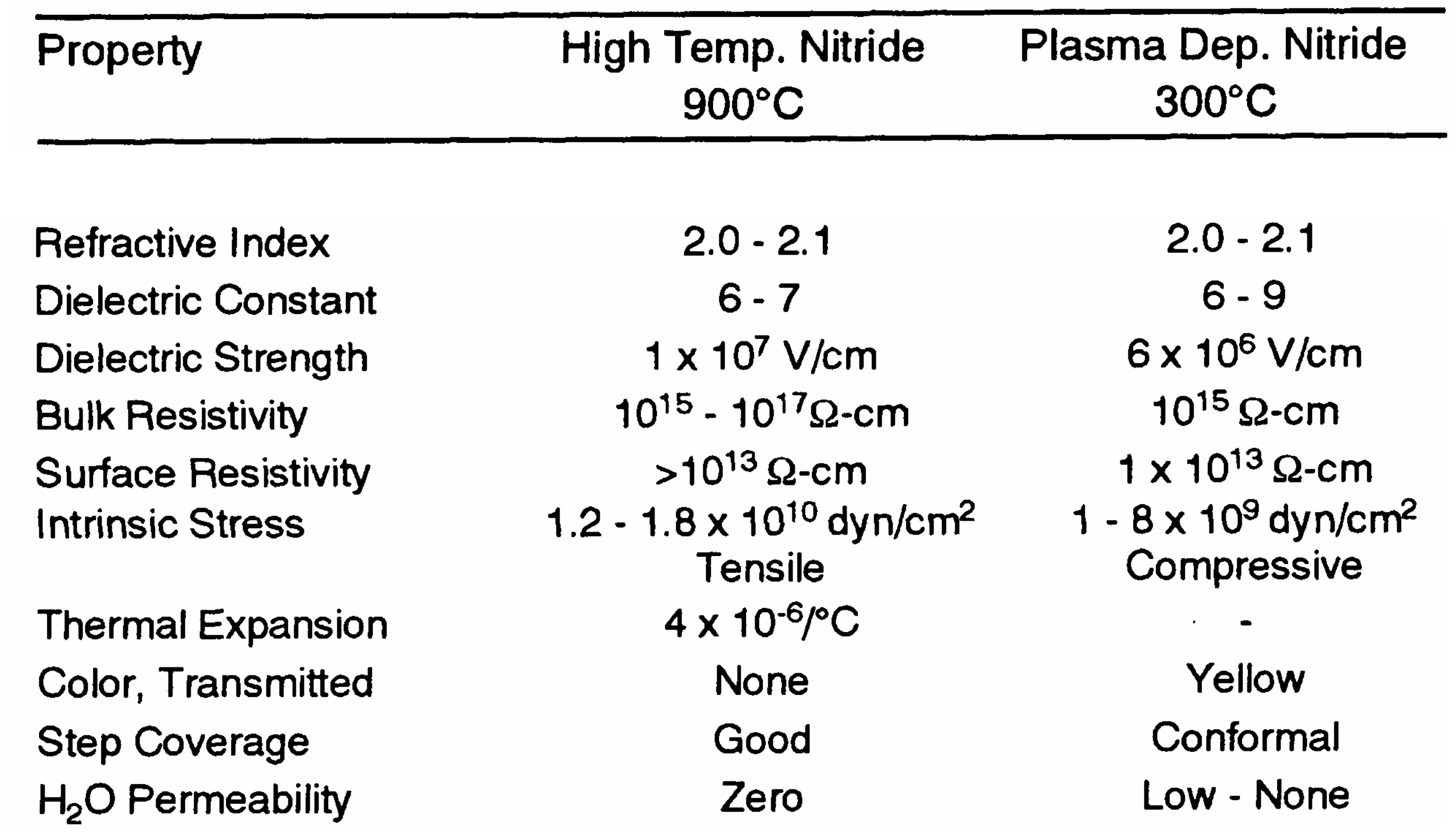
Smith: J.Electrochem.Soc. 137 (1990), p. 614

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

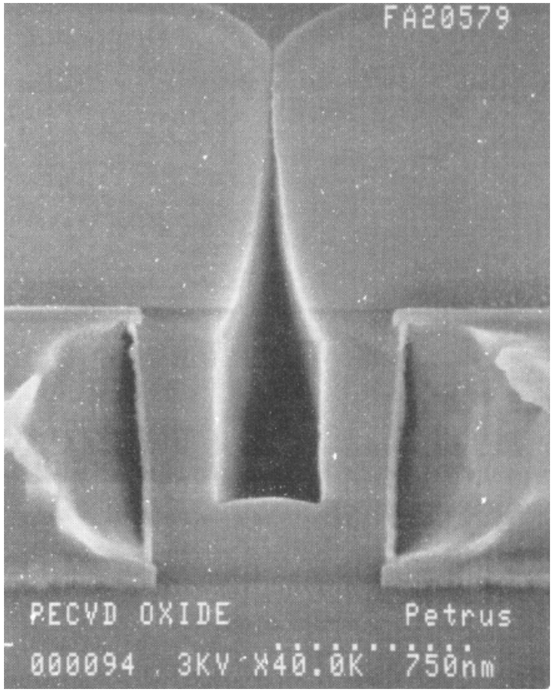
Nitride thermal vs. PECVD (2)



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

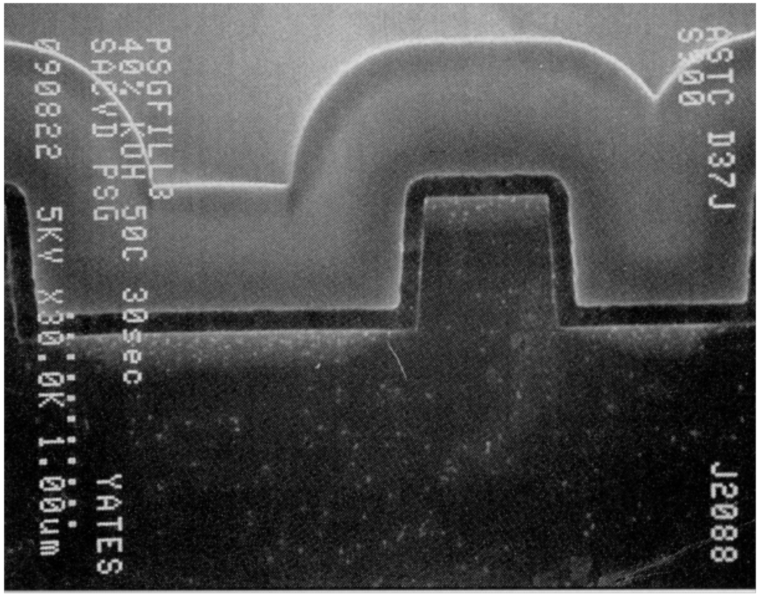
Half-time

Step coverage in CVD



Quite OK, but the "keyhole" might be a minor problem

(PECVD)

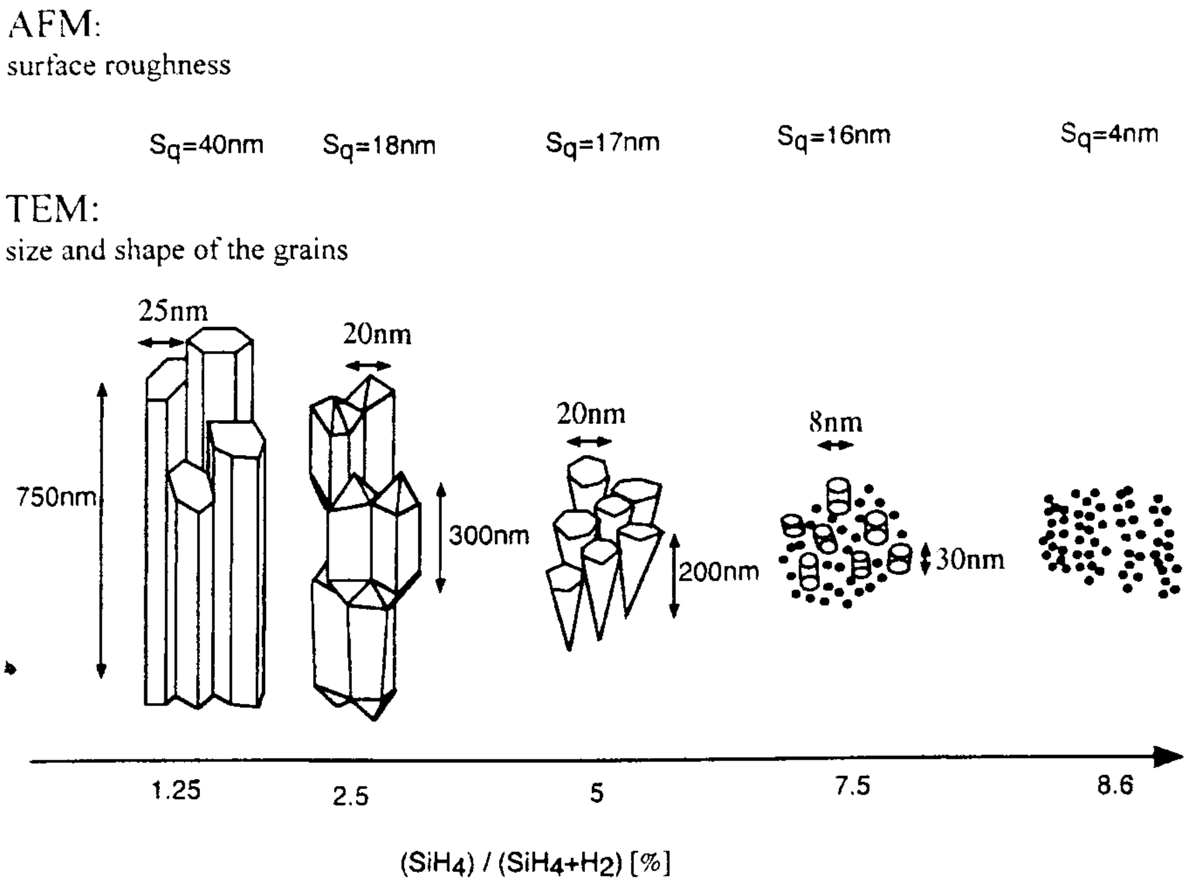


Conformal step coverage

(thermal CVD processes)

Cote, D.R. et al: Low-temperature CVD processes and dielectrics, IBM J.Res.Dev. 39 (1995), p. 437

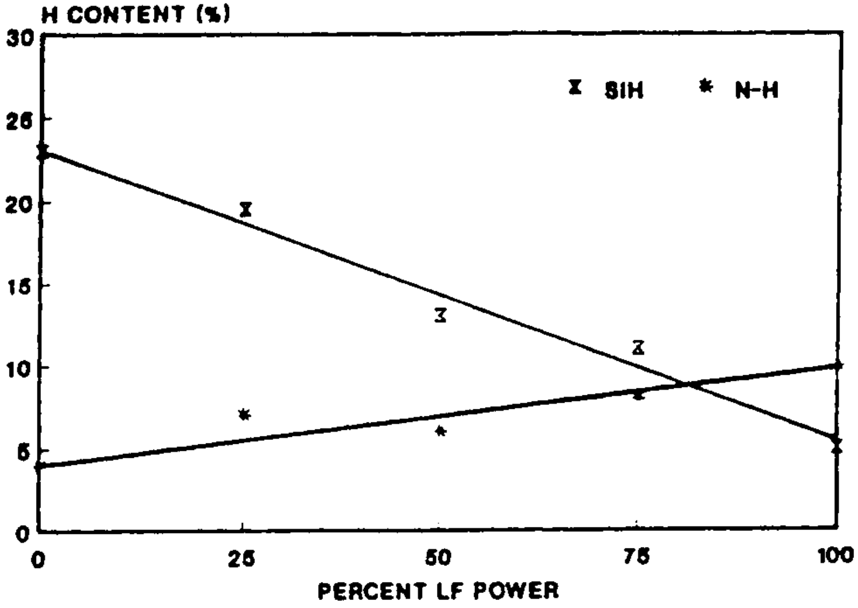
Grain size & roughness

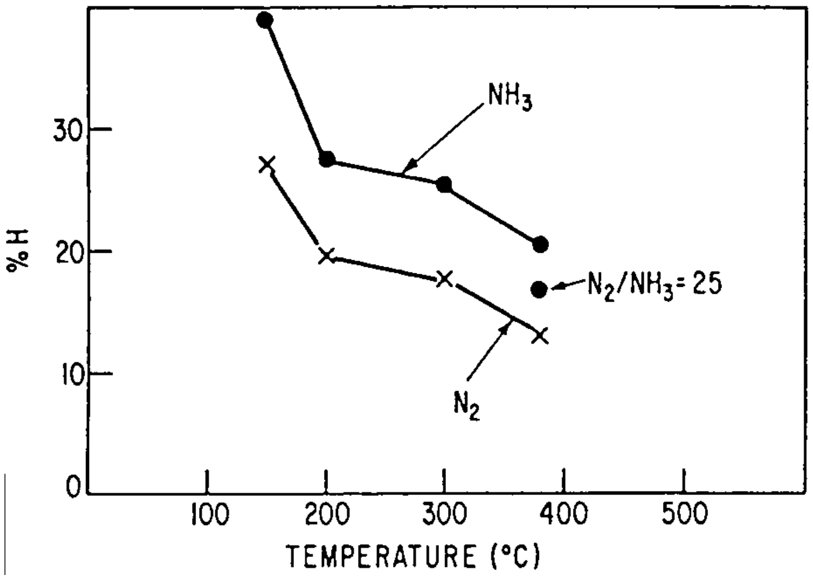


Vallat-Sauvain

Hydrogen in PECVD films

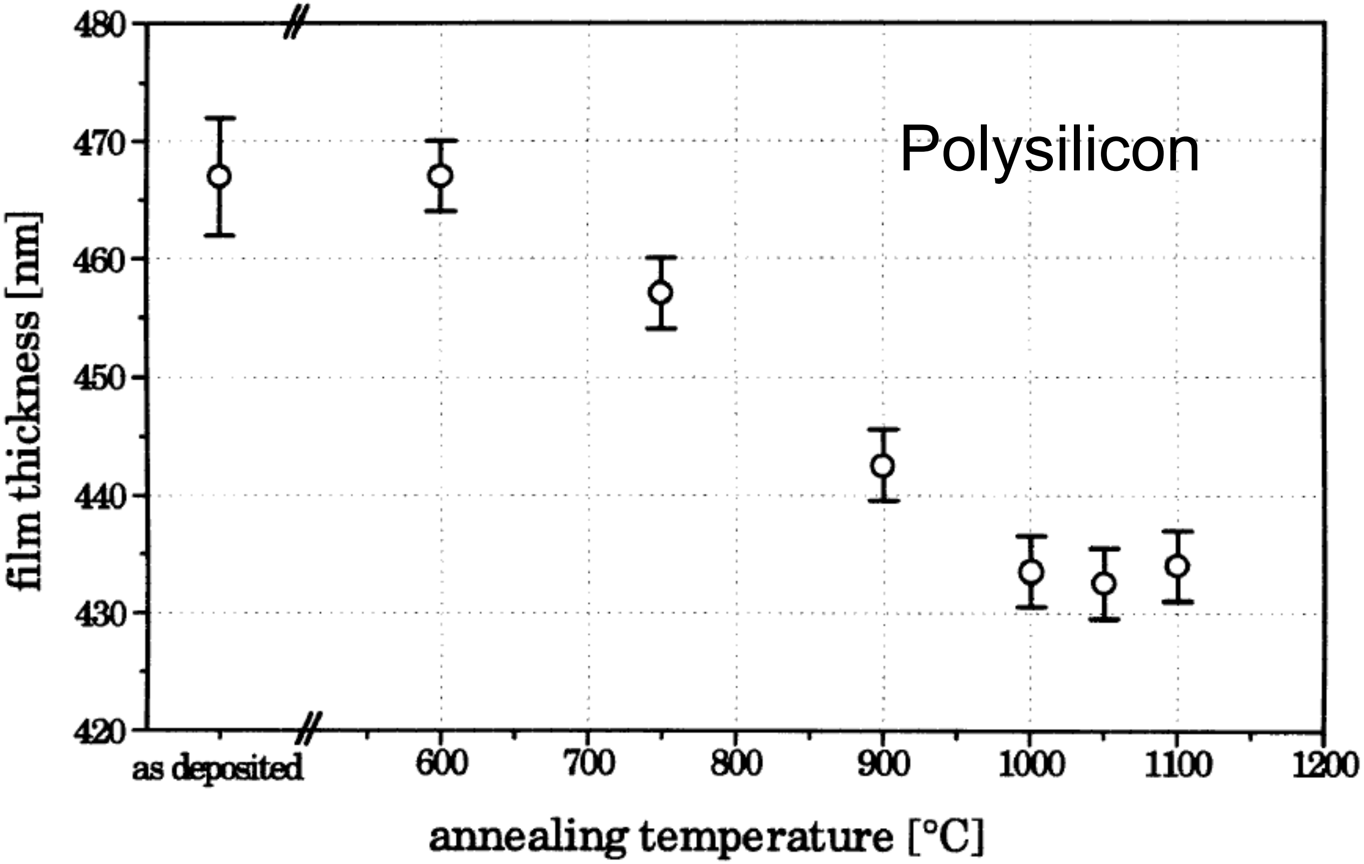
$3SiH_2Cl_2\ (g) + 4\ NH_3\ (g) \Longrightarrow Si_3N_4\ (s) + 6\ H_2\ (g) + 6\ HCl\ (g)$





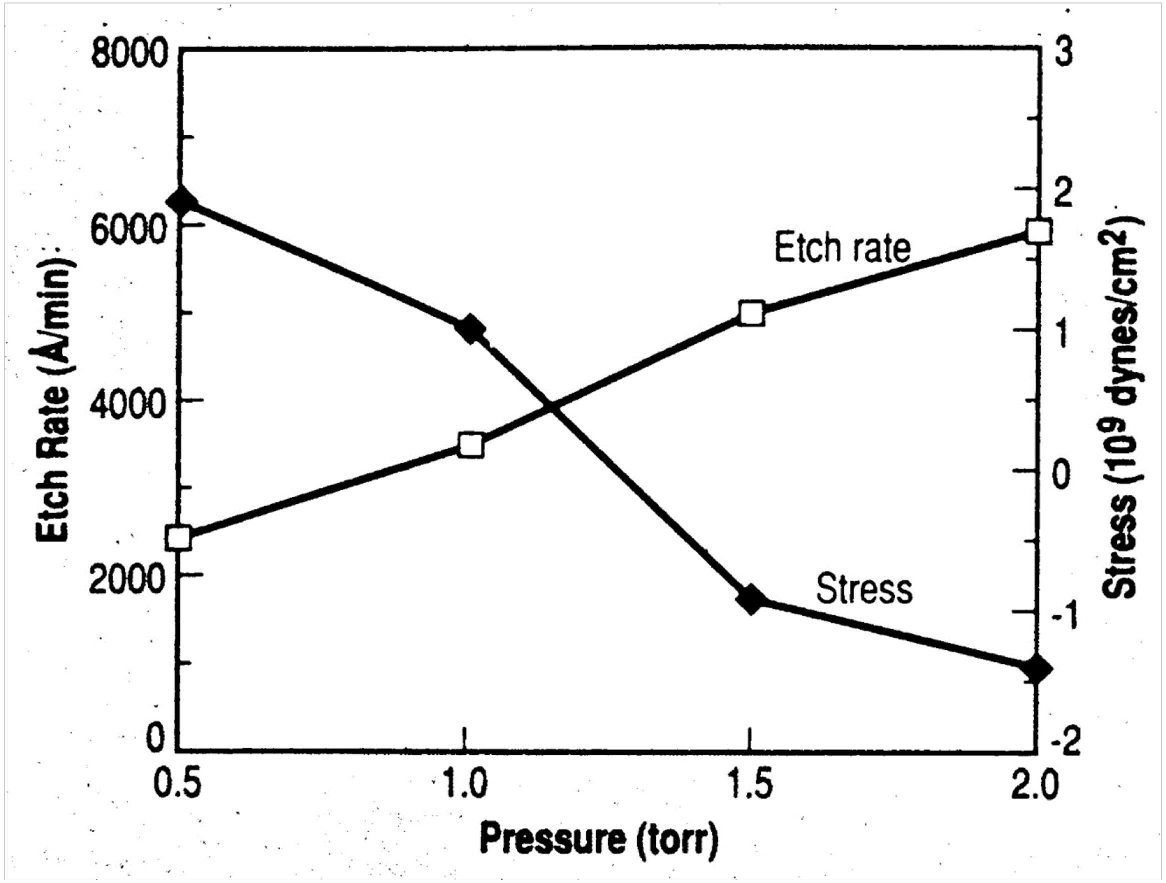
30 at% hydrogen is usual; 3-5% is as small as it gets

CVD films lose thickness upon anneal (H_2 escapes)



J. Micromech. Microeng. 6 (1996) 436–446.

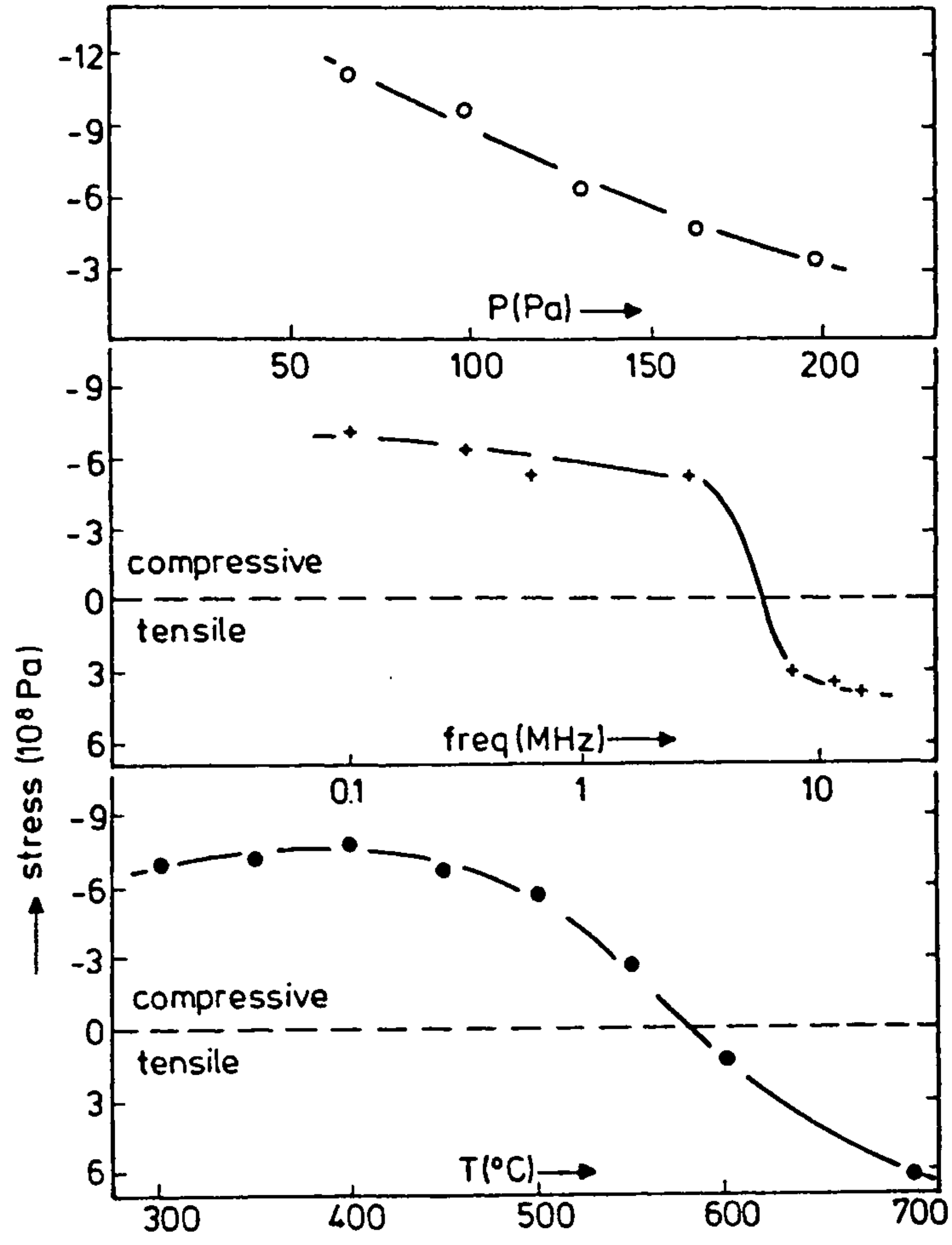
Film quality: etch rate



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



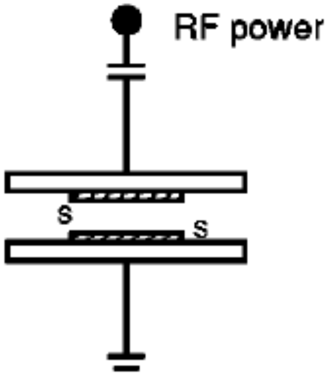
Stress affects by:

pressure

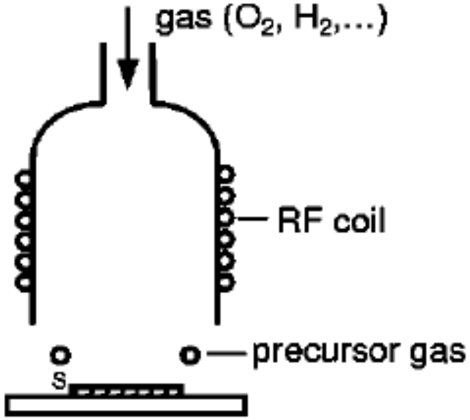
frequency

temperature

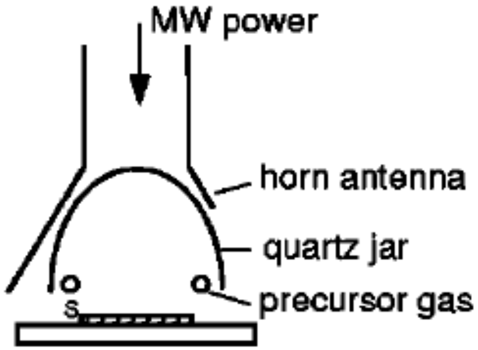
PECVD reactors (1)



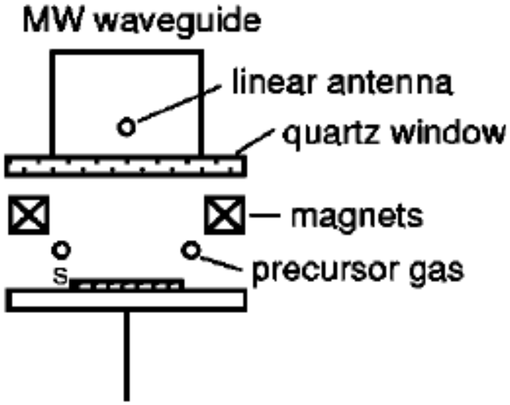
(a) Parallel plate RF PECVD



(b) Remote RF PECVD



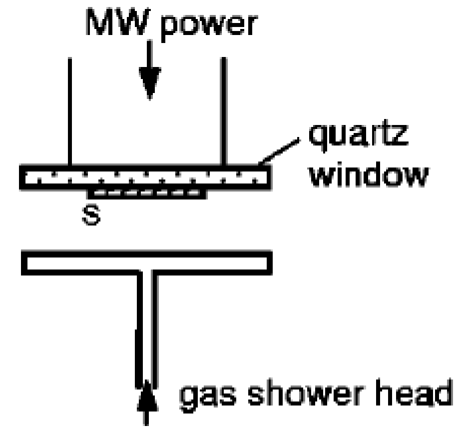
(c) MW PECVD



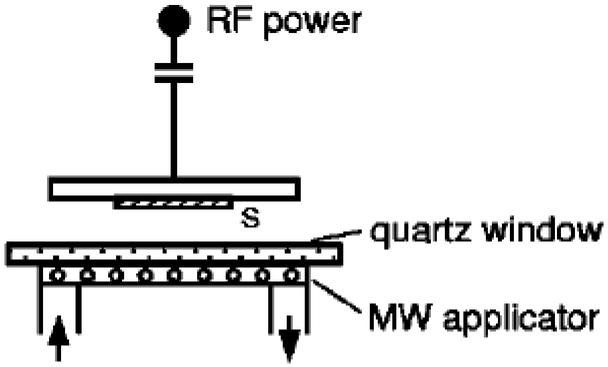
(d) ECR PECVD

L. Martinu and D. Poitras: 2619 J. Vac. Sci. Technol. A 18(6), Nov/Dec 2000

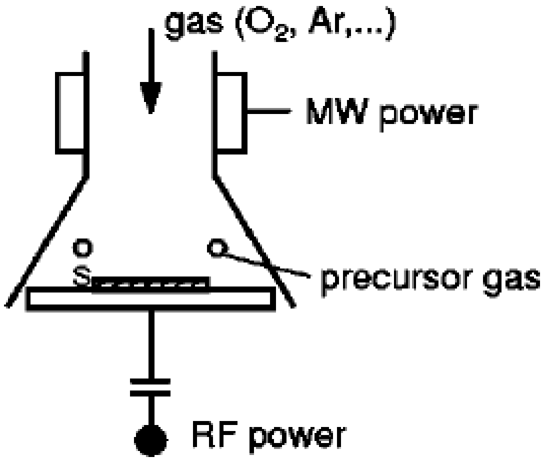
PECVD reactors (2)



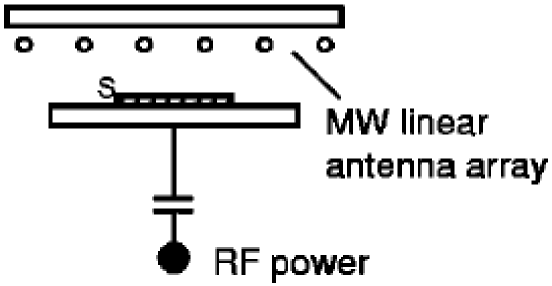
(e) MW PICVD



(f) Dual mode MW/RF PECVD



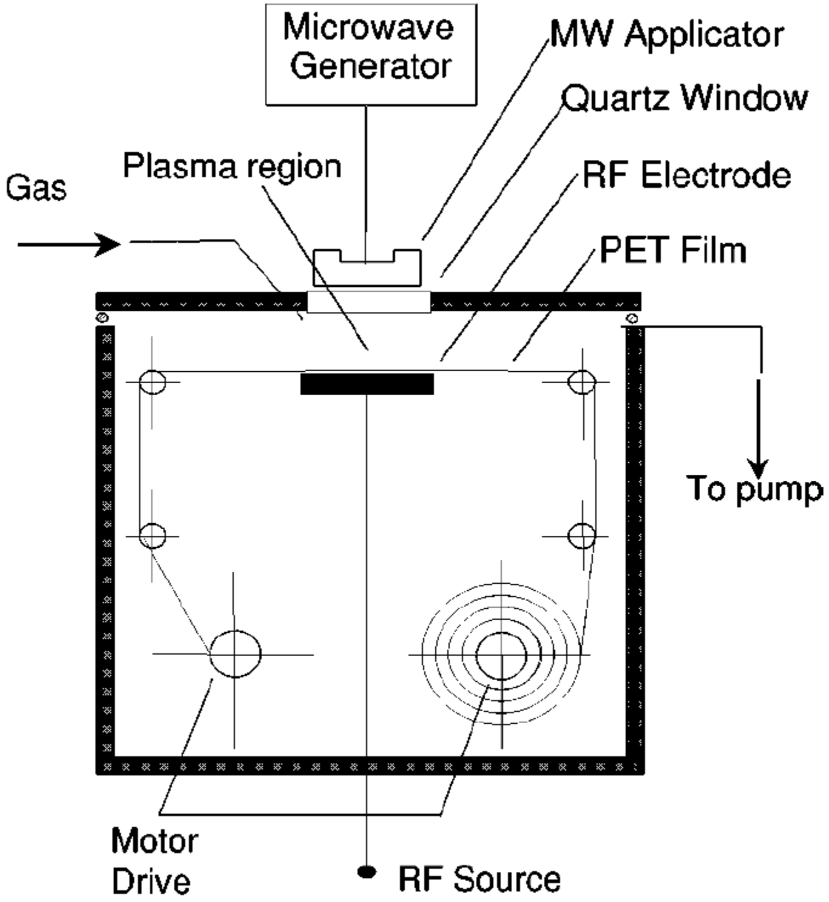
(g) Remote MW/RF PECVD



(h) DECR PECVD

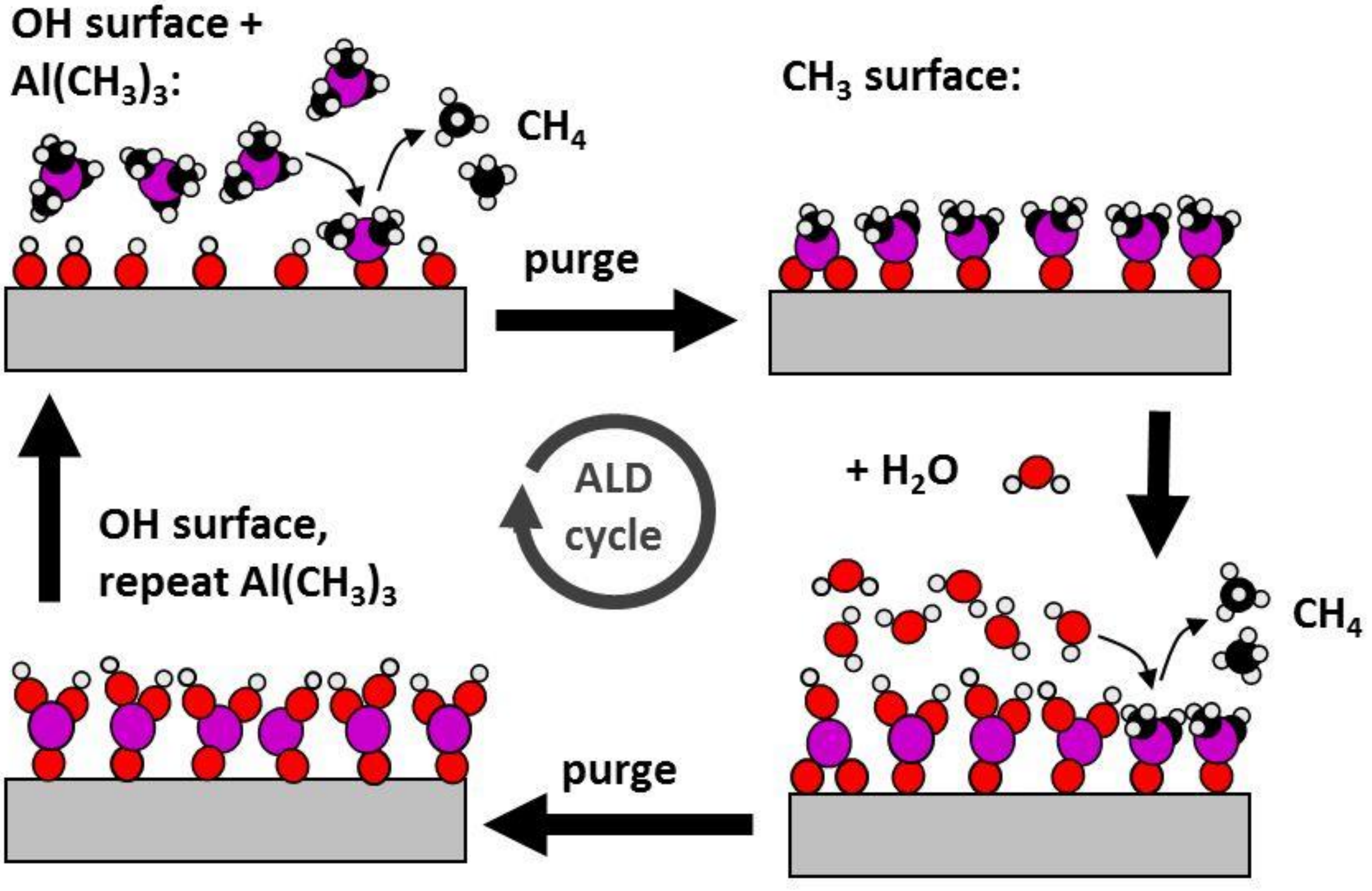
L. Martinu and D. Poitras: 2619 J. Vac. Sci. Technol. A 18(6), Nov/Dec 2000

Roll-to-roll PECVD



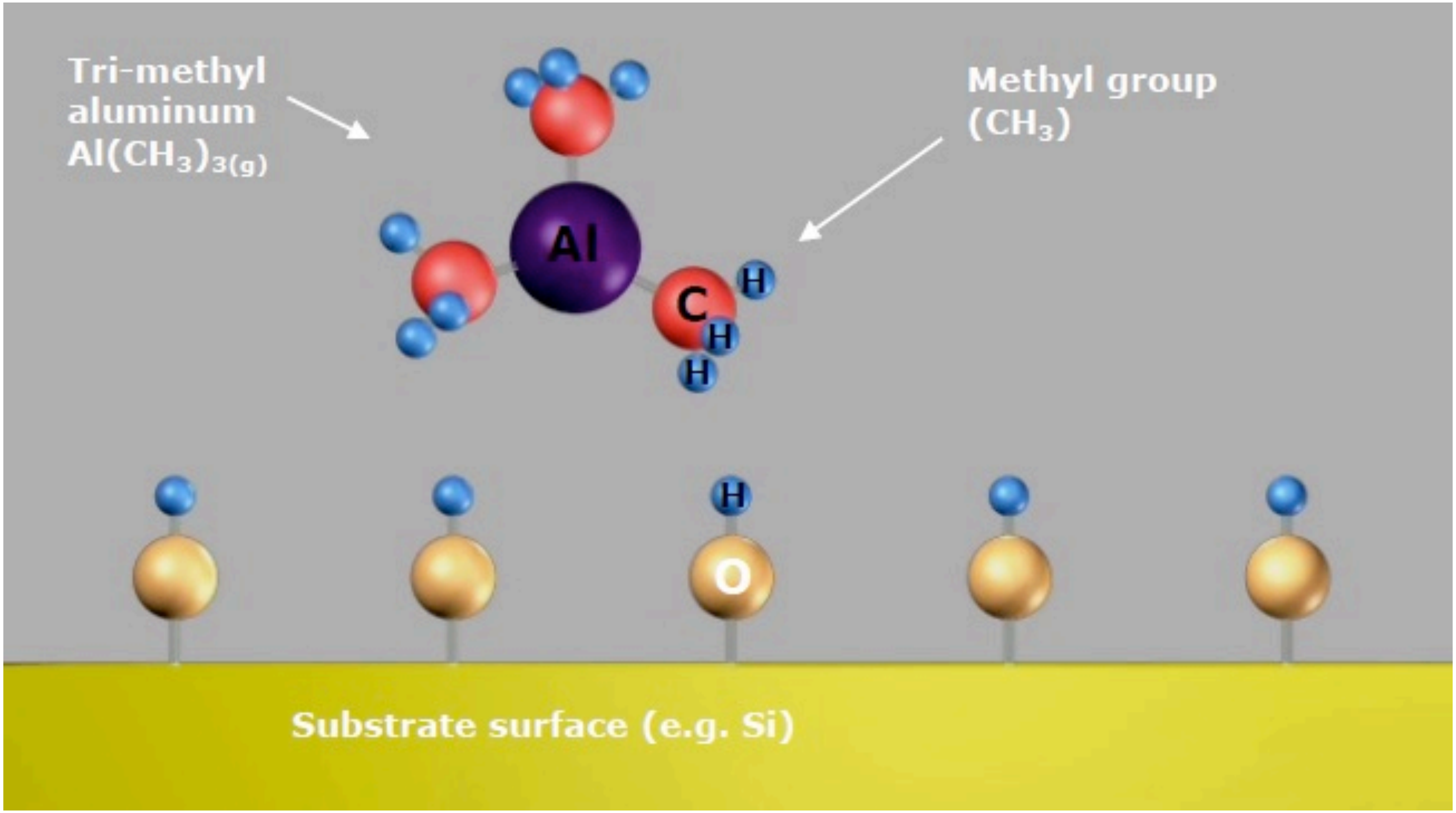
L. Martinu and D. Poitras

ALD: Atomic Layer Deposition



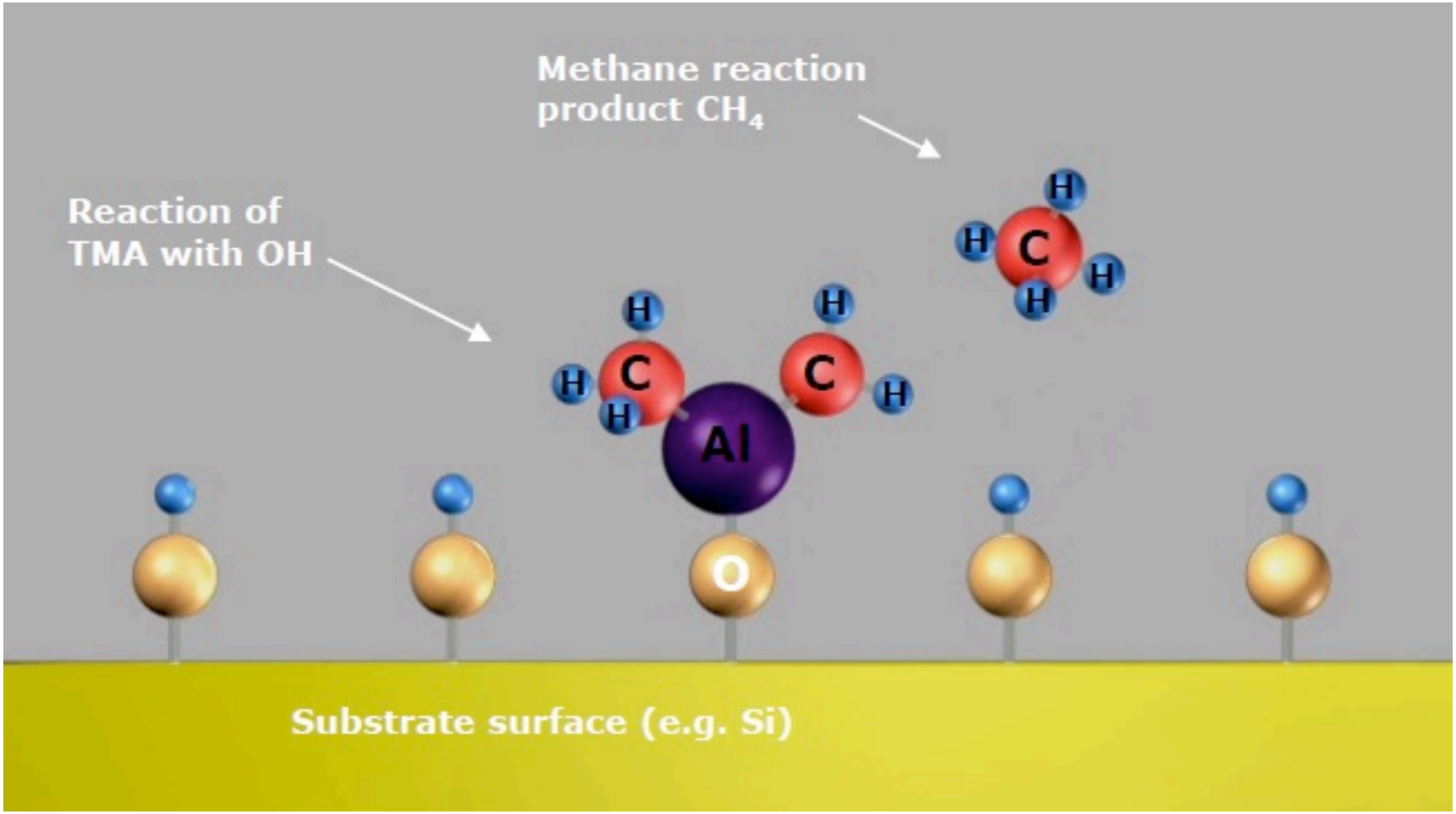
Precursors introduced in pulses, with purging in-between

Step 1: precursor 1 introduction

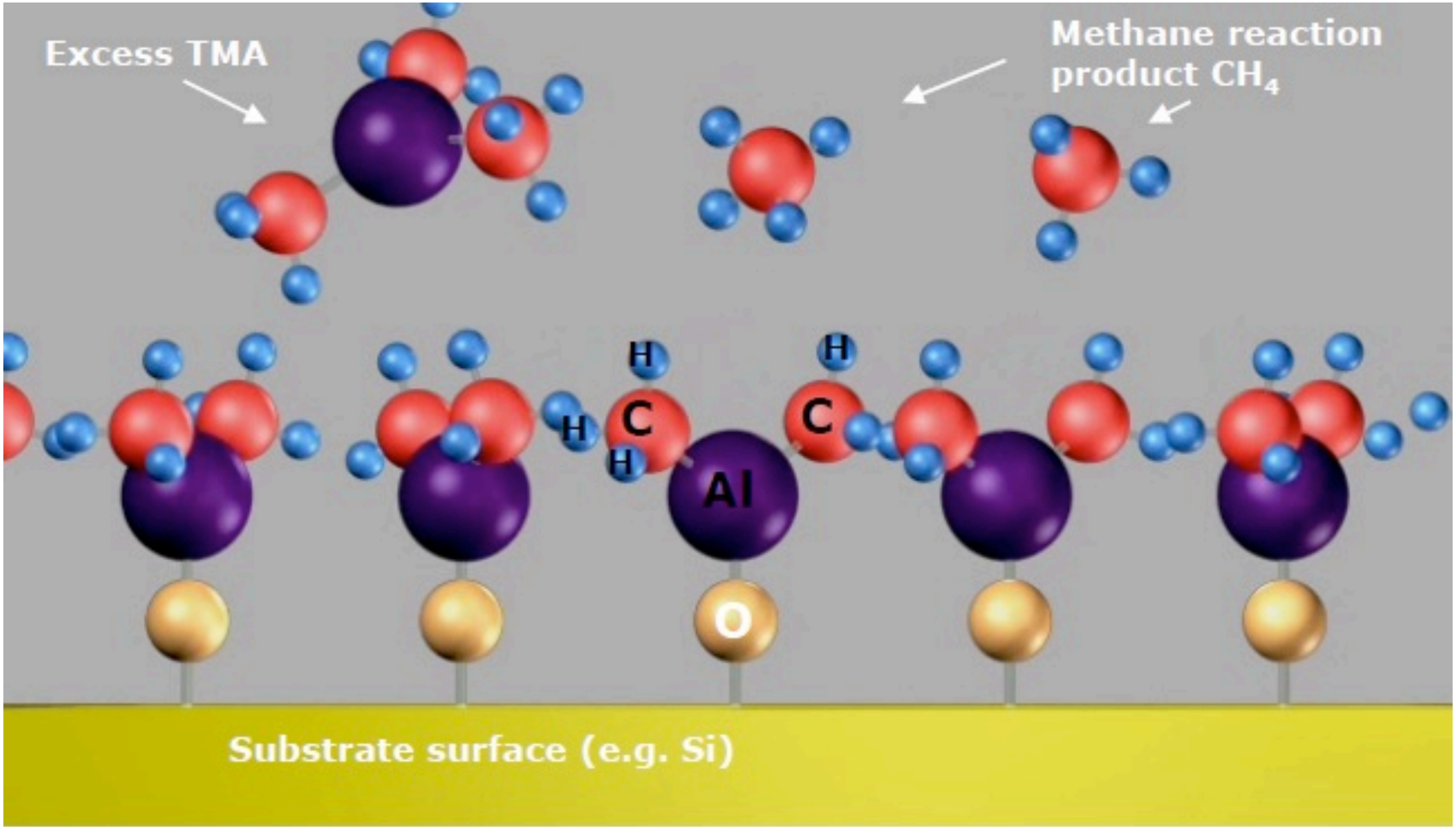


J Provine & Michelle Rincon, Stanford University 2012

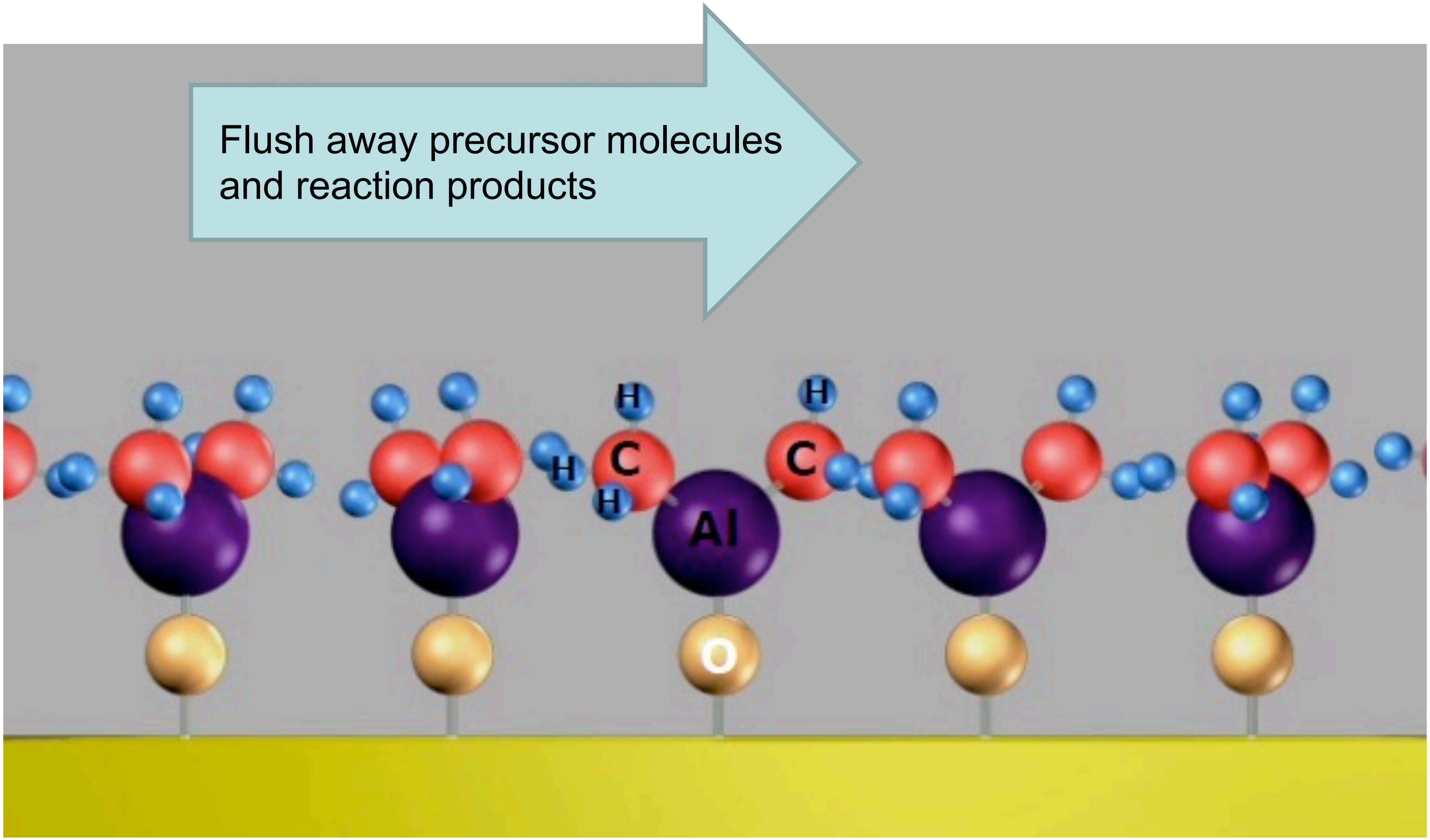
Reaction with hydroxyl moieties



Saturating reaction ➔ monolayer

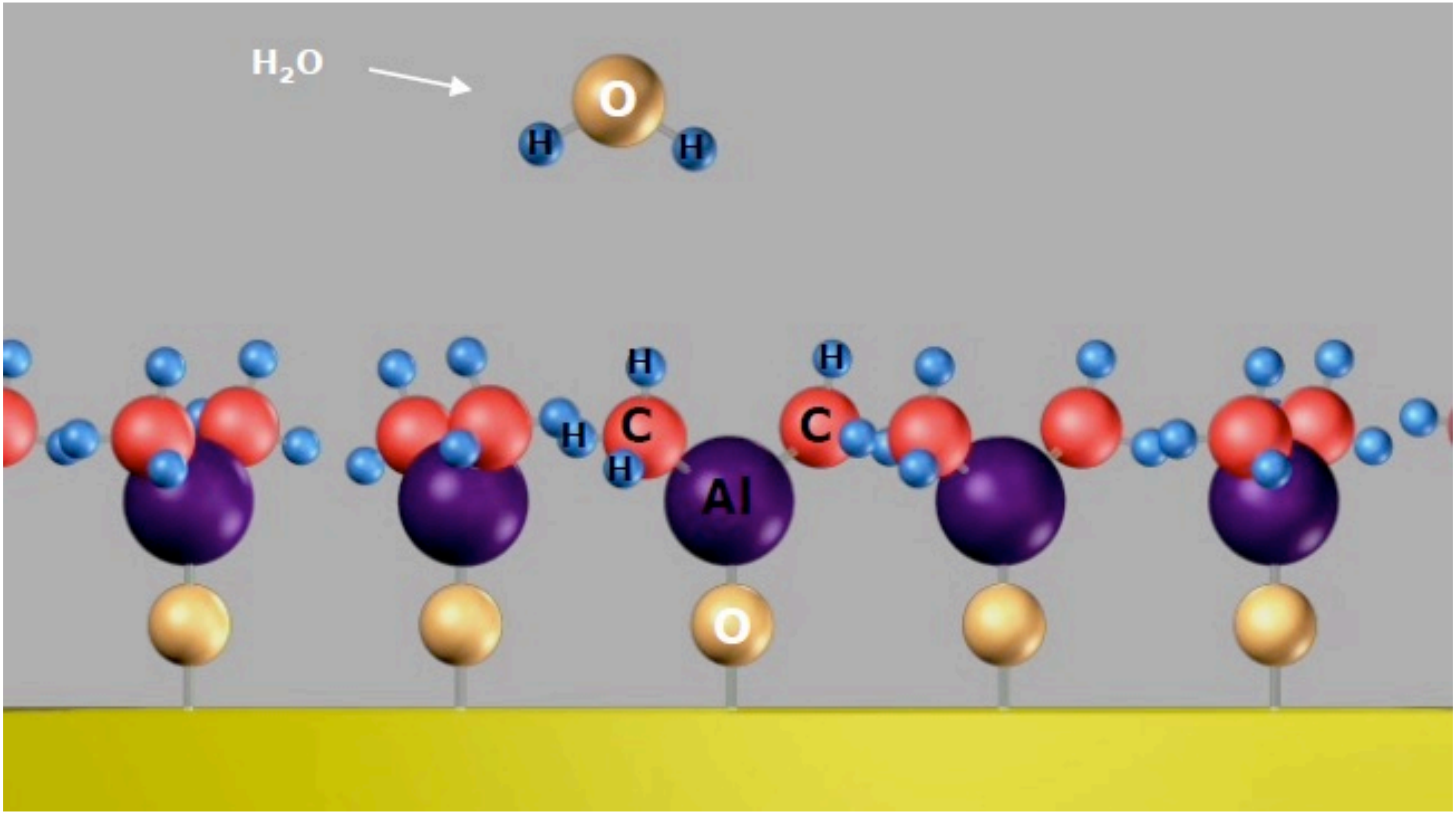


Step 2: purge

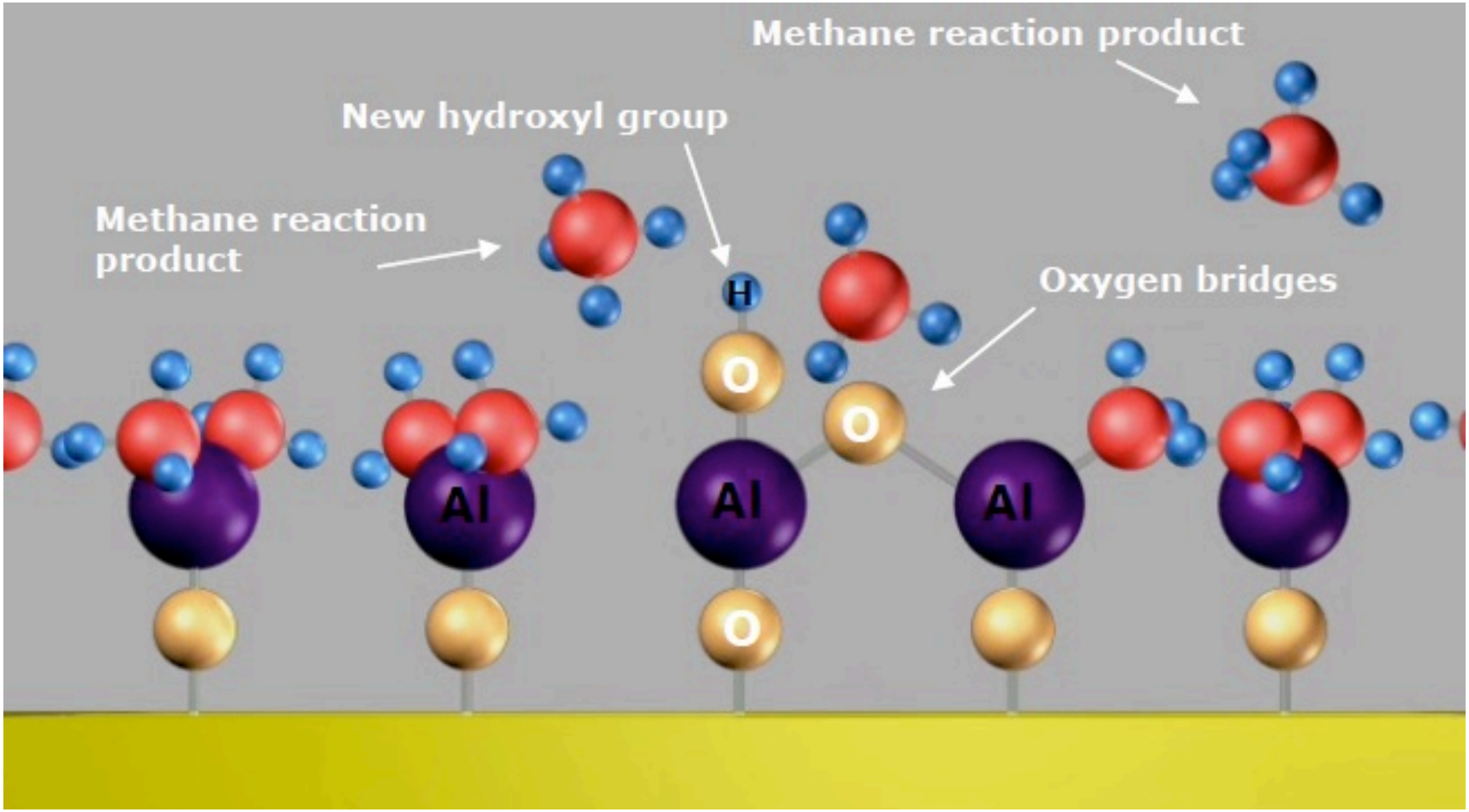


Flush away precursor molecules and reaction products

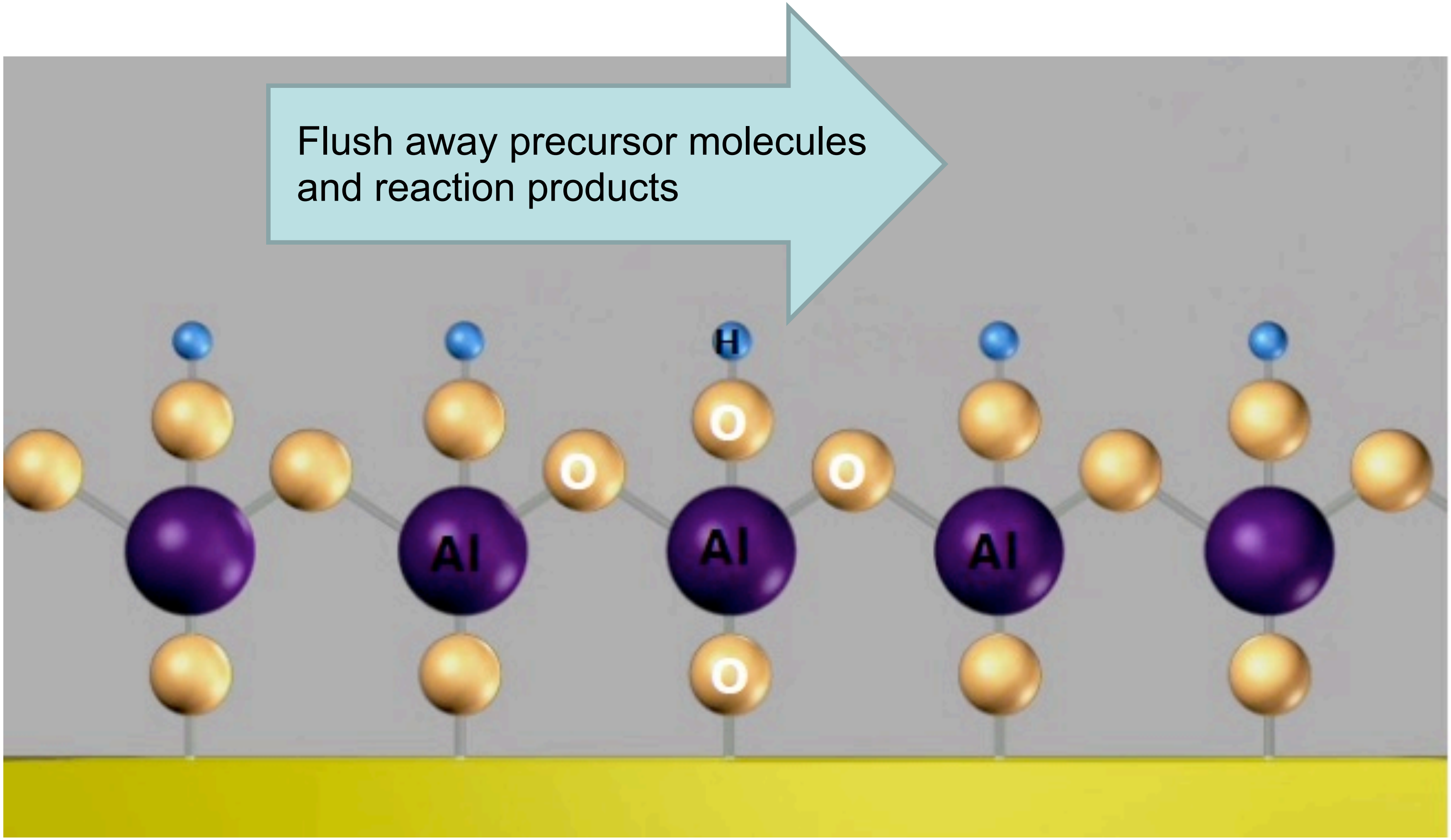
Step 3: second precursor



Second half-reaction

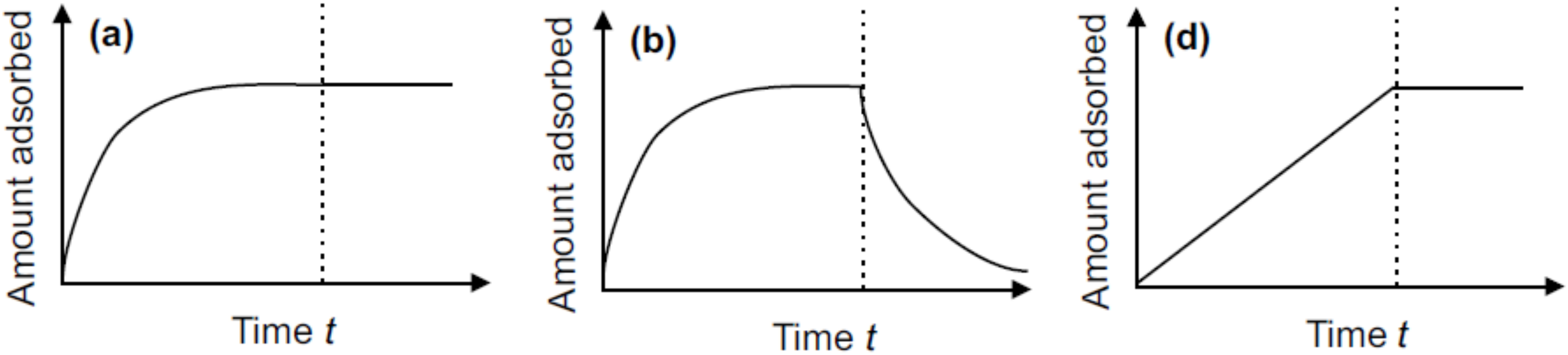


Step 4: purge again



Flush away precursor molecules and reaction products

Surface saturation



Irreversible saturation ALD reactions:

Surface saturates with a monolayer of precursor, strong chemisorption (=chemical bonds formed)

Reversible saturation:

Physisorption only (weak bonds like van der Waals): once precursor flux is stopped, surface specie will desorb.

Irreversible non-saturating.

CVD regime:
more reactants in, more film is deposited (continuosly)

ALD process based on:

Chemisorption

- Suitable temperature for chemical bonding, no thermal decomposition
- Covalent bonding ⇨ excellent adhesion

Saturation

- Sufficient dosing of precursor material
- Self-terminating reactions ⇨ extremely precise dosing not required

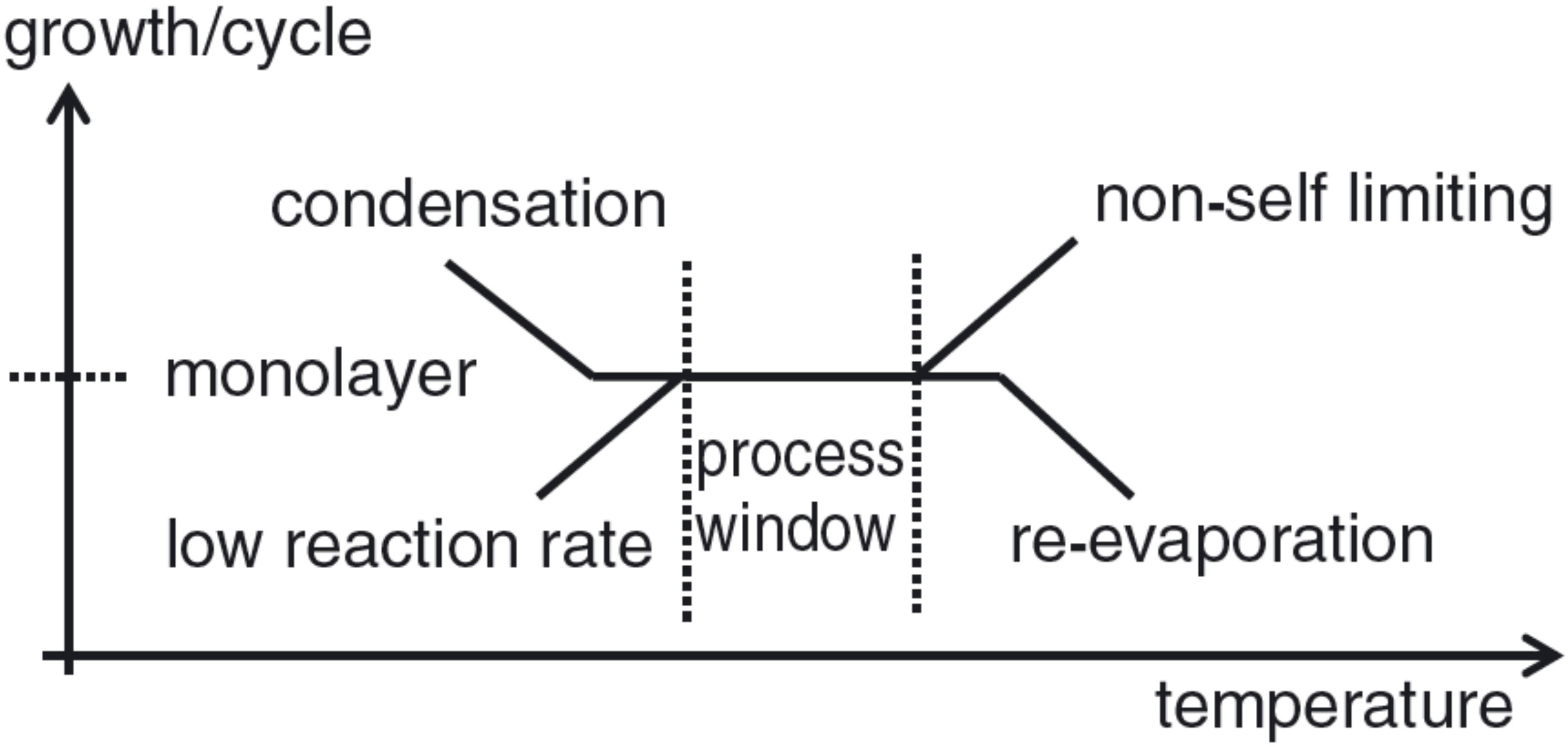
Surface controlled reactions

- Film thickness is independent of substrate geometry ⇨ conformal film onto deep trenches and 3D structures

Sequential

- Digital growth
- Sufficient purging needed between pulses
- Good flow dynamics required to ensure rapid gas changes

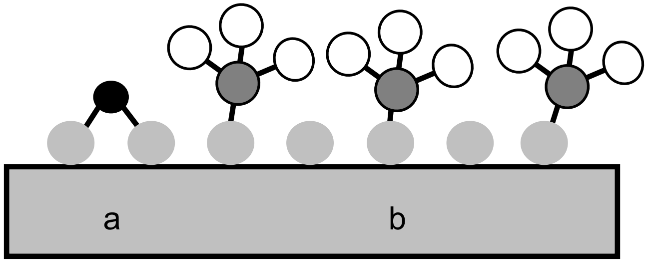
ALD window


growth/cycle
condensation
non-self limiting
monolayer
process window
low reaction rate
re-evaporation
temperature

Deposition rate

Basically one atomic layer per pulse

In practise less than an atomic layer because:



a) Inactive surface sites

b) Steric hindrance: a large precursor molecule prevents another precursor molecule from approaching the reactive site

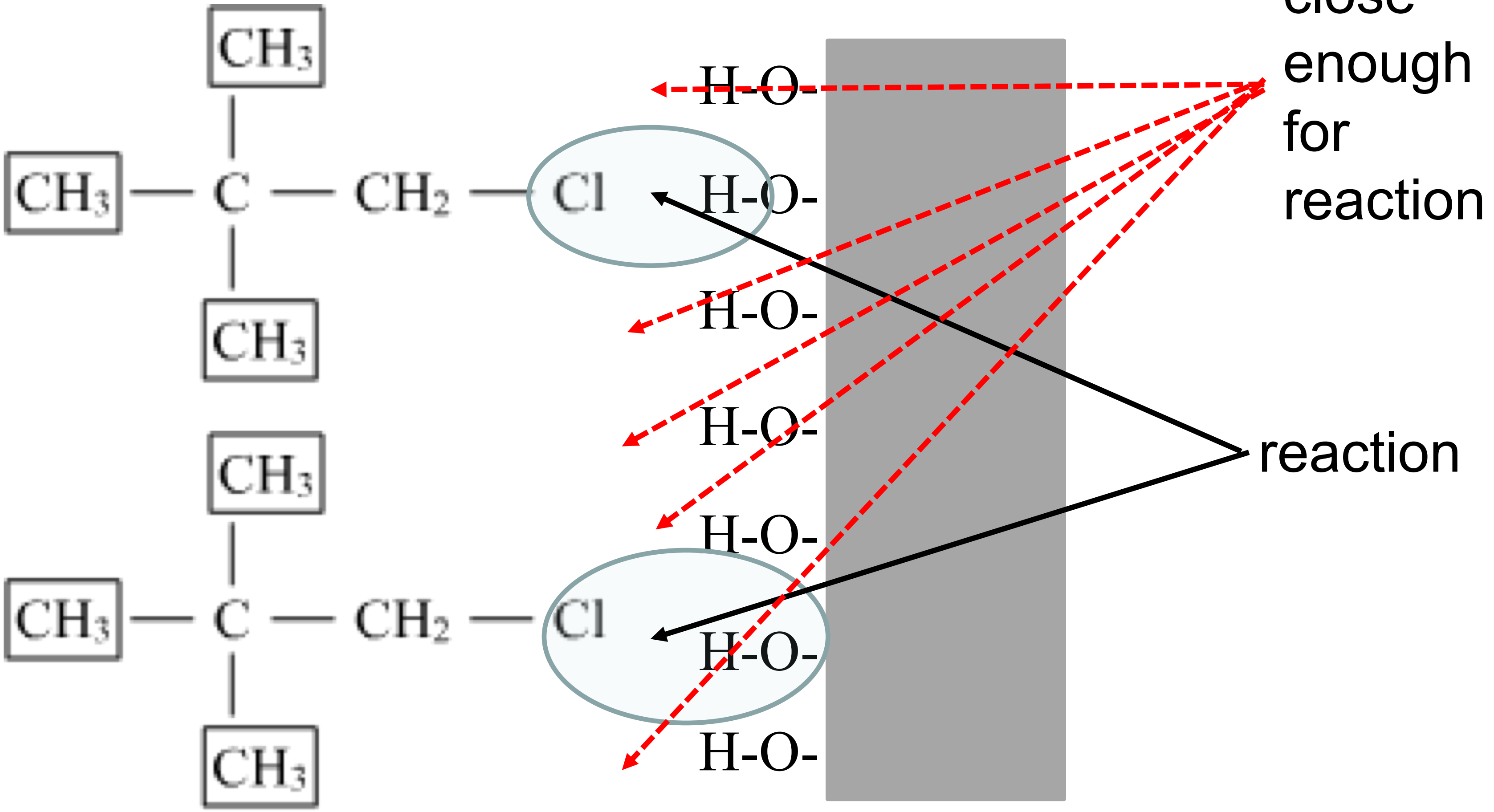
Al_2O_3 deposition it is 1.1 Å/cycle (0.11 nm/cycle)

TiN it is 0.2 Å/cycle

If pulses are one second ➔ 15*monolayer thickness/minute ~ 2 nm/min

If 0.1 second pulses ➔ 20 nm/min max.

Steric hindrance

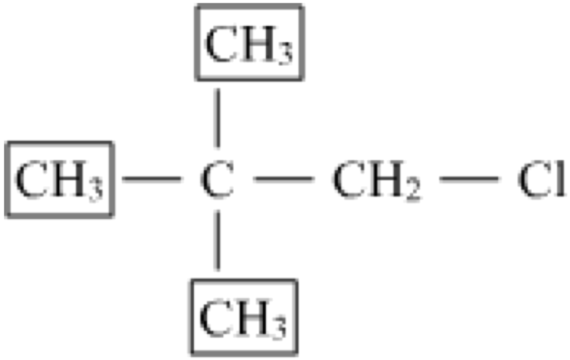


Not close enough for reaction

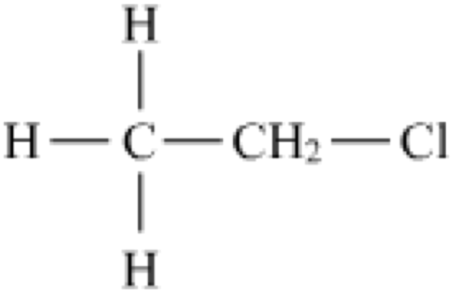
reaction

Most often: not an atomic layer, but less

Precursor design



$$\boxed{\mathrm{CH_3}}-\overset{\boxed{\mathrm{CH_3}}}{\underset{\boxed{\mathrm{CH_3}}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{Cl}$$



$$\mathrm{H}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{Cl}$$

Large size,
Steric hindrance

Small size,
No steric hindrance.

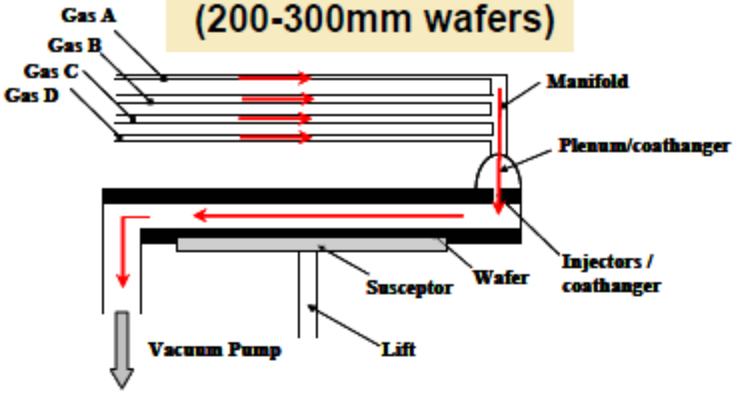
But you also need to consider:

-thermal stability
-vapour pressure
-toxicity
-price…

ALD reactors

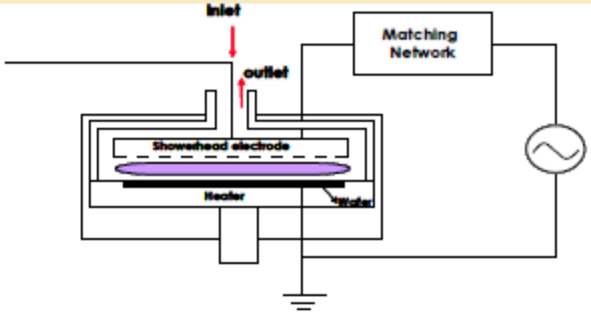
a)

Cross-flow reactor (200-300mm wafers)



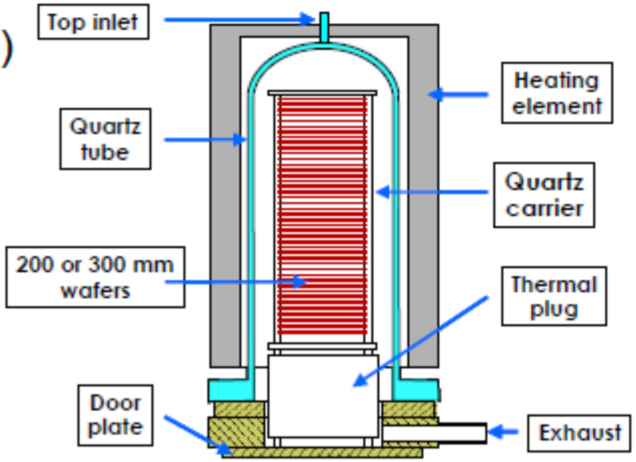
b)

Showerhead ALD or PEALD reactor (200-300mm wafers)



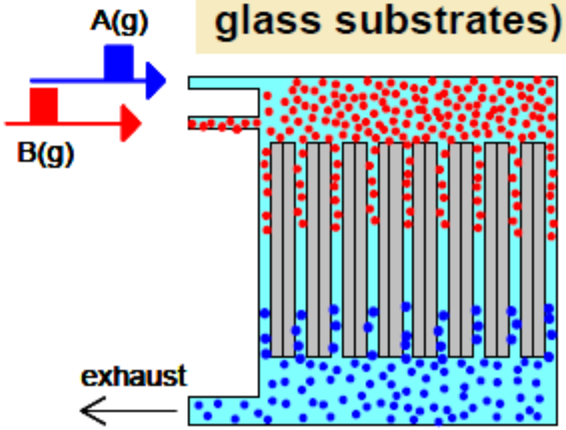
Batch reactor (200-300mm wafers)

c)



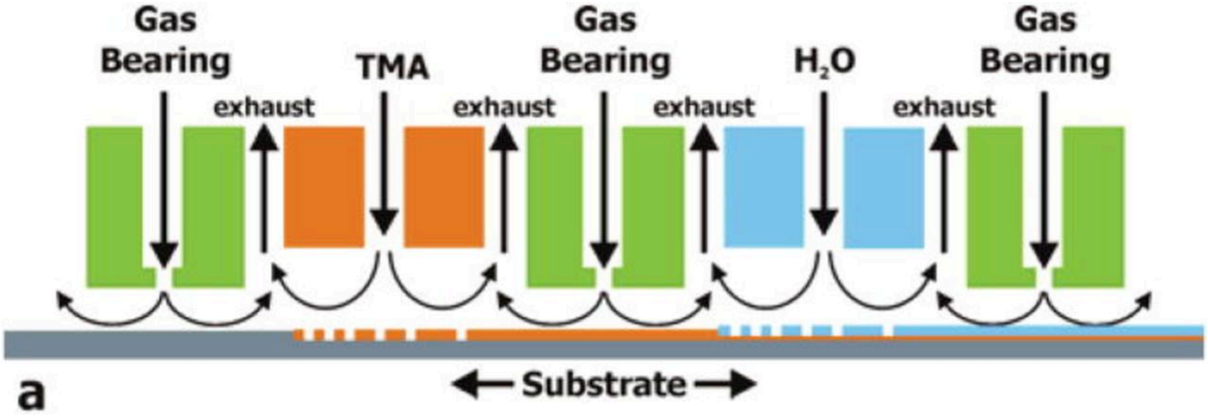
d)

Batch reactor (40x50cm² glass substrates)



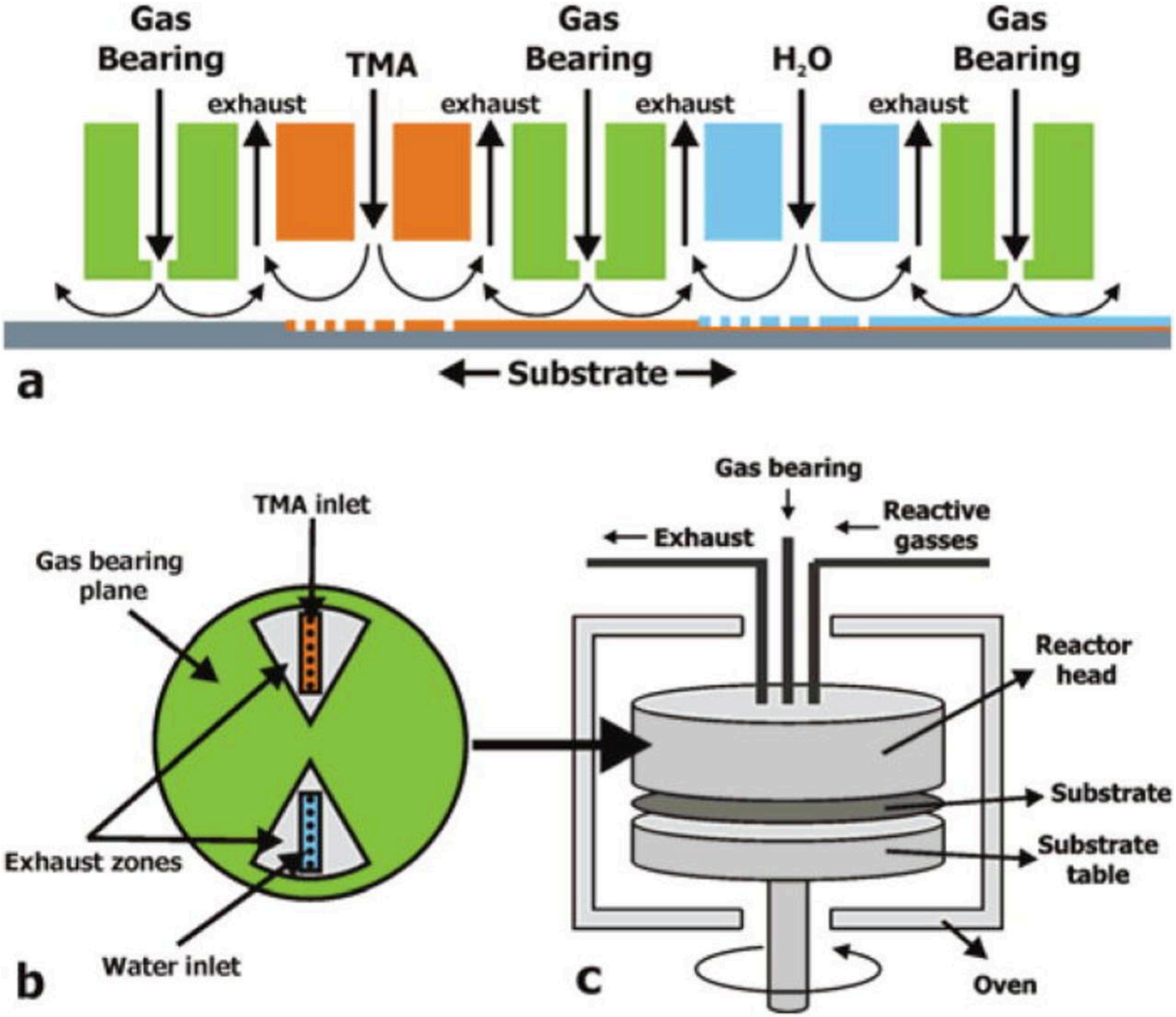
Suvi Haukka 2005

Spatial ALD



jes.ecsdl.org

Spatial ALD



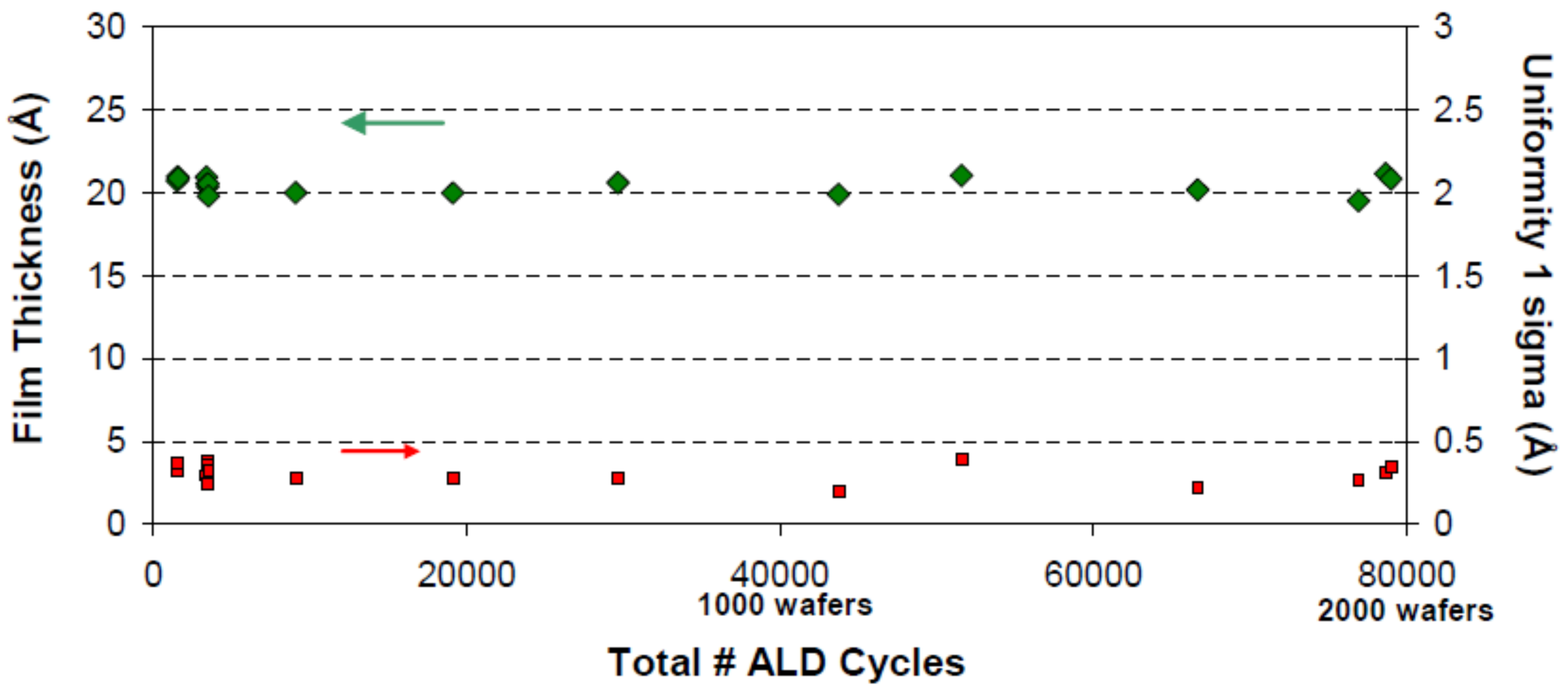
jes.ecsdl.org

Spatial ALD reactors

Deposition upto 10 nm Al_2O_3

www.blog.baldengineering.com

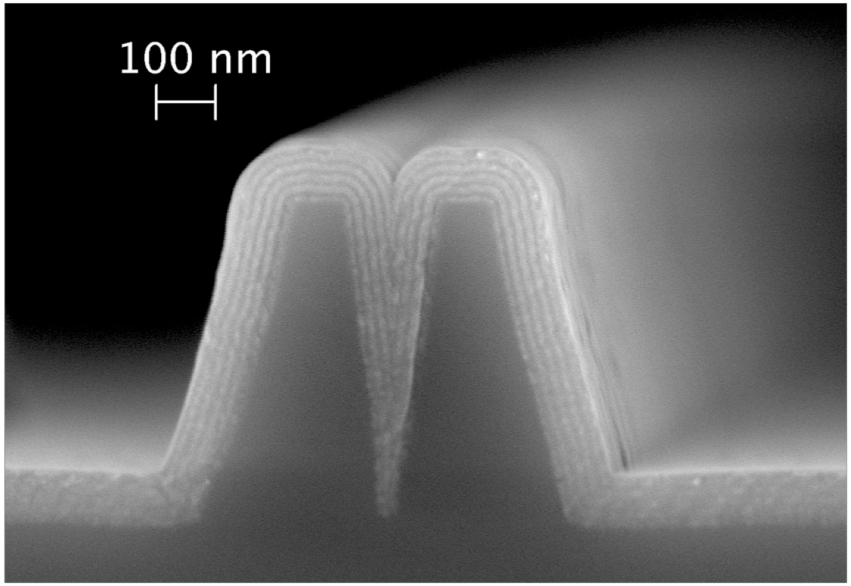
ALD uniformity (=thickness across the wafer)



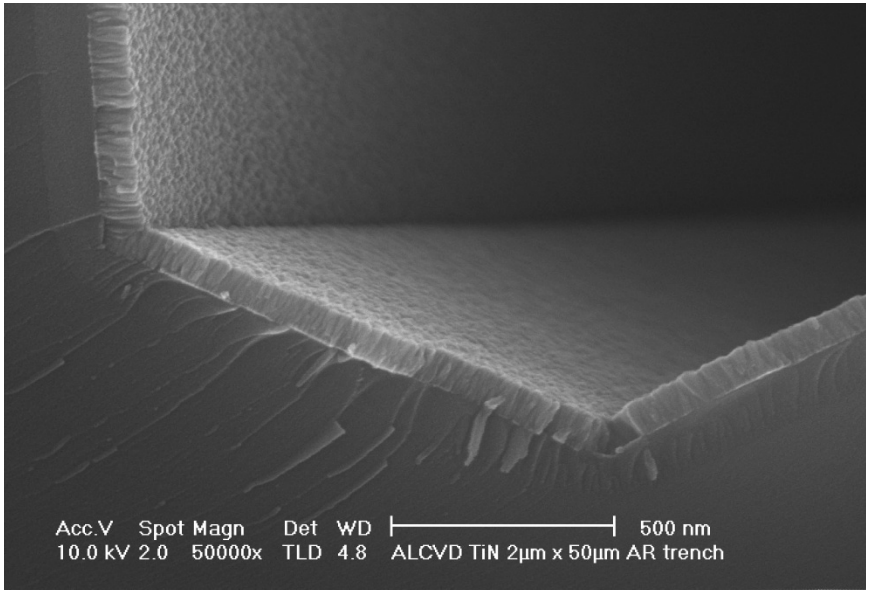
HfO$_2$ dielectric marathon test: 2000 wafers

ALD conformality
(=step coverage in microstructures)

Excellent conformality: all surfaces coated by diffusing gaseous precursors in the surface reaction limited mode.

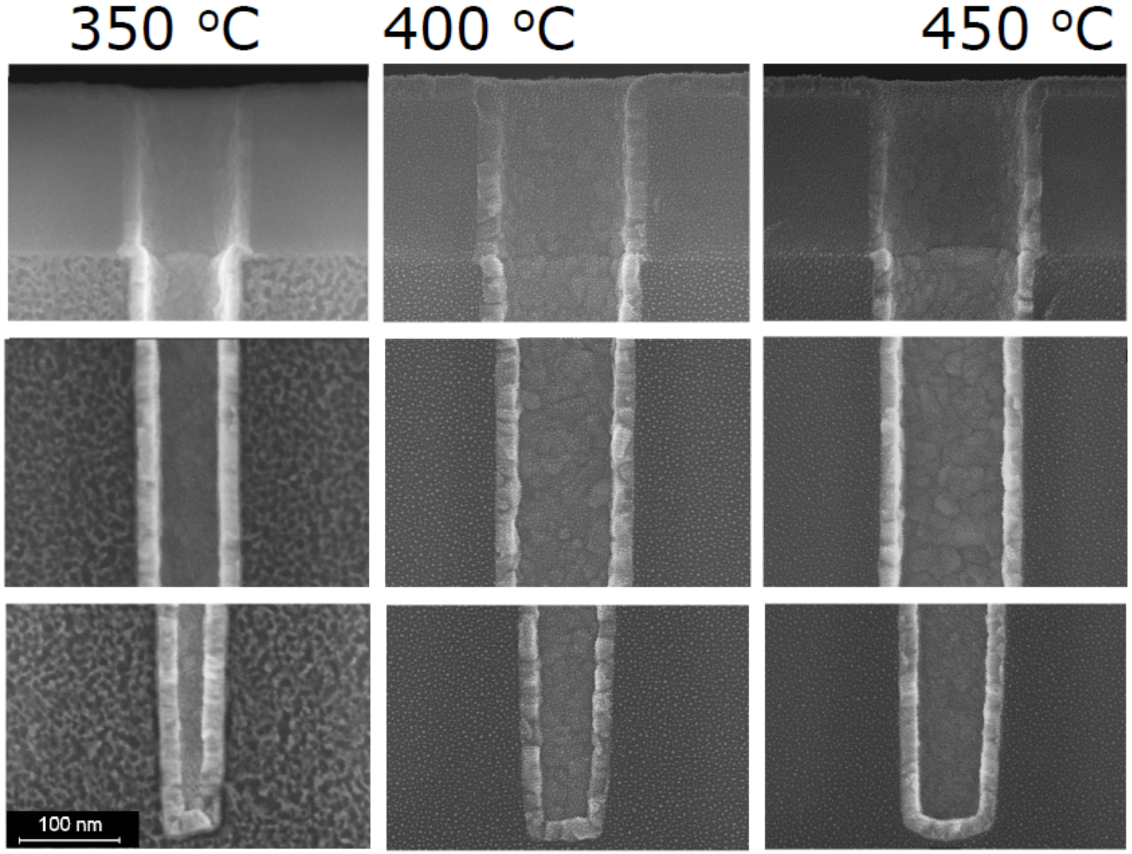


Al_2O_3/TiO_2 nanolaminate



TiN barrier

Step coverage (2)



Step coverage good also in high aspect ratio grooves,

BUT pulse lenghts have to to be increased

(in coating porous materials, pulses last for minutes !!).

Structure:
amorphous vs. polycrystalline ?

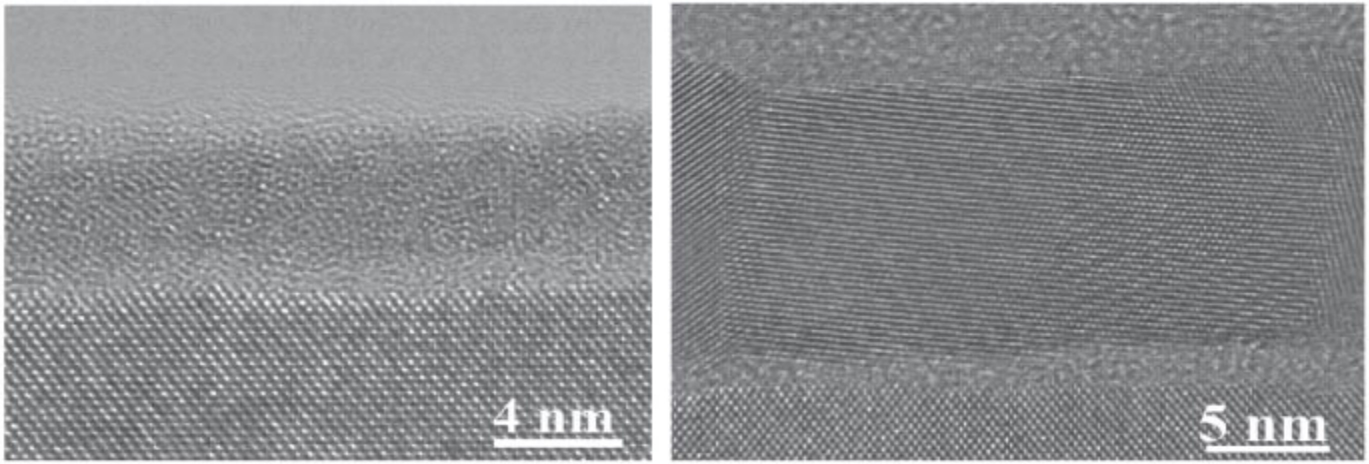
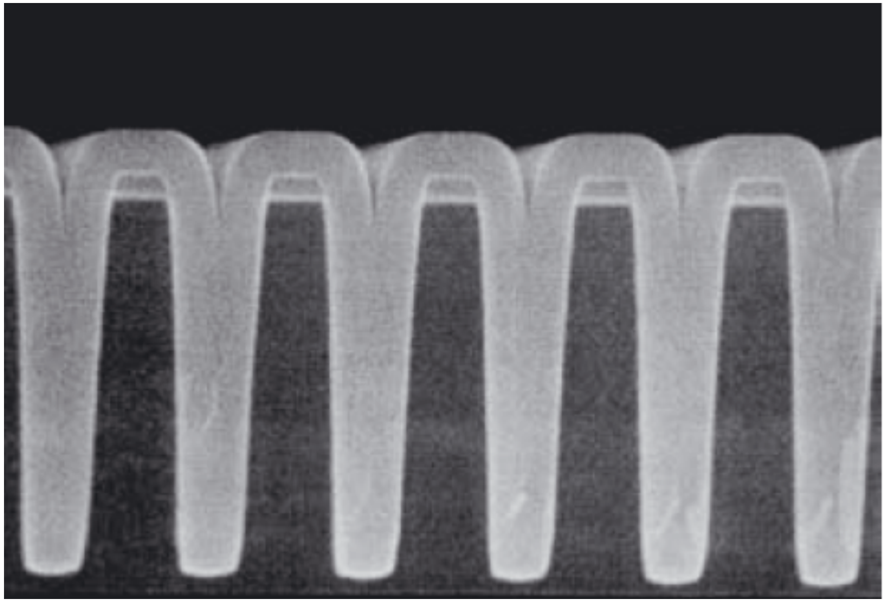


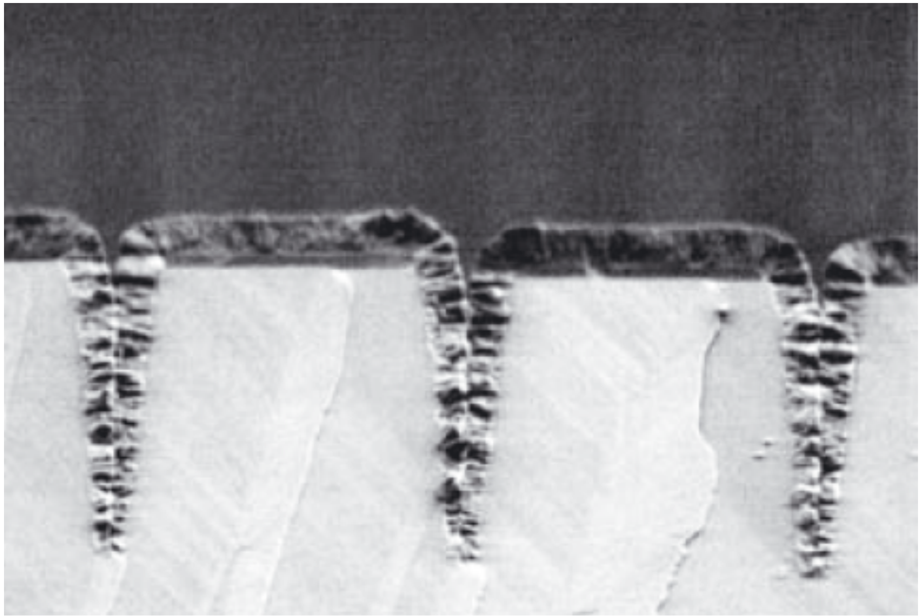
Figure 26-13

ALD ZrO_2: the 4 nm thick film is amorphous but the 12 nm thick film is polycrystalline. Reproduced from Kukli *et al*. (2007), copyright 2007, Elsevier.

Crystallinity



amorphous aluminum oxide



Polycrystalline strontium titanate

Vehkamäki *et al.* (2001)

Materials deposited by ALD

Nitrides	AlN TaN_x NbN TiN MoN W_xN ZrN HfN GaN InN ...
Carbides	TiC NbC TaC ...
Elements	Pt Ru Ir Pd Rh Cu Fe Mo Co Ni W ...
Sulfides	ZnS SrS CaS PbS ...
Fluorides	CaF_2 SrF_2 ZnF_2 MgF_2 LaF_3 ...
Oxides	Al_2O_3 TiO_2 Ta_2O_5 Nb_2O_5 HfO_2 ZrO_2 SiO_2 ZnO MgO La_2O_3 Y_2O_3 Sc_2O_3 Er_2O_3 V_2O_5 CeO_2 SnO_2 ....
Doping	ZnO:Al ZnS:Mn ZnS:Tb SrS:Ce CaS: Eu Al_2O_3:Er ZrO_2:Y ...
Nanolaminates	HfO_2/Ta_2O_5 TiO_2/Ta_2O_5 TiO_2/Al_2O_3 ZnS/Al_2O_3 ATO (AlTiO) HfO_2/TiO_2
Mixed structures	TiAlN AlHfOx AlSiOx HfSiOx TaTiCN ...

Important missing materials:

- silicon
- silicon nitride

ALD applications

1 nm thick catalysts (Pt, Pd)

2 nm thick TiN barrier layers underneath copper

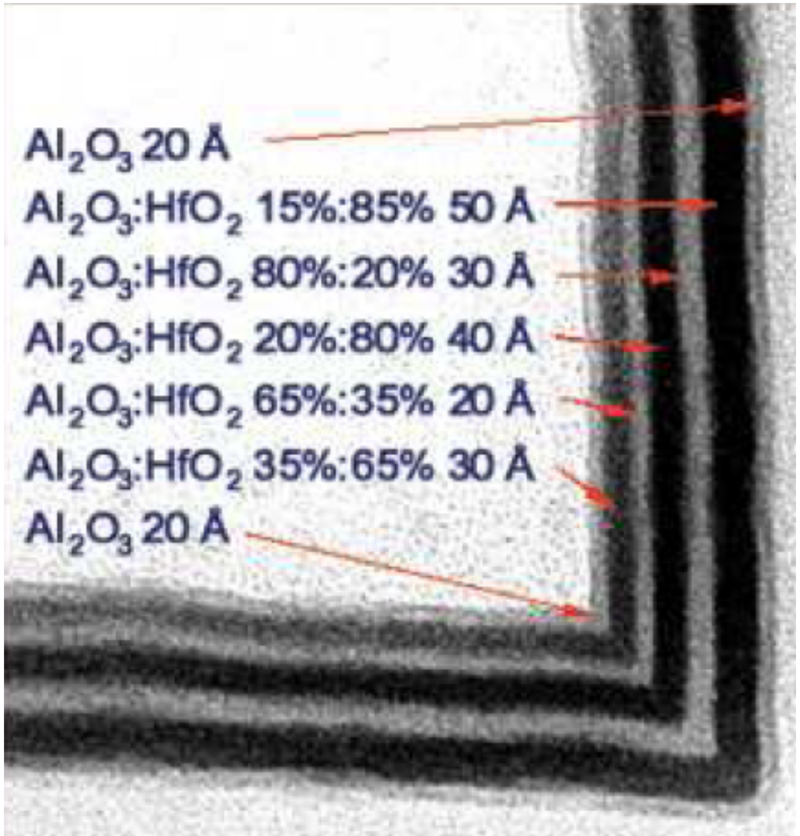
6 nm thick CMOS gate oxides like HfO_2

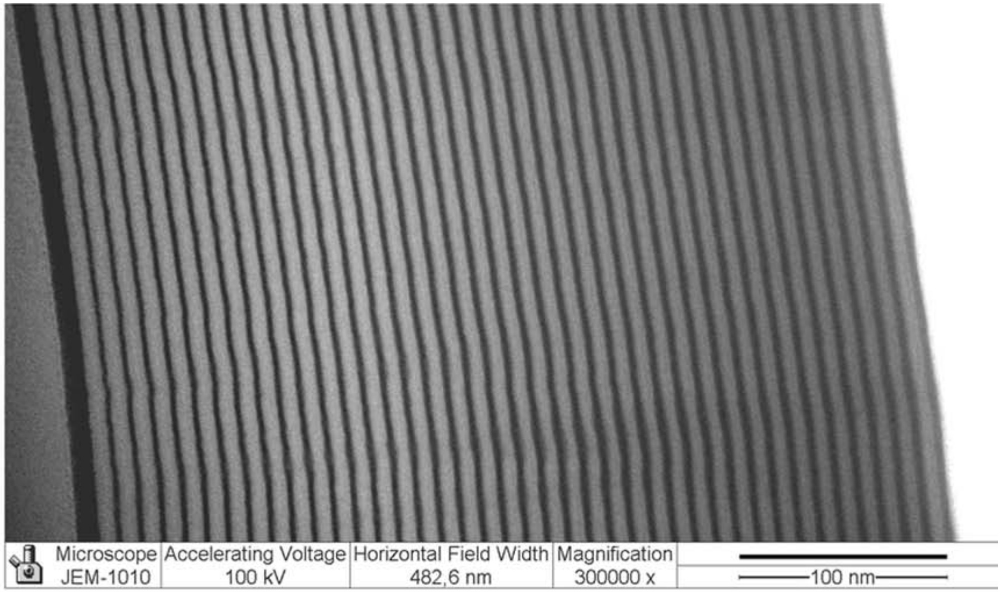
10 nm thick etch masks for plasma etching (Al_2O_3)

30 nm thick antireflection coatings in solar cells (Al_2O_3)

200 nm thick barrier layers in flat panel displays (Al_2O_3)

New materials: nanolaminates

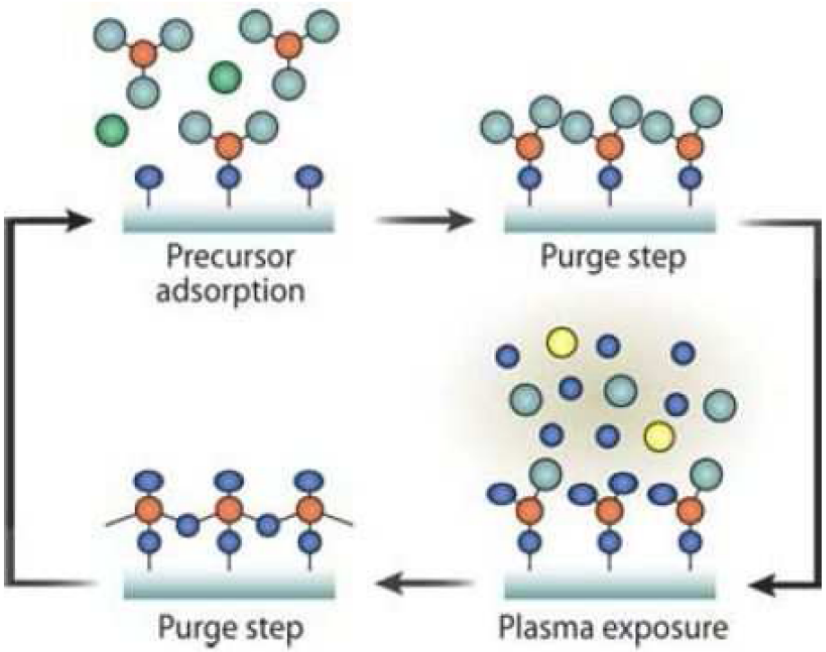


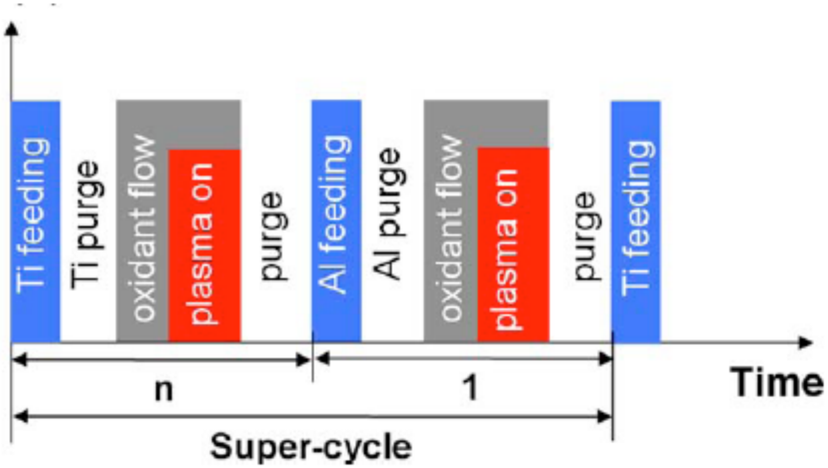


Al2O3 and Ta2O5

Adriana Szeghalmi,Stephan Senz,
Mario Bretschneider, Ulrich Gösele,
and Mato Knez, APL 2009

Plasma ALD (PEALD)





Gyu-Jin Choi, Seong Keun Kim,[a] Seok-Jun Won, Hyeong Joon Kim, and Cheol Seong Hwang[*,z]

Journal of The Electrochemical Society, **156** (9) G138-G143 (2009)

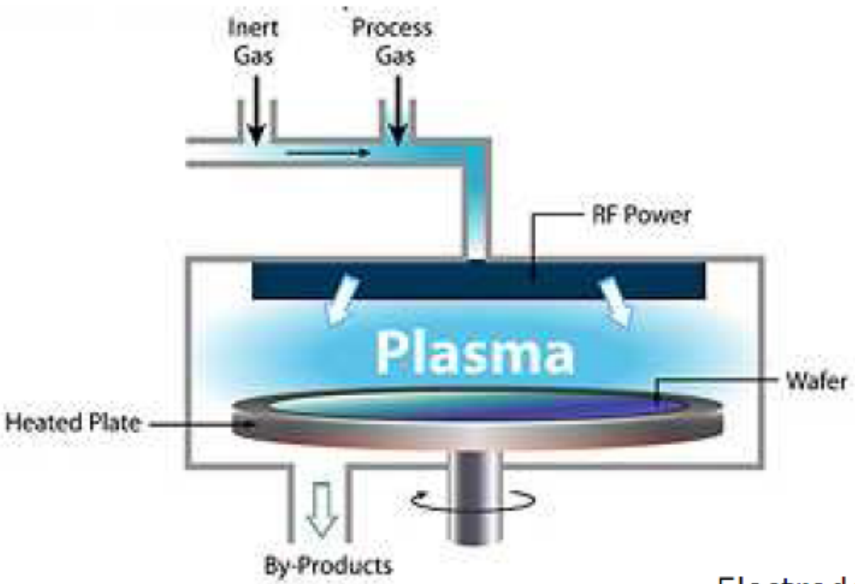
Plasma ALD benefits

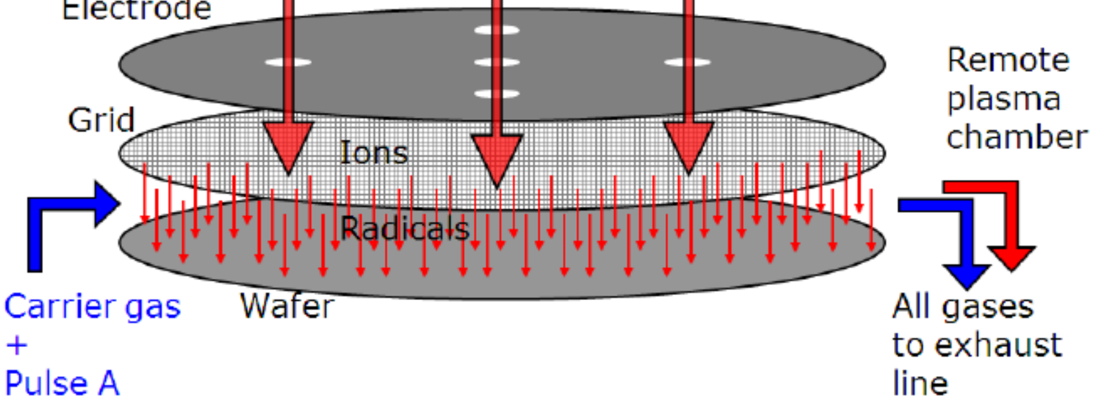
Plasma can break down precursors at lower temperature

New precursors become available because plasma can break down precursors that could not be used in thermal ALD

Ions can kick of loosely bound specie from surface, densifying the film

PEALD equipment





ALD process development

A new microprocessor
with a new gate dielectric

- 2 – 1 years

Gamma phase: a production system
10000 wafers without interruption

10-20 wafers/h

- 3 – 2 years

Beta phase: Only one deposition process for each module in an integrated system, production specs, 1000 consecutive wafers, <1% (1sigma or even 3 sigma)

- 4 – 3 years

Alpha phase: Integrated system 300mm, close to production system, only one deposition process for each module, complete process flow, 250 wafers (minimarathon), less than 10 particles < 0.075um, 2% (1 sigma)

- 6 – 5 years

Concept and feasibility: Scale-up of the precursor synthesis (50-100g), 1 to 3 different precursor chemicals, designed precursor vessel, process studies: 25 consecutive wafers (200-300mm), low particle counts, uniformity less than 5% (1 sigma), real device.

- 10 – 7 years

Exploring phase: Universities and research institutes, chemical suppliers: Development and synthesis of a number of new precursors and first ALD process studies on small substrates.

PVD	CVD & ALD
Atoms as source material	Molecules as source materials
Solid source materials	Solid, liquid, gas precursors
Vacuum/high vacuum	Fluid dynamics important
Elemental films mostly	Molecular/compound films mostly, Chemical bonds broken & formed
Room temperature	Needs elevated temperatures (or plasma activation)
Alloy films easily (W:N)	Elements and compounds OK, alloys more difficult
One process, many materials	Each process materials specific
Al, Au, Cu, Pt, … SiO_2	SiO_2, Si_3N_4, Al_2O_3, HfO_2, … Si, W

Summary

- Thermal CVD: excellent film quality
- PECVD: reasonable film quality at low T
- ALD: excellent film quality at low T

- Thermal CVD: high temperature needed
- PECVD: very high rate possible
- ALD: best for very thin films