

CVD & ALD

(2 hour set for 2023 TFT-course)

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First lecture: CVD

Gas phase
convection

How are gases introduced into a reactor
and how do they flow?

Diffusion through
boundary layer

Basic physics of boundary layer;
LPCVD (Low Pressure CVD);
and how this affects reactor design

Surface processes:

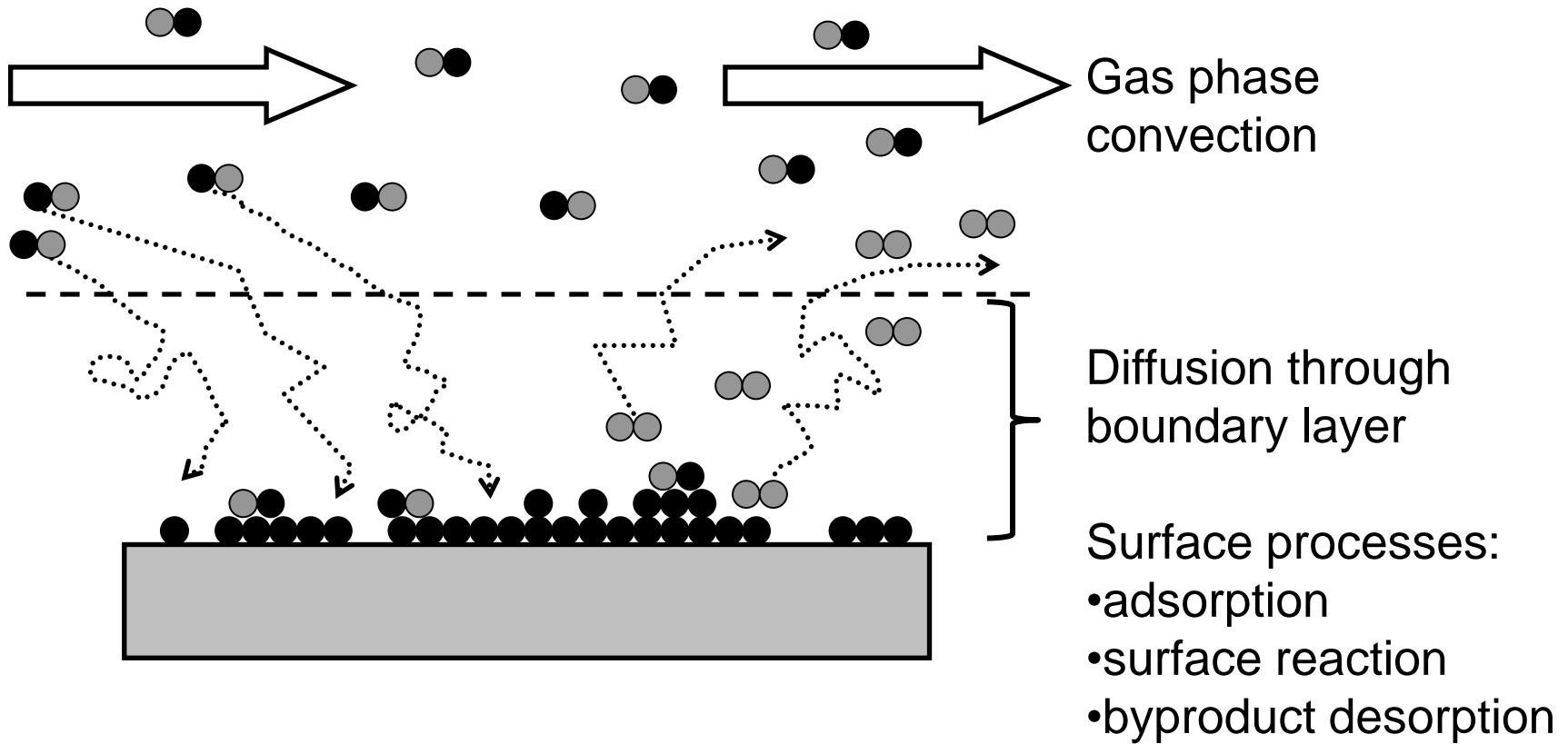
- adsorption
- surface reaction
- byproduct desorption

Not so much on surface processes
(but a lot in case ALD)

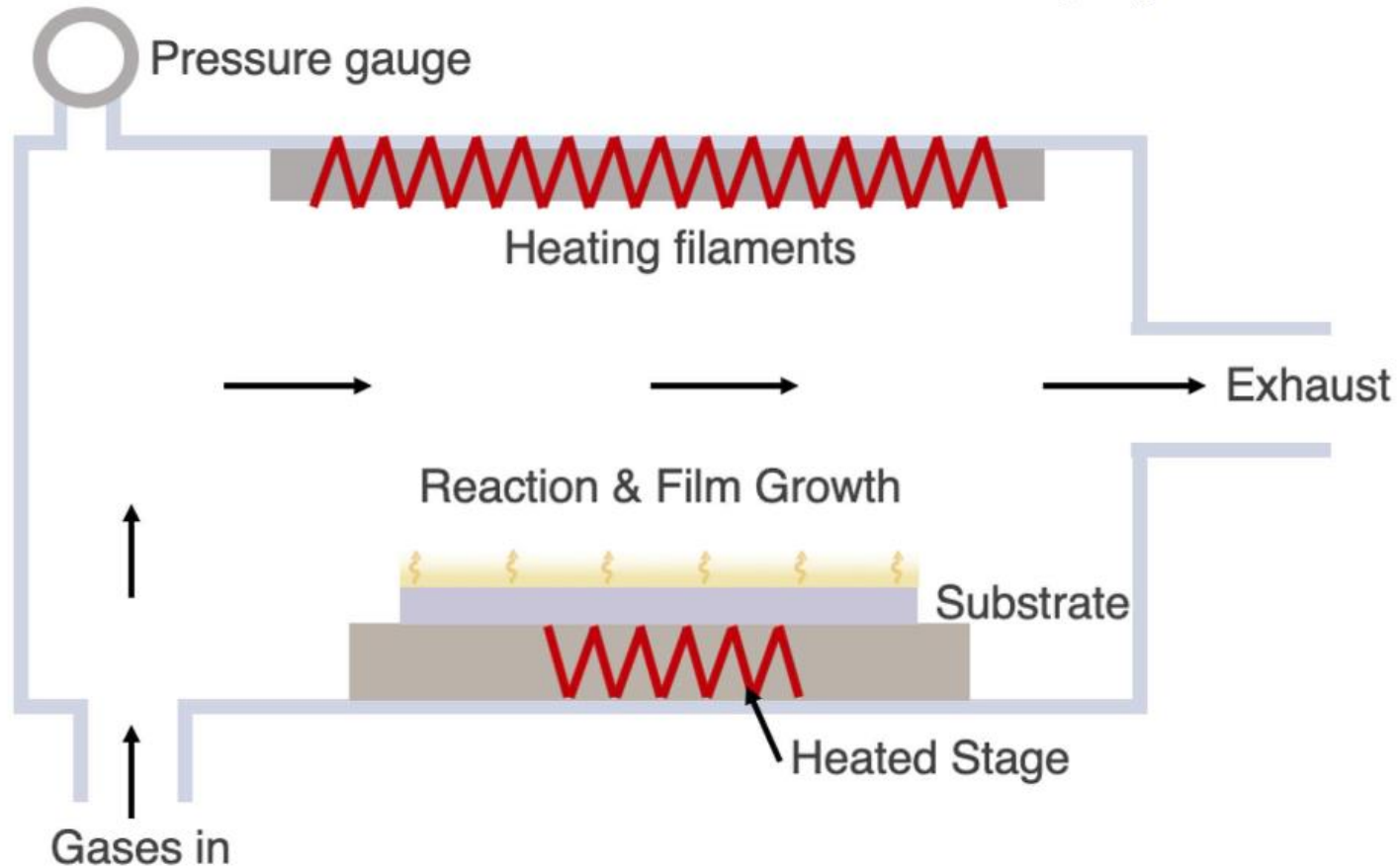
The resulting film

Factors affecting the film structure
Measures of film quality

CVD schematically

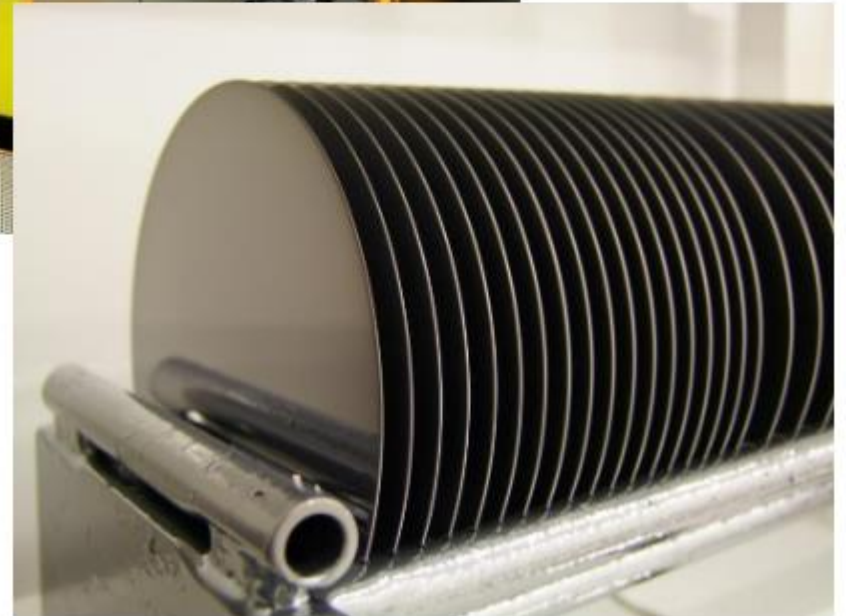


Simple CVD reactor

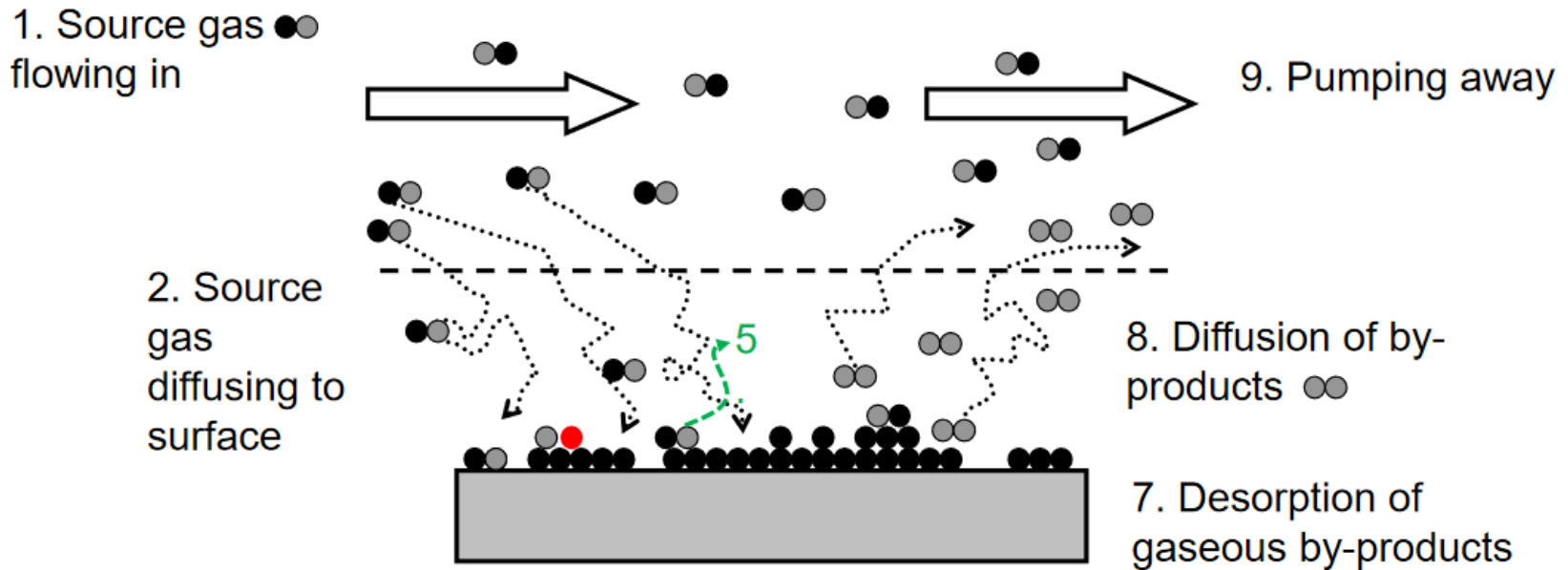




Micronova cleanroom,
CVD (and thermal
oxidation tubes).



CVD: atomic scale



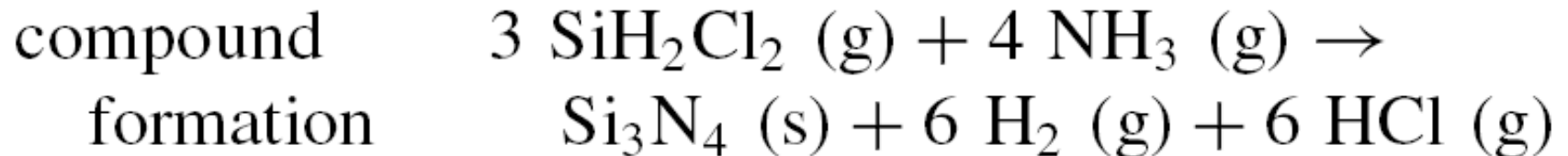
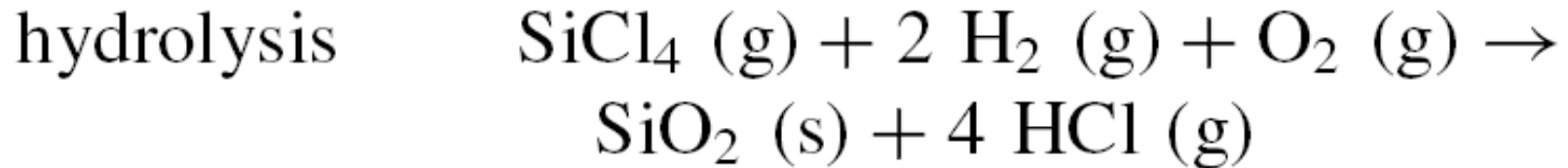
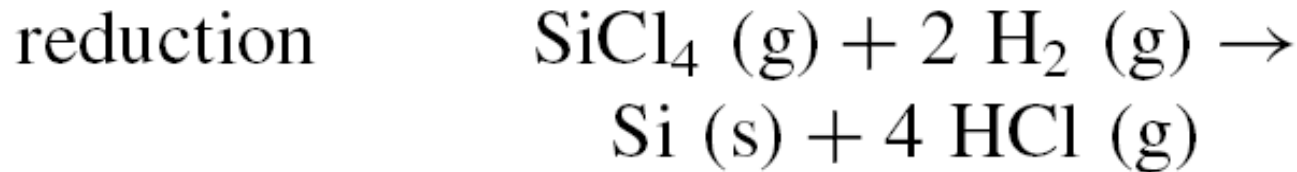
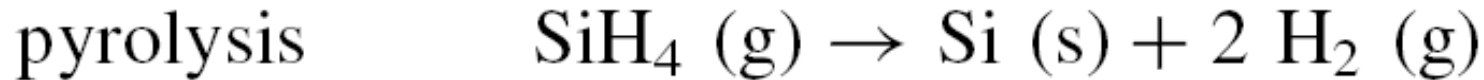
3. Adsorption on surface **6. Surface chemical reaction \approx deposition**

4. Surface diffusion if T high enough

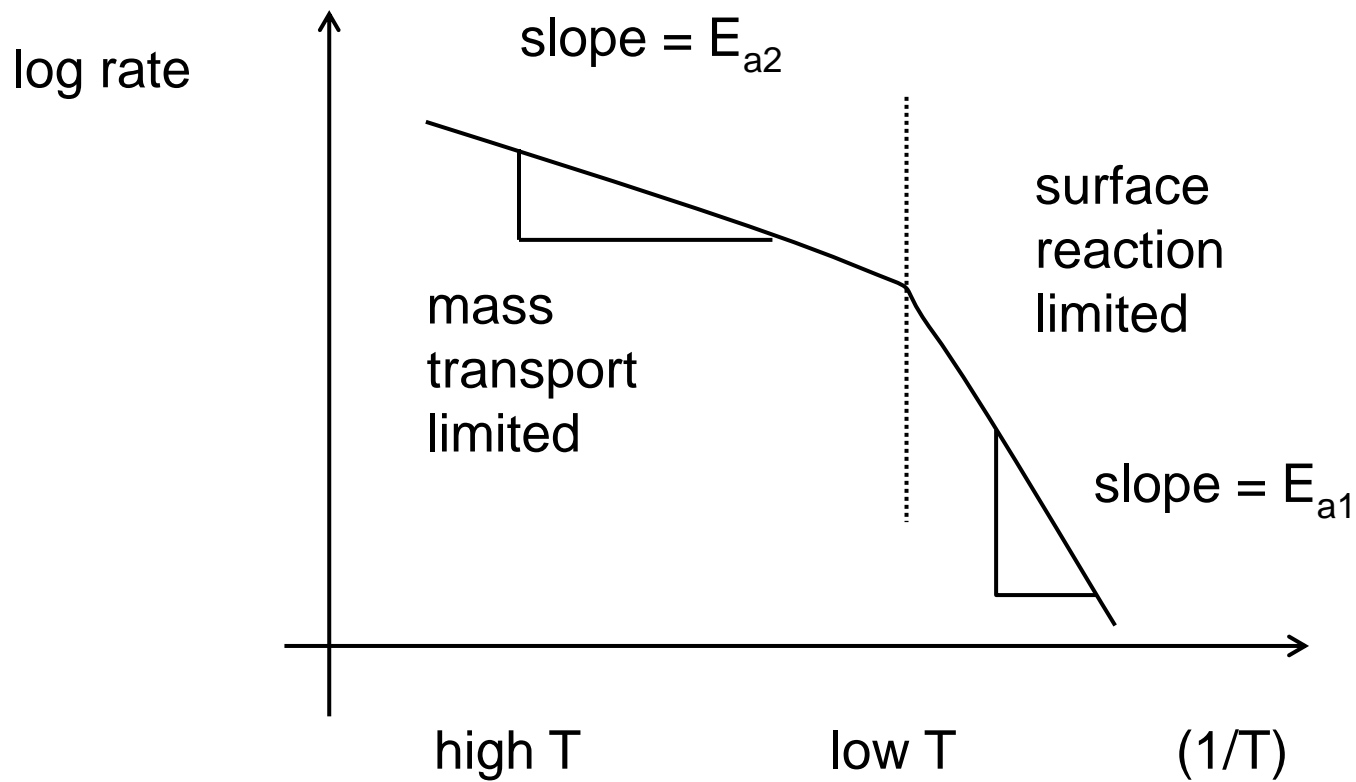
5. Desorption of some source gas molecules (sticking coefficient is <1)

Thermal CVD reactions

Gaseous precursor + surface reaction
→ solid film + gaseous byproducts



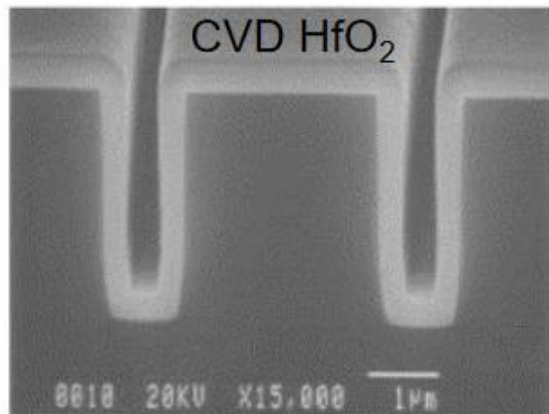
Surface limited vs. mass transport limited reactions



Surface controlled reaction

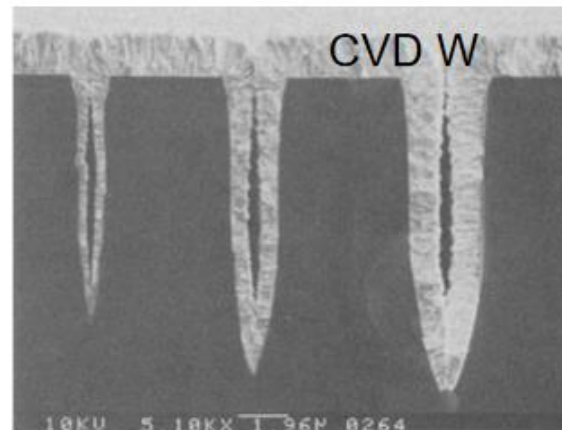
Slow reaction rate (e.g. due to low temperature). Lots of gas available, and only a fraction of it reacts.

All surfaces are exposed to the same gas concentration (because gas has time to diffuse around) → good uniformity and good step coverage.



(d) 450°C

Ohshita et al: *Journal of Crystal Growth*
Volume 235, Issues 1–4, February
2002, Pages 365-370



Note that narrow trenches get clogged and form a “keyhole”

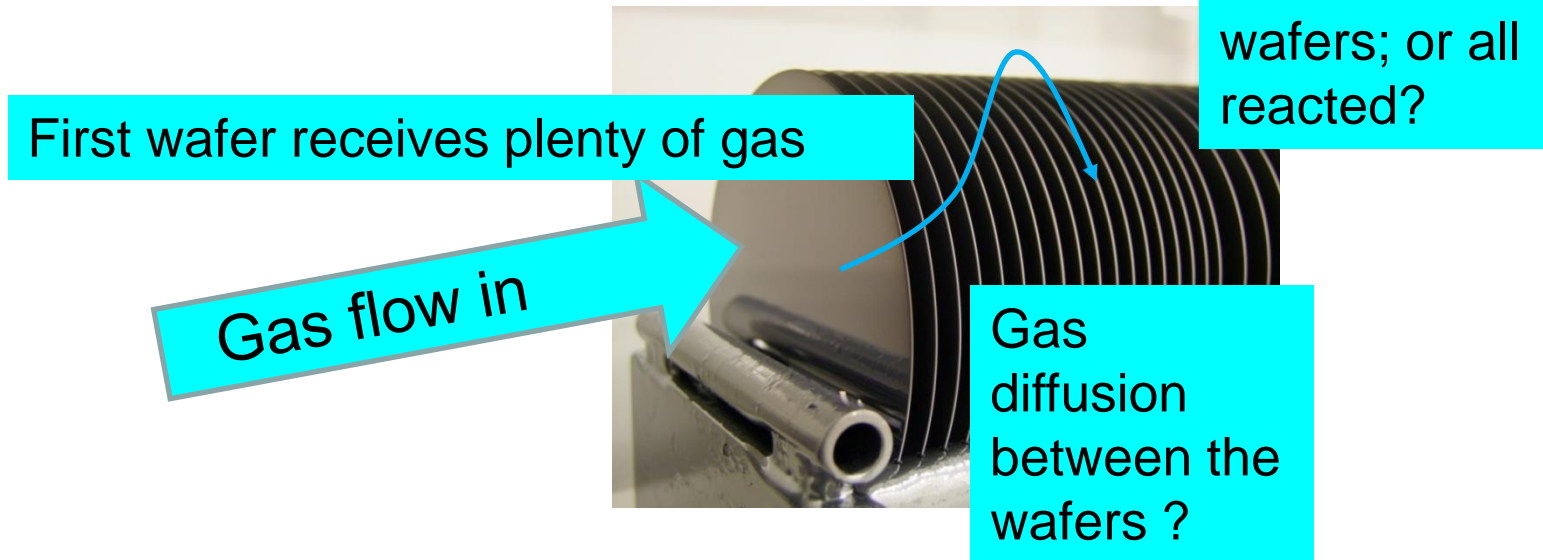
Hasper et al: *J. Electrochem. Soc.*, Vol.
138, No. 6, June 1991

Mass transport limited reaction

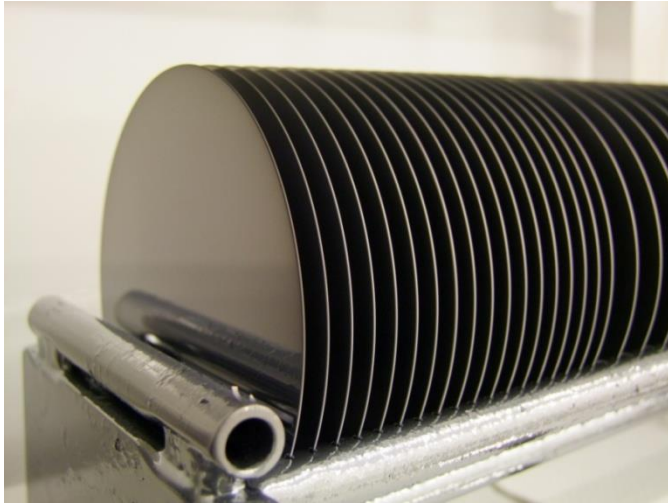
Reaction rate is very fast at high temperatures
(Arrhenius: rate is exponentially temperature-dependent).

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.



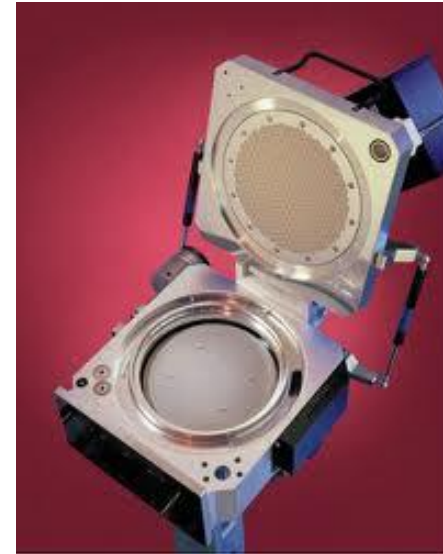
Surface limited vs. mass transport limited reactions



Surface reaction limited mode:

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

Batch reactors



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

Rate modeling

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

Diffusion of precursor gas from main flow to the surface.

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

Boundary layer thickness δ .

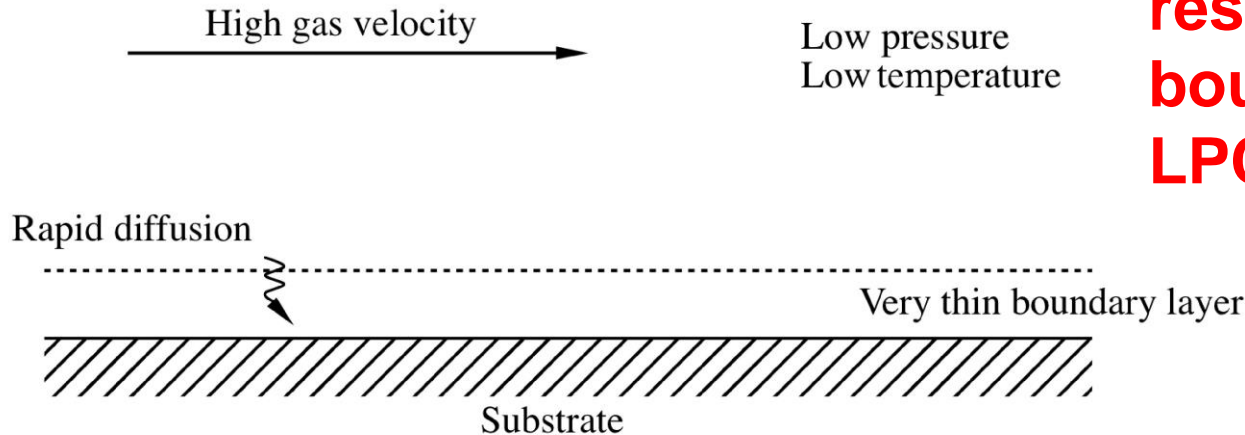
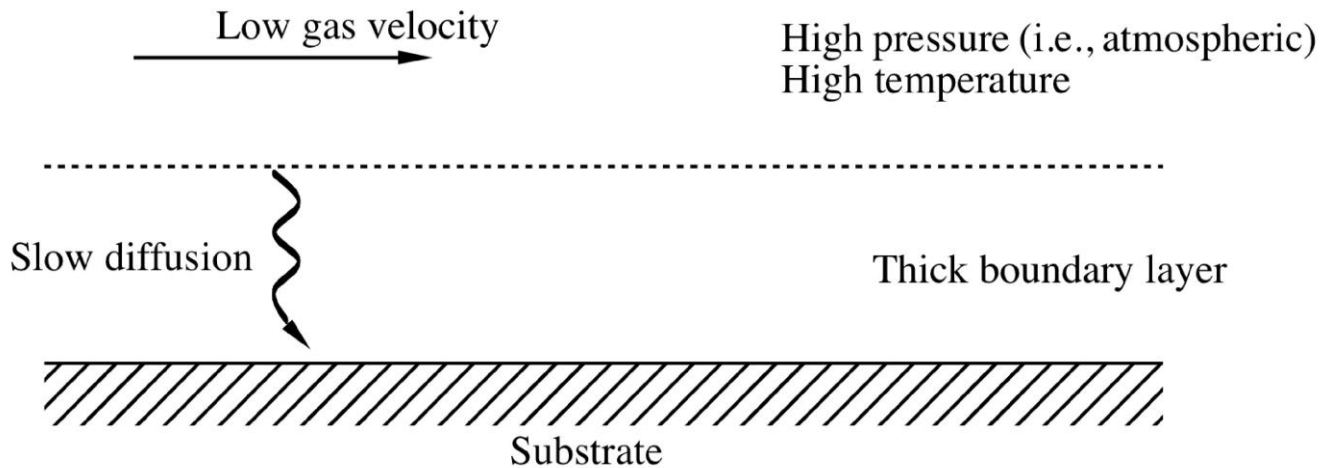
Raising temperature \rightarrow small changes in density, velocity and viscosity

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

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

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

Boundary layer thickness



These variables result in thin boundary layer → LPCVD reactor

CVD reactors are classified by their operating pressure range:

- atmospheric pressure, APCVD
- sub-atmospheric, SACVD 10-100 Torr
- low-pressure, LPCVD at ~Torr
- ultra-high vacuum, UHV-CVD, 10^{-6} Torr base pressure
- In UHV reactors the actual process pressures are 1-10 mTorr when gases are flowing, very much like magnetron sputtering systems. In both cases good base vacuum (of 10^{-6} – 10^{-9} Torr level) is mandatory for removal of residual gases from the chamber.

How are CVD processes developed ?

What reactor parameters to vary ?

What film quality targets ?

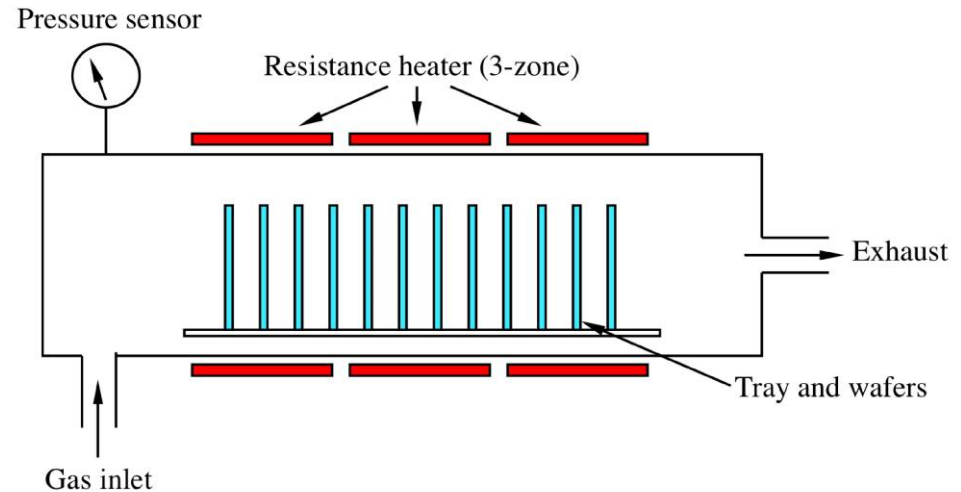
Film quality measurements ?

What productivity targets?

Case: LPCVD polysilicon



- Pressure
- Flow rate
- Temperature
- Source gas purity
- Reactor vacuum (residual gases, leaks)
- Reactor cleanliness (particles)



Targets

Film:

- Crystalline structure (e.g. grain size, orientation)
- Atoms & bonds (e.g. Si-Si bonds vs. Si-H; dangling bonds Si-*)
- Key parameters (t , R_s , n_f , ϵ , ...)
- Uniformity (of thickness & other parameters)
- Impurities and defects

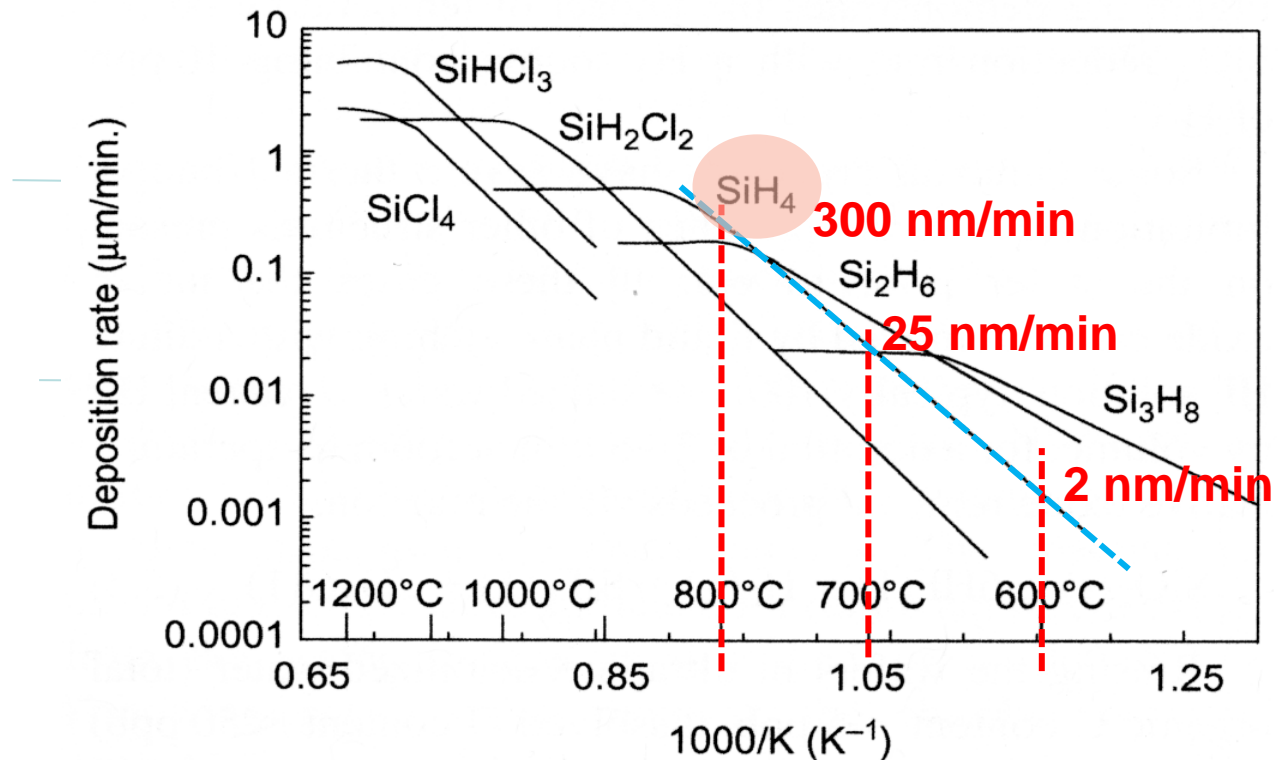
Productivity:

- Deposition rate (in units nm/min)
- Thruput (in units wafers/hour = WPH)
- Reproducibility (run-to-run; day-to-day)
- Yield (particles, out-of-specification thickness...)

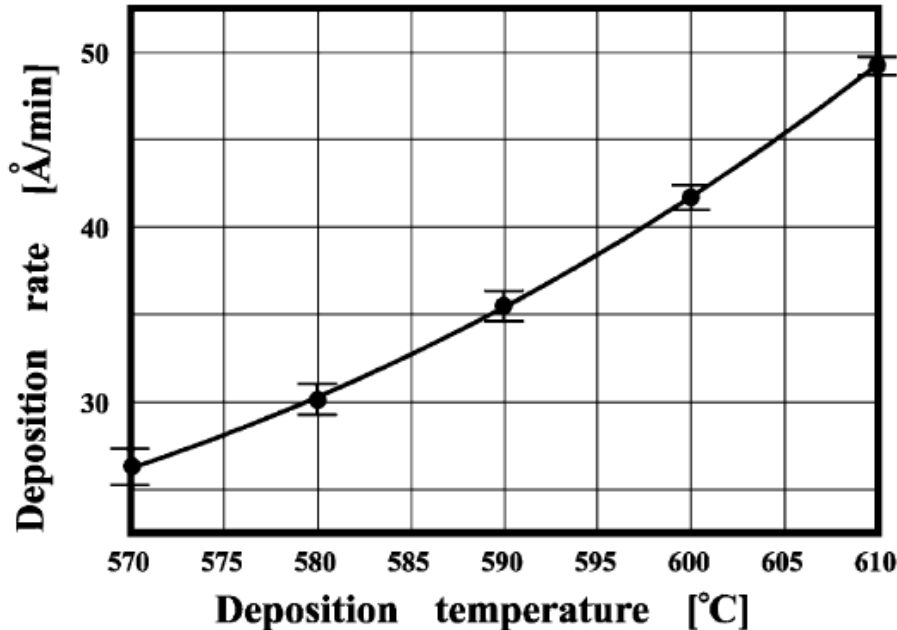
Deposition rate

Arrhenius behavior.

Below 800°C surface reaction controlled.



Deposition rate (2)



Undoped polysilicon

PH_3 dopant (\rightarrow PSG, phosphorous doped silica glass)

Phosphorous retards deposition rate via high rate adsorption of phosphorous which blocks adsorption sites for silane

BCl_3 dopant: (BSG)

Boron enhances deposition rate via unknown mechanism.

Also: PBSG

Structure and Properties of LPCVD Silicon Films

T. I. Kamins*

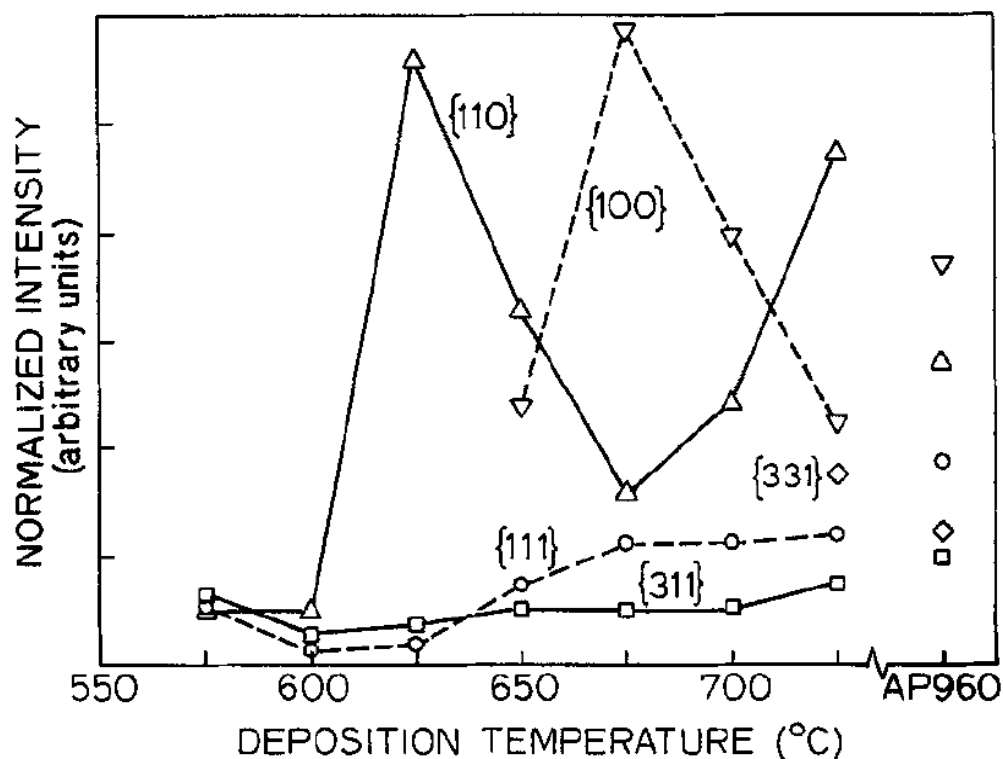
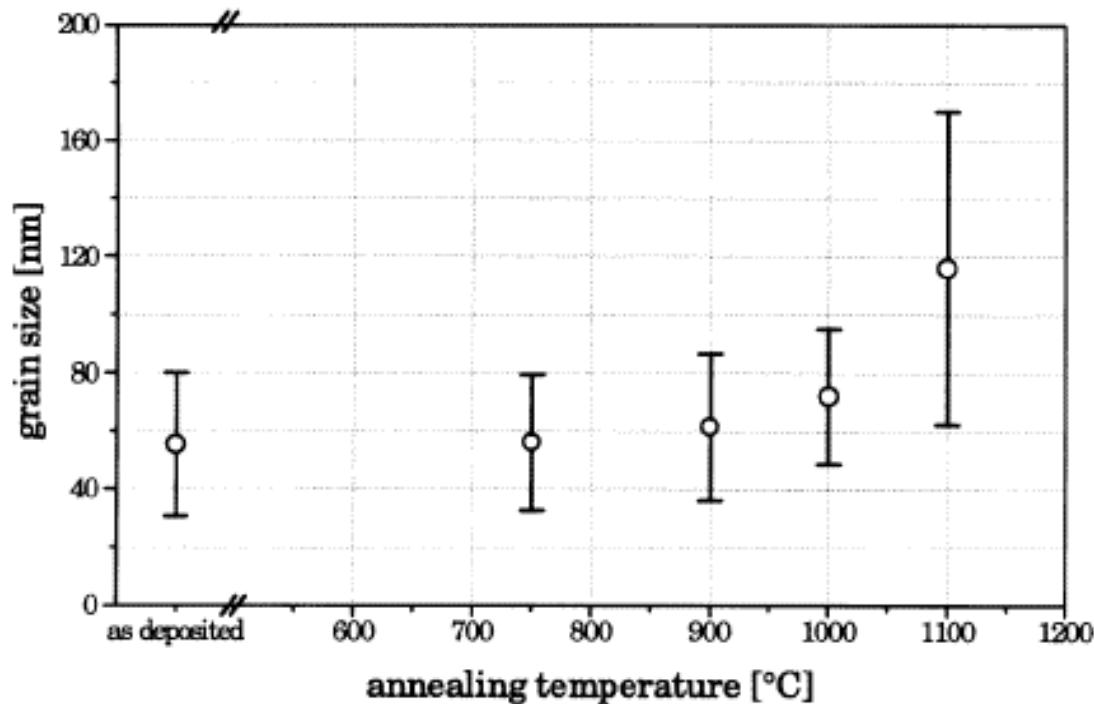


Fig. 1. X-ray texture as a function of deposition temperature for LPCVD silicon films and for an atmospheric pressure film.

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

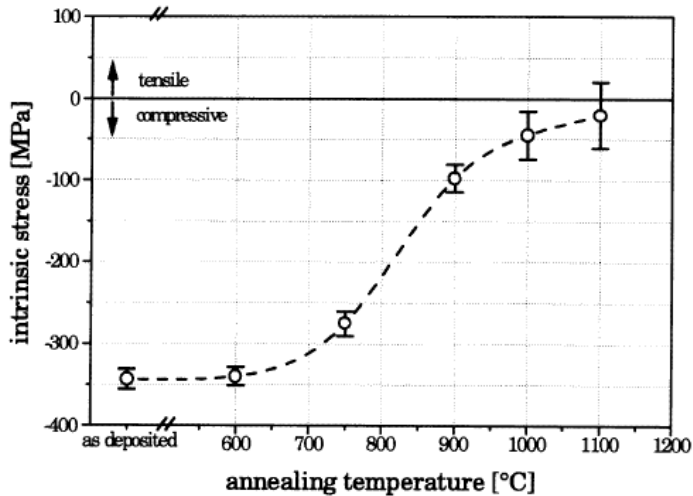
Temperature (°C)	Grain size (nm)
600	55
625	87
650	72
675	74
700	73
725	86

Deposition temperature affects grain size

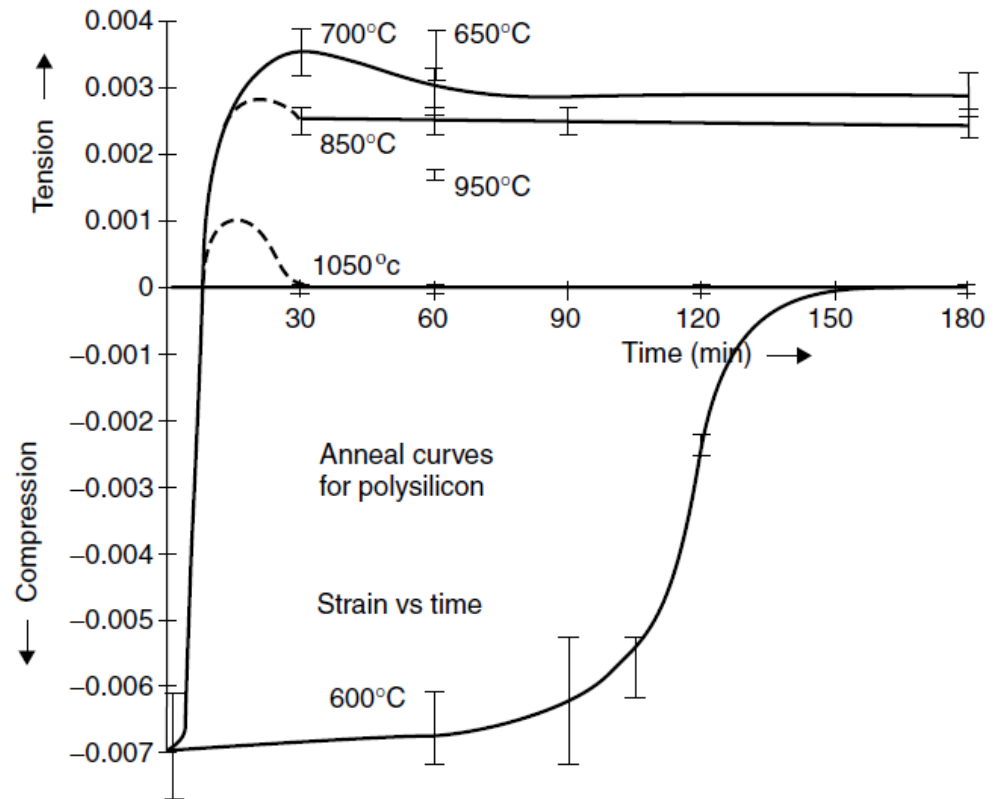


Post-deposition anneal affects grain size

Stress relief anneal



Stress reduction is anneal temperature and time dependent !



580°C deposition, i.e. amorphous initially

a-Si by LPCVD

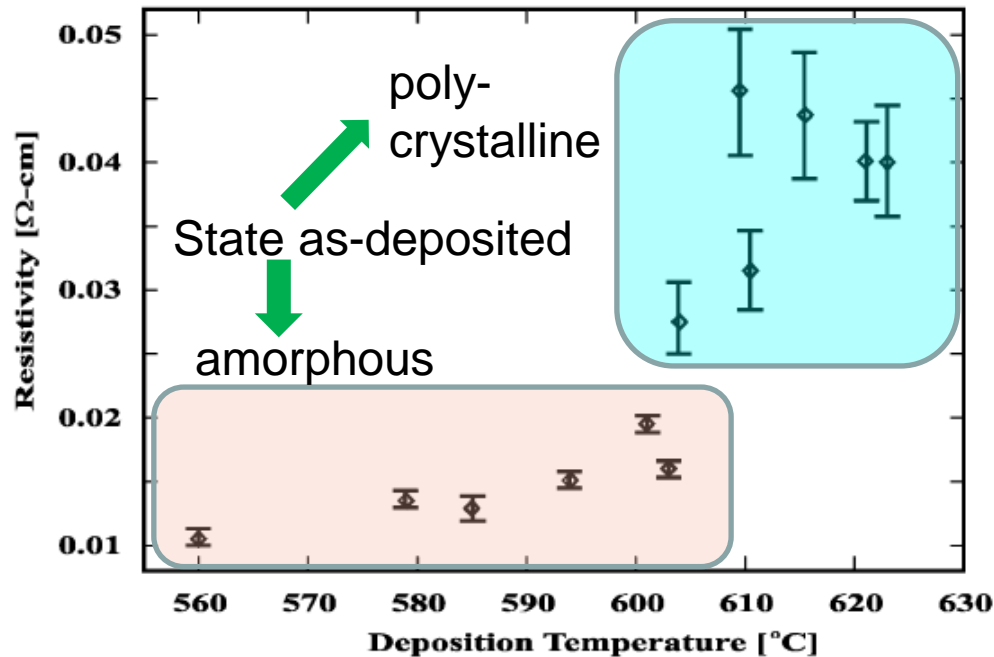
~600°C or lower deposition temperature the resulting film will be amorphous.

When amorphous film is annealed, it will behave differently from polycrystalline.

In polycrystalline film certain things are “frozen”, e.g. crystal directions.

Amorphous film can crystallize in whatever way it wants...

Doping of a-Si vs. poly

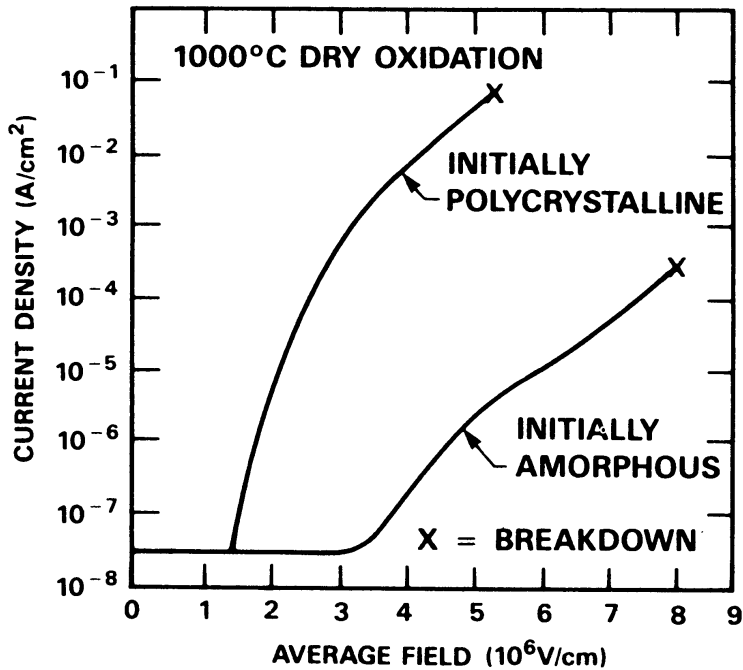


Resistivity after doping:

Ion implantation into film (1×10^{15} ions/cm²) and subsequent anneal (1000 $^{\circ}\text{C}$).

Why the difference ?

Grain boundaries trap dopant atoms; more available in initially amorphous film.

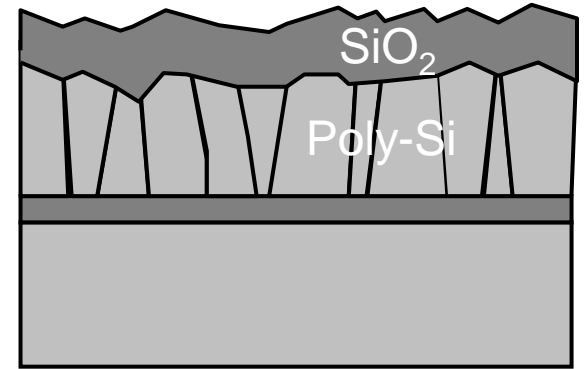
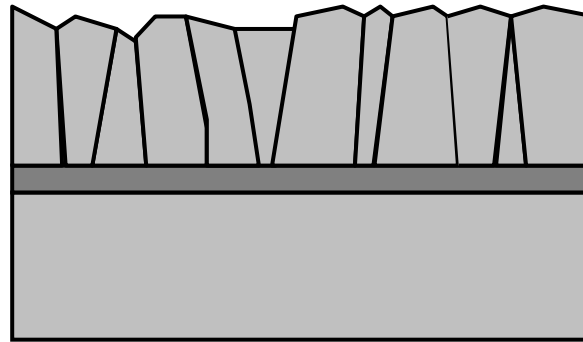
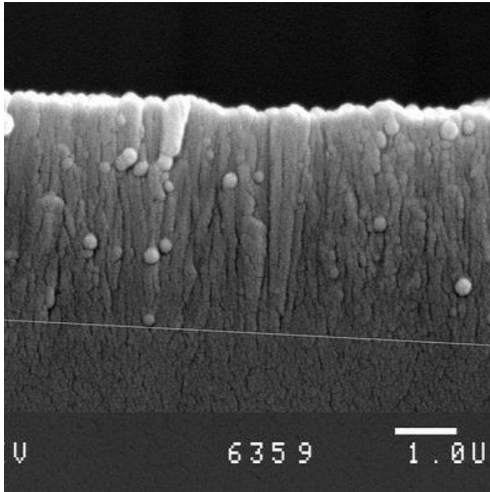


Breakdown field is a common measure of oxide film quality.

Why is initially amorphous film better in terms of oxide breakdown ?

Note: Oxide on monocrystalline silicon ca. 10 MV/cm

Poly oxidation (2)



- Polycrystalline film is rougher than amorphous film
- oxidized polycrystalline film has variable thickness (because grain orientation affects oxidation rate)
- electric field concentration at tips and thin points
- easy breakdown

Grain size & roughness

AFM:
surface roughness

$S_q=40\text{nm}$

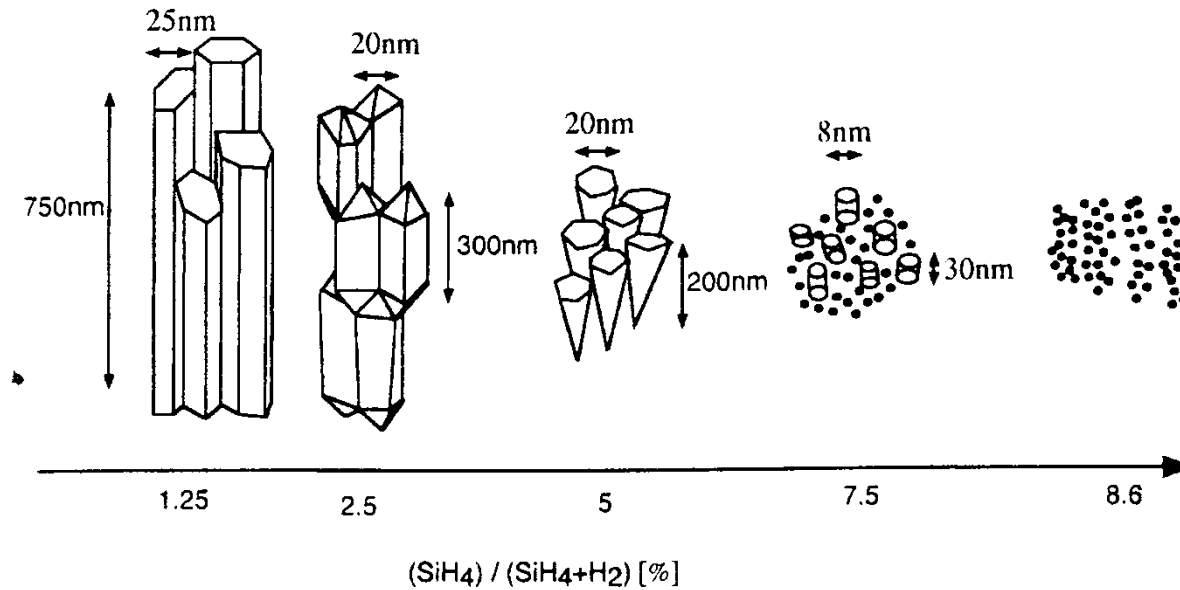
$S_q=18\text{nm}$

$S_q=17\text{nm}$

$S_q=16\text{nm}$

$S_q=4\text{nm}$

TEM:
size and shape of the grains

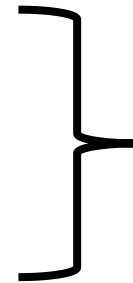


Polysilicon thin film vs. <Si>

Density: same 2.3 g/cm³

Young's modulus: same 170 GPa

CTE: same 2.5 ppm/K

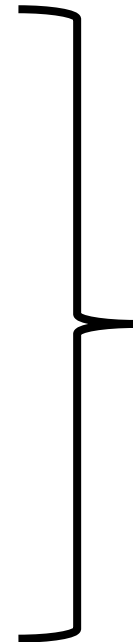


Affected by bond strength and length

Thermal conductivity:

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

poly 32 W/K*m



Affected by grain boundaries; electrons and phonons experience losses at boundaries

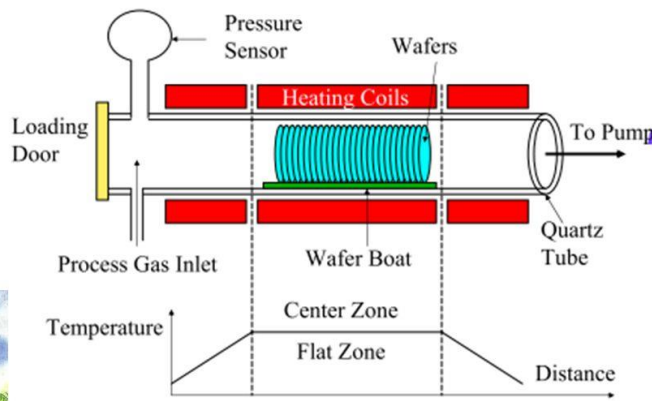
Carrier mobility:

<Si> 100 cm²/Vs

poly 10 cm²/Vs

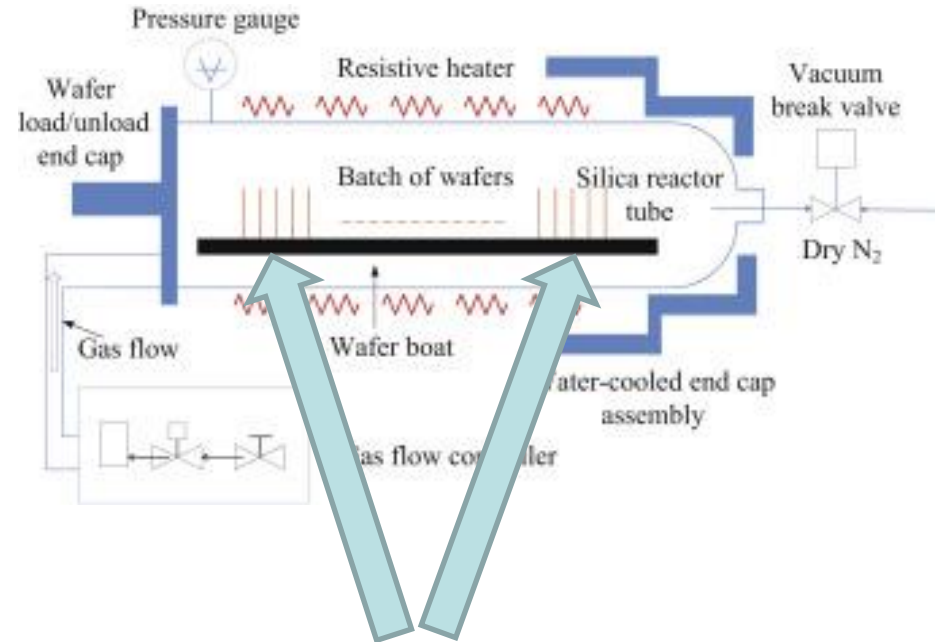
Temperature control zones

LPCVD System



Institute of Electro-Optical and Material Science

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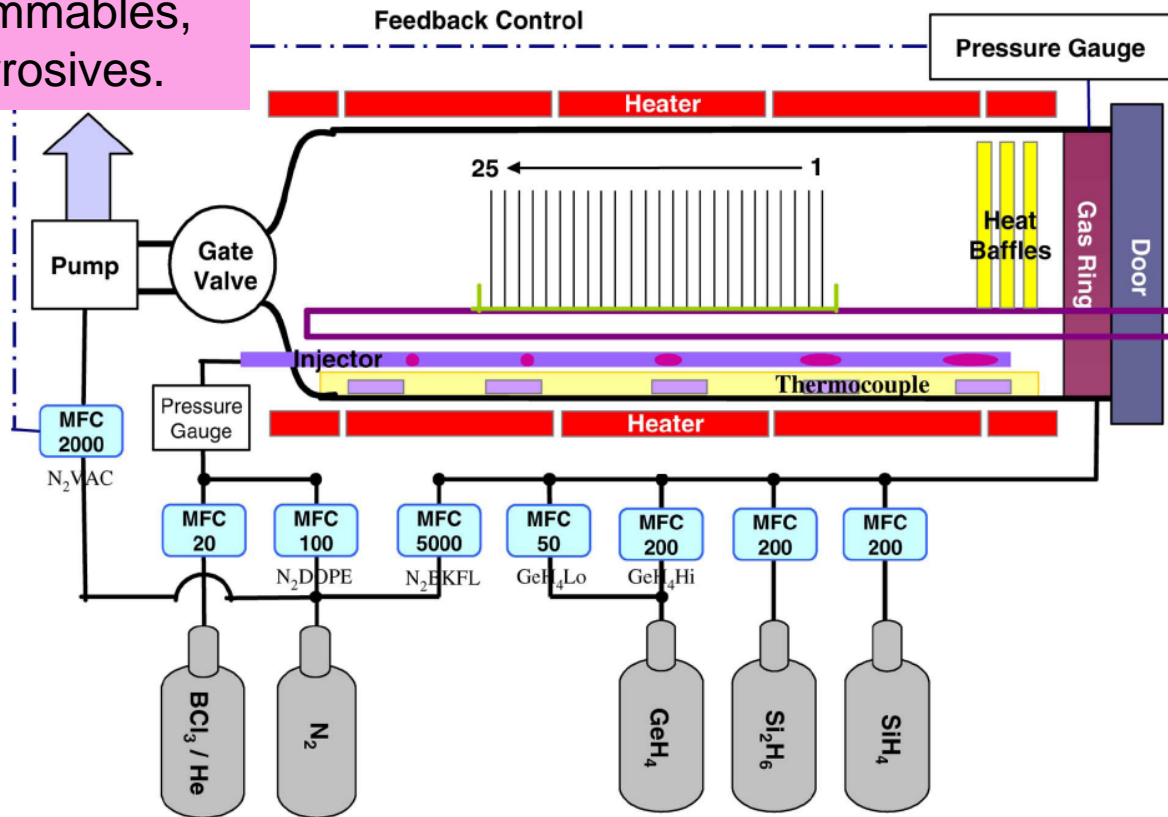


Multiple heater zones ensure flat temperature profile in the central section (maybe little higher in the ends to compensate).

Dummy wafers make sure end of tube thermal losses reduced.

LPCVD reactor

Gas abatement:
remove
toxics,
flammables,
corrosives.

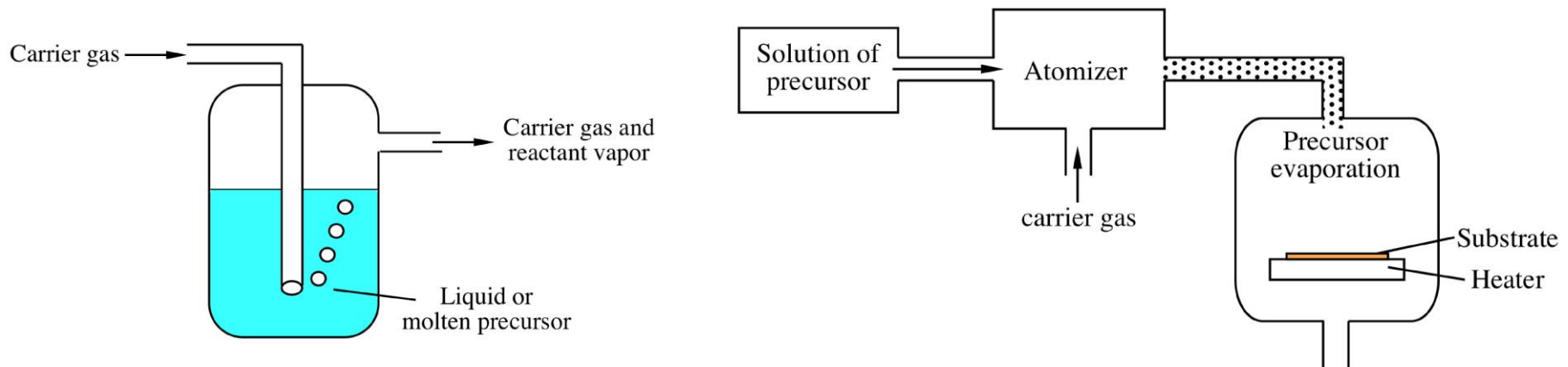
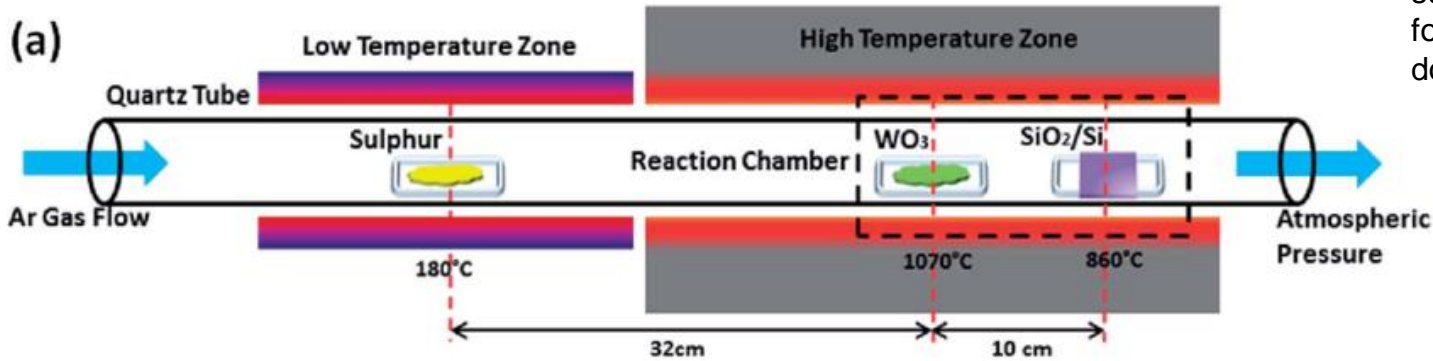


Gas injection:
from below,
from hundreds
of small
injector holes.

Mixing
different
processes in
the same tube
leads to cross-
contamination
(residues).

Solid and liquid precursors

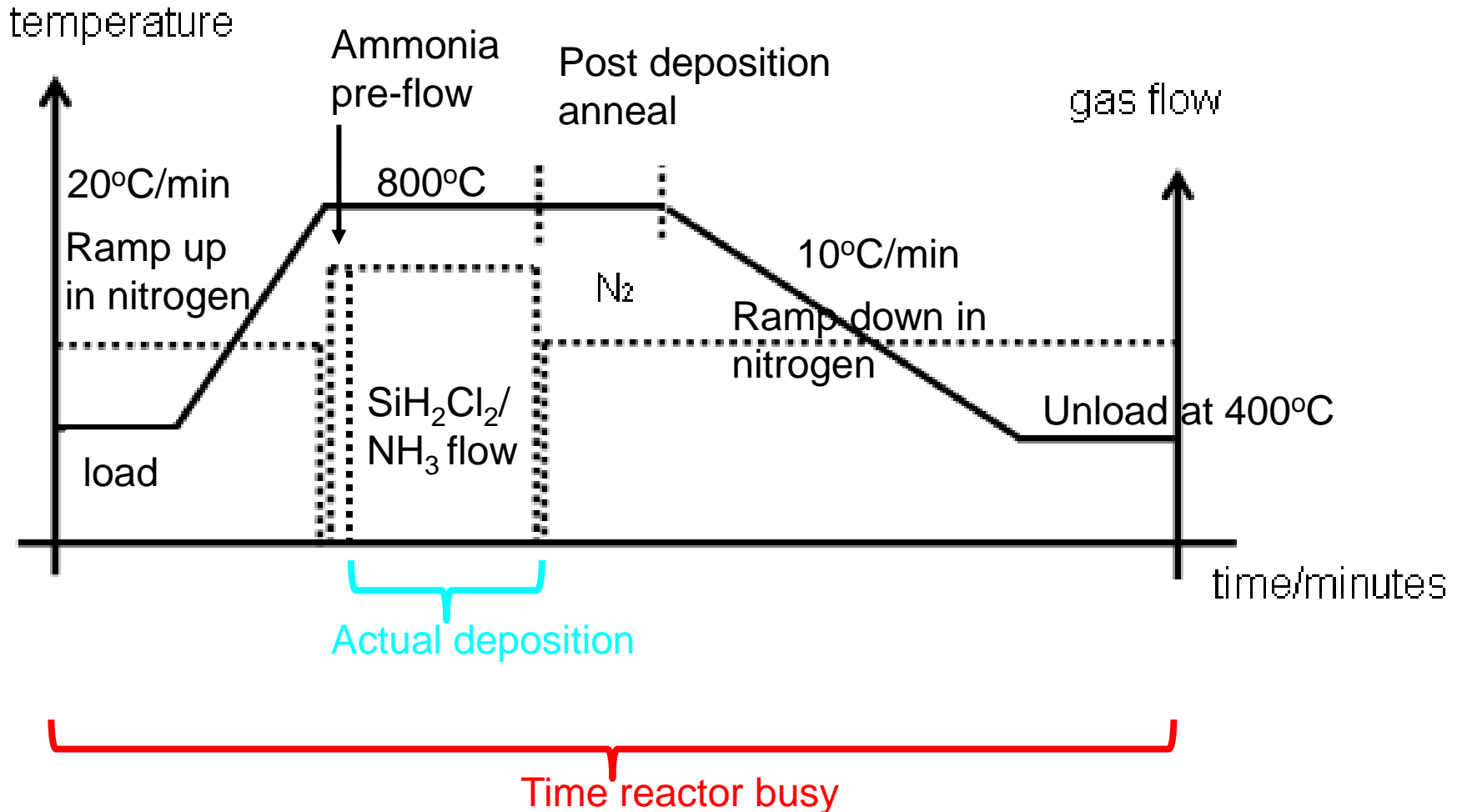
Rong et al: Controlling sulphur precursor addition for large single crystal domains of WS_2 , 2014



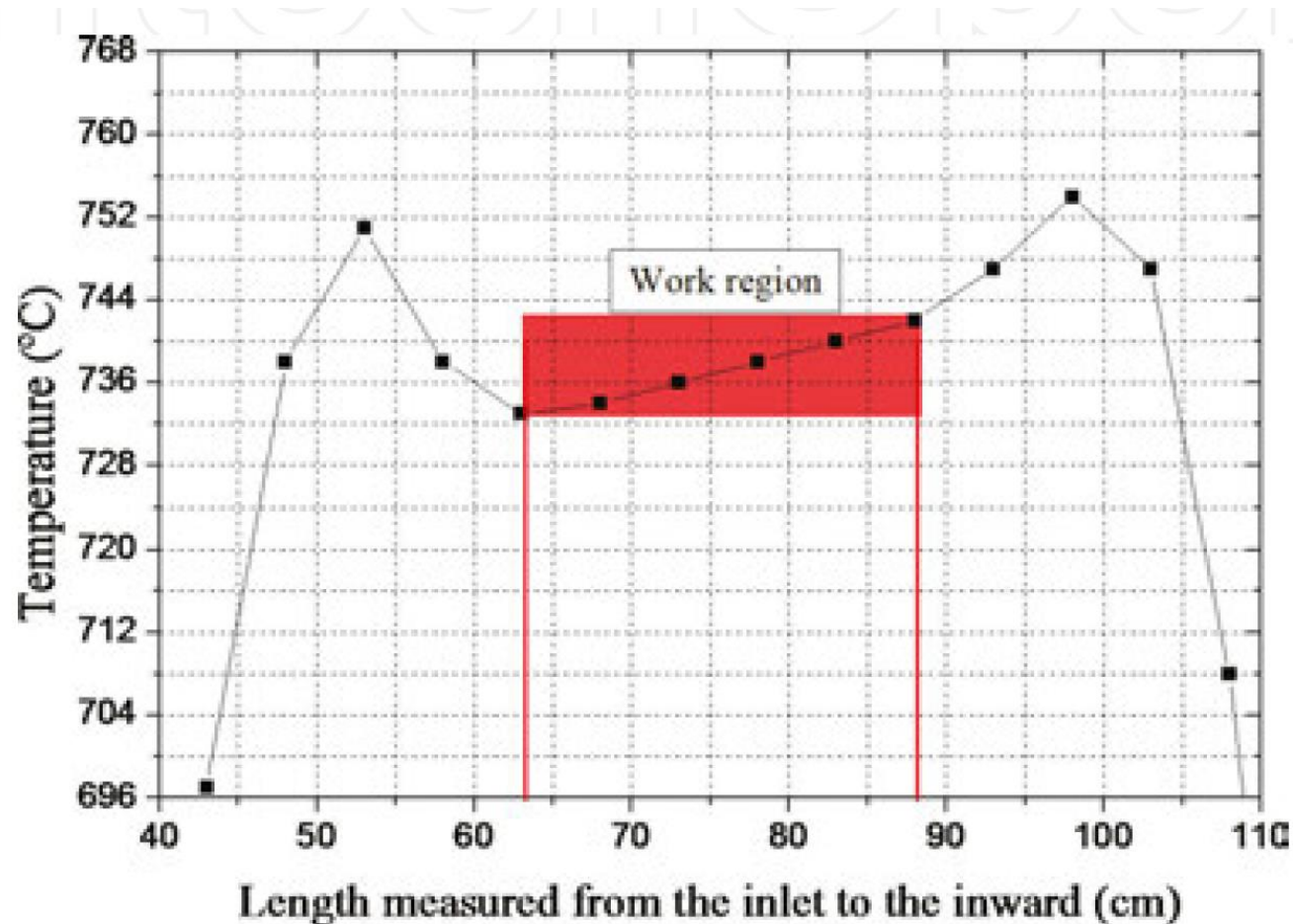
LPCVD of silicon nitride (Si_3N_4)

- Load the boat, fill with dummy wafers to equalize load and flow patterns.
- Ramp temperature from 500°C to 800°C under nitrogen flow, 50 min ($5^\circ\text{C}/\text{min}$)
- Pump to vacuum and perform leak check, 2 min
- Introduce ammonia NH_3 , stabilize flow at 30 sccm, for 1 min
- Introduce dichlorosilane SiH_2Cl_2 , flow 120 sccm, deposition starts
- Deposit at 300 mtorr for 25 min (4 nm/min deposition rate)
- Cool down to 700°C (10 min)
- **Take boat out**
- Monitoring: film thickness and refractive index by ellipsometer

Total cycle time: LPCVD nitride



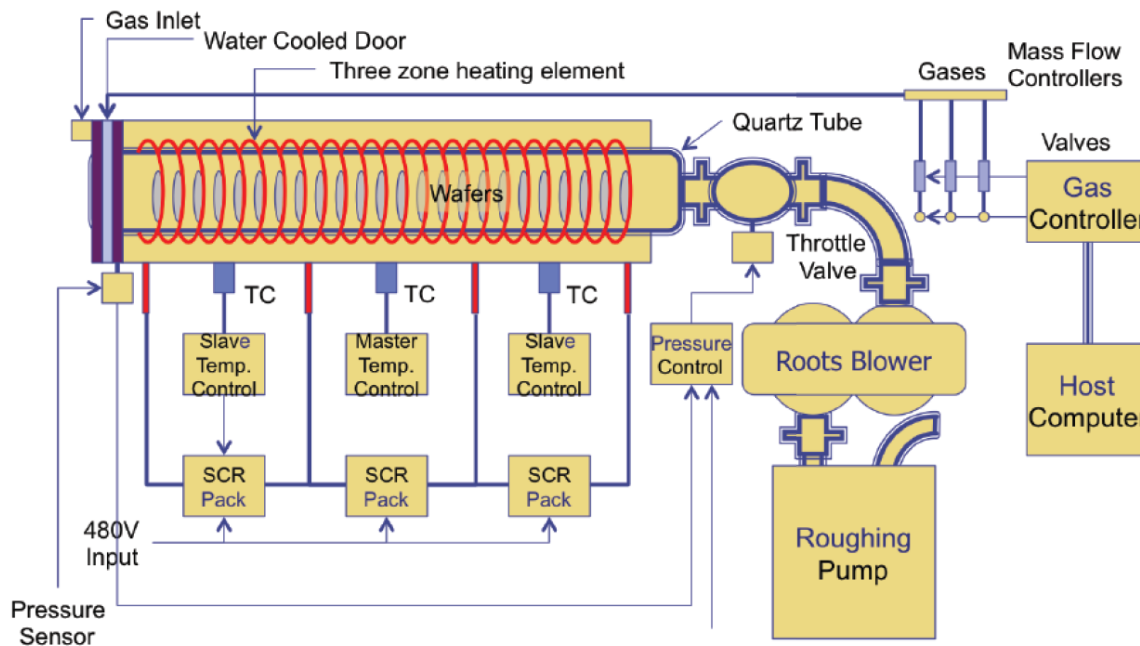
Real temperature profile



Range 9
degrees
!

Does 3-zone temperature work ?

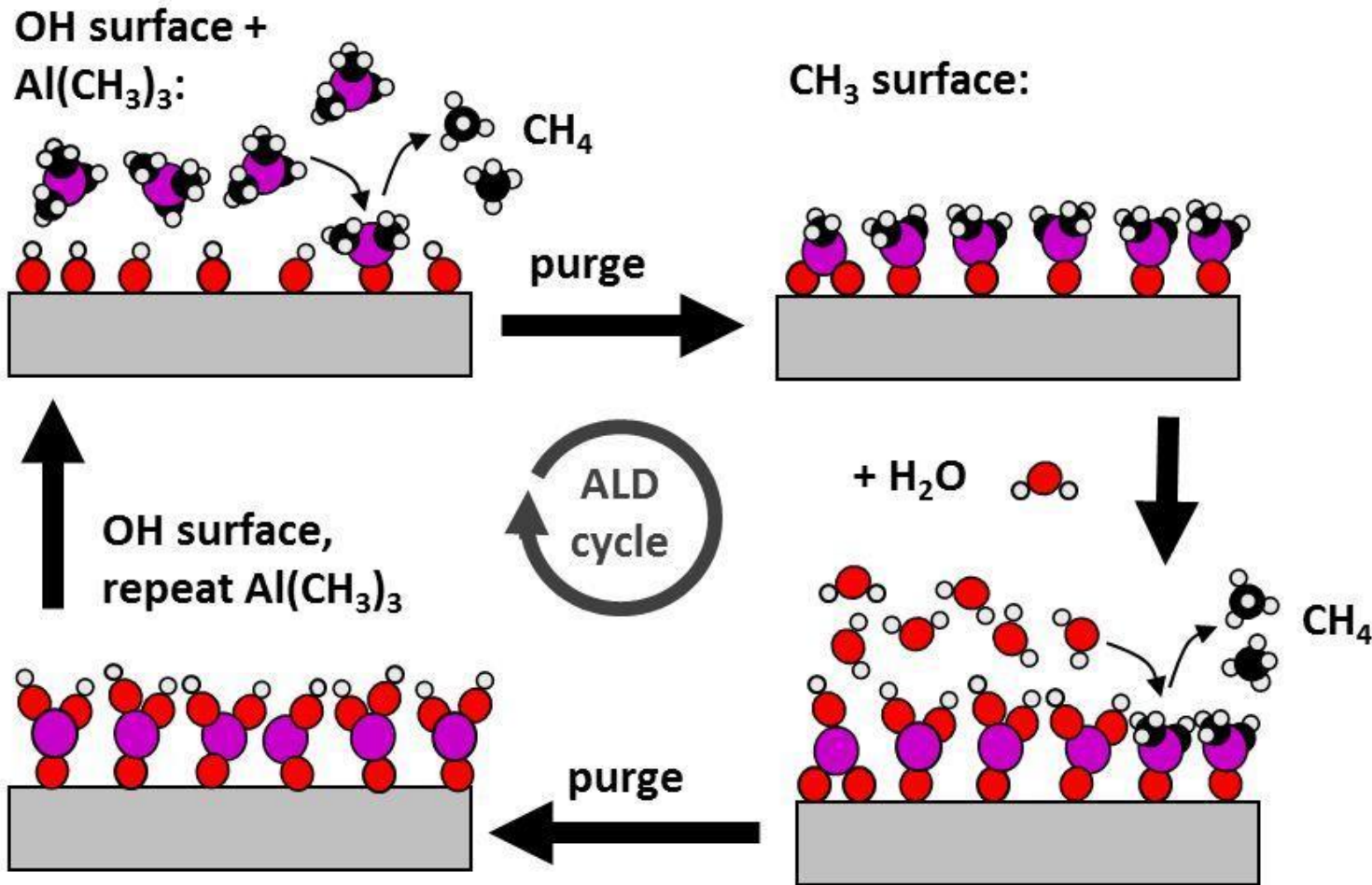
Heating elements are arranged in three zones: e.g. T1: 747 °C, T2: 750 °C, T3: 753 °C for LPCVD silicon nitride. This temperature ramp compensates for the reactant depletion along the tube.



Amorphous films do not matter.
Polycrystalline films show grain size gradient if ΔT .

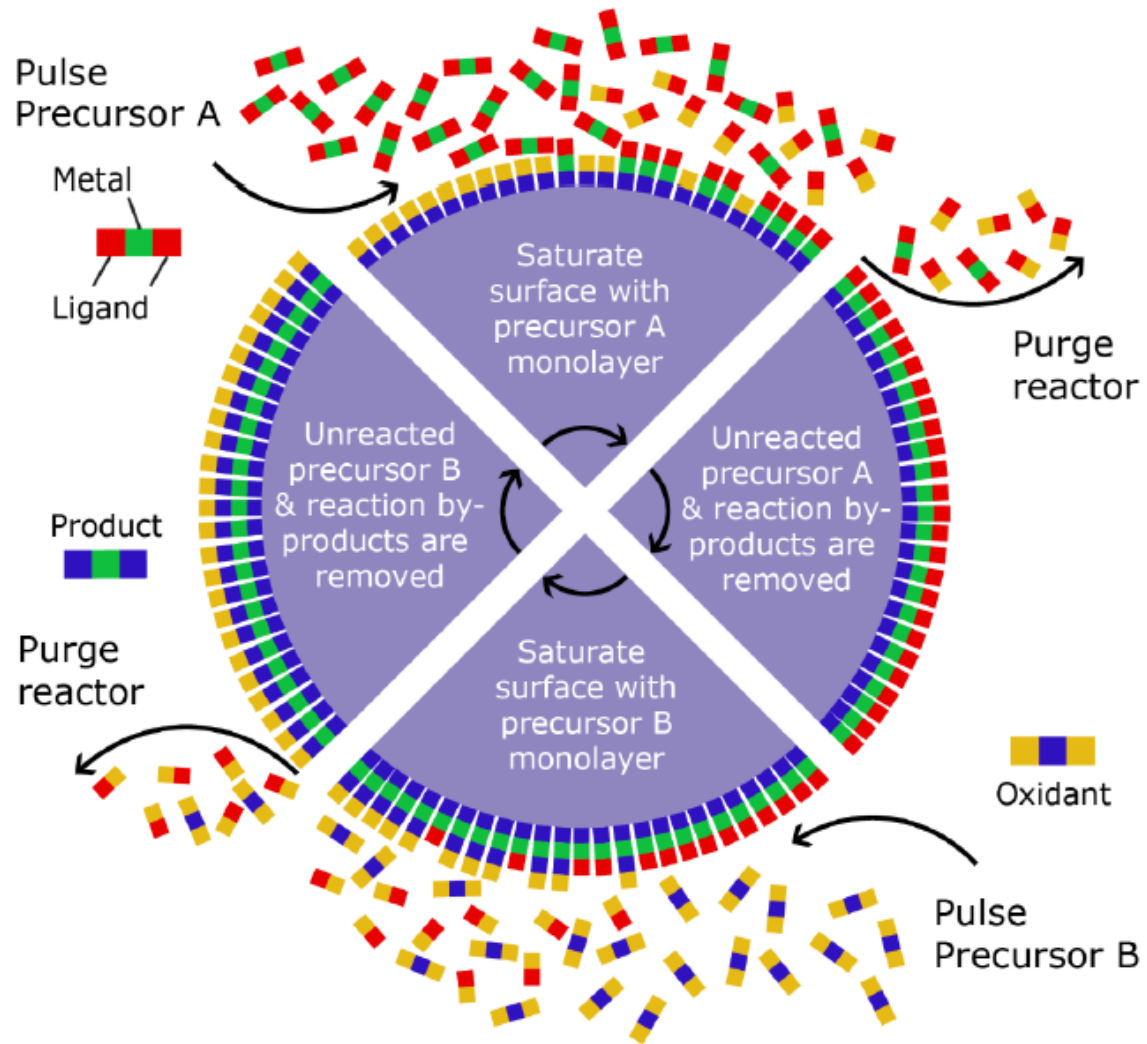
Half-time

ALD: Atomic Layer Deposition



Precursors introduced in pulses, with purging in-between

ALD cycle



ALD process based on:

Chemisorption

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

Saturation

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

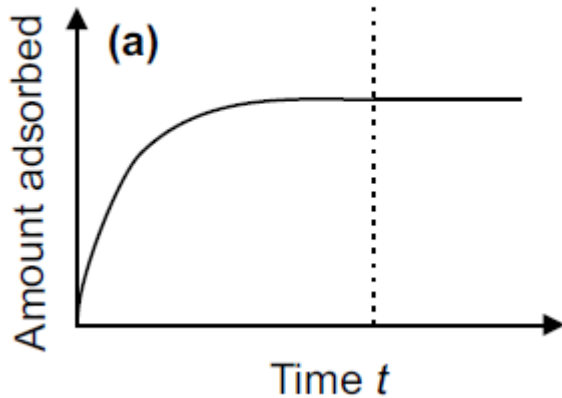
Surface controlled reactions

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

Sequential

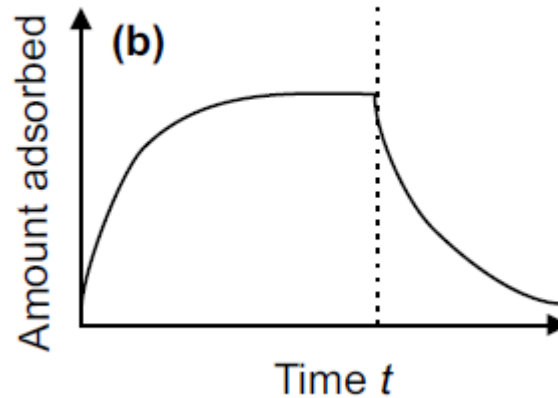
- Digital growth
- Sufficient purging needed between pulses
- Good flow dynamics required to ensure rapid gas changes

Surface saturation



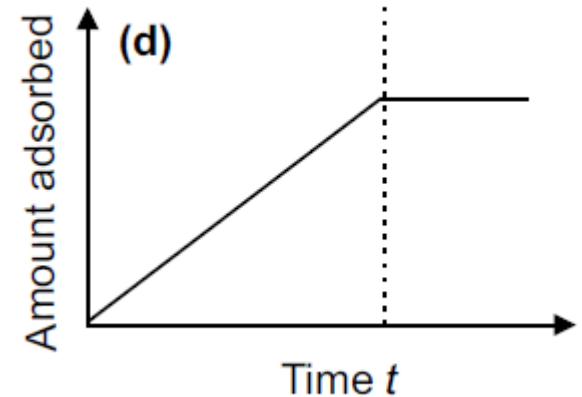
Irreversible saturation
ALD reactions:

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



Reversible saturation:

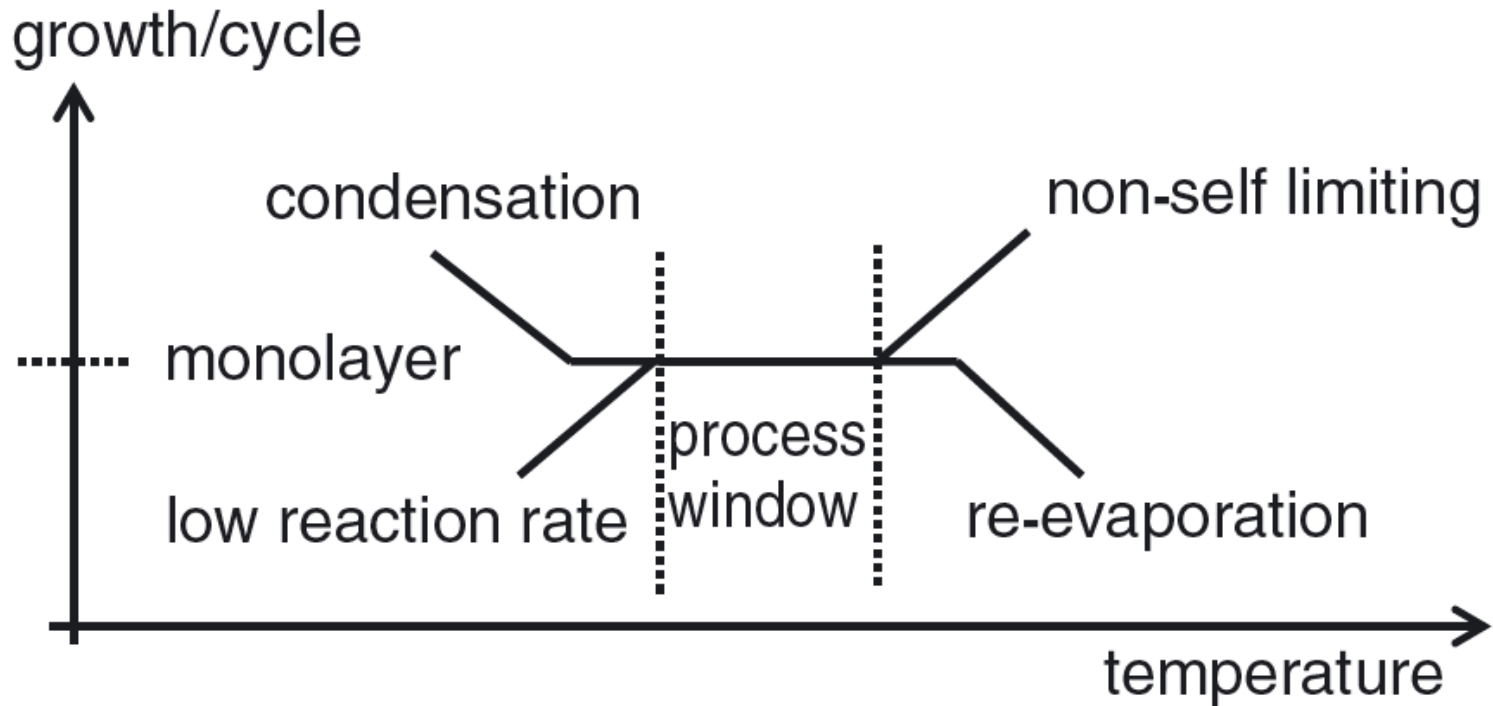
Physisorption only
(weak bonds like van
der Waals): once
precursor flux is
stopped, surface
specie will desorb.



Irreversible non-
saturating.

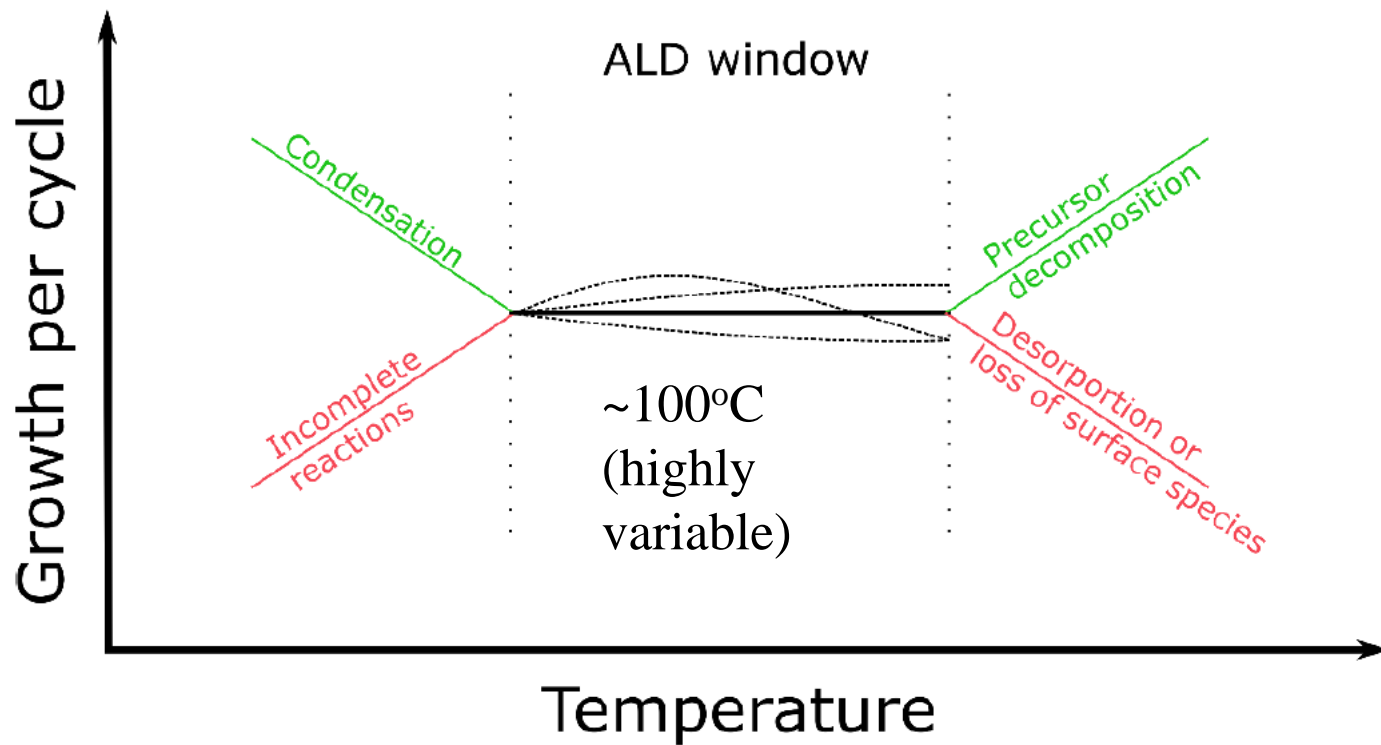
CVD regime:
more reactants in,
more film is
deposited
(continuosly)

ALD window

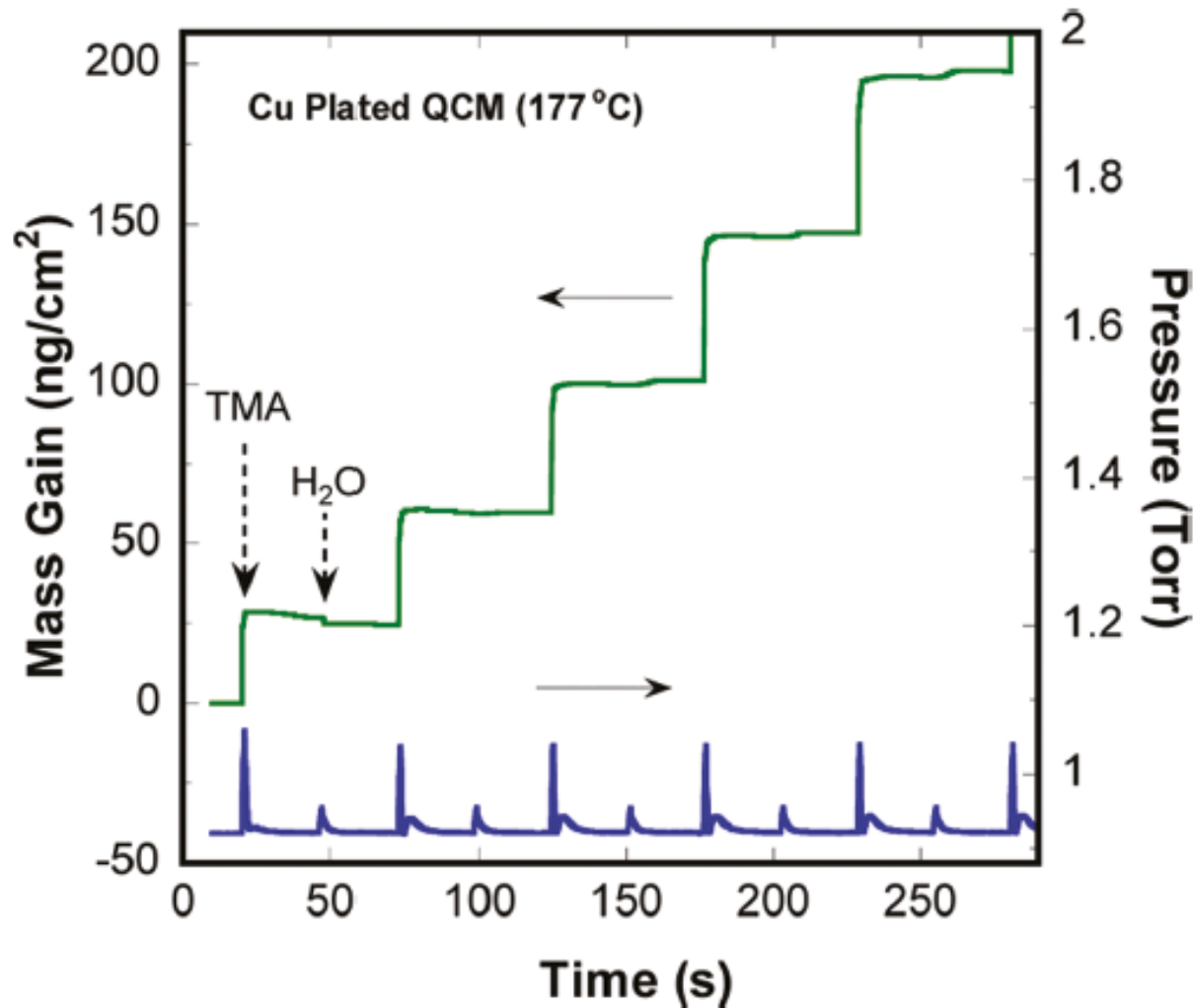


Compare with CVD: exponential (Arrhenius) temperature dependence.

ALD window realistically



Growth per cycle (GPC)



Abdulagatov & S.M. George:
ACS Appl. Mater. Interfaces
2011, 3, 4593–4601

How are ALD processes developed ?

Precursor considerations

Finding ALD window (pulse parameters)

GPC and deposition rate

Characterizing films for

- Uniformity
- Continuity
- Conformality (step coverage)
- Impurities
- Crystallinity

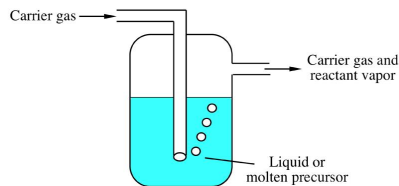
Precursor considerations

Gas precursor dose/flow is easy to measure via mass flow controllers.

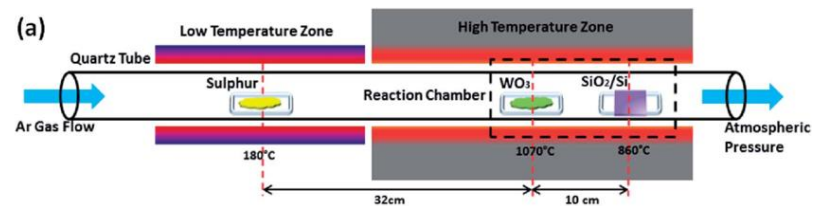
Liquid and solid precursors are also used: they are vaporized by bubbling and/or heating (similar to CVD).

Source temperature then becomes one reactor parameter to optimize.

It is important to all precursors that they do not prematurely dissociate.



Liquid bubbler
Solid source

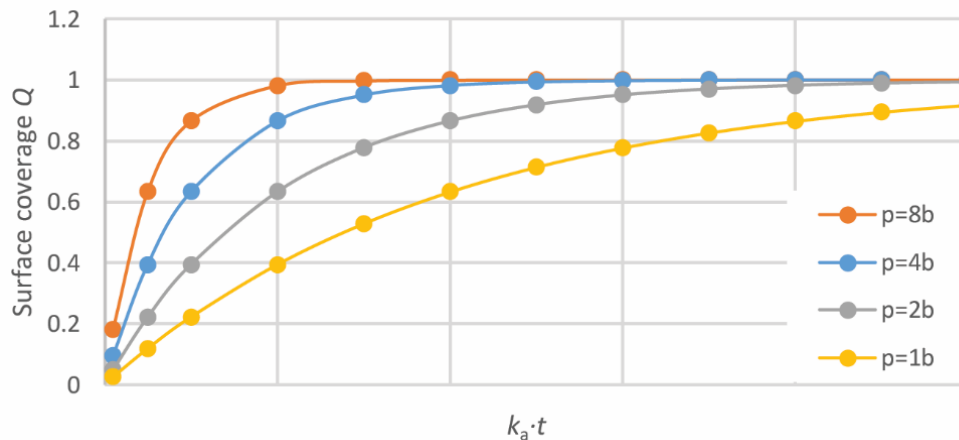


Surface coverage

Irreversible chemisorption case

$$Q = 1 - e^{-k_a p t}$$

Q is chemisorption coverage, k_a reaction rate coefficient, p precursor partial pressure and t time.

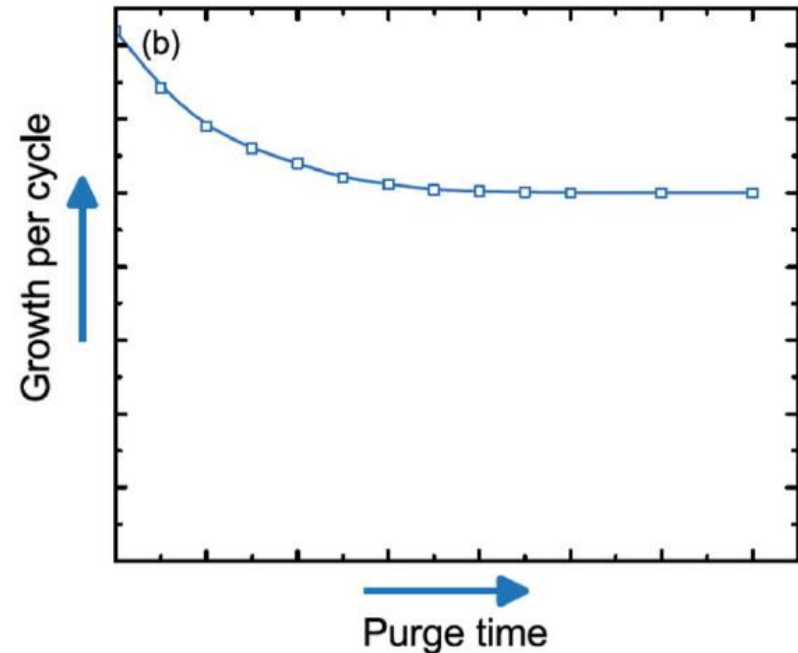
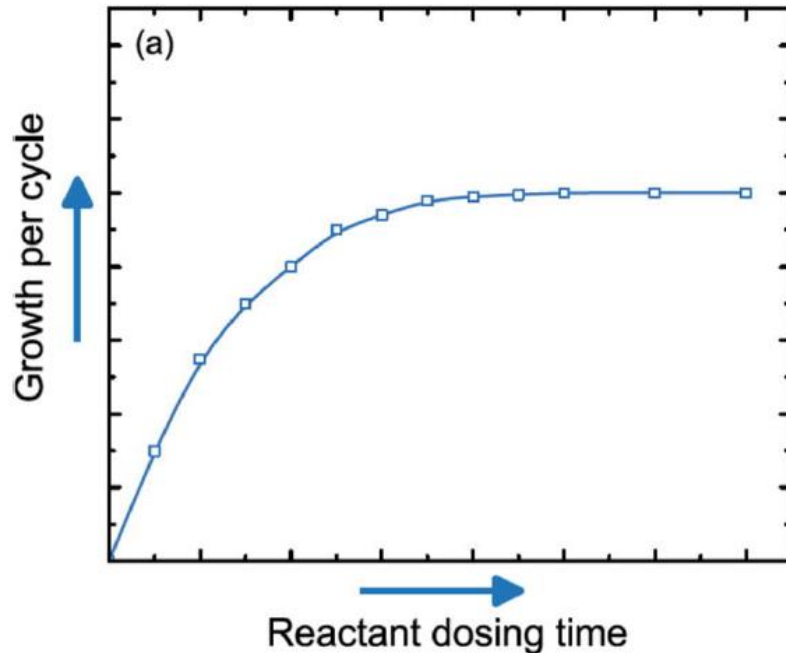


Increasing precursor vapour pressure decreases reaction time needed to reach saturation (but might increase purge pulse duration).

Start with long pulses

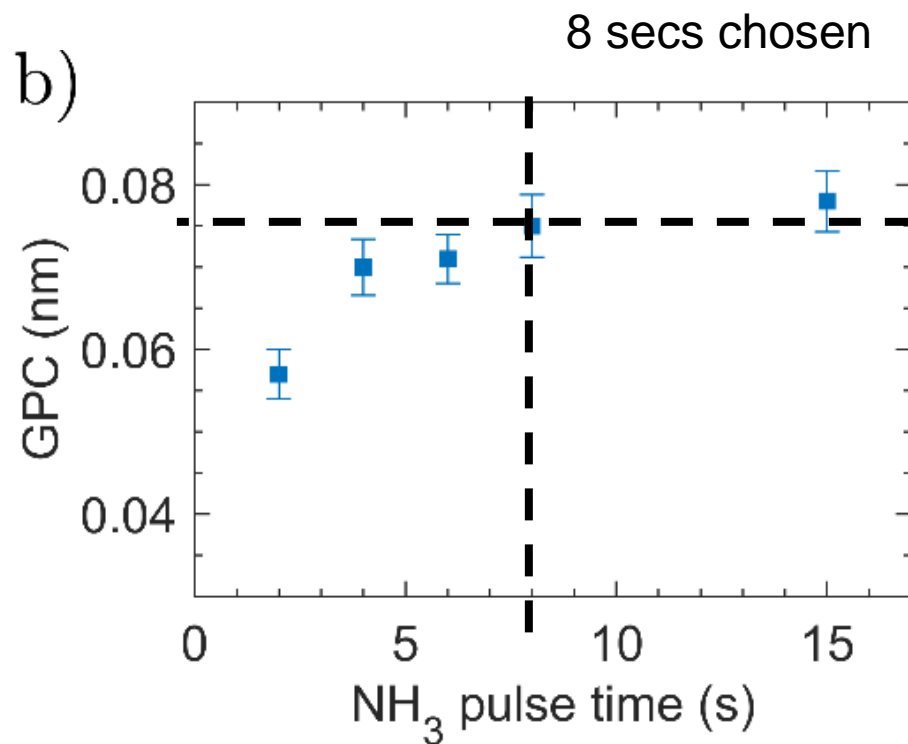
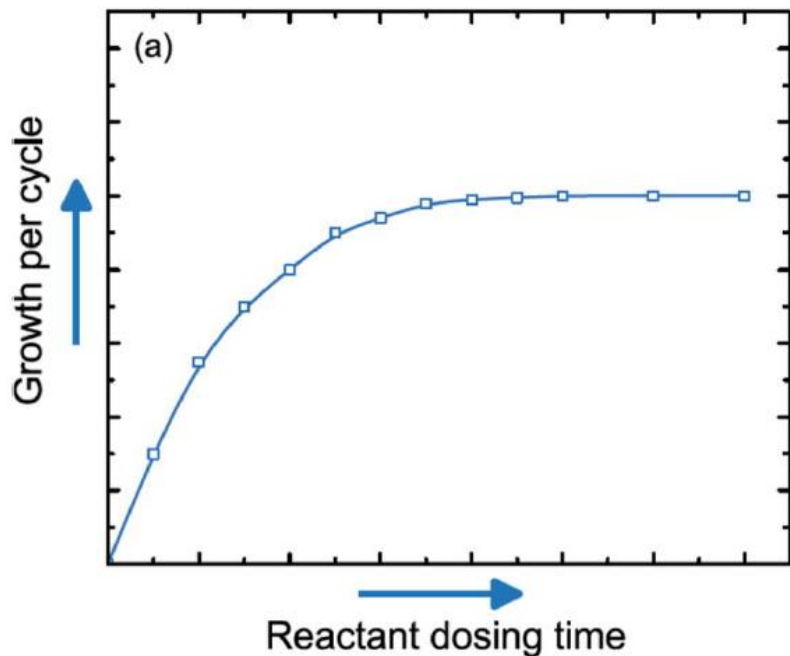
“Initial process development should be performed with long purges to ensure that they are sufficient. When the purge time is too short, precursor pulse A and B are no longer separated from each other and gas phase reactions may occur leading to CVD type deposition. This CVD type growth increases apparent GPC, but the film quality is not as good and the uniformity suffers, which can be detrimental for the application. It can also make it more difficult to optimize the process. Once the saturating pulsing parameters have been established, it is easy to decrease the purge times. The moment when the purge time becomes too short, manifests itself as an increase in GPC and a deteriorated uniformity.”

Finding the pulse times



Find the plateau (← evidence of self-saturating reaction)

Theory vs. practice



Growth saturation graphs
for AlCl₃ and NH₃.

Purge pulse length

Must remove both unreacted precursor and reaction product

Becomes slower as temperature is reduced (volatility reduced)

Water vapor is difficult, esp. $<100^{\circ}\text{C}$;
 O_2 and O_3 easier to pump away

If high aspect ratios or porous materials are coated, pulse lengths increase because of geometry restrictions.

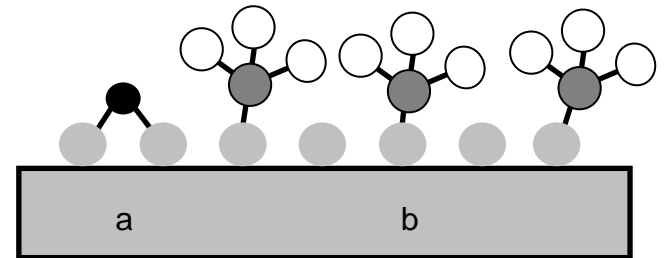
Deposition rate

Basically one atomic layer per pulse

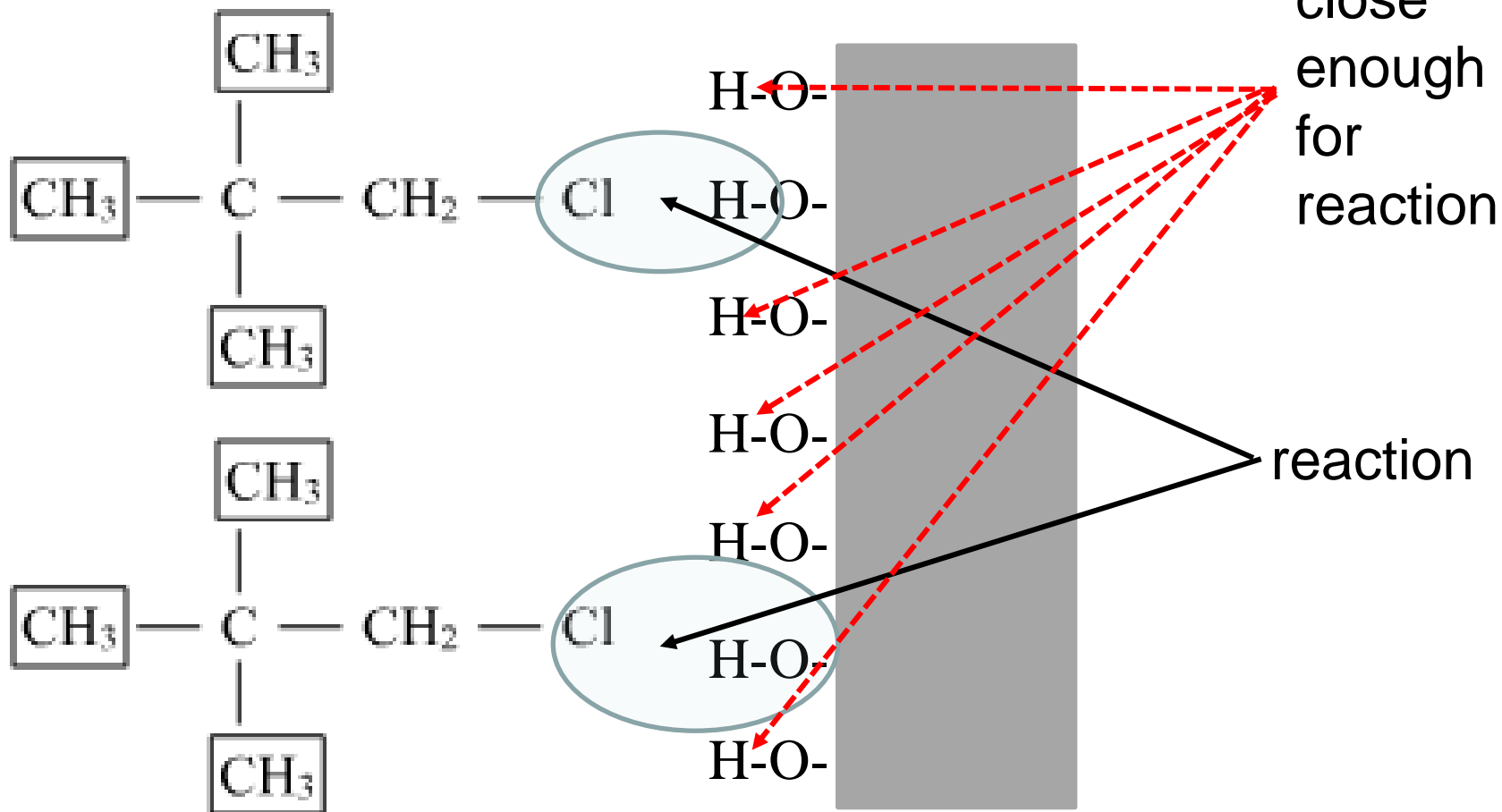
In practise less than an atomic layer because:

a) Inactive surface sites

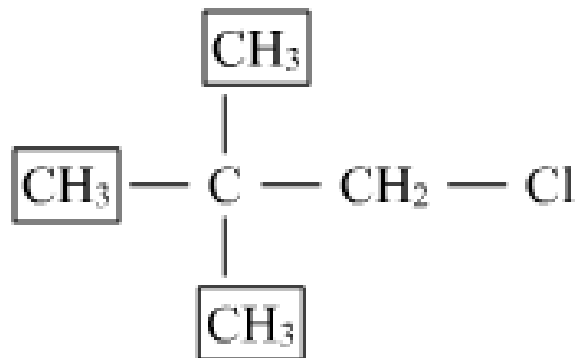
b) Steric hindrance: a large precursor molecule prevents another precursor molecule from approaching the reactive site



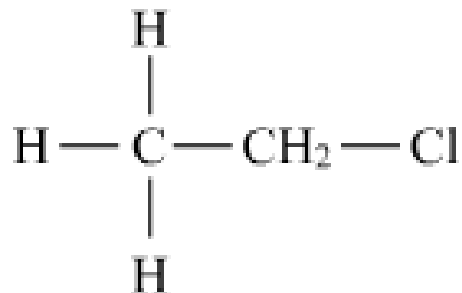
Steric hindrance



Precursor design



Large size,
Steric hindrance



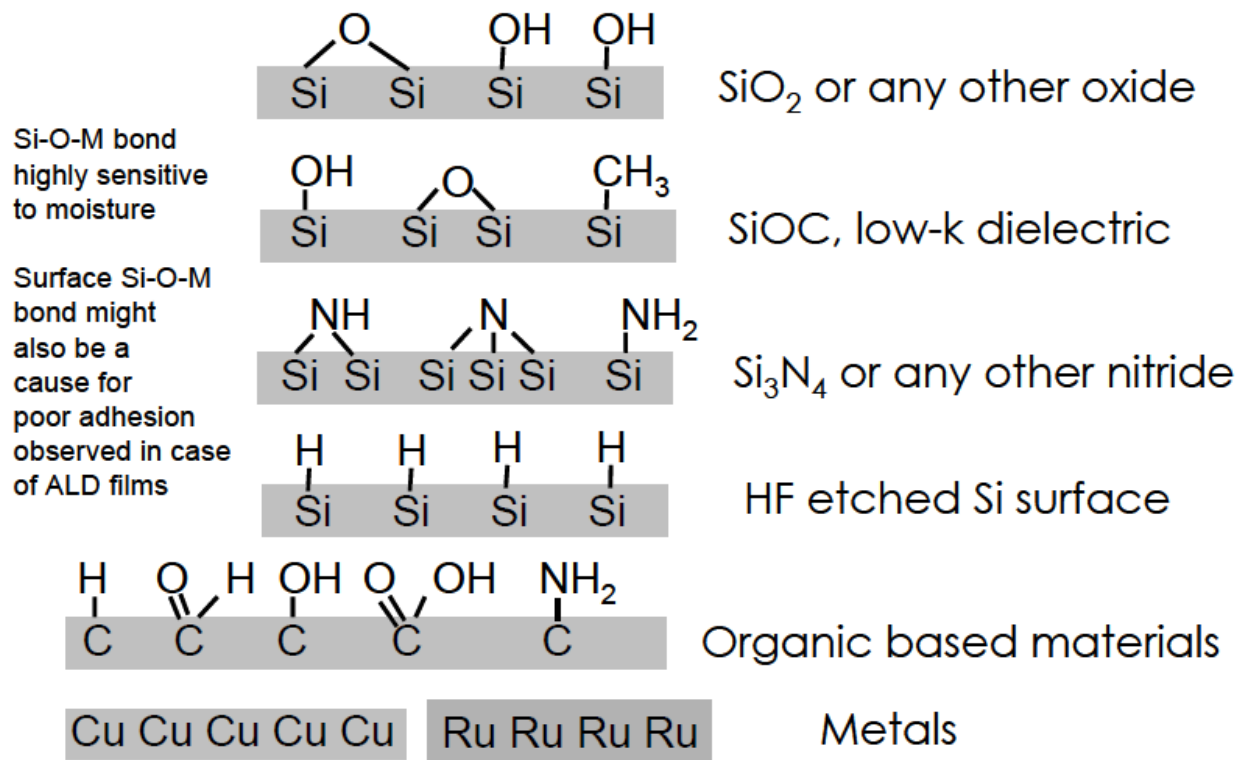
Small size,
Less steric hindrance.

But you also need to consider:

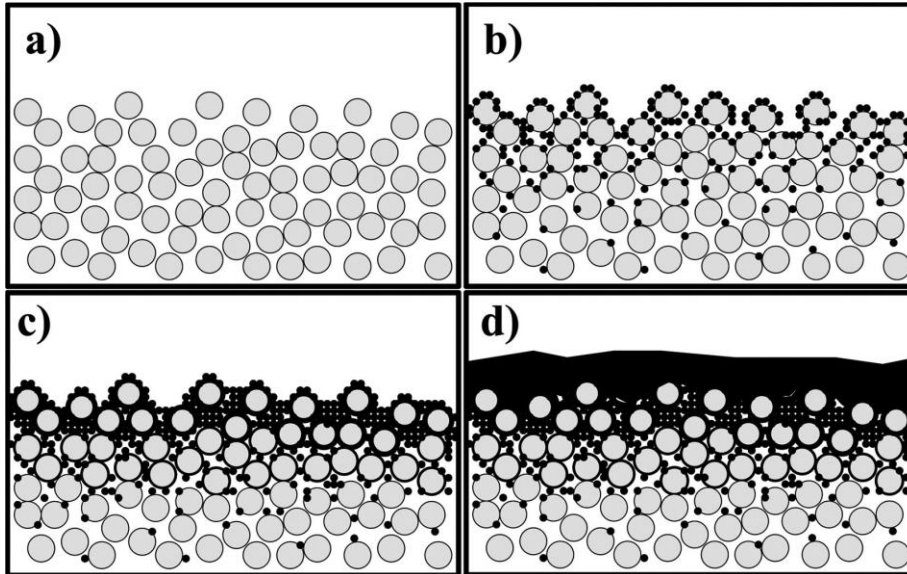
- thermal stability
- vapour pressure
- toxicity
- price...

Available growth sites

Surface preparation step must provide surface with chemically active sites that can react with precursors.



ALD on polymer substrate



No suitable bonds available.

TMA precursor debris acts as a starting surface.

Time lag in initiation.

- (a) a cross section of the polymer chains at the surface of the polymer film,
- (b) Al₂O₃ nucleation clusters formed from H₂O reaction with TMA trapped in the near surface region,
- (c) coalescence of Al₂O₃ clusters and closure of the space between the polymer chains
- (d) formation of a dense Al₂O₃ film that grows on top of the polymer surface.

A misconception often encountered in the literature is that the growth of a full monolayer of MZ_x per cycle would correspond to “ideal ALD”, and growth of less than a monolayer per cycle would correspond to “non-ideal ALD”. It must be emphasized that, for growth from compound reactants, no requirement of a full monolayer growth can be deduced from the basic principles of ALD. In contrast, the theoretical application examples of this work and the real application examples reported elsewhere,^[22] all done under the assumption of ideal ALD, show that achieving a growth per cycle of even half of a monolayer is rare.

ALD \neq one atomic layer/cycle

Al_2O_3 0.9-1.1 Å/cycle (TMA + H_2O)

TiO_2 0.5-0.9 Å/cycle (TiCl_4 + H_2O)

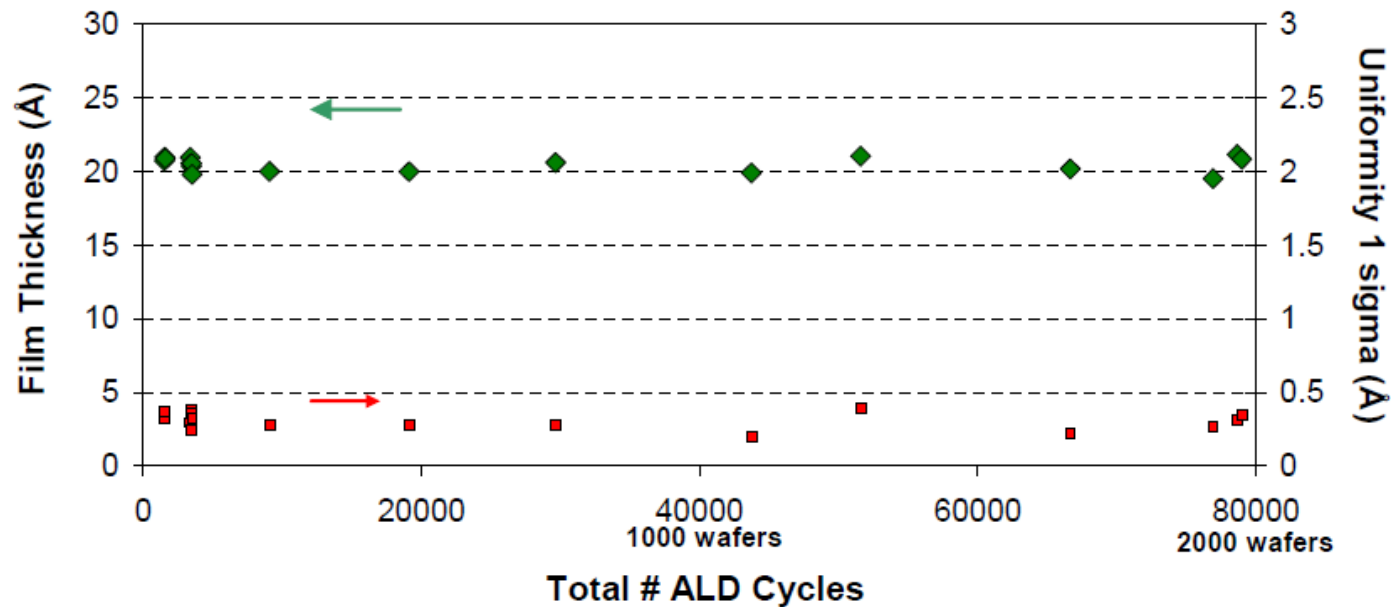
Y_2O_3 0.24 Å/cycle ($\text{Y}(\text{thd})_3$ + O_3)

If pulses are one second \rightarrow 15*monolayer
thickness/minute \sim 2 nm/min

If 0.1 second pulses \rightarrow 20 nm/min max.

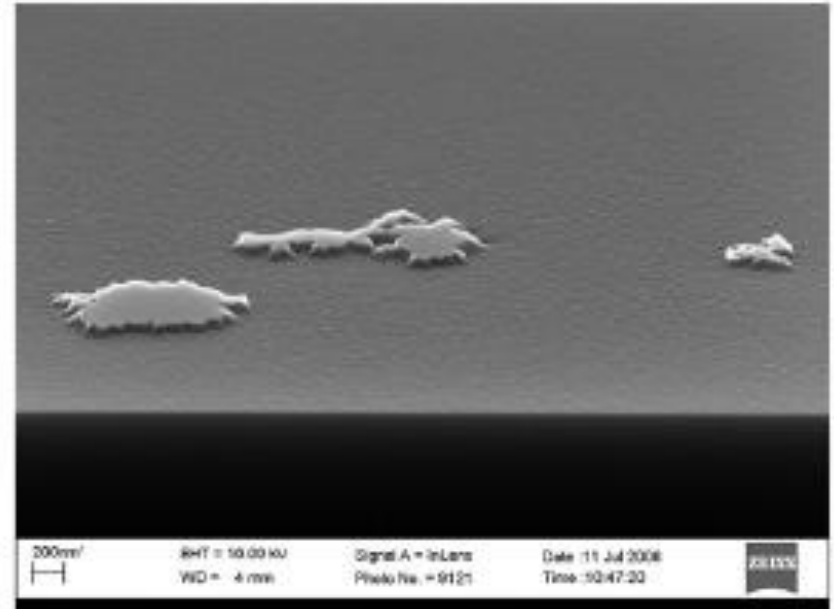
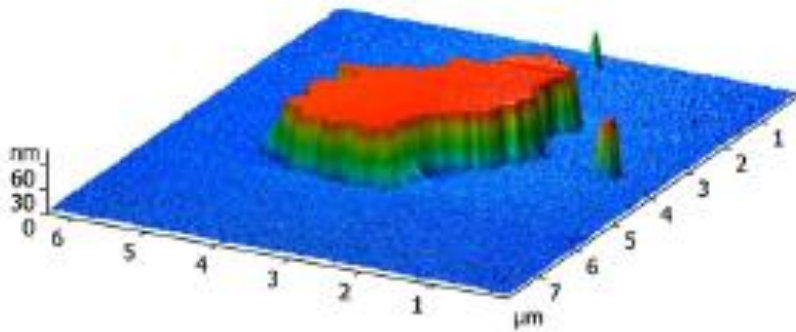
ALD uniformity (=thickness across the wafer)

Good uniformity is a proof of surface controlled reaction.



HfO₂ dielectric marathon test: 2000 wafers

Film continuity



Al_2O_3 of 5 ALD cycles and etched for 2 s cryo-DRIE:
discontinuous film does not protect underlying silicon.

Film continuity (2)

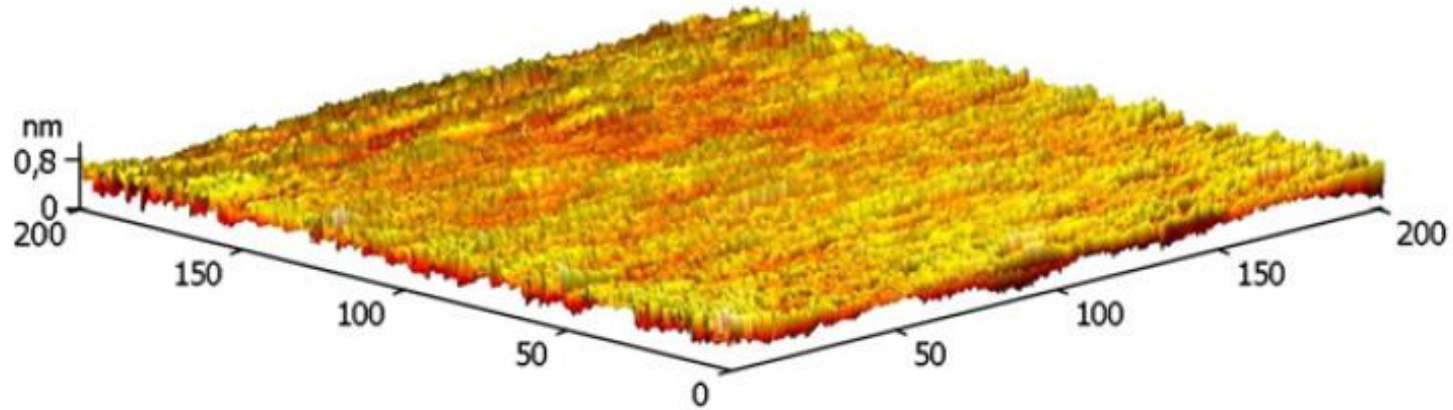
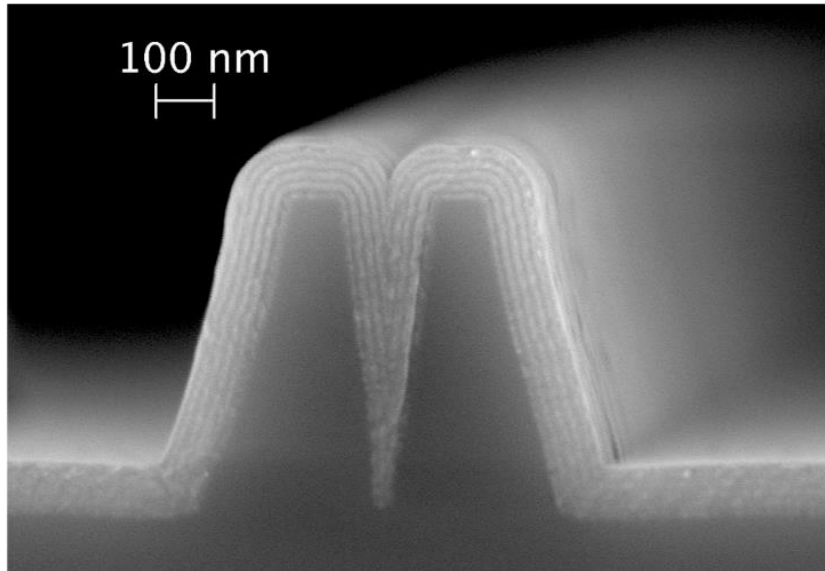


Fig. 4. AFM scan of the structure grown during 10 cycles and etched for 2 s in cryo-DRIE.

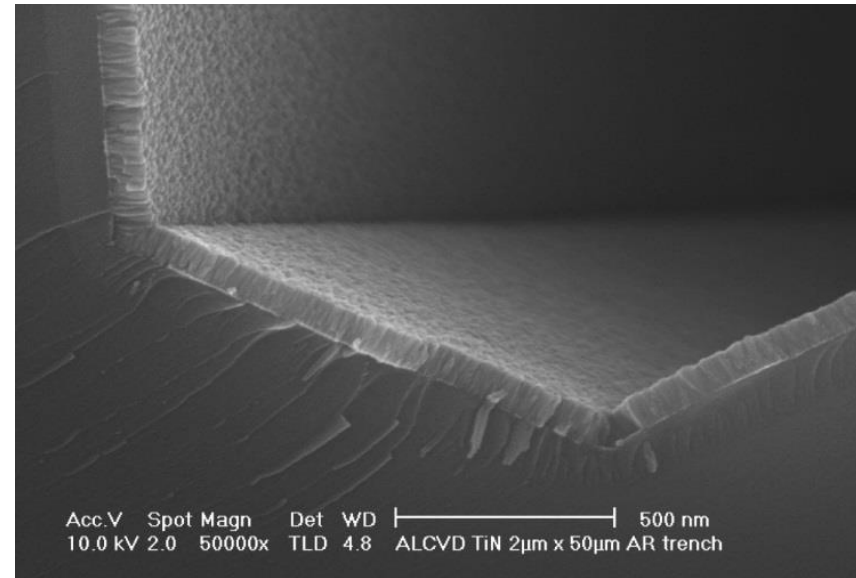
10 cycles (≈ 1 nm) ALD film is continuous and serves as a protective coating.

ALD conformality is excellent (=step coverage 100% in microstructures)

All surfaces coated by diffusing gaseous precursors in the surface reaction limited mode.



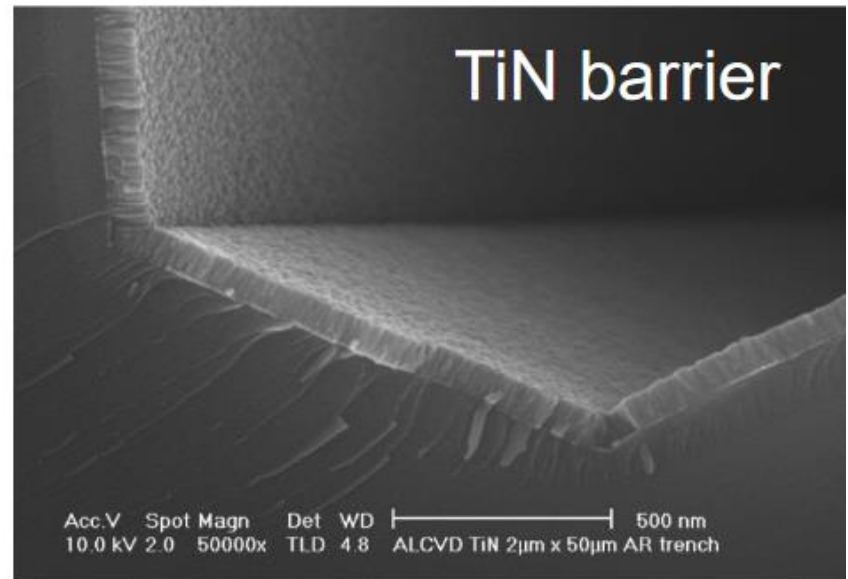
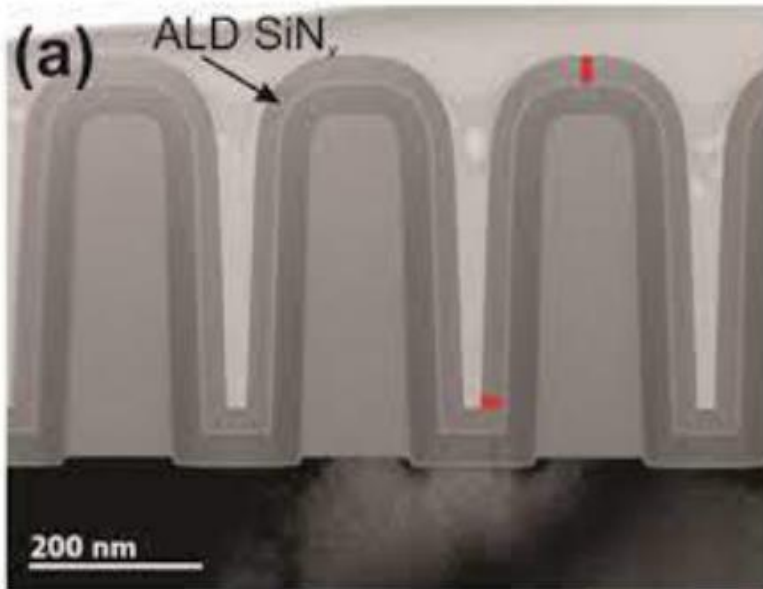
$\text{Al}_2\text{O}_3/\text{TiO}_2$
nanolaminate



TiN barrier

ALD conformality

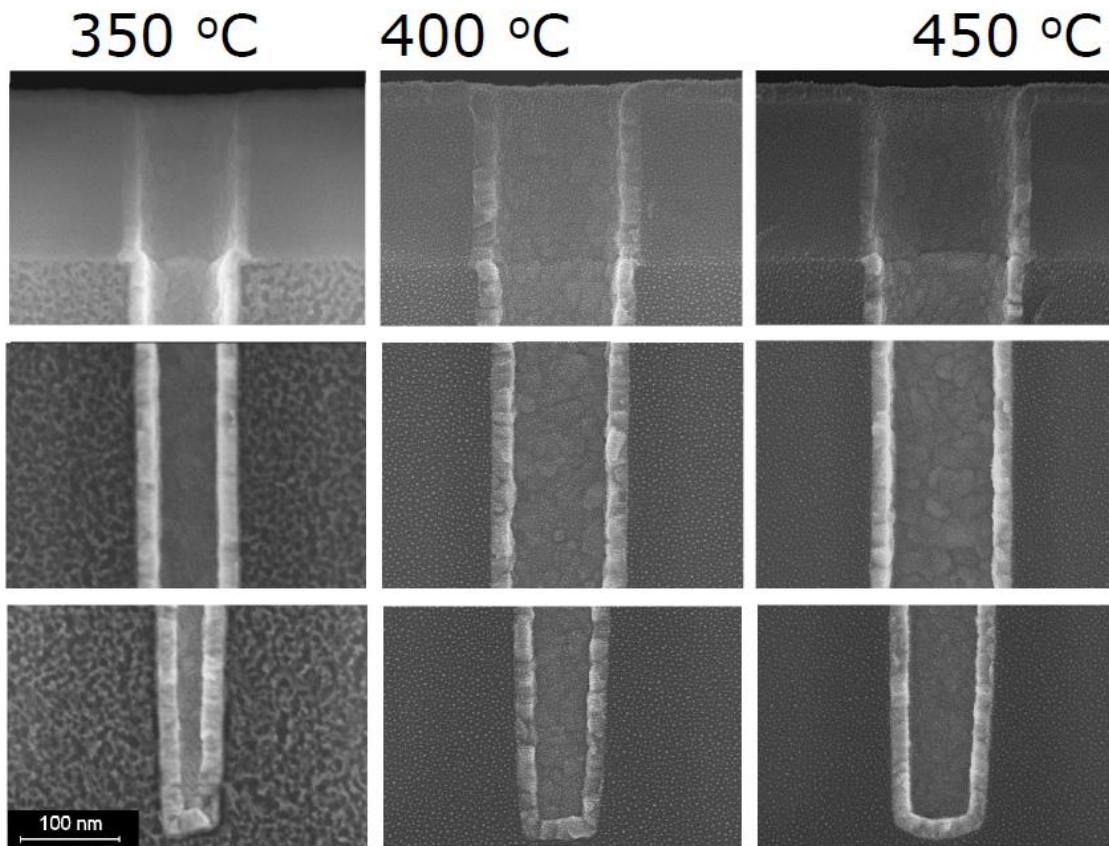
All surfaces coated by diffusing gaseous precursors in the surface reaction limited mode.



Elers et al: CVD

You Jin Ki et al: Appl. Sci. Converg. Technol. 28(5): 142-147
(2019)
<https://doi.org/10.5757/ASCT.2019.28.5.142>

Step coverage (2)



Step coverage
good also in high
aspect ratio
grooves,

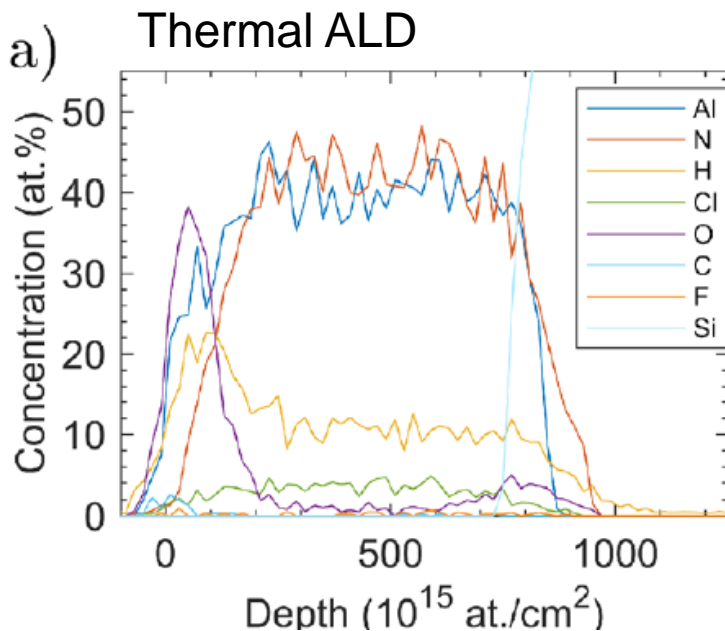
BUT pulse lengths
have to to be
increased

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

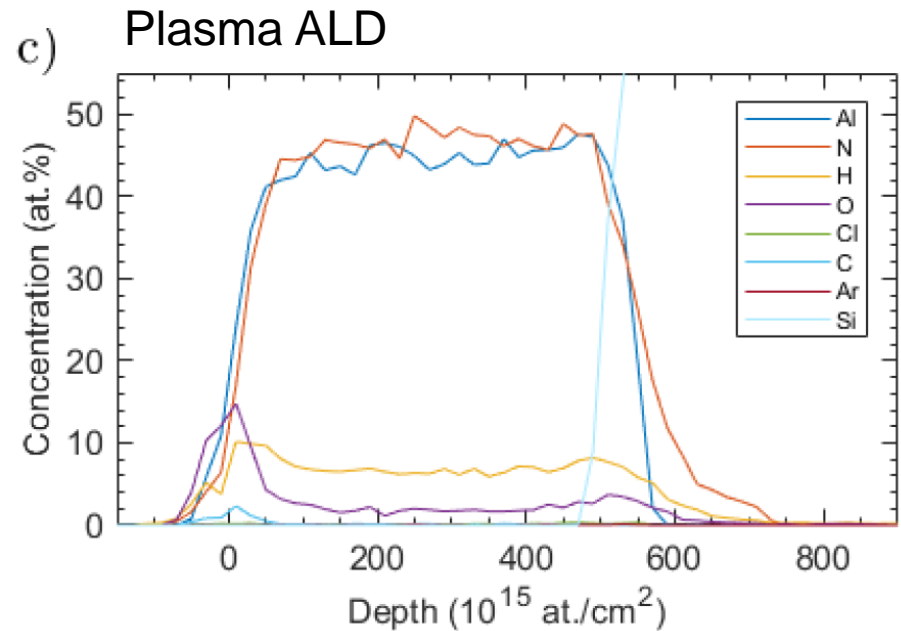
AlN purity by ToF-ERDA

$\text{AlCl}_3 + \text{NH}_3$ process

Oxygen contamination on surface is post deposition

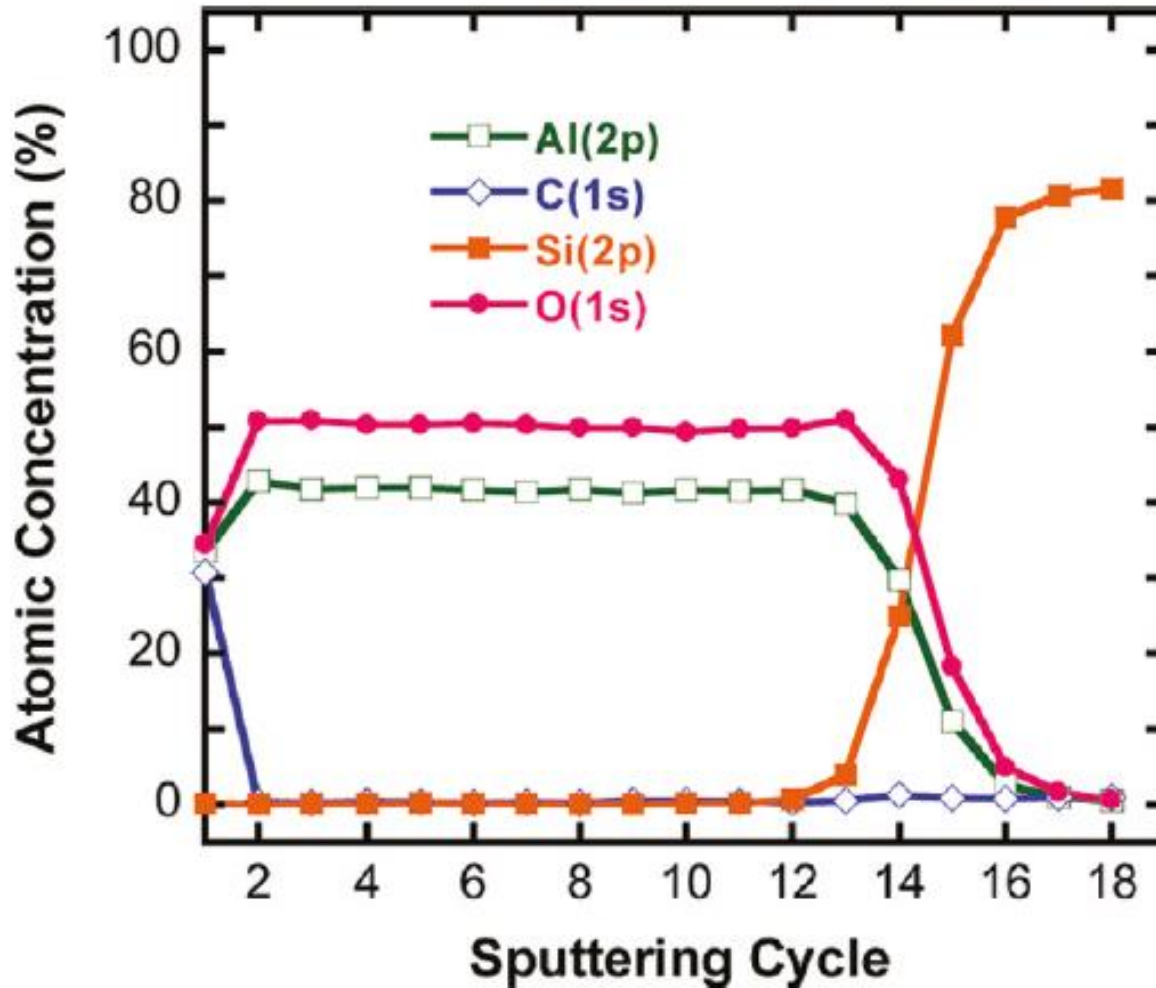


Thermal has much more hydrogen and chlorine.



Overall purity better in PEALD

Al₂O₃ purity by SIMS



Carbon on surface is most likely post deposition contamination.

Crystalline structure: amorphous vs. polycrystalline ?

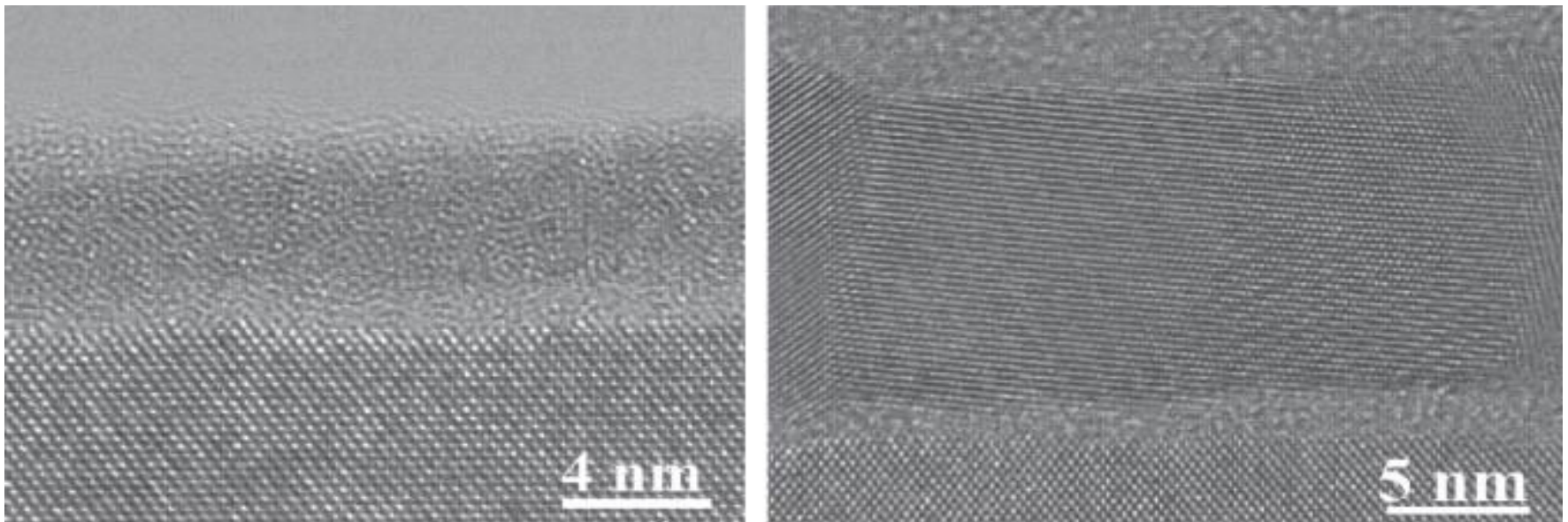
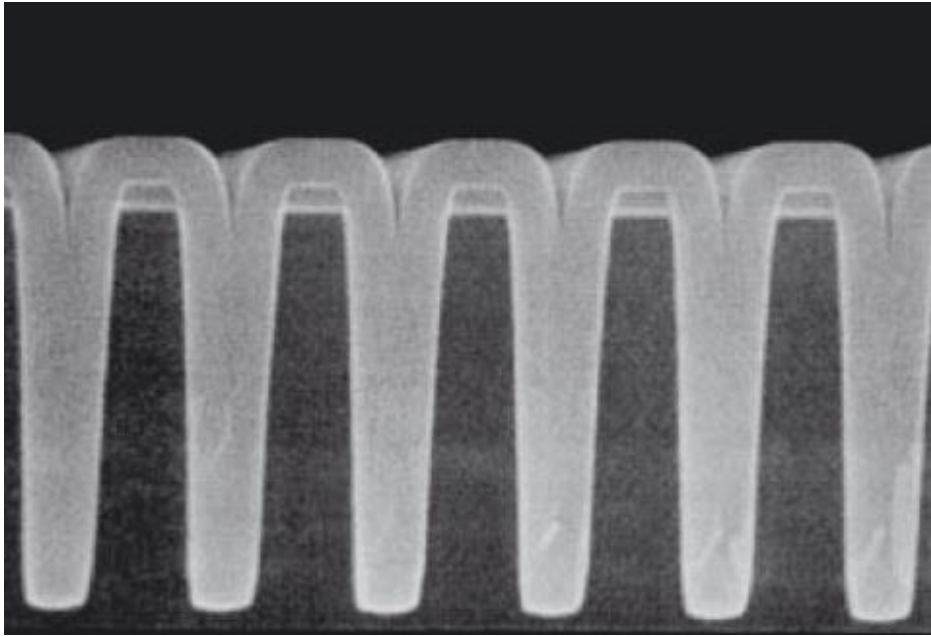


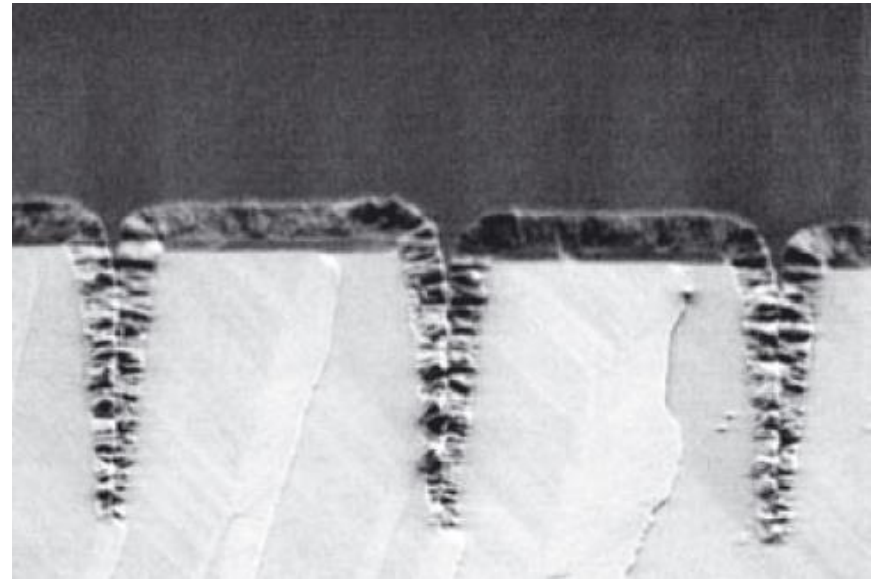
Figure 26-13

ALD ZrO₂: 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 (2)



amorphous aluminum oxide



Polycrystalline strontium titanate

Vehkamäki *et al.* (2001)

Crystallinity: precursors

Metalorganic precursors likely to leave carbon residues
→ amorphous

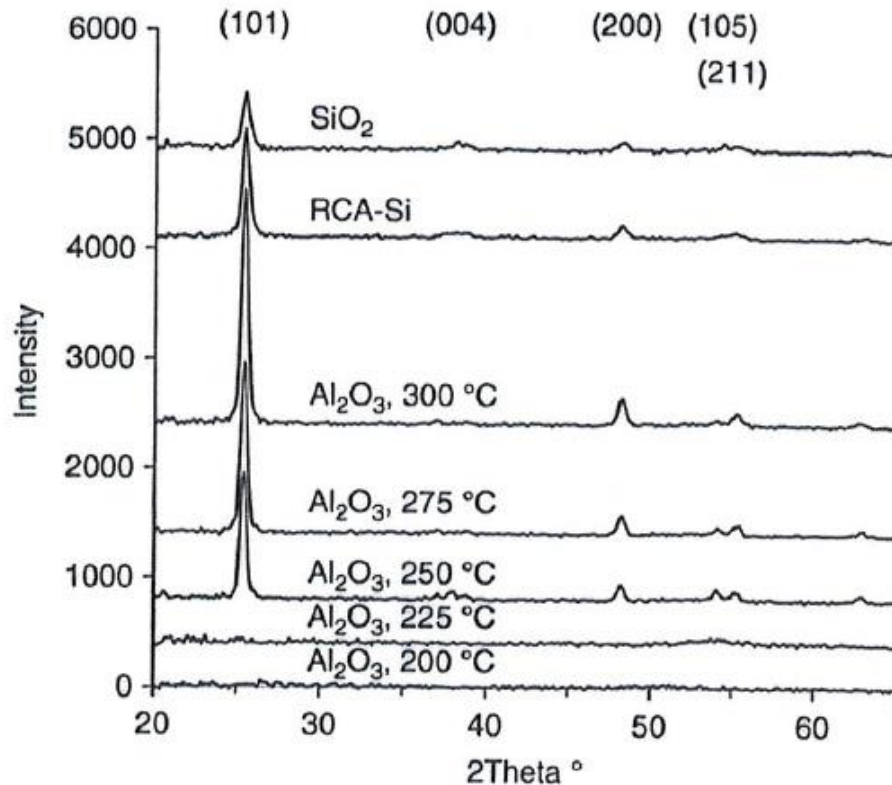
Halide-processes → crystallinity likely

O_2 or O_3 more reactive than H_2O → ligand removed
more efficiently → less contamination → crystalline

Plasma removes residues → crystallinity more likely

H and Cl are "benign" residues, carbon is "bad".

Crystallinity & underlying substrate



TiO₂ ALD film on:

- Amorphous SiO₂
- RCA cleaned <Si>
- Various Al₂O₃ films

Crystalline TiO₂ on high-T amorphous Al₂O₃

When TiO₂ deposited on amorphous low-T Al₂O₃, then amorphous TiO₂

Fig. 2. GIXRD diffractograms for TiO₂ films deposited in 500 cycles on different substrates. Curves have been shifted vertically for clarity.

Evolution of crystallinity

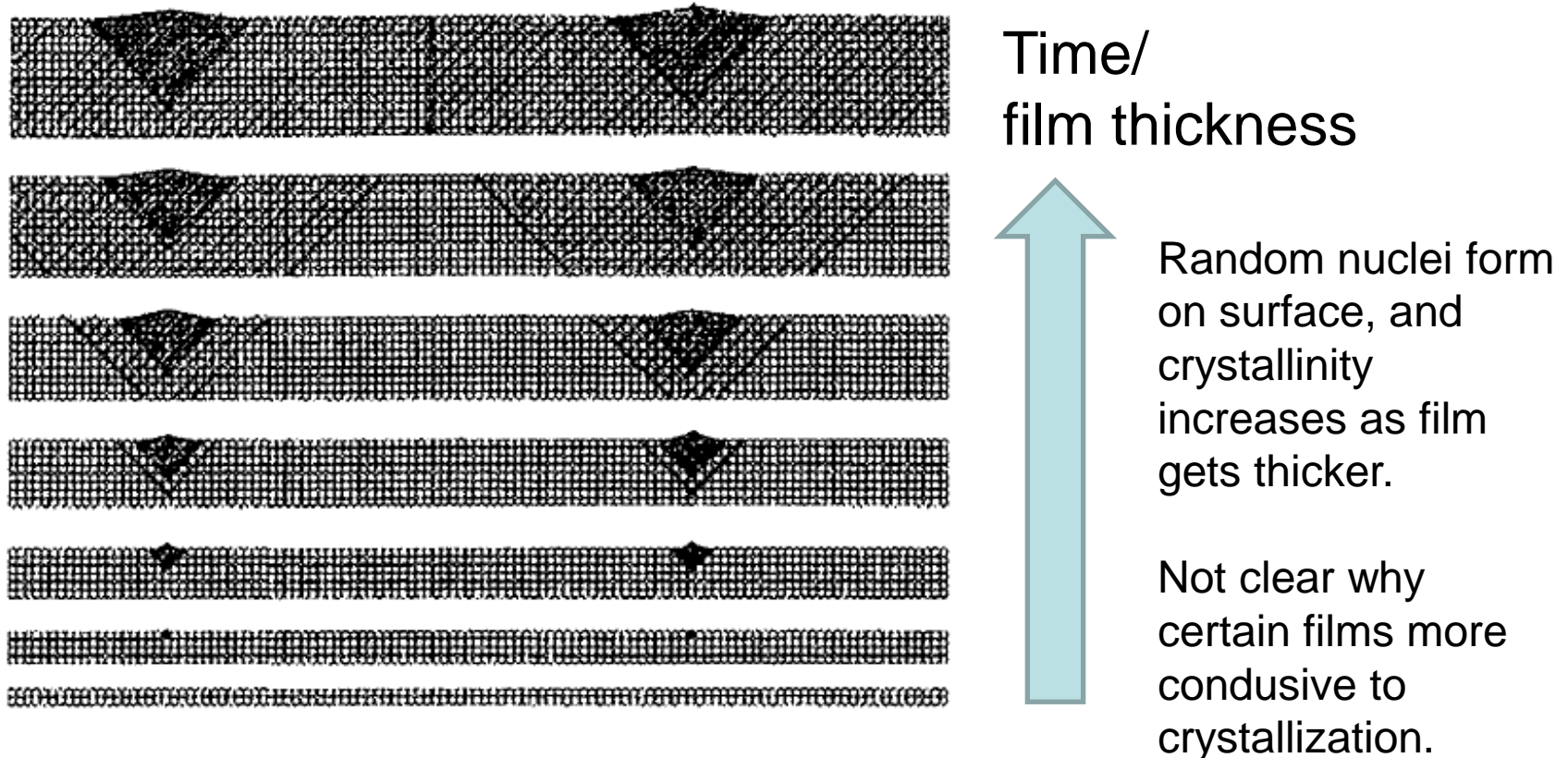
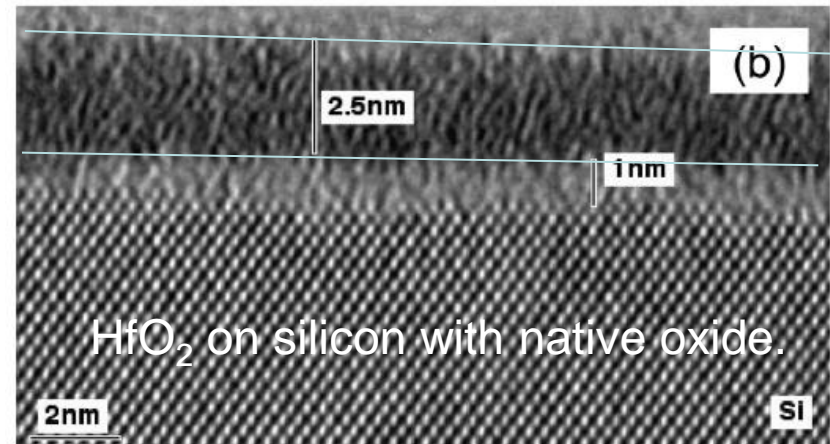
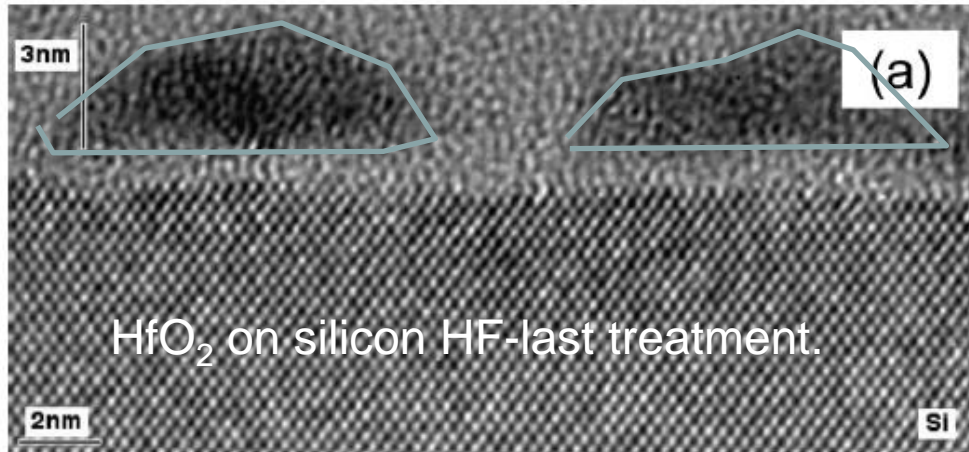


Fig. 10. Scheme for the initial growth of amorphous film (1st from bottom), the formation of crystalline TiO_2 nuclei (2nd from bottom), growth of crystalline TiO_2 grains (3rd–7th from bottom), and through-crystallization of the originally amorphous TiO_2 film (4th–7th from bottom).

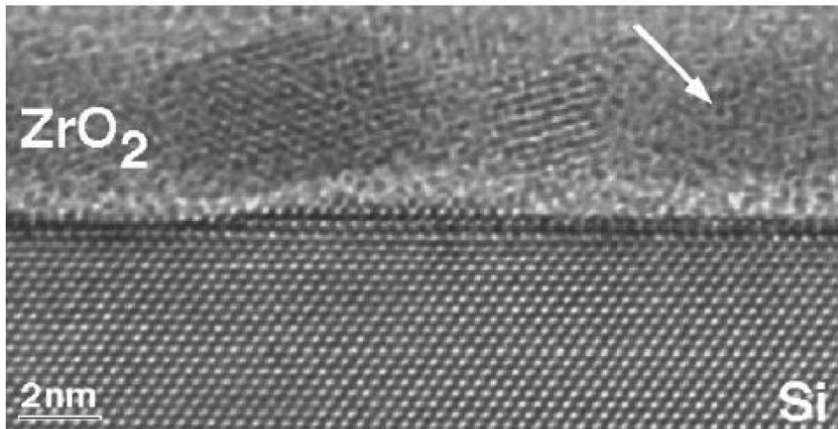
Island growth vs. layer-by-layer growth



“One can observe a uniform, continuous film in the case of HfO₂/SiO₂/Si. For the film deposited directly on Si (after HF last pre-clean), the TEM image reveals the nucleation phenomenon, i.e. the deposited material forms clusters on the surfaces resulting in incomplete coverage of the surface by HfO₂.”



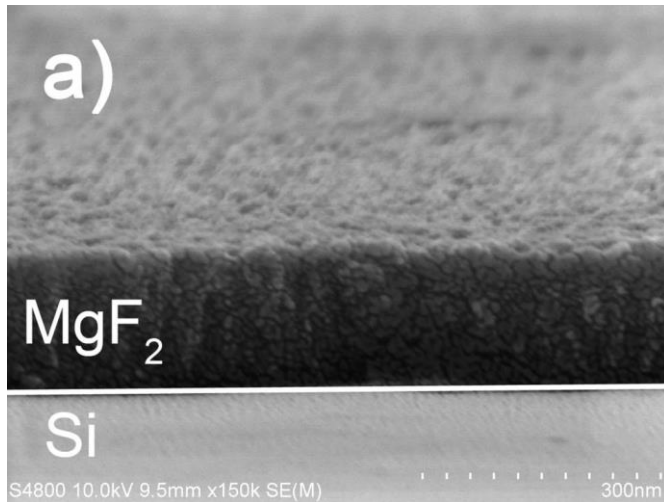
(a)



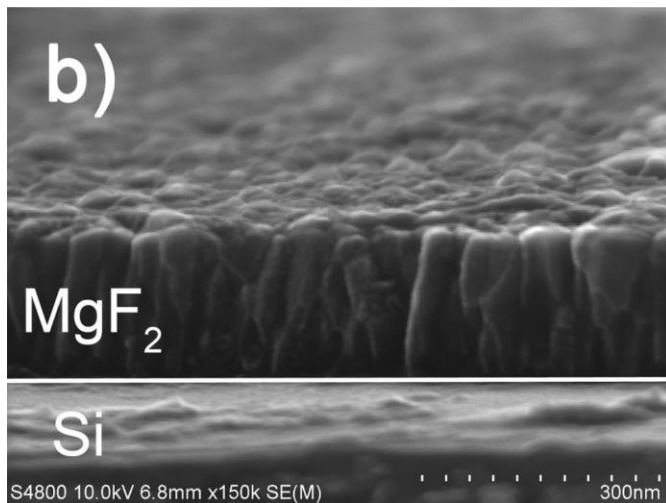
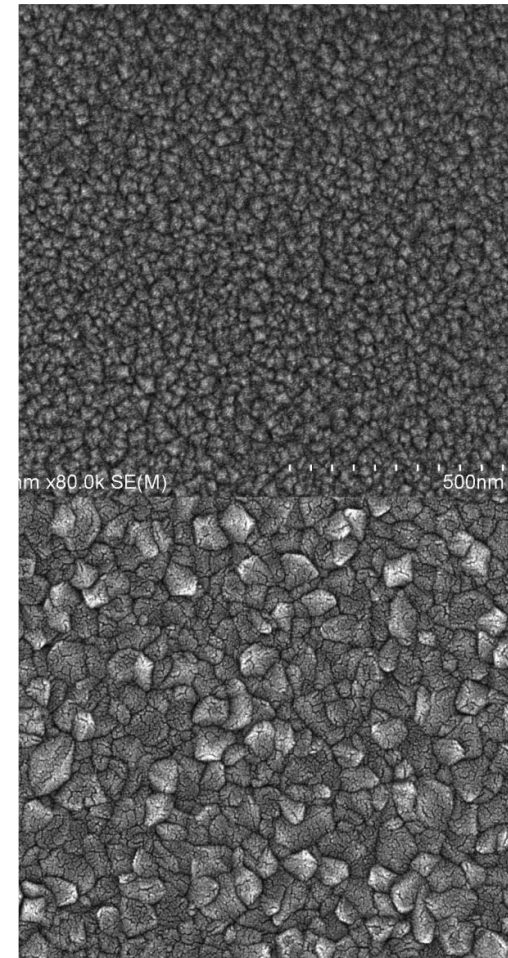
(b)

“On oxidized silicon, ZrO₂ layer is smooth yet clearly polycrystalline. On HF-etched silicon, the nucleation density has been lower and the film shows more or less separate crystallites and is much rougher, because the nuclei have had more time to grow independently before coalescing.”

Crystallinity & depo temperature

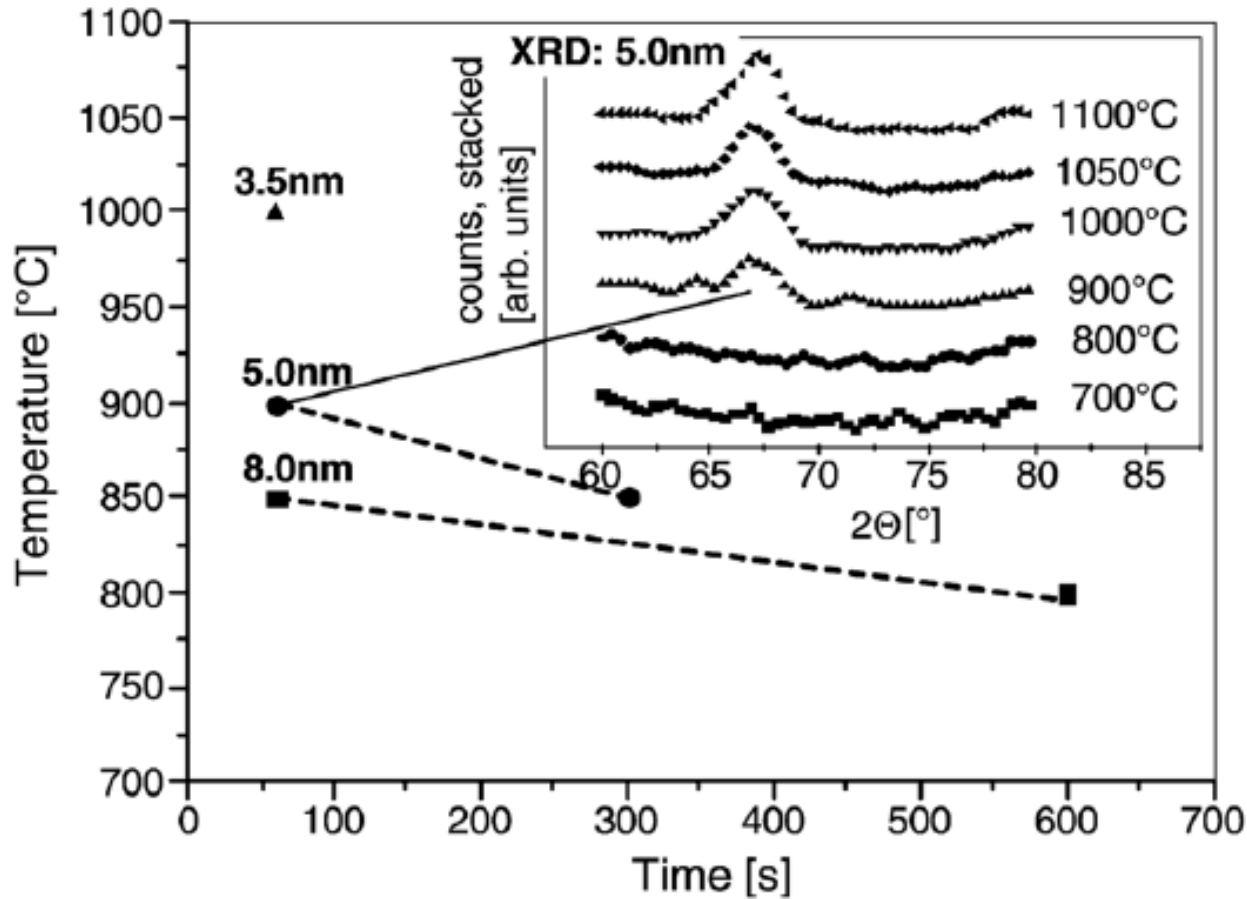


250°C



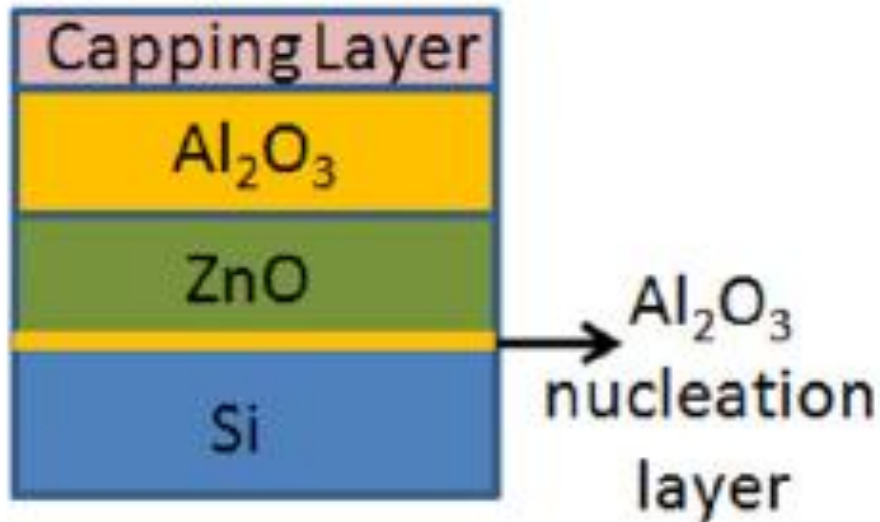
350°C
Higher T
favors
crystallinity

Post deposition annealing



Al_2O_3
turns
crystalline
at ca.
900°C

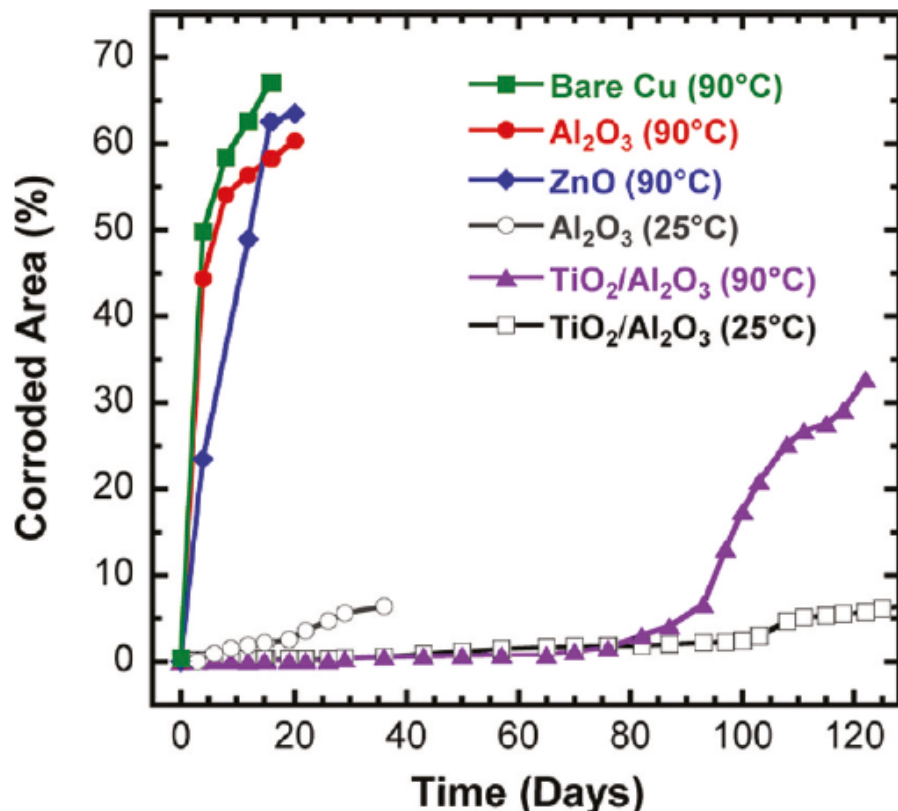
Protective capping layers



Capping Layers

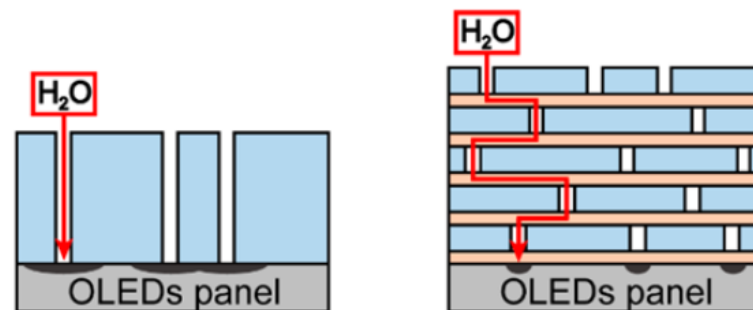
- (1) Ebeam NiO_x
- (2) O₂ Plasma on NiO_x
- (3) Ebeam TiO_x
- (4) O₂ Plasma on TiO_x
- (5) PEALD TiO₂

ALD for corrosion protection



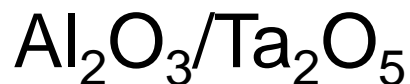
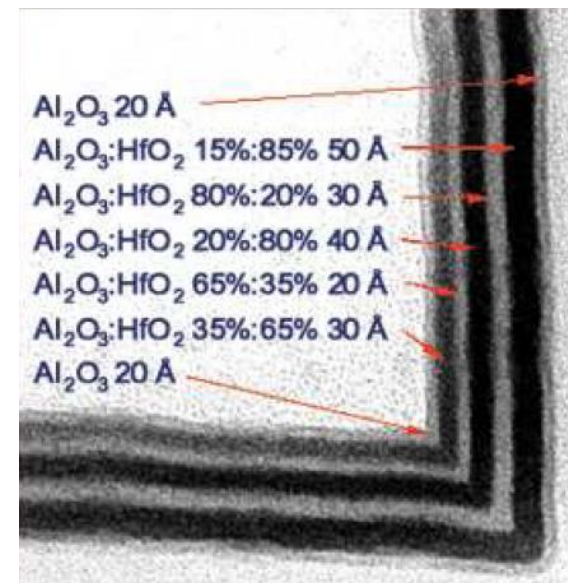
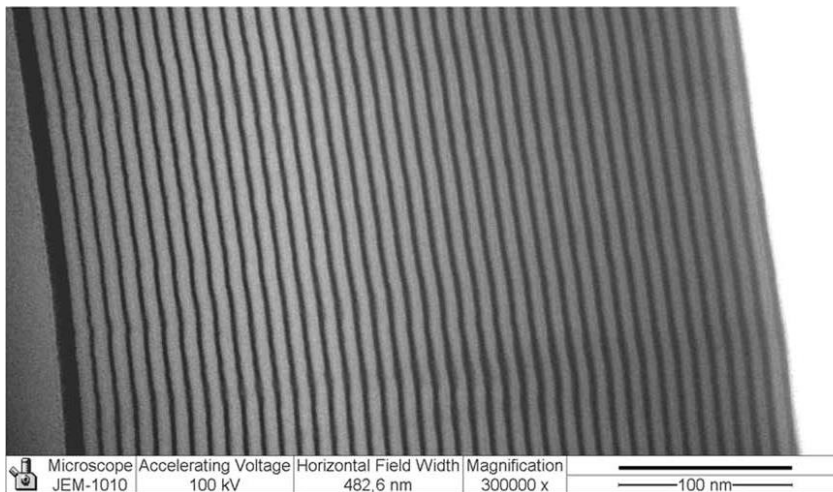
Usually higher deposition temperature results in higher quality film (denser film, less defects, e.g. holes, thinning).

In multilayers the defects are (in theory) non-correlated.



Nanolaminates

- More layers, potentially more effective barrier.
- Lower deposition temperature but more layers maybe a good compromise.



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

PVD

Atoms as source material

Solid source materials

Vacuum/high vacuum

Elemental films mostly

Room temperature

Alloy films easily (W:N)

One process, many materials

Al, Au, Cu, Pt, ... SiO₂

CVD & ALD

Molecules as source materials

Solid, liquid, gas precursors

Fluid dynamics important

Molecular/compound films mostly,
Chemical bonds broken & formed

Needs elevated temperatures
(or plasma activation)

Elements and compounds OK, alloys
more difficult

Each process materials specific

SiO₂, Si₃N₄, Al₂O₃, HfO₂, ... Si, W

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

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