Aalto University
School of Chemical Technology

CVD & ALD

(2 hour set for 2021 TFT-course)

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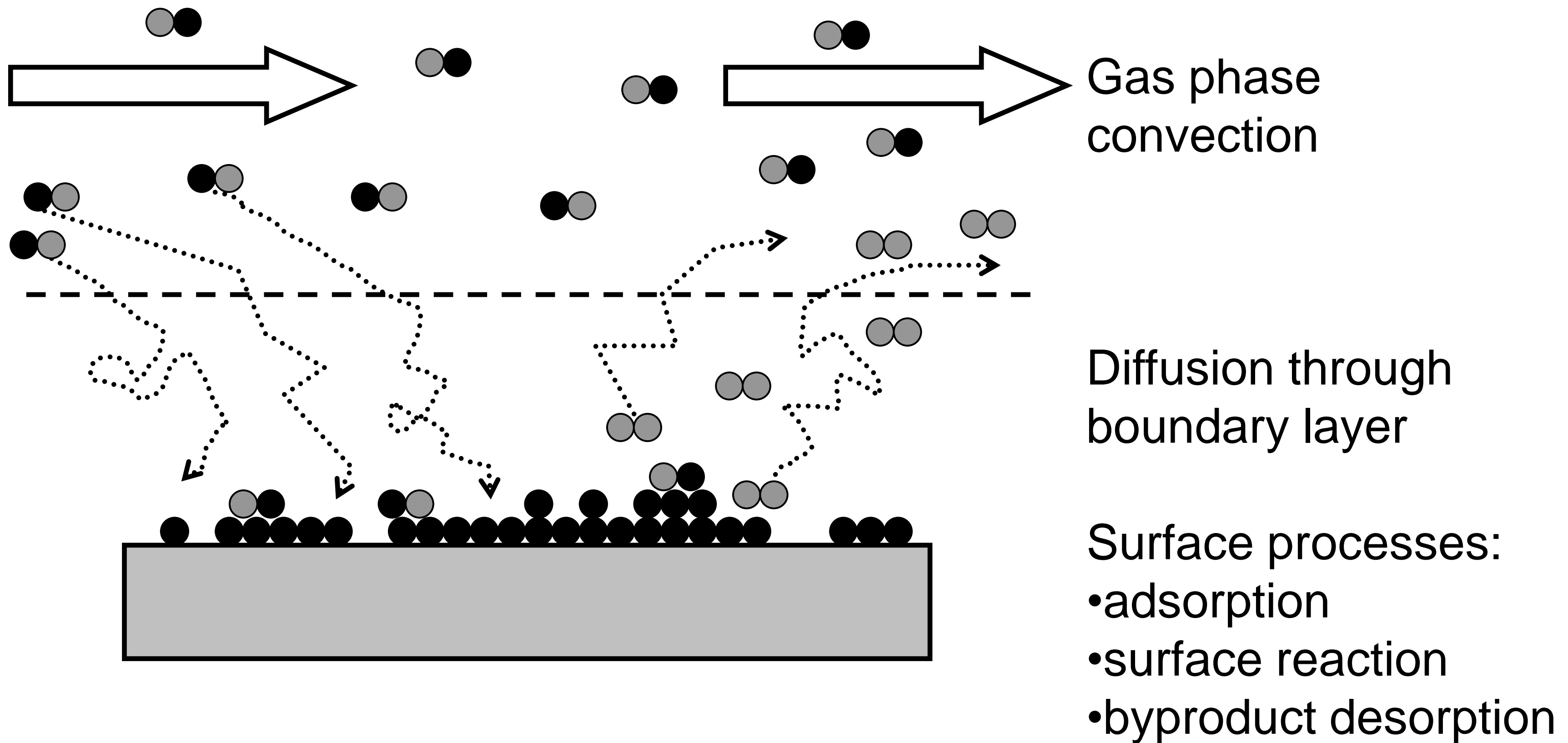
CVD schematically

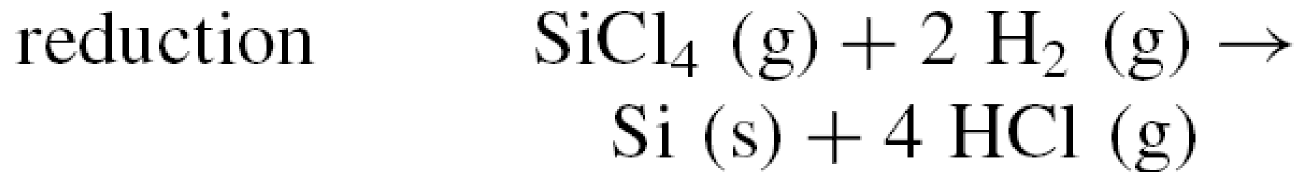


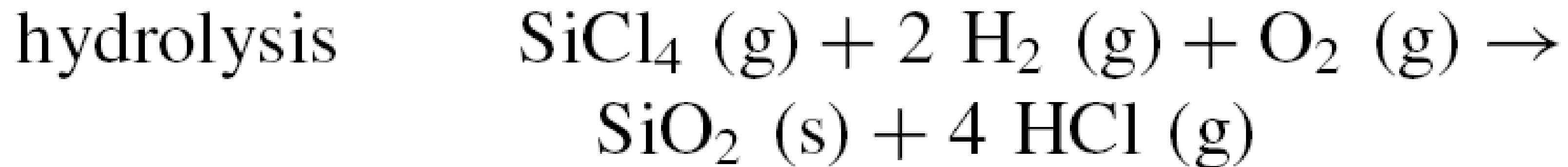
First lecture: CVD

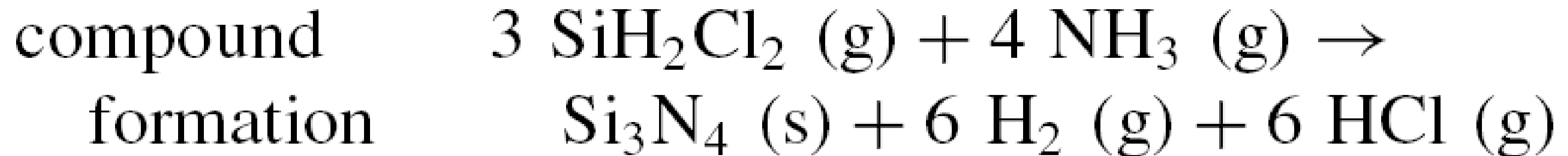
Gas phase convection	How are gases introduced to a reactor and how they flow?
Diffusion through boundary layer	Basic physics of boundary layer; LPCVD (Low Pressure CVD); And how this affects reactor design
Surface processes: •adsorption •surface reaction •byproduct desorption	Not so much on surface processes (but a lot in case ALD)
The resulting film	Factors affecting the film structure Measures of film quality

Thermal CVD reactions

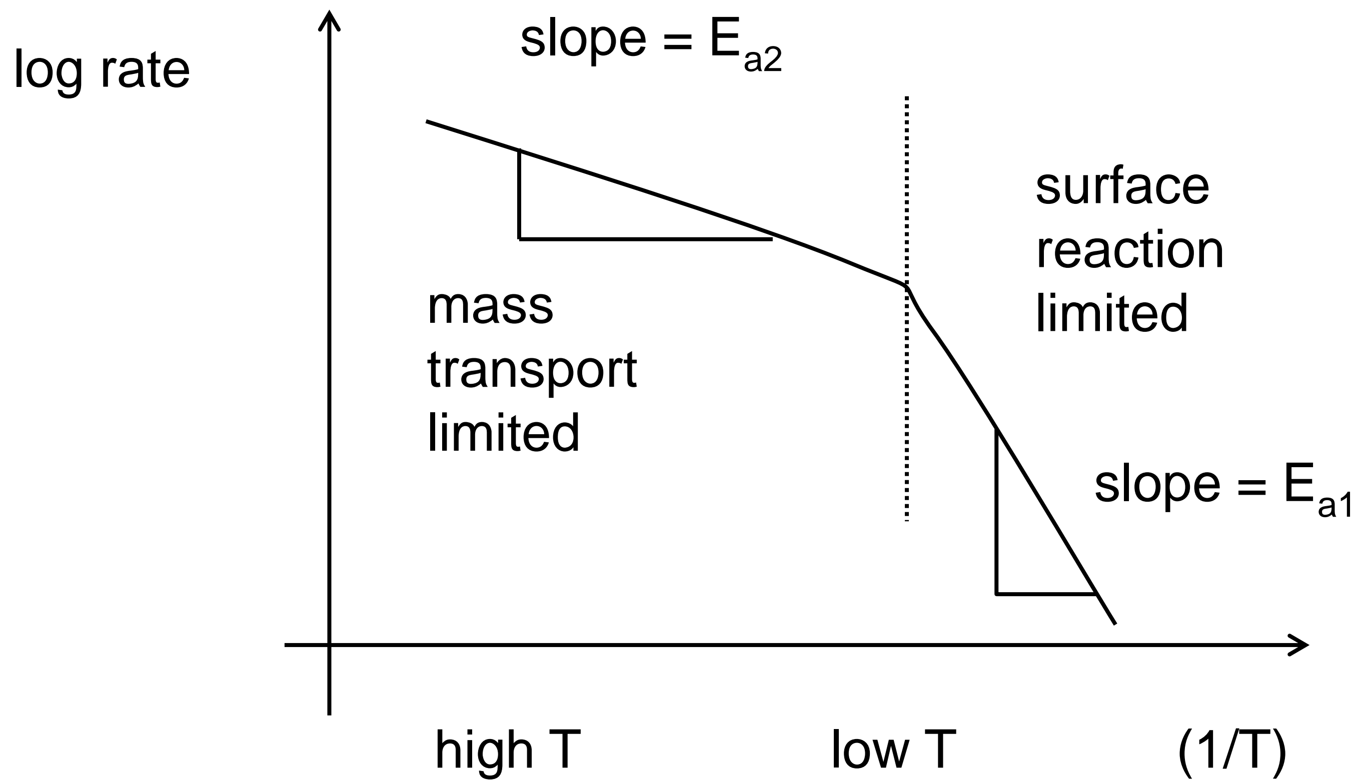
Gaseous precursor + surface reaction
➔ solid film + gaseous byproducts







Surface limited vs. mass transport limited reactions

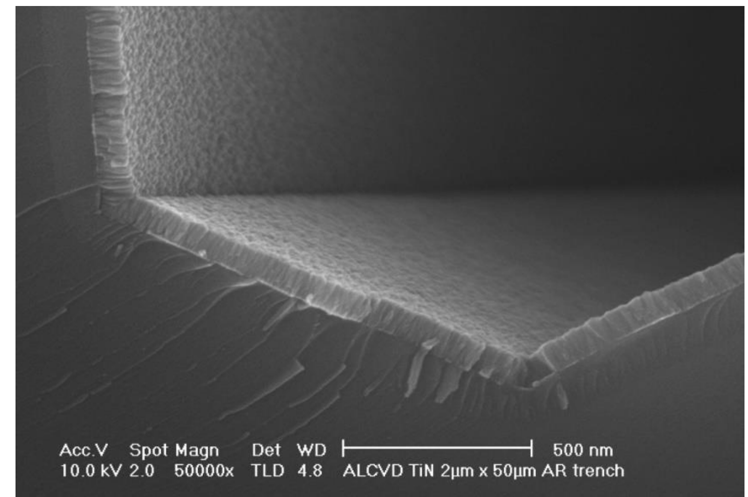


Surface controlled reaction

Slow reaction rate (e.g. due to low temperature). Lots of gas available, and only a fraction of it 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. Thermal CVD (especially LPCVD) also excellent conformality.



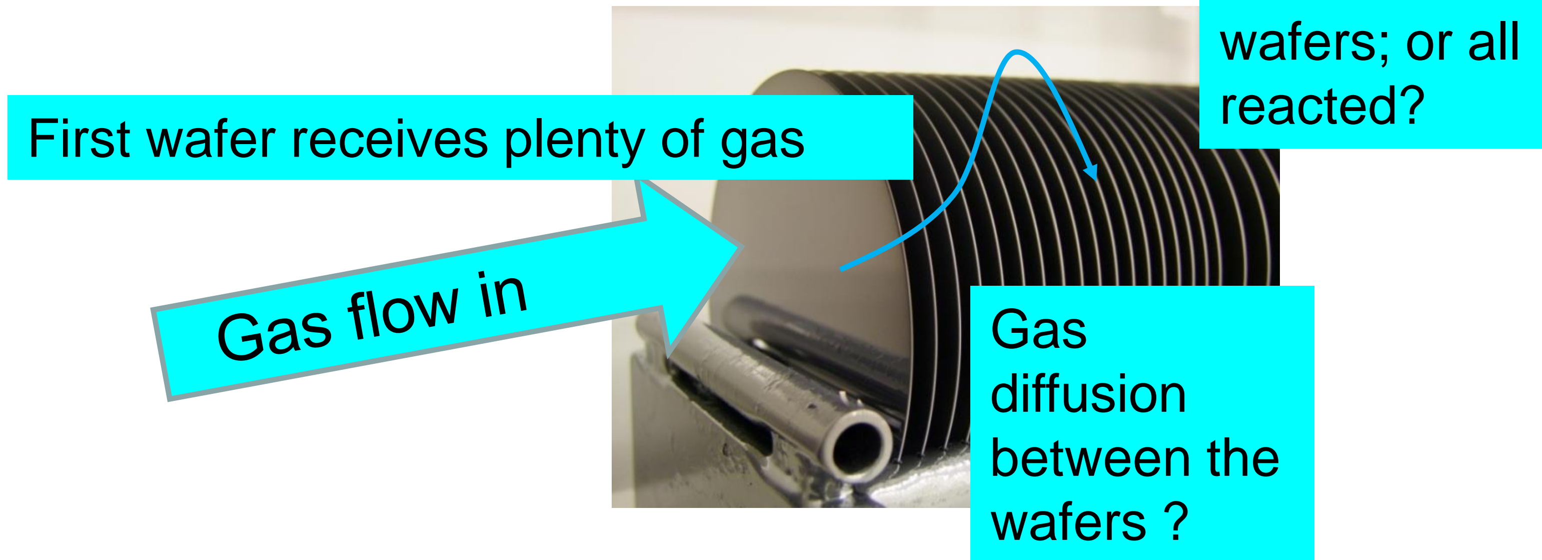
ALD TiN at the bottom of high aspect ratio groove.

Mass transport limited reaction

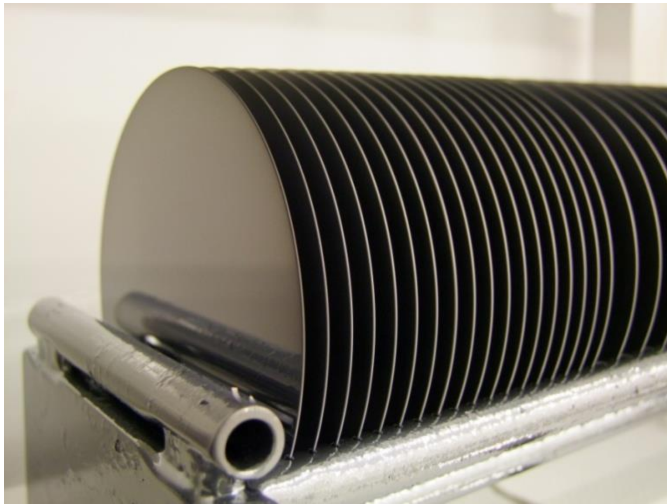
Reaction rate is very fast at high temperatures
(Arrhenius: rate is exponentially temperature-dependent).

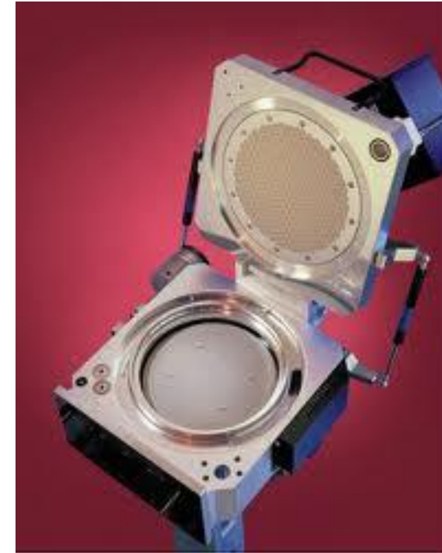
All arriving gases react immediately ➔ need to ensure that gases arrive equally to all parts of reactor. If not, position dependent depo rate.

Reaction is in mass transport limited mode.



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

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

Diffusion of precursor gas from main flow to the surface.

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

Boundary layer thickness δ.

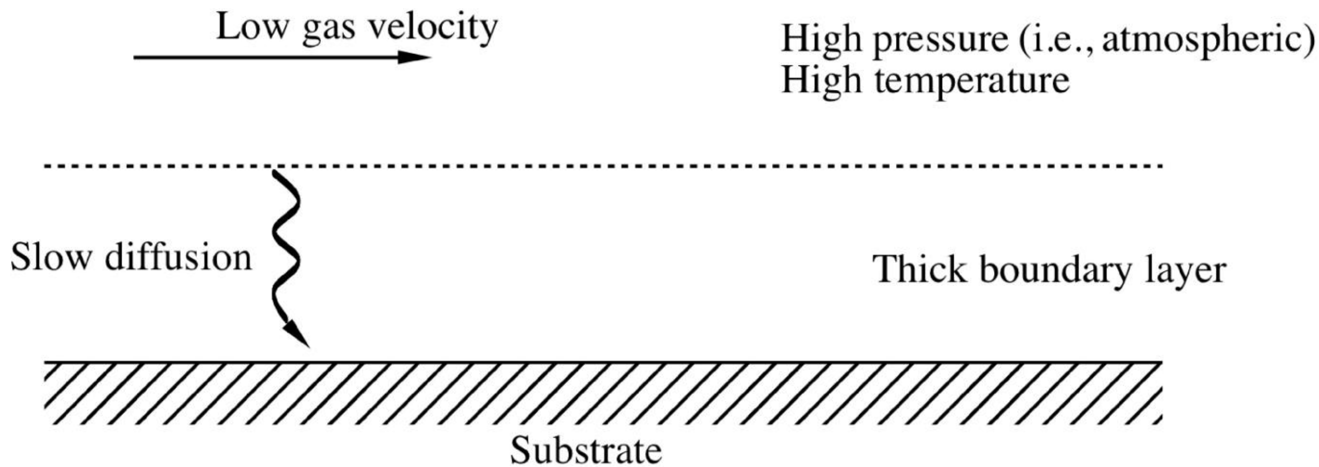
Raising temperature ➔ small changes in density, velocity and viscosity

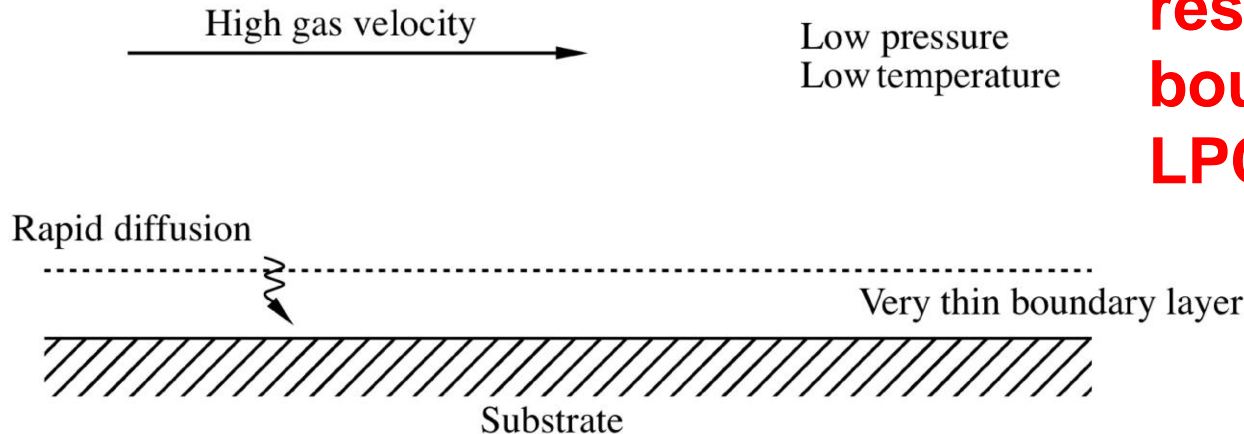
$$D \propto \frac{T^{\frac{3}{2}}}{P}$$

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

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

Boundary layer thickness





These variables result in thin boundary layer → LPCVD reactor

https://cnx.org/contents/m7vjnKhA@2/Chemical-Vapor-Deposition

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 ?

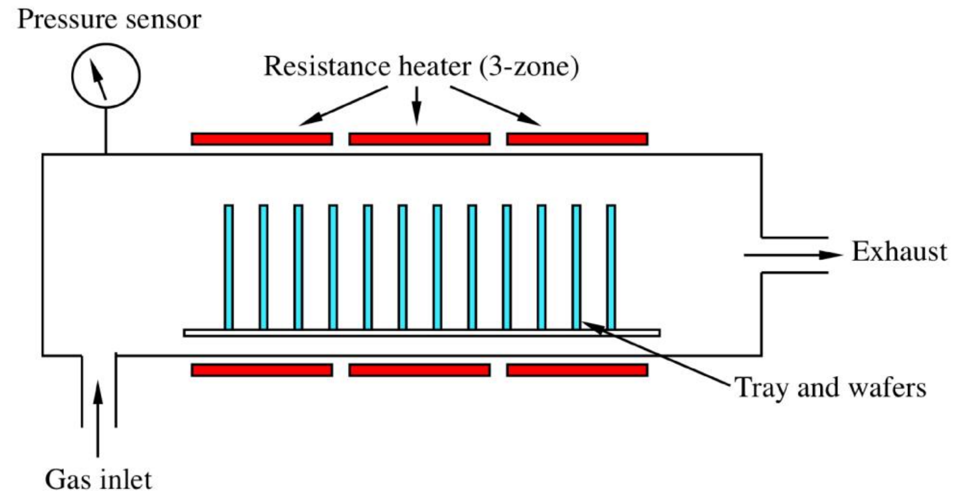
What reactor parameters to vary ?

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)

https://cnx.org/contents/m7vjnKhA@2/Chemical-Vapor-Deposition

Targets

Film:

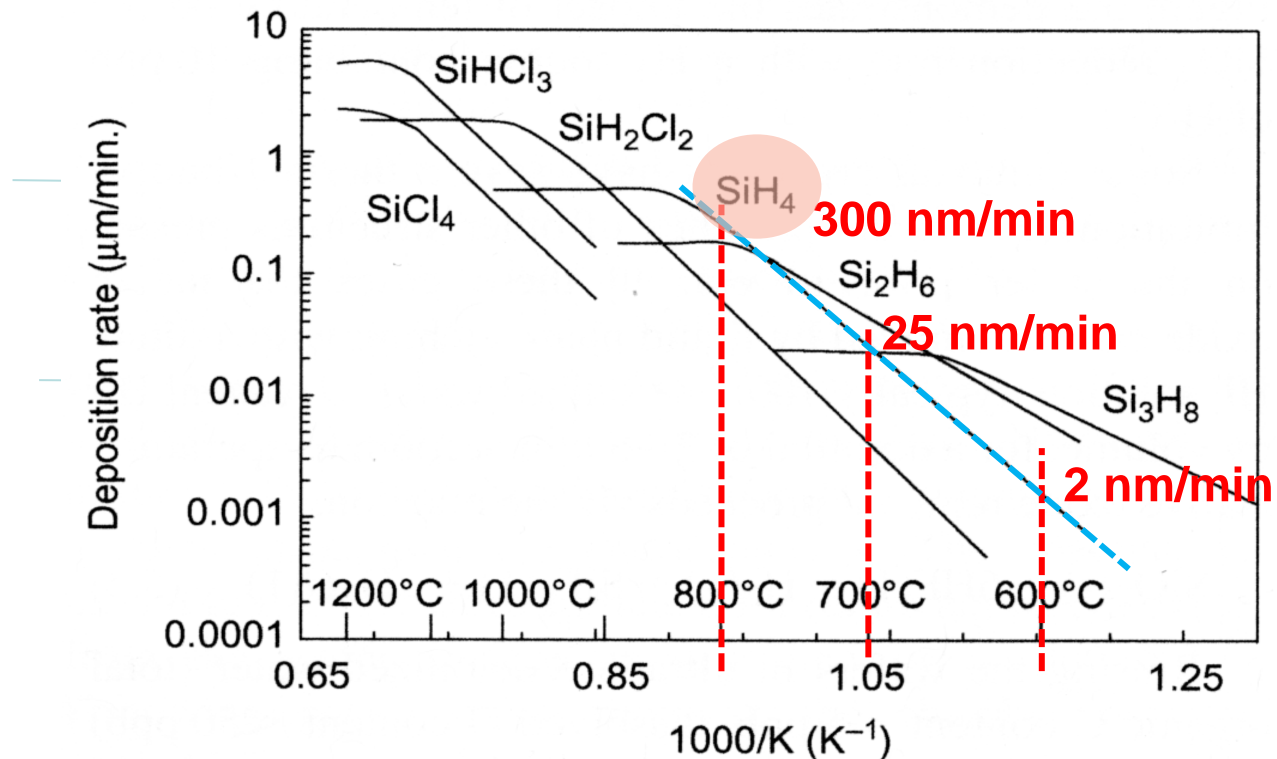
- Crystalline structure (e.g. grain size, orientation)
- Atoms & bonds (e.g. Si-Si bonds vs. Si-H; dangling bonds Si-*)
- Key parameters (t, R_s, n_f, ε, …)
- Uniformity (of thickness & other parameters)
- Impurities and defects

Productivity:

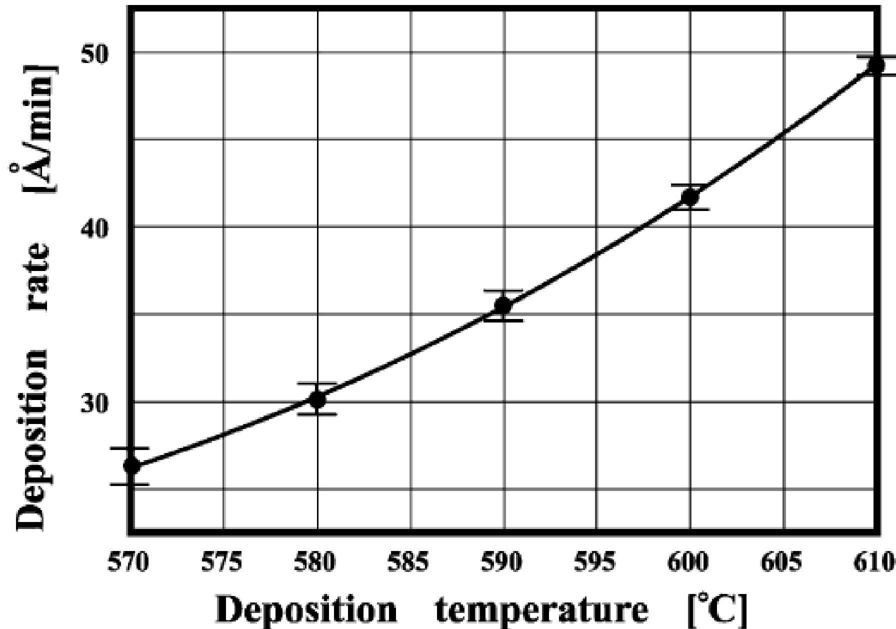
- Deposition rate (in units nm/min)
- Thruput (in units wafers/hour = WPH)
- Reproducibility (run-to-run; day-to-day)
- Yield (particles, out-of-specification thickness…)

Deposition rate

Arrhenius behavior.
Below 800^oC surface reaction controlled.



Deposition rate (2)



Undoped polysilicon

PH_3 dopant (➔ 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*

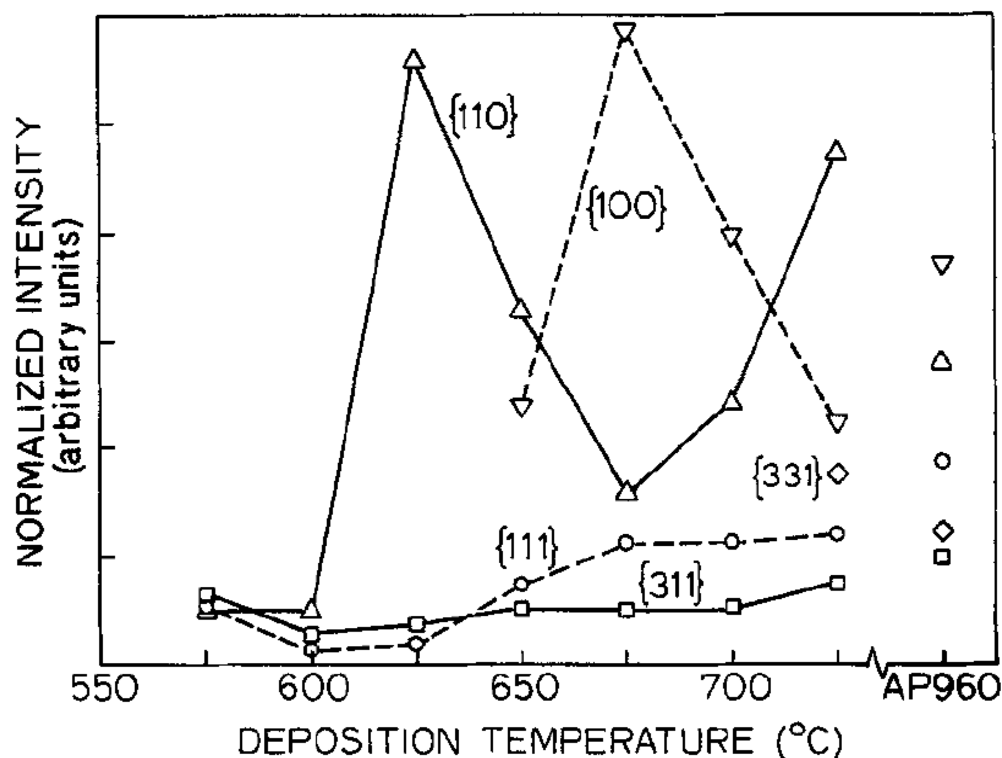
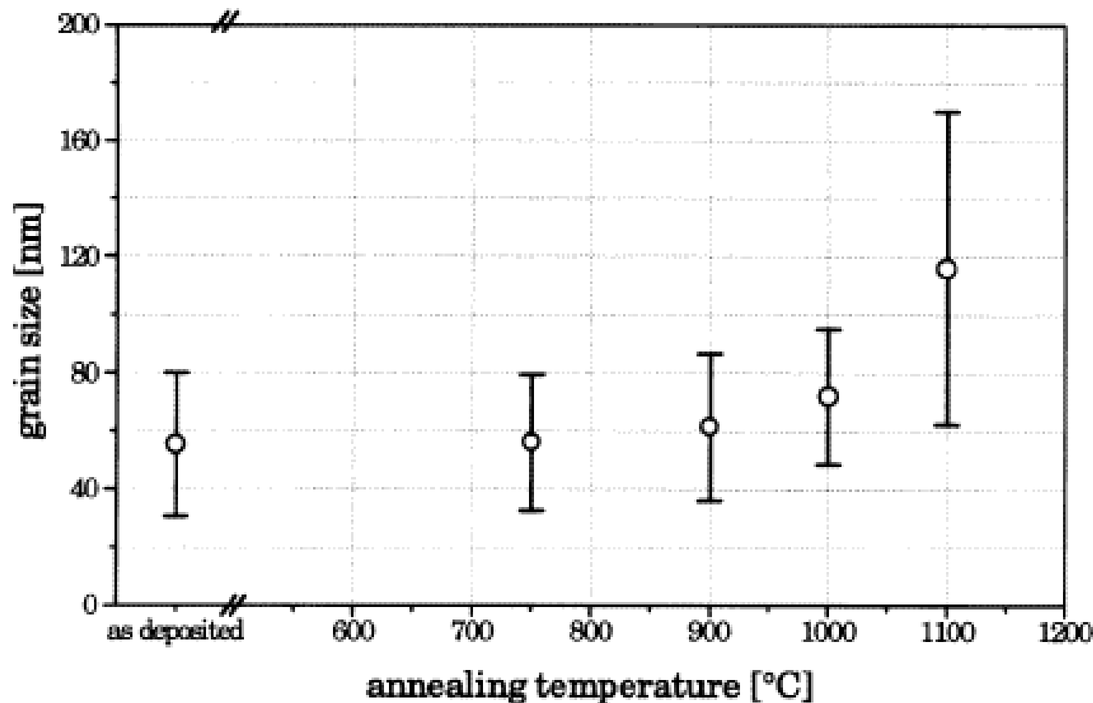


Fig. 1. X-ray texture as a function of deposition temperature for LPCVD silicon films and for an atmospheric pressure film.

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

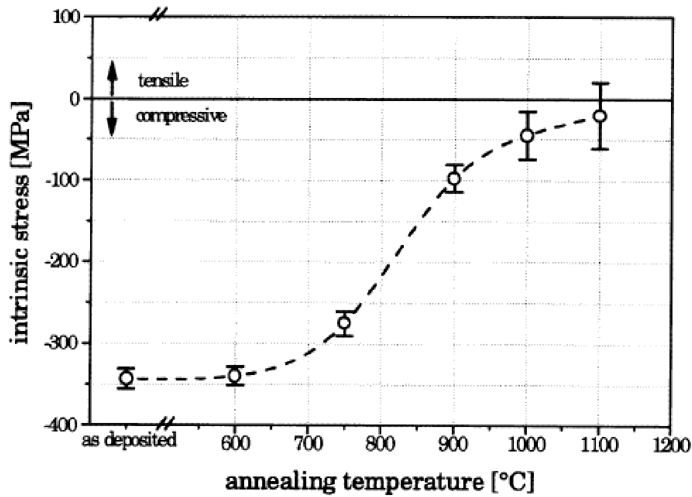
Deposition temperature affects grain size

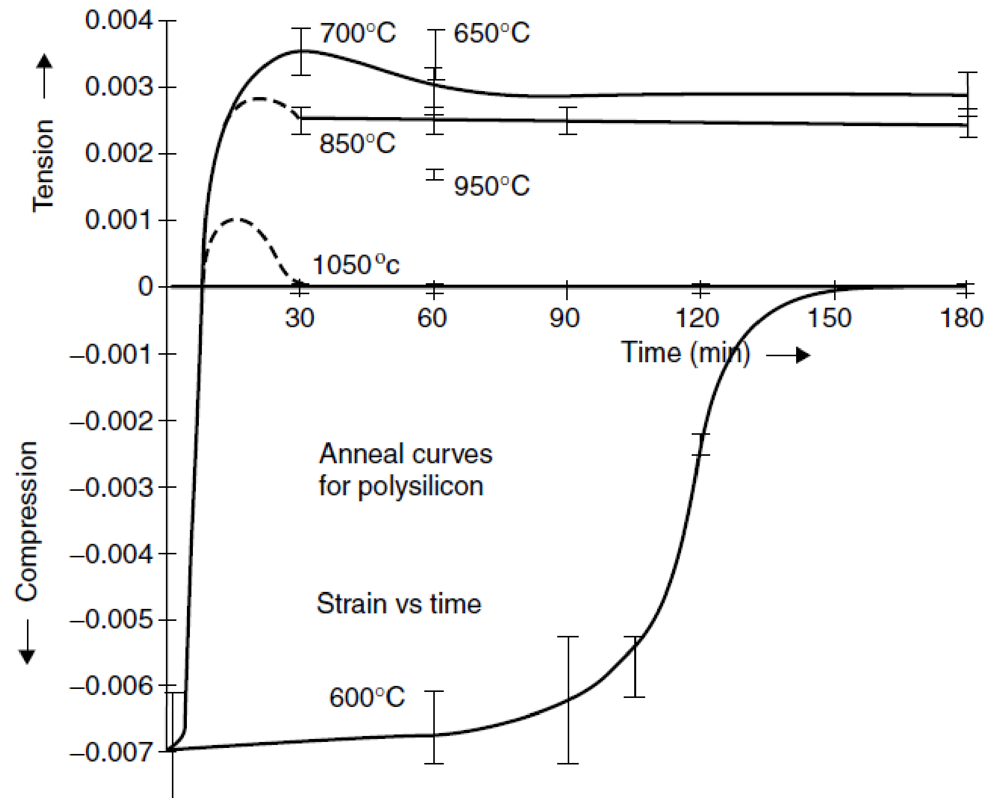


Post-deposition anneal affects grain size

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

Stress relief anneal





Stress reduction is anneal temperature and time dependent !

580°C deposition, i.e. amorphous initially

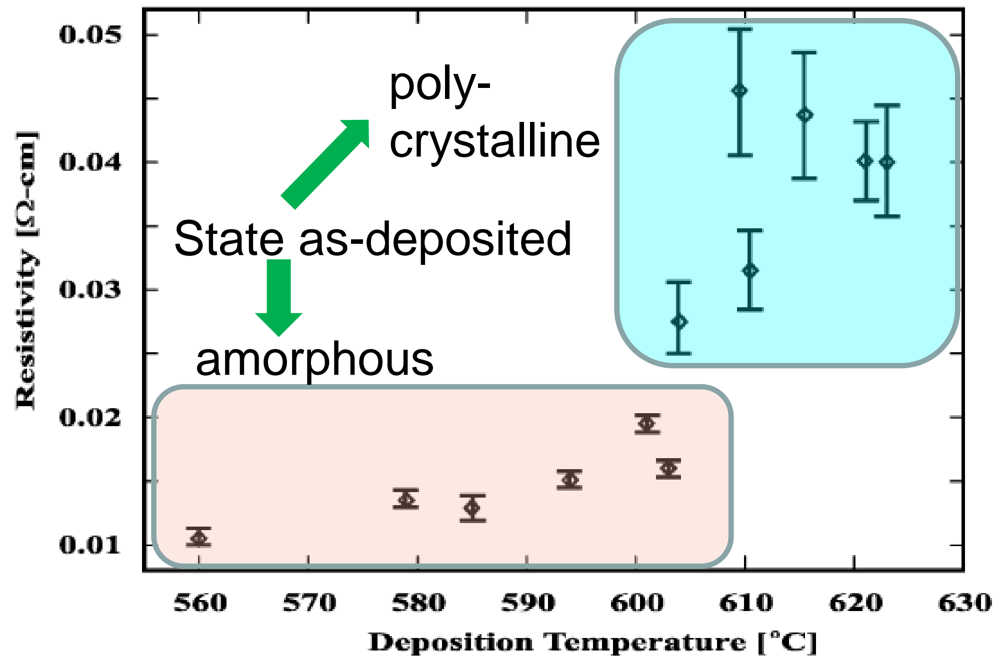
a-Si by LPCVD

~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



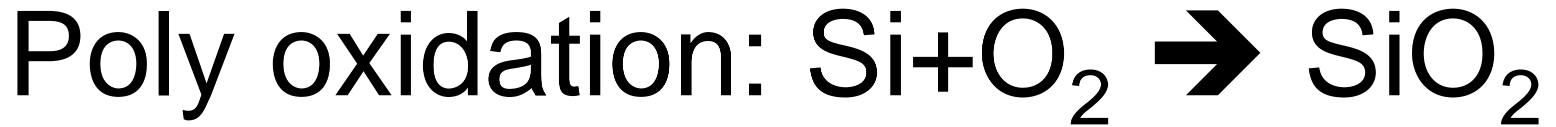
Resistivity after doping:

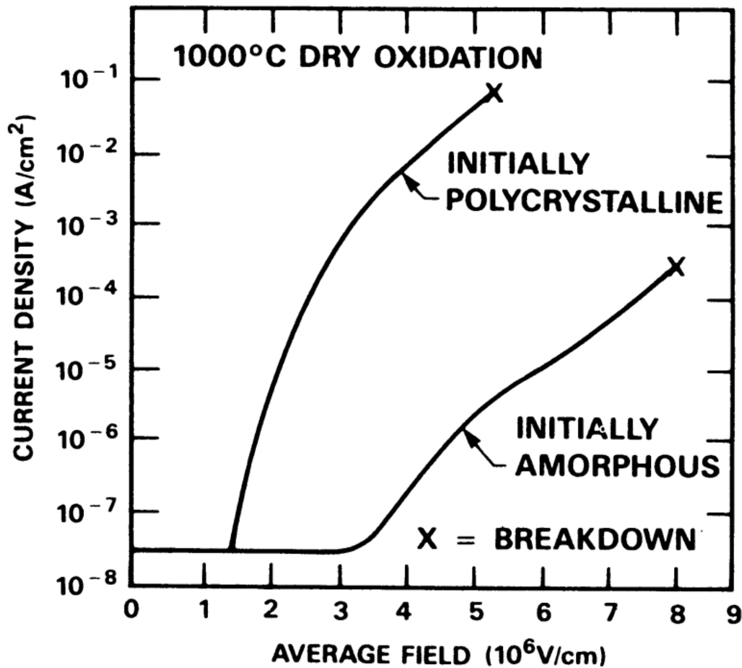
Ion implantation into film ($1*10^{15}$ ions/cm^2) and subsequent anneal (1000°C).

Why the difference ?

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

Paddy French 2002



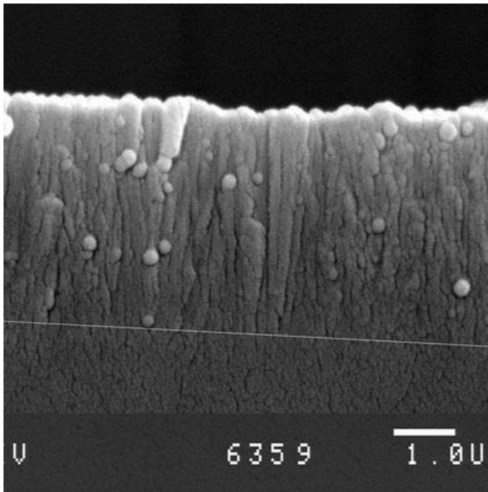


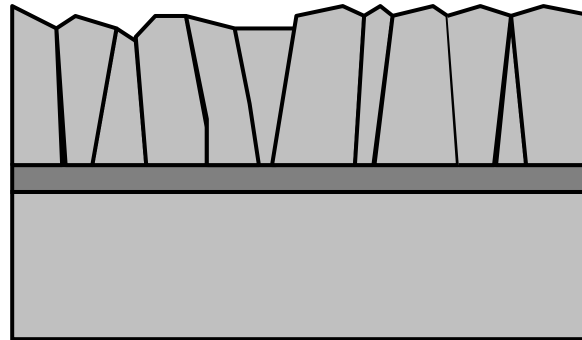
Breakdown field is a common measure of oxide film quality.

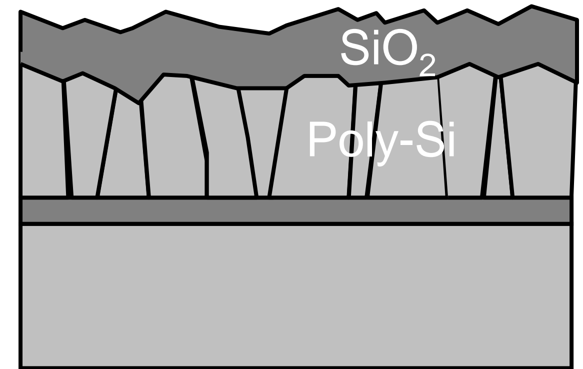
Why is initially amorphous film better in terms of oxide breakdown ?

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

Poly oxidation (2)

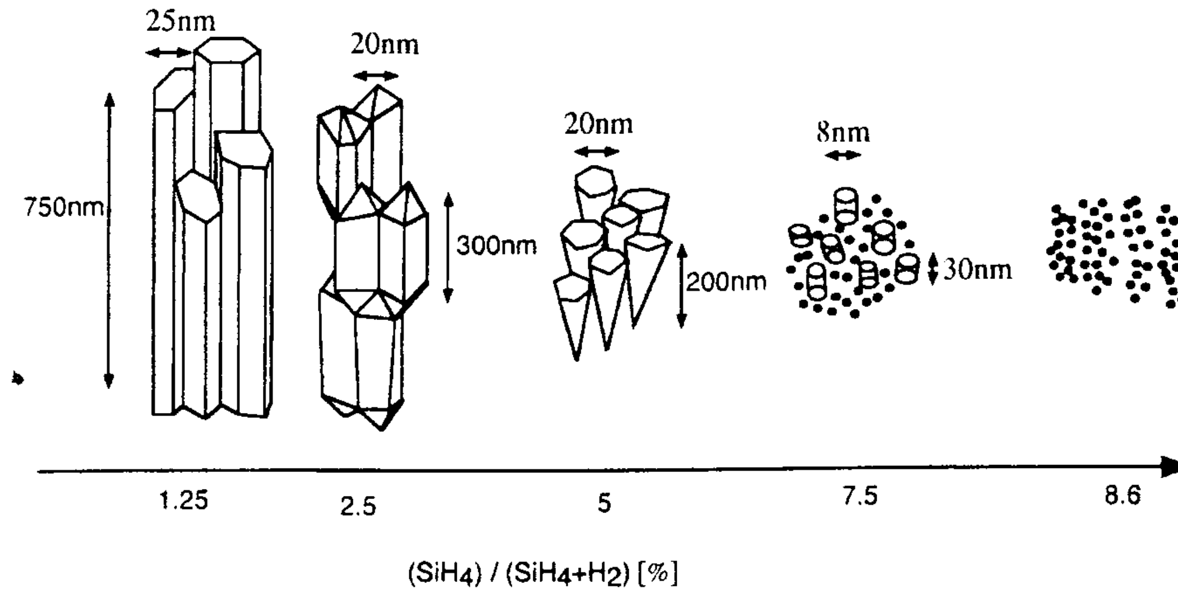






Polycrystalline film is rougher than amorphous film
➔ oxidized polycrystalline film has variable thickness (because grain orientation affects oxidation rate)
➔ electric field concentration at tips and thin points
➔ easy breadown

Grain size & roughness



Vallat-Sauvain

Polysilicon thin film vs. <Si>

Density: same 2.3 g/cm3

Young's modulus: same 170 GPa

CTE: same 2.5 ppm/K

Thermal conductivity:

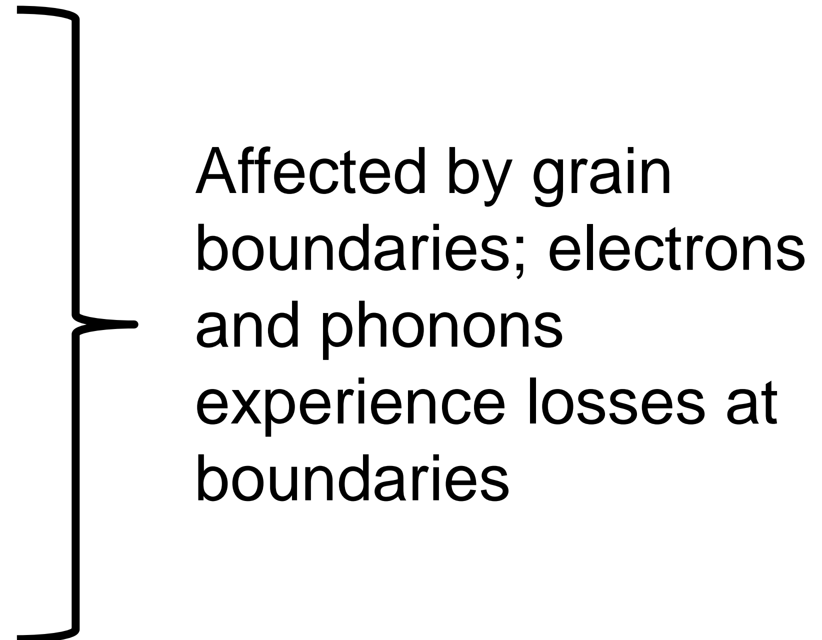
<Si> 156 W/K*m (at room temp)

poly 32 W/K*m

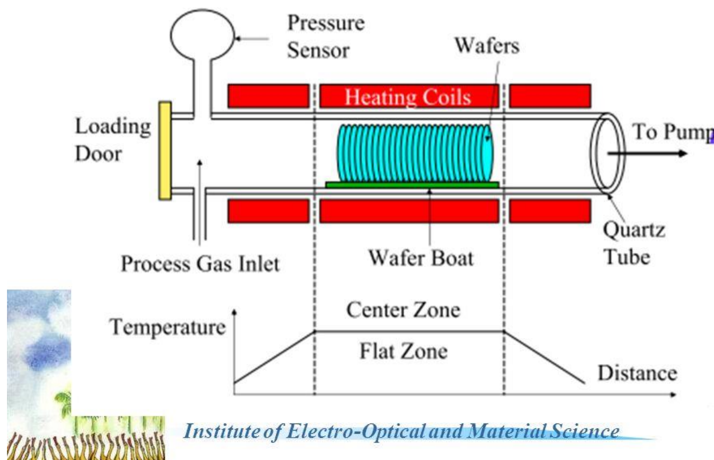
Carrier mobility:

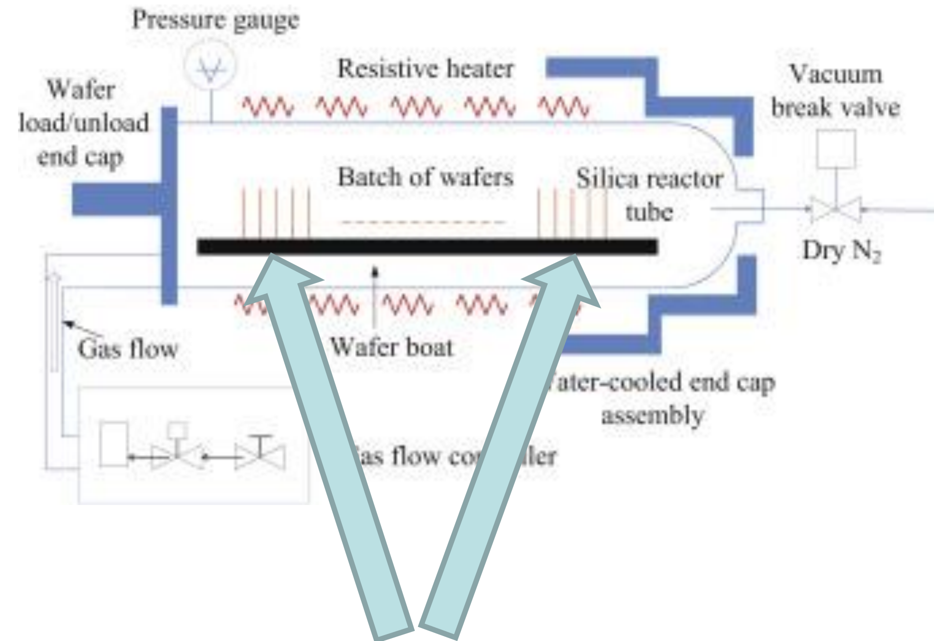
<Si> 100 cm^2/Vs

poly 10 cm^2/Vs



Temperature control zones





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

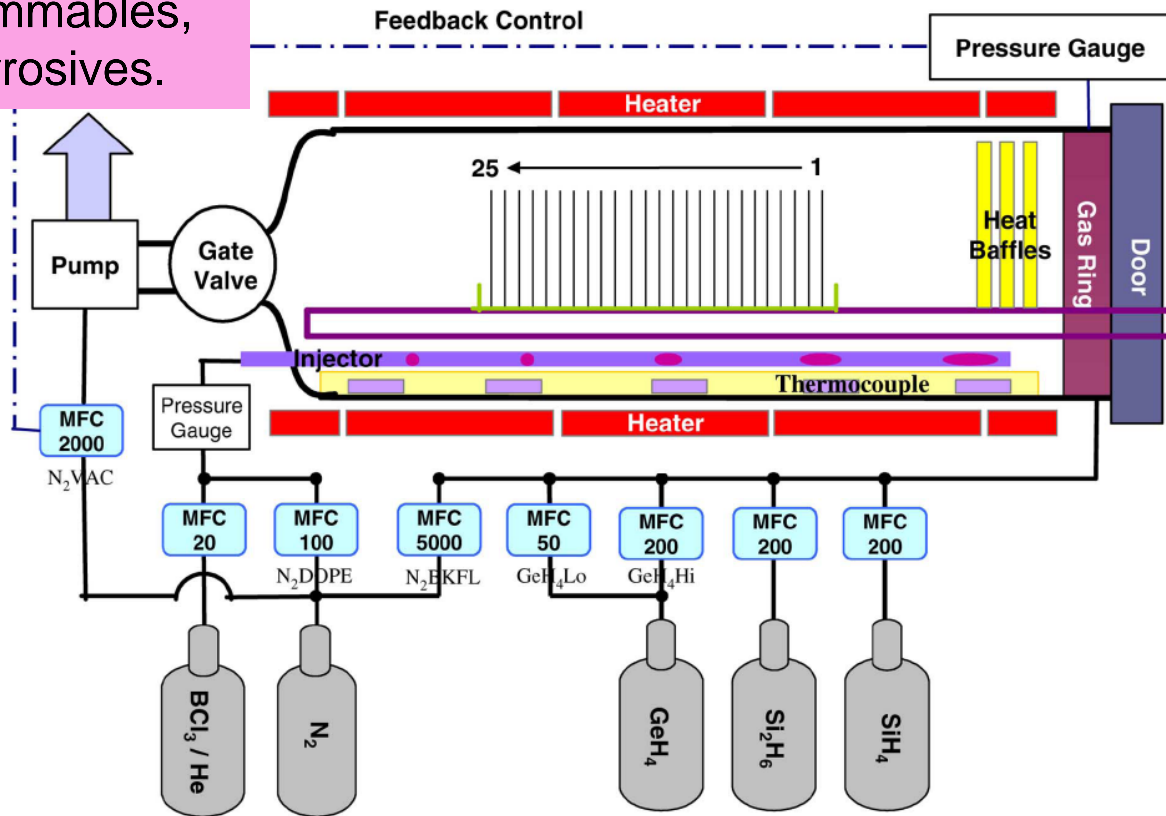
Dummy wafers make sure end of tube thermal losses reduced.

https://slideplayer.com/slide/6820319/

Jiang et al: Materials Science in Semiconductor Processing Volume 43, 1 March 2016, Pages 222-229

LPCVD reactor

Gas abatement: remove toxics, flammables, corrosives.



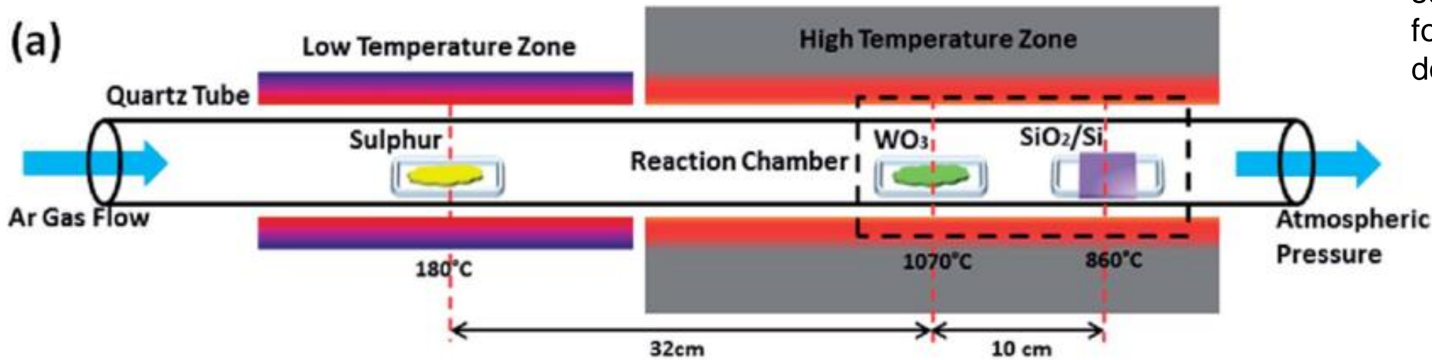
Howe, Stanford

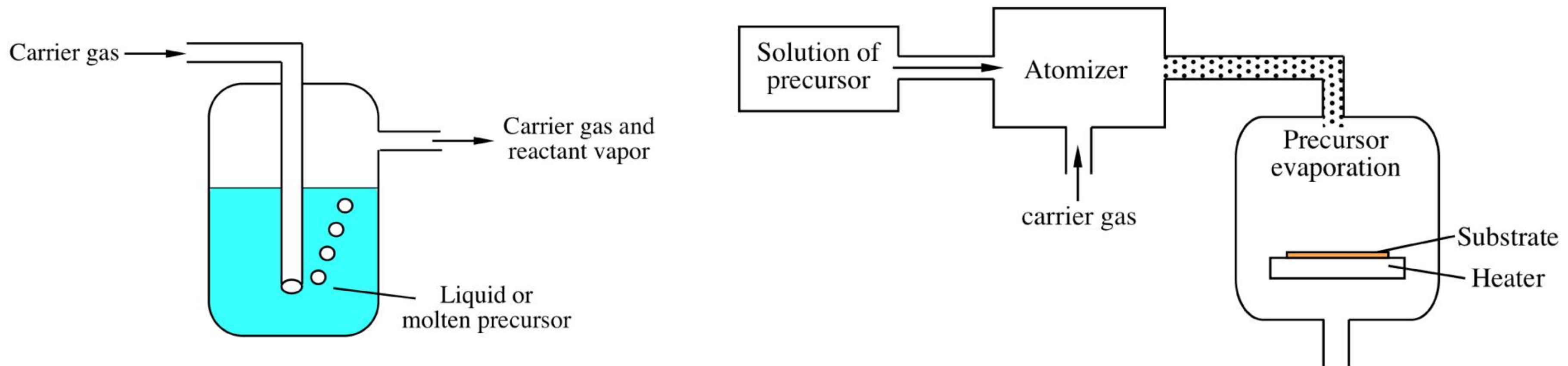
Gas injection: from below, from hundreds of small injector holes.

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



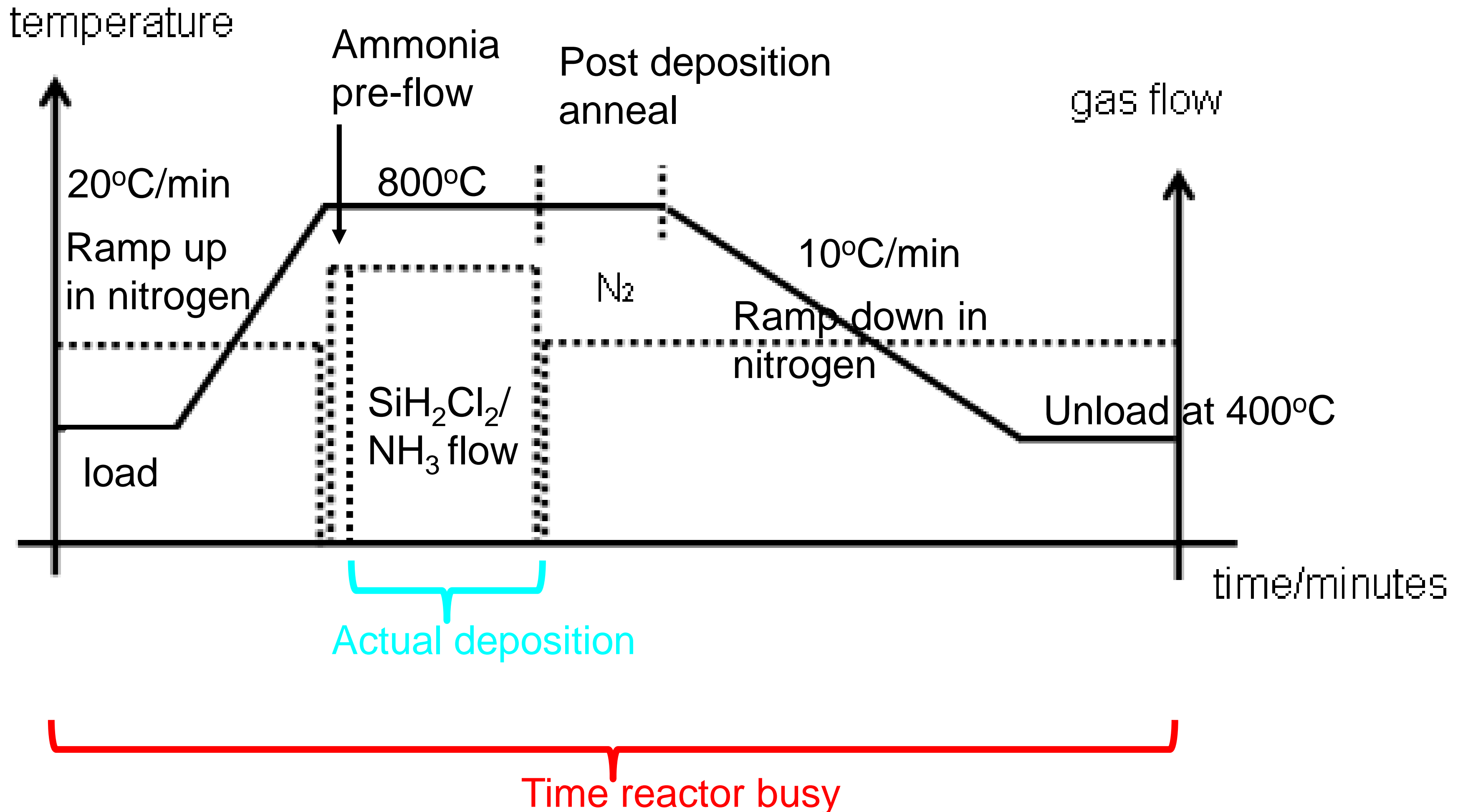


https://cnx.org/contents/m7vjnKhA@2/Chemical-Vapor-Deposition

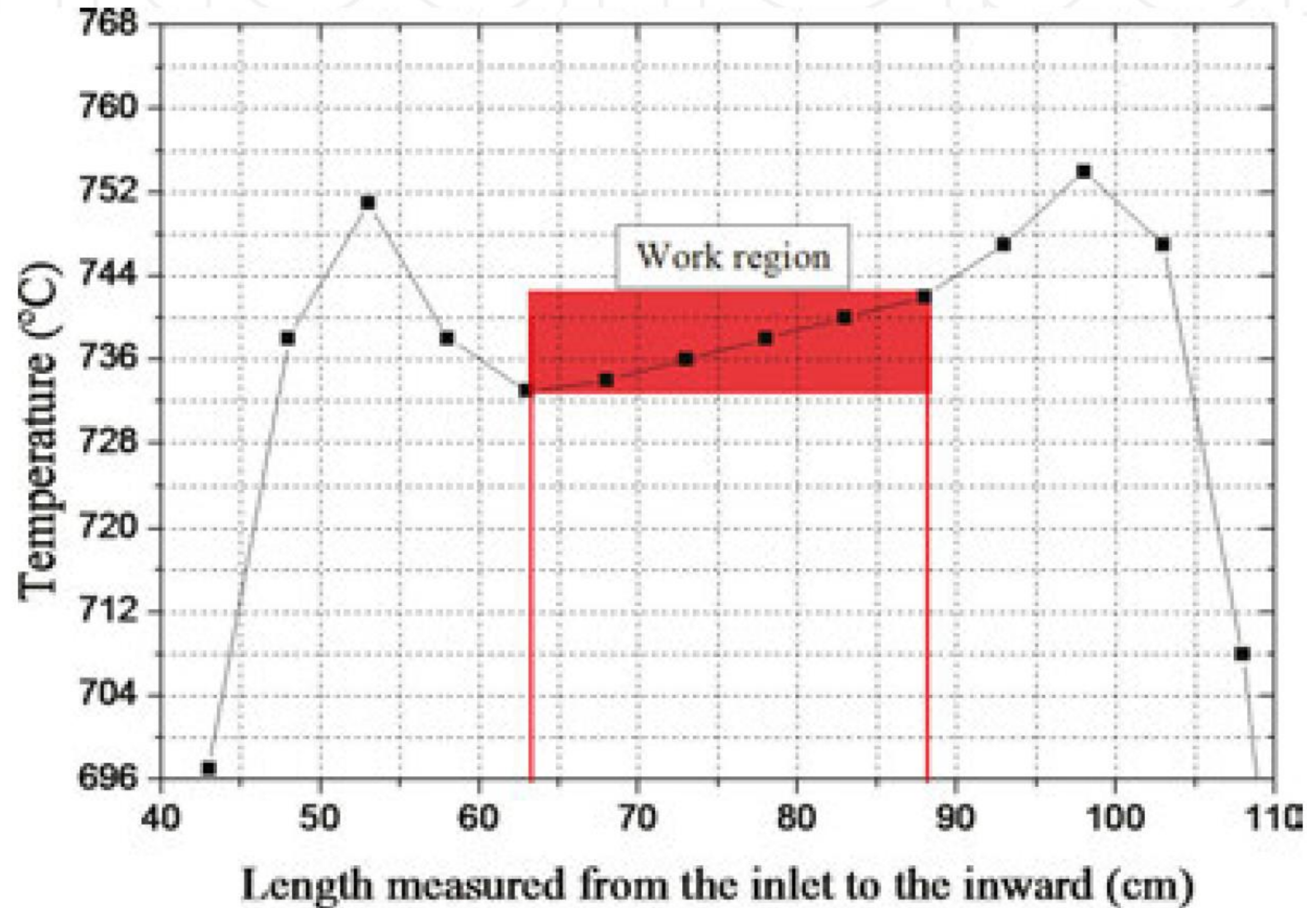
LPCVD of silicon nitride (Si_3N_4)

- Load the boat, fill with dummy wafers to equalize load and flow patterns.
- Ramp temperature from 500^oC to 800^oC under nitrogen flow, 50 min (5^oC/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^oC (10 min)
- **Take boat out**
- Monitoring: film thickness and refractive index by ellipsometer

Total cycle time: LPCVD nitride



Real temperature profile

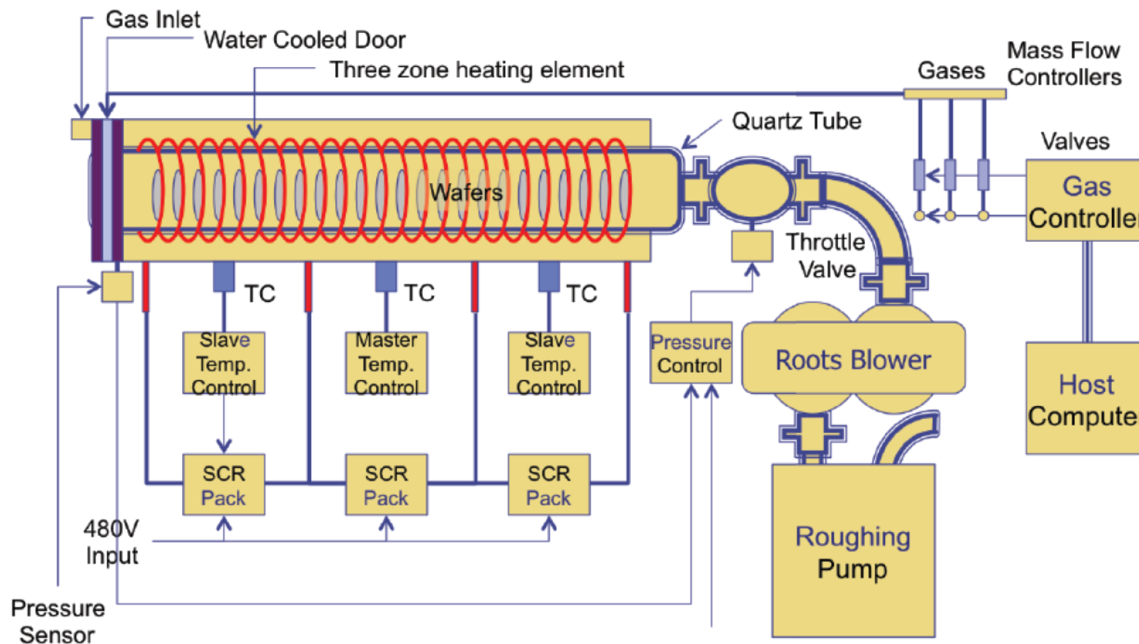


Range 9 degrees !

J. Alarcón-Salazar et al: http://dx.doi.org/10.5772/63012

Does 3-zone temperature work ?

Heating elements are arranged in three zones: e.g. T1: 747 ^oC, T2: 750 ^oC, T3: 753 ^oC 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.

Low Pressure CVD
By Christopher Henderson, Semitracks.com

Purity

Source gas issues:
-oxygen and water vapor oxidize silicon
-hydrogen remains in the film
-purity of source gases ? 99.99% vs. 99.99999%
-oxygen reactive and incorporated into film

Furnace issues:
-base pressure ? What is there to begin with?
-leaks: oxygen, water, backstreaming oils
-tube walls experience film deposition, too
-if these films flake off, they “rain” on wafers as particles

CN-film: PECVD of $NH_3/CH_4/Ar$

XPS results: C, N, O content in films as-deposited and annealed at different T_A

Sample no.	Sputter	C1s (at.%)	N1s (at.%)	O1s (at.%)	N/C ratio
As-deposited	×	66.35	17.80	15.85	0.268
	/	86.45	9.48	4.07	0.110
200 °C	×	73.93	16.10	9.97	0.218
	/	89.29	8.83	1.88	0.099
400 °C	×	77.07	12.01	10.92	0.156
	/	90.02	7.94	2.04	0.088
600 °C	×	82.28	7.42	10.30	0.090
	/	91.61	6.10	2.29	0.067
800 °C	×	85.00	2.80	12.20	0.033
	/	96.73	1.51	1.76	0.016

Note. Sign '×' and '/' mean without and with Ar^+ sputter.

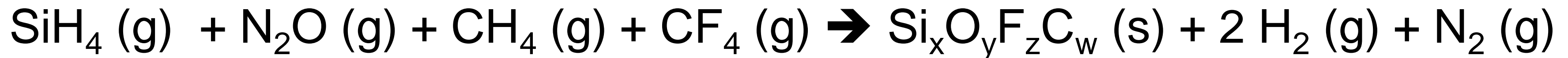
Not stoichiometric (C_3N_4, cf. Si_3N_4)

Oxygen is impurity

Argon ion bombardment during deposition seems to remove oxygen efficiently.

Yu et al: Effects of thermal annealing on amorphous carbon nitride films by r.f. PECVD, 2002

$Si_xO_yF_z$/ $Si_xO_yC_z$ films

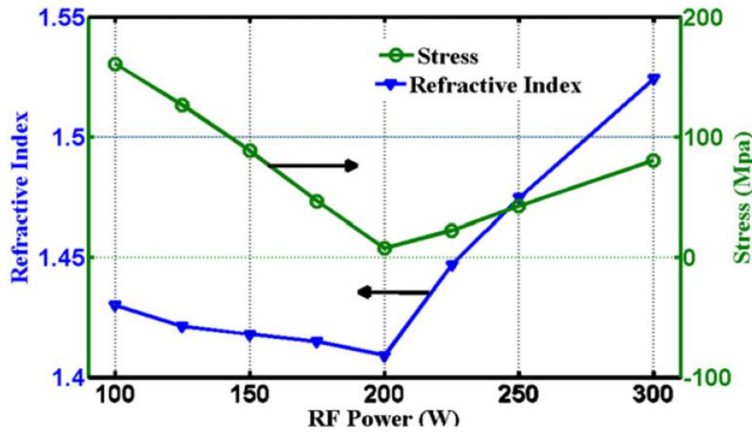


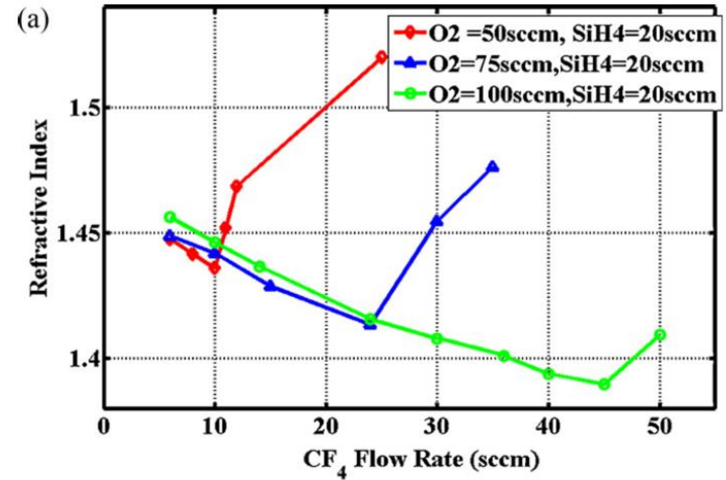
- Low dielectric constants (by chemistry and by porosity)
- Refractive index tailoring
- Composition tailoring
- Stress control

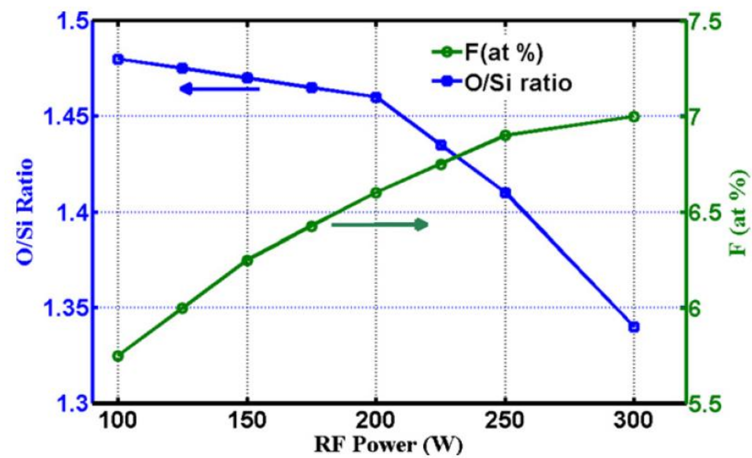
The more variables, the more things to control.

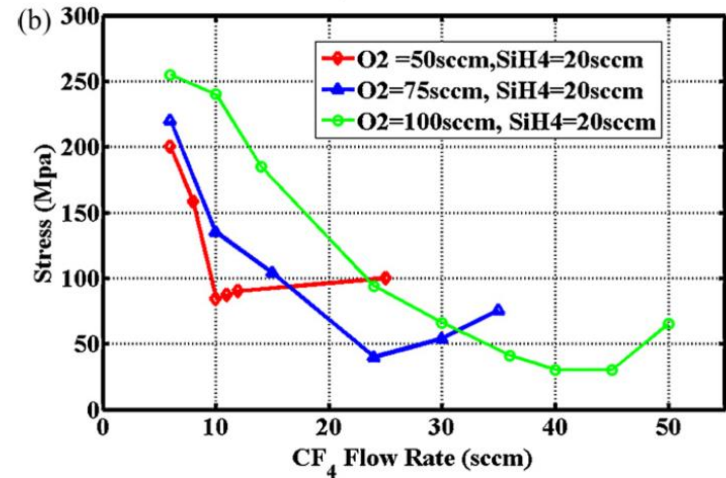
This must be achieved without sacrificing uniformity, reproducibility, stability…

$Si_xO_yF_z$-film



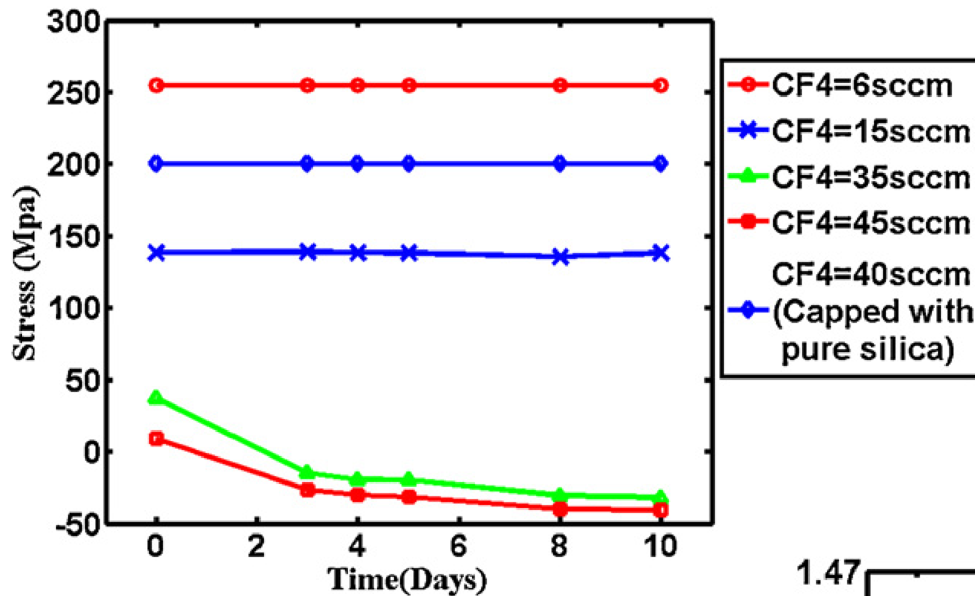




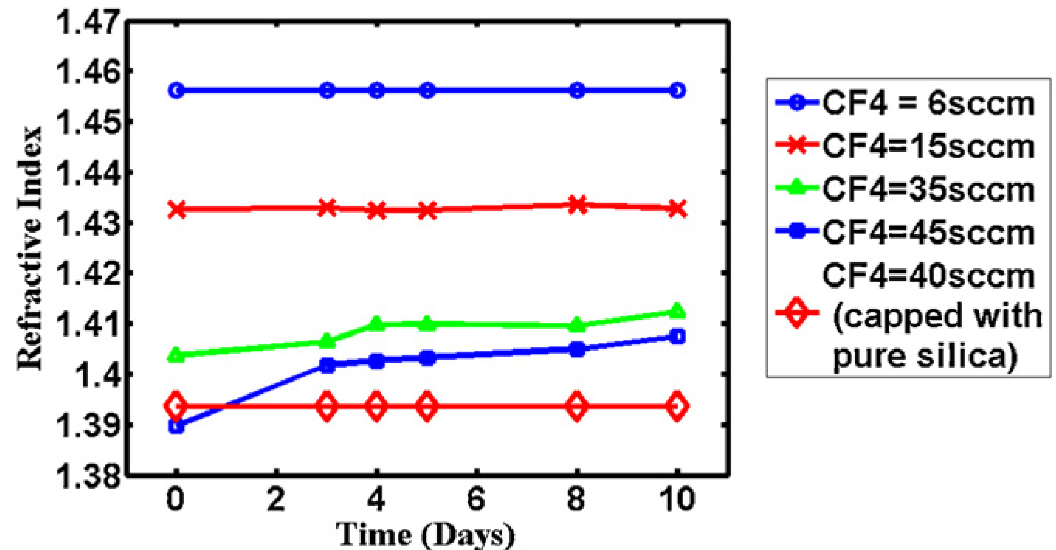


Michael et al: Sensors and Actuators A 178 (2012) 110– 117

$Si_xO_yF_z$ film (in)stability



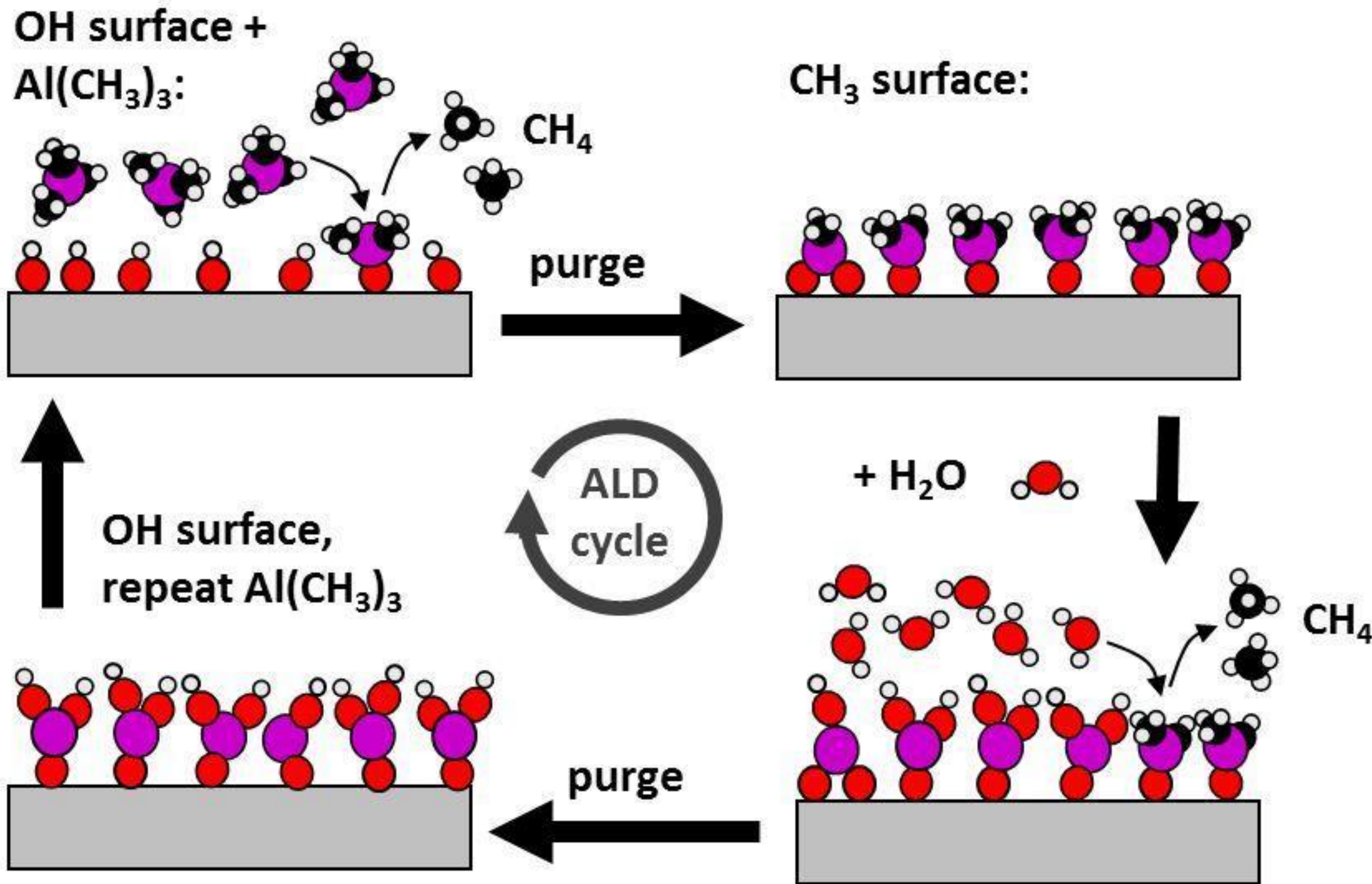
(i) surface effect (due to adsorbed water at the surface), (ii) silanol effect (formation of Si–OH due to diffused water), (iii) adsorbed water dipoles effect



Michael et al: Sensors and Actuators A 178 (2012) 110– 117

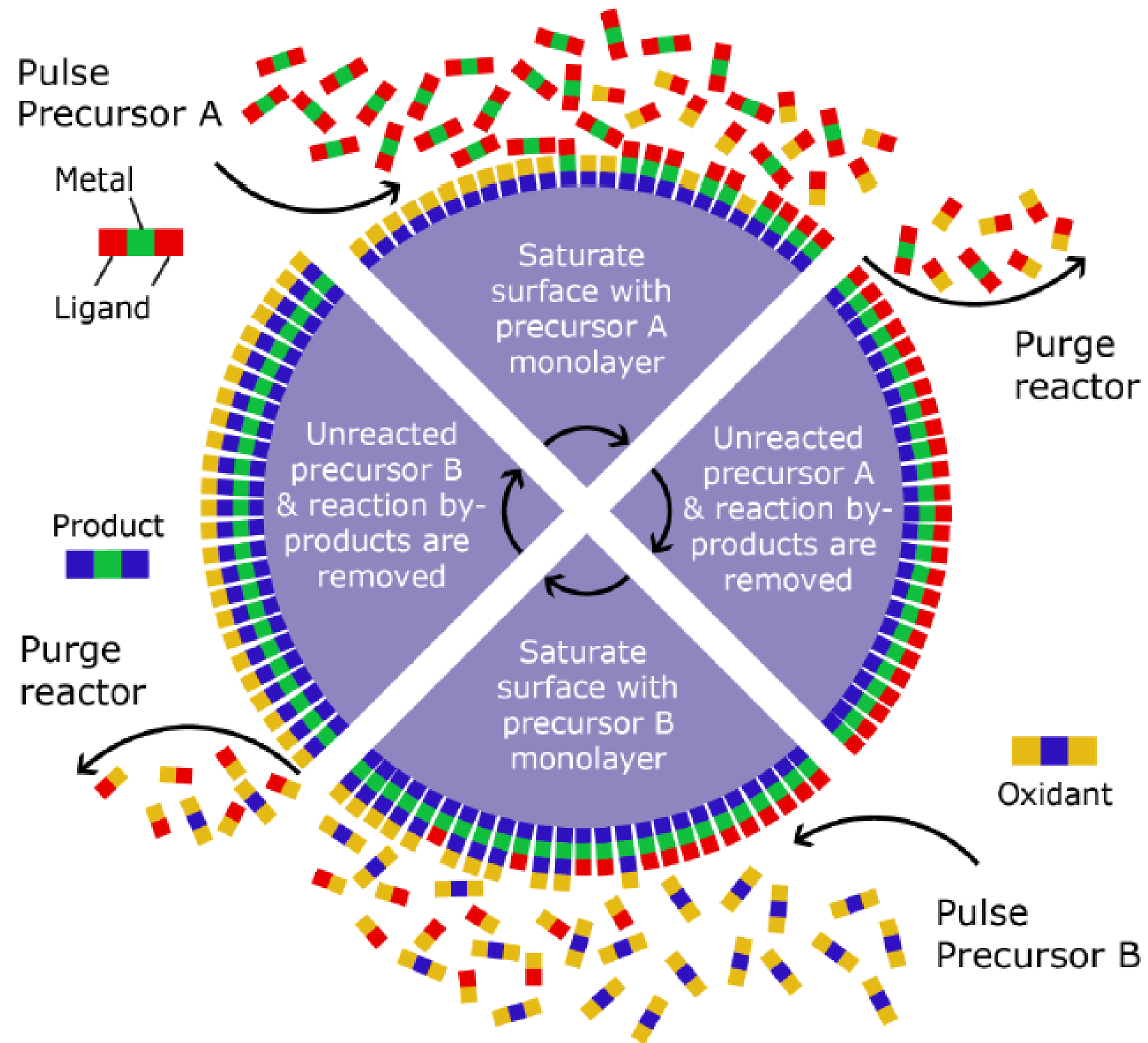
Half-time

ALD: Atomic Layer Deposition



Precursors introduced in pulses, with purging in-between

ALD cycle



Ville Rontu, PhD thesis, Aalto 2020

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

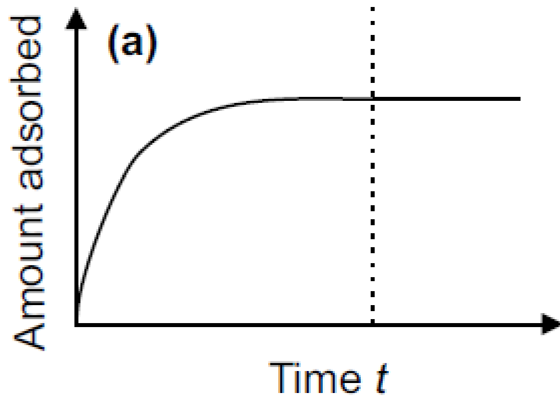
Surface controlled reactions

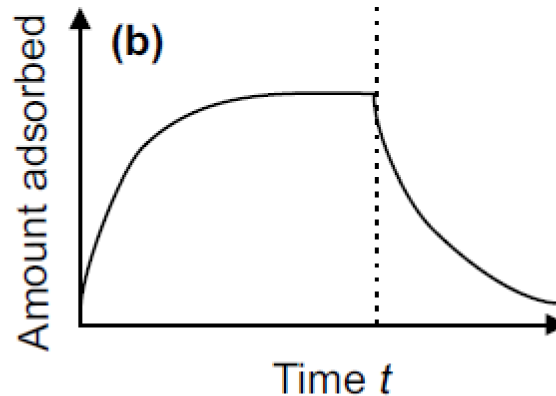
- Film thickness is independent of substrate geometry ⇨ conformal film onto deep trenches and 3D structures

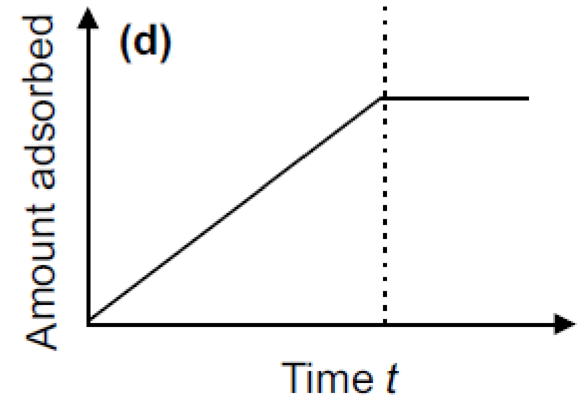
Sequential

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

Surface saturation







Irreversible saturation ALD reactions:

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

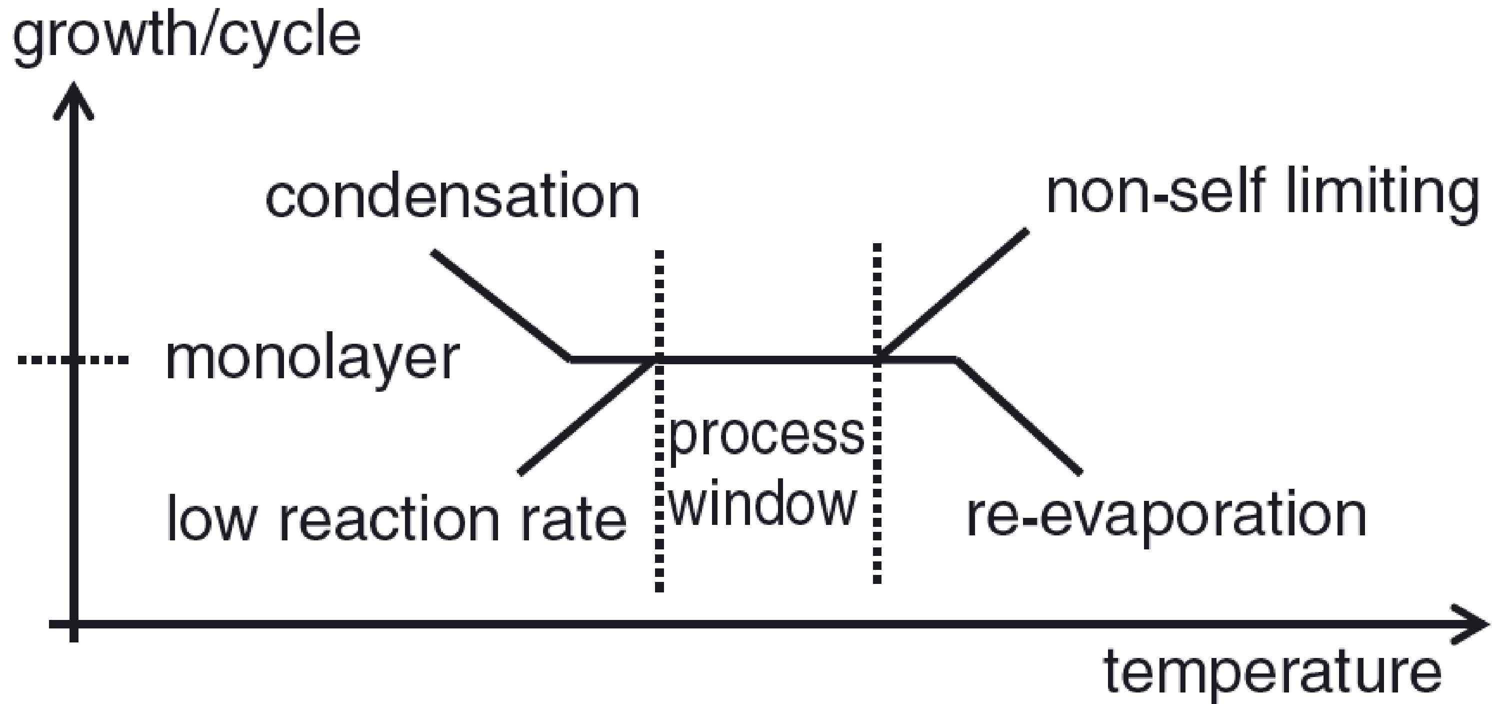
Reversible saturation:

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

Irreversible non-saturating.

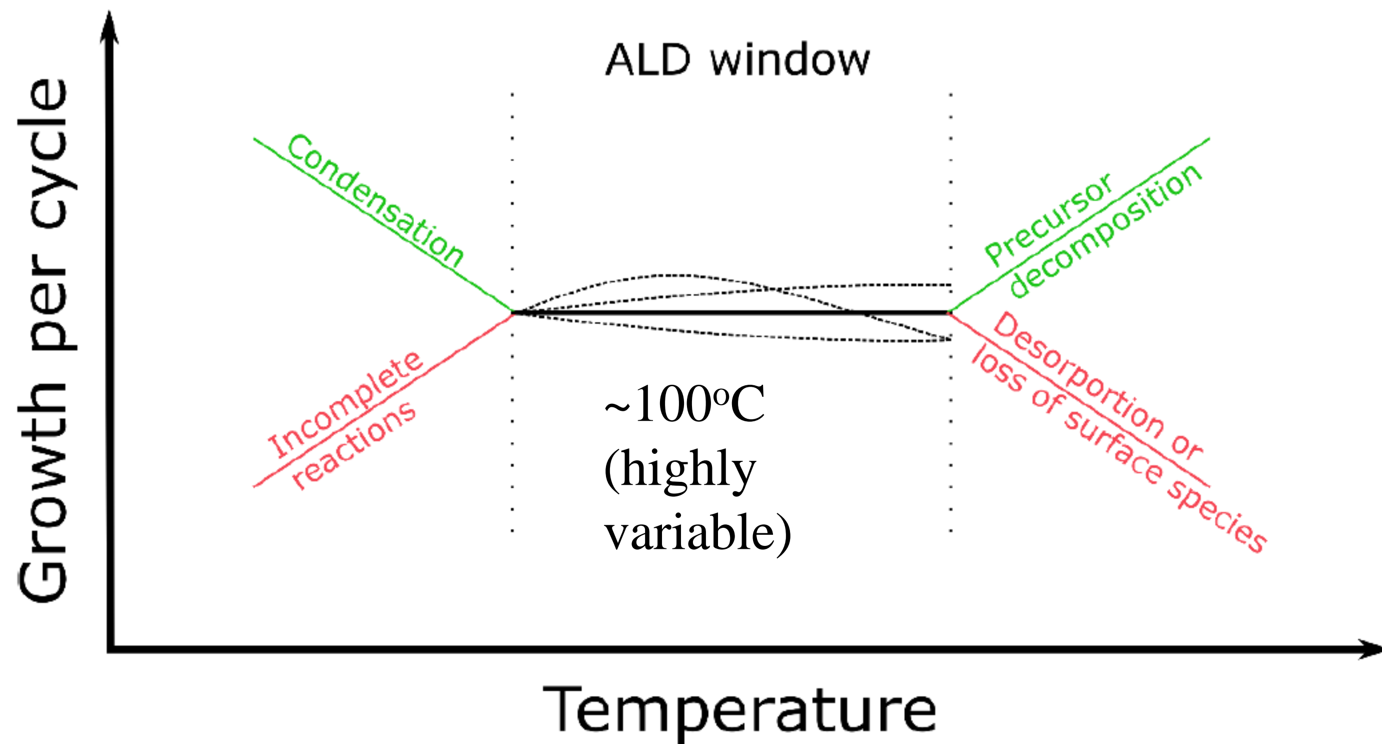
CVD regime: more reactants in, more film is deposited (continuosly)

ALD window



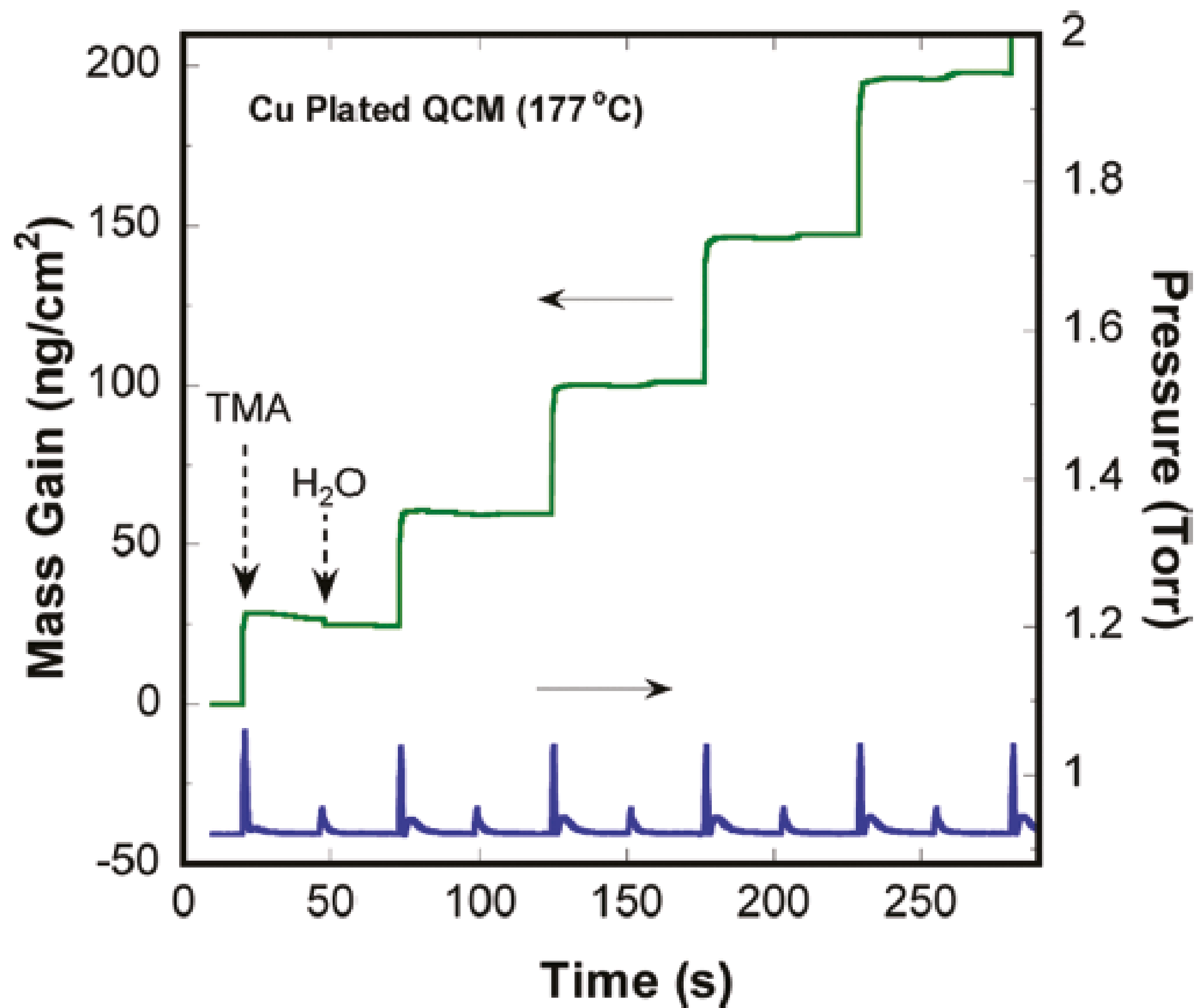
Compare with CVD: exponential (Arrhenius) temperature dependence.

ALD window realistically



Ville Rontu PhD thesis, Aalto 2020

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

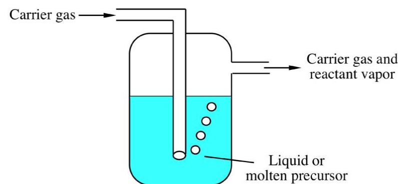
Precursor considerations

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).

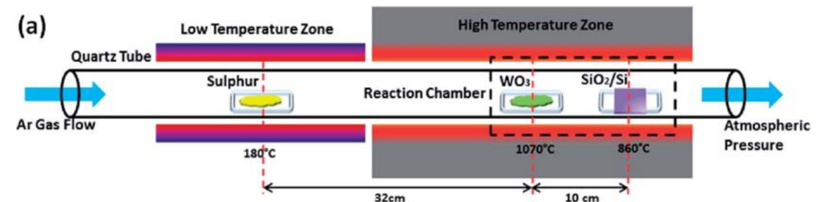
Source temperature then becomes one reactor parameter to optimize.

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



Liquid bubbler

Solid source



https://cnx.org/contents/m7vjnKhA@2/Chemical-Vapor-Deposition

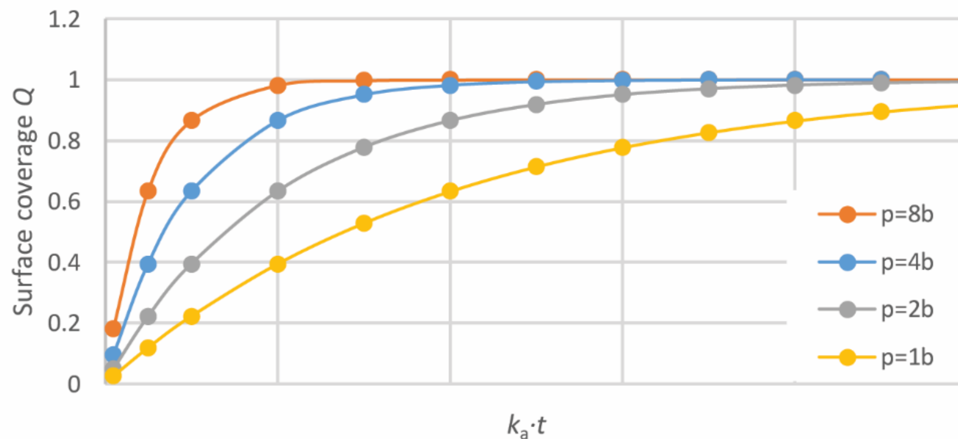
Rong et al: Controlling sulphur precursor addition for large single crystal domains of WS_2, 2014

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).

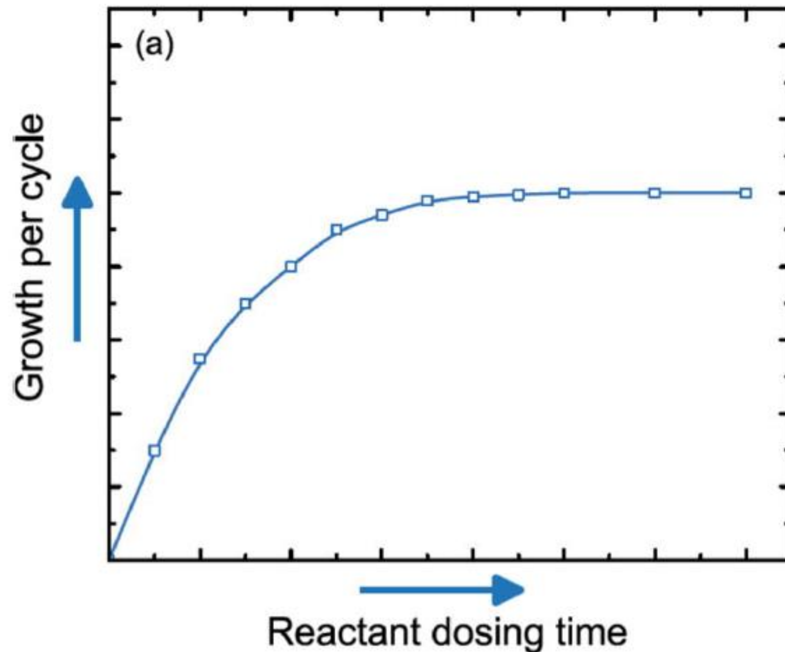
Ville Rontu, PhD thesis, Aalto 2020

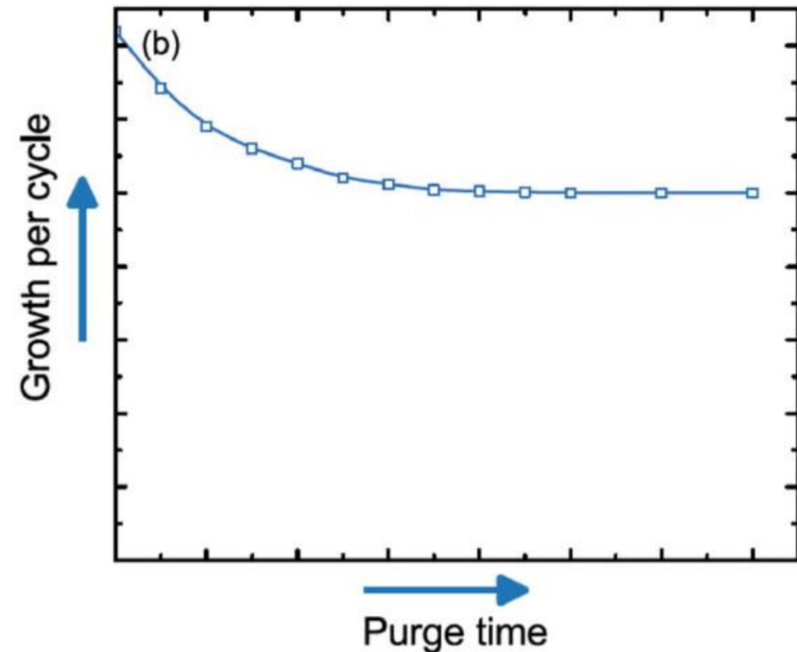
Start with long pulses

"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 deteoriated uniformity."

Ville Rontu, PhD thesis, Aalto 2020

Finding the pulse times

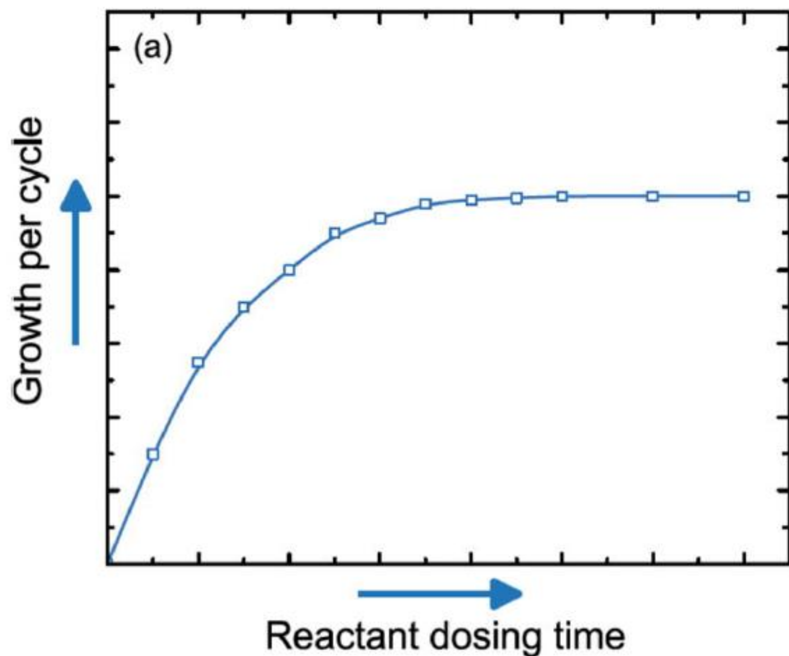


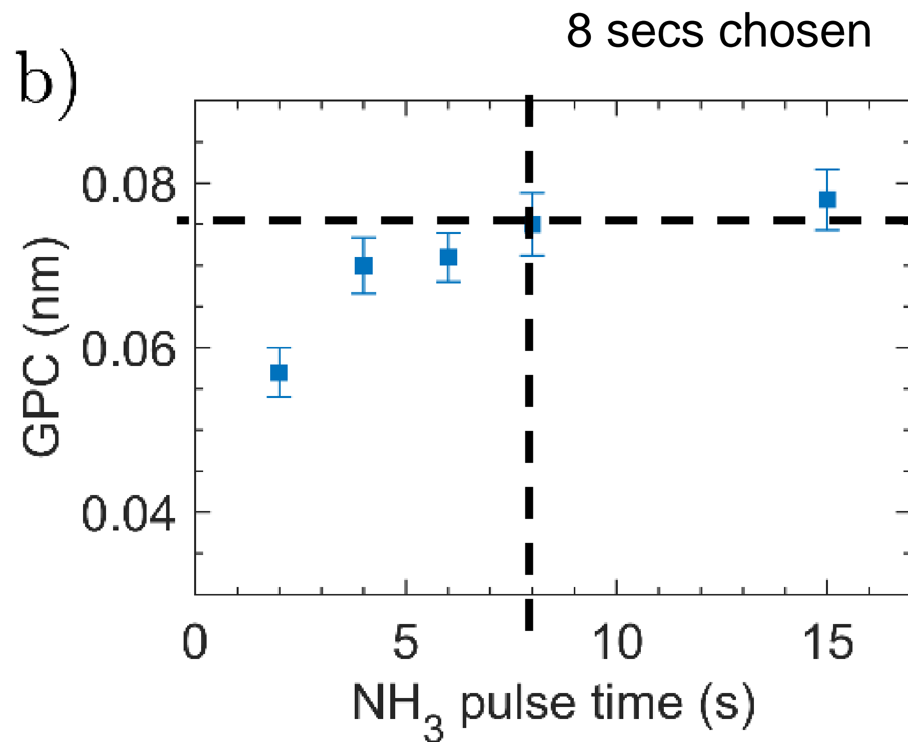


Find the plateau (← evidence of self-saturating reaction)

Ville Rontu, PhD thesis, Aalto 2020

Theory vs. practice





Growth saturation graphs for $AlCl_3$ and NH_3.

Ville Rontu, PhD thesis, Aalto 2020

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^oC;
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.

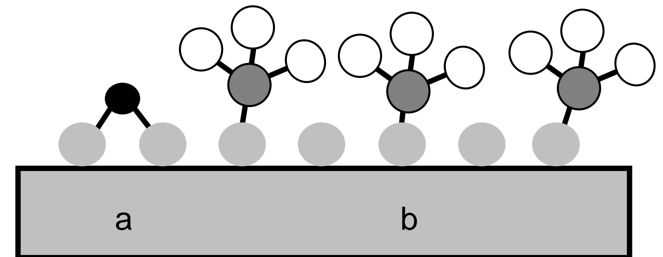
Deposition rate

Basically one atomic layer per pulse

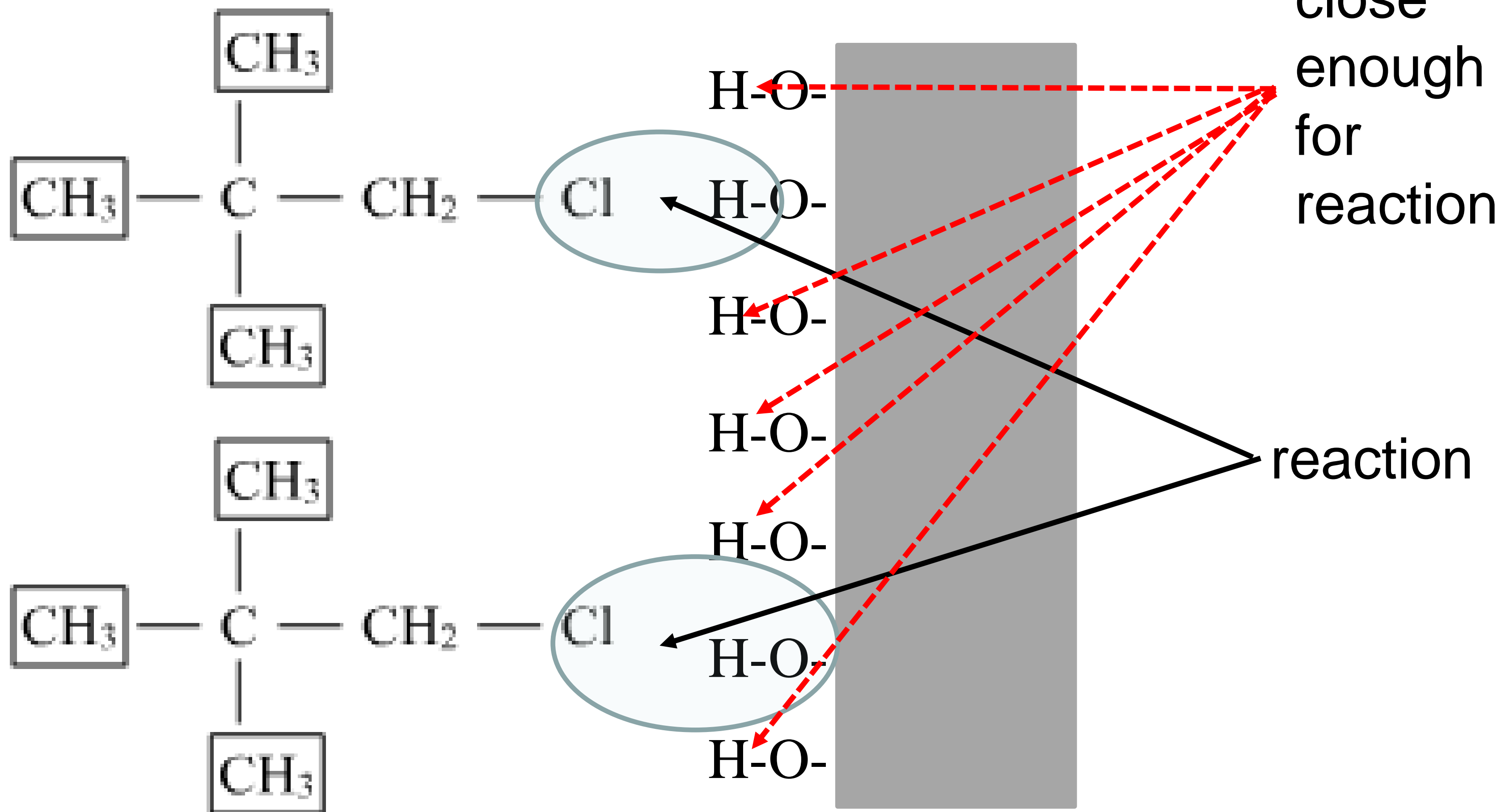
In practise less than an atomic layer because:

a) Inactive surface sites

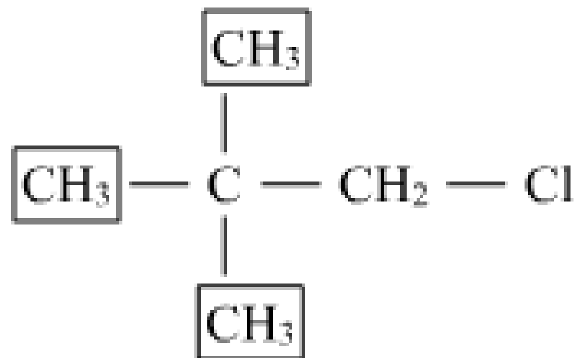
b) Steric hindrance: a large precursor molecule prevents another precursor molecule from approaching the reactive site

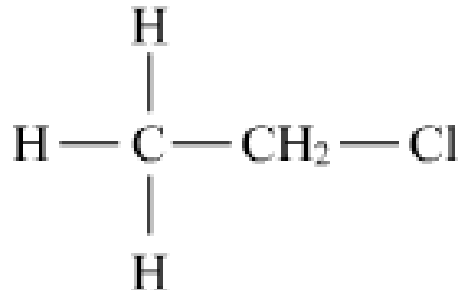


Steric hindrance



Precursor design





Large size,
Steric hindrance

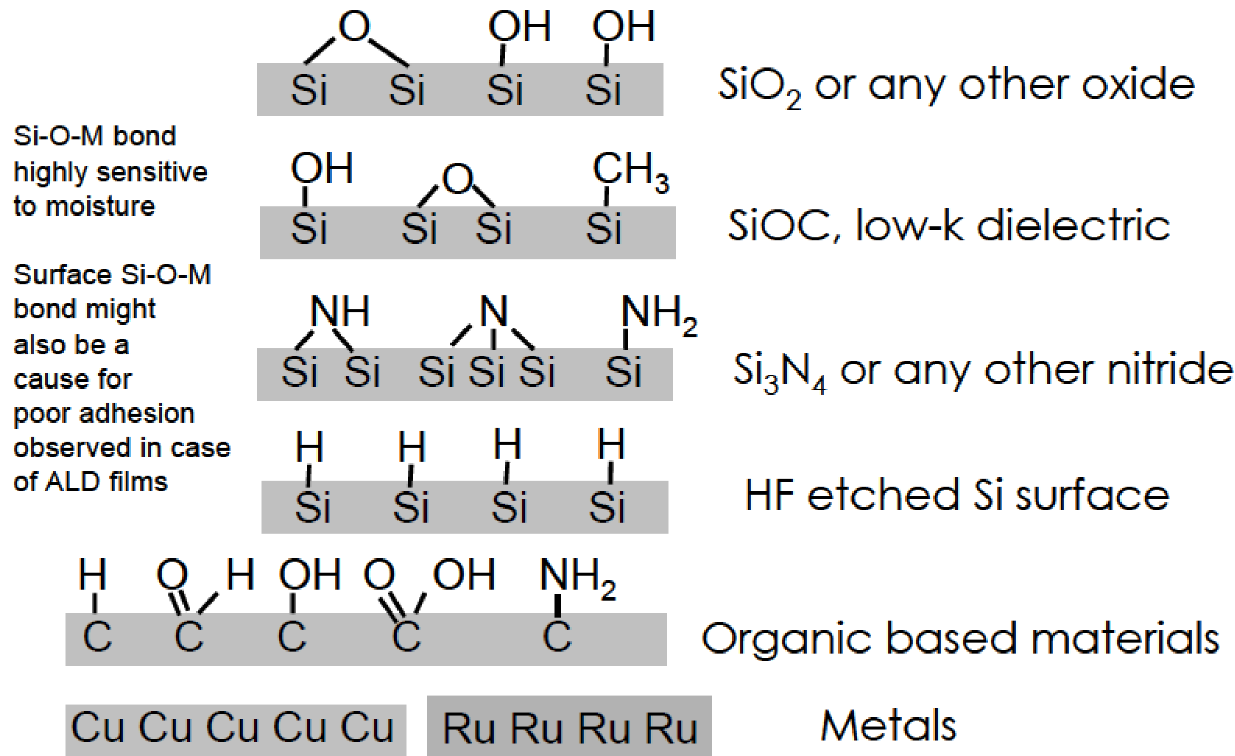
Small size,
Less steric hindrance.

But you also need to consider:

- -thermal stability
- -vapour pressure
- -toxicity
- -price…

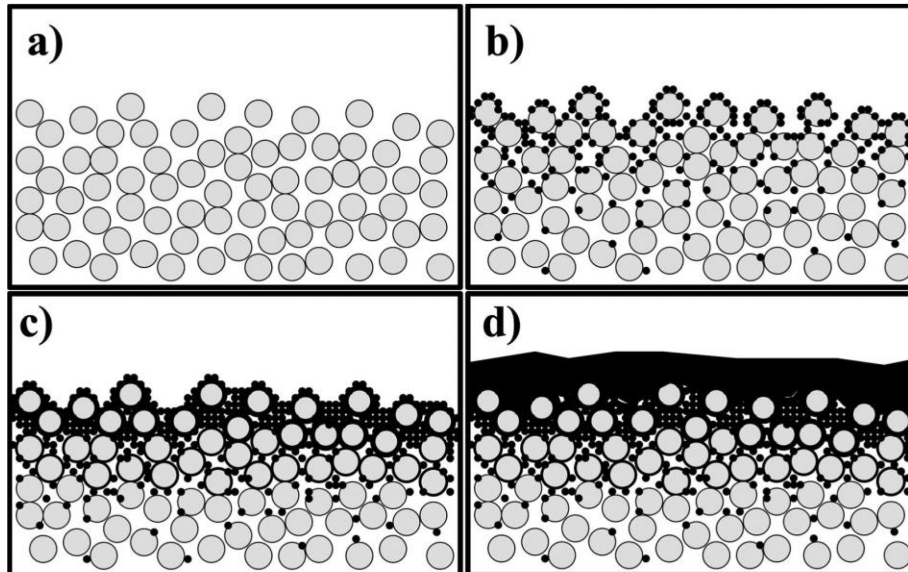
Available growth sites

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



Suvi Haukka, ASM Microchemistry, 2005

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) Al_2O_3 nucleation clusters formed from H_2O reaction with TMA trapped in the near surface region,
(c) coalescence of Al_2O_3 clusters and closure of the space between the polymer chains
(d) formation of a dense Al_2O_3 film that grows on top of the polymer surface.

Wilson, C. A.; Grubbs, R. K.; George, S. M. *Chem. Mater.* **2005**, *17*, 5625.

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.

Puurunen: CVD 2003 p. 249

ALD ≠ one atomic layer/cycle

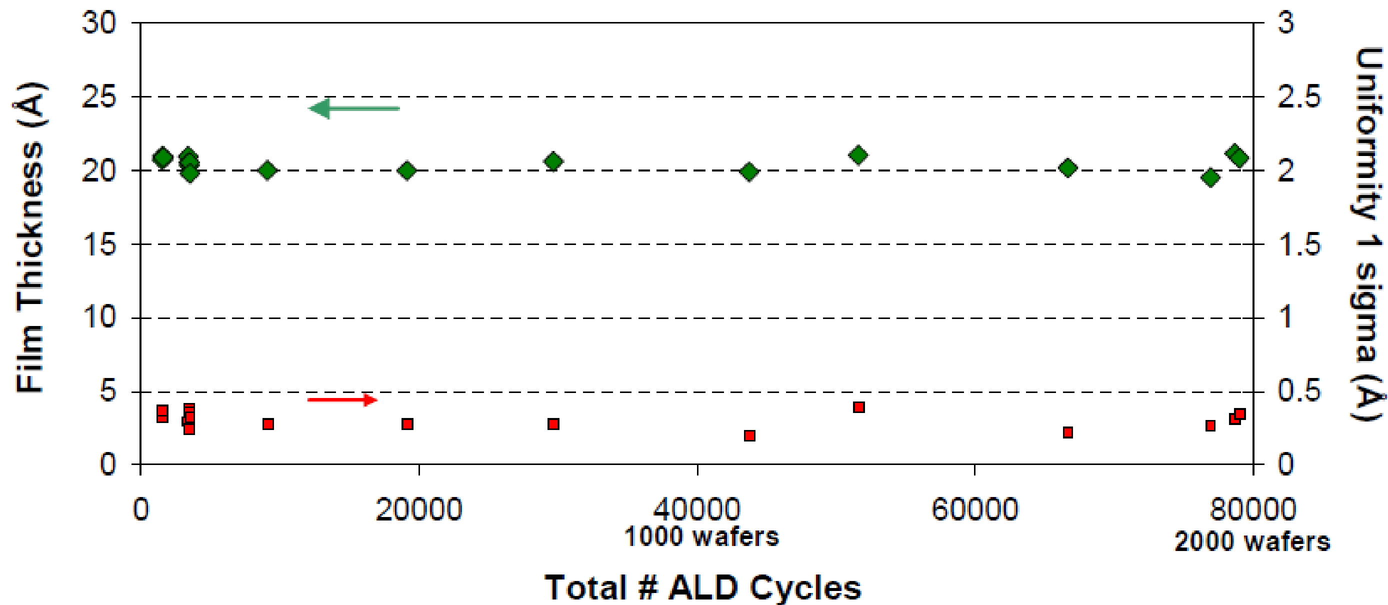
Al_2O_3	0.9-1.1 Å/cycle (TMA + H_2O)
TiO_2	0.5-0.9Å/cycle ($TiCl_4$ + H_2O)
Y_2O_3	0.24 Å/cycle ($Y(thd)_3$ + O_3)

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

If 0.1 second pulses ➔ 20 nm/min max.

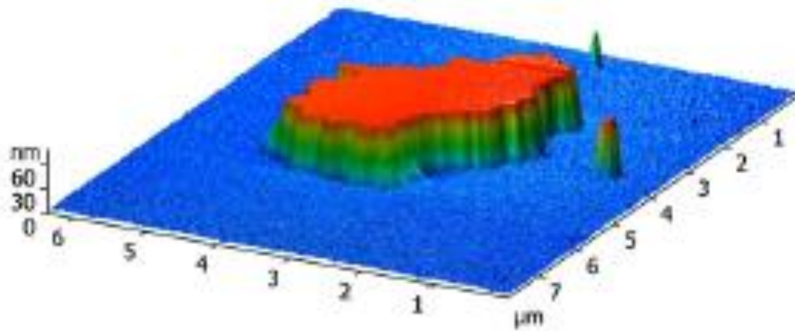
ALD uniformity (=thickness across the wafer)

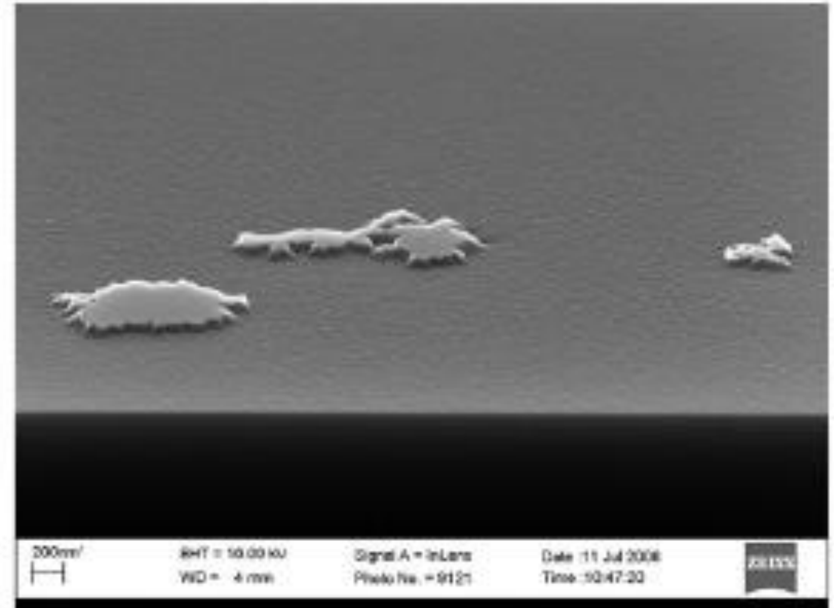
Good uniformity is a proof of surface controlled reaction.



HfO_2 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.

K. Grigoras, S. Franssila, V.-M. Airaksinen 2007

Film continuity (2)

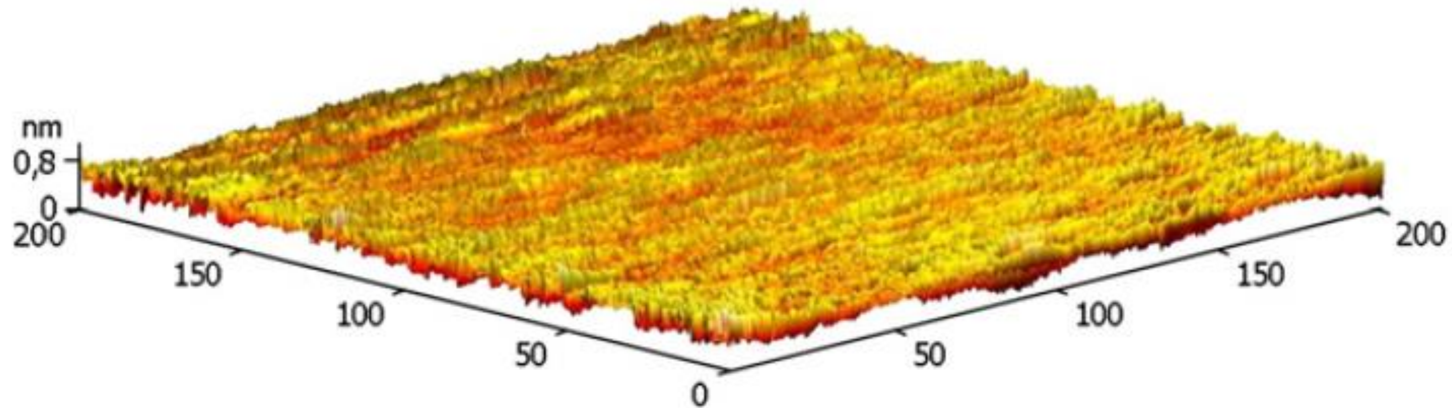


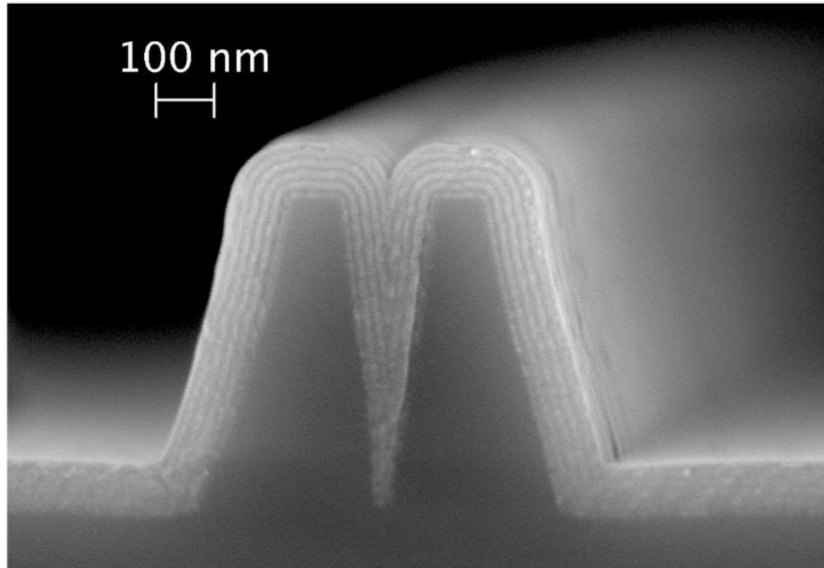
Fig. 4. AFM scan of the structure grown during 10 cycles and etched for 2 s in cryo-DRIE.

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

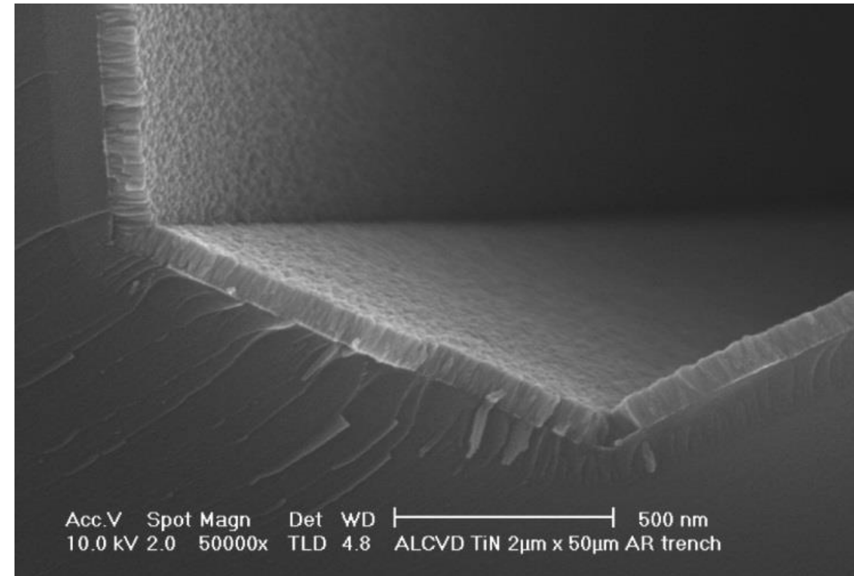
K. Grigoras, S. Franssila, V.-M. Airaksinen 2007

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

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

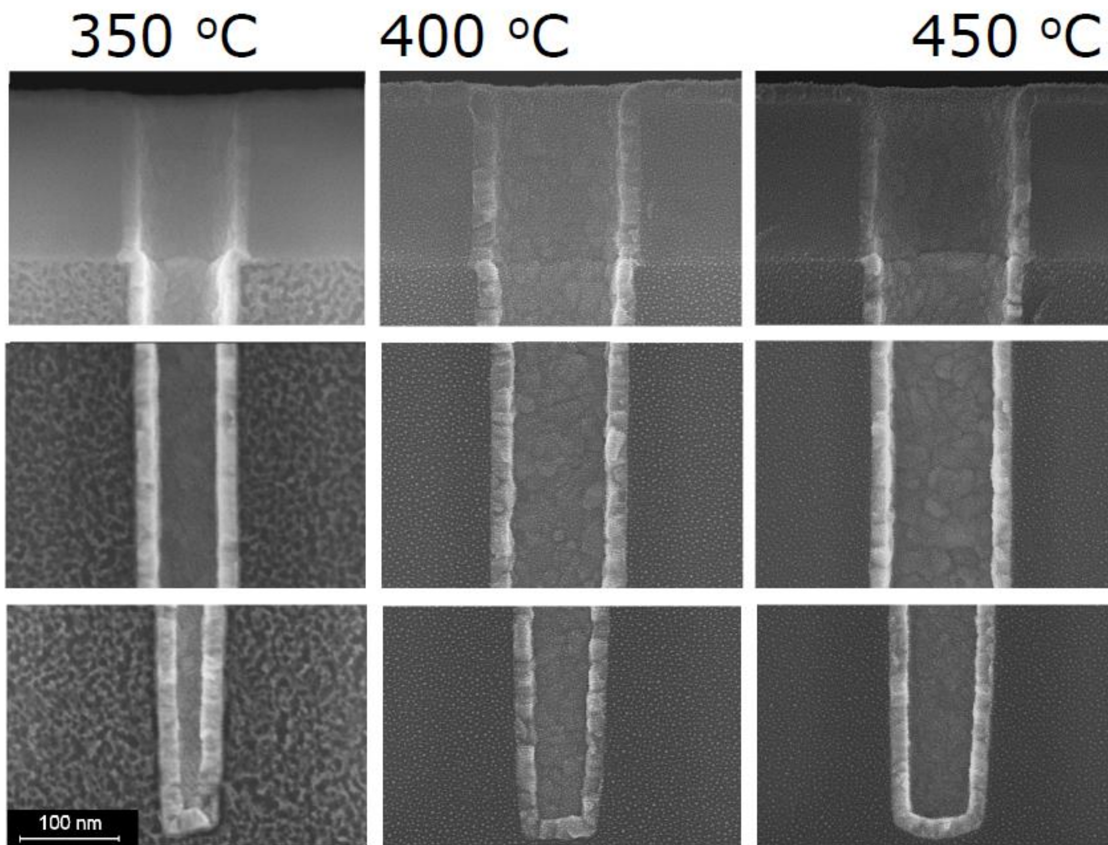


Al_2O_3/TiO_2 nanolaminate



TiN barrier

Step coverage (2)



Step coverage good also in high aspect ratio grooves,

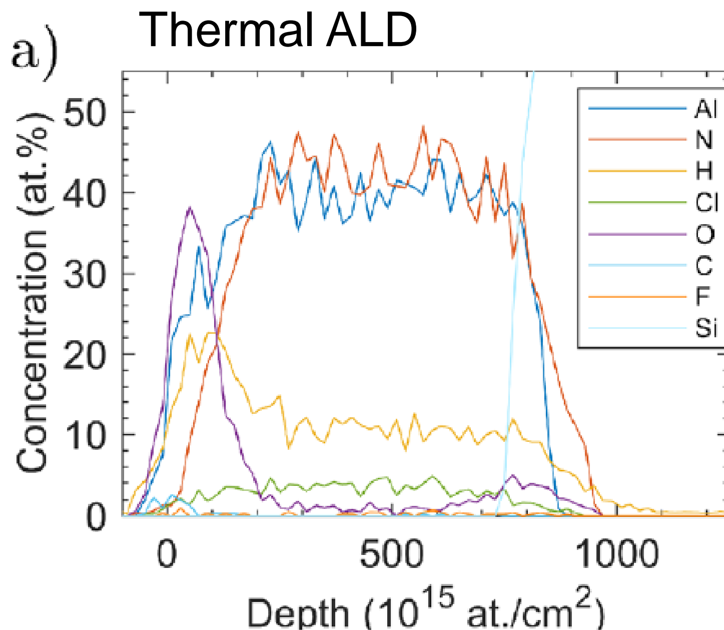
BUT pulse lengths have to to be increased

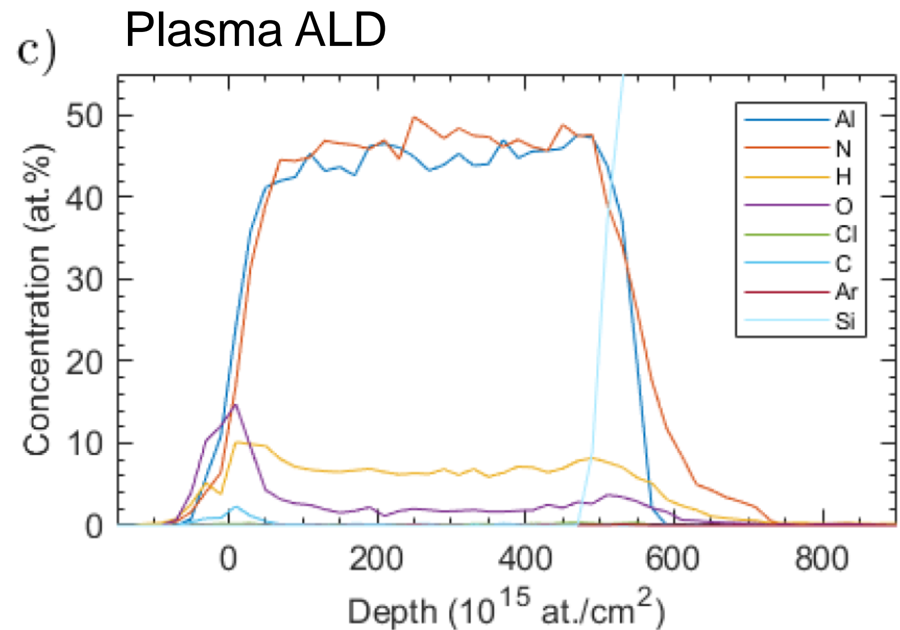
(in coating porous materials, pulses last for minutes !!).

AlN purity by ToF-ERDA

$AlCl_3 + NH_3$ process

Oxygen contamination on surface is post deposition



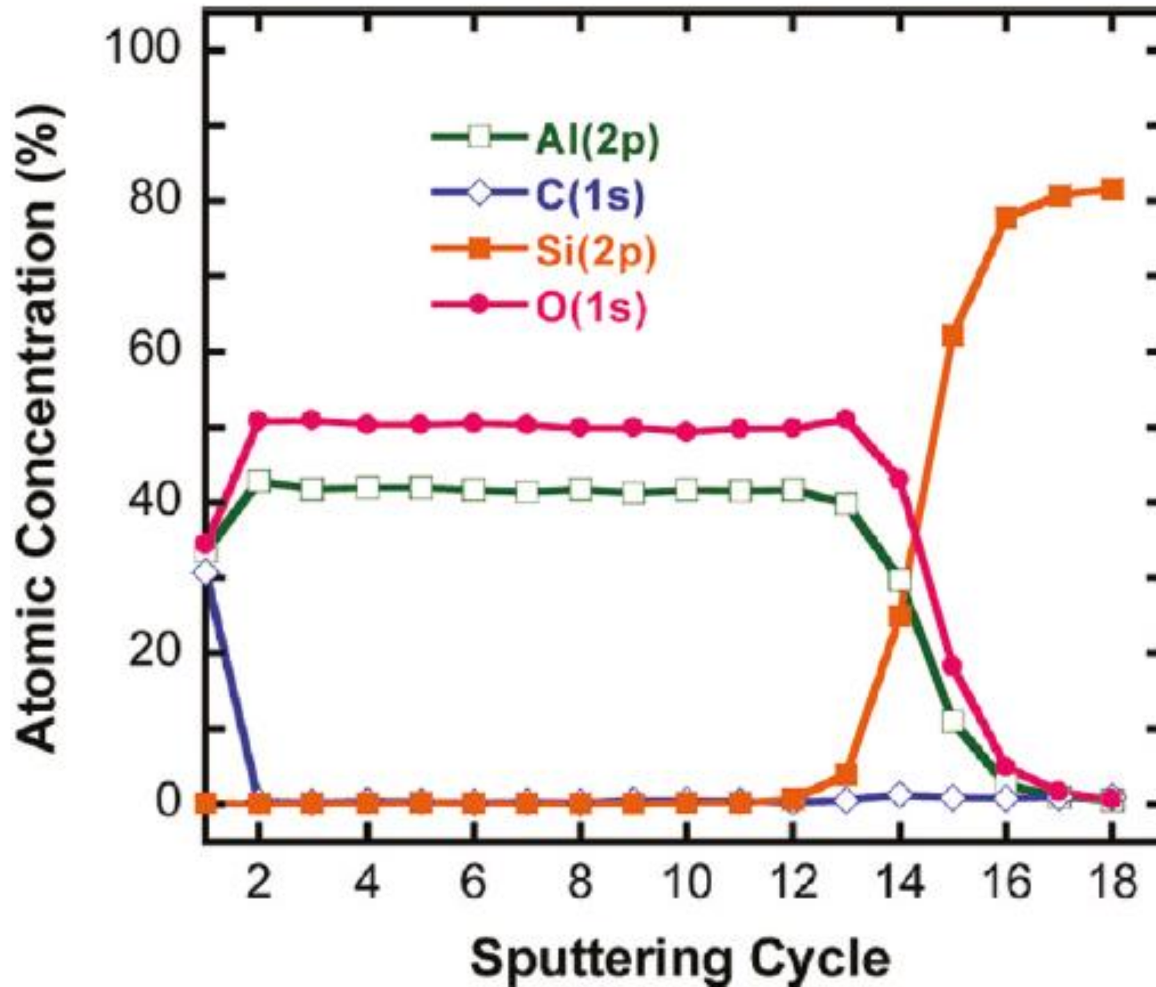


Thermal has much more hydrogen and chlorine.

Overall purity better in PEALD

Ville Rontu, PhD thesis, Aalto 2020

Al_2O_3 purity by SIMS



Carbon on surface is most likely post deposition contamination.

Abdulagatov et al: ACS Appl. Mater. Interfaces 2011, 3, 4593–4601

Crystalline structure: amorphous vs. polycrystalline ?

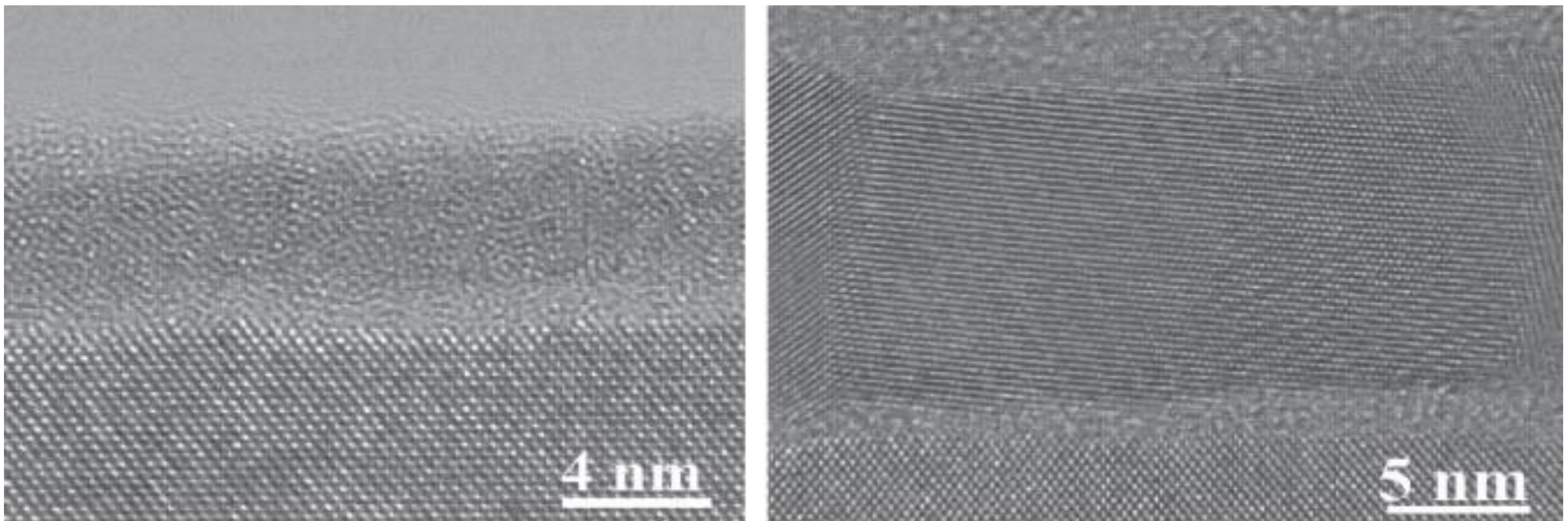
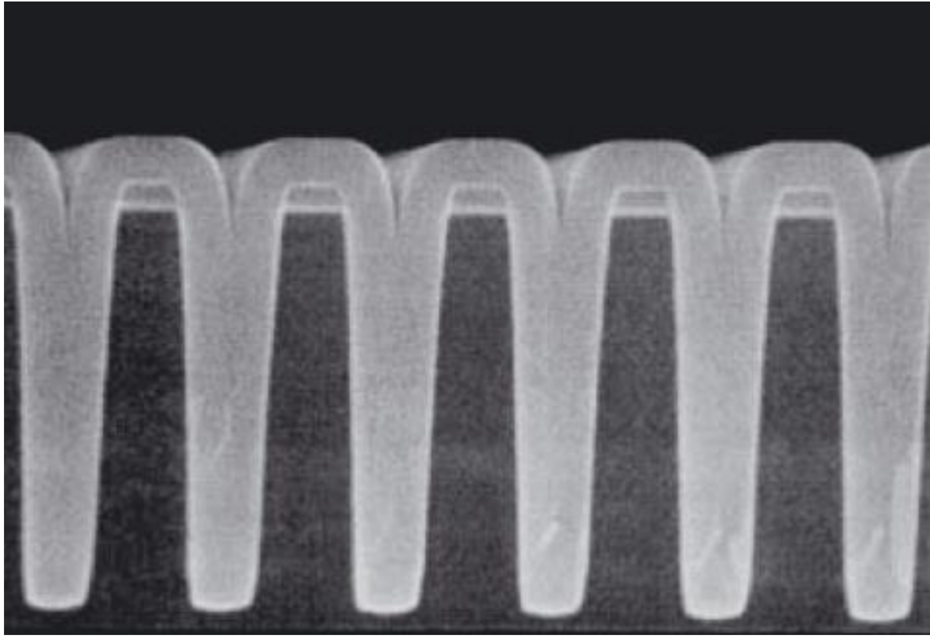


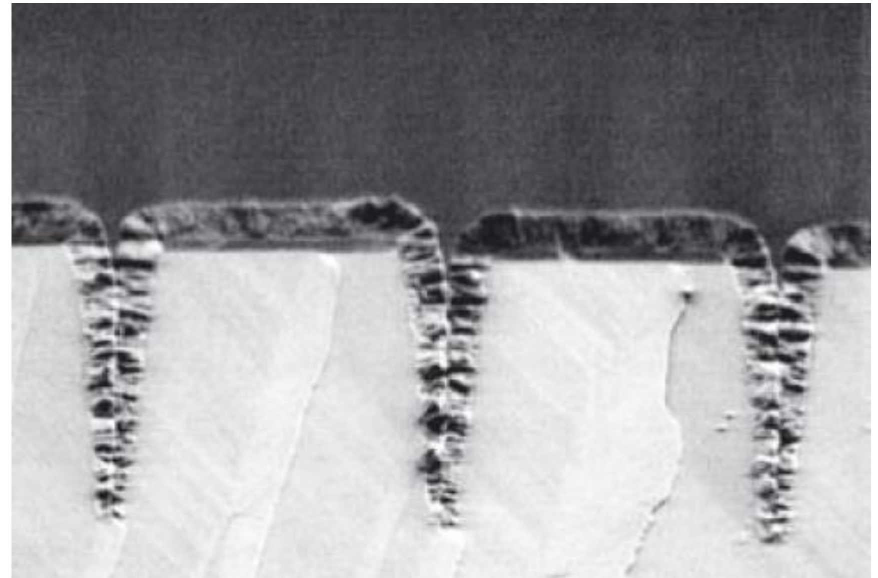
Figure 26-13

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 (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

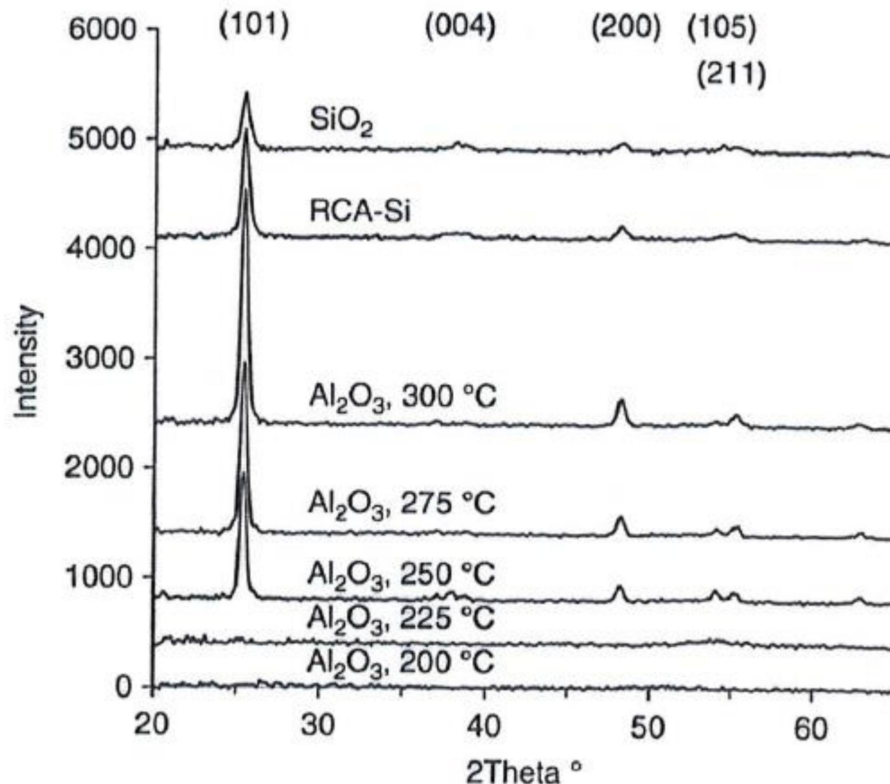


Fig. 2. GIXRD diffractograms for TiO_2 films deposited in 500 cycles on different substrates. Curves have been shifted vertically for clarity.

TiO_2 ALD film on:

- Amorphous SiO_2
- RCA cleaned <Si>
- Various Al_2O_3 films

Crystalline TiO_2 on amorphous Al_2O_3

No crystalline TiO_2 on these amorphous Al_2O_3

Puurunen, J.Nanosci. Nanotechnol. 2011

Evolution of crystallinity

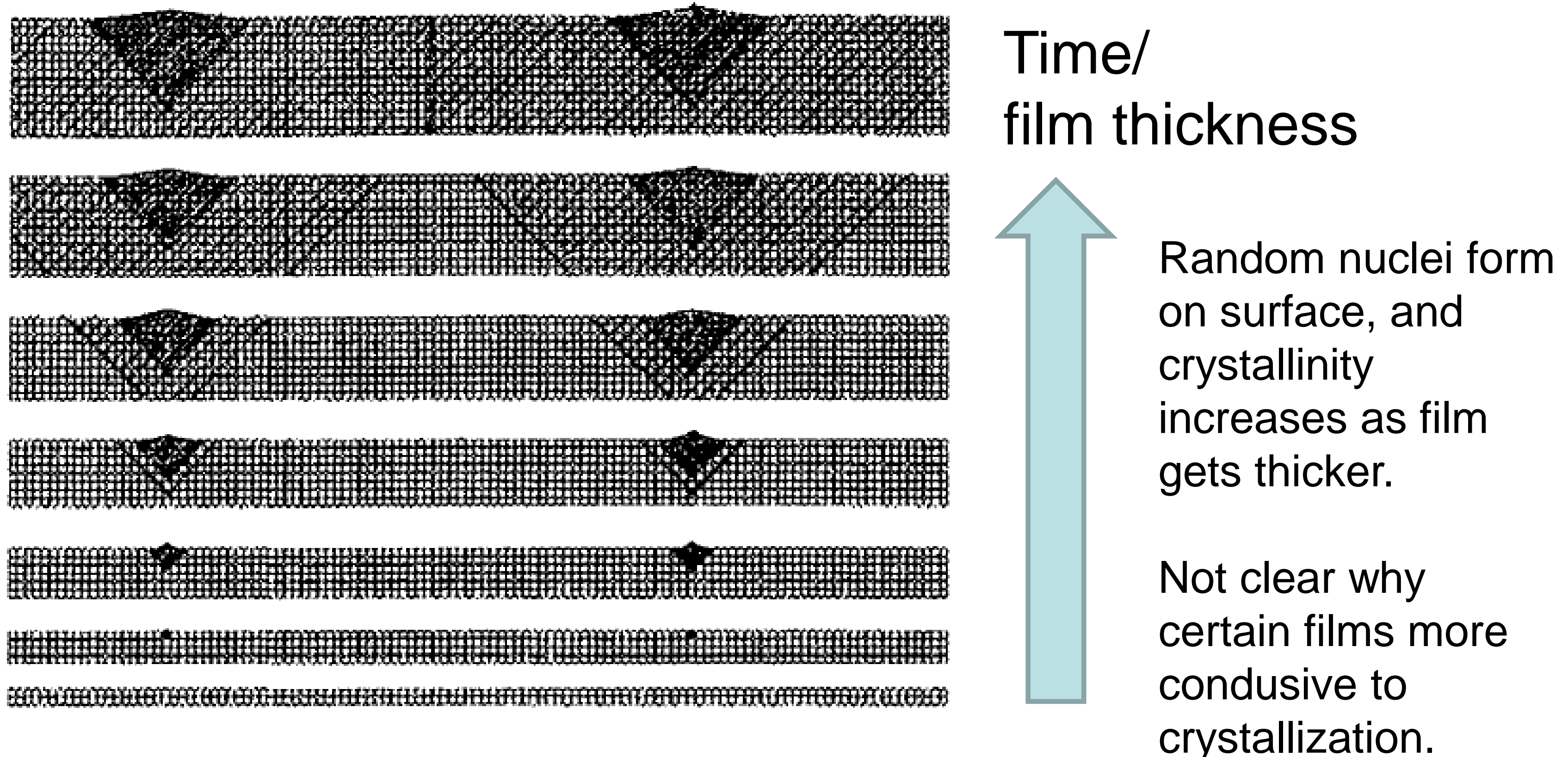
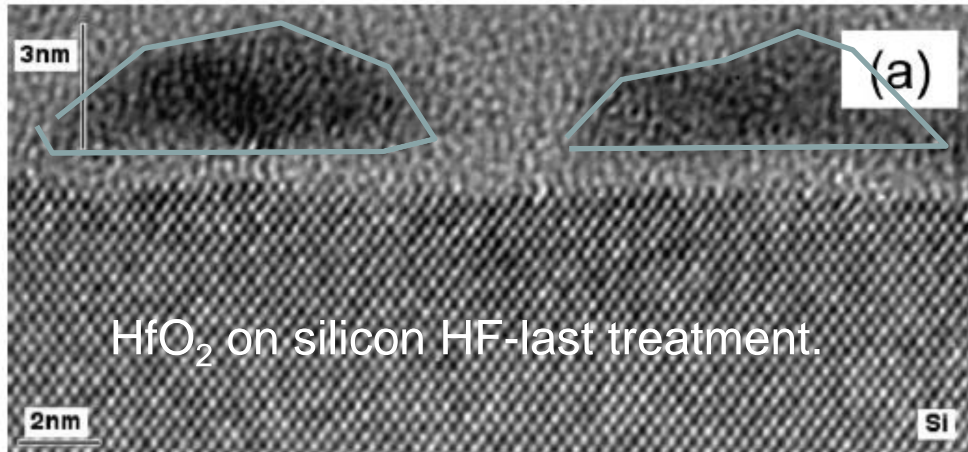
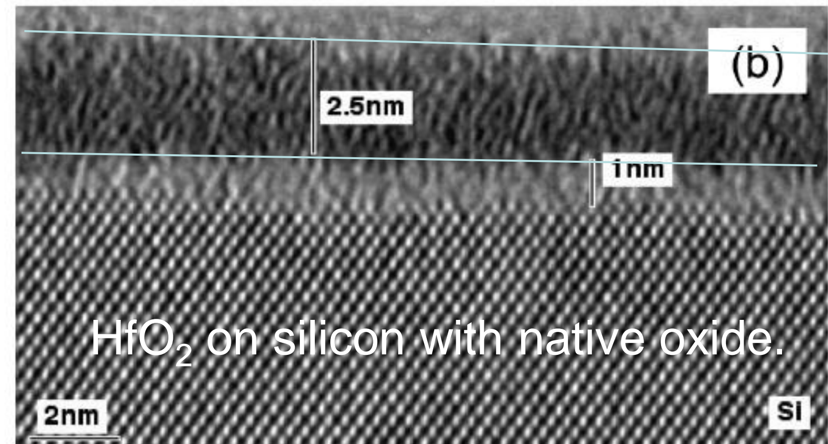


Fig. 10. Scheme for the initial growth of amorphous film (1st from bottom), the formation of crystalline TiO_2 nuclei (2nd from bottom), growth of crystalline TiO_2 grains (3rd–7th from bottom), and through-crystallization of the originally amorphous TiO_2 film (4th–7th from bottom).

Puurunen, J.Nanosci. Nanotechnol. 2011

Island growth vs. layer-by-layer growth

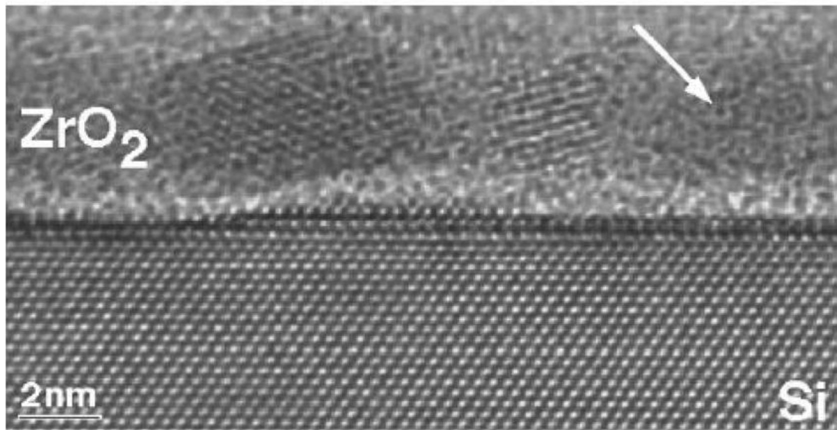




"One can observe a uniform, continuous film in the case of $HfO_2/SiO_2/Si$. For the film deposited directly on Si (after HF last pre-clean), the TEM image reveals the nucleation phenomenon, i.e. the deposited material forms clusters on the surfaces resulting in incomplete coverage of the surface by HfO_2."

Gusev, E. P.; Cabral, C.; Copel, M.; D'Emic, C.; Gribelyuk, M. *Microelectron. Eng.* **2003**, *69*, 145.

(a)

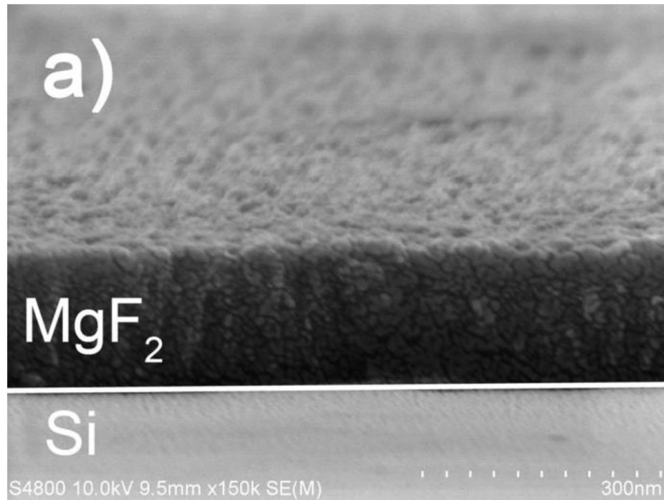


(b)

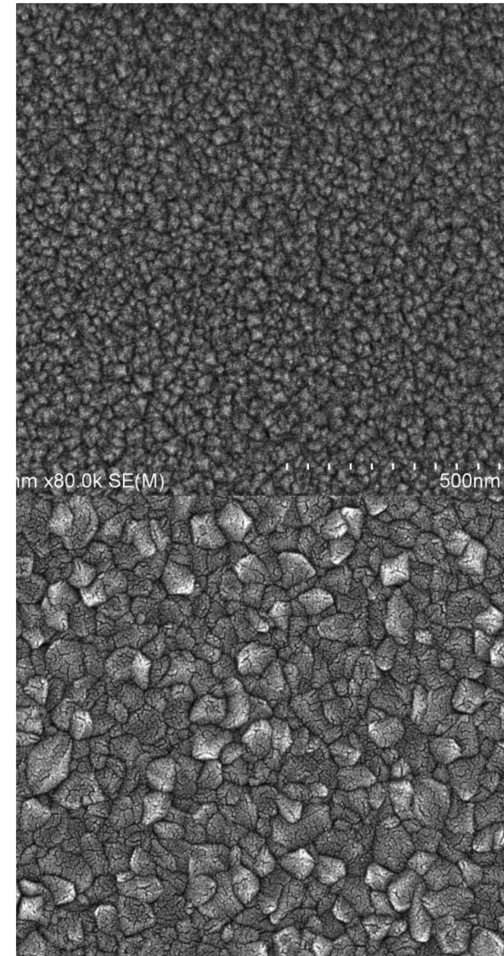
"On oxidized silicon, ZrO_2 layer is smooth yet clearly polycrystalline. On HF-etched silicon, the nucleation density has been lower and the film shows more or less separate crystallites and is much rougher, because the nuclei have had more time to grow independently before coalescing."

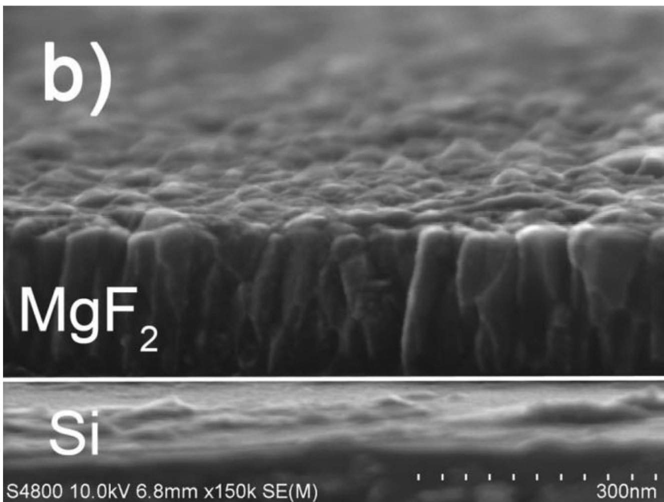
Copel: Appl. Phys. Lett. 76, 436 (2000).

Crystallinity & depo temperature



250°C

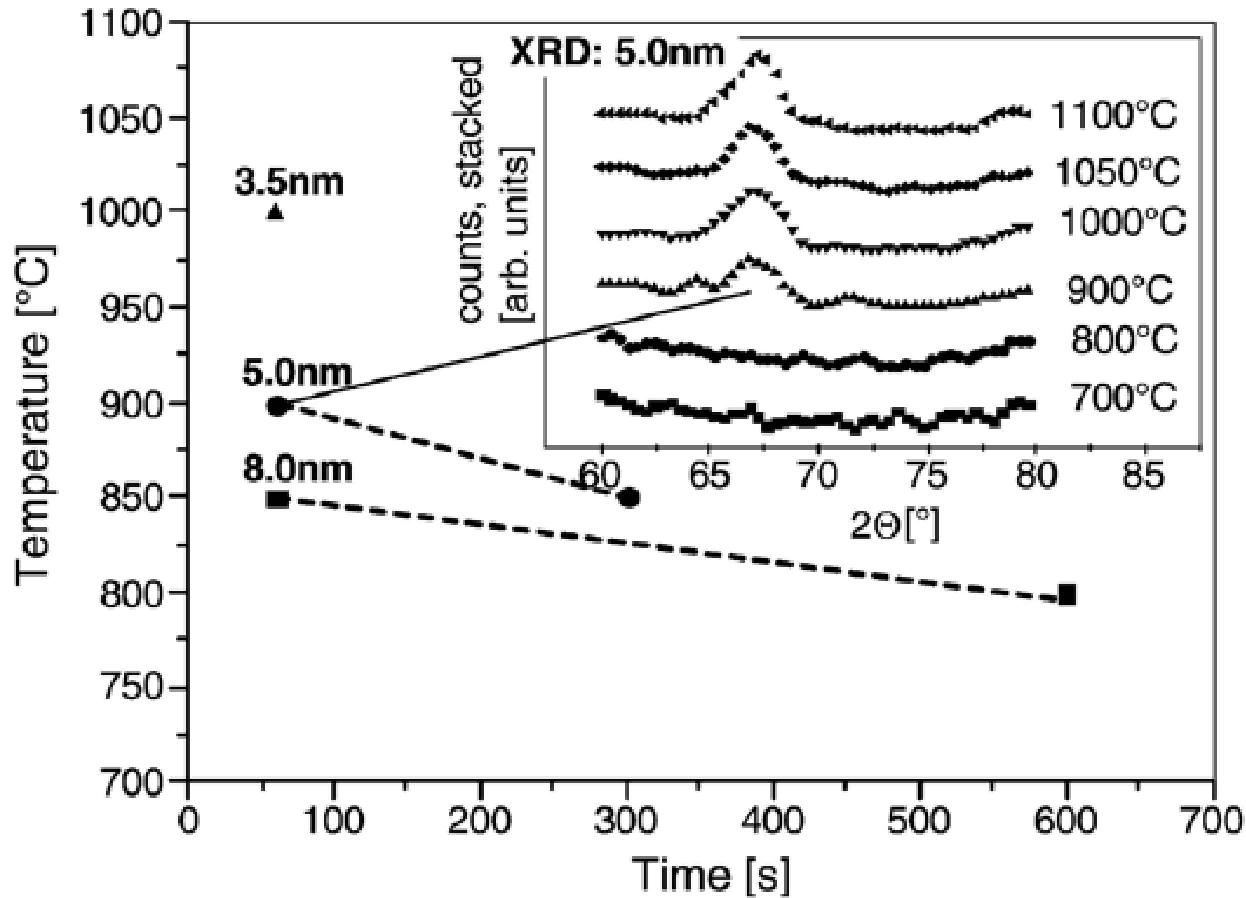




350°C
Higher T favors crystallinity

Pilvi et al: *Chem. Mater.* **2008,** *20,* 5023–5028

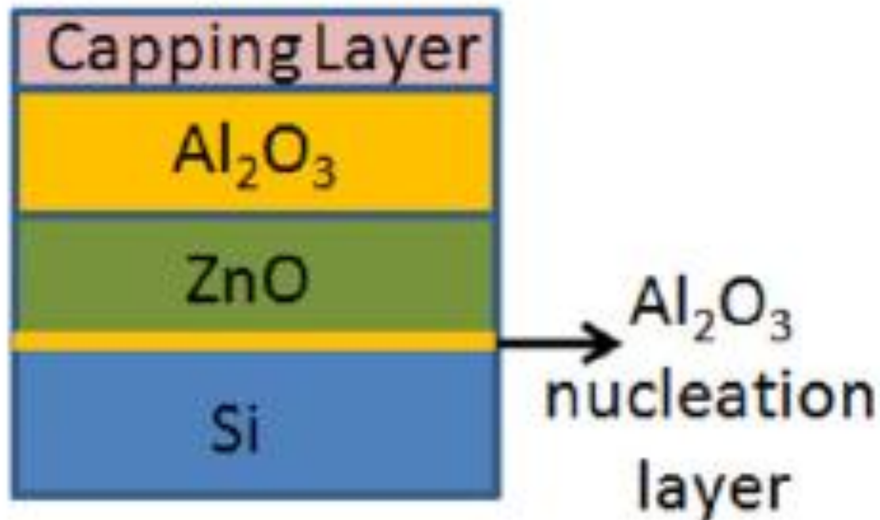
Post deposition annealing



Al_2O_3 turns crystalline at ca. 900°C

S. Jakschik, U. Schroeder, T. Hecht, M. Gutsche, H. Seidl, and J. W. Bartha, Thin Solid Films 425, 216 (2003).

Protective capping layers

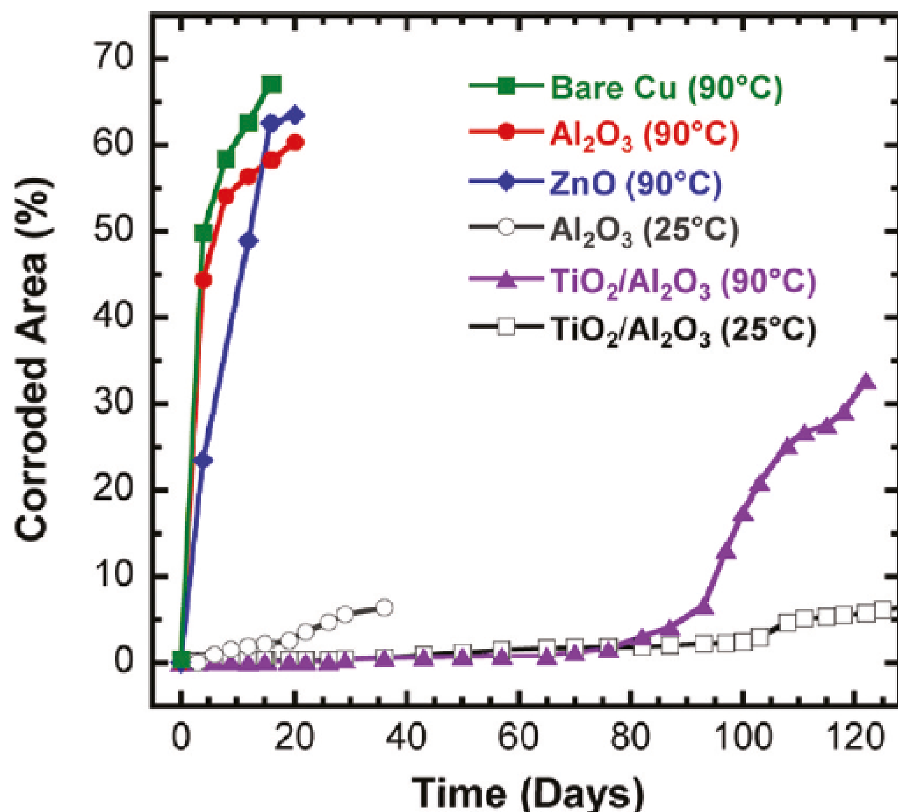


<u>Capping Layers</u>

(1) Ebeam NiO_x
(2) O_2 Plasma on NiO_x
(3) Ebeam TiO_x
(4) O_2 Plasma on TiO_x
(5) PEALD TiO_2

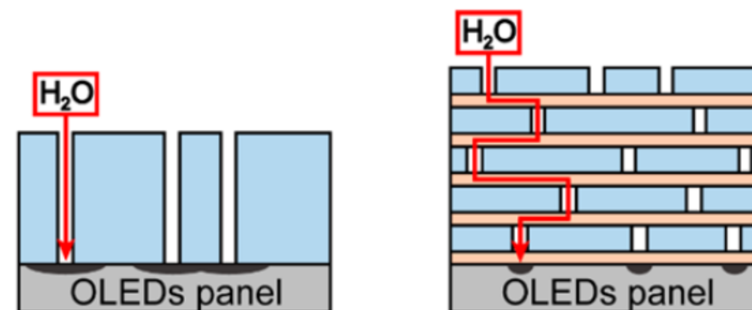
A Bulusu et al: Improving the stability of atomic layer deposited alumina films in aqueous environments with metal oxide capping layers, J. Phys. D: Appl. Phys. 46 (2013) 084014 (10pp)

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.

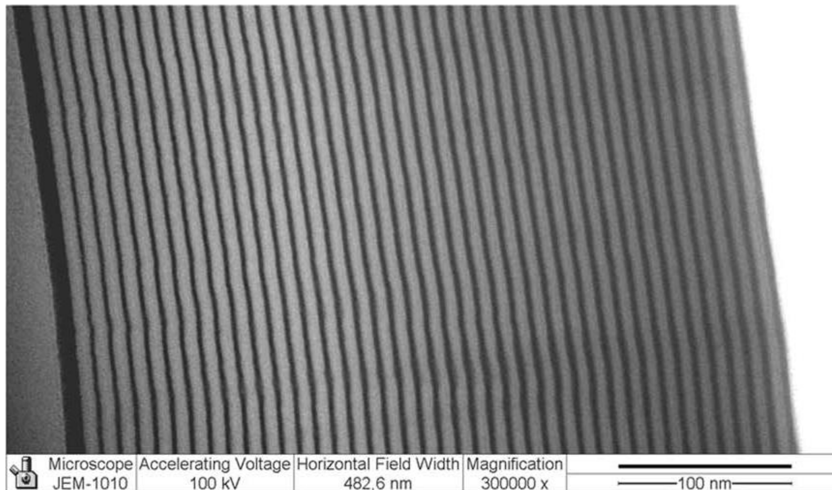


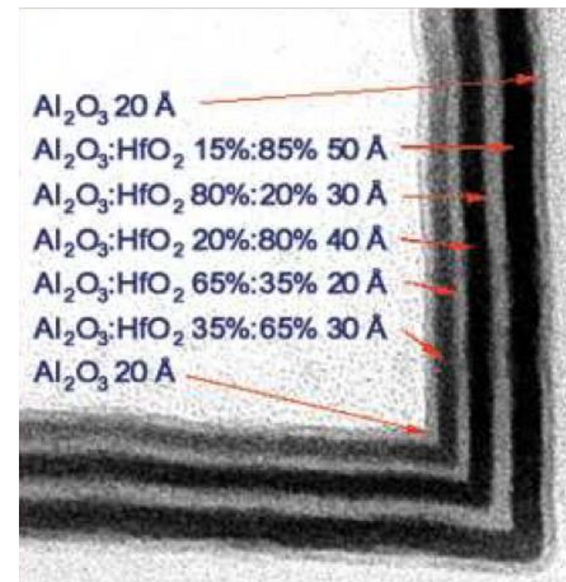
Abdulagatov et al:
ACS Appl. Mater. Interfaces 2011, 3, 4593–4601

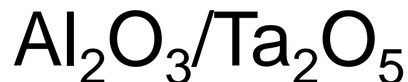
Yoon & Sung: DOI:
10.1021/acsami.6b15404

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	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

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