Aalto University
School of Chemical Technology

CVD and ALD reactors
&
Thin film productivity and quality metrics

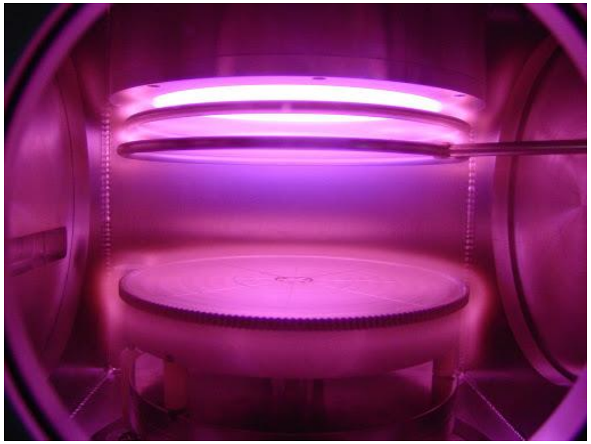
(2 hour set)

sami.franssila@aalto.fi

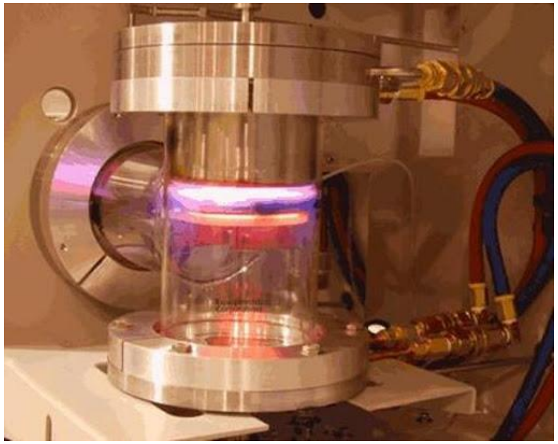
Table of contents

PECVD:
Plasma Enhanced CVD

- Plasma creates active specie (radicals, ions)
- No need of high temperatures because of plasma
- More parameters to work with (power, freq, pulses…)
- Usually single wafer reactors
- Need high rates (1-10 nm/s) (thermal 10% of this)



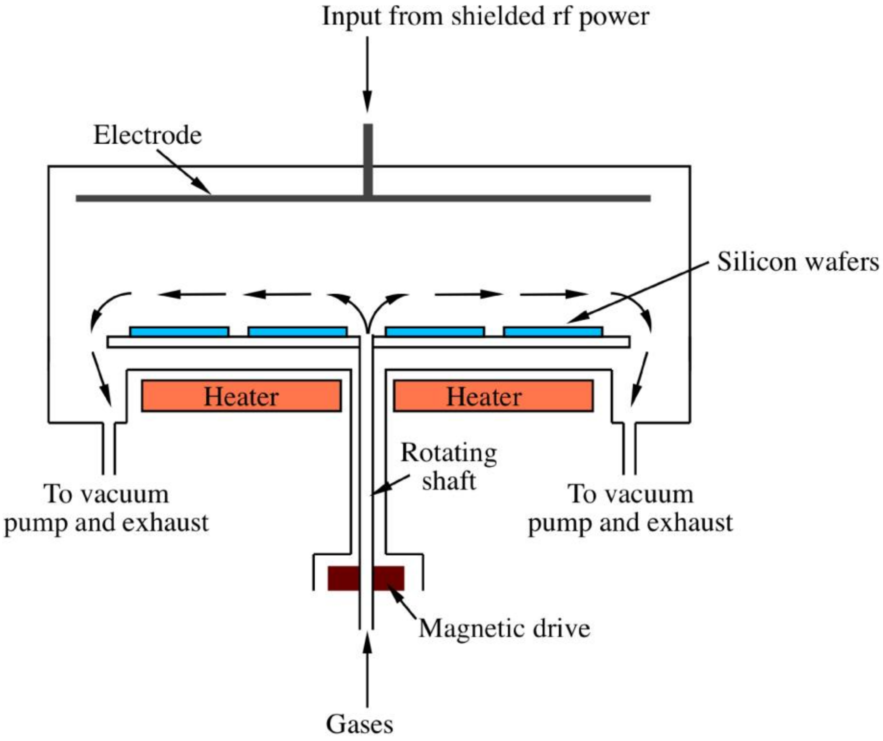
http://www.nanomaster.com/pecvd.html

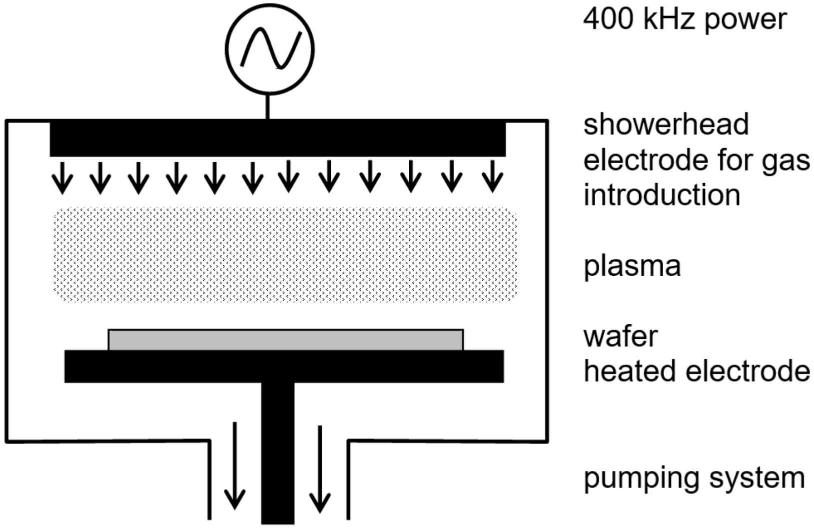


http://thinfilmscience.com/en-US/PECVD.aspx

Radial flow vs. showerhead

In order to work in mass transport limited regime for fast deposition, gas introduction has to ensure uniform gas distribution.

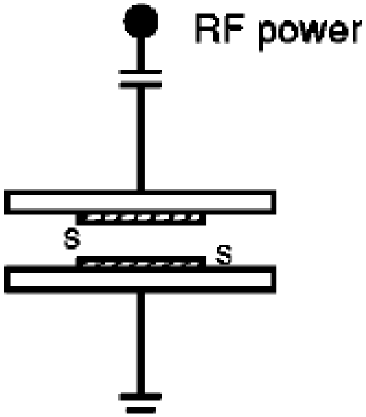




https://cnx.org/contents/m7vjnKhA@2/Chemical-Vapor-Deposition

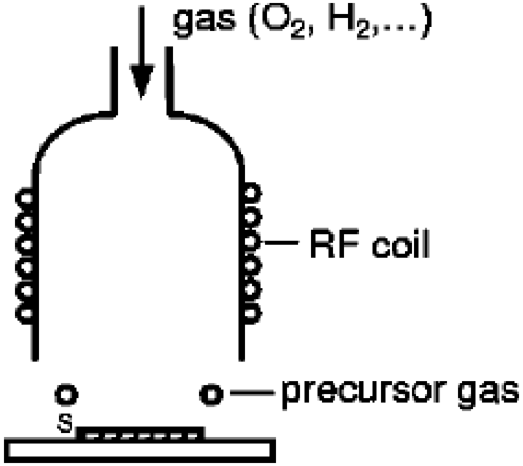
Franssila: Inroduction to Microfabrication, 2010

PECVD reactors (1)



(a) Parallel plate RF PECVD

Capacitively coupled



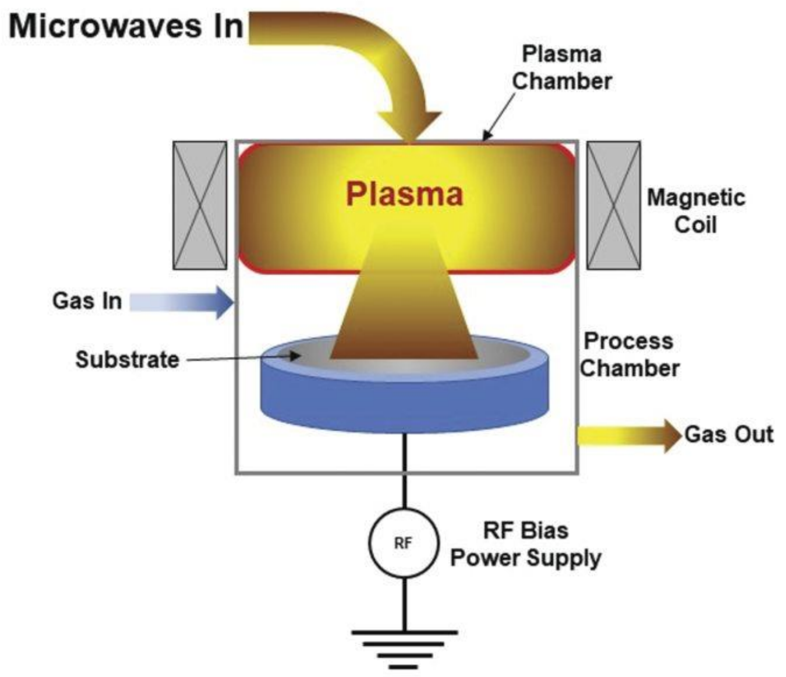
(b) Remote RF PECVD

Increase in power ➔ increase in ion energy (and damage)

Radicals reach wafer by diffusion; little ion bombardment.

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

HDP = High Density Plasma



2 power sources:

GHz-source to generate plasma;
MHz-source to bias the wafer.

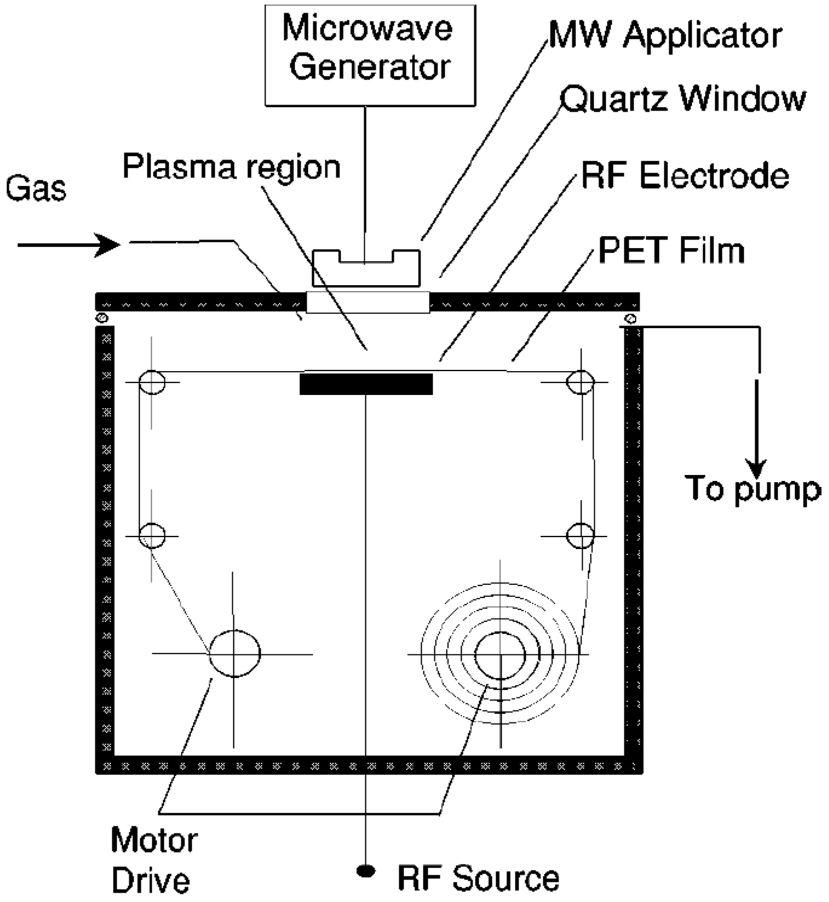
Increasing GHz power does not mean more ion bombardment on the wafer.

HDP: high density plasma, 10^{13} ions/cm^3 vs. 10^{10}-10^{11}/cm^3 for RF plasmas vs. 10^{15} /cm^3 neutrals @100 Torr pressure

→ **Maybe 1% of gas is ionized**

https://www.mksinst.com/n/pecvd-systems

Roll-to-roll PECVD



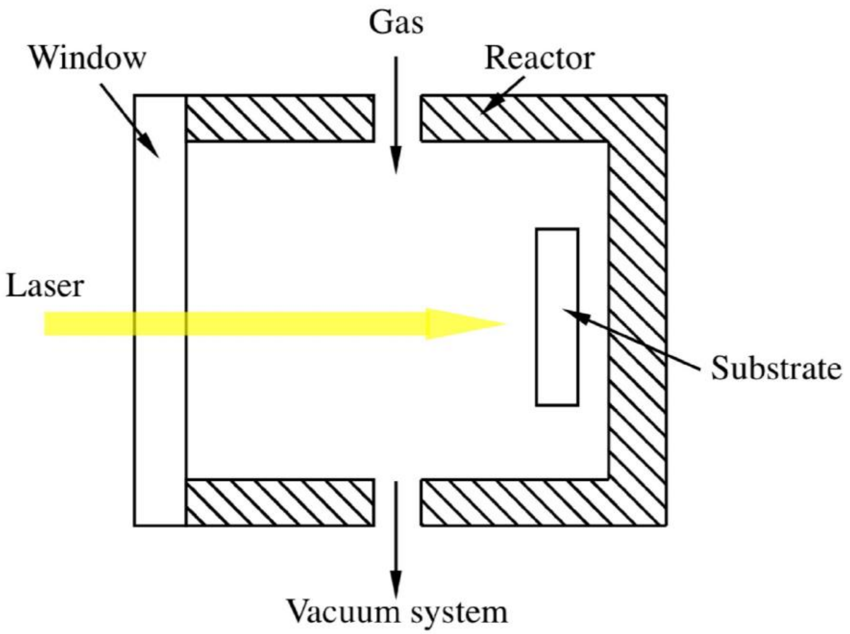
L. Martinu and D. Poitras

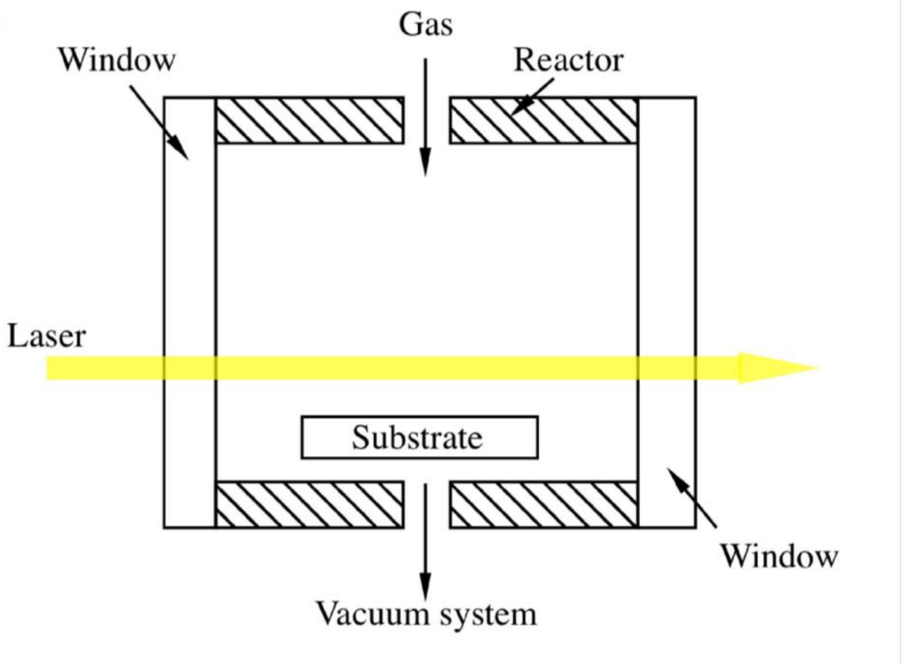
For productivity:

30 cm wide foil coated

Can be 100’s of meters long

Laser-assisted CVD/ALD



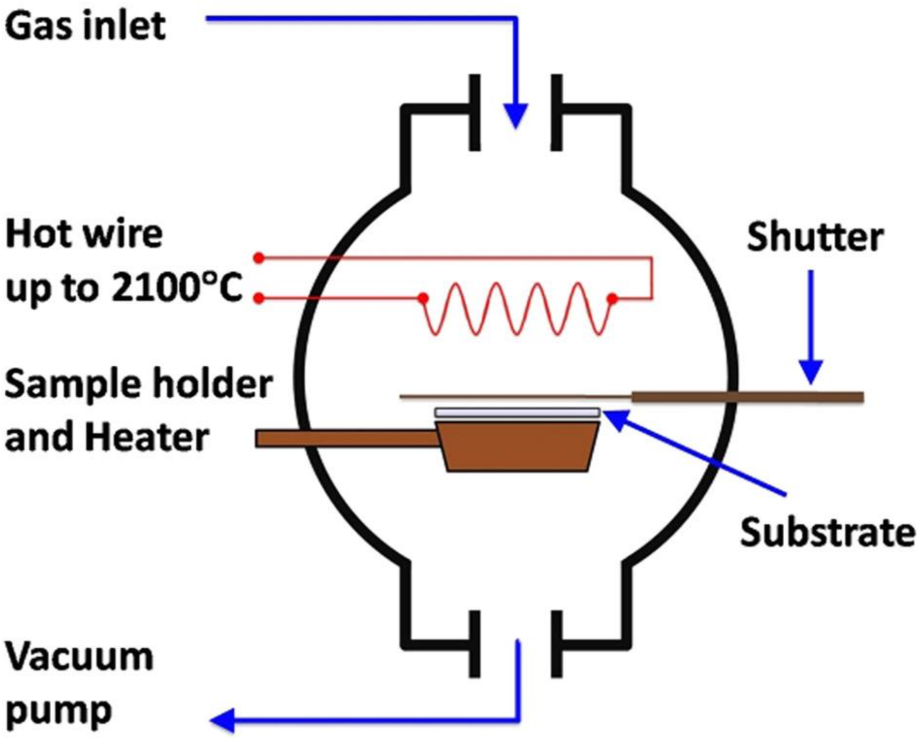


Laser as a heating tool
(photothermal)

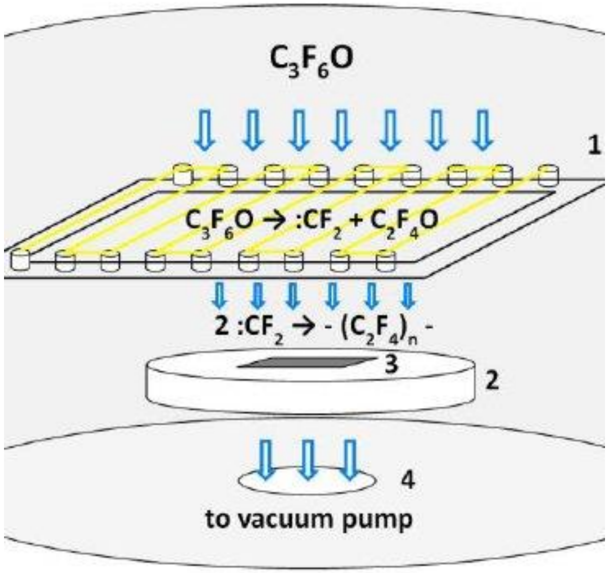
Laser as gas excitation tool
(photochemical)

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

Hot wire CVD



Rai et al: Materials Science in Semiconductor Processing
Volume 67, 15 August 2017, Pages 46-54



Thermal activation of precursors, but substrate temperature can be kept low.

Safonov et al: Deposition and Investigation of
Hydrophobic Coatings, 2015

HW-CVD SiC and diamond

SiC is usually made from $SiH_4/CH_4/H_2$ mixtures.

The mesh temperature was 1600 °C and the substrate temperature 700–800 °C.

At the end of the Si_xC_y composition scale is diamond-like carbon and diamond, which can readily be made by HWCVD using CH_4 and H_2.

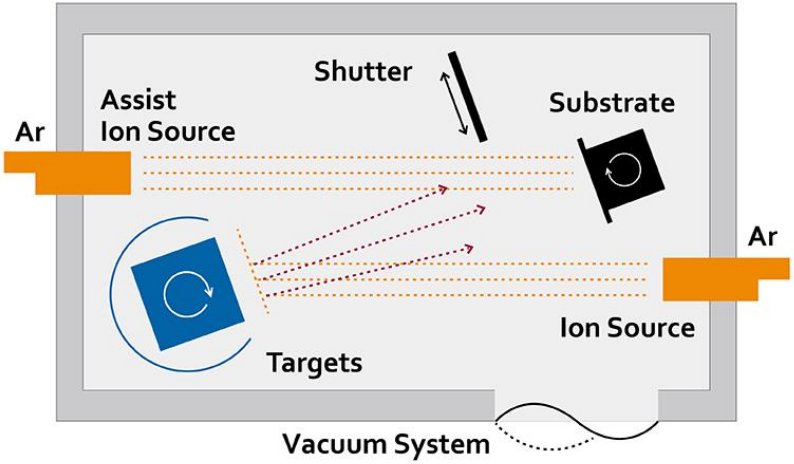
Substrate temperature increased to about 850^{o}C.
The filament temperature was about 2000^{o}C.

Shutter: beam vs. diffusion

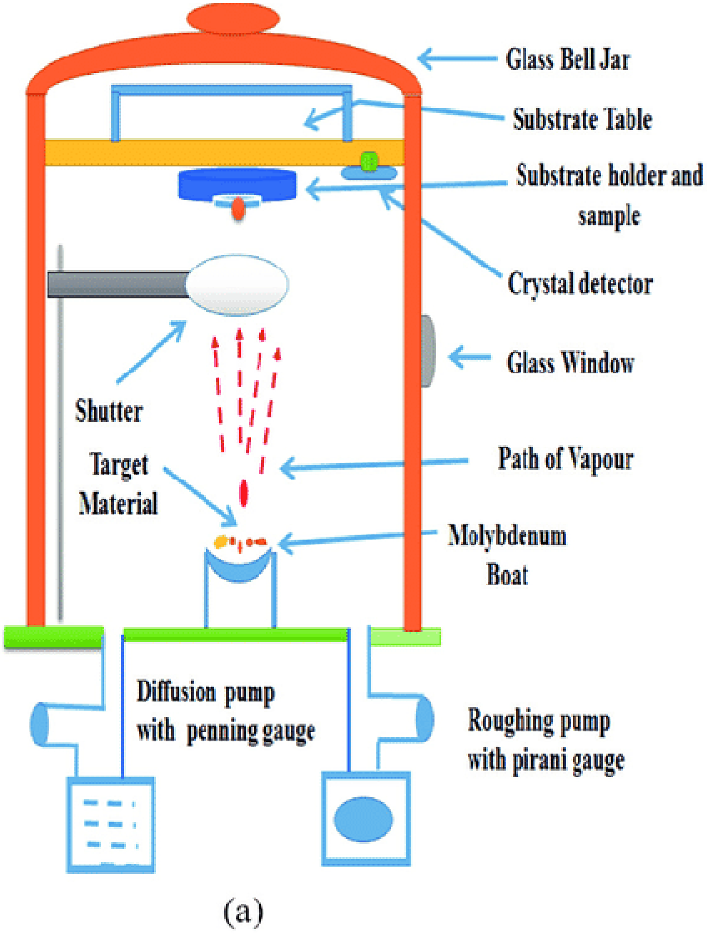
Shutters are generally used to block a beam of atoms; not diffusion of gases.

Shutter is excellent for pre-treatments of substrate or target before actual deposition in PVD.

Shutter is heat shield in HW-CVD.



https://www.dentonvacuum.com/what-is-ion-beam-deposition/



Ganaie et al: Study of Morphological, Electrical and Optical behaviour of Amorphous Chalcogenide Semiconductor, 2020

New parameters by plasma

Plasma power:
-more ions and radicals generated ➔ higher depo rate

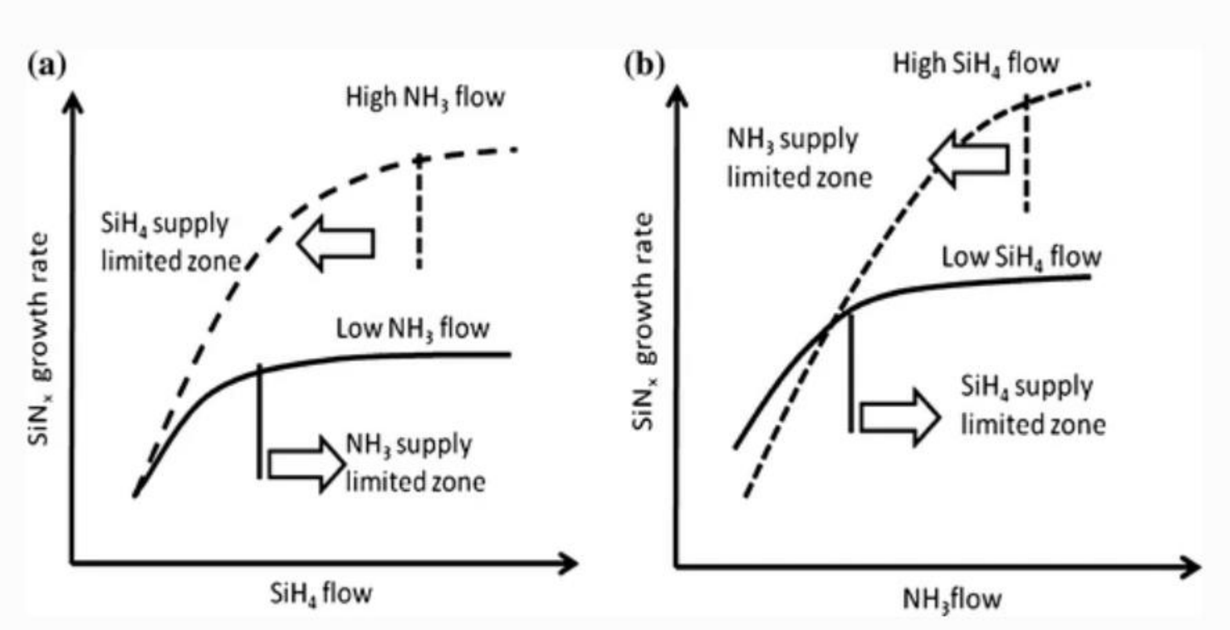
Ion bombardment
-striking loosely bound specie away
-densification of film
-atoms kicked away ➔ slower deposition rate

Pulsed operation:
-generation ions & radicals, but less ion bombardment

Frequency:
-usually fixed at 13.56 MHz or 2.45 GHz, but in theory…

Rate limiting step

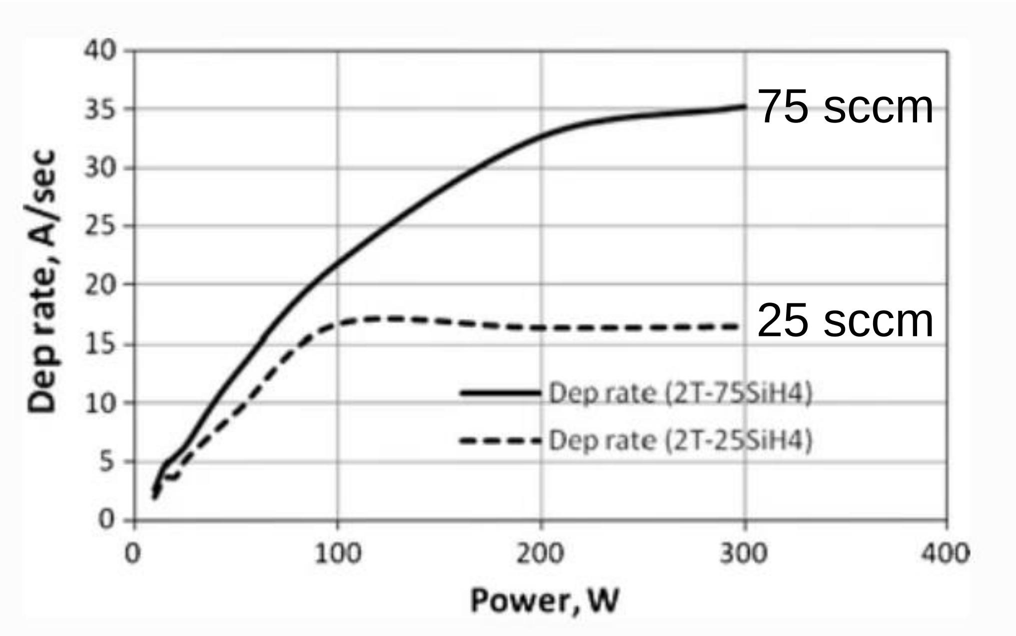
$SiH_4 + N_2O + NH_3 \rightarrow SiO_xN_y + H_2 + N_2$



"Increasing the NH_3 supply will further increase the SiN deposition rate until the Si-containing species concentration becomes the limiting factor again."

Peng, Sue: J Mater Sci (2011) 46:1–37

Rate limiting step (2)



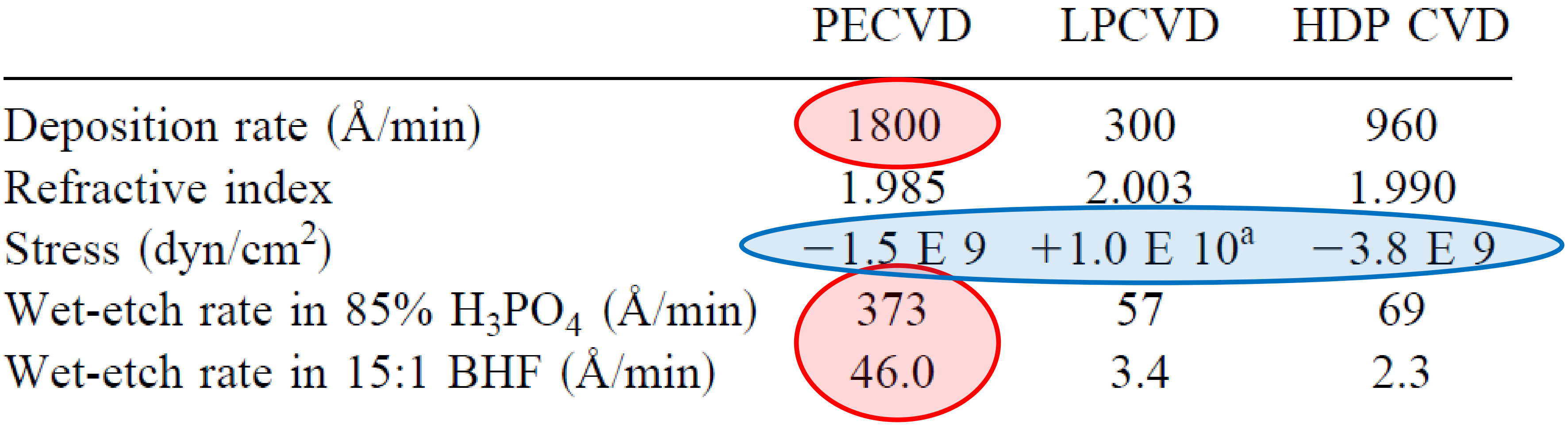
PECVD SiO_xN_y deposition rate at 2 Torr and 250 °C, 10 sccm N_2O flow, 50 sccm He, and 25 sccm NH_3, diluted by N_2 (2000 sccm total flow). Two SiH_4 flow rates: 75 sccm (*solid line*) and 25 sccm (*dashed line*) were plotted here

Peng, Sue: J Mater Sci (2011) 46:1–37

”Assuming 25 sccm of SiH_4 is fully dissociated above 100 W RF power and the diffusion boundary layer is thin enough, SiO_xN_y growth is limited by the lack of a Si-containing precursor supply from the gas phase when O and N are over-saturated.

Thus the growth rate flattens out above 100 W RF power. Increasing the SiH_4 flow from 25 to 75 sccm pushes the growth rate saturation knee to a power level of above 300 W.”

Nitride comparison (1)

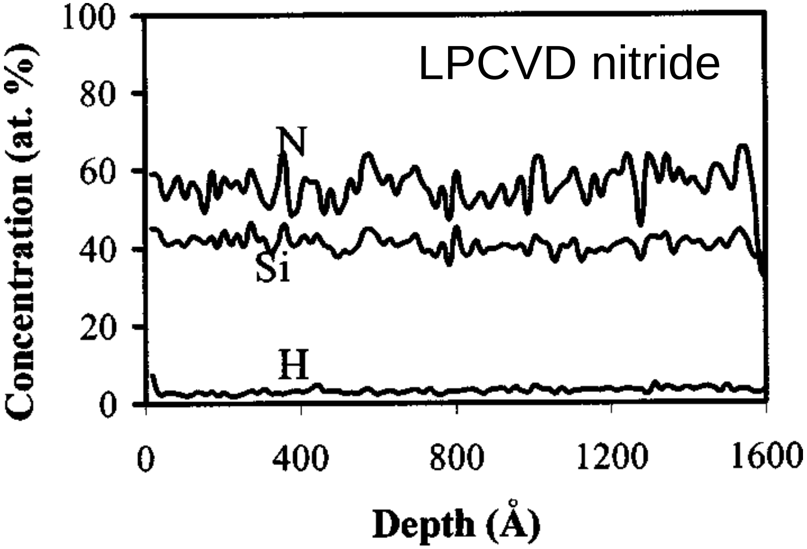


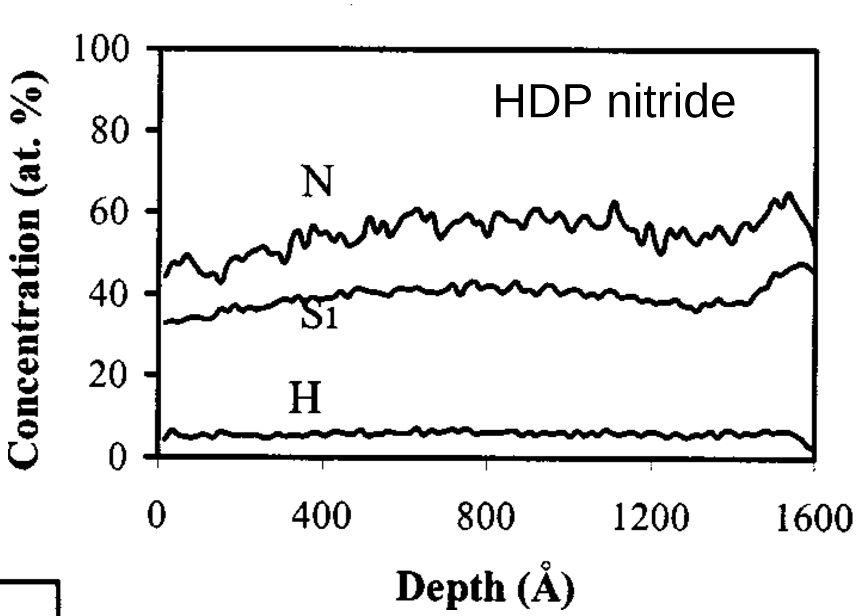
	PECVD	LPCVD	HDP CVD
Deposition rate (Å/min)	1800	300	960
Refractive index	1.985	2.003	1.990
Stress (dyn/cm^2)	−1.5 E 9	+1.0 E 10[a]	−3.8 E 9
Wet-etch rate in 85% H_3PO_4 (Å/min)	373	57	69
Wet-etch rate in 15:1 BHF (Å/min)	46.0	3.4	2.3

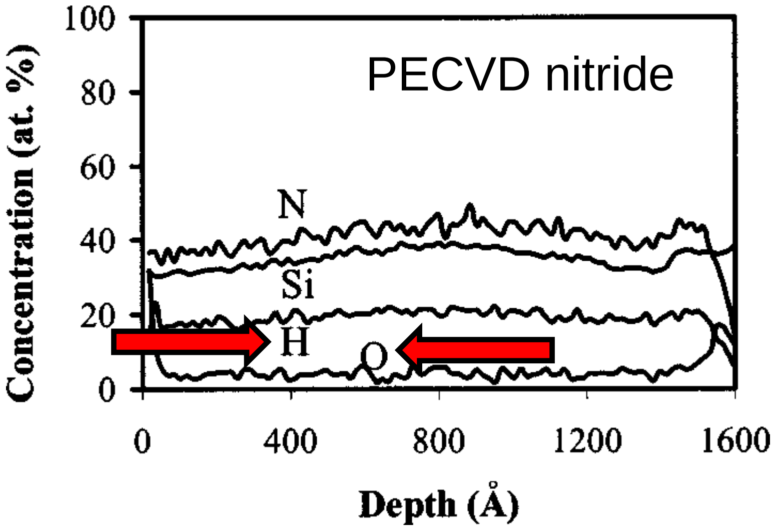
Tradeoff: high deposition rate leads to non-dense film, which is rapidly etched.

Yota et al: JVST A **18**, 372 (2000);

Nitride comparison (2)

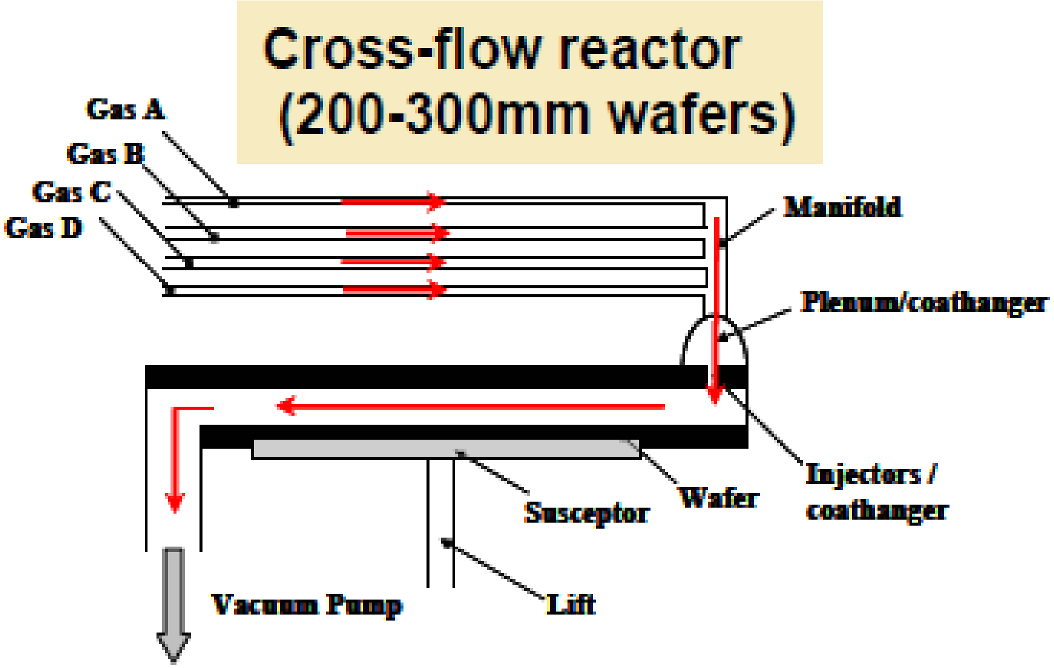






Yota et al: JVST A **18**, 372 (2000);

ALD reactors (1)



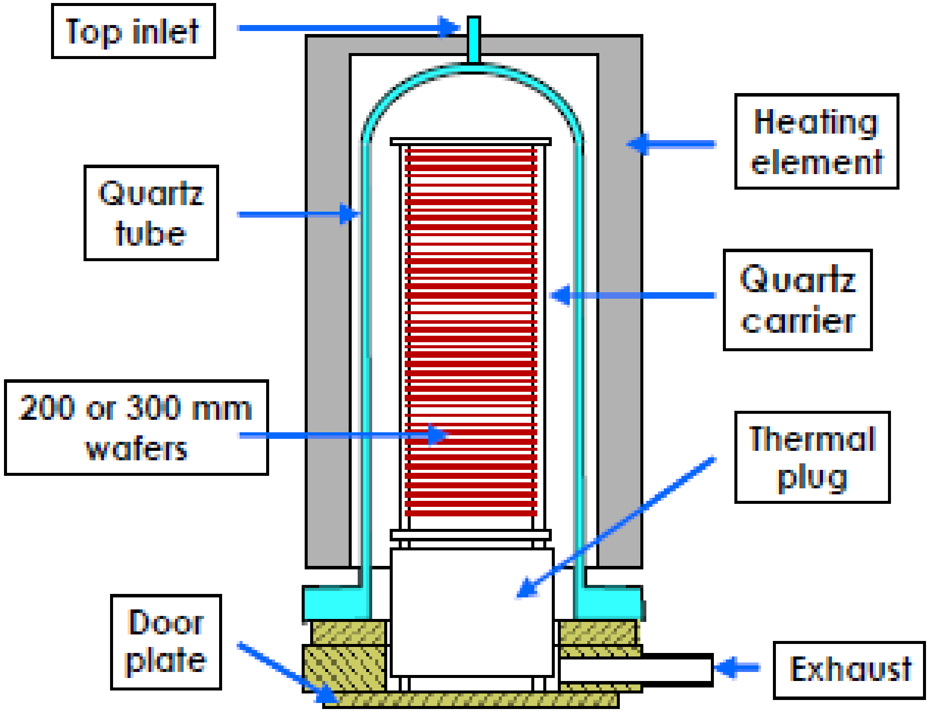
Continuous flow typical.

Stopped flow:introduce precursor pulse, stop pumping; wait for (expensive) precursor to diffuse (into deep cavities).

Suvi Haukka 2005

ALD reactors (2)

Batch reactor (200-300mm wafers)

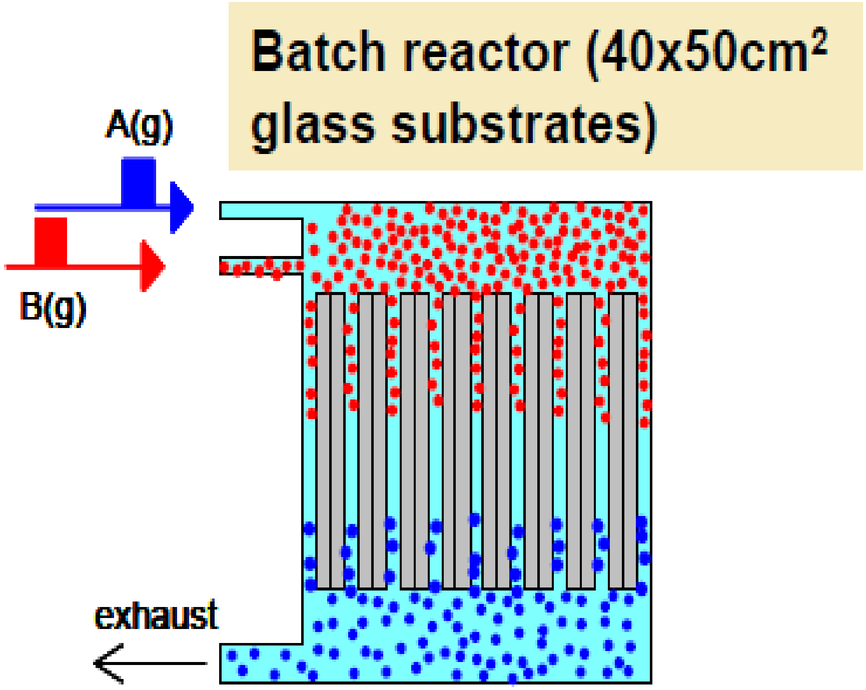


Modern batch reactors, both ALD and CVD are vertical.

This saves precious cleanroom floor space.

Suvi Haukka 2005

ALD reactors (3)

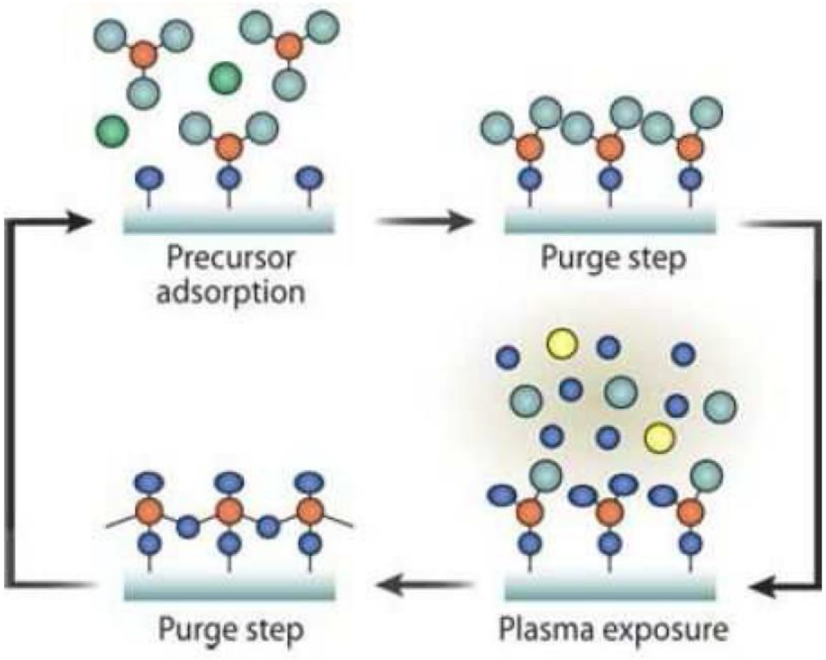


Because ALD is the ultimate surface reaction controlled deposition technique, we can rely on precursor diffusion in tight spaces between substrates.

For 10 nm thick Al_2O_3 passivation film, 3000 WPH has been shown (500 wafers/batch; 10 min each, deposition time 5 min (ca. 100 cycles = 400 gas pulses/300 seconds).

Suvi Haukka 2005

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)

Same benefits as PECVD:

Precursors can be excited at lower temperature;

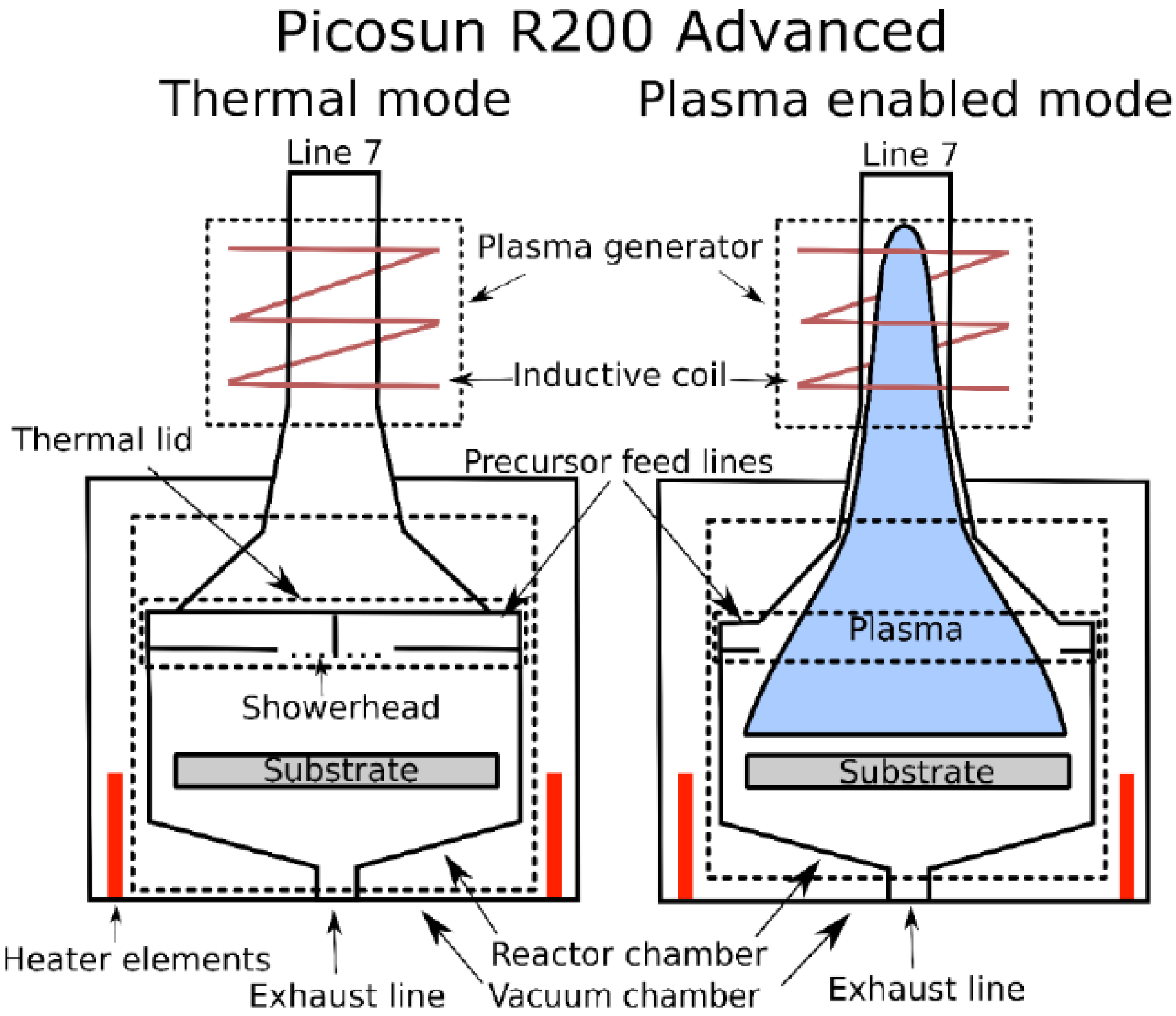
Larger choice of precursors;

Ion bombardment modifies (and damages) film;

Directionality is introduced and ALD excellent conformality is compromised.

Plasma can be ON part of the time during the oxidant pulse; and not at all during metal pulse.

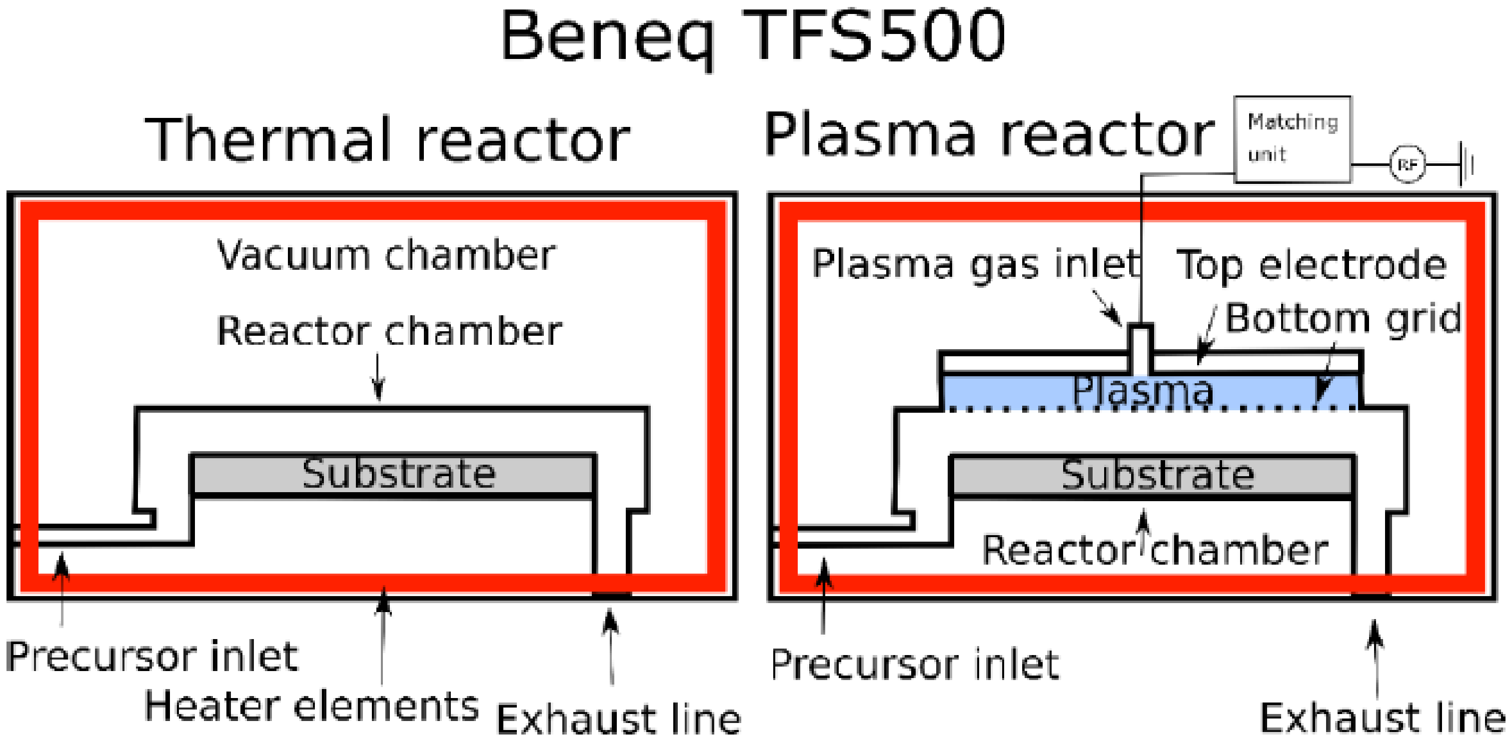
Micronova ALD-tools



The same tool; yes, but you must make hardware changes when you switch modes.

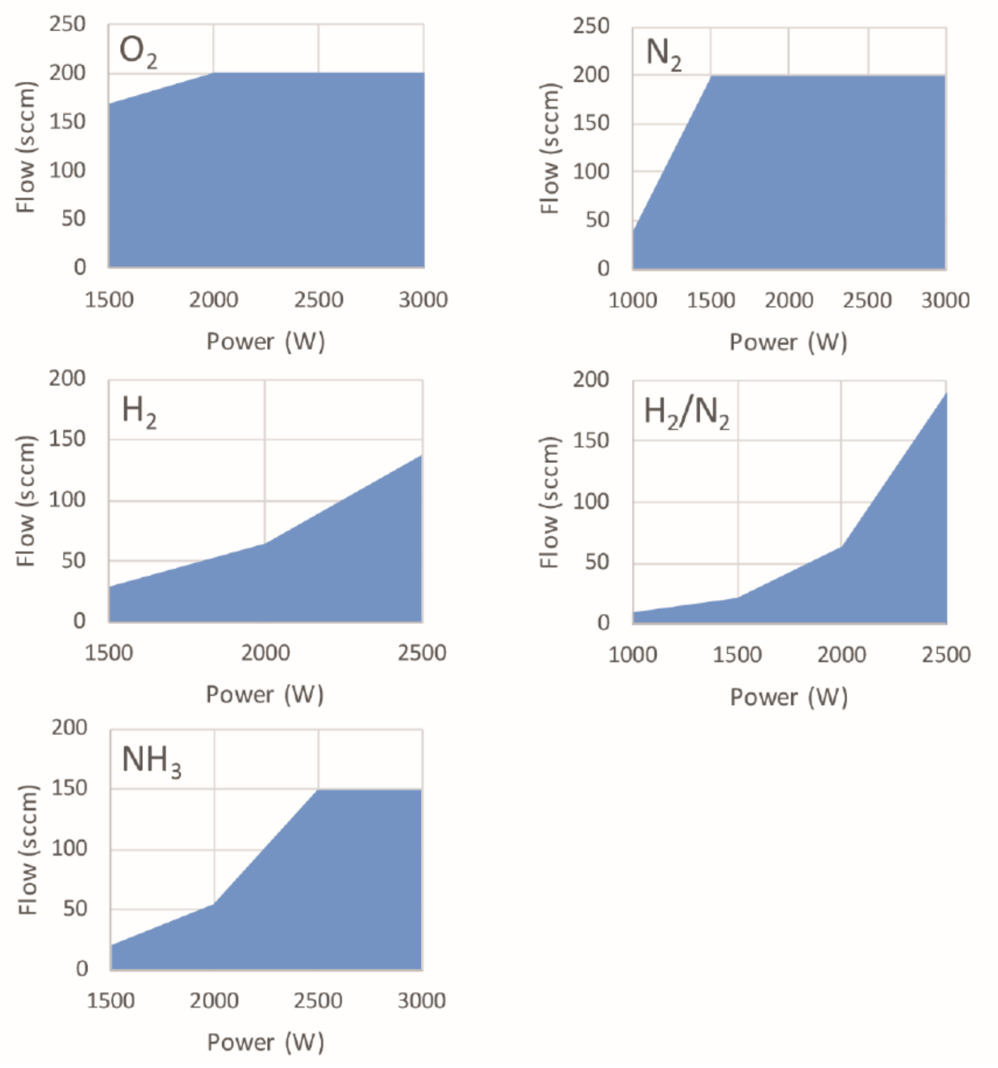
2.45 GHz

Micronova ALD-tools (2)



Capacitively coupled plasma (CCP) with showerhead and the freedom to use direct or remote mode with the same plasma head. 13.6 MHz RF power.

Gas flow rate ← → power



Not all combination of flow and power are available !

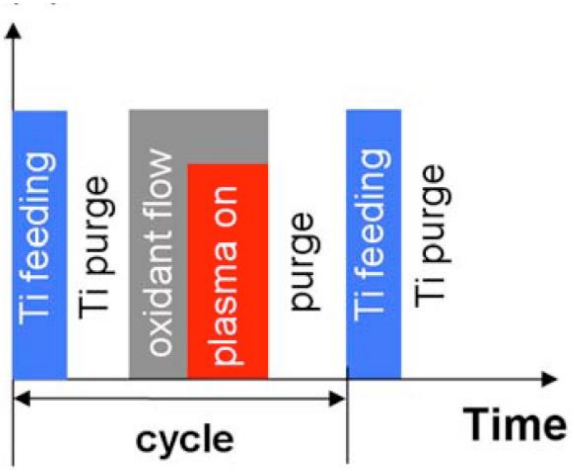
Plasma ignition requires certain pressure, and it may not be reached with given pumps.

Picosun R200 reactor.

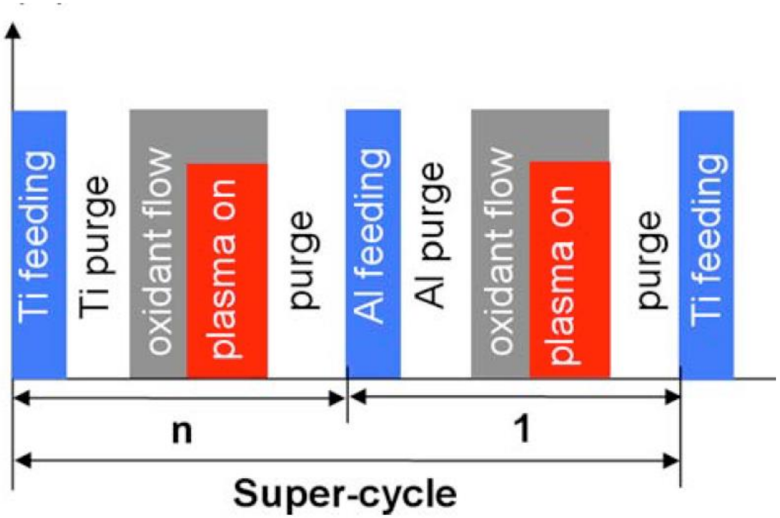
Ville Rontu,
PhD thesis, Aalto 2020

Supercycle PEALD

TiO_2 dielectric thin films



Al-doped TiO_2 dielectric thin films



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.

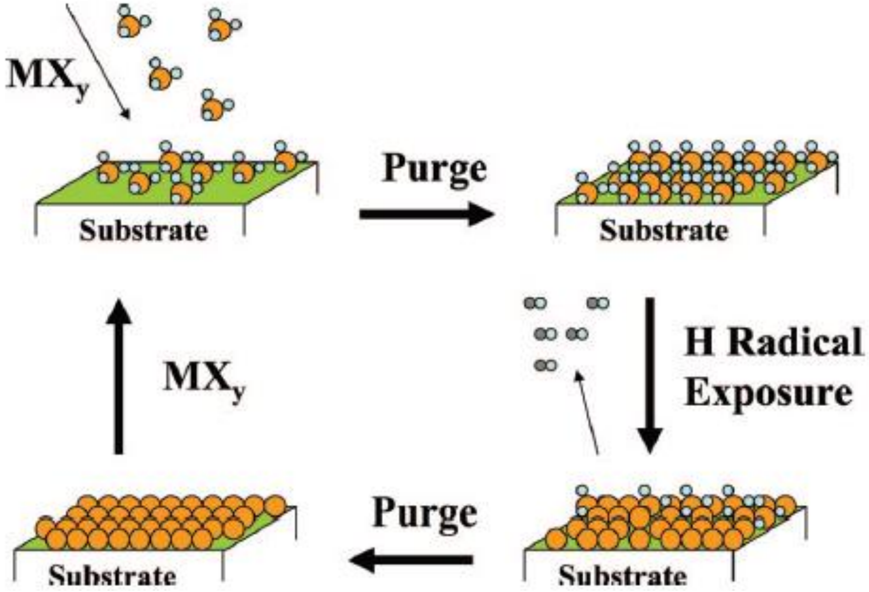
New precursors become available because plasma can break down precursors that could not be used in thermal ALD.
For example, N_2O as oxidant.

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

Radical-enhanced ALD

$$\text{(A) } Ta^* + TaCl_5 \rightarrow TaTaCl_5^*$$

$$\text{(B) } TaCl_5^* + 5H\cdot \rightarrow Ta^* + 5HCl$$



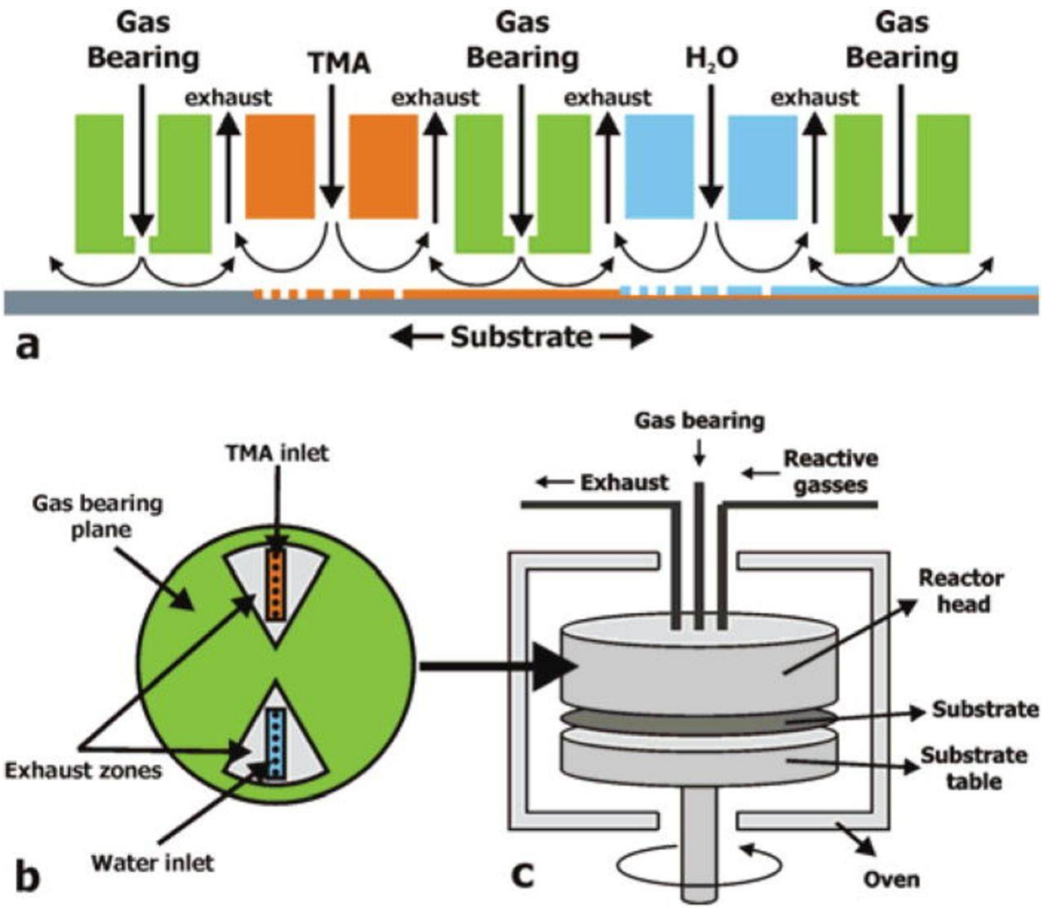
$TaCl_5$ is first exposed to the surface. Subsequently, the hydrogen radicals reduce the Ta atoms and remove the chlorine from the surface.

GPC during Ta ALD is only 0.08 Å per AB cycle. The small growth per cycle is attributed to steric hindrance caused by the large $TaCl_5$ admolecule on the surface.

Ta ALD films have excellent film resistivities.

S.M. George: Chem.Soc.Rev. 2009

Spatial ALD



Wafer is moving past static gas nozzles.

Linear and rotating versions exist.

This was an original idea of Tuomo Suntola in 1970's; reinvented in 2000's.

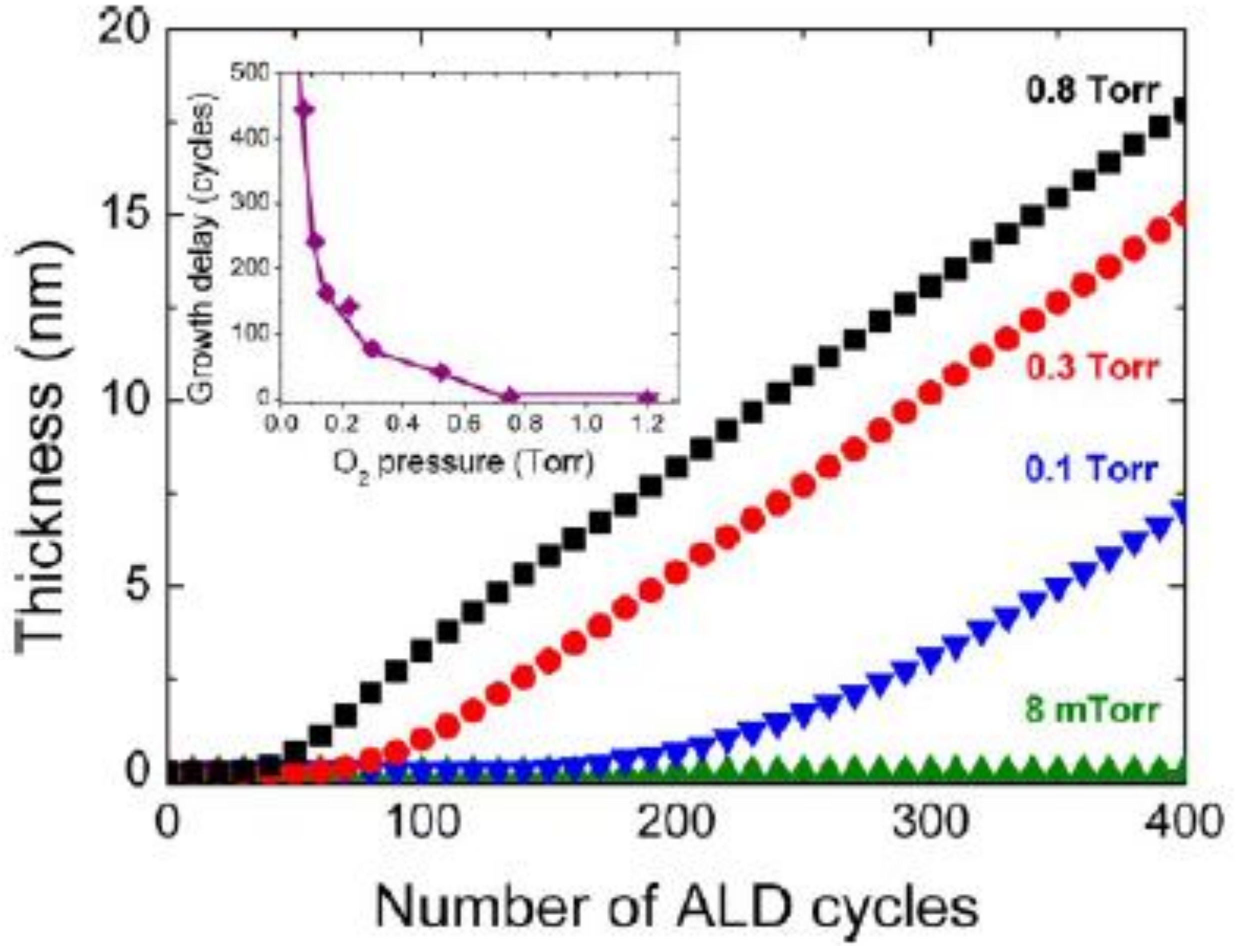
jes.ecsdl.org

Spatial ALD reactors

Deposition upto 10 nm Al_2O_3

www.blog.baldengineering.com

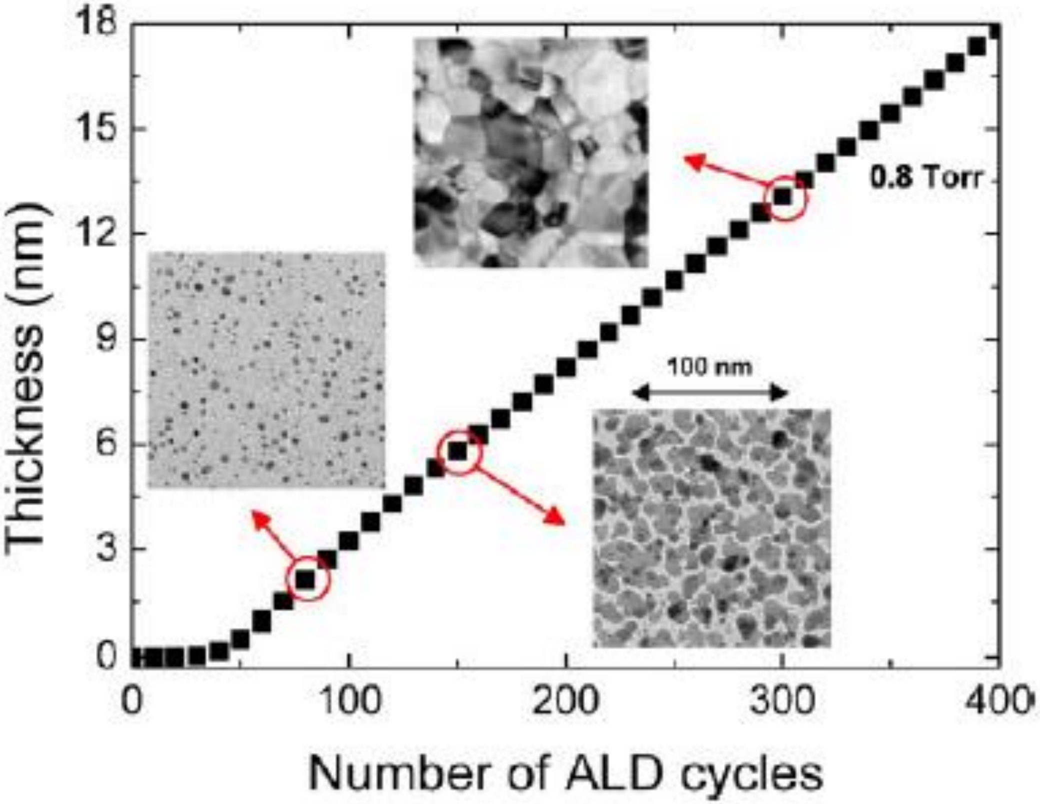
Noble metal ALD: initiation lag



Mackus, Kessels: Chem. Mater. 2013, 25, 1905−1911

“Thickness as a function of the number of ALD cycles as measured by in situ spectroscopic ellipsometry (SE) for different O_2 pressures and a 10 s pulse time. In the inset the growth delay deduced from the nucleation curves is presented as a function of the O_2 pressure.”

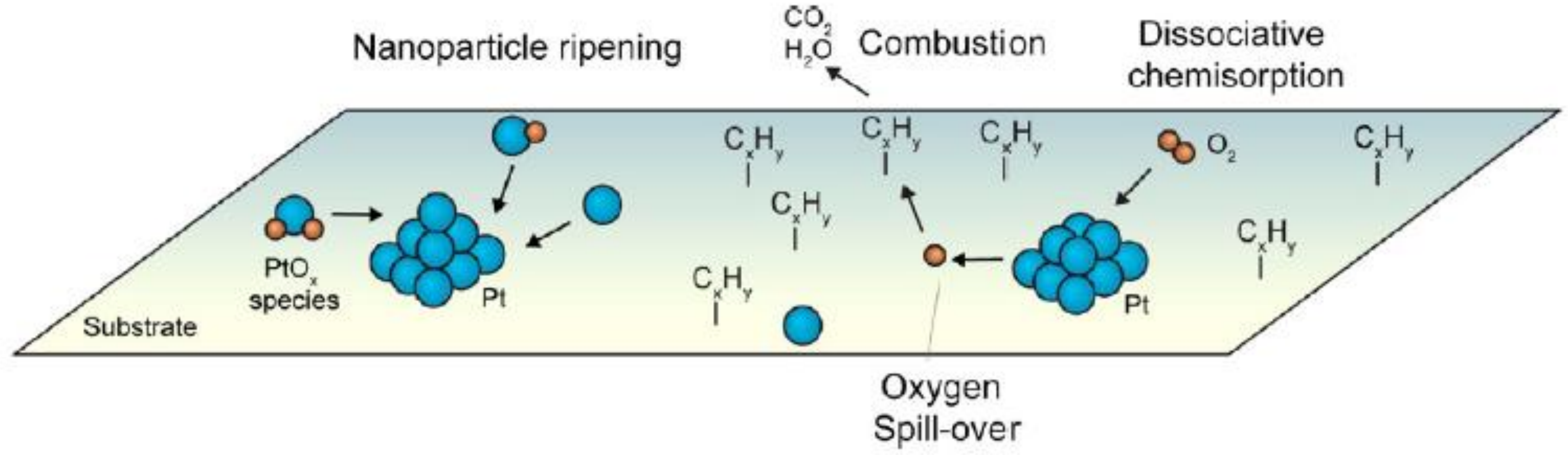
Particle vs. film deposition



“Thickness as a function of the number of ALD cycles as measured by in situ spectroscopic ellipsometry (SE) for an O_2 exposure of 0.8 Torr O_2 for 10 s. The bright field TEM images in the figure illustrate that Pt ALD nucleation evolves from island growth, via island coalescence, to film closure.”

Mackus, Kessels: Chem. Mater. 2013, 25, 1905−1911

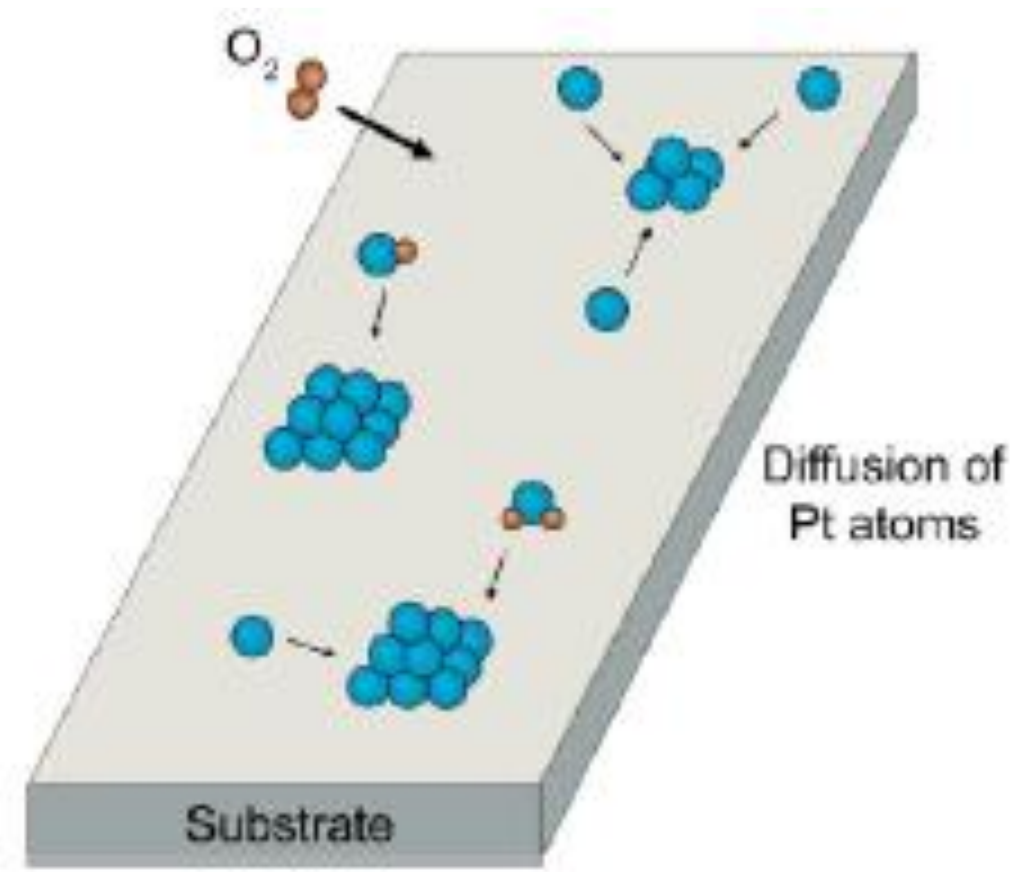
Noble metal ALD mechanism



“Surface reactions during the O_2 pulse of Pt ALD on an oxide substrate.
Hydrocarbon precursor ligands are present as a result of the preceding $MeCpPtMe_3$ pulse.
Exposure to O_2 stimulates the ripening of Pt particles, mainly through the formation of
PtO_x species that diffuse faster as compared to their metallic counterparts.
The formed Pt particles subsequently catalyze the ALD reactions, which
involves dissociative chemisorption of O_2 molecules at the Pt islands, spillover of oxygen, and
combustion of the ligands to CO_2 and H_2O.”

Mackus, Kessels: Chem. Mater. 2013, 25, 1905−1911

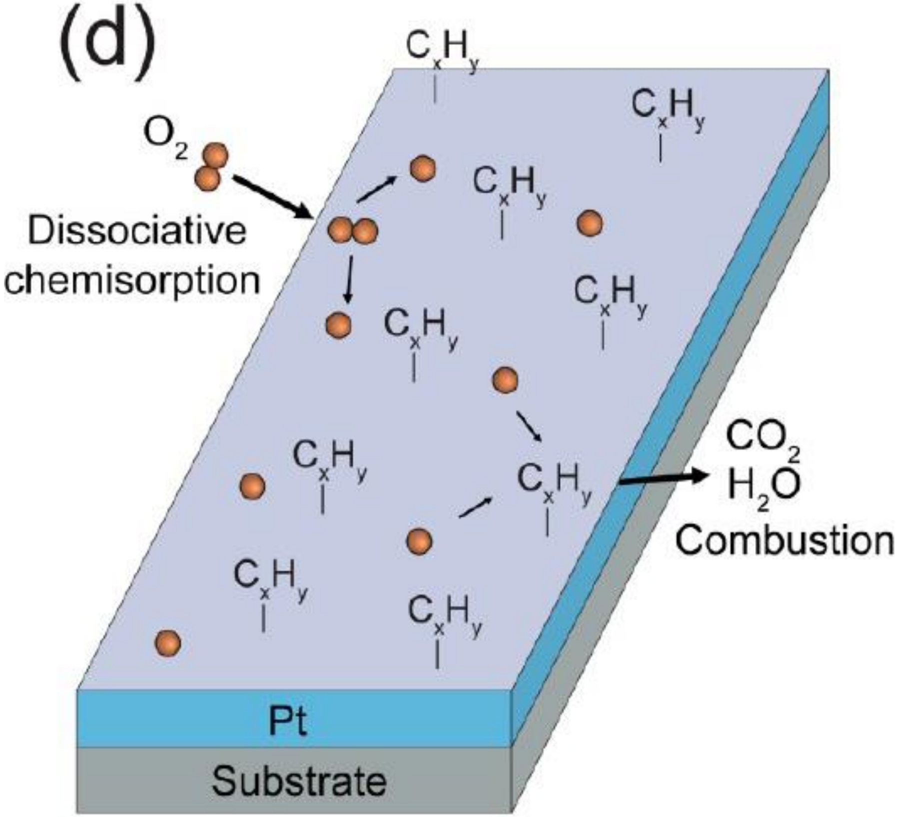
Pt nanoparticle deposition



"O_2 exposure (when being sufficient) enhances the diffusion of single Pt atoms over the oxide surface leading to aggregation of Pt in metal clusters. The particle ripening (i.e., the formation of clusters) can be employed to prepare nanoparticles or, when increasing the number of cycles, to prepare closed films."

Mackus, Kessels: Chem. Mater. 2013, 25, 1905−1911

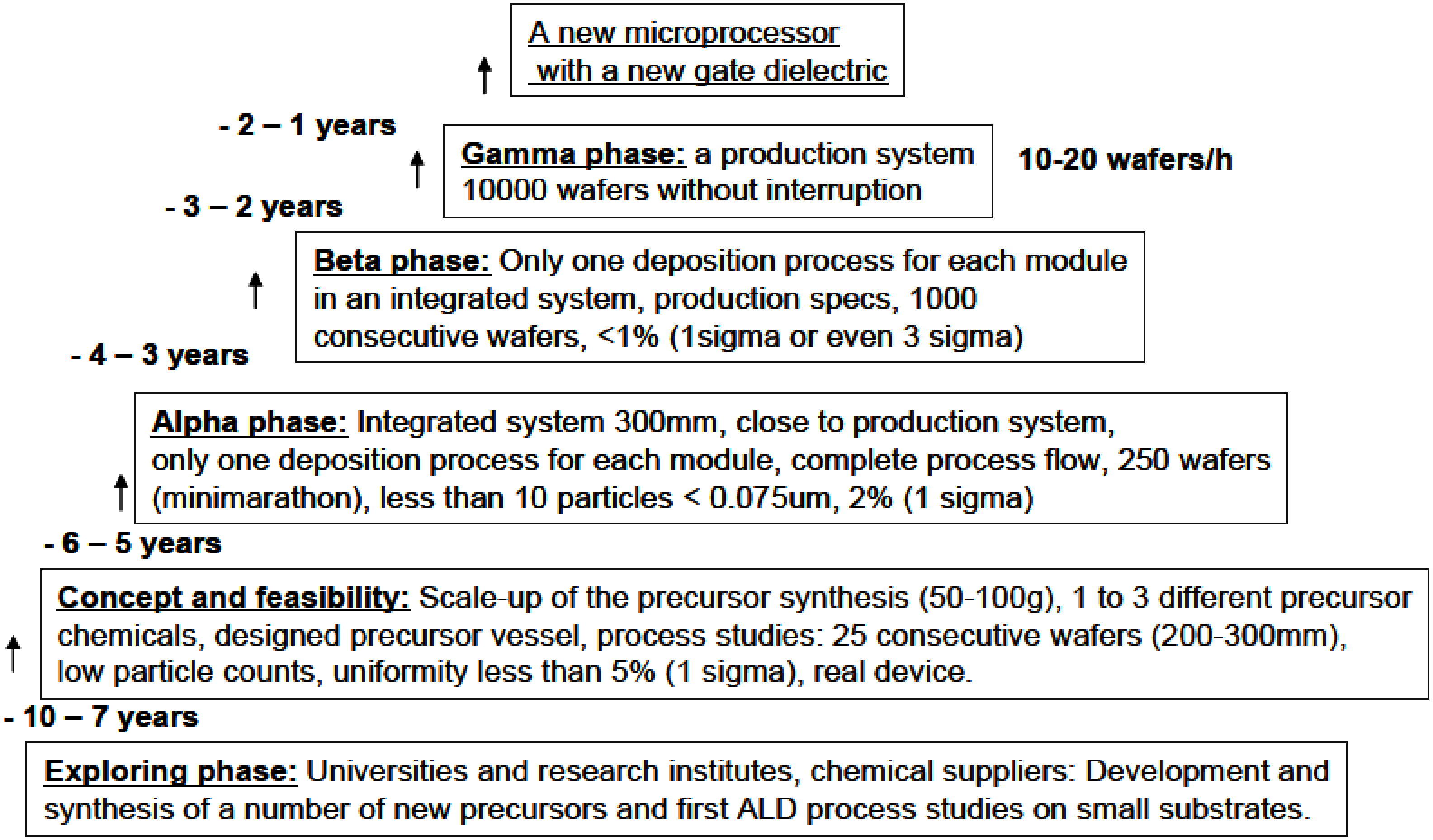
Pt film deposition



O_2 dissociatively chemisorbs on the Pt surface, allowing for subsequent combustion of the ligands remaining from the Pt precursor step.

Mackus, Kessels: Chem. Mater. 2013, 25, 1905−1911

ALD tool 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.

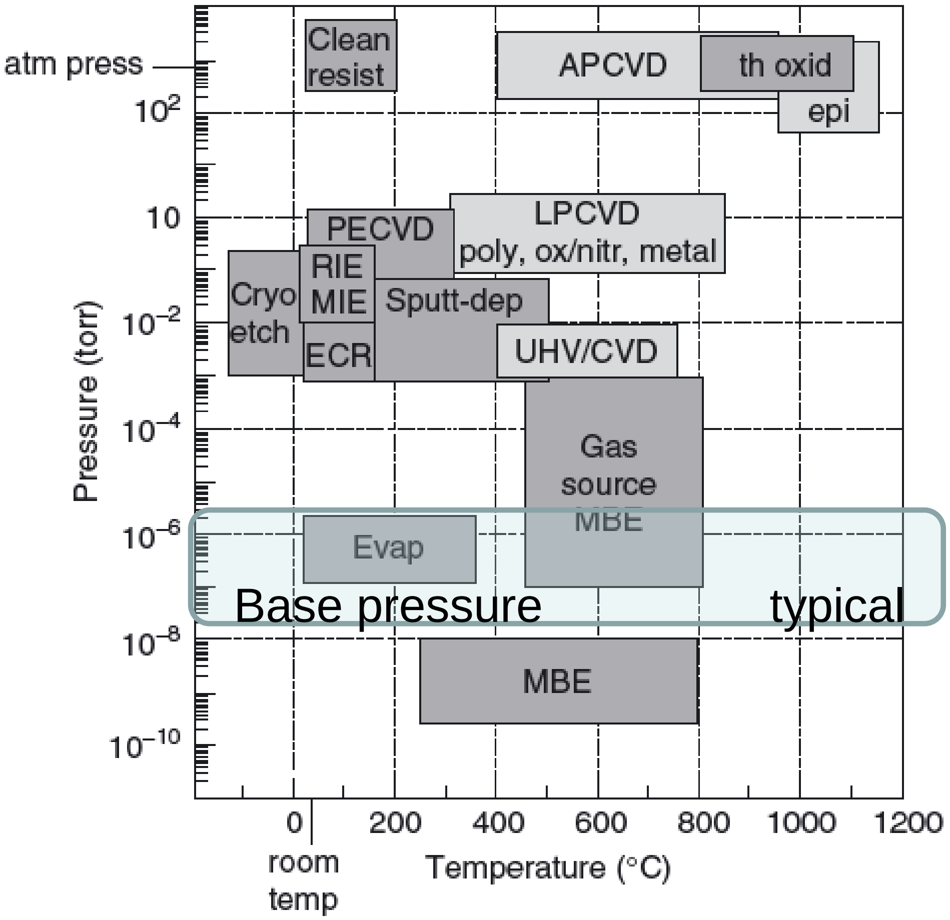
- 10 – 7 years

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.

Suvi Haukka, ASM Microchemistry

Break

Temperature vs. pressure



High vacuum - high temperature is a difficult combo, since stuff evaporates from chamber walls at elevated temperatures.

Base pressure is much lower than process pressure for most processes.

Rubloff, G.W. & D.T. Boronaro: Integrated processing for microelectronics science and technology, IBM J.Res.Dev. 36 (1992), pp. 233

Heating the reactor

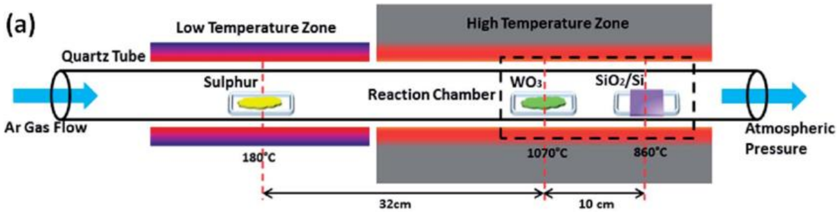
Method	**Equipment**
resistance heating	tube furnace
induction heating	epitaxial reactor
lamp heating	rapid thermal processing RTP
laser heating	LACVD
conduction	hot plates; SW PECVD
convection	resist ovens; gas flow on back

Hot wall vs. cold wall

In hot wall systems all parts are hot ➔ reaction takes place on the walls as well.

At home: oven

Slow ramp rates because huge mass needs to be heated. ~10-100 K/min

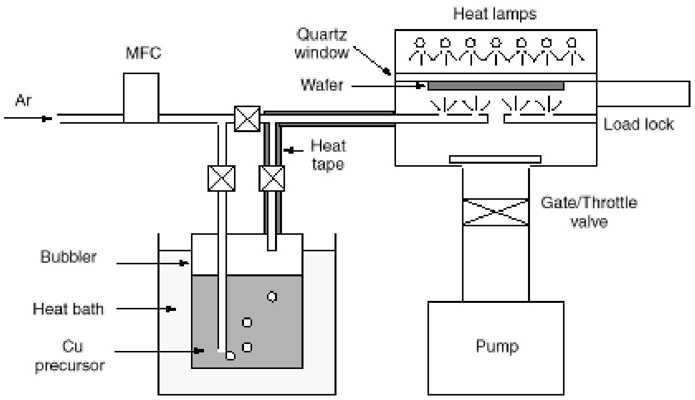


Rong et al: Controlling sulphur precursor addition for large single crystal domains of WS_2, 2014

In cold wall systems only the wafer (and susceptor) is heated.
No deposition on walls.
Heating options: lamp; induction.

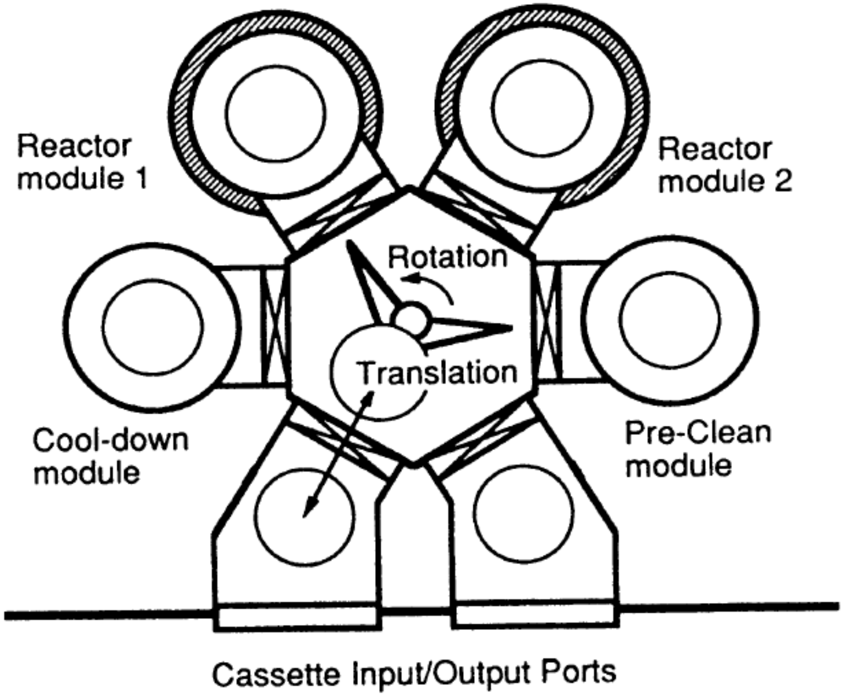
At home: microwave oven.

Fast ramp rates because small mass to be heated, ~ 100-1000 K/s



Changsup Ryu, PhD thesis, Stanford University, 1998

Integrated tools



Pressure regimes:

Reactor module 10^{-8} torr

Central handler 10^{-7} torr

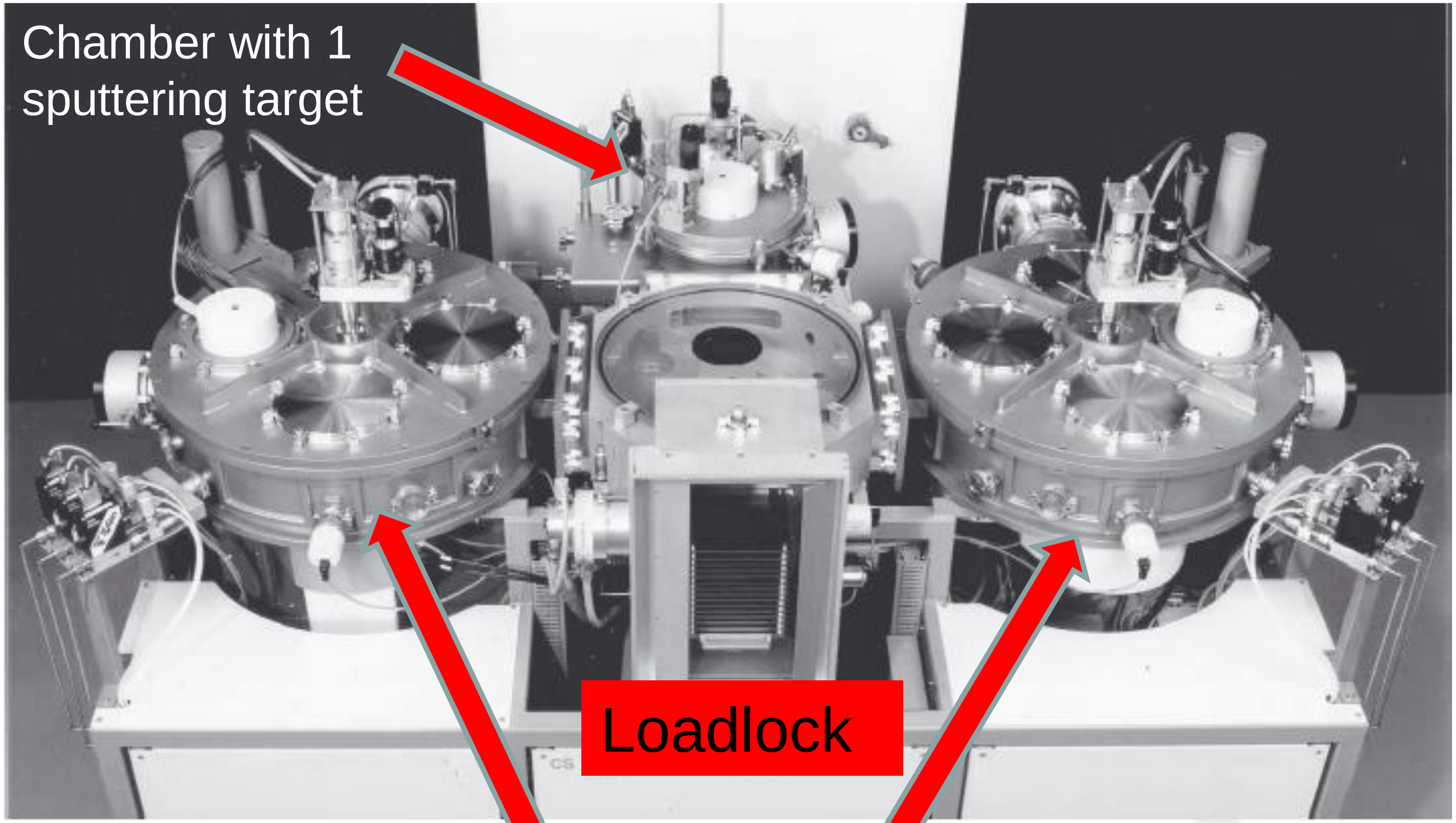
Cool-down/pre-clean 10^{-3} torr

Cassette ports 10^{-3} torr

E.g. TiN by reactive sputtering poisons Ti-target; and subsequent Al deposition prone to form AlN if done in same chamber sequentially.

But if two separate chambers ➔ no cross-over effects between steps.

Micronova von Ardenne

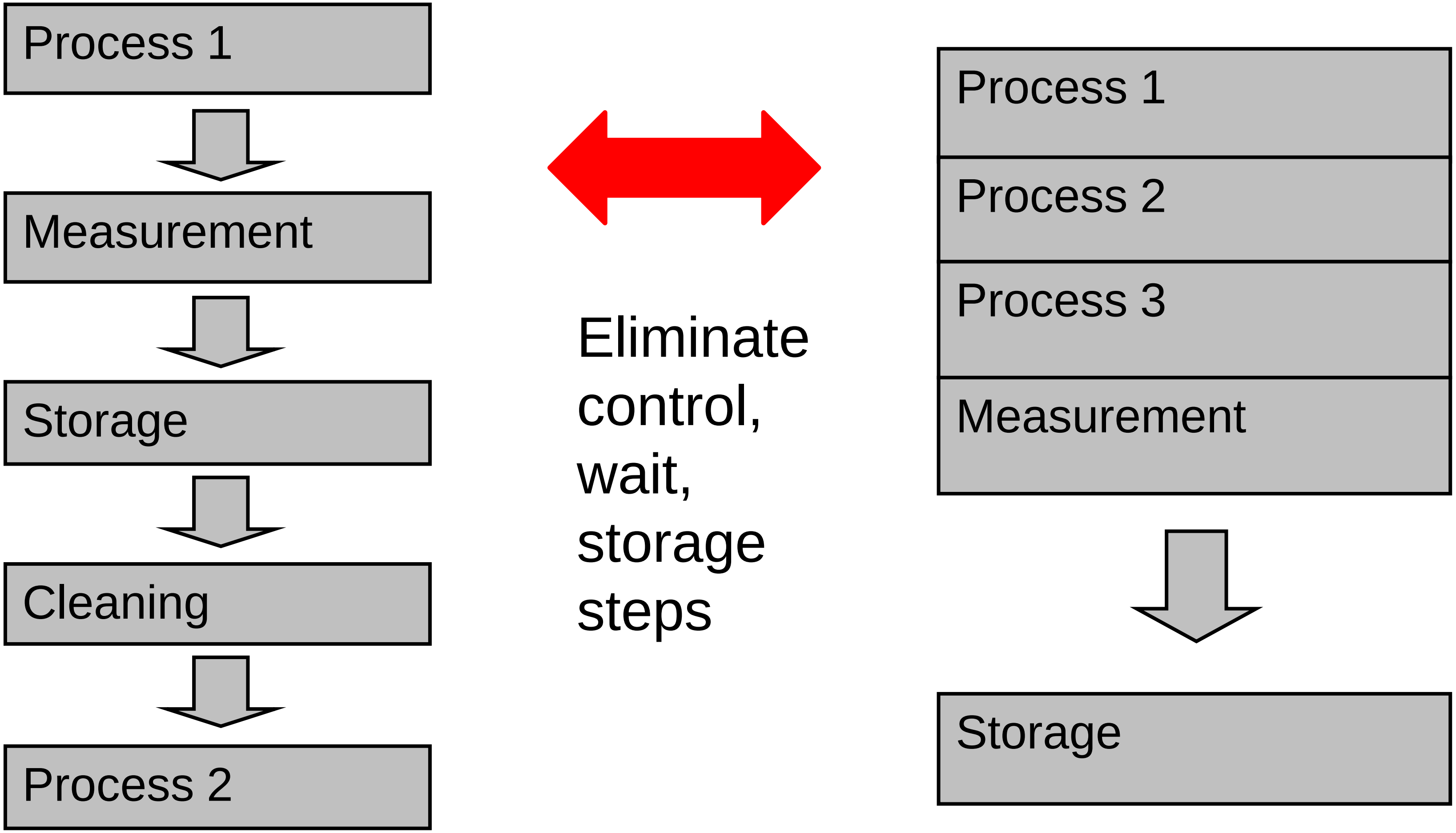


Chamber with 1 sputtering target

Loadlock

2 chambers with 4 sputtering targets each

Integrated processes



Process 1

Measurement

Storage

Cleaning

Process 2

Eliminate control, wait, storage steps

Process 1

Process 2

Process 3

Measurement

Storage

Reactor figures of merit

Uptime/downtime:

Uptime is an overall measure of equipment availability. Uptime is reduced both by scheduled and non-scheduled maintenance. Recalibration/test wafers required to set the process running after a disrupture can contribute significantly to downtime. Scheduled system cleaning is often mandatory for deposition equipment, to prevent film flaking from chamber walls.

Utilization

Utilization is a measure of equipment use: actual productive hours of all available hours. Some tools are needed many times in a process, and some may be reserved for some extra special steps only. The latter have low utilization.

Figures of merit (2)

MTTF
MTBA
MTBC

How long will it work before failure ? Do operators need to interfere with its operation ? How often does it have to be cleaned ? These questions are operationalized by MTTF (mean time to failure), MTBA (mean time between assists) and MTBC (mean time between cleans).

MTBC is process dependent: some products tolerate more defects than others, and more relaxed cleaning intervals apply.

FOM (3)

Footprint

How big is it ? Cleanroom space is premium priced: 10000 $/m^2 is the price range for a class 1 (Fed. Std.) cleanroom. In most cases, just the front panel of the system is in the cleanroom, the rest of the tool is in the service area which has more relaxed particle cleanliness requirements.

Throughput

How many wafers per hours (WPH) can the system handle ? If film thickness is doubled, deposition time is doubled. Throughput, however, might not change much if overhead (loading, pump down, temperature ramp etc.) is high relative to deposition time.

https://www.glassdoor.sg/Photos/Lam-Research-Office-Photos-IMG111691.htm

Deposition rate & thruput

Deposition rate is measured in nm/min.
Thruput is measured in WPH (wafers per hour)

A batch LPCVD polysilicon reactor loads 100 wafers, depo rate is 10 nm/min, which corresponds to time 40 min for 400 nm thick film. Load, ramp etc. take 60 min. ➔ thruput is 60 WPH.

A single wafer PECVD tool deposits silicon at 100 nm/min rate, with load, ramp etc. 1 min/wafer. 400 nm thick film is achieved in 5 min ➔ thruput is 12 WPH.

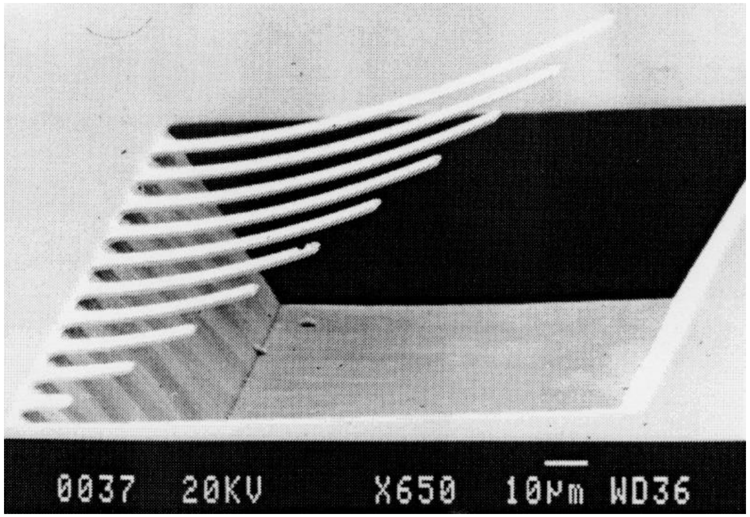
Cost-of-ownership calculation is needed to see if one is superior to other.

Cost of ownership (CoO)

	A	B
Purchase price	1 000 000 €	1 500 000 €
Operating costs	250 000 €/yr	120 000 €/yr
5 years costs	1 750 000 €	2 100 000 €
Uptime	85%	90%
Throughput	45 WPH	55 WPH
Wafers/5 yrs	1.68M	2.17M
Yield	99%	99.8%
Good wafers	1.66M	2.16M
Cost/good wafer	1.05 €	0.97 €

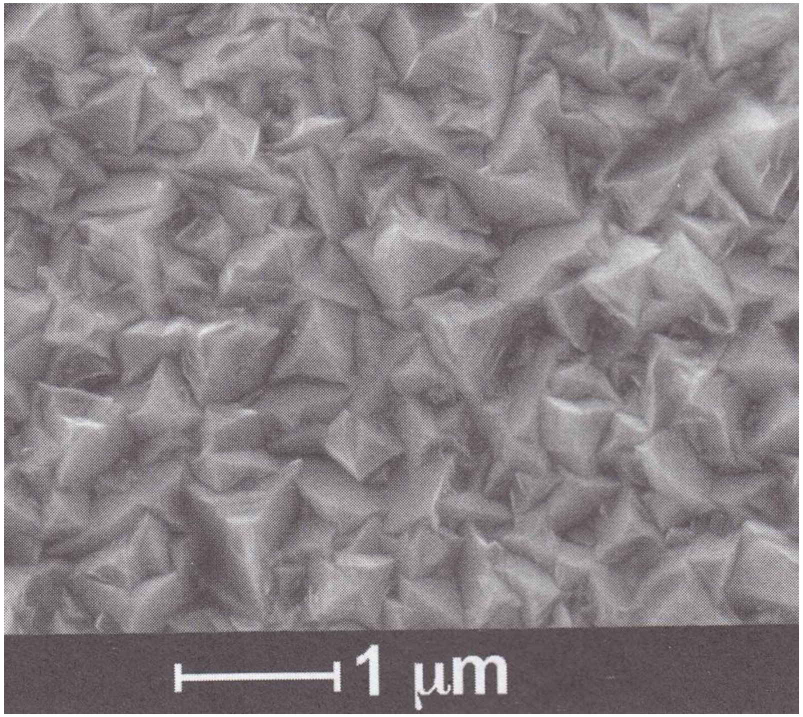
Film quality

- High density (non-porous)
- Step coverage (conformality)
- Low stress (or tailored stress)
- Defect-free
- Low impurity content
- Stability
- Smoothness ?



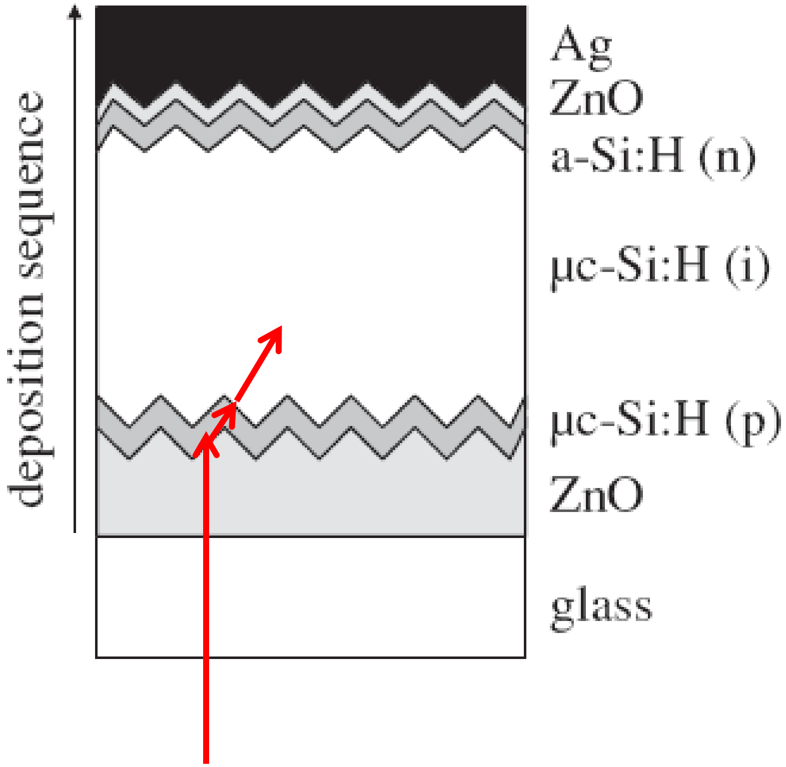
SiO_2/Ti; Weileun Fang

Is smooth good ?



Fluorine-doped zinc oxide (FZO)

Poortmans: Thin film solar cells



Superstrate solar cell:

Repmann

Film quality measures

Uniformity:

across-the-sample uniformity of thickness, resistivity, refractive index…

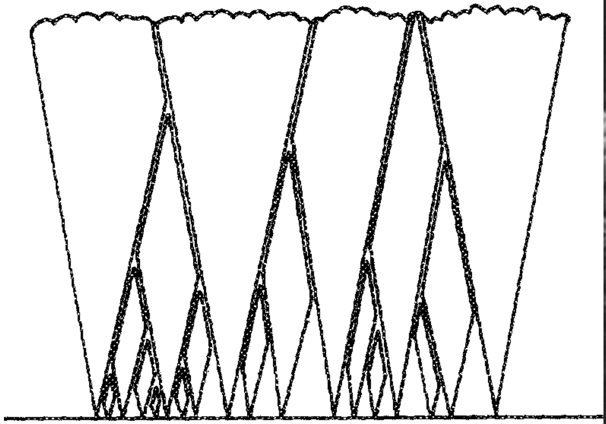
Usually given as U = (max-min):(2*ave), 1-10% typical

Homogeneity:

Film has same structure and composition all over.

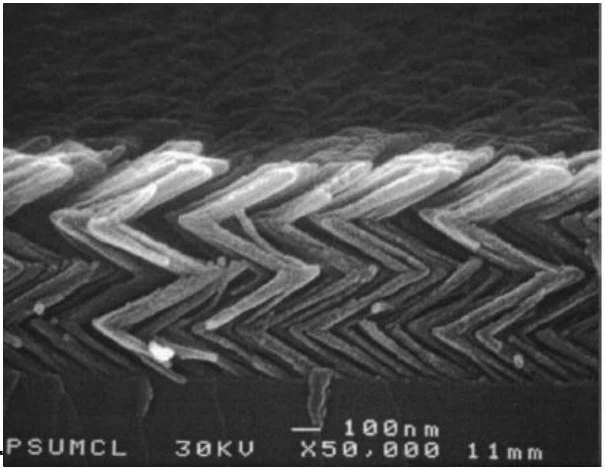
e.g. grain size or dopant concentration is independent of position, no stress gradient, no interfacial layer, …

Inhomogenous films



Grain size gradient

Messier JVST 1986



GLAD/sculpted film: rotation and inclined deposition used to create inhomogenous film on purpose (evaporated MgF_2; Messier book)

PSG (phoshorous doped silica glass) has doped polysilicon partially. PSG is homogenous, but polysilicon displays inhomogenous dopant concentration.

Customer data of Al_2O_3 batch process in a PICOSUN™ P-300B batch ALD tool.

	Target	Measured
Thickness non-uniformity in-wafer	< 1 % 1σ	0.51 % 1σ
Thickness non-uniformity in-batch	< 1 % 1σ	0.80 % 1σ
Deposition rate variation batch-to-batch	< 1 % 1σ	0.18 % 1σ
Added particles/ wafer (>70 nm)	< 8	1-2
Refractive index @ 190 nm	>1.86	>1.864
Film delamination or pinholes after HF etch	no	no
Film stress	< 200 Mpa	< 200 Mpa
Alkali contamination	< 10E10 at/cm^2	< 0.02E10 at/cm^2

MTTM < 4 h

MTBM > 6 months

Uptime > 90 %

Rate vs. impurities

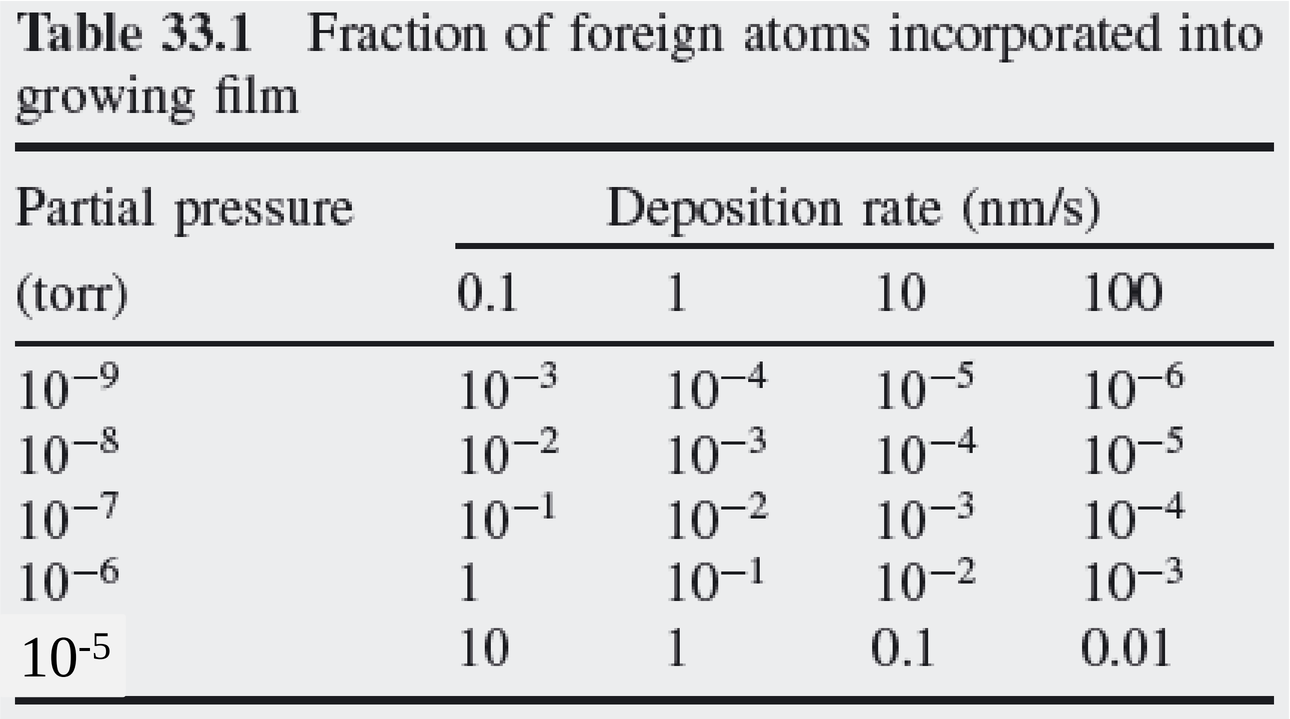


Table 33.1 Fraction of foreign atoms incorporated into growing film

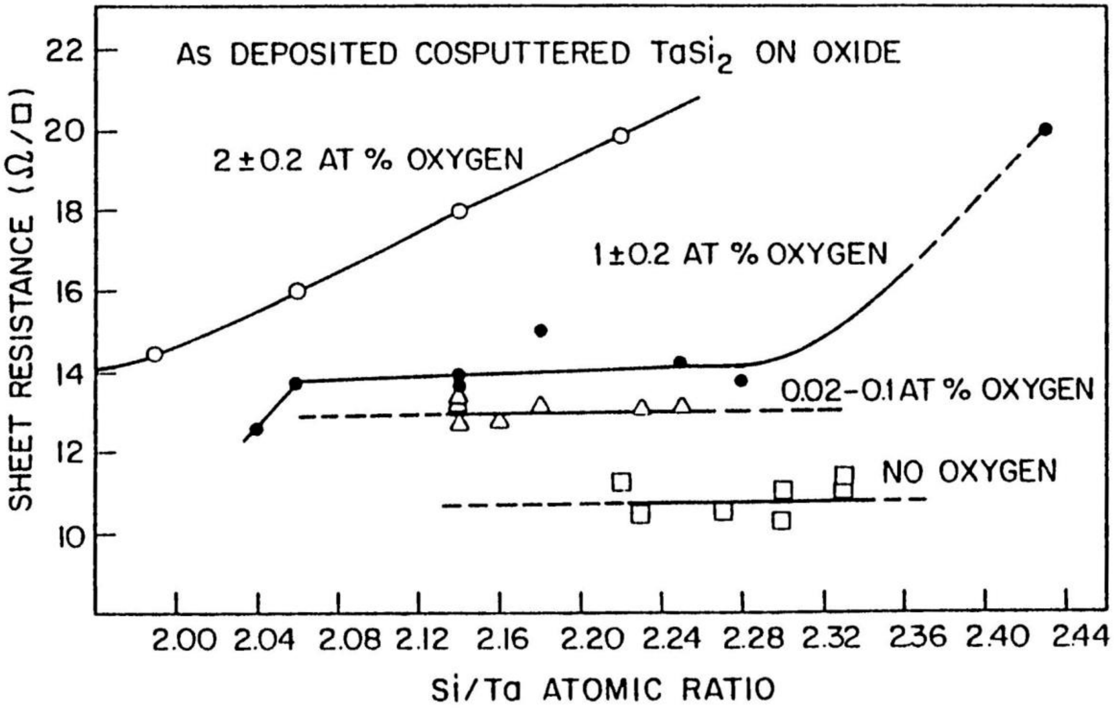
Partial pressure (torr)	Deposition rate (nm/s) 0.1	1	10	100
10^{-9}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
10^{-8}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
10^{-7}	10^{-1}	10^{-2}	10^{-3}	10^{-4}
10^{-6}	1	10^{-1}	10^{-2}	10^{-3}
10^{-5}	10	1	0.1	0.01

In reality sticking coefficient is important: O_2 and H_2O stick readily, N_2 not.

Slow deposition rate means that gas phase impurities in the reactor atmosphere have time to incorporate into growing film. In the previous example then, batch reactor wafers have 10X impurities relative to single wafer reactor.

Franssila: Introduction to Microfabrication

Resistivity: impurity effects

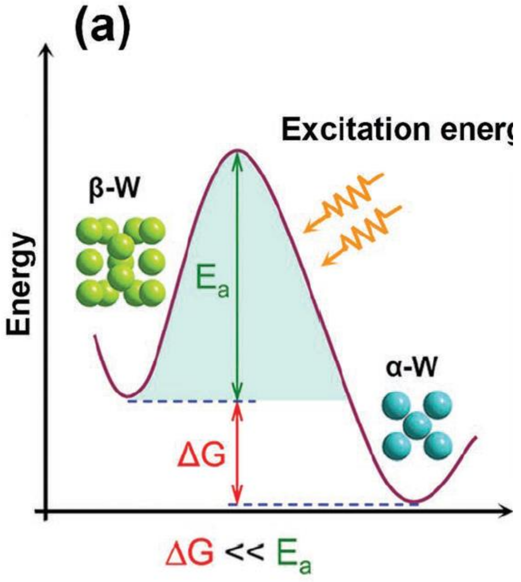


Doubling of $TaSi_2$ resistivity due to 2% oxygen.

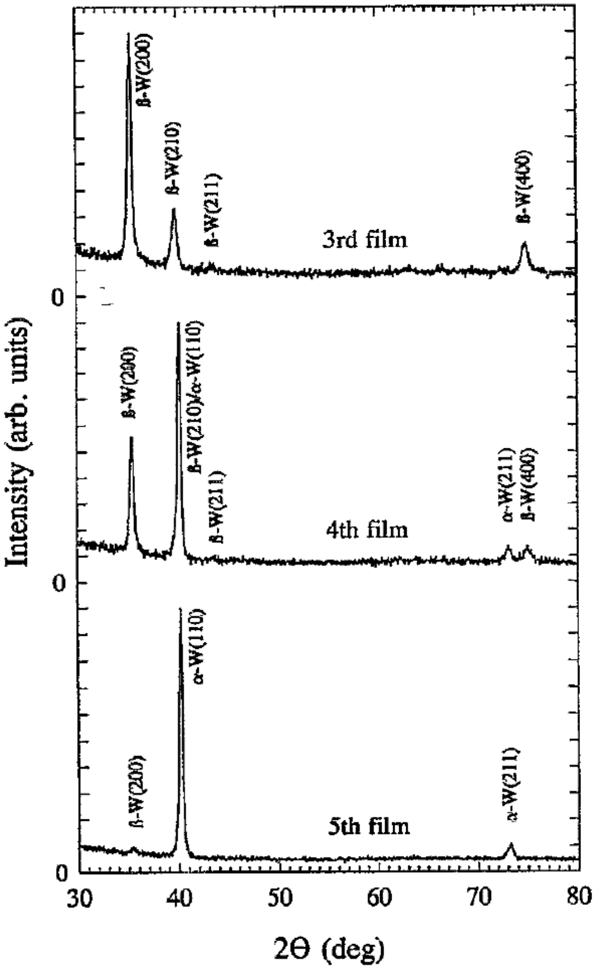
Murarka: Metallization

Oxygen in tungsten film

α-phase is the stable phase, but the metastable β-phase is often found.



Wang & Rogachev: *Adv. Mater. Interfaces* **2019**, *6*, 1900031



Weerasekera et al: APL **64**, 3231 (1994);

8 consecutive sputtering runs:

β-phase is seen in runs 1-3, but the α-phase in runs 5-8; with run #4 as a mixture.

Tungsten getters oxygen, and reactor atmosphere gets purified, and later runs contain less of it, leading to α-phase.

Oxygen impurity in W-films

"The decrease in the lattice parameter of the β-W phase,
and the eventual transition to the α-W phase with increasing sputtering time, strongly suggests that **oxygen impurities stabilize the β -W phase**. Both effects can be accounted for by a decrease in the oxygen partial pressure as the deposition process continues due to the **oxygen gettering ability of freshly sputtered W**.

In this context it is important to note, however,
that the actual amount of incorporated oxygen depends not only on the oxygen partial pressure, but also on the deposition rate. Even though the oxygen partial pressure is relatively low, **the slow deposition rate allows significant amounts of oxygen to be incorporated within the growing films.**"

Weerasekera et al: APL **64**, 3231 (1994);

First wafer effect

1st wafer sees dirtier chamber atmosphere than the following wafers, esp. if long time since last deposition (gettering helps).

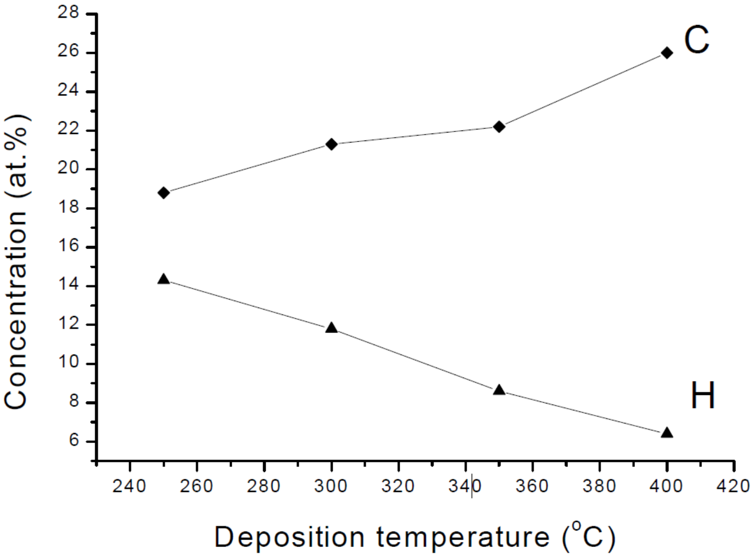
1st wafer experiences cooler chamber than subsequent wafers (most processes use/release heat)

Target may be coated by impurities if it has not been used for a while (pre-sputtering, or evaporation while shutter is in place helps).

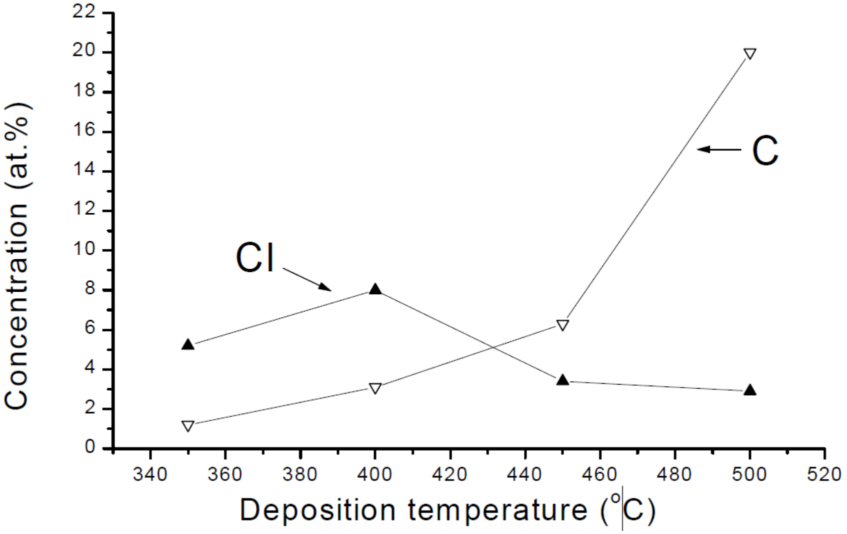
1st wafer has shortest time since previous step, others may have changed during waiting (dehydrated; reacted; absorbed water…)

After chamber cleaning the clean walls may adsorb reactants (molecules, radicals, electrons, ions), and it takes time for wall conditioning.

ALD TaN impurities



Carbon and hydrogen contents determined by TOF-ERDA of films deposited by the TaCl^5-TMA-NH^3 pulsing process as a function of deposition temperature.

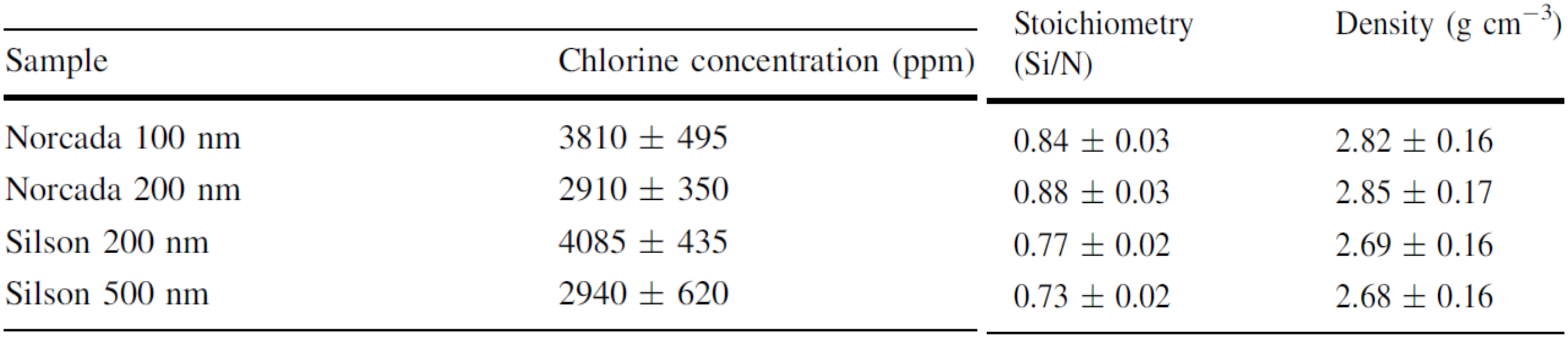


Carbon and chlorine contents of films deposited by the TaCl$_5$-^{t}BuNH$_2$ process as a function of the deposition temperature.

Petra Alen, PhD thesis, University of Helsinki, 2005

Impurities, density, stoichiometry

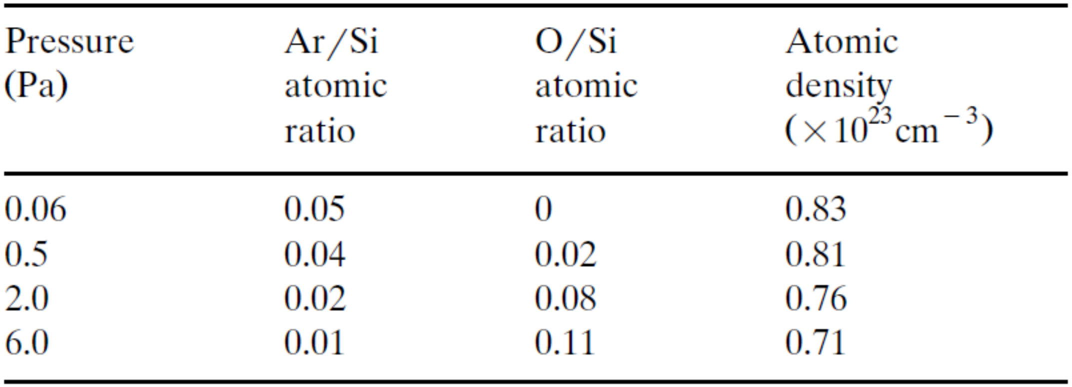
LPCVD nitride



Sample	Chlorine concentration (ppm)	Stoichiometry (Si/N)	Density (g cm^{-3})
Norcada 100 nm	3810 ± 495	0.84 ± 0.03	2.82 ± 0.16
Norcada 200 nm	2910 ± 350	0.88 ± 0.03	2.85 ± 0.17
Silson 200 nm	4085 ± 435	0.77 ± 0.02	2.69 ± 0.16
Silson 500 nm	2940 ± 620	0.73 ± 0.02	2.68 ± 0.16

Huszank: J Radioanal Nucl Chem, 2015

Sputter-deposited nitride:



Pressure (Pa)	Ar/Si atomic ratio	O/Si atomic ratio	Atomic density ($\times 10^{23}$ cm^{-3})
0.06	0.05	0	0.83
0.5	0.04	0.02	0.81
2.0	0.02	0.08	0.76
6.0	0.01	0.11	0.71

“Stoichiometric Si_3N_4 film with extremely low hydrogen content <1% and oxygen content <1% was obtained at the Ar/N_2 partial pressure ratio of 1.5, and total sputtering-gas pressure of less than 0.1 Pa.”

Li et al: Thin Solid Films 384 2001 p.46

Measurement needs

-in-situ: during wafer processing in the process chamber
-in-line: after wafer processing inside the process tool (e.g. exit load lock)
-on-line: in the wafer fab by wafer fab personnel
-ex-situ: outside analytical laboratory by expert users

Measurement needs (2)

	R&D	Pilot production	Volume manufacturing
samples	anything	full wafers (monitors)	full wafers (scribe line measurement)
analysis spot	anything	not a concern	test site
time	anything	minutes/hours	minutes/seconds

Destructive measurement discards the wafer after measurement ➔ measurement cost is >wafer cost.

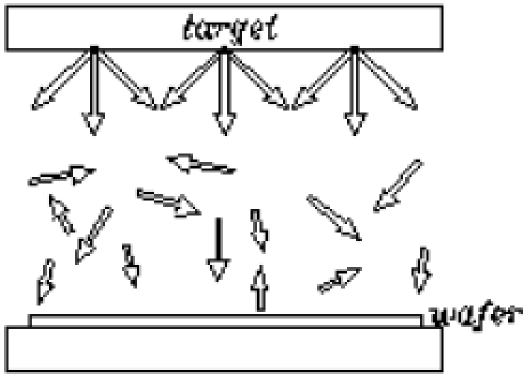
Non-destructive measurement does not destroy the wafer, but maybe it cannot be sold to the customer for cosmetic or reliability reasons.

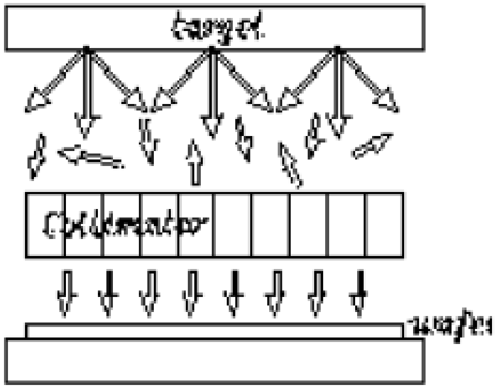
Non-contact measurement does not physically touch the wafer, e.g. thickness by ellipsometer or resisitivity by eddy currents.

Film characterization needs

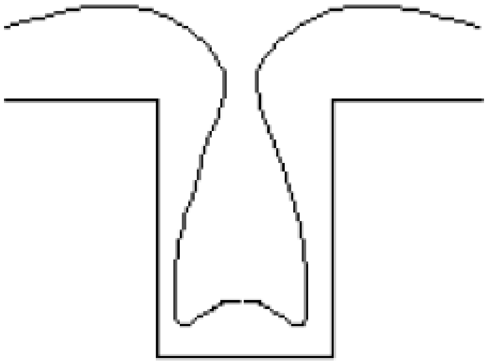
-spatial resolution (image spot size)
-depth resolution (surface vs. bulk properties)
-elemental detection (constituents, impurities)
-structural information (grain structure)
-dimensional characterization (thickness)
-mechanical properties (curvature, stress,…)
-surface properties (roughness, reflectivity,…)
-top view vs. cross sectional imaging
-defects (particles, pinholes,…)

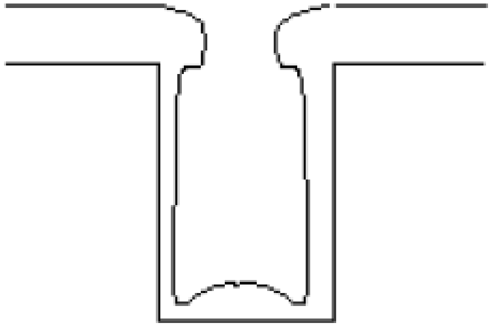
Normal vs. collimated sputtering





Collimator prevents high-angle ions ➔ more directional flux ➔ more uniform step coverage.

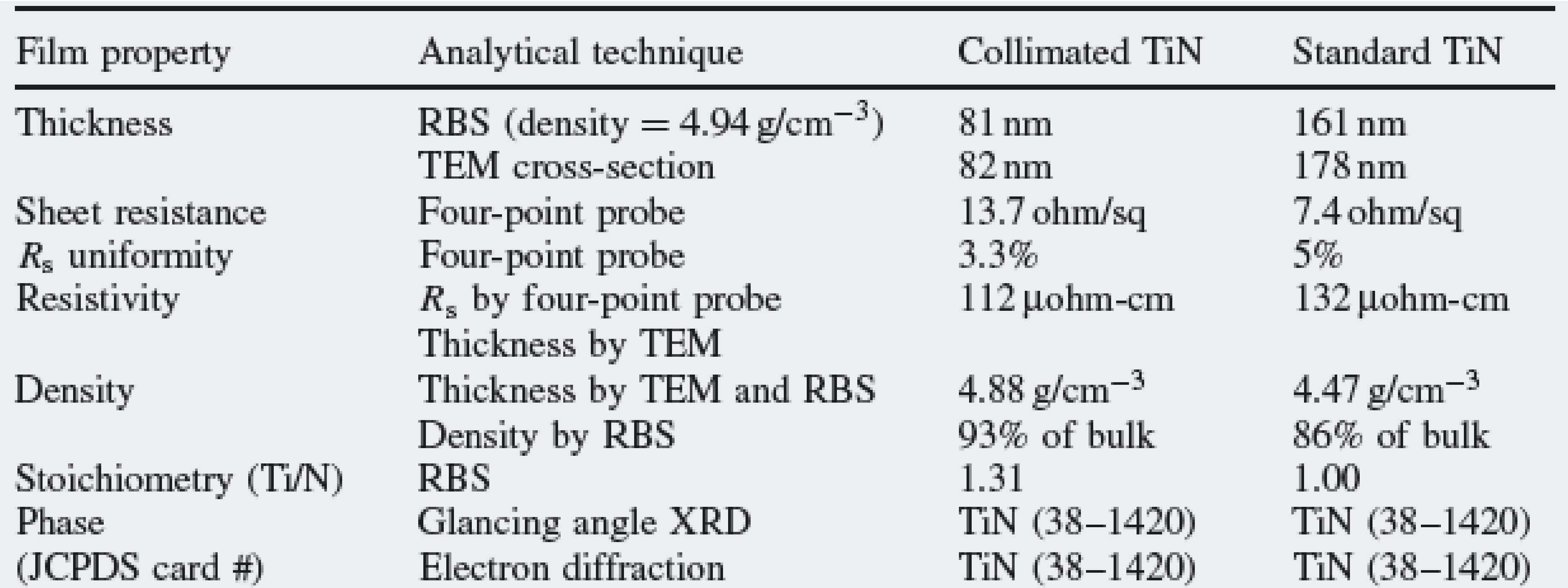




Deposition rate reduced because collimator captures some atoms.

Chia-Hao Chan
lr.nctu.tw.edu

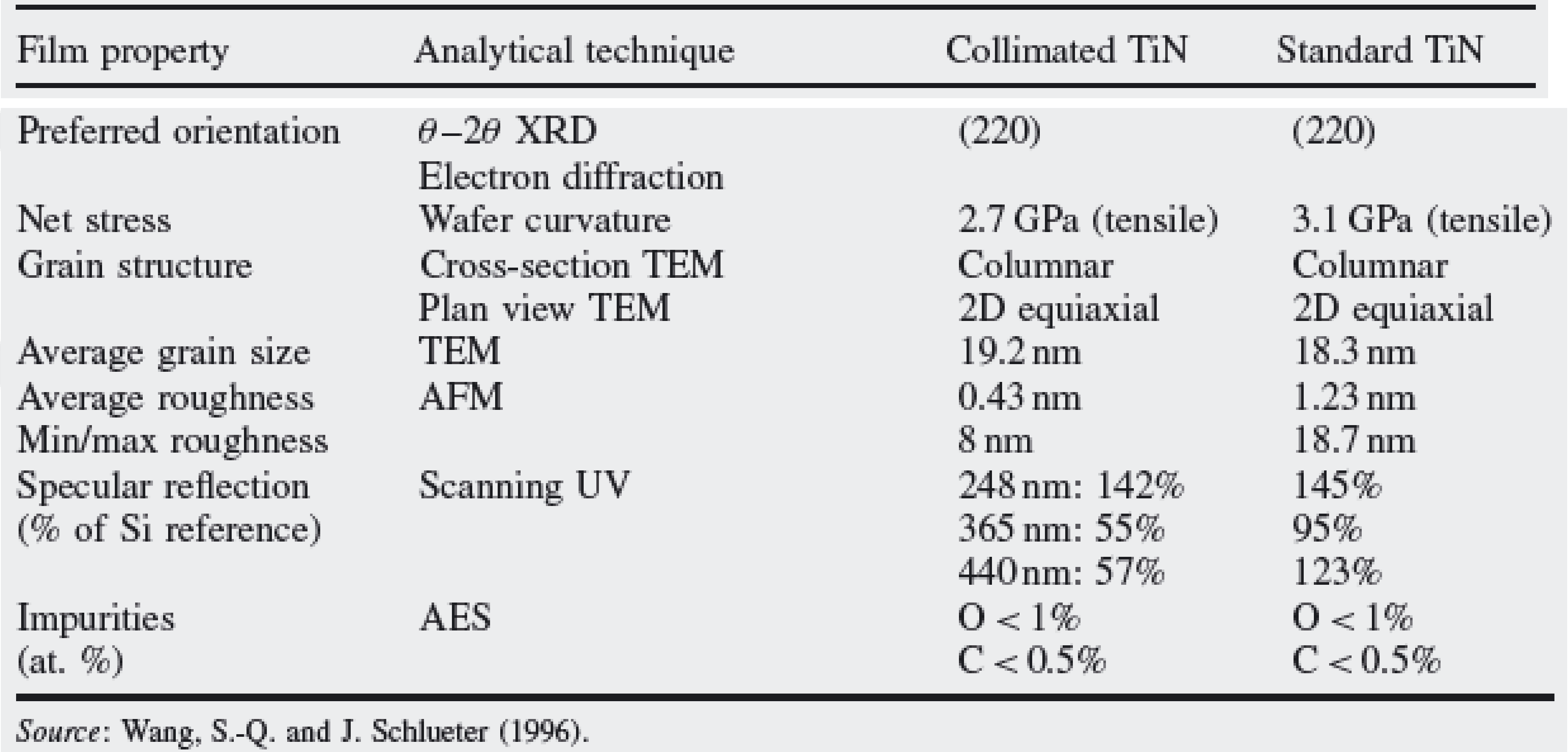
Sputtered TiN characterization



Film property	Analytical technique	Collimated TiN	Standard TiN
Thickness	RBS (density = 4.94 g/cm^{-3})	81 nm	161 nm
	TEM cross-section	82 nm	178 nm
Sheet resistance	Four-point probe	13.7 ohm/sq	7.4 ohm/sq
R_s uniformity	Four-point probe	3.3%	5%
Resistivity	R_s by four-point probe Thickness by TEM	112 μohm-cm	132 μohm-cm
Density	Thickness by TEM and RBS	4.88 g/cm^{-3}	4.47 g/cm^{-3}
	Density by RBS	93% of bulk	86% of bulk
Stoichiometry (Ti/N)	RBS	1.31	1.00
Phase (JCPDS card #)	Glancing angle XRD	TiN (38–1420)	TiN (38–1420)
	Electron diffraction	TiN (38–1420)	TiN (38–1420)

Source: Wang, S.-Q. and J. Schlueter (1996).

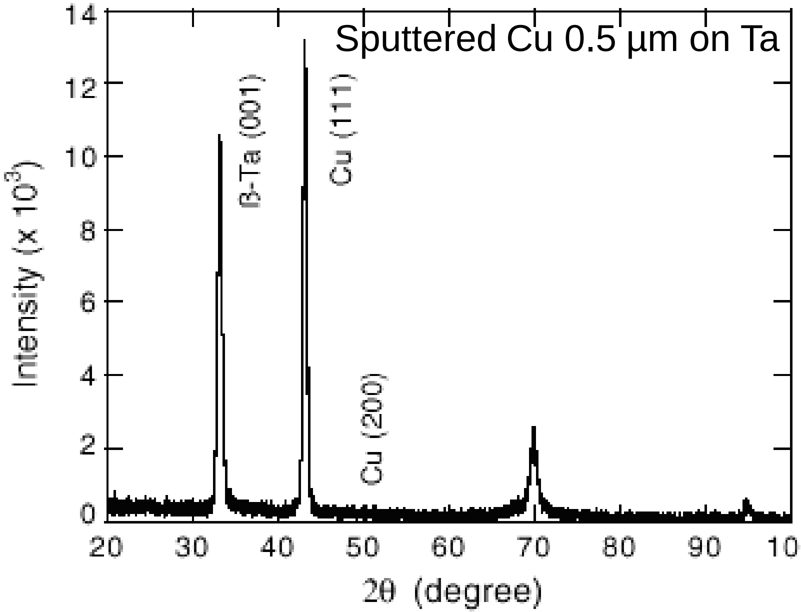
Sputtered TiN (2)

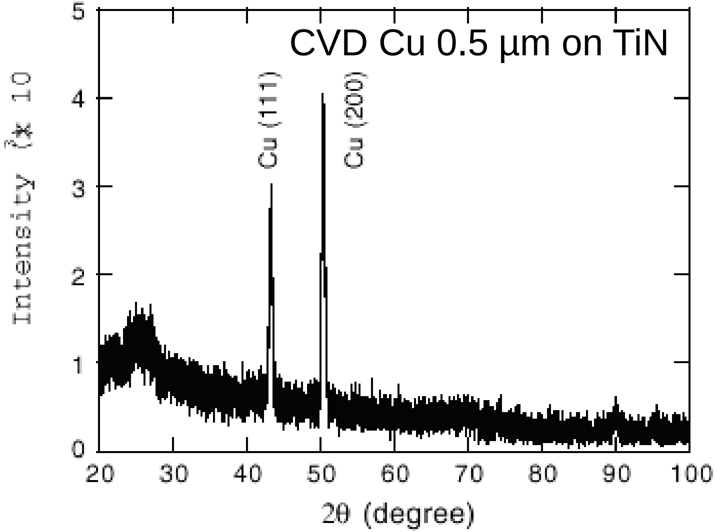


Film property	Analytical technique	Collimated TiN	Standard TiN
Preferred orientation	$\theta - 2\theta$ XRD Electron diffraction	(220)	(220)
Net stress	Wafer curvature	2.7 GPa (tensile)	3.1 GPa (tensile)
Grain structure	Cross-section TEM	Columnar	Columnar
	Plan view TEM	2D equiaxial	2D equiaxial
Average grain size	TEM	19.2 nm	18.3 nm
Average roughness	AFM	0.43 nm	1.23 nm
Min/max roughness		8 nm	18.7 nm
Specular reflection (% of Si reference)	Scanning UV	248 nm: 142% 365 nm: 55% 440 nm: 57%	145% 95% 123%
Impurities (at. %)	AES	O < 1% C < 0.5%	O < 1% C < 0.5%

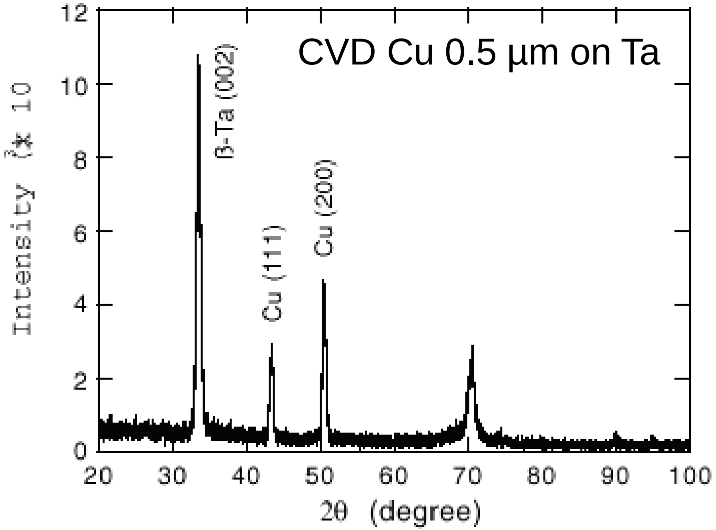
Source: Wang, S.-Q. and J. Schlueter (1996).

Method vs. substrate


Sputtered Cu 0.5 µm on Ta


CVD Cu 0.5 µm on TiN

(a)

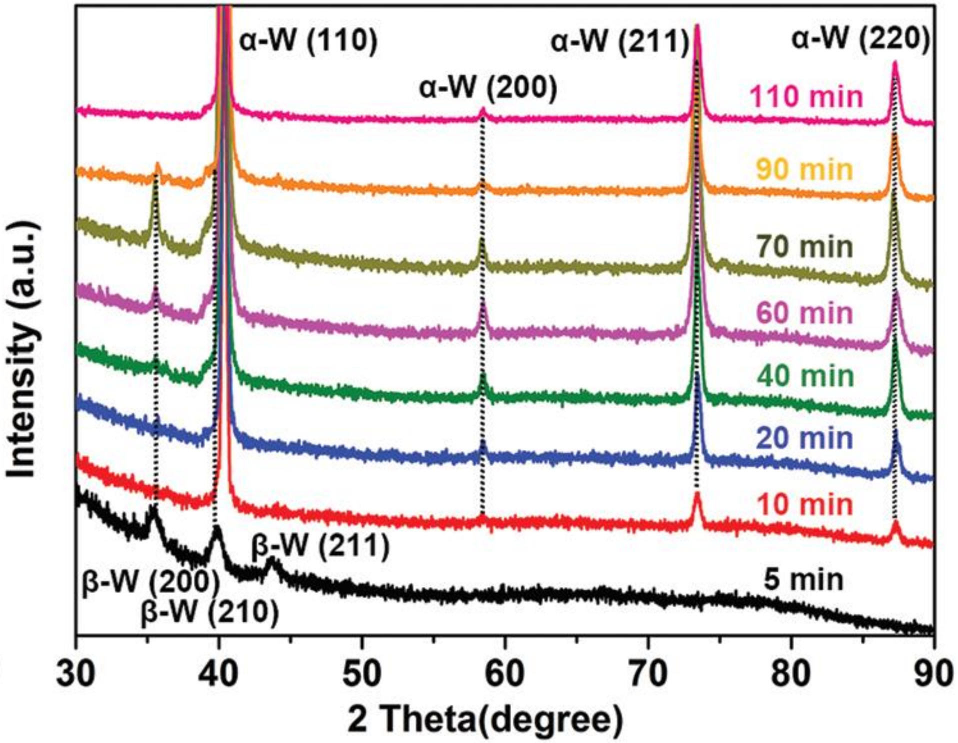

CVD Cu 0.5 µm on Ta

(b)

Effect of substrate and deposition method on film crystallinity.

Monitor wafers have to match product wafers !

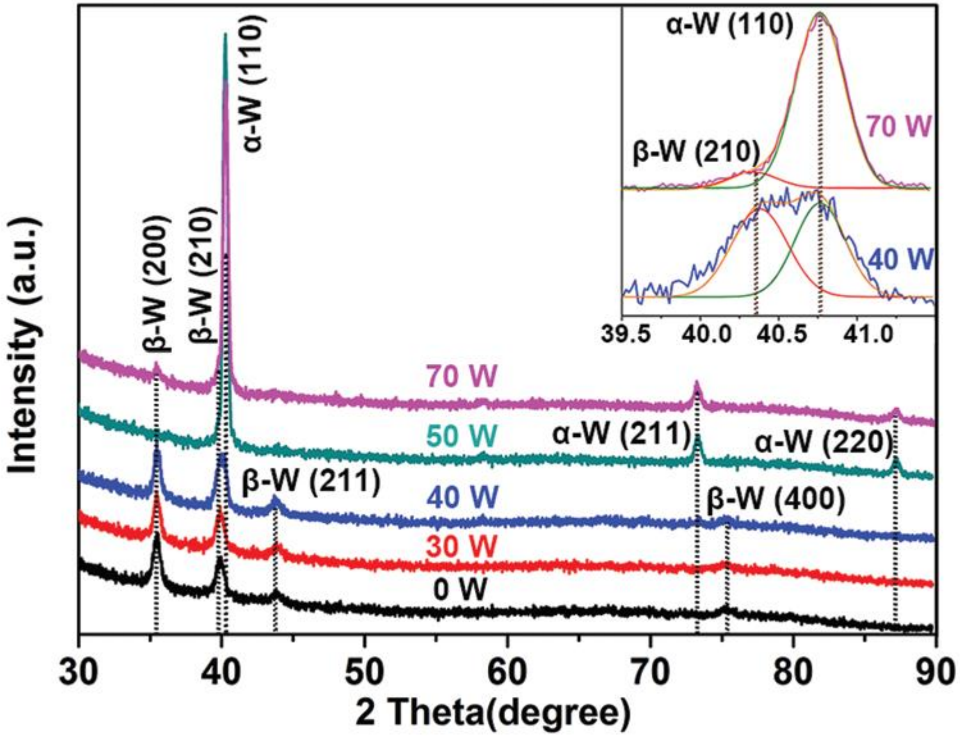
Crystallinity and depo time



Tungsten films deposited under the constant RF bias of 50 W for different durations.

Wang & Rogachev: *Adv. Mater. Interfaces* **2019**, *6*, 1900031

Crystallinity and bias-power

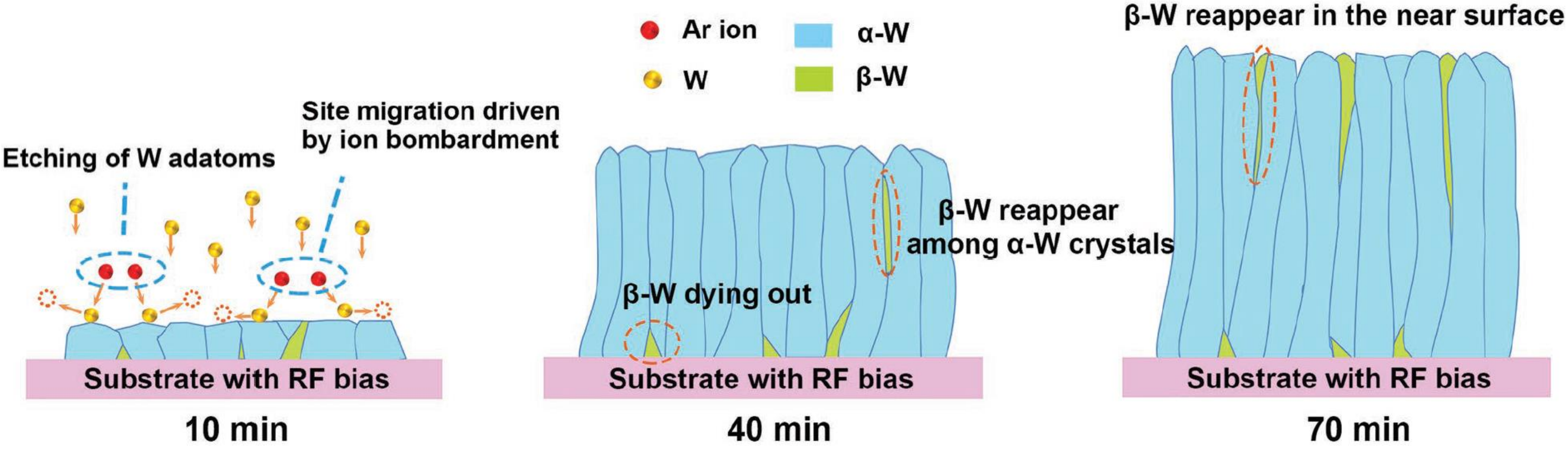


"XRD patterns of W films deposited under various RF biases with a deposition time of 10 min

The inset shows the magnified views of the corresponding diffraction peaks."

Wang & Rogachev: *Adv. Mater. Interfaces* **2019**, *6*, 1900031

Tungsten crystallinity development



“Lattice mismatch, unintentional substrate heating, and oxygen residual (low vacuum ≈$2*10^{-4}$ Pa) are always conducive to form metastable β-W phase.”

“…the competitive growth between α- and β-W happened all the time during the deposition process, where the plasma-assisted ion bombardment on the film surface is crucial to create α-phase-dominated tungsten thin films. In this study, β-phase is like Lord Voldemort, hard to be eradicated completely.”

Wang & Rogachev: *Adv. Mater. Interfaces* **2019**, *6*, 1900031

Nanoindentation test

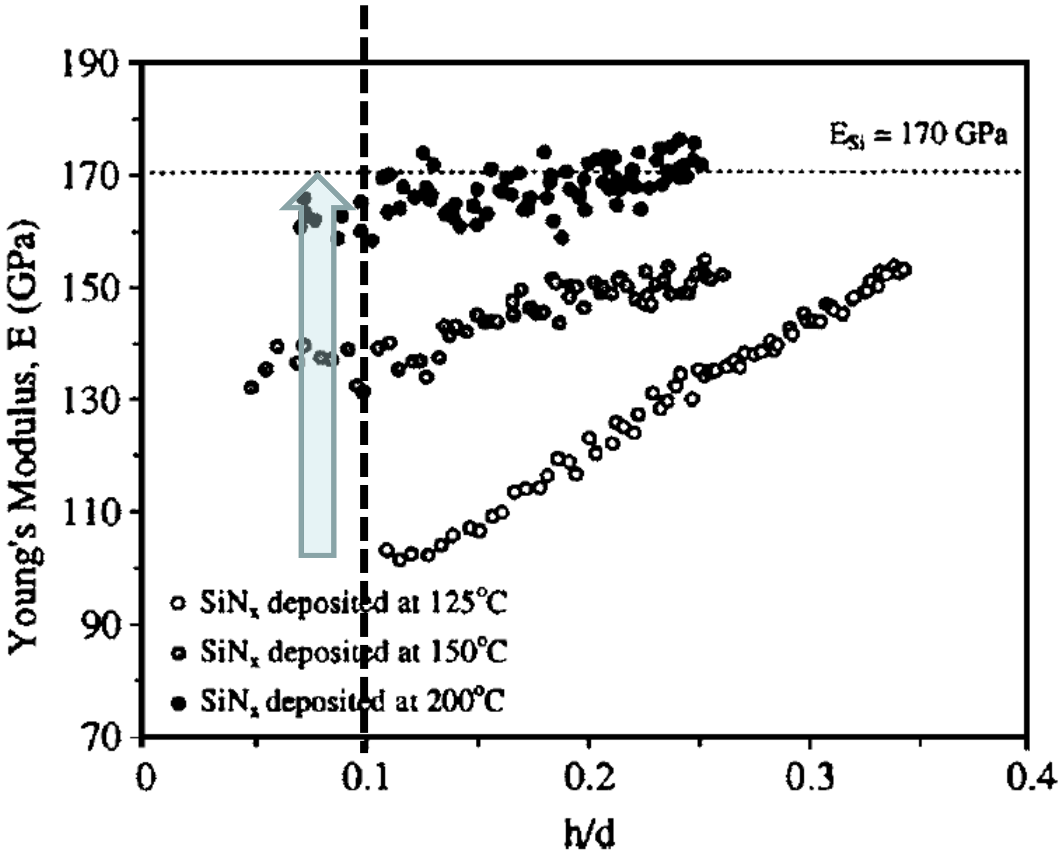


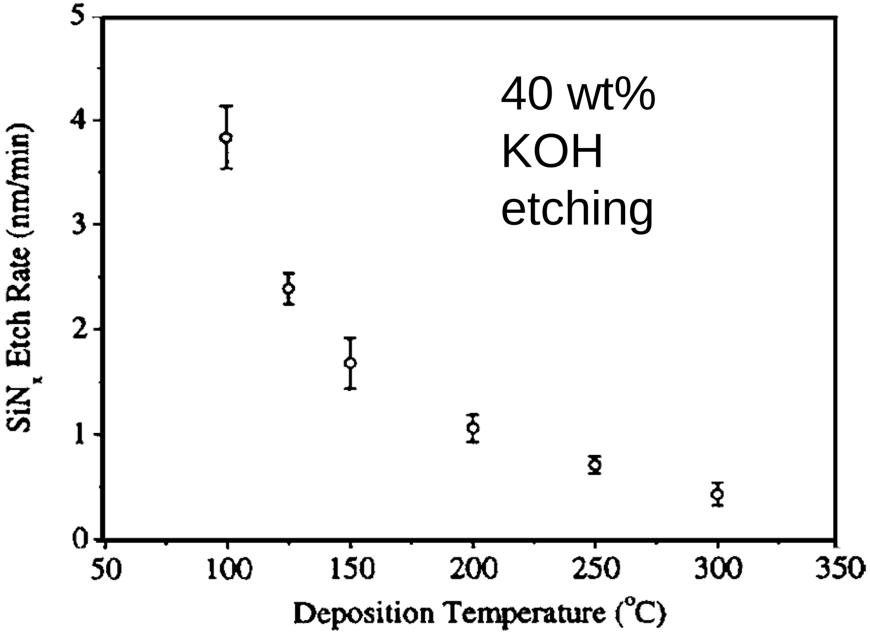
FIG. 7. Normalized nanoindentation data of three PECVD SiN_x films deposited at varying deposition temperatures. On the x axis, h/d is the ratio of indentation depth h to film thickness d.

Higher deposition temperature ➔ better mechanical properties

As a rule of thumb, penetration depth should be ≤10% of film thickness, otherwise we measure substrate properties, not film properties.

Walmsley et al: JOURNAL OF APPLIED PHYSICS **98**, 044904 2005

Etch rate as film quality



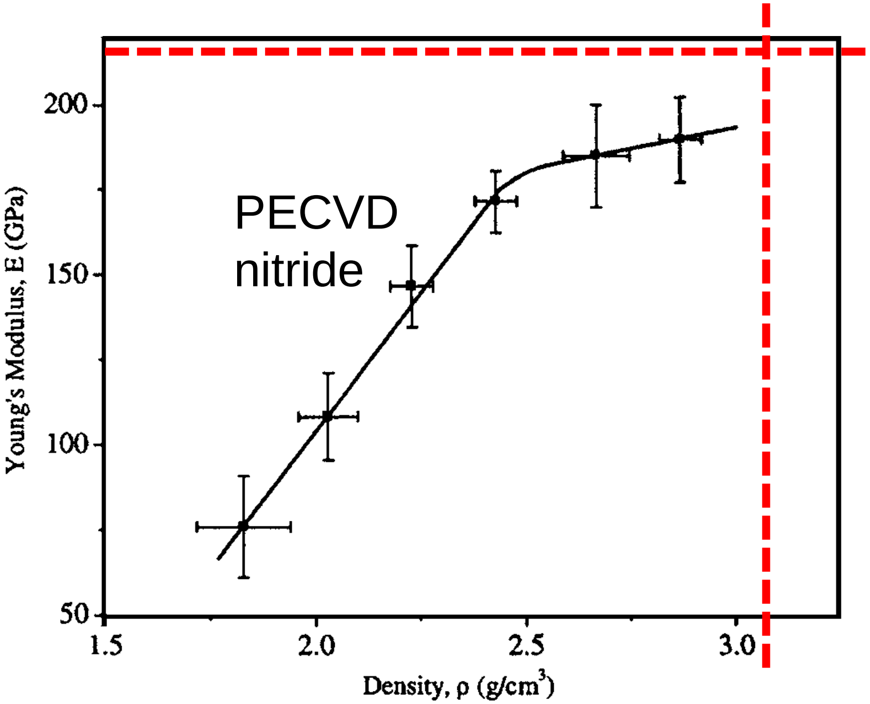
Higher T ➔ denser film ➔ slower etch rate

13.6-MHz Oxford Instruments PECVD 80 system.
Films were deposited from ultra-high-purity gases consisting of silane, ammonia, and nitrogen. Gas flow rates, chamber pressure and RF power were kept constant for all depositions.

Only the substrate temperature was varied, which ranged from 100 to 300 °C.

Walmsley et al: JOURNAL OF APPLIED PHYSICS **98**, 044904 2005

Mechanical quality



LPCVD nitride
Young’s modulus 220 GPa

But:
Size-dependent effective Young’s modulus of silicon nitride cantilevers, Appl. Phys. Lett. 94, 233108 (2009); https://doi.org/10.1063/1.3152772

Stoichiometric LPCVD nitride Si_3N_4 density is 3.1-3.4 g/cm^3.

Walmsley et al: JOURNAL OF APPLIED PHYSICS **98**, 044904 2005

Productivity measures

Deposition rate
Thru-put (very different from rate !)

Wide process window (robust against parameter drift)

Yield of precursors (source gases/targets expensive)

Deposition on one side or both sides simultaneously

Uniformity across the substrate
Uniformity across the batch

Repeatability run-to-run
Repeatability day-to-day

Use quality

What are the stressors the film is going to experience ?

-mechanical (bending, contact wear, particle abrasion…)
-chemical (humidity, sea water, acids, solvents…)
-electrochemical (metal-metal contacts, electrolytes, anodic oxidation…)
-electrical (high current density, high E-field…)
-thermal (high-T, low-T, thermal cycling)
-optical (UV)
-biological (protein adsorption, biofilms,…)