Perfectly Selective Thin Film CVD Using Inhibitor Molecules

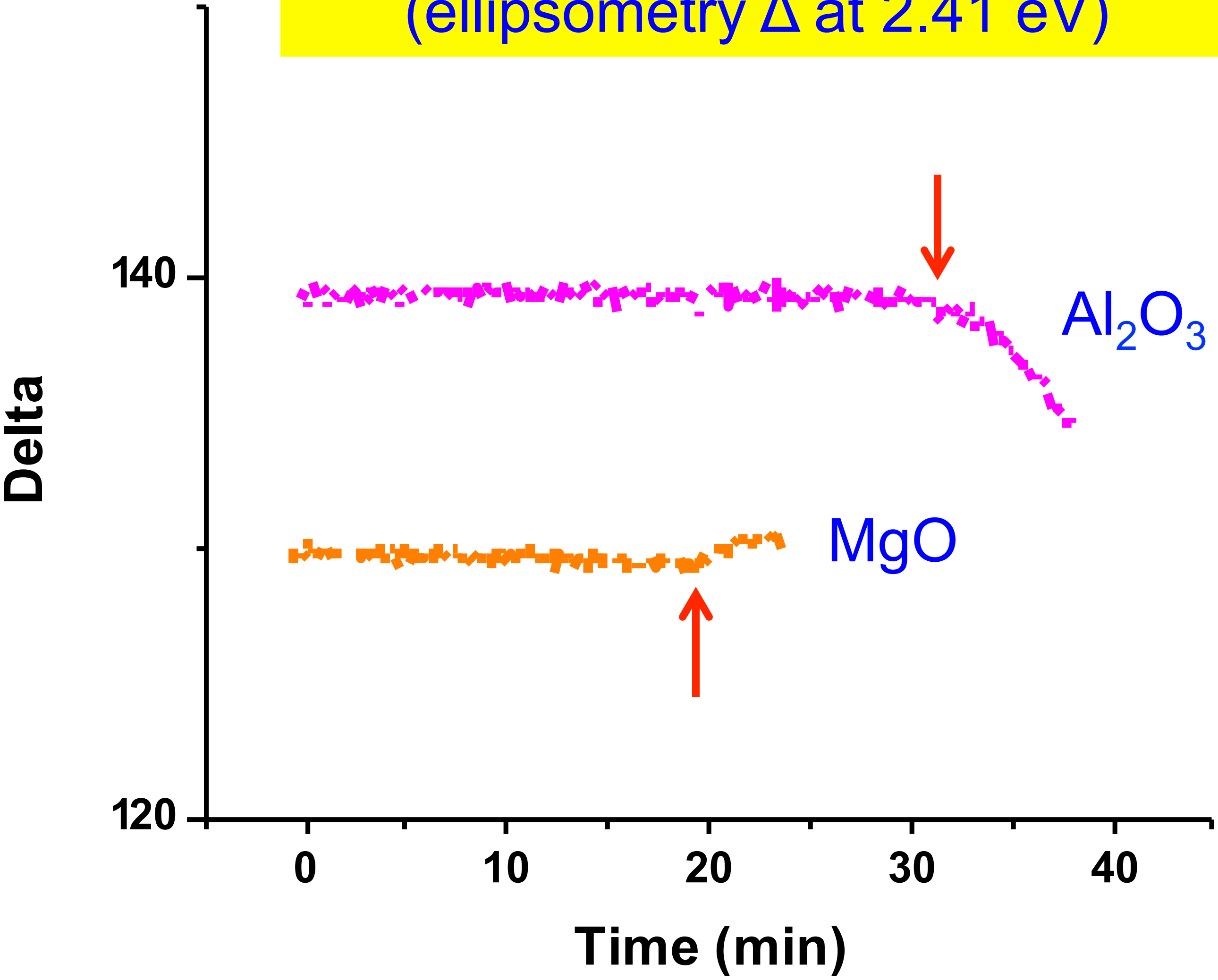
John R. Abelson & Elham Mohimi (MatSE)

Gregory S. Girolami (Chemistry)

UNIVERSITY OF ILLINOIS
AT URBANA-CHAMPAIGN

Intrinsic selectivity: *Fails by stray nucleation*

Onset of metal CVD on dielectrics
(ellipsometry Δ at 2.41 eV)



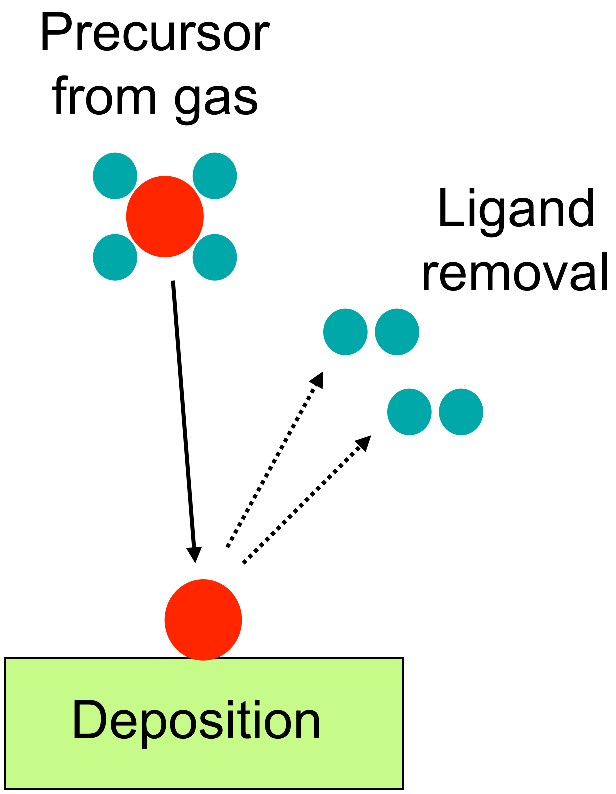
Nucleation: The important role of *defects*

John Venables:
"…there may be defects on the surface which act as preferred nucleation sites...such effects were shown to have played a role in early experiments."

A colleague at an AVS meeting:
"I love the problem of nucleation on oxides."

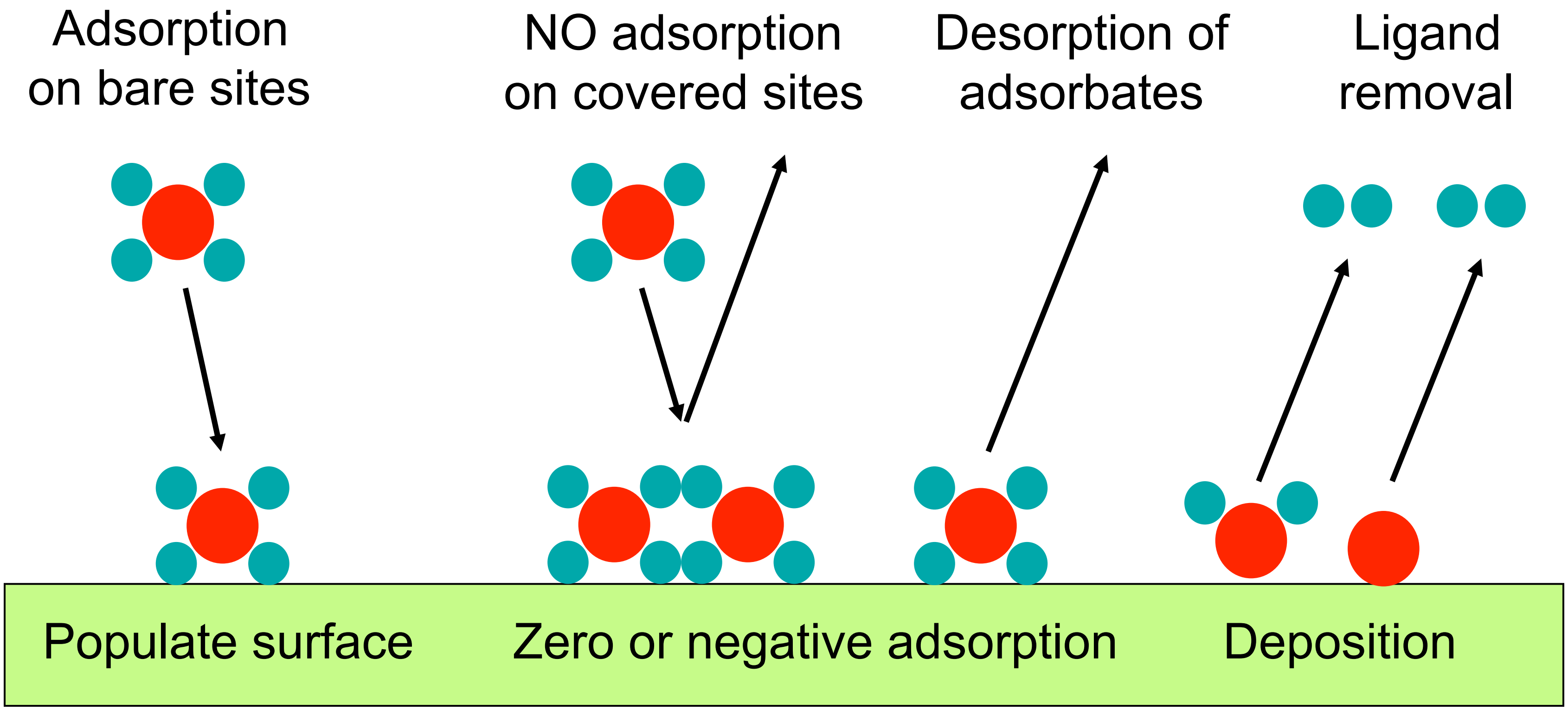
Why?
"I study surface defects – and *the only way I can find them* is to flow a CVD precursor over the surface and form nuclei."

Classic concept of CVD:
precursor rapidly loses ligands



This is correct at higher T, which is required if the precursor is too stable

Low-Temperature CVD: *Surface mostly covered* with adsorbed precursor / product / added inhibitor



Adsorption
on bare sites

NO adsorption
on covered sites

Desorption of
adsorbates

Ligand
removal

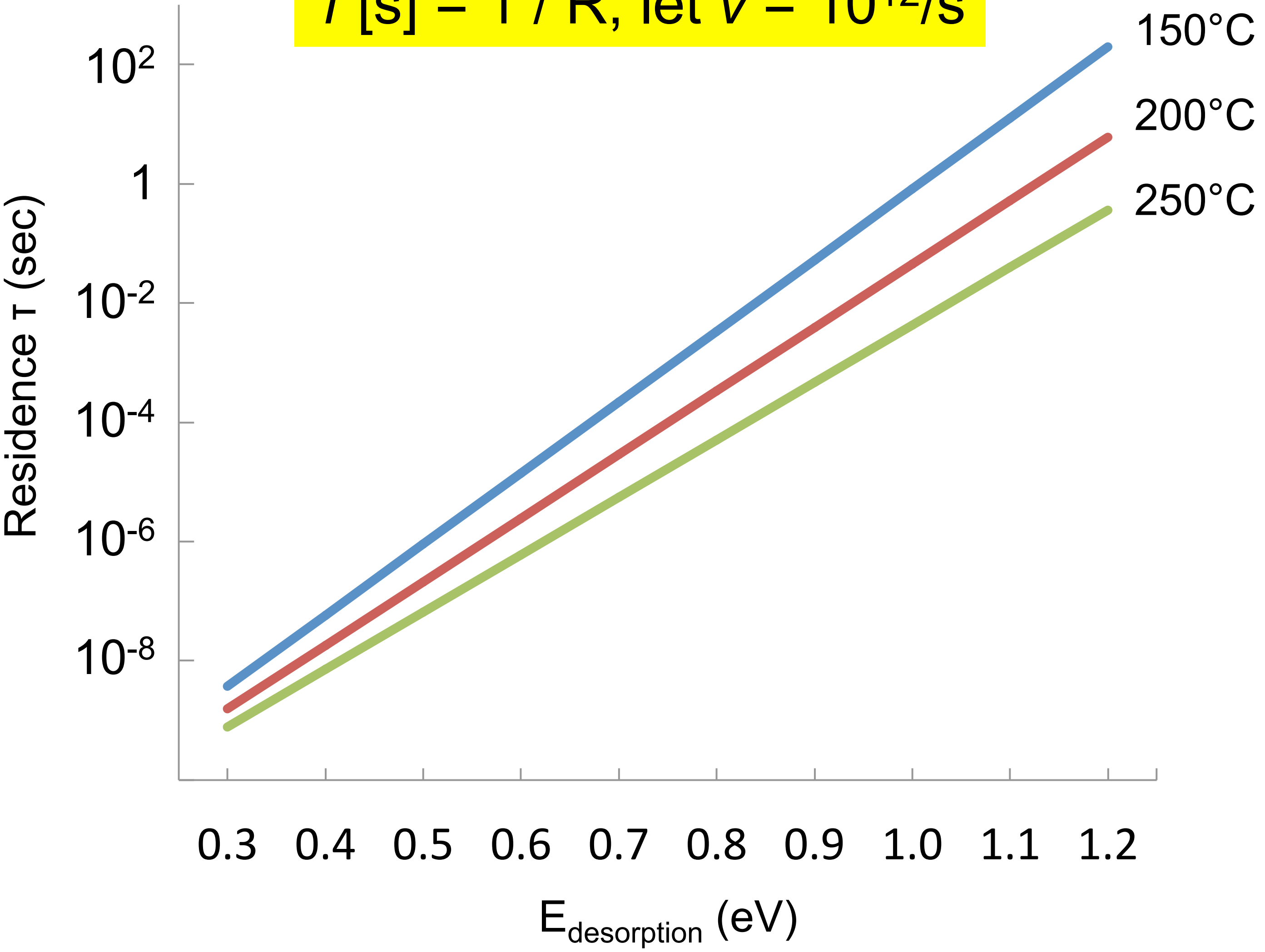
Populate surface

Zero or negative adsorption

Deposition

Adsorbate residence time τ vs. $E_{desorption}$

$R[1/s] = v \exp(-E_{des} / kT)$
$\tau\ [s] = 1 / R$; let $v = 10^{12}/s$



Steady-state with flux from gas phase: Surface coverage θ = *fraction of 1 ML*

$$\vartheta = \frac{k_{ads}}{k_{ads} + k_{des}}$$

where

$$k_{ads} = s\frac{P}{\sqrt{2\pi mkT_{gas}}}$$

$$k_{des} = R_{des}N_{surf}$$

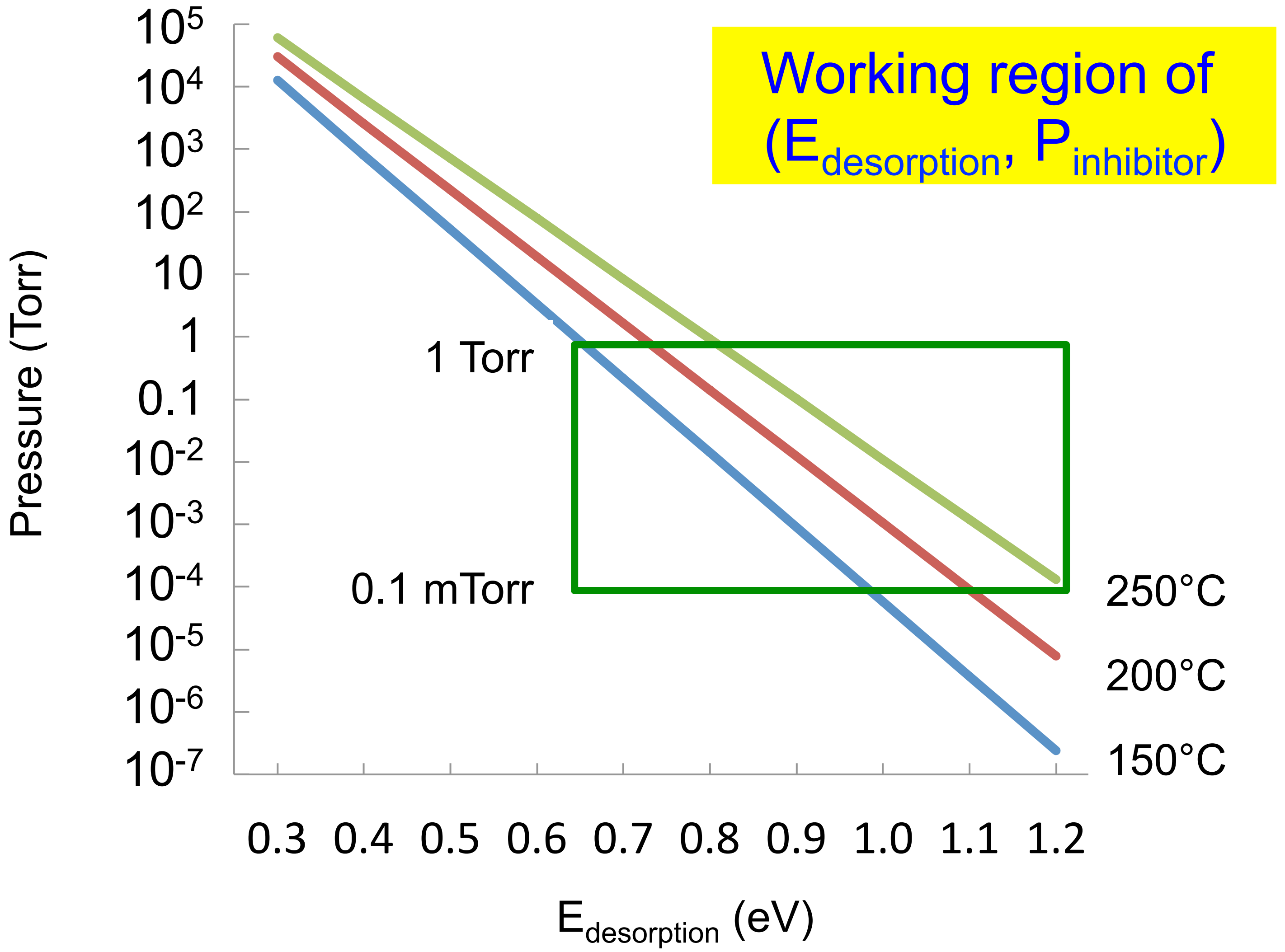
assume

$s = 1$ (sticking coefficient on bare site)

$\nu = 10^{12}[s^{-1}]$ (attempt frequency)

$N_{surf} = 10^{19}[m^{-2}]$ (surface site density)

Adsorbate pressure for steady-state θ = 0.95



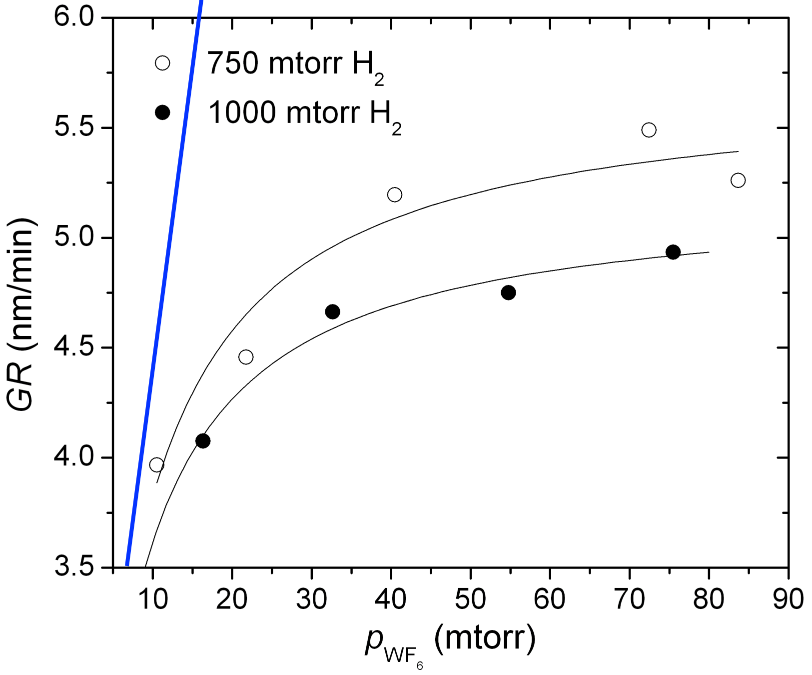
Working region of ($E_{desorption}$, $P_{inhibitor}$)

Example desorption energies

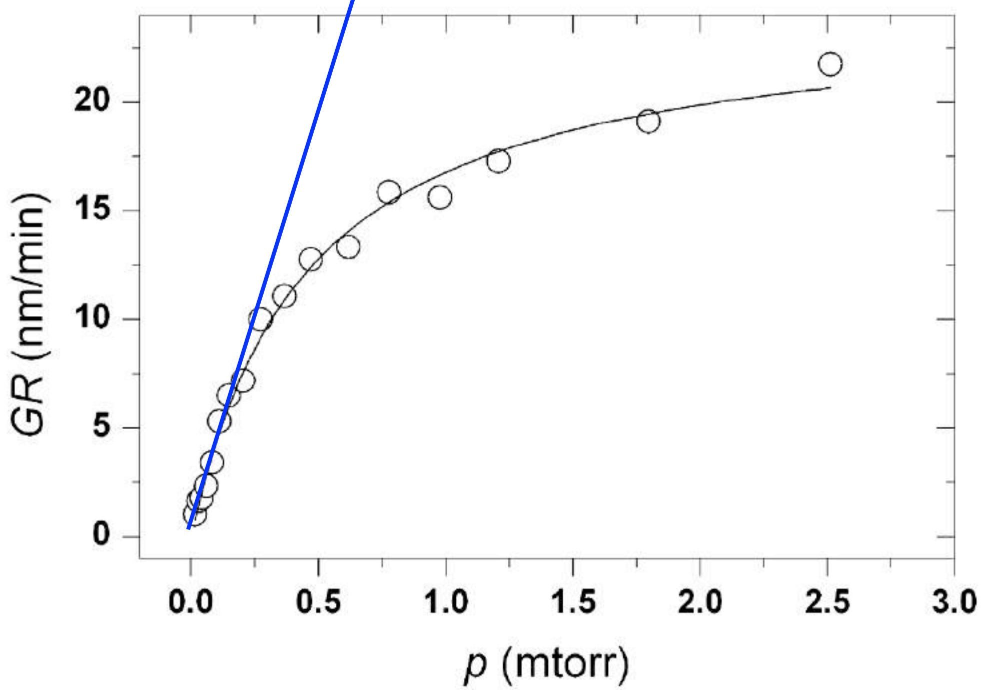
NH_3 on HfB_2	1.30 eV
PMe_3 on Cu(100)	1.21 eV
VTMS on Cu	0.61 - 0.75 eV
COD on Cu(100)	0.61 eV
NH_3 on hydroxilated SiO_2	0.41 eV
Butyne on Cu(100)	0.36 eV

How does the adsorbed layer affect CVD growth?

… if reaction probability were constant …

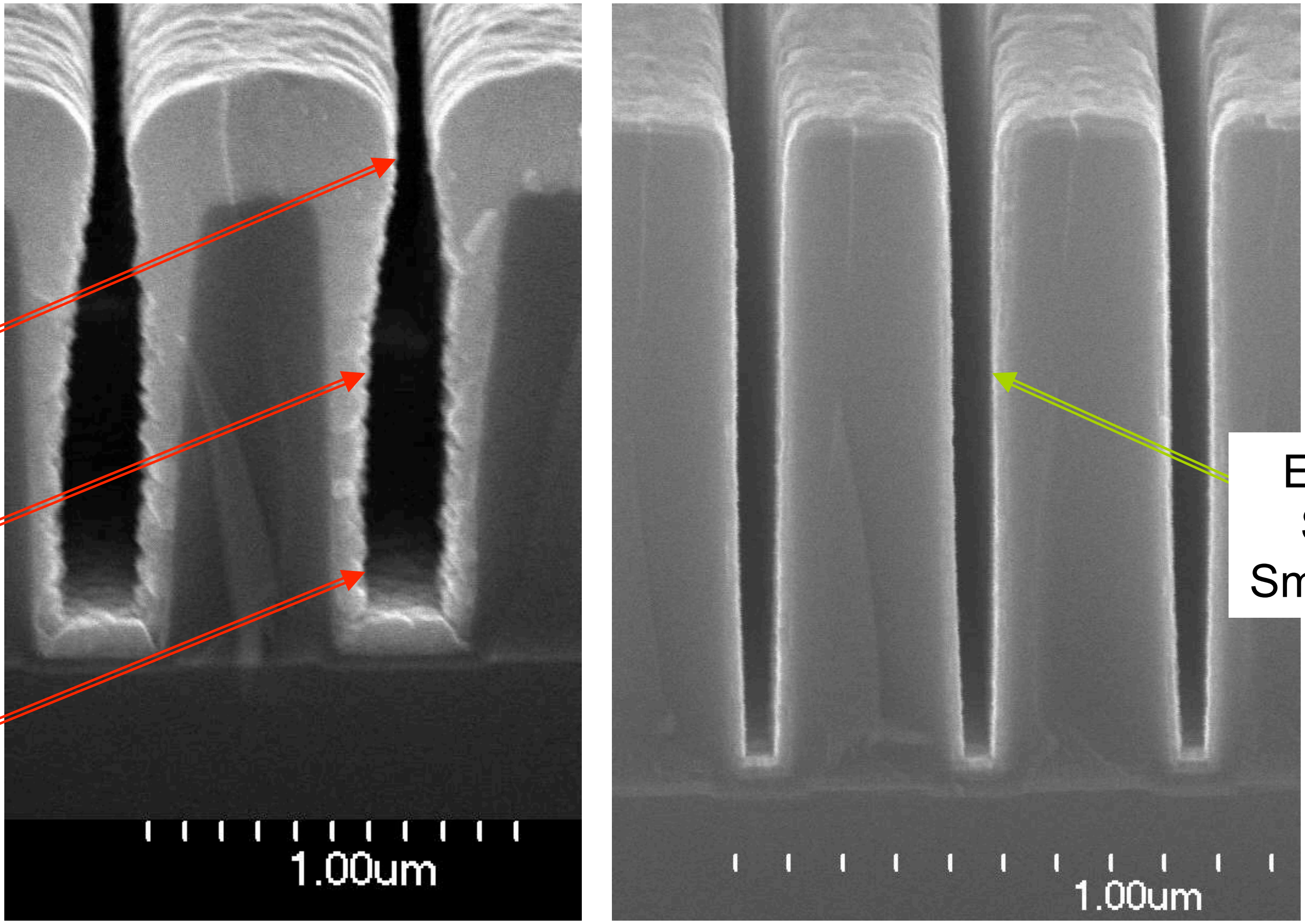

W from WF_6 + H_2

Arora & Pollard (refs therein), JECS (1991)


HfB_2 from $Hf(BH_4)_4$

Yang & Abelson, Chem Mat (2006)

HfB_2 from $Hf(BH_4)_4$ at T_{sub} = 275 °C



Pinch-off

Bad
Morphology

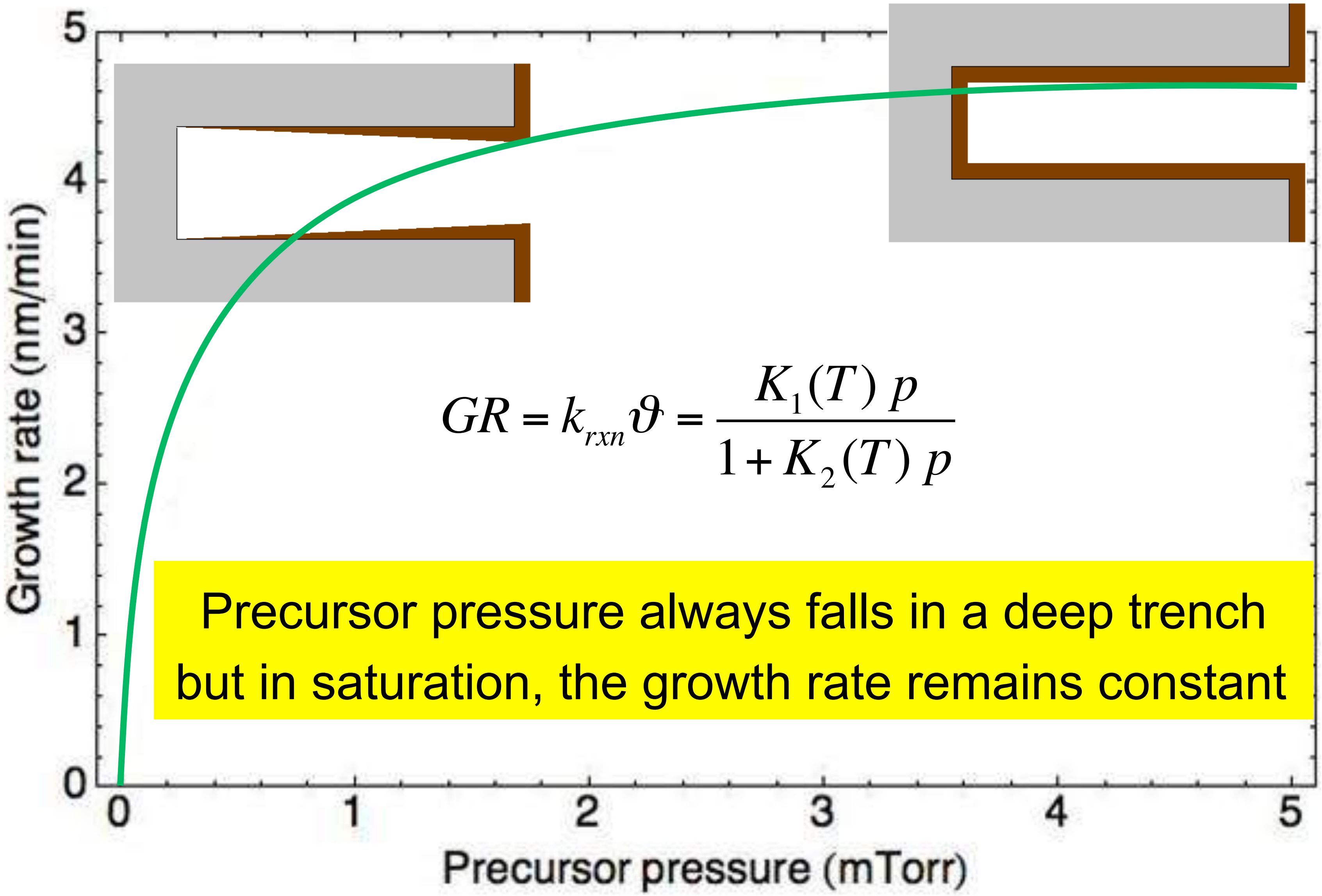
Poor Step
Coverage
(*SC*)

Excellent
SC and
Smoothness

0.1 mTorr

80 mTorr

Saturated growth rate at high P_{pre}: Conformality !



$$GR = k_{rxn}\vartheta = \frac{K_1(T)\,p}{1 + K_2(T)\,p}$$

Precursor pressure always falls in a deep trench but in saturation, the growth rate remains constant

Problem: Many precursors have low vapor P and *never achieve rate saturation*

Solution: Add a *growth inhibitor* to

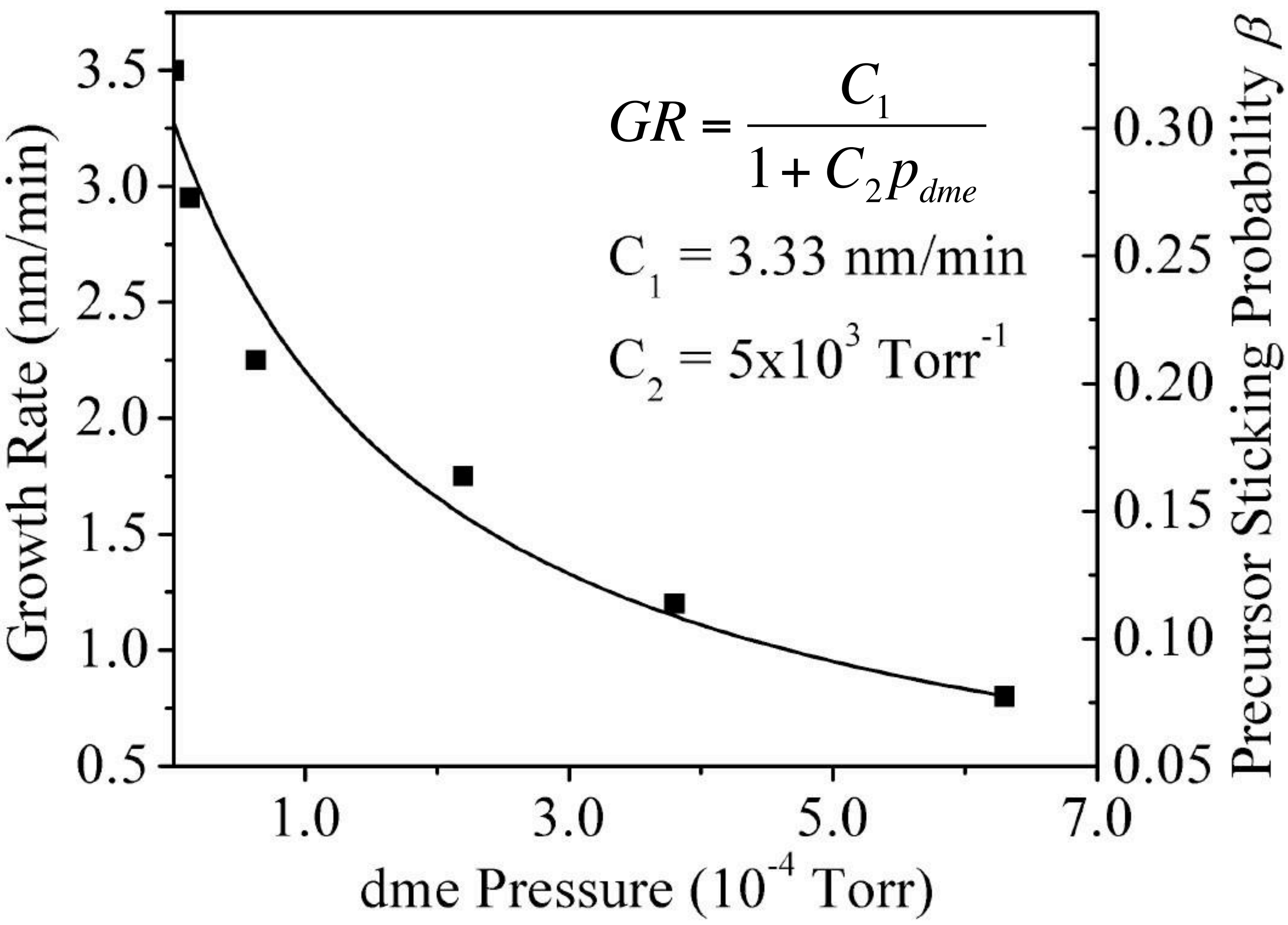
- increase the site blocking effect, and / or
- stimulate associative desorption of the precursor

Example: Growth of TiB_2 from $Ti(BH_4)_3$(dme)

- dme normally desorbs intact from surface
- LeChatelier approach: ***Add an overpressure of dme***

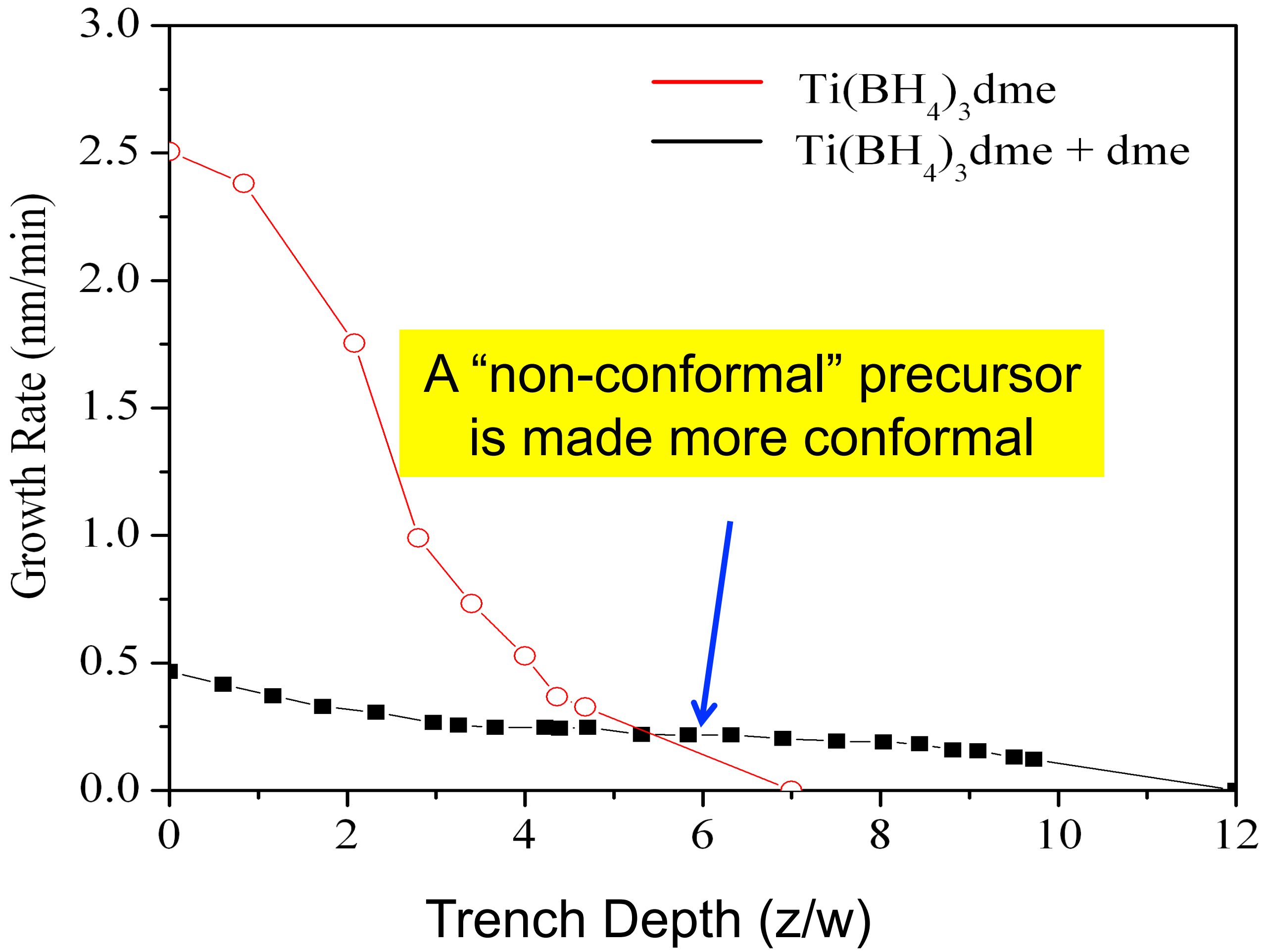
Kumar & Abelson, JACS (2008)

Added dme slows (inhibits) TiB_2 growth



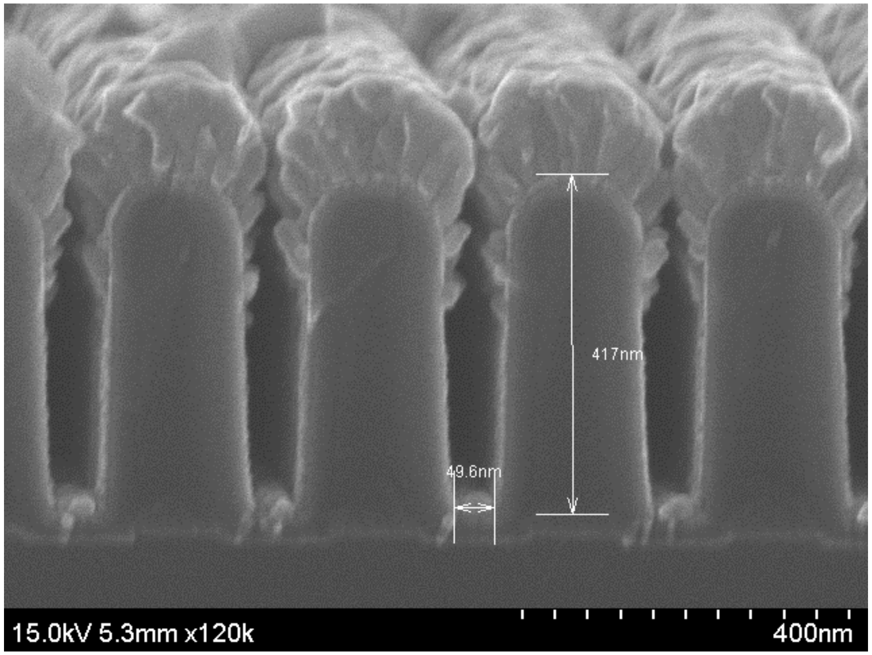
Kumar & Abelson, JACS (2008)

Inhibition by dme affords conformal TiB_2

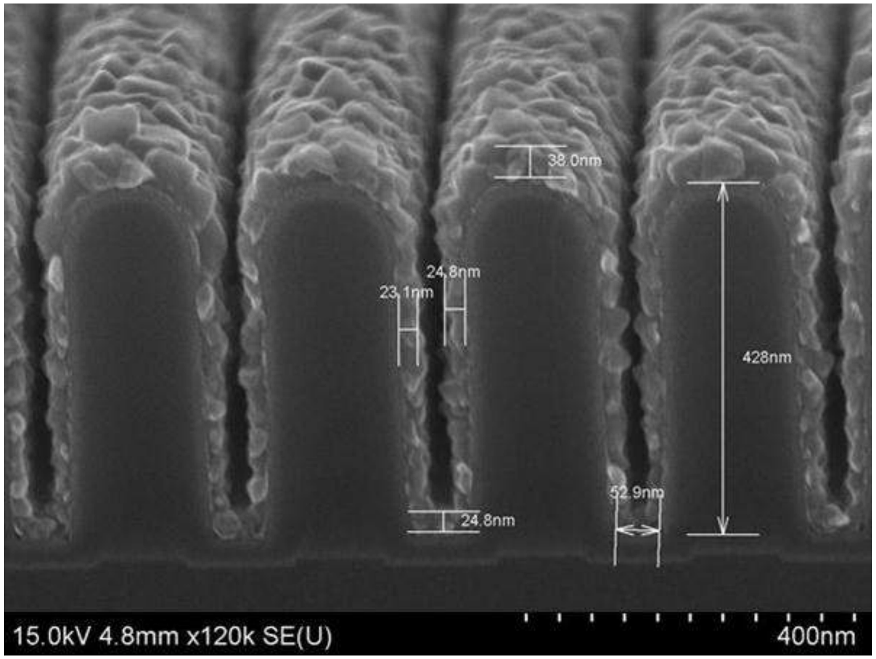


A “non-conformal” precursor is made more conformal

Added CO inhibits Fe growth from $Fe(CO)_5$



Precursor alone



+ 2 mTorr CO

A “non-conformal” precursor is made conformal

Mechanistic interpretation:
Site blocking or *associative desorption* ?

Example:

AB = precursor = $Ti(BH_4)_3$(dme)

B = inhibitor = dme

Site-blocking term

$$GR = k_r\theta_A = \frac{k_r k_{ads} p_{AB}(1-\theta_B)}{k_r + k_{des}\theta_B + k_{ads}p_{AB}}$$

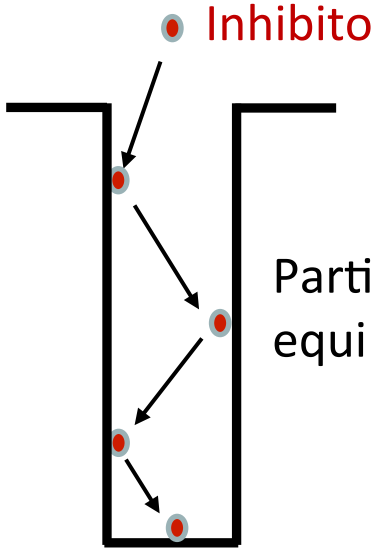
Associative desorption term

One *cannot distinguish* the microscopic mechanism based on a measurement of growth rate!

Inhibitor: Stable vs. consumable?

Stable

either high or low sticking coefficient



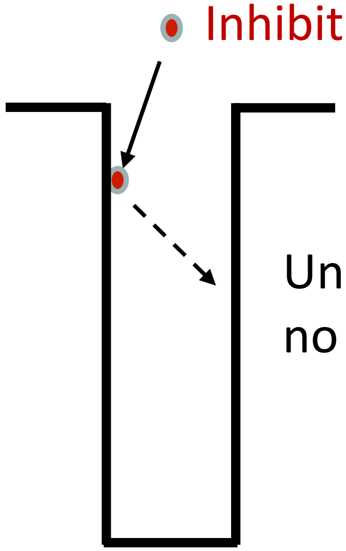
Inhibitor

Partial P equilibrates

Inhibition is same on all surfaces

Consumable

high sticking coefficient



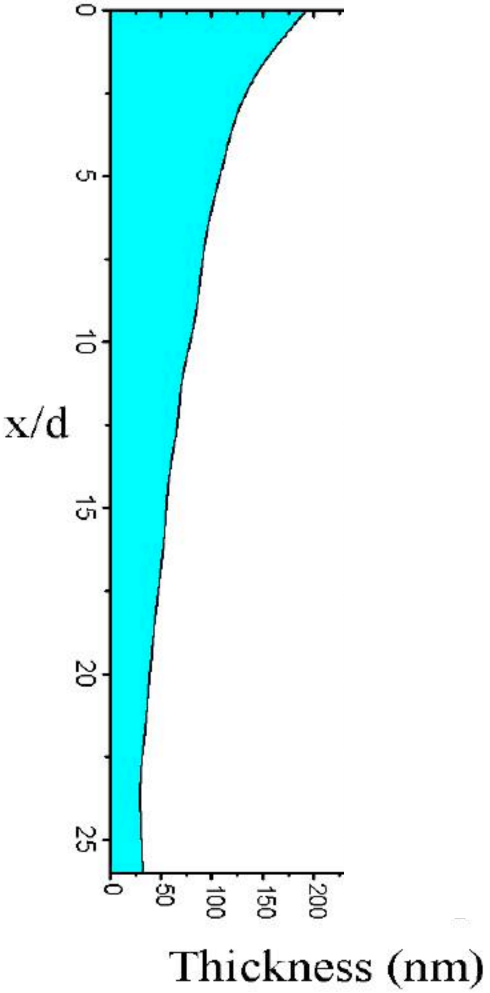
Inhibitor

Unreactive product or no product (incorporated)

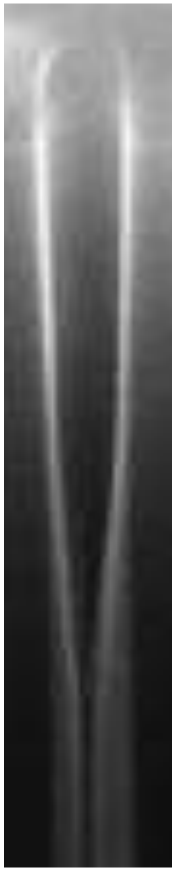
Inhibition on exposed (upper) surfaces only

Consumable inhibitor: Add *$Pd(hfac)_2$* or *H(hfac)* to HfB_2 growth from $Hf(BH_4)_4$

Precursor alone

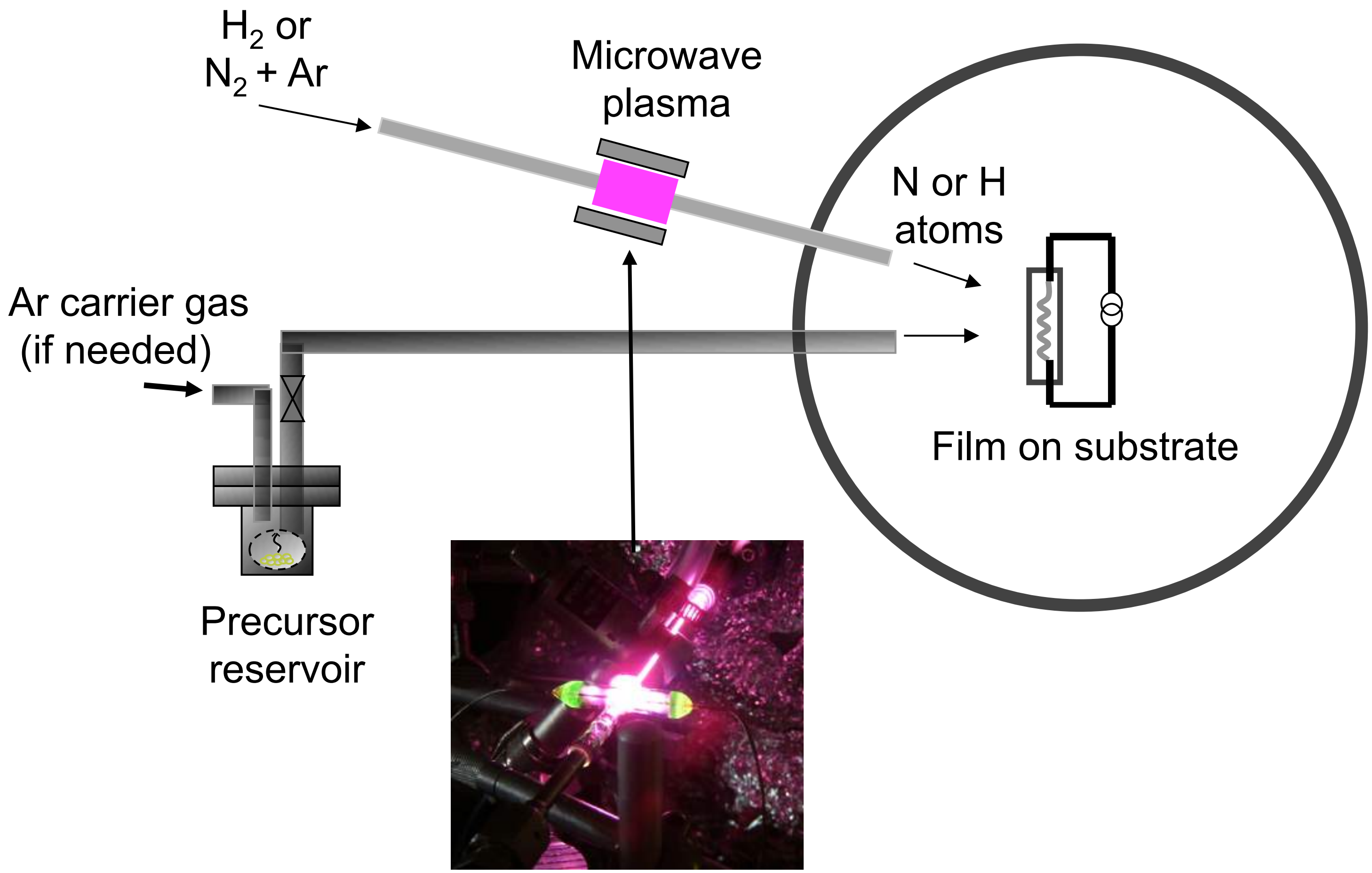


H(hfac) in via



BUT: Pd, F, C in film

Consumable inhibitor: H or N atoms from remote plasma (*no precursor back-streaming*)



H_2 or N_2 + Ar

Microwave plasma

N or H atoms

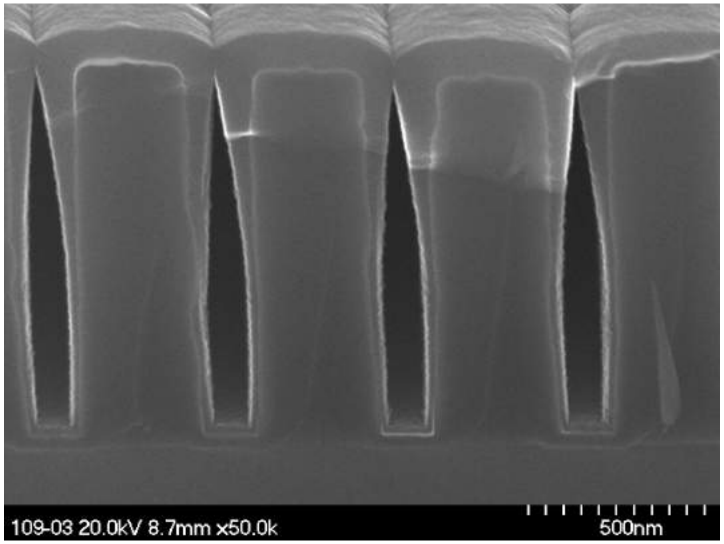
Ar carrier gas (if needed)

Film on substrate

Precursor reservoir

CrB_2 from $Cr(B_3H_8)_2$

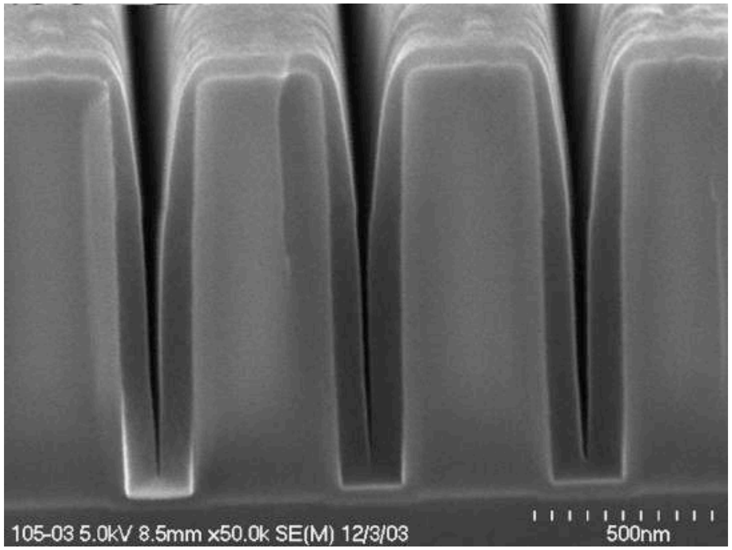
Thermal CVD: *pinch off*



T = 300°C

$P_{precursor} = 4 \times 10^{-5}$ Torr

Add H Atoms: *superconformal*



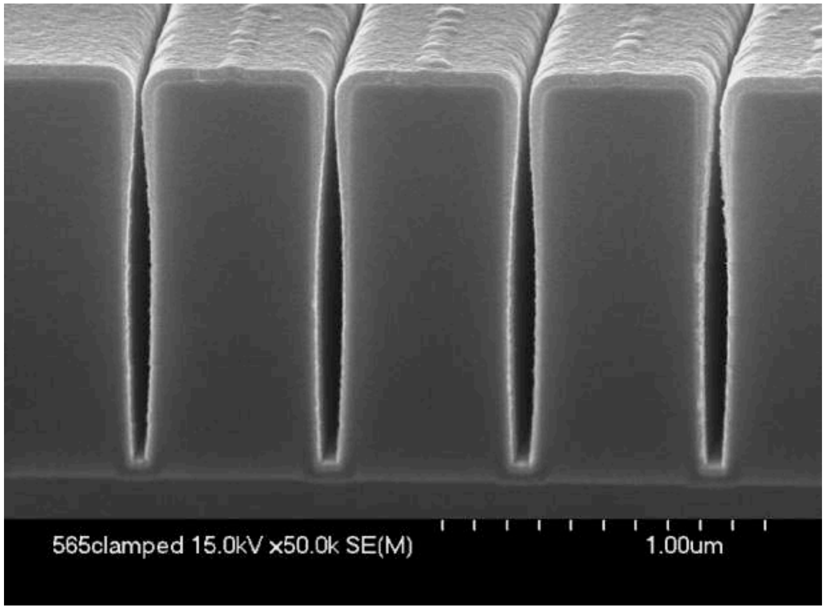
$F_H = 3 \times 10^{14}$ / cm^2-s

Stoichiometry unchanged

Y. Yang (2007)

HfB_2 from $Hf(BH_4)_4$

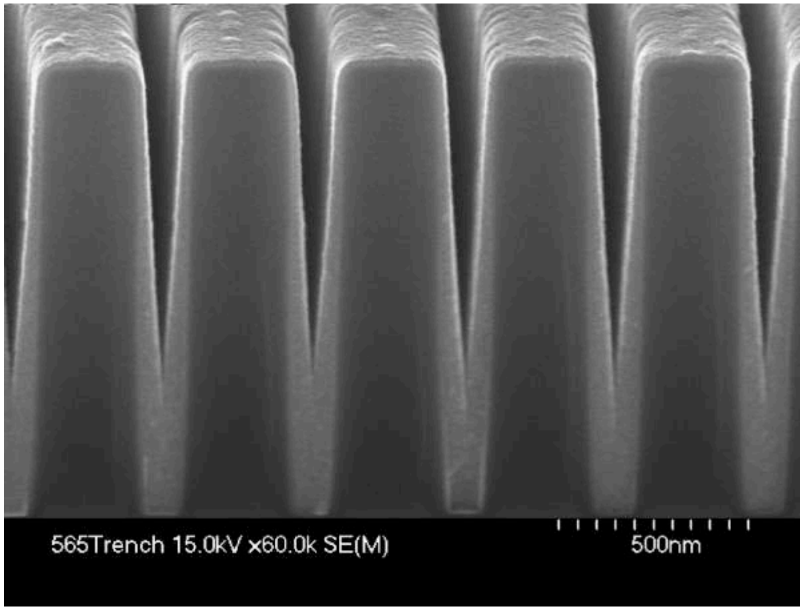
Thermal CVD



$T = 275\ °C$

$P_{precursor} = 1$ mTorr

Add N Atoms



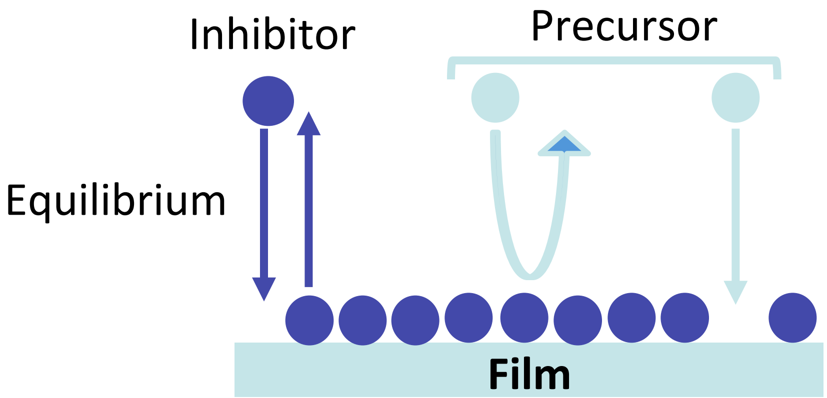
But N incorporation:

$Hf\,B_x\,N_y$

Y. Yang (2007)

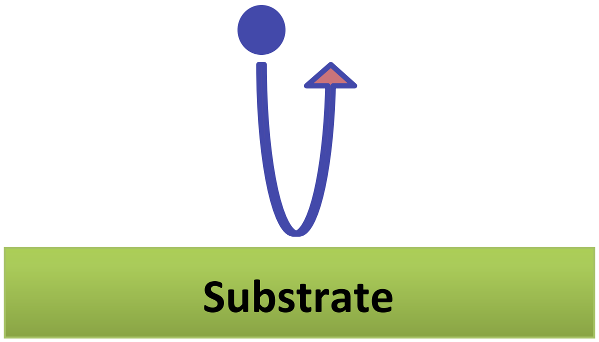
Enhance nucleation density: *Differential inhibition*

Steady-state growth

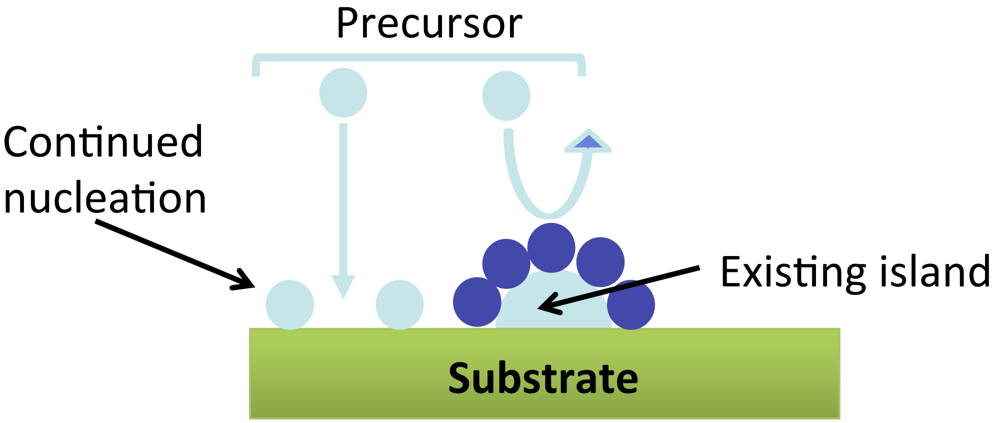


Nucleation

Substrate: ~ No inhibitor coverage

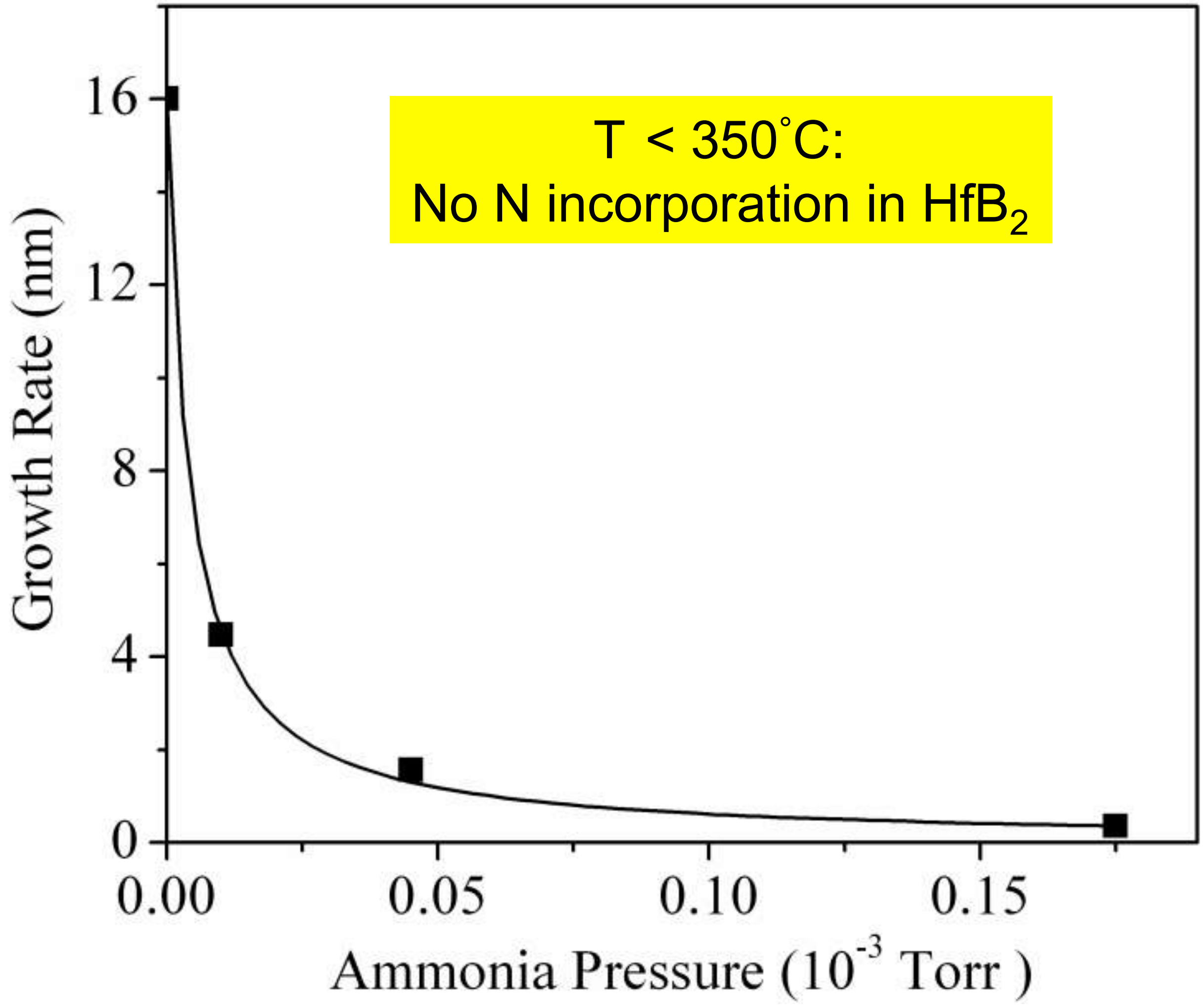


Island: High inhibitor coverage



NH_3 as inhibitor slows HfB_2 growth from $Hf(BH_4)_4$

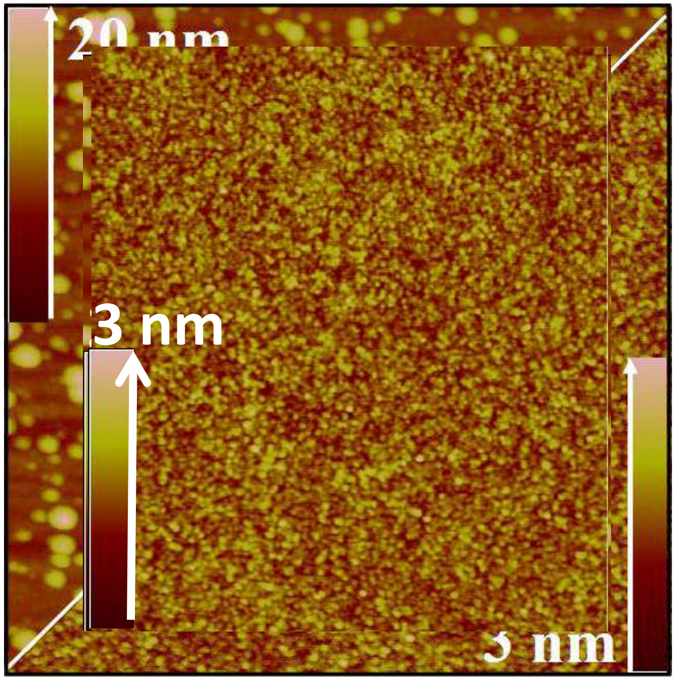
but NH_3 adsorbs weakly on SiO_2



T < 350°C:
No N incorporation in HfB_2

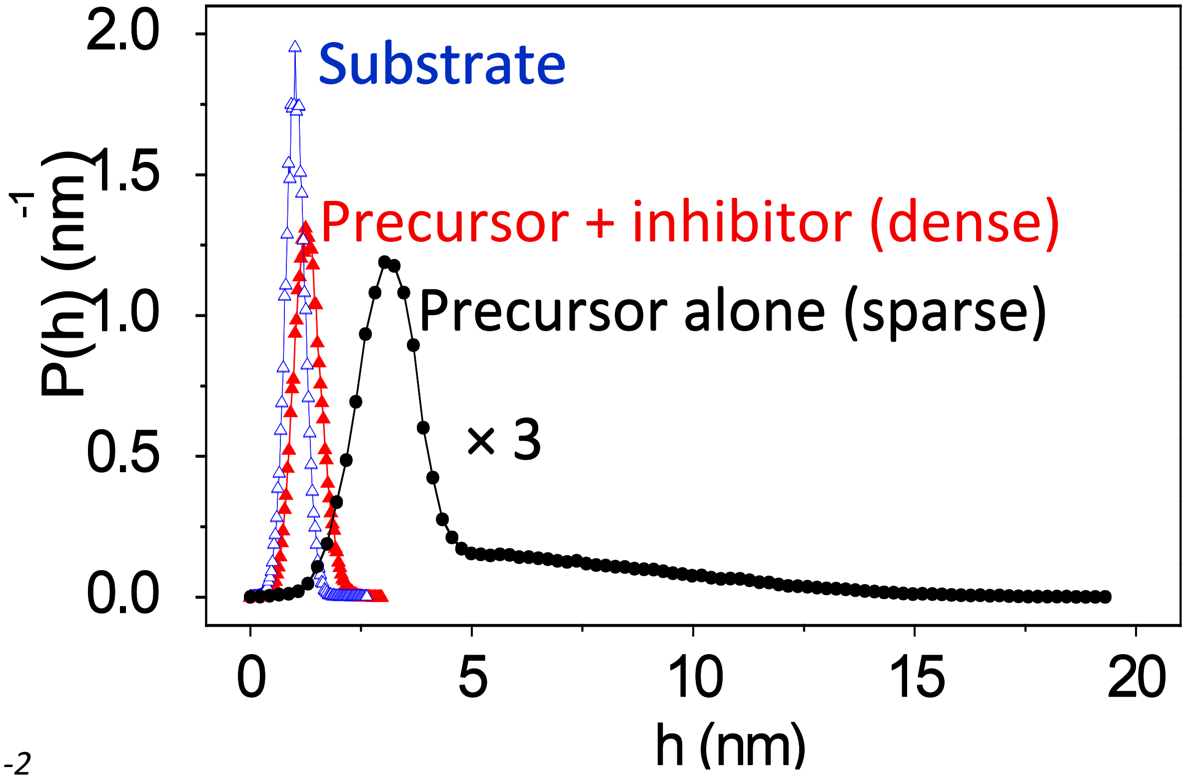
HfB_2 Nucleation on SiO_2 from $Hf(BH_4)_4$

Add NH_3 inhibitor



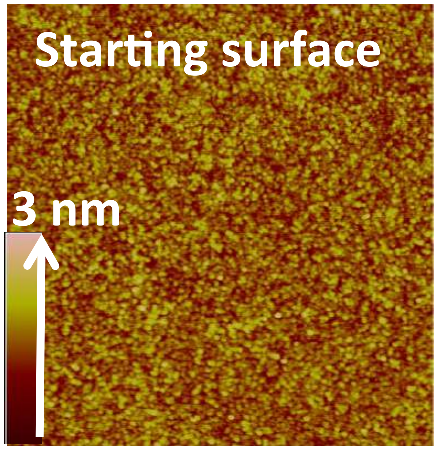
Surface roughness ~ 0.3 nm

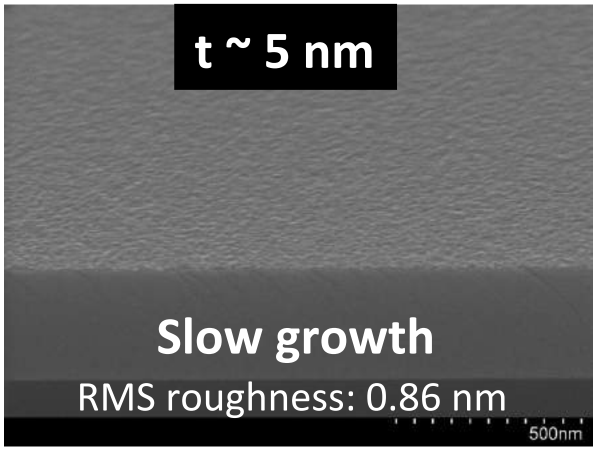
Nucleation density ~ 3 x 10^{12} cm^{-2}

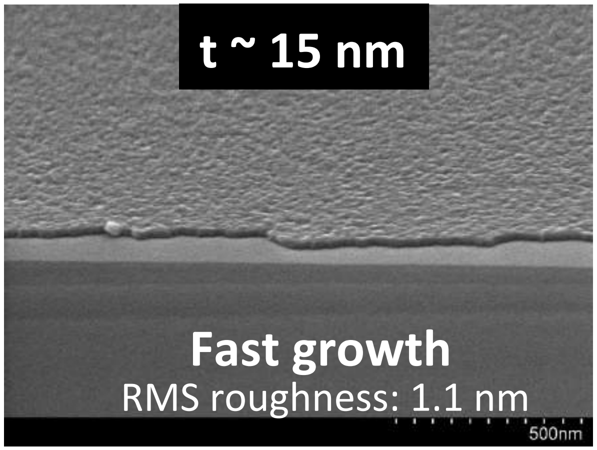


Babar & Abelson, Chem Mats (2013)

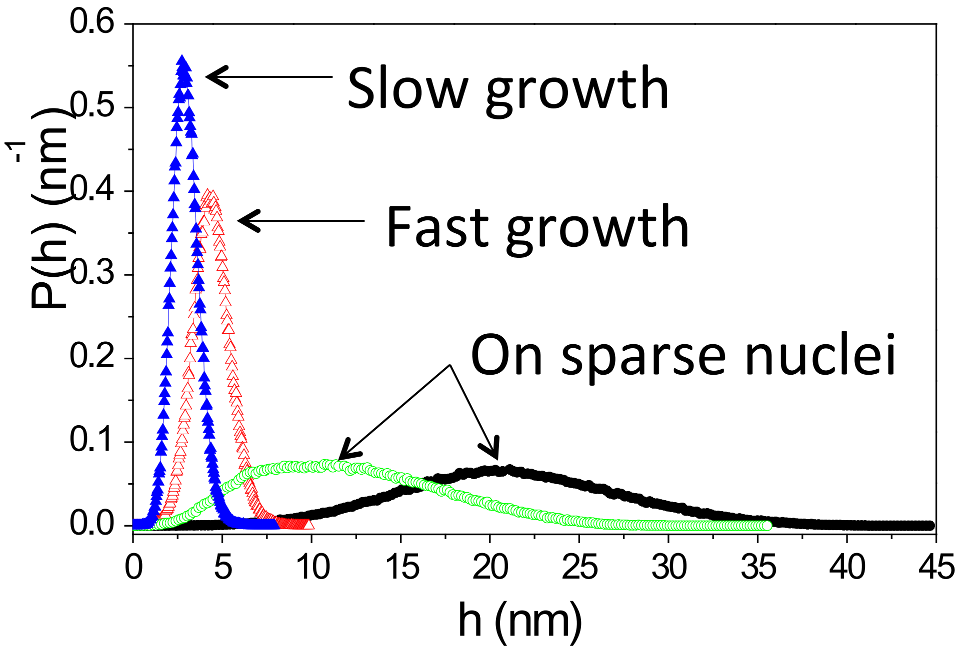
Dense nucleation affords ultra-smooth films







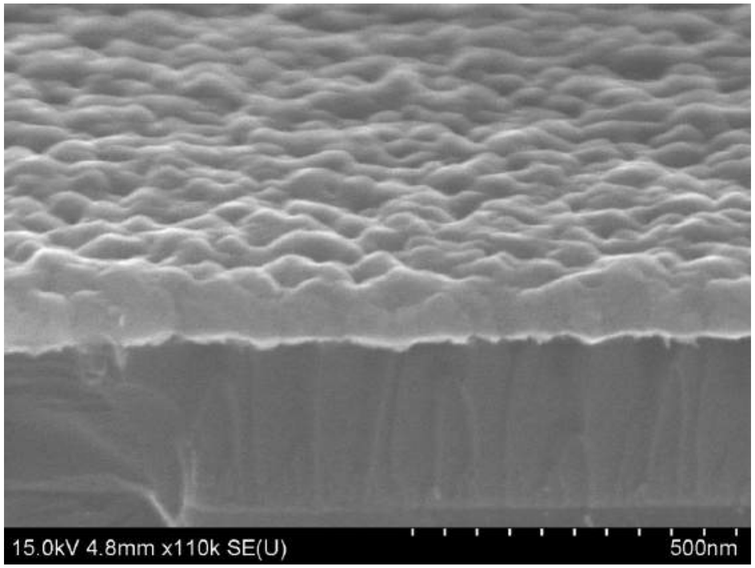
Dense nucleation affords a smooth film, *even with fast growth*



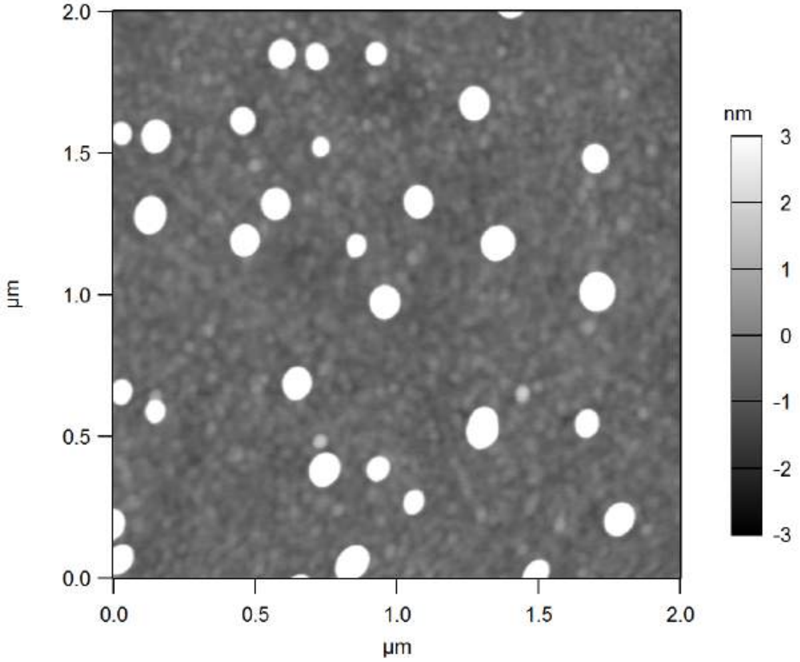
The problem of selective deposition:
eliminate stray nucleation with inhibitors

Cu(hfac)VTMS precursor, $T_{sub.}$= 100˚C, t_{growth}= 30 min

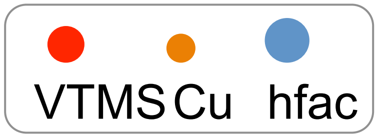
Grow Cu on RuO_x seed layer



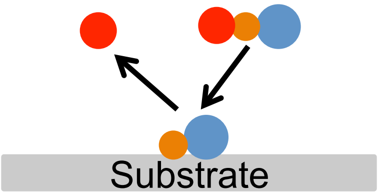
Unwanted Cu islands on SiO_2



Suppress Cu nucleation on SiO_2:
VTMS inhibitor reverses adsorption step

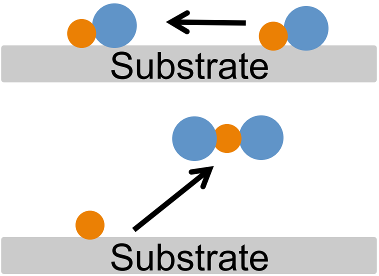


Dissociative adsorption



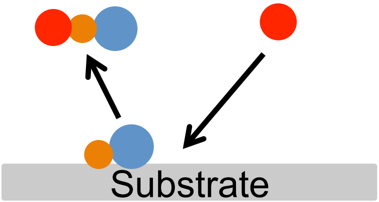
$$Cu(hfac)VTMS_{ads} \leftrightarrow Cu(hfac)_{ads} + VTMS_{g}$$

Disproportionation



$$2Cu(hfac)_{ads} \longrightarrow Cu + Cu(hfac)_{2\,g.}$$

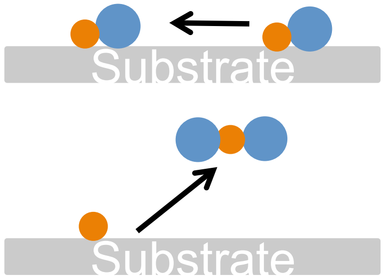
Associative desorption; add VTMS as inhibitor



E.Mohimi et al, ECS JSSST, 4 (7) N60 (2015)

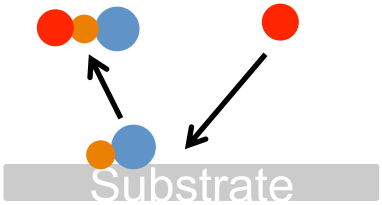
What controls the rate?

Disproportionation



$$Cu^{+1}(hfac)_{ads} + Cu^{+1}(hfac)_{ads} \longrightarrow Cu^{0} + Cu^{+2}(hfac)_{2\,g.}$$

Associative desorption



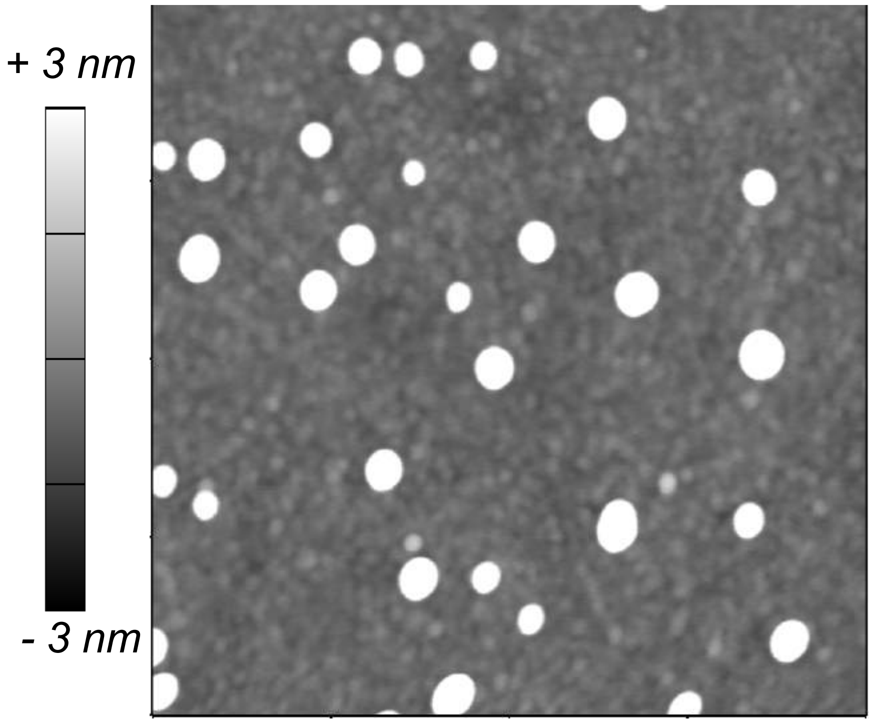
Fast on metals → Dominant mechanism: Disproportionation (Film grows at ~ half the rate)

Slow on dielectrics → Associative desorption (Kills nucleation)

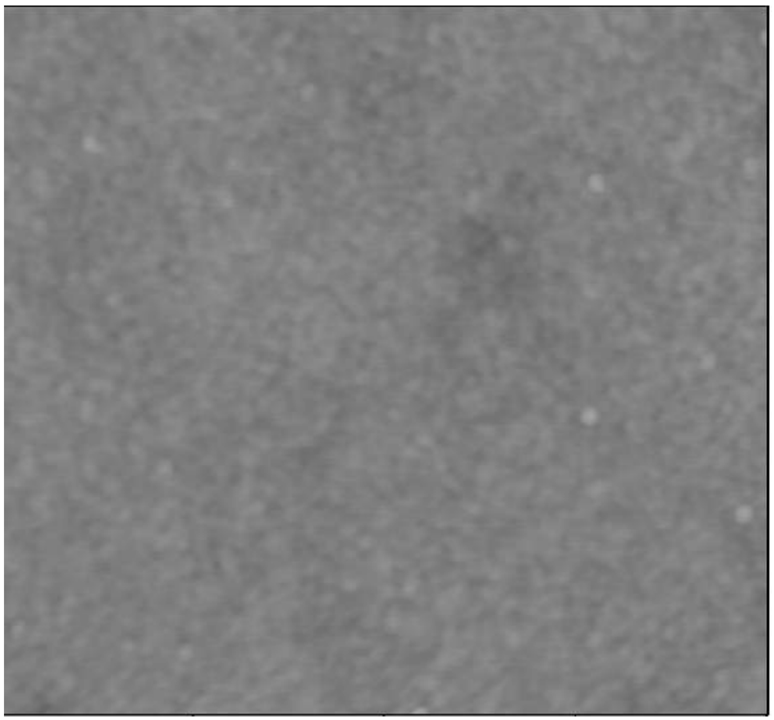
E.Mohimi et al, ECS Journal of Solid State Science and Technology, 4 (7) N60-N63 (2015)

Proof of Concept: VTMS as inhibitor affords selective growth of Cu

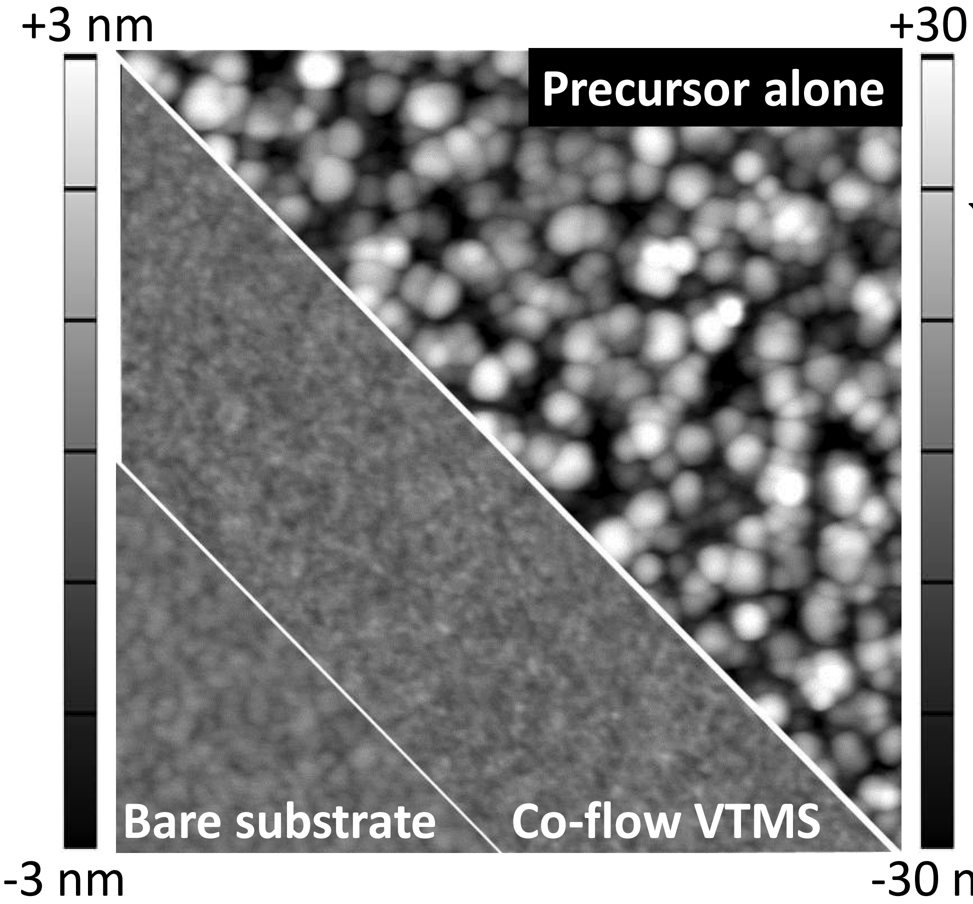
Precursor alone
Stray nucleation

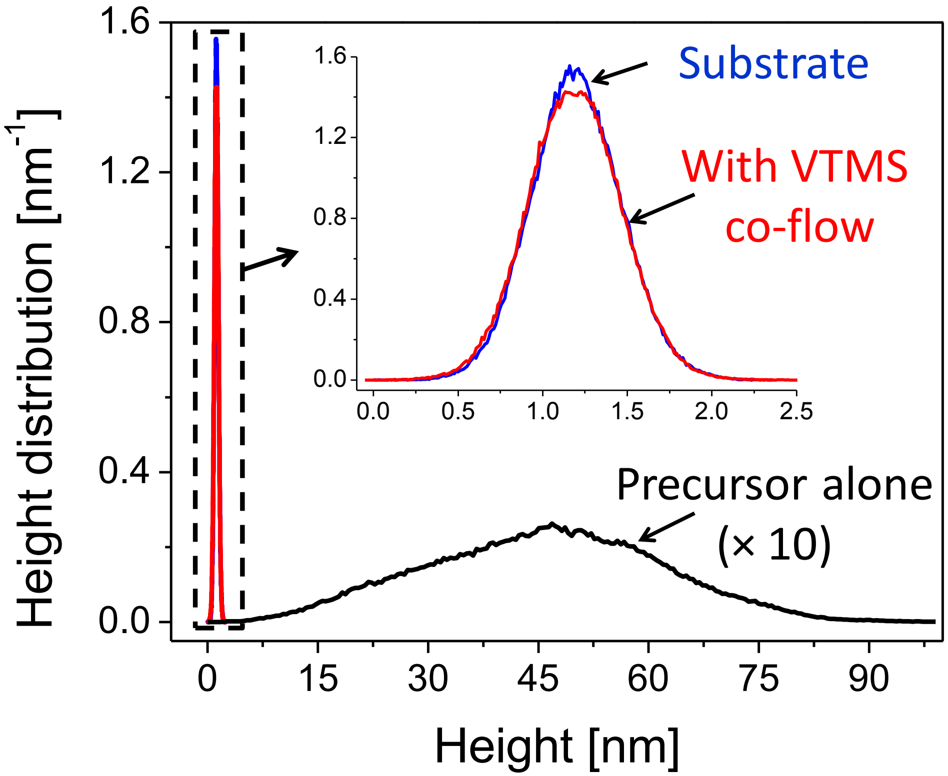


Add VTMS
Zero stray nuclei !

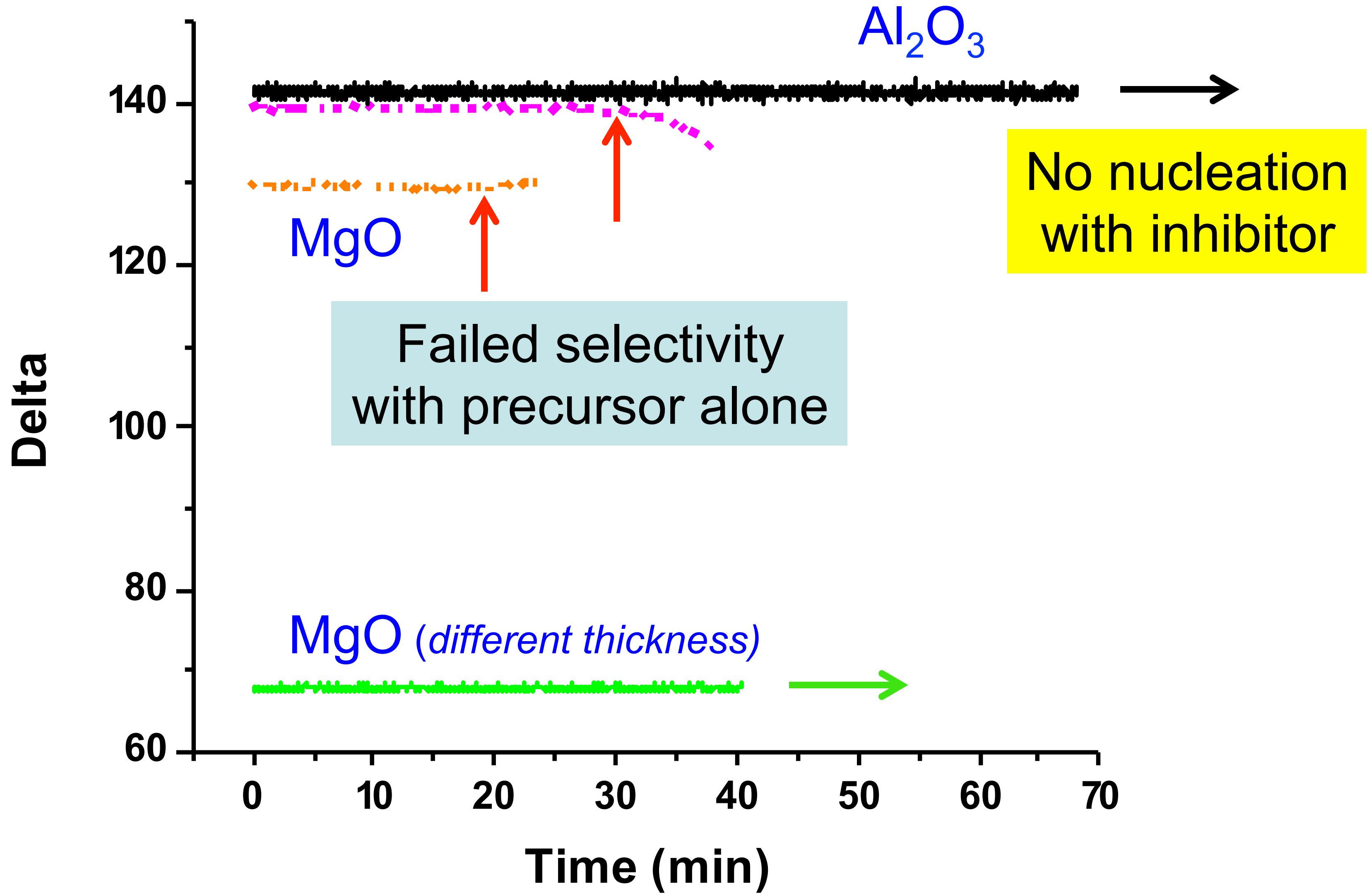


Inhibition works on demanding substrates: Carbon-doped SiO_2 (*Intel 28% C*)





Emerging inhibition work: *No nucleation on oxides* while metal grows on seed areas



No nucleation with inhibitor

Failed selectivity with precursor alone

How can inhibitor suppress nucleation?

Site block almost all surface sites ($\theta \sim 1$)

Passivate surface defects (θ *could be small*)

Reverse precursor adsorption (*helps if growth step is slow*)

Block lateral interaction or transport

Mechanistic understanding hard to obtain !

Tools include isotopes + desorption mass spec, FTIR, …

Conclusions: Low-T CVD

Steady-state adsorbate populations (*Langmuirian*)

Adsorbed layer can moderate growth or halt nucleation

Choose inhibitor for desirable E_{des} and stability (*or lack*)

Control parameters: partial P, substrate T

Can also obtain conformal and superconformal growth

We know little about sites, sterics, and lateral interactions

Why does 1^{st} order Langmuir model work? Because overall rates are limited by slowest kinetic step.

Acknowledgements

Group Members

Y. Yang, N. Kumar, A. Yanguas-Gil, S. Babar, P. Zhang

National Science Foundation

DMR 1005715, CHE 1362931, DMR 1410209

Intel, Lam, Applied Materials, Novellus, Seagate

for patterned substrates

Center for Microanalysis of Materials

Materials Research Laboratory, U. Illinois

ASD17

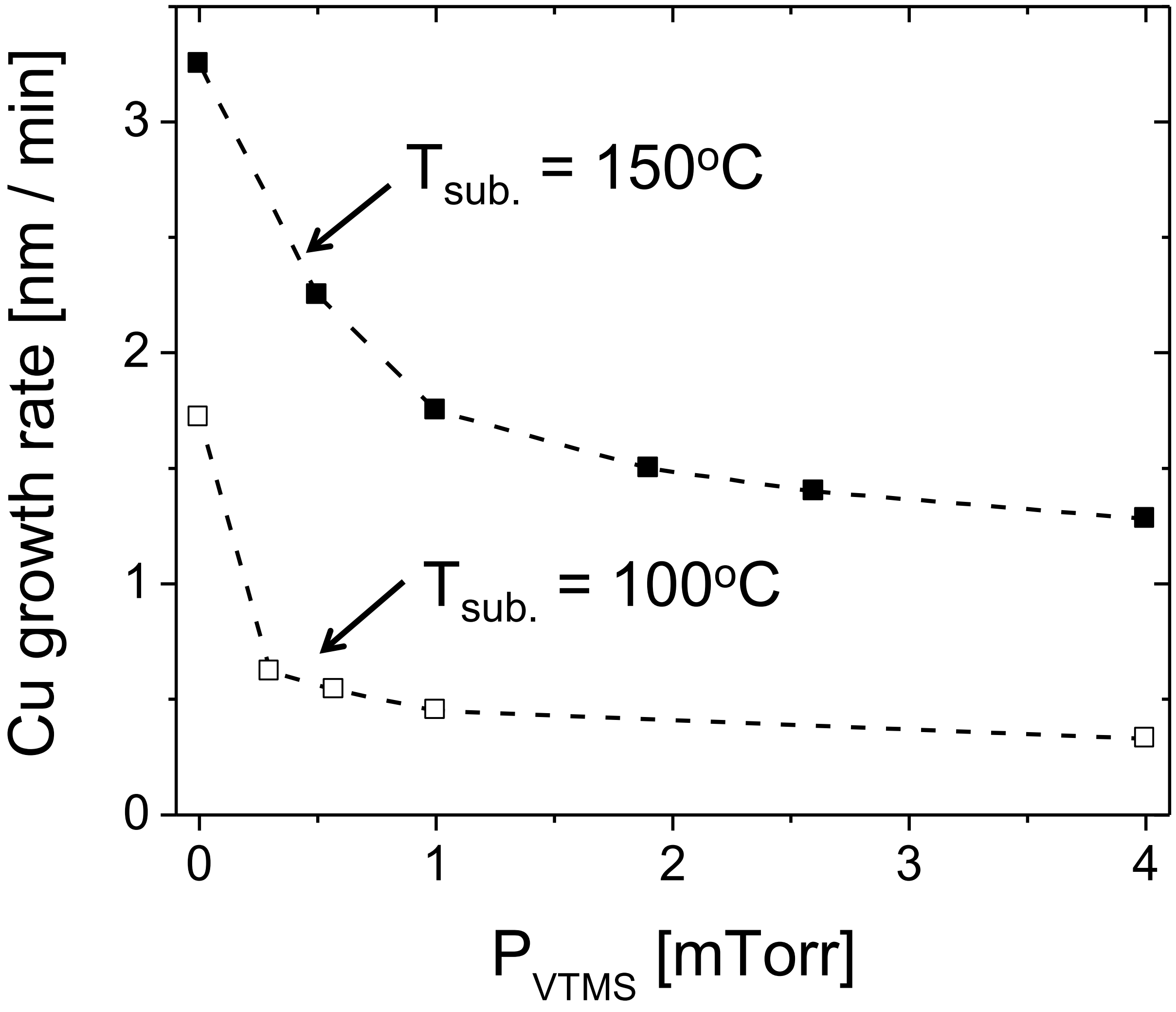
The organizers and sponsors !

Precursors invented by Greg Girolami

Mg(deadb)2	Mg(II)
Mg(dmadb)2	Mg(II)
Ca(dmadb)2(dme)	Ca(II)
Sr(dmadb)2(diglyme)	Sr(II)
Ti(dmadb)2	Ti(II)
Cr(dmadb)2	Cr(II)
Mn(dmadb)2	Mn(II)
Mo(dmadb)2	Mo(II)
La(dmadb)3	La(III)
Ce(dmadb)3	Ce(III)
Pr(dmadb)3	Pr(III)
Nd(dmadb)3	Nd(III)
Sm(dmadb)3	Sm(III)
Eu(dmadb)3	Eu(III)
Gd(dmadb)3	Gd(III)
Tb(dmadb)3	Tb(III)
Dy(dmadb)3	Dy(III)
Ho(dmadb)3	Ho(III)
Er(dmadb)3	Er(III)

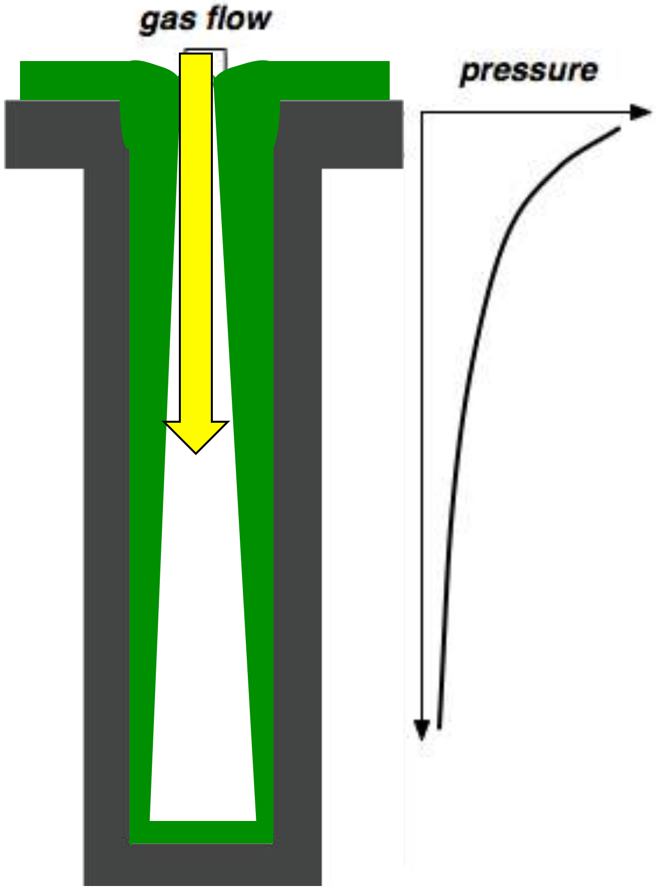
Tm(dmadb)3	Tm(III)
Yb(dmadb)3	Yb(III)
Lu(dmadb)3	Lu(III)
Mn(NtBu2)2	Mn(II)
Fe(NtBu2)2	Fe(II)
Co(NtBu2)2	Co(II)
Ni(NtBu2)2	Ni(II)
Cr(NtBu2)3	Cr(III)
Mg(emadb)2	Mg(II)
Mo(emadb)2	Mo(II)
Mg(meadb)2	Mg(II)
Mg(mmadb)2	Mg(II)
Mg(B3H8)2	Mg(II)
Mg(B3H8)2(OEt2)2	Mg(II)
Cr(B3H8)2	Cr(II)
Ti(BH4)3(dme)	Ti(III)

Added VTMS inhibits Cu growth from Cu(hfac)VTMS



Babar, ECS SST (2014); Kumar, PhD thesis, U. Illinois (2009)

Chemical Vapor Deposition (CVD): The challenge of conformality



Fundamental problem:

Essentially all CVD deposition processes suffer from pinch-off due to faster growth near aperture

Cause: Precursor pressure (and thus growth rate) falls with depth: a *diffusion-reaction problem*

Possible strategies:

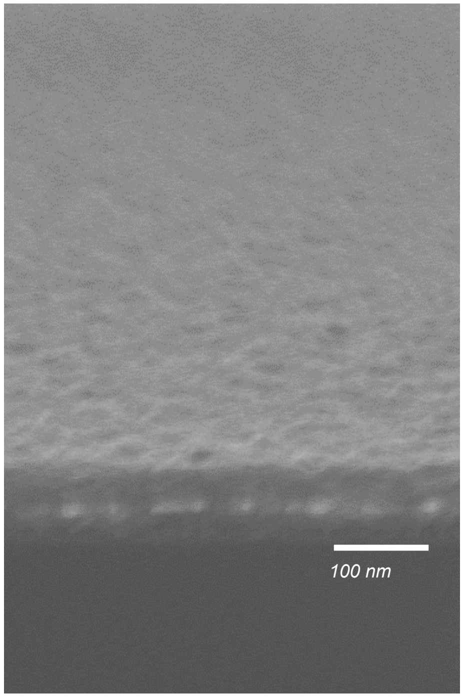
1. Minimize *consumption of precursor*
2. Change *dependence on pressure*

Definitions:

SC (step coverage) = thickness at bottom sidewall / top sidewall

AR (aspect ratio) = trench depth / width

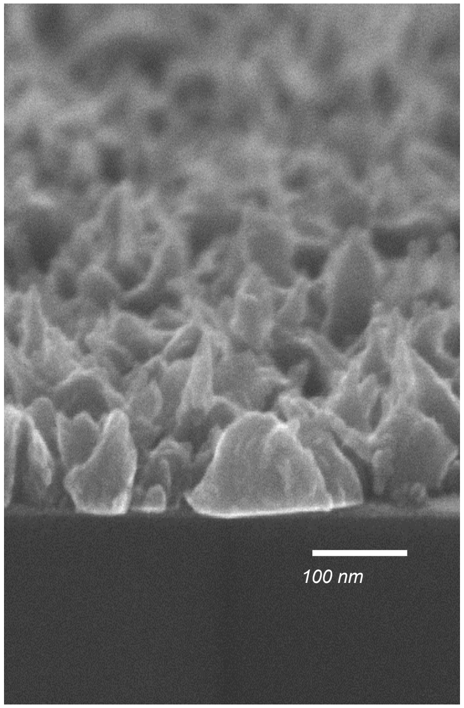
Co CVD (*new results*):
Morphology very sensitive to nucleation !



Ru substrate

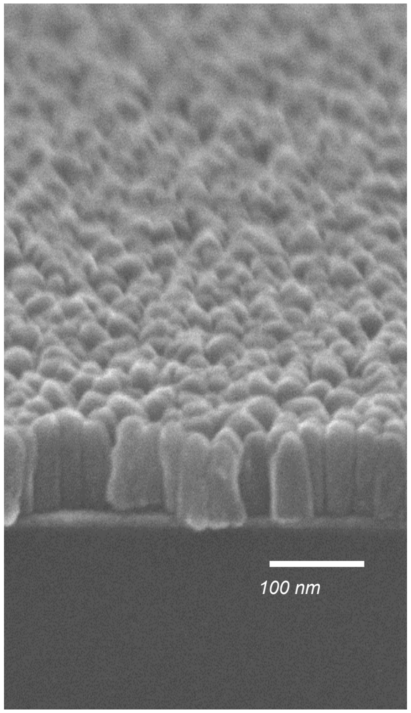
0.05 mTorr $Co_2(CO)_8$,
100°C, 10 min, ~ 60 nm

Sticking s ~ 5 %
onset of conformal regime



Ta substrate

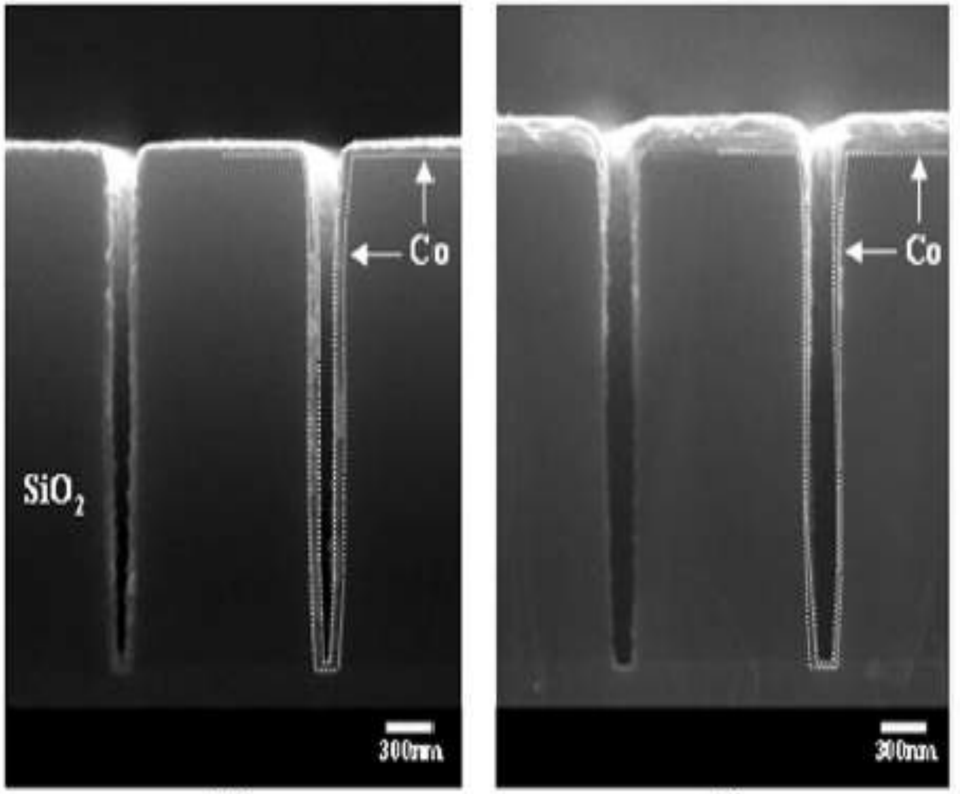
0.05 mTorr $Co_2(CO)_8$,
100°C, 10 min



Ta substrate

0.05 mTorr $Co_2(CO)_8$,
150°C, 10 min

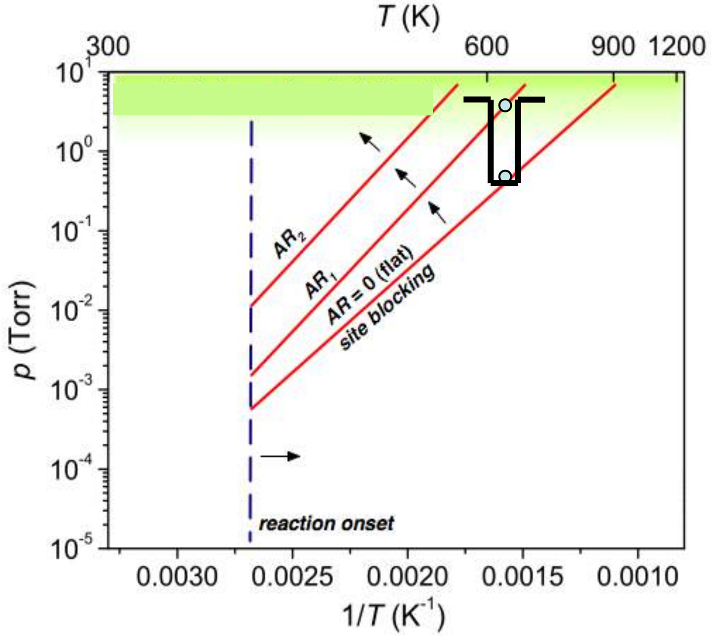
Literature: Conformal CVD of Co at low T, high P



(a) (b)

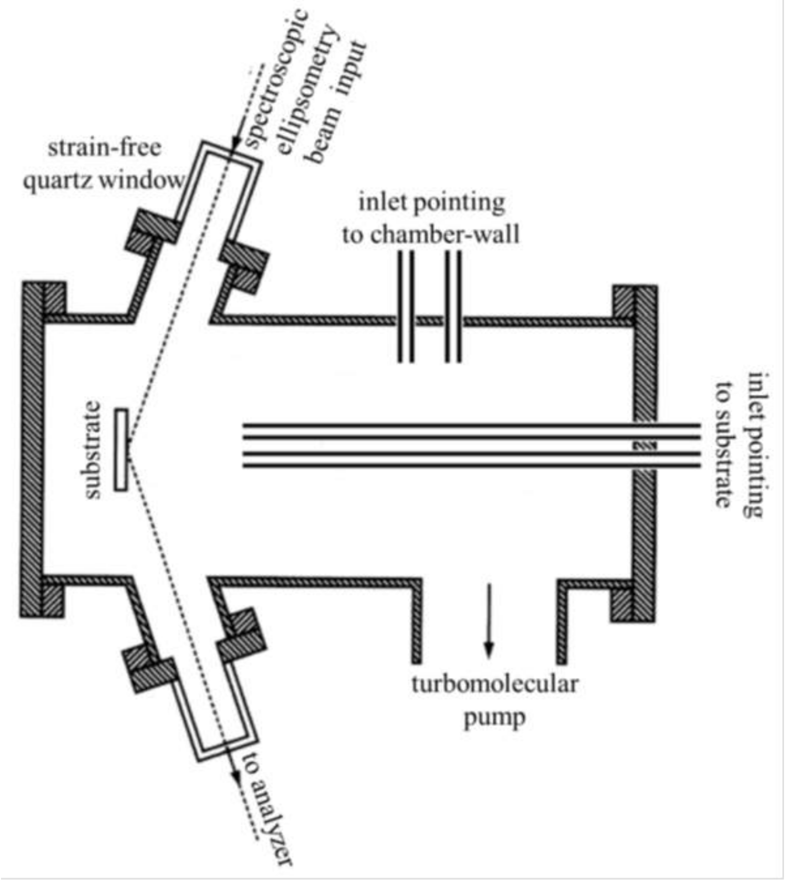
Co deposited in trenches with AR 13:1
using 200 mTorr $Co_2(CO)_8$
(a) 50 °C, (b) 60 °C

J. Lee et. al. JECS 153 (6), G539-G542 (2006)

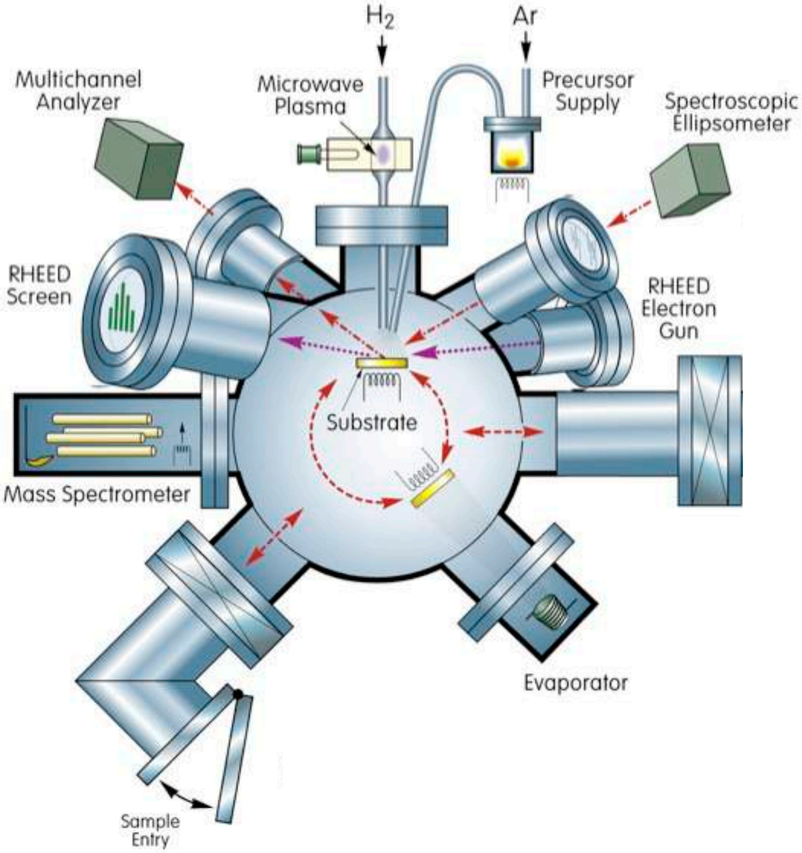


Consistent with prediction of zone diagram: *need high P*

CVD growth systems in Abelson laboratories



Test chamber: simple in design and convenient for oxide growth



Analytical chamber: equipped with multiple surface techniques

Some CVD systems we have investigated

* *precursor invented by GSG*

$Hf(BH_4)_4$ for HfB_2

$Ti(BH_4)_3$(dme)* for TiB_2

$Cr(B_3H_8)_2$* for CrB_2

Cu(hfac)(VTMS) for Cu

$Ru(C_6H_8)(CO)_3$* for Ru

$Mg(DMADB)_2$* + H_2O for MgO

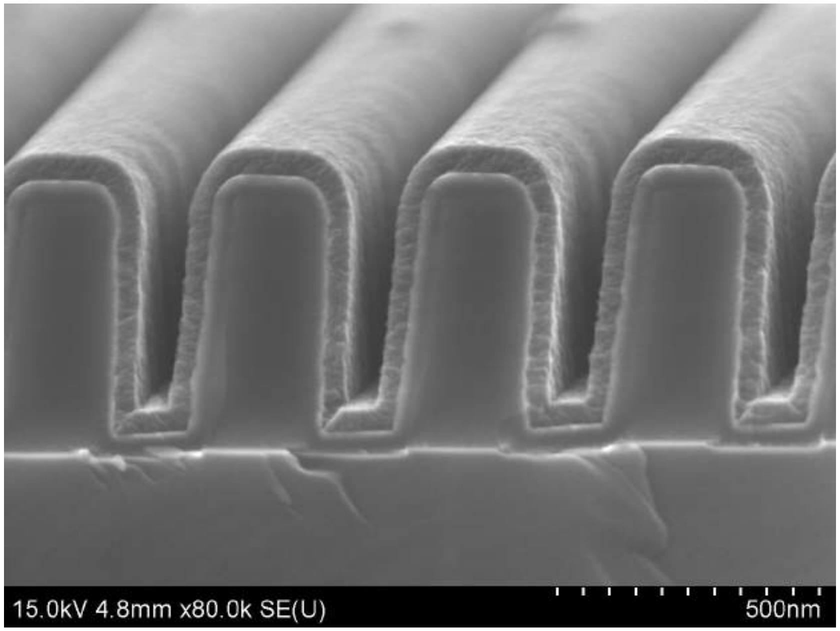
$Fe(CO)_5$ for Fe

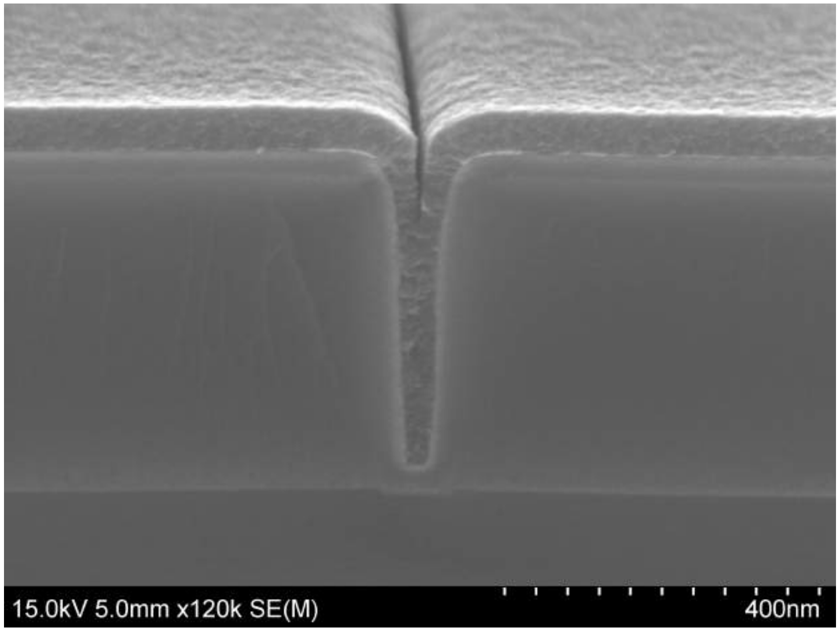
$Co_2(CO)_8$ for Co

$Mn(TMP)_2$* + NH_3 for MnN_x

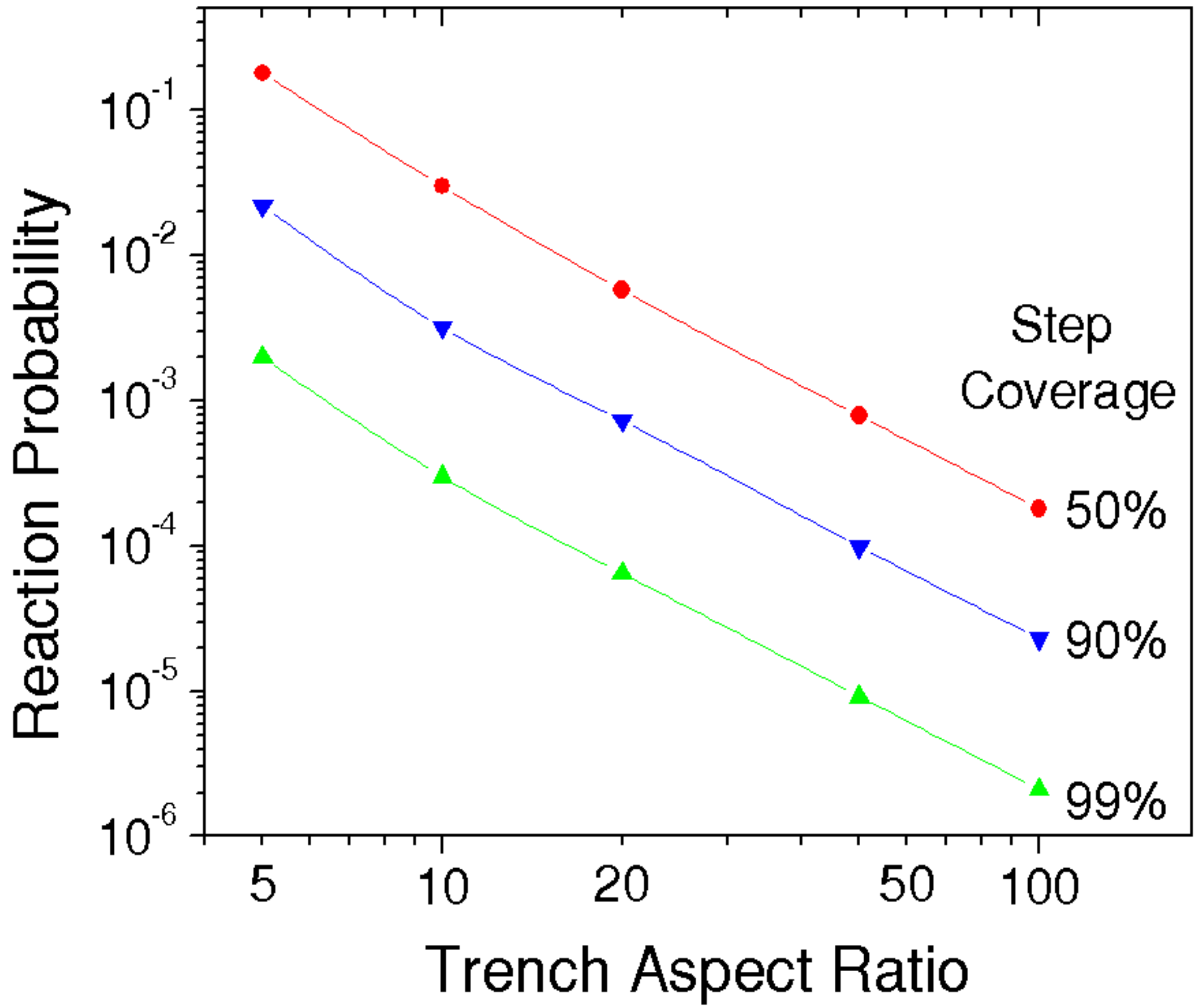
Studies in process: VN, HfO_2, …

New Vanadium Nitride Process
CVD at 150°C





Solution # 1: Minimize reaction probability *β*



Analytic model of conformal coverage in CVD

Fundamental problem:

Pressure drop ΔP from top to bottom of trench

Approximation:

Assume GR = constant; largest possible ΔP

Solve Fick's second law analytically

$$(\Delta p)_{trench} = GR(T)\frac{\rho k_B T}{D_0}(AR)\left(1+\frac{c}{2}(AR)\right) \approx GR(T)\frac{c\rho k_B T}{2D_0}(AR)^2$$

where c = 2,4 for via or trench.

Step coverage SC is then a function of AR and $\frac{\partial GR}{\partial P}$

$$SC = 1 - \frac{\partial GR}{\partial p}\frac{c\rho k_B T}{2D_0}(AR)^2$$

Analytic model for conformal CVD connects GR, AR and SC

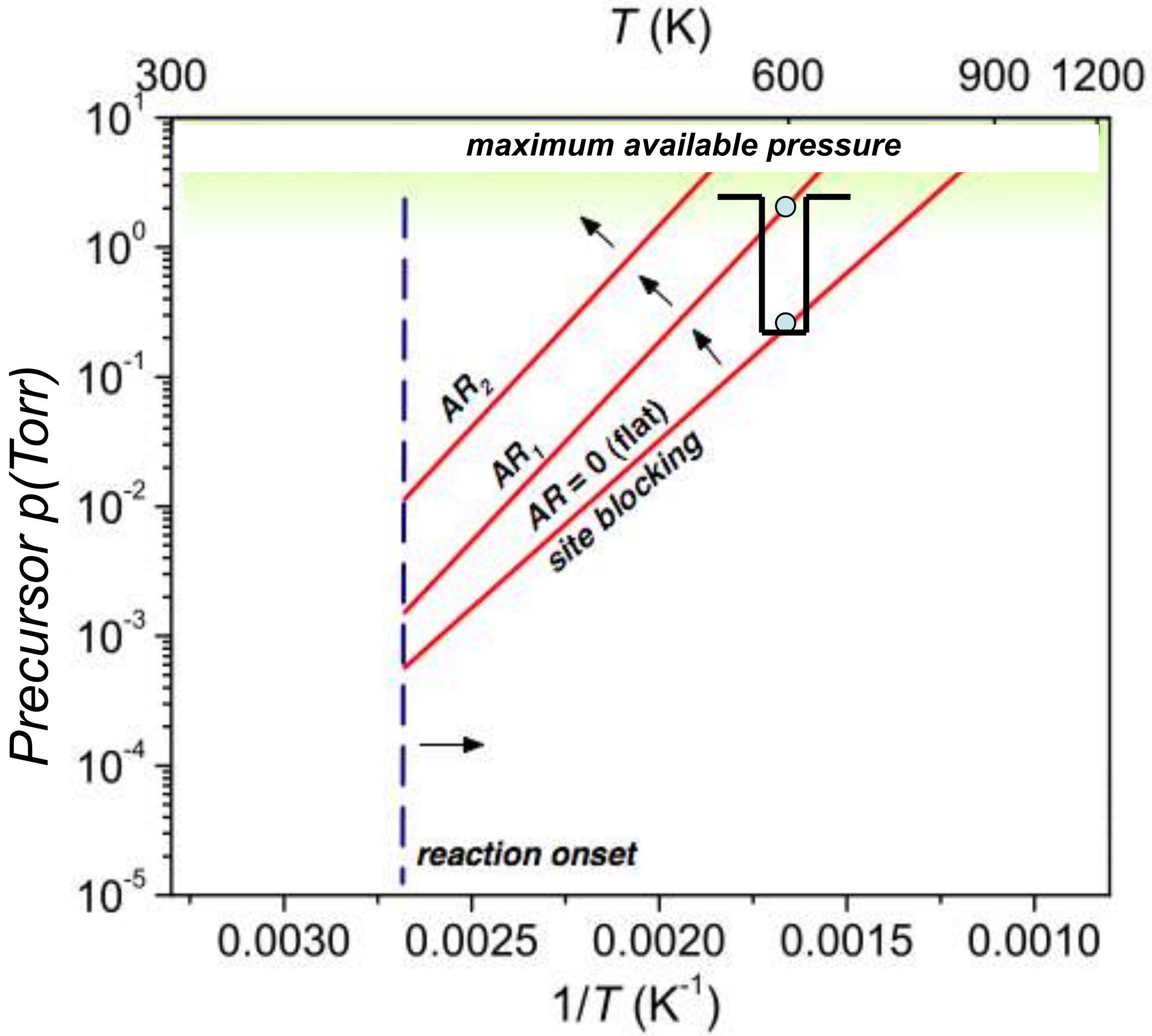
$$p_{precursor} = \frac{GR \times AR}{\sqrt{1-SC}} \sqrt{\frac{c\rho k_B T}{2D_0 K_1(T)}}$$

In CVD, SC is always < 1 (but ~ 0.95 works fine)

High precursor p is essential !

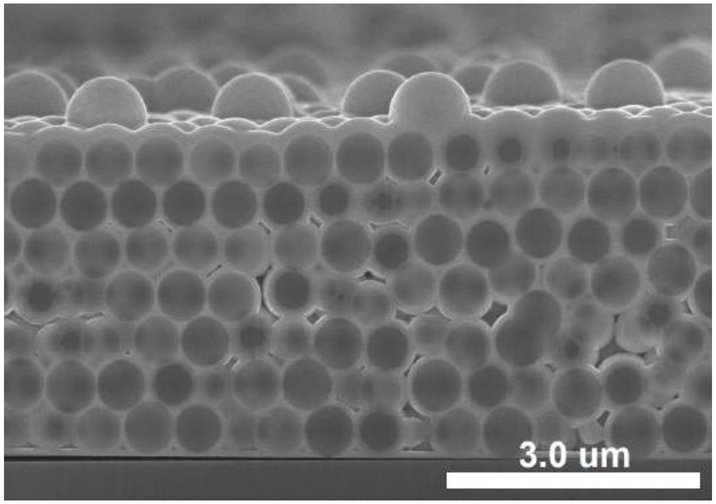
A. Yanguas-Gil, JVST-A (2009)

CVD Conformal Zone Diagram:
Maintain rate saturation at trench bottom



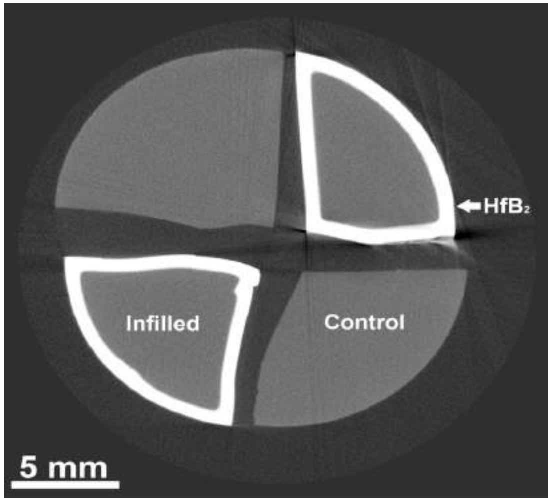
A. Yanguas-Gil, JVST-A (2009)

Use max precursor P and min T for CVD infilling

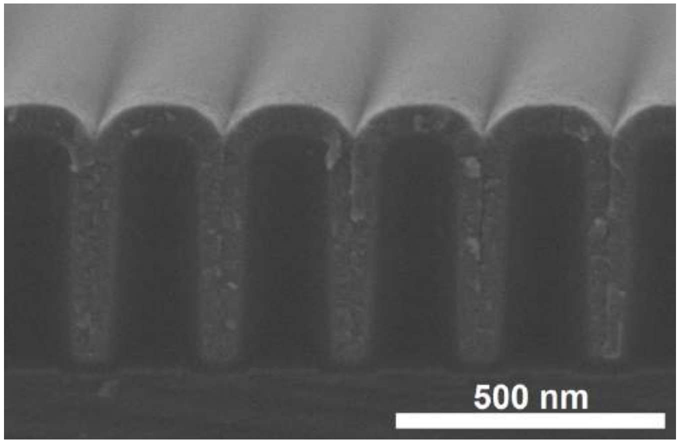


Colloidal crystal

HfB_2



Silica aerogel

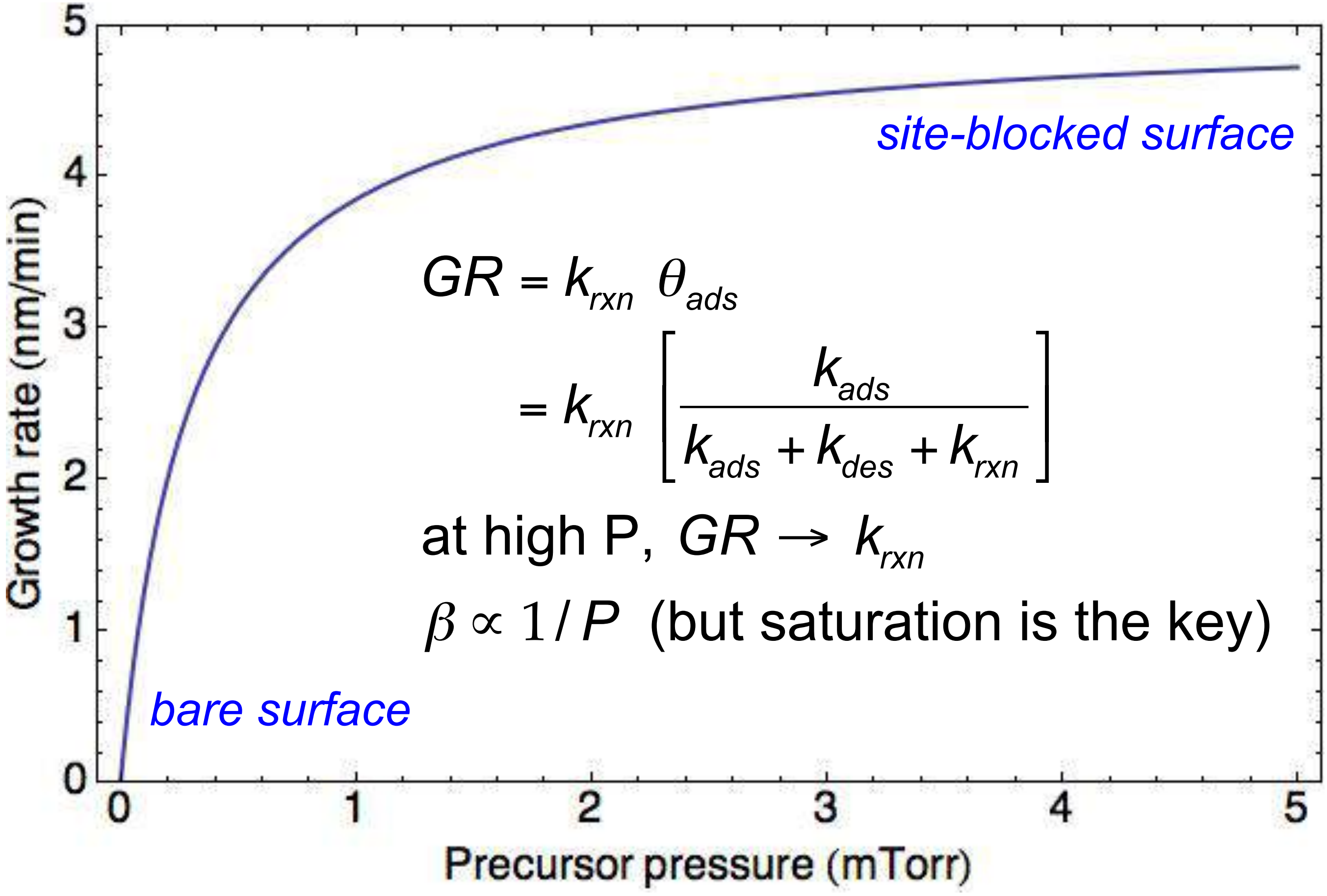


Trench Fill

Fe from $Fe(CO)_5$

Cloud & Abelson,
submitted (2016)

Langmuirian adsorption with film growth



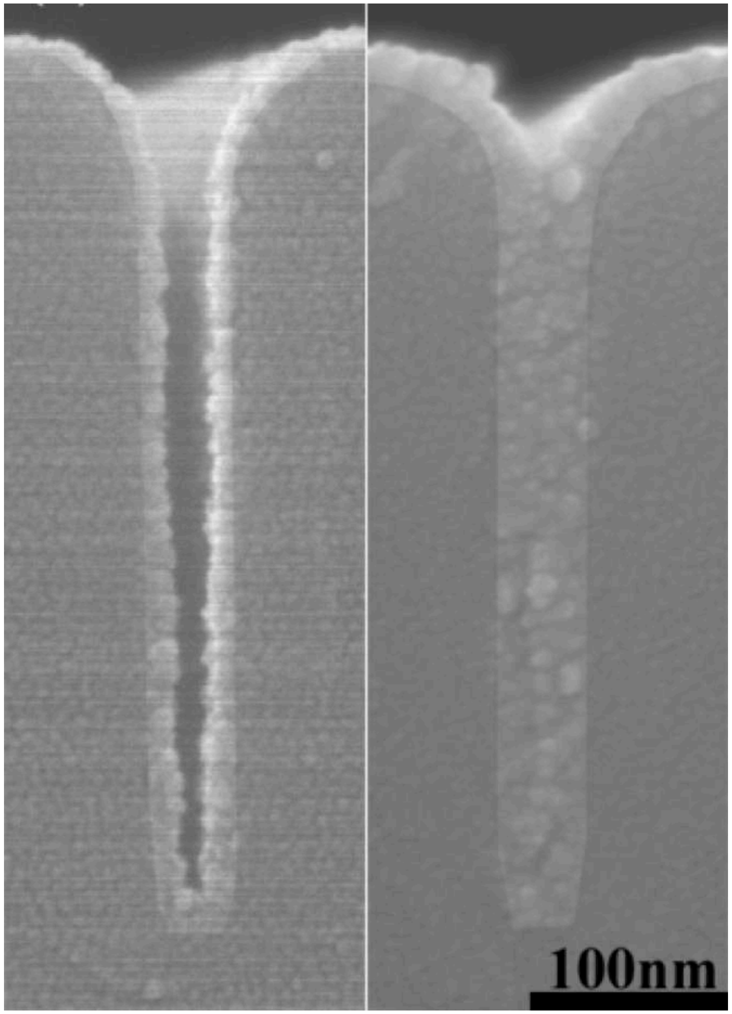
$$GR = k_{rxn}\ \theta_{ads}$$

$$= k_{rxn}\left[\frac{k_{ads}}{k_{ads}+k_{des}+k_{rxn}}\right]$$

at high P, $GR \rightarrow k_{rxn}$

$\beta \propto 1/P$ (but saturation is the key)

We discovered a *superconformal* growth process in two-reactant CVD



$$Mg(DMADB)_2 + H_2O \rightarrow$$
$$MgO + \text{volatile byproducts}$$

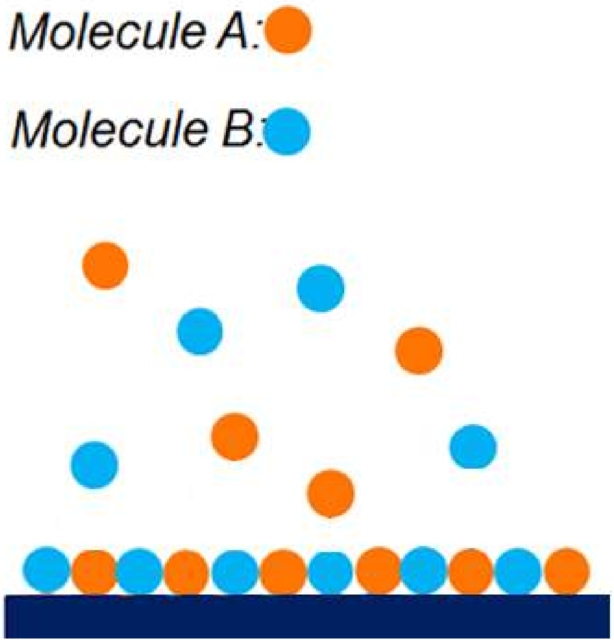
We investigated an unusual process regime, $P_{H_2O} < P_{Mg}$, because we had found that water inhibits growth

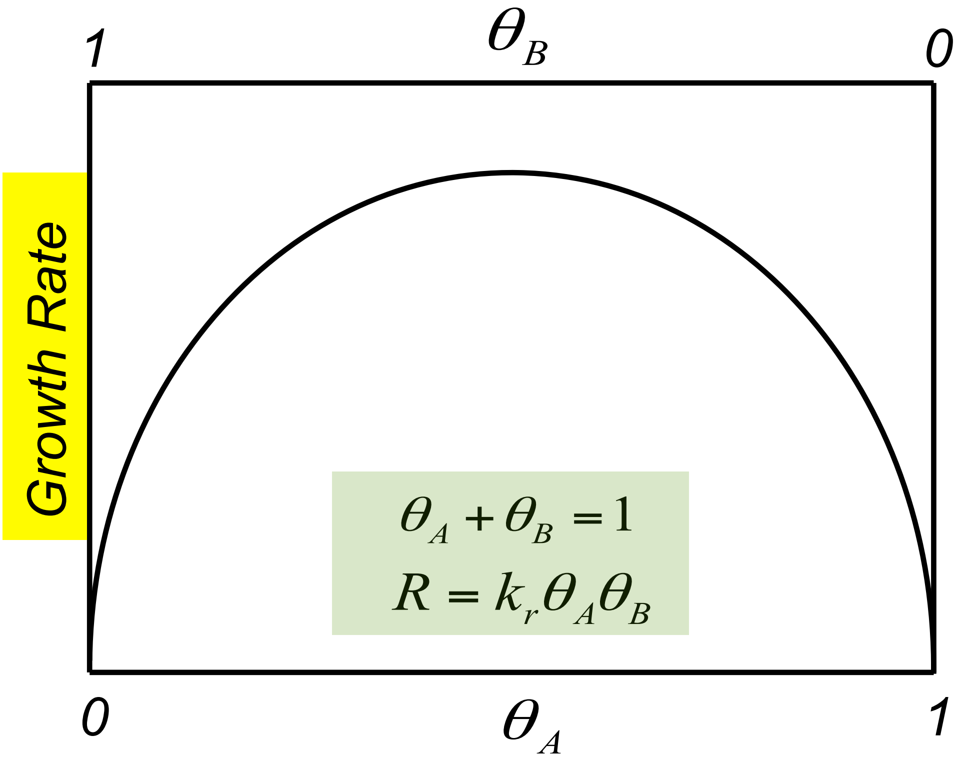
Left image: under these conditions, SC > 1. Film is thicker at bottom !

Right image: continued deposition leads to complete fill !

Abelson, Girolami, et al., *JVST-A* (2014)

Key feature #1:
Co-reactants compete for adsorption sites





$$\theta_A + \theta_B = 1$$
$$R = k_r \theta_A \theta_B$$

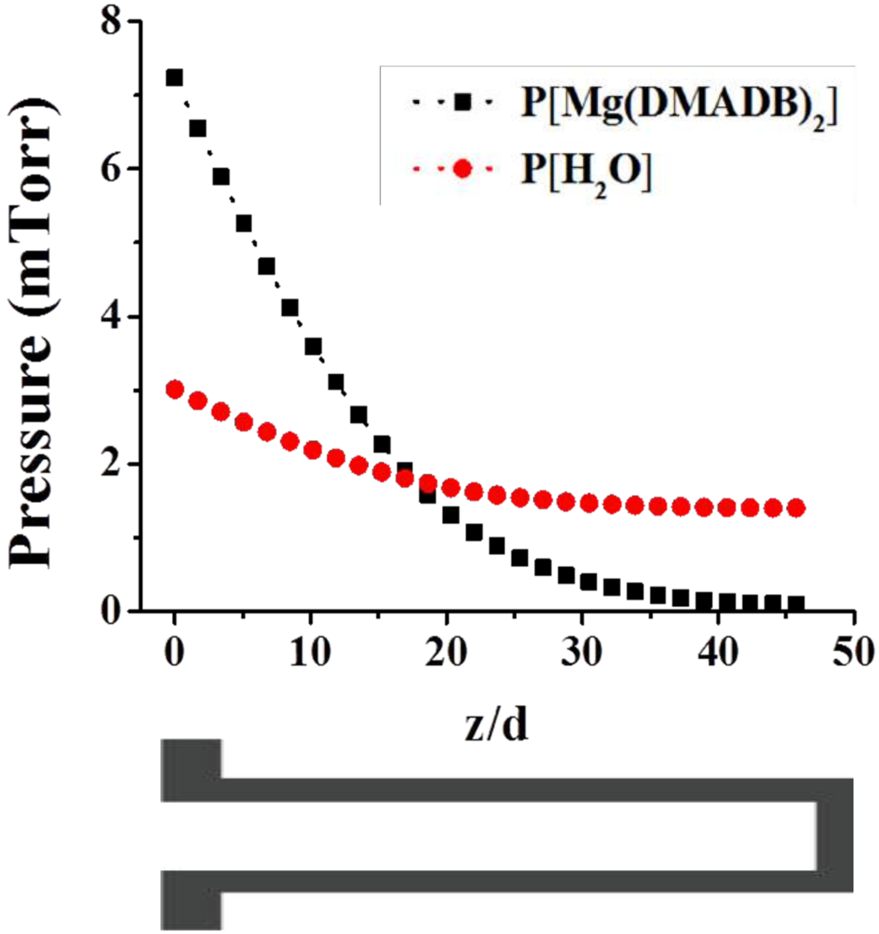
There is a competition of the co-reactants for adsorption sites

Reaction rate is the product of the surface coverages

Thus, water is both necessary for growth *and* an inhibitor of growth

Key feature #2: If molecules *A* and *B* have different molecular weights, *they have different pressure drops*

Example: MgO growth from $Mg(DMADB)_2 + H_2O$



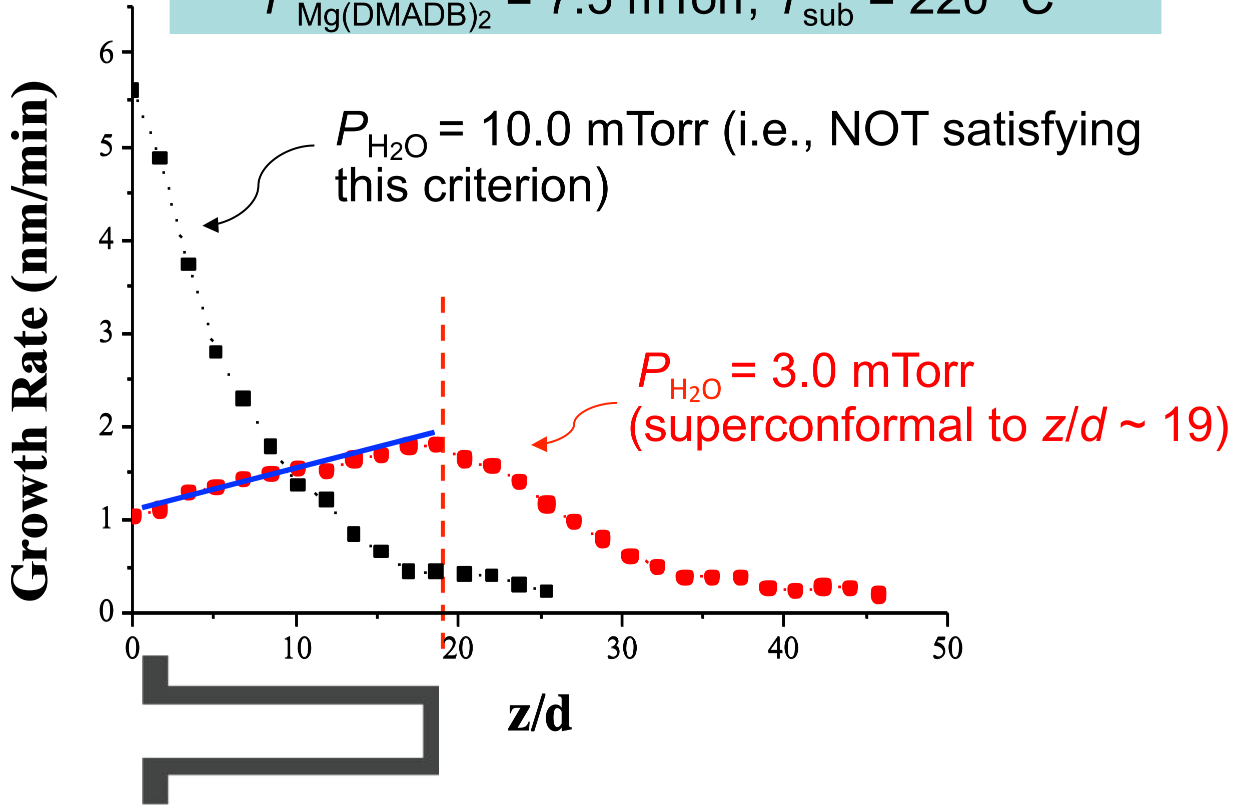
$$\frac{\Delta P_A(z)}{\Delta P_B(z)} = \frac{\rho_A / D_A^k}{\rho_B / D_B^k}$$

Diffusivity, $D \propto 1 / \sqrt{M}$

- ρ_A and ρ_B are the stoichiometric coefficients in the growth reaction ($\rho_A = \rho_B = 1$ for this MgO process)
- High mass Mg precursor has small *D* and thus suffers larger pressure drop down the trench
- The fractional surface coverage of water in the adsorbed growth layer increases with depth in the feature

Combining #1 and #2:
Superconformal if $P_{H_2O} < P_{Mg(DMADB)_2}$ in gas feed

$P_{Mg(DMADB)_2}$ = 7.5 mTorr, T_{sub} = 220 ºC



P_{H_2O} = 10.0 mTorr (i.e., NOT satisfying this criterion)

P_{H_2O} = 3.0 mTorr (superconformal to z/d ~ 19)

If $P_{H_2O} < P_{Mg}$ in the feed, the surface is water starved ($\theta_{H_2O} << 0.5$) at the aperture, and the growth rate is below the maximum

Slower Mg precursor diffusion down feature lessens water starvation at greater depths and leads to faster (i.e., superconformal) growth

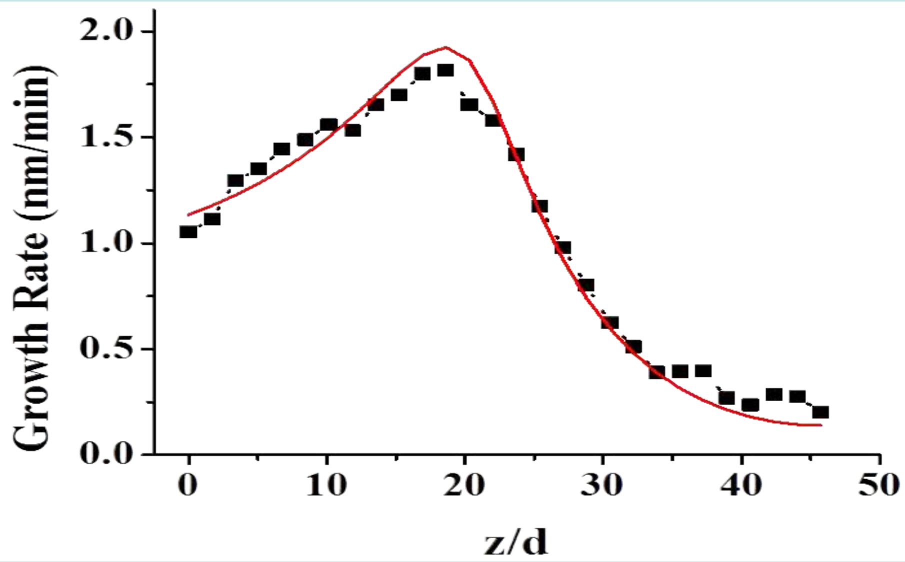
We can fit the growth rate vs. depth data quantitatively to this model

$$\theta_{A,B} = \frac{k_{ads}^{A,B} P_{A,B}(1-\theta_{B,A})}{k_{ads}^{A,B} P_{A,B} + k_{des}^{A,B} + k_r \theta_{B,A}}$$

Competitive Langmurian isotherm with film growth term k_r

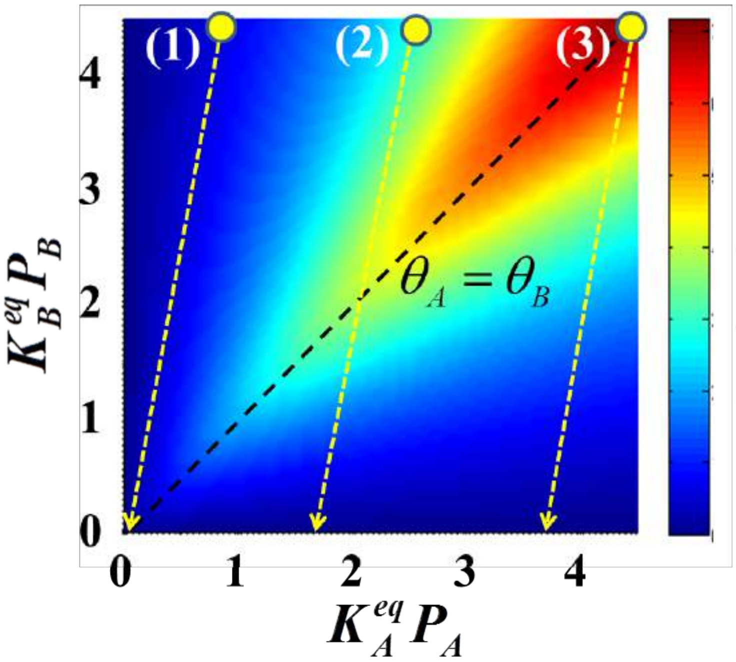
$$R = k_r \theta_A \theta_B$$

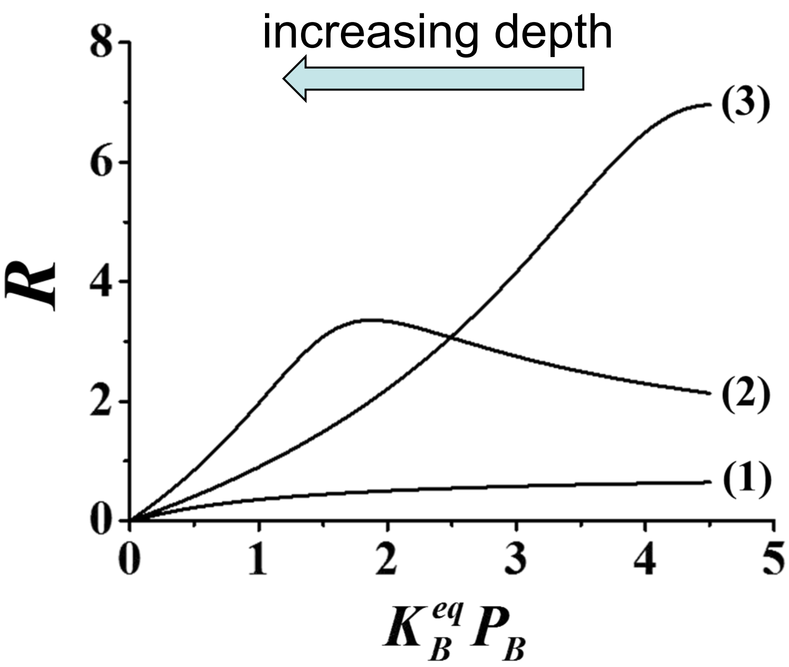
$$\frac{\Delta P_A(z)}{\Delta P_B(z)} = \frac{\rho_A / D_A^k}{\rho_B / D_B^k}$$



This model allows us to predict GR vs depth profiles for any feed conditions (i.e., P_A/P_B and MW ratios)

We can predict growth rate vs. depth profiles from a *trajectory* of P_A vs. P_B down a feature

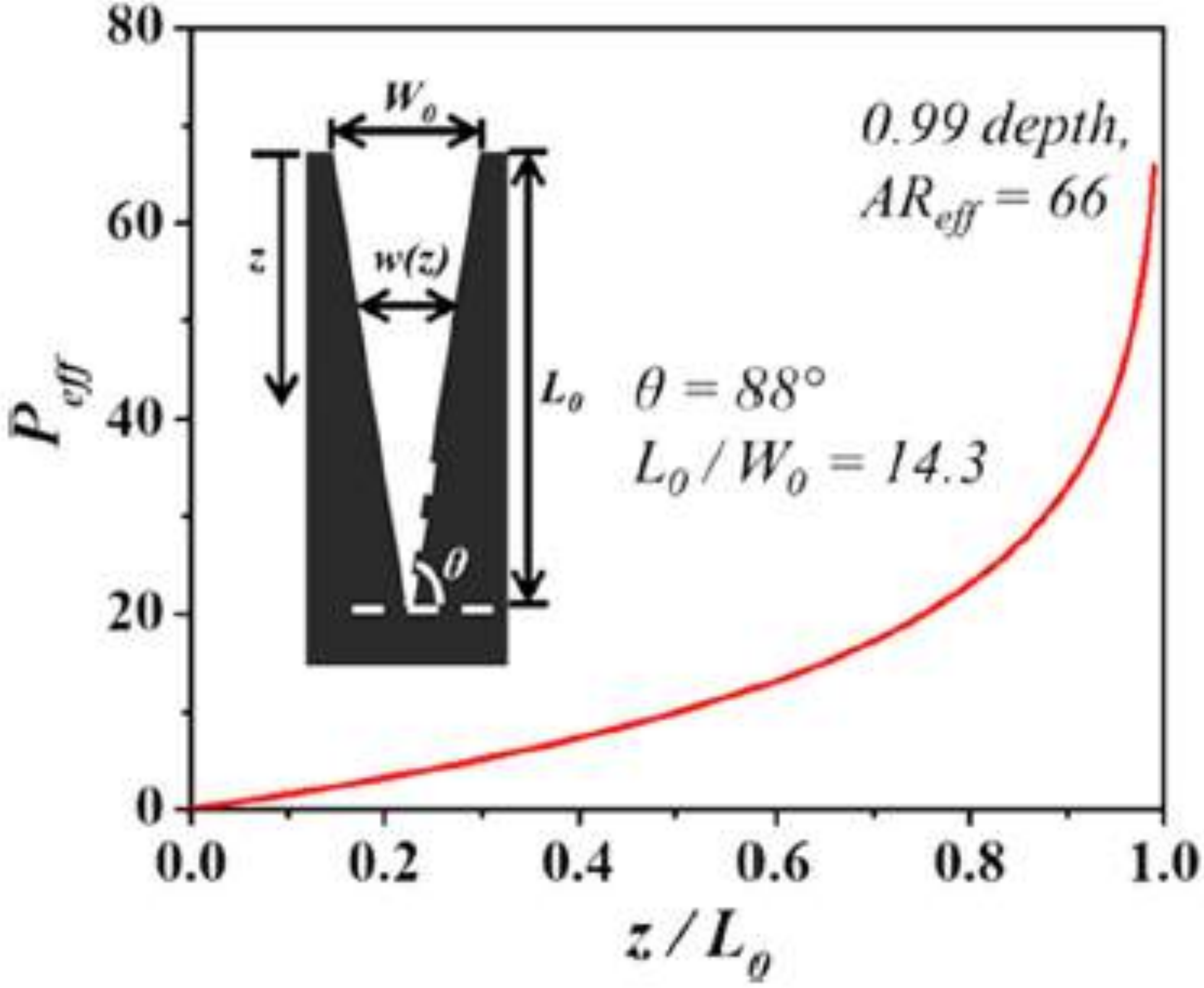




- Case (1) $P_A << P_B$ affords a conformal coating to large depths
- Case (3) $P_A \approx P_B$ affords subconformal coating because the pressures move away from the $\theta_A = \theta_B$ line toward lower GRs
- Case (2) $P_A < P_B$ affords superconformal coating from the starting point to the depth at which the pressures cross the $\theta_A = \theta_B$ line

However, filling a V-shape is not easy:

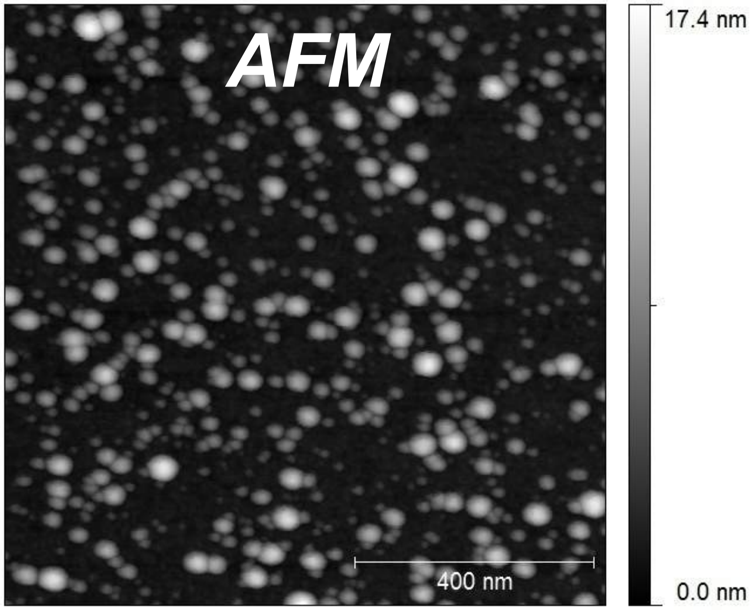
diffusivity diminishes as (1 / trench width) !



W. Wang, JAP 116,194508 (2014)

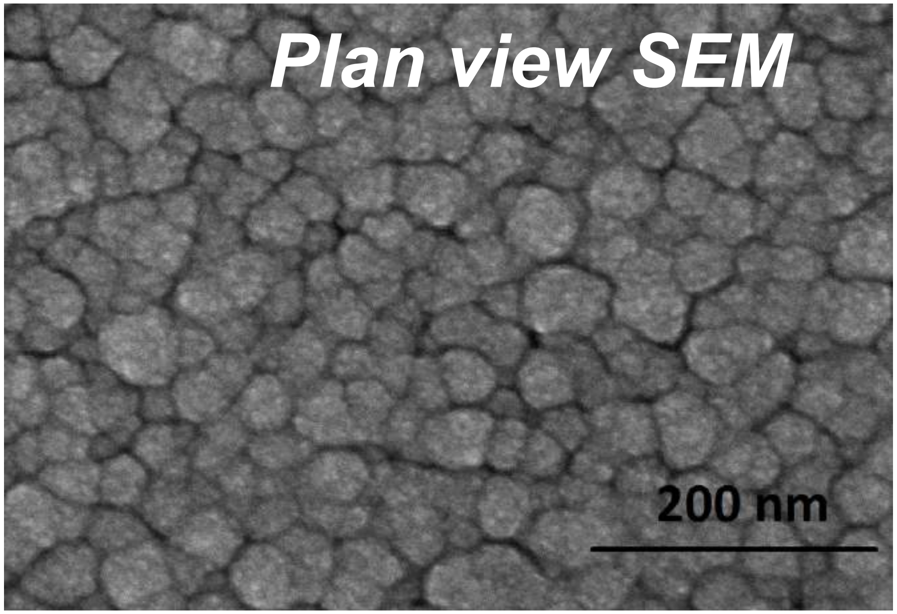
Qualitatively: Nucleation Density Relates to Surface Morphology

Sparse nucleation layer
(without inhibitor)



Thickness = 0.3 nm
RMS roughness = 2.9 nm

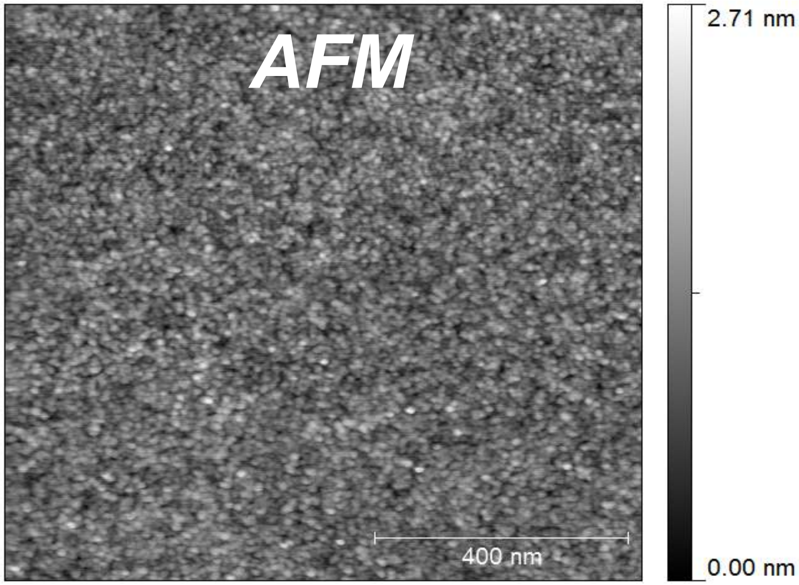
Non-conformal film growth
(without inhibitor) on top



Thickness = 27.5 nm
RMS roughness = 4.3 nm

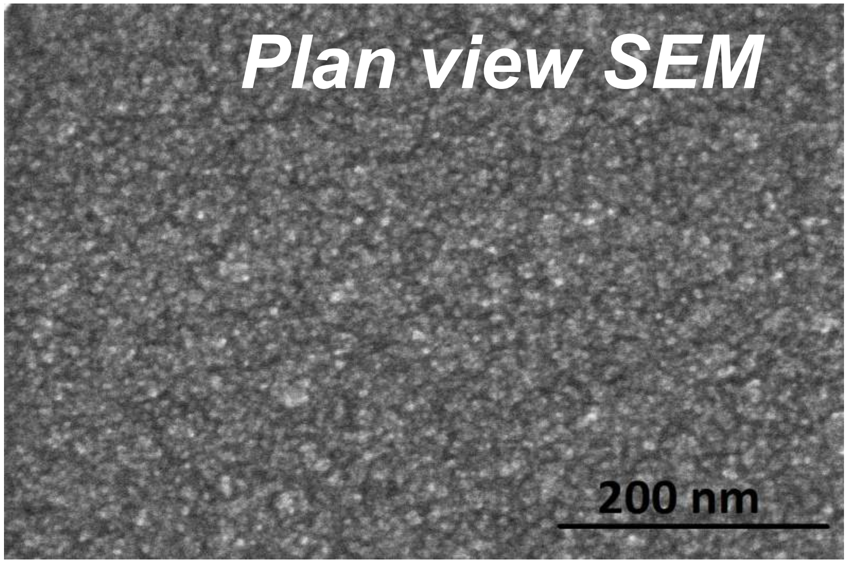
The Smoothest Case:
Dense Nucleation, Conformal Growth

Dense nucleation layer
(with inhibitor)



Thickness = 0.3 nm
RMS roughness = 0.3 nm

Conformal growth
(with inhibitor) on top



Thickness = 35.7 nm
RMS roughness = 1.7 nm

Can We Infer the Mechanisms Leading to Surface Roughness?

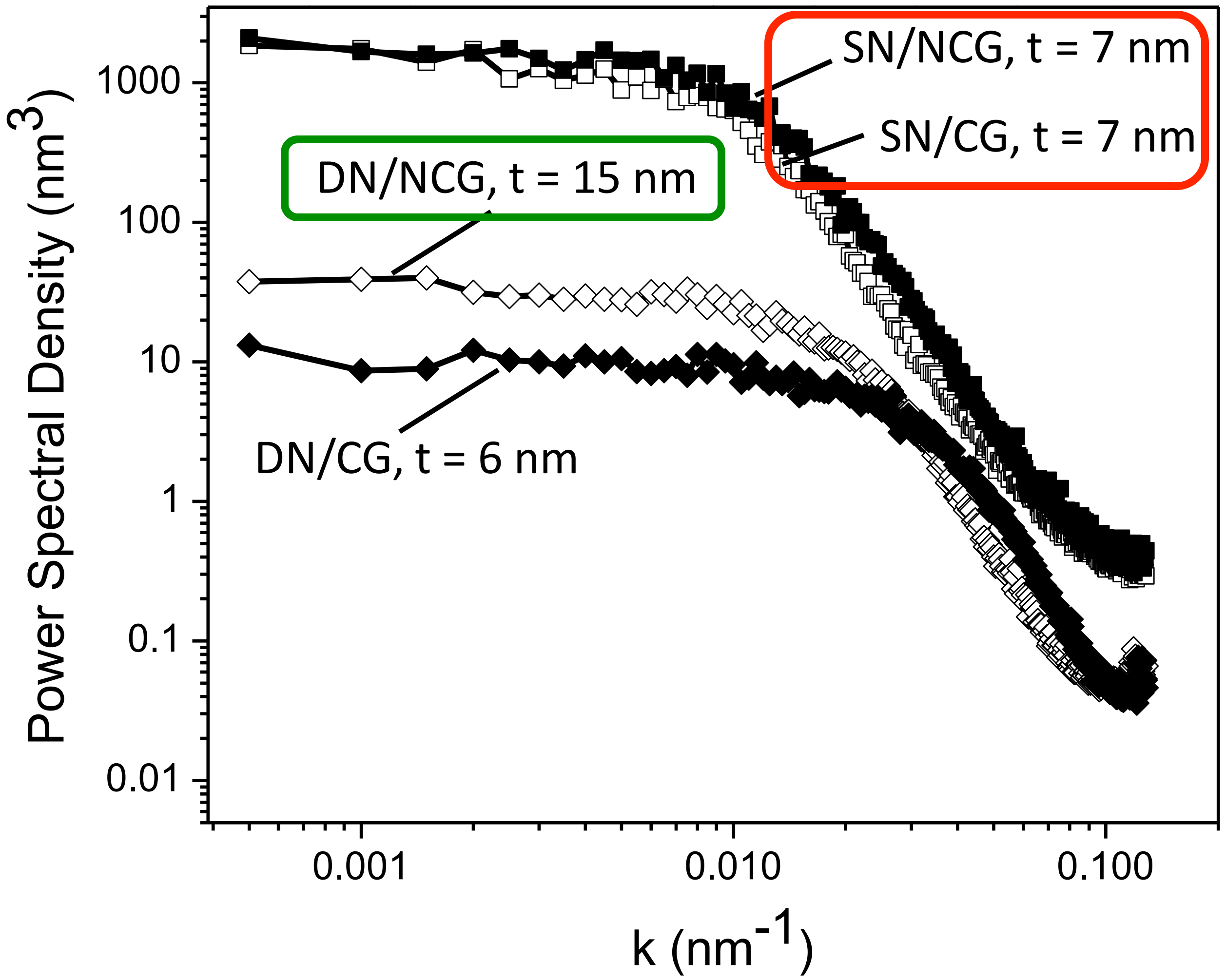
- Measure topography by Atomic Force Microscopy (AFM)
- Compute PSD, the Fourier transform of surface heights *h*

  in reciprocal space *k* :

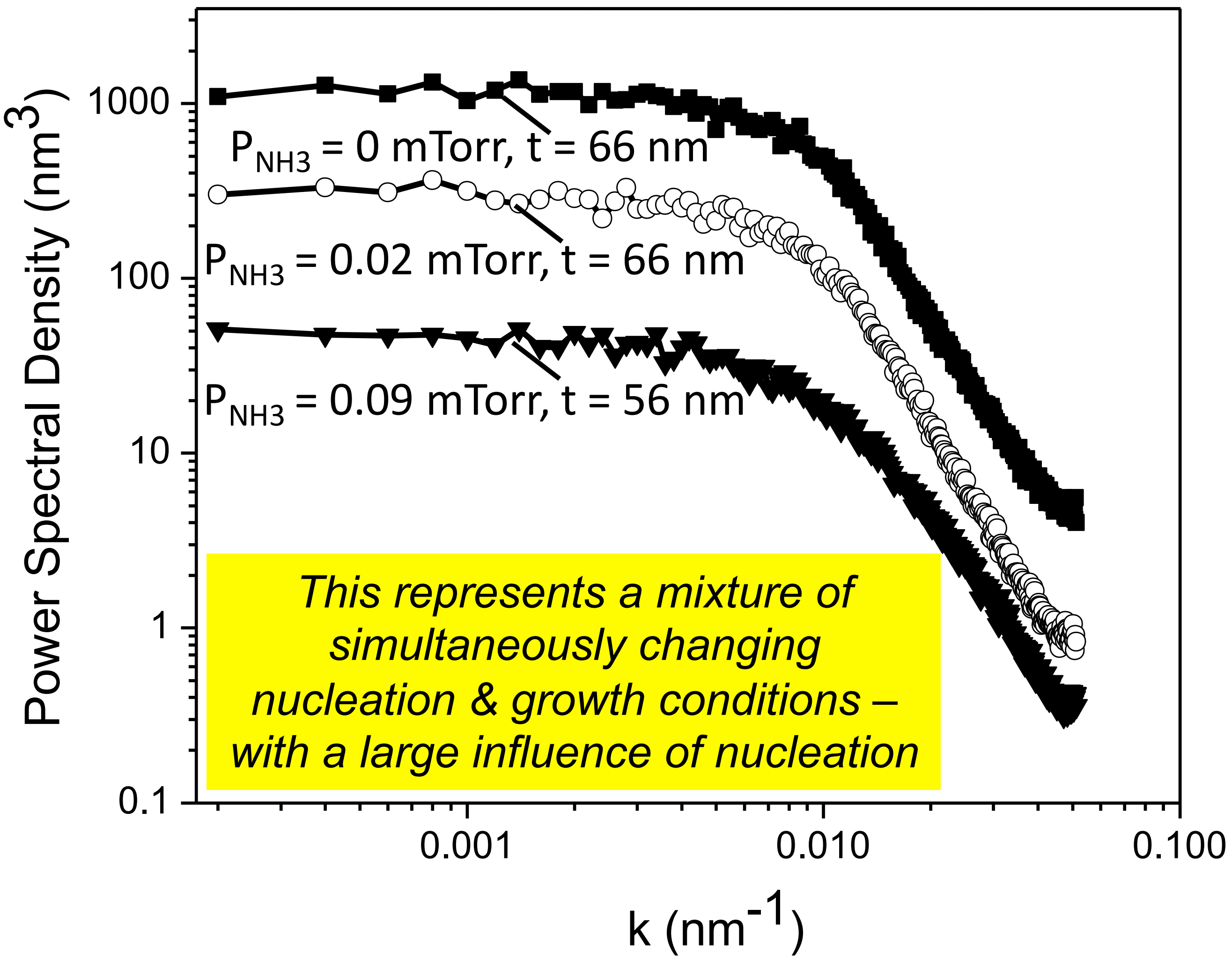
$$P(k) = \left\langle \left| \mathrm{FT}\left[h(\mathbf{x}) \right] \right|^2 \right\rangle_k \qquad \int \mathrm{P(k)dk} = \mathrm{w}^2$$

Use of inhibitor affords independent control of nucleation density and growth conformality

Mixed: Dense Nucleation, *Non-Conformal* Growth vs. Sparse Nucleation, Conformal Growth

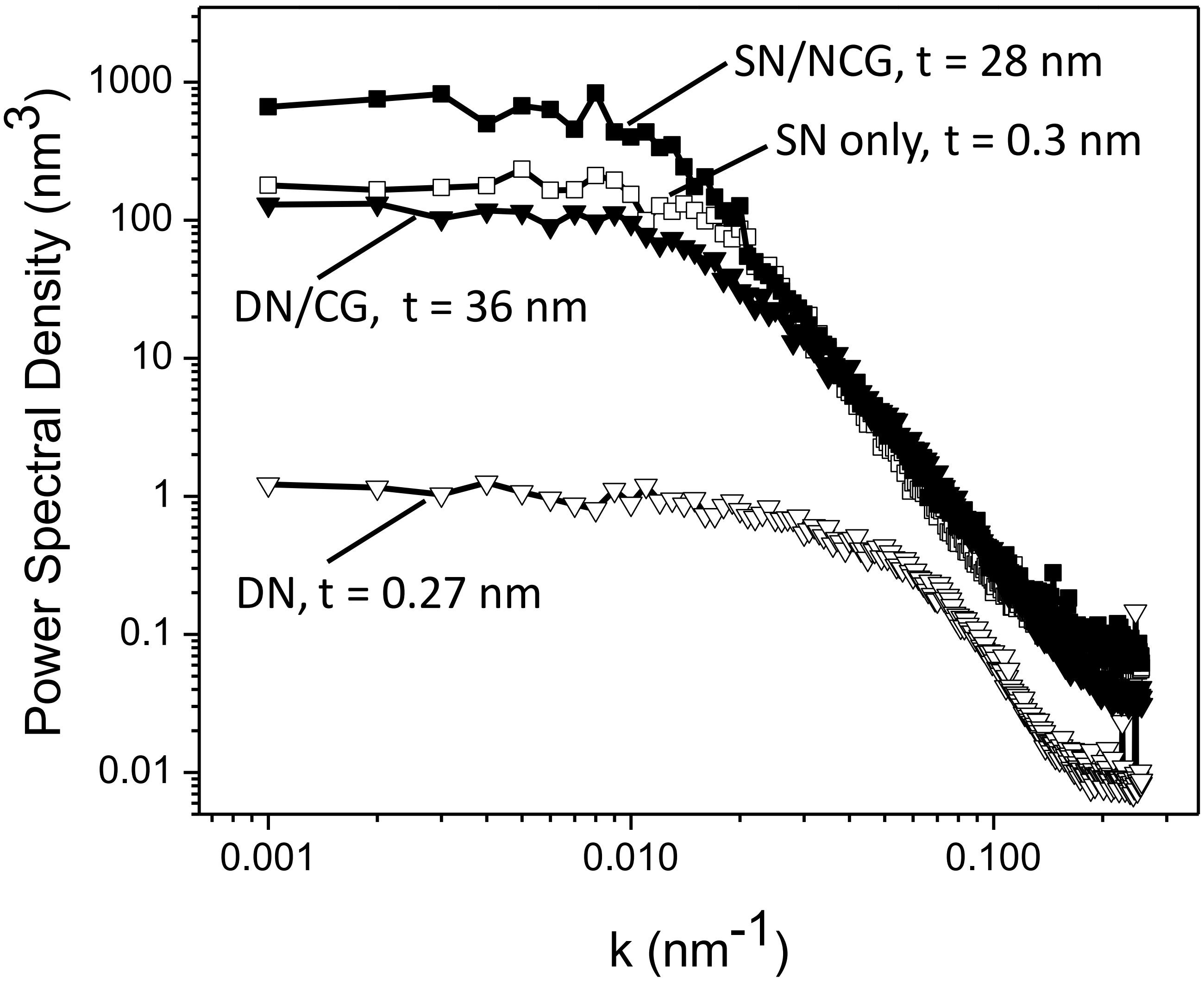


Vary Nucleation and Growth *Together* via Inhibitor Partial Pressure

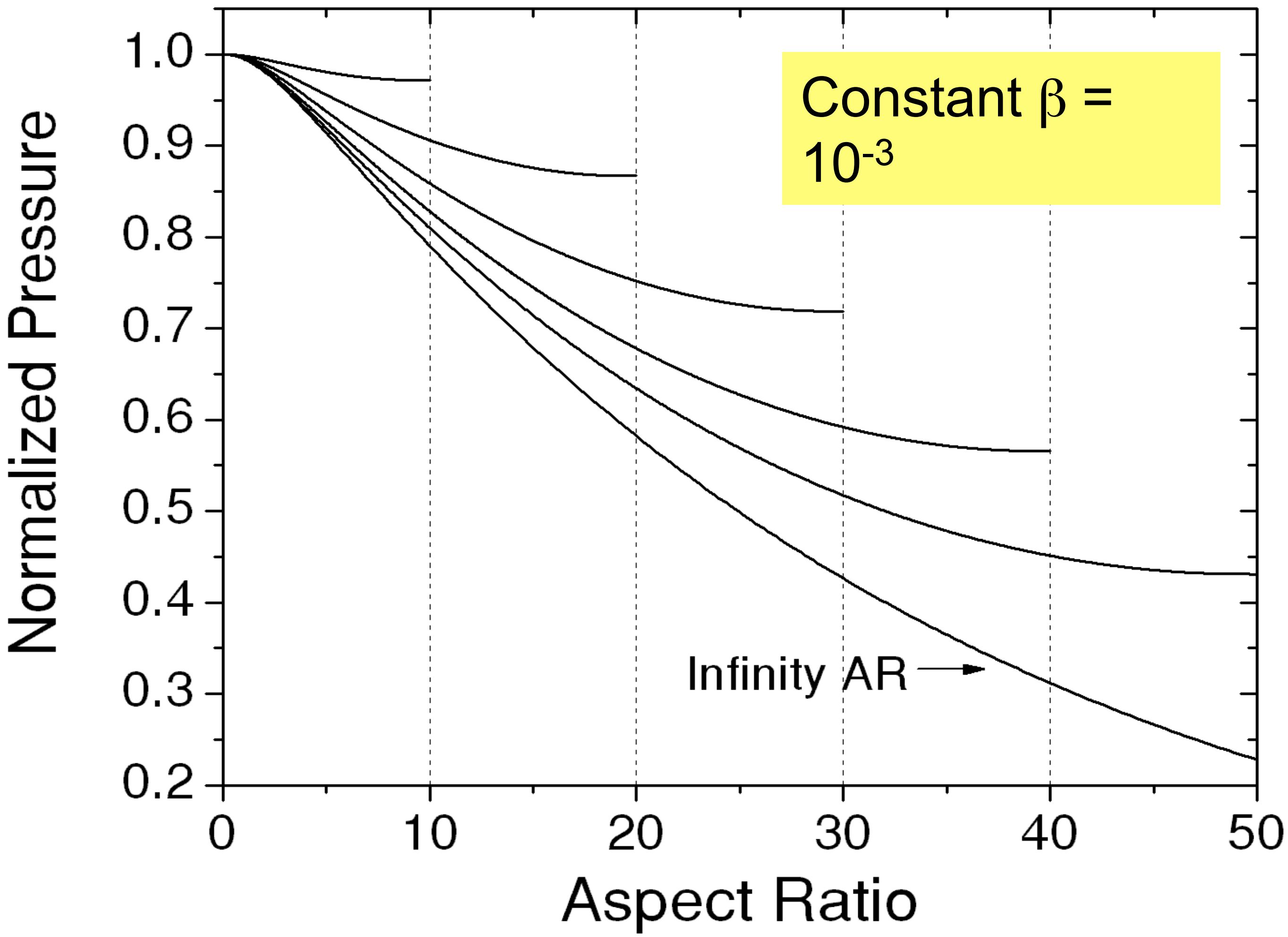


This represents a mixture of simultaneously changing nucleation & growth conditions – with a large influence of nucleation

Extremes: Dense Nucleation, Conformal Growth vs. Sparse Nucleation, Non-Conformal Growth



Note: Conformality improves for shallow ARs



Correspondence

Are the kinetic and Langmuirian models consistent?

$$GR = \frac{K_1(T)\ p}{1 + K_2(T)\ p}$$

$$GR = k_{rxn}\ \ \theta_{ads} = k_{rxn}\ \left[\frac{k_{ads}p}{k_{ads}p + k_{des} + k_{rxn}}\right]$$

Resolution:

- assume k_{rxn} to be small
- ÷ by k_{des}
- $K_1 p = k_{rxn}\, k_{ads} / k_{des}$

Reality Check

Surely someone must have explored inhibition effects before!

YES, but three complications have prevented the general use of inhibition as a means to enhance conformality:

- **The inhibition of hot wall reactions increases the overall transport of reactive intermediates to the substrate**.
Example: TiN growth from TDMAT with DME inhibitor
– *Weiller, Chem. Mat. (1995), JECS (1996)*

- **Re-adsorption of a reaction product (*byproduct inhibition*) occurs readily and depends on gas phase transport.**
Example: TiN growth from TDEAT – *Cale et al., TSF (1993)* or from TDMAT – *Okada & George, Appl. Surf. Sci. (1999)*

- **The inhibition of homogeneous reactions <u>and</u> of surface reactions leads to a complex dependence on geometry.**
Example: SiO_2 growth from TEOS with ethanol inhibitor – *Schlote et al., JECS (1999)*

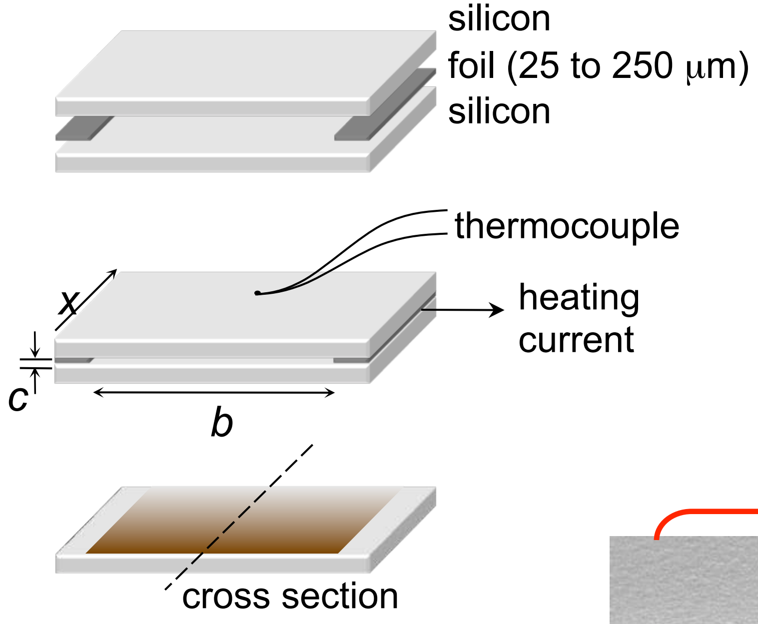
Reality Check

So what is different in the present work using inhibitors?

- Cold wall, low pressure reactor – *no wall or homogeneous reactions.*
- Byproduct inhibition is a weak effect – growth rate is *dominated by the partial pressure of added inhibitor*, which is uniform in the system.

THUS, the experimental behavior can be predicted by a simple model based on *surface reaction-rate control and precursor transport* in a trench*.*

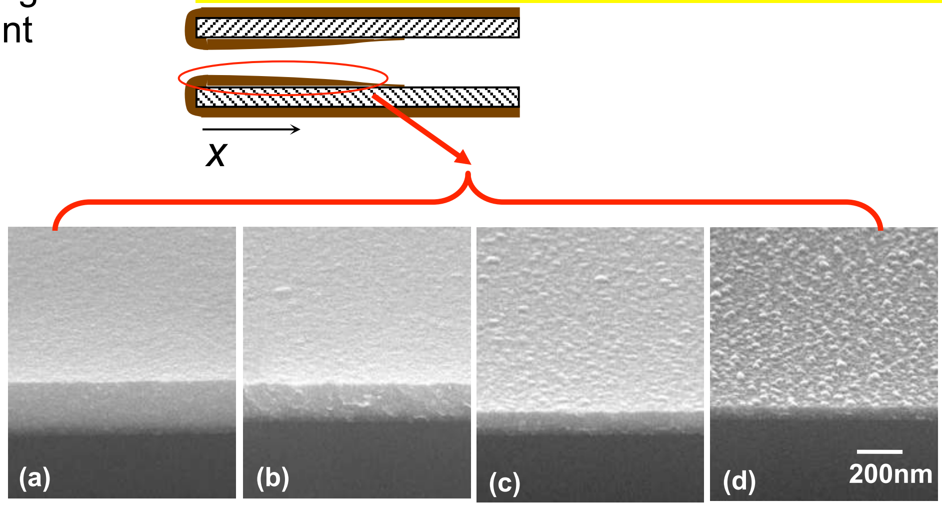
Analyze coverage kinetics using a *Macro-trench*



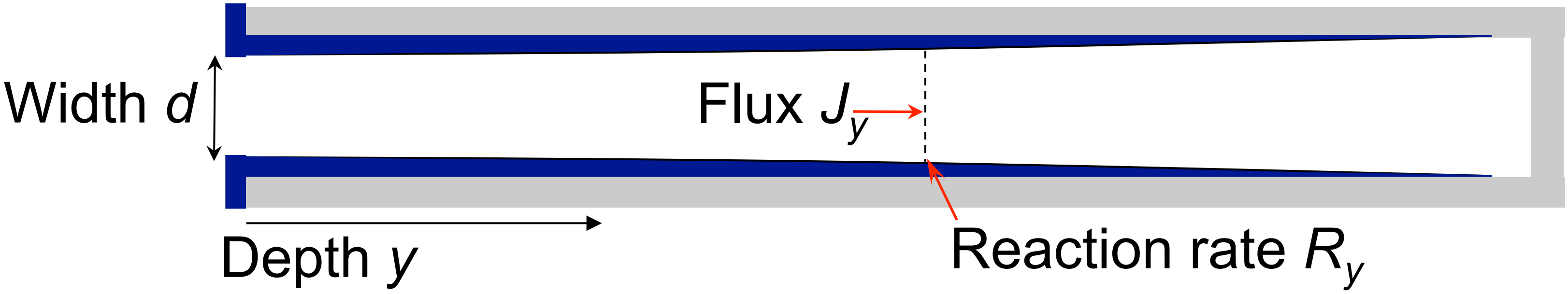
Gas phase λ >> trench dimensions

No pinch-off

High d/w → analytic model



Growth kinetics : Solve the continuity equation



Mass balance

$$\frac{dJ}{dy} = \frac{2R_{growth}}{d}$$

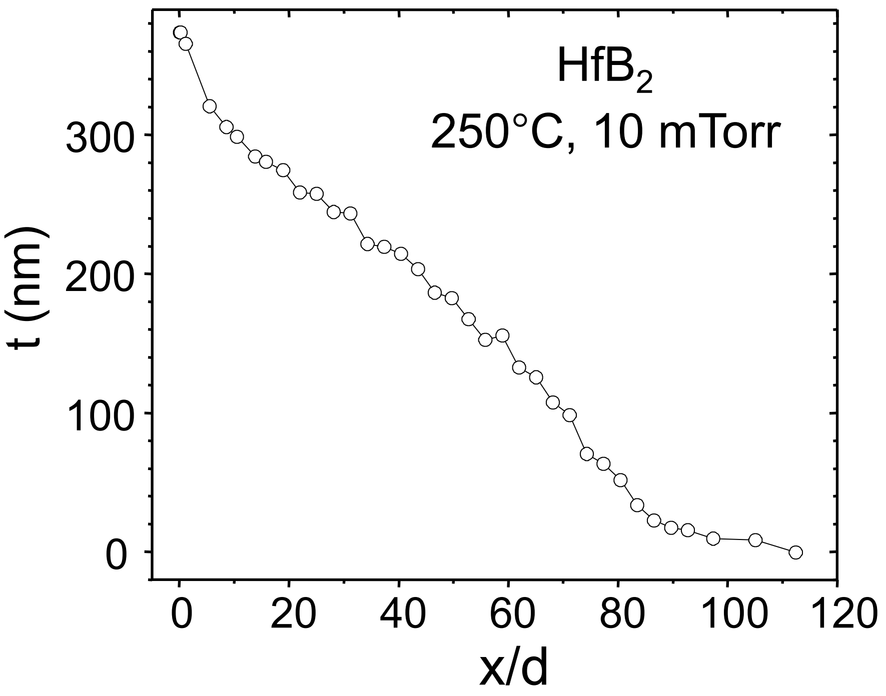
Precursor diffusion

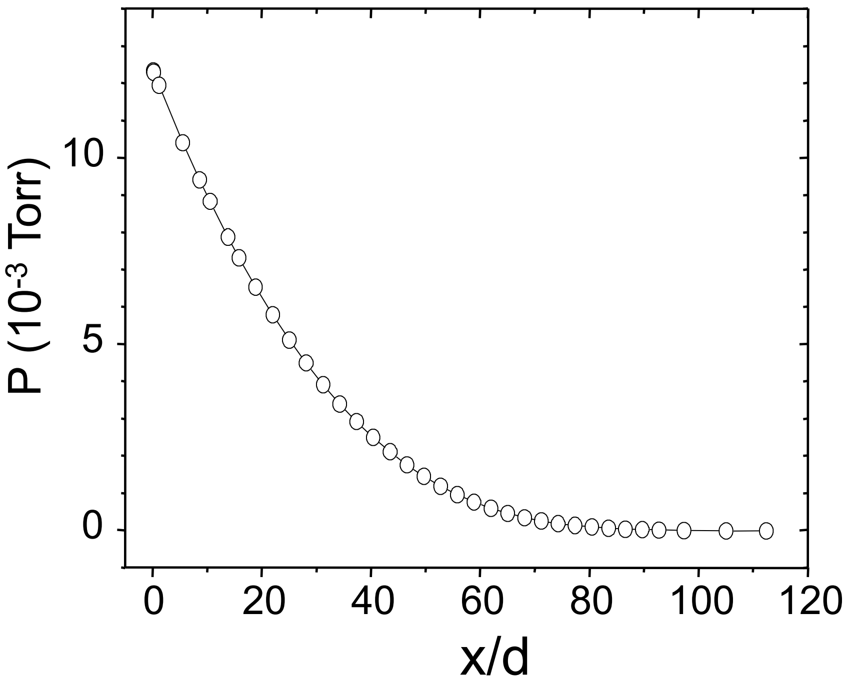
$$J(y) = \frac{D}{kT}\frac{dP}{dy}$$

Molecular flow

$$D = 9708\ d\ \left(\frac{T}{M}\right)^{1/2}$$

Film thickness → Growth flux → Pressure distribution





Growth rate decreases with precursor pressure

as expected due to adsorption saturation