Step Coverage by ALD Films: Theory and Examples of Ideal and Non-Ideal Reactions

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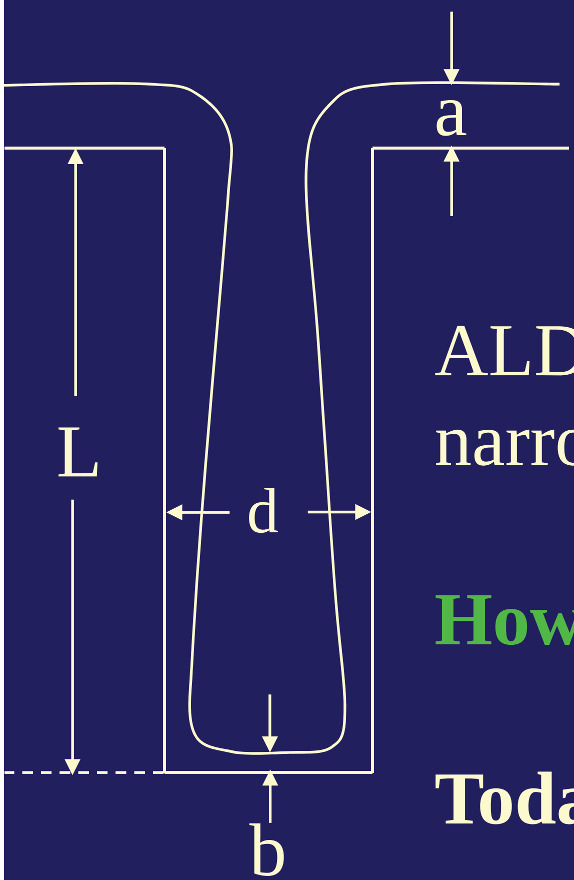
Step Coverage in Holes with High Aspect Ratio



Step coverage = (b/a) x 100%

Aspect ratio = L/d

ALD can give 100% step coverage even in narrow holes with high aspect ratio.

How high an aspect ratio can be coated?

Today: Theoretical and experimental answers

Outline

Theory of Step Coverage in ALD

- assumptions
- formulas for step coverage

Examples of Ideal Reactions

Non-ideal characteristics of some ALD reactions

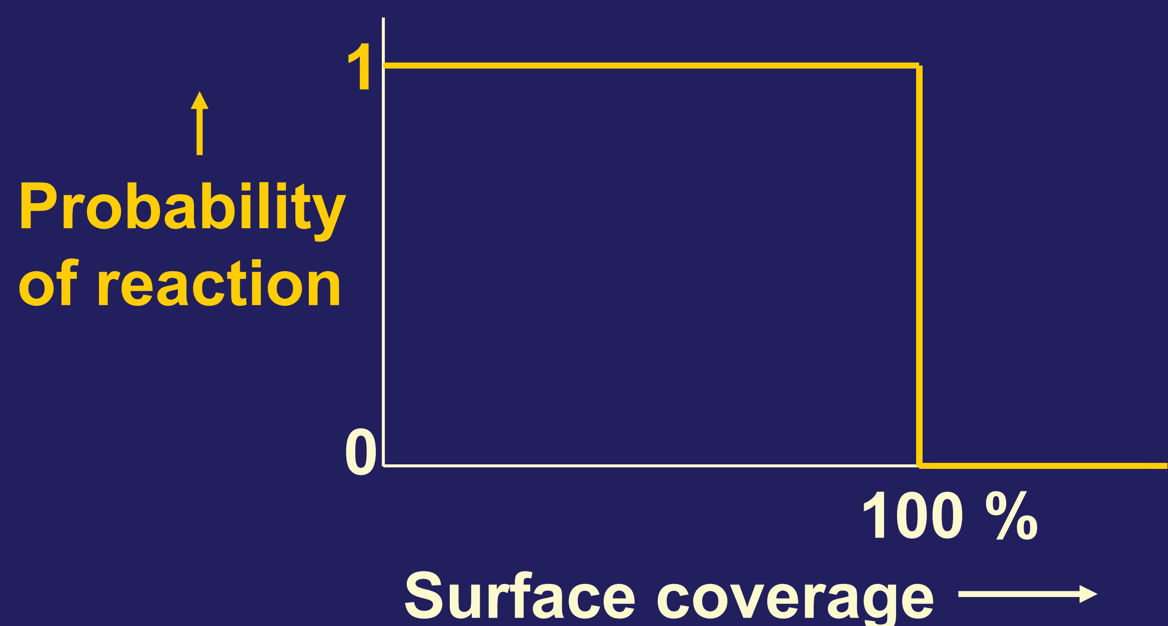
- thermal decomposition
- plasma-radical recombination
- adsorption of reactants into film
- competitive adsorption of byproducts
- etching by reactants or byproducts

Fast Self-Limiting Surface Reactions

Simplifying assumptions:

- Precursor molecules react with probability 1 on each collision with the surface until all reactive sites are filled.

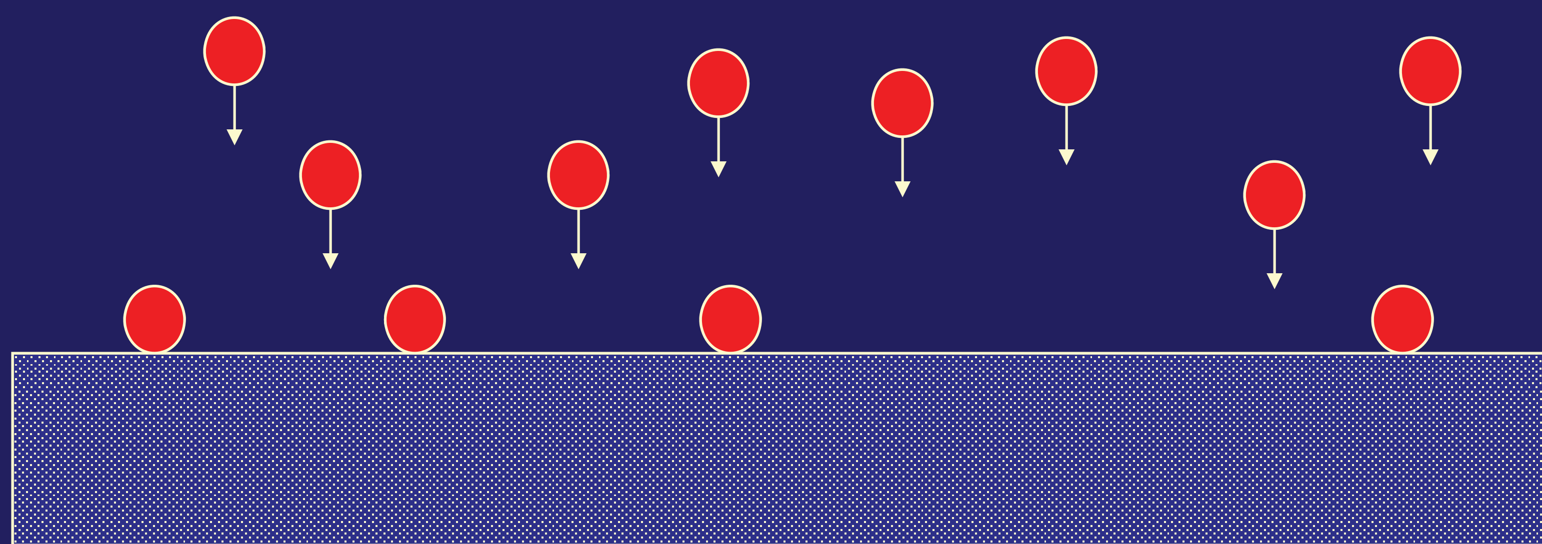
- After all sites have reacted, additional precursor molecules scatter diffusely from the surface.



Deposition on Flat Surfaces

Requirements for Saturation of a Surface Reaction:

1. Minimum **number** of precursor molecules (stoichiometry).
2. Minimum **number of collisions** with surface needed to bind this number of precursor molecules to surface (kinetics).

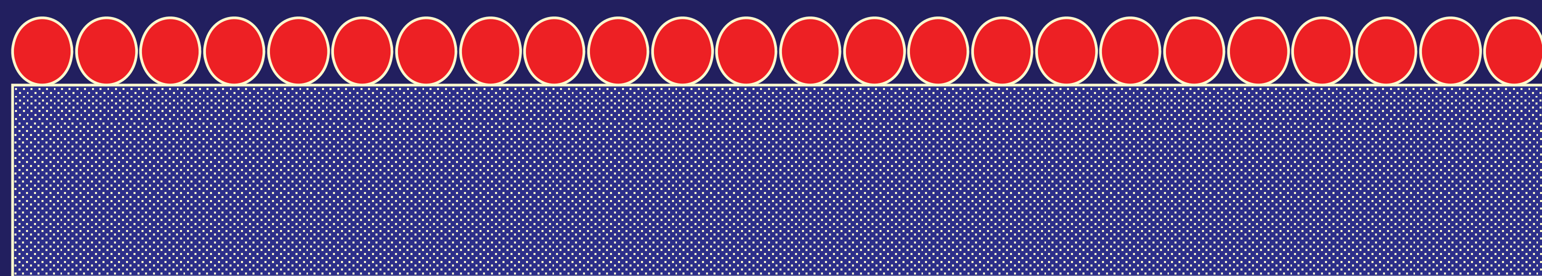


How Many Molecules Saturate a Flat Surface?

S = area density of precursor molecules chemisorbed per m^2:

- X-ray reflectivity (XRR): density×thickness
- Rutherford Backscattering (RBS): integration of peak
- Quartz Crystal Microbalance (QCM)

For example, ALD of 0.1 nm/cycle of HfO_2, density 9.23 g/cm^3, requires $S_{Hf} = 2.5\times10^{18}$ Hf atoms/m^2/cycle

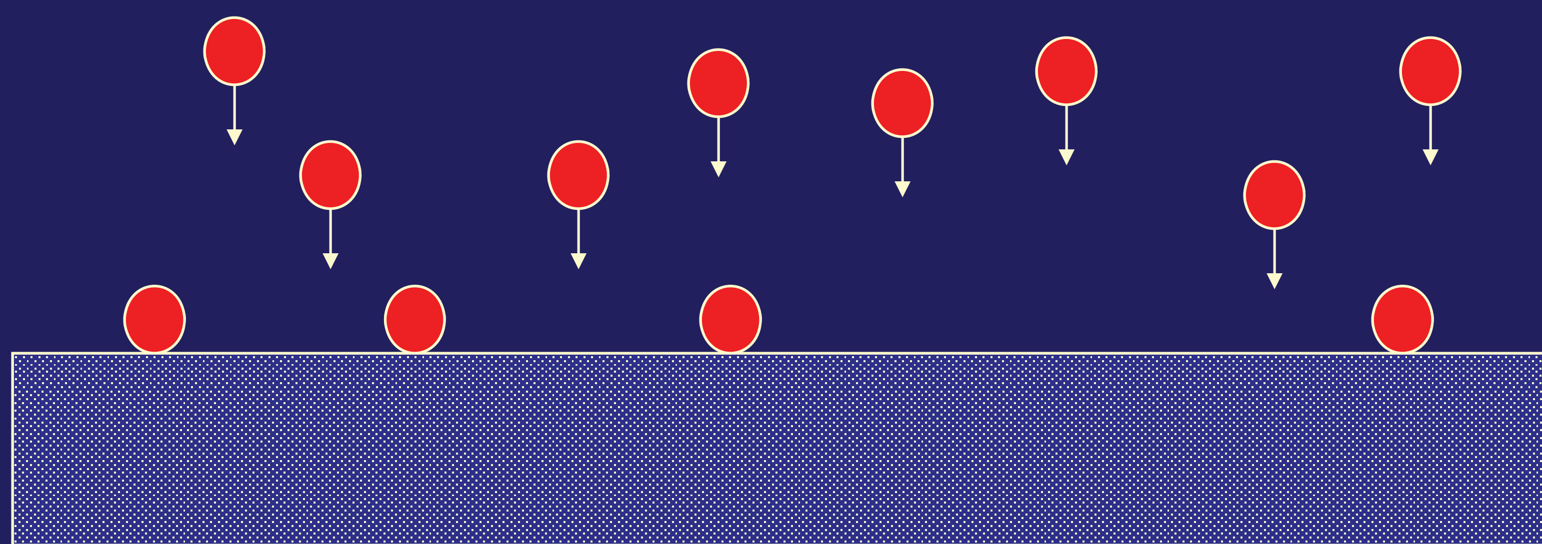


Minimum Time Needed to Saturate Flat Surface

From kinetic theory, Flux $J = P\,(2\pi mkT)^{-1/2}$

Minimum time = Δt = area density/flux = $S / J = S(2\pi mkT)^{1/2}/P$

"Exposure" needed for saturation = $(P\Delta t) = S(2\pi mkT)^{1/2}$



Examples of Fast Self-Limiting Reactions

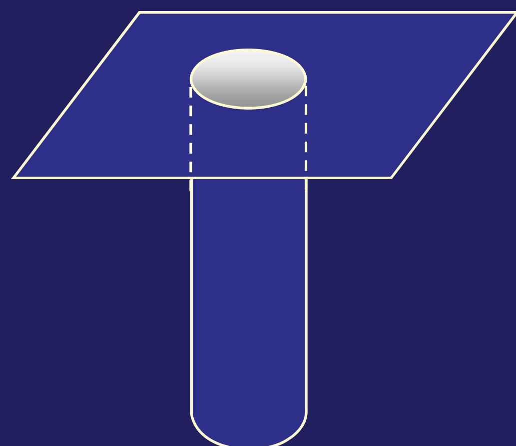
$$(Pt)_{flat} = S(2\pi mkT)^{1/2}$$

precursor	S ($10^{18} m^{-2}$)	M (amu)	T (K)	$(Pt)_{flat}$ (10^{-6} Torr-sec)
Me_3Al	4.4	62	573	2.3
$Hf(NMe_2)_4$	2.5	411	473	3.1
$W(NMe_2)_2(N^tBu)_2$	3.6	414	623	5.2
$La((^iPrN)_2CMe)_3$	2.3	563	573	3.7

Deposition in High-Aspect Ratio Holes

N_{hole} = Additional precursor molecules required for surface area of hole

$(\Delta t)_{hole}$ = Additional time required to saturate surface area of hole



For the following derivation, see Roy G. Gordon, Dennis Hausmann, Esther Kim and Joseph Shepard, *Chemical Vapor Deposition* 9, 73 (2003)

How Many Molecules for 100% Step Coverage?

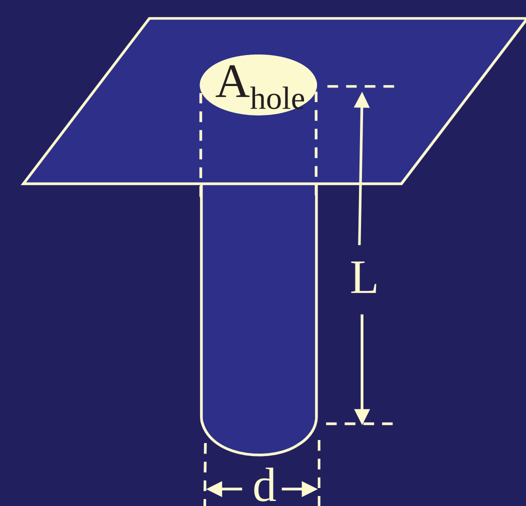
N_{wall} = number of precursor molecules needed to coat wall

$$N_{wall} = S\,Area_{wall} = SA_{hole}\left(\frac{L\pi d}{\frac{1}{4}\pi d^2}\right) = S\,A_{hole}4\left(\frac{L}{d}\right)$$

(define aspect ratio = **a** = L/d = length / diameter)

$$N_{wall} = SA_{hole}4\mathbf{a}$$

If many more molecules
than N_{wall} are available,
then P = constant



Additional Exposure is Also Needed

"Exposure" (in Langmuirs) = time (in micro-seconds) multiplied by precursor partial pressure (in Torr) present at the open end of the hole.

If the precursor concentration varies in time, then the exposure is defined by

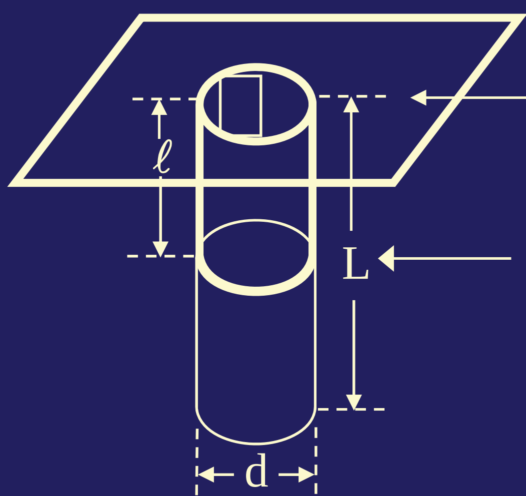
$$\text{Exposure} \equiv \int_0^t P(t')\,dt'$$

We will show that a certain <u>minimum exposure</u> is required for 100% step coverage of a hole.

How Much Additional Exposure is Needed?

Since hole diameter (~100 nm) << mean free path (~ 100 μm), flow regime in a hole is molecular (Knudsen diffusion)

The uncoated lower portion of a hole acts as an ideal vacuum pump:



Flux at entrance to hole = $P(2\pi mkT)^{-1/2}$

Flux at this point reduced by $[1 + (\tfrac{3}{4}\,\ell/d)]^{-1}$

(compare to cryopump at the end of a pipe)

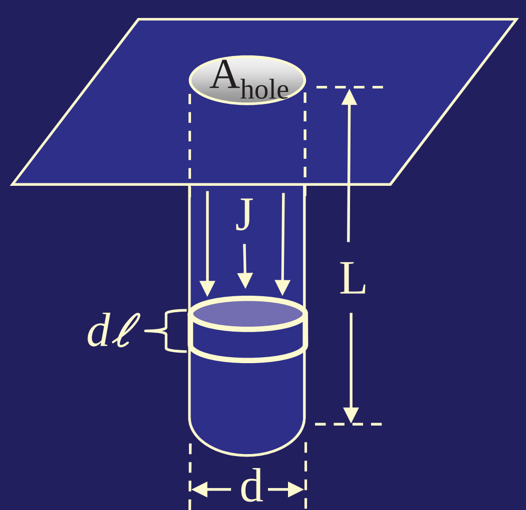
thus $J(\ell) = P(2\pi mkT)^{-1/2}\,[1 + (\tfrac{3}{4}\,\ell/d)]^{-1}$

or $(P/J) = (2\pi mkT)^{1/2}\,[1 + (\tfrac{3}{4}\,\ell/d)]$

Additional Exposure to Coat Walls of a Hole

How much time (dt) is required for enough molecules to diffuse down the coated upper part of a hole to coat an incremental distance ($d\ell$) of the hole?

$$dt = \frac{d(molecules)}{\text{transport rate}} = \frac{S\,d(A_{wall})}{J A_{hole}} = \frac{S\,(\pi d\, d\ell)}{J\,(\frac{1}{4}\pi d^2)} = \left(\frac{4S}{Jd}\right) d\ell$$



$$\text{Exposure} \equiv \int_0^t P\, dt' = P\Delta t$$

$$= (4S/d)\int_0^L d\ell (P/J)$$

Integrate to Find Exposure for Coating Hole

$$(P\Delta t)_{walls} = S(2\pi mkT)^{1/2}\int_0^L d\ell\left[(4/d)+(3/d^2)\right]$$

$$= S(2\pi mkT)^{1/2}\left[4(L/d)+(3/2)(L/d)^2\right]$$

$$= S(2\pi mkT)^{1/2}\left[4a+(3/2)a^2\right]$$

A similar calculation for coating the bottom after the walls are completely coated, gives

$$(P\Delta t)_{bottom} = S\,(2\pi mkT)^{1/2}\,[1 + (3/4)a]$$

Add to get the total exposure for coating both bottom & walls:

$$(P\Delta t)_{total} = S\,(2\pi mkT)^{1/2}\,[1 + (19/4)a + (3/2)a^2]$$

Exposure Needed to Cover a Hole

$$(P\Delta t)_{total} = S\,(2\pi mkT)^{1/2}\,[1 + (19/4)\,a + (3/2)\,a^2]$$

For large aspect ratio a, the a^2 term dominates

$$\text{Exposure } (P\Delta t)_{total} \sim S\,(2\pi mkT)^{1/2}\,(3/2)\,a^2$$

The required exposure increases as the <u>square</u> of the <u>aspect ratio</u>.

$$\text{aspect ratio } a \sim S^{-1/2}(9\pi mkT/2)^{-1/4}\,(\text{exposure})^{1/2}$$

where S = saturation density (from growth per cycle)
m = molecular mass of precursor
k = Boltzmann's constant
T = temperature (K)
$P\Delta t$ = exposure

Minimum Exposure for Conformal Coating

Since $(P\Delta t)_{flat} = S\,(2\pi mkT)^{1/2}$
we can write the exposure as

$$(P\Delta t)_{hole} = (P\Delta t)_{flat}\ \{1 + (19/4)a + (3/2)a^2\}$$

$$\sim (P\Delta t)_{flat}\,(3/2)a^2 \quad \text{for } a >> 1$$

$$a \approx \left(\frac{2 \times \text{exposure for hole}}{3 \times \text{exposure for flat}}\right)^{1/2} \quad \text{for } a >> 1$$

where a = aspect ratio = L/d for a circular hole

Optical Measurement of Step Coverage

Use a test structure with very high aspect ratio hole:

Fused silica capillary tubing with 20 μm inner diameter.

2 cm length gives a hole with 1000:1 aspect ratio.

Mean free path at 200 ^{o}C, 0.2 Torr is 400 μm >> 20 μm; transport is by molecular diffusion as in smaller features.

Image interference pattern with optical microscope

ALD of Tantalum Oxide from $Ta(NMe_2)_5$

Reaction: $2\ Ta(NMe_2)_5 + 5\ H_2O \rightarrow Ta_2O_5 + 10\ Me_2NH$

- Also done with other tantalum alkylamides:
  (*tert*-butylimido)tris(diethylamido)tantalum

- Deposition initiates immediately on hydroxylated surfaces

- ALD rate: about 0.07 nanometers per cycle

- Ideal ALD behavior from 150 to 250 ^{o}C

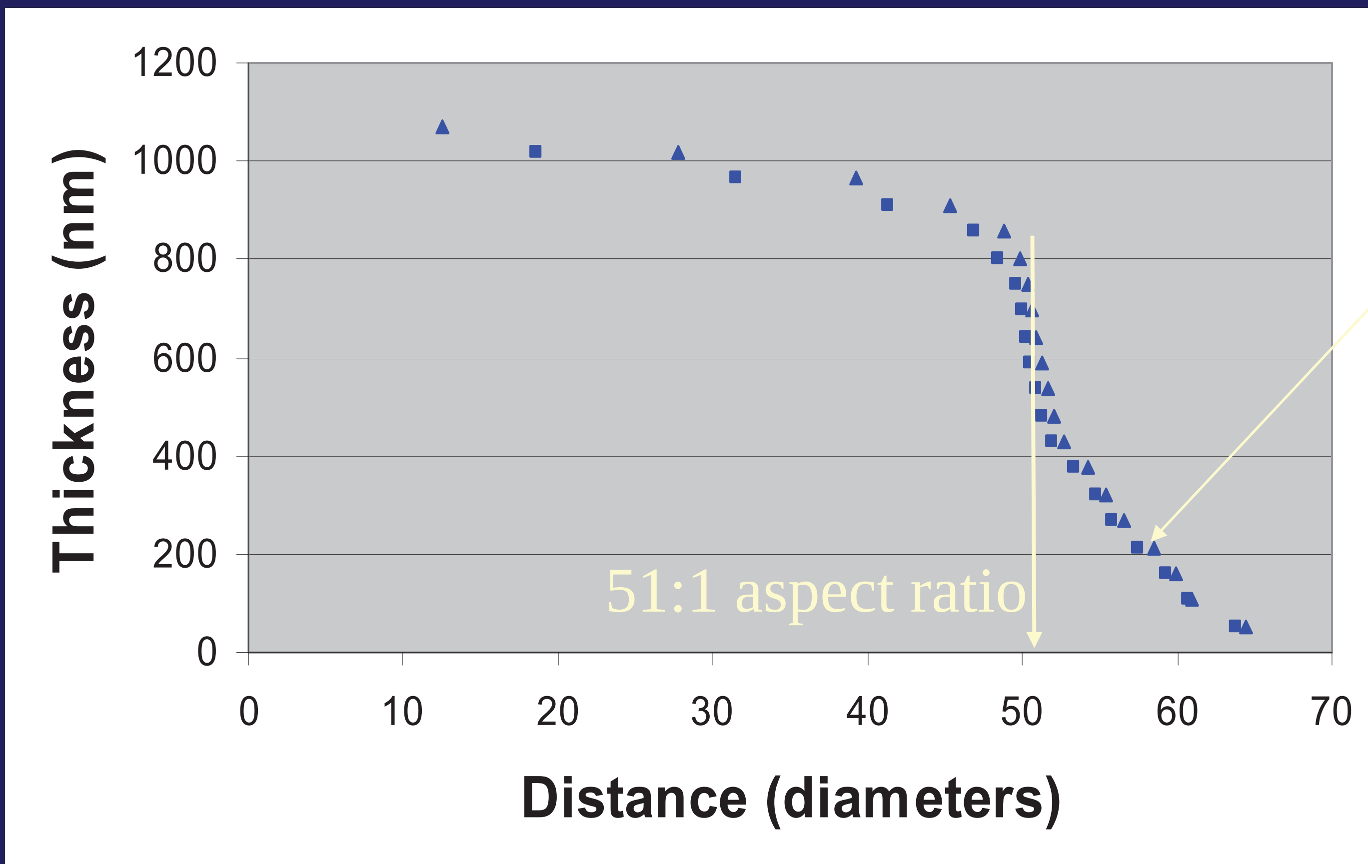
- Yield near 100%

Measurement of Step Coverage

ALD Ta_2O_5 coating 1 μm thick inside 20 μm tubing

Measurement of Step Coverage

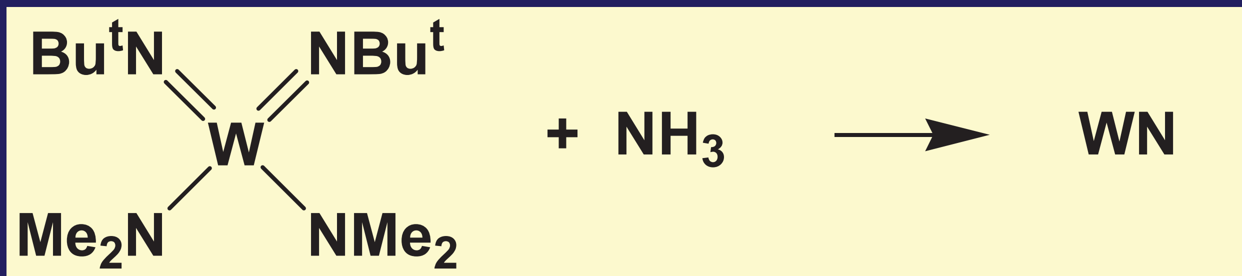
Distribution of ALD Ta_2O_5 coating thickness inside micro-bore capillary tubing



Tail due to sticking coefficient < 100%,

and to narrowing of diameter from 20 μm to 18 μm

ALD of Metallic WN



Bis(*tert*-butylimido)bis(dimethylamido)tungsten, volatile liquid precursor

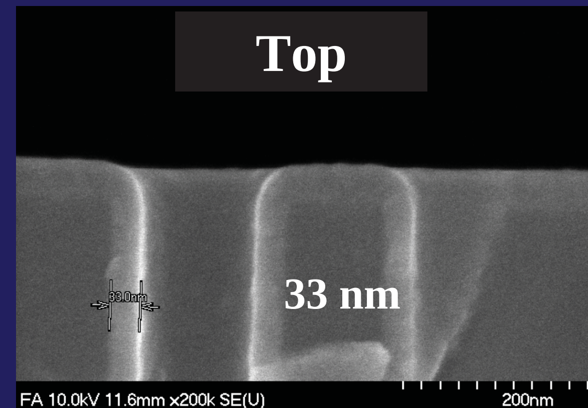
ALD of amorphous tungsten(III) nitride at 270-380 °C

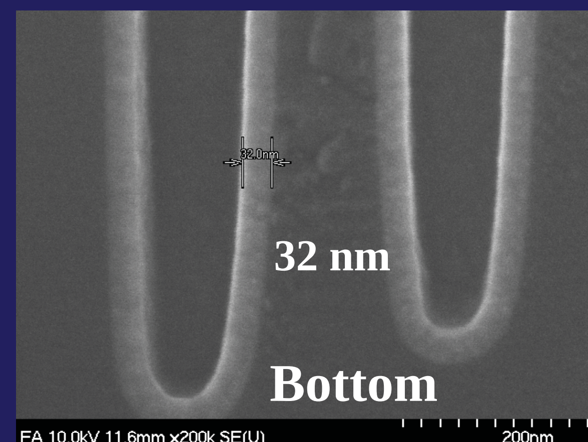
0.1 nm/cycle at 350 °C

Step Coverage of WN

Uniform coverage in holes

with 43:1 aspect ratio





Experimental exposure

2.1 x 10^{-2} Torr-sec / cycle

Theoretical minimum exposure =

$(5.2 \times 10^{-6}) \times \{1 + (19/4)43 + (3/2)43^2\} = 1.5 \times 10^{-2}$ Torr-sec

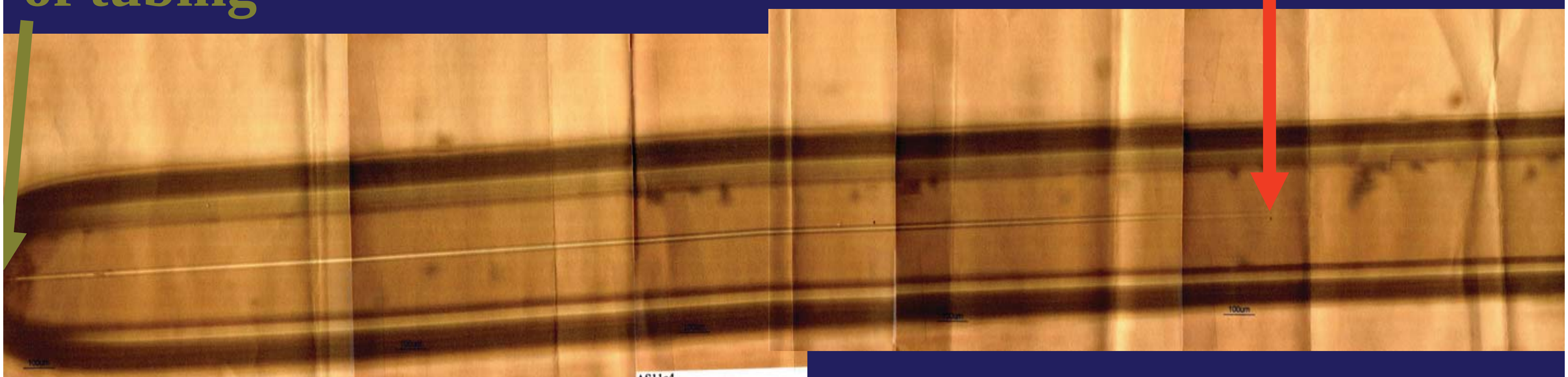
2.1 > 1.5, so complete step coverage predicted and observed

Step Coverage in High Aspect Ratio Holes

ALD WN coating 40 nm thick inside fused silica capillary tubing with 20 micron inner diameter

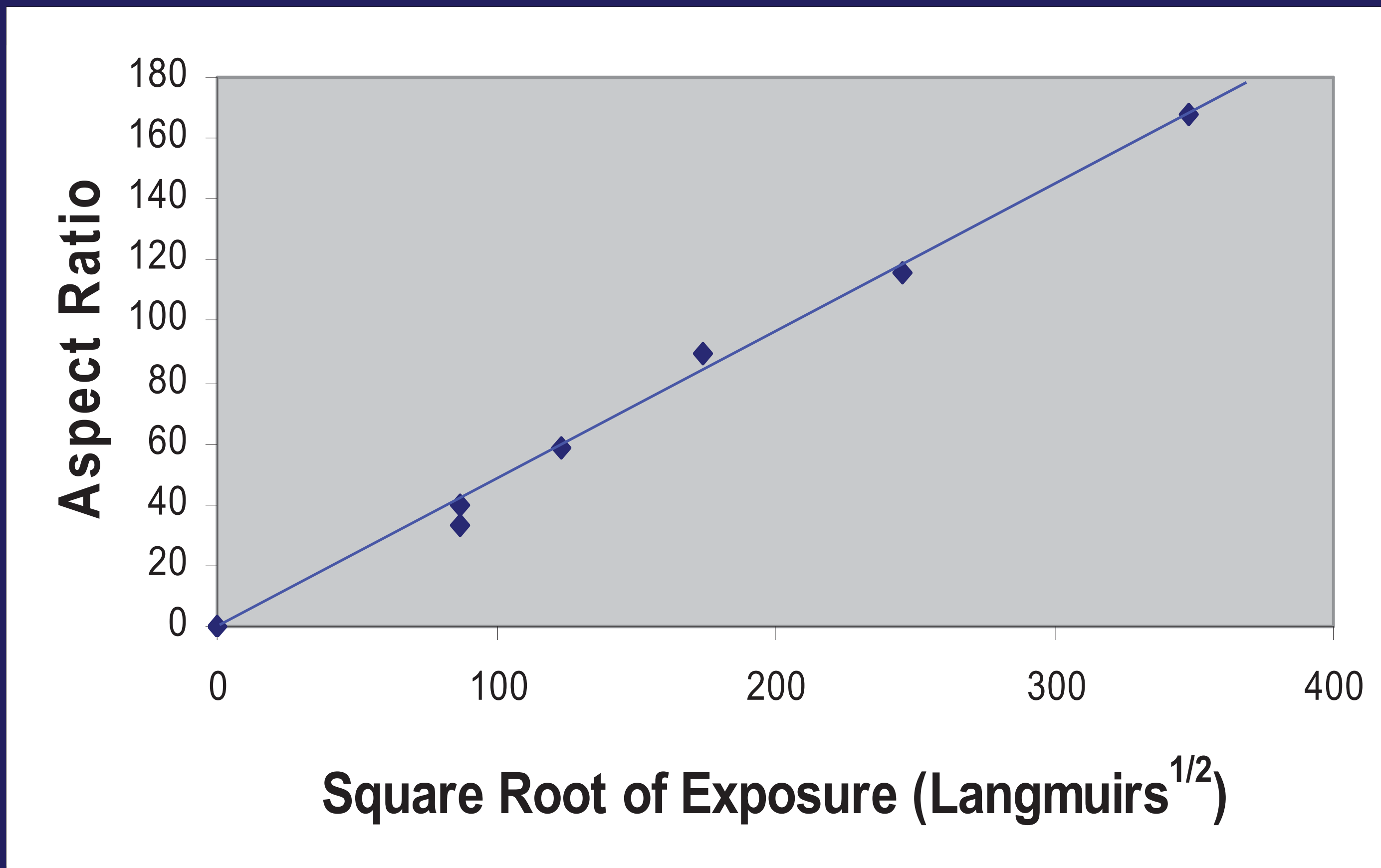
Open end of tubing

End of coating, 210 diameters in



ALD WN Step Coverage vs. Exposure

Aspect ratio $= S^{-1/2}(9\pi mkT/2)^{-1/4}$ $(\text{exposure})^{1/2}$



ALD of Al_2O_3 from TMA and water

Computer simulations of step coverage for the ALD reaction

$$2\ Me_3Al + 3\ H_2O \Rightarrow Al_2O_3 + 6\ CH_4$$

carried out at Infineon (now Qimonda) agree completely with experiments and with the simple formula:

$$(Pt)_{hole} = S(2\pi mkT)^{1/2} \times \{1 + (19/4)a + (3/2)a^2\}$$

$$= (2.3 \times 10^{-6}\ \text{Torr-sec}) \times \{1 + (19/4)a + (3/2)a^2\}$$

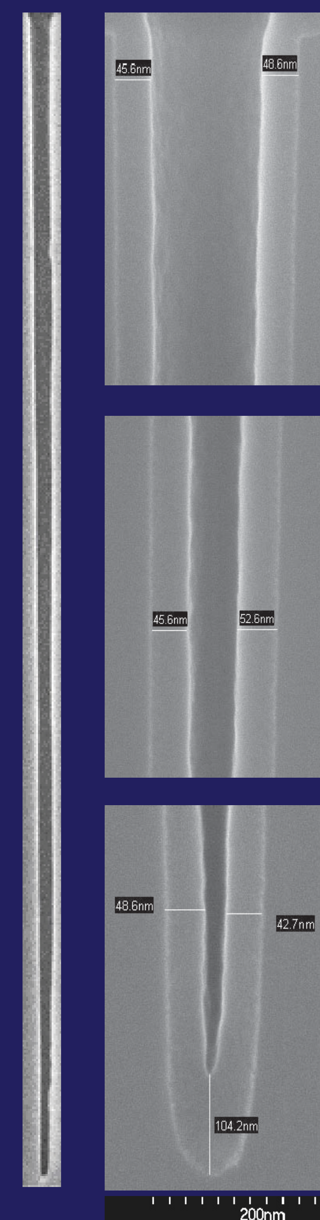
Step Coverage of ALD SiO_2

Aluminum-catalyzed deposition of SiO_2

from tris(*tert*-butoxy)silanol

For high exposures of the silanol, the step coverage is limited by the aluminum from the reaction of Me_3Al.

For a = 43, the Me_3Al exposure must be $> (2.3 \times 10^{-6}$ Torr-sec$) \times \{1 + (19/4)43 + (3/2)43^2\} = 7 \times 10^{-3}$ Torr-sec

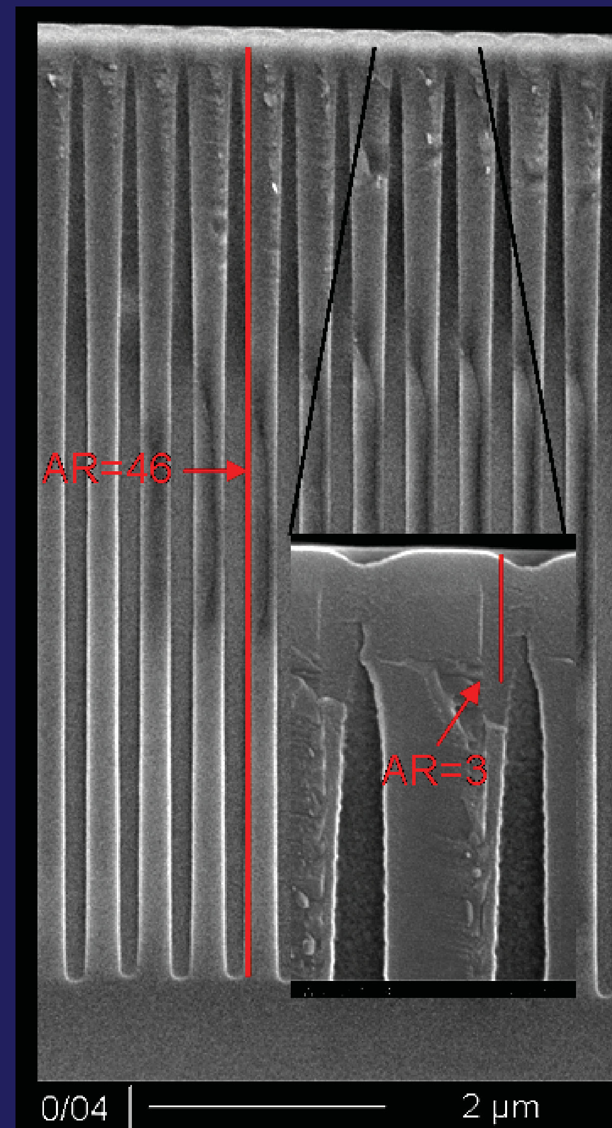


Partial Step coverage of ALD SiO_2

For very small Me_3Al exposures,

~ 6 x 10^{-5} Torr-sec,

the silica deposition is confined to just the top of the holes a ~ 3



Exposure(hole)/exposure(flat) = $6 \times 10^{-5} / 2.3 \times 10^{-6} = 26$

$1 + (19/4)a + (3/2)a^2 = 29$ for a = 3

ALD of Hafnium Oxide from $Hf(NMe_2)_4$

Reaction: $Hf(NMe_2)_4 + 2\ H_2O \rightarrow HfO_2 + 4\ Me_2NH$

- Also done with other hafnium alkyl amides:
  Diethyl amide (NEt_2) and Ethylmethyl amide (NMeEt)

- Deposition initiates immediately on hydroxylated surfaces

- ALD rate: about 0.1 nanometers per cycle

- Ideal ALD behavior from 50 to 350 ^{o}C

- Yield near 100%

Step Coverage of HfO_2

Uniform coverage only down to aspect ratio a = 32:1

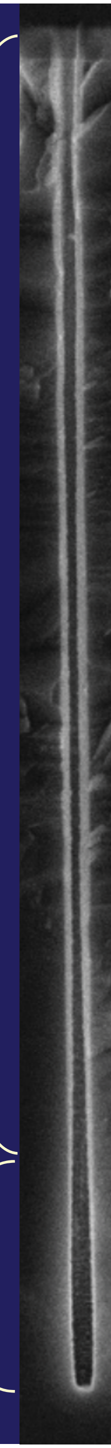
Experimental exposure

4×10^{-3} Torr-sec / cycle

Theoretical exposure

$= (3 \times 10^{-6}) \times \{1 + (19/4)32 + (3/2)32^2\}$

$= 5 \times 10^{-3}$ Torr-sec



Step Coverage of ALD HfO_2

Uniform coverage over

aspect ratio a = 43:1

Experimental exposure

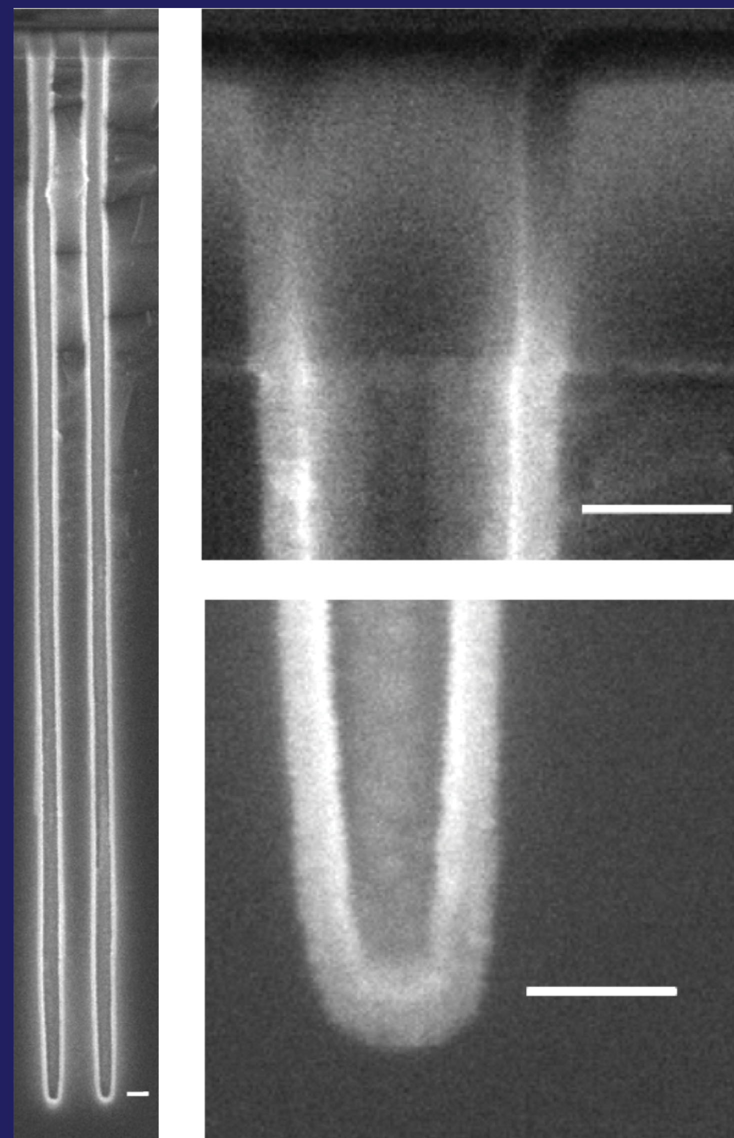
30 x 10^{-3} Torr-sec / cycle

Theoretical min. exposure

$= (3.6 \times 10^{-6}) \times \{1 + (19/4)43 + (3/2)43^2\}$

$= 11 \times 10^{-3}$ Torr-sec

30 > 11, so complete coverage predicted and observed



top

bottom

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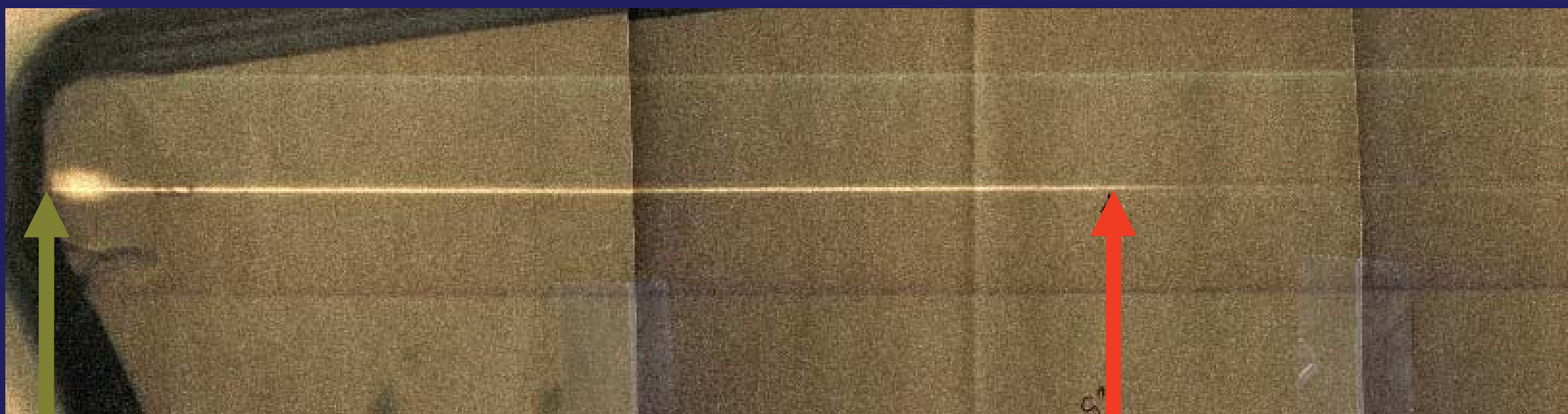
Step Coverage in High Aspect Ratio Holes

ALD HfO_2 coating 80 nm thick inside fused silica capillary tubing with 20 micron inner diameter



Open end of tubing

~ End of coating, 81 diameters in

Predicted aspect ratio

$$a = \left[\frac{2(P\Delta t)_{experimental}}{3(P\Delta t)_{flat}}\right]^{1/2} = \left[\frac{2\times 30\times 10^{-3}}{3\times 3.1\times 10^{-6}}\right]^{1/2} = 80$$

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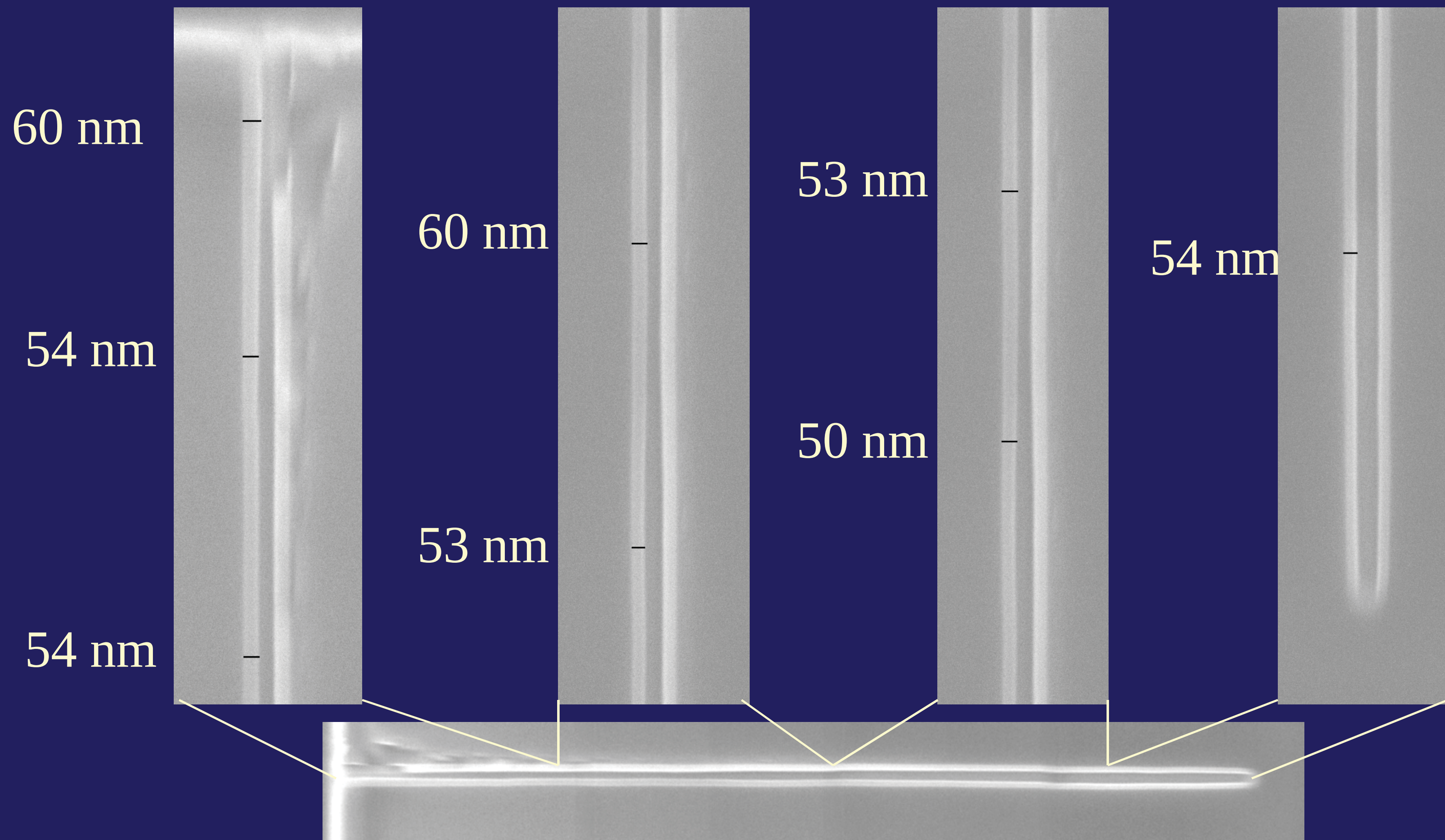
ALD of $LaAlO_3$ with high exposures

$LaAlO_3$ Film 57nm thick by ellipsometer on flat surface



42:1 aspect ratio (initially)

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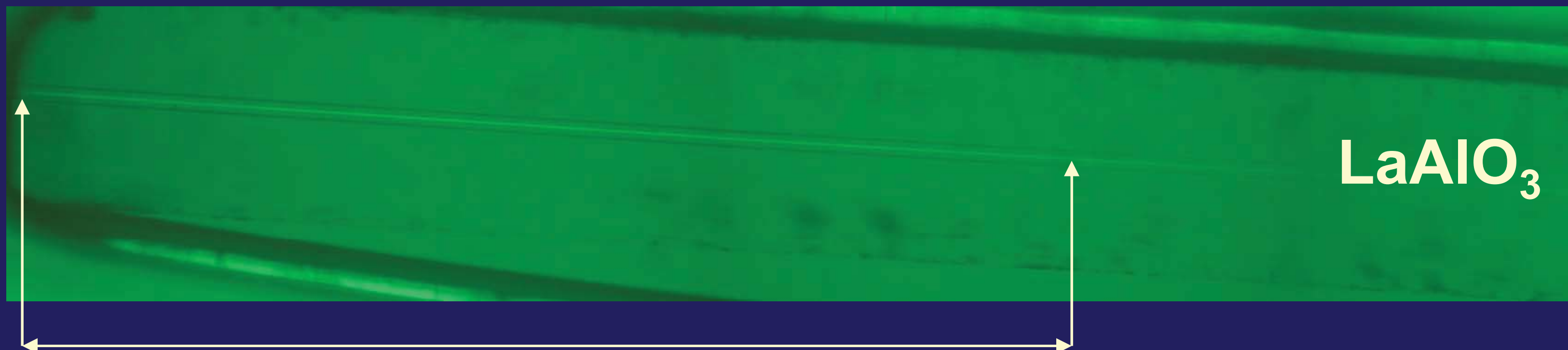
Capillary Test for Very High Aspect Ratios

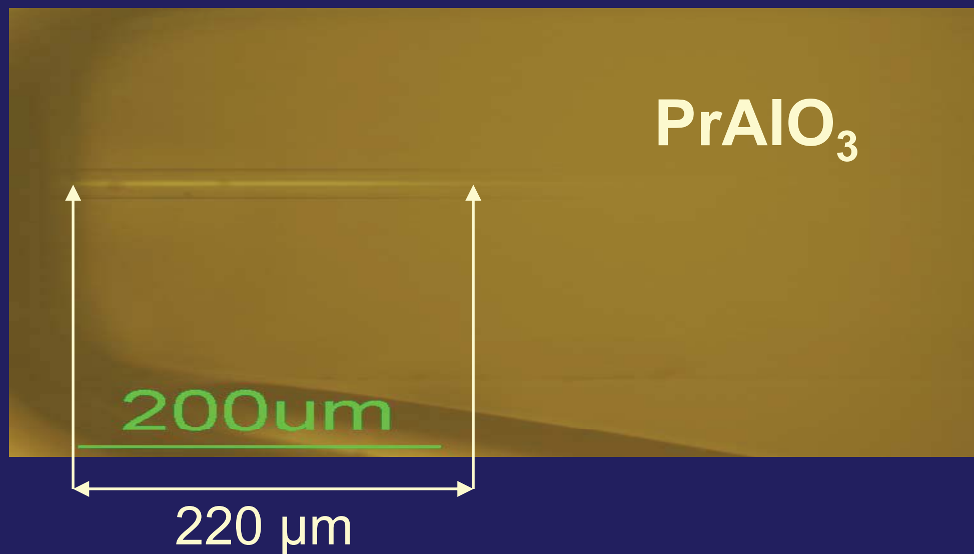


1930 µm/ 20 µm ID = 97 = aspect ratio

Assuming the saturated vapor pressure in the bubbler, the exposure to the La precursor should be 0.06 Torr-sec

From the observed aspect ratio, the La exposure should be
= $(3.7 \times 10^{-6}$ Torr-sec$) \times \{1 + (19/4)97 + (3/2)97^2\}$
= 0.054 Torr-sec

Capillary Test for Very High Aspect Ratios



Aspect Ratio of 11 observed

Equilibrium vapor pressure => exposure of 0.016 Torr-sec

Exposure deduced from the step coverage is 16 x smaller

$\Rightarrow$ **the Pr vapor is limited by the kinetics of sublimation, not by its equilibrium vapor pressure**

Step Coverage in Non-Circular Holes

Generalize to non-circular holes:
Aspect ratio a $\equiv$ (depth) x (perimeter) / 4 (area)

For circular holes:
$a = L\,(2\pi r) / 4(\pi r^2) = L / (2r) =$ depth / width

For trenches:
a = L x (2 x length) / 4 (width x length) = depth / 2 (width)

(Note that for trenches, conventionally a = depth / width)

Same formula for step coverage if this generalized a is used

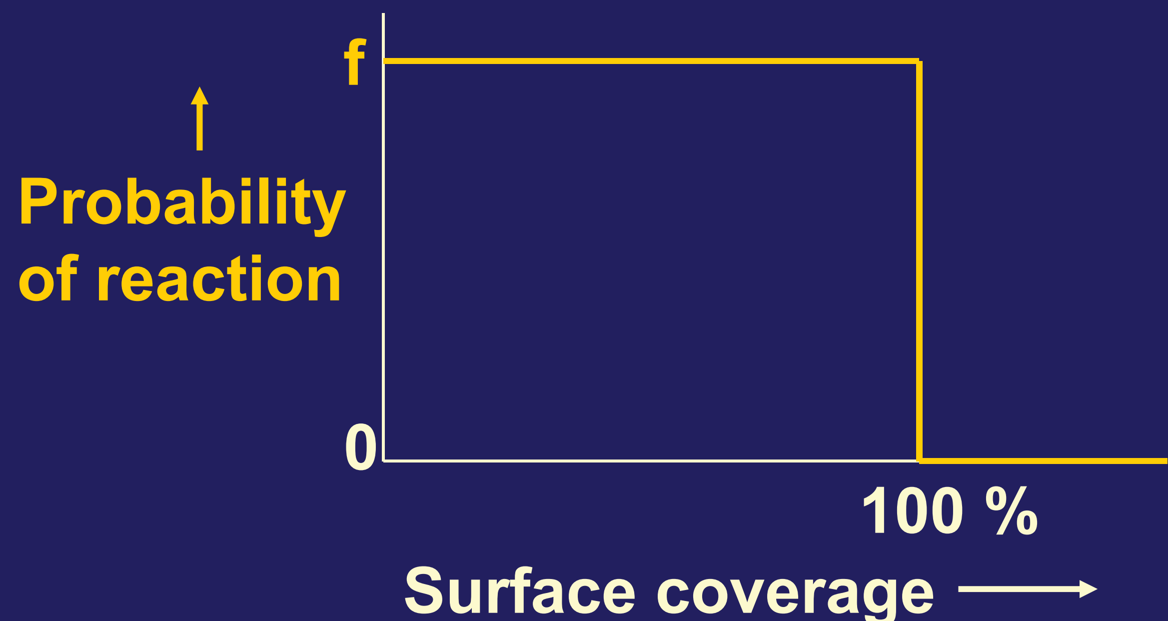
4 x easier to coat trenches than holes with same depth/width

Slow Self-Limiting Surface Reactions

Simplifying assumptions:

- Precursor molecules react with low probability $f \ll 1$ on each collision with the surface until all reactive sites are filled.

- After all sites have reacted, additional precursor molecules scatter diffusely from the surface.



Slow Self-Limiting Surface Reactions

If $f^{-1} \gg \{1 + (19/4)a + (3/2)a^2\}$

the slow step is completing the surface reaction, not diffusion into the hole.

$$(Pt)_{hole} \sim (Pt)_{flat} = S(2\pi mkT)^{1/2} / f$$

An exposure that saturates a flat surface will also coat the inside of a hole uniformly.

Exposures less than this value coat the hole uniformly, but with a thinner than saturated coating.

Examples of Slow Self-Limiting Reactions

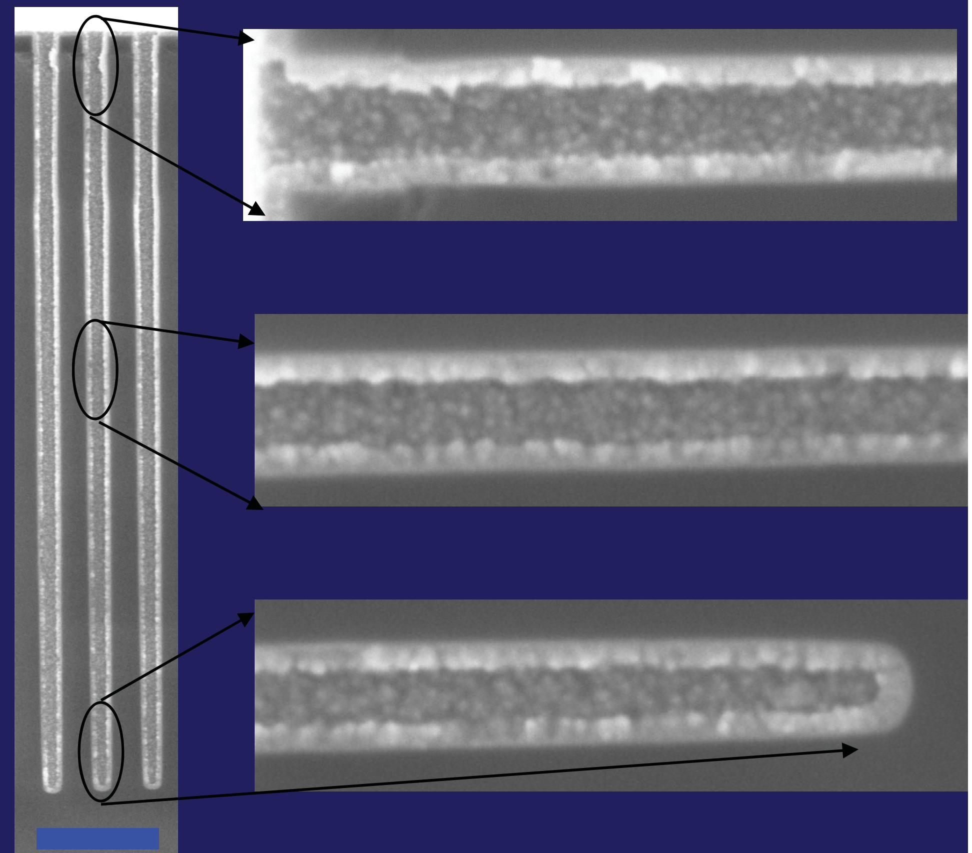
$$(Pt)_{flat} = S(2\pi mkT)^{1/2} / f$$

film	S ($10^{18} m^{-2}$)	M (amu)	T (K)	f	$(Pt)_{flat}$ (Torr-sec)
Cu_3N	1	466	433	$\sim 10^{-6}$	1
Cu	4	466	433	$\sim 2 \times 10^{-5}$	0.15
Co	5	341	523	$\sim 10^{-5}$	0.5

Step Coverage of Cu_3N

Uniform coverage in holes

with 43:1 aspect ratio



Experimental exposure

1 Torr-sec / cycle

(same as for flat surfaces)

minimum exposure for diffusion

$= (1 \times 10^{-6}) \times \{1 + (19/4)43 + (3/2)43^2\} = 0.003$ Torr-sec

=> diffusion time is not limiting; complete step coverage

Step Coverage of Cu

Uniform coverage in holes

with 43:1 aspect ratio

Experimental exposure

0.2 Torr-sec / cycle

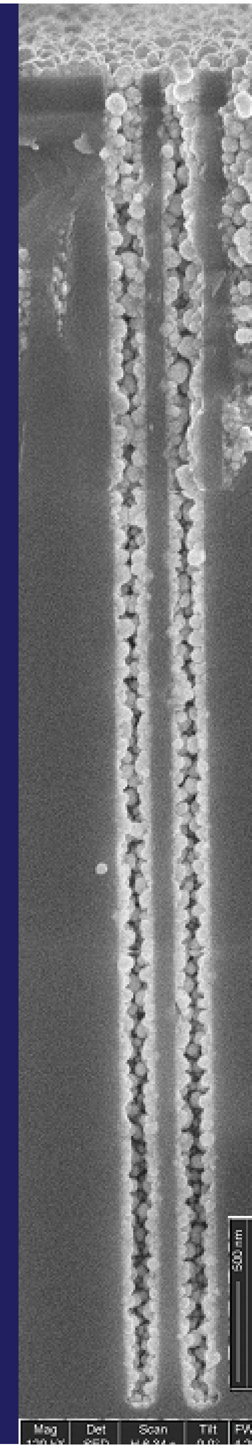
(same as for flat surfaces)

minimum exposure for diffusion

$= (3 \times 10^{-6}) \times \{1 + (19/4)43 + (3/2)43^2\}$

= 0.008 Torr-sec

diffusion is not limiting; complete step coverage



Step Coverage of Cobalt

Co deposited inside quartz capillary tube, 20 μm diameter hole

Aspect Ratio = 220:1

Experimental exposure ~ 0.5 Torr-sec

minimum exposure for diffusion
$= (5 \times 10^{-6}) \times \{1 + (19/4)210 + (3/2)210^2\}$
= 0.4 Torr-sec

Both diffusion and reaction rate limit this coating.
Non-uniform thickness is expected.

Incomplete Step Coverage

- Thermal decomposition

Most metal-organic precursors decompose when the surface temperature is too high.

Me_3Al at T > 350

$Hf(NEtMe)_4$ at T > 280

$La(amd)_3$ at T > 330

$W(NMe_2)_2(NtBu)_2$ at T > 400

=> Thicker coating near entrances to holes

Incomplete Step Coverage

- Recombination of plasmas - atoms and radicals

Most surfaces catalyze the recombination of atoms and radicals into less reactive molecules

$\Rightarrow$plasma-activated ALD reactions have thicker coating near entrances to holes.

H + Me_3Al => Al 75 % step coverage in 5:1 aspect ratio

H + N + $TiCl_4$ => TiN 18 % step coverage in 20:1 aspect ratio

Incomplete Step Coverage

- Reversible absorption of a reactant into film

Example: $2\ LaL_3 + 3\ H_2O \Rightarrow La_2O_3 + 6\ HL$

H_2O is absorbed <u>into</u> the film during the H_2O dose.

The H_2O desorbs reversibly during the purge.

The desorption is rapid when the film is thin (<10 nm).

Desorption from thick films (>10 nm) is slow (minutes).

=> CVD reaction => non-conformal coatings

Incomplete Step Coverage

- Competitive adsorption of byproducts

$$TiCl_4 + 2\,H_2O \Rightarrow TiO_2 + 4\,HCl$$

$$HfCl_4 + 2\,H_2O \Rightarrow HfO_2 + 4\,HCl$$

HCl competes for adsorption sites with MCl_4.

HCl diffuses faster than MCl_4, so HCl reaches the adsorption sites deeper in the hole first.

=> thinner film deeper inside hole.

Incomplete Step Coverage

- Etching of film by byproducts

Deposition: $2\ NbCl_5 + 5\ H_2O \Rightarrow Nb_2O_5 + 10\ HCl$

Etching: $Nb_2O_5 + 6\ HCl \Rightarrow 2\ NbOCl_3 + 3\ H_2O$

$Nb_2O_5 + 3\ NbCl_5 \Rightarrow 5\ NbOCl_3$

=> non-conformal coatings

Incomplete Step Coverage

Aerogels have extremely high aspect ratios, > 10^5 but hard to define exactly because tortuous paths

ALD coating inside aerogels is

<u>Uniform</u> for precursors with high vapor pressure:
WF_6, Me_3Al, Et_2Zn (P > 10 Torr)

<u>Non-uniform</u> for precursors with low vapor pressure:
Ru, Pt, Cu, Fe (P < 1 Torr, so exposure is too low)

S. O. Kucheyev, J. Biener, T. F. Baumann, Y. M. Wang, A. V. Hamza, Z. Li, D. K. Lee and R. G. Gordon, *Langmuir* **24**, 943(2008)

How to Achieve Higher Step Coverage

- Increase amount of precursor per dose
- Reduce pumping speed

Exposure = $P\Delta t$ = $NkT\,\Delta t/V$ = NkT/ Pumping speed

Step coverage α square root(N/Pumping speed)

Change to a precursor that

- is more volatile
- does not decompose
- does not need plasma activation
- does not absorb into the film
- does not etch
- has no etching byproducts
- has no adsorbing byproducts

Summary of Step Coverage

Model Assumptions

- very fast or very slow surface reactions
- diffuse scattering of non-reacting precursors

Kinetic Theory of Step Coverage in Narrow Holes:

- aspect ratio $a \sim (P\Delta t)^{1/2} S^{-1/2} (9\pi mkT/2)^{-1/4}$

$$a \approx \left(\frac{2 \times \text{exposure for hole}}{3 \times \text{exposure for flat}} \right)^{1/2} \quad \text{for } a >> 1$$

Agreement with computer simulations

Summary of Step Coverage

Experimental Measurements of Step Coverage

- SEM in etched holes ($\leq$ 80:1)
- Optical microscopy in capillary tubing

Agreement between theory and experiment, except when vapor pressure is uncertain

Examples of Step Coverage by ALD

insulators		metals	
SiO_2	> 40:1	Cu	> 40:1
HfO_2	81:1	Cu_3N	> 40:1
Ta_2O_5	51:1	Co	~200:1
$LaAlO_3$	97:1	WN	210:1

Summary of Step Coverage

Non-Ideal Reactions

- thermal decomposition of a precursor
- recombination of radicals from plasma
- reversible absorption of a precursor
- growth inhibition by a byproduct
- etching of film by a precursor
- etching of film by a byproduct

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