Beyond A/B/A/B… Unorthodox Pulse Sequences in Atomic Layer Deposition

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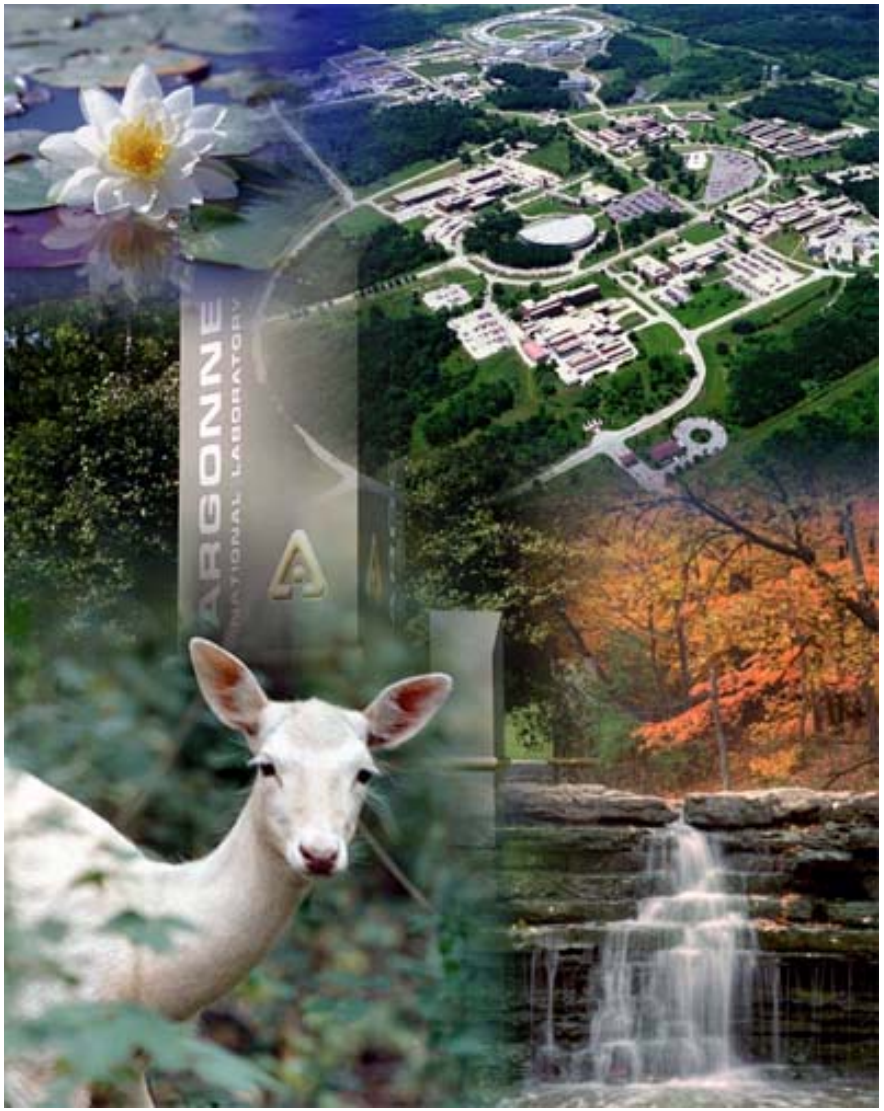
2012 NNIN ALD Symposium
Cambridge, MA, November 30, 2012

Outline

- Introduction
  - Argonne National Laboratory
  - Traditional ALD, A/B/A/B…
- Beyond **A/B/A/B…**
  - Stripe Coating
  - Surface Poisoning
  - Precursor Synergy
  - Nanobowls
- Conclusions

Argonne National Laboratory

- Founded in 1943, designated a national laboratory in 1946
- Managed by The University of Chicago for the U.S. Department of Energy
  - More than 2,800 employees and 5,000+ facility users
  - 1,500-acre, wooded site in DuPage County, Illinois
  - 25 miles southwest of Chicago, Illinois

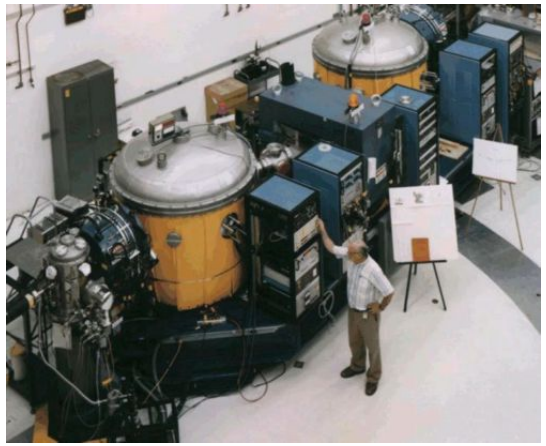


Argonne User Facilities

- Leadership Computing Facility “Blue Gene”

- Advanced Photon Source

- Center for Nanoscale Materials



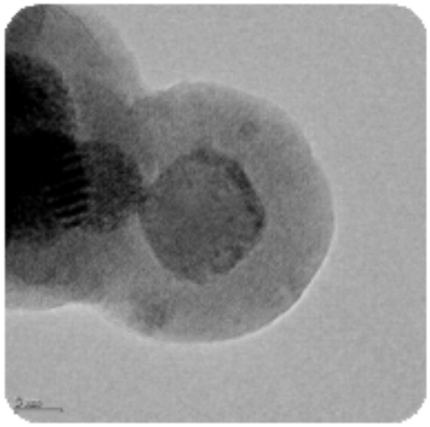
- Argonne Tandem-Linac Accelerator Facility

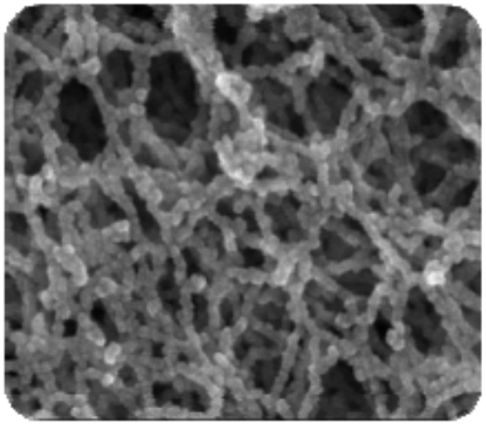
- Electron Microscopy Center

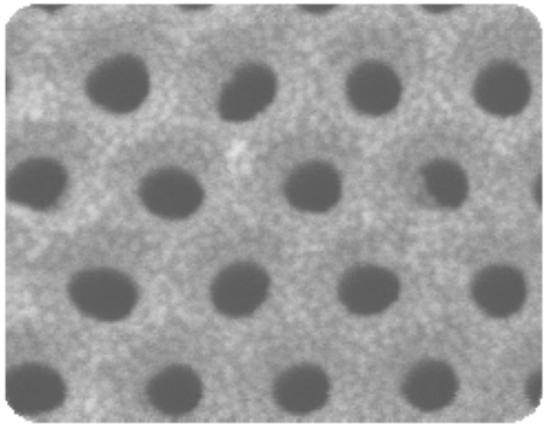
Argonne Atomic Layer Deposition Group

- Develop ALD technology
- Apply ALD to emerging applications:
  - Solar Cells
  - Large Area Photodetectors
  - Lithium Batteries
  - Catalysis

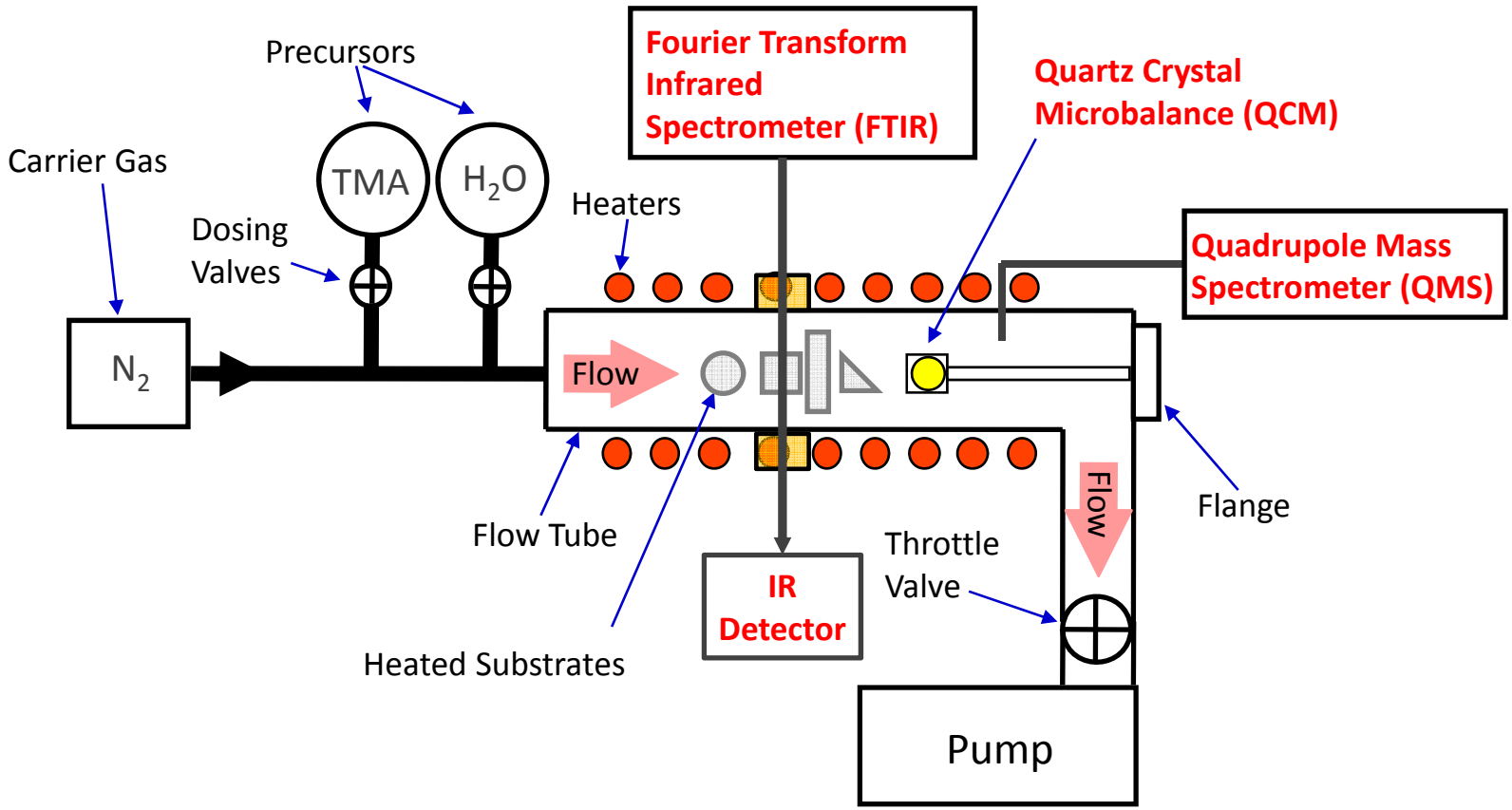
Precise coatings on porous templates:



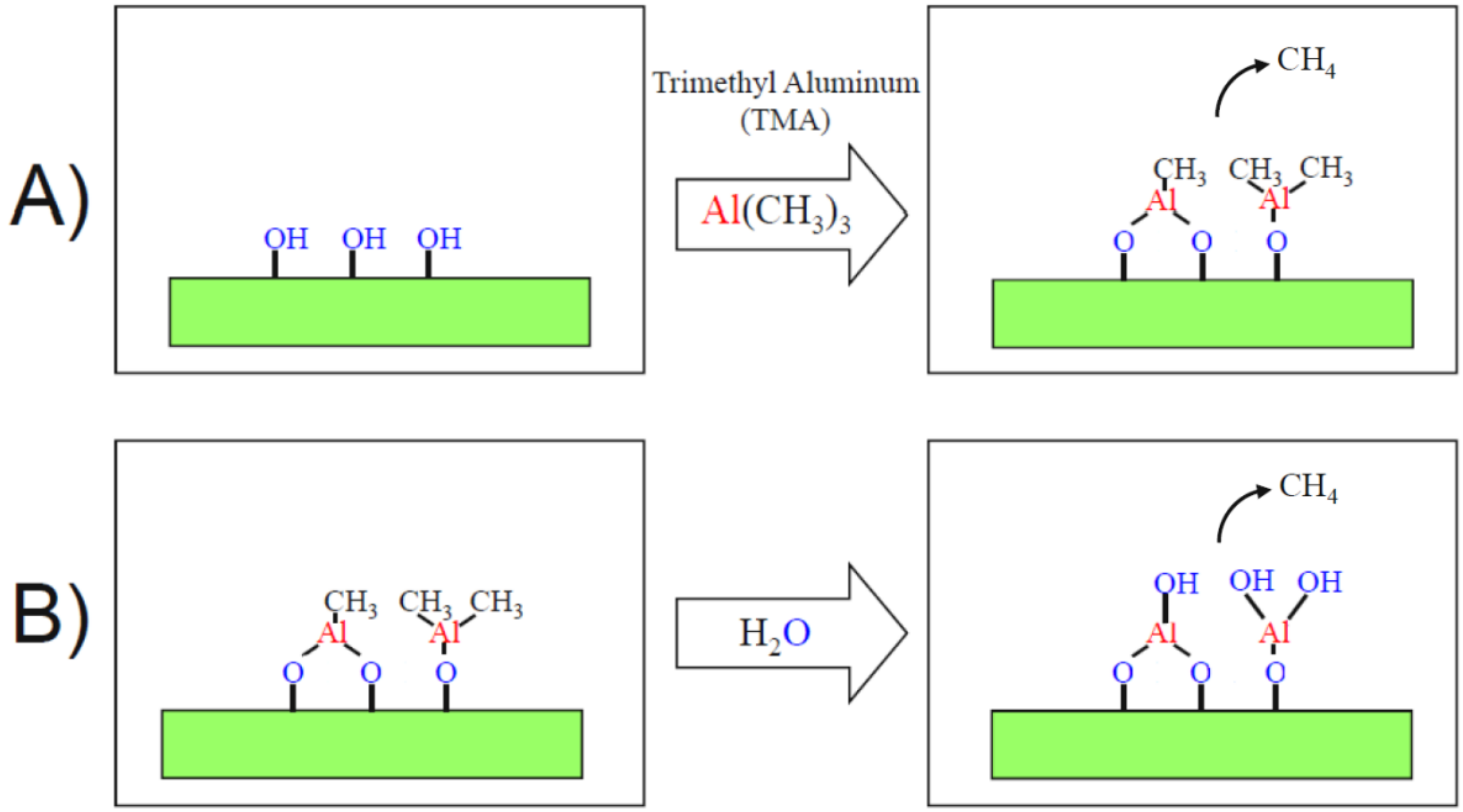




Components of Argonne ALD Systems



Traditional ALD, A/B/A/B…



Self-limiting A/B/A/B… surface chemistry ⇨

- thickness control
- composition control
- uniformity
- conformality
- pinhole-free
- low-temperature
- high purity

Many Examples of A/B/A/B…

Puurunen, J. Appl. Phys. **87**, 121301 (2006)

TABLE III. Overview of ALD processes based on two reactants (Source: ISI Web of Science, status in February 2005). Description of the ligands in Fig. 4.

Z	Material	Reactant A^a	Reactant B	Refs.
5 Boron				
	B_2O_3	BBr_3	H_2O	85
	BN	BCl_3	NH_3	158
		BBr_3	NH_3	159
	$B_xP_yO_z$	$B(OMe)_3$	$POCl_3$	88 and 89

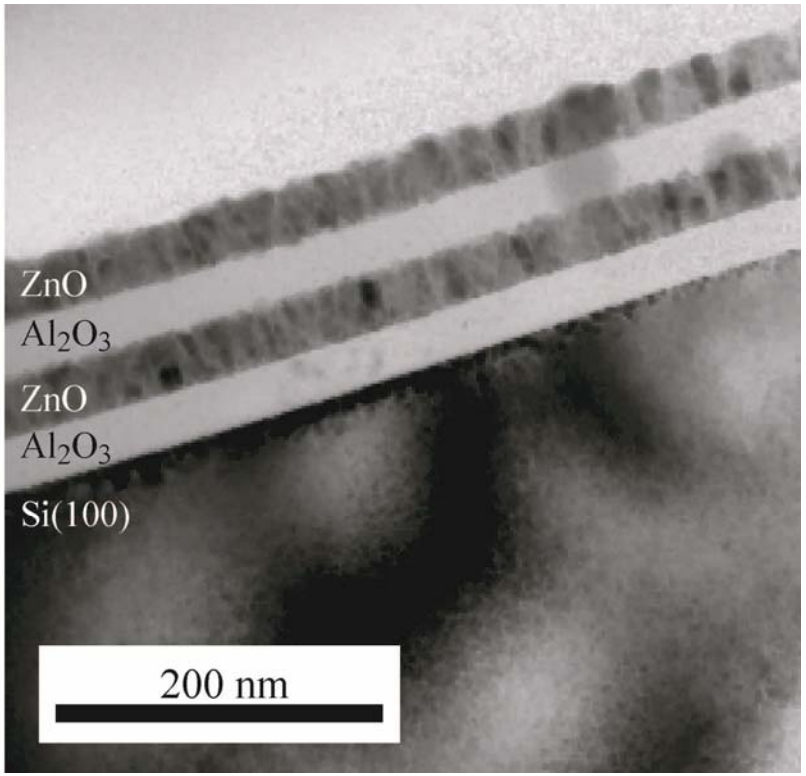
(8 pages!)

	PbS	$PbBr_2$	H_2S	1083
		PbI_2	H_2S	1083
		$Pb(OAc)_2$	H_2S	1083
		$Pb(O^tBu)_2$	H_2S	1084
		$Pb_4O(O^tBu)_6$	H_2S	1084
		$Pb(thd)_2$	H_2S	1083 and 1084
		$Pb(dedtc)_2$	H_2S	1083 and 1084
83 Bismuth				
	BiO_x	$Bi[N(SiMe_3)_2]_3$	H_2O	1085

Beyond A/B/A/B… - Blended Materials

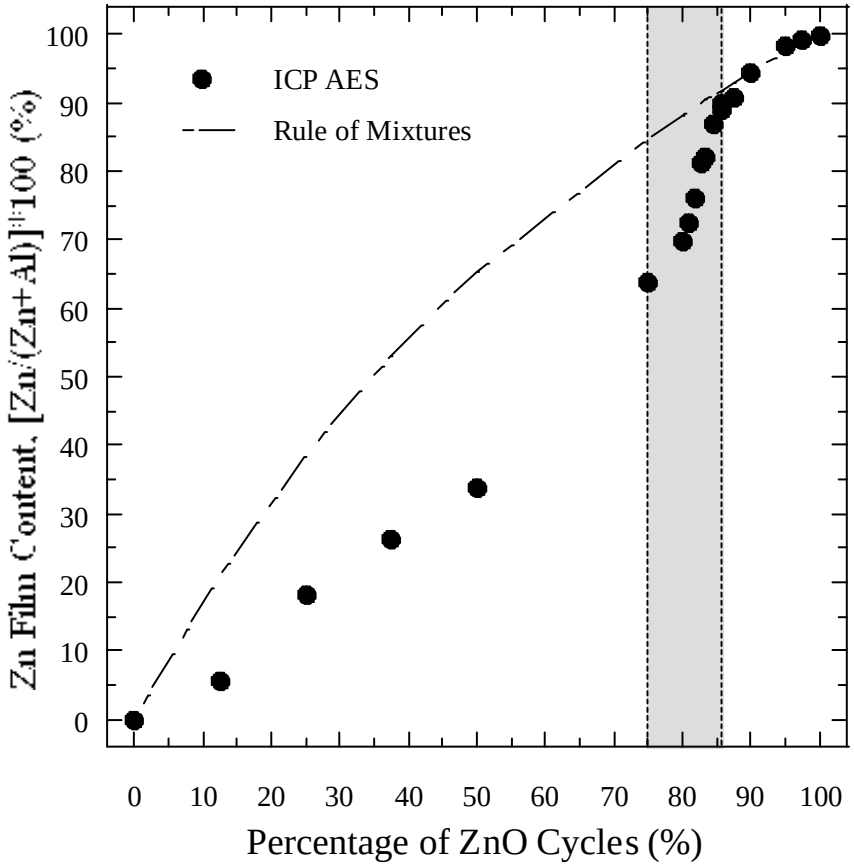
- TMA + $H_2O \rightarrow Al_2O_3$
- DEZ + $H_2O \rightarrow ZnO$

Laminates



Elam, Thin Solid Films **414**, 43, (2002).

Alloys



Elam, Chem. Mater. **15**, 1020, (2003).

Beyond A/B/A/B… - New Processes

Electrochemical and Solid-State Letters, **9** (7) F64-F68 (2006)
1099-0062/2006/9(7)/F64/5/$20.00 © The Electrochemical Society

Effect of Surface Reactive Site Density and Reactivity on the Growth of Atomic Layer Deposited WN_xC_y Films

A. Martin Hoyas,[a,b,z] C. M. Whelan,[a,*] J. Schuhmacher,[a] J. P. Celis,[c] and K. Maex[a,b]

[a]*IMEC, BE-3001 Leuven, Belgium*
[b]*Department of Electrical Engineering, Katholieke Universiteit Leuven , BE-3001 Leuven, Belgium*
[c]*Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, BE-3001 Leuven, Belgium*

- A/B/C…
- $B(C_2H_5)_3/WF_6/NH_3 \rightarrow$ **WN_xC_y**

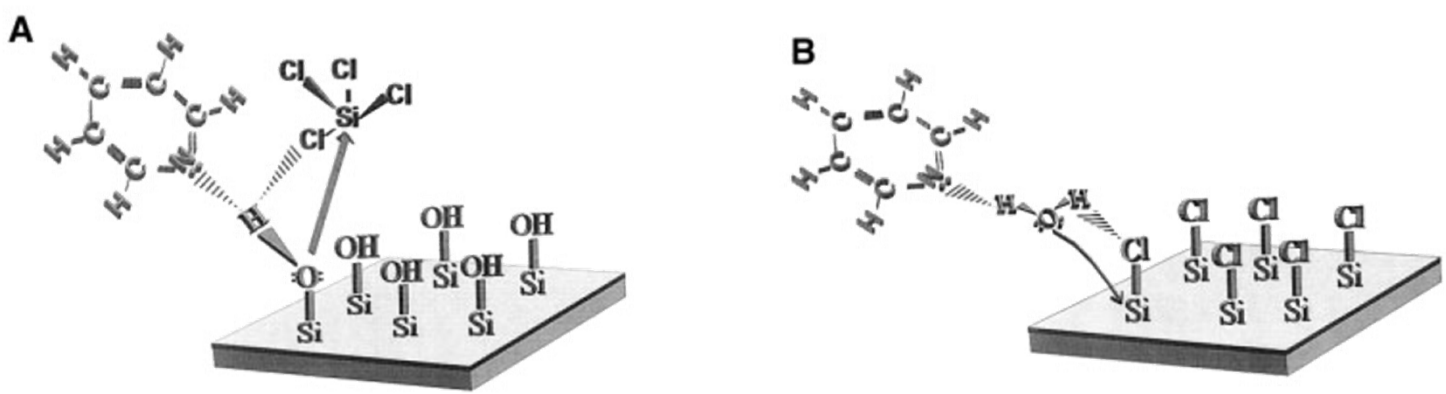
Beyond A/B/A/B… - New Processes

Growth of SiO_2 at Room Temperature with the Use of Catalyzed Sequential Half-Reactions

Jason W. Klaus, Ofer Sneh,* Steven M. George†

SCIENCE • VOL. 278 • 12 DECEMBER 1997

- A+C/B+C…
- $SiCl_4$(Pyridine)/H_2O(Pyridine) → **SiO_2**



Beyond A/B/A/B… - What Else Can We Do?

1) Stripe Coating

2) Surface Poisoning

3) Precursor Synergy

4) Nanobowls

1) Stripe Coating

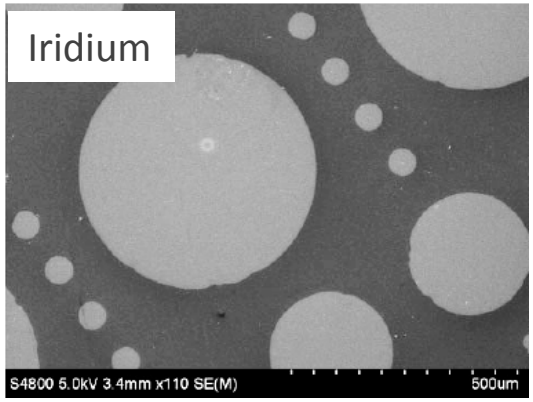
- pattern layers in 3-D, nanoporous materials

- Joseph A. Libera

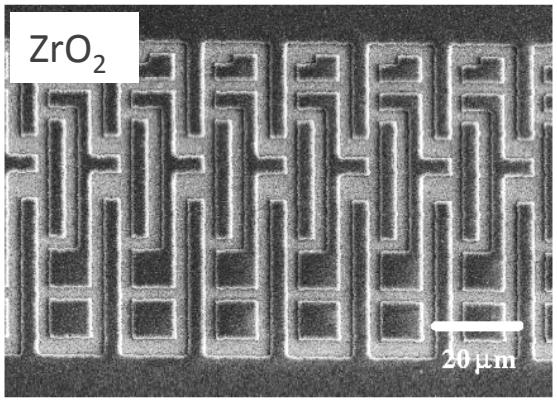
- J. W. Elam, J. A. Libera, P. C. Stair, and M. J. Pellin, Appl. Phys. Lett., **91** 243105-1 – 243105-3, (2007).

Introduction

- Methods exist for selective ALD on planar surfaces



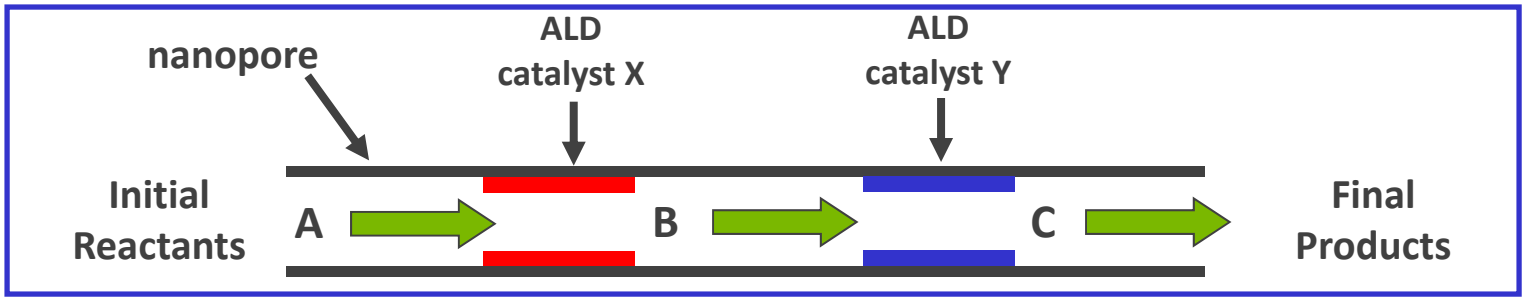
E. Färm et al, CVD **2006**, *12*, 415–417



J. P. Lee et al, JACS **2004**,126, 28-29

- Can we pattern ALD layers inside of porous structures?

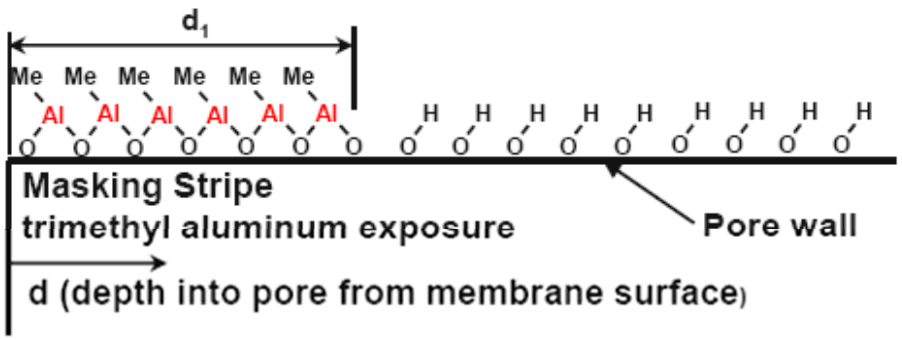
Application - Control of sequential catalytic reactions:



Patterned ALD Layers Inside of Porous Structures

Example: DEZ/H_2O → ZnO

1)



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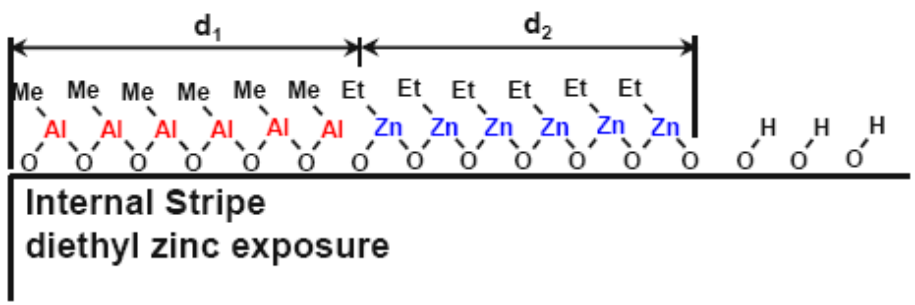
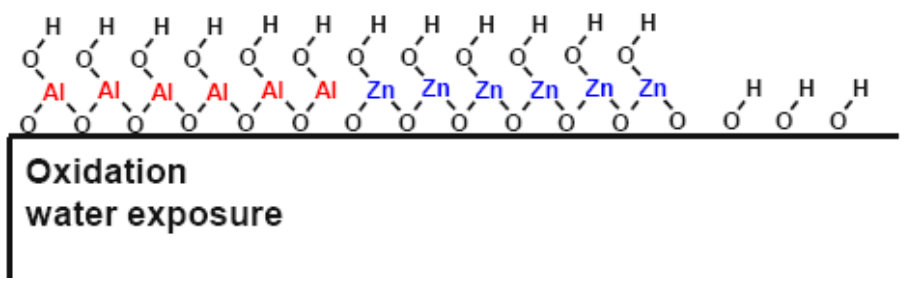
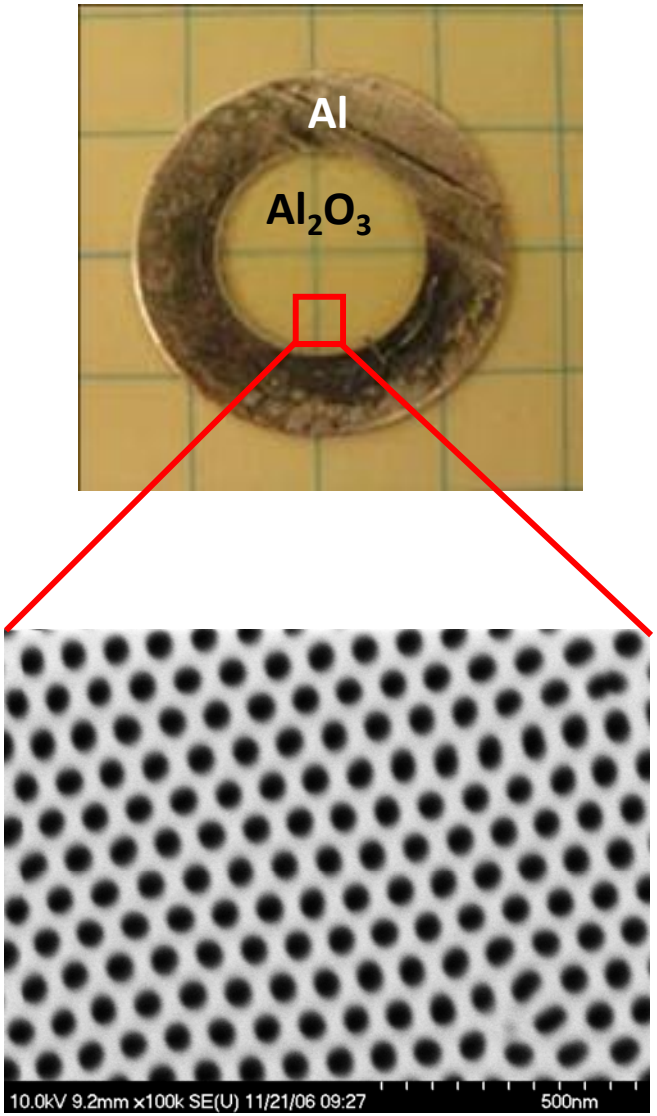


3)



TMA/DEZ/H_2O…
"Stripe Coating"

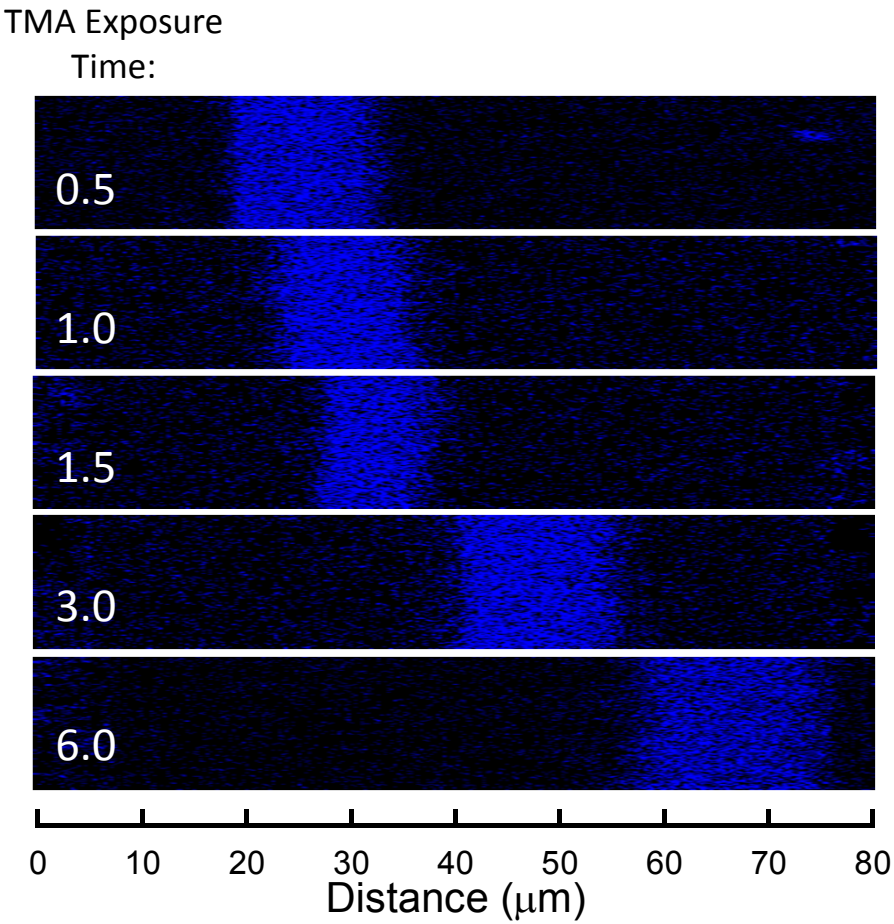
Anodic Aluminum Oxide (AAO) Membranes

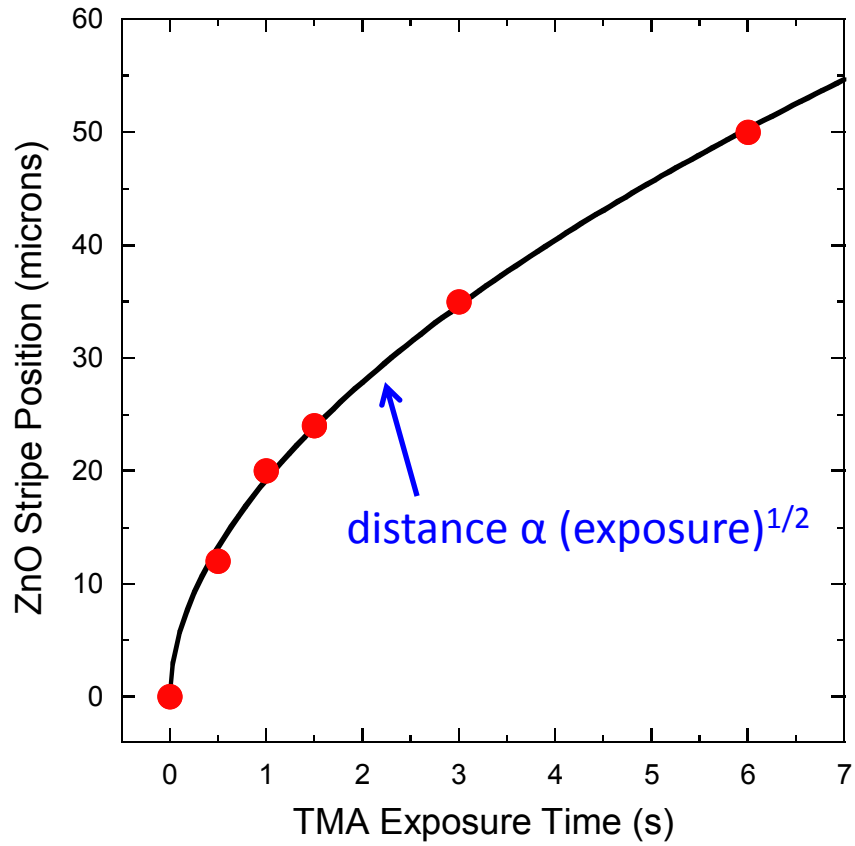


- Electrochemical etching of aluminum metal
- Membrane thickness L=75 μm
- Nanopore diameter d=50 nm
- Aspect ratio L/d = 1400

ZnO Stripes in AAO

- 20 cycles TMA-DEZ-H_2O
- Vary TMA exposure time

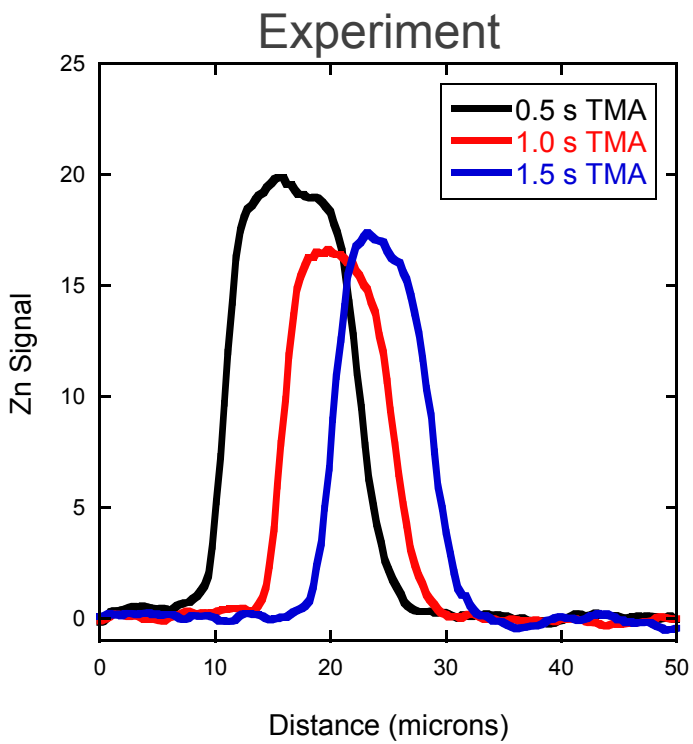


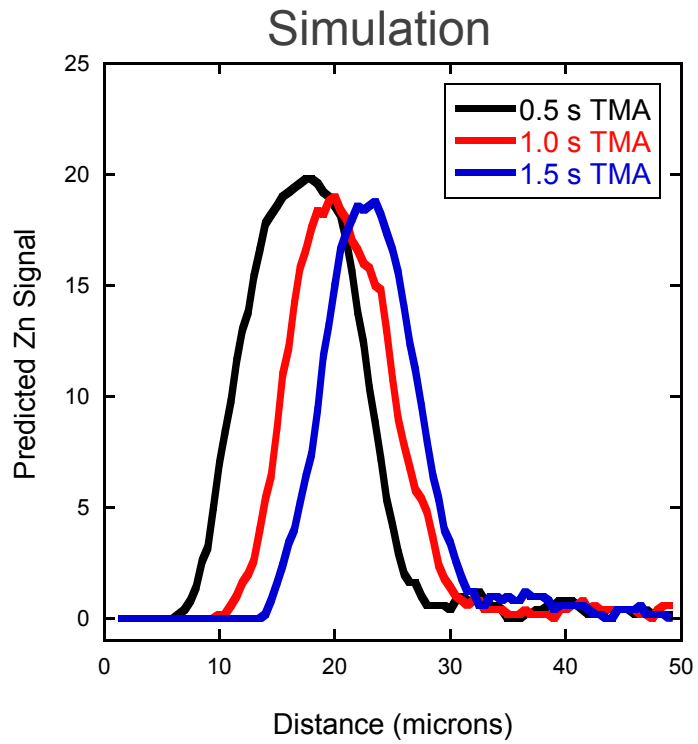


- ZnO stripe position is diffusion-controlled

Monte Carlo Simulation of Stripe Coating

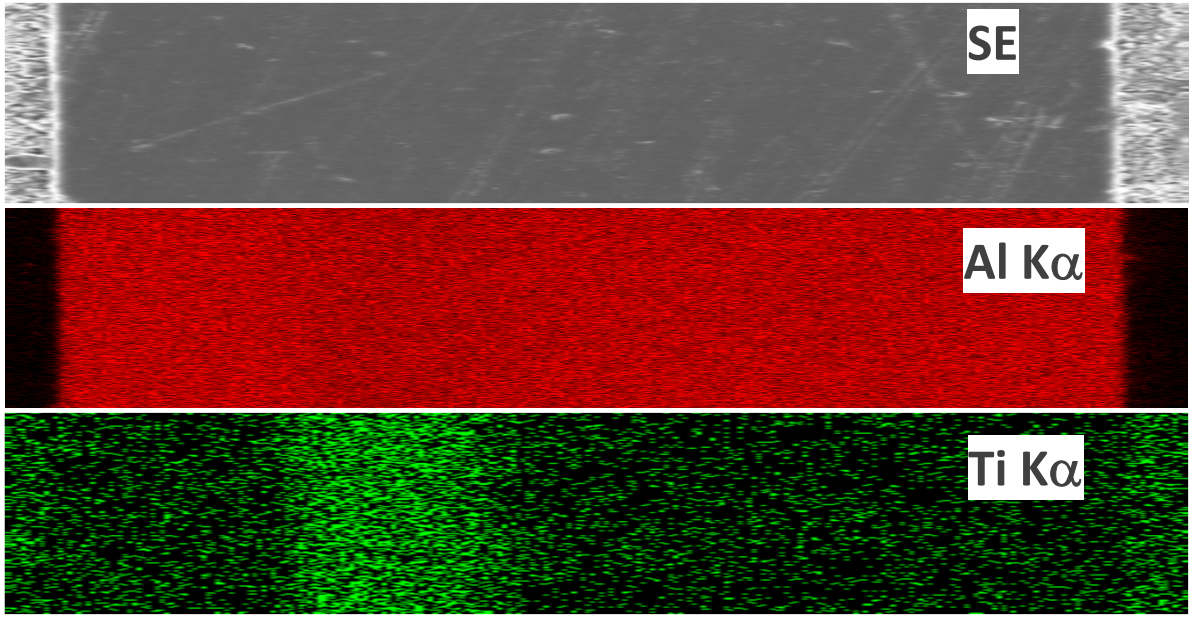
- 1D random walk of hop-length d
- Only model DEZ/TMA half-reaction
- Model trajectory until DEZ/TMA reacts ($S=10^{-3}$) or leaves tube





TiO_2 Stripe Coating in AAO

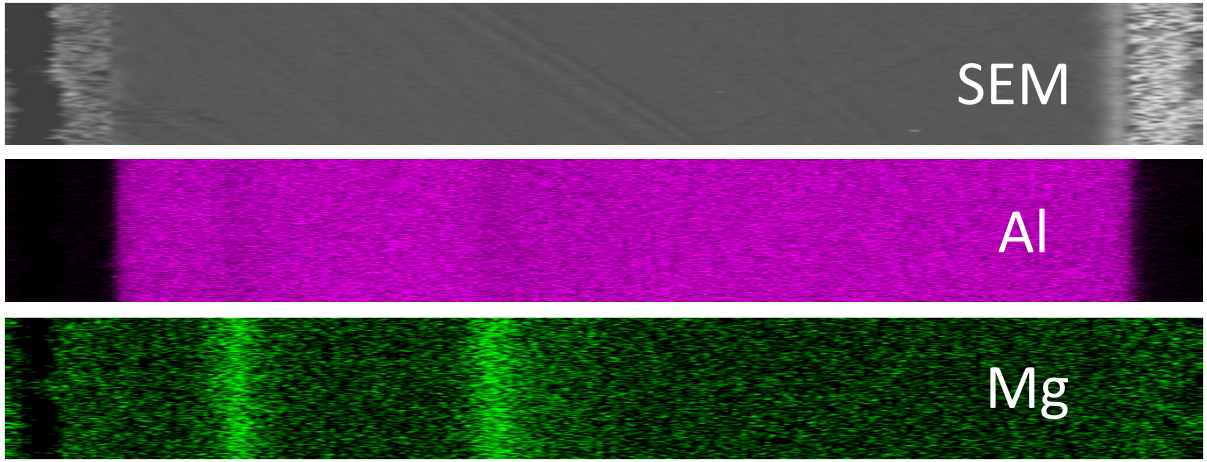
TMA/$TiCl_4$/H_2O



- TiO_2 stripe formed

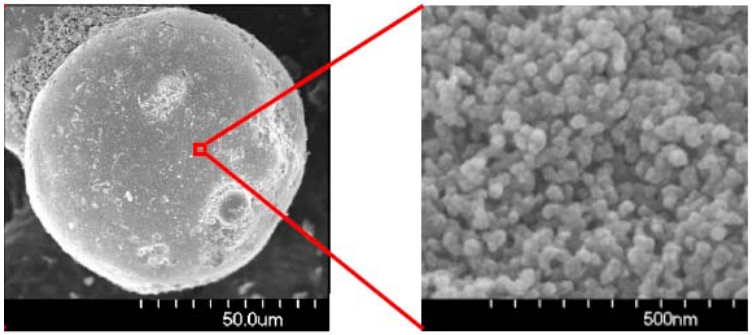
Multiple Magnesium Oxide Stripes

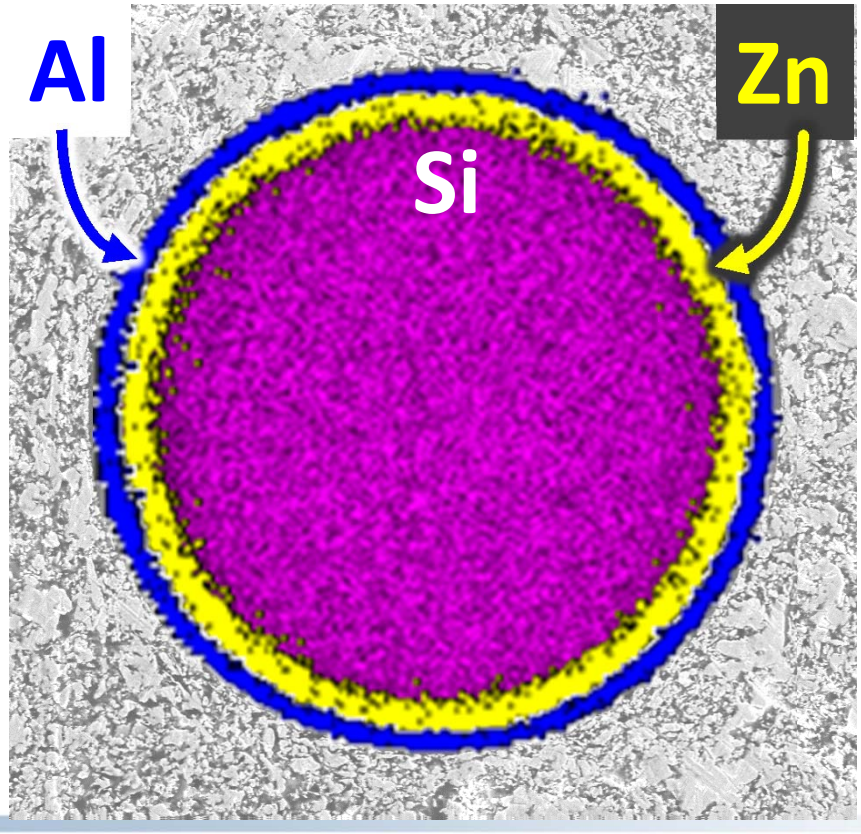
$TMA/MgCp_2/TMA/MgCp_2/H_2O$



- 2 MgO stripes formed

ZnO Stripe in Silica Gel





- TMA/DEZ/H_2O
- Stripe coating works in other porous media

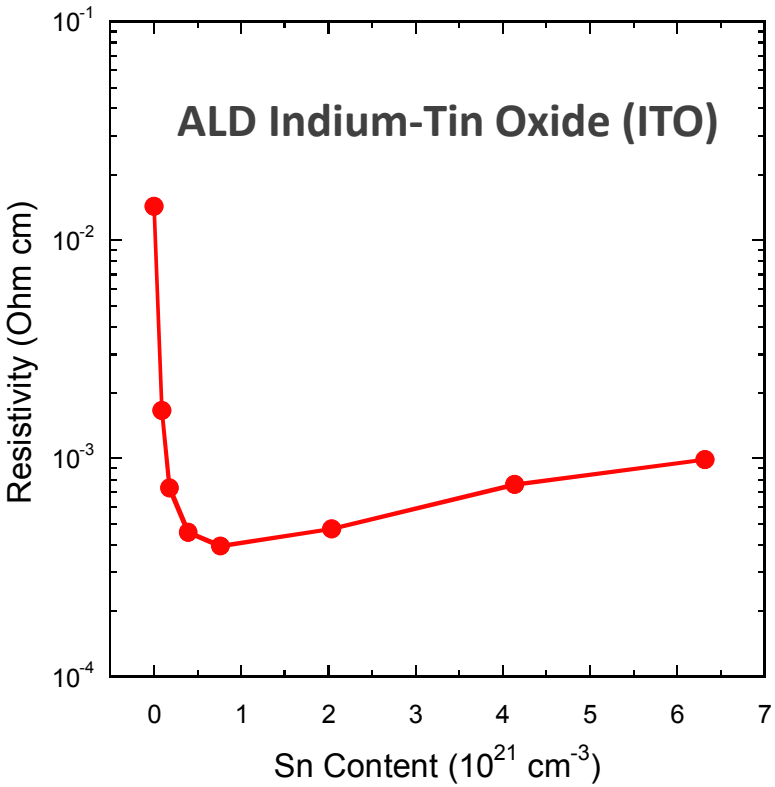
2) Surface Poisoning

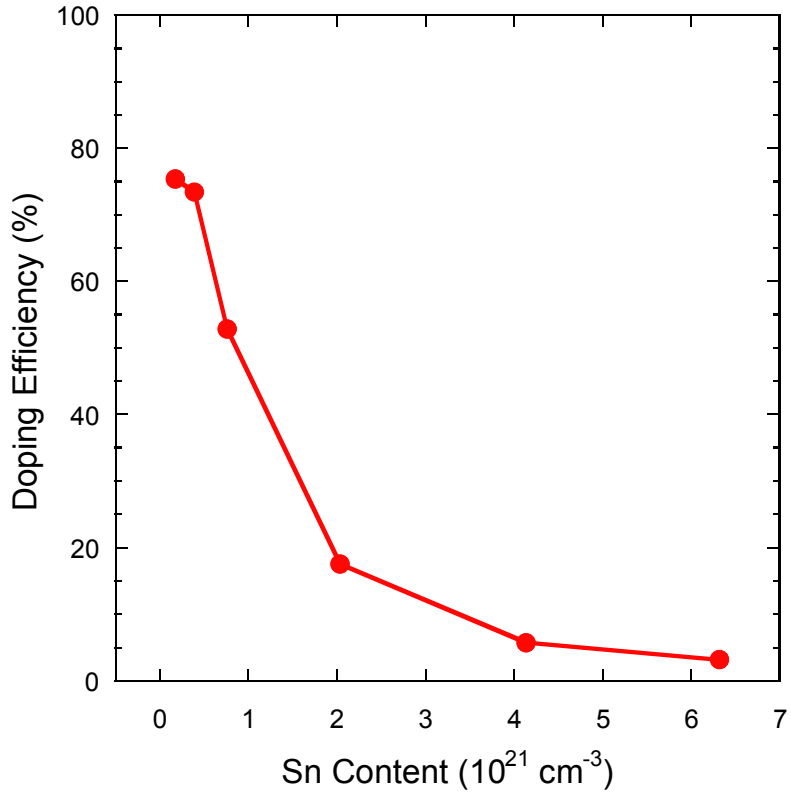
- control spatial location of dopants in a host

- Angel Yanguas-Gil

- A. Yanguas-Gil and J. W. Elam, ECS Trans. **33** (2), 333 (2010).
- A. Yanguas-Gil and J. W. Elam, Chemistry of Materials, **23** (19), 4295-4297, (2011).

What Limits Conductivity in Transparent Conducing Oxides (TCOs)?

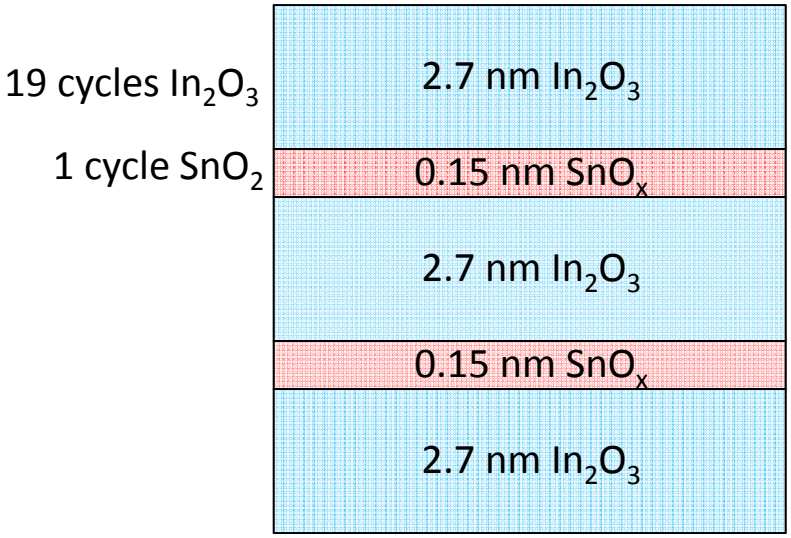




- Doping efficiency decreases with increasing Sn content
- Additional Sn forms non-conducting **Sn-O-Sn** clusters
  - Want a more uniform dispersion of SnOx
  - For ALD TCOs, need a *lower* SnO_2 growth rate

Why lower the ALD dopant growth rate?

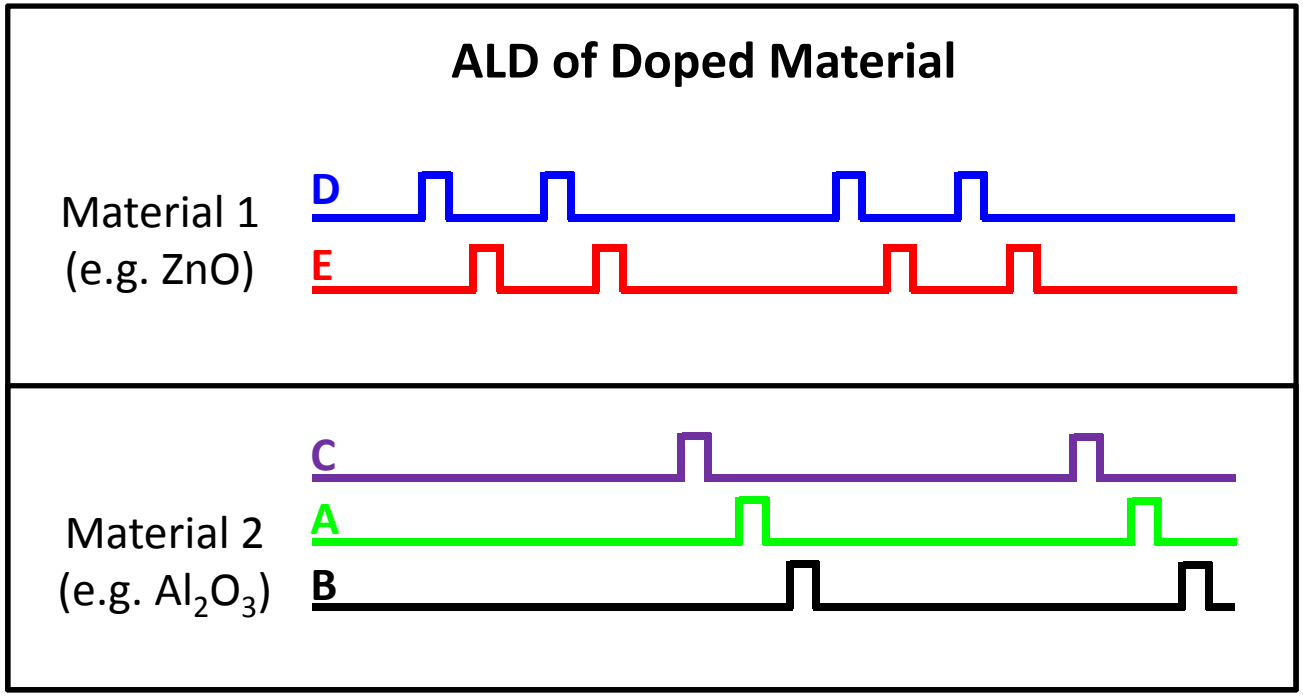
5% ALD ITO:



Achieve a more uniform SnOx dispersion

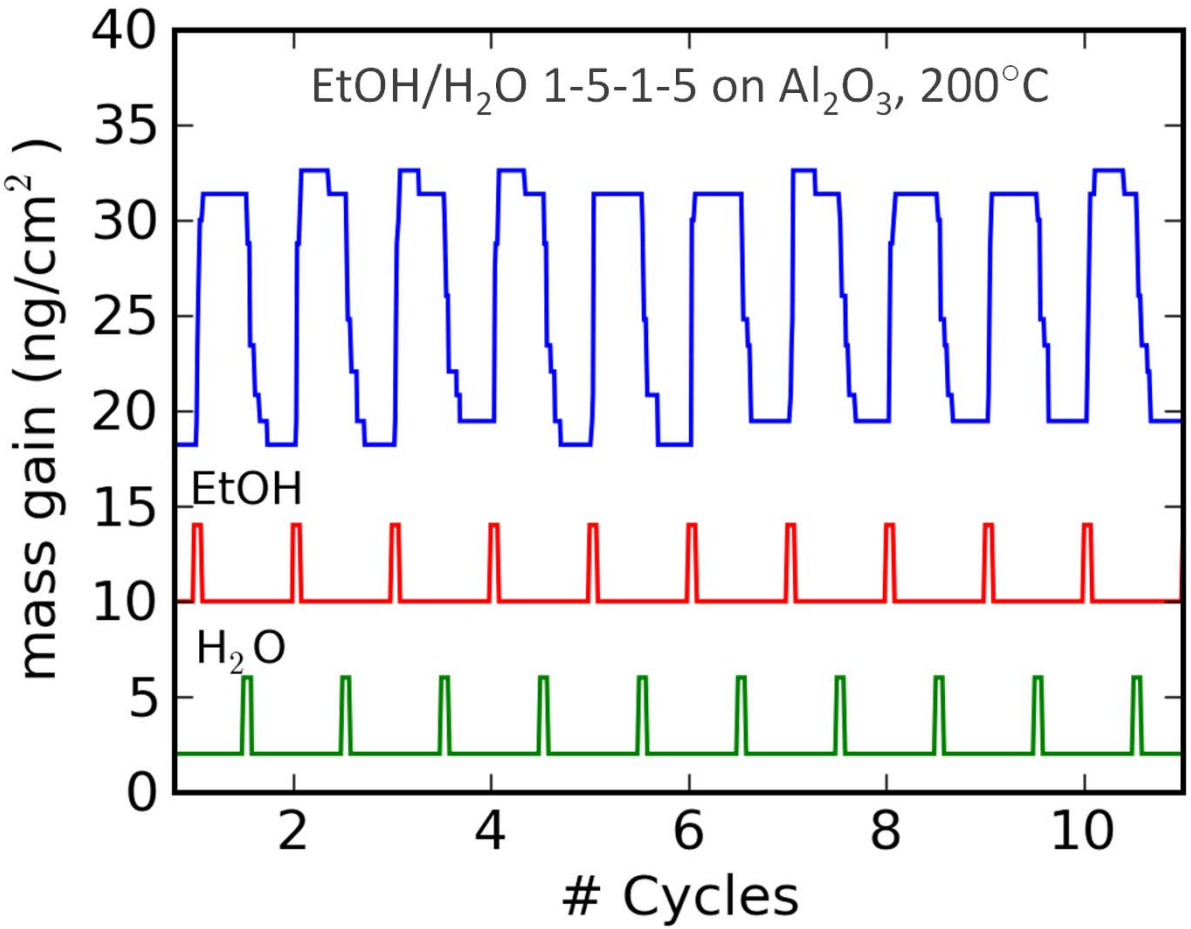
How? – surface poisoning

Strategy: Surface Poisoning



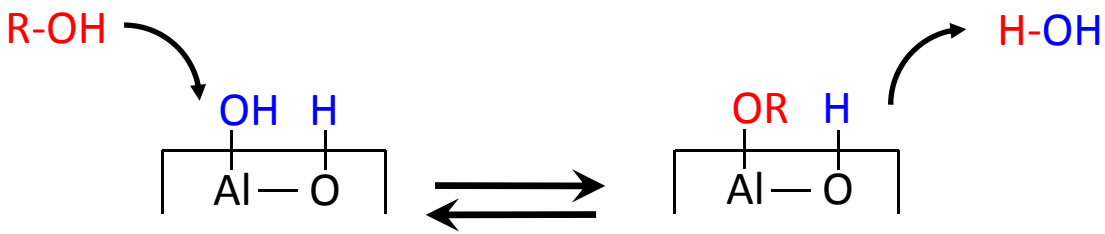
- Growth rate *modulated* by poisoning step
- Initially focus on single-component material: Al_2O_3
- Use alkyl alcohols (ROH) as poison

QCM Measurements of EtOH/H_2O on Al_2O_3



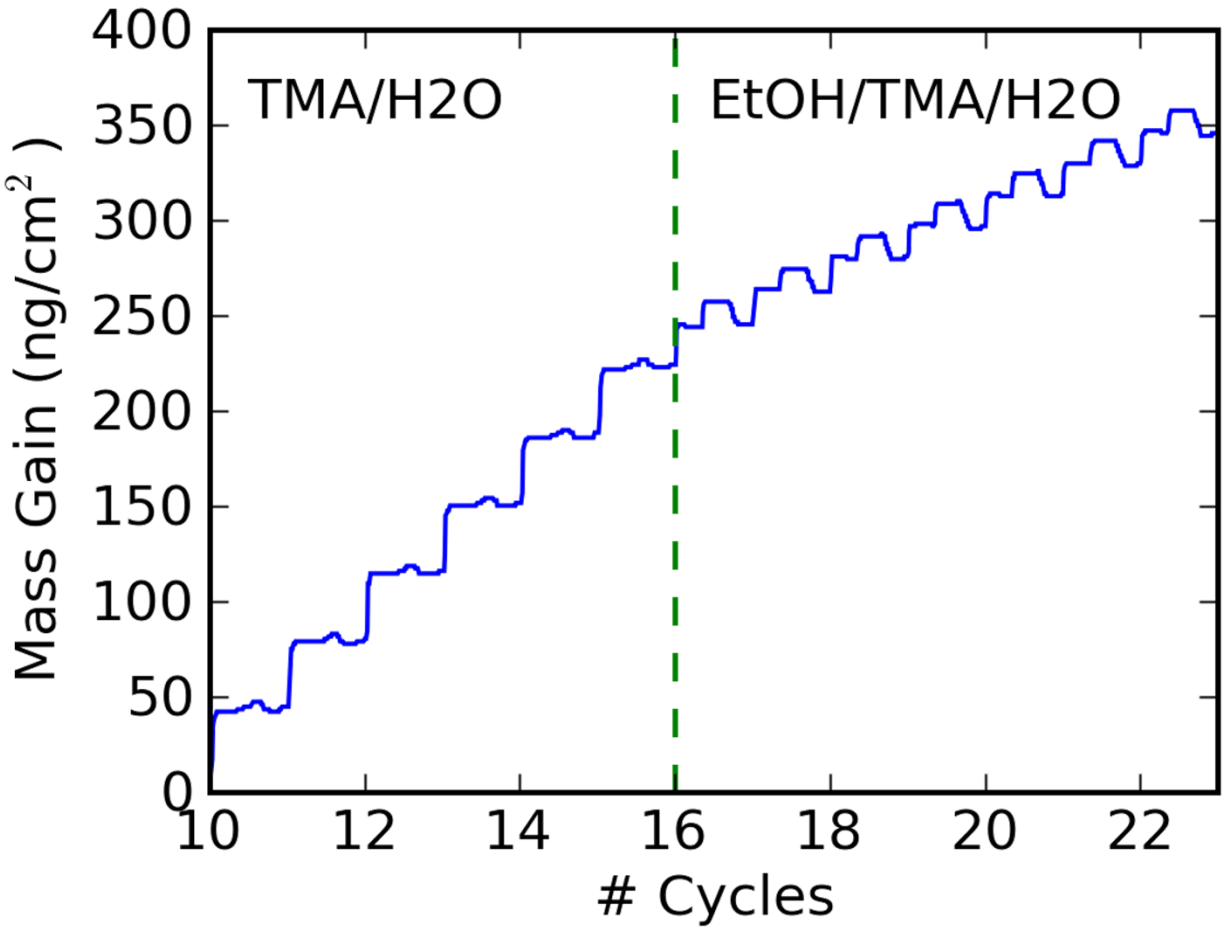
- H_2O displaces EtOH
- EtOH displaces H_2O

Mechanism for ROH Adsorption on Al_2O_3



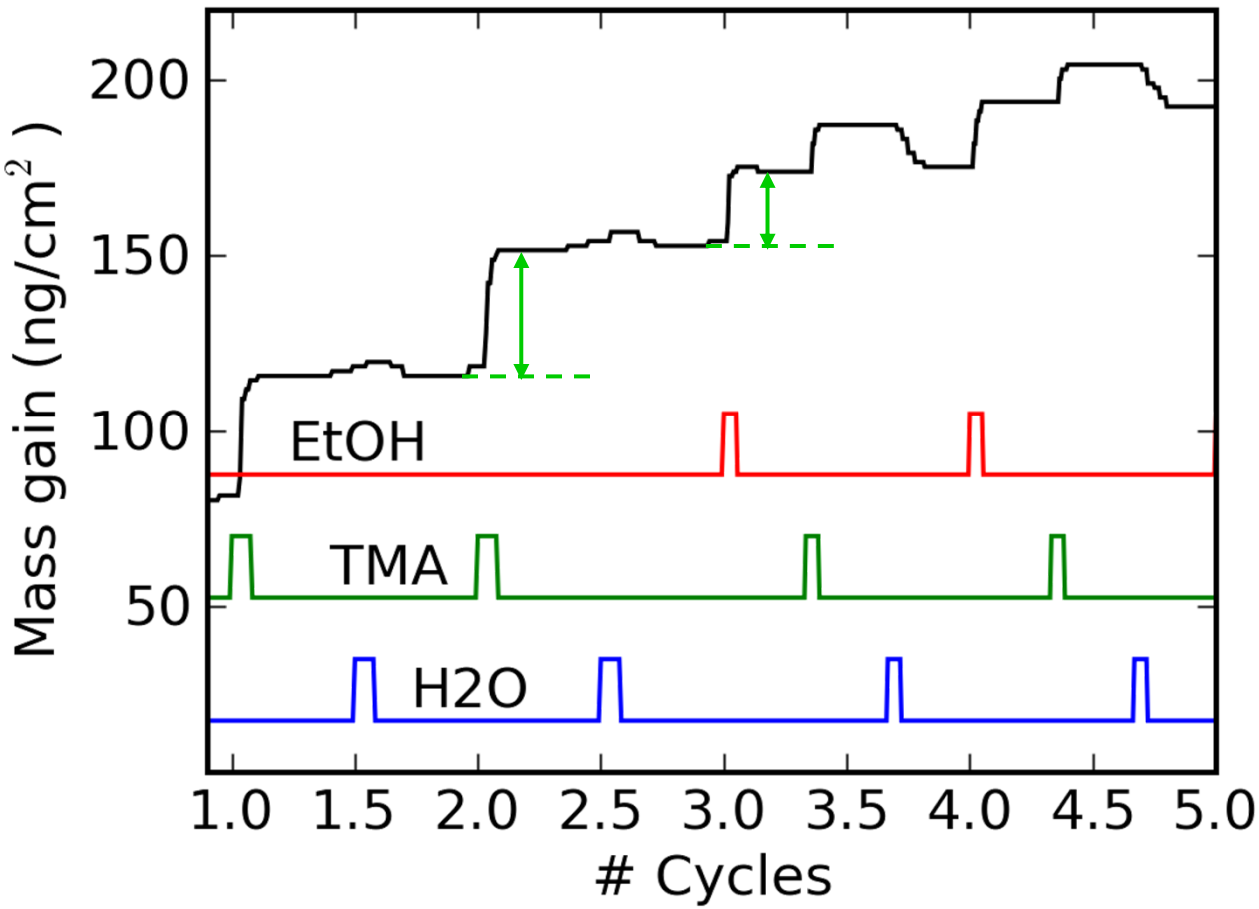
J. Phys. Chem. 1996, *100*, 18183

QCM of Al_2O_3 ALD Using EtOH/TMA/H_2O



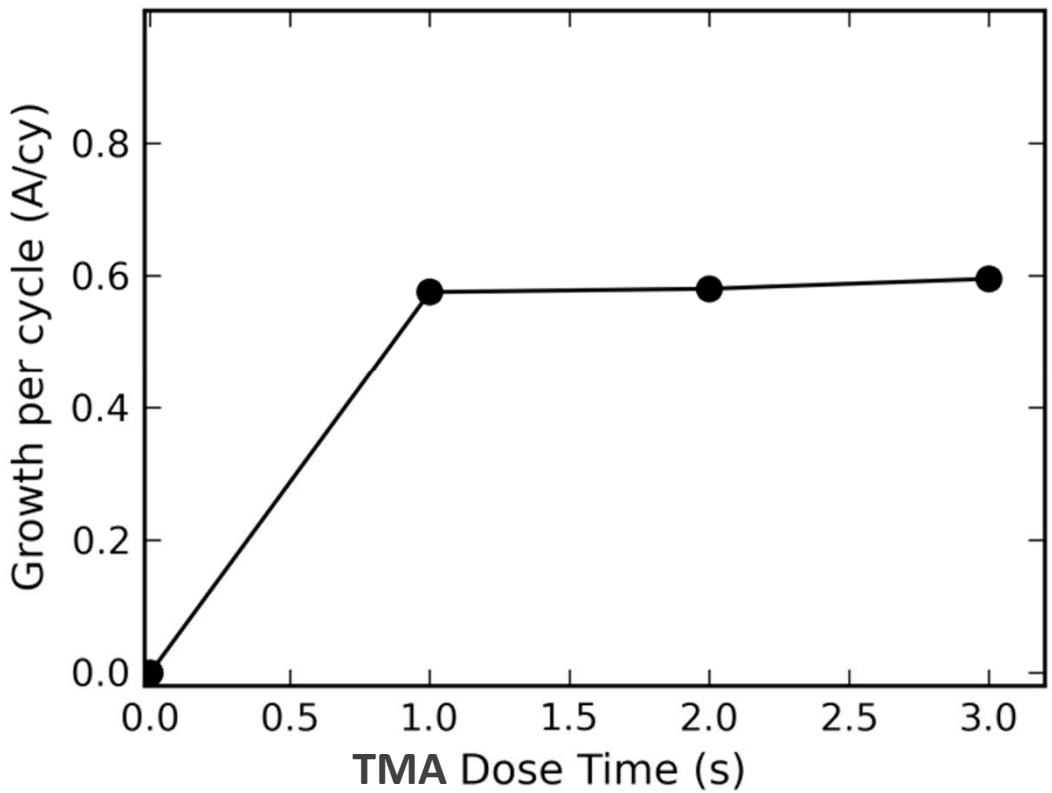
- Al_2O_3 grows more slowly with the EtOH

QCM Pulse Structure During EtOH/TMA/H_2O



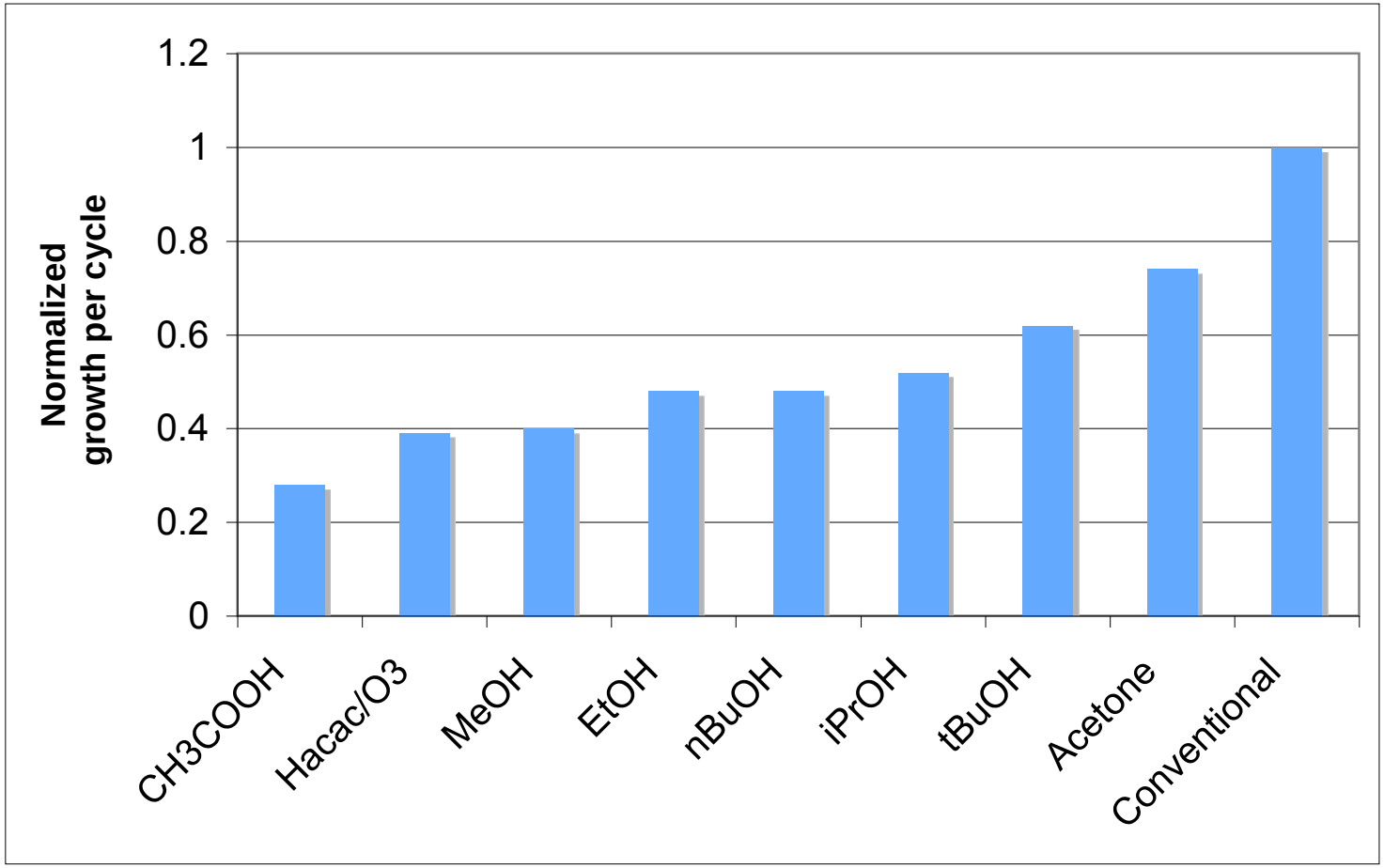
- Mass is gained during TMA exposures
- This mass gain is *smaller* following EtOH

Self-limiting TMA Reaction During EtOH/TMA/H_2O



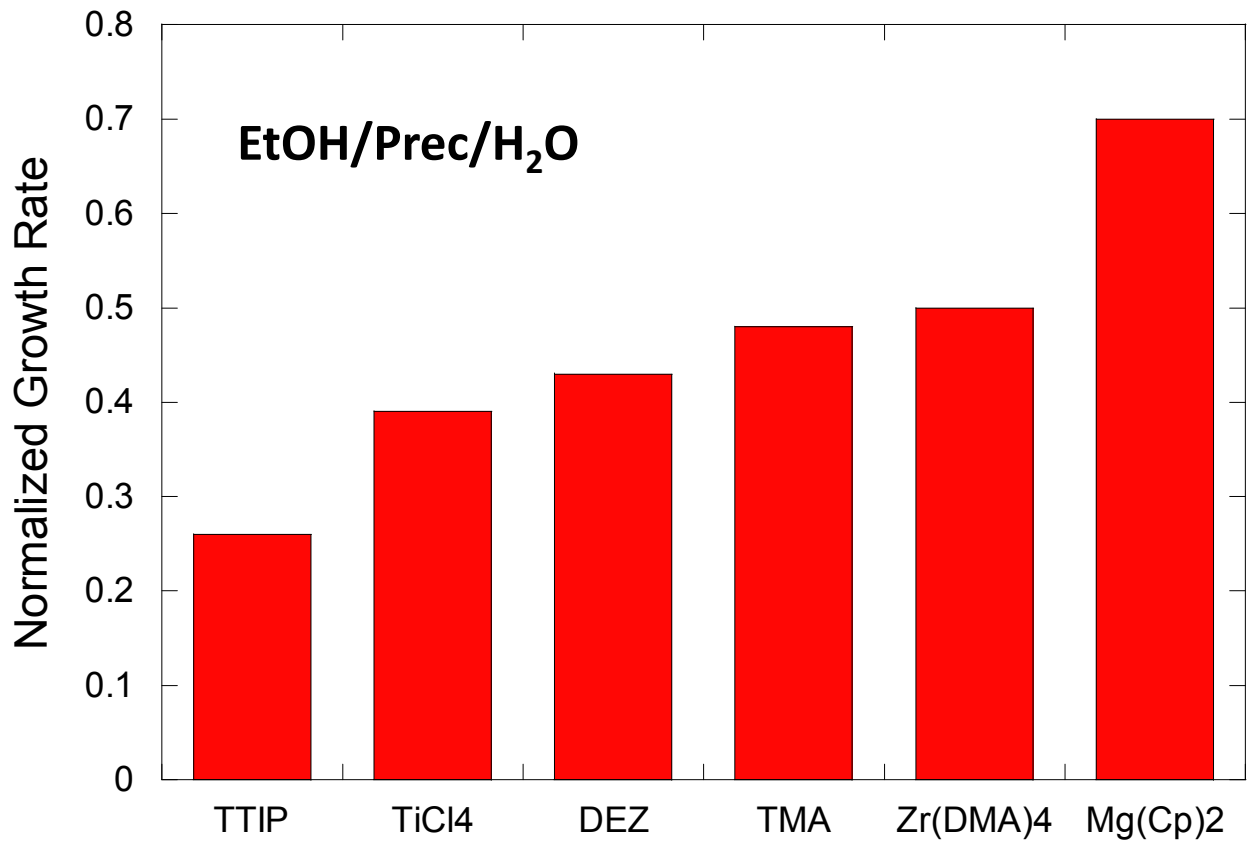
- EtOH/TMA/H_2O is self-limiting
- No growth from EtOH/TMA
- Nominal growth from EtOH/H_2O/TMA/H_2O

Summary of Surface Poisoning Using TMA



- Many organic compounds act as growth inhibitors
- Wide range of Al_2O_3 ALD growth rates

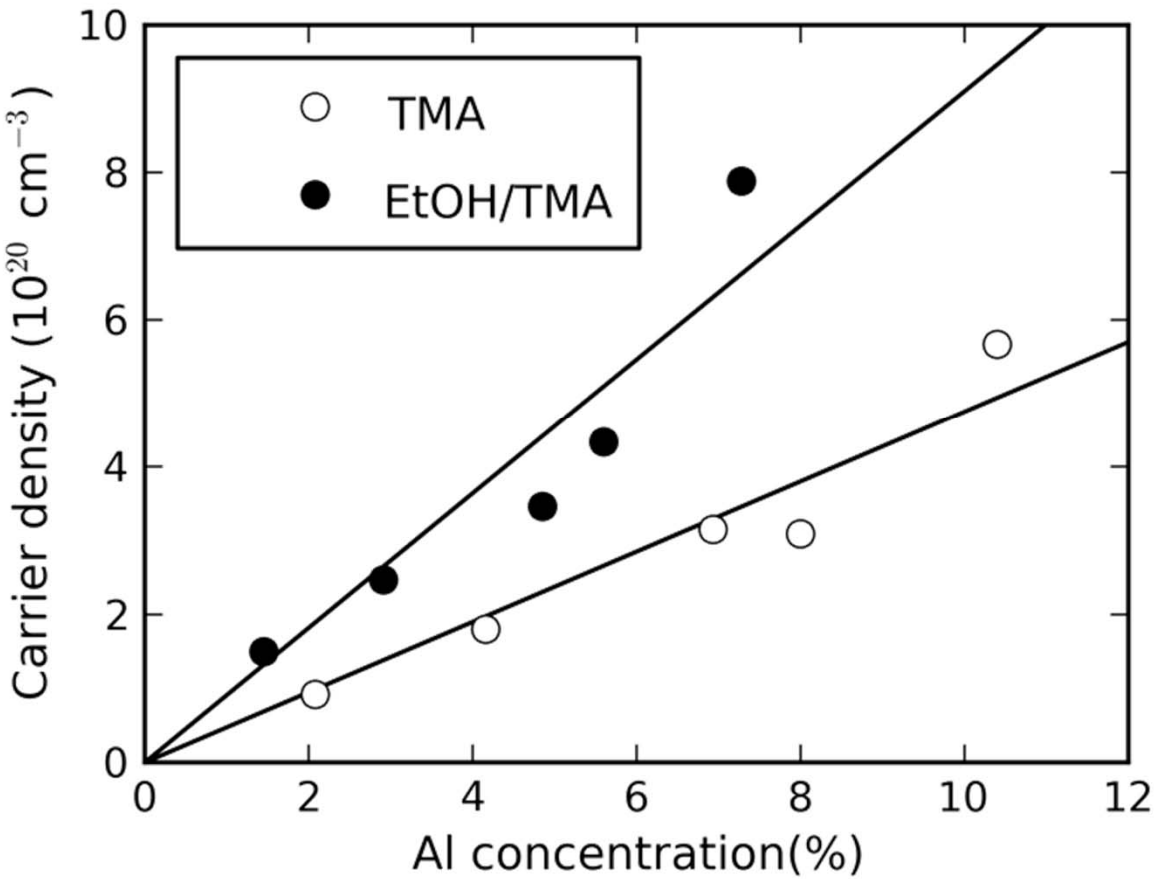
Growth Modulation for Other Precursors



- Surface poisoning works with many ALD materials

Application: Aluminum-Doped ZnO

- Al:ZnO with and without EtOH poisoning
- Measure doping efficiency



- 2x higher doping efficiency with surface poisoning

3) Precursor Synergy

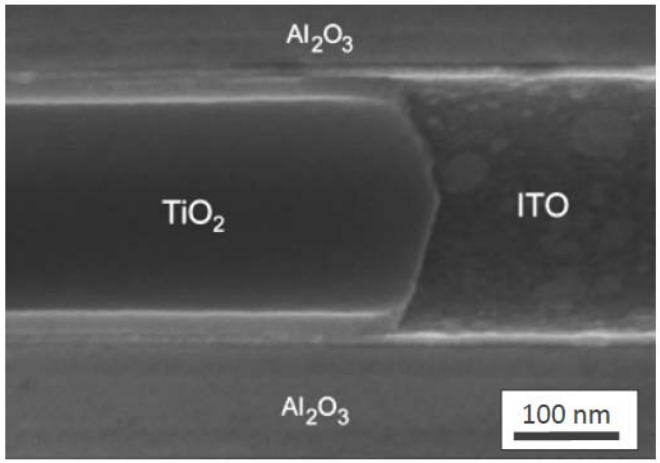
- *make precursors cooperate*

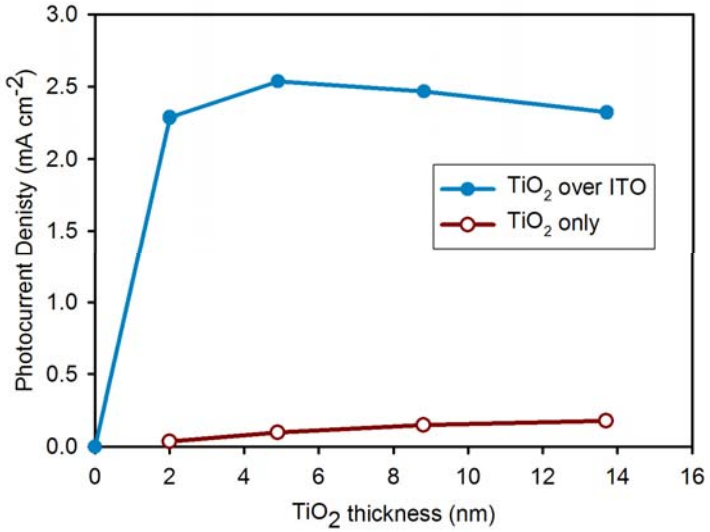
- Joseph A. Libera

- J. A. Libera, J. N. Hryn, and J. W. Elam, Chemistry of Materials (2011).

In_2O_3 ALD using Ozone

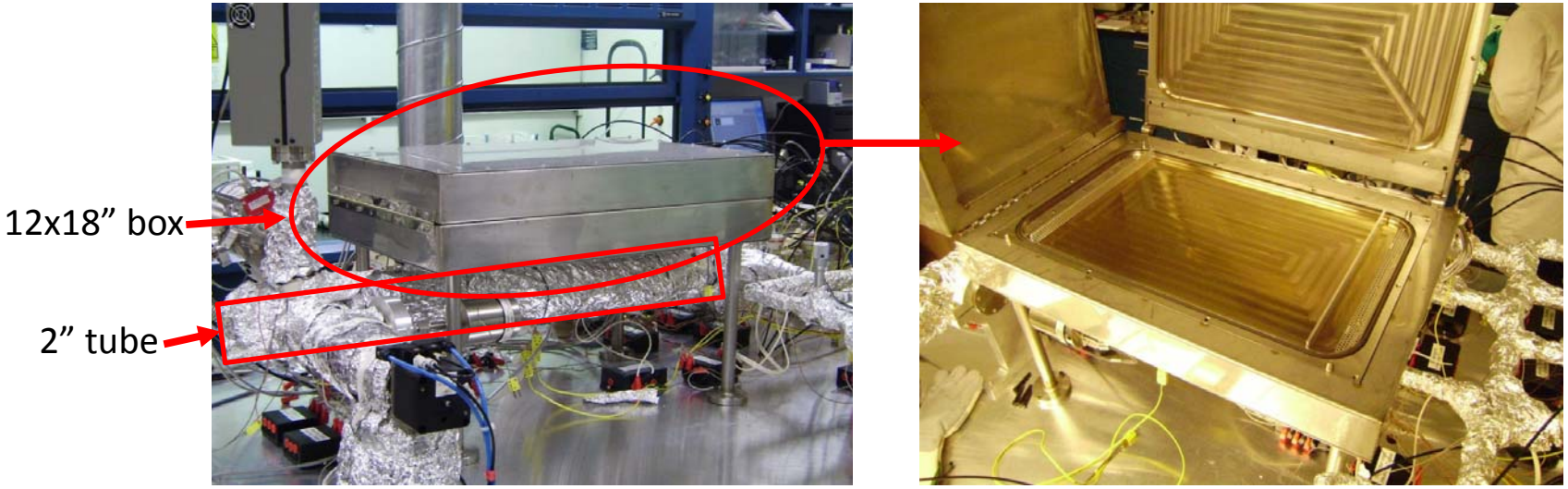
ALD ITO in nanopores (AR=300) for solar cells:

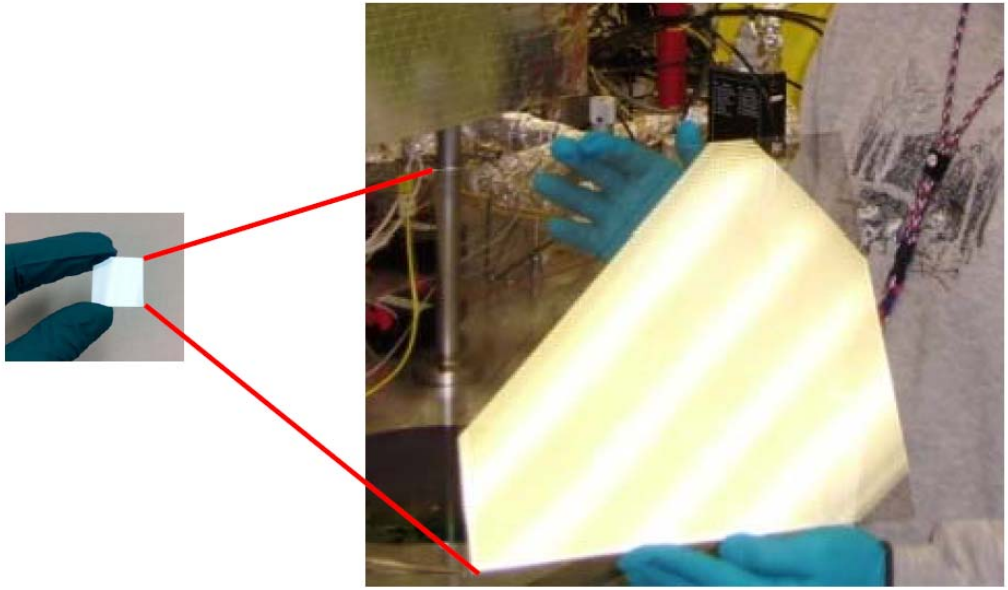




- $InCp + O_3 \rightarrow In_2O_3$ $(In^{+1} \rightarrow In^{+3})$
- In_2O_3 films were thinner downstream in reactor
- $O_3 \xrightarrow{In_2O_3} O^* + O_2$
- Indium oxide catalyzes ozone destruction

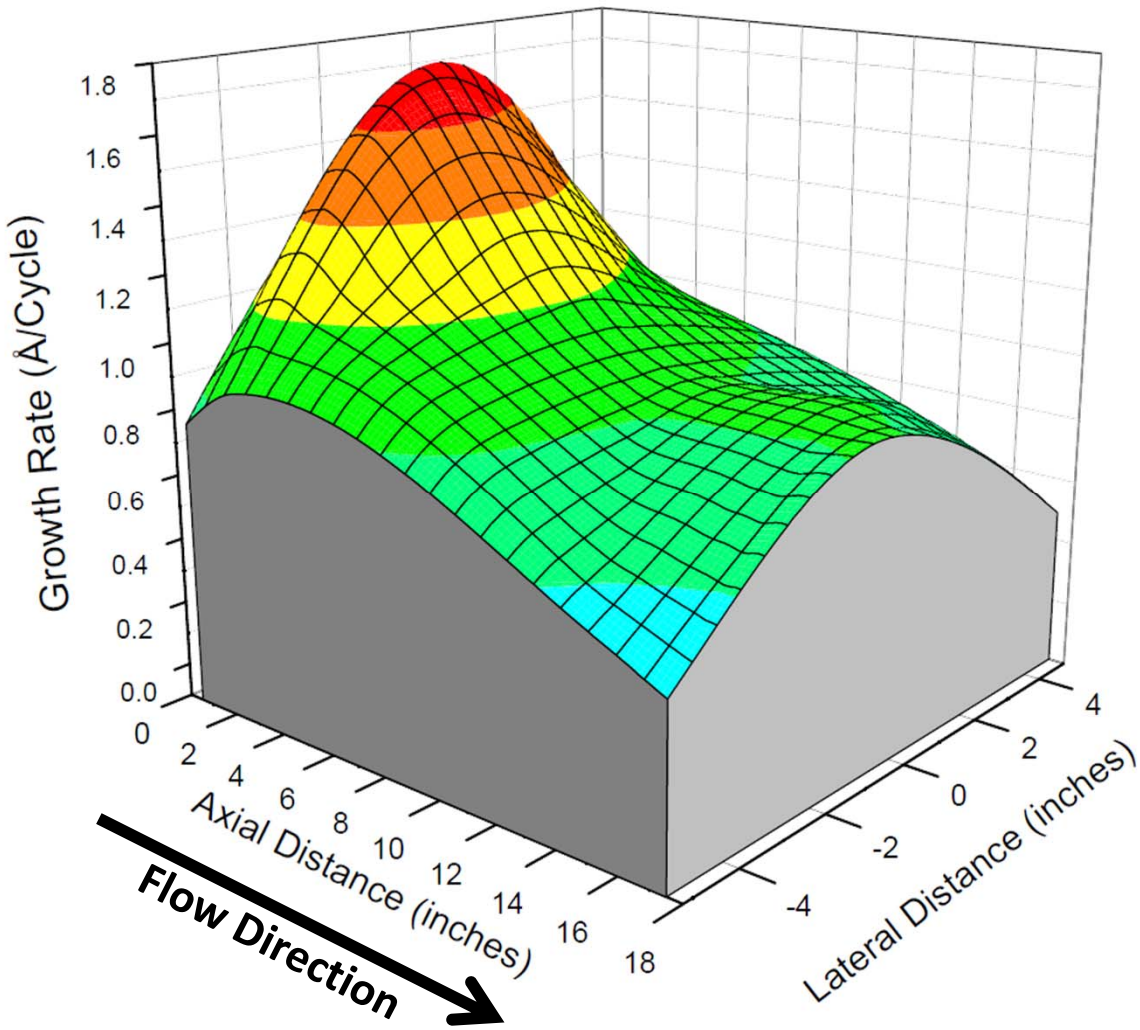
Scale-up of ALD ITO using Large Substrate Reactor





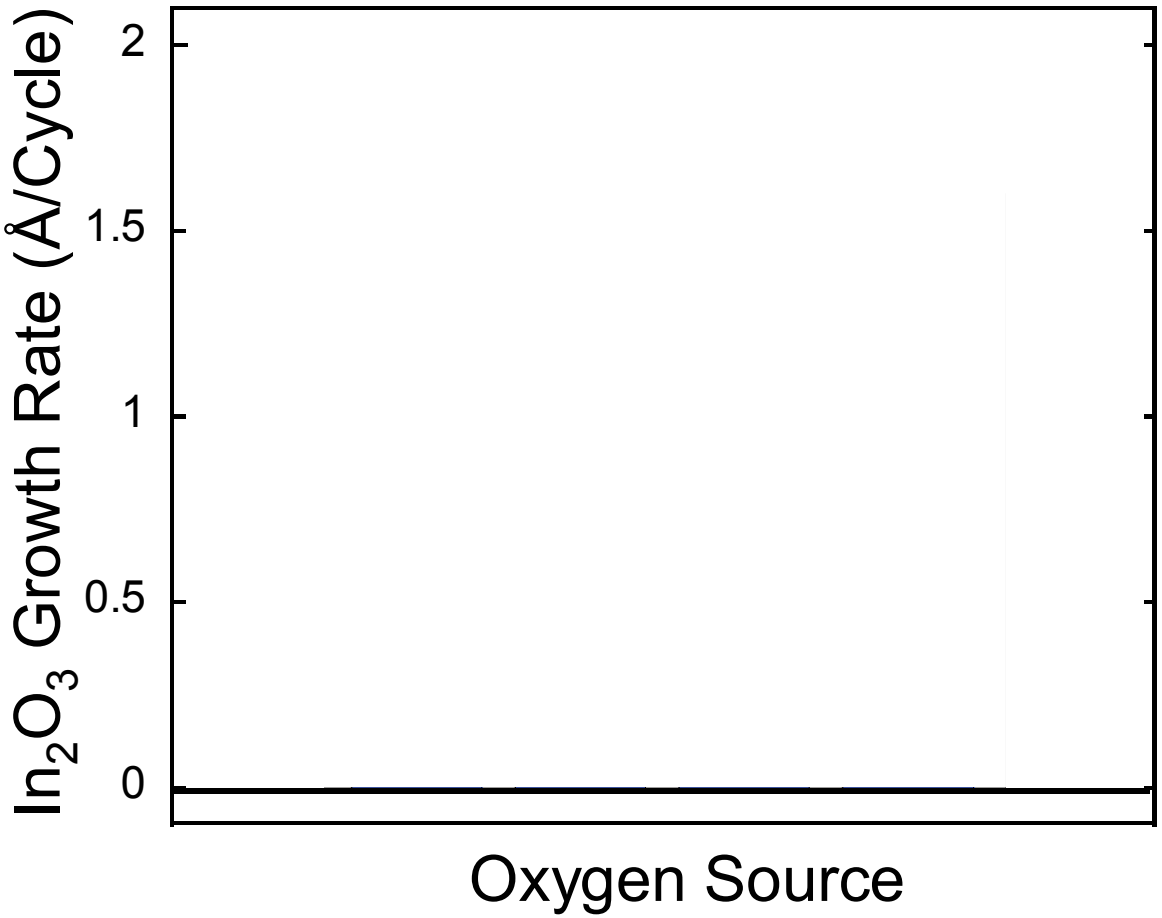
- From 1x1-in plates to 12-in x 18-in plates

Spatial Uniformity of ALD ITO Using InCp/O_3



- Very poor uniformity (± 45%)
- In_2O_3-catalyzed decomposition of O_3
- Can we develop an ALD process that does not require O_3 ?...

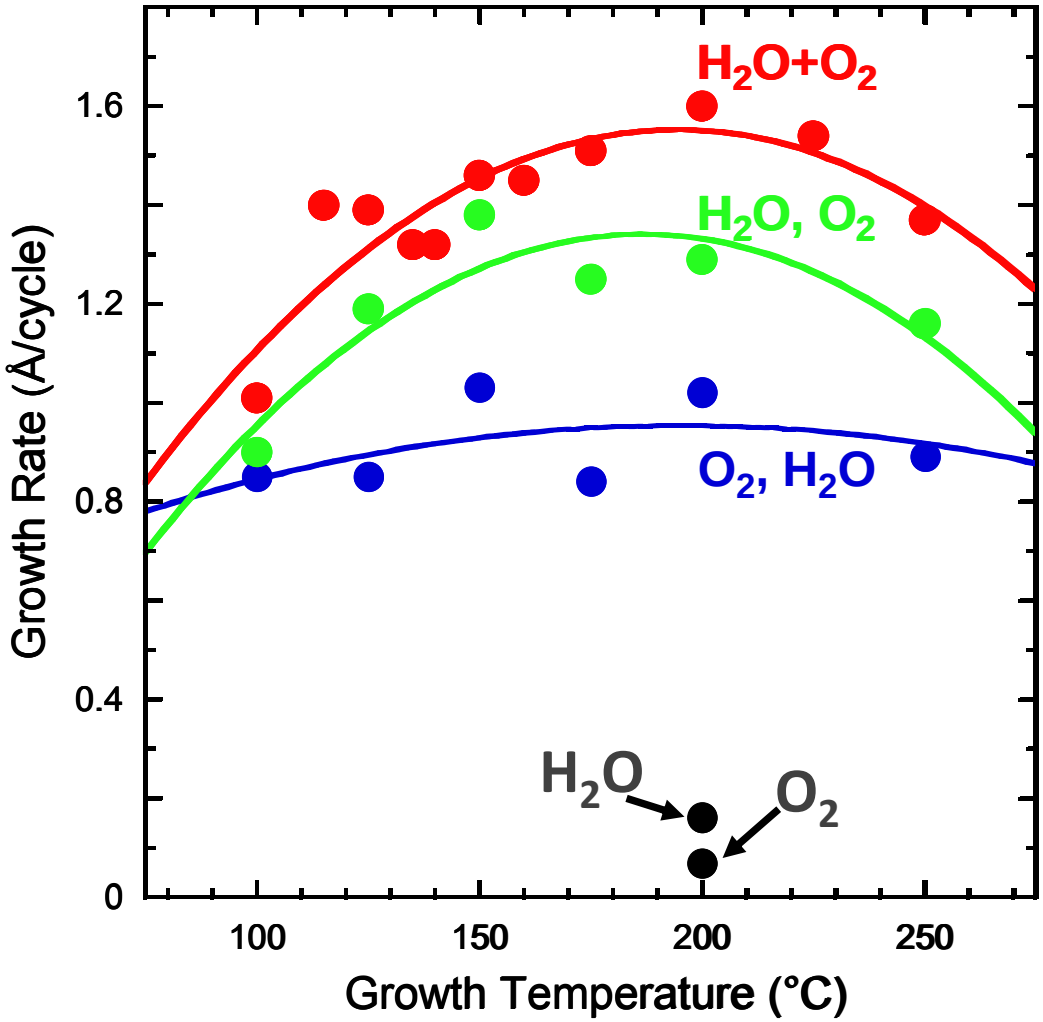
Different Oxygen Sources for In_2O_3 ALD with InCp



- In_2O_3 ALD does not work with either O_2 or H_2O alone
- *Simultaneously* dosing O_2 and H_2O allows In_2O_3 ALD

Growth of ALD In_2O_3 using InCp/(H_2O+O_2)

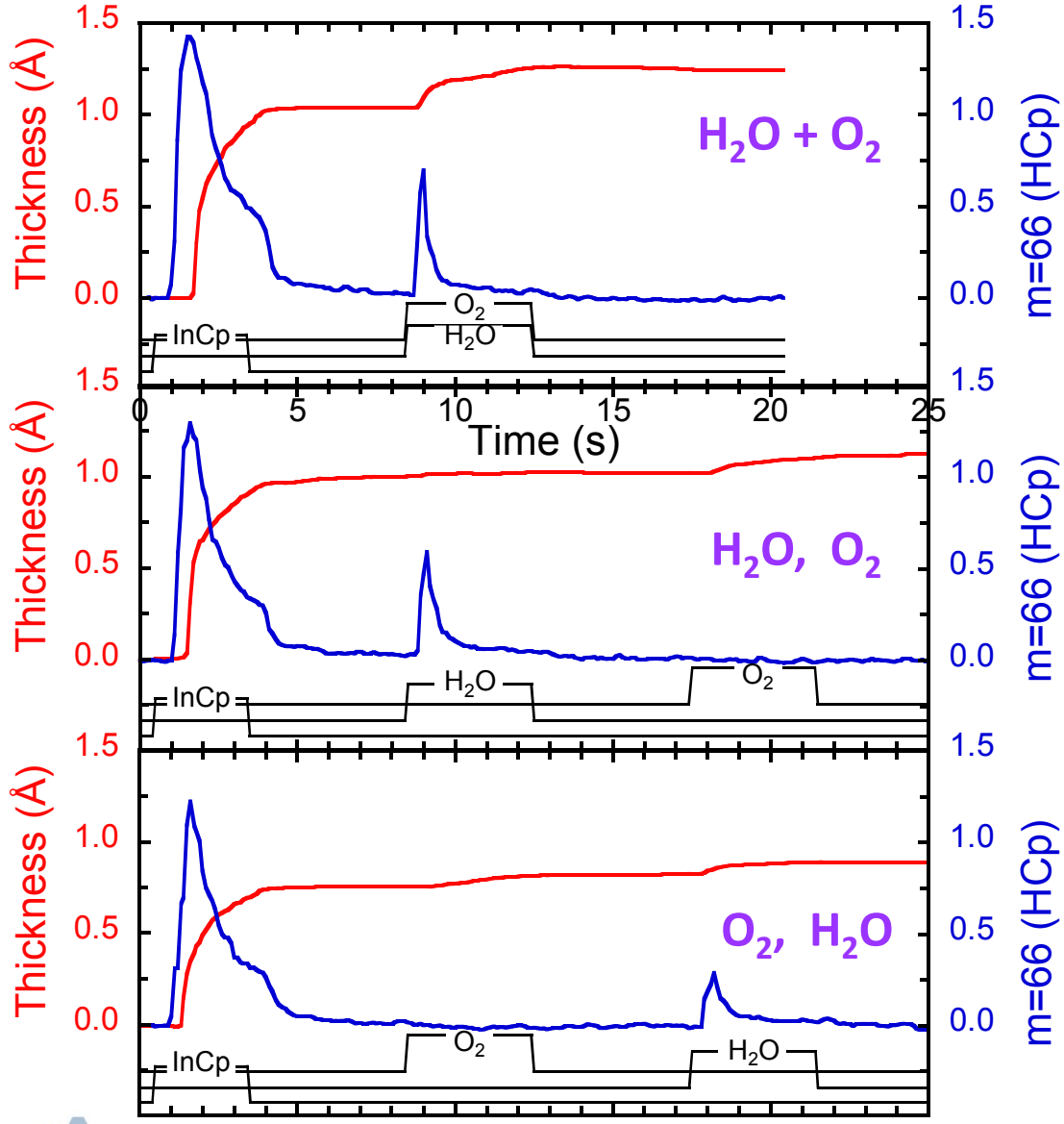
300 cycles on Si(100)
thickness measured by ellipsometry



- High growth rates, 1.0-1.6 Å/cycle
- H_2O and O_2 can be supplied simultaneously or in sequence
- Order is not critical

- What is the mechanism?
- Why are *both* H_2O and O_2 required?

In Situ QCM and QMS During In_2O_3 ALD



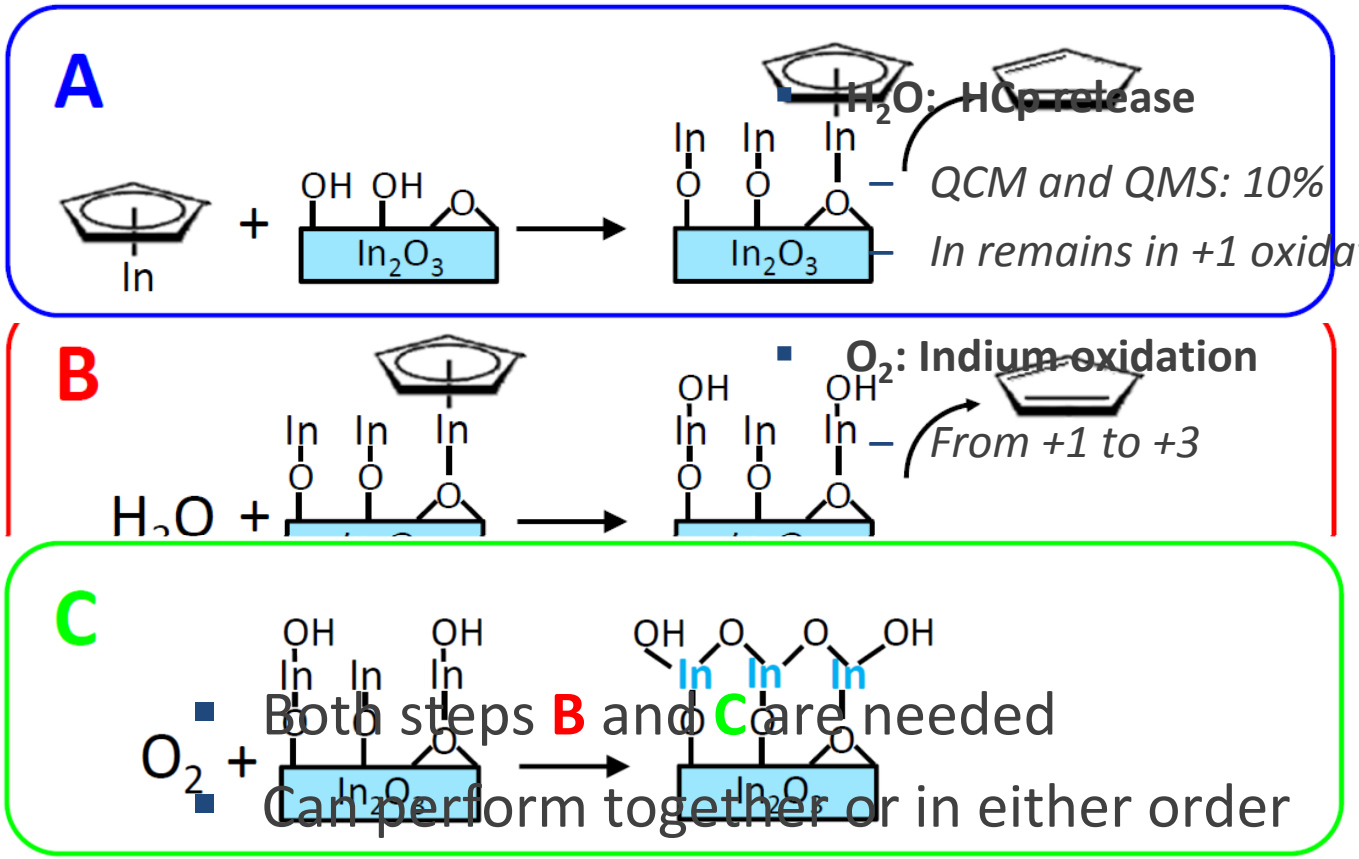
- $O_2 + H_2O$: HCp release and mass gain

- H_2O: HCp release
- O_2: mass gain

- H_2O: HCp release
- O_2: mass gain

Proposed Mechanism for In_2O_3 ALD

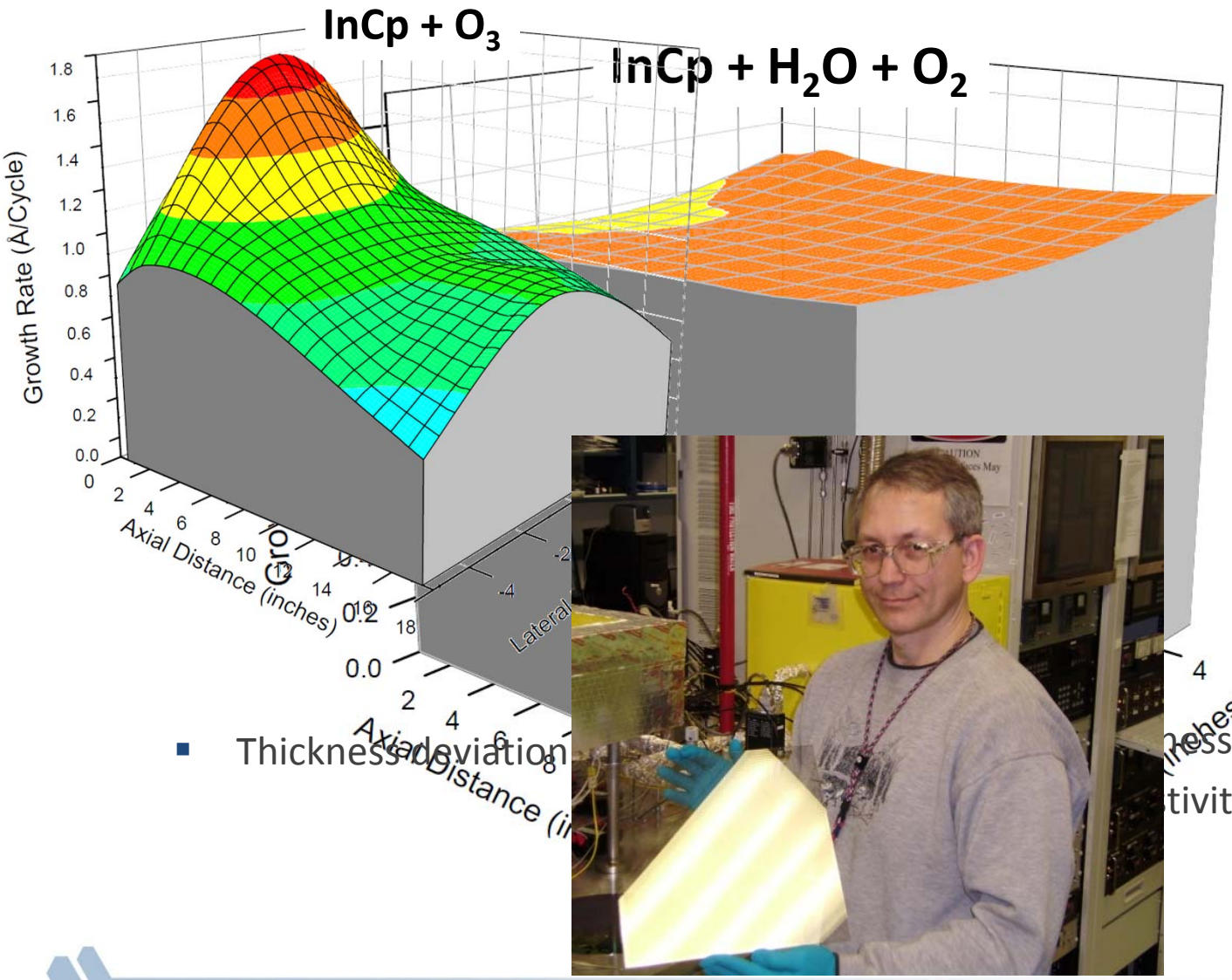
- **InCp: HCp release**
  - *QCM and QMS: 90%*



- **H_2O: HCp release**
  - *QCM and QMS: 10%*
  - *In remains in +1 oxidation state*
- **O_2: Indium oxidation**
  - *From +1 to +3*

- Both steps **B** and **C** are needed
- Can perform together or in either order
- H_2O and O_2 work *synergistically*

Scale-up of ALD In_2O_3 to 12”x18” Substrates



- Thickness deviation
- ness deviation: 2.5%
- tivity deviation: 6%

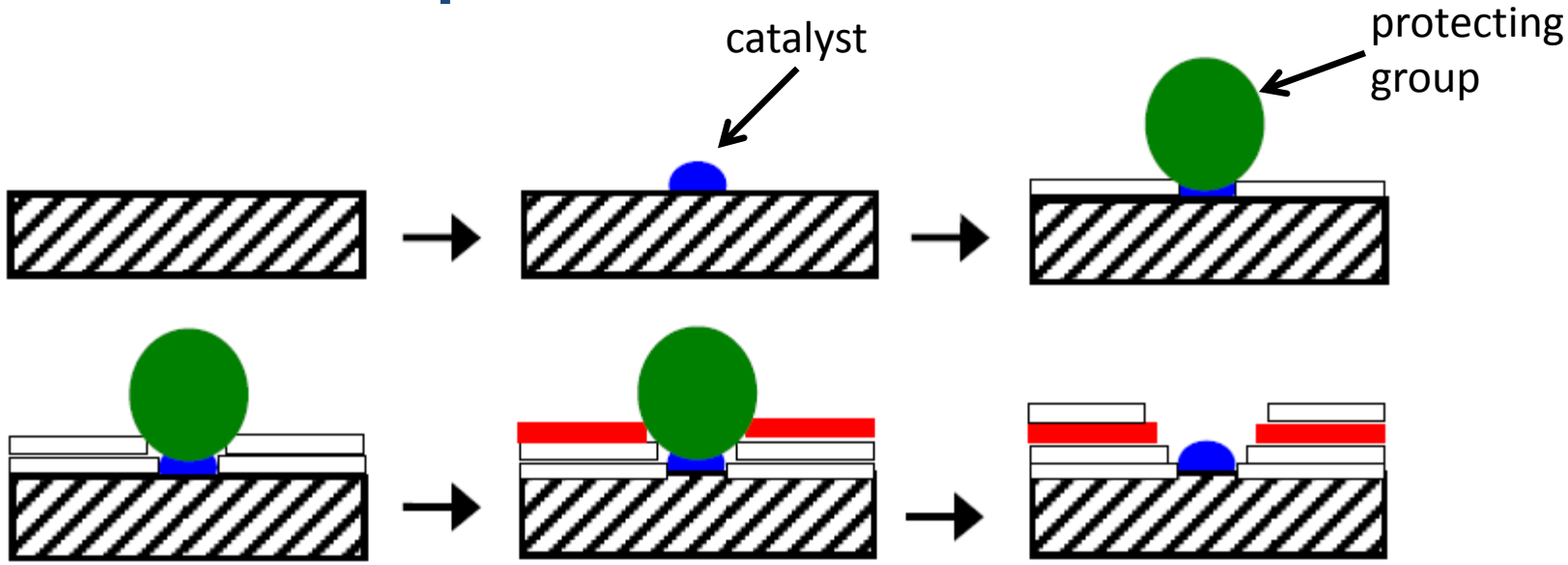
4) Nanobowls

- engineer catalytic environments

- Junling Lu
- Christian Canlas

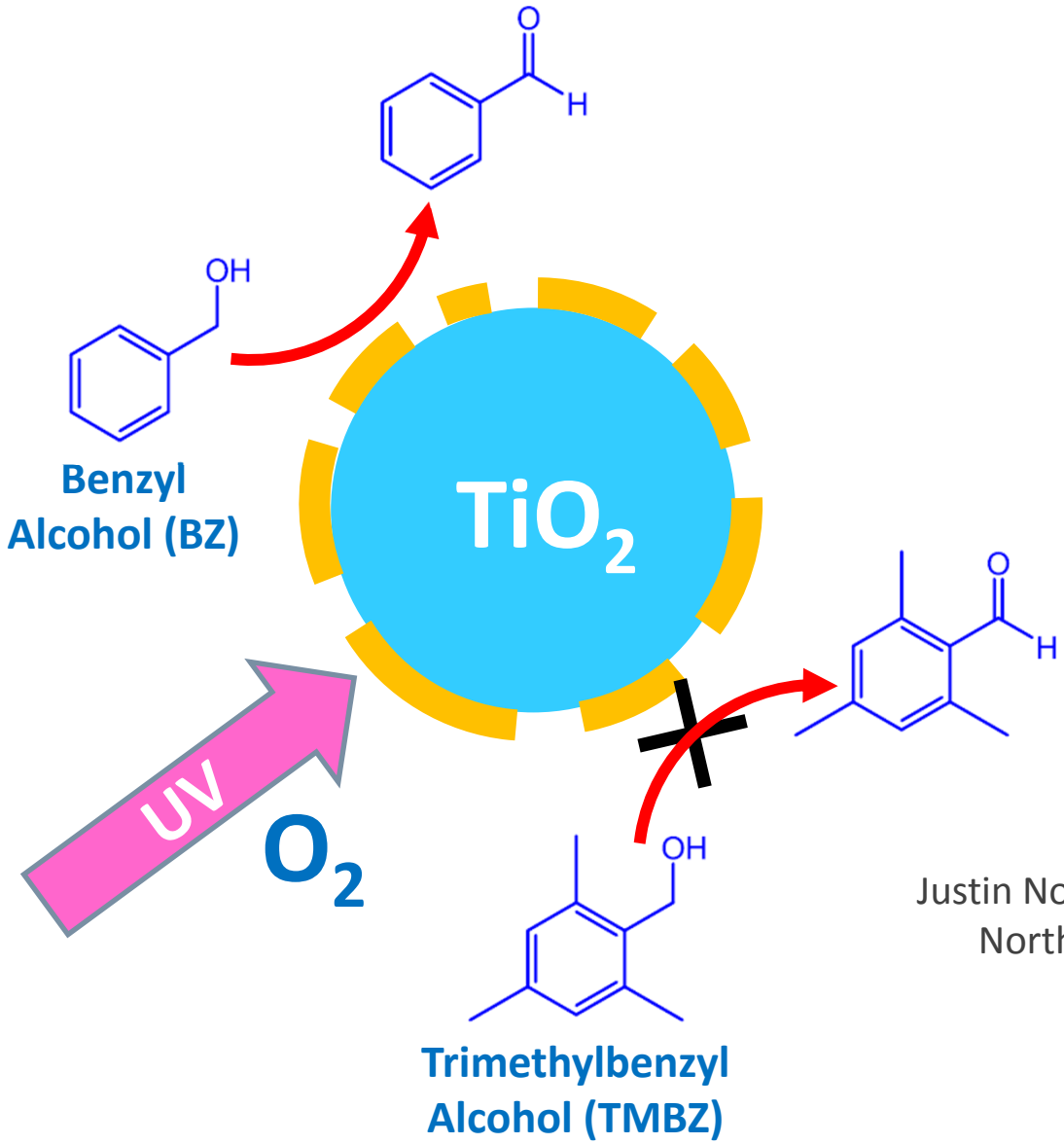
- J. Lu et. al., Science, **335**, 1205 (2012).
- C. Canlas et. al., Nature Chemistry **4**, 1030, (2012).

Nanobowl Concept



- Control composition and relative position of multiple catalytic species
- Impart shape-selectivity
- Stabilize catalyst

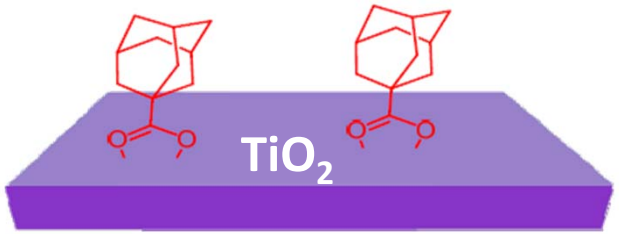
Al_2O_3 Nanobowls on TiO_2: Shape Selective Photocatalysis



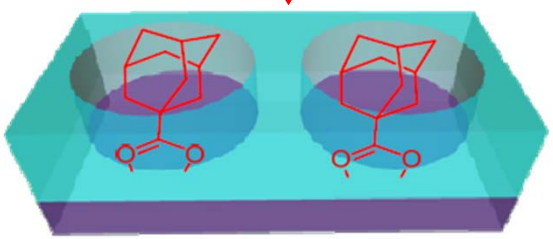
Justin Notstein, Christian Canlas
Northwestern University

C. Canlas et. al., Nature Chemistry **4**, 1030, (2012).

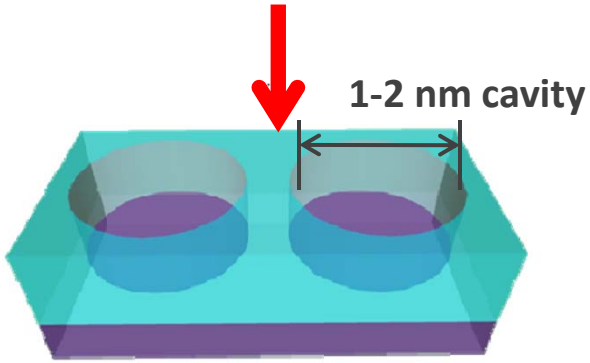
Nanobowls on TiO_2 Photocatalyst



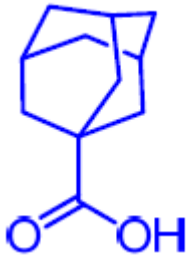
Grafting of ACA template



Al_2O_3 ALD

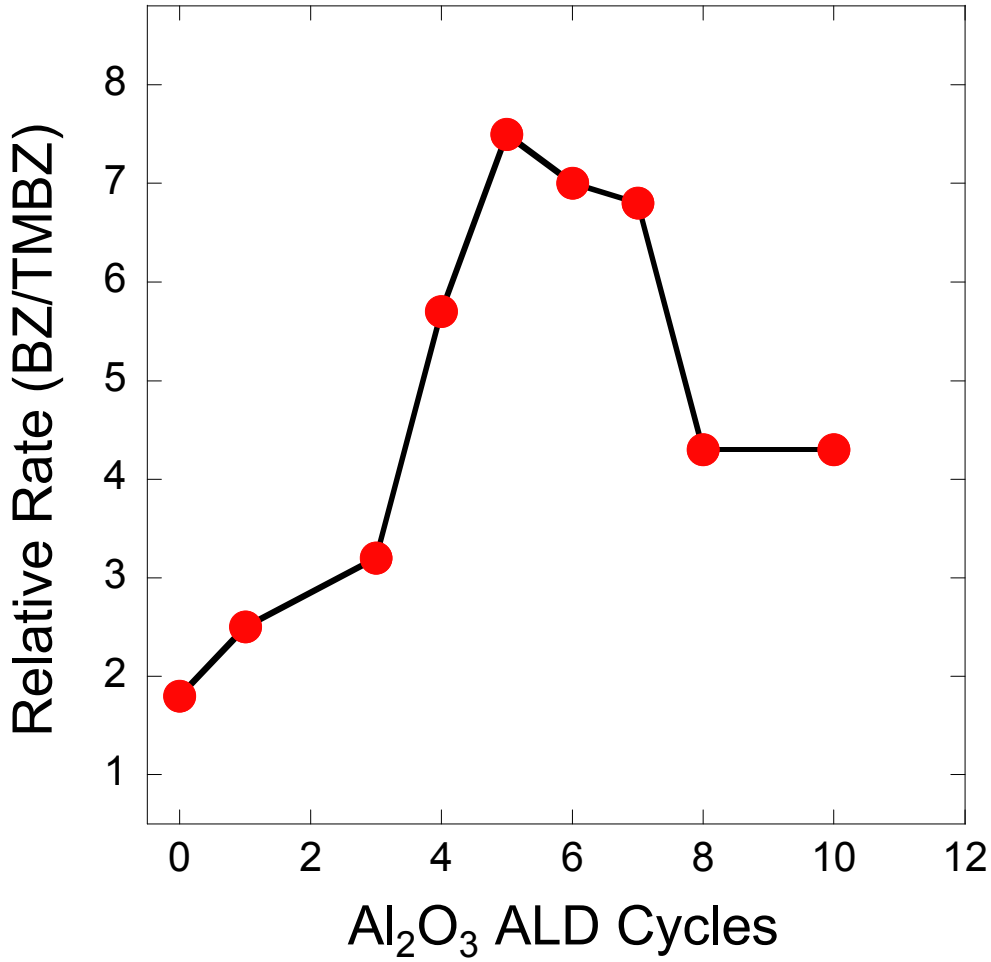


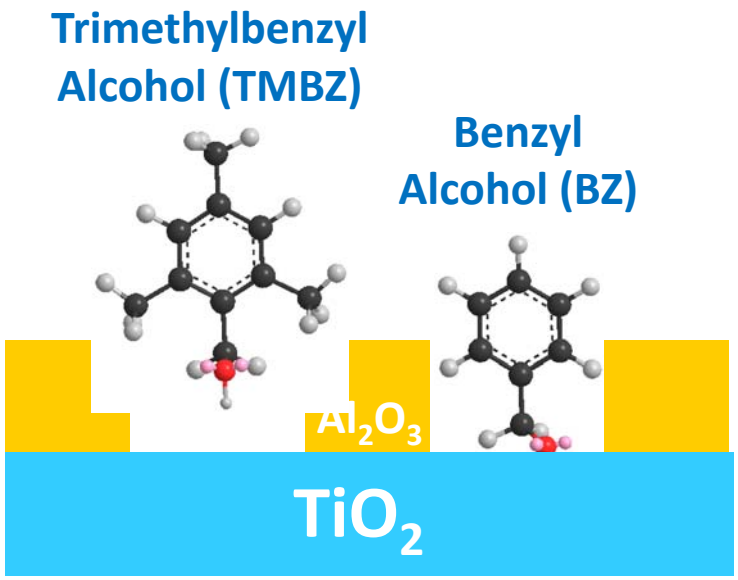
Template removal using ozone



Adamantane carboxylic acid (ACA)

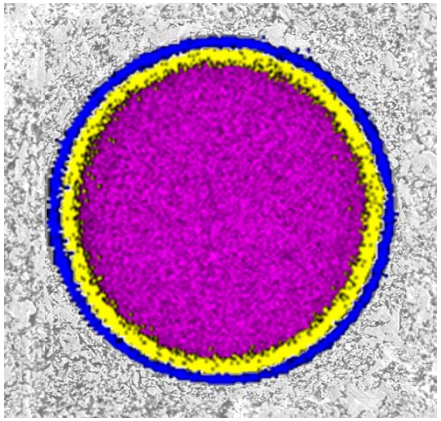
Relative Rates of Photocatalytic Oxidation on Nanobowl Catalysts



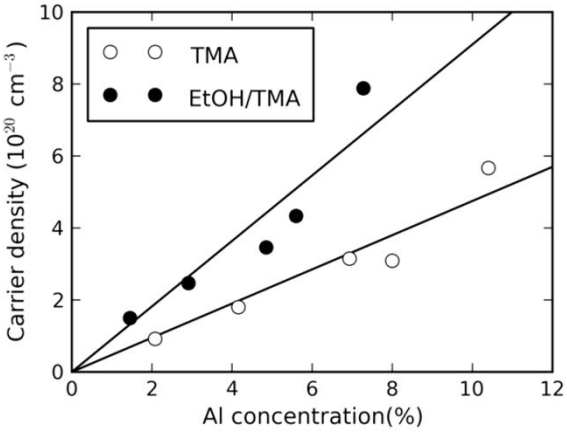


- Remarkable selectivity for BZ after ~5 ALD Al_2O_3 Cycles

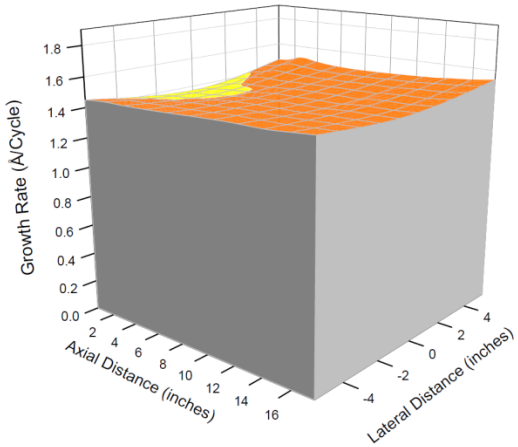
Conclusions- Why look beyond A/B/A/B… ?



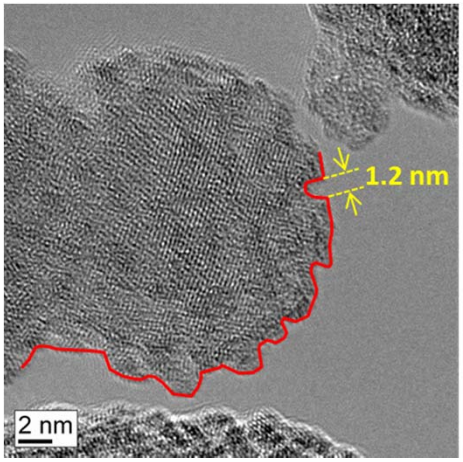
stripe coating



surface poisoning



precursor synergy



nanobowls

Acknowledgements

J. Libera, A. Yanguas-Gil, J. Lu, C. Canlas,
A. Mane, H. Meng, Y. Lei, S. Jokela, S. Mohney,
A. Martinson, J. Hupp, M. Pellin, J. Hryn, A. Hryn, A. Xu, J. Notestein, P. Stair, C. Marshall

Questions?