Improving the Speed of Atomic Layer Deposition Without Sacrificing Chemical Efficiency

Matt Weimer, Dane Lindblad, Sara Harris, Staci Moulton, Arrelaine Dameron, Ofer Sneh
Forge Nano, Thornton, CO

Next-generation nanomaterials and devices rely on precise control via atomic scale processing of conformal, dense, and pin-hole free thin films. For example, conformal coatings in through silicon vias (TSV) as a Cu nucleation and diffusion barrier layers will drive new architectures of enhanced microelectromechanical systems (MEMS). Improved device conversion efficiencies in photovoltaic can be enabled by thin conformal coatings over intricate topographies. Atomic layer deposition (ALD) is unrivaled for gas-phase deposition of atomic precision thin films to non-line-of-sight structures. Used both in additive or subtractive processing to coat nanofeatures or to template and then remove nanofeatures, ALD drives device performance. In traditional gas-phase depositions there is a tradeoff between speed of film growth, conformality, and precursor efficiency. In traditional ALD systems, a more precise film has a slower growth process (i.e., <0.5nm/minute) and suffers from poor precursor usage efficiency (normally >20%). This idea of ALD as slow and inefficient has limited its adoption in various applications due to perception of higher associated costs. Fortunately, progress has been made to increase ALD deposition speed, approaching that of less conformal techniques like CVD, without sacrificing the inherent benefits; perfect thickness conformality and dense, pin-hole free films. This talk will cover the tradeoffs in traditional ALD between uniformity/precursor efficiency and speed, next, a description of the ALDx technology to conformally coat high surface area nanofeatures at speeds exceeding 10 nm/minute, finally some topical examples of applications for ALD technology on industry relevant nanofeatures. True atomic-scale control is enabled by ALDx technology, improving viability of conformal coatings.

https://www.svc.org **DOI: https://doi.org/10.14332/svc23.proc.0001**

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Improving the Speed of Atomic Layer Deposition Without Sacrificing Chemical Efficiency

Atomic Layer Processing

Matt Weimer, Principal R&D Scientist
SVC TechCon May 2023

SVC Society of Vacuum Coaters

TechCon 2023 Washington, D.C

Gaylord National Resort & Convention Center

May 6 – May 11, 2023

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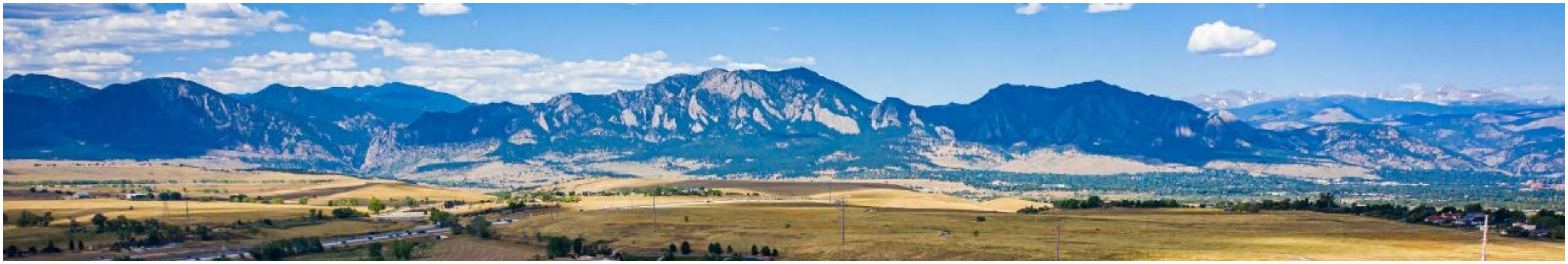
We Make Materials Better



HQ outside Denver, Colorado, USA

Install base and satellite offices across Europe and Asia

World’s largest particle ALD coating equipment

World’s fastest and most efficient object/wafer ALD equipment

Sundew Technologies

Investors

LG Technology Ventures

AIR LIQUIDE ALIAD Venture Capital

VOLKSWAGEN GROUP OF AMERICA

Sumitomo Corporation of Americas

MITSUI KINZOKU

End-to-end Solutions Provider

SVC Society of Vacuum Coaters TechCon 2023 Washington, D.C. Gaylord National Resort & Convention Center May 6 – May 11, 2023

ALD Has Enabled Technology for Decades

- **1965** — Molecular Layering: ALD first published in USSR
- **1974** — Atomic Layer Epitaxy: First ALE Patent in FI
- **1983** — ALD Pilot Production: **Electroluminescent displays**
- **1989** — Atomic Layer Deposition: First ALD of TMA based Al_2O_3
- **1998** — Atomic Layer Deposition: ALD in DRAM devices
- **2007** — ALD Pilot Production: Intel launches ALD of HfO_2 as **high-k metal gate**
- **2012** — ALD Pilot Production: **PERC solar cells** ALD Al_2O_3
- **2020** — ALD Pilot Production: ALD in **3D NAND in channel hole**

Many more applications

- Displays (LED, microLED)
- Micro/nano-electronics (MEMS, RF, Power devices, images sensors, advanced packaging, photonics)
- Advanced photovoltaics
- Catalysts
- Pharmaceuticals and medical devices
- Additive manufacture
- Magnetics
- **Batteries**

Molecular Layering = ML
Atomic Layer Epitaxy = ALE
Atomic Layer Deposition = ALD

The speed and cost of ALD has limited adoption in many areas

ALD Has Enabled Technology for Decades

Molecular Layering
ALD first published in USSR

Atomic Layer Epitaxy
First ALE Patent in FI

ALD Pilot Production
Electroluminescent displays

https://crystal-display.com/

1965 | 1974 | 1983 | 1989 | 1998 | 2007 | 2012 | 2020 | Many more applications

Molecular Layering = ML
Atomic Layer Epitaxy = ALE
Atomic Layer Deposition = ALD

Electroluminescent displays proved ALD can be used in produciton

ALD Has Enabled Technology for Decades

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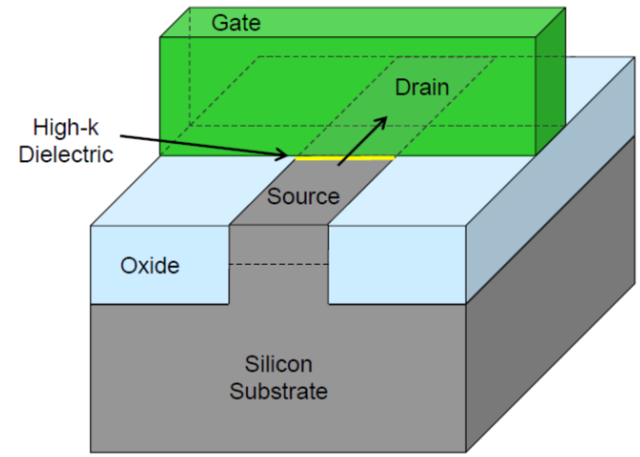

Intel 22nm node

Molecular Layering = ML
Atomic Layer Epitaxy = ALE
Atomic Layer Deposition = ALD

Intel gave ALD it's first moment in the sun!

ALD Has Enabled Technology for Decades

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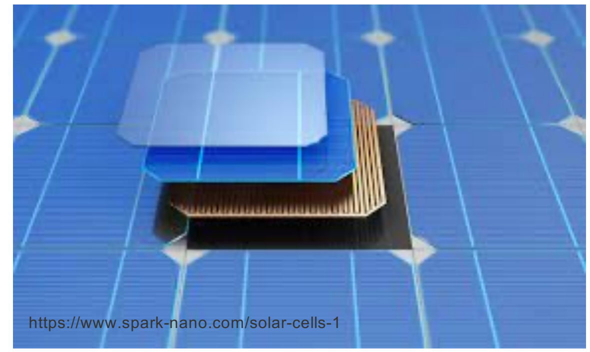
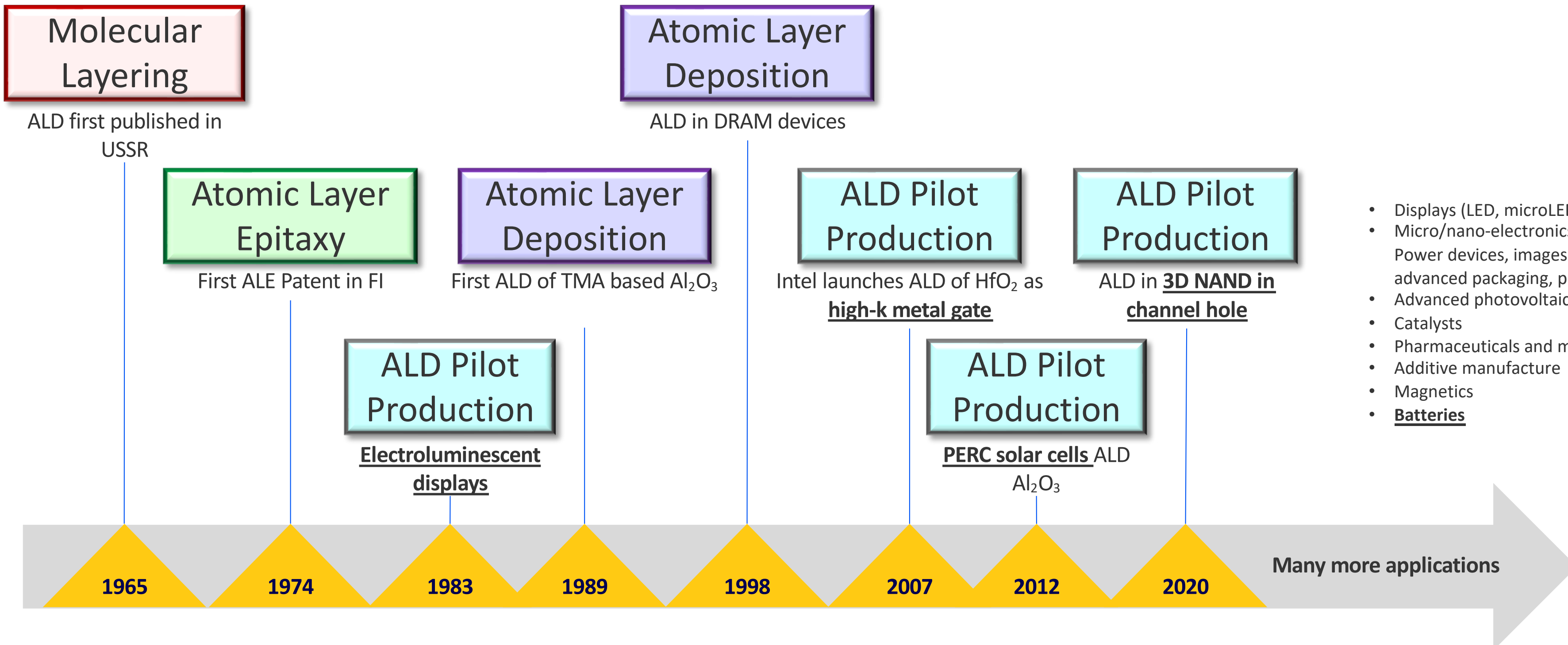


Molecular Layering = ML
Atomic Layer Epitaxy = ALE
Atomic Layer Deposition = ALD

PERC cells are widely available

ALD Has Enabled Technology for Decades



- Displays (LED, microLED)
- Micro/nano-electronics (MEMS, RF, Power devices, images sensors, advanced packaging, photonics)
- Advanced photovoltaics
- Catalysts
- Pharmaceuticals and medical devices
- Additive manufacture
- Magnetics
- **Batteries**

Molecular Layering = ML
Atomic Layer Epitaxy = ALE
Atomic Layer Deposition = ALD

A lot of planned application, but speed/efficiency are barriers

ALD Has Enabled Technology for Decades

Molecular Layering

ALD first published in USSR

Atomic Layer Epitaxy

First ALE Patent in FI

Firs

ALD Pi
Product

Electrolumin
display

Atomic Layer Deposition

D Pilot
duction

n **3D NAND in**
annel hole

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1965 | 1974 | 1983 | 2020 | Many more applications

Molecular Layering = ML
Atomic Layer Epitaxy = ALE
Atomic Layer Deposition = ALD

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Forge Nano overcoming barrier to battery adoption of ALD

ALD Has Enabled Technology for Decades

Molecular

Atomic Layer

Brianna Boeyink – Forge Nano

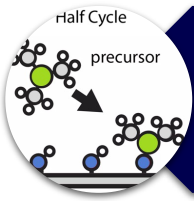
Improved Performance and Safety via ALD-Enhanced Sulfide-Based Solid-State Batteries

RF,

vices

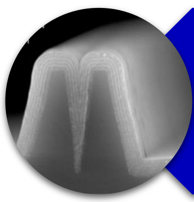
Molecular Layering = ML
Atomic Layer Epitaxy = ALE
Atomic Layer Deposition = ALD

First talk in this session after lunch

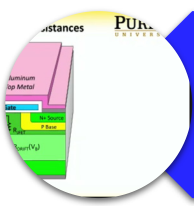


ALD Basics

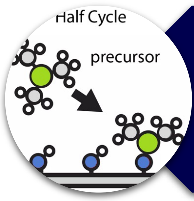
Opportunities for ALD Adoption



R&D Applications for Fast ALD

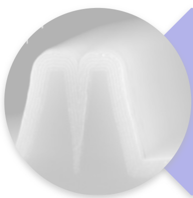


Applications for Production Environments

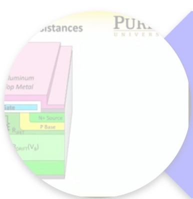


ALD Basics

Opportunities for ALD Adoption



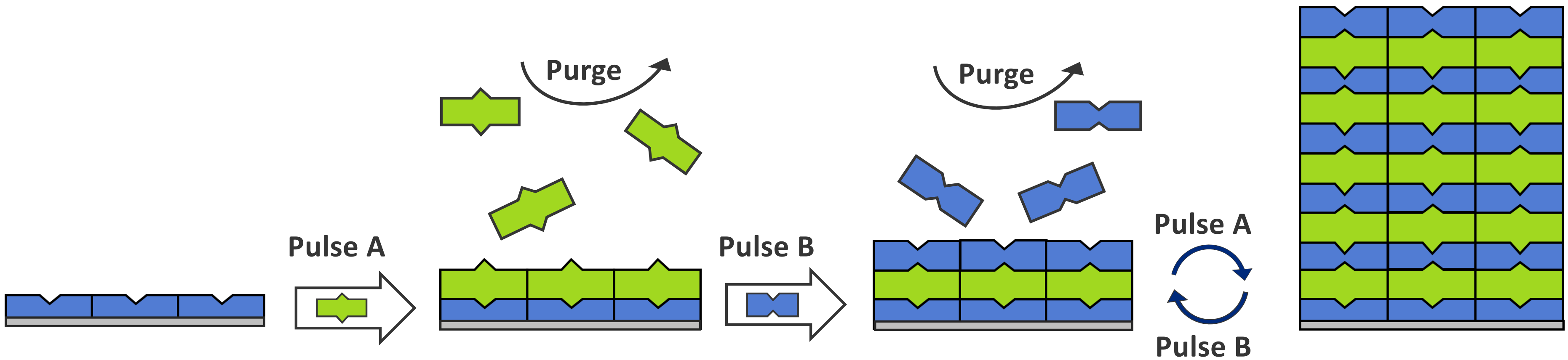
R&D Applications for Fast ALD



Applications for Production Environments

Atomic Layer Deposition – The Basics

ALD is all about sequential surface reactions to deposition thin films atomic layer by atomic layer



How can you visualize surface chemistry?

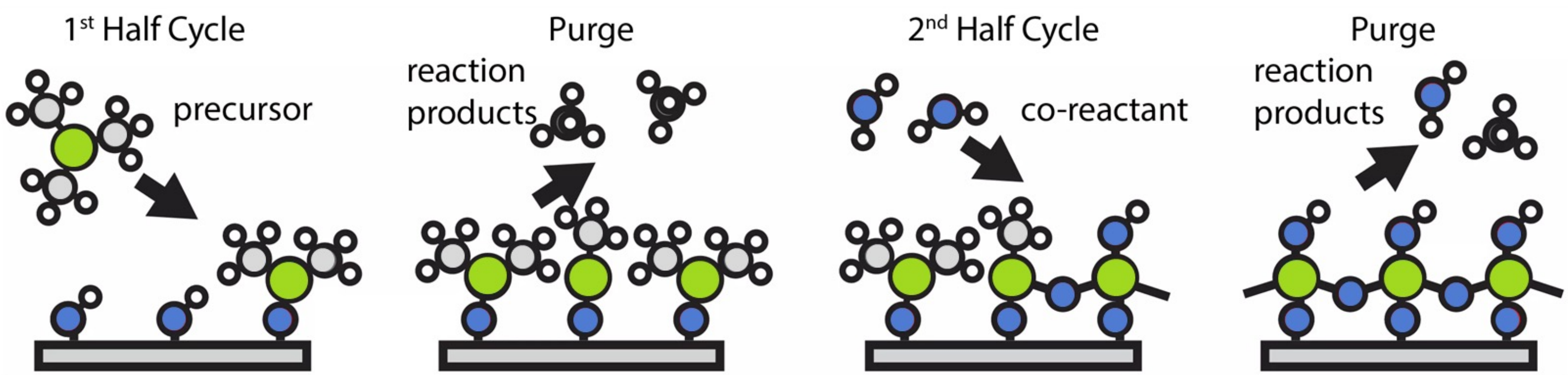
How to Visualize Atomic Scale Manufacturing

http://whiteapronblog.com/2017/06/02/north-carolina-thirteen-layer-cake/

Who doesn't love cake?

Atomic Layer Deposition – Chemistry

Based on spontaneous, sequential, self-limiting thermal reactions that add material with atomic level control

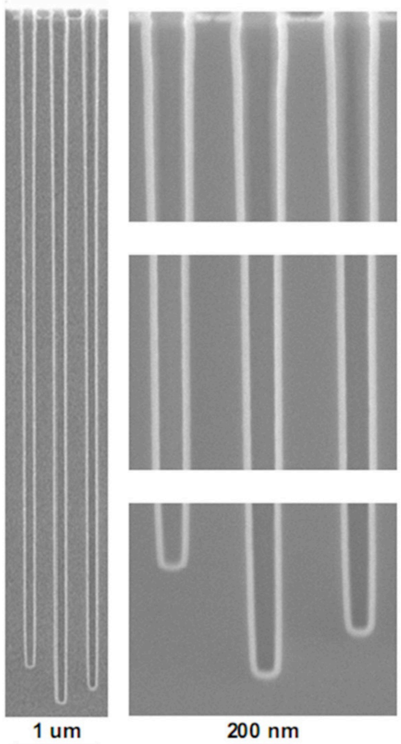


Vervuurt, R.H.J., Kessels, W.M.M.E., and Bol, A.A. (2017) *Adv. Mater. Interfaces*, **1700232**, 1700232

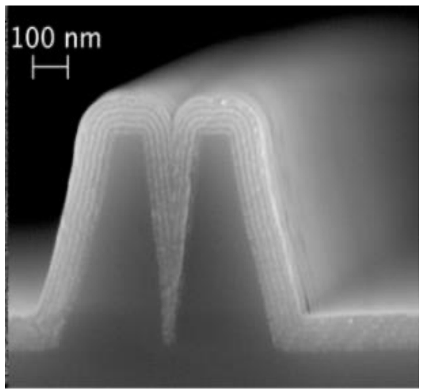
Self-limiting surface chemistry deposits conformal, uniform, pin-hole free films, with good surface adhesion

Self-Limiting Surface Chemistry Advantages

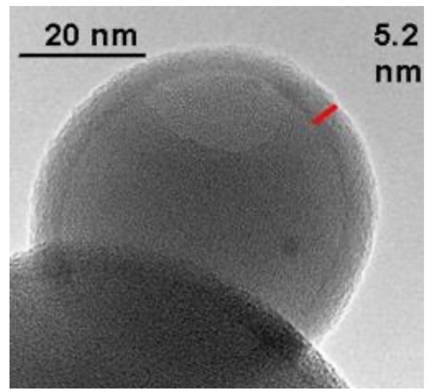
Conformal Coating



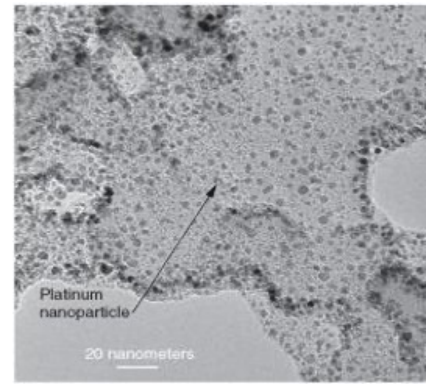
Tailored Multilayers



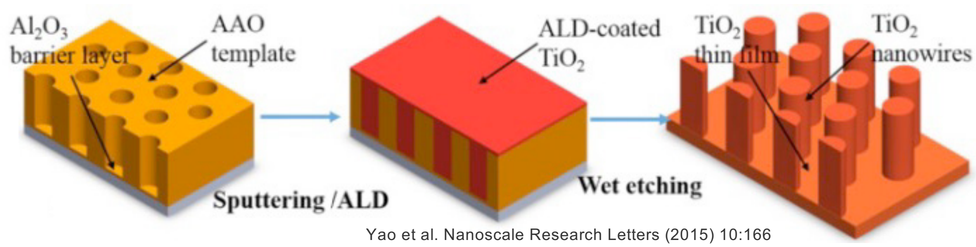
Precision Thickness Control



High Surface Adhesion



High Quality, Low Temperature Films



Yao et al. Nanoscale Research Letters (2015) 10:166

ALD is very useful, but it can't all be good

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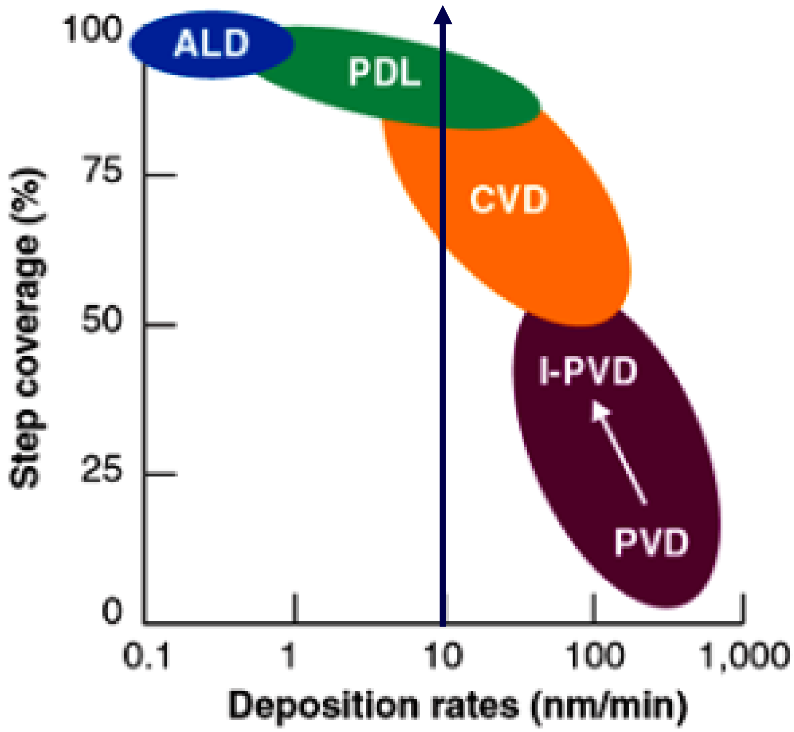
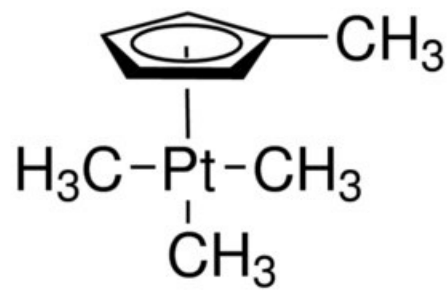
Why isn't ALD Everywhere?

ALD is Slow



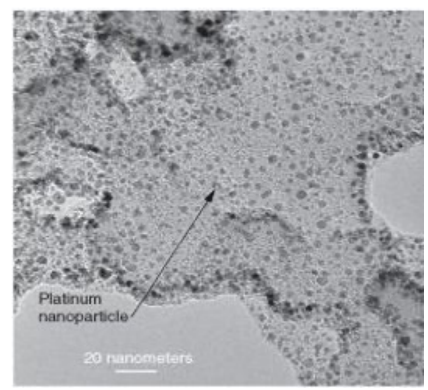
Sputtering Materials for VLSI and Thin Film Devices, 2014, Pages 93-170

ALD is Expensive



Trimethyl(methylcyclopentadienyl)platinum(IV)

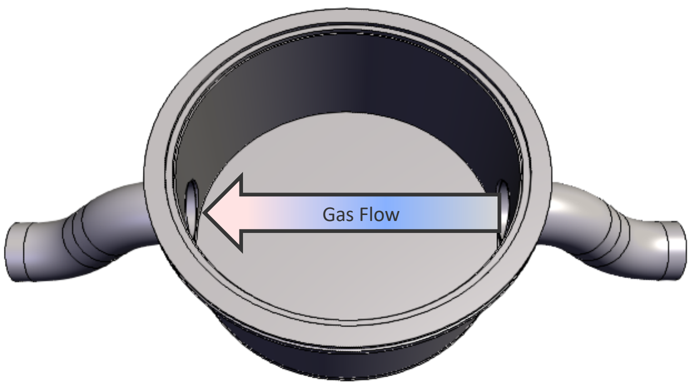
\$450/gram → utilize ~10-20%



How can these barriers be overcome?

Precursor vs Purge Efficiency Tradeoff Barrier

Traditional ALD Reactor

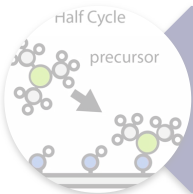


Traditional ALD reactors are stuck in a tradeoff

- Reactor pressure **increase**
  - Precursor use improves (thumbs up)
  - Purge time longer (thumbs down)
- Reactor pressure **decrease**
  - Precursor use degrades (thumbs down)
  - Purge time shorter (thumbs up)

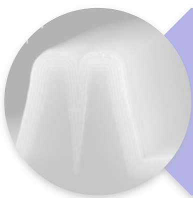
With traditional ALD systems, one must choose between efficient precursor use or efficient purge times

How have people approached improving this tradeoff?

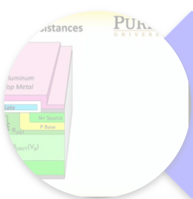


ALD Basics

Opportunities for ALD Adoption

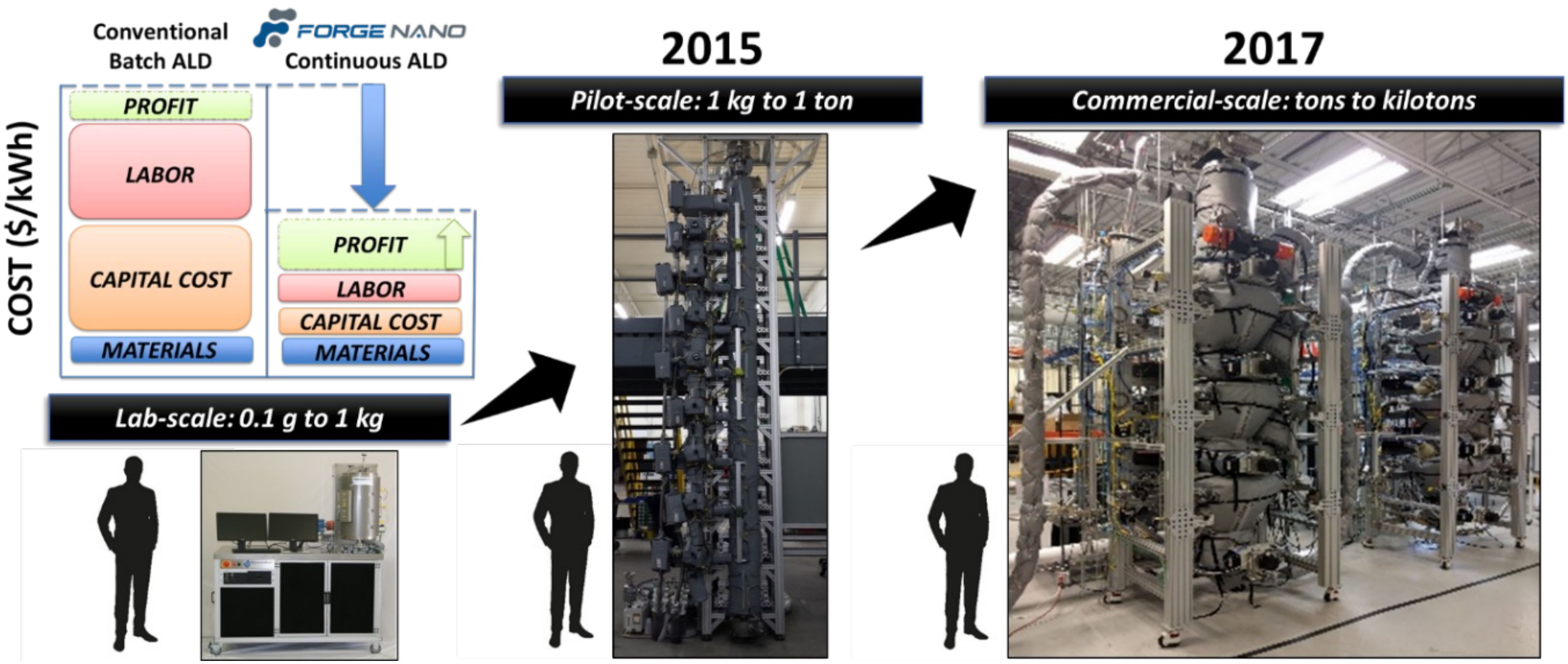


R&D Applications for Fast ALD



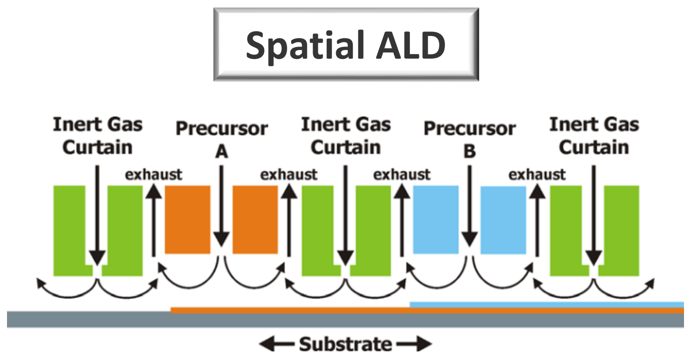
Applications for Production Environments

Powder ALD Production, Get Larger!



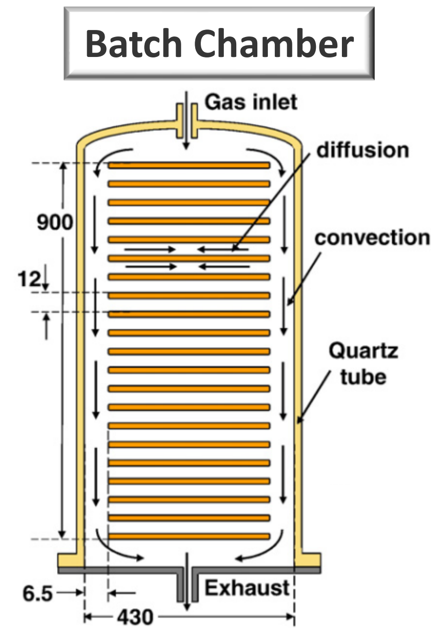
For production scale of powder ALD, it's all about getting bigger!

Wafers and Objects – Move or Get Big



J. Vac. Sci. Technol. A 30, 010802 (2012); https://doi.org/10.1116/1.3670745

Spatial ALD		Batch ALD
Very fast	Speed	Very slow
Slightly better	Precursor Consumption	Much worse
middling	Thickness Uniformity	Very uniform

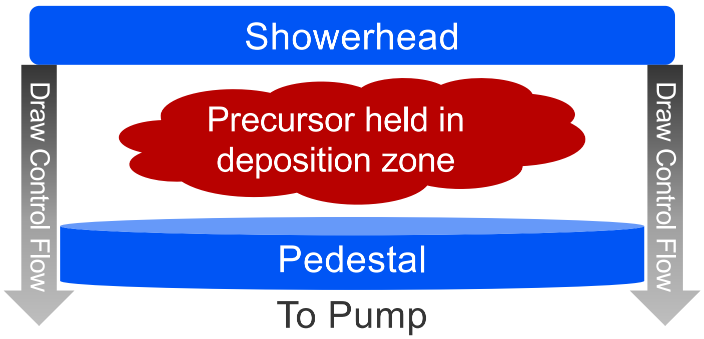


Batch system have high throughput with volume, not speed

Neither addresses the main pressure/consumption tradeoff

ALD^x enables Dynamic Precursor Pressure Control

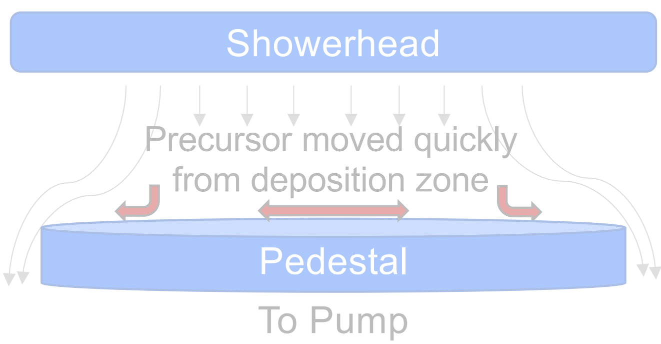
Synchronously Modulated Flow and Draw (SMFD)



Draw Control On

Equal to a long precursor residence time
80-90% chemical utilization

Enables **100x less precursor use**
Typical precursor exposure <50ms



Draw Control Off

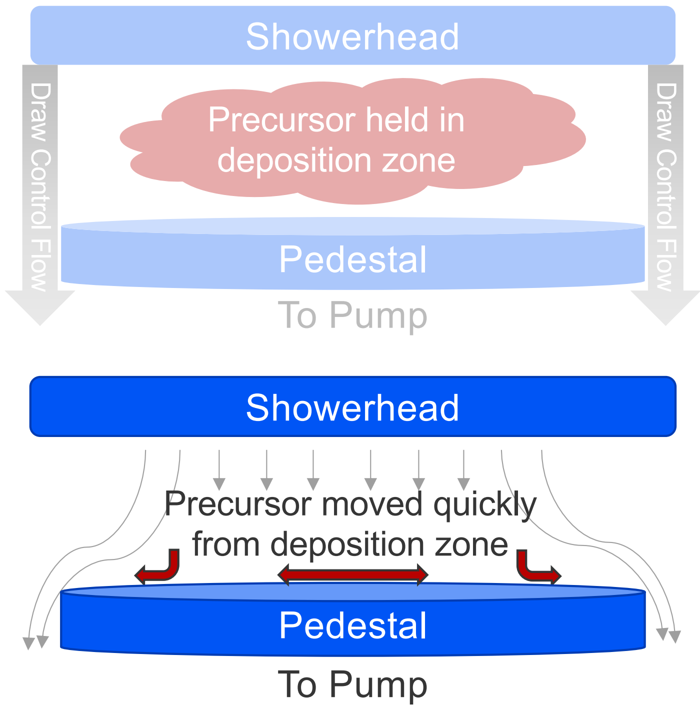
Equal to a short precursor residence time

Enables short cycle time **<1s per cycle**
Typical fast purge time <0.5s

Enabled with proprietary fast pneumatic valves

ALD^x enables Dynamic Precursor Pressure Control

Synchronously Modulated Flow and Draw (SMFD)



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Draw Control Off

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Typical fast purge time <0.5s

True ALD at > 10nm/min with efficient precursor utilization

 FORGE NANO

Fast Pneumatic Valves Enables the SMFD

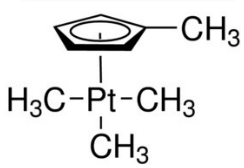
Fast Pneumatic Valves (FPV) enable fast cycling and efficient precursor consumption

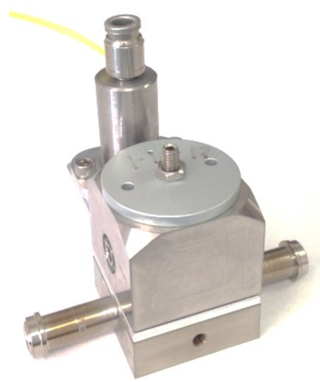
FPVs operate up to 200°C

Can be used for pressure control up to 200°C

Enables most high temperature chemistries

Precursor Cylinder





Flow Dictated By Pressure

1ms Actuation

Full Stack of FPVs

To Reactor

Robust valving shorten purges and enhance consumption efficiency

Forge Nano HfO_2 Performance Difference

HfO_2 ALD at 250°C

- ALD^x
  - ➢ Shorter cycle time => **Higher throughput**
  - ➢ Lower precursor consumption => **Lower COO**
  - ➢ Higher RI, density, near ideal stoichiometry, low impurities => **Better dielectric performance in devices**
- Cross-flow
  - ➢ Performs worse in each category

HfO_2	ALD^x	Cross-Flow	Forge Nano Difference
GPC (Å/cy)	0.99	0.63	**52% faster**
Single cycle (s)	8.9	49.5	**5.5x shorter**
100 nm (hours)	0.42	3.64	**8.7x shorter**
Hf Dose (s)	0.19	9	**47x shorter**
Hf Consumption per 100nm (Torr·s)	93	7143	**77x less**
Thickness non-uniformity (4" full range %)	<2%	<2%	**same**
Density (g/cm^3)	8.9	7.7	**33% more dense**
O:Hf Ratio	2.2	2.4	**0.2 more ideal**
C (%)	1.8	3.2	**1.4% less**
Crystallinity	poly	amorphous	**More order**

ALD^x technology enables higher throughput, reduced precursor consumption, and greater film performance!!

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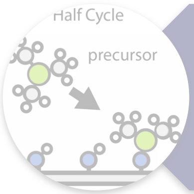
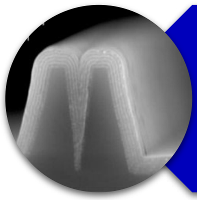
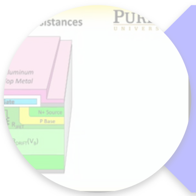


ALD Basics

Opportunities for ALD Adoption

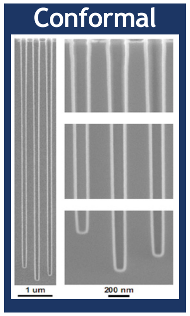


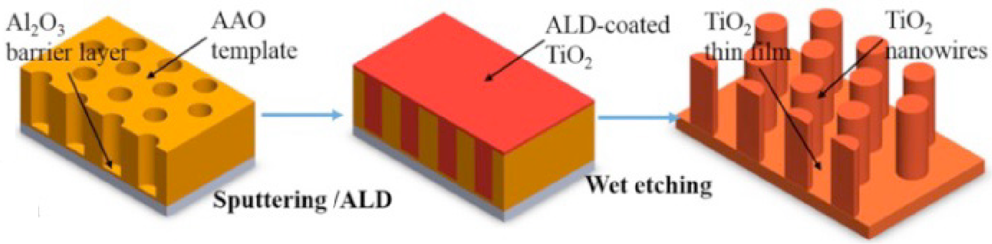
R&D Applications for Fast ALD

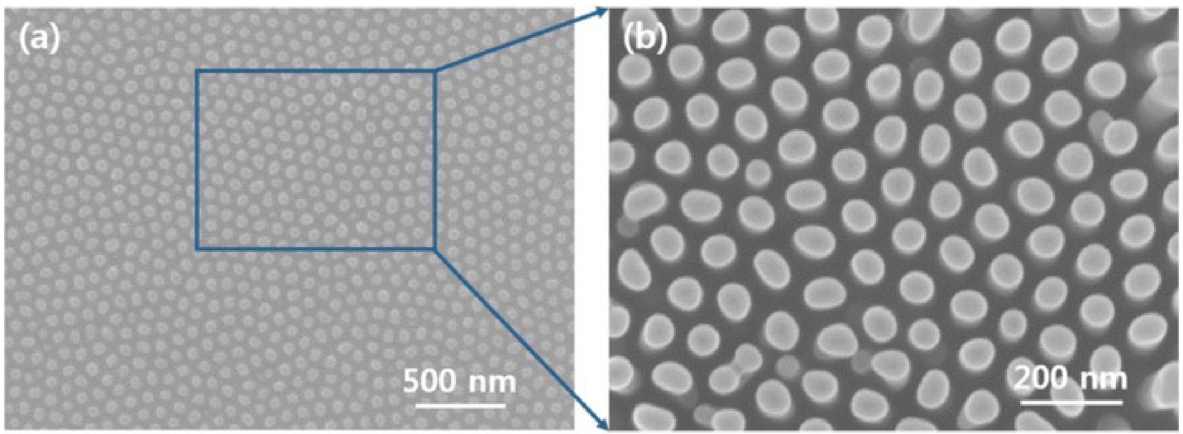


Applications for Production Environments

ALD Fabricated Nanowires or Nanotubes



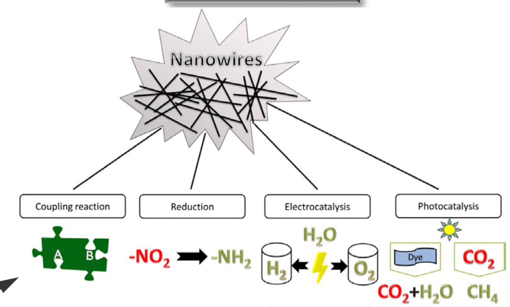




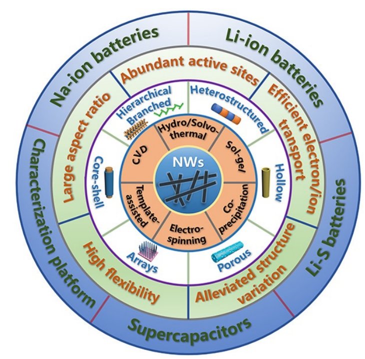
Yao et al. Nanoscale Research Letters (2015) 10:166

Applications

Catalysis



Wasiak and Janas, J. Alloy. Cmpd., (2022) 892, 162158



Zhou et al.Chem. Rev, (2019) 119, 11042

Energy

Subtractive manufacturing enables nanowire research

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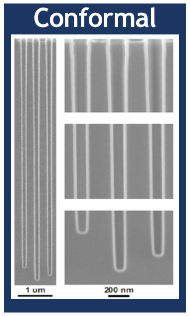
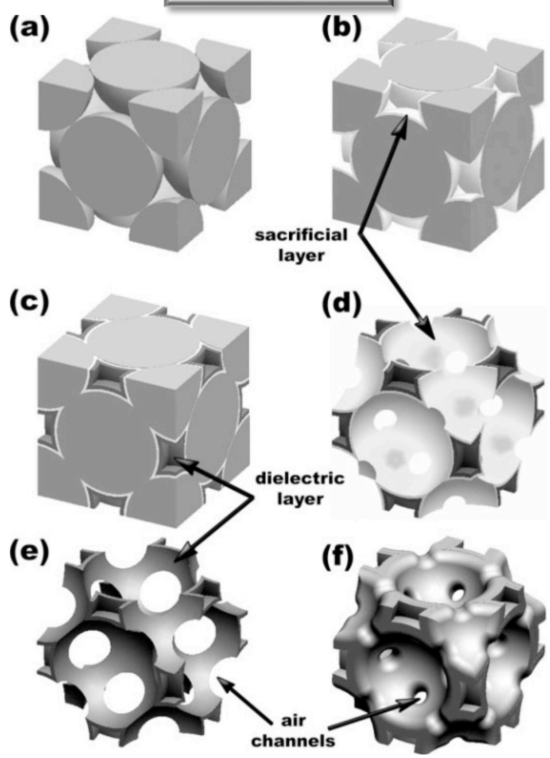


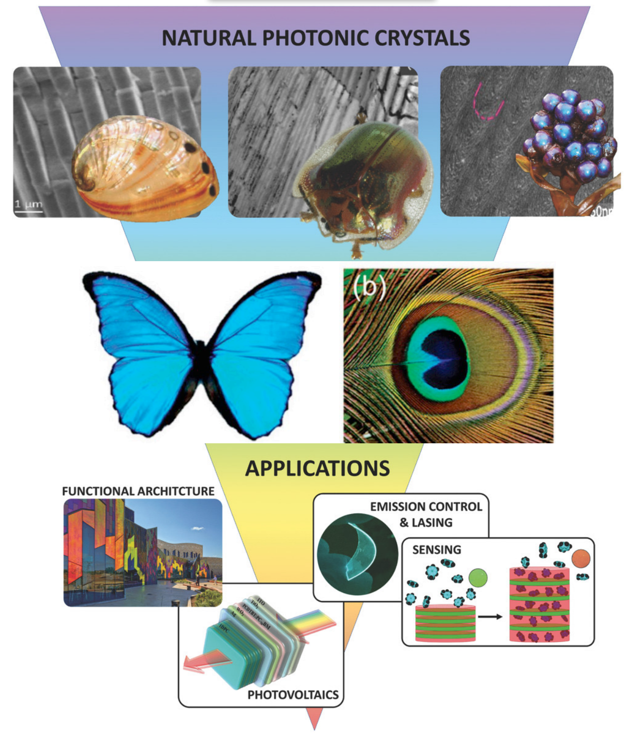
ALD Fabricated Inverse Opal Patterns

Fabrication



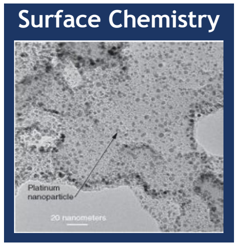
Graugnard, et al. Adv. Funct. Mater. (2006) 16, 1187

Application



Lova et al. Adv. Optic, Mater. (2018) 6, 1800730 and
Armstrong and O'Dwyer J. Mater. Chem. C, 2015, 3, 6109--6143

ALD on polymers is an area of heavy research



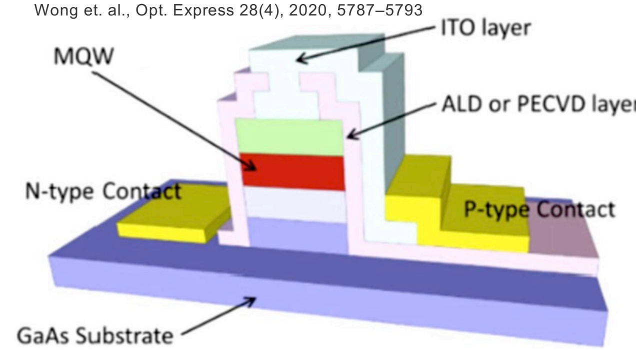
Interface Engineering for MicroLEDs

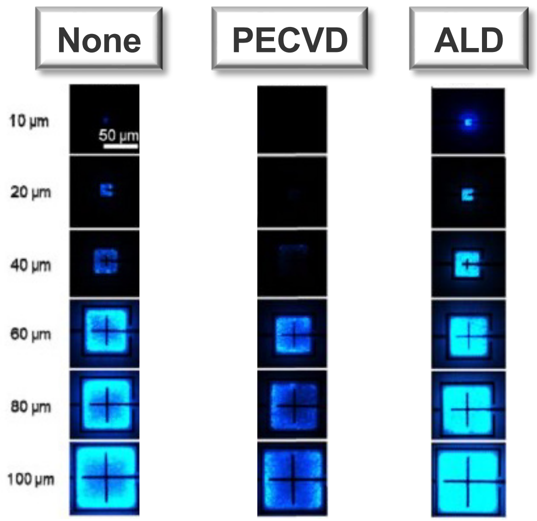
Sidewall passivation with Al_2O_3 ALD

Improve quantum efficiency with thin layer, ~1nm

Reduces etch based defects which cause quenching

Wong et. al., Opt. Express 28(4), 2020, 5787–5793





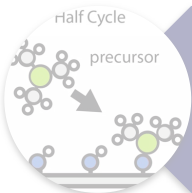
Wong et. al., Opt. Express 26(16), 2018, 21324–21331

Works for Blue, Red, Green

Prof. DenBaar's Group at UCSB at the forefront

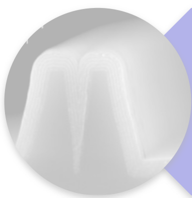
Enables scaling below 60 µm

Micro and nanoLEDs will continue to need ALD R&D

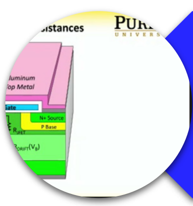


ALD Basics

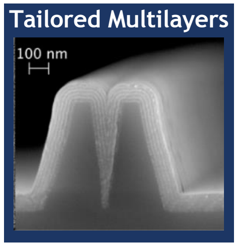
Opportunities for ALD Adoption



R&D Applications for Fast ALD

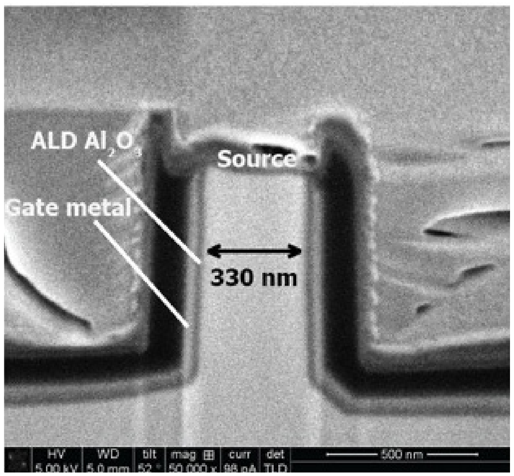


Applications for Production Environments



Tuning Dielectric Barrier and Leakage Current Behavior with ALD

Field Effect Transistor

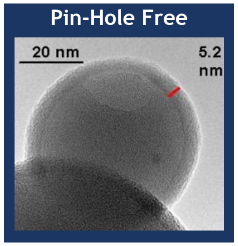


ALD Film Composition	Dielectric Constant (ε)	Dielectric Breakdown Voltage (V_{db} - nFV/mm²)	Leakage Current Density at 50V (J x 10^{-11} A/mm²)
HfO_2 (old gen)	18.8	5.4	7.6
Composition 1	18.1	5.6	5.4
Composition 2	18.3	6	5.8
Composition 3	17.2	5.7	4.5

Dielectric constant, ε, dielectric breakdown voltage, V_{db}, and leakage current density, at 50 V, were measured for monoliths and different laminate compositions

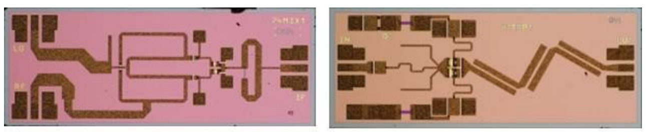
- Direct control over ε, V_{db} and leakage current density
  - One can choose to maximize V_{db} – Composition 2
  - Minimize leakage current – Composition 3
  - Or get a balance of both – Composition 1
- Many ALD oxide available for tuning
  - Al_2O_3, La_2O_3, ZrO_2, Ta_2O_3, Y_2O_3 and many others to tune

High quality dielectric barrier ALD films with tunable properties



ALD^x Enables Superior Moisture Diffusion Barrier Performance

Protect RF MMIC device in harsh environment and smaller scale necessitated by device scaling



https://science.nrao.edu/facilities/cdl/mmics

- PECVD failed every test
- ALD^x Nanolaminate of Al_2O_3 and SiO_2 = ALD-CAP®
  - O_2 Permeability @ atm = $<1\times10^{-7}$ $cm^3\cdot mm/m^2\cdot day$
  - Water vapor transport @ 38°C = $<4\times10^{-10}$ $g\cdot mm/m^2\cdot day$
- 50nm ALD Nanolaminate was solution
  - Total ALD deposition time ~12 minutes

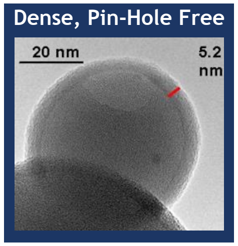
HAST Performance

Coating	Thickness (nm)	96 hours	384 hours
PECVD	>800	Fail	Fail
ALD	10	Pass	Fail
ALD	20	Pass	Pass

JEDEC JESD22-A118 = HAST - 130°C/85% relative humidity

ALD enables ~100x thinner moisture protection

FORGE NANO



Proprietary and Unique SiO_2 CRISP ALD Enhances Dielectric Performance

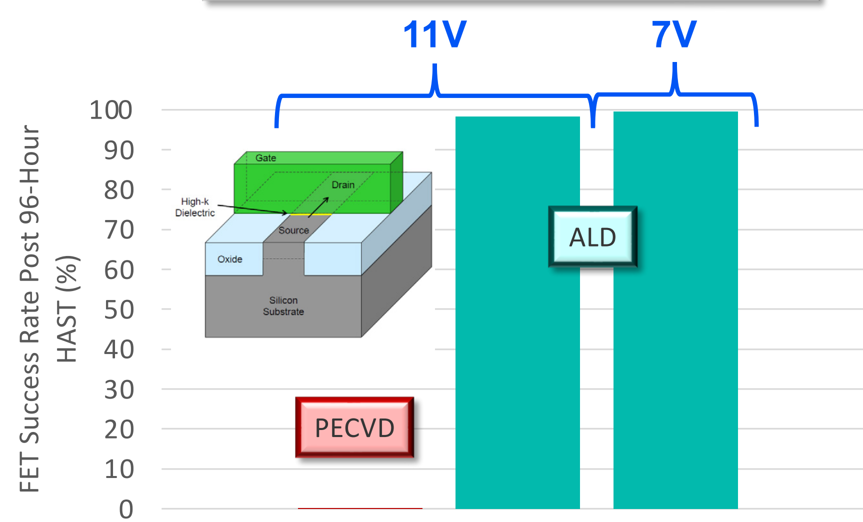
Smaller scale necessitated by customer: ALD^x is the solution!

Unique SiO_2 ALD process
- Use non-metal catalyst
- No trace of impurity/catalyst in film

PECVD failed at every measurement
- SiO_2 CRISP density higher than PEALD SiO_2

ALD^x SiO_2 CRISP at 20nm
- Dielectric constant – 4
- Breakdown Voltage – >12 MV/cm
- Leakage current @2 MV/cm – $<10^{-10}$ A/mm^2

FET Failure Performance



JEDEC JESD22-A110 = HAST - 130°C/85% relative humidity
Test biased at pinchoff, failure measured by leakage current
CS Mantec, 2013

Proprietary SiO_2 CRISP ALD has superior performance over PECVD

ALD^x SiO_2 Outperforms PEALD SiO_2

SiO_2 ALD at 250°C

ALD^x

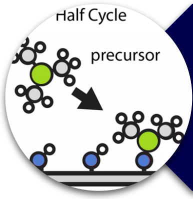
- Shorter cycle time => **Higher throughput**
- Lower precursor consumption => **Lower COO**
- Higher density, ideal stoichiometry, no impurities, better dielectric properties => **Better film performance in devices**

PEALD

- Performs comparable or worse in each category
- Plasma can damage incoming surface

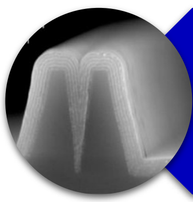
SiO_2	ALD^x	PEALD (BTBAS)	Forge Nano Difference
GPC (Å/cy)	1.2	1.1	**9% faster**
100 nm (hours)	0.7	2.1	**3x shorter**
Si Consumption per 100nm (Torr·s)	275	18,175	**66x less**
Thickness non-uniformity (6" full range %)	<2%	<4%	**2% more uniform**
RI (633nm)	1.44	1.45	**0.01 lower**
Density (g/cm^3)	2.32	2.19	**6% higher**
O:Si Ratio	2.0	2.1	**FN ideal**
Dielectric Constant	4.0	4.1	**0.1 lower**
Breakdown Voltage (MV/cm)	>12	>9	**33% higher**
Leakage Current @ 2MV/cm (A/mm^2)	$<10^{-10}$	$<10^{-10}$	**Same**

Proprietary SiO_2 CRISP ALD outperforms bleeding edge ALD tools

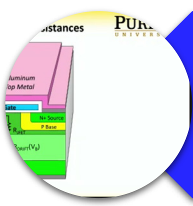


ALD Basics

ALD Breaks the Mold



R&D Applications for Fast ALD



Applications for Production Environments

Thank you!
Questions?

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FORGE NANO

SVC Society of Vacuum Coaters
TechCon 2023 Washington, D.C
Gaylord National Resort & Convention Center
May 6 – May 11, 2023