



# Atomic Layer Deposition

## An Introduction to Theory and Applications

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October 4, 2011

Cambridge**NanoTech**  
*Simply ALD*

# Agenda



- Atomic Layer Deposition Overview
- History
- Applications
- Summary
- Cambridge NanoTech

# Methods for Depositing Thin Films

Method	ALD	MBE	CVD	Sputter	Evapor	PLD
Thickness Uniformity	good	fair	good	good	fair	fair
Film Density	good	good	good	good	fair	good
Step Coverage	good	poor	varies	poor	poor	poor
Interface Quality	good	good	varies	poor	good	varies
Low Temp. Deposition	good	good	varies	good	good	good
Deposition Rate	fair	fair	good	good	good	good
Industrial Applicability	varies	varies	good	good	good	poor

# The ALD Cycle

- ALD is a thin film deposition technique where precursors are sequentially introduced to the surface, where they **react directly with the surface**, to form *sub-monolayers* of film
- A single ALD cycle consists of the following steps:
  - 1) Exposure of the first precursor
  - 2) Purge or evacuation to remove by-products
  - 3) Exposure of the second precursor
  - 4) Purge or evacuation of the reaction chamber

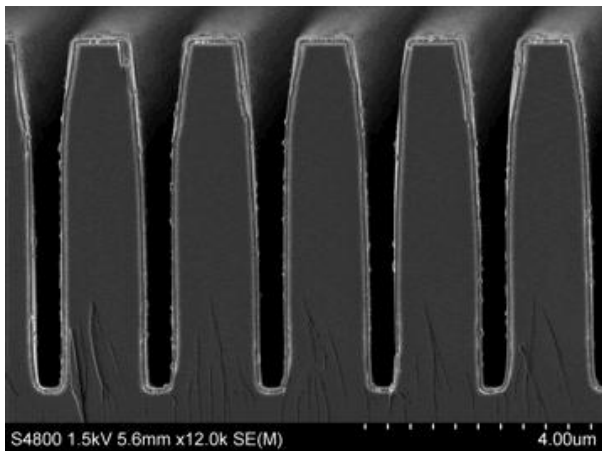
# ALD Deposits Thin Inorganic Films



# Benefits of ALD



100 nm  $\text{Al}_2\text{O}_3$  coating on Si wafer

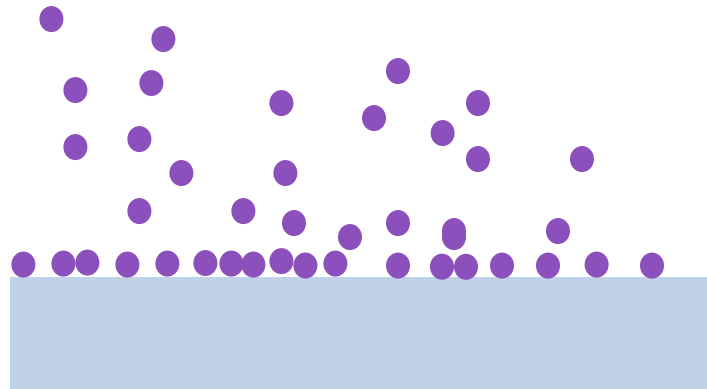


- **Perfect films**
  - Digital control of film thickness
  - Excellent repeatability
  - High film density
  - Amorphous or crystalline films
  - Ultra thin films: <10nm possible
- **Conformal Coating**
  - Perfect 3D conformality
  - Ultra high aspect ratio (>2,000:1)
  - Large area thickness uniformity
  - Atomically flat and smooth coating
- **Challenging Substrates**
  - Gentle deposition process for sensitive substrates
  - Low temperature and low stress
  - Excellent adhesion
  - Coats challenging substrates – even teflon

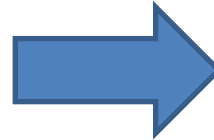
Typical ALD Film thickness 10 Å – 2000 Å

# ALD is a Two-Part Reaction

Step A

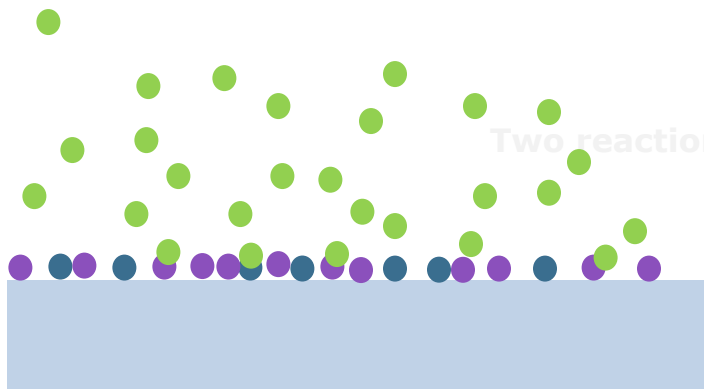


Organometallic chemisorption

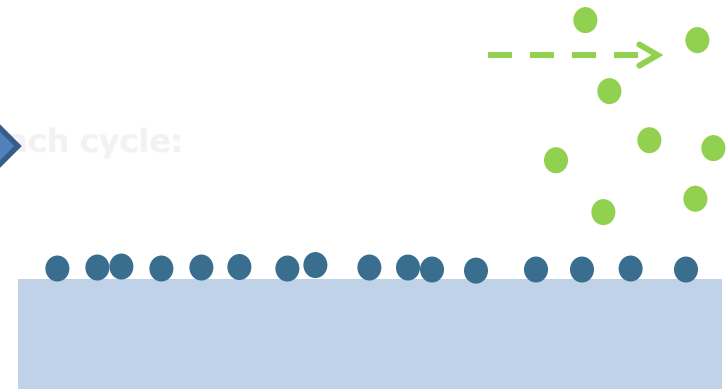
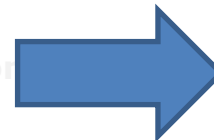


Purge

Step B



Surface Passivation

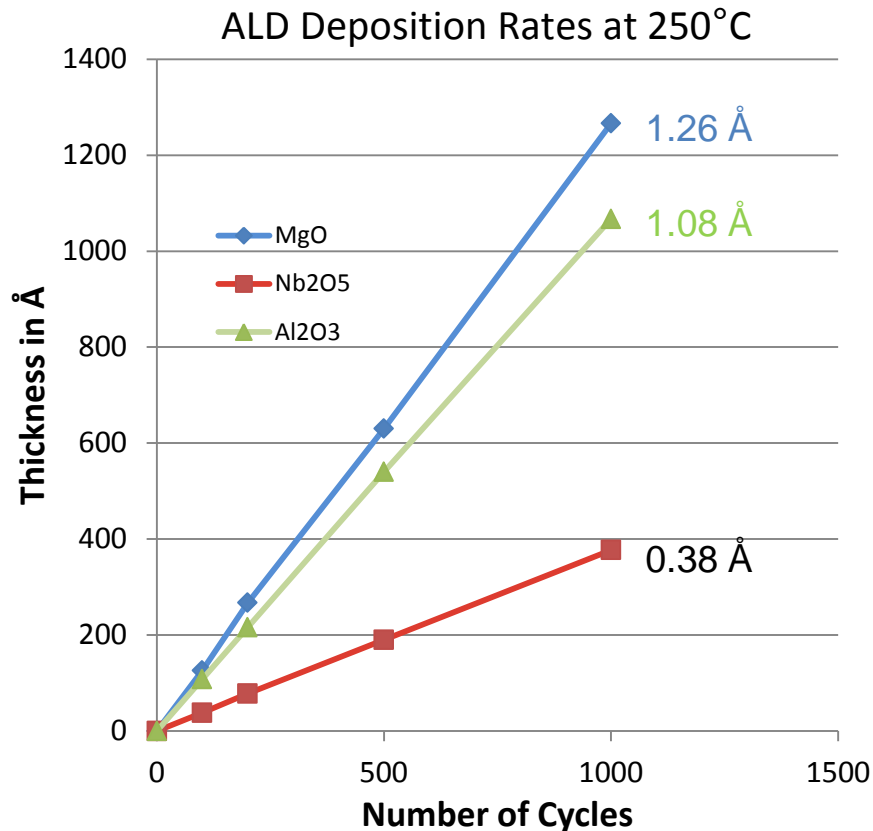


Purge

Two reaction cycle:

# ALD Films

- Films deposited with digital control of thickness; “built layer-by-layer”
- Each film has a characteristic growth rate for a particular temperature



## Oxides

Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZnO, ZrO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, ITO, FeO<sub>x</sub>, NiO<sub>2</sub>, MnO<sub>x</sub>, Nb<sub>2</sub>O<sub>5</sub>, MgO, Er<sub>2</sub>O<sub>3</sub>, WO<sub>x</sub>

## Nitrides

WN, Hf<sub>3</sub>N<sub>4</sub>, Zr<sub>3</sub>N<sub>4</sub>, AlN, TiN, TaN, NbN<sub>x</sub>

## Metals

Ru, Pt, W, Ni, Co, Pd, Rh, Cu

## Sulphides

ZnS, SnS, Cu<sub>2</sub>S



# ALD Periodic Table

## Periodic Table | ALD Films

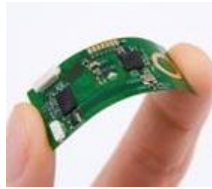
<div>H1</div>	<div><div>O:Oxide</div><div>C:Carbide</div><div>N:Nitride</div><div>F:Flouride</div><div>M:Metal</div><div>D:Dopant</div><div>P:Phosphide/Asenide</div><div>S:Sulphide/Selenide/Telluride</div></div>																<div>He2</div>				
<div><div></div><div>Li3</div></div>	<div>Be4</div>															<div><div></div><div>B5</div></div>	<div>C6</div>	<div>N7</div>	<div>O8</div>	<div>F9</div>	<div>Ne10</div>
<div>Na11</div>	<div><div></div><div>Mg12</div><div>F</div></div>															<div><div></div><div>Al13</div><div>P</div></div>	<div><div></div><div>Si14</div><div>C</div></div>	<div>P15</div>	<div>S16</div>	<div>Cl17</div>	<div>Ar18</div>
<div>K19</div>	<div><div></div><div>Ca20</div><div>S</div><div>F</div></div>	<div><div></div><div>Sc21</div></div>	<div><div></div><div>Ti22</div><div>S</div></div>	<div><div></div><div>V23</div></div>	<div><div></div><div>Cr24</div></div>	<div><div></div><div>Mn25</div><div>S</div><div>D</div></div>	<div><div></div><div>Fe26</div></div>	<div><div></div><div>Co27</div></div>	<div><div></div><div>Ni28</div></div>	<div><div></div><div>Cu29</div><div>S</div><div>D</div></div>	<div><div></div><div>Zn30</div><div>S</div><div>F</div><div>D</div></div>	<div><div></div><div>Ga31</div><div>P</div><div>D</div></div>	<div><div></div><div>Ge32</div><div>O</div><div>M</div></div>	<div><div></div><div>As33</div></div>	<div><div></div><div>Se34</div></div>	<div><div></div><div>Br35</div></div>	<div><div></div><div>Kr36</div></div>				
<div>Rb37</div>	<div><div></div><div>Sr38</div><div>S</div><div>F</div></div>	<div><div></div><div>Y39</div></div>	<div><div></div><div>Zr40</div><div>O</div><div>N</div></div>	<div><div></div><div>Nb41</div><div>O</div><div>N</div></div>	<div><div></div><div>Mo42</div><div>O</div><div>N</div><div>M</div></div>	<div><div></div><div>Tc43</div></div>	<div><div></div><div>Ru44</div><div>O</div><div>M</div></div>	<div><div></div><div>Rh45</div><div>O</div><div>M</div></div>	<div><div></div><div>Pd46</div><div>O</div><div>M</div></div>	<div><div></div><div>Ag47</div><div>O</div><div>M</div></div>	<div><div></div><div>Cd48</div><div>S</div></div>	<div><div></div><div>In49</div><div>P</div><div>S</div></div>	<div><div></div><div>Sn50</div><div>O</div><div>S</div><div>D</div></div>	<div><div></div><div>Sb51</div><div>O</div><div>M</div><div>D</div></div>	<div><div></div><div>Te52</div></div>	<div><div></div><div>I53</div></div>	<div><div></div><div>Xe54</div></div>				
<div>Cs55</div>	<div><div></div><div>Ba56</div><div>S</div></div>	<div><div></div><div>La57</div><div>S</div><div>F</div></div>	<div><div></div><div>Hf72</div><div>S</div><div>F</div></div>	<div><div></div><div>Ta73</div><div>O</div><div>N</div><div>M</div><div>C</div></div>	<div><div></div><div>W74</div><div>O</div><div>N</div><div>M</div></div>	<div><div></div><div>Re75</div><div>O</div></div>	<div><div></div><div>Os76</div><div>O</div></div>	<div><div></div><div>Ir77</div><div>O</div><div>M</div></div>	<div><div></div><div>Pt78</div><div>O</div><div>M</div></div>	<div><div></div><div>Au79</div></div>	<div><div></div><div>Hg80</div><div>S</div></div>	<div><div></div><div>Tl81</div></div>	<div><div></div><div>Pb82</div><div>O</div><div>S</div><div>D</div></div>	<div><div></div><div>Bi83</div><div>O</div></div>	<div><div></div><div>Po84</div></div>	<div><div></div><div>At85</div></div>	<div><div></div><div>Rn86</div></div>				
<div>Fr87</div>	<div>Ra88</div>	<div>Ac89</div>	<div>Rf104</div>	<div>Db105</div>	<div>Sg106</div>	<div>Bh107</div>	<div>Hs108</div>	<div>Mt109</div>													

# Applications for ALD



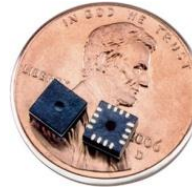
## Optical

Antireflection  
Optical filters  
OLED layers  
Photonic crystals  
Transparent conductors  
Electroluminescence  
Solar cells  
Lasers  
Integrated optics  
UV blocking  
Colored coatings



## Semi / Nanoelectronics

Flexible electronics  
Gate dielectrics  
Gate electrodes  
Metal Interconnects  
Diffusion barriers  
DRAM  
Multilayer-capacitors  
Read heads



## MEMS

Etch resistance  
Hydrophobic /  
antistiction



## Chemical

Catalysis  
Fuel cells



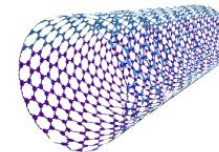
## Other applications

Internal tube liners  
Nano-glue  
Biocompatibility  
Magnetic materials



## Wear resistant

Blade edges  
Molds and dies  
Solid lubricants  
Anti corrosion



## Nanostructures

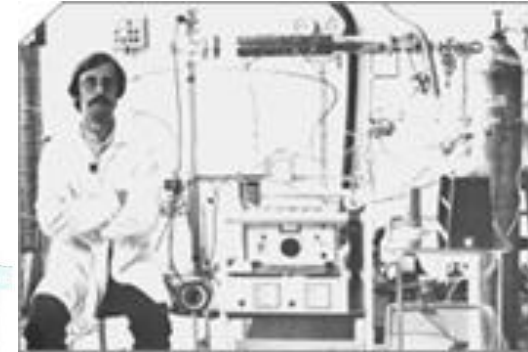
Inside pores  
Nanotubes  
Around particles  
AFM tips  
Graphene functionalization

# ALD History

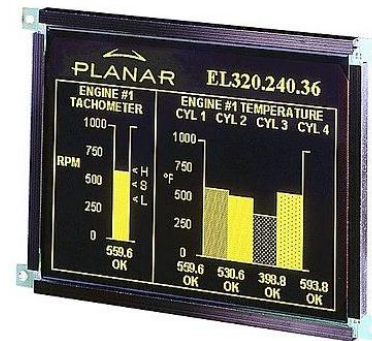
1950-1962: “Molecular Layering” Prof. S.I. Kol'tsov and Prof. V.B. Aleskovskii, Russia

1972: “Atomic Layer Epitaxy” : Dr. T. Suntola, Finland

Mid 1970-1980s: Thin Film Electroluminescent Displays  
Mass produced using “ALE” ZnS



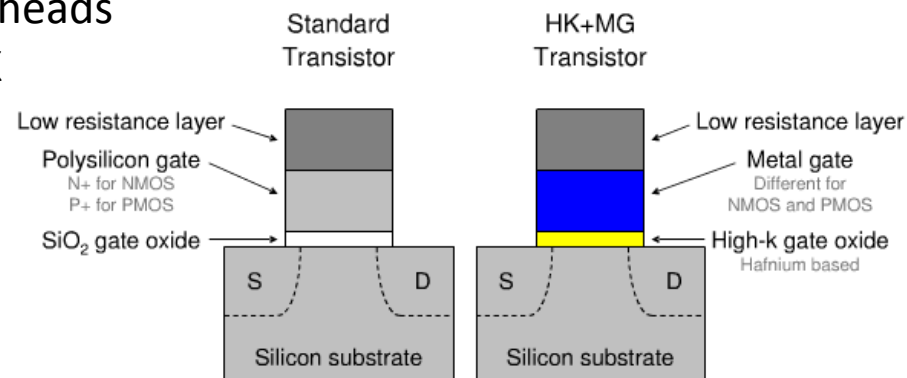
1980s-1990s: “Dark Ages of ALD”



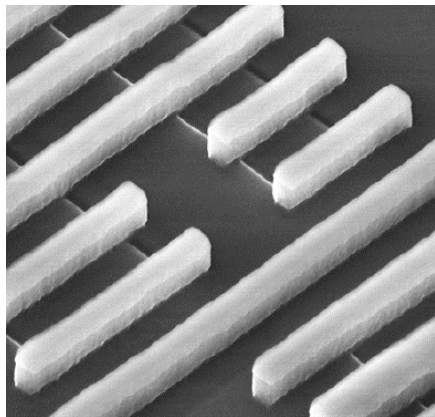
Mid 1990s: research interest in ALD renewed – Microelectronics

Early 2000s: HDD Write heads

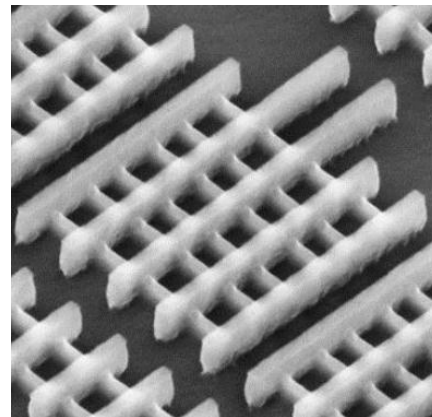
2007: Intel 45nm High-K



# ALD For Microelectronics



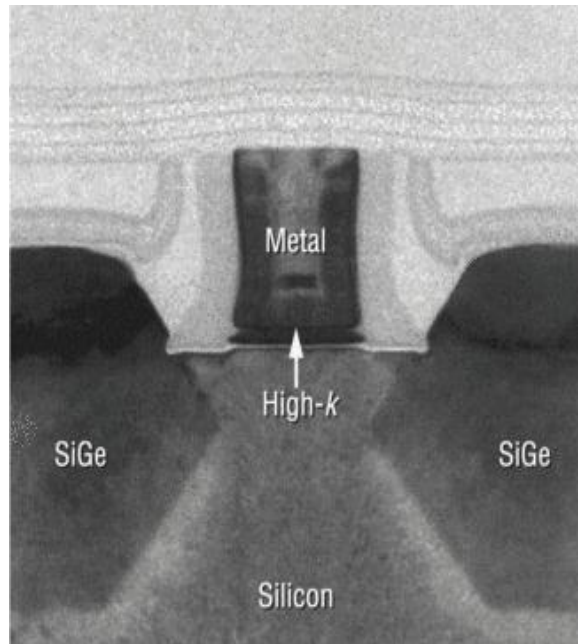
32nm Planar Transistor



22nm 3-D Transistor

# ALD For Microelectronics

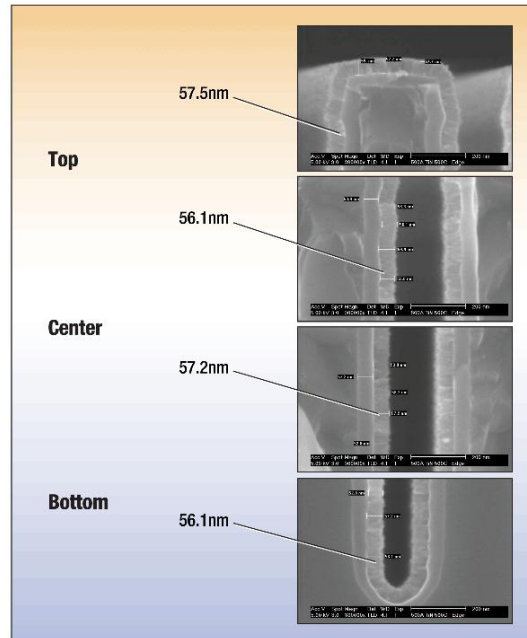
## High-K



$\text{HfO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  
 $\text{HfSiO}$ ,  $\text{ZrSiO}$ ...

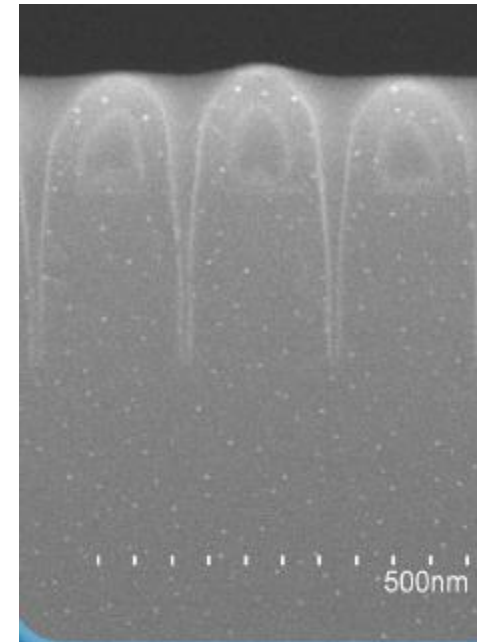
## Diffusion Barrier

Step coverage of batch ALD TiN film in 32:1 trenches



$\text{TiN}$ ,  $\text{TaN}$ ,  $\text{TaCN}$ ,  $\text{WN}$ ,  
 $\text{WC}_x\text{N}_y$ ,  $\text{Ru}$ ,  $\text{TiSiN}$ ...

## Glue/Seed Layer



$\text{Ru}$ ,  $\text{Cu}$ ,  $\text{Mn}$ ,  $\text{Pd}$

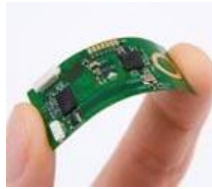


# Applications for ALD



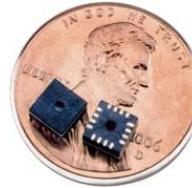
## Optical

Antireflection  
Optical filters  
OLED layers  
Photonic crystals  
Transparent conductors  
Electroluminescence  
Solar cells  
Lasers  
Integrated optics  
UV blocking  
Colored coatings



## Semi / Nanoelectronics

Flexible electronics  
Gate dielectrics  
Gate electrodes  
Metal Interconnects  
Diffusion barriers  
DRAM  
Multilayer-capacitors  
Read heads



## MEMS

Etch resistance  
Hydrophobic /  
antistiction



## Chemical

Catalysis  
Fuel cells



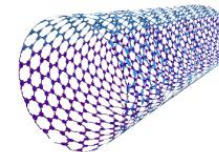
## Other applications

Internal tube liners  
Nano-glue  
Biocompatibility  
Magnetic materials



## Wear resistant

Blade edges  
Molds and dies  
Solid lubricants  
Anti corrosion

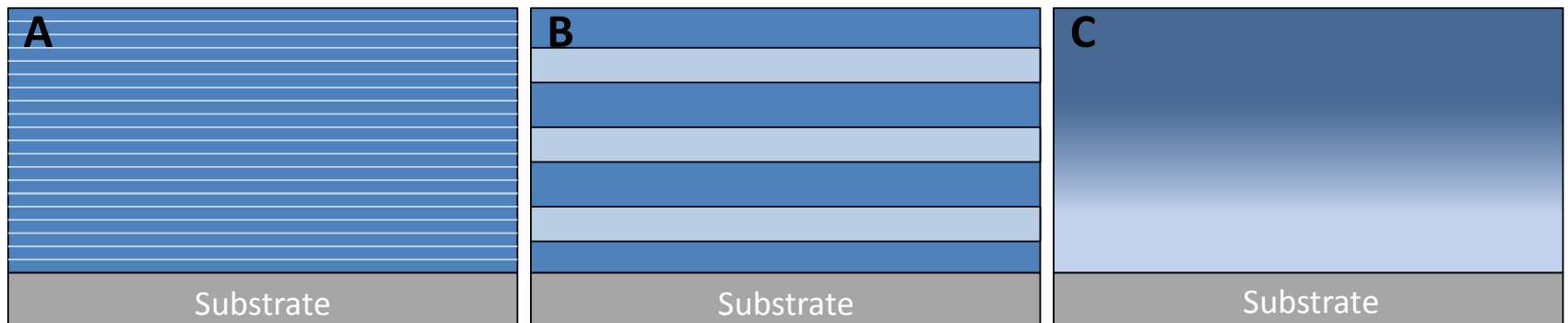


## Nanostructures

Inside pores  
Nanotubes  
Around particles  
AFM tips  
Graphene functionalization

# Variety of Films Possible

- (A) Doped films: single “layers” of dopant film in between bulk
- (B) Nanolaminate Films: stacks of alternating layers
- (C) Graded films: composition slowly changes from material A to material B

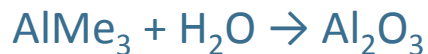


# Tunable Film Properties

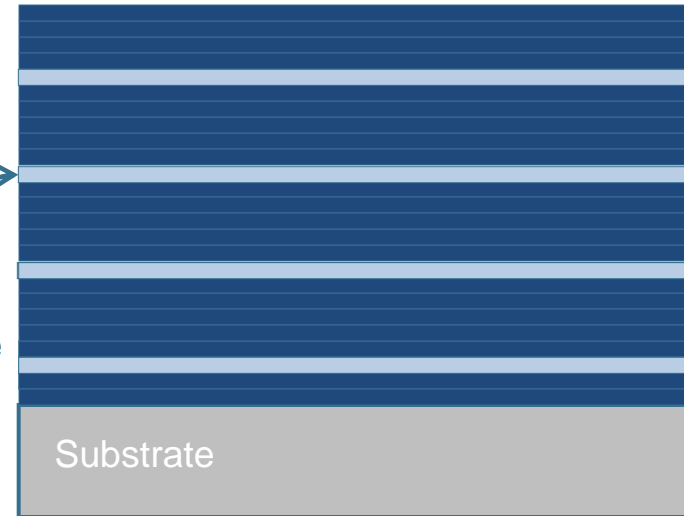
Main Film component:



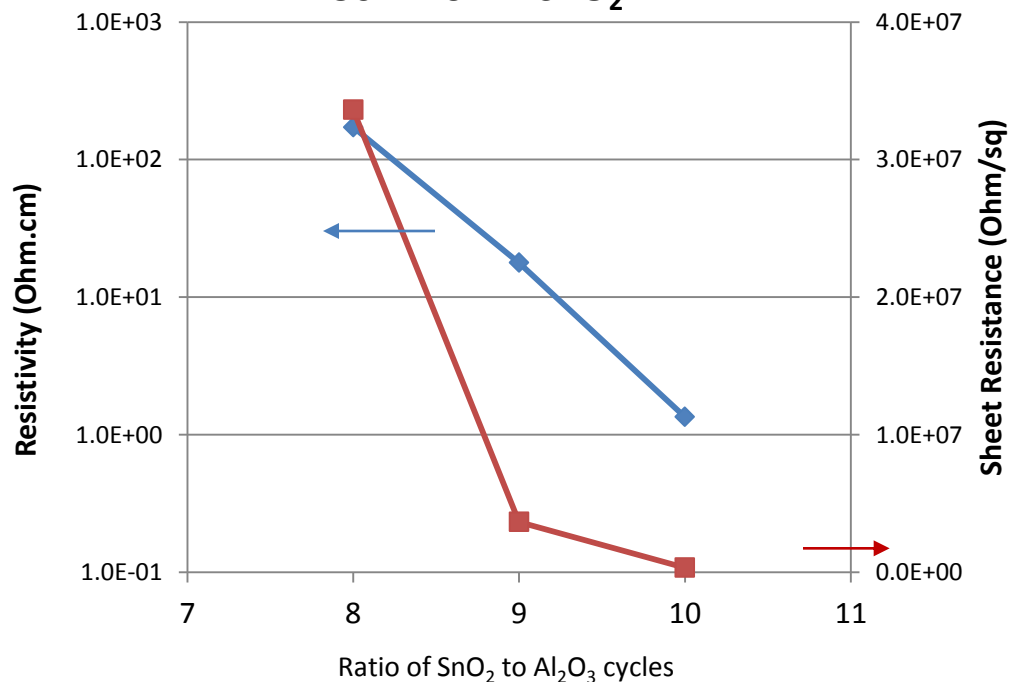
Dopant:



Dopant cycle



50nm of Al:SnO<sub>2</sub>



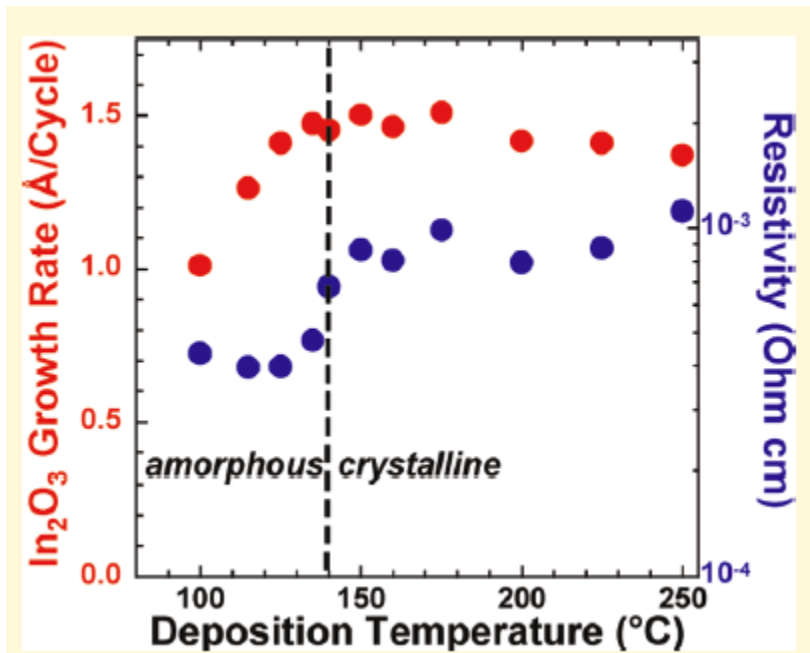
- Electrical resistivity tunable
- Films behave as bulk, doped films
- No post-deposition activation



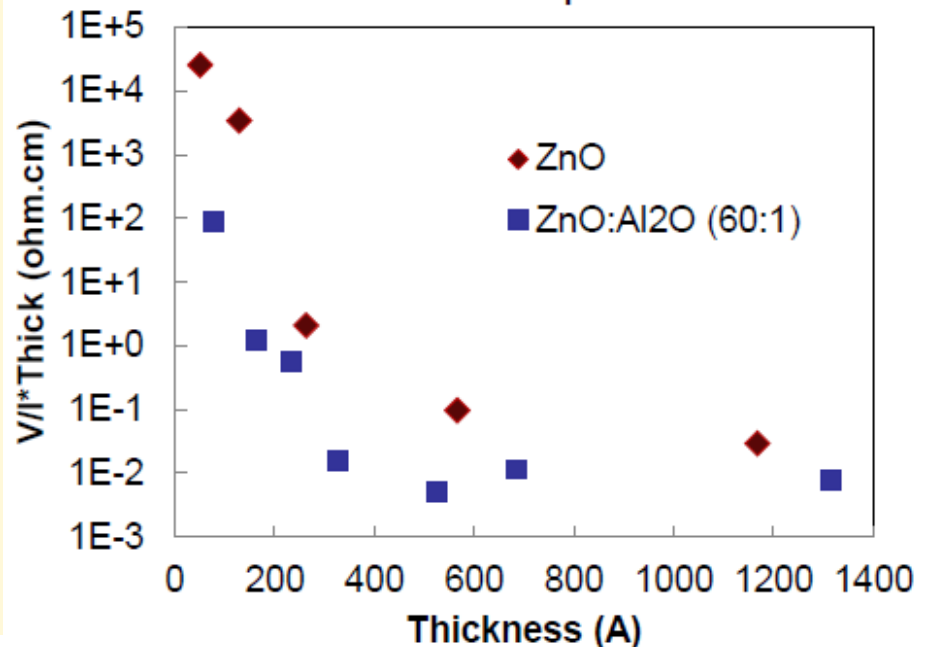
# ALD for TCOs

- Current “gold standard” TCOs are F:SnO<sub>2</sub> or ITO; low resistivity, high transparency
- Both ITO and ZnO:D systems can be tuned for optical transparency, substrate effects

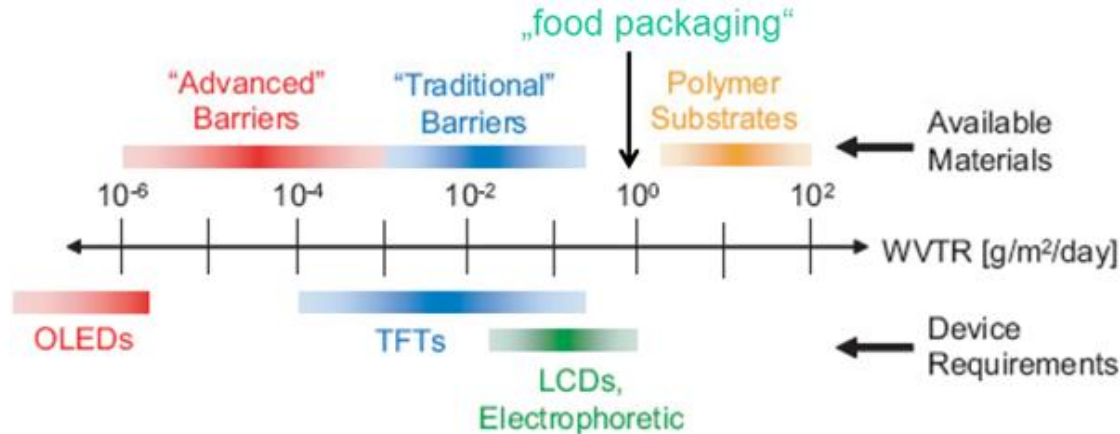
In<sub>2</sub>O<sub>3</sub> only



Aluminum-doped ZnO

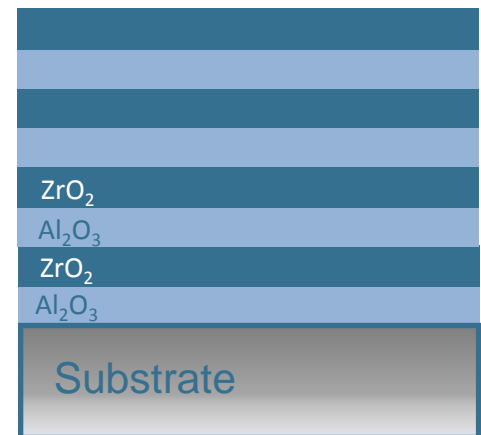
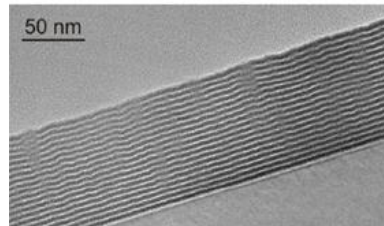


# ALD for Moisture Barriers



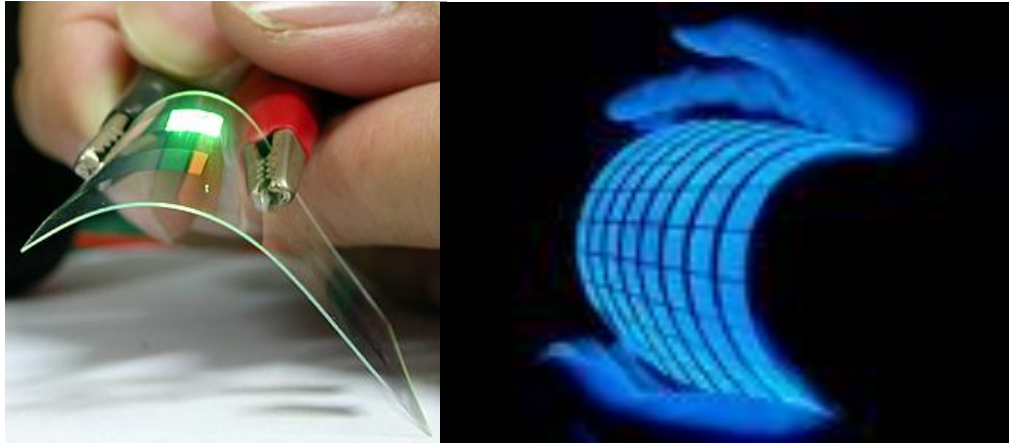
- Improved performance water and oxygen barrier by using nanolaminate layers of 5nm  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$
- Water Vapor Transmission Rate (WVTR)  $<10^{-6}$  g/m² day demonstrated

*Advanced Materials* **2009**, 21, 1845-1849

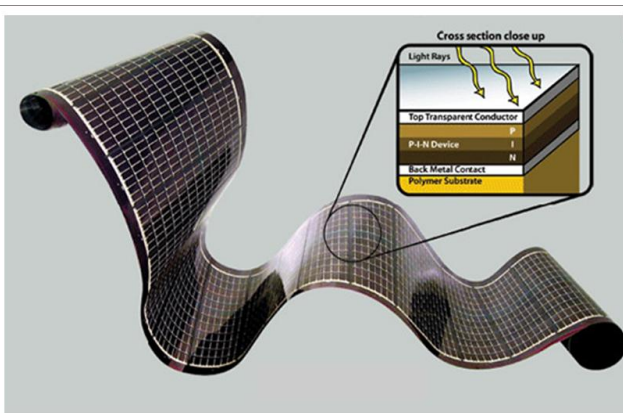


# Flexible Electronics

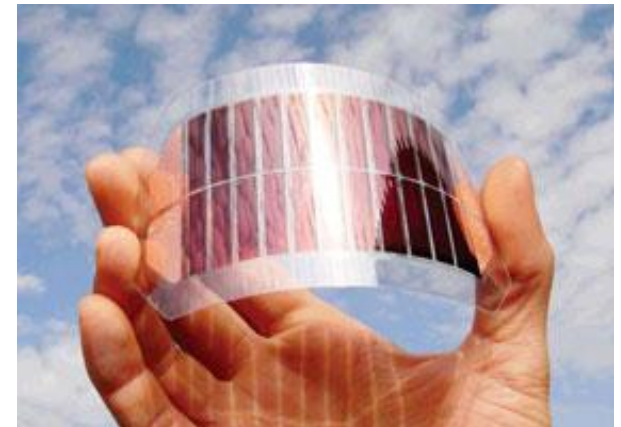
OLEDs



ePaper



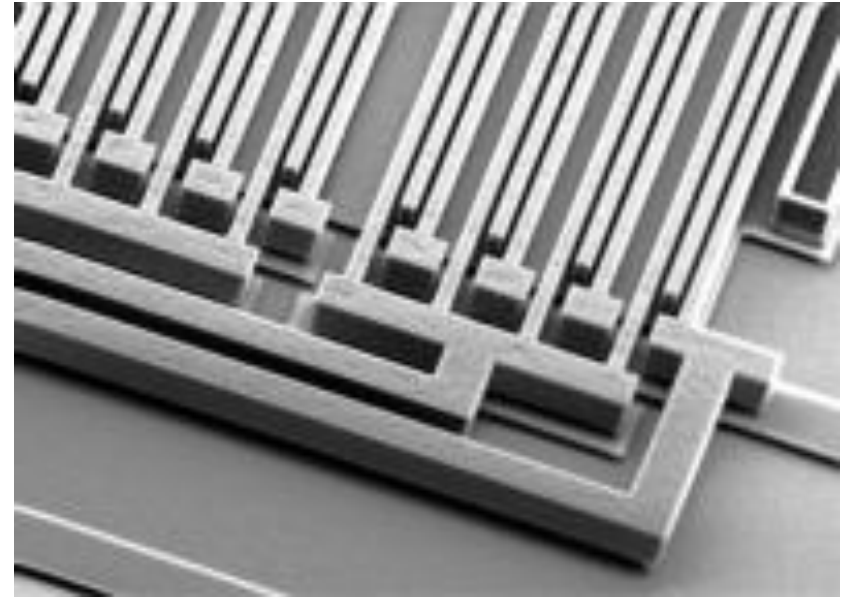
Flexible Solar



Low Cost Electronics (Jet-Printed)

# MEMS – ALD is a good fit...

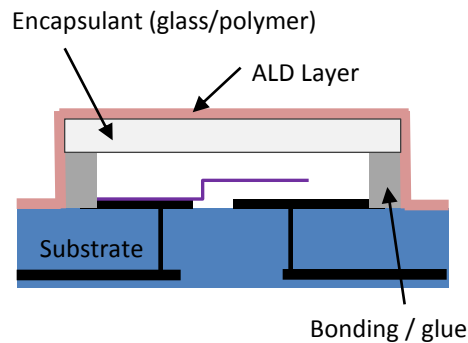
## Micro Electromechanical Systems



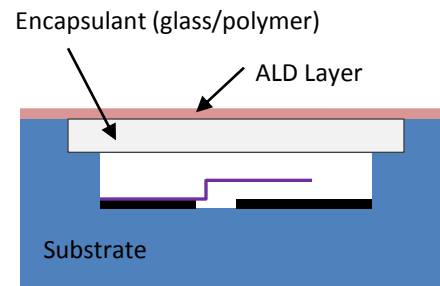
- Billion dollar market - CURRENTLY
- Pressure sensors, accelerometers, blood pressure, displays...
- ALD MEMS applications: conformal dielectric, lubrication / anti-stiction, anti-wear, thermionic layer, encapsulation

# MEMS - Encapsulation Films

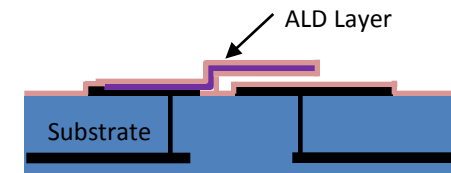
## Different Types of Hermetic Sealing



ALD Layer acts as supplement to **bonding** layer



ALD Layer acts as supplement to **encapsulating** layer



ALD Layer is the **encapsulating** blanket layer

- Different type of hermetic sealing based on different device architecture
- ALD “blanket” layer can act as anti-stiction, dielectric, etc. layer as well as hermetic layer



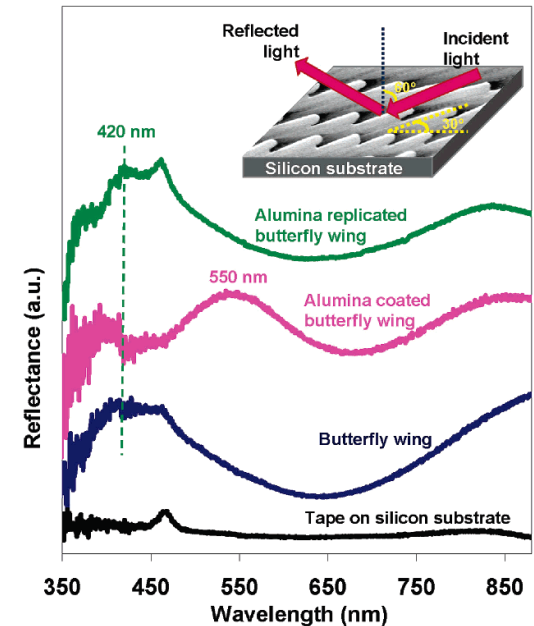
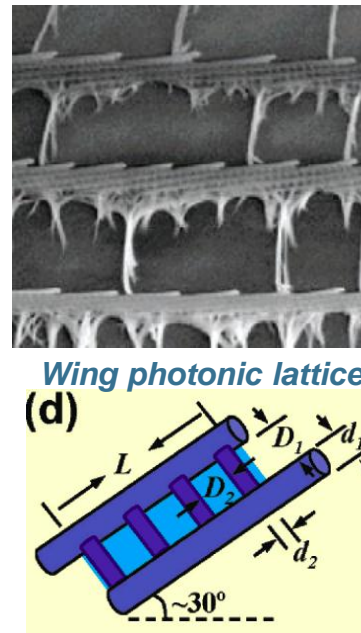
# Low Temperature ALD

- Some ALD processes can deposit films < 150°C:  $\text{Al}_2\text{O}_3$ ,  $\text{HfO}_2$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{SnO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{MgO}$ ,  $\text{In}_2\text{O}_3$
- With plasma, also add, Pt, Ru, Pd, Cu....
- Ideal for merging organics with inorganics
- Compatible with photoresist, plastics, biomaterials



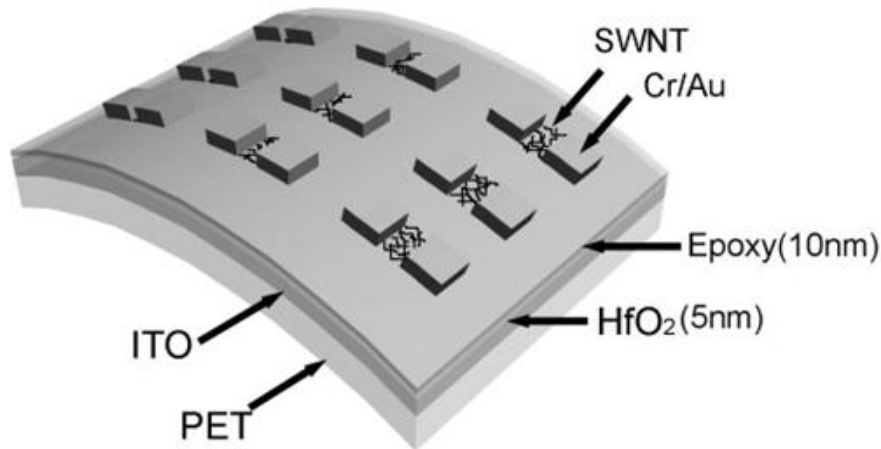
*Morpho Peleides butterfly*

Huang J. Y. *Nano Letters*. 2006, 6, 2325

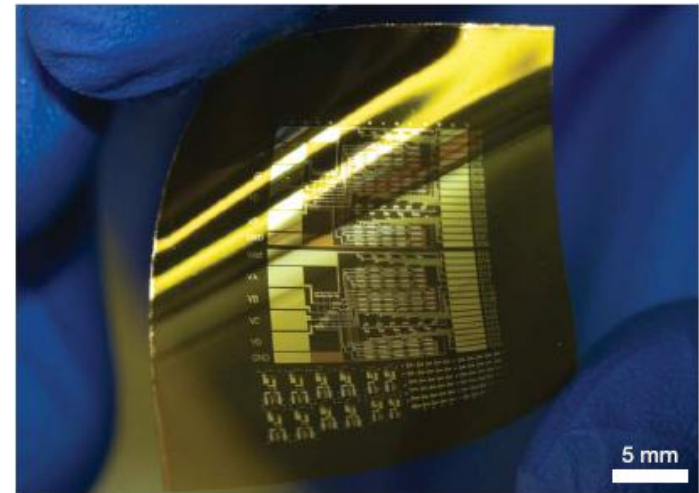
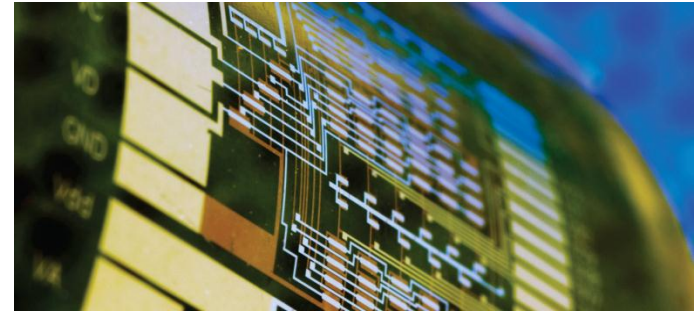


# ALD for Flexible Electronics

- High quality  $\text{HfO}_2$  gate dielectric, deposited at  $100^\circ\text{C}$
- Low stress film - flexible



*Advanced Functional Materials*, **2006**, 16, 2355-2362.  
*Nature*, **2008**, 454, 495-500.



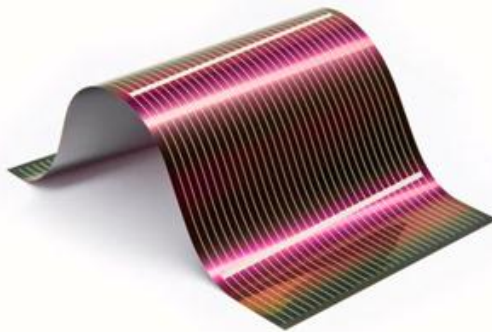
large capacitance (up to ca.  $330 \text{ nF cm}^{-2}$ ), and low leakage current (ca.  $10^{-8} \text{ A cm}^{-2}$ )

# ALD – Solar Cells

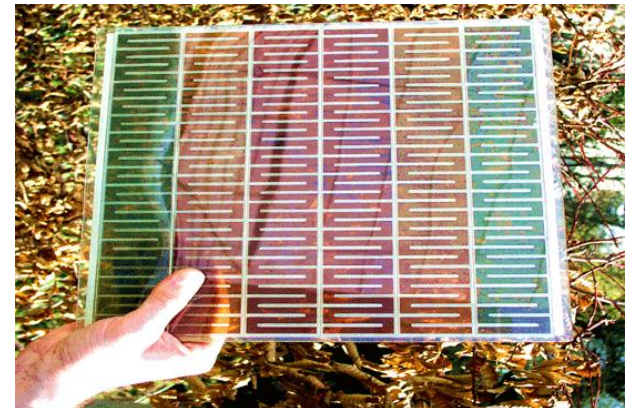
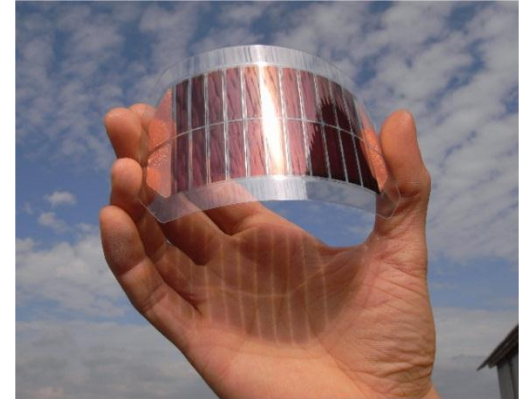
Silicon



Thin Film

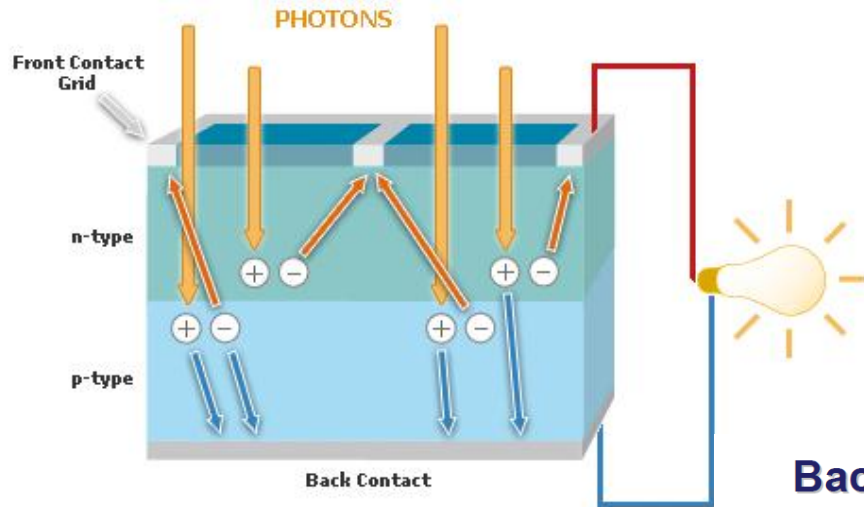


Organic PV





# Silicon Solar Cell Passivation

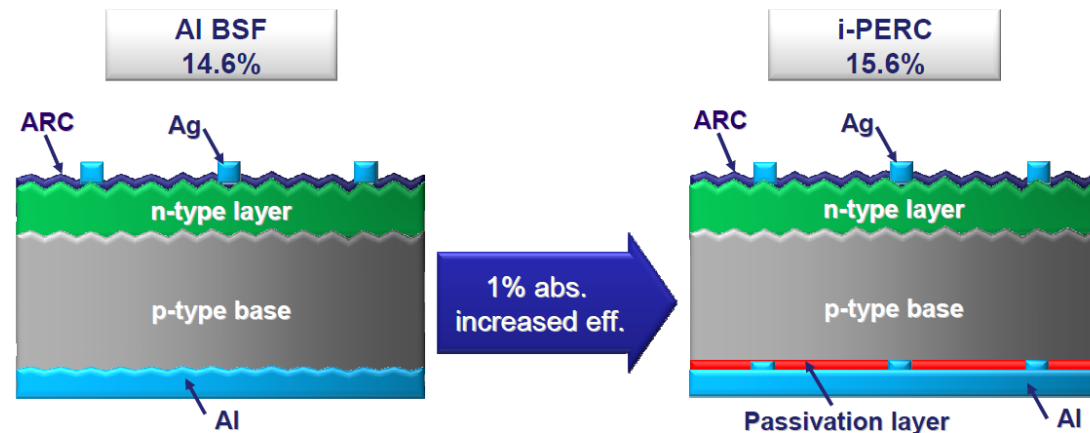


ALD  $\text{Al}_2\text{O}_3$  passivation removes defects of dangling bonds on Si

Helps prevent surface recombination

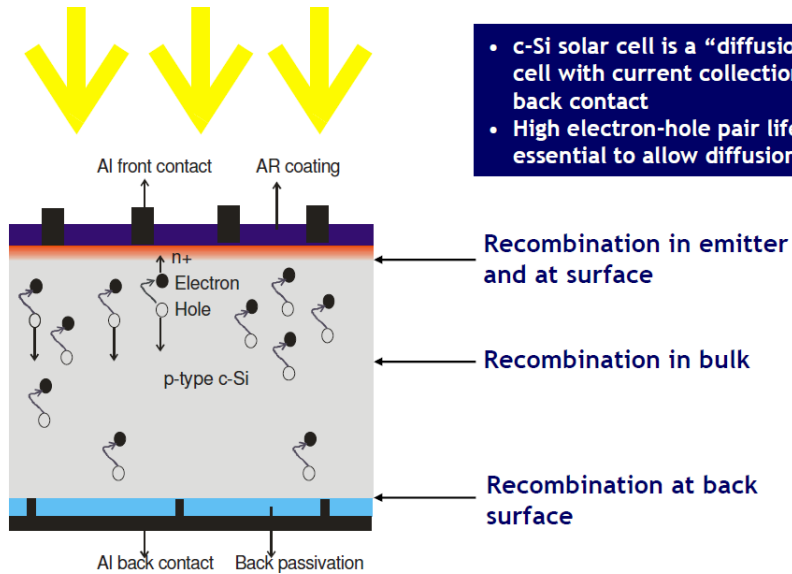
## Backside passivation of Si solar cells

- $\text{Al}_2\text{O}_3$  acts as a *surface passivation layer* in silicon solar cells\*  
→ Higher efficiency → Thinner wafers → lower costs/ $W_p$



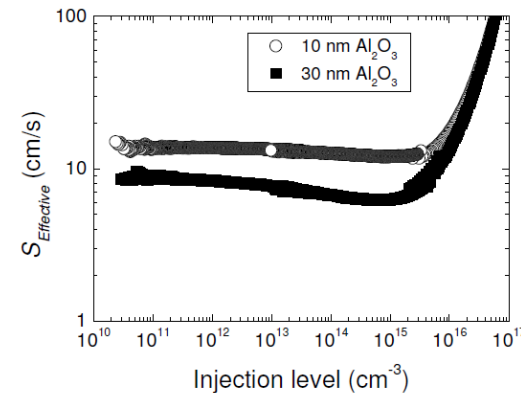
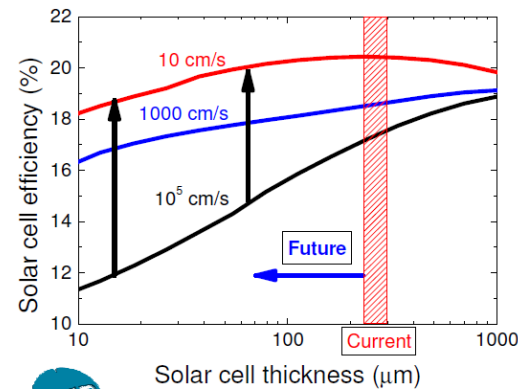
Passivated Emitter and Rear Cell (PERC), 140 EFG, 140  $\mu\text{m}$ , 100  $\text{cm}^2$   
(imec, Crystal Clear, EUPVSEC 2009)

# Silicon Solar Cell Passivation



- c-Si solar cell is a “diffusion” type solar cell with current collection at front and back contact
- High electron-hole pair lifetime  $\tau_{\text{eff}}$  is essential to allow diffusion to the surfaces

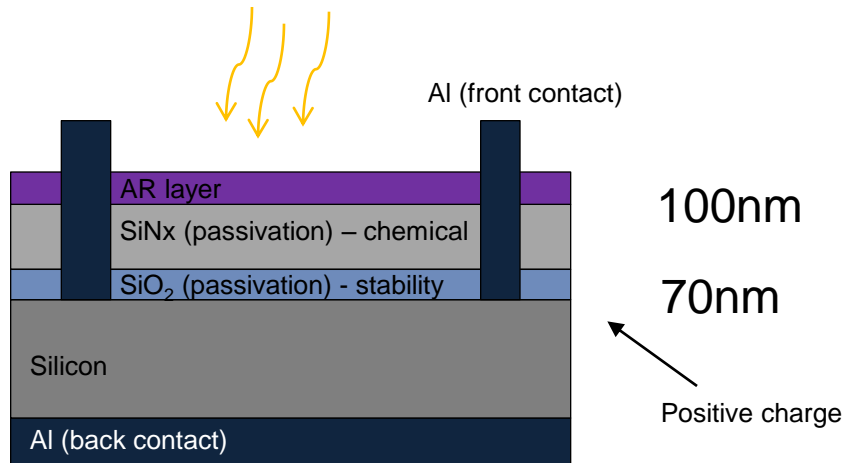
- Surface passivation on the back is essential when decreasing solar cell thickness
- Current technology (Al BSF) yields only  $\sim 1000 \text{ cm/s}$  on the back side!



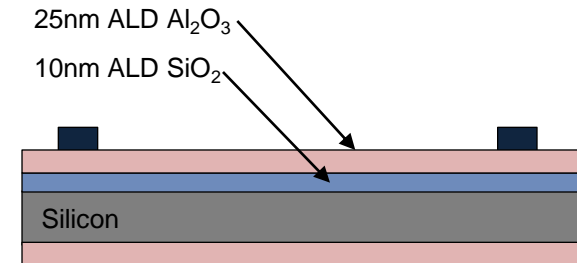
- c-Si surface can effectively be passivated by Al<sub>2</sub>O<sub>3</sub>
- Al<sub>2</sub>O<sub>3</sub> exhibits low interface density
- Al<sub>2</sub>O<sub>3</sub> has a high amount of negative built-in charge ( $\sim 10^{12}$ - $10^{13} \text{ cm}^{-2}$ )

# Silicon Solar Cells

Traditional Silicon



With ALD



- Highly doped p-type or n-type c-Silicon solar cells
- Chemical passivation (interface trap density) – dangling bonds (SiO<sub>2</sub> or SiN<sub>x</sub> passivates)
- Field effect passivation (negative fixed charge in Al<sub>2</sub>O<sub>3</sub>) passivates SiO<sub>2</sub> at the Si-SiO<sub>2</sub>

# Thin Film Solar Cells

- Thin film solar cells can have higher efficiencies than silicon cells >28% for single junction in natural sunlight
- Substrate can also be metal foil, polymer, glass – cheaper than c-Si
- **But there are some issues....**

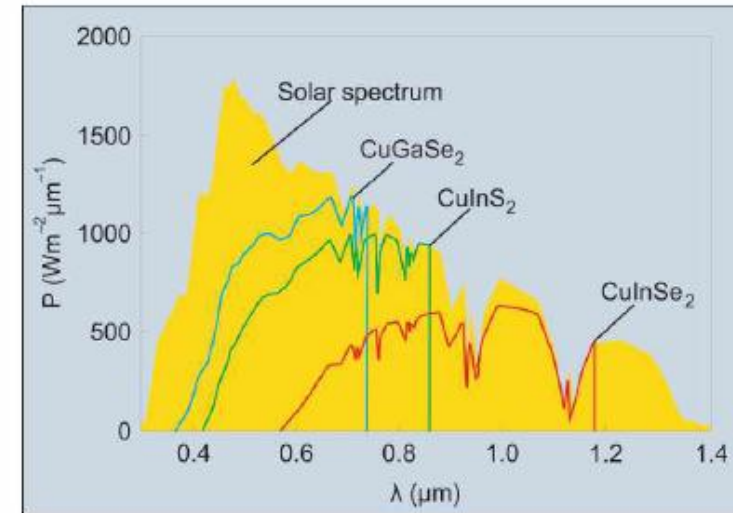
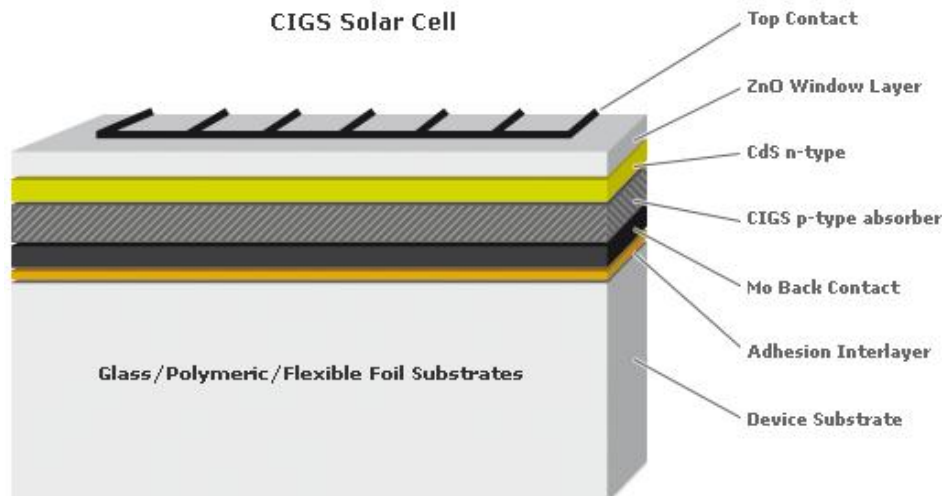


Figure 10. Solar spectrum and response of CIGS materials, showing possibilities for multi-junction solar cells.

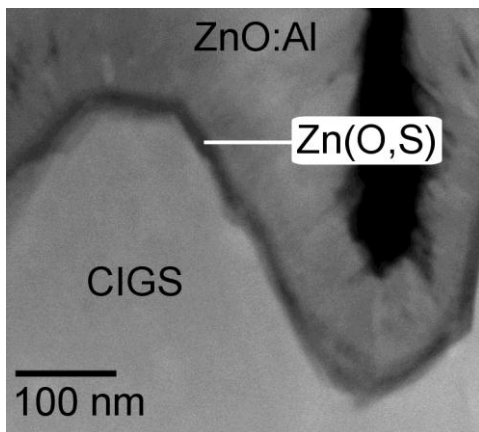


# Thin Film Solar Cells

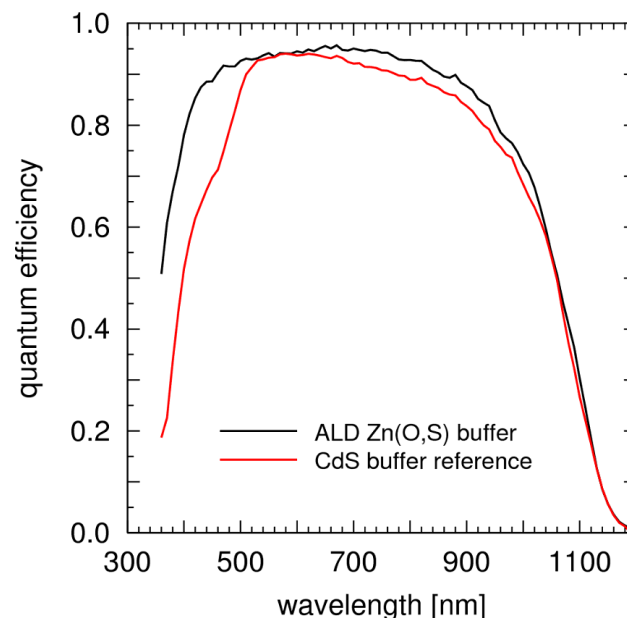
Key feature: Absorber / Buffer / TCO combination determine spectral capture range

ALD Insertion points:

- TCO layer
- Encapsulation
- **buffer layer: replacement for CdS**



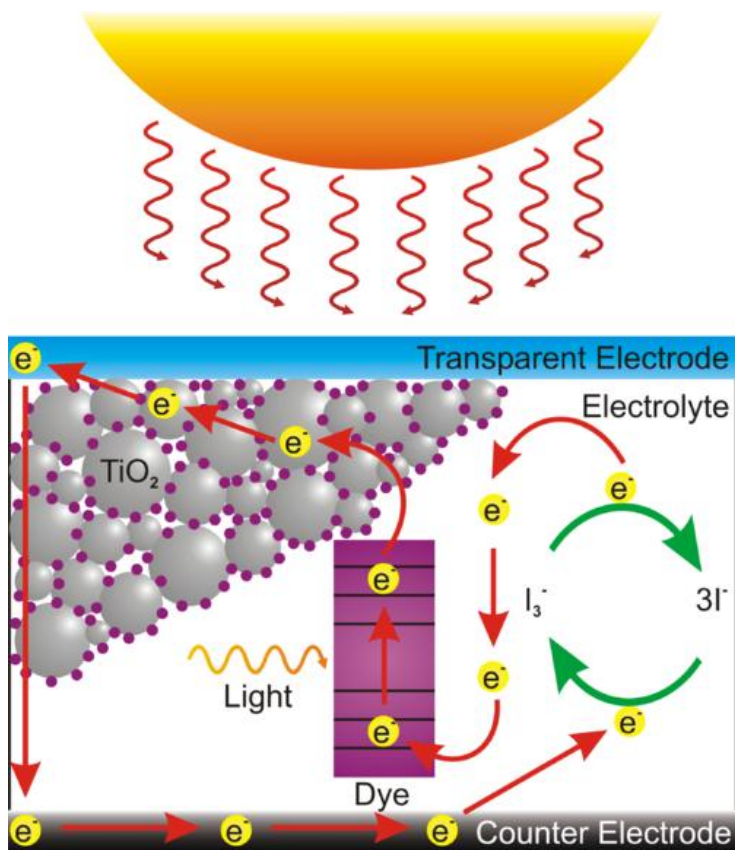
Cross section TEM image of a CIGS solar cell with ALD grown Zn(O,S) buffer layer. The buffer layer is the dark band between the CIGS grains and the columnar ZnO:Al front contact layer. The dark area to the right is a void.



Quantum efficiency measurement for a cell with ALD Zn(O,S) buffer layer and a reference cell with CdS buffer.

# Dye Sensitized Solar Cells (DSSC)

## Dye-Sensitized Solar Cell Schematic



DSSCs still have comparably low efficiency compared to thin film / c-Si solar cells

## Many interfaces require optimization in DSSCs:

## How can ALD help?

Tune interface of dye/photoanode:  
- suppress recombination

Prasittichai, C.; Hupp, J. T. *J Phys Chem Lett.* **2010**, *1*, 1611.

Bills, B., Shanmugam, M., et al. MRS Symp. Proc. 2010, vol. 1260.

## Novel photoanode

Hamann, T. W.; Martinson, A. B. F.; Elam, J. W.; Pellin, M. J.; Hupp, J. T. *J. Phys Chem. C* **2008**, 112, 10303

## Novel structure to minimize electron transfer distance

Silica Aerogel - Li, T. C., et al. *J Phys Chem. C.* **2011**, *115*, 11257-11264.

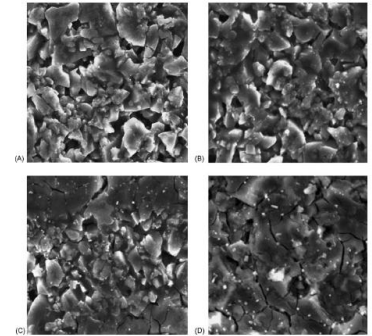
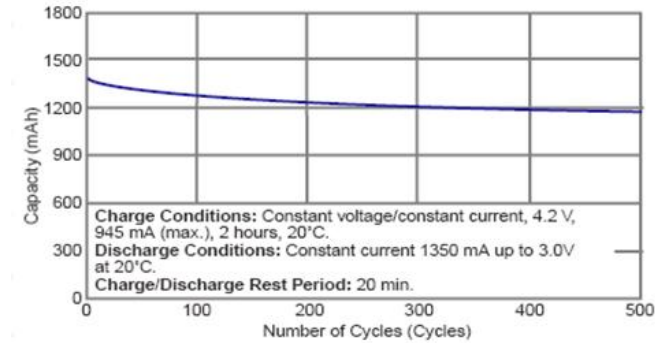
AAOs - Martinson, A. B. F., Hamann, T. W., Pellin, M. J., & Hupp, J. T.  
*Chem. Euro J.* **2008**, *14*, 445



# Current Li-ion Battery Limitations

Lithium ion batteries are promising but current issues prevent need to be addressed

1. Specific charge capacity decreases rapidly with number of charge-discharge cycles
2. Slow charge up time
  - Fast charge or discharge can result in damage to the electrode material
3. Safety issues with liquid electrolyte being exposed to
  - Lithium electrolyte is pyrophoric
4. Low power density
  - Large batteries are cumbersome for increasingly smaller consumer devices



Continuous fast charging alters microstructure of cathode/anode

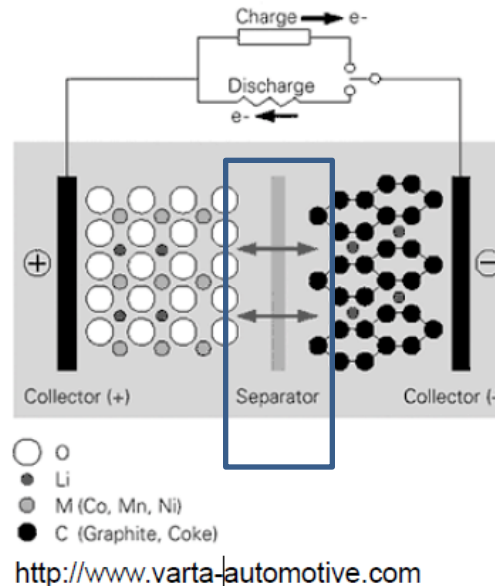


# Li Ion Batteries

Can ALD help increase cycle lifetime?

## Cathode materials:

$\text{LiCoO}_2$   
 $\text{LiMn}_2\text{O}_4$   
 $\text{LiNiO}_2$   
 $\text{LiFePO}_4$   
 $\text{V}_2\text{O}_5$   
 $\text{MnO}_2$   
*etc.*



## Anode materials:

Graphite ( $\text{LiC}_6$ )  
Si  
 $\text{TiO}_2$   
 $\text{Li}_4\text{Ti}_5\text{O}_{12}$   
 $\text{Sn}_3\text{N}_4$   
*etc.*

- Anode – cathode separator is a thin plastic membrane coated with ceramic paste;
- typically 30-40% of total cost of Li-ion battery,
  - Failure mechanism - loss of charge capacity due to fouling of membrane
  - Li ions cannot effectively move across separator after cycling

Can ALD layers replace the ceramic paste in the separator to reduce fouling / plugging?

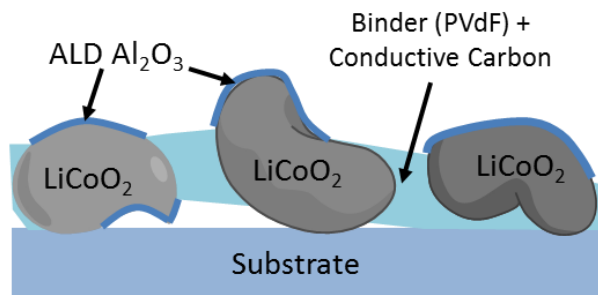


# Li Ion Batteries

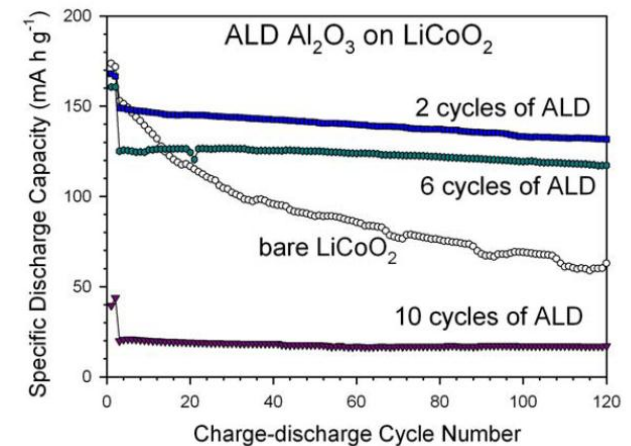
## ALD layers help to improve long term specific charge capacity

- Prevent corrosion of cathode with thin  $\text{Al}_2\text{O}_3$  layer

ALD  $\text{Al}_2\text{O}_3$  films (2-8 cycles) improve the capacity retention of cathode material,  $\text{LiCoO}_2$ , from 45% to 89% after repeated cycling



Lee, J. T.; Wang, F. M.; Cheng, C. S.; Li, C. C.; Lin, C. H. *Electrochimica Acta* **2010**, 55, 4002.



Y.S Yung et al. *J. Electrochem. Soc.* **2010**, 157, A75-A81.

Interface engineering is possible by ALD

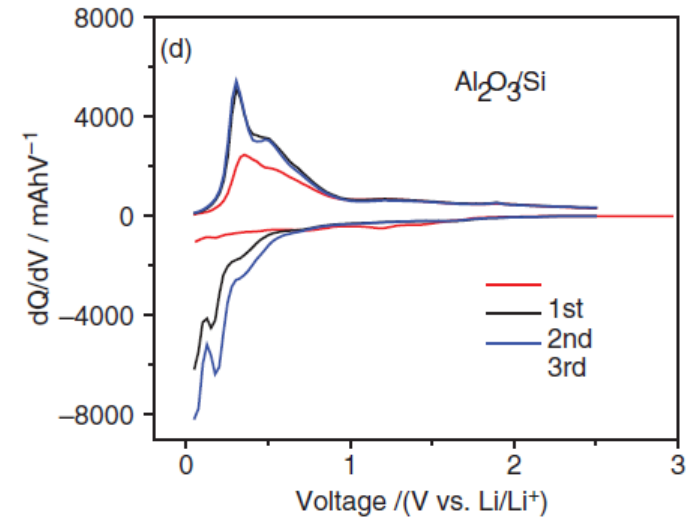
# Li Ion Batteries

ALD layers directly improve specific charge capacity by improved performance of cathode

Typically, charge capacity decreases after first charge/discharge cycle.

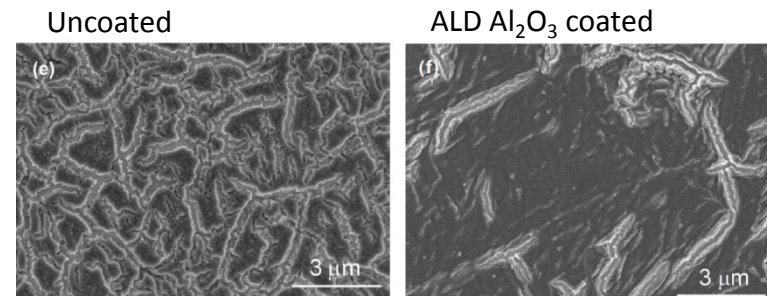
A few cycles of ALD  $\text{Al}_2\text{O}_3$  increases charge capacity after first cycle: Formation of thin and stable SEI layer is enhanced by ALD  $\text{Al}_2\text{O}_3$  -  $\text{LiAlO}_2$  forms after first charge/discharge cycle; helps to lower energy barrier for Li diffusion into and out of anode

-  $\text{Al}_2\text{O}_3$  helps to improve mechanical stability as well as corrosion resistance, SEI layer



Xiao, X., Lu, P., & Ahn, D. *Adv. Mat.* **2011** ASAP  
doi:10.1002/adma.201101915

## Cycled Silicon Anode



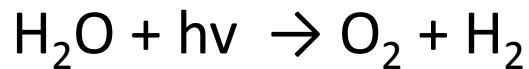
# Solar Energy Harvesting

Issues with Solar Energy:

## IT GETS DARK AT NIGHT

Can we develop a strategy to harvest energy and store it to do work later?

## Photocatalysts for water oxidation



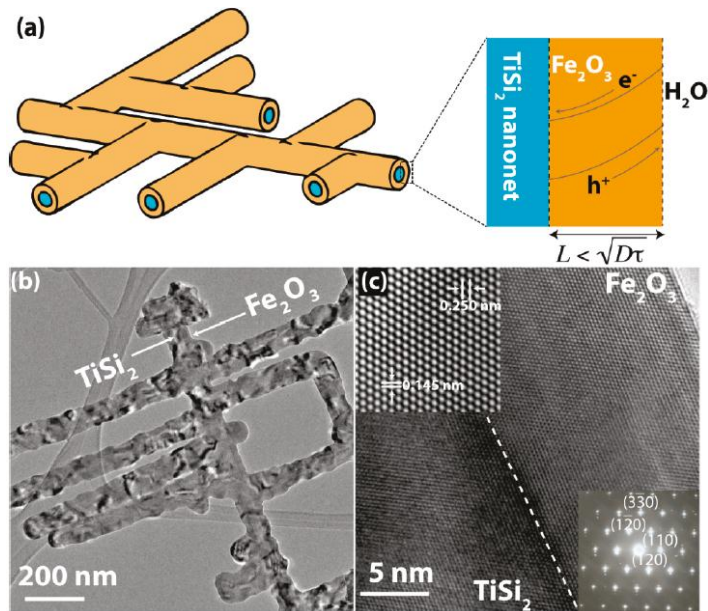
Materials need to have the following characteristics:

- Strong absorption in the visible range
- Separate charges using absorbed photons
- Collect and transport charges for oxidation reaction
- Difficult to find materials which do all of these things
- Good photoabsorbers ( $\text{Fe}_2\text{O}_3$ ,  $\text{Cu}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{WO}_3$ ) have short charge diffusion lengths



# ALD Photocathodes

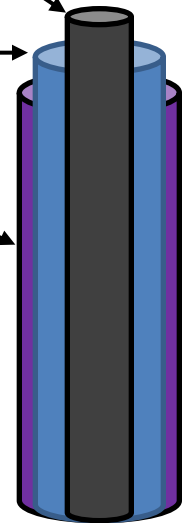
Use nanostructures to create new materials: overcome charge diffusion issues



Charge collector – TiS<sub>2</sub>

ALD deposited  
Photocathode

Oxygen evolving  
catalyst (optional)  
MnO<sub>x</sub> x = 2-5



Photocurrent of 2.7 mA/cm<sup>2</sup> using Fe<sub>2</sub>O<sub>3</sub>; quantum efficiency 46% at  $\lambda = 400$  nm (without OEC)

Fe<sub>2</sub>O<sub>3</sub> - Lin, Y.; Zhou, S.; Sheehan, S. W.; Wang, D. *J. Am. Chem. Soc.* **2011**, 133(8), 2398-401

WO<sub>3</sub> - Liu, R., Lin, Y., Chou, L.-Y., Sheehan, S. W., He, W., Zhang, F., et al. *Angew. Chem. Int. Ed.* **2011**, 3(3), 499-502.

TiO<sub>2</sub> - Lin, Y., Zhou, S., Liu, X., Sheehan, S., & Wang, D. *J. Am. Chem. Soc.* **2009**, 131(8), 2772-3.

# ALD Improved Photocatalysts

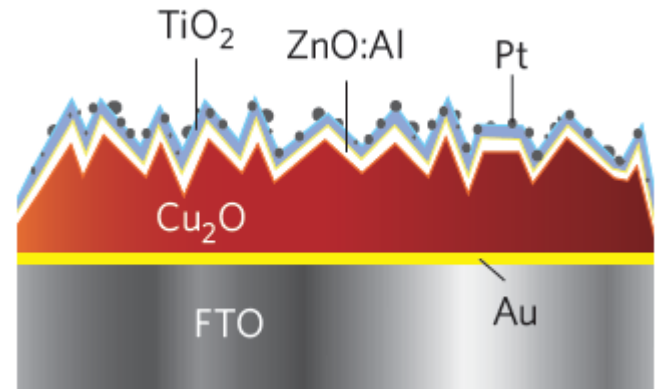
## ALD layers used for interface control:

- repairs defects in electrodeposited  $\text{Cu}_2\text{O}$  surface;
- prevents degradation to cathode material;
- improves performance of device

ALD  $\text{TiO}_2$  helps prevent corrosion /degradation of  $\text{Cu}_2\text{O}$   
ALD  $\text{ZnO}:\text{Al}$  films used as photon extraction layer

Highest recorded photo current  $7.6 \text{ mA} / \text{cm}^2$   
Photon-to-current efficiency was 40% between  
350 and 480 nm

Pt nanodot (hydrogen evolving catalyst) also possible by  
ALD; as are other layers i.e.)  $\text{MnO}_x$

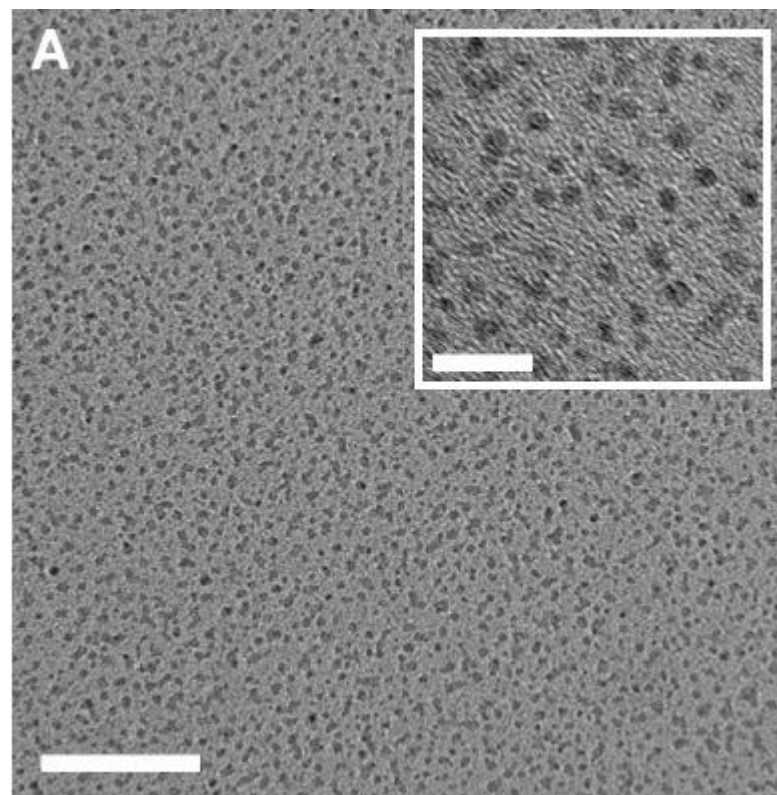


Paracchino, A. Laporte, V.; Sivula, K.; Grätzel, M.; Thimsen, E. *Nat. Mater* **2011**, 10, 457.



# Ru Nucleation - Nanodots

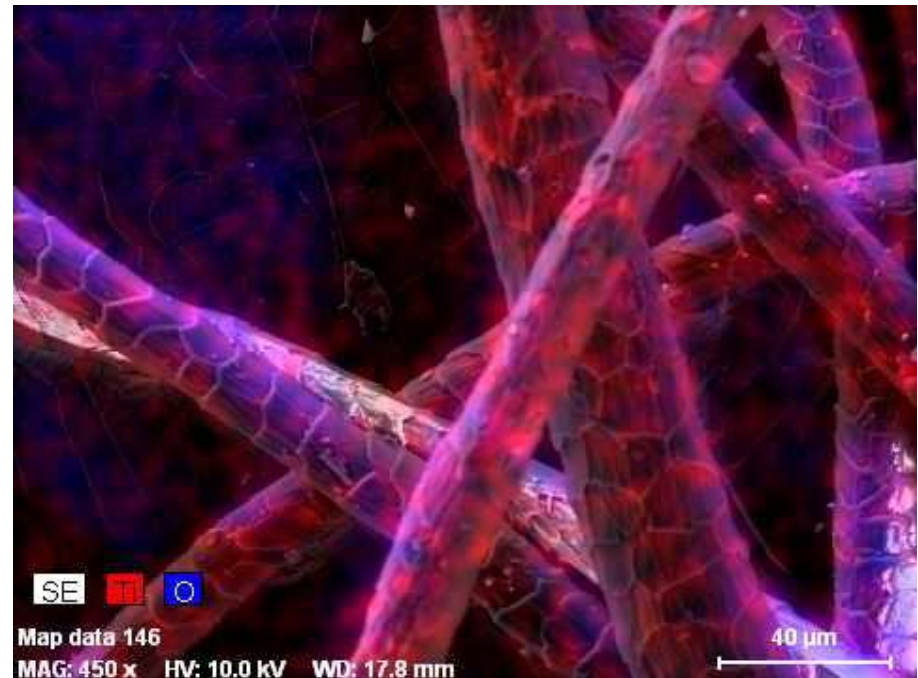
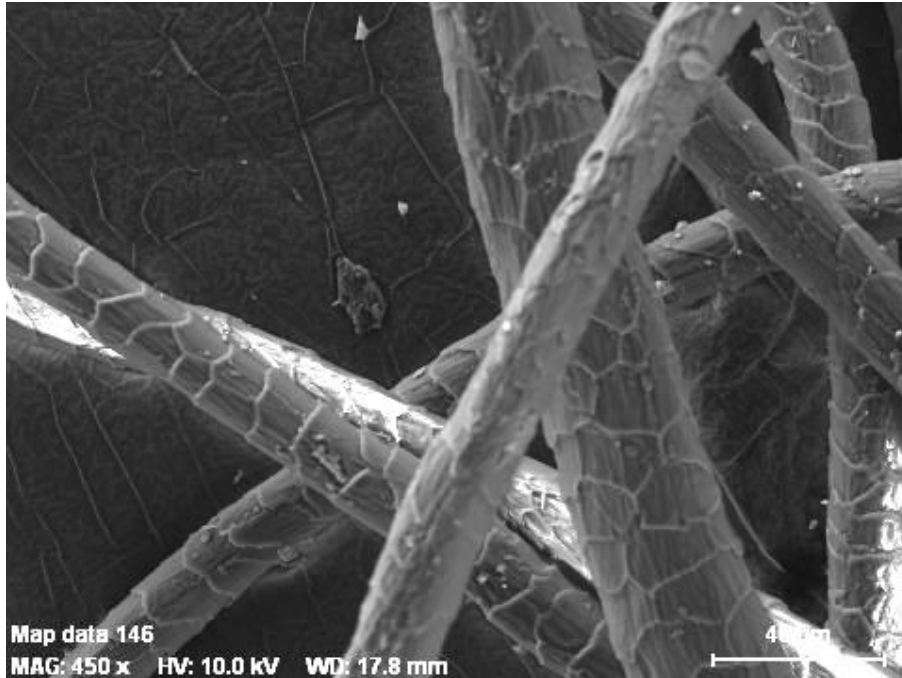
- Nucleation of Ru is substrate dependent
- Allows for formation of nanodots; diameters of  $\sim 1\text{-}2\text{nm}$ , 5-10 atoms across
- Takes advantage of slow nucleation of Ru on oxide
- film will become continuous with enough cycles



40nm scale bar. 10nm in inset

Interesting applications for catalysis – controlled “active sites” with size distribution

# Textiles

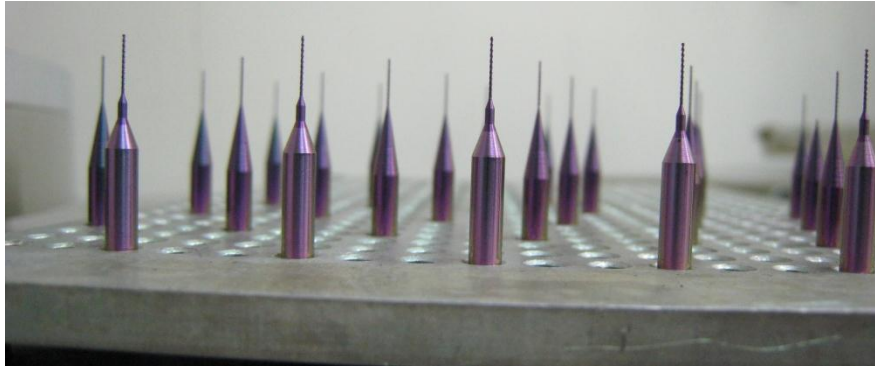


Wool fabric coated with ALD  $\text{TiO}_2$

EDS X-ray map of the wool

- Spill resistant fabrics – SAMs hydrophobic coatings
- High moisture absorbancy fabric (sportswear) – SAMs Hydrophilic coating
- Abrasion resistant fabrics –  $\text{Al}_2\text{O}_3$  coatings
- Anti-microbial coatings –  $\text{TiO}_2$  coating

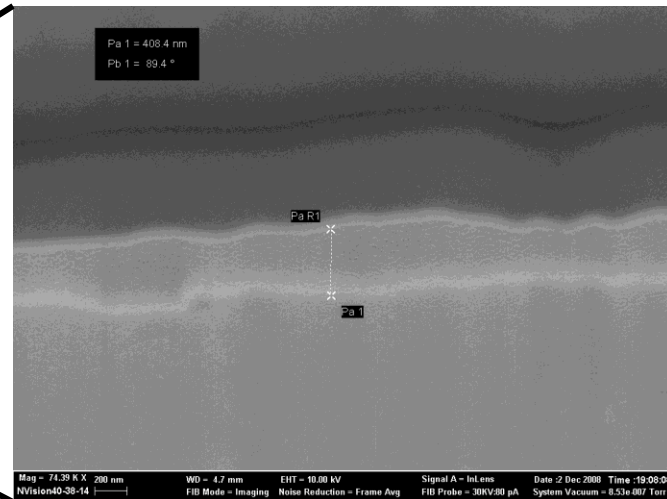
# Macroscopic Coatings



Drill bits with  $\text{ZrO}_2$  coatings



Coiled stainless steel tubing



FIB Cross-section of interior coated with ALD deposited Ru

Protective layer of Carbon

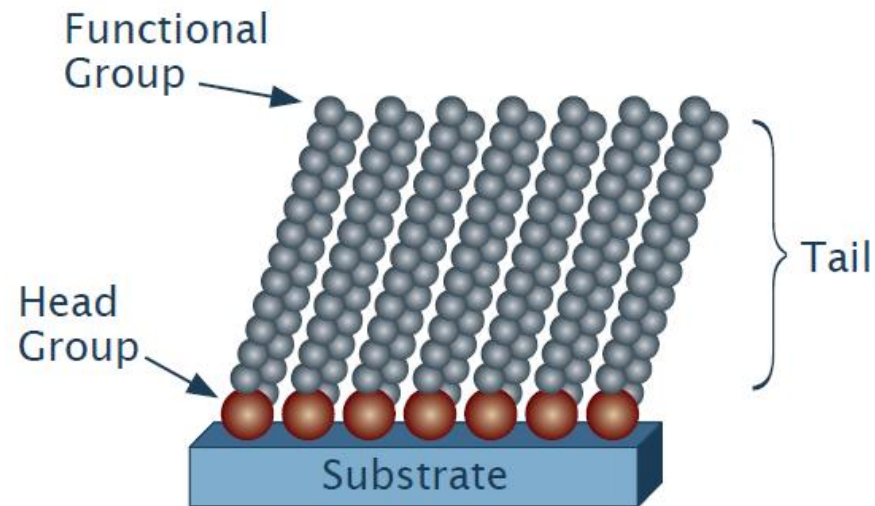
Conformal Ru coating

Stainless Steel



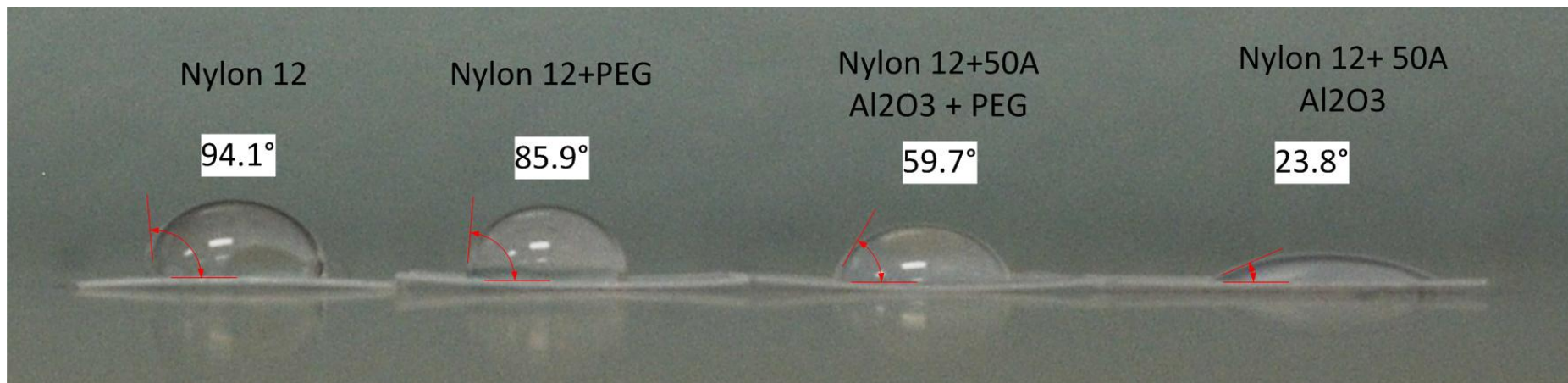
# MLD: SAMs: 2-D Self-Assembly

- Self-assembly in liquid or vapor phase driven by amphiphilic character of the molecules
- Ordered molecular 2D assemblies formed spontaneously by the chemisorption of the head group to a substrate.
- Head group
  - Affinity to substrate to induce chemisorbed surface reactions
  - High energy chemical bond (100 kJ/mol) provides molecular stability (thermal, chemical, biological)
- Tail group
  - Closed-packed structure driven by Van der Waals interaction between alkyl chains
- Functional group
  - Defines properties of monolayer, e.g., hydrophobicity/hydrophilicity, affinity to anchor with biological entities



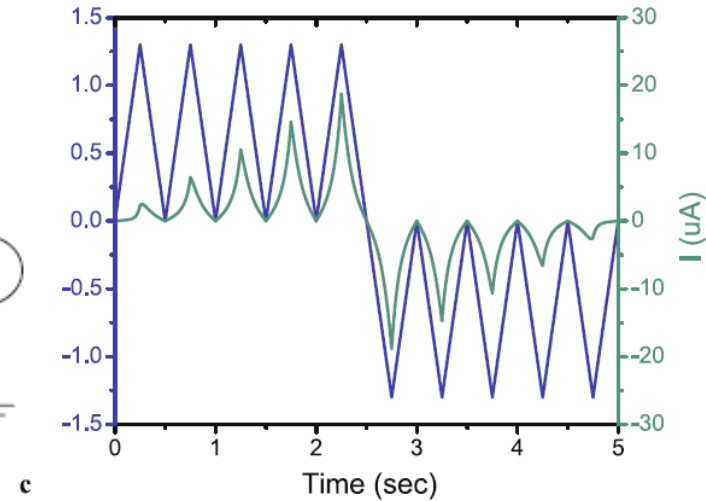
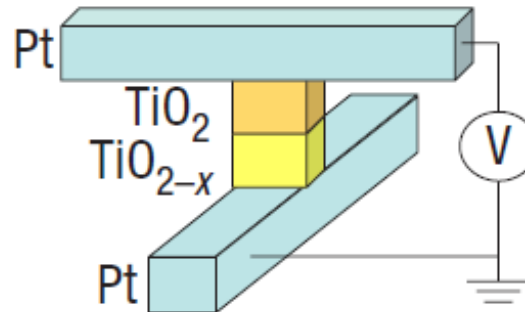
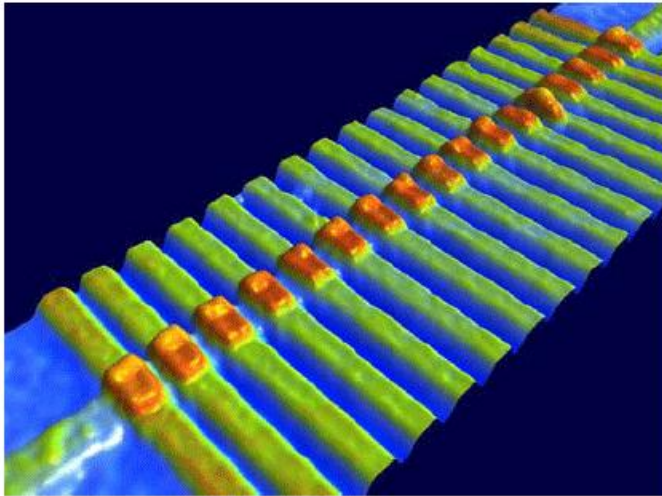
# PEG hydrophilic coating on Nylon

Tuning coating performance by combining ALD and SAMs



- Precursor: 2Methoxy(polyethyleneoxy)propyl)trimethoxysilane
- Source @ 100°C, Reactor 50°C
- Sample: Nylon12
- Sample prep: Al<sub>2</sub>O<sub>3</sub> ALD seed layer deposited at 50°C
- Result: nylon made more hydrophilic by combination of ALD+ polyethylene glycol coating

# ALD for Memristor



- No energy required to store data
- 3-D structure (can be stacked on top of each other)
- Memristive material changes states (based on oxygen vacancies for oxides)
- Many different logic states: not just 0:1

Different Oxygen Vacancies:  
Different Logic States

0:	$\text{MO}_x$
1:	$\text{MO}_{x-0.5}$
2:	$\text{MO}_{x-1}$
3:	$\text{MO}_{x-1.5}$
4:	$\text{MO}_{x-2}$

ALD Memristive materials:  $\text{HfO}_2$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{Cu}_2\text{S}$

# Summary

- Interest in ALD remains strong from the microelectronics industry
  - High-K gate oxides, metallization, “zero-thickness” barrier layers
  - Novel device structures
  - Low cost, printed or flexible electronics
- Applications such as lighting /displays, solar, energy storage, anti-corrosion/anti-wear, biocompatibility are large opportunities for using ALD
- Much research left to be done:
  - Novel precursors for new ALD films
  - Nanolaminates / doped films
  - Plasma-enhanced ALD

# Cambridge NanoTech

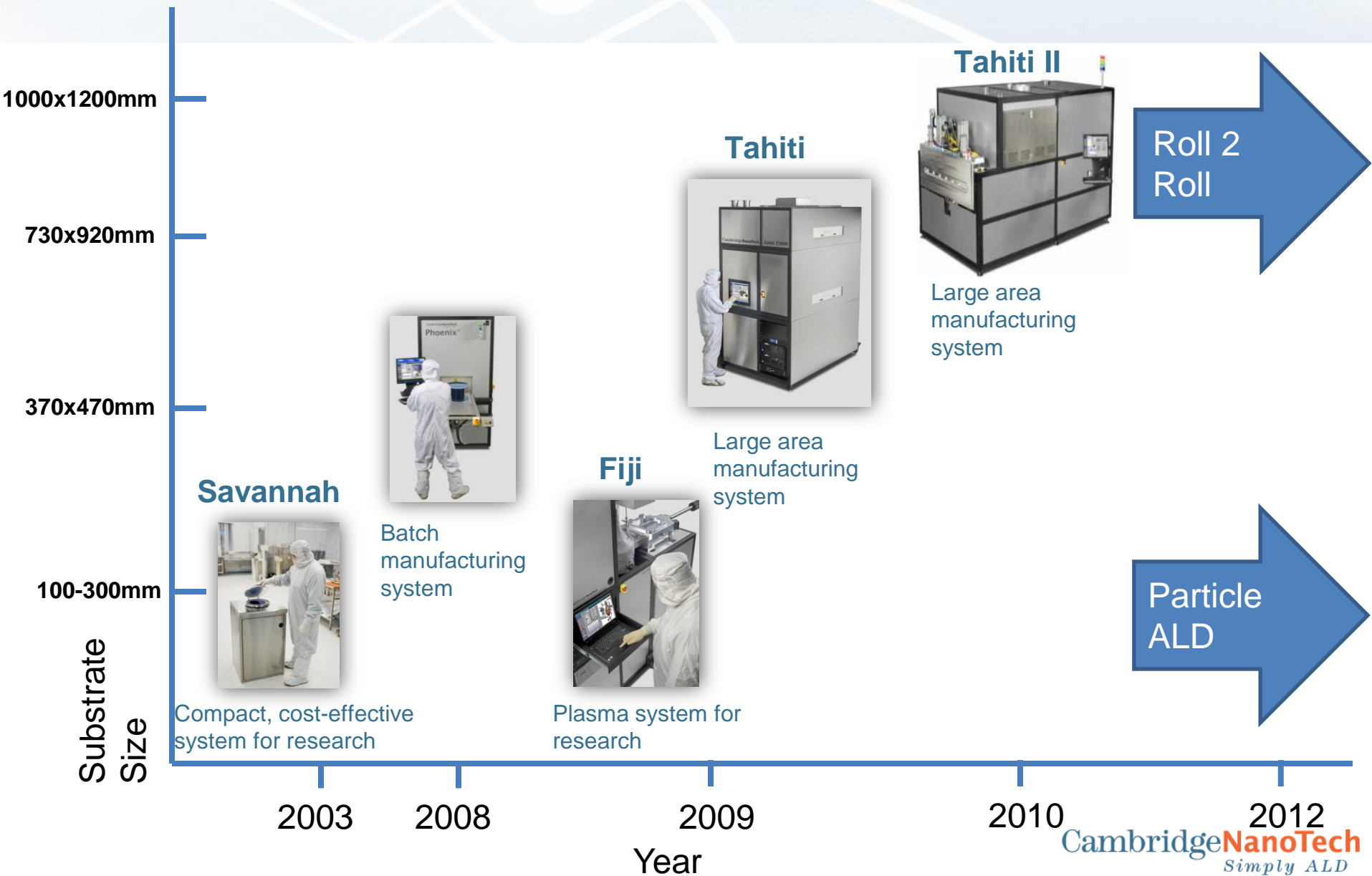


- Founded in 2003 by Dr. Jill Becker
- Located in Cambridge, MA
- Grew directly out of Gordon Lab at Harvard University
- Dedicated to advancing the science and technology of ALD
- Multiple ALD product lines serving many applications and industries
- Rapid response to custom applications and projects
- Full staff of Ph.D. research scientists
- Strategic partnerships deliver complete ALD solution



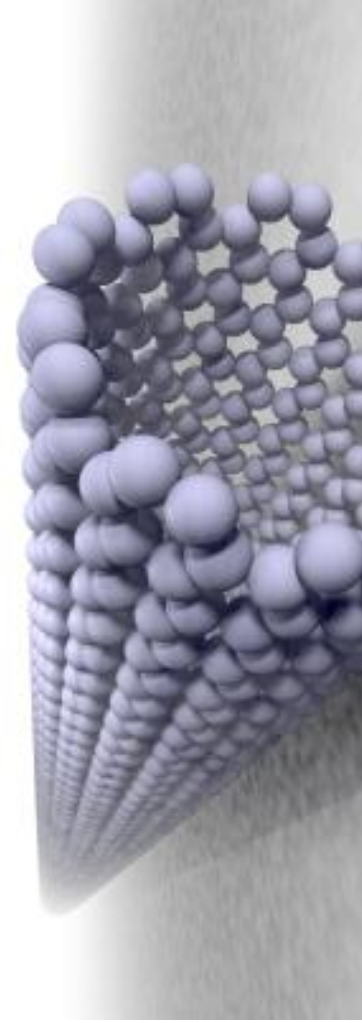
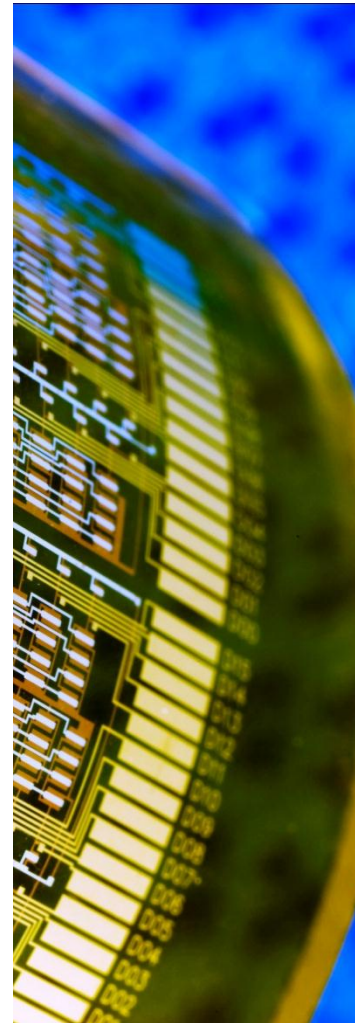
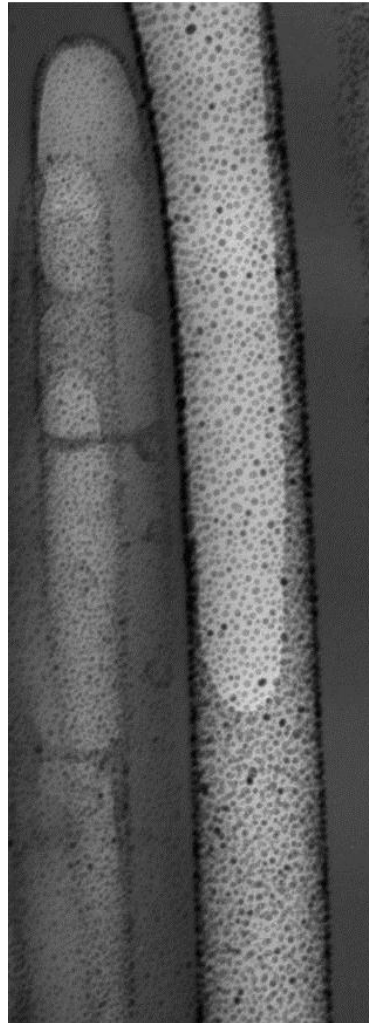


# ALD Systems





# The Promise of ALD



# ALD Applications



For application and process help:  
[support@cambridgenanotech.com](mailto:support@cambridgenanotech.com)

Cambridge**NanoTech**  
*Simply ALD*