## Atomic Layer Deposition for Nano-Manufacturing

June 24, 2010 Eric Deguns, Ph.D.



## Outline



- About Cambridge NanoTech
- Atomic Layer Deposition (ALD)
- Selected Applications
- Manufacturing Considerations
- ALD Reactors
- Summary



### About 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

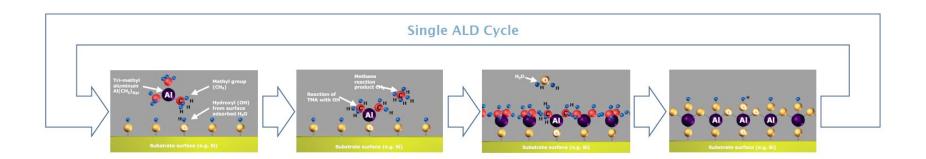


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# The ALD Cycle

- 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
- In the example below, precursors Trimethylaluminum (TMA) and H<sub>2</sub>O are alternately pulsed to deposit an Aluminum Oxide (Al<sub>2</sub>O<sub>3</sub>) film





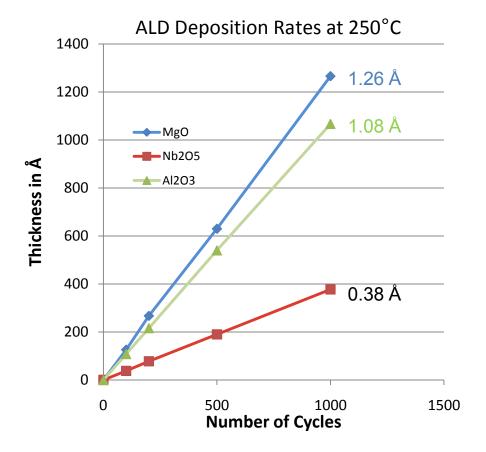
### **ALD Deposits Thin Inorganic Films**





# **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

 $\begin{array}{l} AI_{2}O_{3}, \ HfO_{2}, \ La_{2}O_{3}, \ SiO_{2}, \ TiO_{2}, \ ZnO, \\ ZrO_{2}, \ Ta_{2}O_{5}, \ In_{2}O_{3}, \ SnO_{2}, \ ITO, \ FeO_{x}, \\ NiO_{2}, \ MnO_{x}, \ Nb_{2}O_{5}, \ MgO, \ Er_{2}O_{3} \end{array}$ 

### **Nitrides**

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

### Metals

Ru, Pt, W, Ni, Co



# **Benefits of ALD**



100 nm Al<sub>2</sub>O<sub>3</sub> coating on Si wafer

### Perfect films

- Digital control of film thickness
- Excellent repeatability
- 100% 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

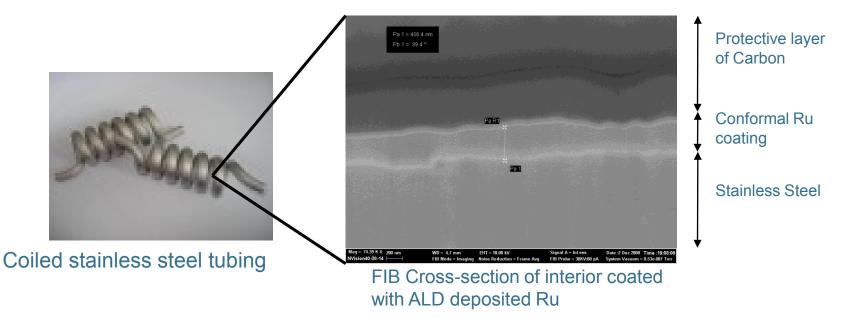
#### Challenging Substrates

- Gentle deposition process for sensitive substrates
- Low temperature and low stress
- Excellent adhesion
- Coats challenging substrates even teflon



### **Successful Coating of Irregular Shapes**

- Conformal coating of irregular topographies
- ALD film will deposit where ever precursor can infiltrate, without shadowing or line-of-sight issues

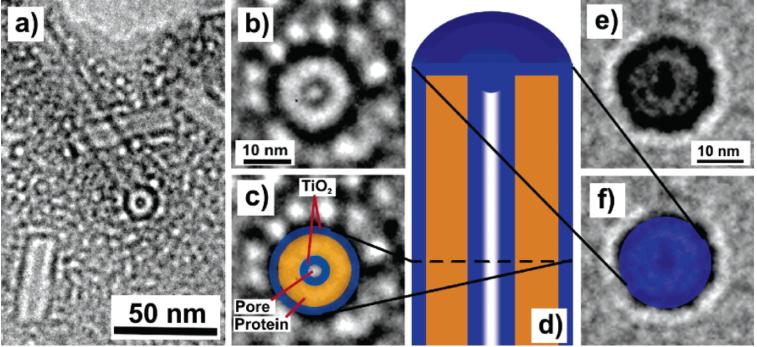




# **ALD on Biological Templates**

 Biological macromolecules enable fabrication of 3-D semiconducting / metallic/ insulative nanostructures

Deposition of  $TiO_2$  inside and around tubular shaped tobacco mosaic virus length 300 nm, OD 18 nm, ID 4 nm. Grown <  $80^{\circ}C$ 

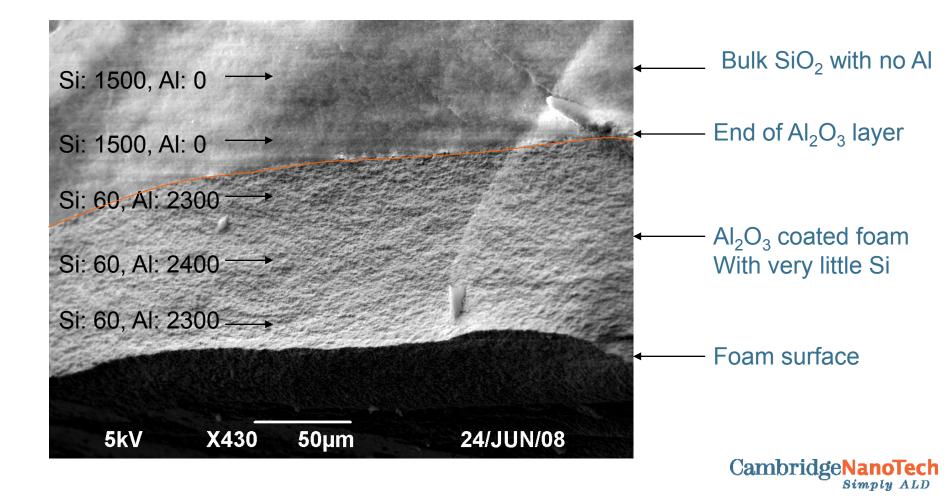


Courtesy of M. Knez, MPI Halle



# Al<sub>2</sub>O<sub>3</sub> Infiltration – Silica Aerogel

Successful conformal coating of 2000:1 aspect ratio inside porous aerogel



## **ALD Applications**



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



<u>MEMS</u> Etch resistance Hydrophobic / antistiction





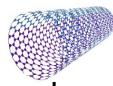
Chemical Catalysis Fuel cells



Other applications Internal tube liners Nano-glue Biocompatibility Magnetic



Wear resistant Blade edges Molds and dies Solid lubricants Anti corrosion



Nanostructures

Inside pores Nanotubes Around particles AFM tips Graphene



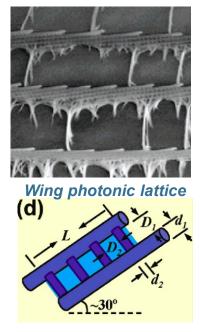
### Low Temperature ALD

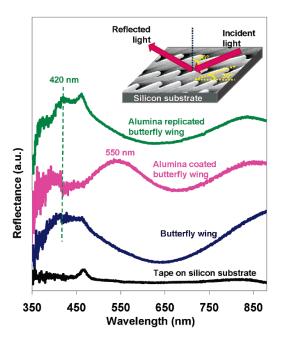
- Films deposited < 150°C:  $Al_2O_3$ ,  $HfO_2$ ,  $SiO_2$ ,  $TiO_2$ , ZnO,  $ZrO_2$ ,  $Ta_2O_5$ ,  $SnO_2$ ,  $Nb_2O_5$ , MgO
- Ideal for merging organics with inorganics
- Compatible with photoresist, plastics, biomaterials



Morpho Peleides butterfly

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

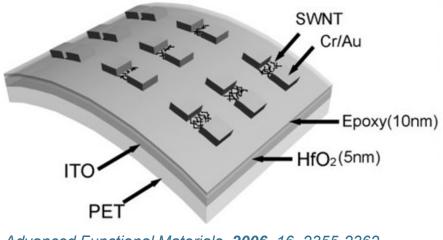




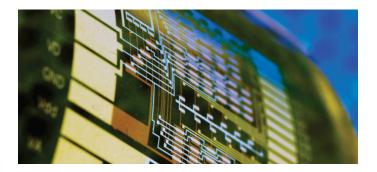
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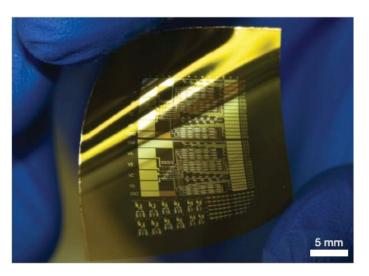
## **ALD for Flexible Electronics**

- High quality HfO<sub>2</sub> gate dielectric, deposited at 100°C
- Low stress film flexible



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



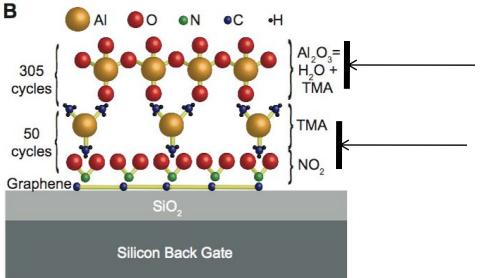


large capacitance (up to ca. 330 nF cm<sup>-2</sup>), and low leakage current (ca. 10<sup>-8</sup> A cm<sup>-2</sup>)



# **Functionalizing Graphene**

- To make useful devices need to control carriers
- Need to first functionalize the Graphene surface.
- Requirements:
  - Non interacting layer with Graphene and yet a good material for the growth of the gate dielectric  $(Al_2O_3)$



Done at 225°C in an ALD reactor (gate dielectric growth)

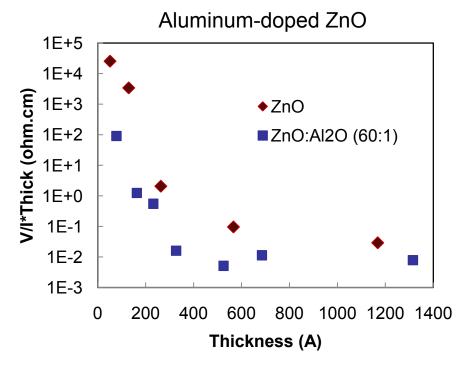
Done at room temperature in an ALD reactor (functionalization step)

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### **ALD for Transparent Conducting Oxides**

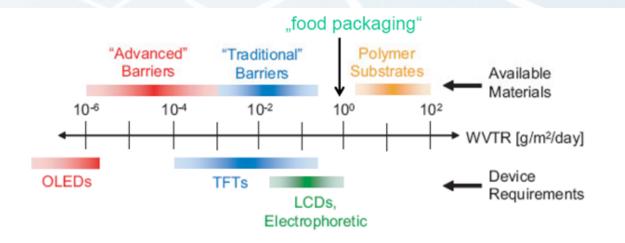
- ALD deposited Indium-Tin Oxide (ITO) at 250°C
  - Resistivity: 2 30 X 10<sup>-4</sup> Ω.cm, Thickness >200 Å
- Sensitive substrates require low process temperatures <120°C



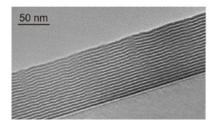
- Al<sub>2</sub>O<sub>3</sub>-doped ZnO<sub>2</sub> resistivity: – 2.8 X 10<sup>-3</sup>  $\Omega$ ·cm at 120°C
- Optical transparency, bandgap tunable without consequence on resistivity

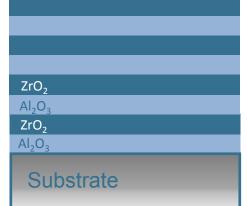


## **ALD for Moisture Barriers**



- Improved performance water and oxygen barrier by using nanolaminate layers of 5nm Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>
- Water Vapor Transmission Rate (WVTR) <10<sup>-6</sup> g/m<sup>2</sup> day demonstrated





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

## **ALD Process Considerations**

- Not all materials/processes are available for deposition by ALD or are appropriate for high-volume manufacturing
- Why?

### **Precursors**

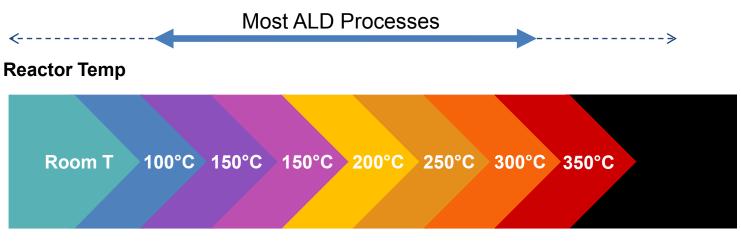
- Most precursors are air-sensitive: requires inert atmosphere or vacuum
  - Appropriate precursor chemistry
    - Must be thermally stable
    - Volatile / Reactive
    - Commercially produced and cost-effective
    - Compatibility with substrate / manufacturing



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### **ALD Reaction Temperatures**

- ALD is a chemistry driven process
- Based on precursor volatility/reactivity



Lower precursor volatility, Slow desorption of precursors Faster cycle time, poor thermal stability of precursors



## **ALD Process Considerations**

### **Process Pressure**

- ALD is generally pressure insensitive: can be performed at atmosphere
- Typical ALD reactors operate between 1-500mTorr
- Lower volatility precursors require lower process pressures

### Hardware Design

- Sizing of vacuum pump to clear byproducts cycle times (sub 1 second possible)
- Precursor introduction / distribution to ensure saturation



# **Manufacturing Considerations**

### **Process Times**

- Typical process time 1-30 seconds per cycle
- 20-500Å of material typically deposited
- "Batch" reactor will accommodate one hundred 200mm wafers
- Less than 2 hours of reactor time for 250Å

### **ALD for Manufacturing**

• Integration of ALD hardware into process line



### **In-line Systems**

- Air exclusion; reduction of process time (eliminates pump down time)
- Large flexible substrates (displays, solar, roll-to-roll)



Batch cassette for 300mm wafers



## **Product Portfolio**

Cambridge NanoTech ALD systems are engineered for a wide variety of applications from research to high-volume manufacturing.





### Production



## **Time to Production**

**<u>Case Study</u>**: MEMS technology <u>**Application**</u>: two layers, one to prevent stiction of MEMS device and another to prevent degradation via atmosphere (water)

#### R&D: - "Savannah" 200mm reactor

- Tested ALD layers for anti-stiction on R&D samples
- found ALD layers solved stiction issue, also acts as enhanced H<sub>2</sub>O barrier



200mm Savannah



**Phoenix Batch System** 

#### Pilot Scale: - "Phoenix" Batch System

-Scaled ALD deposition conditions from R&D reactor to "batch" pilot machine for qualification testing in less than one week -Five 370 X 470mm glass plates per batch -Identical film properties to R&D reactor

#### Manufacturing: "Tahiti" Production System

- Designed, built and qualified Production system in under 6 months
- Scaled ALD depositions conditions to manufacturing POR in 10 runs
- Identical film properties to R&D and Pilot Scale batch reactor
- Currently in production for commercial product; 920 X 730 mm plate



Tahiti – large format system

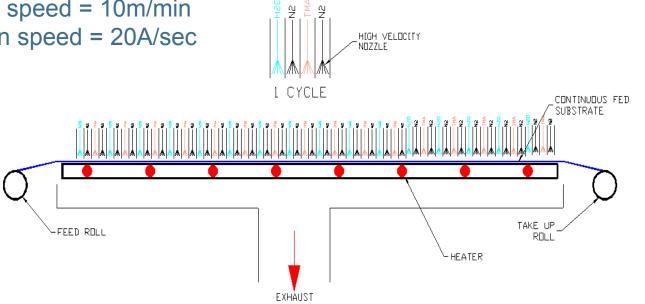
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## **Roll-to-Roll ALD Processing**

Funding for R2R project approved by consortium of Flexible Electronics companies. Delivery slated for 2012

### Project Goals

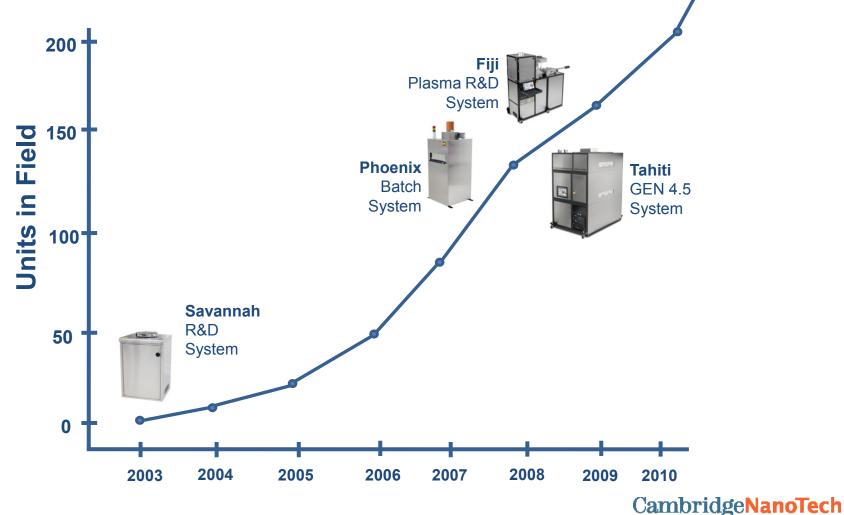
- Sub-second cycle time •
- Ability to handle web sizes >1m
- Substrate speed = 10m/min
- Deposition speed = 20A/sec



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### Industry Leader: Installed ALD Systems

• Recently shipped our 200<sup>th</sup> system



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## **ALD Experts**



Savannah S300

 Cambridge NanoTech offers a wide variety of ALD tools:

- Research
- Plasma
- Batch manufacturing
- Large area manufacturing
- Coating Services for ALD film evaluation
- ALD Consulting Services
- Partnerships with industry leaders to provide our customers with a complete ALD solution

