Atomic Layer Deposition for Nano-Manufacturing

June 24, 2010
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NanoTech
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
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$_2$O are alternately pulsed to deposit an Aluminum Oxide (Al$_2$O$_3$) film
ALD Deposits Thin Inorganic Films
- Films deposited with digital control of thickness; “built layer-by-layer”
- Each film has a characteristic growth rate for a particular temperature

**Oxides**
- \( \text{Al}_2\text{O}_3 \), \( \text{HfO}_2 \), \( \text{La}_2\text{O}_3 \), \( \text{SiO}_2 \), \( \text{TiO}_2 \), \( \text{ZnO} \), \( \text{ZrO}_2 \), \( \text{Ta}_2\text{O}_5 \), \( \text{In}_2\text{O}_3 \), \( \text{SnO}_2 \), \( \text{ITO} \), \( \text{FeO}_x \), \( \text{NiO}_2 \), \( \text{MnO}_x \), \( \text{Nb}_2\text{O}_5 \), \( \text{MgO} \), \( \text{Er}_2\text{O}_3 \)

**Nitrides**
- \( \text{WN} \), \( \text{Hf}_3\text{N}_4 \), \( \text{Zr}_3\text{N}_4 \), \( \text{AlN} \), \( \text{TiN} \), \( \text{TaN} \), \( \text{NbN}_x \)

** Metals**
- Ru, Pt, W, Ni, Co
Benefits of ALD

- **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

100 nm $\text{Al}_2\text{O}_3$ coating on Si wafer
Successful Coating of Irregular Shapes

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

Coiled stainless steel tubing

FIB Cross-section of interior coated with ALD deposited Ru

Protective layer of Carbon

Conformal Ru coating

Stainless Steel
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°C

Courtesy of M. Knez, MPI Halle
Al₂O₃ 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

**MEMS**
- 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: Al₂O₃, HfO₂, SiO₂, TiO₂, ZnO, ZrO₂, Ta₂O₅, SnO₂, Nb₂O₅, MgO
- 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 HfO$_2$ gate dielectric, deposited at 100°C
- Low stress film - flexible


large capacitance (up to ca. 330 nF cm$^{-2}$), and low leakage current (ca. $10^{-8}$ A cm$^{-2}$)
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 ($\text{Al}_2\text{O}_3$)

Done at 225°C in an ALD reactor (gate dielectric growth)
Done at room temperature in an ALD reactor (functionalization step)
ALD for Transparent Conducting Oxides

- ALD deposited Indium-Tin Oxide (ITO) at 250°C
  - Resistivity: 2 – 30 \times 10^{-4} \ \Omega \cdot \text{cm}, \text{Thickness} > 200 \ \text{Å}

- Sensitive substrates require low process temperatures <120°C

- \text{Al}_2\text{O}_3\text{-doped ZnO} resistivity:
  - 2.8 \times 10^{-3} \ \Omega \cdot \text{cm} at 120°C
- Optical transparency, bandgap tunable without consequence on resistivity
• Improved performance water and oxygen barrier by using nanolaminate layers of 5nm Al₂O₃ and ZrO₂

• Water Vapor Transmission Rate (WVTR) <10⁻⁶ g/m² day demonstrated

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

Most ALD Processes

Reactor Temp

Room T 100°C 150°C 200°C 250°C 300°C 350°C

Lower precursor volatility,
Slow desorption of precursors
Faster cycle time,
poor thermal stability of precursors
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
  - Glovebox, clustering, robot loading, batch cassette integration

In-line Systems
- Air exclusion; reduction of process time (eliminates pump down time)
- Large flexible substrates (displays, solar, roll-to-roll)
Cambridge NanoTech ALD systems are engineered for a wide variety of applications from research to high-volume manufacturing.

**Product Portfolio**

Savannah
- Compact, cost-effective system for research

Fiji
- Plasma system for research

Phoenix
- Batch manufacturing system

Tahiti
- Large area manufacturing system

Research  Production
Time to Production

Case Study: MEMS technology

Application: 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$_2$O barrier

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
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
Recently shipped our 200th system
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