# [Atomic Layer Deposition](http://www.cambridgenanotech.com/)

A Tutorial by Cambridge NanoTech Inc. Cambridge, MA 02139 USA

Contact us to receive the Powerpoint version!

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# **About Atomic Layer Deposition (ALD)**

Atomic Layer Deposition (ALD) is used to deposit thin films with special qualities.

 The principle of ALD is based on sequential pulsing of chemical precursor vapors, both of which form about one atomic layer each pulse. This generates pinhole free coatings that are extremely uniform in thickness, even deep inside pores, trenches and cavities.



100 nm Al $_2$ O $_3$  coating on Si wafer.

#### Cambridge NanoTech Inc. ALD systems



**The Cambridge NanoTech Inc. Atomic layer deposition systems are controlled with a convenient Labview-PC-USB interface.**

**They are hot wall ALD systems with cross flow travelling wave precursor deposition. Nitrogen carrier gas is used for high speed pulse-purge cycles.**

> **Prior to deposition, a substrate is inserted into the ALD reactor, and is heated usually between 50-400°C**

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#### ALD example cycle for Al $_{2} \mathrm{O}_{3}$  deposition



In air H<sub>2</sub>O vapor is adsorbed on most surfaces, forming a hydroxyl group. **With silicon this forms: Si-O-H (s)**

**After placing the substrate in the reactor, Trimethyl Aluminum (TMA) is pulsed into the reaction chamber.**



**Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product**

 $\overline{A}$ **Al(CH<sub>3</sub>)**<sub>3 (g)</sub> + : Si-O-H <sub>(s)</sub>  $\longrightarrow$  :Si-O-Al(CH<sub>3</sub>)<sub>2 (s)</sub> + CH<sub>4</sub>

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**Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, until the surface is passivated. TMA does not react with itself, terminating the reaction to one layer. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.**



**After the TMA and methane reaction product is pumped away,**  water vapor (H<sub>2</sub>O) is pulsed into the reaction chamber.



H<sub>2</sub>O reacts with the dangling methyl groups on the new surface forming aluminum**oxygen (Al-O) bridges and hydroxyl surface groups, waiting for a new TMA pulse. Again metane is the reaction product.** 

2 H<sub>2</sub>O<sub>(g)</sub> + :Si-O-Al(CH<sub>3</sub>)<sub>2 (s)</sub> 
$$
\longrightarrow
$$
 :Si-O-Al(OH)<sub>2 (s)</sub> + 2 CH<sub>4</sub>



The reaction product methane is pumped away. Excess H<sub>2</sub>O vapor does not react with **the hydroxyl surface groups, again causing perfect passivation to one atomic layer.**



One TMA and one H<sub>2</sub>O vapor pulse form one cycle. Here three cycles are shown, with **approximately 1 Angstrom per cycle. Each cycle including pulsing and pumping takes e.g. 3 sec.**

**Two reaction steps in each cycle:**

$$
AI(CH_3)_{3(g)} + :AI-O-H_{(s)} \longrightarrow :AI-O-Al(CH_3)_{2(s)} + CH_4
$$
  
2 H<sub>2</sub>O<sub>(g)</sub> + :O-Al(CH<sub>3</sub>)<sub>2(s)</sub>  $\longrightarrow$  :Al-O-Al(OH)<sub>2(s)</sub> + 2 CH<sub>4</sub>



**The saturative chemisorption of each layer and its subsequent monolayer passivation in each cycle, allows excellent uniformity into high aspect ratio 3D structures, such as DRAM trenches, MEMS devices, around particles etc.**

Animation of the ALD process!

see our website

http://www.cambridgenanotech.com/animation

### **ALD Deposition advantages**

Alternating reactant exposure creates unique properties of deposited coatings:

- Digital thickness control to atomic level.
- 3D conformality (100% step coverage).
- Large area uniformity.
- Easy batch scalability (small material sources and substrate stacking).
- **Pinhole free films, even over very large areas.**
- **Excellent repeatability (wide process window)**
- **Low defect density**
- Excellent adhesion due to chemical bonds at the first layer.
- Nanolaminates and mixed oxides possible.
- Gentle deposition process for sensitive substrates, no plasma.
- **Low temperature deposition possible (RT-400C)**
- Atomically flat and smooth, copies shape of substrate perfectly.
- **Low stress because of molecular self assembly**
- **100% dense guarantee ideal material properties (n,**  $E_{\text{hd}}$ **, k, etc).**
- **Relatively insensitive to dust.**
- Oxides, nitrides, metals, semiconductors possible (standard recipes).
- **Amorphous or crystalline depending on substrate and temperature.**
- **Coats on everything, even on teflon.**
- **Higher yields**
- Not all materials possible yet

#### Thin film deposition methods compared



 $ALD =$  atomic layer deposition, MBE = molecular beam epitaxy. CVD = chemical vapor deposition, PLD = pulsed laser deposition.





#### Our ALD products

see also:

#### http://www.cambridgenanotech.com/Products/products.php

# Savannah 100 & 200 ALD



- Travelling wave cross flow reactor
- Affordable for research labs
- Expandable (ozone, plasma, analytical systems)
- Small footprint (19 x 22 inches)



#### **CNT Customer testimonials:**

From Old Dominion University, Prof. Baumgart:

One of my students " Kanda Tapily " enjoyed numerous helpful contacts with you and appreciates your valued technical advise on whatever issues and questions did arise during his work. The Cambridge Nanotech ALD system works really fine and we are very happy about the tool. This ALD tool can be easily managed by graduate students in a university environment and *works like a charm.*

From a customer who asked their startup company is not mentioned:

"Cambridge NanoTech has been most excellent to provide expertise and starting points for developing processes to push our technology to the next level. *Their customer support is excellent. We've been using the Savannah system to grow films from the first day it was installed*."

Email received from customer Dr. Thomas W. Scharf:

"UNT is using the Cambridge NanoTech ALD system to deposit solid lubricant and nanocrystalline lubricous oxides for moving mechanical assembly (MMA) applications, such as fully assembled, miniature steel rolling element bearings and silicon MEMS. *UNT is very happy with the system, technical support, ALD expertise and timeliness in responses from Cambridge NanoTech*."

Professor Goldhaber-Gordon from Stanford University wrote:

*The ALD system runs smoothly,* producing conformal, high-breakdown aluminum oxide on a variety of substrates (we'll soon try depositing other materials). Cambridge Nanotech support is great -- they always respond to technical questions very fast and give useful suggestions.

Email received from Prof. Marek Godlewski PAS Poland:

We are very happy with the new ALD system SAVANNAH 100, which we bought from Cambridge NanoTech Inc. *We have grown more than 100 samples within the first 5 months after the purchase of this ALD*  system and the system worked perfectly. Presently we work on thin films of ZnO and ZnMnO, the first material for new electronics applications, the latter material for spintronics applications. It turned out to be very crucial to grow ZnO and ZnMnO at very low temperatures. In the case of ZnMnO we could avoid so-called spinodal decomposition and also accumulation of foreign Mn oxide phases. The obtained material was very homogeneous showing preferential magnetic properties.

From Marcello Zucca, Laboratorio di Chimica per le Tecnologie Università di Brescia, Italy

ALD system of Cambridge Nanotech is a perfect instrument to deposit nanometric films of metal oxides. The instrument is very reliable and thanks to interface it's very easy to use. We are able to deposit without problems titanium and zinc oxide and soon other oxides. We have obtained great results also thanks to the constant support of cambridge Nanotech. The customer assistance has always been helpful, fast and kind.

# Applications: High-k dielectrics for CMOS



100NodeLength (nm) Length (nm) Gate length 10 **EOT** 1Si atom diam eter2000 2005 2010 2015year

Intel 2007 production in 45 nm chips!

- Smaller transistors => short channel effect
- Need stronger electrostatic coupling of gate =>
- Thinner gate dielectrics but
- SiO<sub>2</sub> tunneling current => high-*k* dielectrics



### Choice of high-k dielectric material

#### 5 conditions -

- •High enough dielectric constant *k*
- • Stable - no reaction with Si
	- Oxides with high heat of formation
	- Preferred HfO<sub>2</sub>, Zr, Y, La, Al
- Stable up to 1050°C
	- Low diffusion, amorphous HfSiO<sub>v</sub>:N
- •Wide band gap for low leakage
- •Good interface, low impurities, traps



#### Applications: Semiconductor memory

High aspect ratio ALD of Ta2O5 in vias of 170 nm dia, 7 microns

deep

3D DRAM needs conformal coating of high-k dielectric and metal electrode

- $\bullet$  C=kA/d: Al $_2$ O $_3$ , ZrO $_2$ , Ta $_2$ O $_5$
- DRAM crown
- DRAM trench

Si

Poly-Si

 $AI<sub>2</sub>O<sub>2</sub>$ 



100 nm100 nm

Samsung uses ALD for DRAM manufacture!

*Hausmann et al. Thin Solid films 2003.*

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### Applications: Gate dielectrics on non-Si devices



 $(b)$ 



*NanoTech Client: Prof. C.M. Marcus, Harvard University.*

(a) Schematic of finger gated devices. Mo gates (150 nm wide 10 nm thick) were defined lithographically on a Si/ SiO2 substrate and subsequently coated with 25 nm of HfO2 grown by low-temperature ALD. Nanotubes were grown across these local gates by CVD and contacted with Ti/Au electrodes. Not to scale.

(b) Atomic force micrograph of nanotubes grown across Mo finger gates and contacted (far left and far right) by Ti/Au leads. Note that one finger gate passes directly underneath the nanotube-metal contact. Arrows indicate the location of the nanotube. Finger gates are labeled as in the text.

*Local gating of carbon nanotubes, Biercuk, Nano Letters 2003*

#### **Applications: ALD liftoff**

Low-temperature atomic-layer-deposition lift-off method for microelectronic and nanoelectronic applications, Biercuk, APL 2003.

![](_page_22_Picture_3.jpeg)

FIG. 3. SEM image of 15-nm-thick  $HfO<sub>2</sub>$  on  $Si/SiO<sub>2</sub>$ , patterned by electronbeam lithography. Device critical dimensions  $\sim 80$  nm as measured using the SEM. Inset: region of the device showing smallest features.

ABLE I. Properties of several high- $\kappa$  materials grown using the same low-temperature ALD process as used for lift-off, measured at 20 K and room temperature  $(T_M)$ : breakdown field,  $E_{BD} = V_{BD}/d$  ( $V_{BD}$  is breakdown voltage,  $d$  is film thickness), dielectric constant  $\kappa$ , and charge density at breakdown,  $Q_{BD} = CV_{BD}$ .

![](_page_22_Picture_67.jpeg)

#### Applications: Gate dielectrics on non-Si devices

*Client: Nobel laureate Prof. Tsui, Princeton University*

Undoped high mobility two-dimensional hole-channel  $GaAs/Al_{\alpha}Ga_{\alpha}$  As heterostructure field-effect transistors with atomic-laver-deposited dielectric

T.M. Lu.<sup>1,\*</sup> D.R. Luhman.<sup>1</sup> K. Lai.<sup>1,†</sup> D.C. Tsui.<sup>1</sup> L.N. Pfeiffer.<sup>2</sup> and K.W. West<sup>2</sup>

<sup>1</sup>Department of Electrical Engineering, Princeton University, Princeton, New Jersey  $08544$ <sup>2</sup>Bell Laboratories, Lucent Technologies, 700 Mountain Avenue, Murray Hill, New Jersey 07974

We have fabricated undoped p-channel  $GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As heterostructure field-effect transistors$ with nearly ideal drain current-voltage characteristics, using atomic-layer-deposited  $A_1O_3$  as the dielectric, and measured their transport properties. At 0.3K, the densities and mobilities of the two dimensional holes can be tuned up to  $2.9 \times 10^{11}$ /cm<sup>2</sup> and  $6.4 \times 10^5$ cm<sup>2</sup>/Vs respectively. The variable density high mobility two-dimensional hole system provides a large parameter space for the study of two-dimensional physics. Appl. Phys. Lett. 90, 112113 (2007)

High mobility two-dimensional electron gases (2DEGs) have benefited research in condensed matter physics and brought about many interesting physical phenomena [1]. Conventionally there are two ways of realizing 2DEGs. Modulation-doping is the most widely used technique for  $GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As heterostructures, in which electrons$ transfer from dopants in the barrier layer to the heterojunction interface and form the high mobility 2DEG. Metal-oxide-semiconductor field-effect transistors (MOS-FETs) are quite popular for Si-based systems, utilizing a high quality thermal oxide not available in other semiconductors. In a MOSFET, the 2DEG is induced at the interface of the semiconductor and the amorphous oxide by an electric field. The nature of disorder in the two types of 2DEGs is significantly different and is expected to have impact on their physical properties.

![](_page_23_Figure_7.jpeg)

FIG. 1: Schematic view of the device structure of an undoped p-channel GaAs heterostructure transistor. The "+" signs denote the capacitively induced 2D hole layer.

### Applications: Gate dielectrics on non-Si devices

APPLIED PHYSICS LETTERS 89, 162505 (2006)

#### Electric-field control of ferromagnetism in (Ga, Mn)As

#### D. Chiba. F. Matsukura. and H. Ohno<sup>a)</sup>

Semiconductor Spintronics Project, Exploratory Research for Advanced Technology, Japan Science and Technology Agency, Kitamemachi 1-18, Aoba-ku, Sendai 980-0023, Japan; and Laboratory for Nanoelectronics and Spintronics, Research Institute of Electrical Communication, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

(Received 21 July 2006; accepted 29 August 2006; published online 17 October 2006)

The authors show modulation of Curie temperature  $T_c$  and coercivity  $\mu_0 H_c$  by applying external electric fields  $E$  in a ferromagnetic semiconductor (Ga,Mn)As, where a field-effect transistor structure with an Al<sub>2</sub>O<sub>3</sub> gate insulator is utilized. Application of  $E=+5$  (-5) MV/cm decreases (increases)  $T_c$  of the channel layer.  $\mu_0 H_c$  also decreases (increases) with increasing (decreasing) E below  $T_c$ . The mechanism of the modulation of  $\mu_0H_c$  by E is discussed.  $\odot$  2006 American Institute of Physics. [DOI: 10.1063/1.2362971]

*Client: Prof. Ohno, Tohoku University, Japan.*

![](_page_24_Figure_8.jpeg)

# Applications: ALD lift-off technology

![](_page_25_Picture_1.jpeg)

FIG. 3. SEM image of 15-nm-thick HfO<sub>2</sub> on Si/SiO<sub>2</sub>, patterned by electronbeam lithography. Device critical dimensions  $\sim 80$  nm as measured using the SEM. Inset: region of the device showing smallest features.

*Cambridge NanoTech Client: C.M. Marcus, Harvard University.*

&ABLE I. Properties of several high- $\kappa$  materials grown using the same low-temperature ALD process as used for lift-off, measured at 20 K and room temperature  $(T_M)$ : breakdown field,  $E_{BD} = V_{BD}/d$  ( $V_{BD}$  is breakdown voltage,  $d$  is film thickness), dielectric constant  $\kappa$ , and charge density at breakdown,  $Q_{BD} = CV_{BD}$ .

![](_page_25_Picture_68.jpeg)

Cambridge NanoTech co-authored publication, Applied Physics Letters 2003.

### WN metal barrier for Cu interconnects

![](_page_26_Figure_1.jpeg)

- Refractory nature
- Amorphous
- Acts as an adhesion promotor for Cu and Co

*Cambridge NanoTech co-authored publication*

![](_page_26_Figure_6.jpeg)

#### **Applications: Porous structures**

#### **Atomic Layer Deposition in Porous Alumina (Top view)**

![](_page_27_Figure_3.jpeg)

#### **Applications: Porous structures**

#### **Atomic Layer Deposition in Porous Alumina (Bottom view)**

![](_page_28_Figure_3.jpeg)

#### **Applications: Porous structures**

*Cambridge NanoTech Client: K. Nielsch, Max Planck Germany*

![](_page_29_Figure_2.jpeg)

TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> coaxial nanotubes grown with ALD inside porous alumina.

*K. Nielsch, Max Planck Institute, 2006*

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### Applications: ferromagnets

#### Nickel nanotubes grown in porous alumina, then alumina etched away

![](_page_30_Picture_2.jpeg)

![](_page_30_Figure_3.jpeg)

*K. Nielsch, Max Planck Institute, 2006*

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*Cambridge NanoTech Client: K. Nielsch,* 

*Max Planck Germany*

### **Applications: Nanotube formation**

#### Monocrystalline spinel nanotube fabrication based on the Kirkendall effect

HONG JIN FAN\*, MATO KNEZ, ROLAND SCHOLZ, KORNELIUS NIELSCH, ECKHARD PIPPEL, DIETRICH HESSE. MARGIT ZACHARIAS<sup>+</sup> AND ULRICH GÖSELE

*Nature Materials 2007* Published online: 2 July 2006; doi:10.1038/nmat1673

![](_page_31_Picture_4.jpeg)

#### *cambridge NanoTech Client: K. Nielsch, Max Planck Germany*

![](_page_31_Figure_6.jpeg)

Figure 1 Schematic diagram of the formation process of  $ZnAl_2O_4$  spinel nanotubes. a, Single-crystal ZnO nanowires are grown by the vapour-liquid-solid mechanism using Au nanoparticles as a catalyst. b, The nanowires are coated with a uniform layer of  $Al_2O_3$  by ALD, forming core-shell ZnO-Al $_2O_3$  nanowires. c, Annealing the core-shell nanowires leads to the formation of ZnAl<sub>2</sub>O<sub>4</sub> nanotubes by a spinel-forming interfacial solid-state reaction involving the Kirkendall effect.

### Play-LD: coating of virus

Deposition of Al $_2\rm{O}_3$  inside and around tubular shaped tobacco mozaic virus length 300 nm, OD 18 nm, ID 4 nm. Grown < 80C

![](_page_32_Figure_2.jpeg)

#### M. Knez et al., Nano Lett. 6, No. 6, 1172 (2006).

*cambridge NanoTech Client: K. Nielsch, Max Planck Germany*

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#### Play-LD: butterfly PC waveguide

#### **Controlled Replication of Butterfly Wings for Achieving Tunable Photonic Properties**

Jingyun Huang, t, t, \$ Xudong Wang, t, \$ and Zhong Lin Wang\*, t

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, P. R. China

Received August 8, 2006; Revised Manuscript Received September 5, 2006

#### **NANO LETTERS**

2006 Vol. 6, No. 10  $2325 - 2331$ 

![](_page_33_Picture_7.jpeg)

*Morpho Peleides* **butterfly** *Wing photonic lattice*

![](_page_33_Picture_9.jpeg)

![](_page_33_Picture_11.jpeg)

*Cambridge NanoTech Client: Zhong Lin Wang, Georgiatech.*

#### Play-LD: butterfly PC waveguide

![](_page_34_Picture_1.jpeg)

![](_page_34_Figure_2.jpeg)

www.cambridgenanotech.com www.cambridgenanotech.com 35 *Cambridge NanoTech Client: Zhong Lin Wang, Georgiatech.*

#### Applications: Anti-reflection coatings

*ALD good for AR coatings: large area precision thickness control and batch coating.*

=> Graded index coatings posssible by varying the number of Al2O3/TiO2 low n/high n layers inside a nanolaminate stack

![](_page_35_Figure_3.jpeg)

FIG. 1. Film thickness as a function of the number of cycles, and corresponding structure of the laminated film constructed of alternating Al<sub>2</sub>O<sub>1</sub>-TiO<sub>2</sub> sublayers.

![](_page_35_Figure_5.jpeg)

FIG. 2. Refractive index of  $AI_2O_3-TiO_2$  nanoscale laminated films as a function of the volume concentration of  $Al_2O_3$  ( $C_{Al_2O_2}$ ) defined by Eq. (2).

![](_page_35_Figure_7.jpeg)

FIG. 3. Reflection spectra of silicon substrate with and without the singlelayer nanoscale laminated coating consisting of 60  $Al_2O_3 - TiO_2$  bilayers.

*Zaitsu et al. Applied Phyics Letters, 80, 2442, 2002*

#### **Applications: Transparent conductors**

ALD-ZnO transparent conductors advantages:

- No costly indium as in ITO
- Good optical transmission
- Low resistivity (1 mOhmcm)
- Large area uniformity
- Very smooth films in contrast to ITO

Thin film transistors:

ALD of ZnO active matrix thin film transistors possible as well.

Japanese Journal of Applied Physics Vol. 44, No. 7, 2005, pp. L242-L245

C2005 The Japan Society of Applied Physics

**Characteristics of Organic Light Emitting Diodes** with Al-Doped ZnO Anode Deposited by Atomic Layer Deposition Sang-Hee Ko PARK<sup>\*</sup>, Jeong-Ik LEE, Chi-Sun HWANG and Hye Yong CHU

![](_page_36_Figure_12.jpeg)

Fig. 3. Transmittance spectra of ZnO:Al films (film A: ZnO surface; film B:  $Al_2O_3$  surface) and ITO film on a glass substrate.

#### **Applications: humidity barriers**

Water vapor transmission rate of 25 nm ALD Al2O3 better than 1 mm polymer encapsulation!

WVTR <10−5 g/m2 day demonstrated

![](_page_37_Figure_3.jpeg)

FIG. 1. (Color online) Cross section of a Ca-test cell consisting of 16 semitransparent Ca squares,  $5 \times 5$  mm<sup>2</sup>, evaporated on a glass substrate, epoxied to a plastic (PEN) lid coated on one side with a thin-film barrier material.

![](_page_37_Figure_5.jpeg)

FIG. 2. (a) (Color online) Change in optical transmission with aging for a representative Ca thin-film square in a test cell where the lid was PEN, coated with 25 nm thick  $AI_2O_3$ , grown by atomic layer deposition. Aging was at 38 °C (85% RH) and 60 °C (85% RH). (b) Optical images of Ca, protected by ALD Al<sub>2</sub>O<sub>3</sub> barrier before and after aging for over 3000 h, and after  $\sim$ 16 h in ambient for a plastic lid without a barrier.

![](_page_37_Figure_7.jpeg)

For more applications see:

#### http://www.cambridgenanotech.com/ALD-applications.php

and

http://www.cambridgenanotech.com/clientmap/clientpapers.php

#### **Our website**

www.cambridgenanotech.com

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