

## Atomic Layer Deposition Techniques and Films by the University of Colorado

### Atomic layer deposition (ALD):

ALD is a thin film growth technique that relies on two sequential, self-limiting surface reactions between gas-phase precursor molecules and a solid surface as illustrated in Figure 1 [1]. The surface is first exposed to reactant A, which reacts with initial surface sites. Then, after the products from reaction A are purged, the surface is exposed to reactant B. This reaction regenerates the initial functional groups and prepares the surface for the next exposure to reactant A. The film is grown to the desired thickness by repeating this AB sequence. As the reactions are self-limiting, ALD does not require line-of-sight for deposition and high surface area to volume ratio structures and complex geometries can be conformally coated. Atomic force microscopy (AFM) inspection of Al<sub>2</sub>O<sub>3</sub> ALD films deposited on planar surfaces reveals pinhole-free coatings with nearly the same surface roughness as the underlying substrate. Smooth, dense films result when the two reactions are allowed to go to completion. ALD techniques exist for depositing a variety of substances including oxides, nitrides, and metals.

ALD has many important benefits over other more standard thin film deposition techniques such as chemical vapor deposition (CVD). During CVD, the surface is exposed to both reactants at the same time. This allows for gas-phase reactions, which can cause particle formation and poorly controlled growth. During ALD, only one reactant is present at a time so that only *surface* reactions occur. This insures smooth conformal films with atomic level control over growth. Additionally, ALD can be performed at temperatures well below typical CVD temperatures, thus allowing the coating of relatively fragile materials, such as polymers, without damage.

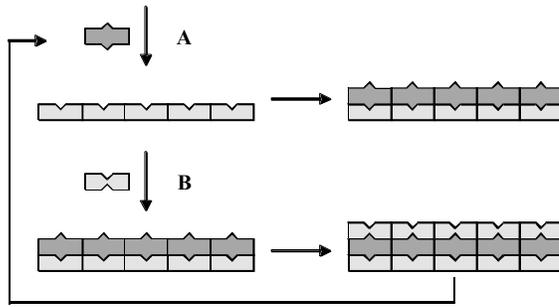


Figure 1: A schematic drawing of the AB reaction sequence during atomic layer deposition

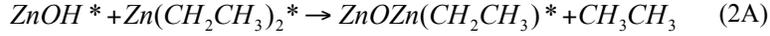
Al<sub>2</sub>O<sub>3</sub> ALD films are deposited using alternating exposures of trimethylaluminum (Al(CH<sub>3</sub>)<sub>3</sub>, TMA) and water. The chemistry of Al<sub>2</sub>O<sub>3</sub> ALD occurs via the following equations where the asterisk represents surface species



At a deposition temperature of 177 °C, the growth rate for Al<sub>2</sub>O<sub>3</sub> ALD determined using an *in-situ* quartz crystal microbalance (QCM) is 1.2 Å/cycle and the typical cycle time is 12 seconds [2]. Al<sub>2</sub>O<sub>3</sub> films grown by ALD techniques are insulating, amorphous and smooth [3]. Furthermore, the Al<sub>2</sub>O<sub>3</sub> ALD surface chemistry is very favorable to growth on a wide variety of substrates including oxides, nitrides, metals, semiconductors [4], and polymeric surfaces [5]. This allows for devices of almost any material to be coated with ALD films. Al<sub>2</sub>O<sub>3</sub> ALD can be used for a variety of applications (see list below for some examples).

1. Al<sub>2</sub>O<sub>3</sub> ALD films on electrostatically actuated polysilicon cantilever beams prevent electrical shorting and increase the number of actuation cycles before device failure [6].
2. Al<sub>2</sub>O<sub>3</sub> ALD films on bilayer (Au/Si) cantilever beams prevent creep during high temperature holding [7].
3. Al<sub>2</sub>O<sub>3</sub> ALD films on surface-micromachined gears can serve as friction and wear-resistive coatings [8].
4. Thin Al<sub>2</sub>O<sub>3</sub> ALD films (25Å) can serve as adhesion layers for the attachment of hydrophobic precursor molecules, which results in robust and reliable hydrophobic coatings to prevent moisture-induced stiction [9, 10].
5. Alloys of Al<sub>2</sub>O<sub>3</sub> ALD and ZnO ALD can be used to prevent stiction due to dielectric charging in gold RF-MEMS devices [11, 12].
6. In a biocompatibility test, adherence of vascular smooth muscle cells was superior on Al<sub>2</sub>O<sub>3</sub> ALD surfaces when compared to glass surfaces [13].
7. Al<sub>2</sub>O<sub>3</sub> ALD films have been used to construct nano-scale devices such as deformable membranes and cantilever beams [14].

Diethylzinc (Zn(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, DEZ) and water are the reactants used during ZnO ALD. The AB reaction sequence for ZnO ALD is as follows



At a deposition temperature of 177 °C, the growth rate for pure ZnO ALD is 2.0 Å/cycle as determined with an in-situ QCM. A typical AB cycle takes 12 seconds. In contrast to the Al<sub>2</sub>O<sub>3</sub> ALD films, ZnO ALD films are conducting, polycrystalline and rough [3].

### Al<sub>2</sub>O<sub>3</sub>/ZnO ALD Alloys:

It has been previously established that the resistivity of Al<sub>2</sub>O<sub>3</sub>/ZnO ALD alloy films can be tuned over a wide range by varying the amount of Zn in the film [15]. Al<sub>2</sub>O<sub>3</sub>/ZnO ALD alloy films can therefore be designed with a dielectric constant high enough to provide a large down-state capacitance and a resistivity low enough to promote the dissipation of trapped charges. In order to create alloys of Al<sub>2</sub>O<sub>3</sub> ALD and ZnO ALD, a percentage of the TMA exposures are replaced by exposures of DEZ [16]. An Al<sub>2</sub>O<sub>3</sub>/ZnO alloy with 33% DEZ exposures, for example, can be grown by substituting every third TMA exposure with a DEZ exposure. By evenly distributing the DEZ exposures, the Al<sub>2</sub>O<sub>3</sub>/ZnO ALD alloy is as homogeneous as possible.

In order to perform as an effective dielectric layer, the Al<sub>2</sub>O<sub>3</sub>/ZnO ALD alloy films must have a high dielectric constant similar to pure Al<sub>2</sub>O<sub>3</sub> ALD. Table 1 shows the dielectric constants [12] and resistivities [15] for Al<sub>2</sub>O<sub>3</sub>/ZnO ALD alloy films. The dielectric constants for the films containing zinc are very similar to the value for the pure Al<sub>2</sub>O<sub>3</sub> ALD film, while the resistivities of the films varied from 10<sup>13</sup> to 10<sup>16</sup> Ω·cm.

Table 1: Dielectric constants and resistivities for Al<sub>2</sub>O<sub>3</sub>/ZnO ALD films.

% DEZ exposures	0	10	25	33	50
Dielectric Constant	6.8 ± 0.5	6.5 ± 0.4	6.9 ± 0.3	7.2 ± 0.2	6.6 ± 0.3
Resistivity (Ω·cm)	~10 <sup>16</sup>	~5 x 10 <sup>15</sup>	~5 x 10 <sup>14</sup>	~10 <sup>14</sup>	~10 <sup>13</sup>

### Hydrophobic ALD Coating:

The chemical modification of micromachined surfaces can also be achieved using ALD techniques. After completing the H<sub>2</sub>O reaction, the Al<sub>2</sub>O<sub>3</sub> layer is left with a very high coverage of AlOH\* hydroxyl groups at the surface [17]. At room temperature, this hydroxyl coverage is almost twice as large as the coverage of hydroxyl groups on SiO<sub>2</sub> surfaces. Consequently, Al<sub>2</sub>O<sub>3</sub> can be used as a seed layer to which precursors that modify the chemical properties of the surface can be attached. Using this technique, highly hydrophobic films have been demonstrated [9, 10]. In this example, hydrophobic perfluorinated alkylsilane precursors are attached through reactions with surface OH groups on the Al<sub>2</sub>O<sub>3</sub> ALD surface. This deposition technique results in a dense and conformal hydrophobic film with a water contact angle of 108 ± 2°. When annealed in air to 300 °C for 10 minutes, the hydrophobic ALD films remained hydrophobic with a contact angle greater than 90°. Using MEMS poly silicon cantilever beam arrays, hydrophobic ALD-coated beams were determined to have an adhesion energy of 0.11 ± 0.03 mJ/m<sup>2</sup> at 100% humidity as compared with an adhesion energy of 12 ± 1 mJ/m<sup>2</sup> for the same beams without any coating.

### Summary of Measured Properties:

- ZnO
1. Young's modulus (nanoindentation, T<sub>Dep.</sub>=100°C) = 120 - 140 GPa
  2. Hardness (nanoindentation, T<sub>Dep.</sub>=100°C) = ~5 GPa
  3. Resistivity (T<sub>Dep.</sub>=177°C) = 1x10<sup>-2</sup> Ω·cm
  4. Index of refraction (T<sub>Dep.</sub>=177°C) = 1.95
  5. Density (T<sub>Dep.</sub>=177°C) = 5.62 g/cm<sup>3</sup>

- Al<sub>2</sub>O<sub>3</sub>
1. Young's modulus (nanoindentation, T<sub>Dep.</sub>=100°C) = 150 - 155 GPa
  2. Hardness (nanoindentation, T<sub>Dep.</sub>=100°C) = ~8 GPa
  3. Residual stress (T<sub>Dep.</sub>=177°C, thickness = 30 nm) = 37 MPa
  4. Index of refraction (T<sub>Dep.</sub>=177°C) = 1.65
  5. Density (T<sub>Dep.</sub>=177°C) = 3.06 g/cm<sup>3</sup>; (T<sub>Dep.</sub>=100°C) = 2.7 g/cm<sup>3</sup>
  6. Table summarizing electrical properties of Al<sub>2</sub>O<sub>3</sub> ALD:

Thickness (nm)	Deposition temperature (°C)	Resistivity (Ω·cm)	Leakage current (A/cm <sup>2</sup> )	Electric field strength (MV/cm)	Catastrophic breakdown (MV/cm)	Dielectric constant
115	177	1.00E+16	1.00E-10	1		7.5
64	100					6.8
12	177	1.00E+15	2.00E-09	3	5.3	5.9

## References

- [1] S. M. George, A. W. Ott, and J. W. Klaus, "Surface chemistry for atomic layer growth," *Journal of Physical Chemistry*, vol. 100, pp. 13121-13131, 1996.
- [2] J. W. Elam, M. D. Groner, and S. M. George, "Viscous flow reactor with quartz crystal microbalance for thin film growth by atomic layer deposition," *Review of Scientific Instruments*, vol. 73, pp. 2981-2987, 2002.
- [3] J. W. Elam, Z. A. Sechrist, and S. M. George, "ZnO/Al<sub>2</sub>O<sub>3</sub> nanolaminates fabricated by atomic layer deposition: growth and surface roughness measurements," *Thin Solid Films*, vol. 414, pp. 43-55, 2002.
- [4] M. D. Groner, J. W. Elam, F. H. Fabreguette, and S. M. George, "Electrical characterization of thin Al<sub>2</sub>O<sub>3</sub> films grown by atomic layer deposition on silicon and various metal substrates," *Thin Solid Films*, vol. 413, pp. 186-197, 2002.
- [5] J. W. Elam, C. A. Wilson, M. Schuisky, Z. A. Sechrist, and S. M. George, "Improved nucleation of TiN atomic layer deposition films on SILK low-k polymer dielectric using an Al<sub>2</sub>O<sub>3</sub> atomic layer deposition adhesion layer," *Journal of Vacuum Science & Technology B*, vol. 21, pp. 1099-1107, 2003.
- [6] N. D. Hoivik, J. W. Elam, R. J. Linderman, V. M. Bright, S. M. George, and Y. C. Lee, "Atomic layer deposited protective coatings for micro-electromechanical systems," *Sensors and Actuators A-Physical*, vol. 103, pp. 100-108, 2003.
- [7] K. Gall, M. Hulse, M. L. Dunn, D. Finch, S. M. George, and B. A. Corff, "Thermomechanical response of bare and Al<sub>2</sub>O<sub>3</sub>-nanocoated Au/Si bilayer beams for microelectromechanical systems," *Journal of Materials Research*, vol. 18, pp. 1575-1587, 2003.
- [8] T. M. Mayer, J. W. Elam, S. M. George, P. G. Kotula, and R. S. Goeke, "Atomic-layer deposition of wear-resistant coatings for microelectromechanical devices," *Applied Physics Letters*, vol. 82, pp. 2883-2885, 2003.
- [9] C. F. Herrmann, F. W. DelRio, V. M. Bright, and S. M. George, "Hydrophobic coatings using atomic layer deposition and non-chlorinated precursors," *17th IEEE International Conference on Micro Electro Mechanical Systems*, pp. 653-656, 2004.
- [10] C. F. Herrmann, F. W. DelRio, V. M. Bright, and S. M. George, "Conformal Hydrophobic Coatings Prepared Using Atomic Layer Deposition Seed Layers and Non-Chlorinated Precursors," *Journal of Micromechanics and Microengineering*, under review, 2004.
- [11] F. W. DelRio, C. F. Herrmann, N. D. Hoivik, S. M. George, V. M. Bright, J. L. Ebel, R. E. Strawser, R. Cortez, and K. D. Leedy, "Atomic layer deposition of Al<sub>2</sub>O<sub>3</sub>/ZnO nano-scale films for gold RF MEMS," *Microwave Symposium Digest, 2004 IEEE MTT-S International*, vol. 3, pp. 1923 - 1926, 2004.
- [12] C. F. Herrmann, F. W. DelRio, S. M. George, and V. M. Bright, "Properties of atomic layer deposited Al<sub>2</sub>O<sub>3</sub>/ZnO dielectric films grown at low temperature," *Proceedings of SPIE*, in press, 2005.
- [13] D. Finch, K. Ramadurai, T. Oreskovic, C. F. Herrmann, and S. M. George, "Cytotoxicity Study of Vascular Smooth Muscle Cells Applied to Conformal Atomic Layer Deposited Alumina Thin Films for Bio-MEMS Applications," *Biomaterials*, to be submitted, 2005.
- [14] M. K. Tripp, C. F. Herrmann, S. M. George, and V. M. Bright, "Ultra-thin multilayer nanomembranes for short wavelength deformable optics," *17th IEEE International Conference on Micro Electro Mechanical Systems*, pp. 77-80, 2004.
- [15] J. W. Elam, D. Routkevitch, and S. M. George, "Properties of ZnO/Al<sub>2</sub>O<sub>3</sub> alloy films grown using atomic layer deposition techniques," *Journal of the Electrochemical Society*, vol. 150, pp. G339-G347, 2003.
- [16] J. W. Elam and S. M. George, "Growth of ZnO/Al<sub>2</sub>O<sub>3</sub> alloy films using atomic layer deposition techniques," *Chemistry of Materials*, vol. 15, pp. 1020-1028, 2003.
- [17] A. C. Dillon, A. W. Ott, J. D. Way, and S. M. George, "Surface-Chemistry of Al<sub>2</sub>O<sub>3</sub> Deposition Using Al(CH<sub>3</sub>)<sub>3</sub> and H<sub>2</sub>O in a Binary Reaction Sequence," *Surface Science*, vol. 322, pp. 230-242, 1995.