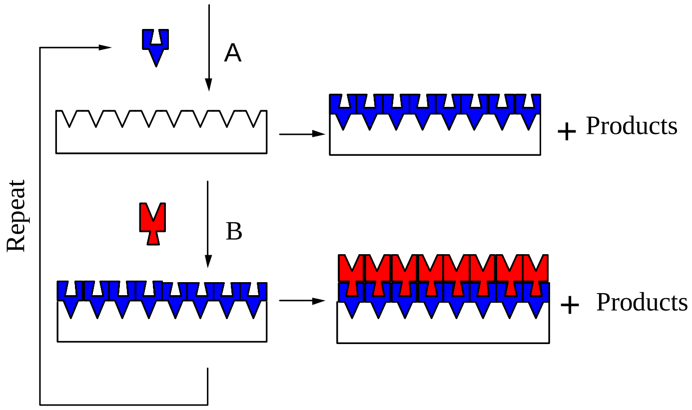
Introduction to Atomic Layer Deposition & Molecular Layer Deposition

Miniaturization to the nanometer scale has been one of the most important trends in science and technology over the last several years. The chemistry to fabricate nanolayers, the engineering for nanocomposite design and the physics of nanostructure properties have created many exciting opportunities for research. These new interdisciplinary areas in nanoscience and nanotechnology supersede the more traditional disciplines and demand new paradigms for collaboration.

Our research is focusing on the fabrication, design and properties of ultrathin films and nanostructures. We are developing new surface chemistries for thin film growth, measuring thin film nanostructures and characterizing thin film properties. This research is relevant to many technological areas such as semiconductor processing, flexible displays and MEMS/NEMS. Our research bridges many disciplines and we have collaborators in the Departments of Chemistry, Chemical Engineering, Mechanical Engineering and Physics on campus and many others at universities, industries and national laboratories off campus.

Many of our surface chemistry and thin film growth investigations utilize atomic layer deposition (ALD) techniques [1]. ALD is based on sequential, self-limiting surface reactions as illustrated in the accompanying figure. This unique growth technique can provide atomic layer control and allow conformal films to be deposited on very high aspect ratio structures. ALD methods and applications have developed rapidly over the last few years. In particular, ALD is on the semiconductor road map for high-k gate oxides and diffusion barriers for backend interconnects.

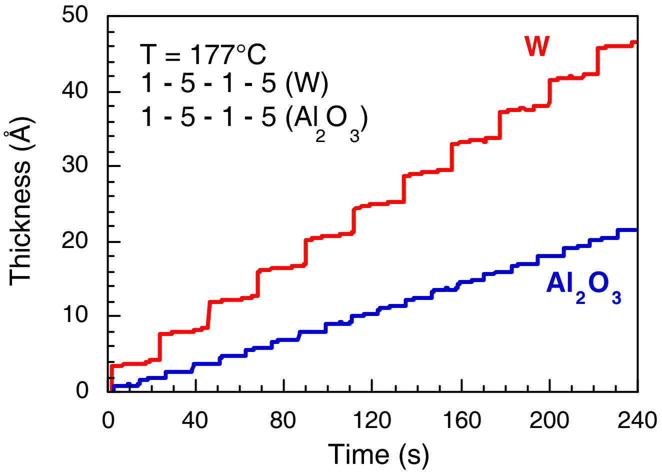


ALD is based on sequential, self-limiting surface chemical reactions. For example, for Al_2O_3 deposition, the binary reaction: $2Al(CH_3)_3 + 3H_2O \rightarrow Al_2O_3 + 6CH_4$ can be split into the following two surface half-reactions [2,3]:

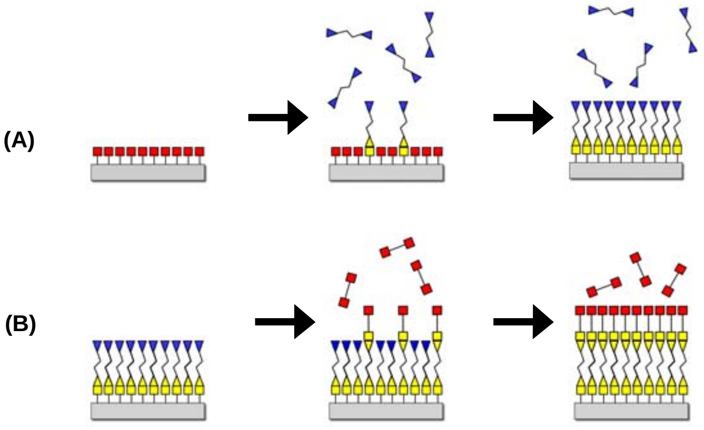
A) $AlOH^{*} + Al(CH_3)_3 \rightarrow AlOAl(CH_3)_2^{*} + CH_4$

B) $AlCH_3^{*} + H_2O \rightarrow AlOH^{*} + CH_4$

where the asterisks denote the surface species. In the (A) reaction, $Al(CH_3)_3$ reacts with the hydroxyl (OH^{*}) species and deposits aluminum and methylates the surface. The (A) reactions stops after all the hydroxyl species have reacted with $Al(CH_3)_3$. In the (B) reaction, H_2O reacts with the $AlCH_3^{*}$ species and deposits oxygen and rehydroxlates the surface. The (B) reactions stops after all the methyl species have reacted with H_2O. Because each reaction is self-limiting, the Al_2O_3 deposition occurs with atomic layer control.



By applying these surface reactions repetitively in an ABAB... sequence, Al_2O_3 ALD is achieved with a growth rate of 1.1 Å per AB cycle [3]. This approach is general and can be applied to many important binary materials such as SiO_2 [4], MgO [5] and TaN [6]. We have also extended the ALD method to deposit single-element metal films. For example, the binary reaction for tungsten deposition: $WF_6 + Si_2H_6 \rightarrow W + 2SiHF_3 + 2H_2$ can be split into separate WF_6 and Si_2H_6 half reactions to obtain W ALD [7]. Film growth during Al_2O_3 and W ALD can be recorded using a variety of techniques including the quartz crystal microbalance (QCM) [8]. QCM results for Al_2O_3 and W ALD are shown in the accompanying figure.



Similar self-limiting surface reactions can be employed for the growth of organic polymer films. This film growth is described as molecular layer deposition (MLD) because a molecular fragment is deposited during each reaction cycle [9]. The precursors for MLD have typically been homobifunctional reactants. A cartoon illustrating the MLD process is shown in the nearby figure. MLD methods have been developed for the growth of organic polymers such as polyamides [10,11]. The polyamides have been deposited using dicarboxylic acid and diamines as the reactants. New approaches to MLD involve heterobifunctional and ring-opening precursors.

In addition to organic polymers, the precursors for ALD and MLD can be combined to grow hybrid organic-inorganic polymers [9]. For example, $Al(CH_3)_3$ (trimethylaluminum (TMA)) and $HO(CH_2)_2OH$ (ethylene glycol (EG)) can be reacted to obtain an aluminum alkoxide polymer known as "alucone" [12]. Many other hybrid organic-inorganic polymers are possible by mixing various ALD and MLD reactants. The hybrid organic-inorganic MLD films are very interesting because their chemical and mechanical properties can be tuned by varying the nature of the organic group.

1. S.M. George, A.W. Ott and J.W. Klaus, "Surface Chemistry for Atomic Layer Growth", *J. Phys. Chem.* **100**, 13121 (1996).

2. A.C. Dillon, A.W. Ott, S.M. George, and J.D. Way, "Surface Chemistry of Al_2O_3 Deposition Using $Al(CH_3)_3$ and H_2O in a Binary Reaction Sequence", *Surf. Sci.* **322**, 230 (1995).

3. A.W. Ott, J.W. Klaus, J.M. Johnson and S.M. George, "Al_2O_3 Thin Film Growth on Si(100) Using Binary Reaction Sequence Chemistry", *Thin Solid Films* **292**, 135 (1997).

4. B. B. Burton, S. W. Kang, S.W. Rhee and S.M. George, "SiO_2 Atomic Layer Deposition Using Tris(dimethylamino)silane and Hydrogen Peroxide Studied by in situ Transmission FTIR Spectroscopy", *J. Phys. Chem. C* **113**, 8249 (2009).

5. B.B. Burton, D.N. Goldstein and S.M. George, "Atomic Layer Deposition of MgO Using Bis(ethylcyclopentadienyl)magnesium and H_2O", *J. Phys. Chem. C* **113**, 1939 (2009).

6. B.B. Burton, A.R. Lavoie and S.M. George, "Tantalum Nitride Atomic Layer Deposition Using Tris(diethylamido)(*tert*-butylimido)tantalum and Hydrazine", *J. Electrochem. Soc.* **155**, D508 (2008).

7. J.W. Klaus, S.J. Ferro and S.M. George, "Atomic Layer Deposition of Tungsten Using Sequential Surface Chemistry with a Sacrificial Stripping Reaction", *Thin Solid Films* **360**, 145 (2000).

8. R.K. Wind, F.H. Fabreguette, Z.A. Sechrist and S.M. George, "Nucleation Period, Surface Roughness and Oscillations in Mass Gain per Cycle during W Atomic Layer Deposition on Al_2O_3", *J. Appl. Phys.* **105**, 074309 (2009).

9. S.M. George, B. Yoon and A.A. Dameron, "Surface Chemistry for Molecular Layer Deposition of Polymers", *Acc. Chem. Res.* **42**, 498 (2009).

10. Y. Du and S.M. George, "Molecular Layer Deposition of Nylon 66 Films Examined Using In Situ FTIR Spectroscopy" *J. Phys. Chem. C* **111**, 8509 (2007).

11. N.M. Adamczyk, A.A. Dameron and S.M. George, "Molecular Layer Deposition of Poly(p-phenylene terephthalamide) Films Using Terephthaloyl Chloride and p-Phenylenediamine", *Langmuir* **24**, 2081 (2008).

12. A.A. Dameron, D. Seghete, B.B. Burton, S.D. Davidson, A.S. Cavanagh, J.A. Bertrand and S.M. George, "Molecular Layer Deposition of Alucone Polymer Films Using Trimethylaluminum and Ethylene Glycol", *Chem. Mater.* **20**, 3315 (2008).