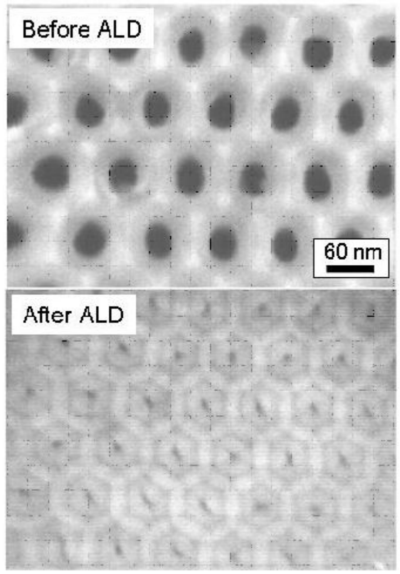
Energy Systems

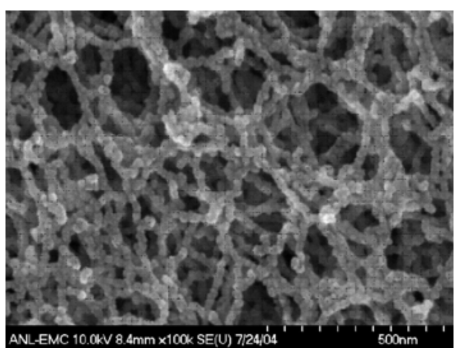
Atomic Layer Deposition

The program is a joint initiative of the Materials Science and Energy Systems Divisions that combines basic and applied sciences. We are expanding ALD into new fields and deposition platforms, and developing ALD thin film technologies that address a wide variety of our nation's energy challenges. In particular, we are focusing our attention on solar cells, catalysis, separation membranes, and superconductivity.

Bench-scale ALD thin film deposition systems designed and constructed at Argonne National Laboratory are used to deposit materials with atomic-level precision onto nearly any substrate .



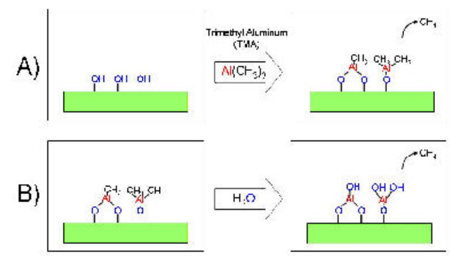
AAO membrane before and after 15 nm ALD Al_2O3 coating



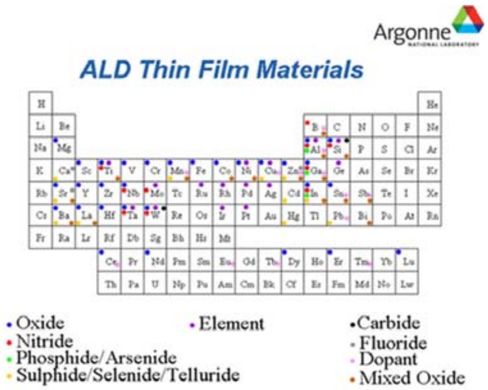
Low-density silica aerogel conformally coated by ALD ZnO layer

ALD uses alternating, saturating reactions between gaseous precursor molecules and a substrate to deposit films in a layer-by-layer fashion. By repeating this reaction sequence in an ABAB… fashion, films of virtually any thickness, from atomic monolayers to micrometer dimensions, can be deposited with atomic layer precision. This alternating reaction strategy eliminates the *line-of-sight* or *constant-exposure* requirements that limit conventional methods such as physical- or chemical-vapor deposition.

As an example, consider the following binary reaction sequence for the ALD of Al_2O:



In reaction A, the substrate surface is initially covered with hydroxyl (OH) groups. The hydroxyl groups react with trimethyl aluminum (TMA) to deposit a monolayer of aluminum-methyl groups and give off methane (CH4) as a byproduct. Because TMA is inert to the methyl-terminated surface, further exposure to TMA yields no additional growth beyond one monolayer. In reaction B, this new surface is exposed to water regenerating the initial hydroxyl-terminated surface and again releasing methane. The net effect of one AB cycle is to deposit one monolayer of Al_2O_3 on the surface. The layer-by-layer ALD growth process allows digital film thickness control at the monolayer level.
ALD can deposit a wide variety of materials including oxides, nitrides, sulfides and metals. An integral component of the Argonne ALD research program is to invent new binary reaction sequence chemistries that extend the range of useful thin film materials.



We currently have three bench-scale ALD thin film deposition reactor systems that were designed and constructed at Argonne. These unique reactor systems are very flexible and allow us to deposit a wide range of materials with atomic level precision onto nearly any substrate. We deposit ALD materials onto nano-porous templates such as anodic aluminum oxide (AAO) membranes and low-density aerogels, catalytic supports, and tubes, (up to one meter in length, 10 cm in diameter). We are also designing larger, application specific reactors. To enable detailed studies of new ALD chemistries, our bench-scale reactor systems are equipped with in-situ measurement capabilities including quartz crystal microbalance (QCM) and quadrupole mass spectrometry (QMS). We also developed GaPO4 sensors for improved diagnostics. In addition, we have a full range of thin-film measurement tools (AFM, XPS, SIMS, WVASE, XRF, etc.) Our ALD research benefits enormously from ready access to Argonne's remarkable suite of measurement facilities such the Advanced Photon Source and the Electron Microscopy Center.

Primary Focus Projects

- Solar Cells (**In_2O_3, SnO_2, TiO_2**) – Transparent conducting oxide layers as well as semiconducting oxide films are deposited using ALD to form novel light-harvesting devices.
- Novel Selective Oxidation Catalysts: We are developing new techniques for the manufacture of catalysts by ALD for the selective oxidative dehydrogenation of alkanes, for example, ethane to ethylene, or propane to propylene. As one template for these catalysts, we are coating commercial silica gel powders comprised of ~100 micron diameter silica beads that are agglomerates of ~10 nm particles. These silica gel beads possess a very high surface area and pose unique challenges for coating.
- Nanostructured Catalytic Membranes: We are synthesizing, characterizing and testing nanostructured catalytic membranes fabricated using ALD. As a starting template, we use anodic aluminum oxide (AAO) membranes comprised of hexagonal arrays of uniform pores. We coat the inner surfaces of the pores with ALD Al_2O_3 to reduce the pore diameter. Next, we deposit a catalytic support layer. Finally, we deposit the active catalyst.
- Nanoporous Separations Membranes: We coat the interior of AAO pores with atomic level precision using atomic layer deposition (ALD) techniques. Next, using ALD of selected materials, the chemical nature of the pore wall coating is tuned to allow further specificity during separations. The result is a nanoporous separation membrane (NSM) with excellent molecular size and chemistry selectivity.
- High Temperature Superconductors – (**$YBa_2Cu_3O_7$**) HTS Ceramic materials are deposited conformally on conducting substrates to enable the efficient fabrication of second generation coated conductors.

Additional Projects:

- Aerogels – Aerogels due to their extremely low density, low thermal conductivity, and high specific surface area have found diverse applications in sensing, catalysis, aerospace and high-energy physics. By conformally coating aerogels using atomic layer deposition (ALD), we can both precisely define the surface chemical properties and dramatically enhance the physical properties of the aerogels to greatly extend their utility. Carbon aerogels coated by ALD tungsten have applications as spallation targets for the production of radioactive ion beams.
- Hydrogen Economy – (**Pd**) Nanoporous scaffolds are coated with ultra-thin metal layer for efficient hydrogen production, storage and sensing.
- Hermetic Coatings – (**Y_2O_3, ZrO_2, Al_2O_3**) Conformal amorphous layers are deposited on all surfaces fully encapsulate a device for medical implantation, or to be used in corrosive environments.
- Chemical Sensors – (**ZnO, SnO_2**) Nanoporous anodic alumina and aerogel templates are coated with ultra-thin conducting oxide layers to form chemical sensors.
- Optical Nanosensors – Noble metal nanoparticles coated with dielectric films act as optical biosensors and chemosensors based on the localized surface plasmon resonance (LSPR) effect. Consequently, the optical properties of LSPR sensors can be tailored using ALD coatings. (Collaboration with Northwestern University).

Publications

G. Xiong, J. W. Elam, H. Feng, C. Y. Han, H.–H. Wang, L. E. Iton, L. A. Curtiss, M. J. Pellin, M. Kung, H. Kung, and P. C. Stair, "Effect of Atomic Layer Deposition Coatings on the Surface Structure of Anodic

Aluminum Oxide Membranes", J. Phys. Chem. B., 109 (29), 14059-14063 (2005).

J. W. Elam and M. J. Pellin, "$GaPO_4$ Sensors for Gravimetric Monitoring during Atomic Layer Deposition at High Temperatures", Anal. Chem., 77, 3531 (2005).

M. J. Pellin, P. C. Stair, G. Xiong, J. W. Elam, J. Birrell, L. Curtiss, S. M. George, C. Y. Han, L. Iton, H. Kung, M. Kung, H.–H. Wang, "Mesoporous Catalytic Membranes: Synthetic Control of Pore Size and Wall Composition", Catalysis Letters, 102 (3-4), 127-130 (2005).

V. Whitney, J. W. Elam, S. Zou, A. V. Zinovev, P. C. Stair, G. C. Schatz and R. P. Van Duyne, "Localized Surface Plasmon Resonance Nanosensor: A High-Resolution Distance Dependence Study using Atomic Layer Deposition", J. Phys. Chem. B, 109 (43), 20522-20528, (2005).

S. O. Kucheyeva, J. Biener, Y. M. Wang, T. F. Baumann, K. J. Wu, T. van Buuren, A. V. Hamza, and J. H. Satcher, Jr., J. W. Elam and M. J. Pellin, "Atomic Layer Deposition of ZnO on Ultralow-Density Nanoporous Silica Aerogel Monoliths", Appl. Phys. Lett., 86, 083108 (2005).

Posters from the ALD 2005 Conference

J. W. Elam, P. W. Klamut, J. E. Gerbi, G. Xiong, C. Y. Han, H. H. Wang, J. N. Hryn, M. J. Pellin, "Nucleation, Growth and Crystallization of ALD Catalytic Oxide Layers."
Jeffrey W. Elam, Alex Zinovev, Catherine Y. Han, Hau H. Wang, Ulrich Welp,

John N. Hryn and Michael J. Pellin, "Atomic Layer Deposition of Palladium Films on Al_2O_3 Surfaces."

Jeffrey W. Elam and Michael J. Pellin, "$GaPO_4$Sensors for Gravimetric Monitoring During Atomic Layer Deposition at High Temperatures."

For more information, please contact:
Catherine Foster
630-252-5580
cfoster@anl.gov

Collaborators

- Argonne Chemistry Division
- Argonne Chemical Engineering Division
- Argonne Physics Division
- Northwestern University Department of Chemistry
- Lawrence Livermore National Laboratory
- University of Nevada, Las Vegas Department of Chemistry
- University of Notre Dame, Department of Electrical Engineering