Process Models and Metrologies for Atomic Layer Deposition

NIST is providing validated, predictive process models and associated in situ metrologies for atomic layer deposition (ALD) process diagnostics and control in microelectronic manufacturing. ALD process models are being created by incorporating chemical reaction mechanisms developed at NIST into commercially available computational fluid dynamics (CFD) code that simulates the gas flow and temperature fields in an ALD reactor.

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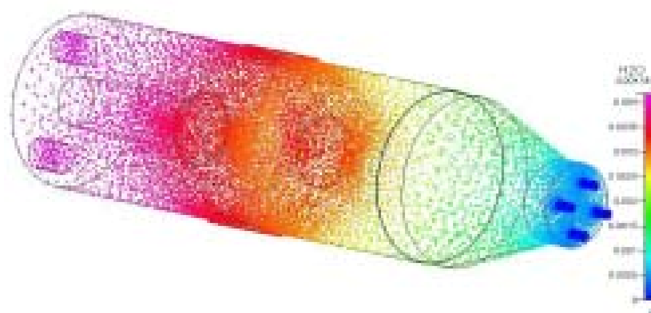
Atomic layer deposition is increasingly being utilized to deposit the thin (nanometer-scale), conformal layers that are required for many microelectronics applications, including high κ gate dielectric layers, diffusion barrier layers, and DRAM dielectric layers. However, significant developmental issues remain for many of these applications. The goal of this work is to provide validated, predictive atomic layer deposition (ALD) models and in situ diagnostics for ALD processes.

Technology computer-aided design (TCAD) has become a vital design tool for the semiconductor industry. ALD is a relatively new fabrication critical to the complex manufacture of today's and next generation semiconductor devices. Validated, predictive ALD process models are critical to successful prediction of equipment influences on film properties, thereby providing potential solution to many atomic layer deposition (ALD) process development issues. TCAD has been identified in the 2005 International Technology Roadmap for Semiconductors (ITRS) as "one of the few enabling methodologies that can reduce development cycle times and costs." [2005 ITRS, Modeling and Simulation, page 1] However, many difficult challenges to the development of validated, predictive ALD process models have also been identified, including chemical data (e.g., rate constants, cross sections, surface chemistry); reaction mechanisms, and reduced models for complex chemistry. In addition to a lack of reliable fundamental physical and chemical data, experimental validation has been identified as a "key difficult challenge across all modeling areas." [2005 ITRS, Modeling and Simulation, page 1] Further, with respect to experimental validation, "One of the major efforts required for better model validation is sensor development and metrology, especially for models predicting the fabrication and behavior of ultra-thin films". [2005 ITRS, Modeling and Simulation, page 17]

This project involves two primary research directions: development of *in situ* metrologies sensitive to ALD chemistry and development of ALD chemical reaction mechanisms. ALD process models are being created by incorporating chemical reaction mechanisms developed at NIST into commercially available computational fluid dynamics (CFD) code that simulates the gas flow and temperature fields in an ALD reactor. Unlike chemical vapor deposition processes which is dominated by gas phase processes and are still widely used for relatively thick film deposition, atomic layer deposition is a surface chemical process that deposits films at or near single molecular thickness. This is accomplished by dosing the deposition surface initially with a monolayer of water molecules followed by the admission of the second reactant to the process chamber and reaction with the water layer to form the desired film.



A three dimensional mass fraction profile in an optically-accessible reactor showing the water mass fraction distribution after 3 s helium purge following a 0.1 s water injection.

Experimental validation of overall process models are accomplished by modeling the performance of custom-built, research-grade ALD reactors with optimized optical accessibility and benchmarking the numerical results with experimental data. These data are obtained using various measurement techniques, including vibrational spectroscopies and mass spectrometry. Hafnium oxide (HfO_2) ALD, using tetrakis(ethyl-methylamino) hafnium (TEMAH) and water or tetrakis(dimethylamino) hafnium (TDMAH) and water, has been selected as the chemical system for primary investigation.

NIST validated, predictive atomic layer deposition (ALD) models and *in situ* diagnostics for ALD processes are expected to improve the microchip manufacturing process.

Research-grade, optically-accessible ALD reactors have been designed and constructed with full optical access for surface and gas-phase Raman and FTIR spectroscopic measurements. An associated pulsed gas delivery system has been designed and constructed. HfO_2 films have been deposited with ALD under a variety of process parameters using TEMAH or TDMAH and water. Films have been characterized with a number of techniques, including vacuum ultraviolet spectroscopic ellipsometry (VUV-SE), X-ray photoelectron spectroscopy, atomic force microscopy, X-ray diffraction, Fourier-Transform infrared (FTIR) spectroscopy, and deep UV Raman spectroscopy.

In situ gas phase FTIR spectroscopic measurements have been performed during HfO_2 film deposition and have been shown to be sensitive to deposition reactants, TEMAH, and products, N-methyl-ethanamine. In addition, *in situ* FTIR measurements during TEMAH injection pulses were shown to be sensitive to TEMAH decomposition in the delivery system. Adequate reference spectra could not be located for TEMAH or N-methyl-ethanamine (MEA), a gas phase product of the TEMAH and water ALD reaction. Hence, infrared and Raman vibrational frequencies were calculated with Density Functional Theory using the B3LYP/LANL2DZ method. The calculated frequencies were compared to measured infrared spectra obtained in the ALD reactor and tentatively identified as TEMAH and MEA.

Process Models: Three dimensional CFD models for gas flow and temperature fields have been developed for various reactor geometries, including optically-accessible reactor designs, and used to model flow and temperature under various process conditions. In addition, time-resolved precursor distributions have been modeled. The results from these models have been used to help optimize reactor designs, especially optical window design, and deposition conditions. Chemical reaction mechanism models for HfO_2 ALD are being developed for use with these three dimensional flow and temperature models to simulate the entire ALD process.

Chemical Kinetics Mechanisms: Molecular structures and energies for precursors, adsorbates, intermediates, and transition states have been calculated using ab initio and density functional theory quantum calculations for ALD of Al_2O_3 from TMA and water and HfO_2 from TEMAH or TDMAH and water. Although the primary focus of this work is on HfO_2 ALD, Al_2O_3 ALD is also being investigated as a model system for two main reasons. First, there has been significant work on Al_2O_3 ALD, and consequently, there are adequate experimental data for use in chemical mechanism validation. Second, aluminum is more amenable to quantum calculations than hafnium, a transition metal. It is expected that lessons learned in developing an ALD model for Al_2O_3 ALD will be useful in development of an HfO_2 ALD model. For Al_2O_3 ALD, prototypical small cluster ($Al_xO_yH_z$) species have been utilized to represent the surface layer. Rate expressions based on calculated structures and energies have been derived using transition state theory. High level ab initio calculations, up to CCSD(T)/aug-cc-pVnZ (n=2-4) have been done for small species to benchmark heats of formation and bond dissociation energies for AlH_nX species (n = 0-2, X = H, F, Cl, OH, NH_2, CH_3). Additional calculations will be done to provide higher level corrections (*e.g.*, core-valence, relativistic, etc).

A Website containing Chemical Kinetics Mechanisms has been made available through the NIST Standard Reference Data website.
http://srdata.nist.gov/ckmechx/

This site currently contains bibliographic and thermochemical information of silicon hydrides, halocarbons, and organometallic compounds import to semiconductor processes, including information pertaining to ALD and chemical vapor deposition of aluminum, Al_2O_3, and other related ALD systems (*e.g.*, Zr, Hf, etc.), as well as a significant amount of information pertaining to hydrocarbon-based reactions.

Future Directions: During the upcoming year, *in situ* gas phase and surface optical measurements will continue in an effort to provide model validation data as well as develop suitable *in situ* diagnostics for ALD processes. Concurrently, we will search for correlations between specific film deposition steps uncovered by the more sophisticated optical methods with signals from conventional process monitors, such infrared absorption spectroscopy and mass spectrometers. In addition, we will attempt to correlate data measured *in situ* at or near the deposition surface with data measured in the exhaust stream in an effort to qualify the results of sensors designed for use on reactor exhaust lines.

Publications:

D.R. Burgess, Jr., J.E. Maslar, W.S. Hurst, E.F. Moore, W.A. Kimes, and N.V. Nguyen, **"Atomic Layer Deposition: Process Models and Metrologies,"** Characterization and Metrology for ULSI Technology: 2005 International Conference, edited by D. G. Seiler et al., AIP Conference Proceedings 788, Melville, NY: American Institute of Physics, 2005, pp. 141-146.

J.E. Maslar, W.S. Hurst, D.R. Burgess, Jr., W.A. Kimes, and N.V. Nguyen, **"*In Situ* Characterization Of Gas-Phase Species Present During Hafnium Oxide Atomic Layer Deposition,"** Electrochemical Society Transactions, 2006, in press.