Time-Dependent Simulations of the ALD Process

CAPP-ALD-1 (v1.0) December 15, 2007

Summary

This application note demonstrates two ways of simulating a time-dependent ALD process.

Project Description

The CHEMKIN transient Perfectly Stirred Reactor Model runs relatively quickly and is useful for developing and initial testing of the chemical reaction mechanism. The transient stagnation flow model more realistically simulates a production-scale shower-head ALD reactor by including mass-transport effects. The process operates at a pressure of 1 Torr, and a relatively low surface temperature (compared to CVD) of 450° C (723 K). This example demonstrates four cycles of the flow sequence including: metalorganic precursor in argon; argon purge; ozone in oxygen and argon; and argon purge. The four cycles are sufficient, in this case, to characterize the process.

The chemistry set describes the atomic layer deposition (ALD) of alumina from trimethylaluminum (TMA) and ozone. This mechanism is deliberately simplistic, for illustration purposes only. It demonstrates one way of describing the ALD of alumina, but it should generally be considered as illustrative only and not used as a source of kinetic data for this process. This mechanism is designed to deposit stoichiometric alumina, with three oxygen atoms being deposited for each two aluminum atoms. If the goal of a simulation were to track the elemental make-up of a material with a wide range of possible compositions, the choice of surface species and reactions would have to be quite different.

The fact that the different chemicals are separately pulsed into the system, rather than being mixed in the gas, prevents many possible gas-phase reactions from occurring in this process. The gas-phase chemistry described in the chemistry input file, *chem.inp,* has five elements: Al, C, H, O, and Ar; and six gas-phase species: $AlMe_3$, O, O_2, O_3, C_2H_6 and Ar. There are only two gas-phase reactions; the collisionally-induced decomposition of ozone and the reaction of O atoms with ozone to form molecular oxygen. The rate parameters are from Benson and Axworthy.[1] This mechanism does not include reactions for TMA decomposition because it was determined to be too slow at the temperatures of interest. If such reactions were included, they would be listed in the same chemistry input file. The temporal separation of the gas mixtures is accounted for by omitting reactions between gas-phase species that would not be present in the reactor at the same time, such as reactions between TMA and O atoms. A reaction mechanism for alumina CVD, in contrast, would need to include all such reactions.

[1] S. W. Benson and A. E. Axworthy, *Jr., J. Chem. Phys.*, **26**:1718 (1957).

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The surface chemistry described in the *surf.inp* file defines three surface species: O(S), ALME2(S) and ALMEOALME(S), with the last species occupying two surface sites, plus the bulk alumina AL2O3(B). There are only three surface reactions, each of which represents several elementary surface processes.

- The first surface reaction represents the dissociative adsorption of TMA on the oxygenated surface species O(S) to form the ALME2(S), combined with the recombination of two methyl groups and desorption of an ethane molecule. This reaction has been given a moderately high sticking coefficient of 0.1, and is written in terms of a half ethane molecule in order to have a balanced reaction that is first order in TMA. This reaction only occurs in the presence of TMA, and will terminate when all of the O(S) surface species have reacted.
- The second surface reaction describes gas-phase oxygen atoms reacting with the two ALME2(S) to form the ALMEOALME(S) species and a gas-phase ethane molecule.
- The third surface reaction describes an O atom reacting with the ALMEOALME(S) species to deposit AL2O3(B), regenerate O(S), and form gas-phase ethane, where fractional molecules are used to write balanced reactions. Oxygen atoms are expected to be very reactive, so these reactions have been given high sticking coefficients of 1.0. These reactions only occur in the presence of O atoms, which are generated from ozone decomposition, and will terminate when all the methylated surface species have reacted.

All the surface reactions are irreversible. As a result, the thermodynamic properties for surface species provide the elemental composition of the surface species, but the polynomial fitting parameters are merely placeholder values.

Project Setup

The two reactor diagrams in this application each contain three gas inlets and either a Perfectly Stirred Reactor or a Stagnation-flow CVD Reactor Model. In this application, the names of the gas inlets, and their corresponding input panels, have been modified from the default names of R1_IN1, etc, to **METORG**, **OXIDIZER** and **PURGE**, which reflect the function of the gas flowing through the inlets. The listings of flow rate as a function of time for each gas-flow inlet are saved as time-dependent profile files.

In this case, the profiles of total flow rates for each gas inlet are in volumetric flow units of sccm, but flow profiles can also be specified in mass flow units. The PSR and stagnation-flow models use the same flow-profile files.

Transient PSR

The names of the flow-profile files are designated on the Stream Property Data tab of each Gas Inlet panel. In this case, inlet temperatures are not specified on the Gas Inlet panel, as this is a fixed-gas temperature simulation. You will specify the composition of each reactant gas inlet on the Species-specific Property panel of the corresponding Gas Inlet panel.

Use the Problem-type dropdown list on the Reactor Physical Property tab of the C1_ PSR panel to choose the fixed gas temperature for this simulation.. The gas temperature, pressure, volume and surface area (which are generally representative of ALD reactors) are also input here. In this case, the gas temperature for the PSR simulation was chosen to reproduce the degree of ozone decomposition to O atoms and match the deposition rate observed in the higher dimensional simulation. The surface temperature is different from the gas temperature, and it is also specified on the Reactor Physical Properties tab. On the Species-specific Data tab, specify the starting gas composition of pure argon on the Initial Gas Fraction sub-tab, the starting surface composition of complete O(S) coverage on the Surface Fraction sub-tab, and an activity of 1.0 for AL2O3(B) on the Bulk Activity sub-tab. These correspond to a reasonable starting condition where the substrate might have an initial oxide coating, and the system was purged with argon after loading.

You can specify an end time of the transient simulation on the Basic tab of the Solver panel, along with the solver step time, interval for saving the solution, and the interval for printing data to the diagnostic output file.

Transient Stagnation Flow Reactor

The names of the flow-profile files are designated on the Stream-property panel of each Gas Inlet panel. In this case, the gas energy equation is being solved, so set the inlet temperatures to 150° C (423 K) for each gas inlet. The composition of each reactant gas inlet is specified on the Species-specific Property tab of the corresponding Gas Inlet panel.

On the Reactor Physical Property tab's Basic sub-tab of the C1_Stagnation Flow panel, you can control options such as Solve a Transient problem; Include the Gas Energy Equation; Use Multicomponent Diffusion but Not the Soret Effect; etc. Use this sub-tab to input the process pressure and surface temperature, along with the name of file containing the initial guess for the gas temperatures as a function of height above the disk, and a cross sectional flow area used for translating volumetric flow rates to linear flow velocities. There are no entries on the other sub-tabs of the Reactor Physical Property tab.

The Initial Grid Property tab of the C1_ Stagnation Flow panel allows the input of the number of points in the grid of distance above the substrate, along with the ending axial distance. In transient simulations, the grid currently does not adapt as it does in steady-state stagnation flow simulations. Thus, you should specify a reasonably dense initial grid, and the adaptive gridding parameters are ignored. Note that the surface is defined as being at a coordinate value of $x = 0$, and the maximum

distance of 1.2 cm is the location of the gas inlets (showerhead). In other words, the solution is given as a function of distance from the surface.

On the Species-specific Data tab of the C1_ Stagnation Flow panel, the starting gas composition of pure argon is specified on the Initial Gas Fraction sub-tab, and you should specify the starting surface composition of complete O(S) coverage on the Surface Fraction sub-tab and an activity of 1.0 for AL2O3(B) on the Bulk Activity sub-tab. These are the same as were used in the PSR simulation, and correspond to a reasonable starting condition, where the substrate might have an initial oxide coating, and the system was purged with argon after loading.

The end time of the transient simulation is specified on the Basic tab of the Solver panel, along with the interval for printing data to the output file and some tolerance parameters that have been relaxed from the default values. The Advanced tab of the Solver panel contains a time-step specification and a solver parameter that have been altered from the default values.

Project Results

Figure 1 shows the gas pulses used in this example for the metal-organic and oxidizer gas inlets. The pure-argon purge gas pulses are not shown. The metal-organic gas pulses are considerably shorter than the oxidizer gas pulses, but appear to be sufficient. The contour plot of one TMA pulse from the stagnation-flow simulation in *Figure 2* clearly shows that the TMA is consumed at the surface only at the beginning of the pulse. By the end of the pulse, all the TMA flowing into the reactor is also flowing out again.

Figure 1 Time-dependent ALD Simulations—PSR, Total Flow Rates vs. Timec

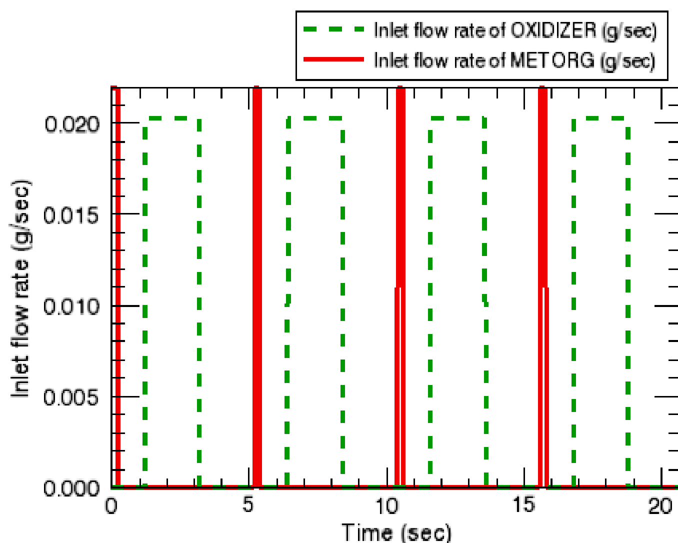
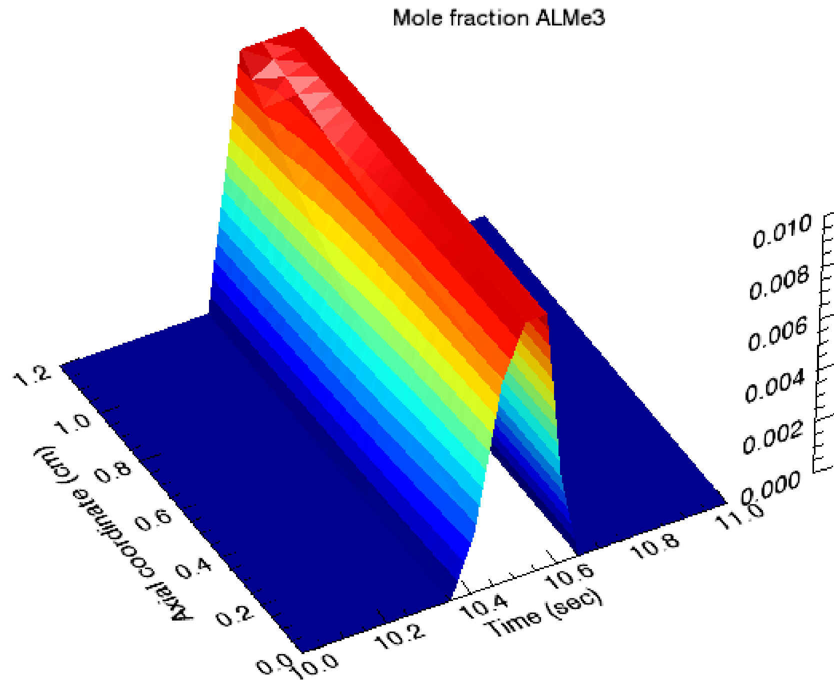


Figure 2 Time-dependent ALD Simulations—TMA Contour Plot



The chemistry that occurs during the oxidizer pulses is more complex. The contour plot of O atom mole fractions in *Figure 3* show how the O atoms are formed by gas-phase decomposition of ozone in the hotter regions of the gas, and then react away at the surface. The site fractions in *Figure 4* show that the methylated surface species, ALME2(S) and ALMEOALME(S), are not completely converted to O(S) during the oxidizer pulse. This probably results from the fact that the oxidation occurs as two sequential steps and the kinetics are limiting the process. The O atom mole fractions in *Figure 5* shows that the O atoms are not being depleted at the surface in the stagnation flow simulations, which suggests a kinetic limitation, possibly resulting from the default reaction orders in this simple mechanism. The incomplete oxidation of the methylated surface species in turn leads to less than unity O(S) coverage at the beginning of the TMA pulse, which in turn leads to less efficient use of TMA and some notable differences between the first and subsequent pulses.

Figure 3

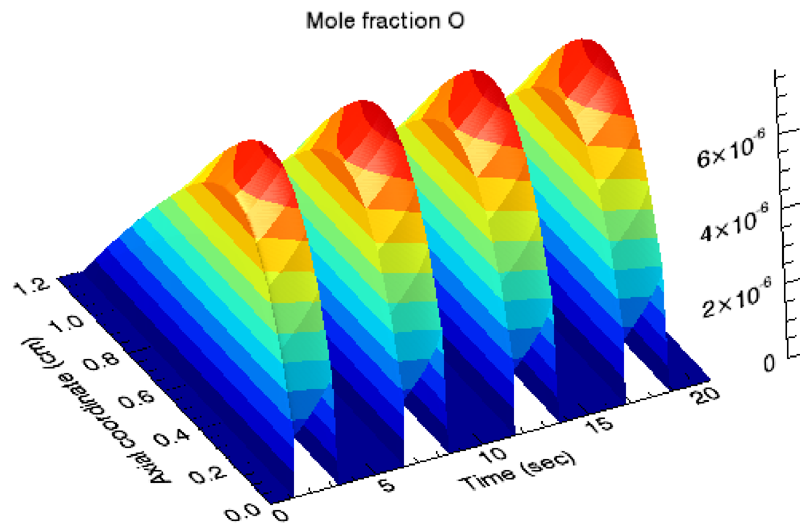


Figure 4 Ti

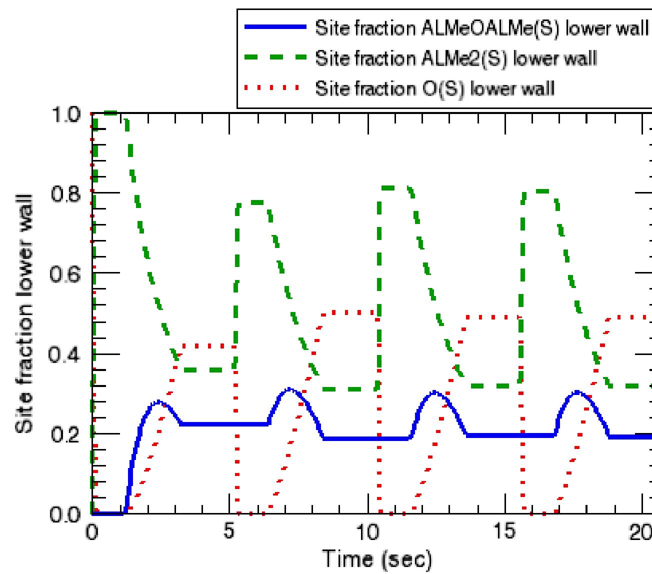
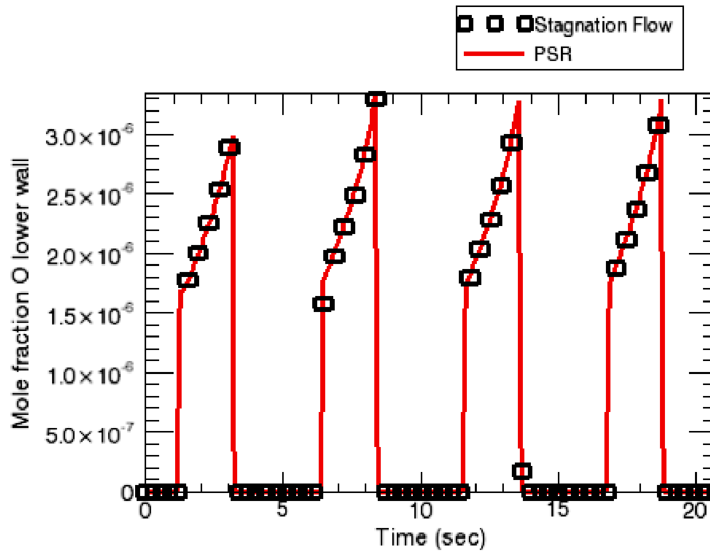
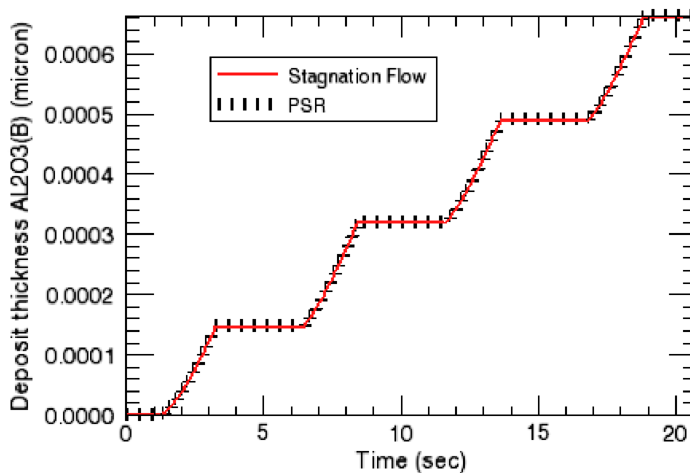


Figure 5 Time-dependent ALD Simulations—O Mole Fractions Comparison



The O atom mole fractions in *Figure 5* from the stagnation flow simulations agree well with those from the PSR simulations. Within the limits of this simple deposition chemistry, this directly leads to the good agreement for deposition thickness shown in *Figure 6.* The agreement between the two models, in this case, results from the fitting of the gas-phase temperature in the PSR simulation to reproduce the O atom mole fractions in the higher-dimensional simulation. This kind of a calibration allows the faster-running PSR simulation to be used to quickly explore a wide range of pulse sequences and other experimental conditions of interest, before returning to higher-dimensional simulations for more careful study.

Figure 6 Time-dependent ALD Simulations—Deposition Thickness Comparison



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