PSR Analysis of Steady-State Thermal CVD

APP-CVD-2 (v2.0) August 30, 2010

Summary

This application note presents a model for the CVD of silicon nitride in a steady-state PSR.

Project Description

The process operates at a low pressure of 1.8 Torr, and a high temperature of 1440 C, which makes it reasonable to approximate this system as a PSR. In the PSR model, the CVD reactor is described using a volume, surface area, and gas flow rate. This is a fixed-temperature simulation that uses continuations to see the effects of changing the SiF_4/NH_3 ratio in the input gas. It also uses sensitivity and rate-of-production (ROP) options to analyze the chemistry occurring in the system.

The chemistry set used for this application describes the deposition of silicon nitride (Si_3N_4) from a mixture of SiF_4 and NH_3.[1] This mechanism demonstrates one way of describing the deposition of a compound solid, but it should generally be considered as illustrative only and not as a source of kinetic data for Si_3N_4 deposition.

The chemistry input file, *chem.inp*, includes 4 elements, 17 gas-phase species and 33 reactions. The first 27 of these reactions describe the pyrolysis of ammonia, and are taken from published models for ammonia oxidation and De-NOx.[2] The other six reactions describe SiF_4 decomposition and likely cross reactions between Si and N-containing species. Rate parameters were not available in the literature for these reactions, so the mechanism uses estimates based on bond strengths and analogies with related gas-phase reactions.

Thesurface chemistry input file, *surf.inp*, defines six surface species in the Si_3N_4 surface phase and the Si_3N_4 solid, which is defined in terms of two bulk phases, SI(D) and N(D). The surface species all occupy more than one site, and have placeholder thermodynamic data. Six irreversible surface reactions are also defined in this file. The surface reactions are “lumped” reactions, meaning that they each represent several elementary steps that have been combined into one reaction. Rate parameters for these surface reactions were determined by fitting the model results to experimental deposition-rate data. The activation energies for the surface reactions are all zero, which reflects the limitations of the experimental data set used to derive the rate parameters. Although it is not immediately obvious, the surface species and reactions were designed to produce a bulk-phase stoichiometry of 3 Si to 4 N. The

[1]M. E. Coltrin, P. Ho, Sandia National Laboratories, private communication.
[2]J. A. Miller, M. D. Smooke, R. M. Green, and R. J. Kee, *Comb. Sci. Technol.* **34**:149 (1983).

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densities of bulk species has been defined to force the linear deposition rates of either Si(D) or N(D) match the experimentally observed deposition rate for Si_3N_4. These reactions have zero for activation energies because they were fit to an experimental data set taken at one temperature. These rates would therefore not be likely to be valid at other temperatures.

Project Setup

This reactor diagram contains only one inlet, one Perfectly Stirred Reactor, and an output Product icon. You specify the inlet flow rate (11300 sccm, standard cubic centimeters per minute) on the Stream Property Data tab of the Inlet Stream panel. The inlet gas composition is input on the Species-specific Property tab of the Inlet Stream panel.

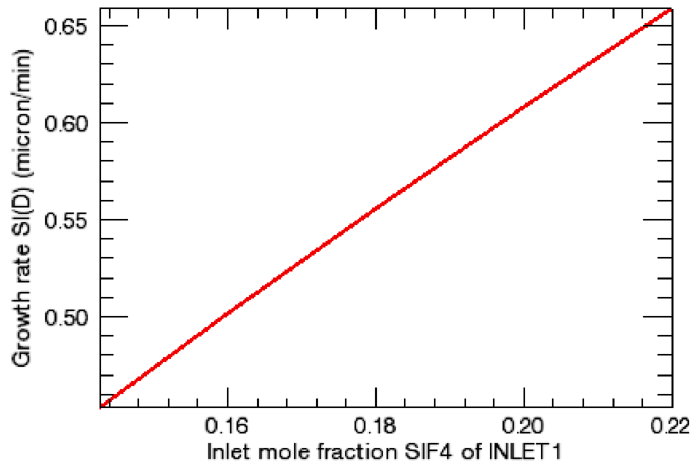
The Reactor Physical Property tab of the (C1_) PSR panel provides options so you can specify the constant reactor temperature (1440 C), pressure (2.368E-3 atm), volume, and internal surface area. In this sample problem, no estimated gas mole fractions are input on the Initial Gas Fraction sub-tab of the Species-specific tab of the (C1_) PSR panel. Solution estimates for the surface site concentrations and bulk phase activities are input on the corresponding sub-tabs of the Species-specific tab of the (C1_) PSR panel. You do not need to input values on the Bulk-phase-specific Data tab of the (C1_) PSR panel because this is a deposition rather than an etching system.

Use an Output Control threshold of 0.001 for filtering A-factor sensitivities, and use a threshold of 0.01 for ROP. The Species Sensitivity and ROP tab allows you to specify that sensitivities should be calculated and saved for only particular species, in this case HF, SiF_4 and NH_3. Also, there are choices for printing ROP information for particular species in the output file. The Continuations panel has options for specifying four more simulations to be done with increasing SiF_4/NH_3 ratios.

Project Results

Figure 1 shows that the predicted deposition rate increases with increasing SiF_4/NH_3 ratio, as expected under these conditions of excess ammonia. Although this particular plot shows the growth rate of Si(D), choosing to plot the growth rate of N(D), BULK1 or BULK2 would give essentially the same result.

Figure 1 Steady-state Thermal CVD—Deposition Rate vs. SiF_4 Mole Fraction



In studying a CVD system, it is often useful to know the relative importance of gas-phase and surface reactions. For this system, the model shows that very little gas-phase decomposition occurs under these conditions. Figure 2 shows the total rates of production (ROPs) for SiF_4 and NH_3 due to gas-phase and surface reactions. In these cases, the negative numbers indicate that these are really loss rates rather than production rates. However, these results clearly show that surface reactions (rather than gas reactions) dominate the decomposition of these starting materials. Sensitivity analysis gives complementary information to the ROP analysis. Figure 3 shows the silicon nitride growth rate is most sensitive to surface reaction #2, which is the reaction of SiF_4 at the surface. Figure 4 shows that the NH_NH2(S) site fraction is much larger than the site fractions of the other surface species.

Figure 2 Steady-state Thermal CVD—ROP Comparison

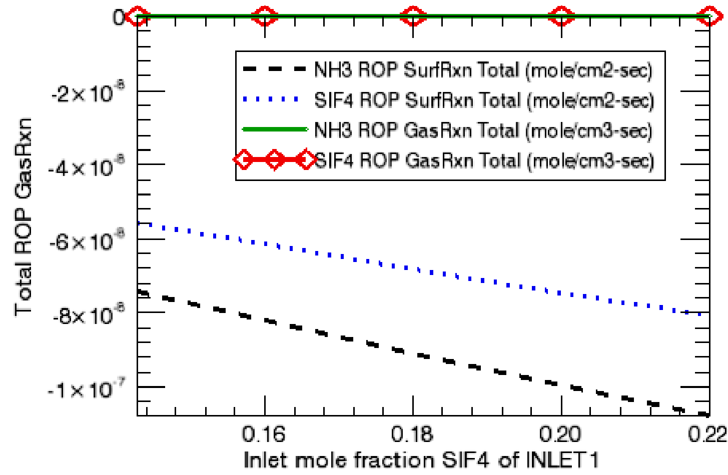


Figure 3 Steady-state Thermal CVD—Growth Rates

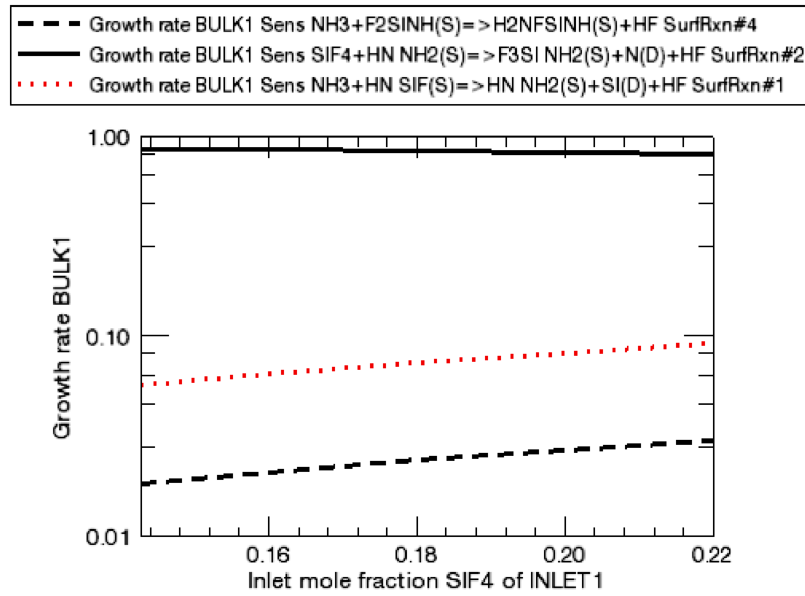
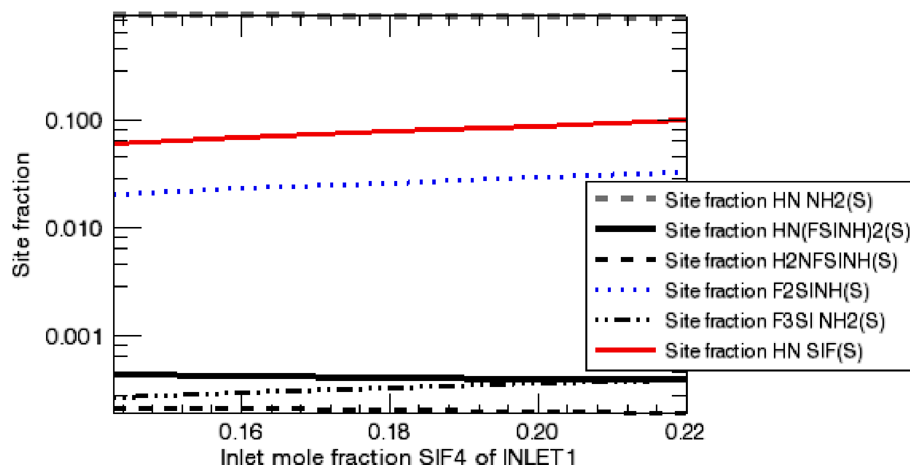


Figure 4 Steady-state Thermal CVD—Site Fractions



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