Chemical vapor deposition (CVD) of silicon nitride (Si_3N_4) film from a mixture of SiF_4 and NH_3

Background

Accurate modeling of chemical processes on the surface is of fundamental importance for heterogeneous catalysis, semiconductor device fabrication, fuel cells, self-assembled monolayers etc. CWB incorporates several reactor models that can be used for the modeling of such processes. These models assume that chemical reactions can occur in the gas phase, at the surface, and in the bulk of the condensed phase. A surface sites formalism was used to describe heterogeneous reactions that occur at the surface, between the surface and the gas phase, and between the surface and the condensed phase. Within this formalism, the surface and condensed phases can possess several different types of sites at which heterogeneous reactions can occur and the rates of these reactions are calculated according to formal kinetics rules. Reactor models calculate the steady state or the time dependence of the chemical composition of the medium (gas phase, condensed phase, and surface) by solving a set of differential equations for each chemical component and a set of heat- and mass-transfer equations.

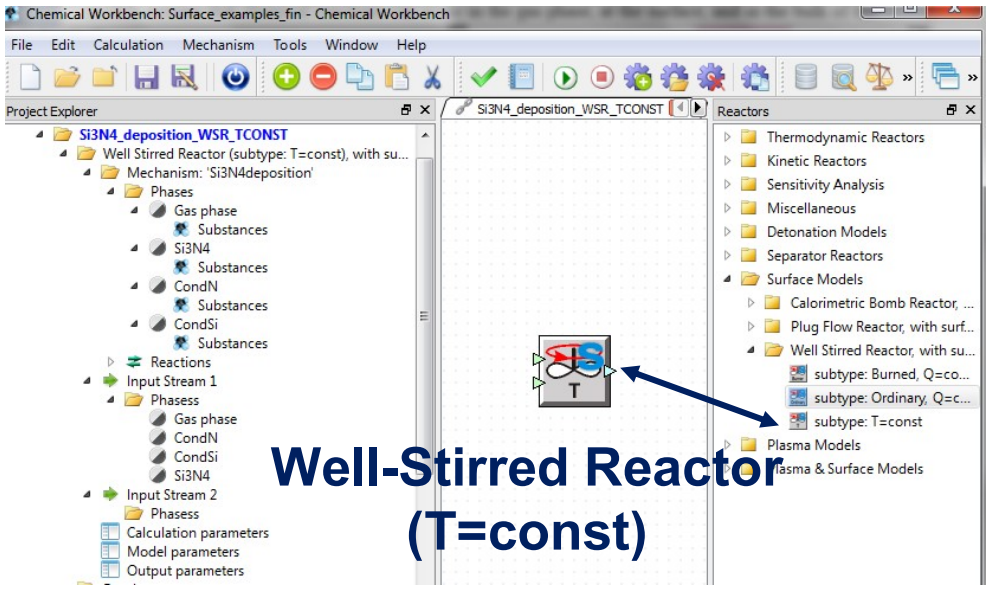
Problem statement

It is required to calculate silicon nitride film growth from SiF_4 and NH_3 mixture of various composition. Overall process can be described as $4NH_{3\ g} + SiF_{4\ g} = Si_3N_{4bulk} + 12HF_{gas}$. The pressure of gas mixture is low (about several Torrs) so gas-phase decomposition of reactants is slow, temperature is fixed to 1440 K (typical value for chemical vapor deposition CVD experiments). Mole fraction of tetrafluorosilane gas (SiF_4) is varied from 5 to 35 %.

Problem setup in Chemical Workbench

This example includes the calculation of the deposition of Si_3N_4 film as a function of gas phase compossitions. The process operates at a low pressure of ~2 Torr and a high temperature of 1440 K, so it can be assumed that heat- and mass-transfer processes inside the reactor are so fast that provide the uniform distribution of the reagents and the gas-phase reaction products which makes it reasonable to approximate this system as a **Well-Stirred Reactor Model**. This reactor model describes the process of deposition from the gas phase in a flow 0-dimensional reactor. As a result of heterogeneous chemical reactions, the steady-state chemical compositions of the gas, condensed, and surface phases and the steady-state rate of the film growth are calculated.

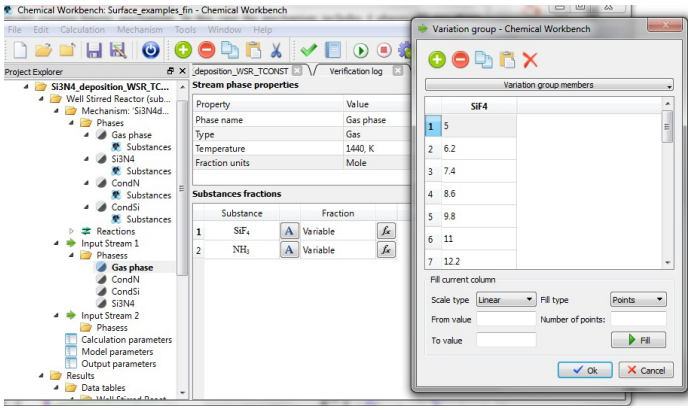
This example is a fixed temperature simulation demonstrating the effects of changing the SiF_4/NH_3 ratio in the input gas, so a **Well-Stirred Reactor with constant temperature** is used. The mixture of SiF_4 and NH_3 gases is set at the reactor inlet.



Parameters setup in Chemical Workbench

Well-Stirred Reactor requires the following parameters:

- Kinetic mechanism,
- Input streams,
- Calculation parameters,
- Model parameters.

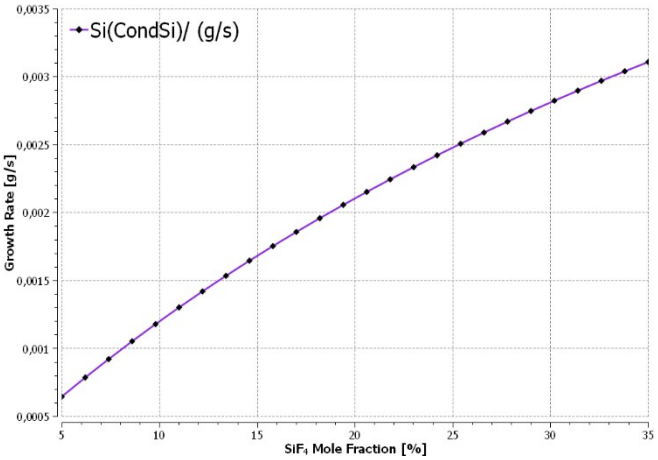


In this example, the SiF_4/NH_3 ratio in the Input Stream 1 is variable, T = 1440 K, P = 2 Torr, flow rate 0.2268 g/s, reactor volume 2000 cm^3 with surface area 950 cm^2.

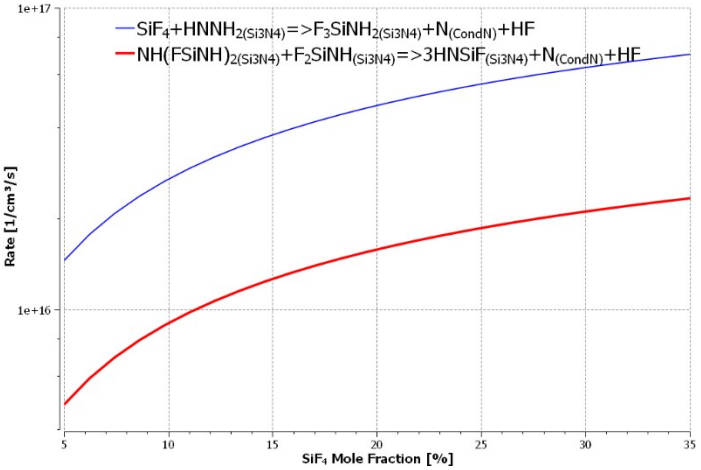
Kinetic mechanism of chemical vapor deposition of Si_3N_4 films was taken from literature (M. E. Coltrin et al J. Phys. Chem. 98:10138 (1994) and J. A. Miller et al, Comb. Sci. Technol. 34:149 (1983)). It includes 4 phases, 33 gas-phase reactions and 6 irreversible on-surface reactions.

Results

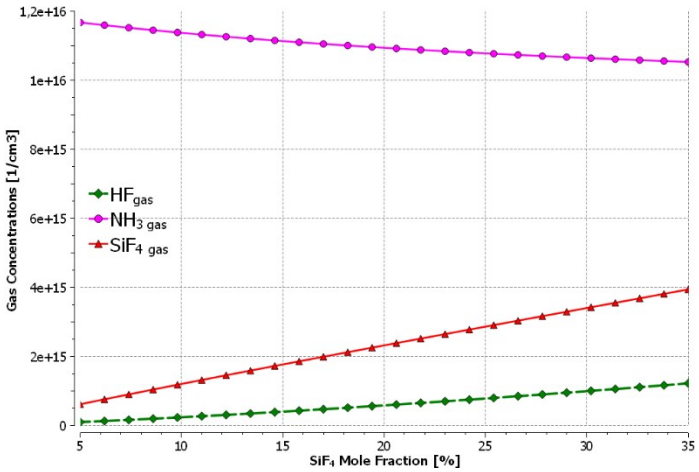
Simulated results are shown in figures below:

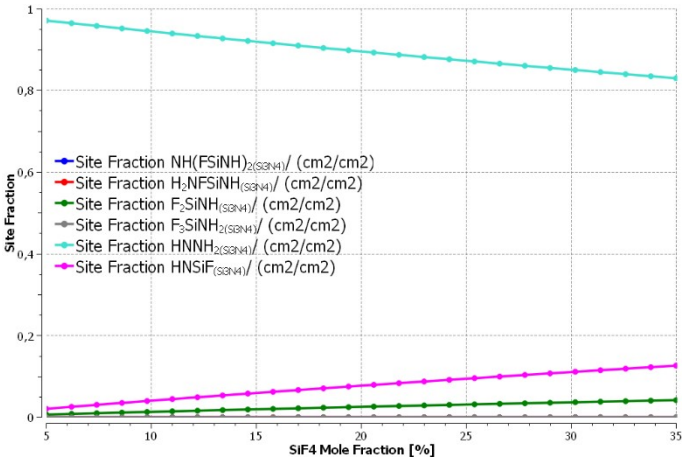


Predicted film deposition rate (in g/s) increases with increasing mole fraction of SiF_4 gas.



Sensitivity analysis showing nitride growth rate is most sensitive to surface reaction with SiF_4.





Concentrations of gas species (left) and surface species (right): the reactants SiF_4 and NH_3 are depleted, main gaseous product HF forms; site fractions of surface species changes for different gas mixtures.

Next steps

This example can be extended further:

1. Change reactor parameters like reactor volume, surface area, inlet temperature etc.
2. Compare predictions of different chemical kinetic mechanisms, for conditions of interest for you.