Trichlorosilane CVD in a Planar Channel Flow Reactor

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Summary

This application note presents a model for the CVD of silicon in a steady-state planar shear-layer flow reactor.

Project Description

The process operates at atmospheric pressure, and a relatively high temperature (1398 K). This is a fixed-temperature simulation that represents a horizontal cross-flow reactor of the type used to deposit epitaxial silicon layers. In this case, the upper wall temperature is held at a temperature (773 K) that is significantly lower than the deposition substrate, but higher than the inlet gas temperature (623 K).

The chemistry set describes the deposition of silicon from trichlorosilane in a hydrogen carrier gas. This mechanism is built on a significant number of independently published chemical kinetic parameters, and is described in more detail in a publication by Ho, et al.[1]

The chemistry input file, *chem.inp*, includes 3 elements, 11 gas-phase species, and 9 reversible gas-phase reactions. The gas-phase reactions are reversible decomposition reactions of various chlorosilanes and chlorinated disilanes. These reactions cause the conversion of some of the initial chlorosilane starting material to these other gas-phase species, which can be significant because the less-chlorinated molecules have higher surface reactivities. These reactions are written as unimolecular decomposition reactions at their high-pressure limit, so this reaction mechanism would tend to overstate the importance of gas-phase chemistry if it were used at lower total pressures.

The surface input file, *surf.inp*, has three surface species: open silicon surface sites, hydrogen-covered sites, and chlorine-covered sites, plus solid silicon as a bulk phase. There are 10 surface reactions, all written as irreversible reactions with placeholders for the thermodynamic data of the surface species. These reactions include the dissociative adsorption of $SiCl_3H$, $SiCl_2H_2$ and $SiCl_4$, which result in the formation of deposited silicon and hydrogenated/chlorinated silicon surface species. These are "lumped reactions" to the extent that the initial adsorption event, plus the successive transfer of H and Cl atoms from the initially adsorbed Si to other surface Si atoms, are all described as one step. The physical

[1] "Chemical Kinetics for Modeling Silicon Epitaxy from Chlorosilane", P. Ho, A. Balakrishna, J. M. Chacin, A. Thilderkvist, B. Haas, and P. B. Comita, in "Fundamental Gas-Phase and Surface Chemistry of Vapor-Phase Materials Synthesis", T. J. Mountziaris, M. D. Allendorf, K. F. Jensen, R. K. Ulrich, M. R. Zachariah, and M. Meyyappan, Editors, PV 98-23, p. 117-122, Proceedings of the 194th Meeting of the Electrochemical Society, 11/1-6/98, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).

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interpretation of this "lumping" is that adsorption of the gas-phase species is assumed to be slow compared to subsequent transfer of H and Cl atoms on the surface. For a chemically balanced reaction, this is written as involving four open sites, which by default would make the reaction fourth order in open sites, so the coverage dependence option has been used to set the kinetics to a more reasonable first-order dependence. Other reactions include the dissociative adsorption and associative desorption of H_2, HCl and $SiCl_2$, plus the dissociative adsorption of HSiCl. In many cases, the rate parameters are based on experimental surface-science studies, in other cases they are the result of fitting a model to experimental silicon deposition rate data from a specific CVD reactor.

Project Setup

The reactor diagram contains one inlet, one planar shear-flow reactor, and an outlet. You can specify the properties of the inlet gas on the C1_Inlet panel. Enter the inlet gas temperature and inlet gas velocity on the Stream Property Data tab. The Axial Velocity should be the maximum gas-phase velocity at the inlet. For this application, which is in cartesian coordinates, the average velocity equals two-thirds of the maximum velocity of the parabolic velocity profile. Enter the composition of the inlet gas on the Species-specific Property tab of the C1_Inlet panel.

You enter parameters describing the reactor geometry and wall temperatures on the Reactor Physical Property tab of the C1_ Planar Shear Flow panel. The temperatures for the upper wall and deposition surface (lower wall) are also input on this tab, as well as an optional parameter specifying the distance over which the wall temperatures are smoothly transitioned from the inlet gas temperature to the desired wall temperature. Use this tab to also specify the pressure, grid parameters, and the use of multicomponent diffusion and thermal diffusion (the Soret effect). The Species-specific Data tab allows the specification of initial guesses for the gas composition adjacent to the surface, which is not used in this example, as well as estimated values for the surface site fractions and bulk activities, which are provided.

Project Results

The gas temperatures in *Figure 1* show that the gas heats up substantially near the deposition surface, with the hot zone expanding with axial distance, as expected. The inlet gas temperature is lower than the upper wall temperature, such that the coolest gas lies in a region near to, but below the top wall. This cooler gas region is reflected in the trichlorosilane mole fraction contours shown in Figure 2. Depletion as a result of chemical reaction causes the low $SiCl_3H$ mole fractions near the lower wall, but thermal diffusion causes the heavier gas to move away from the upper wall. A simulation run without thermal diffusion gives uniform $SiCl_3H$ mole fractions in the upper part of the reactor. Figure 3 shows how the deposition rate of solid silicon varies as a function of axial distance. Initially, the deposition rate is quite high, but it drops rapidly as the $SiCl_3H$ near the surface is depleted, indicating that the deposition process is transport-limited in this system. Figure 4 shows gas-phase mole fractions near the lower surface as a function of axial distance. The extent of $SiCl_3H$ depletion and HCl formation is

notably larger than the formation of the other silicon-chlorine species ($SiCl_2$, $SiCl_2H_2$ and $SiCl_4$), which indicates that deposition of solid silicon is the dominant reaction pathway.

Figure 1 Trichlorosilane CVD—Gas Temperatures vs. Axial and Radial Distance

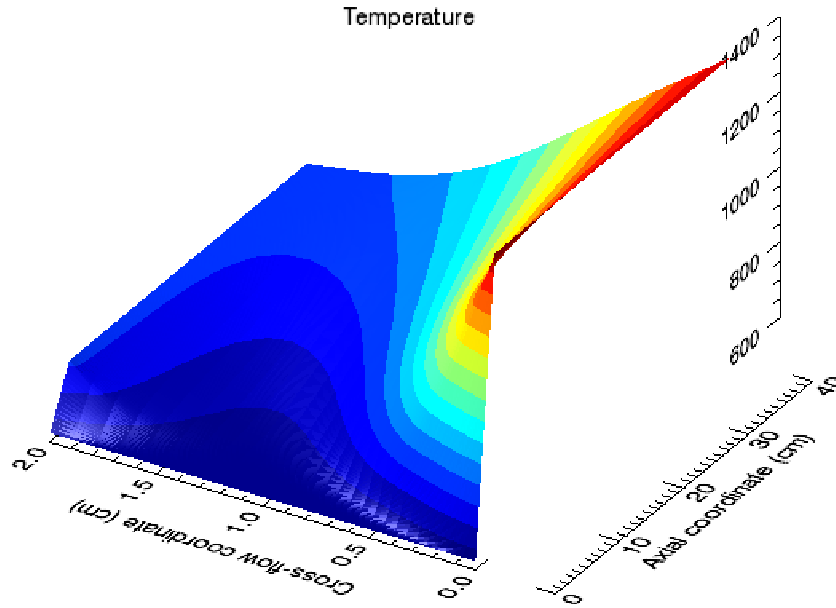


Figure 2 Trichlorosilane CVD—Trichlorosilane Mole Fraction

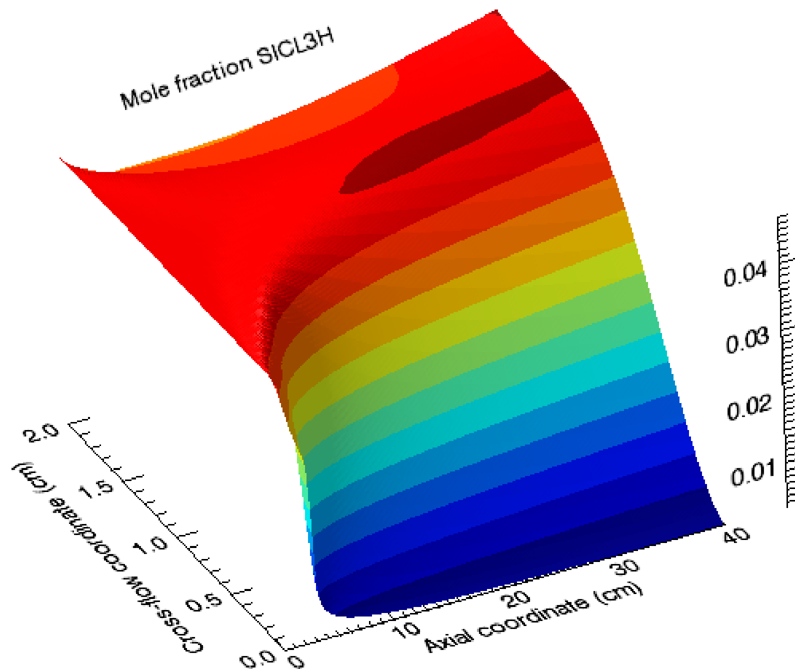


Figure 3 Trichlorosilane CVD—Silicon Deposition Rate

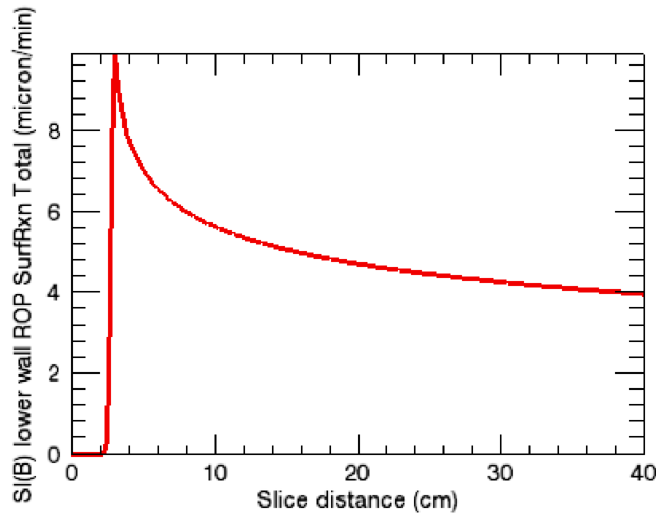
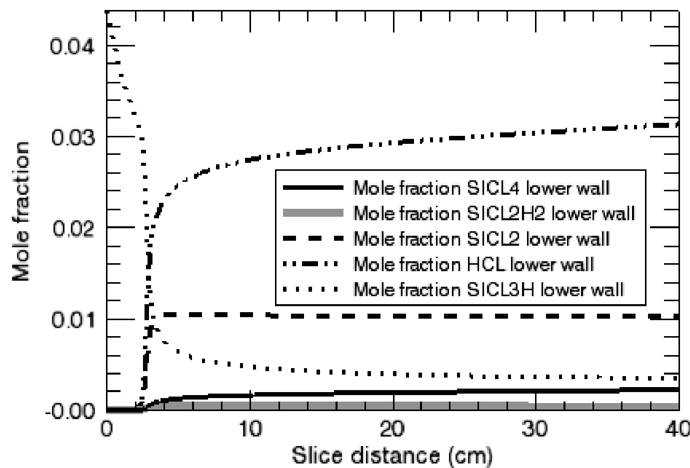


Figure 4 Trichlorosilane CVD—Mole Fractions



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