Equilibrium Analysis of Chlorosilane CVD

APP-CVD-1 (v2.0) August 30, 2010

Summary

This application note presents a multi-phase equilibrium calculation of the Si-Cl-H system.

Project Description

A constant pressure and temperature equilibrium calculation gives the maximum amount of solid product that could be formed in the absence of kinetic or transport limitations. This can be a valuable screening tool in choosing operating conditions for a CVD process. In this case, adding HCl to a mixture of $SiCl_3H$, H_2, and solid silicon alters the Si/Cl ratio in the system enough to change the equilibrium composition from one that would result in deposition of more solid Si, to one that would result in etching.

Project Setup

This application requires only one Equilibrium calculator. The equilibrium calculation only needs a list of species with their thermodynamic data; a reaction list is not needed. It is important to include all likely radical species as well as the desired and undesired product species in the calculation. It is generally better to include some unimportant species than to leave out ones that turn out to be important. The chemistry input file, *chem.inp*, includes 3 elements and 22 gas-phase species and no reactions. In the interest of completeness, a number of species such as SiH_4 or atomic Cl were added that are not expected to be important at standard CVD conditions, but that might be more important under different conditions. The surface chemistry input file, *surf.inp*, includes only solid silicon in the bulk (condensed) phase.

Setting up this problem first involves the C1_Equilibrium panel. You enter the problem type, temperature (1400 K) and pressure (1 atm) on the Reactor Physical Property tab. Then enter the starting composition on the Reactant Species tab. Starting with a molecular mixture will give the same equilibrium composition as starting with elemental Si, H, and Cl with the same Si/Cl and H/Cl ratios. On the Continuations panel, three additional simulations with increasing amounts of HCl are added, replacing some of the hydrogen carrier gas. Notice that all components of the starting mixture have been re-entered, because the composition must be entered as a set.

Project Results

Figure 1 shows the initial and equilibrium amounts of solid silicon for an initial mixture of 10% (by volume) $SiCl_3H$ in hydrogen with increasing amounts of HCl at 1 atm total pressure and 1400 K. With no added HCl, the

equilibrium mole fraction of solid silicon is larger than the initial amount, indicating that this gas mixture is likely to result in the deposition of silicon. As the HCl content increases, the mole fraction of Si(B) expected at chemical equilibrium decreases below the initial mole fraction. This initial gas mixture is thus expected to result in etching, rather than deposition of Si under these conditions. This primarily results from the decreasing Si/Cl ratio in the system. As shown in

Figure 2 Chlorosilane CVD—Mole Fractions, the most prevalent gas-phase species at equilibrium are the hydrogen carrier gas and various chlorinated silicon species. Increasing the relative amount of Cl in the system favors the formation of these gas-phase species.

Figure 1 Chlorosilane CVD—Equilibrium Calculations

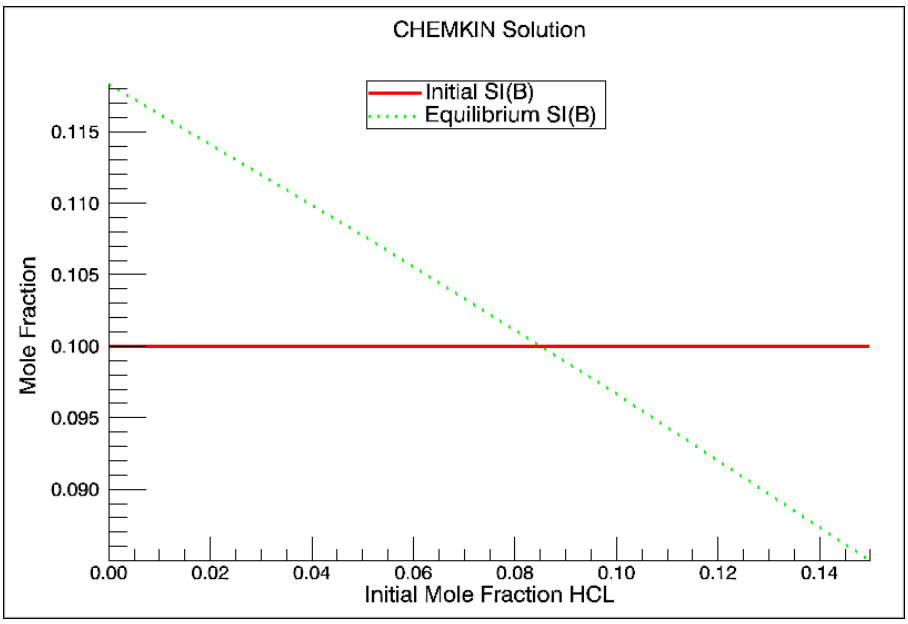
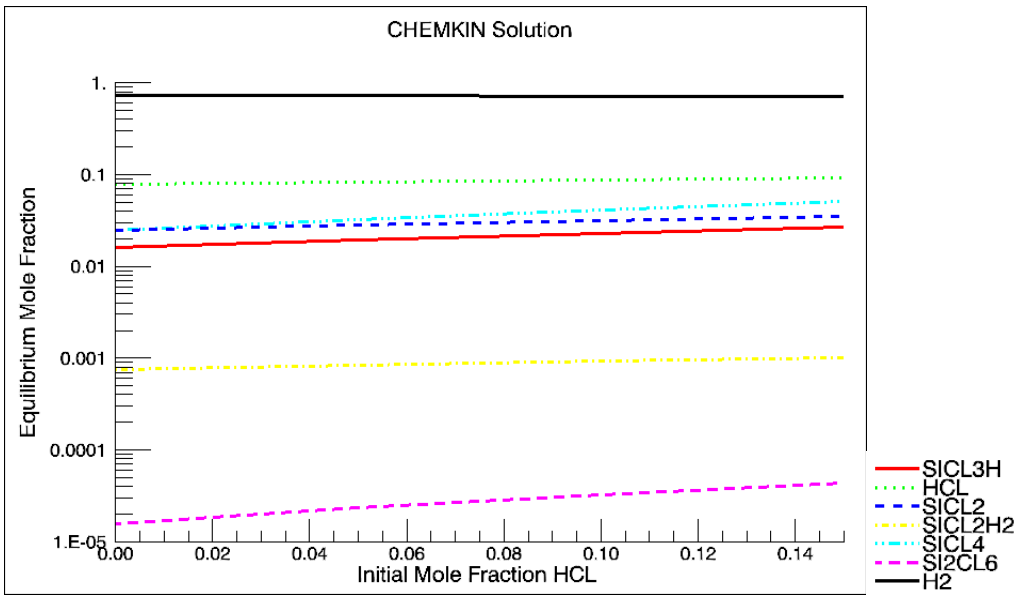


Figure 2 Chlorosilane CVD—Mole Fractions



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