Multiplicity of Steady States in the Codeposition of Silicon Carbide and Carbon

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Past studies have suggested that the process of chemical vapor deposition of SiC and C from mixtures of methyltrichlorosilane (CH_3SiCl_3, MTS), ethylene and hydrogen may exhibit multiple steady states in some regions of its space of operating parameters and conditions. This phenomenon was studied systematically and experimentally in a hot-wall chemical-vapor deposition reactor, in which small substrates hung from the sample arm of a sensitive microbalance are used for continuous monitoring of the deposition rate. Multiplicity of steady states occurs in a wide region of the space of process operating parameters, which covers a considerable portion of the range of conditions where deposition of SiC from MTS usually occurs. All cases studied manifest themselves as two stable (observable) deposition states at the same condition, differing by at least one order of magnitude. Various experimental observations and results of the thermochemical equilibrium analysis in the gas phase of the deposition system prove that the appearance of multiplicity in the $MTS-C_2H_4-H_2$ system manifests the heterogeneous chemistry of the deposition process, not of the homogeneous chemistry or the interactions of the transport and reaction processes. The composition analysis of the deposits reveals that sudden changes of the composition from almost pure carbon at the low deposition rate branch to SiC with excess carbon at the high deposition branch take place at the two limits of the multiplicity region. It indicates that one must operate outside the range of multiple steady states to obtain deposit compositions over the whole range from C to SiC.

Introduction

Multiplicity of steady states is a phenomenon in which a physicochemical system exhibits more than one stable (and, therefore, experimentally observable) steady state at a given set of operating conditions. In a chemical vapor deposition (CVD) system, multiplicity of steady states may be manifested as differences in deposition rate, deposit microstructure, or deposit composition (for codeposition systems). Among the few studies that have reported multiplicity phenomena in CVD systems, Haupfear and Schmidt (1993) have observed the presence of multiple steady states in a cold wall CVD system used to deposit TiC from $TiCl_4$ and C_3H_8, and Papasouliotis and Sotirchos (1995, 1998) presented conclusive evidence on the existence of multiple steady states in the deposition of SiC from methyltrichlorosilane (MTS) and H_2 mixtures.

In their early studies of SiC deposition from MTS, Papasouliotis and Sotirchos (1995) observed three distinct temper-

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ature regions in the variation of the deposition rate with the temperature in Arrhenius coordinates: a lower region where solid deposition was practically absent, an intermediate temperature region (about 25–50°C wide) where the deposition rate could change by almost four orders of magnitude, depending on how the reactor was brought to the operating conditions, and an upper temperature range of high deposition rate where the apparent activation energy decreases with increasing temperature. Further studies (Papasouliotis and Sotirchos, 1998) showed that the aberrant behavior of the deposition rate in the second region was due to the existence of multiple steady states.

A much clearer picture of the multiplicity region with a well-defined hysteresis loop was obtained in experiments with HCl added to the reactor feed. Multiple steady states were found to occur in a relatively broad range of operating conditions covering a considerable part of the region in which SiC is deposited in industrial CVD and chemical vapor infiltration (CVI) processes and experimental studies are carried out. Even though an explicit reference to the existence of multiple steady states in SiC deposition from MTS has not been made in other studies of the literature, in several of them it has been found that HCl, the main byproduct of SiC deposition from MTS (Hopfe et al., 1995; Jonas et al., 1995; Mosebach et al., 1995), inhibits the deposition process of SiC in a complex way (Besmann et al., 1992; Loumagne et al., 1993, 1995; Neuschutz et al., 1995), possibly by blocking reactive surface sites (Schulberg et al., 1995). Allendorf and Outka (1993) proposed as a possible inhibition mechanism dissociative adsorption of HCl on the SiC surface, with chlorine forming a strong Si/Cl bond. The addition of HCl to the MTS/H_2 mixture (Lespiaux et al., 1995) was found to decrease the nucleation rate, an indication that HCl affects surface reactions. Ohshita (1990) reported a similar decrease in the nucleation rate with HCl addition during SiC deposition from $SiH_2Cl_2/C_3H_8/H_2$ mixtures.

In a previous investigation of the codeposition of SiC and C from $MTS/C_2H_4/H_2$ mixtures (Kostjuhin and Sotirchos, 2001), it was found that the addition of HCl to the feedstream decreased the deposition rate and raised the carbon content of the deposit. However, in some region of the space defined by the operating parameters of the process, the deposition rate exhibited abrupt changes between two values differing by a few orders of magnitude as the HCl concentration or some other operating parameter (such as the temperature) crossed certain values. As in the study of Papasouliotis and Sotirchos (1998), this was found to be a manifestation of the existence of two stable (observable) deposition rates at the same operating conditions. The analysis of the composition of the deposit revealed that the abrupt change in the deposition rate was followed by a change in the composition of the deposit from a silicon carbide-rich SiC/C composite structure on the branch of high deposition rates to a deposit consisting mainly of carbon on the low deposition-rate branch.

This result is of immense importance for the preparation of SiC/C composite structures through chemical-vapor deposition from $MTS/C_2H_4/H_2$ mixtures, since it implies that when operation is carried out in the region of the parametric space of the problem where multiple deposition rates are present, the preparation of coatings in a range of intermediate SiC:C ratios is not possible. Composite SiC/C materials are of interest for a number of applications, such as matrix of interface material in fiber reinforced composites (for example, Deng et al., 1999; Maury and Aguillo, 1995) and protective layers of C/C composites (for example, De Castro and McEnaney, 1992; Hirai, 1993; Zhu et al., 1999). Being able to obtain the whole range of compositions from C to SiC is very important in the last area of applications since a very attractive class of protective coatings is that of functionally graded materials (FGM), in which the composition is varied smoothly from pure carbon in contact with the C/C material to a SiC outer layer.

The presence of multiplicity of steady states in the codeposition of SiC and C from $MTS/C_2H_4/H_2$ mixtures is investigated in a comprehensive manner in the present study. Ethylene was chosen as the additional carbon source in our studies, since several past studies of the literature and our own preliminary studies have shown that this hydrocarbon shows relatively high reactivity for carbon deposition (Kostjuhin and Sotirchos, 2001). Chemical-vapor deposition experiments are carried out in a hot-wall chemical-vapor deposition reactor of tubular configuration, in which deposition takes place on small substrates hung from the sample arm of a sensitive microbalance. This permits continuous *in situ* monitoring of the deposition rate and thus makes it possible to obtain multiple measurements of the deposition rate under the same conditions, but with the system brought to that set of operating conditions from a different previous state. Results are obtained on the effects of operating conditions on the appearance of a multiplicity of steady states in a rather broad region of the operating space of the codeposition process. The results are discussed in light of thermochemical equilibrium results for the gas-phase species that may be present in the chemical reactor at the conditions of solid deposition and a mechanistic scheme for SiC and C deposition from $MTS/C_2H_4/H_2$ mixtures.

Experimental Apparatus and Procedures

The CVD reactor used in the deposition experiments consists of a quartz tube with 15-mm internal diameter, in vertical position, with a resistance furnace. The reactive mixture entered the reactor from the top, and the flow rates of all gases, including that of the MTS vapor, were controlled using mass flow controllers. A mechanical vacuum pump, along with a pressure measurement and control system, was employed to control the pressure in the reactor at subatmospheric levels. The furnace had a 25-cm heating zone, and temperature measurements showed that this established in the reactor tube a region of about 23 cm in length in which the temperature was within $\pm 5°C$ of the set point value. The beginning of this almost isothermal zone practically coincided with the beginning (top) of the heating zone of the furnace. In the region of the reactor that preceded the isothermal zone, the temperature varied almost linearly with the distance, in such a way that the temperature rose from about 50% of its setpoint to the setpoint value within about 7 cm. More details about the experimental system in the configuration used for SiC deposition from MTS/H_2 mixtures and for SiC and C deposition from $MTS/C_2H_4/H_2$ mixtures are given by Papasouliotis and Sotirchos (1995, 1999) and Kostjuhin and Sotirchos (2001).

Deposition-rate measurements were carried out within the isothermal part of the tubular, hot-wall CVD reactor. The reactor served as the sample tube of a microbalance (Cahn

D-101 with 1-μg sensitivity), and this permitted continuous monitoring of the deposition rate on small substrates hung from the sample arm of the beam of the balance. The substrates were cut from plates of high-density graphite. A few minutes of deposition time were sufficient for the accurate determination of the deposition rate. Assuming linear variation of the deposition rate over the length of the substrate (which was typically about 1−1.5 cm), the measure deposition rate was assumed to be representative of that at the middle of the substrate. It was corrected for the weight of material deposited on the thin refractory wire from which the substrate was suspended by weighing both the wire and the substrate before and after an experiment and assuming that in each experiment the ratio of the material deposited on the substrate to that deposited on the wire was the same for all experimental points collected in that experiment. In most cases, this correction was less than 5%. More information is provided by Kostjuhin and Sotirchos (2001).

The presence of multiple steady states was examined by varying an operating parameter in small steps, in an increasing or decreasing direction, and measuring the deposition rate at each value of this variable. When the deposition rate was observed to undergo a sharp change (increase or decrease), the operating parameter was changed back to its previous value to see whether this change was the result of the presence of multiple steady states. If that was the case, that is, the reaction rate did not attain the value it had previously at that point, the variation of the parameter in the reverse direction was continued in small steps to locate the other limit of the multiplicity region and construct the complete hysteresis loop. Figure 1 shows the graph of deposition rate vs. parameter P that is obtained by the preceding procedure, as parameter P is varied when multiple steady states are present. Points A and B correspond to the limits of the multiplicity region at which a discontinuous change in the deposition rate is observed. The dashed portion of the curve gives the nonobservable (experimentally) part of the graph that corresponds to an unstable steady state.

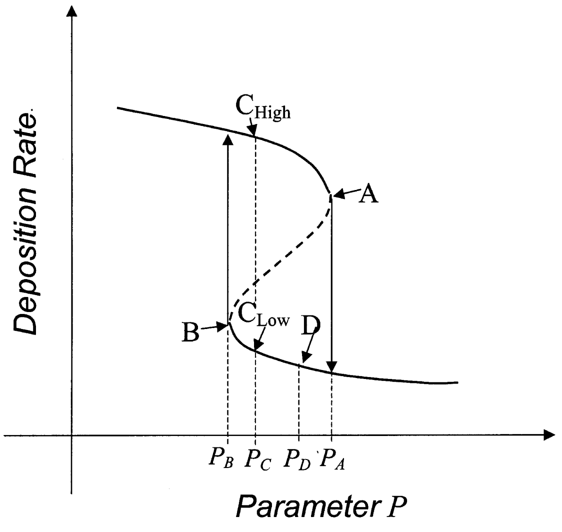

Figure 1. Qualitative plot of deposition rate vs. parameter *P* (any parameter) in the presence of multiplicity.

Experiments involving changes of the feed composition were much easier to conduct than experiments involving a change in the temperature or of the pressure of the operation. For large deviations of the latter from their set point values, the system could be temporarily brought outside the limits of the multiplicity region, and thus end up on a different steady-state branch from the one observed for a monotonic, or with smaller deviations, the approach of the varied parameter to its new value. This point can be made clearer by using the qualitative picture shown in Figure 1. Suppose that the system is for some value of the operating parameter P, P_D, which is between the values bounding the multiplicity region, P_A and P_B, at point D on the low deposition-rate branch. If the value of P is reduced from P_D to P_C, one would expect the system to remain on the low deposition-rate branch and move to point C_{Low}. However, if the control system used to change parameter P brings it below the value that corresponds to the lower limit of the multiplicity region (P_B), the CVD system may move toward the branch of high deposition rates. Therefore, when P eventually reaches P_C, the system may end up at the steady state that corresponds to the high deposition rate, C_{High}. This happened to be the case in the experiments of Sotirchos and Papasouliotis (1995), where as the temperature was changed from one set point value to another, the high thermal inertia of the Pt-Rh/Pt thermocouple that was used for temperature measurement in the control system caused very large transient deviations of the temperature outside the interval defined by the two set-points.

Experimental Results

Multiplicity of steady states was observed in a relatively broad range of operating conditions. Multiple steady states could be observed by varying the composition of the feed or by varying the temperature. Some of the more representative cases of the obtained results are discussed in the following sections. All deposition-rate data shown in the figures represent the result of a single experimental measurement. Multiple measurements of the deposition rate at the same conditions and in the same experiment showed very small differences among the measured values. Of course, when multiple steady states were present, this was true only for deposition-rate measurements on the same branch of the steady-state solution. These observations were also valid for the results of different experiments at the same conditions.

Effects of feed composition

The results of preliminary experiments where HCl was added while keeping the flows of all other reactants constant (the total flow rate was varied in this case) are shown in Figures 2 and 3, for MTS mole fractions equal to 0.02 and 0.06, respectively. The deposition rate initially decreased and then experienced an abrupt change as the HCl mole fraction was increased beyond a certain value. As can be seen in Figures 2 and 3, this value increased with increasing MTS concentration. At this point, the signal of the microbalance indicated that deposition had practically stopped. When the HCl mole fraction was decreased from the region with negligible depo-

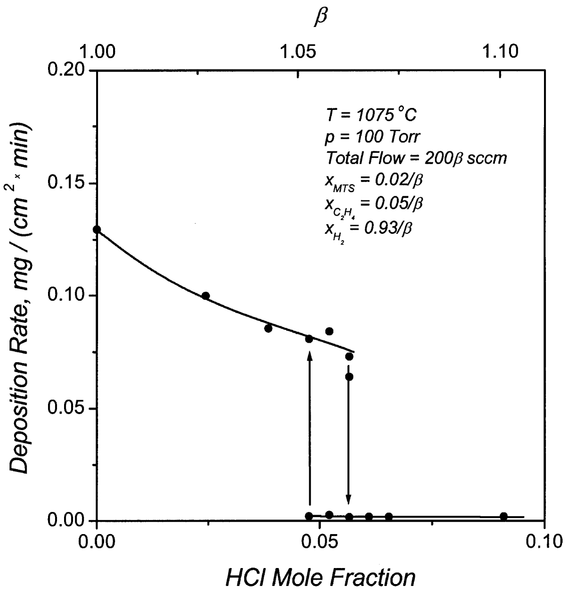

Figure 2. Variation of the deposition rate with the HCl mole fraction for 2% MTS and 5% C_2H_4 in the feed.

sition, an abrupt increase in the deposition rate was observed, but at an HCl concentration lower than the one where the deposition was stopped. Thus, the typical hysteresis loop that is reported in the literature for systems with steady-state multiplicity could be generated (see Figure 1). Arrows are used at the limits of the multiplicity region to indicate the direction in which the deposition rate changes as the HCl mole fraction passes through them. The mole fraction of HCl in Figures 2 and 3 was changed by varying the flow rate of this gas without changing the other flow rates. This causes

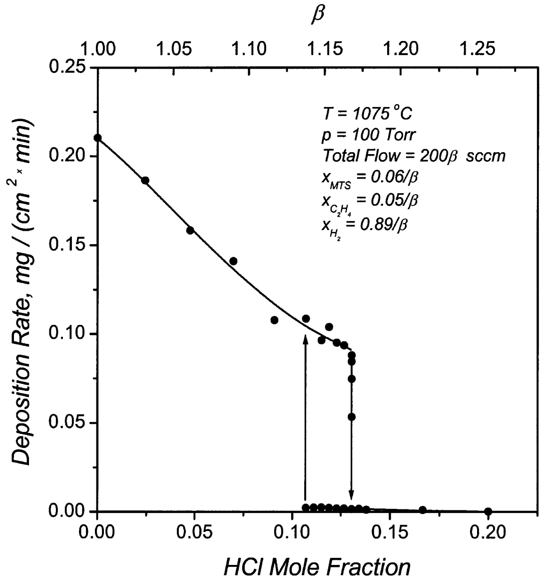

Figure 3. Variation of the deposition rate with the HCl mole fraction for 6% MTS and 5% C_2H_4 in the feed.

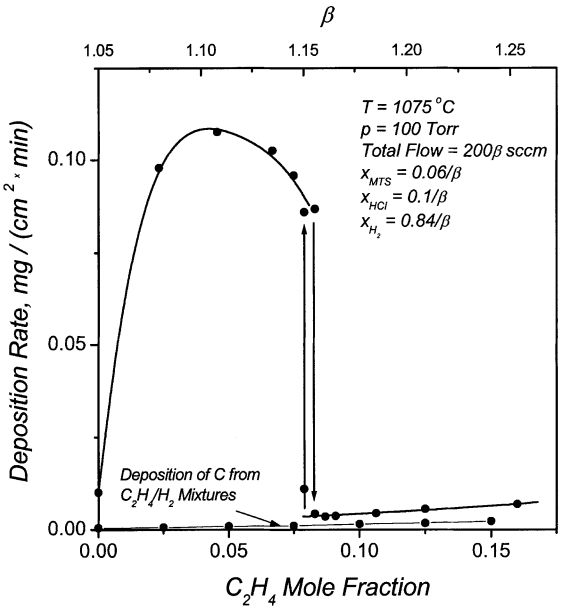

Figure 4. Variation of the deposition rate with the C_2H_4 mole fraction for 6% MTS and 10% HCl in the feed.

the total flow rate and the mole fractions of the other gases to vary as well. The factor β given at the top axis of these figures, as well as in some other figures, can be used to find the values of these variables at a given value of the abscissa using the equations given on the figures.

All operating parameters influenced the appearance of multiple steady states. As Figure 4 shows, it is possible to observe multiplicity in the presence of HCl by changing the flow rate of ethylene only. The main difference between the results of Figure 4 and those of Figures 2 and 3 is that in the former the region of C_2H_4 mole fraction values in which multiplicity is observed is considerably smaller than the range of HCl mole fraction over which multiple steady states are present in Figures 2 and 3. For other values of the HCl mole fraction in the feed or of the other experimental parameters, the variation of the concentration of C_2H_4 may not reveal the presence of multiple steady states. As shown in Figure 5, this turns out to be the case at the conditions of Figure 4 in the absence of HCl from the feed. (In Figure 5, the total flow rate was maintained constant by keeping the sum of the flow rates of H_2 and C_2H_4 constant.) The introduction of C_2H_4 causes a dramatic rise in the deposition rate. A further increase in the concentration of C_2H_4 leads to a maximum in the deposition rate and then to a slow decrease. This slow decrease is followed in Figure 4 by an abrupt drop in the deposition rate to a very low value, whereas in Figure 5, the deposition rate goes through a sharp minimum, beyond which it increases monotonically with the mole fraction of C_2H_4 in the feed.

Repeated measurements of the deposition rate at the same conditions by increasing and decreasing the concentration of C_2H_4 in the feed did not suggest the presence of multiple steady states at the conditions of Figure 5. Figure 5 also shows results on the variation of the composition of the deposit with the mole fraction of C_2H_4. The composition data were ob-

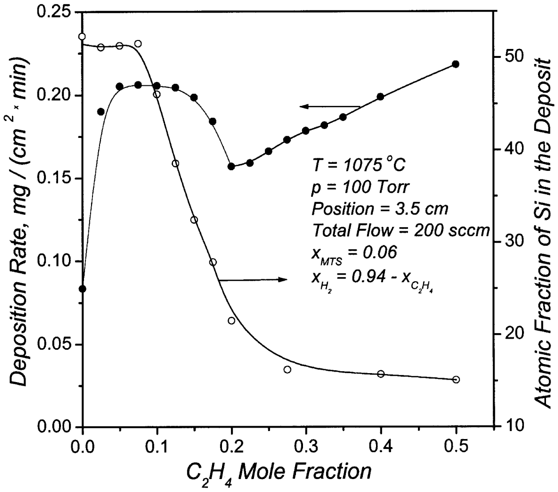

Figure 5. Variation of the deposition rate and of the deposit composition with the C_2H_4 mole fraction at the conditions of Figure 4, but without HCl present in the feed.

tained using energy dispersive X-ray analysis (EDXA). According to these results, the initial increase in the deposition rate upon the introduction of C_2H_4 is not accompanied by a change in the composition of the deposit. Si and C are present in the deposit at the stoichiometry of SiC, and X-ray diffraction analysis showed that SiC was present in the β-SiC form. The atomic fraction of Si in the deposit starts to decrease in the region of decreasing deposition rate, reaching after the minimum a value of about 7%, which remains almost constant in the region of the linearly increasing deposition rate. The analysis of the composition of deposits prepared at the conditions of Figure 4 did not reveal significant changes in the composition (from that of stoichiometric SiC) up to the point where the abrupt drop in the deposition rate took place. However, the deposits that were obtained on the low deposition-rate branch consisted almost entirely of carbon. More results on the effects of C_2H_4 on the deposition rates of C and SiC in the MTS/C_2H_4/H_2 system in the absence of multiple steady states were presented in a past publication (Kostjuhin and Sotirchos, 2001).

Figure 4 shows the deposition rate of C from mixtures of C_2H_4 and H_2. This deposition rate is by about a factor of 3 smaller than the total deposition rate in the codeposition process on the lower branch in Figure 4, and it is by almost two orders of magnitude smaller than the total deposition rate in Figure 5 after the minimum even though the major content of the deposit is carbon. These observations suggest that the abrupt change in the deposition rate in Figure 4 at the upper limit of the multiplicity region reflects both a drop in the deposition rate of SiC and a drop in the deposition rate of C. Since the deposit on the lower branch of Figure 4 consists of carbon and the main content of the deposit in Figure 5 for C_2H_4 mole fractions greater than the value at which the minimum takes place is carbon, one concludes that the deposition rate of carbon (in addition to that incorporated in SiC) in the codeposition process is much higher than the rate of deposition at the same conditions of carbon from mixtures containing C_2H_4 and hydrogen only. Therefore, the presence of silicon compounds in the gas phase must have an enhancing (catalytic-like) effect on the rate of carbon deposition.

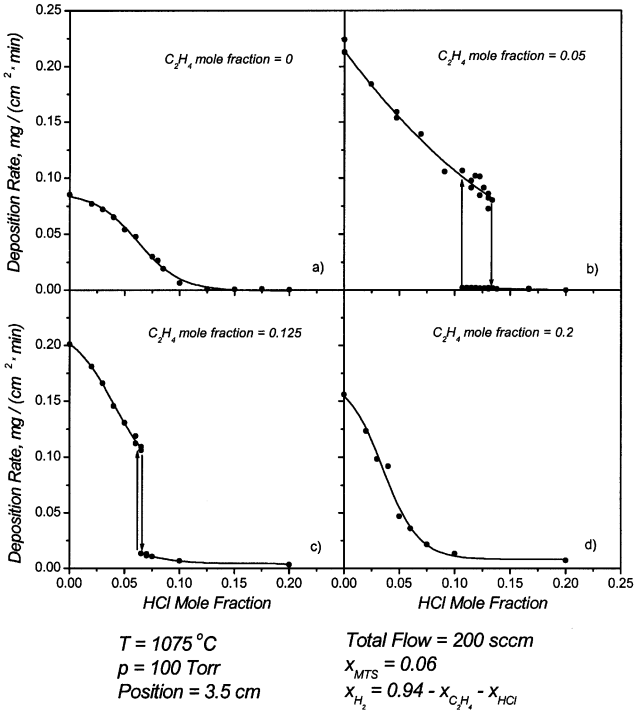

Figure 6. Evolution of the deposition rate vs. HCl mole fraction graph with the C_2H_4 mole fraction in the feed with 6% MTS in the feed.

The results shown in Figures 2–5 were obtained at a fixed position in the reactor. Since the gas-phase composition changes dramatically along the length of the reactor (because of the occurrence of the homogeneous and heterogeneous reactions and the transfer of material to the deposition surfaces), the deposition rate varies significantly with the distance from the entrance of the reactor. As a result, the results of Figures 2–5 are not representative of the situation encountered at other locations in the reactor. In their study of steady-state multiplicity in the CVD of SiC from MTS/H_2 mixtures, Papasouliotis and Sotirchos (1998) found that at some reaction conditions, the deposition rate could present multiple steady states with the variation of HCl in the front section of the reactor but not close to the exit.

More results on the effects of the feed mole fractions of MTS, C_2H_4, and HCl on the appearance of multiple steady states in the codeposition of SiC and C from MTS and C_2H_4 mixtures can be seen in Figures 6 and 7. These figures present the variation of the total deposition rate with the HCl mole fraction for different MTS and C_2H_4 concentrations in the feed. In contrast to the results of Figures 2–4, the results of Figures 6 and 7, like those of Figure 5, were obtained by keeping the total flow rate constant. For each value of the MTS mole fraction, there is a range of C_2H_4 mole fractions within which there are multiple deposition-rate values for a range of HCl mole fraction values. As in Figures 2–4, the deposition rates at the two branches differ by a few orders of magnitude. In general, the results of Figures 6 and 7 indicate

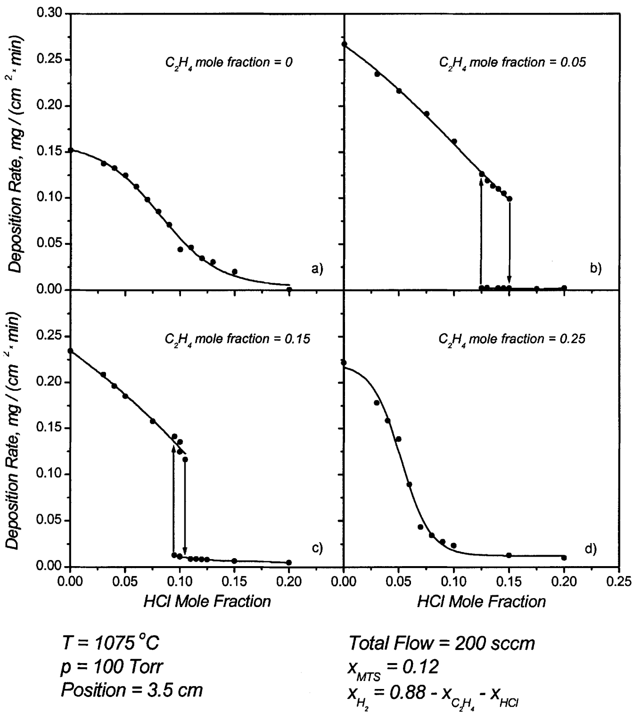

Figure 7. Evolution of the deposition rate vs. HCl mole fraction graph with the C_2H_4 mole fraction in the feed with 12% MTS in the feed.

that as the concentration of MTS increases, the region where multiple solutions occur tends to move toward larger C_2H_4 mole fractions and larger HCl mole fractions.

In presenting the results of Figures 4 and 5, it was mentioned that the analysis of the composition of deposits obtained at the high and low rate branches of the multiplicity region revealed that a discontinuous change took place in the composition of the deposit at the limits of the multiplicity region. The deposit at the high-rate branch consisted primarily of SiC, whereas the content of the deposit obtained at the low-rate branch was predominantly C. This situation was found to occur in all cases where the multiplicity of steady states was encountered. A similar observation was made by Papasouliotis and Sotirchos (1998, 1999) in their study of SiC deposition from MTS, but since no extra source of carbon was employed in this case, the deposition rate along the lower branch was extremely low. The increase in the concentration of HCl led to some increase in the carbon content of the deposit in the upper branch, but most of the change toward pure carbon occurred between the two stable branches. In the cases in which there was no presence of multiplicity, the reduction of the deposition rate to very low values through the introduction of HCl in the feed was accompanied by a smooth change in the composition of the deposit toward pure carbon. This can be seen in Figure 8, which presents deposition-rate and deposit-composition results for Figure 7d. As in Figure 5, the composition data were obtained using EDXA. The introduction of HCl leads to a smooth change in the composition of the deposit from 22% Si, the value at C_2H_4 mole fraction equal to 0.20 in Figure 5, to more than 98% carbon. From the results of Figures 4 and 8, one draws the conclusion that in order to be able to increase the C content of the deposit smoothly using HCl to suppress the rate of SiC deposition, multiplicity of steady states must be avoided.

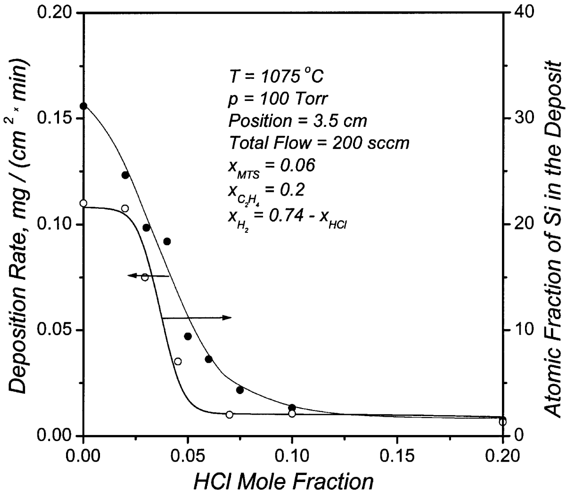

Figure 8. Variation of the deposition rate and of the deposit composition with the HCl mole fraction at the conditions of Figures 4 and 6 with 20% C_2H_4 in the feed.

Effects of temperature

Preliminary experiments on the variation of the deposition rate with the temperature showed that without ethylene or with a small amount of C_2H_4 added, the deposition abruptly stopped at about 850°C—possibly manifesting the jump between two multiple steady states—while in the presence of relatively large concentrations of C_2H_4 in the system, this effect was not observed. This behavior is the opposite of that seen in the results of HCl addition experiments at the conditions of Figures 6 and 7 where multiplicity was not observed in the absence of ethylene, but was present in a range of mole fractions of C_2H_4.

The effects of temperature on the appearance of multiplicity was investigated with experiments at various temperatures in the range from 925°C to 1,125°C, conducted by changing the HCl concentration and keeping all other parameters constant except the H_2 concentration, which was adjusted to keep the total flow of reactants constant. Some of the obtained results are shown in Figure 9 for the case in which 5% ethylene is present in the feed. The system does not exhibit multiplicity of steady states, as the feed mole fraction of HCl is varied at 950°C. However, at the two higher temperatures, multiple steady states appear within a certain range of HCl mole fraction, which is broader at the higher temperature. Since the deposition rate in the high deposition branch increases strongly with the temperature, the differences between the two deposition rates in the multiplicity region become larger as the temperature is increased. The multiplicity region moves toward higher values of the HCl mole fraction, and thus larger concentrations of HCl are needed to bring the deposition rate to a low value.

A more informative picture of the evolution of the multiplicity of steady states with the temperature and the HCl mole

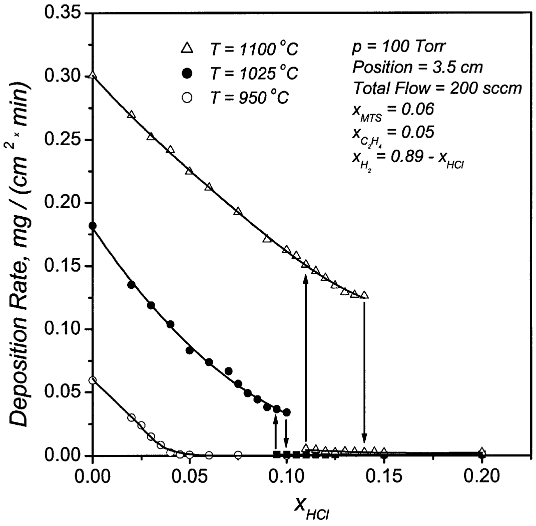

Figure 9. Effect of temperature on the deposition rate vs. HCl mole fraction diagram for 6% MTS and 5% C_2H_4 in the feed.

fraction is obtained by constructing a surface plot of the deposition rate over the plane of temperature and HCl mole fraction. Such a surface plot, shown in Figure 10, was generated by carrying out several experiments like those shown in Figure 9 in the 900–1,150°C range. The projection of the limits of the multiplicity region on the (HCl mole fraction, temperature) plane is presented in Figure 11. The upper-branch limit corresponds to the conditions where the deposition rate drops to a low value during an increase of HCl mole fraction, whereas the lower-branch limit gives the conditions where deposition at a high rate is obtained when the concentration of HCl is reduced. Between these two branches of limit points lies the region of experimental conditions with two steady states. The two branches meet at a point [hysteresis (cusp) point], which may be used to find the temperature and HCl mole fraction limits below which multiplicity of steady states is not observed at the conditions of Figure 10.

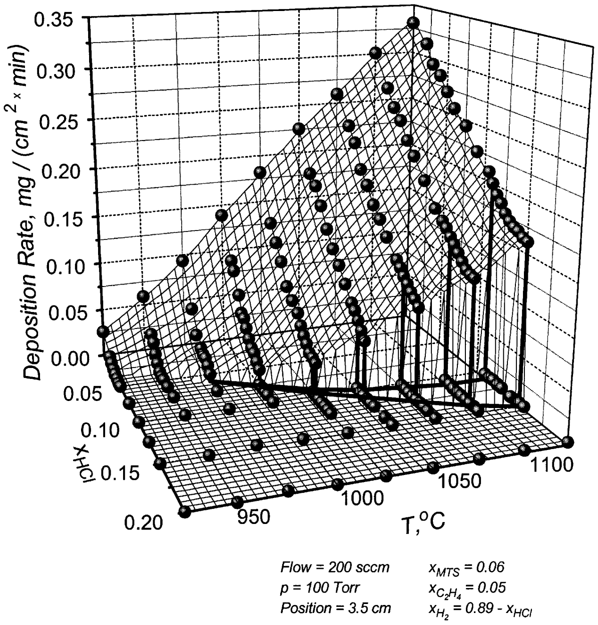

Figure 10. Evolution of the multiplicity region with the temperature at the conditions of Figure 9.

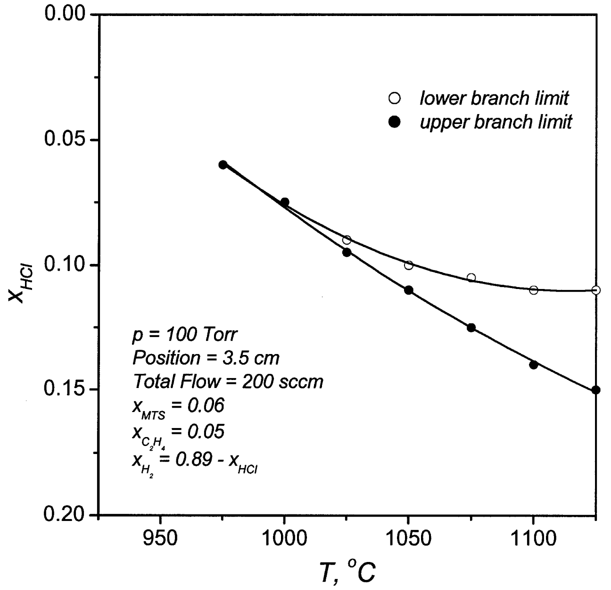

Figure 11. Locus of the limits (turning points) of the multiplicity region at the conditions of Figures 9 and 10 on the (temperature, HCl mole fraction) plane.

Independent experiments carried out at a fixed HCl concentration and varying temperature produced graphs consistent with those extracted from the results shown in Figure 10. For example, for 10% HCl in the feed, the results of Figure 10 indicate that the deposition rate should jump to a much higher value at the lower-branch limit, but change moderately (drop to a lower value) at the upper-branch limit. The graph of Figure 12, constructed from an independent experiment in which the temperature was varied, shows that this is indeed the case. The quantitative agreement between the results of Figures 10 and 12 is also excellent. This agreement offers an indication of the reproducibility characteristics of our experiments. The data points in Figure 12 were obtained from a single experiment, whereas each point in Figure 10 at 0.1 HCl mole fraction was measured in a different experiment. It must also be noted that the use of a microbalance permits multiple measurements of a deposition rate at a certain set of reaction conditions, and thus the repeatability of a measurement can be tested routinely. In general, insignificant differences were observed among measurements conducted at the same conditions.

Discussion

The overall reactions that lead to SiC and C deposition from mixtures of methyltrichlorosilane and hydrogen are

$$CH_3SiCl_3 \rightarrow SiC + 3HCl$$

$$C_2H_4 \rightarrow 2C + 2H_2$$

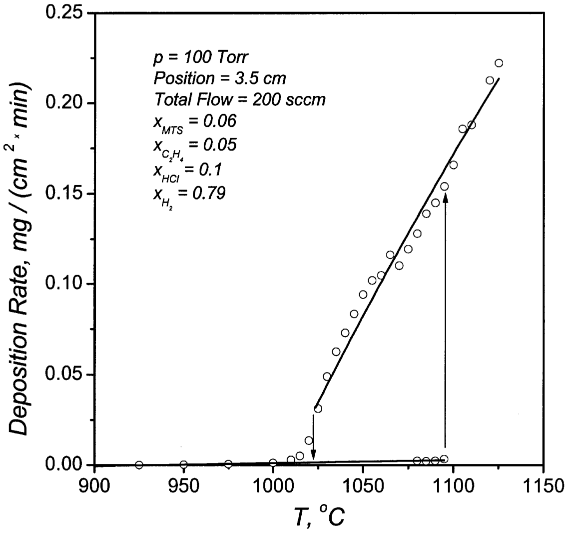

Figure 12. Deposition rate vs. temperature for 10% HCl in the feed at the conditions of Figures 9 and 10.

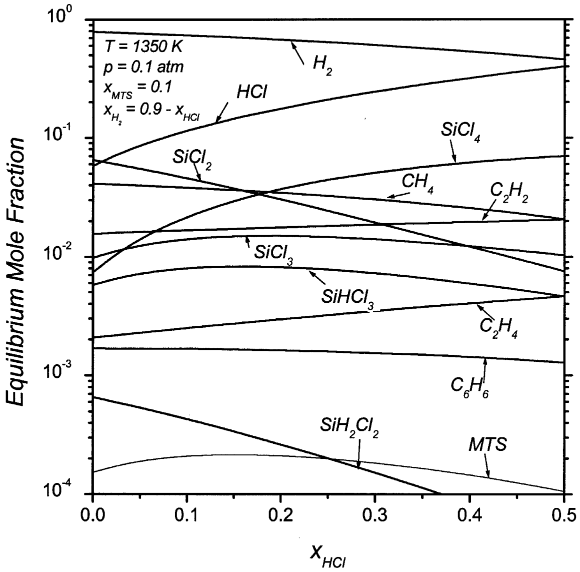

Figure 13. Effect of HCl addition in the feed on the equilibrium mole fractions of the major gas-phase species (with mole fraction greater than 10^{-4}) in the MTS/H_2 system.

These equations represent only overall macroscopic balances for the codeposition process. The actual chemical mechanism of the deposition process involves many heterogeneous and homogeneous chemical reactions, in which a very large number of gas-phase species and species adsorbed on the surface of the growing film participate. Since HCl is a product of the overall reaction of SiC deposition, one would expect an increase in the concentration of this species in the gas phase to have an inhibitory effect on the SiC deposition rate. Moreover, for the given values of the concentrations MTS and of the other species in the gas phase, there should be a limiting value for the concentration of HCl, above which deposition of SiC is not thermodynamically feasible. The concentration of the HCl in the gas phase is expected to increase with increasing loading of the gas phase in Cl; this can happen through the addition of HCl in the feed or through the transfer of Si and C to the deposition surface.

Computations on the thermochemical equilibrium of the reacting mixture were carried out to examine the relationship between the reduction of the rate of SiC deposition and the eventual stoppage of the deposition of this species and the changes in the gas-phase composition of the reactive mixture that take place as HCl is added in the feed or Si and C are transferred to the deposition surfaces. A code based on the Gibbs free energy minimization was used to compute equilibrium gas-phase mole fractions in the Si/C/H/Cl deposition system for over 120 gaseous species using a database (Papasouliotis, 1997) assembled mainly from the JANAF Thermochemical Tables (Chase et al., 1985) and two additional sources (Gurvich et al., 1990; Barin, 1989).

Results of the effect of HCl addition on the gas-phase composition are presented in Figure 13 for the major species (with mole fractions above 10^{-4}). The most important changes in the equilibrium composition of the gas phase of the major silicon-containing species are the decline in the concentration of $SiCl_2$ and an increase in the $SiCl_4$ concentration. The concentrations of $SiCl_3$ and $SiHCl_3$ remain almost unaffected. $SiCl_2$ is considered to be among the main precursors for Si incorporation in the deposition from mixtures containing chlorosilanes. The changes in the concentration of major hydrocarbon species are mainly due to the reduction in the H_2 mole fraction in the feed to keep the total flow rate constant as the HCl mole fraction is increased. The weak effect of HCl on the concentrations of the hydrocarbon species agrees with the observation (made in our experiments) that HCl does not have significant effects on carbon deposition from ethylene/hydrogen mixtures. The equilibrium mole fraction of MTS is a very small fraction of the feed mole fraction, and it is affected less strongly by the addition of HCl in the feed than the mole fractions of $SiCl_2$ and $SiCl_4$.

The results of Figure 13 were obtained by allowing only gas-phase species to form in the chemical reactor. This was done because the residence times needed to transfer to the deposition surfaces of a typical CVD reactor the amounts of elements (Si and C) that are required for complete gas–solid equilibrium to be attained are much longer than the actual residence times. Therefore, if thermodynamic equilibrium is going to be reached in the reactor, this will most probably happen in the gas phase alone. The gas-phase equilibrium results can be employed to assess the feasibility of the deposition of a certain solid. To do that, we consider a chemical reaction (any reaction) that leads to deposition of the solid of interest and involves gaseous species present in the equilibrium mixture. Deposition of that solid is feasible if this reaction is thermodynamically allowed to proceed in the direction of solid deposition at the conditions prevailing in the gas phase.

Results obtained using the preceding procedure on the effect of HCl addition on the feasibility of SiC formation at conditions similar to those used in our experiments are presented in Figure 14. The ordinate axis in this figure gives the

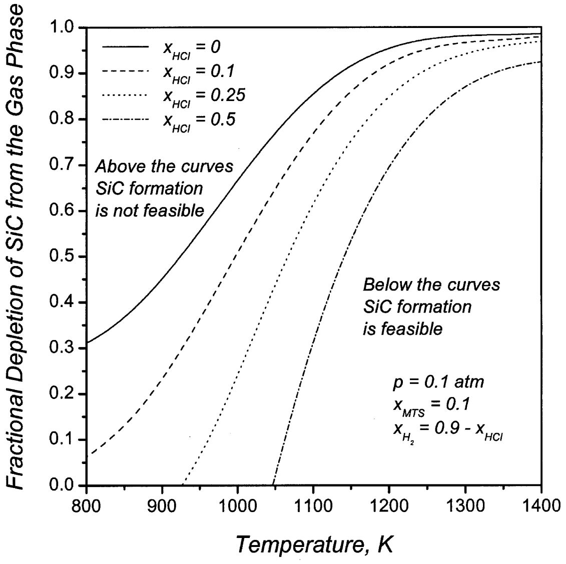

Figure 14. Evolution with the temperature, as Si and C are removed from the gas phase as SiC at the conditions of Figure 13, of the boundary of the region in which deposition of β-SiC is thermodynamically allowed.

fractional depletion of Si and C from the gas phase because of the deposition of SiC on the walls of the reactor. This is actually the situation that arises as the mixture makes its way toward the exit of the reactor. However, since MTS can be stoichiometrically decomposed to one molecule of SiC and three molecules of HCl, an equivalent situation can be obtained by introducing additional HCl in the feedstream. The results of Figure 14 show that as more HCl is added to the feed or more SiC is removed from the gas phase, higher temperatures are needed to make the deposition of SiC feasible. The boundary in Figure 14 between the region where SiC deposition is possible and the region where it is not corresponds to the conditions where reactions leading to SiC deposition and involving gas-phase species from the equilibrated gas phase are at equilibrium.

The results in Figure 14 show that the addition of HCl or the removal of Si and C from the gas phase can lead to stoppage of SiC deposition. However, this stoppage cannot be the same as that seen in cases where multiplicity of steady states appears. As we have seen in the experimental results, the deposition rate in those cases changes suddenly between two values that may differ by a few orders of magnitude. The quantitative agreement between experimental and thermodynamic results is rather poor. Although the conditions used to obtain the results of Figure 14 are comparable with those used in the experiments, the thermodynamic equilibrium results predict that 50% HCl must be added in the feed to stop the SiC deposition at 1,050 K (780°C), whereas the experimental results of Figure 9 indicate that about 5% HCl added to the feed can reduce the deposition rate to practically zero at 950°C, and less than 15% can have the same effect at 1,100°C.

Even though the subject of this study is the codeposition of SiC and C, in Figure 14 we have dealt only with the feasibility of the deposition of SiC. The feasibility of carbon deposition at the conditions in Figures 13 and 14 and under any other conditions can be assessed by following the same procedure as for SiC deposition. The addition of HCl affects weakly the concentrations of hydrocarbons (see Figure 13), and thus its influence on the feasibility of C deposition is rather weak. The deposition of carbon is favored to occur at all conditions in Figures 13 and 14, but when deposition experiments at similar conditions are carried out, one finds (for example, see Papasouliotis and Sotirchos (1999)] that the deposit contains excess silicon and not excess carbon. This is exactly the reason for which C_2H_4 was employed to obtain excess carbon in the deposit as an extra carbon source in the present study.

The disparity between the thermodynamic equilibrium results and the experimental results points to the conclusion that even when multiple solutions are not present, the reduction of the deposition rate of SiC to essentially zero levels is not a consequence of thermodynamic limitations on the process, but of the interactions of the various transport and reaction processes that are involved in the overall process. Both in the experiments that were presented in our past study (Kostjuhin and Sotirchos, 2001) and in those we carried out in the present study, it was observed that the deposition rate of SiC and C at a certain location in the reactor was practically independent of the exact location of the substrate on the cross section of the reactor and the local geometry of the deposition surface. Since the location of the substrate in the reactor and the local geometry usually have strong effects on the mass-transfer coefficient from the gas phase to the deposition surface, this observation indicates the absence of significant mass-transport limitations from the process. Transport-reaction interactions should therefore be excluded as a cause of the multiplicity phenomenon. The occurrence of multiplicity is most probably a manifestation of the interactions of the elementary reactions that are involved in the heterogeneous chemistry of the process.

A model for the chemical-vapor deposition of SiC from mixtures of MTS and H_2 was presented by Sotirchos and Papasouliotis (1992) and Papasouliotis and Sotirchos (1994). The simplest mechanism that can describe the deposition of SiC in this model is

$$\mathrm{SiCl_2} + [\mathrm{S}] \rightarrow [\mathrm{SiCl_2}]_s \tag{1}$$

$$\mathrm{C_2H_4} \rightarrow 2[\mathrm{CH_2}]_s \tag{2}$$

$$[\mathrm{CH_2}]_s + [\mathrm{SiCl_2}]_s \rightarrow \mathrm{SiC}_b + 2[\mathrm{S}] + 2\mathrm{HCl}, \tag{3}$$

where subscript b is used to denote bulk species, [S] represents an active site on the surface, and the brackets [ ] with subscript s are used to denote adsorbed species on the deposition surface. In their investigation of multiplicity phenomena in the deposition of SiC from MTS and H_2, Papasouliotis and Sotirchos (1998) showed that this model is capable of yielding multiple steady states and explaining several observations made in the experiments.

Since it is the rate of deposition of SiC that undergoes a dramatic change at the limits of the multiplicity region between the upper and the lower branches of the observable steady states in the codeposition of SiC and C from $MTS/C_2H_4/H_2$ mixtures, a deposition model that includes the reactions given by Eqs. 1–3 can also describe the behavior seen in this deposition system. However, steps leading to carbon deposition must be included in such a model to explain the presence of excess carbon in the deposit. Sotirchos and Papasouliotis (1992) and Papasouliotis and Sotirchos (1994) used the following two reaction steps in their deposition model to allow for the deposition of Si and C from MTS and H_2 mixtures

$$[\mathrm{SiCl}_2]_s + \mathrm{H}_2 \rightarrow \mathrm{Si}_b + [\mathrm{S}]_{\mathrm{Si}} + 2\mathrm{HCl} \tag{4}$$

$$[\mathrm{CH}_2]_s \rightarrow C_b + [\mathrm{S}]_{\mathrm{C}} + \mathrm{H}_2, \tag{5}$$

where $[\mathrm{S}]_{\mathrm{C}}$ and $[\mathrm{S}]_{\mathrm{Si}}$ are free active sites corresponding to the C and Si atoms on the surface, respectively. Since the active sites on the surface are differentiated between the Si and C sites, the reaction for the deposition of bulk SiC (Eq. 3) is rewritten as

$$[\mathrm{CH}_2]_s + [\mathrm{SiCl}_2]_s \rightarrow \mathrm{SiC}_b + [\mathrm{S}]_{\mathrm{C}} + [\mathrm{S}]_{\mathrm{Si}} + 2\mathrm{HCl}. \tag{6}$$

Equation 5 can account for the production of excess carbon, but it cannot describe the enhancement in the deposition rate of excess carbon in the presence of MTS in the feed or the inhibitory effect of HCl on carbon deposition in the codeposition process. In view of this, Kostjuhin and Sotirchos (2001) postulated that steps involving both Si and C species on the surfaces of the general form

$$[\mathrm{SiCl}_x]_s + \left[\mathrm{C}_y\mathrm{H}_z\right]_s \rightarrow \mathrm{C} + \mathrm{HCl}$$

must be included in the mechanism to describe these phenomena. As a possible reaction step consistent with the trends in the variation of the rate of carbon deposition, they proposed the following

$$[\mathrm{CH}]_s + [\mathrm{SiCl}_3]_s \rightarrow \mathrm{C}_b + [\mathrm{S}]_{\mathrm{C}} + [\mathrm{SiCl}_2]_s + \mathrm{HCl}. \tag{7}$$

The theoretical investigation of the occurrence of multiplicity of steady states in the codeposition of SiC and C from $MTS/C_2H_4/H_2$ mixtures using a deposition model built around the reactions given by Eqs. 1, 2, and 4–7 is among the subjects of our current studies.

Summary and Conclusions

The phenomenon of the occurrence of multiple steady states, that is, more than one stable deposition rate under the same conditions, in the chemical-vapor codeposition of SiC and C for $MTS/C_2H_4/HCl/H_2$ mixtures was investigated in a comprehensive manner in the thermogravimetric chemical-vapor deposition (CVD) system over a wide region of the system's operating space. Multiplicity of steady states was found to occur in a relatively large region of the space of the operating parameters of the process, which covers a considerable portion of the range of conditions where deposition of SiC from MTS is usually carried out. In all cases where multiplicity of steady states was encountered in this study, it manifested itself as two stable (observable) deposition states at the same condition, differing by at least one order of magnitude. For one set of operating conditions, measurements of the deposition rate vs. the HCl mole fraction at various temperatures were used to obtain a complete map of the surface of the deposition over the (HCl mole fraction, temperature) plane.

The results obtained indicated a complex dependence of the multiplicity structure on the problem or the operating parameters. In general, the introduction of C_2H_4 in the feed made the appearance of multiplicity in the deposition process more likely. In cases where there was no multiplicity in the deposition rate vs. HCl mole fraction graph for deposition from $MTS/H_2/HCl$ mixtures, multiplicity could show up in a range of C_2H_4 values. For a given value of C_2H_4 mole fraction in the feed, multiple steady states appeared on the deposition rate vs. HCl mole fraction graph above some temperature limit, and the multiplicity region became broader and moved toward higher values of the HCl mole fraction as the temperature was increased.

When multiplicity of deposition rates was present, the deposition rate at the lower branch was much smaller (by more than a few orders of magnitude in some cases) than that at the upper branch. The thermochemical equilibrium analysis of the gas phase of the deposition process indicated that the addition of HCl in the feed or, equivalently, the removal of Si and C because of deposition of SiC on the walls of the reactor, could lead to conditions where deposition of SiC is not thermodynamically allowable. However, the difference between the limiting HCl mole fraction predicted by the thermodynamic analysis for stoppage of SiC deposition and that given by the experiments for transition from the upper steady-state branch to the lower one was very large. Moreover, the thermochemical equilibrium analysis gave a smooth variation of the equilibrium mole fractions of the gas-phase species, whereas the experimentally observed change in the deposition rate was abrupt. On the basis of these results and other observations made in the experiments, it was concluded that the appearance of multiplicity is due to interactions of the reaction steps in the heterogeneous chemistry of the process. For the case of SiC deposition from $MTS/H_2/HCl$ mixtures, Papasouliotis and Sotirchos (1998) showed that rather simple surface chemistry mechanisms of SiC deposition can describe the appearance of multiple steady states.

The analysis of the composition of the deposits revealed that a sudden change in the composition from almost pure carbon at the lower branch to SiC with excess carbon at the high deposition branch takes place at the two limits of the multiplicity region. Intermediate compositions between these two extremes apparently occur along the unstable branch of deposition rates, that is, under physically unrealizable conditions. This result is of immense importance for the development of processing schemes aimed at the preparation of functionally graded SiC/C material for the protection of C/C composites for oxidation and other applications. These materials present continuous variation of their composition between C and SiC, and so, operation outside the range of multiple steady states is needed to get compositions covering the whole gamut from C to SiC.

Acknowledgments

This research was supported by grants from the National Science Foundation and the U.S. Department of Energy. The help of Mr. Brian McIntyre with the characterization of the deposits is gratefully acknowledged.

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Manuscript received Jan. 22, 2002, and revision received May 24, 2002.