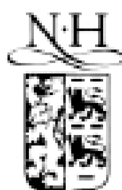

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Thermodynamic approach to the chemical vapor deposition process

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Abstract

The portion of the free energy change which is solely dissipated for deposition in the chemical vapor deposition (CVD) process is examined. The partial pressure of the species to be deposited in the supersaturated gas phase is determined by minimizing the Gibbs free energy without the condensed phase. The supersaturation ratio for deposition is defined as the ratio of this partial pressure to the equilibrium vapor pressure of its solid. The supersaturation ratio for deposition is the same as the activity when the solid phase is chosen as the standard state. It can be expressed in terms of the partial pressures of the other species which satisfy the law of mass action, allowing the estimation of the supersaturation ratio of the compound whose stoichiometry is not maintained in the vapor phase. This supersaturation ratio is consistent with the CVD phase diagram, being unity along the phase boundary and less than unity in the gas phase region. Based on this scheme, the line of the iso-supersaturation ratio for deposition or etching can be introduced to the conventional CVD phase diagram and the dependence of the CVD processing variables on the supersaturation can be assessed. By applying this scheme to the Si–Cl–H system, the supersaturations for deposition of silicon are evaluated with respect to temperature, pressure and composition.

1. Introduction

Chemical vapor deposition (CVD) is widely used in preparing various kinds of films, especially for solid state devices [1–4]. Thermodynamic analyses provide a basic guideline for the process. From equilibrium thermodynamic calculations the CVD phase diagram [3,5,6] can be drawn, which predicts deposition or etching of the given solid phase and a theoretically obtainable amount of a deposit under the specified experimental conditions.

The CVD process is the precipitation of the solid phase from the gas phase reaction. The driving force for precipitation of the solid phase should be distinguished from the driving force for the overall CVD process. The free energy change between the initial reactants and the final equilibrium products is the driving force for the overall CVD process. This free energy change is dissipated not only in the precipitation process but also in various other processes such as producing the new gas species, entropy of mixing of all gases

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and in some cases, the diffusion of the reactant gases. Only a small portion of this free energy change will be dissipated in the precipitation of the solid phase.

The initial reactant gases are always unstable with respect to the final equilibrium, where all the gas species involved in the reactions exist in their due proportions to minimize the total free energy. Even when the solid phase is not stable in the final equilibrium, the chemical reactions of the initial reactant will proceed. In this case, the free energy that drives the overall process does not contribute to deposition at all; it is dissipated in the chemical reactions and diffusion of the reactant gases. The free energy difference between the initial state and the final equilibrium is always negative, regardless of the initial composition. However, the free energy change dissipated solely for deposition should be negative only when the solid phase is predicted by the composition of the initial reactant gases in the CVD phase diagram. The driving force for precipitation should be consistent with the CVD phase diagram which shows the equilibrium region for deposition and etching; along the phase boundary of the gas/(gas + solid), the driving force should be zero and in the etching region, its sign should be reversed.

The driving force for deposition is the difference in the chemical potential of the species to be deposited between the gas and the solid phases. In this paper, the chemical potential of that species in the supersaturated gas phase is suggested to be approximated by the value determined by the gas phase equilibrium. We will use two terminologies, "the gas phase equilibrium" and "the final equilibrium" or "the gas–solid equilibrium". By the first we mean the equilibrium among the gas phase species excluding any condensed phases. The gas phase equilibrium is determined by the Gibbs free energy minimization excluding the condensed phases. By the second we mean the total equilibrium including the condensed phases, which minimizes the total Gibbs free energy of the system.

The detailed description of this scheme in relation to other driving forces in the CVD process is described elsewhere [8]. The driving force determined by this scheme would be the maximum driving force that can be achieved by the chemical reactions among gases. This scheme will be a good approximation especially when the chemical reactions among gases are sufficiently fast [8,9]. With the suggested scheme, the activity of the species to be deposited can be evaluated quantitatively in terms of the CVD-independent variables such as the temperature, the pressure and the compositions of the reactant gases, and the iso-supersaturation ratio or the iso-activity lines can be introduced into the CVD phase diagram. This scheme is applied to the deposition of silicon in the Si–Cl–H system.

2. Supersaturation ratio for deposition

The following reaction involving three gas and one solid species will be considered:

$$A + B = C_{solid} + D. \quad (1)$$

The supplied gases A and B react to form the solid C, which is to be deposited, and the gas D which diffuses away from the substrate during the process. The species C will be regarded as the gas unless it has the subscript "solid". The gas species are assumed to be ideal so that the fugacity of each gas can be replaced with its partial pressure.

The supersaturation ratio for deposition from the vapor phase is defined as the ratio of the pressure deviated from equilibrium to the equilibrium vapor pressure of the solid [10]. If this definition is extended to the CVD process, the supersaturation ratio, α, for deposition in the CVD process can be written as

$$\alpha = P_C / P_C^f, \quad (2)$$

where P_C is the partial pressure of the species C exerted in the gas phase which has deviated from equilibrium and P_C^f the equilibrium vapor pressure of the solid C. The equilibrium vapor pressure P_C^f is the pressure exerted by the species C in the gas phase in the final equilibrium. The supersaturation is defined as $\alpha - 1$ [10]. Thus, along the phase boundary of the CVD phase diagram, which is equivalent to the equilibrium

solubility line, the supersaturation ratio and the supersaturation are unity and zero, respectively.

P_C^f depends only on temperature. P_C adjacent to the growing surface determines the supersaturation ratio for deposition in the CVD process. Before the reaction of Eq. (1) starts, P_C is zero. As the reaction proceeds, P_C is built up. In order for deposition to take place, P_C in Eq. (2) should be higher than P_C^f. P_C depends not only on the thermodynamic conditions, but also on the kinetics of the chemical reactions. The steady-state value of P_C for the fast chemical reaction will be higher than that for slow one. The maximum value of P_C is determined by the gas phase equilibrium [8,9].

For the ideal gas, the activity is defined as the ratio of the partial pressure of the species in that state to its pressure in its standard state [11]. When the standard state of the species to be deposited is set to be that of its solid phase, the activity of the species C in the gas phase becomes the same as Eq. (2); the activity becomes the supersaturation ratio for deposition.

The maximum supersaturation ratio for deposition can be written as [8,9]

$$\alpha = P_C^*/P_C^f, \tag{3}$$

where the asterisk represents the partial pressure in the gas phase equilibrium. P_C^* will be the limit of the metastability of the species C in the gas phase with respect to the solid C. The driving force for deposition is the difference in chemical potential of the species C between the solid and the gas phases. The maximum driving force for deposition per mole of the species C will be

$$\Delta\mu_C = -RT \ln\left(P_C^*/P_C^f\right). \tag{4}$$

Eqs. (3) and (4) will be valid only when the chemical reactions are sufficiently fast so that the metastable gas phase equilibrium may be maintained adjacent to the growing surface. Katz and Donohue [12] reported previously the same scheme as Eq. (4) for nucleation involving the chemical reactions. The concept similar to Eq. (3) was suggested by Piekarczyk et al. [13], who derived the supersaturation for deposition by comparing the super-equilibrium solubility with the equilibrium solubility of solid in the gas phase [14]. To our understanding, the terminology of "the super-equilibrium" that they used corresponds to "the gas-phase equilibrium" in this paper. The CVD phase diagram describes the region where the concerned phase is stable or not. It can predict whether deposition is possible or not for the composition of the source gases. The phase boundary in the CVD phase diagram normally demarcates the one-phase region of the gas phase and the two-phase region of the gas and the solid phases. In the one-phase region of the gas phase, the supersaturation ratio is less than unity, in which case etching is predicted and in the two-phase region, it is higher than unity, in which case deposition is predicted. Eqs. (3) and (4) are consistent with the CVD phase diagram: deposition or etching will take place depending on whether the overall composition falls in the two-phase (gas + solid) region or in the one-phase region of gas. Along the boundary of the gas/(gas + solid), the driving force for deposition given by Eq. (4) is zero.

3. Deposition of a compound or a solid solution

When the species to be deposited is a compound or a solid solution, the partial pressure or the equilibrium vapor pressure is often difficult to define. For example, some compounds do not have vapor species corresponding to the same stoichiometry of the solid phase. Assume that the compound A_aB_b does not have vapor species of the same stoichiometry. Here, A and B are the elements. From Eq. (3), the supersaturation ratio becomes

$$\alpha = P_{A_aB_b}^*/P_{A_aB_b}^f. \tag{5}$$

However, $P_{A_aB_b}^*$ and $P_{A_aB_b}^f$ do not exist and thus cannot be obtained in the equilibrium calculation. If the gas species that are in equilibrium with the hypothetical $P_{A_aB_b}^*$ and $P_{A_aB_b}^f$ are considered, the supersaturation ratio can be obtained. Consider the following two hypothetical equilibria: one for the gas phase equilibrium and the other for the final equilibrium:

$$a\ A^* + b\ B^* = A_aB_b^*, \tag{6}$$

$$a\ A^f + b\ B^f = A_aB_b^f. \tag{7}$$

From these two equilibria, the following relationship is derived:

$$\frac{P^*_{A_aB_b}}{P^f_{A_aB_b}} = \frac{(P^*_A)^a (P^*_B)^b}{(P^f_A)^a (P^f_B)^b}. \tag{8}$$

P^*_A, P^*_B and P^f_A, P^f_B can be determined in the gas phase equilibrium and in the final equilibrium, respectively. The supersaturation ratio of the compound is expressed by

$$\alpha = \frac{(P^*_A)^a (P^*_B)^b}{(P^f_A)^a (P^f_B)^b}. \tag{9}$$

The driving force for deposition per mole of the compound A_aB_b becomes

$$\Delta\mu = -RT \ln\left(\frac{(P^*_A)^a (P^*_B)^b}{(P^f_A)^a (P^f_B)^b}\right). \tag{10}$$

This result for the compound can be extended to the solid solution by assuming that the stoichiometry coefficients a and b can continuously change within the solid solution range with the restraint that the sum of the stoichiometry is unity, that is $a + b = 1$, which is needed because the driving force is evaluated per mole of the solid solution. For an example, the deposition of silicon carbide by the following overall reaction will be considered.

$$SiH_4 + CH_4 = SiC + 4\,H_2. \tag{11}$$

By considering the gas phase equilibrium and the final equilibrium of this reaction, the supersaturation ratio for deposition of silicon carbide can be obtained in terms of the partial pressures of the other gases in their gas phase and the final equilibriums as

$$\frac{P^*_{SiC}}{P^f_{SiC}} = \frac{P^*_{SiH_4} P^*_{CH_4} (P^f_{H_2})^4}{P^f_{SiH_4} P^f_{CH_4} (P^*_{H_2})^4}. \tag{12}$$

The supersaturation ratio can be obtained from any reactions satisfying the law of mass action. Consider the following simpler hypothetical gas phase and final equilibriums.

$$Si + C = SiC. \tag{13}$$

Since P_{Si} and P_C can be determined by the gas phase and the final equilibria, the supersaturation ratio can be expressed as

$$\frac{P^*_{SiC}}{P^f_{SiC}} = \frac{P^*_{Si} P^*_C}{P^f_{Si} P^f_C}. \tag{14}$$

The supersaturation ratio for deposition of SiC can be determined either by Eq. (12) or by Eq. (14).

4. Supersaturation ratio for deposition in the Si–Cl–H system

The thermodynamic scheme of Eqs. (3) and (4) will be applied to the deposition of silicon. Starting reactant gases may be the mixtures of $SiCl_4$, SiH_4, and H_2. For the overall composition of the reactant gases and the given reactor pressure and the substrate temperature, the gas phase and the final equilibria can be calculated. Consider any reaction which produces silicon. For example, the following reaction is considered.

$$SiCl_4 \longrightarrow Si + 2\,Cl_2. \tag{15}$$

From the gas and the final equilibriums, the following relation can be derived.

$$\frac{P^*_{Si}}{P^f_{Si}} = \frac{P^*_{SiCl_4}}{P^f_{SiCl_4}} \frac{(P^f_{Cl_2})^2}{(P^*_{Cl_2})^2}. \tag{16}$$

The supersaturation ratio for deposition of silicon, α, can be determined from either the left side or the right side of eq. (16). The driving force for deposition per mole of silicon will be

$$\Delta\mu = -RT \ln(P^*_{Si}/P^f_{Si}). \tag{17}$$

Based on Eq. (16), the line along which the supersaturation ratio for deposition or the activity is the same can be drawn in addition to the CVD phase diagram. The lines of the iso-supersaturation ratio can provide additional information compared to the conventional CVD phase diagram such as the effect of the independent CVD variables on the supersaturation ratio for deposition. The dependence of the supersaturation ratio on the CVD processing variables will

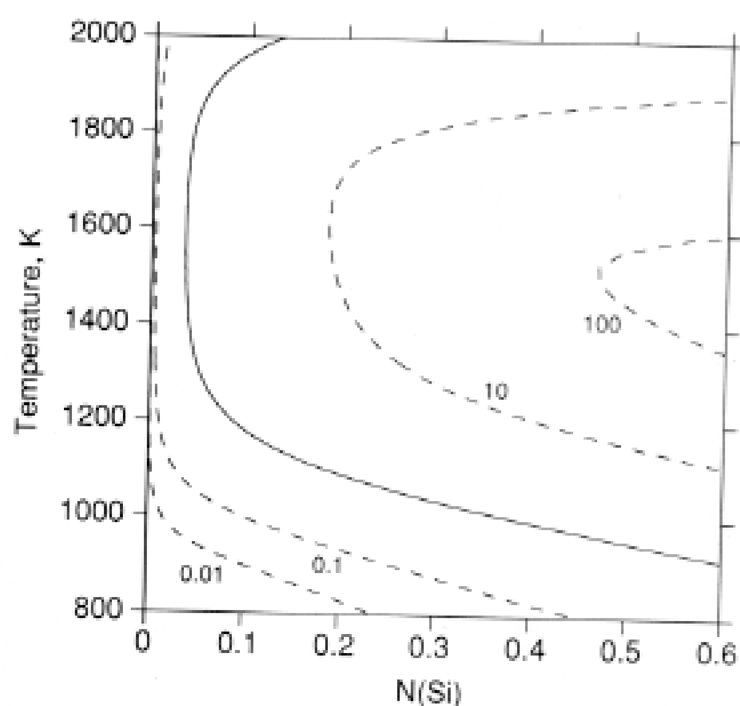
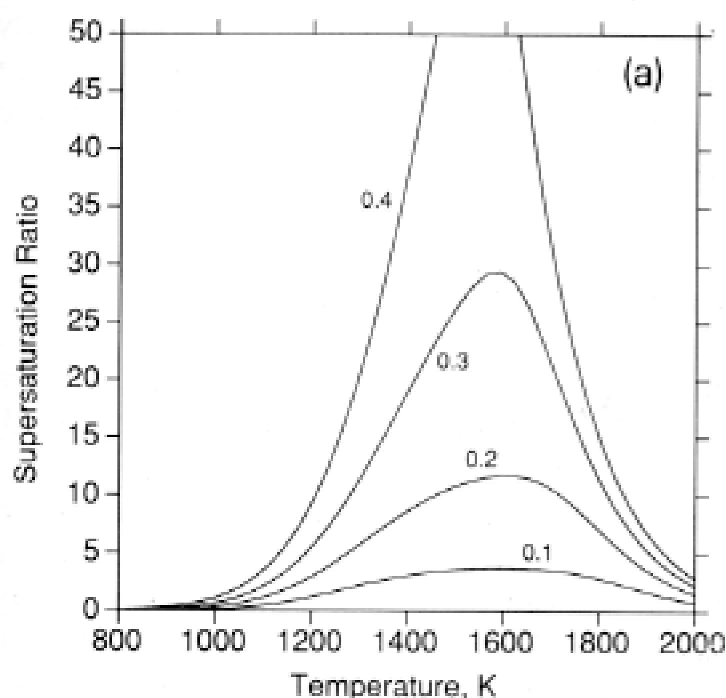


Fig. 1. CVD phase diagram of the Si–Cl–H system at 10666 Pa and composition of $N(\mathrm{H}) = 200$ and $N(\mathrm{Cl}) = 1$. The dashed lines of the iso-supersaturation ratios, 0.1, 0.01, 10, and 100 are calculated from Eq. (16).

also be evaluated. All thermodynamic calculations in this paper are done by the Thermo-Calc software [15] based on the thermodynamic data of the related species in the database of the software.

The CVD phase diagram in the Si–Cl–H system at 10666 Pa is shown in Fig. 1, together with the dashed lines of the iso-supersaturation ratios of 0.1, 0.01, 10, and 100. The solid line in Fig. 1 is the phase boundary of the gas/(gas + solid), which corresponds to the supersaturation ratio of unity. Fig. 1 is the temperature versus $N(\mathrm{Si})$ plot for a fixed mole of $N(\mathrm{Cl}) = 1$ and $N(\mathrm{H}) = 200$, where N means the number of moles. Fig. 1 shows the effect of temperature and $N(\mathrm{Si})$ on the supersaturation ratio. A melting point of the solid silicon is 1687 K and above this temperature the solid silicon is metastable with respect to its liquid. By this scheme, a map of the supersaturation or the driving force for deposition can be made with respect to the independent CVD thermodynamic variables.

Figs. 2a and 2b show the supersaturation ratio versus temperature plot with $N(\mathrm{Si}) = 0.1$, 0.2, 0.3, and 0.4 for the two different amounts of a chlorine content of $N(\mathrm{Cl}) = 1$ and $N(\mathrm{Cl}) = 0.2$, respectively, at 10666 Pa for the fixed mole of $N(\mathrm{H}) = 200$. Note that the ordinate in Fig. 2b is in logarithmic scale. Decreasing the chlorine content from $N(\mathrm{Cl}) = 1$ to $N(\mathrm{Cl}) = 0.2$ increases enormously the supersaturation ratio for deposition. Fig. 2a shows that with increasing $N(\mathrm{Si})$, the supersaturation ratio varies more sensitively with temperatures. The supersaturation tends to be maximum around 1600 K in Fig. 2a. This maxi-



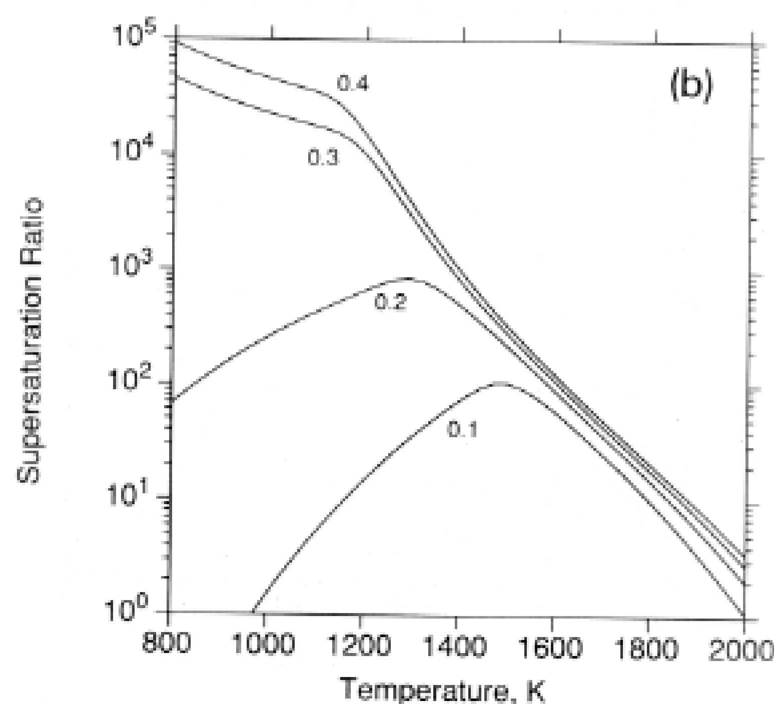


Fig. 2. Plot of the supersaturation ratio versus temperature for $N(\mathrm{Si}) = 0.1$, 0.2, 0.3, and 0.4 for (a) $N(\mathrm{Cl}) = 1$ and (b) $N(\mathrm{Cl}) = 0.2$ at 10666 Pa and $N(\mathrm{H}) = 200$.

mum tends to shift to lower temperatures with increasing content of silicon. When the content of silicon is larger than that of chlorine, the supersaturation ratio monotonically increases with decreasing temperature, as shown in Fig. 2b. Figs. 2a and 2b indicate that the supersaturation ratio depends very strongly on the ratio of silicon to chlorine. When this ratio is sufficiently large, gas phase nucleation above the surface is expected, while when it is sufficiently low, etching instead of deposition of silicon is expected.

Fig. 3 shows the supersaturation ratio versus pressure plot at 1400 K for $N(\mathrm{Si}) = 0.1$, 0.2, 0.3, and 0.4 for a fixed mole of $N(\mathrm{Cl}) = 1$ and $N(\mathrm{H}) = 200$. For $N(\mathrm{Si}) = 0.1$, the supersaturation is insensitive to pressures but with increasing $N(\mathrm{Si})$, it becomes more sensitive to them. In the chosen range of pressures, the supersaturation in the intermediate range around 10^3 Pa tends to be maximum. It should be noted that the deposition rate of silicon is not only related to the supersaturation, but also to the hypothetical partial pressure of silicon [16] because all silicon-containing gas compounds can contribute to deposition.

The driving force for deposition can be evaluated from Fig. 2 by Eq. (17). Fig. 4 shows the driving force versus temperature plot for thermodynamic conditions of Fig. 2a. Depending on the sign of the driving force, the deposition is possible or not. When the driving force for precipitation of the solid from the gas phase reactions is determined, the nucleation kinetics can be evaluated, which are closely related to the microstructural evolution. The dependence of the supersaturation or the driving force on the CVD variables is determined by the relatively simple expressions of Eqs. (16) and (17), regardless of the complexity of the involved chemical reactions. It should be noted that 17 gas species are involved in the Si–Cl–H system.

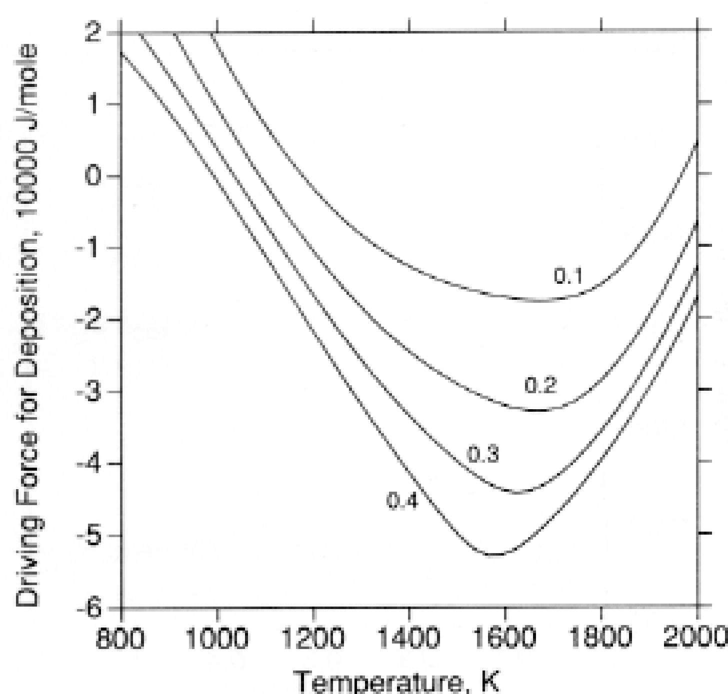


Fig. 4. Plot of the molar Gibbs energy change for deposition versus temperature for $N(\mathrm{Si}) = 0.1$, 0.2, 0.3, and 0.4 at 10666 Pa, $N(\mathrm{H}) = 200$ and $N(\mathrm{Cl}) = 1$.

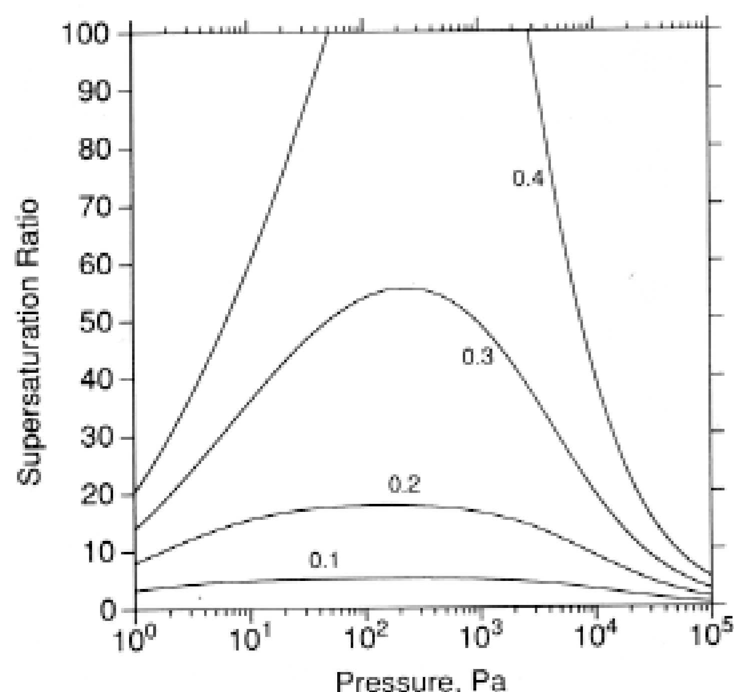


Fig. 3. Plot of the supersaturation ratio versus pressure for $N(\mathrm{Si}) = 0.1$, 0.2, 0.3, and 0.4 at 1400 K, $N(\mathrm{H}) = 200$ and $N(\mathrm{Cl}) = 1$.

5. Consideration of the substrate

In the previous sections, the role of the substrate or the growing surface has not been considered, although the gases normally undergo heterogeneous reactions on the surface. The atoms that are attached to the kink sites mostly come from the adatom by diffusion on the surface not directly from the gas phase. The composition of the adsorbed species can be different from that of the gas phase because the desorption energies are different for each species.

Eq. (2) for the gas phase can be extended to the adsorbed state when the equilibrium adsorption concentration of the species C and the adsorption concentration of C deviated from equilibrium replace P_C^f and P_C in Eq. (2), respectively. Especially, when the gas phase is in equilibrium with the adsorbed species, the chemical potential of the species to be deposited might be the same for the gas phase and the adsorbed state. In this case, the supersaturation ratio given by Eq. (3) can be directly applied to the adsorbed state.

However, the difference in the rates of each species for incoming to and outgoing away from the substrate might make the local composition different from that of the initial reactant gases. Normally the species to be deposited tends to be depleted because it is lost faster by being deposited than the others which have to diffuse away. The depletion would reduce the driving force for deposition. This depletion will be affected by the gas flow rates and the gas flow patterns, the pressure of the reactor and the temperature of the substrate. Non-uniformity of the deposition rate might be related to the non-uniformity of this depletion.

6. Conclusion

The chemical potential of the species to be deposited is suggested to be approximated by the value determined at the gas phase equilibrium where the condensed phase is excluded in the minimization of the Gibbs free energy. This approximation will be valid when the gas phase reactions are sufficiently fast. From this scheme, the iso-supersaturation or iso-activity line can be added to the conventional CVD phase diagram and the dependence of the supersaturation and the driving force for deposition on the CVD independent variables can be evaluated.

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