

# Thermodynamic analysis of the chemical vapor deposition of diamond in the C–H, C–O and C–H–O systems

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Thermodynamic analysis has been made in order to evaluate the effect of the chemical vapor deposition (CVD) processing variables on the driving force for precipitation of carbon from the gas phase in the C–H, C–O and C–H–O systems. It is suggested that when the chemical reactions are involved, the chemical potential of carbon in the gas phase increases monotonically as the chemical reactions proceed and becomes maximum in the metastable gas phase equilibrium. The maximum supersaturation ratio for deposition of diamond is suggested to be the ratio of the partial pressure of carbon in the metastable gas phase equilibrium to the equilibrium vapor pressure of diamond. The lines of the iso-supersaturation ratio are added to the CVD phase diagram. The phase boundary of the CVD phase diagram corresponds to the line of the iso-supersaturation ratio of unity.

## 1. Introduction

The chemical vapor deposition (CVD) of diamond has been studied intensively using various processes such as hot filament CVD [1–4] and plasma CVD [5,6]. From the thermodynamic point of view, the overall process is the precipitation of the solid carbon from the chemical reactions in the gas phase. In order to approach the process on a thermodynamic basis, the driving force for precipitation or deposition of the solid carbon from the gas phase should be determined. The driving force for deposition is only a part of the total driving force that drives the overall CVD process.

Previously, Sommer et al. [7] and Piekarczyk et al. [8] reported the phase diagram of the C–H system in relation to the CVD diamond process. The phase diagram of the CVD system represents the phase equilibrium between the gas and the solid phases. In the CVD phase diagram, the deposition of the solid phase is possible only in the two-phase region where the solid and the gas phases coexist. In the single phase region, where only the gas phase is stable, etching instead of deposition of the solid phase should take place.

The proposed driving force for deposition should be consistent with the phase diagram of the CVD system. Along the line of the solubility limit in the CVD diagram, which is the phase boundary, the driving force and the supersaturation ratio should be zero and unity, respectively. Depending on whether the composition of the initial reactant gases is in the two-phase region or in the single phase region, the driving force should predict deposition or etching.

The purpose of this paper is to provide the thermodynamic scheme to determine the driving force for deposition or etching of diamond in terms of the CVD independent variables. By adding the lines of the iso-supersaturation ratio to the conventional phase diagram of the C–H, C–O and C–H–O systems, the gradient of the driving force with respect to the independent variables can be evaluated. By determining the effect of the process variables on the driving force for deposition, the optimization of the CVD process can be approached systematically.

In a previous report [9], we dealt with the possibility of the dominant nucleation of the metastable diamond. In this paper, only the phase equilibrium between diamond and the gas phase

and the deviation from equilibrium will be pursued. Since the capillary effect of the small carbon cluster is not considered in the thermodynamic treatment of this paper, the possibility of the dominant formation of the metastable diamond will not be dealt with.

## 2. Supersaturation or driving force for deposition

When the given irreversible phenomena are approached on a thermodynamic basis, the degree of the irreversibility is quantitatively described by the driving force for the process. When the state has deviated from equilibrium, the driving force to restore equilibrium is evolved, which is given by the free energy change between equilibrium and the state deviated from equilibrium.

In the CVD diamond process, the reactant gases are a mixture of the hydrocarbon and the hydrogen. Normally the mixture of  $\text{CH}_4$  and  $\text{H}_2$  is used as the reactant gas, and the product species are the various other hydrocarbons, atomic hydrogen, and carbon. The final equilibrium products are composed of 25 gas species and one solid phase of graphite in their due proportions to minimize the Gibbs free energy of the system. The C-H-O system is also commonly used [10], where 40 gas species are involved in the final equilibrium. Since diamond is the metastable phase, it does not appear in the final equilibrium. However, it is possible to evaluate the driving force for the precipitation of diamond from the gas phase.

The Gibbs free energy of the CVD system comprising the various gases and the solid species is expressed by

$$G = \sum_j \mu_j n_j, \quad (1)$$

where  $\mu_j$  and  $n_j$  are the chemical potential and the number of moles of the species  $j$ , respectively. If it is assumed that the gas species follow the ideal gas behavior, the chemical potential of the species  $j$  is given by

$$\mu_j = \mu_j^s + RT \ln P_j, \quad (2)$$

where  $\mu_j^s$  is the chemical potential in the standard state and  $P_j$  is the partial pressure of the species  $j$ .

The thermodynamic calculations minimizing eq. (1) will not allow the carbon chemical potential in the gas to exceed unity in the presence of solid carbon and the driving force for the precipitation of solid carbon cannot be estimated. Therefore, to free this constraint in equilibrium calculations, one must exclude solid carbon in the calculations. The free energy excluding the solid carbon can be expressed as

$$G^{\text{gas}} = \sum_j \mu_j n_j, \quad (3)$$

which is the same as that of eq. (1) except that the species  $j$  does not contain the solid carbon. The free energy of the gas phase given by eq. (3) continues to decrease with reactions. The reactants and products monotonically decrease and increase, respectively, and their behavior is similar to that given by eq. (1). However, one striking difference is that the chemical potential which carbon can have in the system excluding the solid carbon can be much higher than that of the solid carbon, evolving the driving force for deposition.

If  $P_C^{\text{gas}}$  is assumed to be the steady-state value of the partial pressure of carbon maintained during the CVD process, the chemical potential of carbon in the gas phase would be given by

$$\mu_C^{\text{gas}} = \mu_C^s + RT \ln P_C^{\text{gas}}, \quad (4)$$

where  $\mu_C^s$  is the chemical potential of carbon in the standard state.

The chemical potential of carbon in the solid carbon can be expressed in terms of its equilibrium vapor pressure,  $P_C^{\text{VP}}$ , when the standard state is set to be the same as that of the gas phase. It is given by

$$\mu_C^{\text{solid}} = \mu_C^s + RT \ln P_C^{\text{VP}}. \quad (5)$$

From eqs. (4) and (5), the chemical potential difference of carbon between the gas phase and the solid carbon is given by

$$\Delta\mu_C = -RT \ln(P_C^{\text{gas}}/P_C^{\text{VP}}), \quad (6)$$

which is the driving force solely dissipated in the

deposition process. The supersaturation ratio for deposition would be

$$\alpha = P_C^{\text{gas}} / P_C^{\text{VP}}. \quad (7)$$

When the states are not in equilibrium, the thermodynamic calculation is not possible and eqs. (6) and (7) cannot be evaluated. We will restrict our considerations to the case of equilibrium, which might be metastable or stable. The stable equilibrium of the total system can be determined by the minimization of eq. (1). This equilibrium will be called "the final equilibrium" or "the gas-solid equilibrium". The metastable equilibrium among the gas species excluding the solid carbon can be determined by the minimization of eq. (3). This metastable equilibrium will be called "the gas phase equilibrium".

The chemical potential of carbon in the gas phase would increase monotonically with reactions and become maximum in the gas phase equilibrium, which is given by

$$\mu_C^* = \mu_C^s + RT \ln P_C^*, \quad (8)$$

where the asterisk represents the gas phase equilibrium. The maximum chemical potential difference of carbon between the gas and the solid phases, which is the maximum driving force for deposition, is given by

$$\Delta\mu_C = -RT \ln(P_C^* / P_C^{\text{VP}}). \quad (9)$$

The maximum supersaturation ratio becomes

$$\alpha = P_C^* / P_C^{\text{VP}}. \quad (10)$$

This thermodynamic scheme is similar to the well-established way of determining the driving force for precipitation of the solid from the matrix solid solution [11], where the driving force is the free energy change between the final equilibrium state and the metastable equilibrium where the phase to be precipitated is not included. Thus, the metastable state without the concerned phase, the precipitation of which the driving force is referred to, is regarded as the state deviated from equilibrium. The supersaturation ratio given by eq. (10) is consistent with the CVD phase diagram. It is unity along the phase boundary and is less or larger than unity, depending on whether

the composition predicts etching or deposition in the CVD phase diagram. When the thermodynamic condition is changed from deposition to etching, the sign of the driving force given by eq. (9) is correctly reversed and eq. (10) predicts the supersaturation ratio to be less than unity. The supersaturation ratio given by eq. (10) will be valid only when the chemical reactions are sufficiently fast, so that the metastable gas phase equilibrium may be maintained in the gas phase. Otherwise, the partial pressure of carbon in the gas phase,  $P_C^{\text{gas}}$ , will be less than  $P_C^*$  and the supersaturation ratio will be less than that given by eq. (10).

Sommer et al. [7] and Wang et al. [12] developed a thermodynamic analysis of the CVD diamond based on the quasi-equilibrium model, where the non-equilibrium steady state depositions of diamond and graphite are analyzed using equilibrium thermodynamics. They calculated the solubility limit of carbon for diamond, which corresponds to the line of the iso-supersaturation ratio of unity for diamond calculated by eq. (10) in this paper. Piekarczyk et al. [8,13] defined the supersaturation in the CVD diamond system, which is similar in concept to eq. (10). Previously, Katz and Donohue [14] suggested a similar scheme in treating the nucleation when chemical reactions are involved.

With the driving force and the supersaturation ratio given by eqs. (9) and (10), respectively, the iso-driving force line or the iso-supersaturation ratio lines can be added to the conventional CVD phase diagram. The phase boundary in the CVD phase diagram corresponds to the supersaturation ratio of unity. In the following evaluation of the iso-supersaturation ratio lines in the C-H, C-O and C-H-O systems, we will assume that the gas phase reactions are sufficiently fast and that the maximum supersaturation is maintained in the CVD process.

### 3. C-H system

Normally, in the filament CVD process of the diamond film, various forms of hydrocarbon diluted by hydrogen are used as reactants [15]. The



thermodynamic independent variables in the process are the composition ratio of carbon to hydrogen, the chamber pressure and the substrate temperature. Based on the supersaturation ratio described by eq. (10), the effect of these variables can be evaluated in terms of their effect on the partial pressure of carbon in the gas phase equilibrium. Depending on whether we use the equilibrium vapor pressure of diamond or of graphite, the supersaturation ratio given by eq. (10) would be for precipitation of diamond or for that of graphite. The thermodynamic data of diamond will be used to evaluate the supersaturation ratio for the precipitation of the solid carbon. But the solubility limit of graphite in the gas phase will be evaluated in order to compare with that of diamond. All the thermodynamic analyses were done using the Thermo-Calc software [16].

In fig. 1, the solubility limits of carbon for diamond and graphite, which corresponds to the supersaturation ratio of unity, are drawn as the solid and the dashed lines, respectively, with the other lines of the iso-supersaturation ratio in the temperature versus composition plot of the C-H system for the total pressure of 2700 Pa. The ordinate represents the carbon fraction with respect to hydrogen. The supersaturation ratio, which is the ratio of the partial pressure of carbon in the metastable gas phase equilibrium to the equilibrium vapor pressure of diamond, be-

comes of the same value as the activity of carbon when diamond is set to be the standard state. Fig. 1a shows the region of the relatively high carbon content and thus the line of the iso-supersaturation ratio as high as 100, while fig. 1b shows mainly the undersaturated region of the low carbon content and the line of the iso-supersaturation ratio as low as 0.01.

The lines of the iso-supersaturation ratio in fig. 1 together with eqs. (9) and (10) provide additional information compared to the previous phase diagram of the C-H system [7,8]. While the conventional CVD phase diagram just predicts the deposition or the etching for the given thermodynamic condition, the lines of the iso-supersaturation ratio in fig. 1 or eqs. (9) and (10) permit evaluating the driving force for deposition or etching for the given thermodynamic condition.

Fig. 1a shows that the gradient of the driving forces for the deposition of the solid carbon is steepest with the carbon fraction for the temperatures being around 1300 K. Thus, the driving force for deposition will be sensitively affected by the carbon fraction around 1300 K. Fig. 1b shows that the driving force for etching is very sensitive to the carbon fraction around the temperature of 1700 K. With a further decrease of the carbon fraction, the driving force for etching will become much larger and in the absence of carbon, the

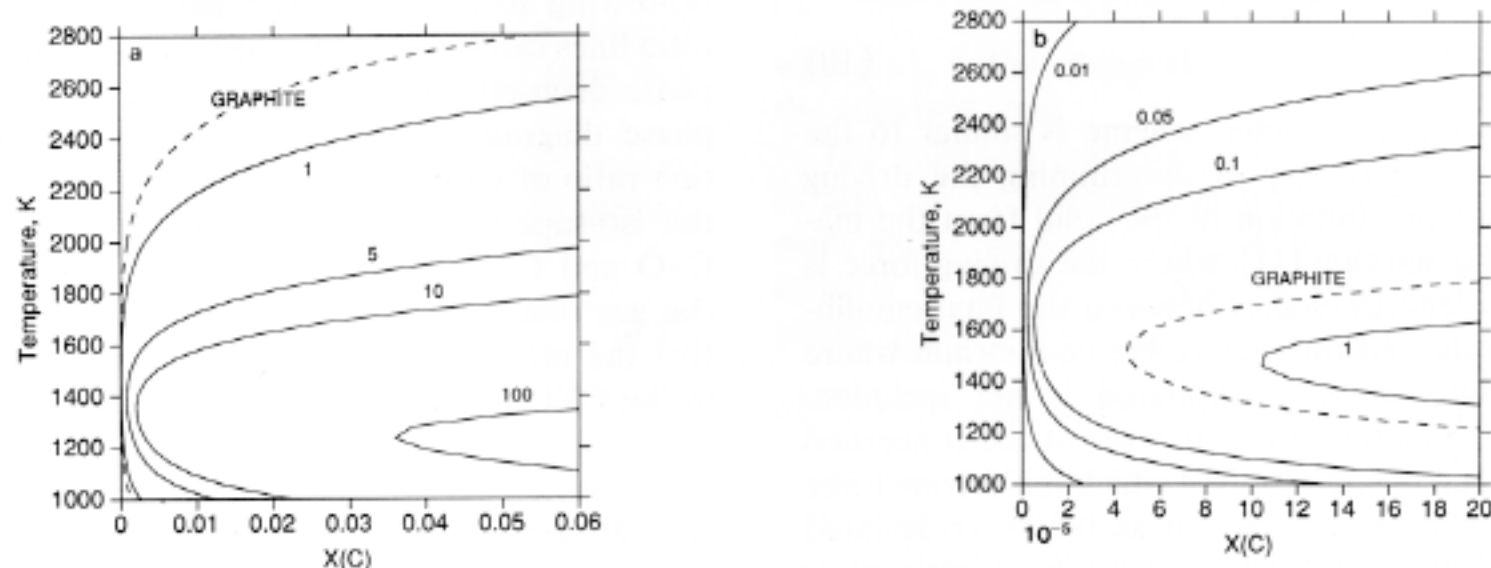


Fig. 1. The temperature versus pressure plot of the C-H system at 2700 Pa showing several lines of the iso-supersaturation ratio in the composition range of the mainly supersaturated region (a) and the mainly undersaturated region (b). The dashed line is the solubility limit of carbon for graphite. The line of the iso-supersaturation ratio of unity corresponds to the solubility limit of carbon for diamond. The value of the  $x$ -axis in (b) should be multiplied by  $10^{-5}$ .

driving force for etching will go to infinity. In the temperature versus composition plot in the C-H system, the lines of the iso-supersaturation ratio are a C-shaped curve, which means that the driving force for deposition or etching will be relatively insensitive to the carbon content in the high and low temperatures, but sensitive to it in the intermediate temperatures.

Fig. 2 shows the pressure versus composition plot at 1200 K which is often adopted as the substrate temperature in the CVD diamond process. The lines of the iso-supersaturation ratio from 0.1 to 100 are calculated. The dashed line is the solubility limit of carbon in the gas phase with respect to graphite. As the pressure decreases, the driving force for deposition tends to increase, and this increase is sensitive to the carbon content at low pressures. It should be noted that fig. 2 is the isothermal section at 1200 K. At different temperatures, the shape of the curves will be different.

#### 4. C-O and C-H-O systems

Thermodynamically, the chemical potential of carbon is produced in the C-O system as well as in the C-H system. However, the C-O system is

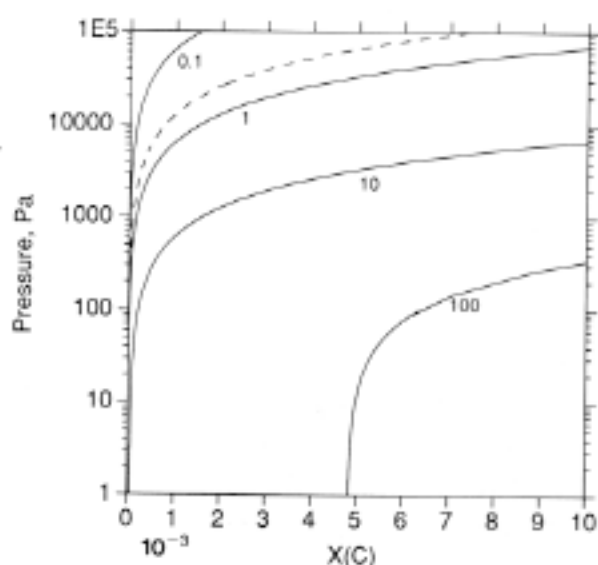


Fig. 2. The pressure versus composition plot of the C-H system at 1200 K showing several lines of the iso-supersaturation ratio. The dashed line is the solubility limit of carbon for graphite. The value of the  $x$ -axis should be multiplied by  $10^{-3}$ .

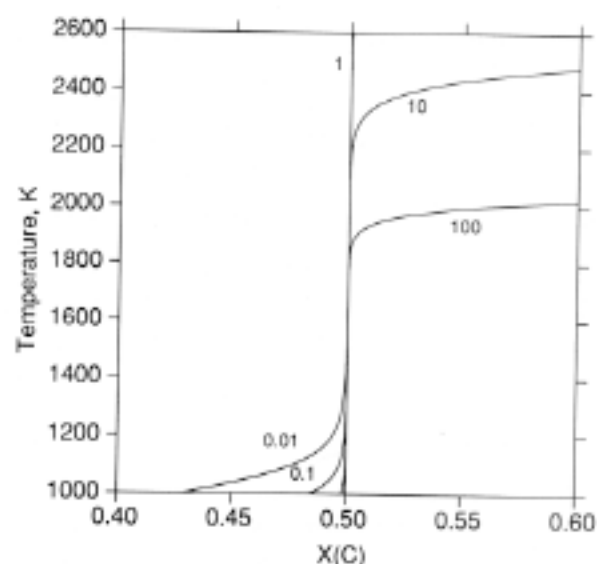


Fig. 3. The temperature versus composition plot of the C-O system at 2700 Pa showing five different lines of the iso-supersaturation ratio.

not used for the CVD diamond process. In this section, the reason why the C-O system is inappropriate for the CVD diamond process will be approached on a thermodynamic basis. The growth of the CVD diamond in the C-H-O system is frequently reported [10]. Bachmann [10] compiled the previously reported diamond CVD data and suggested the diamond deposition map in the C-H-O system, where irrespective of the sources of reactants and method of processes, deposition of diamond is possible along the narrow range of composition centered on the carbon monoxide line and in the carbon-rich side of this range the non-diamond deposition results and in the oxygen-rich side no growth results. In terms of the dependence of the driving force for deposition of carbon on the CVD process variables, the C-H-O system is intermediate between the C-H and the C-O systems. These aspects will be approached by the thermodynamic analysis.

We will analyze the C-O system first and then extend the result to the C-H-O system. Fig. 3 shows the temperature versus composition plot of the C-O system. Five different lines of iso-supersaturation ratios, 0.01, 0.1, 1, 10 and 100, are calculated at a pressure of 2700 Pa. There are the striking differences in the composition dependence on the driving force between C-H and C-O systems. The chemical potential of carbon in the gas phase is much more sensitive to the

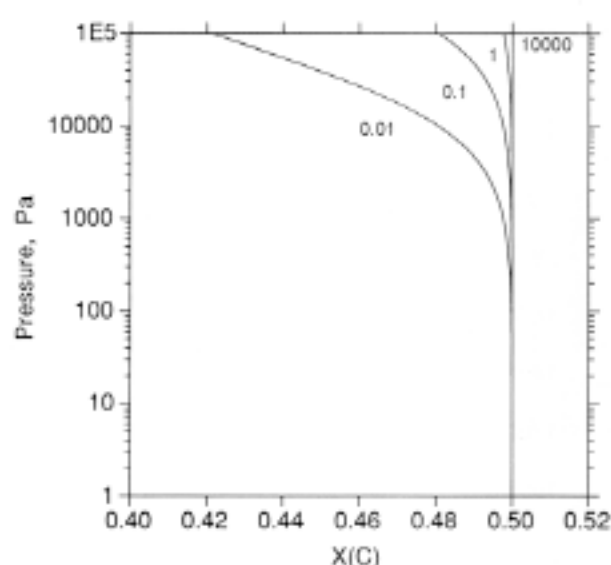


Fig. 4. The pressure versus composition plot of the C-O system at 1200 K showing four different lines of the iso-supersaturation ratio.

carbon content in the C-O system. Fig. 3 shows that at the temperatures lower than 1800 K, the supersaturation ratio is very sensitive to the carbon content and it increases abruptly to high values when the carbon fraction deviates in a very small amount above the carbon monoxide composition of C:O = 1:1. Note that the range of the carbon fraction in the ordinate is from 0.4 and 0.6. In the high temperature range above 1400 K, the driving force for etching is very sensitive and

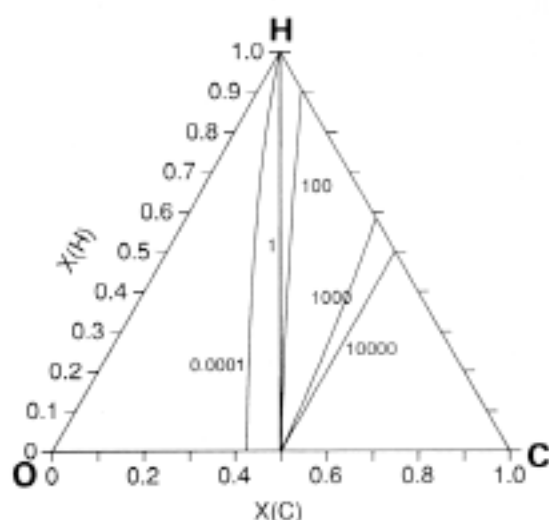


Fig. 5. The ternary diagram of the C-H-O system at 1200 K under 2700 Pa showing five different lines of the iso-supersaturation ratio.

the small deficiency of carbon from the composition of C:O = 1:1 results in the very high driving force for etching.

Fig. 4 shows the pressure versus composition plot at a temperature of 1200 K. At 1200 K, the driving force for deposition is expected from fig. 3 to be extremely sensitive to the composition, while the driving force for etching is relatively less sensitive. These expectations are revealed in fig. 4. Note that the line of the iso-supersaturation ratio of 10000 coincides with the carbon monoxide line, while the line of the iso-supersaturation ratio of 0.01 deviates relatively wide from the carbon monoxide line.

Because of this sensitive dependence of the composition on the driving force in the C-O system, the processing condition for the appropriate driving force for the diamond deposition might be extremely difficult to control in the C-O system compared to the C-H system. This sensitive variation of the driving force when there is a deviation from the composition of C:O = 1:1 might be related to two facts: one is the very high value of the free energy of formation of carbon monoxide and the other is that very few species are involved in the C-O system. The thermodynamic calculations of the C-O system indicate that the carbon monoxide is the only major species with a small amount of carbon dioxide,  $C_2O$ , and  $C_3O_2$ . The rest of the species are oxygen and carbon. This is in contrast with the case of the C-H system, where various forms of hydrocarbon exist in an appreciable amount.

When the amount of carbon is larger than that of oxygen, most of the excess carbon after forming the carbon monoxide is used to build up the chemical potential of carbon in the gas phase, resulting in the very high values of the chemical potential of carbon in the gas phase. When the amount of carbon is less than that of oxygen, almost all carbon is consumed to make the carbon monoxide, making the chemical potential of carbon in the gas phase extremely small. These tendencies would be relieved when hydrogen is added to the C-O system.

Fig. 5 shows the C-H-O ternary plot at 1200 K under 2700 Pa. In the overall compositions, the driving force for deposition and etching is sensi-

tive to the relative ratio of carbon to oxygen. Increasing hydrogen content tends to reduce this tendency. These thermodynamic aspects might be related to the reports that diamond deposition is possible along the narrow composition region near the carbon monoxide line in the C-H-O systems [10].

The line of the solubility limit of the solid carbon in the gas phase in the C-H-O diagram or the line of the iso-supersaturation ratio of unity is along the carbon monoxide, as shown in fig. 5 at a substrate temperature of 1200 K. The carbon-rich and oxygen-rich sides are the regions for deposition and etching, respectively. The five different lines of iso-supersaturation ratios are shown. It should be noted that the lines of the iso-supersaturation ratio as high as 100 and as low as 0.0001 are close to the carbon monoxide lines.

Prijaya and Angus [17] also reported the thermodynamic analyses in the C-H-O system, but the results of their thermodynamic calculations seem to be somewhat different from those in this paper. One possibility of the difference is that they included only fifteen gas species in the calculation, while forty gas species are involved in the C-H-O system. In this paper, all thermodynamic calculations are done by Thermo-Calc software [16] and the thermodynamic data of all species are from the database of the software.

## 5. Conclusion

We provide a thermodynamic scheme to determine the driving force for deposition or etching in the CVD diamond processing. By this scheme, the effect of each process variable on the driving force can be evaluated. The maximum supersaturation ratio is suggested to be the ratio of the partial pressure of the species to be deposited in the metastable gas phase equilibrium to its equilibrium vapor pressure.

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## References

- [1] B.V. Derjaguin and D.B. Fedoseev, Growth of Diamond and Graphite from the Gas Phase (Nauka, Moscow, 1977) ch. 4.
- [2] S. Matsumoto, Y. Sato, M. Tsutsumi and N. Setaka, *J. Mater. Sci.* 17 (1982) 3106.
- [3] S. Matsumoto, Y. Sato, M. Kamo and N. Setaka, *Japan. J. Appl. Phys.* 21 (1982) L183.
- [4] A. Sawabe and T. Inuzuka, *Thin Solid Films* 137 (1986) 89.
- [5] K. Suzuki, A. Sawabe, H. Yasuda and T. Inuzuka, *Appl. Phys. Letters* 50 (1987) 728.
- [6] M. Kamo, Y. Sato, S. Matsumoto and N. Setaka, *J. Crystal Growth* 62 (1983) 642.
- [7] M. Sommer, K. Mui and F.W. Smith, *Solid State Commun.* 69 (1989) 775.
- [8] W. Piekarczyk, R. Messier, R. Roy and C. Engdahl, *J. Crystal Growth* 106 (1990) 279.
- [9] N.M. Hwang, G.W. Bahng and D.N. Yoon, *Diamond and Related Materials* 1 (1992) 191.
- [10] P.K. Bachmann, D. Leers and H. Lydtin, *Diamond and Related Materials* 1 (1991) 1.
- [11] M. Hillert, in: *Lectures on the theory of Phase Transformations*, Ed. H.I. Aaronson (AIMMPE, New York, 1982).
- [12] R.B. Wang, M. Sommer and F.W. Smith, *J. Crystal Growth* 119 (1992) 271.
- [13] W. Piekarczyk, R. Roy and R. Messier, *J. Crystal Growth* 98 (1989) 765.
- [14] J.L. Katz and M.D. Donohue, *J. Colloid Interface Sci.* 85 (1982) 267.
- [15] K.E. Spear, *J. Am. Ceram. Soc.* 72 (1989) 171.
- [16] B. Sundman, B. Jansson and J.O. Andersson, *CALPHAD* 9 (1985) 153.
- [17] N.A. Prijaya and J.C. Angus, presented at *Diamond Films '92*, Heidelberg, 1992.