Driving force for deposition in the chemical vapour deposition process

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Chemical vapour deposition (CVD) is widely used in preparing various kinds of films, especially for solid-state devices [1–4]. In this process various gaseous, liquid and solid chemicals are employed as sources of the elements of which the thin film is to be made. Thermodynamic approaches in CVD allow prediction of the behaviour of the process under various conditions and thus provide some guidelines for optimizing the process.

Although CVD is widely used, the driving force for its deposition is not clearly defined, and it seems it is not distinguished from the driving force for the chemical reaction [2–5]. The driving force for deposition should be defined as the chemical potential difference of the species to be deposited between the gas and the solid states. Katz *et al.* [6] reported a similar concept in which they analysed the driving force for nucleation when the chemical reactions were involved. The purpose of this letter is to clarify the driving force for deposition in CVD, which is distinguished from the driving force for the chemical reaction.

We will show that the chemical potential of the species to be deposited is negative infinity before the chemical reaction starts and continues to increase as the chemical reaction proceeds. Deposition is not possible until the chemical potential of the species becomes higher than that of its solid phase, which is achieved when the chemical reaction proceeds further than the solid–gas equilibrium. This result does not depend on whether the gas phase reactions take place above or on the growing surface.

In order to compare the driving force for the chemical reaction and the driving force for deposition, the following reaction involving three gas species and one solid species will be referred to

$$A + B \rightarrow C_{\text{solid}} + D \qquad (1)$$
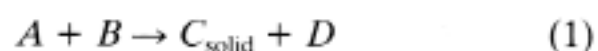
where the supplied gases A and B react to form the solid C, which is to be deposited, and the gas D, which diffuses away from the substrate during the process. If the gaseous species are assumed to be ideal, the fugacities of the gases can be replaced with their partial pressures. And when the standard state of the solid phase is set to be the same as that of the gas species, the activity of the solid phase would be its equilibrium vapour pressure.

In the conventional treatment [2, 3] the driving force or the supersaturation for CVD was defined by the same approach as is used for growth from the melt. Thus, the driving force was regarded as the difference in thermodynamic potential between the left and the right sides of Equation 1 and is given as

$$\Delta\mu = -RT \ln \frac{P_A^i P_B^i P_C^f P_D^f}{P_A^f P_B^f P_C^i P_D^i}, \qquad (2)$$

and the supersaturation becomes

$$\alpha = \frac{P_A^i P_B^i P_C^f P_D^f}{P_A^f P_B^f P_C^i P_D^i} \qquad (3)$$

where the superscripts 'i' and 'f' represent the initial state and final equilibrium states, respectively. (These notations will have the same meaning throughout this report.) Before the chemical reaction starts, the partial pressures of the gas state of C and D (P_C^i and P_D^i in Equations (2) and (3)) are zero, and thus the driving force and the supersaturation ratio go to infinity. This infinite driving force and supersaturation come from the entropy of mixing between the pre-existing and the newly formed species. The infinite driving force and supersaturation will decrease markedly as soon as the chemical reaction starts.

In reality, this infinite driving force is not used. Instead, the supersaturation ratio is expressed only in terms of the reactant gases [4] and when the gas species D is also supplied, the following supersaturation ratio is used [5]

$$\alpha = \frac{P_A^i P_B^i P_D^f}{P_A^f P_B^f P_D^i} \qquad (4)$$

We think that the conventional use of Equation (4) instead of equation (3) is to avoid the difficulty of the infinite supersaturation.

It should be noted that the supersaturation ratio in Equations (3) and (4) is related to the chemical reaction, which should be distinguished from the driving force for deposition. In order to define the driving force for deposition, the free energy change between the initial and the final states should be considered. In order to simplify the argument, the total number of moles of the system is assumed not to change during the chemical reaction; otherwise,

the molar Gibbs free energy would be difficult to define during the chemical reaction.

In the initial state before the chemical reaction starts, species C and D are absent and the molar free energy would be

$$G_m^i = X_A^i \mu_A^i + X_B^i \mu_B^i, \tag{5}$$

where X_A^i and X_B^i are initial mole fractions of A and B. It should be noted that even though μ_C^i and μ_D^i go to negative infinity, X_C^i and X_D^i are zero and their contribution to the free energy is zero.

As the chemical reaction proceeds, the fractions of A and B will decrease and those of C and D will increase. In the final equilibrium, the molar free energy becomes

$$G_m^f = X_A^f \mu_A^f + X_B^f \mu_B^f + X_C^f \mu_C^f + X_D^f \mu_D^f \tag{6}$$

The free energy change between the initial and the final states becomes

$$\Delta G_m = G_m^f - G_m^i \tag{7}$$

ΔG_m would be the driving force for the overall CVD process in terms of one mole of the system. ΔG_m in Equation (7) should be distinguished from $\Delta \mu$ in Equation (2), which represents the driving force for the forward chemical reaction.

The driving force ΔG_m can be decomposed into four contributions from each species of A, B, C and D in terms of the variations of their chemical potentials. The chemical potential of any species, 'j', is expressed by

$$\mu_j = \mu_j^o + RT \ln P_j, \tag{8}$$

where μ_j^o and P_j are the chemical potential of the standard state and the partial pressure, respectively. The chemical potential of each species increases logarithmically with its partial pressure, and as the reaction goes on the chemical potentials of A and B continue to decrease while those of C and D continue to increase.

Among contributions from four species to the free energy change ΔG_m in Equation (7), two contributions from species A and B are negative and those from species C and D are positive. The chemical potential of species C increases from negative infinity at the initial state to the chemical potential of the solid at final equilibrium. This means that by comparing only the initial state and final equilibrium, the driving force is for etching rather than deposition of species C. It appears to be contradictory but it is directly derived from Equations 5–7. In order for deposition to be possible, the chemical potential of the species C in the gas phase should be higher than that of the solid, since the driving force for deposition would be the chemical potential difference of species C between the gas phase and the solid state. Considering Equations 5–7, it is evident that species C is undersaturated with respect to its solid, which is the final equilibrium product of species C.

But what actually happens in CVD is that the chemical reaction does not stop at the final solid–gas equilibrium but proceeds further, and as a result species C in the gas phase becomes supersaturated with respect to its solid. The limit that the reaction can proceed to is the gas phase equilibrium, which is metastable with respect to the solid–gas equilibrium. Thus, species C in the gas phase equilibrium has the maximum supersaturation for deposition.

As mentioned earlier, when the standard state of the solid phase is set to be that of the gas, the activity of the solid will be replaced by its equilibrium vapour pressure. The chemical potential of C in the solid state will be expressed as

$$\mu_{C_{solid}} = \mu_C^o + RT \ln P_C^{v.p.}. \tag{9}$$

where 'v.p.' represents the equilibrium vapour pressure of the solid C. The chemical potential of C in the gas phase will be expressed as

$$\mu_{C_{gas}} = \mu_C^o + RT \ln P_C^{gas} \tag{10}$$

The chemical potential difference will be

$$\Delta \mu_C = -RT \ln \frac{P_C^{gas}}{P_C^{v.p.}} \tag{11}$$

and the supersaturation ratio will be

$$\alpha = \frac{P_C^{gas}}{P_C^{v.p.}} \tag{12}$$

Thus, in order for deposition to be possible, the partial pressure of C in the gas phase should be higher than its equilibrium vapour pressure. Initially, C is absent and, thus, the partial pressure of C in the gas phase will be lower than its equilibrium vapour pressure. In this case, the supersaturation ratio in Equation (12) is less than unit, resulting in undersaturation, and etching of the solid C will take place instead of being deposited. Only when the chemical reaction proceeds to such a degree that the supersaturation in Equation (12) becomes larger than unity does species C in the gas phase become metastable or supersaturated with respect to its solid.

Both thermodynamics and kinetics should be considered to determine P_C^{gas} in Equation (12). Depending on the kinetics of CVD under the given thermodynamic condition, P_C^{gas} will vary from zero to P_C^*, which is the partial pressure of C in the gas phase equilibrium. When the gas phase reaction on the growing surface is sufficiently fast, gas phase equilibrium will be maintained during processing. The maximum supersaturation ratio can be expressed as

$$\alpha_{max} = \frac{P_C^*}{P_C^{v.p.}} \tag{13}$$

where P_C^* represents the partial pressure of C in the gas phase equilibrium. The gas phase equilibrium can be determined by excluding the condensed phases of species C in considering Gibbs free energy minimization. The behaviour of the supersaturation ratios in Equation (12) and Equation (4) is quite different in each case; the ratio in Equation (12) is minimum before the chemical reaction starts and continues to increase as the chemical reaction

proceeds, while the ratio in Equation (4) varies in the reverse way.

Comparison of the real CVD processing data between Equations (4) and (13) reveals that the supersaturation ratio estimated from Equation (4) is usually much higher than that from Equation (13). A marked difference between these two supersaturation ratios arises when the initial composition of the supplied gas species predicts no solid phase in the final equilibrium. In this case, the supersaturation ratio from Equation (4) is still higher than unity while that from Equation (13) is less than unity, which result is consistent with the prediction of the absence of the solid phase in the final equilibrium.

It should be noted that the major conclusion of this report does not depend on whether the gas phase reactions take place above the substrate or on the substrate. By the newly suggested supersaturation, when the gas phase equilibrium is assumed to be maintained during CVD, the effects of the various independent variables in the process such as pressure, substrate temperature and the composition of the supplied gases, can be easily estimated in terms of their effect on the partial pressure of the species to be deposited in the gas phase equilibrium, regardless of how many gas species are involved in the process.

References
1. C. E. MOROSANU, in "Thin films by chemical vapor deposition" (Elsevier, Amsterdam, 1990) p. 91.
2. J. BLOEM, *J. Cryst. Growth* **50** (1980) 581.
3. G. B. STRINGFELLOW, in "Crystal growth of electronic materials", edited by E. Kaldis (North-Holland, Amsterdam, 1985) p. 248.
4. W. A. BRYANT, *J. Mater. Sci.* **12** (1977) 1285.
5. L. CHAPUT, R. CADORET and M. MIHAILOVIC, *J. Cryst. Growth* **112** (1991) 691.
6. J. L. KATZ and M. D. DONOHUE, *J. Colloid Interface Sci.* **85** (1982) 267.