Application of thermodynamics to chemical vapor deposition

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Abstract

Processing of thin films by chemical vapor deposition (CVD) is accompanied by chemical reactions, in which the rigorous kinetic analysis is difficult to achieve. In these conditions, thermodynamic calculation leads to better understanding of the CVD process and helps to optimise the experimental parameters to obtain a desired product. A CVD phase diagram has been used as guide lines for the process. By determining the effect of each process variable on the driving force for deposition, the thermodynamic limit for the substrate temperature that diamond can deposit is calculated in the C-H system by assuming that the limit is defined by the CVD diamond phase diagram. The addition of iso-supersaturation ratio lines to the CVD phase diagram in the Si-Cl-H system provides additional information about the effects of CVD process variables.

Keywords: thermodynamic limit, substrate temperature, C-H, Si-Cl-H

Introduction

Chemical vapor deposition (CVD) is an irreversible process which dissipates the free energy. The direction of the irreversible process is toward an equilibrium state, in which the free energy is minimized. Because the thermodynamic function such as free energy or entropy is a state function, the application of the thermodynamic concept to the CVD process is a relatively simple and a fundamental way to the systematic approach of the process. The optimization of the process with respect to the microstructural evolution can be made systematically by the knowledge of the related thermodynamic property.

In order to apply the thermodynamics to the CVD process, the first step should be to identify the driving force for the process. Many irreversible processes are involved in the CVD process such as chemical reactions, spontaneous mixing, diffusion and nucleation. Each irreversible process is associated with its driving force or the free energy change. The irreversible process we are most interested in is the precipitation process of the solid phase from the gas phase. Thus, we need to identify the free energy dissipated in the precipitation or the deposition process. Once the driving force for precipitation or deposition is identified, the possibility for deposition or etching can be estimated; besides, the nucleation rate can be estimated and the microstructure evolution of the films can be predicted.

In order to define the driving force for deposition, the supersaturation ratio for precipitation should be defined first. According to Hwang et al. [1,2], this supersaturation ratio should be defined as the ratio of the fugacity of the species to precipitate in the gas phase adjacent to the growing surface to that of the solid phase. If the gas follows the ideal gas law, the fugacity can be replaced by the partial pressure. In this case, the supersaturation ratio becomes the ratio of the partial pressure in the gas phase adjacent to the growing surface to the equilibrium vapor pressure of the solid phase. If the species to deposit is designated 'A', the supersaturation ratio is expressed as

$$\alpha = \frac{P_A}{P_A^{eq}} \qquad (1)$$

where P_A is the partial pressure of 'A' adjacent to the growing surface and P_A^{eq} is the equilibrium vapor pressure of the solid 'A' at the given temperature. During the CVD process, the partial pressure, P_A, would have a steady-state value. P_A depends on the chemical reaction. Usually, P_A increases with increasing rate of chemical reactions and becomes maximum when the gas phase equilibrium is maintained. The gas phase equilibrium is attained when the gas phase reaction is sufficiently fast without the precipitation of solid. This state is the maximum deviation from the final equilibrium and defines the maximum supersaturation ratio or the maximum driving force for precipitation. This value of supersaturation ratio can be easily

determined by the metastable gas phase equilibrium, in which the Gibbs free energy is minimized excluding all the condensed phases.

$$\alpha_{max} = \frac{P_A^{gas}}{P_A^{eq}} . \quad (2)$$

This value can be approximated as the supersaturation ratio during the process if the gas phase nucleation does not take place. The driving force for precipitation is derived as

$$\Delta\mu = -RT \ln \alpha_{max} . \quad (3)$$

This driving force is the difference in chemical potential of the species 'A' between the gas and the solid phases.

With these thermodynamic schemes for determining the supersaturation ratio and the driving force for precipitation, the thermodynamic calculation will be applied to the well-known systems of C-H and Si-Cl-H. The first system is for the deposition of diamond in a low pressure synthesis of diamond and the second system is for the deposition of silicon, which is widely used in the field of microelectronics. In the C-H system, the lower limit of the substrate temperature for diamond deposition will be determined. In the Si-Cl-H system, the iso-supersaturation ratio will be determined, which can be a useful guideline for the selective epitaxial growth. Thermodynamic calculations presented in this paper were carried out using the Thermo-Calc software [3].

Lower limit of substrate temperature for deposition of diamond

The most popular choice of a gas mixture to deposit diamond by CVD is hydrogen with a small percentage of methane. The mixture of CH_4 - H_2 produces various kinds of the other gas compounds. In the thermodynamic analysis of the C-H system, 35 gas species were considered.

In this paper, the growth mechanism will not be considered and the thermodynamic analysis will be the primary concern. The growth mechanism of the CVD diamond was pursued in other papers [5,6]. The determination of the lower limit of the substrate temperature will be valid independent of the growth mechanism.

Figure 1 shows the thermodynamic calculations based on the suggested scheme in the introduction. The calculations show the dependence of the driving force on the temperature for the two different pressures of 101325 Pa and 10.1325 Pa for the gas mixture of 1%CH_4-99%H_2.

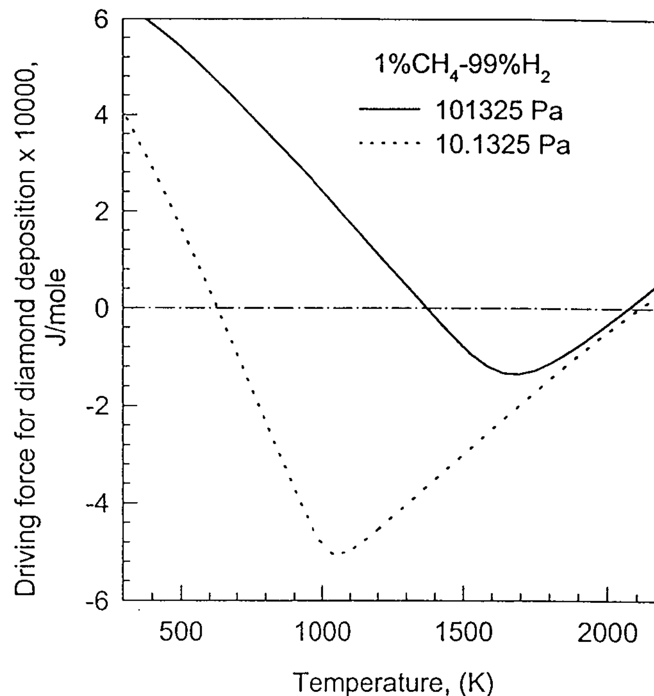

Figure 1 Driving force for diamond deposition versus temperature in the C-H system.

The driving force predicts deposition and etching when it is negative and positive, respectively. If this thermodynamic scheme is correct, the thermodynamic region where deposition is predicted by the negative driving force should correspond to the two-phase region of solid and gas in the CVD phase diagram. At the same time, the thermodynamic region where etching is predicted by the positive driving force should correspond to the one-phase region of gas in the CVD phase diagram. It is confirmed that the thermodynamic region for deposition and etching corresponds exactly to the two-phase and the one-phase regions in the CVD phase diagram, respectively.

At atmospheric pressure, the driving force for diamond deposition decreases with temperature and becomes zero for temperatures of 1375 K and 2025 K. Thus, in order to deposit diamond, the temperature range should be between these two values. The lower limit for the substrate temperature is 1375 K. A maximum driving force for diamond deposition is shown to be at ~1700 K. If the operating pressure is reduced to 10.1325 Pa, the temperature range for a diamond deposition becomes between 600 K and 2100 K (dashed curve). In this case, the lower limit of the substrate temperature is 600 K, which is about 735 K lower than that of the atmospheric pressure. These thermodynamic analyses indicate that the lower limit of the substrate temperature for diamond deposition should decrease with increasing the pressure of the CVD reactor, which is in agreement of the general experimental observations in the C-H system.

It can be said from the above analysis that for the low temperature deposition, the total pressure should be decreased. However, it should be noted that the pressure decrease leads to the decrease in the deposition rate. Besides, the pressure decrease has an additional adversary effect. In the case of the hot-filament reactor, The pressure decrease will increase the evaporation rate of the filament because of the reduced adsorption on the filament. In the case of the microwave plasma, the reactor pressure decrease would reduce the plasma density or make it difficult to stabilize the plasma. Therefore, the C-H system is not appropriate for the lower substrate temperature. If the C-H-O system is used, however, the substrate temperature can be decreased markedly without decreasing pressure. The detailed thermodynamic analysis of the C-H-O system will be published elsewhere [7].

Thermodynamic analysis for silicon deposition by CVD

The CVD process is widely used to deposit silicon thin films. The thermodynamic analysis of the Si-Cl-H system has been extensively studied. However, the thermodynamic analysis in this paper adopted the most updated data [3,4]. Besides, with the thermodynamic scheme used in this paper, we can estimate the dependence of the supersaturation on the independent thermodynamic variables in the CVD process. 21 gas species have been considered in order to calculate silicon solubility in the Si-Cl-H system. The iso-supersaturation lines (0.5, 1 and 5) for precipitation of silicon are drawn in Fig. 2. Once the supersaturation ratio is determined, the driving force for precipitation can be evaluated by Eq. (3).

The iso-supersaturation line of unity corresponds to the CVD phase diagram and along this line, the driving force for deposition or precipitation of silicon from the gas phase is zero. Therefore, this line separates the thermodynamic region into two: the gas phase region and the (gas + solid) phase region. In the one phase region of gas, the driving force is for etching and in the two-phase region of gas + solid, the driving force is for deposition. Figure 2 shows that the solubility of silicon in the gas phase is minimal at ~1700 K, which means that if the gas phase nucleation of silicon takes place, the driving force at the substrate temperature becomes for etching.

Conclusion

By applying the suggested thermodynamic scheme to diamond and silicon deposition by CVD, the driving force for deposition and etching could be evaluated in the C-H and the Si-Cl-H system. The dependence of the driving forces and/or supersaturation ratio on the CVD independent variables could also be evaluated.

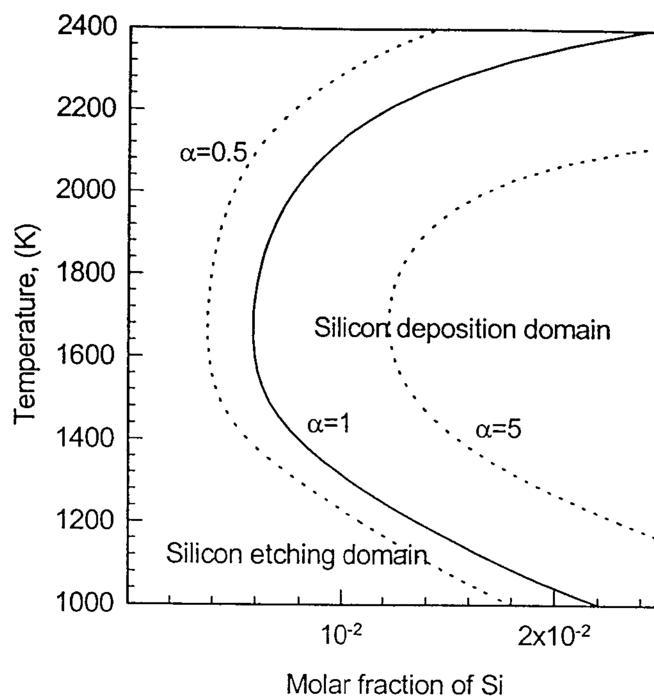

Figure 2 Temperature dependence of the supersaturation ratio on the molar fraction of Si in the Si-Cl-H system with N(Cl)=4, N(H) =95 and the pressure of 101325 Pa.

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