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REACTIVE-FLOW SIMULATION ON THE GROWTH OF CVD DIAMOND

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<Abstract>

Two-dimensional reactive-flow simulations on the growth of diamond in a hot-filament chemical vapor deposition (HFCVD) system were carried out. The model combines equations of the conservation of mass, momentum, energy and chemical species with appropriate boundary conditions. The coupled partial differential equations were solved numerically to determine the gas velocity, temperature and gas-phase composition profiles in a reactor. The model was then used to investigate the effects of CH_4 -source gas- concentration and the filament temperature on the production of CH_3 that is known as the diamond precursor in HFCVD system. From the result, the predicted chemical species concentrations are well agreed with previously measured experimental values and the concentration of CH_3 is shown to increase with increasing CH_4 concentration and the filament temperature. This means that the growth rate of diamond increases also at higher CH_4 concentration and the filament temperature.

CVD 다이아몬드의 성장에 관한 반응유동 전산모사

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<요 약>

열-필라멘트 화학증착법(HFCVD)에 의해 생성된 다이아몬드의 성장에 관하여 2차원 반

응유동 전산모사를 수행하였다. 모델식은 질량, 운동량, 에너지 및 각 화학종들의 보존식을 적절한 경계조건으로 결합하였다. 이 결합된 편미분방정식들을 수치적으로 풀어서 반응기 내의 가스속도, 온도 및 가스상의 농도분포를 결정하였다. 이 모델로부터 HFCVD계에서 다이아몬드 성장의 전구체로 알려진 CH_3의 생산량에 미치는 CH_4 -원료가스- 의 농도와 필라멘트온도의 영향을 조사하였다. 그 결과 예측된 화학종들의 농도는 이전의 실험으로 직접 측정된 값들과 잘 일치하였고 또한 CH_3의 농도는 CH_4의 농도와 필라멘트의 온도에 비례하여 증가한다는 것을 알았다. 이것은 다이아몬드의 성장속도 역시 메탄의 농도와 필라멘트의 온도에 비례하여 증가한다는 것을 의미한다.

I. Introduction

Chemical-vapor-deposited (CVD) diamond is currently grown using many different techniques[1] such as hot-filament CVD (HFCVD), microwave plasma CVD, arc-jet plasma CVD and oxygen-acetylene torch CVD. The more conventional techniques frequently uses CH_4 as a carbon-bearing feedstock and dilute this gas with large amounts of H_2 to achieve inlet mixtures containing less than 1 mol% CH_4. Studies of the gas-phase environment in which diamond nucleation and growth occurs are of considerable interest since a knowledge of the gas composition at the substrate may give important clues regarding the kinetic mechanism leading to diamond formation.

The gas-phase chemistry for diamond deposition has been intensively studied so that the growth mechanism proceeding under metastable conditions can be elucidated. Numerical simulation can provide extensive information on the gas-phase chemistry, especially of the behavior of radicals that would play important roles in the growth reaction. Therefore, many numerical studies[2] have been made on various kinds of CVD techniques. However, in order to simplify the numerical models, most of these studies involved crucial assumptions; viz., a one-dimensional plug-flow system or chemical equilibrium system. A satisfactory model of the gaseous environment requires solving for the velocity, temperature and concentration fields, including both convective and diffusive transport, together with a detailed reaction mechanism. Only a few researchers including Goodwin and Gavillet[3], Kondoh et al[4] and Coltrin and Dandy[5] have conducted the simulation of diamond growth by applying the exact mass, momentum, energy and chemical species. However, their initial process parameters such as pressure, temperature, inlet gas velocity, etc., are considerably different from each other. So in this study, Process parameters were chosen to represent the real HFCVD system, and compare calculating results with the available experiment data for species concentrations and film growth rate.

II. Theoretical model

A. Model equations

A theoretical model is based on mass, momentum and energy conservation for a reacting gas flow at steady state. The appropriate conservation equations are as follows.

$$\mathrm{div}(\rho \mathbf{u}) = 0 \quad \text{(continuity equation)}$$

$$\rho(\mathrm{u} \cdot \mathrm{grad})\mathbf{u} - \mu \Delta \mathbf{u} = -\,\mathrm{grad}\ P \quad \text{(momentum conservation equation)}$$

$$\mathrm{div}(\rho \mathrm{u h}) - \chi\ \mathrm{div}(\mathrm{grad}\ T) = 0 \quad \text{(energy conservation equation)}$$

$$\mathrm{div}(\rho \mathbf{u} Y_i) - \mathrm{div}(\rho\ D_i\ \mathrm{grad}\ Y_i) = S_i \quad \text{(chemical species conservation equation)}$$

Where, density ρ, viscosity μ, specific enthalpy h and thermal conductivity χ are physical properties calculated by considering all the species in the reactor. Y_i, D_i and S_i are mass fraction, mixture diffusivity and production rate of i component, respectively; **u**, P, T means gas velocity, reactor pressure and temperature. In order to evaluate transport parameters such as μ, χ, D_i, the transport property software package from Sandia National Laboratories[6] was used. Also, to calculate the equilibrium constants and the reaction rate expressions necessary in conservation equations, CHEMKIN-II subroutine package[7] was used. In this model, 13 chemical species such as H_2, H, CH_4, CH_3, CH_2, CH, C, C_2H, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6 were considered.

B. Boundary conditions

Fig. 1 is the coordinate system for the HFCVD reactor used in the simulation and actual calculating domain is area abcd. In this area, boundary conditions are specified for the x and y components of velocity vector **u** (u and v), temperature T and species concentrations at the inflow and outflow of the reactor and on the walls as followers:

inflow:

$T = T_{inlet}$, $C_i = C_{i0}$, $u = u_0$, $v = 0$

outflow:

$\partial u/\partial y = \partial T/\partial y = \partial C_i/\partial y = 0$

filament wall:

$T = T_{fila}$, $u = 0$

$\partial u/\partial y = \partial T/\partial y = \partial C_i/\partial y = 0$

substrate wall:

$T = T_{sub}$, $v = 0$

$\partial v/\partial x = \partial T/\partial x = \partial C_i/\partial x = 0$

C. Numerical computation

The foregoing set of partial differential equations with the defined boundary conditions and the thermal and caloric equations of state are solved for a 66×12 grid, using a control-volume based difference method[8]. The equations are discretized on a nonuniform grid and solved iteratively, using a line-by-line method with TDMA(Tri-Diagonal Matrix Algorithm). SIMPLER(Semi-Implicit Method for Pressure Linked Equations Revised) algorithm and power-law scheme are adopted for correct solution and program stability. Typical computational times were about 14 hours when carrying out on a 100 Mhz pentium-based PC.

III. Result and Discussion

A. Distribution of flow-vector and temperature

Fig. 2 represent flow-vector and temperature distribution within area abcd shown in Fig. 1 and its calculating conditions are total flow rate 200 sccm, filament temperature 2500K, substrate temperature 1000K and methane concentration 1%. It shows that the gas temperature between filament and substrate is decreased almost linearly toward substrate side. Linear decrease means that mass transport is occurred mainly by diffusion of gas species rather than convection[9] i.e. diffusion is more important transport mechanism of gas species than convection.

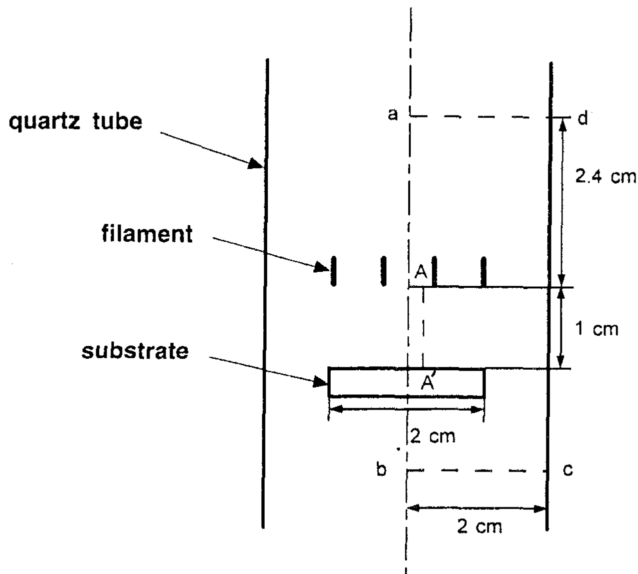

Fig. 1 Two-dimensional coordinate system for the HFCVD reactor used in the simulation

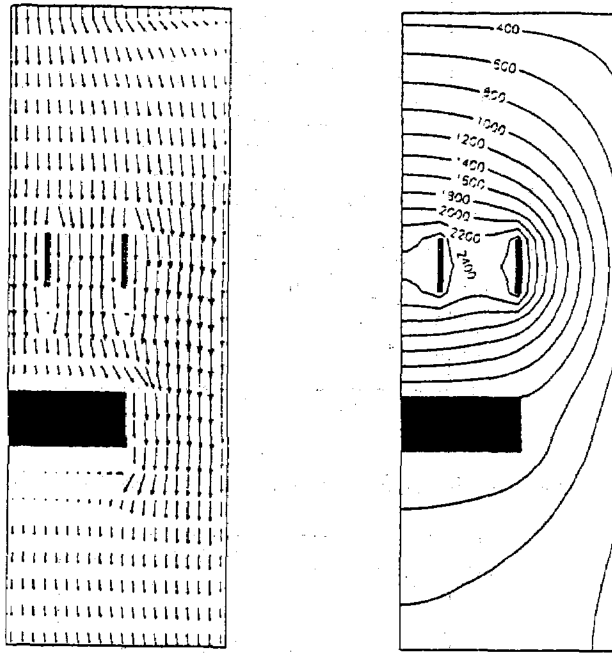

Fig. 2 Velocity and temperature distribution of the simulated HFCVD reactor

B. Distribution of chemical species

Fig. 3 shows the special distribution of the products concentrations along line AA′ in Fig. 1 and its calculating conditions are the same as in Fig. 2. Each species has a similar profile. The concentration increases gradually in the x direction, being a maximum around the filament; and slowly increases or decreases depending on species toward substrate. The nearly flat concentration distribution of chemical species means that the diffusion is more important than chemical reaction. Because the products generated by thermal decomposition such as H, CH_3, and C_2H_2 are almost same as between in filament region (2500K) and in substrate region (1000K). In order to estimate the effect of gas species diffusion, a calculation was carried out for the case in which the diffusion was ignored. The result shown in Fig. 4 demonstrates the importance of gas phase diffusion in diamond growth. In present knowledge, it is believed that the main precursor of diamond is CH_3 rather than C_2H_2[9] in HFCVD system. The equilibrium calculation, however, is shown that the more plentiful of hydrocarbon species in around gas temperature 1000K is C_2H_2[10]; and this fact is agreed with Fig. 4. If diffusion effect is considered in HFCVD system, the result is completely reversed, i.e. concentration of CH_3 is more plentiful than C_2H_2 as shown in Fig. 3. So the hypothesis that the main precursor is methyl radical(CH_3) is acceptable and this is owing to the diffusion effect.

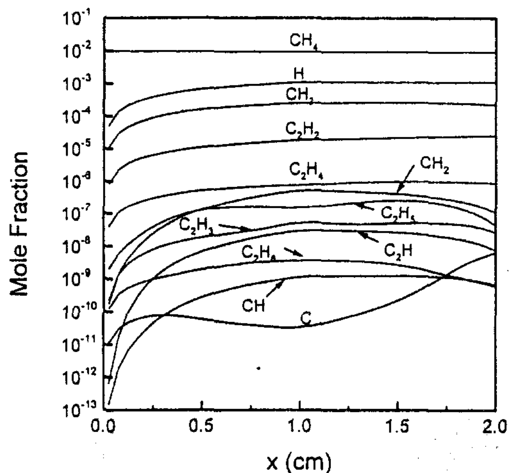

Fig. 3 Distribution of chemical species along the line AA′ shown in Fig. 1

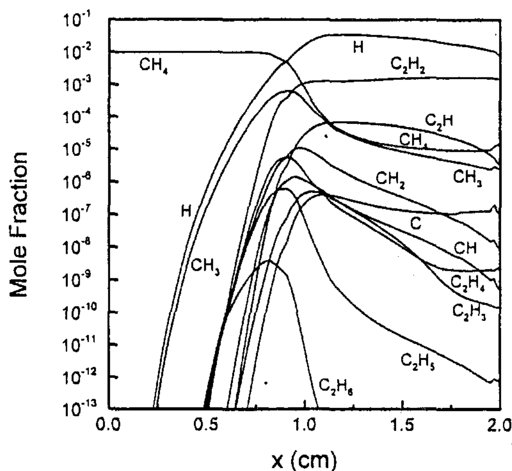

Fig. 4 Distribution of chemical species along the line AA′ shown in Fig. 1 without allowing for diffusion

C. The effects of methane concentration and the filament temperature.

Fig. 5, 6 show the dependence of the methane concentration and the filament temperature upon the gas phase composition at the position of the substrate. Hsu[11] and Harris and Weiner[12] have measured the concentrations of H, CH_3, CH_4 and C_2H_2 in the HFCVD gas ambience as a function of the methane concentration by using a mass spectrometer. Putting their results together, the H concentration decreased continuously, whereas the concentrations of H, CH_3, CH_4 and C_2H_2 increased with increasing methane concentration; in this respect, the effect of methane concentration is well consistent with present results. A comparison between the diagnostic measurements just referred to and present results are summarized in Table 1. Clearly the reported values are in

fairly good agreement with present simulation except C_2H_2 whose concentration differ on the order of 2. Celii and Butler[13] were determined CH_3 concentration on filament temperature using the REMPI(Resonance-Enhanced Multiphoton Ionization) technique. Their result showed that CH_3 concentration was proportionally increased with filament temperature in the range of 2000-2600K. This agrees well with the results in Fig. 6.

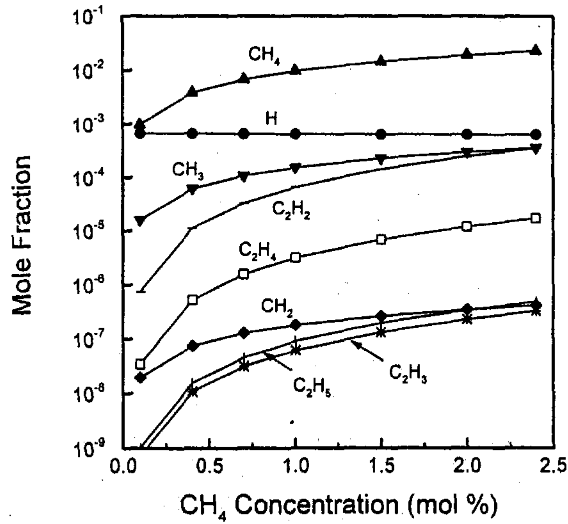

Fig. 5 Effect of methane concentration on the mole factions of chemical species at substrate. (Filament temperature 2500K, substrate temperature 1000K)

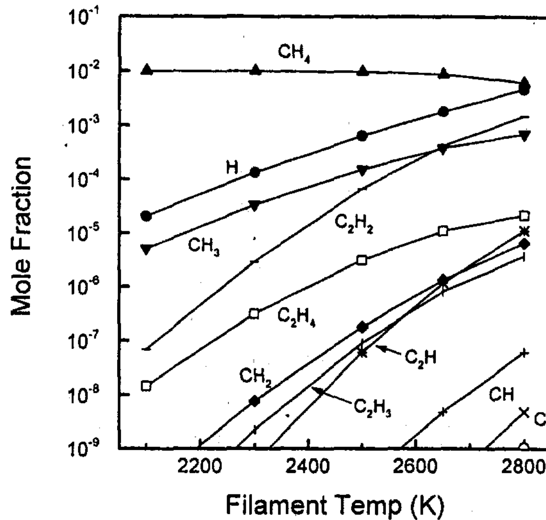

Fig. 6 Effect of filament temperature on the mole fractions of chemical species at substrate. (Substrate temperature 1000K, Methane concentration 1 mol%)

Species	Hsu[6]	Harris and Weiner[7]	Celii et al [8]	present work
H	2.3×10^{-3}	7.0×10^{-3}		1.1×10^{-3}
CH_3	9.1×10^{-5}	2.0×10^{-4}	1.6×10^{-5}	2.2×10^{-4}
CH_4	3.9×10^{-4}	1.1×10^{-3}	6.3×10^{-3}	9.4×10^{-3}
C_2H_2	3.6×10^{-3}	1.6×10^{-3}	1.6×10^{-3}	3.0×10^{-5}

Table 1. Comparison with measured and calculated mole fractions for various gaseous species. The methane percentage in the feed gas is approximately 1%.

IV. Conclusion

From the simulation work performed to 2-D reactive-flow, the following conclusions were obtained:

1. The temperature distribution within the reactor shows that primary mass transport mechanism of gas phase is the diffusion of chemical species. Consequently, the species profiles are largely independent of the gas velocity **u**.
2. Predicted species concentrations are well agreed with published experimental work and the result shows that there exist super-equilibrium concentration of CH_3.
3. Increasing the methane concentration, CH_3 concentration also increases, while H concentration decreases monotonically. From this result, there may be a maximum growth rate of diamond between 0.5% to 2% CH_4 feed gas.

Acknowledgment

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