Numerical simulation of hydrogen dissociation and recombination by gas-surface reactions in HFCVD process

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Abstract: The numerical simulation for understanding the HFCVD process has been carried out as considering dissociation and recombination of hydrogen gas by gas-surface reactions. This numerical method used in this simulation could consider simultaneously the gas-surface reactions and gas-phase reactions. The production of hydrogen atom was anticipated, which showed good agreement with prior studies. And the concentration of CH_3 which is known as the important species for producing diamond film was very similar with the measured result.

Keywords: Numerical simulation, HFCVD, Gas-surface reaction, Hydrogen

1. Introduction

HFCVD (Hot Filament Chemical Vapor Deposition) process has been used to produce a diamond film. Although it is not clearly demonstrated that the diamond is synthesized on a substrate, favourable conditions for producing high quality film have been found through a lot of studies. The concentration profile of activated species near the substrate is one of them [1-6], which is significantly affected on temperature distribution between filament and substrate [7-9].

The numerical approaches had been developed to analyze the correlation between the temperature and concentration by using CFD (Computational Fluid Dynamics) code with considering chemical reactions [2,3,10-13]. Among various physical and chemical phenomena in the HFCVD process, production of hydrogen atom by hydrogen dissociation is the most important phenomenon in order to similarly reproduce the environment of HFCVD process. Since production of hydrogen atom is almost achieved on the filament surface, however, this phenomenon is not easily to be able to be considered in the numerical simulation. Thus the production rate of hydrogen atom has been assumed as the constant in former numerical studies [12,13].

In this present work, the numerical method which is able to include the heterogeneous gas-surface reaction in conjunction with gas-phase reaction has been introduced in order to anticipate the production of hydrogen atom in the HFCVD process.

2. Simulation Method

In order to verify the numerical method used in this simulation, the calculated mass fraction of hydrogen atom and hydrogen molecules on the filament and concentration distribution of hydrogen atom were compared with the results calculated by Martinez *et al.* [13], and the calculated concentration profile of CH_3 from filament to substrate was compared with the results measured by Whal *et al.* [6].

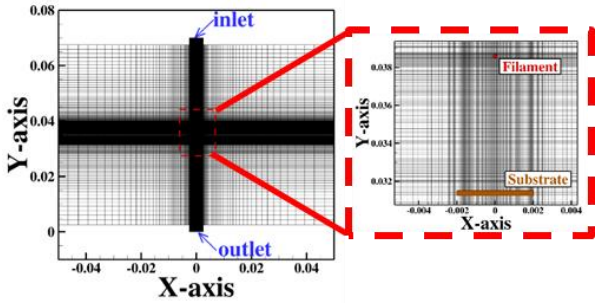

Fig. 1. The two-dimensional geometry for the reactor reported by Whal [6]

Fig. 1 is the two-dimensional geometry used in this work, which was modelled on the reactor reported by Whal *et al.* [6]. The reactor has one filament with diameter of 0.2 mm and a substrate with width of 4 mm and thickness of 0.25 mm. And the distance from filament to substrate is 7 mm.

Table 1 indicates the gas-phase governing equations. Equation (1) states the total mass conservation equation. Equation (2) to (5) describe the components of the gas velocity (v_x and v_y), the gas temperature (T) and the species concentration (Y), respectively, as function of position inside the reaction chamber.

The gas-phase reactions and heterogeneous gas-surface reactions were be able to be applied by using Arrhenius equation. The gas-phase and gas-surface reaction

Table 1. Gas-phase governing equations [13]

Overall continuity :	$\vec{\nabla}\cdot\rho\vec{v}=0$	(1)
Momentum in x direction :	$-\vec{\nabla}\cdot(\rho v_x\vec{v})-\vec{\nabla}\cdot\vec{\tau}_x-\frac{\partial P}{\partial x}=0$	(2)
Momentum in y direction :	$-\vec{\nabla}\cdot(\rho v_x\vec{v})-\vec{\nabla}\cdot\vec{\tau}_x-\frac{\partial P}{\partial x}+\rho g_y=0$	(3)
Energy :	$-\rho\vec{v}\cdot C_p\vec{\nabla}T-\vec{\nabla}\cdot\vec{q}-\sum_{i=1}^{n}h_iM_i\dot{\omega}_i=0$	(4)
Species continuity of species i :	$-\vec{\nabla}\cdot\vec{n}_i+M_i\dot{\omega}_i=0$	(5)

mechanism and the coefficient for rate constant used in Arrhenius equation are shown in the table 2.

The filament temperature is assumed as constant value of 2,300 K. The inlet gas were composed of H_2 and CH_4, of which ratio were 99.5% and 0.5% (vol. %), respectively. The ANSYS-FLUENT (Ver19.2) was used to calculate the equations (1) to (5)

Table 2. Reaction mechanism and coefficients for rate constant used in this work

	Gas-phase reaction [13]	A[a]	β[a]	E_a[a]
1	$C_2H_6 + H_2 = CH_3 + CH_3 + H_2$	5.52×10^{42}	-8.90	452.09
2	$CH_4 + H_2 = CH_3 + H + H_2$	1.34×10^{33}	-6.18	451.96
3	$C_2H_5 + H_2 = C_2H_4 + H + H_2$	6.28×10^{37}	-8.24	186.89
4	$C_2H_2 + H + H_2 = C_2H_3 + H_2$	3.12×10^{35}	-7.61	31.73
5	$CH_4 + H = CH_3 + H_2$	2.20×10^{4}	3.0	36.63
6	$CH_3 + CH_3 = C_2H_4 + H_2$	1.00×10^{16}	0	133.10
7	$CH_3 + CH_4 = C_2H_5 + H_2$	1.00×10^{13}	0	96.29
8	$C_2H_5 + H = CH_3 + CH_3$	1.00×10^{14}	0	0
9	$C_2H_3 + H = C_2H_2 + H_2$	4.00×10^{13}	0	0
10	$C_2H_4 + H = C_2H_3 + H_2$	1.10×10^{14}	0	35.58
11	$C_2H_6 + H = C_2H_5 + H_2$	5.40×10^{2}	3.5	21.81
12	$H + H + H_2 = H_2 + H_2$	9.20×10^{16}	-0.6	0
	Gas-surface reaction on filament [14]	A[a]	β[a]	E_a[a]
1	$S_F^b + H_2 \rightarrow S_FH^b + H$	1.69×10^{12}	0.5	20.736
2	$S_FH^b + H \rightarrow S_F^b + H_2$	9.03×10^{12}	0	0
3	$S_FH^b \rightarrow H + S_F^b$	1.00×10^{13}	0	82.944
4	$S_F^b + H \rightarrow S_FH^b$	1.72×10^{13}	0	0
	Gas-suface reaction on substrate [15]	A[a]	β[a]	E_a[a]
1	$S_S^b + H_2 \rightarrow S_SH^b + H$	1.51×10^{7}	1.12	14.93
2	$S_SH^b + H \rightarrow S_S^b + H_2$	1.39×10^{12}	0	7.00
3	$S_SH^b \rightarrow H + S_S^b$	3.70×10^{15}	-0.72	95.48
4	$S_S^b + H \rightarrow S_SH^b$	3.13×10^{11}	0	0

[a]Arrhenius parameters for the rate constants in the forward direction written as the form $k = AT^{\beta}exp(E_a/RT)$. The units of A are given in terms of moles, cubic centimeters, and seconds, E_a is in kcal mol^{-1}

[b]S_F, S_S and SH mean an activated site of filament, activated site of substrate and hydrogenated surface site, respectively.

3. Result and Discussion

In the case of the simulation of Martinez *et al.* [13], which was the research about the simulation referring the reactor reported by Whal [6], the production of hydrogen atom on the filament is assumed by using constant mass fraction of hydrogen atom and hydrogen molecules on filament of 0.036 and 0.933, respectively. As a result of the simulation used in this work, the mass fraction of hydrogen atom and hydrogen molecules near the filament was 0.008 and 0.924, respectively. While the value of hydrogen molecules was similar with the value calculated by Martinez *et al.* [13], there was a little difference among mass fraction results of the hydrogen atom. This difference

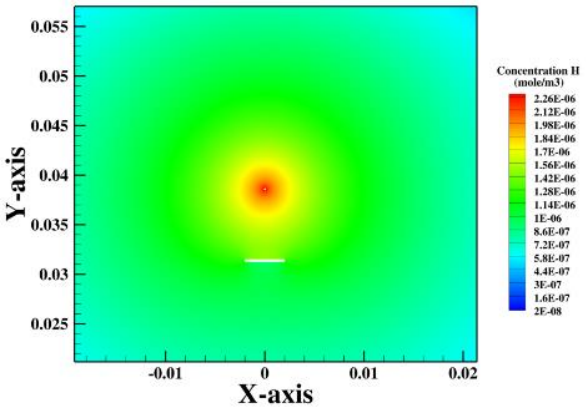

Fig. 2. Concentration distribution of hydrogen atom calculated by this simulation method.

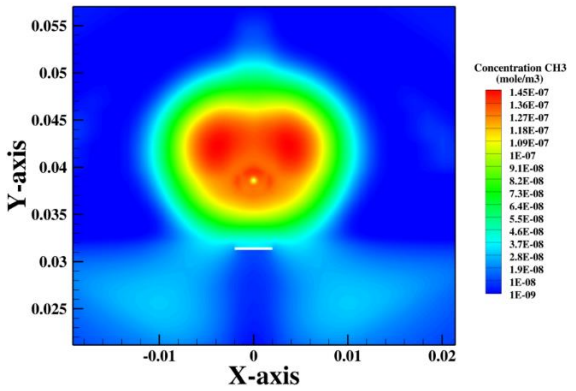

Fig. 3. Concentration distribution of CH_3 calculated by this simulation method.

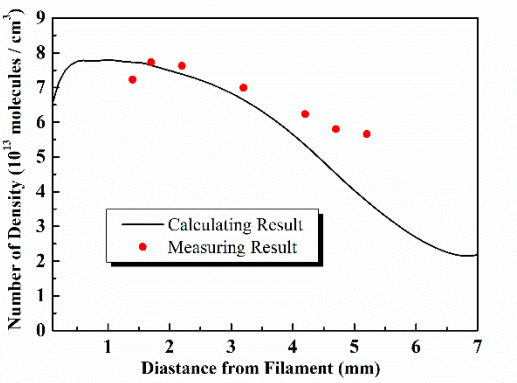

Fig. 4. The comparison between calculated and measured number density of CH_3; the measured result was extracted from Ref. [6].

could be caused by the fact that some of hydrogen atom was been adsorbed on filament, creating the S_FH. While this absorption was took into account in the numerical method used in this work, the method by Martinez *et al.* neglected it. The concentration distribution of hydrogen atom shown in the Fig. 2 is also be able to be presented as the reason indicating the verification of this numerical

method. Although the concentration of hydrogen atom near the substrate was largely calculated, the overall order and distribution appearance were equal with the results calculated by Martinez *et al.* [13].

Fig. 3 is the concentration distribution of CH_3, which also indicates the accuracy of this method. The hydrogen atom was known as taking role of triggering the homogeneous chemical reaction [3,11,13]. Thus, only if the production of the hydrogen atom is reflected well, the concentration of CH_3 also is able to be accurate. In the case of this simulation, the number density of CH_3 was similar with the result measured by Whal *et al.* [6] like shown in the Fig. 4. Therefore, the numerical method that the hydrogen dissociation by the heterogeneous gas-surface reaction on filament is considered in conjunction with gas-phase reaction has been verified by demonstrating the comparison between calculated results by this work and results calculated and measured by Martinez *et al.* and Whal *et al.*

4. Conclusion

The numerical method which is able to consider gas-surface reactions in conjunction with gas-phase reactions has been developed by this work. By comparing with other researches, this method has been verified, showing the good agreement about the concentration distribution of CH_3 and the mass fraction of the hydrogen atom on the filament. This method is able to be applied to correctly predict the concentration distribution of chemical species and temperature distribution in designing the large-scale HFCVD process.

5. References

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