Evaluation of Ion and Radical Fluxes in CH₄/H₂ Plasma for CNT Growth

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Keywords: carbon nanotubes, radio-frequency discharge plasmas, hydrocarbon plasmas, fluid model, simulation

We simulated CH₄/H₂ RF capacitively coupled plasma using a 1-dimensional fluid model. We focused on distributions and fluxes of ions and radicals. Evaluation of ions and neutrals fluxes onto the grounded electrode are important in order to understand the mechanism of growth of carbon nanotube (CNT) and to optimize its growth condition. We fixed CH₄ partial pressure at 1 Torr and varied H₂ partial pressure to be 0−9 Torr.

Number densities of higher order molecules CₓHᵧ (x, y ≥ 2) increased to about 1/100 of CH₄/H₂, primary plasma medium until the end of the simulation, 10⁵ RF cycles (Fig 1). Their density would increase further more during the gas residence time in the chamber (about 10⁷ RF cycles).

We estimated the influence of CₓHᵧ on the ion and radical production. Mean electron energy in pure CH₄ and in CH₄/CₓHᵧ was calculated by a Boltzmann equation solver “Bolsig+:” Mean electron energy in CH₄/CₓHᵧ was 0.1−3.3 eV lower than that in pure CH₄ at the reduced electric field of 0.1−2000 Td (Fig. 2). With this result, we estimated ionization rate of H₂ (H₂ + e → H₂⁺ + 2e, threshold energy 12.60 eV) as an example of the ion production. H₂ ionization rate in CH₄/CₓHᵧ was about 2/3 of that in pure CH₄. Other rates of ionization and dissociation will show similar tendency because their threshold energy is close to that of H₂. Consequently, whole production of ions and radicals in CH₄/CₓHᵧ will be significantly lower than that in CH₄. We consider that it is possible to evaluate production of ions and radicals more realistically by including the accumulation of CₓHᵧ in the model.

When the H₂ mixture ratio was 0.1, fluxes of H₂⁺ and H₃⁺ were respectively 5 and 10 times larger than those in the case without H₂ mixing (Fig 3). In our previous experiment, slight mixture of H₂ promoted the CNT growth, and we inferred that the cause of promotion is that H₂ maintained the activity of the catalyst particle from which CNT grew. Present numerical result supports our conjecture.

It was pointed out that we need to include the interaction between precursor and catalyst on the substrate in the simulation for further understanding of mechanism of CNT growth.

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Fig. 1. Spatially averaged molecular number densities as a function of simulation time (RF cycles) at the condition of Pᵣ = 0

Fig. 2. Mean electron energy ⟨ε⟩ as a function of reduced electric field E/N, CH₄/CₓHᵧ (CH₄ 70.9%, C₂H₂ 4.7%, C₃H₄ 5.8%, CₓHᵧ 5.8%, C₃H₈ 12.8%)

Fig. 3. Dependence of calculated onto the grounded electrode on the pressure ratio Pᵣ = Pᵣ₂/(PᵣCH₄ + PᵣH₂)
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A CH₄/H₂ radio frequency capacitively coupled plasma used for synthesis of carbon nanotubes (CNTs) was simulated with a 1-dimensional fluid model. The pressure of CH₄ was fixed at 1 Torr and that of H₂ varied from 0 to 9 Torr. When the H₂ mixture ratio was 0.1, the fluxes of H₂⁺ and H₃⁺ to the substrate were respectively about 5 and 10 times those for the case without H₂ mixing. In our previous experiment, a slight mixture of H₂ promoted CNT growth. We inferred that this was because H₂ maintained the activity of the catalyst particle from which CNT grew. The present numerical result supports our hypothesis. In addition, CₓHᵧ (x, y ≥ 2) accumulated with time. This accumulation is not negligible because it lowers the electron temperature. We estimated the H₂ ionization rate in CH₄/CₓHᵧ is about 2/3 of that in CH₄. It is pointed out that we need to consider the accumulation of CₓHᵧ to improve the accuracy of the estimation of CNT growth.

Keywords: carbon nanotubes, radio-frequency discharge plasmas, hydrocarbon plasmas, fluid model, simulation

1. Introduction

Carbon nanotubes (CNTs), which consist of rolled graphene sheets, have attracted considerable attention because they have many excellent properties such as high current density, aspect ratio (a diameter of nanometer order and length of micron to millimeter order), and thermal conductivity(1). Furthermore, their electrical feature, whether metallic or semiconducting, is variable depending on their chirality. There is great expectation for the application of CNTs to electronic devices(2).

Plasma-enhanced chemical vapor deposition (PECVD) is one technique used for CNT production and CH₄/H₂ capacitively coupled plasma (CCP) is used for carbon nanostructure production including that of diamond-like carbon(3) and CNTs.

To optimize the experimental condition of the CNT growth and control the property of CNTs, in this paper, we simulated CH₄/H₂ RF (radio frequency, 13.56 MHz) CCP for CNT growth using a 1-dimensional (1D) fluid model. We investigated the plasma properties, especially from a viewpoint of the effect of the H₂ mixture.

In the present calculation, we fixed the CH₄ pressure at 1 Torr and varied the H₂ pressure from 0 to 9 Torr. We investigated the effect of the mixture of H₂ on particle number densities and fluxes onto the grounded electrode, especially at low mixture ratios of H₂ of about 0.1. At such a mixture ratio, it has been reported that long CNTs are obtained with a high density(4).

To understand the mechanism of the CNT growth, we focused on fluxes of ions and radicals onto the grounded electrode. The densities of higher-order molecules such as CₓHᵧ and CₓHᵧ increased with time, and the mean electron energy in CH₄/CₓHᵧ (x, y ≥ 2) is lower than in pure CH₄. Therefore, it is inferred that accumulation of CₓHᵧ prevents the production of ions and radicals that are incident to the grounded electrode and contribute to the CNT growth. It is necessary to evaluate the plasma properties in the presence of CₓHᵧ such as C₂H₄ and C₂H₆ quantitatively.

2. Simulation Method

2.1 One-dimensional Fluid Model

The electrode configuration assumed in this study is shown in Fig. 1. The diameter of the circular parallel-plane electrodes was 6.4 cm, and the electrode distance was 1.5 cm. These dimensions were taken from our experimental apparatus previously reported(5).

The 1D fluid model consists of the three following governing equations:

the continuity equation of species \( j \)
\[
\frac{\partial n_j}{\partial t} + \frac{\partial F_j}{\partial x} = S_j; \tag{1}
\]

Poisson’s equation
\[
\frac{\partial^2 V}{\partial x^2} = \frac{P}{\varepsilon_0}; \tag{2}
\]

and an electron energy conservation equation

\[
\frac{\partial}{\partial t} \frac{\partial V}{\partial x} = \frac{P}{\varepsilon_0}.
\]

Fig. 1. The electrode configuration assumed in the simulation(5)
particles are incident to the electrode, they stick to the surface with probabilities of sticking to the wall surface of the chamber in their article. We assumed that particles that stuck to the substrate contributed to the growth of CNTs. Here, because we confirmed experimentally that CNT do not grow in thermal CVD phase and this effect maintained the catalyst activity.

2.2 Boundary Conditions CNTs grow from catalyst particles on the substrate placed on the grounded electrode. When particles are incident to the electrode, they stick to the surface with the sticking probability \( \beta \). The \( \beta \) values for each species were set as: ions, 1; molecules, 0; H, 0.001; CH\(_2\), CH\(_3\), C\(_2\)H\(_4\), C\(_2\)H\(_5\), C\(_3\)H\(_8\) and C\(_3\)H\(_9\)) and radicals (H, CH, CH\(_2\), CH\(_3\) and C\(_2\)H\(_2\)). The simulation included 39 electron–neutral collisions (excitation, ionization and dissociation), 18 neutral–neutral reactions, and 9 ion–neutral reactions. The rate coefficient of each reaction was estimated from electron collision cross sections of H\(_2\), CH\(_4\), CH\(_2\), CH\(_3\), C\(_2\)H\(_2\), C\(_2\)H\(_3\), C\(_2\)H\(_4\) and C\(_2\)H\(_5\)) and radicals (H, CH, CH\(_2\), CH\(_3\) and C\(_2\)H\(_2\)).

2.3 Simulation Condition Okita et al.\(^{(4)}\) grew CNTs experimentally and simulated the plasma at various CH\(_4\)/H\(_2\) ratios at a constant total pressure of 10 Torr. In these conditions the CH\(_4\) pressure decreased inversely to the increase in the H\(_2\) pressure. At a ratio \( P_1 = P_{CH_4}/P_{H_2} = 0.1 \), they yielded a high number density of the smallest diameter CNTs, which grew for a longer time than in pure CH\(_4\). They considered that H\(_2\) reduced the catalyst not only in the preparation phase but also in the growth phase and this effect maintained the catalyst activity.

On the basis of this consideration, in this paper we fixed the CH\(_4\) pressure at 1 Torr and varied the H\(_2\) pressure from 0 to 9 Torr, to investigate the effect of H\(_2\) mixing on the plasma properties.

The voltage applied to the electrodes was varied from 432 to 600 V to keep the power density constant at 0.31 W/cm\(^3\), which is the typical value calculated for pure CH\(_4\). We set the gas temperature at 650°C, and the power source frequency 13.56 MHz. The initial number densities of the electron, H\(_2^+\) and CH\(_4^+\) were set at 1.0×10\(^6\), 0.5×10\(^8\) and 0.5×10\(^6\) cm\(^{-3}\), respectively. We simulated the temporal variations of the species mentioned above for 10\(^5\) RF cycles.

3. Results and Discussion

3.1 Behavior of Electrons and H\(_2^+\) in Plasma Figure 2 shows spatiotemporal distributions of (a) the electric field \( E \), (b) the electron density \( n_e \), and (c) the electron temperature \( T_e \). The plasma bulk was built in a region 0.7–0.8 cm from the electrode. In this region, electron density was almost constant through an RF cycle. \( T_e \) at the bulk was 3.8–4.5 eV. The highest value of \( E \) was 1430 V/cm in the vicinity of the electrode, where the highest \( T_e \) was 57.1 eV.

Figure 3 shows spatiotemporal distributions of (a) number density \( n_{H2^+} \), (b) net production rate \( S_{H2^+} \) (production – loss), and (c) flux \( \Gamma_{H2^+} \). The bright spots indicating higher \( \Gamma_{H2^+} \) values distribute along the edges of the electron distribution and cyclically move toward and away from the electrode (see also Fig. 2). Figure 3 depicts that H\(_2^+\) ions were produced and accumulated around \( x = 1.25 \) cm during a period of \( t = 0.0–0.5 \) RF cycles (Fig. 3(a) and (b)), and many of them were incident to the substrate during \( t = 0.5–1.0 \) RF cycles because of high \( \Gamma_{H2^+} \) (Fig. 3(c)).
Therefore, we consider that there was a time lag of 0.5 RF cycles between the production phase and the incidence phase of H2⁺.

### 3.2 Accumulation of C₂H₄ and C₂H₆

Figure 4 shows the dependence of the number densities of the neutral species on the pressure ratio \( P_r = P_{H_2}/(P_{CH_4} + P_{H_2}) \). The values shown in Fig. 4 are spatially averaged values 10⁵ RF cycles after the start of the simulation. The densities of C₂H₆ and C₂H₄ reached an order of about 1/100 of that of CH₄/H₂, which was the primary species of the plasma medium. Figure 5 shows the time dependence of the spatially averaged number densities. Figure 5 indicates the number density of CₓHᵧ \((x, y \geq 2)\) will increase further because equilibrium has not been achieved even at 10⁵ RF cycles. We consider the accumulation of CₓHᵧ affects the ionization and dissociation rate because in most cases \( T_e \) in CₓHᵧ is lower than that in CH₄. For more realistic simulation, we need to treat the gas mixture as CH₄/H₂/CₓHᵧ rather than CH₄/H₂. A more detailed discussion will be presented in section 4.

### 3.3 Fluxes onto the Grounded Electrode

Figure 6 shows the dependence of the calculated fluxes of ions and radicals onto the grounded electrode on which the substrate was placed. The drift term was dominant in the ion flux. On the other hand, the gradient of the radical number density was overwhelmingly larger than that of the ion. Therefore, ion fluxes were smaller than those of radicals because of the small densities of ions.

From the comparison of sticking probabilities between ions and radicals, it seems that CH₃⁺ and C₂H₅⁺ are the main precursors of CNT growth among the species considered in the present work. The fluxes of H₂⁺ and H₃⁺ at \( P_r = 0.1 \) are about 5 and 10 times those at \( P_r = 0 \), respectively. The result of Okita et al. shows a similar tendency.

Considering the experimental result in Okita et al. (mentioned in subsection 2.3), which obtained narrower CNTs with a slight
mixture of H2, we suppose that H2+ and H3+ maintain the activity of the catalyst and decrease the catalyst particle size. To investigate the effect of the ions on the catalyst on the surface of the substrate, we need to take account of the interaction between the catalyst and the precursor in future simulations.

4. Effect of Accumulation of C3H8

Oda et al. (9) discussed the effect of the accumulation of C3H8 on mean electron energy \( \varepsilon \) as mentioned in subsection 3.2. From their calculation result, the number densities of C2H2, C2H4, C2H6 and C3H8 increased to non-negligible values.

The CNT growth experiment by Okita et al. (4) was carried out in a flow system. The residence time \( \tau_r \) of the gas in the chamber is estimated from the dimensions of the experimental apparatus as follows.

\[
\tau_r = \frac{V_p}{B}, \quad \text{Eq. (6)}
\]

\[
B = \frac{Q}{n_0}, \quad \text{Eq. (7)}
\]

where \( V_p \) is the velocity of the region where the plasma is produced, \( B \) is the exhaust velocity, \( Q \) is the flow rate, and \( n_0 \) is the gas pressure in equilibrium (\( dp/dt = 0 \)). \( B \) and \( \tau_r \) were respectively estimated to be \( 3.80 \times 10^{-2} \text{ l/s} \) and \( 1.27 \text{ s} \), from the experimental condition of Okita et al. (4) (\( p_0 = 10 \text{ Torr}, Q = 30 \text{ scem} \)) and Eqs. (6) and (7). This residence time is equivalent to \( 1.72 \times 10^7 \text{ RF cycles} \).

The accumulation of C3H8 through this long period will affect \( \varepsilon \) significantly. Therefore, in the future it will be necessary to simulate the C3H8 accumulation over \( 10 \times 10^7 \text{ RF cycles} \), which is 10 times longer than the simulation time of the present calculation. From the rate of CH4 decomposition, which was about \( 1 \times 10^{15} \text{ cm}^{-3} \text{s}^{-1} \) in the result described in section 2, it is estimated that most CH4 is consumed in the gas residence time.

Oda et al. (9) calculated the number densities of neutral species using a model that includes the supply and exhaust of gas. Their results were number densities for CH4, C2H2, C2H4, C2H6, and C3H8 of \( 6.1 \times 10^{16}, 0.4 \times 10^{16}, 0.5 \times 10^{16}, 0.5 \times 10^{16} \) and \( 1.1 \times 10^{16} \text{ cm}^{-3} \), respectively (almost uniform over the space between the electrodes). We calculated \( \varepsilon \) by a Boltzmann equation solver “Bolsig+.” The mixture ratios of CH4, C2H2, C2H4, C2H6, and C3H8 were set at 70.9%, 4.7%, 5.8%, 5.8% and 12.8%, respectively, to reflect the above calculation results.

The calculated \( \varepsilon \) values are shown in Fig. 7. \( \varepsilon \) in CH4/C3H8 was 0.01–3.3 eV lower than that in pure CH4 in an \( E/N \) range of 0.1–2000 Td. We consider that at such a low \( \varepsilon \), dissociation and ionization occur much less than in pure CH4; the threshold energies of dissociation and ionization are relatively high (8.9–15.4 eV). Therefore, the number of ions and radicals supplied to the substrate surface in CH4/C3H8 will be less than in the case of pure CH4 shown in subsection 3.3.

Let us estimate the change in the ionization rate \( S_{H2ion} \) for the reaction of \( H_2 + e \rightarrow H_2^+ + 2e \) as an example of the processes of ion production. The threshold energy \( \varepsilon_0 \) is 12.60 eV. \( S_{H2ion} \) is given as \( S_{H2ion} = k_{H2ion}n_Hn_e \), where \( k_{H2ion} \) is the rate coefficient of H2 ionization (see Fig. 8) and \( n_H \) is the density of H2. We estimated \( S_{H2ion} \) in three regions, around Fig. 3(b) (i) \( x = 0.9 \text{ cm}, t = 0.8 \text{ RF cycles} \), Fig. 3(b) (ii) \( x = 1.0 \text{ cm}, t = 0.6 \text{ RF cycles} \), and Fig. 3(b) (iii) \( x = 1.3 \text{ cm}, t = 0.1 \text{ RF cycles} \). \( S_{H2ion} \) takes its peak values. Pure CH4, \( S_{H2ion} = 1.06 \times 10^{14}, 2.46 \times 10^{14} \) and \( 2.64 \times 10^{14} \text{ cm}^{-3} \text{s}^{-1} \), respectively in regions (i), (ii), and (iii). In CH4/C3H8, \( S_{H2ion} = 7.91 \times 10^{13}, 1.42 \times 10^{14} \) and \( 1.71 \times 10^{14} \text{ cm}^{-3} \text{s}^{-1} \), respectively in the same regions. The values of ionization rate in CH4/C3H8 were about 2/3 times those in CH4 on average.

Therefore, there is a possibility that the H2+ number density will be significantly lower than that of the conventional model, which does not include C3H8 in the plasma media. Although we picked H2 ionization for the present example, the rates of other ionizations and dissociations with threshold energies close to that of H2 ionization will show a similar tendency. As a result, the total number of ions and radicals contributing to the growth of a CNT will be significantly lower than that estimated in the conventional model. This consideration may explain a result in Okita et al. (4); the numerical estimation of the amount of carbon atoms related to the CNT growth was about twice that estimated from the experimental result.

5. Conclusion

An RF CH4/H2 CCP was simulated by a 1D fluid model. It was revealed that CH4/C3H8, such as C2H2 and C2H4, accumulated to about 1/100 of the CH4/H2 content during \( 10^3 \text{ RF cycles} \). The accumulation of CH4 would become more significant during a gas residence time over \( 10^7 \text{ RF cycles} \). Our estimation showed that the mean electron energy in CH4/C3H8 is lower than that in CH4, and the decrease in the mean electron energy leads to a significant decrease in the ionization rate. It was indicated that the production
rate of ions and radicals contributing to the growth of a CNT would be significantly lower than that for the conventional model. We consider it is possible to evaluate the production of ions and radicals more realistically by including the accumulation of $C_2H_5^+$ and $H_3^+$ as major species as precursors for CNT growth.

In our previous experiment, $H_2$ promoted the growth of CNTs, while in the present calculation, fluxes of $H_2^+$ and $H_3^+$ onto the substrate at $P_r = 0.1$ are about 5 and 10 times the fluxes in the case of $P_r = 0$. It was suggested that $H_2^+$ and $H_3^+$ are candidates for key species that contribute to CNT growth. This seems consistent with the empirical explanation that $H_2$ maintains the catalyst activity.

It was pointed out that we need to include the interaction between precursor and catalyst on the substrate in the simulation for further understanding of the mechanism of CNT growth.

Acknowledgments

Publication of this paper was supported by the Center for Engineering Education Development, Hokkaido University.

Work by Mr Okita was supported by the Japan Society for the Promotion of Science.

(Manuscript received Jan. 10, 2008, revised March 14, 2008)

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