Microwave CH_4 /H_2 Plasma Composition Analysis for Diamondlike Carbon Film Synthesis

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Abstract

Microwave CH_4/H_2 plasmas were useful for diamondlike carbon (DLC) film synthesis. The effects of the plasma compositions on the DLC film qualities were investigated. The DLC film was deposited with a microwave plasma source using a resonant cavity. The plasma compositions were examined from plasma diagnostic measurements and kinetic calculations.

I. INTRODUCTION

Diamondlike carbon (DLC) films, which are a very attractive material for industrial application, are easily deposited by microwave-plasma-enhanced chemical vapor deposition (CVD) using mixture of hydrogen and hydrocarbon gas. The film quality depends on the composition of C sp^3 and C sp^2 bonds within the film and is parametrically controlled by composition of working gas, discharge chamber pressure and microwave power. These parameters influence the plasma compositions (neutrals, ions and electrons). To precisely control the film quality, we have to understand the correlation between the plasma composition and the film quality. However, plasma compositions are not clear.

In the present paper, compositions of CH_4/H_2 plasma, used for deposition of diamondlike carbon, were analyzed by means of plasma diagnostic measurements and kinetic calculations.

Ⅱ. EXPERIMENTAL APPARATUS

Figure 1 shows the microwave plasma source using a resonant cavity for chemical vapor deposition of DLC films [1-4]. Microwaves of 2.45 GHz are introduced into a cavity and resonantly produce plasma in a 24-mm inner diameter quartz discharge tube. Electrostatic double probe measurements and plasma emission spectroscopic measurements were conducted for plasma composition analysis at the same location where DLC films were deposited. Table 1 shows the deposited condition of the DLC films. The deposited film features were examined with Fourier transform infrared spectroscopy (FTIR). From the FTIR analysis, the films were composed of C sp^3 and C sp^2 bonds. The composition ratio of C sp^3 to C sp^2 bonds increases with pressure and decreases with increasing CH_4 concentration.

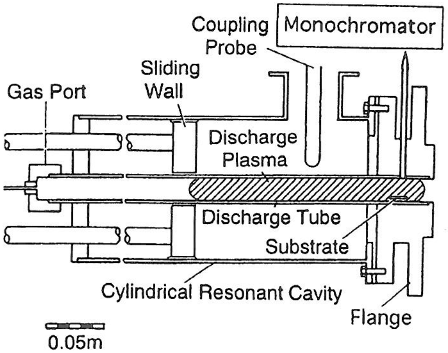

Fig. 1 Microwave plasma source using resonant cavity.

Table 1 DLC film deposition condition.

Working Gas	CH_4+H_2
Chamber Pressure	133.3～666.5Pa
Total Flow Rate	200 sccm
CH_4 Concentration	4.0～10.0 vol%
Microwave Power	350 W
Substrate	Quartz glass

Ⅲ. KINETIC CALCULATION

Various particles are produced in the CH_4/H_2 plasma. In the above plasma diagnostic measurements, little is known about plasma composition. To examine the plasma compositions, we simulated the plasma using a kinetic model. 14 species of neutrals and 16 species of ions were analyzed as shown in Table 2. From reaction rate equations of each particles, differential equations were derived and numerically

Table 2 List of simulated particles.

Neutrals (14 species)	Ions (16 species)
CH_4 , CH_3 , CH_2, CH, C, C_2H_6, C_2H_5, C_2H_4, C_2H_3, C_2H_2, C_2H, C_2 , H_2 ,H	$CH_5{}^+$, $CH_4{}^+$, $CH_3{}^+$, $CH_2{}^+$, CH^+ , C^+, $C_2H_6{}^+$, $C_2H_5{}^+$, $C_2H_4{}^+$, $C_2H_3{}^+$, $C_2H_2{}^+$, C_2H^+, $C_2{}^+$, $H_3{}^+$, $H_2{}^+$, H^+

solved to find out the particle number densities [3-6]. Electrons are assumed to obey a maxwellian distribution. Also, the electron temperatures and densities, which were measured with an electrostatic double probe, were used in this analysis.

From the plasma emission spectroscopic measurement, the emission of hydrogen balmer line (Hβ) was observed. To verify the above numerical result experimentally, we used this spectrum. The emission intensity of Hβ is proportional to the number density of H atoms excited in an energy quantum level of 4. It was also calculated from the reaction rate equation between electrons and H atoms. The sum of number density of the ground state and the excitation state is equal to the above numerical result of H atom number density. The number density of H atom excitation level of 4 was compared with the emission intensity of Hβ.

IV. RESULTS AND DISCUSSION

In the spectroscopic measurements, emissions of Hβ, Hγ lines and CH-, C_2- bands were observed. Figure 2 shows the plasma density and peak emission intensity at 1 % of CH_4 concentration. Each spectral intensity has a maximum between 60 and 100 Pa. Also, the plasma density has a maximum at 67 Pa. Above 30 Pa, the peak intensity of Hβ and Hγ lines decreased with increasing CH_4 concentration. On the other hand, the peak intensities of CH and C_2 bands increased with CH_4 concentration. An increase in CH_4 concentration activates the CH_4 dissociation and produces CH, C_2 and other various fragments. However, we could not observe other fragments from the emission spectrum.

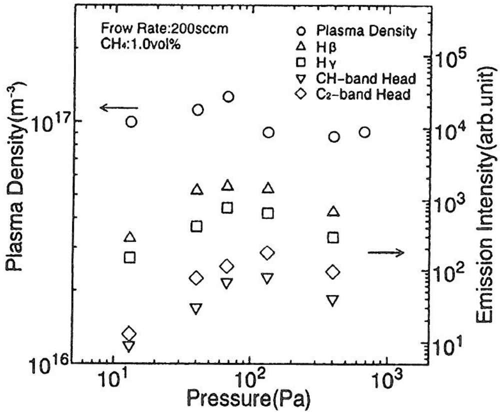

Fig. 2 Plasma density and peak emission intensities measured for various pressures.

Figure 3 shows the numerical results of eight neutral species at 1 % of CH_4 concentration. The number density of each species increases with pressure. Most of H_2 and CH_4 exist in plasma without dissociation and ionization. Except H_2 and CH_4, H atom is the most popular species and proportionally increases with pressure. On the other hand, CH_3 and CH increase with the pressure and saturated above 300 Pa. Although the number densities of C and C_2 are very low under 100 Pa, they rapidly increase with pressure.

Figure 4 shows the numerical results of eight neutral species at 4 % of CH_4 concentration. This is roughly the same plasma composition at 1 % of CH_4

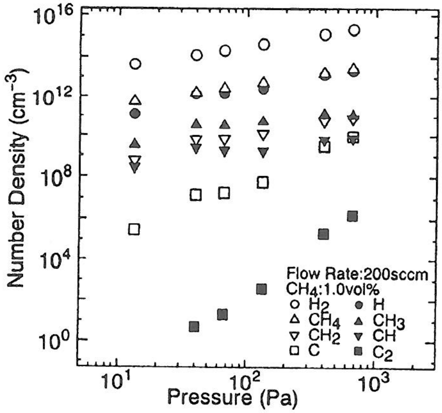

Fig. 3 Calculated particle densities for various pressures (CH_4: 1 vol%).

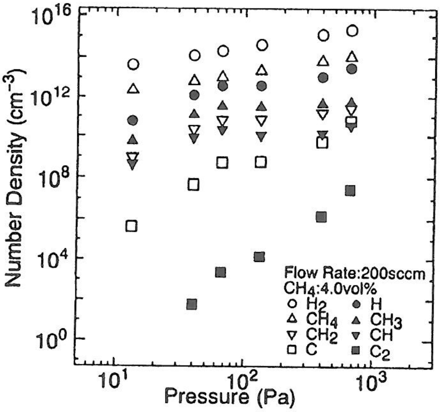

Fig. 4 Calculated particle densities for various pressures (CH_4: 4 vol %).

concentration. The number densities of dissociated species of CH_4 increase with CH_4 concentration at various pressures. However, the number density of H atom is almost unchanged.

Figure 5 shows the pressure dependence of calculated number density of excited H atoms and emission intensities of Hβ line. At 1 % and 4 % of CH_4 concentration, they agree with together. As shown in Figs. 3 and 4, the number density of H atom increased with the pressure. However, the plasma density decreases with increasing pressure around 67 Pa, as shown in Fig.2. Consequently, the number density of excited H atom decreased above 67 Pa. At 7 % CH_4 concentration, they greatly differ above 100 Pa. In the calculation of excited H atom, we only consider the collision between H atom and electron. At high CH_4 concentration and high pressure, excitation of H atom due to collisions with other species cannot be ignored. However, the number density of excited H atom is very low compared with other neutral species. It is considered to have little effect on the plasma composition

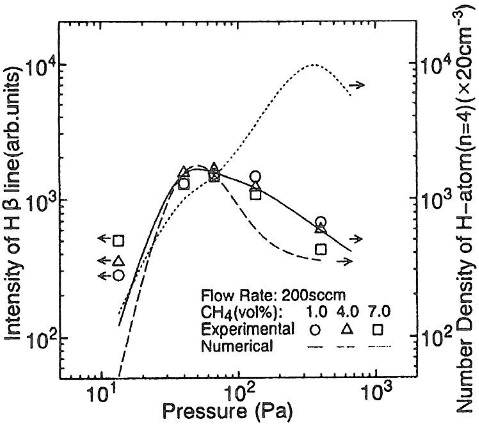

Fig. 5 Comparison of Hβ emission intensities with excited H-atom number densities for various pressures.

V. CONCLUSION

Microwave CH_4/H_2 plasma compositions were investigated by plasma diagnostics and kinetic calculations to examine the correlation between the plasma composition and the film quality. From the spectroscopic measurement, an increase in CH_4 concentration activated the CH_4 dissociation and produces CH, C_2 and other various fragments. From the kinetic calculation, CH_3 and CH increased with pressure and saturated above 300 Pa. Although the number densities of dissociated species of CH_4 increased with CH_4 concentration at various pressures, the number density of H atom was almost unchanged. At 1 % and 4 % of CH_4 concentration, both results agreed with together. At 7 % CH_4 concentration, they greatly differed above 100 Pa. Both results showed that the number densities of dissociated species of CH_4 were increased with pressure and CH_4 concentration. At the deposited condition for DLC film, CH_3 molecules and H atoms were expected to become main species within plasma.

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