Spectroscopic Measurement of DC Plasma Jet in Diamond Synthesis

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In synthesis of diamond with a plasma jet under medium pressure, the morphology of the deposited particles depends strongly on the ratio of the methane gas flow rate to the hydrogen gas flow rate and the distance from the feed ring exit to the substrate. The relationship between the morphology of the deposited particles and the chemical species in the plasma jet is studied by means of emission spectroscopy, with a view toward achieving large-area deposition at a high rate. The intensity ratio of the CH to the Hα spectrum is strongly correlated with the quality of the diamond synthesized and the deposition area.

KEY WORDS: diamond synthesis, plasma jet, spectroscopic measurement, thermal plasma, chemical vapor deposition

1. Introduction

Thermal plasma jets have the advantage that they can be used to synthize diamond at a higher rate than possible with any other chemical vapor deposition method, because thermal plasma jets have high temperature, speed and plasma density. On the other hand, since the plasma diameter is small and the radial gradient of the plasma parameters is steep, thermal plasma processing has the disadvantages that the deposition area is small and the film thickness and the film quality are not uniform. For scale-up of diamond synthesis with use of thermal plasma to the industrial level, it is important to achieve large-area deposition of diamond film at a high rate, and to clarify the mechanism of the diamond synthesis.

Several methods of achieving large-area deposition have been reported. One is the plasma production method, in which a large-volume plasma jet generated by three plasma jet generators[1] or a one cathode-three anode type plasma jet generator[2] is used. Another is a deposition method, in which the substrate is rotated[3] or moved linearly by use of an X-Y stage.[4]

We have also developed a method of large-area diamond film synthesis,[5,6] which involves use of a plasma jet under medium pressure where states of the produced plasma jet could be controlled from conventional thermal plasma to cold plasma states. We have studied the effects of processing conditions such as ambient gas pressure, substrate temperature, etc., on diamond synthesis and found that with use of a medium-pressure plasma jet, diamond films as large and uniform as ones synthesized by cold plasma processing can be synthesized at a high rate of the same order of magnitude as in

thermal plasma processing. In this report, we will discuss the correlation between the optical emission spectra for the plasma jet and the deposited diamond, with a view toward increasing the deposition area of the diamond film.

2. Experimental Setup

A schematic diagram of the experimental setup for the diamond synthesis is given in Fig. 1. A forced constricted type plasma jet generator with a feed ring (5mm diam.)[7] is mounted on the vacuum vessel (160mm diam., 500mm long). The plasma jet is generated by DC arc discharge and ejected into the vacuum vessel. The plasma gas is a mixture of argon and hydrogen. The carbon source, methane, is injected through the feed ring into the plasma jet. The vessel is continuously pumped by the mechanical booster pump ($1200m^3/h$) and the vessel pressure is adjusted to a desired value ranging from 3 to 760 Torr using a choke valve. Diamond particles or films are deposited on the molybdenum or silicon substrate. The luminance temperature of the substrate is monitored by an optical pyrometer. The diamond quality is determined by micro-Raman spectroscopy and its morphology is assessed by scanning electron microscopy (SEM).

Optical emission spectra for the plasma jet are measured using a condenser lens, an optical fiber and a spectrometer with a CCD array. For measurement of the two-dimensional distributions of the emission spectra, the condenser lens and the optical fiber are set on a stage which moves in both the axial and radial direction of the plasma jet. With the assumption that the plasma jet is axially symmetric and optically thin, the measured line intensity is converted to a radial

coefficient of the spectrum by means of Abel inversion.

The experimental conditions are as follows: working gas (Ar) flow rate, 20 l/min; jet power, 3 kW; chamber pressure, 3 -760 Torr; methane gas flow rate, 0.1 - 0.6 l/min; hydrogen gas flow rate, 5 l/min; distance from the feed ring exit to the substrate, 25 - 120 mm; and substrate temperature, 1050±50 ℃.

3. Experimental Results and Discussion

In diamond synthesis with this thermal plasma jet reactor, the ratio of the methane gas flow rate to the hydrogen gas flow rate (CH_4/H_2), the distance from the feed ring exit to the substrate (L), the chamber pressure (Pt) and the substrate temperature (Ts) are very important parameters because the morphology of the deposited particles depends strongly on these parameters. Typically three types of particles are synthesized. SEM images and micro-Raman spectra of these particles are shown in Fig. 2. Type A particles are polyhedral. Type B particles are spherical and include crystal planes (100). Type C particles are spherical and include no crystal planes. According to the Raman spectroscopy results, type A and type B particles are diamond, but type C particles are not. Type A diamond is of better quality than type B diamond.[8)]

Figure 3 shows the relationship between the morphology of the deposited particles and the CH_4/H_2 flow rate ratio for a constant Ts of 1050±50 ℃ and L (75 mm and 85 mm) as a parameter. With decreasing CH_4/H_2, particles are deposited in the order type C, type B and type A. That is to say, the diamond quality of the particles increases.[5)]

Figure 4 shows a photograph of the plasma jet during diamond synthesis. The jet is composed of a red core region and a green outer flame. A flow pattern of diamond shock can be observed in the plasma jet near the feed ring exit with the naked eye, though it is difficult to recognize the diamond shock in this photograph. According to this flow pattern, the jet is ejected at faster than the velocity of sound.

For clarification of the relationship between the morphology of the deposited particles shown in Fig. 2 and the chemical species in the plasma jet, emission spectra were measured. The spectra of Balmer series hydrogen (Hα, Hβ and Hγ), the hydrocarbon radical CH and the dicarbon, C_2, have attracted special interest, because they seem to be related to the morphology of the deposited particles.

Figure 5 shows a typical example of the two-dimensional distribution of the optical emission spectrum for the plasma jet, which is converted from the measured line intensity by means of Abel inversion. The spectral intensity decreases with increasing distance from the feed ring exit, but increases again in the vicinity of the substrate. The diameter of the plasma flame also decreases slightly with increasing distance from the feed ring exit and then rapidly increases in front of the substrate.[8] These results indicate that the plasma stagnates in front of the substrate. We consider this stagnation of the plasma flow to be strongly correlated with the quality of the deposited particles and the deposition area.

Figure 6 shows the radial distributions of Hα (656.2 nm), C_2 (516.5 nm) and CH (431.4 nm) at 1 mm above the substrate for methane gas flow rates Q_{CH_4} of 0.15, 0.3 and 0.5 l/min. These three flow rates correspond to deposition of type A, type B diamond and type C

particles, respectively. Under the conditions of the high quality diamond (type A) particle deposition, the Hα line intensity is the highest and the intensities of the C_2 and the CH spectra are the lowest. On the other hand, under the conditions of non-diamond particle (type C) deposition, the Hα intensity is the lowest and the intensities of the C_2 and the CH spectra are the highest. From these results, we can conclude that diamond is synthesized under conditions of a high H atom density and low CH and C_2 molecular densities.

The intensity ratios among the spectra shown in Fig. 6 seem to be important in terms of the quality of the deposited diamond particles. Figure 7 shows the radial distributions of the intensity ratio of CH to Hα (CH/Hα), corresponding to the three types of deposited particles. These distributions are calculated by division of the intensity of the CH spectrum by that of the Hα spectrum shown in Fig. 6. Apparently, diamond particles (type A and type B) are synthesized under the condition that CH/Hα is rather small. With increasing CH/Hα, the deposited particles vary from diamond to graphite. Furthermore, the radial distributions of CH/Hα were compared with the area of the diamond films obtained by 20 min of deposition. As shown in Fig. 7, CH/Hα, in the case of Q_{CH_4} = 0.15 l/min, remains nearly constant from the substrate center to radius r= 8 mm and increases suddenly beyond r= 8 mm. The radius of the diamond film obtained under the same conditions is about 7 mm. This diamond film radius is almost equal to the radius ($R_{CH/H\alpha}$) at which CH/Hα remains

nearly constant. In the case of QCH4 = 0.3 l/min, the radius of the diamond film is also found to be nearly equal to $R_{CH/H\alpha}$. That is to say, diamond is synthesized in the region where CH/Hα has a certain small constant value. In Figs. 6 and 7, the parameter is QCH4. For the relationship between the radius of the diamond film and $R_{CH/H\alpha}$, the same tendency is observed when the parameters are the distance from the feed ring exit to the substrate and the ambient gas pressure. In conclusion, the deposition area of the diamond film can be estimated by monitoring CH/Hα.

Furthermore, we investigated the possibility of changing CH/Hα or modifying the quality of the deposited diamond by injection of additional hydrogen into the plasma jet. We fed the additional hydrogen into the plasma fringe near the substrate using a copper tube as shown in Fig. 1. With increasing additional hydrogen flow rate, CH/Hα increases at the plasma fringe and, at the same time, the quality of the deposited diamond film deteriorates. Therefore, we have reconfirmed that the intensity ratio CH/Hα is a promising parameter for monitoring of diamond synthesis. It may be possible to increase the area of diamond synthesis by optimizing the conditions for the additional hydrogen injection.

4. Conclusions

Optical emission spectra for a plasma jet in diamond synthesis were measured as functions of key parameters (gas flow rate ratio, pressure and L). We have confirmed that the quality of the deposited

diamond depends strongly on the intensity ratio of the CH (431.4 nm) spectrum to the Hα (656.2 nm) spectrum and that the deposition area of the diamond film coresponds to the region where CH/Hα has a certain small constant value. Therefore, the intensity ratio of the CH spectrum to the Hα spectrum is used to monitor the diamond deposition in a plasma jet.

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Figure captions

Fig.1 A schematic diagram of the experimental setup for the diamond synthesis and measurement of the emission spectra.

Fig.2 SEM images of three types of particles and their micro-Raman spectra. Experimental conditions are as follows: Pt = 55 Torr and deposition time = 10 min.

Fig.3 The relationship between the morphology of the deposited particles and CH_4/H_2. Experimental conditions are as follows: Pt = 20 Torr and deposition time = 10 min.

Fig.4 A photograph of the plasma jet during diamond synthesis. Experimental conditions are as follows: Pt = 20 Torr, L = 75 mm and ratio of methane flow rate to hydrogen flow rate = 3 %.

Fig.5 A typical example of the two-dimensional distribution of the optical emission spectrum (Hα 656.2 nm) for the plasma jet. Experimental conditions are as follows: Pt = 20 Torr, L = 75 mm and ratio of methane flow rate to hydrogen flow rate = 3 %.

Fig.6 The radial distributions of (a) Hα (656.2 nm), (b) C_2 (516.5 nm) and (c) CH (431.4 nm) at 1 mm above the substrate for methane gas flow rates Q_{CH_4} of 0.15, 0.3 and 0.5 l/min. These three flow rates correspond to deposition of type A, type B diamond and type C particle, respectively. Experimental conditions are as follows: Pt = 20 Torr and L = 75 mm

Fig.7 The radial distributions of the intensity ratio of CH to Hα (CH/Hα), corresponding to the three types of the deposited particles. All the experimental conditions are the same as those for Fig.6.

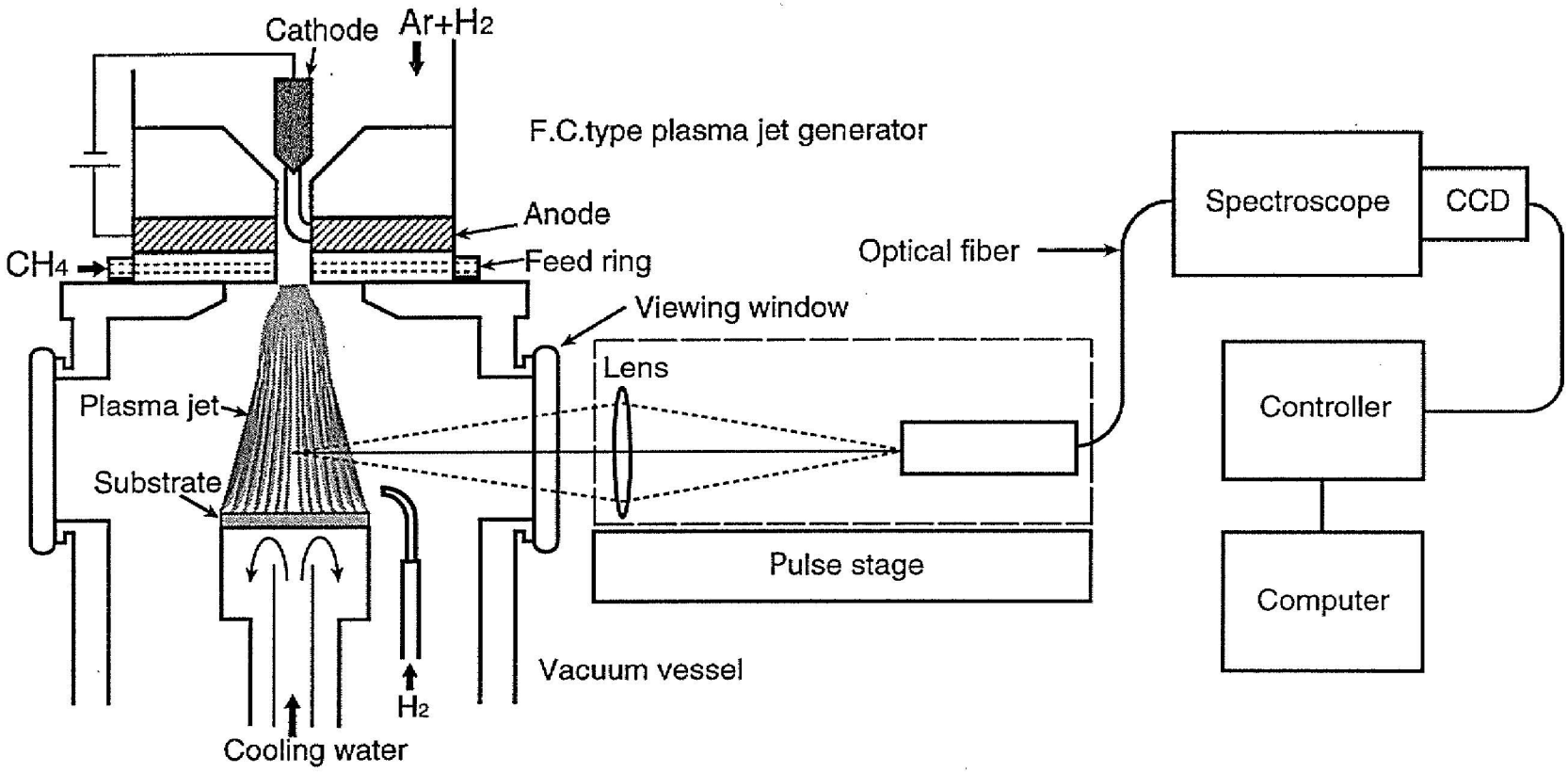

Cathode
Ar+H2
F.C.type plasma jet generator
Anode
CH4
Feed ring
Optical fiber
Spectroscope
CCD
Viewing window
Lens
Plasma jet
Controller
Substrate
Pulse stage
Computer
Vacuum vessel
H2
Cooling water

Fig.1

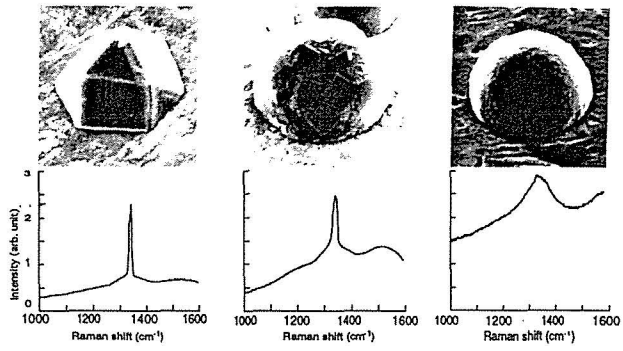

Intensity (arb. unit)
0
1
2
3
1000
1200
1400
1600
Raman shift (cm⁻¹)
(a) Type A
(b) Type B
(c) Type C

Fig.2

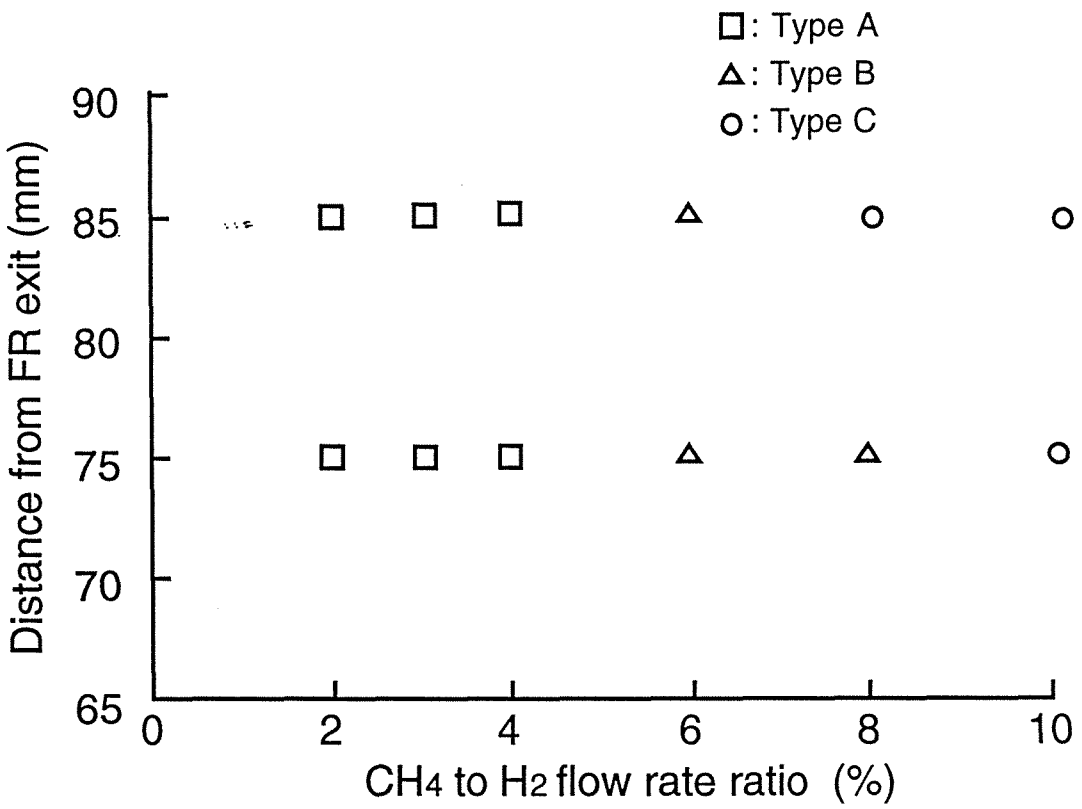

□: Type A
△: Type B
○: Type C
Distance from FR exit (mm)
90
85
80
75
70
65
0
2
4
6
8
10
CH4 to H2 flow rate ratio (%)

Fig.3

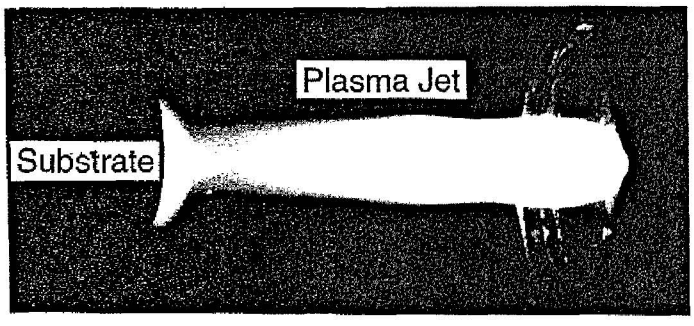


Fig.4

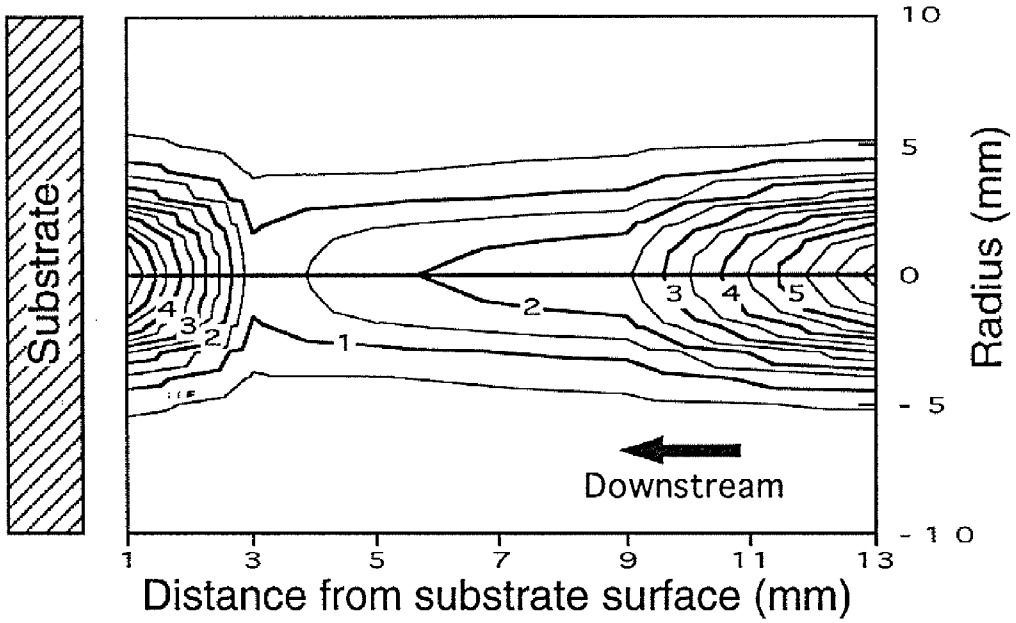
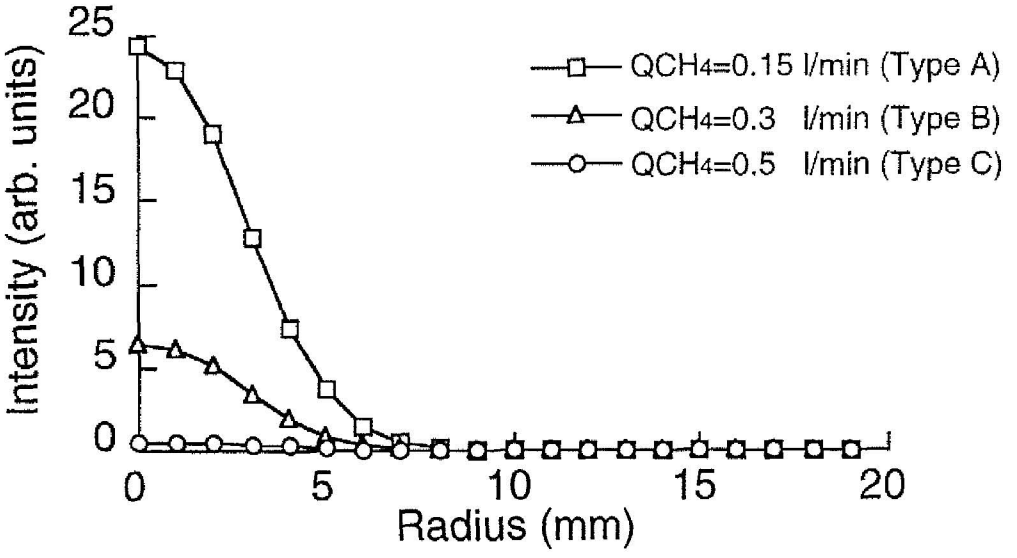
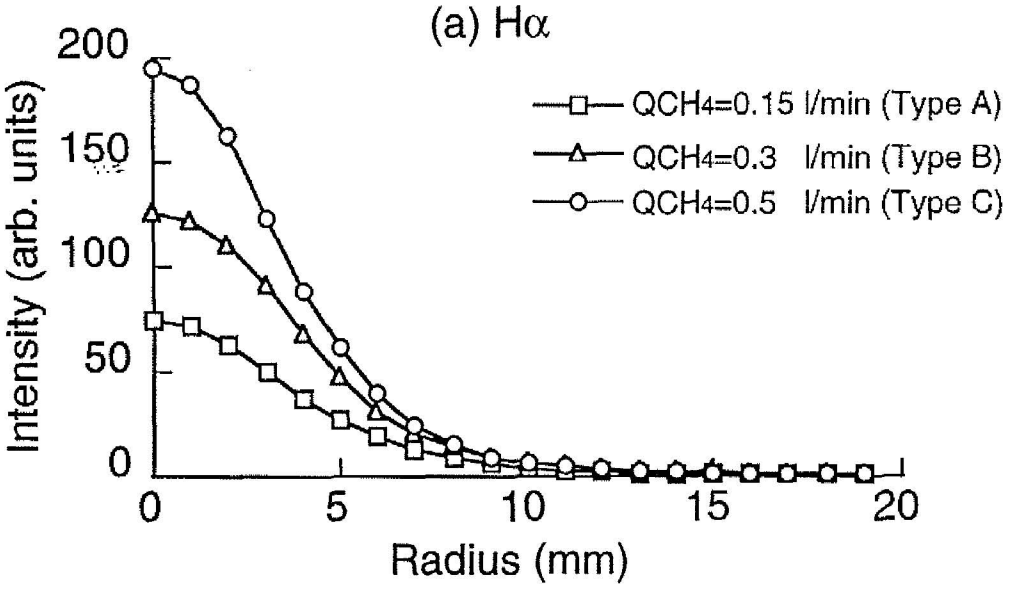

Substrate
10
5
0
- 5
- 10
Radius (mm)
1
2
3
4
5
Downstream
1
3
5
7
9
11
13
Distance from substrate surface (mm)

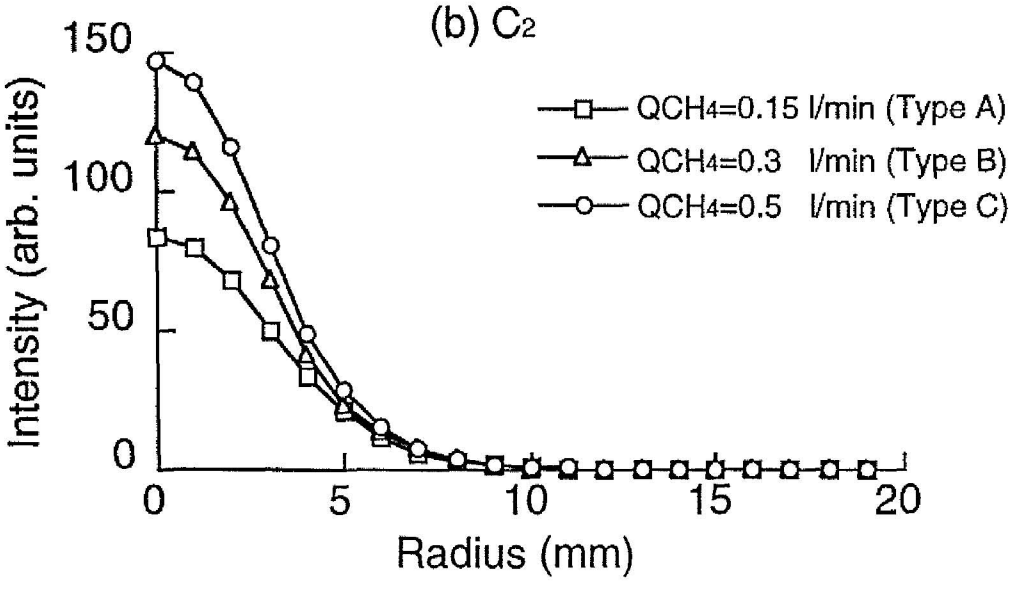
Fig.5



(a) Hα



(b) C_2



(c) CH

Fig.6

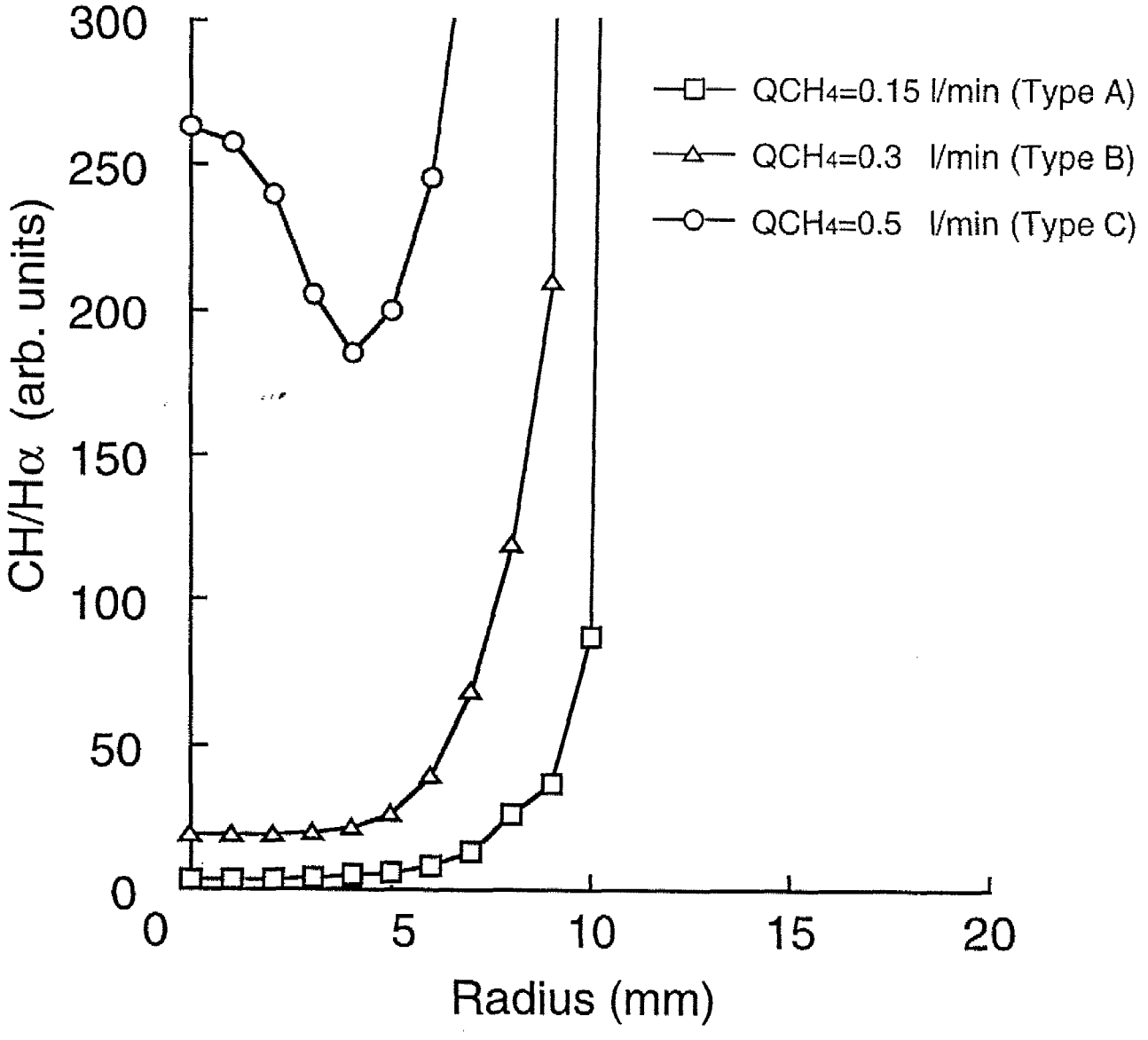

300
250
200
150
100
50
0
0
5
10
15
20
CH/Hα (arb. units)
Radius (mm)
QCH4=0.15 l/min (Type A)
QCH4=0.3 l/min (Type B)
QCH4=0.5 l/min (Type C)

Fig.7