Decomposition and polymerization of perfluorinated compounds in microwave-excited atmospheric pressure plasma

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Decompositions and polymerizations of perfluorinated compounds gases were demonstrated employing atmospheric pressure plasmas with continuous-wave microwave excitations. The atmospheric pressure plasma was generated at a low gas temperature of 520 K. Spherical-shaped particles of approximately 50–120 nm in diameter were synthesized in CF_4/He and C_4F_8/He plasma on Si substrate with dc voltage biasing, which was set in the plasma downstream region. The gas temperature in plasma was important to generate particles because particles were not generated at a high gas temperature of 850 K. The particles were determined to consist of carbon and fluorine atom composition from an energy dispersive x-ray spectroscopy. Furthermore, the effect of H_2 addition on the CF_4/He plasma was investigated. The decomposition efficiency of CF_4 was increased with H_2 addition and obtained over 80% without emissions of carbon dioxide. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1931034]

I. INTRODUCTION

Perfluorinated compounds (PFCs) gases have been widely used in the etching processes of dielectric films, in the deposition processes of fluorocarbon films and in the cleaning processes of chemical vapor deposition (CVD) chambers and so on. It is well known that PFCs cause a serious environmental problem due to their high global warming potentials (GWP) and long atmospheric lifetimes. In particular, CF_4 with a lifetime exceeding 50 000 years is generated as a by-product after the etching and CVD processing employing PFCs gases. Therefore, it is an important issue in the worldwide semiconductor industry to reduce the emission of PFCs gases into the atmosphere. Decomposition is a method of reducing the emission of PFCs. There exist many methods.

Several methods for the decomposition of PFCs gases have been proposed, employing plasma, thermal, and catalytic techniques. In the plasma technique, the point-of-use plasma abatement (PPA) has been proposed as a reduction method of PFCs emissions in the ultra large scale integration (ULSI) manufacturing. Excellent PFC oxidation characteristics in PPA method were shown by using a microwave plasma at pressures from hundred milliTorr to several Torr.[1,2] Furthermore, a rf plasma system for the abatement of C_2F_6 was investigated by Sawin and Vitale.[3] Fiala *et al.* showed that CF_4 can be generated at significant proportions in the abatement of a C_2F_6/O_2 mixture using an inductively coupled plasma (ICP) from a modeling study.[4] In these plasma, PFCs are changed to COF_2, CO, and CO_2 by oxidation. The conversion from CF_4 to CO_2 with greenhouse effect is considered not to be a final solution for preventing global warming. Therefore, it is necessary to decompose PFCs without the emission of CO_2.

Low gas temperature plasmas sustained at the atmospheric pressure have attracted much attention because plasma processings of materials at atmospheric pressure are able to be performed at the low temperature. To produce low gas temperature, several attempts have been proposed, such as corona discharges[5] and dielectric barrier discharges.[6] Kono *et al.* reported a low gas temperature and high-density plasma at the atmospheric pressure using microwave-excited discharge.[7] In the report, a high-density ($n_e = \sim 10^{15}$ cm^{-3}) nonequilibrium plasma was produced continuously by using microgap electrodes. The plasma source enables them to etch, deposit, and synthesize materials at low temperatures.

Recently, we have developed an environmentally benign silicon oxide (SiO_2) etching process using a solid material instead of PFCs gases.[8,9] A solid-state recovery process, where the exhaust PFCs after the etching process are polymerized to synthesize particles and where particles are collected, enables us to develop the etching process without uses of PFCs gases and emissions of CO_2. Therefore, we have proposed a technique of PFC abatement which converts PFCs to particles employing the atmospheric pressure plasma with microwave excitation.

It was necessary to abate PFCs in N_2 mixtures because N_2 was used as a purge gas for dry pumps. In this study, however, the PFC abatement was performed using He/PFCs mixture instead of N_2/PFCs mixture, because it is necessary to investigate the possibility that PFCs were converted to particles without CO_2 emission. Furthermore, by-products included nitrogen atom could be also formed in N_2/PFCs mixture. Therefore, the decomposition and polymerization of PFCs were investigated by using the rare gas. Recently, we produced atmospheric pressure plasma with microwave excitations employing N_2, Ar, or He gas.[10]

The PFC abatements in N_2 mixture at atmospheric pressure with microwave plasma have been investigated by other studies.[11,12] They reported good decomposition efficiency of PFCs by O_2 addition. In this study, we have demonstrated the decomposition and polymerization of C_4F_8 and CF_4 gases

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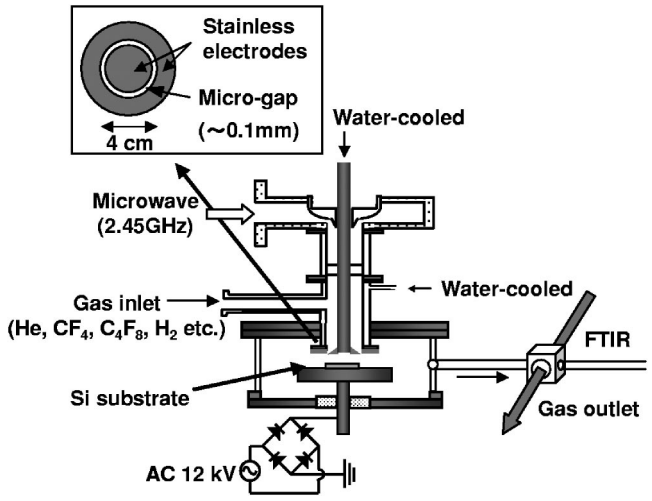

FIG. 1. Schematic diagram of the atmospheric pressure discharge system using microwave excitations.

employing the atmospheric pressure plasma with the microwave excitation. The syntheses of fluorocarbon particles from PFCs gases in atmospheric pressure plasmas have been never reported. The high decomposition efficiency of CF_4 gas over 80% was obtained without emissions of CO_2.

II. EXPERIMENT

Figure 1 shows a schematic diagram of the atmospheric pressure discharge system using microwave excitations. Microwaves (2.45 GHz) are converted to a coaxial mode through the rectangular-coaxial transfer, and then propagate along a water-cooled coaxial line to a ring microgap electrode with a gap distance of 0.1 mm. A plasma ring (40 mm in diameter) was generated between the microgap electrodes. The gas mixtures (He, CF_4, C_4F_8, or H_2) were introduced into the electrodes from an upper side of the electrode, and decomposed by the plasma generated between the electrodes. Fluorocarbon particles were collected on the Si substrate, which acted as an electrode supplied at 12-kV dc.

Fourier transform infrared (FTIR) absorption spectroscopy was performed for the analysis of exhaust gases. The decomposition efficiency of CF_4 in the atmospheric plasma was derived from the IR peak ratio of CF_4 (1283 cm^{-1}) before and after the discharge. The morphology and chemical structure of the synthesized fluorocarbon particles were evaluated by a scanning electron microscopy (SEM) and an energy dispersive x-ray spectroscopy (EDS).

A small amount of N_2 (0.05%) was added to the atmospheric pressure plasma employing He gas in order to evaluate the gas temperature. The gas temperature was measured by an optical emission spectroscopy (OES). The gas temperature was determined by comparing results between an experimental and a theoretical spectrum on the (0-2) band of the N_2 second positive system ($C\,^3\Pi_u - B\,^3\Pi_g$). The rotational temperature of the N_2 molecule was used to determine the gas temperature. In this study, Honl–London factors were used as the intensity distribution and Hund's case (a) was assumed. Each rotational line was represented by an expression of the instrumental line shape.[13]

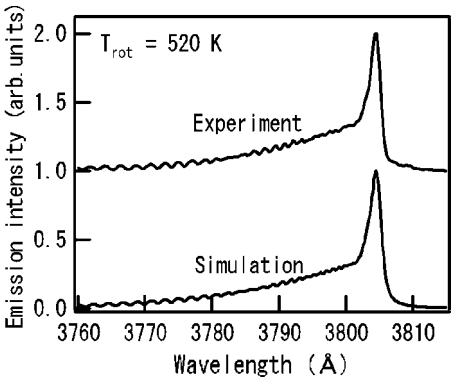

FIG. 2. Typical example of a measured emission spectrum and a calculated emission spectrum of the N_2 second positive system. The gas temperature was determined to be 520 K.

Figure 2 shows a typical example of a measured emission spectrum and a calculated emission spectrum of the N_2 second positive system. The emission intensity in He plasma including 0.05% N_2 gas were subtracted by one of pure He plasma. The gas temperature was evaluated to 520 K in the condition of a microwave power of 400 W, a total pressure of 10^5 Pa, and a gas flow rate of He=2000 SCCM (SCCM denotes cubic centimeter per minute at STP).

III. RESULTS AND DISCUSSIONS

A. Polymerization of fluorocarbon gases using the atmospheric pressure plasma at the low gas temperature

Fluorocarbon particles were fabricated using atmospheric pressure plasmas with microwave excitations. Figure 3 shows SEM images of particles synthesized after 2 min in

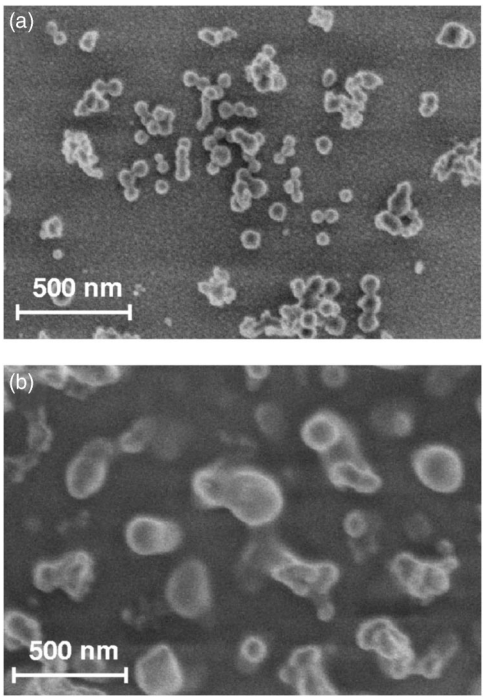

FIG. 3. SEM images of particles synthesized after 2 min in the condition of a microwave power of 400 W, a total pressure of 10^5 Pa, and gas flow rates of (a) CF_4/He=2.5/497.5 SCCM and (b) C_4F_8/He=2.5/497.5 SCCM.

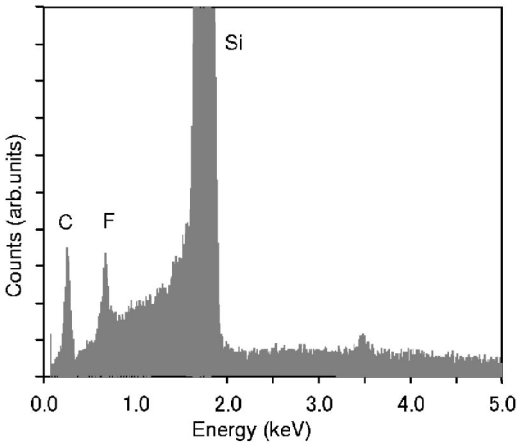

FIG. 4. EDS spectrum of the particles in Fig. 3(a).

the condition of a microwave power of 400 W, a total pressure of 10^5 Pa, and gas flow rates of (a) $CF_4/He = 2.5/497.5$ SCCM and (b) $C_4F_8/He = 2.5/497.5$ SCCM. The substrate was placed on the distance of 1 cm below plasma region, and biased at 12-kV dc. The negatively charged particles in the plasma region were accelerated toward the positively biased electrode. As a result, the particles were collected efficiently on the Si substrate. If some charged plates are used as an electrostatic precipitator, the particles could be collected more effectively. Spherical-shaped particles of approximately 50–250 nm in diameter were synthesized, as shown in Fig. 3. The particles in C_4F_8/He plasma were larger than the particles in CF_4/He plasma.

Gas temperature is an important parameter in atmospheric pressure plasma because particles are generated by three-body reactions in gas phase. The gas temperature was increased from 520 to 850 K without the water-cooled electrodes. Particles were not fabricated at the high gas temperature of 850 K in both C_4F_8/He plasma and CF_4/He plasma. Therefore, reduction of gas temperature is important to generate particles in the atmospheric pressure plasma. Formations of the particles were not also reported using the atmospheric pressure plasma at the high gas temperature over 1000 K in other studies.[12] Some techniques to reduce gas temperatures in the atmospheric pressure plasma were reported.[10]

Figure 4 showed the EDS spectrum of the particles in Fig. 3(a). The particles were shown to consist of carbon and fluorine atom composition. The peaks at 1.74 and 3.49 keV came from Si substrate used in this study.

B. Effects of H_2 additions on the decomposition of CF_4 with gas flow

The effect of a H_2 addition on the decomposition of CF_4 was investigated in $CF_4/He/H_2$ plasma. Figure 5 shows FTIR spectra of the exhaust gas with and without plasma in the condition of a microwave power of 600 W, a total pressure of 10^5 Pa, and gas flow rates of $CF_4/He/H_2 = 1/2000/6$ SCCM. The peak of HF was observed with the H_2 addition around 4000 cm^{-1}. Figure 6 shows the dependence of decomposition efficiency of CF_4 and the absorbance

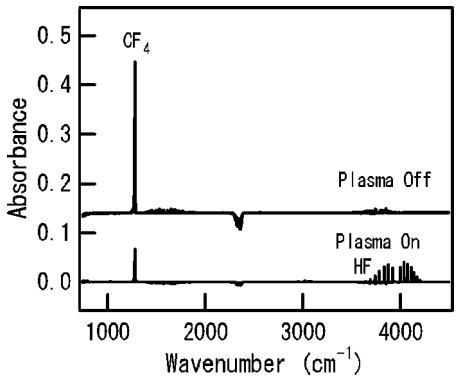

FIG. 5. FTIR spectra of the exhaust gas with and without plasma in the condition of microwave powers of a microwave power of 600 W, a total pressure of 10^5 Pa, and gas flow rates of $CF_4/He/H_2 = 1/2000/6$ SCCM.

of HF as a function of the H_2 flow rate. The decomposition efficiency of CF_4 was calibrated from the peak ratios of CF_4 (1283 cm^{-1}) with and without discharge, and the absorbance of HF was calibrated from the peak at 4039 cm^{-1}. As the H_2 flow rate was increased, the decomposition efficiency of CF_4 was increased from 12% to 85%, and saturated at the H_2 flow rate of 2 SCCM. The behavior of decomposition efficiency was similar to that of the HF absorbance. Therefore, these results indicated that the F abstraction reactions with H atoms were contributed greatly to the decomposition.

The generation of HF can be explained by reactions of H atoms with $CF_x(x=1-3)$ radicals and F atom, for example,

$$CF_3 + H \Rightarrow CF_2 + HF, \tag{1}$$

$$CF_2 + H \Rightarrow CF + HF, \tag{2}$$

$$CF + H \Rightarrow C + HF, \tag{3}$$

$$F + H + M \Rightarrow HF + M, \tag{4}$$

$$F + H_2 \Rightarrow HF + H. \tag{5}$$

The rate constants for reactions in Eqs. (1)–(3) are of the order of 10^{-11} cm^3/s, which are considerably large.[14] The reaction in Eq. (4) is the third-body association, and HF can be generated easily in the gas phase at the atmospheric pressure as compared with the low pressure. H atom was gener-

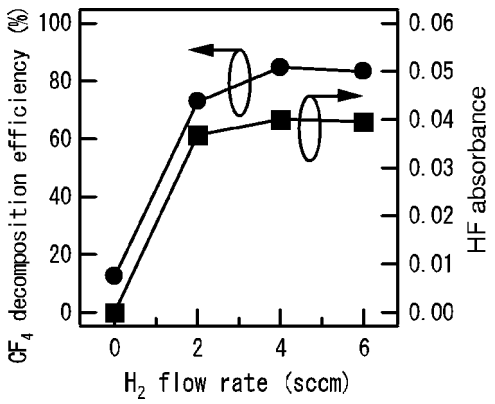

FIG. 6. The decomposition efficiency of CF_4 and the absorbance of HF as a function of the H_2 flow rate.

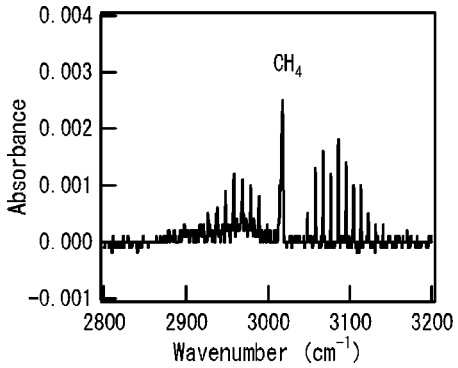

FIG. 7. The detailed FTIR spectrum around 2800−3200 cm^{-1} in Fig. 5.

ated not only by electron dissociation, but also by H abstraction reaction between F atoms and H_2 molecule, as shown in Eq. (5), where the rate constant is 8.27×10^{-12} cm^3/s.[15]

On the other hand, H atoms are less likely to react with feed molecular.

$$CF_4 + H \Rightarrow \text{products}. \tag{6}$$

The rate constant is $\sim10^{-36}$ cm^3/s, which is much smaller than those for reactions in Eqs. (1)–(3) and (5). The abstraction reaction of H atoms with CF_x ($x=1-3$) radicals and the reduction of F atoms seem to suppress the recombination of CF_x ($x=1-3$) radicals with F atoms. Furthermore, it was reported that when H_2 gas was added to the fluorocarbon plasma, the generation of fluorocarbon radicals is mainly dominated not by electron impact dissociation but by F abstraction due to H atoms with increasing gas pressure.[16] It is considered that the reduction of F atoms due to H_2 addition led to a high decomposition efficiency in the atmospheric pressure plasma. Fluorocarbon radicals might be distinguished in the gas phase by the recombination as follows, for example,

$$CF + CF_2 \Rightarrow C_2F_3 \Rightarrow C_xF_y. \tag{7}$$

Figure 7 shows the detailed FTIR spectrum around 2800−3200 cm^{-1} in Fig. 5. The peak of CH_4 was not observed in Fig. 5 because the absorbance of CH_4 was much smaller than that of CF_4 and HF. CH_4 around 3018.4 cm^{-1} was observed in the $CF_4/He/H_2$ plasma. CH_4 is known to be a greenhouse effect gas as well as CO_2, and is regulated in the COP3 Kyoto protcol. Figure 8 shows the CH_4 absorbance

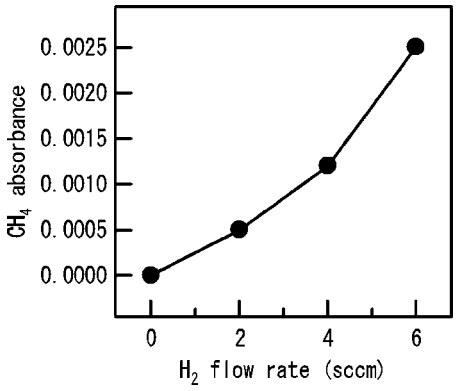

FIG. 8. CH_4 absorbance as a function of the H_2 flow rate.

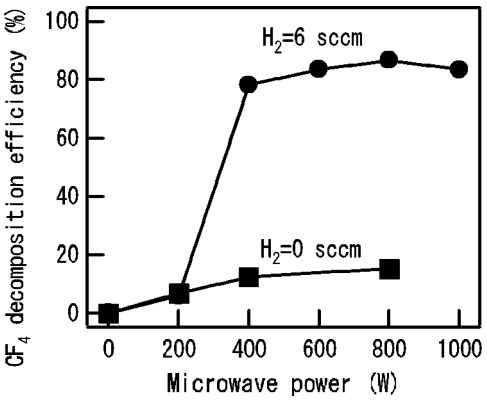

FIG. 9. Dependence of CF_4 decomposition efficiency on the microwave power at a microwave power of 0–1000 W, a total pressure of 10^5 Pa, and a gas flow rate of $He/CF_4/H_2=2000/1/0$ or 6 SCCM.

as a function of the H_2 flow rate. It was found that CH_4 was increased monotonously with increasing H_2 flow rate from 0 to 6 SCCM. On the other hand, the decompositon efficiency of CF_4 was saturated at the H_2 flow rate of 2 SCCM, as shown in Fig. 6. Therefore, it is necessary to add an optimum amount of H_2 gas because the addition of excess amount of H_2 gas led to the generation of CH_4.

Figure 9 shows the dependence of CF_4 decomposition efficiency on the microwave power. In the case without H_2 addition, the decompositon efficiency of CF_4 was increased with microwave power, but the efficiency was below 20%. On the other hand, in the case with H_2 addition ($H_2=6$ SCCM), the decomposition efficiency was increased to over 80% at microwave powers of more than 200 W. The H_2 gas was useful for the suppression of recombination between

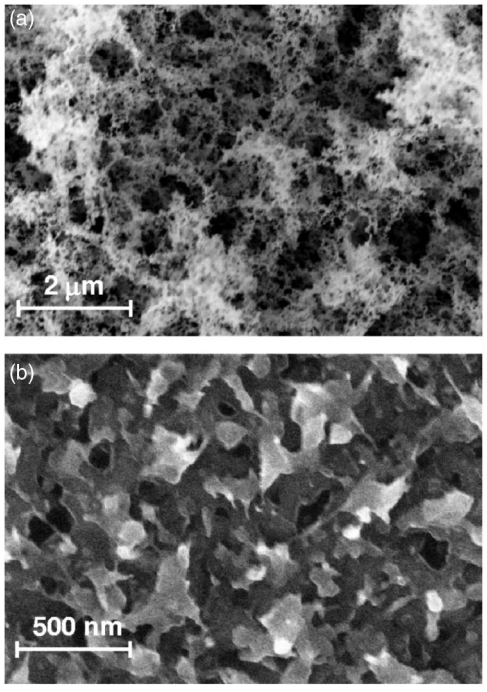

FIG. 10. SEM images of particles collected on the Si substrate at a microwave power of 600 W, a total pressure of 10^5 Pa, a discharge time of 20 min, and a gas flow rate of (a) $He/CF_4/H_2=2000/1/2$ SCCM and (b) $He/CF_4/H_2=2000/1/6$ SCCM.

F atom and CF_x radicals, and the generation of carbon particles as by-products without the emission of CO_2.

Figure 10 shows the SEM images of particles collected on the Si substrate in the condition of a microwave power of 600 W, a total pressure of 10^5 Pa, a discharge time of 20 min, and gas flow rates of (a) $CF_4/He/H_2=1/2000/2$ SCCM and (b) $CF_4/He/H_2=1/2000/6$ SCCM. In the case of $H_2=2$ SCCM the particles seemed to be a tubelike fragment, and in the case of $H_2=6$ SCCM the particles were thin films. As shown in Fig. 3, the spherical-shaped particles were synthesized without H_2 addition. It was reported that polymerization reactions in gas phase were suppressed due to the H_2 dilution in atmospheric pressure $CH_4/H_2/He$ discharge from the observation of Mie scattering.[17] The variation of the structure of particles was due to the differences of the polymerization reaction and the chemical bond. In conventional PFCs abatement, PFCs could be converted to CO, CO_2, and COF_2 with the addition of O_2.[3,11] At these plasmas, byproducts included carbon atoms were emitted, and therefore carbon particles were not produced. In this study, it was demonstrated that the low gas temperature and the H_2 addition without O_2 were useful to polymerize and decompose PFCs using the atmospheric pressure plasma.

IV. CONCLUSIONS

Atmospheric pressure plasma with microwave excitations were applied to the decomposition of PFCs. CF_4 and C_4F_8 gases were decomposed without emissions of CO_2, and fluorocarbon particles were synthesized. It was found that the gas temperature in plasma was an important parameter to generate particles in atmospheric pressure plasma. Furthermore, the effect of H_2 addition on the CF_4/He plasma was investigated. It was demonstrated that the low gas temperature and the H_2 addition without O_2 was useful to polymerize and decompose PFCs in the atmospheric pressure plasma.

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