

Effects of H, OH, and CH₃ radicals on diamond film formation in parallel-plate radio frequency plasma reactor

M. Ikeda, H. Ito,^{a)} M. Hiramatsu,^{b)} M. Hori, and T. Goto

Department of Quantum Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

(Received 3 March 1997; accepted for publication 7 July 1997)

Diamond films were successfully synthesized in both parallel-plate radio frequency (rf: 13.56 MHz) CH₄ and CH₃OH plasmas with injection of H and OH radicals generated in the remote microwave (2.45 GHz) H₂/H₂O plasma. Effects of H, OH, and CH₃ radicals on the diamond film formation in the rf plasma reactor were investigated by the formation of diamond films employing radical injection technique and the measurement of density in the plasma. Under the condition of diamond film formation, CH₃ density was measured by infrared diode laser absorption spectroscopy (IRLAS). The kinetics of CH₃ in rf CH₄ and CH₃OH plasmas with injection of H and OH radicals were evaluated from the results of optical emission spectroscopy and lifetime of CH₃ radicals estimated by IRLAS. © 1997 American Institute of Physics. [S0021-8979(97)06419-0]

I. INTRODUCTION

Diamond has many excellent properties such as negative electron affinity, mechanical hardness, high thermal conductivity, and wide band gap. These properties have been expected to be applied to field emitters, mechanical cutting tools, heatsinks of semiconductor, and semiconductors in a high temperature operation. Therefore, various techniques of diamond film formation, represented by a hot filament chemical vapor deposition (HFCVD) and a plasma enhanced chemical vapor deposition (P-CVD), have been developed.¹⁻⁵

In order to realize the synthesis of diamond films with high quality, the clarification of mechanism of diamond film formation is necessary. Up to now, the mechanism of diamond film formation has been studied by theoretical calculations and experimental methods. Through these studies, some models of diamond film growth have been proposed. Harris reported the epitaxial growth on (100) diamond crystal through the surface reaction due to CH₃ and H radicals.⁶ Moreover, existence of CH₃ radicals on the surface of diamond film deposited by P-CVD was confirmed using a scanning tunneling microscope.⁷ However, some researchers have reported the growth of diamond through species containing carbon other than CH₃ radicals. Zhang *et al.*⁸ reported that C atoms had a potential for the diamond formation by the theoretical calculation in the gas phase. Gruen *et al.*⁹ reported the deposition of diamond film from C₂ in the microwave plasma employing C₆₀ and mixture gases of Ar and H₂. However, the mechanism of diamond film growth has not been clarified entirely.

In order to clarify the mechanism of the diamond film growth, it is indispensable to get the information on the behavior of radicals in the plasma with relation to the characteristics of diamond films. In our previous studies, we have proposed a radical injection technique (RIT) to control radi-

cals in the plasma with keeping the plasma parameter constant. RIT has also enabled us to investigate the effect of radicals of interest on the process. Using this RIT, diamond has been successfully synthesized in the parallel-plate rf plasma reactor for the first time.¹⁰⁻¹² Moreover, H and OH radicals have been found clearly to play a critical role in etching of nondiamond phases during the diamond formation.^{10,12} However, there was no information on CH₃ radicals in the plasma with injection of H and OH radicals in our previous studies. Since the CH₃ radicals has been regarded as important precursor for the deposition of the diamond films, investigations of the kinetics of CH₃ radicals together with H and OH radicals in the gas phase are necessary for better understanding of the mechanism of diamond film formation.

In this article, effects of H, OH, and CH₃ radicals on the diamond film formation in the parallel-plate rf (13.56 MHz) plasma reactor employing RIT were investigated by the measurement of radical density in the plasma. Films were deposited in the parallel-plate rf CH₄ and CH₃OH plasmas assisted by injection of H and OH radicals generated in the remote microwave (2.45 GHz) H₂/H₂O plasma. The behaviors of CH₃ radicals in these plasmas were investigated by using infrared diode laser absorption spectroscopy (IRLAS) measurement. The kinetics of CH₃ radicals in the plasma are evaluated from the results of optical emission spectroscopy (OES) and lifetime of the CH₃ radicals estimated by IRLAS.

II. EXPERIMENT

A main reaction chamber used for the diamond film formation was equipped with circular parallel-plate electrodes of 8.5 cm in diameter with a separation of 4 cm. The remote microwave plasma system for the generation of radicals to be injected into the rf plasma region was attached to the side wall of the main reaction chamber as described in Refs. 10 and 11. CH₃OH or CH₄ gas was introduced into the rf plasma region. H₂ and H₂O gases were fed through the quartz tube equipped with the discharge cavity, and were excited by a microwave plasma. The inner diameter of quartz tube was 1.0 cm and the distance from the center of micro-

^{a)}Also with: Electronics Department, Nagoya Municipal Industrial Research Institute, Atsuta-ku, Nagoya 456, Japan.

^{b)}Also with: Department of Electrical and Electronic Engineering, Meijo University, Tempaku-ku, Nagoya 468, Japan.

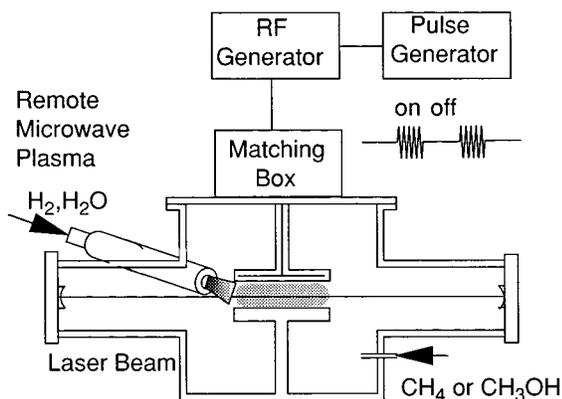


FIG. 1. Schematic diagram of experimental system.

wave plasma region to the edge of quartz tube was 6.3 cm. A substrate was set on the electrically isolated stainless block on the grounded electrode and was biased positively during the deposition. The substrate was a (100) Si, which was polished for 1 h with 30–40 μm diamond powders in the solution with an ultrasonic vibrator. The polished Si substrates were rinsed with acetone for 10 min.

The thickness of deposited films was measured using a tally step. A deposition rate of films was obtained by dividing the thickness of deposited films by deposition period. Deposited films were characterized by a scanning electron microscope (SEM), an x-ray diffraction (XRD), and a Raman spectroscopy.

Figure 1 shows an rf P-CVD chamber used for the measurement of CH_3 radical density. It was the same as the system reported in Ref. 13 except for a remote radical source (Superior microwave radical source, Irie Koken Co., Ltd.). The size of the chamber was 40 cm in inner diameter and 40 cm in height. The rf plasma chamber was equipped with a pair of circular parallel-plate electrodes of 20 cm in diameter the chamber with a separation of 4.5 cm. The microwave plasma system for the generation of radicals to be injected was attached to the side wall of the rf plasma chamber. The radicals source employed in the present study has been described in detail in Ref. 14. The diameter of an orifice in front of the microwave plasma cavity was about 0.5 cm, which was made from hexagonal boron nitride. The distance between the orifice and center of the electrode was about 20 cm.

CH_3OH or CH_4 gas was introduced into the rf plasma region. Moreover, a small amount of Ar gas was added to the rf plasma to obtain the information on the electron density and electron temperature in the plasma. The partial pressure of Ar gas was 0.13 Pa. H_2 and H_2O gases were introduced into the microwave plasma region and then dissociated species were injected into the rf plasma region. An rf power was modulated by the square wave signal with an on-period of 20 ms and an off-period of 38 ms and was applied to the upper electrode. The microwave power was continuously applied to the discharge cavity.

In rf CH_4 and CH_3OH plasmas with H radical injection, CH_3 radical density was measured as a function of micro-

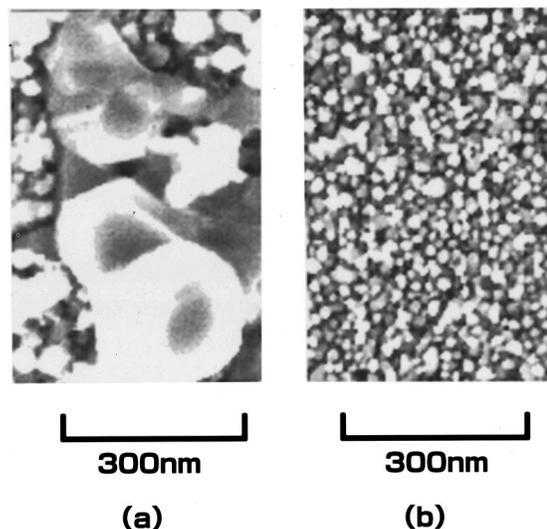


FIG. 2. SEM images of surface of deposited films (a) in rf CH_3OH plasma assisted by H radical injection, which is cited from Ref. 12 and (b) in rf CH_4 plasma assisted by H radical injection.

wave power. In these measurements, the density of H radicals injected into the rf plasma was controlled by varying the microwave power. Experiments were carried out at a CH_3OH or CH_4 partial pressure of 2.67 Pa, an H_2 partial pressure of 10.7 Pa, and an rf power density of 0.83 W cm^{-2} . The lifetime of the CH_3 radicals in the plasma was also measured from the decay curve of CH_3 radical density after the termination of rf plasma.

In CH_3OH and CH_4 plasmas with H and OH radical injection, CH_3 radical density was measured as a function of mixture ratio of H_2 and H_2O gases at a total pressure of 13.3 Pa, a CH_3OH or CH_4 partial pressure of 2.67 Pa, an rf power density of 0.83 W cm^{-2} , and a microwave power of 300 W.

In the measurement of CH_1 radical density, the IR laser beam was passed 40 times through the rf plasma region at the position of 2 cm above the lower electrode. The absorption length is assumed to be 800 cm (20 cm of electrode diameter \times 40 times of number of crossing the plasma). The temperature is estimated to be 400 K from the linewidth of absorption profile due to CH_3 radicals.

In the OES measurement, emission intensities of Ar^* [$750.4 \text{ nm } 4s'(1/2)^0-4p'(1/2)$ transition], OH ($308.9 \text{ nm } A^2E^+-X^2\Pi$ transition), and O ($777.4 \text{ nm } 3p^5P-3s^3S^0$ transition) were used. The light emitted from the rf plasma region was focused on the monochromator using lens and detected with photomultiplier tube.

III. RESULTS AND DISCUSSION

A. Effects of H radical injection on diamond formation

In the case of film formation using rf CH_3OH and CH_4 plasmas assisted by the H radical injection, films were deposited at pressures of $\text{CH}_3\text{OH}/\text{H}_2=0.66/13.3 \text{ Pa}$ and $\text{CH}_4/\text{H}_2=0.66/13.3 \text{ Pa}$, a substrate temperature of 600°C , a substrate bias of +5 V, an rf power of 100 W, and a microwave power of 100 W. Figures 2(a) and (b) show the SEM

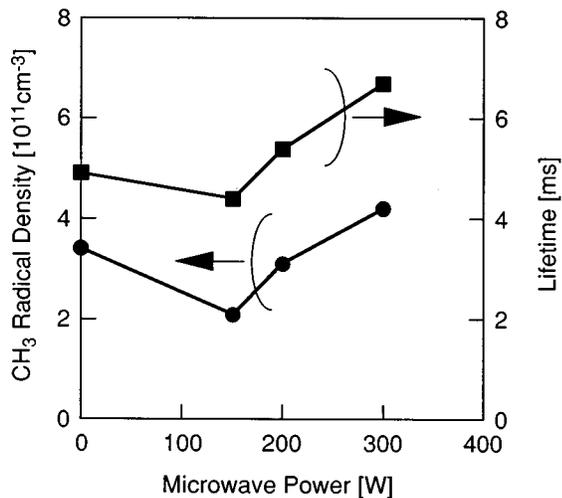


FIG. 3. The density and lifetime of CH₃ radical in the rf CH₃OH plasma with H radical injection as a function of microwave power.

images of the surface of films deposited using rf CH₃OH and rf CH₄ plasmas, respectively. Figure 2(a) is cited from our previous results in Ref. 10. In the case of rf CH₃OH plasma with injection of H radicals, diamond nuclei with grain size of 200–300 nm and ball-like deposits 50–100 nm in size were observed from Fig. 2(a). In the case of rf CH₄ plasma with H radical injection, on the other hand, only ball-like nondiamond phases with 10–30 nm in size were observed and the diamond nuclei were not formed as shown in Fig. 2(b). Therefore, it is worth noting that the diamond formation is considerably influenced by feed gases used in this system.

B. Kinetics of CH₃ radicals in rf plasma with H radical injection

In order to investigate the influence of feed gases on the diamond film formation in this study, CH₃ radical density was measured in rf CH₃OH and CH₄ plasmas with H radical injection using IRLAS. Figure 3 shows the density and lifetime of CH₃ radicals in the rf CH₃OH plasma with H radical injection as a function of microwave power. The density of H radicals injected into the rf plasma was controlled by the variation of microwave power. CH₃ radical density decreased at the microwave power of 150 W, and then increased with further increasing the microwave power. At the microwave power of 300 W, CH₃ radical density was estimated to be $4 \times 10^{11} \text{ cm}^{-3}$ in the rf CH₃OH plasma with the H radical injection. In the same manner, the lifetime of CH₃ radicals decreased at the microwave power of 150 W and then increased with further increasing the microwave power.

Figure 4 shows Ar* emission intensity as a function of microwave power. Ar* emission intensity increased up to the microwave power of 150 W and then was almost constant with further increasing the microwave power.

Figure 5 shows the density and lifetime of CH₃ radicals in the rf CH₄ plasma with H radical injection as a function of microwave power. It was found that both CH₃ radical density

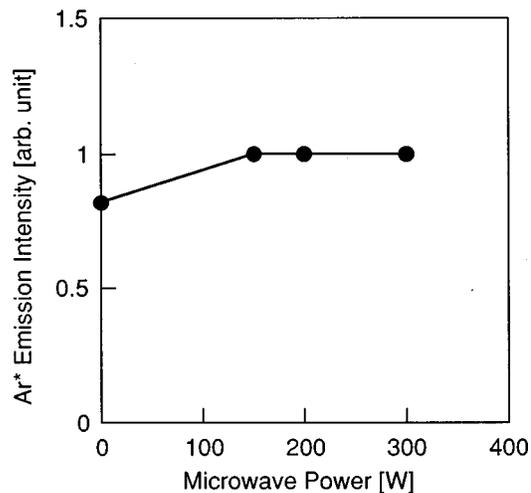


FIG. 4. The optical emission intensities of Ar* in the rf CH₃OH plasma with H radical injection as a function of microwave power.

and the lifetime of CH₃ radicals decreased with increasing the microwave power. At the microwave power of 300 W, CH₃ radical density was estimated to be $3 \times 10^{11} \text{ cm}^{-3}$ in the rf CH₄ plasma with H radical injection.

Figure 6 shows Ar* emission intensity as a function of microwave power. The emission intensity of Ar* was almost constant with the variation of microwave powers up to 200 W, and then increased with further increasing the microwave power.

The effects of H radical injection on CH₃ radicals in rf CH₃OH and CH₄ plasmas are discussed by reactions of H radicals with CH₃ radicals and parent gases. The production and loss reactions of CH₃ radicals due to H radicals in rf CH₃OH and CH₄ plasmas are listed in Table I.

Using these reaction rate constants and measured CH₃ radical density as shown in Fig. 3, the production rate of CH₃ radicals due to the reaction of Eq. (1) was estimated to be

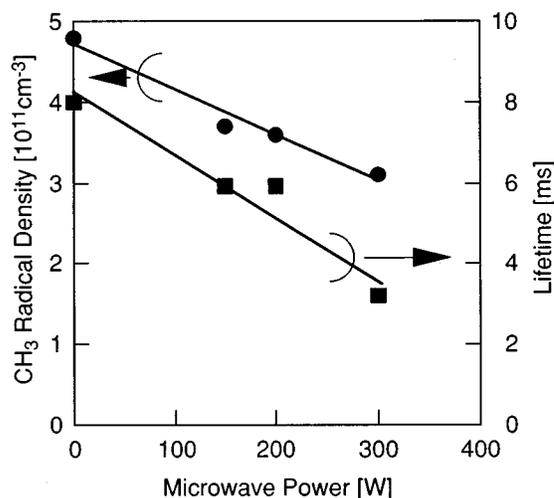


FIG. 5. The density and lifetime of CH₃ radical in the rf CH₄ plasma with H radical injection as a function of microwave power.

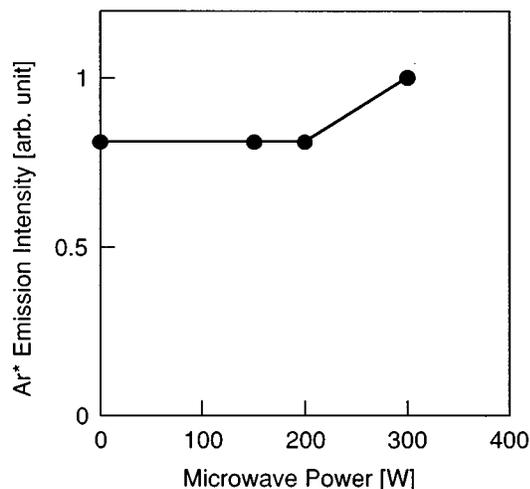


FIG. 6. The optical emission intensities of Ar* in the rf CH₄ plasma with H radical injection as a function of microwave power.

52 s⁻¹ in the rf CH₃OH plasma under the present condition of [CH₃OH]=6×10¹⁴ cm⁻³. On the other hand, the loss rate due to the reactions of Eqs. (3) and (4) was estimated to be 16 s⁻¹ under the present condition of [CH₃]=4×10¹¹ cm⁻³. The production rate of CH₃ radicals due to H radicals was larger than the loss rate due to the H radicals reaction, which caused the increase of the lifetime of CH₃ radicals in the case of H radical injection. Ar* emission intensity represents the product of the electron density and electron temperature in the plasma. In the rf CH₃OH plasma with H radical injection, the product of the electron density and electron temperature was almost constant at microwave powers above 150 W. This result suggests that the generation of CH₃ radicals from CH₃OH molecules by the electron impact dissociation was almost constant. Therefore, the increase of CH₃ radical density was caused by the production of CH₃ radicals due to the reaction of H radicals with parent CH₃OH molecules.

In the rf CH₄ plasma with H radical injection, the production rate of CH₃ radicals due to the reaction of Eq. (2) in Table I was estimated to be 2×10⁻³ s⁻¹ under the present condition of [CH₄]=6×10¹⁴ cm⁻³. On the other hand, the loss rate due to the reaction between CH₃ and H radicals was estimated about 10 s⁻¹ with [CH₃]=3×10¹¹ cm⁻³. The loss rate due to the reaction between CH₃ and H radicals was much larger than the production rate due to the reaction of H radicals with parent CH₄ molecules because the reaction rate constant between H and CH₃ radicals was much larger than that between H and parent CH₄ molecules. With increasing the density of H radicals injected into rf plasma region, the

TABLE I. Generation and loss reactions of CH₃ radical due to the injection of H radicals in rf CH₃OH plasma and CH₄ plasma.

Chemical reaction	Reaction rate constant	Reference
CH ₃ OH+H→CH ₃ +H ₂	k ₁ =8.6×10 ⁻¹⁴ cm ³ s ⁻¹ (1)	15
CH ₄ +H→CH ₃ +H ₂	k ₂ =3.2×10 ⁻¹⁸ cm ³ s ⁻¹ (2)	16
CH ₃ +H→CH ₂ +H ₂	k ₃ =3.3×10 ⁻¹¹ cm ³ s ⁻¹ (3)	17
CH ₃ +H→CH ₄	k ₄ =7.0×10 ⁻¹² cm ³ s ⁻¹ (4)	18

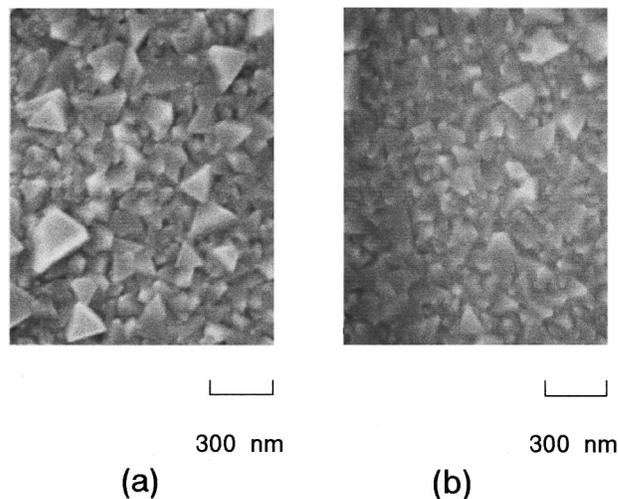


FIG. 7. SEM images of surface of deposited diamond films (a) in the rf CH₃OH plasma assisted by H and OH radical injection and (b) in the rf CH₄ plasma assisted by H and OH radical injection.

lifetime of CH₃ radicals decreased due to the loss reaction between CH₃ and H radicals Ar* emission intensity representing the generation of CH₃ radicals due to the electron impact dissociation did not decrease with increasing microwave power. Observed decay curves of CH₃ radical density were well fitted to the single exponential. Moreover, the lifetime of CH₃ radicals was two orders of magnitude shorter than the residence time of feed gases. These results indicate that the loss process of CH₃ radicals was through the reaction loss. Therefore, the density and lifetime of CH₃ radicals decreased due to the increase in the the loss reaction between CH₃ and H radicals in the rf CH₄ plasma.

When H radicals were injected into rf CH₃OH and CH₄ plasmas at the same amount, CH₃ radical densities in both plasmas were almost the same, and were of the order of 10¹¹ cm⁻³ at the rf power density of 0.83 W cm⁻². However, the diamond was successfully formed only using the rf CH₃OH plasma assisted by H radical injection. The diamond formation cannot be explained by the difference of CH₃ radical density between rf CH₃OH and CH₄ plasmas with H radicals injection.

C. Effects of OH radical injection on diamond film formation

Figures 7(a) and 7(b) show SEM images of the surface morphology of films deposited in rf CH₃OH and CH₄ plasmas with injection of OH radicals together with H radicals, respectively. These experiments were carried out at a total

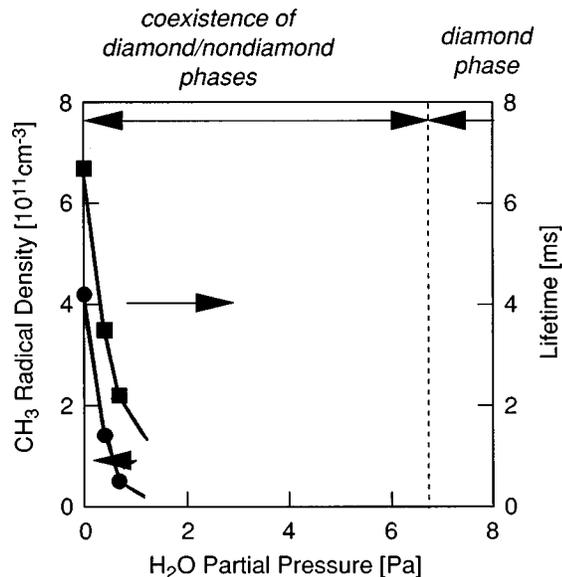


FIG. 8. The density and lifetime of CH_3 radical in rf CH_3OH plasma with H and OH radicals injection as a function of H_2O pressure.

pressure of 13.3 Pa, $\text{H}_2/\text{H}_2\text{O}$ pressures of 5.34/6.67 Pa, a substrate temperature of 600 °C, a substrate bias of +5 V, an rf power of 100 W, and a microwave power of 100 W. In our previous paper, a diamond peak at 1333 cm^{-1} was observed in deposited films using this system from the Raman spectroscopy.¹¹ In both rf CH_3OH and CH_4 plasmas, diamond films were successfully deposited by the injection of OH radicals in addition to H radicals. The deposition rates of these films were almost the same and the value was 33 nm/h. The quality of diamond in these films was almost the same by the measurement of XRD. It was found that OH radical injection is effective on the diamond film formation using the parallel-plate rf plasma.

D. Kinetics of CH_3 radicals in rf plasma with OH radical injection

Figure 8 shows the density and lifetime of CH_3 radicals in the rf CH_3OH plasma as a function of H_2O partial pressure. The CH_3 radical density decreased rapidly at H_2O partial pressures up to 0.67 Pa and then the absorption signal attributed to CH_3 radicals could not be detected with further increasing H_2O pressure. The density of CH_3 radicals at H_2O partial pressures above 0.67 Pa was estimated to be less than

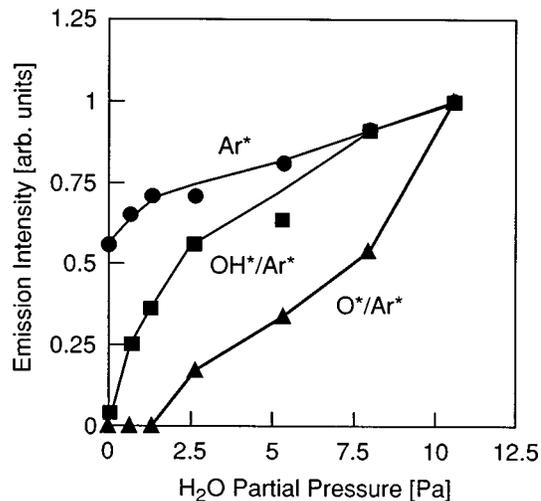


FIG. 9. The optical emission intensities of Ar^* , OH, and O in rf CH_3OH plasma with H and OH radicals injection as a function of H_2O pressure.

$4.0 \times 10^{10}\text{ cm}^{-3}$ from the detection limit of 0.1% absorption. The lifetime of CH_3 radicals also decreased with increasing H_2O pressure.

Figure 9 shows emission intensities of Ar^* , OH, and O in the rf CH_3OH plasma as a function of H_2O partial pressure. Emission intensities of OH and O were normalized by Ar^* emission intensity and then all emission intensities were normalized to unity at the H_2O pressure of 10.7 Pa. The emission intensities of Ar^* , OH, and O increased with increasing H_2O partial pressure. Especially, the emission intensities of OH and O increased considerably.

Here, effects of injected OH and O radicals on CH_3 radicals in the rf CH_3OH plasma are discussed on the basis of the reactions of CH_3 radicals with OH and O radicals. The production and loss reactions of CH_3 radicals with OH and O radicals in rf CH_3OH and CH_4 plasmas are listed in Table II.

There has been no data for the production of CH_3 radicals due to reactions of OH and O radicals with parent CH_3OH molecules. These production rate of CH_3 radicals would be negligibly small. The loss reactions of CH_3 radicals with OH and O radicals are given by Eqs. (9) and (10). The reaction rate constants for the reactions of CH_3 with OH and O radicals were of the order of 10^{-11} and $10^{-10}\text{ cm}^{-3}\text{ s}^{-1}$, respectively, which are rapid reaction rates. Using these reaction rate constants listed in Table II, loss rates of CH_3 radicals due to the reaction with OH and O were estimated to

TABLE II. Generation and loss reactions of CH_3 radical due to OH and O radicals in rf CH_3OH plasma and CH_4 plasma.

Chemical reaction	Reaction rate constant	Reference
$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_3 + \text{products}$	no data	(5)
$\text{CH}_3\text{OH} + \text{O} \rightarrow \text{CH}_3 + \text{products}$	no data	(6)
$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	$k_7 = 3.3 \times 10^{-15}\text{ cm}^3\text{ s}^{-1}$	(7)
$\text{CH}_4 + \text{O} \rightarrow \text{CH}_3 + \text{OH}$	$k_8 = 6.6 \times 10^{-18}\text{ cm}^3\text{ s}^{-1}$	(8)
$\text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{OH}$	$k_9 = 3.5 \times 10^{-11}\text{ cm}^3\text{ s}^{-1}$	(9)
$\text{CH}_3 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	$k_{10} = 1.3 \times 10^{-10}\text{ cm}^3\text{ s}^{-1}$	(10)

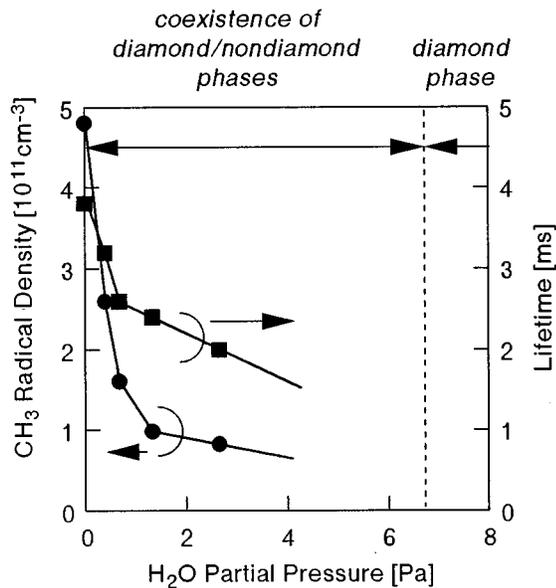


FIG. 10. The density and lifetime of CH_3 radical in rf CH_4 plasma with H and OH radicals injection as a function of H_2O pressure.

be 10 and 30 s^{-1} , respectively, under the present condition of $[\text{CH}_3]=3 \times 10^{11} \text{ cm}^{-3}$. With the injection of OH and O radicals into the rf CH_3OH plasma, only loss reactions of CH_3 radicals are considered to occur.

The behavior of CH_3 radicals shown in Fig. 8 is explained by the results of emission intensities in Fig. 9 and chemical reactions described in Table II. From the emission intensities, OH and O radicals contributing to the loss of CH_3 radicals increase with increasing H_2O partial pressure. Although Ar^* emission intensity representing the generation of CH_3 radicals due to the dissociation of feed gas by the electron impact increased with increasing H_2O partial pressure, the variation of Ar^* emission intensity was relatively small compared with those of OH and O emission intensities. Observed decay curves of CH_3 radical density were well fitted to the single exponential. Moreover, the observed lifetime of CH_3 radicals was two orders of magnitude shorter than the residence time of feed gases. These results indicate that the loss process of CH_3 radicals was due to the reaction loss. Therefore, the density and lifetime of CH_3 radicals were decreased by the increase in the loss reaction of CH_3 radicals with OH and O radicals.

Figure 10 shows the density and lifetime of CH_3 radicals in the rf CH_4 plasma as a function of H_2O pressure. In the same manner as rf CH_3OH plasma, the density and lifetime of CH_3 radicals decreased with increasing H_2O partial pressure and CH_3 radicals could not be detected at H_2O pressures above 5.34 Pa.

Figure 11 shows emission intensities of Ar^* , OH, and O in the rf CH_4 plasma as a function of H_2O partial pressure. Emission intensities of OH and O were normalized by the Ar^* emission intensity and all emission intensities were normalized to unity at the H_2O pressure of 10.7 Pa. The emission intensity of Ar^* was almost constant with the variation of H_2O partial pressure. On the other hand, emission inten-

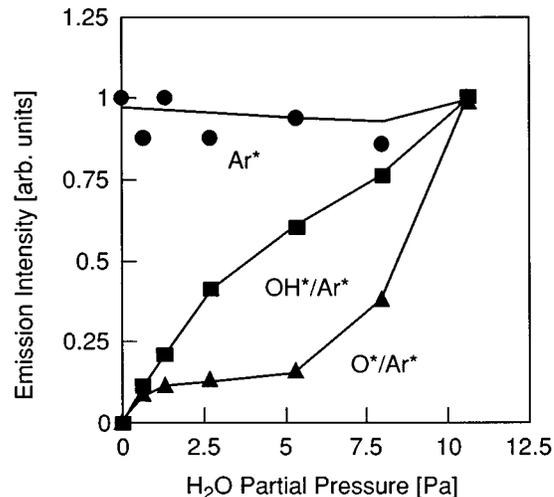


FIG. 11. The optical emission intensities of Ar^* , OH, and O in rf CH_4 plasma with H and OH radicals injection as a function of H_2O pressure.

sities of OH and O radicals increased considerably with increasing H_2O partial pressure.

In the case of rf CH_4 plasma, the production reactions of CH_3 radicals through the reactions between injected OH and O radicals and the parent CH_4 molecules are shown in Table II. In Table II, the loss reaction of CH_3 radicals with OH and O radicals are also described in Eqs. (9) and (10).

Using reaction rate constants in Table II, the production and loss rates of CH_3 radicals due to the reaction with OH radicals were estimated to be 4 and 10 s^{-1} , respectively, under the present condition of $[\text{CH}_4]=6 \times 10^{14} \text{ cm}^{-3}$ and $[\text{CH}_3]=3 \times 10^{11} \text{ cm}^{-3}$. Moreover, the production and loss rates of CH_3 radicals due to the reaction with O radicals were estimated to be 4×10^{-2} and 30 s^{-1} , respectively. In the reactions of OH radicals with CH_3 radicals and parent CH_4 molecules, the loss rate of CH_3 radicals was larger than the production rate. Moreover, in the case of the reactions of O radicals with CH_3 radicals and parent CH_4 molecules, the loss rate of CH_3 radicals was three orders of magnitude larger than the production rate.

The behavior of CH_3 radical density shown in Fig. 10 is explained by using emission intensities shown in Fig. 11 and chemical reactions described above. OH and O radicals contributing to the loss of CH_3 radicals increase with increasing the H_2O partial pressure. On the other hand, Ar^* emission intensity was almost constant with varying H_2O partial pressure. The decrease in the density and lifetime of CH_3 radicals with increasing H_2O pressure was caused by the increase in the loss rate due to the reactions with O and OH radicals.

In the parallel-plate rf CH_4 plasma without radical injection, the CH_3 radical density was measured, which was of the order of 10^{12} cm^{-3} .²¹ In that system, since CH_3 radical density was high, it was concluded that the CH_3 radicals are the dominant precursor for the amorphous carbon thin film. On the other hand, in the present rf CH_3OH or CH_4 plasma with OH radical injection, CH_3 radical density decreased with increasing OH radicals injected into the rf plasma. These re-

sults indicate the increase in the loss reaction of CH₃ radicals with OH and O radicals.

The flux of CH₃ radicals was estimated to be less than $7.5 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ under the present conditions that CH₃ radical density was less than $4.0 \times 10^{10} \text{ cm}^{-3}$. When we assume that the CH₃ radicals are the major species as a carbon source for the diamond growth, the deposition rate of the diamond film was estimated to be less than $1.0 \times 10^{-10} \text{ cm s}^{-1}$ using the sticking probability of CH₃ radical of 0.02.^{22,23} On the other hand, the deposition rate of diamond films obtained in Fig. 7 was $9.2 \times 10^{-10} \text{ cm s}^{-1}$. Comparing these values, the contribution of CH₃ radicals was estimated to be 10% or less. In the present system, other species such as C or C₂ with a high sticking probability may contribute to the diamond film formation. Further detailed study such as measurements of other species and estimation of their contributions to the diamond film formation are necessary to clarify the mechanism of diamond film formation completely.

It is necessary for the formation of diamond film to etch nondiamond phases such as amorphous carbon and graphite. H and OH radicals injected into the rf plasma made the etching of the nondiamond phases during the diamond film formation as reported in our previous paper.^{10,12} OH radicals especially, played an important role in the selective etching of nondiamond phases. Moreover, etching of diamond film by the OH radical was negligible because the etch rate of diamond film by the OH radical was much smaller than the deposition rate of diamond film.¹² In this study, the etching of nondiamond phases by H and OH radicals was considerably effective for the diamond film formation in the parallel-plate rf plasma.

The deposition rate of diamond films in the present system was small compared with the conventional microwave plasma CVD. This might be due to the small CH₃ radical density in the plasma because of large loss reaction rate of CH₃ radical with OH and O radicals injected into the rf plasma. Therefore, the cyclic process of deposition through CH₃ radicals and etching of nondiamond phases through H and OH radicals will be considered to be necessary to form diamond with a high rate, and this process is under preparation to be investigated.

IV. CONCLUSION

With H radical injection, diamond nuclei were formed in the rf CH₃OH plasma, while diamond nuclei were not formed in the rf CH₄ plasma. With injection of OH radicals together with H radicals, diamond film was successfully formed in both rf CH₃OH and CH₄ plasmas. OH radicals were found to be important species for the diamond formation in the parallel-plate rf plasma in addition to H radicals.

OH radicals especially, play role in the selective etching of nondiamond phases during the diamond film formation.

The kinetics of CH₃ radicals in the rf CH₃OH and CH₄ plasmas with H and OH radical injection were clarified by IRLAS measurement. With injection of OH radicals together with H radicals into rf CH₃OH and CH₄ plasmas, CH₃ radical density decreased with the increasing amount of injected OH radicals due to the increase in loss reaction of CH₃ radical with OH and O radicals.

ACKNOWLEDGMENTS

The authors would like to thank Shoji Den (Irie Koken Co., Ltd.), Dr. Akihiro Kono (Nagoya University), and Dr. Masafumi Ito (Nagoya University) for valuable advice and discussion in this study. This work is supported by a Grant-in-Aid for Scientific Research (A) from the Ministry of Education, Science, Sports and Culture.

- ¹S. Matsumoto, Y. Sato, M. Kamo, and N. Setaka, *Jpn. J. Appl. Phys.*, Part 2 **221**, L183 (1982).
- ²Y. Hirose and Y. Terasawa, *Jpn. J. Appl. Phys.*, Part 2 **225**, L519 (1986).
- ³M. Kamo, Y. Sato, S. Matsumoto, and N. Setaka, *J. Cryst. Growth* **62**, 642 (1983).
- ⁴H. Kawarada, K. S. Mar, and A. Hiraki, *Jpn. J. Appl. Phys.*, Part 2 **226**, L1032 (1987).
- ⁵K. Suzuki, A. Swabe, H. Yasuda, and T. Inuzuka, *Appl. Phys. Lett.* **50**, 728 (1987).
- ⁶S. J. Harris, *Appl. Phys. Lett.* **56**, 2298 (1990).
- ⁷H. Sasaki and H. Kawarada, *Jpn. J. Appl. Phys.*, Part 2 **232**, L1771 (1993).
- ⁸Y. E. Zhang and D. Dunn-Rankin, *J. Appl. Phys.* **74**, 6941 (1993).
- ⁹D. M. Gruen, S. Liu, A. R. Krauss, and X. Pan, *J. Appl. Phys.* **75**, 1758 (1994).
- ¹⁰M. Ikeda, M. Hori, T. Goto, M. Inayoshi, K. Yamada, M. Hiramatsu, and M. Nawata, *Jpn. J. Appl. Phys.*, Part 1 **134**, 2484 (1995).
- ¹¹M. Hiramatsu, M. Inayoshi, K. Yamada, E. Mizuno, M. Nawata, M. Ikeda, M. Hori, and T. Goto, *Rev. Sci. Instrum.* **67**, 2360 (1996).
- ¹²M. Ikeda, E. Mizuno, M. Hori, T. Goto, K. Yamada, M. Hiramatsu, and M. Nawata, *Jpn. J. Appl. Phys.*, Part 1 **135**, 4826 (1996).
- ¹³S. Naito, H. Nomura, and T. Goto, *Rev. Laser Eng.* **20**, 746 (1992).
- ¹⁴S. Den, M. Ikeda, H. Muto, M. Ito, M. Hori, and T. Goto, in *Proceedings of the 3rd. International Conference on Reactive Plasma and 14th Symposium on Plasma Processing*, edited by K. Tachibana and Y. Watanabe (The Japan Society of Applied Physics, Nara, 1997), p. 421.
- ¹⁵Y. Matsui, and M. Sahara, *Jpn. J. Appl. Phys.*, Part 1 **128**, 1023 (1989).
- ¹⁶R. Shaw, *J. Phys. Chem. Ref. Data* **7**, 1179 (1978).
- ¹⁷A. Rhallabi and Y. Catherine, *IEEE Trans. Plasma Sci.* **19**, 52 (1992).
- ¹⁸L. E. Kline, W. D. Partlow, and W. E. Bies, *J. Appl. Phys.* **65**, 70 (1989).
- ¹⁹H. Oser, N. D. Stothard, R. Humpfer, and H. H. Grotheer, *J. Phys. Chem.* **96**, 5359 (1992).
- ²⁰I. R. Slagle, D. Sarzynski, and D. Gutman, *J. Phys. Chem.* **91**, 4375 (1987).
- ²¹S. Naito, N. Ito, T. Hattori, and T. Goto, *Jpn. J. Appl. Phys.*, Part 1 **133**, 5967 (1994).
- ²²A. Hatta, H. Suzuki, K. Kadota, H. Makita, and A. Hiraki, *Plasma Sources Sci. Technol.* **5**, 235 (1996).
- ²³M. Shiratani, J. Jolly, H. Videlot, and J. Perrin, in *Proceedings of the 3rd International Conference on Reactive Plasma and 14th Symposium on Plasma Processing*, edited by K. Tachibana and Y. Watanabe (The Japan Society of Applied Physics, Nara, 1997), p.293