重点領域研究

フリーラジカルの科学

平成5,6,7,8年度　研究成果報告書

研究代表者

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第４班課題「プラズマプロセスにおけるフリーラジカルに関する研究」

分担課題　：　分光法による気相中のラジカル計測の研究

平成５年度，平成６年度および平成７年度研究成果報告書

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要約

１．研究成果

平成５年度，平成６年度および平成７年度を通して，当初の研究計画をほぼ達成した．研究成果の概要を以下に列記する．これらの成果は３９件の論文，４５件の国際会議発表，１６２件の国内学会発表として公表されている．

（１）赤外半導体レーザー吸収分光法（ＩＲＬＡＳ）を用いて，エッチングプロセスにおけるＲＦ励起CF_4，CHF_3プラズマおよびＥＣＲ励起CF_4，CHF_3，C_2F_6，C_4F_8プラズマ中のＣＦ，CF_2，CF_3ラジカル密度を初めて計測し，その振舞いを明らかにした．

（２）オンオフ放電変調方式によって，ＥＣＲ励起CHF_3プラズマ中のＣＦ，CF_2，CF_3ラジカルの密度比を制御できることを示した．さらに，これらのラジカルとフルオロカーボン膜の堆積速度，組成との関係を調べ，高精度エッチングプロセスにおけるフルオロカーボン膜の形成にCF_2ラジカルが寄与していることを明らかにした．

（３）CF_2ラジカルを選択的に生成し，ラジカルをＥＣＲプラズマのダウンフロー領域に注入する新しいラジカル制御方式を開発した．本方式を用いることで，イオンによる基板表面の活性効果があれば，CF_2ラジカルはフルオロカーボン膜の重要な前駆体になることを明らかにした．また，カーボンリッチな膜がSiO_2／Ｓｉの高選択比エッチングで重要な役割を果たしていることを明らかにした．

（４）ＲＦ励起CH_4プラズマ中のCH_3ラジカル密度がＸｅ希釈ガス中で増加することを見出し，その密度増加機構を解明した．さらに，CH_3ラジカル密度とカーボン膜の堆積速度との関係を調べ，CH_3ラジカルがカーボン膜形成の重要な前駆体であることを明らかにした．

（５）ＩＲＬＡＳおよび紫外吸収分光法を用いて，アモルファスＳｉ薄膜形成プロセスにおけるＥＣＲ励起SiH_4／H_2プラズマ中のSiH_3，Ｓｉラジカル密度を初めて計測し，ラジカルの組成がＲＦ励起と異なることを明らかにした．

（６）オンオフ放電変調法とレーザー誘起蛍光法を組み合わせた計測法（ＭＬＩＦ）を用いてＲＦ励起SiH_4プラズマ中のSiH_2ラジカルの密度を計測することに成功した．ＲＦ励起SiH_4プラズマ中におけるSiH_2およびSiH_3ラジカルの希釈ガス（H_2，Ｈｅ，Ａｒ，Ｘｅ）依存性を系統的に明らかにした．さらに，ＳｉＨおよびSiH_2ラジカルとSiH_4との反応が１Ｔｏｒｒ以下の低圧力下において三体反応であることを明らかにするとともにその反応速度定数をはじめて決定した．

（７）平行平板型ＲＦ励起CH_3OHプラズマ中にマイクロ波励起プラズマで生成したＨラジカルおよびＯＨラジカルを注入するプロセスを開発し，平行平板型ＲＦ励起プラズマによるダイヤモンドの形成に初めて成功した．

２．予算

平成５年度	１３，５００，０００円	（後藤，菅井）
平成６年度	１２，９００，０００円	（後藤，菅井，村岡）
平成７年度	１６，１００，０００円	（後藤，菅井，村岡，田頭，安田）

The 4th Group Theme:Study on Free Radicals in Plasma Process .

Studies on Measurements of Radicals in the Gas Phase Using Spectroscopic Techniques

Report on the results obtained during the 1993~1995 Fiscal Years

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Abstract

Research Results

In 1993-1995 fiscal years, the proposed research programs have been almost achieved.

The outlines of the obtained results are as follows. These results have been published in 39 papers, 45 presentations in international conferences and 162 presentations in domestic conferences.

(1)Using infrared laser diode absorption spectroscopy (IRLAS), the CF, CF_2 and CF_3 radical densities in the etching process employing RF discharge CF_4 and CHF_3 plasma and ECR discharge CF_4, C_2F_6, C_4F_8 and CHF_3 plasmas were measured for the first time and the behaviors of these radicals in the plasmas were clarified.

(2)The ratios of the CF, CF_2 and CF_3 radical densities in ECR discharge CHF_3 plasma were successfully controlled by on-off plasma modulation technique. Furthermore, it was elucidated that the CF_2 radical contributed to the growth of polymer films in the high precision etching process on the basis of measured results of these radical densities, fluorocarbon polymer deposition rate and the film composition.

(3)A new technique was developed for injecting the CF_2 radical into downstream region of ECR plasma . By this technique, it was clarified that CF_2 radical was the important precursor for fluorocarbon film formation with the assistance of surface activation by plasma exposure, and that the carbon-rich film played an important role in the high etching selectivity of SiO_2/Si.

(4)The CH_3 radical density in RF discharge CH_4/Xe plasma was found to increase with Xe dilution and the mechanism of the increase in the CH_3 radical density was made clear. It was elucidated that the CH_3 radical was one of the most important precursors in the formation of carbon film through the investigation of the relation between the CH_3 radical density and the deposition rate of carbon film in the plasma.

(5)Using IRLAS and UV absorption spectroscopy, the SiH_3 and Si radicals in ECR discharge SiH_4/H_2 plasma were measured for the first time and it was found that the behavior of these radicals in ECR discharge plasma was different from that in RF discharge plasma.

(6) Using laser induced fluorescence spectroscopy combined with the on-off plasma modulation (MLIF), the SiH_2 radical in RF discharge SiH_4 plasma was successfully measured and the behaviors of the SiH_2 and SiH_3 radicals were systematically studied in RF discharge SiH_4 plasmas with Xe, Ar, He, and H_2 dilution gases. Furthermore, the reaction of SiH and SiH_2 radicals with SiH_4 was shown to be three body reaction in a low pressure range below 1Torr and the rate constants of these reaction were determined.

(7)The new process, where the H and OH radicals generated in the microwave discharge H_2 and H_2O plasmas, respectively, was preferentially injected into the parallel plate RF discharge CH_3OH plasma, was developed for the synthesis of diamond film. Using this process, diamond film was successfully synthesized for the first time in the parallel plate RF discharge plasma.

1. Introduction

In the microelectronics field, plasma process has been a basis technology for deposition or etching of materials. In this process, neutral radicals produced in the plasma arrive at the substrate through reactive collisions with electrons, ions and other radicals, and react with the solid surface. Therefore, in order to develop such a plasma process, it is indispensable to obtain information about the behavior of radicals in the gas phase and on the solid surface.

The purpose of this research is to measure various kinds of key radicals for the deposition and etching plasma processes, to clarify the behavior of these radicals in the gas phase using spectroscopic techniques and furthermore to investigate the correlation between the behavior of these radicals and the characteristics of deposition film and etching in the plasma processing.

In this study, using IRLAS (Infrared Diode Laser Absorption Spectroscopy), we have measured for the first time fluorocarbon radicals such as CF_x (x : 1-3) systematically in RF CF_4 and CHF_3 plasmas and ECR CF_4, CHF_3, C_2F_6 and C_4F_8 plasmas. The kinetics of these radicals in the gas phase and surface have been also investigated. By on-off modulation of ECR CHF_3 plasma, it was found that the ratio of the CF and CF_2 radical densities to the CF_3 radical and/or F atom densities has been successfully controlled. On the basis of measured results of CF_x (x : 1-3) radical densities in the ECR CHF_3 and CHF_3/H_2 plasmas, the polymer deposition rates on Si and SiO_2 surfaces, and the composition of these polymer films, the important precursors for the growth of polymer films in the ECR CHF_3 and CHF_3/H_2 plasmas have been discussed.

Moreover, a new radical injection technique (RIT) has been developed for clarifying the important radical in the plasma etching process. Using the RIT, the surface reactions of CF_2 radicals injected selectively into the plasma have been investigated and the role of CF_2 radicals in the fluorocarbon film formation for the highly selective SiO_2 etching process has been clarified.

In the case of the deposition process of amorphous silicon (a-Si : H) films, the measurement technique of SiH_2 radical density in the plasma has been developed using MLIF (Modified Laser Induced Fluorescence Spectroscopy). The behavior of SiH_x (x : 0-3) radicals has been investigated in RF SiH_4 plasma with dilution gases (Xe, Ar, He, and H_2) and ECR SiH_4/H_2 plasma using IRLAS, MLIF, and ultraviolet absorption spectroscopy (UVAS). Furthermore, from the decay rate of SiH_2 and SiH densities in the afterglow of RF SiH_4/Ar and SiH_4/He discharge, the rate constants for the reactions of SiH_2 and SiH radical with SiH_4 have been determined for the first time at pressures below 1Torr.

In the diamond and amorphous carbon film formation processes, the CH_3 radical densities in RF CH_4 and CH_3OH plasmas and ECR CH_4 and CH_3OH plasmas have been measured and the contribution of the CH_3 radical to the film properties has been discussed. Diamond films have been successfully synthesized for the first time using a parallel-plate RF CH_3OH plasma assisted by injection of H and OH radicals. The roles of H and OH radicals in the formation of diamond films have been discussed.

2. Experimental

The measurements of radicals were performed in the RF and ECR discharge plasma experiment systems. A typical RF discharge plasma chamber was used here. It had plane parallel electrodes of

20cm diameter, 3cm separation, and the on-off modulated RF (13.56MHz) power was fed to the electrode [1] . The ECR plasma experiment system consisted of a plasma chamber and a process chamber [2] . The ECR plasma was produced in the ECR region (2.45GHz microwave, 875G resonance magnetic field) . The plasma was directed in the divergent magnetic field to the process chamber. A substrate plate of 20 cm diameter was placed at an axial position of 22 cm downstream from the plasma chamber. White type multi-reflection system was fitted to the plasma chamber in order to obtain a larger absorption signal by increasing the absorption length in the absorption spectroscopic technique.

IRLAS [2] was used for the measurements of the SiH_3 radical density in RF and ECR SiH_4 plasmas, the CH_3 radical density in RF CH_4 and CH_3OH plasmas and ECR CH_4 and CH_3OH plasmas, and the CF_x (x : 1-3) radical densities in RF and ECR plasmas. The laser beam was introduced into the plasmas and absorbed partly there with the aid of the White type multi-reflection system. The radical absorption signal in the selected infrared rovibrational transition line was measured with the HgCdTe detector and transient wave memory. UVAS using a ring laser and a hollow cathode lamp was applied to the measurement of Si atom density in the RF and ECR plasmas, respectively.

In the radical injection technique, a new source for injecting CF_2 radical was attached to the side wall of the ECR plasma chamber described above. Ar or H_2/Ar mixture gas was introduced from the top of the ECR source. The cylindrical tube of diameter 1.3cm was set at the boundary between the plasma and process chambers to prevent hexafluoropropyleneoxide (HFPO) from being dissociated by electron impact in the ECR plasma region. This allowed CF_2 radical to be injected into the ECR Ar and H_2/Ar downstream plasmas region.

The SiH_2 radical density in the RF SiH_4 plasma was measured by MLIF. In this technique, a LIF method combined with the plasma modulation and photon counting technique was used. The absolute density of SiH_2 radical was derived from the comparison of the saturated LIF intensity with the Rayleigh scattering intensity from a known pressure of N_2.

Diamond film was synthesized using a parallel-plate RF CH_3OH plasma assisted by injection of H and OH radicals generated by the microwave H_2 and /or H_2O plasma.

The characteristics of fluorocarbon films deposited on the substrates were investigated using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) . The diamond films were characterized by scanning electron microscopy (SEM) , X-ray diffraction (XRD) and reflection high-energy electron diffraction (RHEED) .

3. Behaviors of CF, CF_2 and CF_3 Radical Densities in RF CF_4, CHF_3, ECR CHF_3 and C_4F_8 Etching Plasmas

In RF CF_4 and CHF_3 etching plasmas, the measurements of CF_x (x : 1-3) radical densities have been performed as a function of the input RF power, the CF_4 and CHF_3 gas pressure and the distance from the electrodes. The absolute density of CF_2 radical was estimated to be of the order of 10^{12} cm^{-3} and 10^{13} cm^{-3} in CF_4 and CHF_3 plasma, respectively, the CF radical density in CF_4 plasma and the CF and CF_3 radical densities in CHF_3 plasmas were estimated to be of the order of 10^{12} cm^{-3} at a gas pressure of 30Pa, input power of 100W (0.48W/cm^2) , and distance of 2.0 cm above the ground electrode.

Using the balance equation of production and loss processes on the basis of the measured results, the behaviors of CF_x radicals were clarified. In RF CF_4 plasma, the variation of CF and CF_2 radical densities are explained well from the production by electron-impact dissociation of CF_4 and the loss by wall removal. In RF CHF_3 plasma, however, the radical kinetics becomes different from that in CF_4 plasma mainly due to the formation of fluorocarbon film on the electrode surface, which brings about the reduction of surface loss probability of CF_x (x : 1-3) radicals and the production of radicals by chemical sputtering (CF) or by neutralization of incident positive ion on the electrodes (CF_3) .

The influence of fluorocarbon formation on CF_x (x : 1-3) radicals was observed in the discharge duration dependence of CF_x (x : 1-3) radical densities measured in RF CHF_3 plasma at various CHF_3 pressures. Figure 1 shows the discharge duration dependence of CF_x (x : 1-3) radical densities in RF CHF_3 plasma at 8Pa and input power of 100W. It was found that the CF and CF_3 densities in the plasma increased for 20 minutes until the electrode surface is covered with the fluorocarbon film of 30nm in thickness, while the slow increase in CF_2 density over an hour is due to the gradual change of chamber wall condition with the fluorocarbon film formation at a slow rate.

In high density etching plasmas, CF_4, C_2F_6 and C_4F_8 gases and the mixtures of these gases with H_2 gas have been commonly employed for etching SiO_2. The CF_x (x : 1-3) radical densities in ECR CF_4, C_2F_6 and C_4F_8 plasmas have been systematically measured at 25 cm downstream lower from the ECR region. In the C_4F_8 plasma, CF_2 radical density was found to be of the order of $10^{13}cm^{-3}$ at microwave powers below 300W and decreases to be of the order of $10^{12}cm^{-3}$ with further

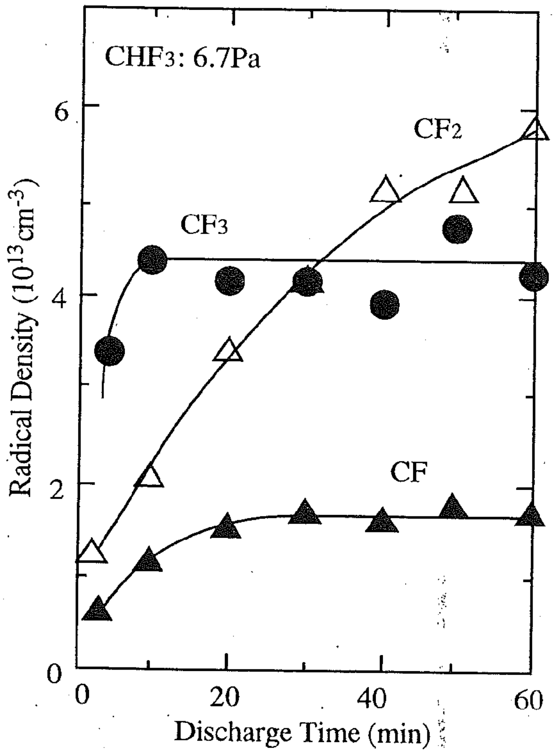

Fig.1. Discharge duration dependence of CF_x(x=1-3) radical densities in RF CHF_3 plasma at 8 Pa and 100W.

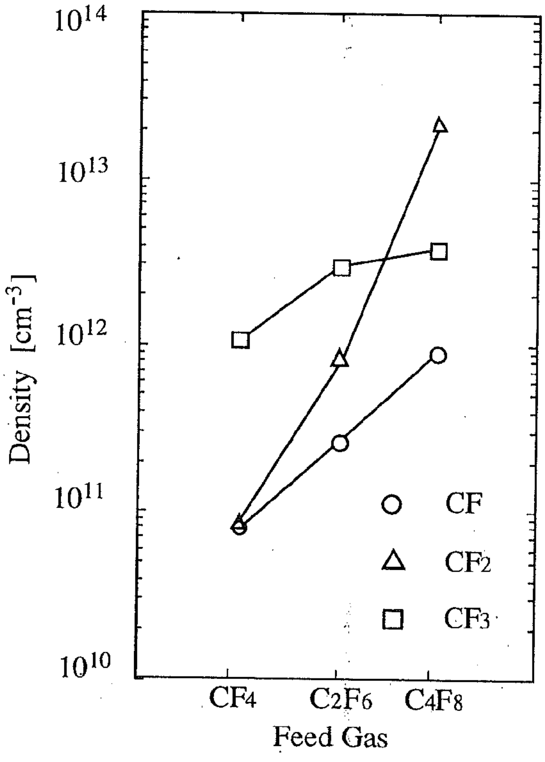

Fig.2. CF_x(x=1-3) radical densities in CF_4, C_2F_6 and C_4F_8 plasmas as a function of C/F ratios of feed gases at 0.4 Pa and 100W.

increase of microwave power at 0.4Pa. CF and CF_3 radical densities were estimated to be of the order of $10^{11}cm^{-3}$ and 10^{12} cm^{-3}, respectively at above conditions. It is noteworthy that CF_2 radical density in C_4F_8 ECR plasma is considerably high compared to CF and CF_3 radical densities at microwave powers below 300W.

Figure 2 summarizes CFx (x : 1-3) radical densities in CF_4, C_2F_6 and C_4F_8 plasmas as a function of carbon/fluorine (C/F) ratios of feed gases at 0.4Pa and 100W. The CF and CF_2 radical densities increased exponetially with decrease in C/F ratio. This fact suggests that composition of CFx radicals in fluorocarbon plasma is strongly affected by C/F ratio of feed gases.

4. Control of CF, CF_2 Radical Densities to CF_3 Radical Density in ECR CHF_3 Etching Plasmas by On-Off Modulation

Figure 3 shows the dependences of CFx (x : 1-3) radical densities on the duty ratio at a CHF_3 pressure of 0.4 Pa and microwave on-power of 300 W. The CF, CF_2 and CF_3 radical densities were normalized to unity at an on-period of 15ms. In the case of ECR CHF_3 plasma, the absolute density of CF radical was estimated to be of the order of 1×10^{12} cm^{-3} and those of both CF_2 and CF_3 radicals were estimated to be of the order of 10^{13} cm^{-3}. It was observed clearly in Fig.3 that the ratio of CF and CF_2 radical densities to CF_3 radical density was controlled by varying the on-off period in ECR CHF_3 plasma.

Figure 4 shows the dependences of the deposition rates for Si and SiO2 surfaces on the duty

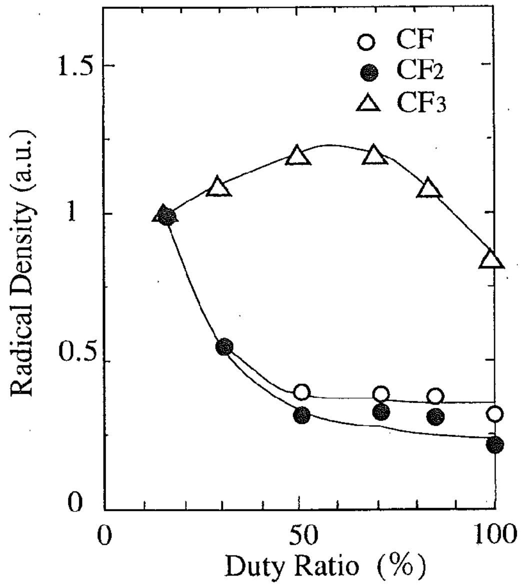

Fig.3. The dependences of CFx radical densities on the duty ratio at 300W in the pulse cycle of 100ms.

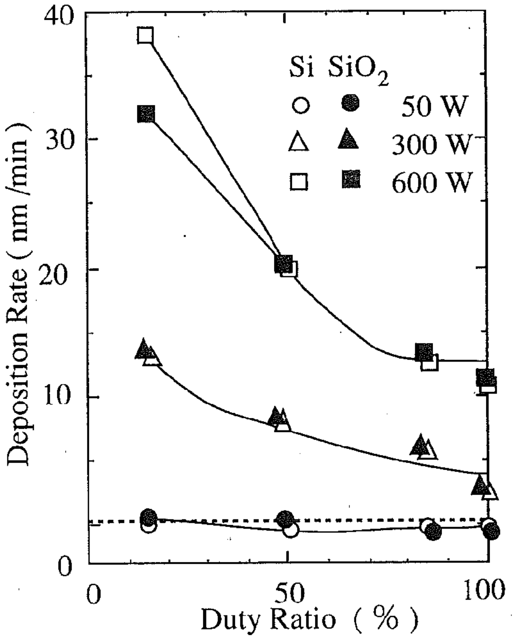

Fig.4. The dependences of deposition rates on the duty ratio at 50, 300 and 600W in the pulse cycle of 100ms.

ratio at the CHF_3 pressure of 0.4Pa and microwave power of 50, 300, and 600W. The deposition rate was obtained by dividing the polymer thickness by the plasma duration of the on-period. From Fig.4, the deposion rates of polymer films were found to be controlled by varying the on-off period as well as CF and CF_2 radical densities. On the basis of the behaviors of CF and CF_2 radicals, the deposition rates, and supplementary XPS analysis of the composition of polymer films, it was elucidated that the CF_2 radical contribited to the growth of polymer films. Furthermore, the etching selectivity of SiO_2/Si was found to decrease gradually with increasing the duty ratio in supplying the rf bias to the substrate plate. Thus, the on-off modulated plasma technique enabled us to control the CF_x radical densities, polymer deposition rates, and SiO_2/Si etching selectivity.

5. Effect on radical densities in CHF_3/H_2 ECR plasma by the change in composition of films deposited on the chamber wall

Figure 5 shows CF and CF_2 radical densities (after pure CHF_3 plasma exposure and CHF_3/H_2 (50%) plasma exposure) as a function of H_2 partial pressure at the duty ratio of 15%, the microwave power of 300W and CHF_3 pressure of 0.4 Pa. In the case of pure CHF_3 plasma exposure pretreatment, CF radical density increased rapidly and then decreased with the increase in H_2 pressure while CF_2 radical density decreased monotonically. Therefore, although the CF_2 radical density is five times as high as the CF radical density in the pure CHF_3 plasma, the CF radical density becomes even higher than the CF_2 radical density at H_2 pressures above 0.02Pa.

The dominant precursor of the polymer film formation in the pure CHF_3 plasma is believed to be the CF_2 radical. However, it is expected from the result shown in Fig.5 that the contribution of the CF radical to the polymer film formation increased rapidly with the increase in H_2 pressure and the CF radical became the dominant precursor of the polymer film formation.

In the case of CHF_3/H_2 (50%) plasma exposure pretreatment, the behavior of CF radical was considerably different from that after the pure CHF_3 plasma exposure pretreatment. The CF radical density decreased gradually increasing H_2 partial pressures. With regard to the CF_2 and CF_3 radicals, it was observed that these radical densities were not affected by the different pretreatments.

Furthermore, a small amount of Ar gas was added into the plasma and the Ar emission intensities were meaured to obtain information on the electron density and temperature in the plasma. These intensities were not sensitive to the variation of plasma exposure pretreatment.

From these results and XPS analysis of the films

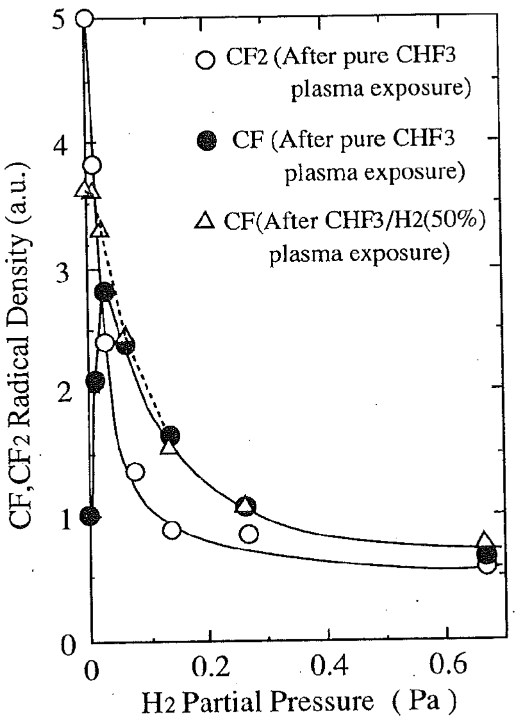

Fig.5. CF and CF_2 radical densities as a function of H_2 partial pressure.

deposited on the chamber wall, it was clarified that the surface loss probability of CF radical on fluorocarbon films deposited on the wall was dependent on the F/C ratio of the films.

6. Control and qualification of precursor in SiO_2 high selective etching employing radical injection technique

In a radical injection technique, CF_2 radical was selectively formed from a pyrolysis of HFPO in a resistively heated 1/8 in. stainless-steel tube. The heated HFPO gas pressure and flow rate were 0.67Pa and 10sccm, respectively. The CF_2 radical density was estimated to be about $1\times10^{13}cm^{-3}$ at the inner wall temperature of 900K while the CF and CF_3 radical densities were on the order of $10^{11}cm^{-3}$ or less, respectively, which was negligibly small compared with the CF_2 radical density. The CF_2 radical was injected into the ECR downstream plasma region through the tube and the CF_2 radical density was fixed at about $1\times10^{13}cm^{-3}$. Ar or H_2/Ar gases was employed as source gases of the ECR plasma. In the ECR Ar plasma, the Ar pressure and flow rate were 0.8Pa and 14 sccm, respectively. In the H_2/Ar plasma, the H_2 pressure and flow rate were 0.26Pa and 10sccm, respectively, and the Ar pressure and flow rate were 0.4Pa and 7sccm, respectively. The electron density and temperature were estimated to be on the order of 10^8cm^{-3} and about 2eV, respectively, from the probe measurement, in ECR Ar downstream plasma at the Ar pressure of 0.8Pa and the microwave power of 800W. The fluorocarbon film was formed negligibly without plasma exposure, and the deposition rates increased linearly with the microwave power in the Ar and H_2/Ar plasmas although the injected CF_2 radical density was fixed. It was suggested that fluorocarbon film formation occurred due to the reaction of CF and CF_2 radicals with the surface activated by ion bombardment.

Figure 6 shows the etching rates of Si and SiO_2 as a function of bias voltage to the substrate at the microwave power of 800W in the ECR Ar and H_2/Ar downstream plasmas with CF_2 radical injection. In the ECR Ar plasma, the fluorine-rich (F/C=1.5) fluorocarbon films were formed on the Si and SiO_2 surfaces at bias voltages up to -30V. The SiO_2/Si etching selectivity did not change with bias voltage. On the contrary, in the ECR H_2/Ar plasma where the carbon-rich (F/C=0.4) fluorocarbon films were formed, Si was not etched while the SiO_2 was etched at bias voltage of -400V. Thus, it was clarified that CF_2 radical was the important precursor for fluorocarbon film formation and the carbon-rich film played an important role in high etching selectivity.

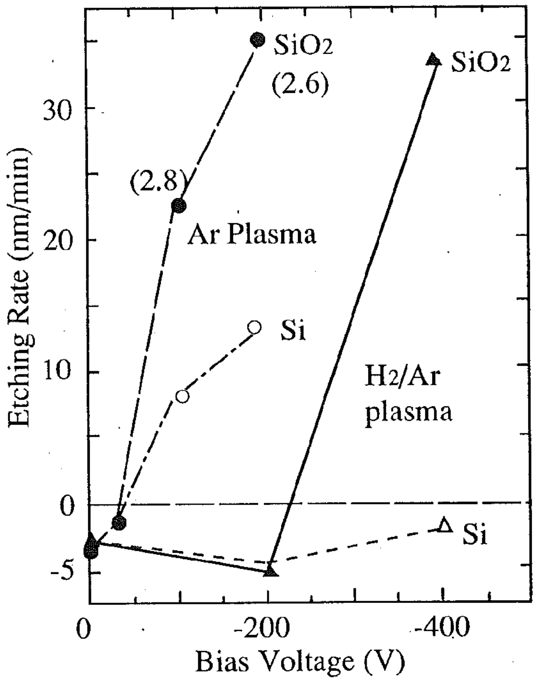

Fig.6. Etching rates of Si and SiO_2 as a function of the bias voltage in the ECR downstream plasmas with CF_2 radical injection.

7. Effect of Xe Dilution on CH_3 Radical Density and Correlation between CH_3 Radical Density and Carbon Thin-Film Formation in RF CH_4 Plasma

We have successfully measured the CH_3 radical densities in CH_4/rare gases (Xe, Kr, Ar, Ne and He) plasmas and investigated systematically the behavior of CH_3 radical for dilution gases.

Figure 7 shows the Xe partial pressure dependence of the CH_3 radical density and the excited Xe^* atom densities in the lowest metastable state $^3P_2$ and the resonance state $^3P_1$. The absolute CH_3 radical density was about $10^{12}cm^{-3}$ at a CH_4 prcssure of 7Pa and input power of 260W (0.83W/cm^2) . It was found that the CH_3 radical density increased with increasing partial pressure of Xe. In order to investigate the mechanism of increase in the CH_3 radical density, Xe^* ($^3P_2$ and $^3P_1$) atom densities were also measured through the absorption spectroscopy using a Xe hollow cathode lamp. These densities were of the order of 10^8 cm^{-3} and increased with increasing Xe partial pressure as shown in Fig.7. The effect of Xe^* atoms on the CH_3 radical density was investigated quantitatively and thus it was indicated that the increase in the CH_3 radical density in CH_3/Xe plasma was mainly caused by the collisions of Xe^* atoms with CH_4 molecules.

Furthermore, the correlation between the CH_3 radical density and the deposition rate of carbon thin film was investigated with controlling CH_3 radical density in RF CH_4/Xe plasma and the CH_3 radical was found to be one of the most important precursors in carbon thin film formation.

8. Measurements of Si and SiH_3 Radical Densities in ECR SiH_4 Plasma

Figure 7 shows the Si atom and SiH_3 radical densities in ECR SiH_4 (50%) /H_2 plasma as a function of the microwave power at a total pressure of 1.3Pa. The SiH_3 radical density increases rapidly up to 100W and amounts to $1.3x10^{10}cm^{-3}$. As the microwave power increases more, it becomes almost saturated.

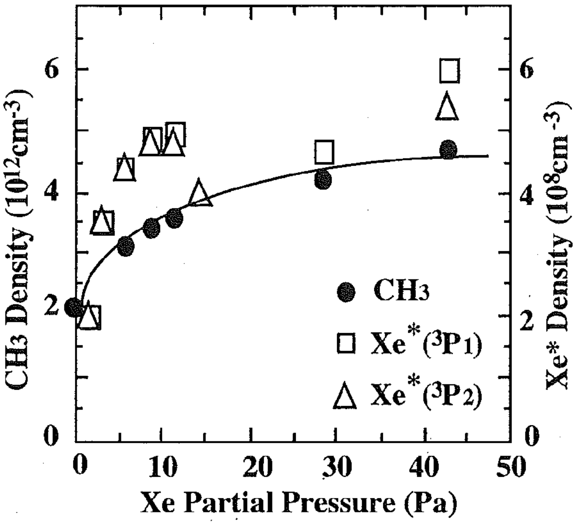

Fig.7. Xe pressure dependence of CH_3 radical density and Xe^*($^3P_2$ and $^3P_1$) atom densities in CH_4/Xe plasma.

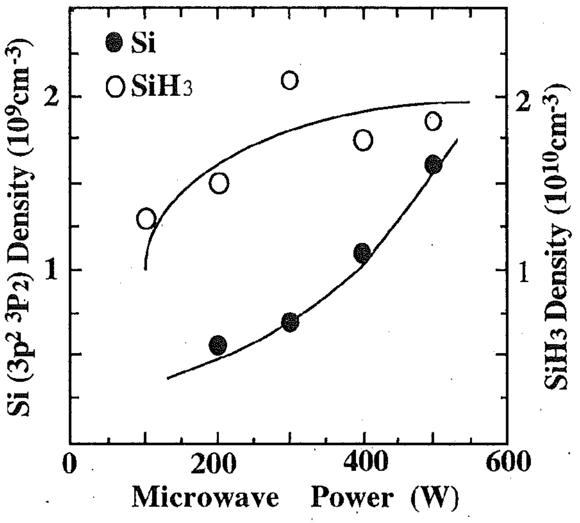

Fig.8. Si and SiH_3 radical densities as a function of microwave power in ECR SiH_4(50%)/H_2.

On the other hand, the Si $(3p^2\ ^3P_2)$ atom density increases slightly more than linearly with increasing in the microwave power and the density was estimated to be 3.6×10^9cm^{-3} at a microwave power of 400W. The SiH3 radical density in the ECR plasma was smaller by about one order of magnitude than that in the RF plasma, while the Si atom density in the ECR plasma was larger by one order of magnitude than that in the RF plasma. These results suggest that Si atom plays an important role for the film formation in the ECR SiH4/H2 plasma.

9. SiH2 and SiH3 Radical Densities in RF SiH4 Plasma with Xe, Ar, He and H2 Dilution Gases

The SiH2 and SiH3 radical densities have been measured using MLIF and IRLAS, respectively, in a parallel plate RF SiH4 as a function of SiH4 fraction for Xe/, Ar/, He/, and H2/SiH4 plasmas.

Figure 9 summarizes the effect of four kinds of dilution gases on the SiH2 radical density at a pressure of 5.3 Pa and RF power of 40W in RF SiH4 plasmas with Xe, Ar, He and H2 dilution gases.

The SiH2 radical density was estimated to be of the order of 10^9 cm^{-3}. The SiH2 radical density increased greatly with the increase in the Ar and Xe mixing ratios. The SiH3 radical density in was also estimated to be of the order of 10^{11} cm^{-3} at a pressure of 4Pa and RF power of 200W in RF SiH4 plasmas with Xe, Ar, He and H2 dilution gases.

On the basis of the behaviors of SiH2 and SiH3 radical densities for dilution gas ratios, it was made clear that in highly diluted SiH4/Xe and SiH4/Ar mixtures, the production of SiH2 and SiH3 radicals via energy transfer from metastable Xe* and Ar* atoms to SiH4 was important over direct electron impact dissociation of SiH4.

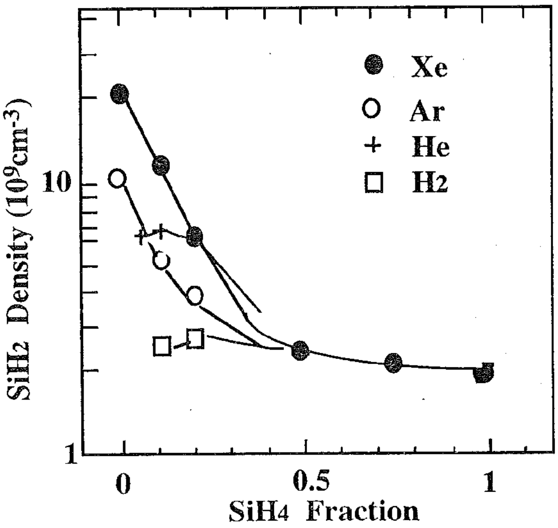

Fig.9. SiH2 radical density as a function of SiH4 fraction in Xe, Ar, He and H2 in 40W and 40mTorr.

10. Rate Constants for the Reactions of SiH2 and SiH Radicals with SiH4

The rate constants of SiH2+SiH4 and SiH+SiH4 reactions have been measured in low pressures below 1Torr where a-Si : H films are usually synthesized. These rate constants were evaluated from the decay waveforms of the SiH2 and SiH radical densities in the afterglow of SiH4/Ar and SiH4/He plasmas.

Figure 10 shows the pressure dependence of the SiH2+SiH4 reaction rate constant using Ar and He dilution gas. The rate constants obtained using Ar and He dilution gases decreased with desreasing total pressure. The results indicate that under low-pressure conditions below 1Torr, the three-body reaction that $SiH_2 + SiH_4 \rightarrow Si_2H_6$ is the dominant reaction pathway. The rate constant of the SiH+SiH4 reaction was estimated in the same manner. It also decreased with decreasing total gas pressure. The dominant reaction channel of SiH is the three-body reaction, $SiH + SiH_4 \rightarrow Si_2H_5$. Therefore, in the RF-SiH4 plasma process, the insertion reactions producing Si2H6 and Si2H5, respectively are the important reaction channels even in the low pressure condition of RF-SiH_4 plasma process.

11. Synthesis of Diamond Using CH_3OH Plasma CVD Assisted by H and OH Radical Injection

Diamond was synthesized successfully for the first time using a parallel plate RF CH_3OH plasma CVD system assisted by the injection of H and/or OH radicals generated in the microwave discharge H_2 or H_2O/H_2 plasma. Figures 11 (a) and (b) show SEM images of the surface morphology of the films deposited at a substrate temperature of 600℃, RF power of 100W, pressures of CH_3OH/H_2 : 0.66Pa/13Pa and $CH_3OH/H_2/H_2O$: 0.67/3.3/9.3Pa, with injections of H and OH radicals, respectively. With the injection of H radicals, diamond nuclei with grain size of 200-300nm were observed, while only the non-diamond phases like ball with 20-50nm in size were observed without H radical injection. It was confirmed that the difficulty in the diamond formation using a parallel plate RF plasma CVD reactor was caused by the insufficient dissociation of H_2 molecules. In the case of OH radical injection, the well-defined diamond grains were observed over the whole area of deposited film.

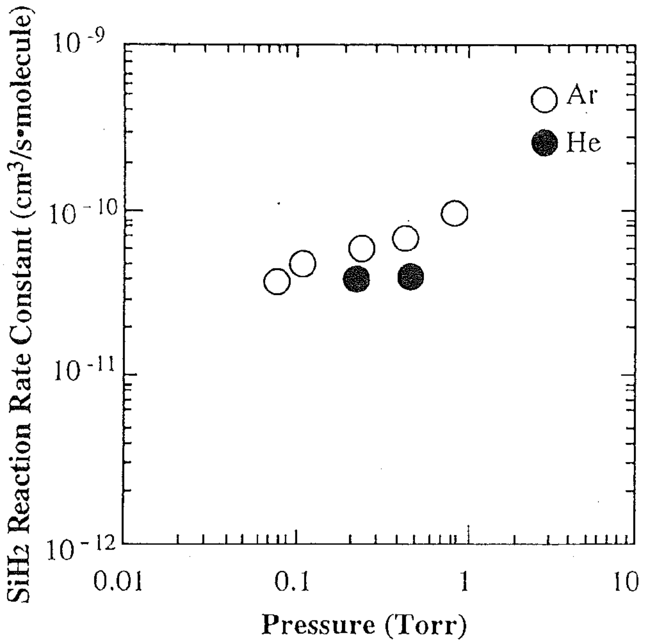

Fig.10. Pressure dependence of SiH_2+SiH_4 reaction rate constants in RF SiH_4 diluted using Ar and He.

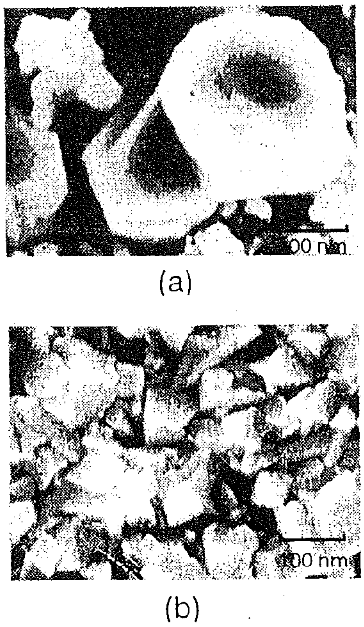

Fig.11. SEM images of the surface on deposited films: (a) H radical injection and (b) OH radical injection.

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