Novel process for SiO_2/Si selective etching using a novel gas source for preventing global warming

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A novel gas source replacing fluorocarbon feed gases has been developed for preventing global warming. The novel gas source was designed to generate fluorocarbon species from polytetrafluoroethylene by CO_2 laser ablation. The species generated from the gas source were introduced into an electron cyclotron resonance (ECR) plasma employing Ar gases. To characterize the gas source, CF_x ($x=1-3$) radical densities with and without plasmas were measured by infrared diode laser absorption spectroscopy. In the ECR plasma employing the novel gas source, CF_x ($x=1-3$) radical densities were estimated to be of the order of $10^{12}-10^{13}\,cm^{-3}$. The gas source has been applied to the selective etching of SiO_2 to Si using the ECR plasma. As a result, the etching characteristics by ECR plasma employing the novel gas source were equivalent to those by a conventional ECR plasma employing C_4F_8 gas. Therefore, this novel gas source is applicable to etching processes for preventing global warming. © *1999 American Vacuum Society.*
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I. INTRODUCTION

A large amount of fluorocarbon gases are used in dry etching processes for thin-film patterning and chamber cleaning after film depositions. Particularly, highly selective etching of SiO_2 to Si for fabrication of ultra-large-scale integrated circuits (ULSIs) has been developed by using plasmas employing fluorocarbon gases. In these etching plasma processes, fluorocarbon polymer films formed on Si and SiO_2 affect the etching rate and selectivity. In particular, CF_x ($x=1-3$) radicals generated from the dissociation of fluorocarbon gases have been reported as precursors for the formation of fluorocarbon polymer films in plasma etching processes.[1–7] Therefore, fluorocarbon plasma chemistry is very important to perform highly selective etching of SiO_2 to Si. However, fluorocarbon gases cause a serious environmental problem, namely, global warming. The global warming potentials of fluorocarbon gases is thousands of times as high as that of CO_2 gas because of long lifetimes in the atmosphere. Therefore, the productive restriction on fluorocarbon gases is discussed intensively and the use of fluorocarbon gases in industries would be prohibited in the near future.

Recently, the semiconductor industries have been taking some measures for the negative impact of fluorocarbon gases on global warming. For example, the technology for elimination of emission of fluorocarbon gases to the atmosphere has been investigated and alternative feed gases having short lifetimes have been developed. However, conventional fluorocarbon gases and new alternative gases are usually supplied by using gas cylinders. These gas cylinders have many problems, for example, a high risk of gas leakage during transportation and consumption. Additionally, the legal restriction on gases makes us need a large waste gas disposal apparatus corresponding to the feed gas volume kept in gas cylinders.

In this study, we have developed a novel fluorocarbon gas source without using fluorocarbon feed gases for preventing global warming, where polytetrafluoroethylene (PTFE) is ablated by a CO_2 laser and the generated fluorocarbon species such as radicals and molecules are introduced into the plasma reactor. In this gas source system, a solid material is used to replace the gases. This gas source system, therefore, has many advantages. For example, it enables us to reduce the capacity of the waste gas disposal apparatus because of low risk for leakage of fluorocarbon gas, and so this system is very compact and safe because the gas cylinder is basically unnecessary. To evaluate the possibility of the novel gas source, CF_x ($x=1-3$) radical densities generated from the novel gas source were measured by infrared diode laser absorption spectroscopy (IRLAS). Moreover, the gas source was applied to the SiO_2/Si selective etching using an electron cyclotron resonance (ECR) plasma. The behaviors of the radical densities and etching characteristics with the novel gas source were compared with those of C_4F_8 gas.

II. EXPERIMENT

Figure 1 shows the ECR plasma process system equipped with a novel gas source and the infrared diode laser absorption spectroscopy system. The novel gas source consists of a PTFE target and a CO_2 laser.

The process chamber, made of stainless steel, was 40 cm in diameter and 40 cm in height. Two magnetic coils were arranged symmetrically and they provided a divergent magnetic field. A 2.45 GHz microwave was introduced into the top of the reactor. An ECR region of 875 G was created at the position of 10 cm below the quartz window.

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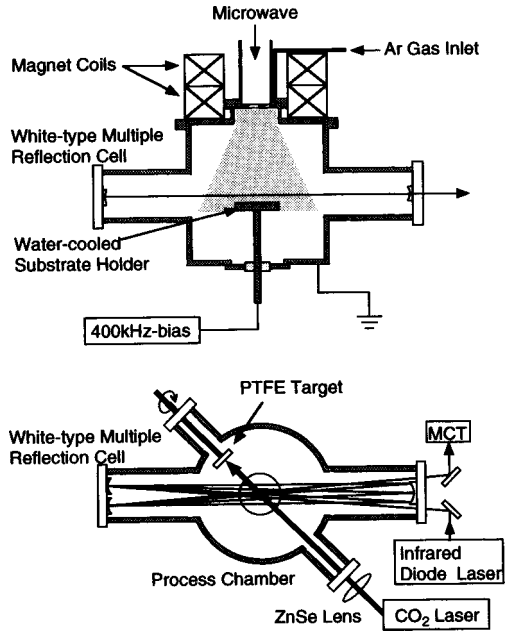

FIG. 1. ECR plasma process system equipped with a novel gas source and an infrared diode laser absorption spectroscopy (IRLAS) system.

In the novel gas source, a cw CO_2 laser (10.6 μm) was used for ablation of the PTFE target. The cw CO_2 laser was very compact (W70×H97×L425 mm; Synrad Inc.). The cw CO_2 laser beam was focused by a ZnSe lens and irradiated on the surface of the PTFE target in the reaction chamber through the ZnSe window. The CO_2 laser beam irradiated on the PTFE target was 3 mm in diameter. The power of the CO_2 laser was maintained to be 30 W. Before starting the ablation, the process chamber was pumped down to a pressure of 1.33×10^{-3} Pa by 200 and 700 l/s turbomolecular pumps. The ablation of the PTFE target was performed at room temperature. A PTFE target of 5 mm in thickness was used in this work. The molecular weight of PTFE is 107 g/mol and the melting point is 327 °C. The PTFE target was rotated at 333 rpm automatically.

IRLAS has enabled us to measure CF_x ($x=1-3$) radical densities in various kinds of fluorocarbon plasmas.[8–12] A White-type multiple reflection cell of 200 cm in length was installed at a process chamber to increase the absorption length of the infrared laser beam used for the radical density measurements. The laser beam was passed 12 times for the measurement of the CF_2 radical density at 2 cm above the substrate plate through the ECR downstream plasma using the White-type multiple reflection cell and 40 times for those of CF, CF_3 radicals densities. Absorption signals were detected by an infrared detector (MCT). The absorption lines used in this study were the $R_1(4.5)$ and $R_2(4.5)$ lines for CF radicals,[13] a ${}^{Q}R_4$ (26) line for CF_2 radicals,[14] and a ${}^{R}R_{18}(18)$ line for CF_3 radicals.[15] The calculation procedures of the radical densities have been described in detail in Ref. 8. In these calculation procedures, the rotational temperature was assumed to be 350 K. CF_x ($x=1-3$) radical densities generated from PTFE by CO_2 laser ablation were measured. Furthermore, CF_x ($x=1-3$) radical densities were measured as a function of the microwave power from 200 to 800 W in the ECR Ar plasma where the fluorocarbon species generated from PTFE by CO_2 laser ablation were introduced. The Ar gas partial pressure and Ar gas flow rate were fixed at 0.4 Pa and 20 sccm, respectively.

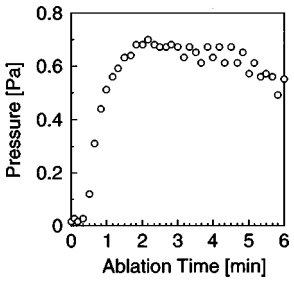

FIG. 2. Gas pressure as a function of ablation time at CO_2 laser power of 30 W, and exhaust rate of 84 l/s.

In the etching experiments, a stainless-steel substrate plate of 9 cm in diameter was used. The substrate plate was coupled with a 400 kHz rf power supply to generate self-bias voltage (V_{dc}) and cooled by water. In order to compare the etching results using the novel gas system with those using C_4F_8 gas, we performed etching of the SiO_2 films and Si substrates at a C_4F_8 gas flow rate of 16 sccm and a C_4F_8 gas pressure of 0.33 Pa by changing the microwave powers in the identical ECR plasma reactor.

III. RESULTS AND DISCUSSION

Figure 2 shows the gas pressure as a function of ablation time. The gas pressure was not increased for the first 30 s, because the PTFE target was not heated enough. The pressure was increased to about 0.7 Pa at an ablation time of 2 min and then saturated. The gas pressures were almost flat with an increase of ablation time to 5 min. Therefore, the stable gas supply was realized in this system. After ablation times of 5 min, the gas pressure was decreased slowly. The PTFE target of 5 mm in thickness irradiated by the CO_2 laser beam was found to be consumed completely at 20 min. It has been reported that polytetrafluoroethylene is ablated at a high rate by a CO_2 laser[16] and synchrotron radiation (SR).[17] The consuming rate of PTFE in this study was estimated to be 250 μm/min. This fact indicates the gas supply will be stopped at 5 min. This problem can be easily solved by scanning the PTFE target. The gas flow rate was calculated from the gas pressure and exhaust rate. The exhaust rate was estimated on the basis of the condition that the Ar gas flow rate and Ar gas pressure were 20 sccm and 0.4 Pa, respectively. Figure 3 shows the gas flow rate as a function of CO_2 laser power and revolution speed of the PTFE target. The PTFE was not ablated at CO_2 laser powers below 20 W. The gas flow rate increased with an increase of CO_2 laser power. The gas flow rate was estimated to be 34 sccm at the CO_2 laser power of 30 W and the PTFE target revolution speed of 333 rpm. The gas flow rate was increased with a decrease of the PTFE target revolution speed at CO_2 laser powers above 25 W. The gas flow rate was estimated to be 40 sccm at the CO_2

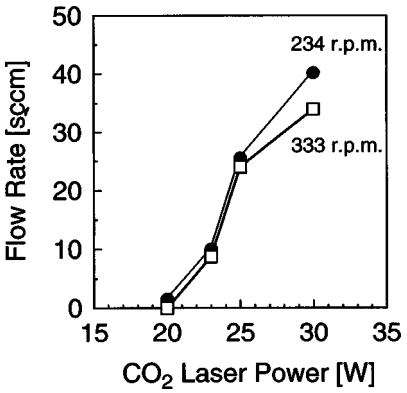

FIG. 3. Gas flow rate as a function of CO_2 laser power and revolution speed of the PTFE target at exhaust rate of 84 l/s.

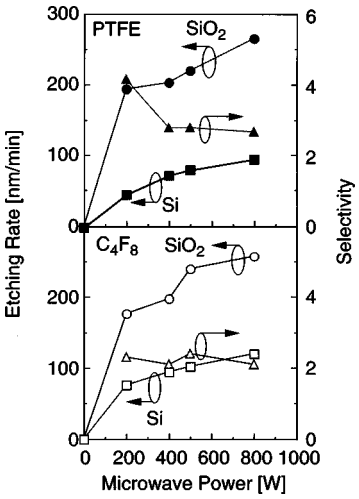

FIG. 5. Etching rates of SiO_2 and Si, and the etching selectivity (SiO_2/Si) as a function of microwave power at CO_2 laser power of 30 W, pressure of 0.33 Pa, bias voltage (V_{dc}) of −420 V, and exhaust rate of 211 l/s.

laser power of 30 W and the PTFE target revolution speed of 234 rpm. It was found that the gas flow rate could be successfully controlled by changing the CO_2 laser power and revolution speed of the PTFE target.

To characterize the gas component generated from the PTFE target, CF_x ($x=1-3$) radical densities were measured by IRLAS. Furthermore, CF_x ($x=1-3$) radical densities were evaluated in the ECR Ar plasma where the gas component generated from the PTFE target was injected. Figure 4 shows CF_x radical densities as a function of microwave power. The CF_2 radical density was estimated to be $2.2\times10^{12}\,cm^{-3}$ without the ECR Ar plasma while both CF and CF_3 radical densities were not detected, and so were estimated to be less than $1\times10^{11}\,cm^{-3}$ from the detection limit of IRLAS. When the Ar discharge turned on, it was found that CF and CF_3 radicals were observed together with CF_2 radicals. At a microwave power of 200 W, the CF_2, CF, and CF_3 radical densities were $4.5\times10^{13}\,cm^{-3}$, $4.0\times10^{11}\,cm^{-3}$, and $4.2\times10^{12}\,cm^{-3}$, respectively. CF_2 and CF_3 radical densities were saturated with an increase of microwave power. The CF radical density increased with increasing microwave power. CF_x ($x=1-3$) radical densities after discharge turned on increased by one order of magnitude compared with those before the discharge turned on. These results indicate that larger molecules, such as $C_xF_y(x\geq2)$, are generated by the PTFE ablation and then they are dissociated into smaller fragments, such as CF_x ($x=1-3$), by electron impacts. The behaviors of CF_x ($x=1-3$) radical densities were equivalent to those at the same ECR plasma apparatus employing C_4F_8 gas in a previous study.[11] Therefore, it is expected that this technique can be applied to the selective etching process.

We performed, therefore, the SiO_2/Si selective etching in the ECR plasma employing the novel gas source. Figure 5 shows the etching rates of SiO_2 and Si, and the etching selectivity (SiO_2/Si) as a function of microwave power. The SiO_2 and Si etching rates increased with an increase in microwave power and the etching selectivity was about 3. In the same conditions, except the novel gas source, SiO_2/Si selective etching was also performed in the ECR plasma em-

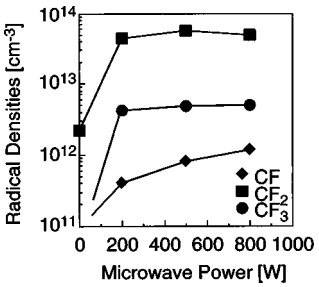

FIG. 4. CF_x ($x=1-3$) radical densities as a function of microwave power at CO_2 laser power of 30 W, Ar gas flow rate of 20 sccm, Ar gas partial pressure of 0.4 Pa, total pressure of 10.7 Pa, and exhaust rate of 84 l/s.

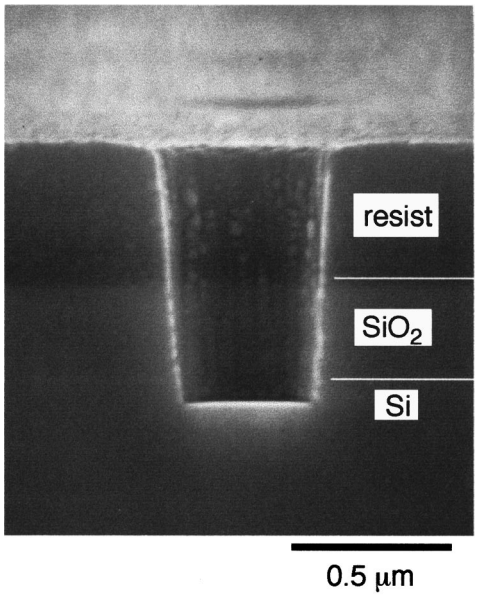

FIG. 6. SEM image of the etched contact hole at CO_2 laser power of 30 W, microwave power of 800 W, pressure of 0.4 Pa, bias voltage (V_{dc}) of −420 V, and exhaust rate of 211 l/s.

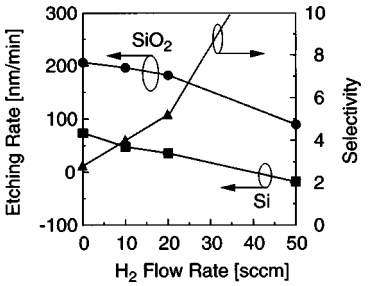

FIG. 7. Etching rates of SiO_2 and Si and the selectivity as a function of H_2 flow rate at CO_2 laser power of 30 W, microwave power of 400 W, pressure of 0.33 Pa, bias voltage (V_{dc}) of -420 V, and exhaust rate of 211 l/s.

ploying C_4F_8 gas. As a result, the SiO_2 and Si etching rates, and the selectivity obtained by using C_4F_8 gas are almost equivalent to those by using the novel gas source. Figure 6 shows the SEM image of the contact hole 0.5 μm in diameter. This image shows that the anisotropic etching of SiO_2 was successfully realized under this condition by using the novel gas source.

Figure 7 shows the etching rates of SiO_2 and Si and the selectivity as a function of the H_2 flow rate. The SiO_2 and Si etching rates decreased with an increase in the H_2 flow rate. At a H_2 flow rate of 50 sccm, SiO_2 was etched at 100 nm/min while Si was not etched. Under this condition, very high selectivity of SiO_2/Si was obtained. By using the novel gas source, the selective etching of SiO_2 to Si, equivalent to those by using conventional fluorocarbon feed gases, was realized in this study. Therefore, this technique is considered to be compatible with the conventional etching process employing fluorocarbon feed gases and makes a breakthrough in the plasma etching process for preventing global warming.

IV. CONCLUSIONS

We have developed a novel fluorocarbon gas source for preventing global warming where the fluorocarbon gas was generated from PTFE by CO_2 laser ablation. CF_x ($x=1-3$) radical densities were of the order of $10^{12}-10^{13}\,cm^{-3}$ in ECR Ar plasma using the novel gas source. These radical densities were almost the same as those in the ECR C_4F_8 plasma. Selective etching of SiO_2 to Si was performed in ECR plasma employing the novel gas source. The etching characteristics by the novel gas source were equivalent to those by a conventional ECR C_4F_8 plasma. Very high selectivity of SiO_2/Si was obtained in ECR H_2 plasma employing the novel gas source. Therefore, it is expected that this novel gas source is applicable to the selective etching of SiO_2 to Si and replaces the conventional gas source in order to prevent global warming.

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