PRECURSORS OF FLUOROCARBON FILMS FORMED
USING LOW GLOBAL WARMING GAS PLASMAS
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Abstract
Precursors of fluorocarbon films formed using low global warming potential gas plasmas, which is employed in low-dielectric film formation and contact hole etching processes for fabricating ultra large scale integrated circuits, have been investigated by the single-path infrared laser diode spectroscopy combined with laser-induced fluorescence and so on. These results suggest that fluorocarbon polymer films are formed by atomic carbon and polymeric species.

1. Introduction
Multilevel interconnection technologies are essential to realize the high performance in ultralarge scale integrated circuits (ULSIs). In advanced logic devices with sub-quarter micron design rules, the number of interlayer dielectrics has increased to four or five, so that interconnection delays are beginning to dominate the total signal delay and to limit the signal transmission rate of devices in ULSIs. As these interconnection delays are caused by the parasitic capacitance, the reduction of parasitic capacitance with employing lower dielectric constant materials for interlayer dielectrics is indispensable for improving the signal transmission rates. Many techniques of synthesizing low dielectric constant films have been investigated. In particular, fluorocarbon films formed by plasma chemical vapor deposition (CVD) employing fluorocarbon gases attracted great attention.

As wafers become larger, with approaching to 12 inches in diameter, the process uniformity over the entire area of large wafers are strongly required. Therefore, the measurement of the spatial distribution of absolute radical densities in the plasma reactor and the clarification of the formation mechanisms are indispensable to achieve the high performance plasma processing. In our previous study, the spatial distribution of absolute CF and CF₂ radicals densities in electron cyclotron resonance (ECR) C₄F₈ plasma were measured with high accuracy by combining the single-path infrared laser absorption spectroscopy (IRLAS) with laser-induced fluorescence (LIF) techniques.

The feed gases such as C₄F₈ have been also employed in the formation process of fluorocarbon films such as low-dielectric constant interlayer. The fluorocarbon gases, however, are kinds of the greenhouse effect gases. The global warming potential (GWP) of CF₄, CHF₃, C₂F₆, and C₄F₈ are 6,300, 12,100, 12,500, and 8,700, respectively. The use and production of these fluorocarbon gases with high GWP would be prohibited in the near future.

In this study, we have measured the spatial distributions of the absolute densities of CF and CF₂ radicals in ECR plasmas employing low GWP fluorocarbon gases of hexafluorobutadiene (C₄F₈) and hexafluoropropene (C₃F₆), and a conventional octafluorocyclobutane (c-C₄F₈) by combining the single-path IRLAS and LIF techniques. Moreover, the behaviors of ions, atomic fluorine, and atomic carbons have been investigated by using quadrupole mass spectrometry (QMS), actinometric optical emission spectroscopy.
(AOES), and vacuum ultraviolet absorption spectroscopy (VUVAS), respectively. The distribution of deposition rate of fluorocarbon films on Si wafer is evaluated. On the basis of these results, the precursors for the fluorocarbon film formation are discussed.

2. Experimental

$C_4F_8$ and $C_6F_6$ were used as low GWP source gases. The conventional $C_4F_8$ gas with high GWP was also used for the comparison. $C_4F_8$ and $C_6F_6$ gases have C–C double bond, which leads to be not only low GWP but also high reaction rates because the bonding energy of the double bond is lower.

For investigating the precursor of the deposited film, the spatial distributions of the absolute CF and CF$_2$ radical densities were measured in ECR plasma reactor by combining the single-path IRIAS and LIF techniques. Details of the plasma chamber and the laser guiding system for IRIAS and LIF were given in our previous paper.

A continuous 2.45 GHz microwave was introduced into the plasma reactor at the top of the reactor. The mirror-type magnetic field was formed by a main and two sub magnet coils, and the ECR plasma was confined within a region of 25 cm in diameter. An 8 inch Si wafer was placed on the substrate holder. The substrate was heated at 350°C and the chamber wall was maintained at 80°C.

Behaviors of atomic carbon were measured in the same reactor described above by using VUVAS method. The VUVAS system employing a high-pressure microdischarge hollow cathode lamp (MHCIL) as a light source has been used for the measurement of absolute H and N atom densities. In this study, helium (He) gas containing a small amount of CO$_2$ gas was used for the source gas of carbon emission line in the MHCIL. In this study, the absorption intensity indicative of the density of atomic carbons were measured because the spectral profile and self absorption due to atomic carbons in the light source have not been evaluated yet.

Fluorocarbon ions were measured by quadrupole mass spectrometer (QMS) attached on the side wall of plasma chamber. The distance between the orifice and the center of ECR layer was about 10 cm horizontally and about 5 cm normally, so the orifice was located at the plasma region. F atom densities in the ECR plasma were measured by AOES. X-ray photoelectron spectroscopy (XPS) was used to investigate the surface structure of fluorocarbon polymer deposited on the substrate.

3. Results and discussion

Figure 1 shows the deposition rates of fluorocarbon polymer films formed at the center of Si substrate employing the different gases as functions of (a) microwave power and (b) pressure. The negative values of deposition rate in Fig. 1 mean the etching. Fluorocarbon polymers were formed on the Si substrate in $C_4F_8$ and $C_6F_6$ plasmas. In particular, at 2.5 kW of microwave power, the high deposition rates

![Fig. 1 Deposition rates of fluorocarbon polymer films formed at the center of Si substrate employing the different gases as functions of (a) microwave power and (b) pressure.](image-url)
of fluorocarbon polymers of 600 nm/min were achieved at a substrate temperature of 350 °C in both \textit{C}_{4}\textit{F}_{8} and \textit{C}_{6}\textit{F}_{6} plasmas. On
the other hand, the deposition was not observed at any condition in the \textit{C}_{6}\textit{F}_{6} plasmas. However, the film was deposited
with low rate on the substrate attached on chamber wall, which was heated at 80 °C
and not exposed to the plasma.

Figure 2 shows the C1s XPS spectra of Si substrate surface in \textit{C}_{4}\textit{F}_{8} plasma as functions of (a) microwave power and (b)
pressure. Plasma conditions were the same as those in Fig. 1. At the conditions of high
microwave powers or low pressures, where the high deposition rates were obtained.
C-CF\textsubscript{3} and C\textsubscript{2} bond spectra appeared strongly in the deposited polymers. The
dielectric constants and the ratio C/C\textsubscript{2} of the
deposited polymers were 3.1 and 1.1, respectively, which were almost the same as
those (3.0 and 1.2) in \textit{C}_{6}\textit{F}_{6} plasma. Thus, the fluorocarbon film of low dielectric constant
was formed at high deposition rates by using
\textit{C}_{4}\textit{F}_{8} and \textit{C}_{6}\textit{F}_{6} gases.

Figure 3 shows the spatial distribution of polymer deposition rate in \textit{C}_{4}\textit{F}_{8} and \textit{C}_{6}\textit{F}_{6}
plasmas. Fluorocarbon polymers were deposited at a pressure of 0.4 Pa, a
microwave power of 1.0 kW, and a source gas flow rates of 60 sccm.

Figures 4 shows the spatial distributions of the absolute CF\textsubscript{2} radical density as a
function of microwave power in the \textit{C}_{4}\textit{F}_{8}
plasma, which were measured by combining the single-path IRIAS and LIF techniques.
A total pressure and a flow rate of \textit{C}_{4}\textit{F}_{8} were
1.3 Pa and 60 sccm, respectively. The CF\textsubscript{2}
radical density decreased with increasing microwave power. Moreover, the CF\textsubscript{2}
radical densities had hollow-type distributions, where the density at the center of the wafer
was lower than that in the vicinity of the chamber wall. At a microwave power of 0.5 kW, the
CF\textsubscript{2} radical density above the center of wafer was \(0.2 \times 10^{14}\) cm\(^{-3}\) and it increased slowly in
the plasma region. Then, near the boundary of plasma region, CF\textsubscript{2} radical density increased
rapidly and reached to \(1.6 \times 10^{14}\) cm\(^{-3}\) in the vicinity of the wall. These distributions of CF\textsubscript{2}
radical density were almost the same as those in the \textit{C}_{6}\textit{F}_{6} plasmas obtained in our previous
study.\(^1\) However, the hollow-type distribution of CF\textsubscript{2} radical in the \textit{C}_{4}\textit{F}_{8} plasma was shallower
than that in the \textit{C}_{6}\textit{F}_{6} plasma at a microwave power of 0.5 kW as shown in Fig. 4. CF\textsubscript{2} radical
density near the chamber wall in the \textit{C}_{6}\textit{F}_{6} plasma was almost twice of that in the \textit{C}_{4}\textit{F}_{8} plasma. These
results might be caused by the difference of those gas structures. CF\textsubscript{2} radical will be
easily generated in the \textit{C}_{4}\textit{F}_{8} plasma compared with that in the \textit{C}_{6}\textit{F}_{6} plasma because \textit{C}_{6}\textit{F}_{6}
molecule forms a ring of CF₂ bonds.

Figure 5 shows the spatial distribution of the absolute CF radical density in the C₄F₆ plasma as a function of microwave power. The plasma was generated at a C₂F₆ gas flow rate of 60 scm and under a pressure of 1.3 Pa. At a microwave power of 2.5 kW, CF radical density had a hollow-type distribution like CF₂ radical density. On the other hand, at 0.5 and 1.0 kW, CF radical densities in the plasma region were almost the same or higher than those outside the plasma. In C₃F₈ plasma, CF radical densities were higher than CF₂ ones in the plasma region but lower outside the plasma region, whereas CF radical densities in C₄F₆ plasma were lower than those in C₃F₈ plasma and CF and CF₂ radical densities were almost the same in plasma region.

The spatial distributions of the absolute CF₂ and CF radical densities in the C₄F₆ plasma as a function of microwave power were also measured. The CF₂ radical densities had hollow-type distributions for every microwave power, and the overall density decreased with increasing microwave power in a similar manner to the results of C₃F₈ plasma. The absolute CF₂ radical densities in the C₄F₆ plasma were almost the same as those in the C₃F₈ plasma at a microwave power of 1.0 and 2.5 kW. On the other hand, CF₂ radical densities in C₃F₈ plasma at 0.5 kW were clearly higher than those at 1.0 kW and were higher than those in C₄F₆ plasma at 0.5 kW, while CF radical densities in C₃F₈ plasma were lower than those in C₄F₆ plasma and a hollow-type distribution was never observed at a microwave power of 2.5 kW.

Figure 6 shows F atom densities in C₄F₆, C₃F₈, and C₄F₈ plasmas as a function of microwave power. From this result, F atom density increased with increasing microwave power in every source gas plasma and was the highest in C₃F₈ plasma. Comparing the structure of C₃F₈ with that of C₄F₆, C₃F₈ gas has higher F atom component ratio (F/C) resulting in higher F atom density in C₃F₈ plasma. On the other hand, the difference of behaviors of F atom between C₃F₈ and C₄F₆ plasmas with the same component ratio (F/C=2) might be due to that of dissociation reactions because C₃F₈ gas has a C=C bond.

Figure 7 shows the absorption intensity of C atoms measured by VUVAS as functions of (a) microwave power and (b) pressure in C₄F₆, C₃F₈, and C₄F₈ plasmas. These absorption intensities of C atom are indicative of relative densities of C atom in the plasma. Therefore, it was found that C atom density was higher at lower pressures or at higher microwave powers.
Moreover, the absorption intensity of C atom was the highest in the $\text{C}_4\text{F}_6$ plasma. $\text{C}_4\text{F}_6$ gas has the highest C atom component ratio in the gas structure among those source gases and is easily dissociated into smaller species such as F and C atoms because of two C=O bonds in the gas structure. Therefore, a large amount of C atoms are considered to be produced from the $\text{C}_4\text{F}_6$ gas.

Each signal intensity of QMS for $\text{CF}_x^+$ (X=1-3) ions observed in the $\text{C}_4\text{F}_6$ plasma was almost the same as that in the $\text{C}_4\text{F}_6$ plasma, which was different from that in the $\text{C}_4\text{F}_6$ plasma. These signal intensities increased with increasing microwave power in the $\text{C}_4\text{F}_6$ and $\text{C}_4\text{F}_6$ plasmas, while decreased in the $\text{C}_4\text{F}_6$ plasmas.

Moreover, the variations of pressure after the discharges turned on were measured. The pressure increased in the $\text{C}_4\text{F}_6$ plasma while the pressures decreased in the $\text{C}_4\text{F}_6$ and the $\text{C}_4\text{F}_6$ plasmas. It is suggested that, in the $\text{C}_4\text{F}_6$ plasma, the source gas was mostly dissociated into smaller species with electron-impact dissociation while, in the $\text{C}_4\text{F}_6$ and $\text{C}_4\text{F}_6$ plasmas, the dissociated products seem to be polymerized to form polymeric species such as higher-order radicals with the plasma resulting in the decrease of gas species in the plasma chamber. These polymeric species seemed to increase with increasing microwave power in the plasma employing $\text{C}_4\text{F}_6$ and $\text{C}_4\text{F}_6$ gases. The hollow-type distributions of $\text{CF}_x$ radical densities in $\text{C}_4\text{F}_6$ and $\text{C}_4\text{F}_6$ plasmas indicate shallower ones than those in $\text{C}_4\text{F}_6$ plasma. In the $\text{C}_4\text{F}_6$ and $\text{C}_4\text{F}_6$ plasmas, $\text{CF}_2$ radical densities in the plasma region were higher than those in the $\text{C}_4\text{F}_6$ plasma. These results also suggest that $\text{CF}_2$ radicals are produced from the dissociation of polymeric species in the plasma region in $\text{C}_4\text{F}_6$ and $\text{C}_4\text{F}_6$ plasmas.

As shown in Fig. 3, the deposition rate of polymers in $\text{C}_4\text{F}_6$ plasma was almost twice of those in $\text{C}_4\text{F}_6$ plasma. This result can be explained by the difference of density of F atom, which works as an etchant of fluorocarbon film, since F atom densities were higher in $\text{C}_4\text{F}_6$ plasma than that in $\text{C}_4\text{F}_6$ as shown in Fig. 6.

The deposition rates of fluorocarbon polymers at the center of wafer were higher than those at the edge of wafer in both plasmas, that is, hill-type distributions were observed as shown in Fig. 3. These distributions of deposited films were quite different from those of CF.
and CF$_2$ radical densities. Moreover, CF and CF$_2$ radical densities above the substrate decreased with increasing microwave power, which were also much different from those of the deposition rate of films. These facts indicate that CF and CF$_2$ radical did not work so much as precursors of fluorocarbon polymer. If CF$_4^-$ ions were precursors of films and/or contributed to the polymer deposition, the fluorocarbon polymer should not be deposited on the silicon wafer surface in the C$_4$F$_8$ plasma like the C$_4$F$_8$ plasma because in the C$_4$F$_8$ plasma, the CF$_4^-$ ion densities were lower and the F atom densities were higher than those in C$_4$F$_8$ plasma. Therefore, the contribution of CF$_4^-$ ions to the polymer deposition seems to be very low.

On the other hand, the behaviors of C atoms indicated the similar tendency to those of film deposition rates. In the C$_4$F$_8$ plasma, C atom density and the film deposition rate were the highest among those source gases. Therefore, C atoms with relatively high sticking coefficient will be a precursor of polymer deposition. However by using only C atom-chemistry, it can not be explained enough why deposited films had strong C-CF$_4$ and CF$_2$ bond spectra and the film never formed in C$_4$F$_8$ plasma, where the C atom density was almost the same as that in C$_4$F$_8$ plasma. Recently, Booth et al. proposed that the fluorocarbon films are formed through the reaction combined with CF$_2$ radical and high-order species in the high-pressure and relatively low-density fluorocarbon plasmas. From the results of gas species and film deposition rates measured in this study, we consider that not only C atoms but also polymeric species contribute dominantly to the high rate deposition of fluorocarbon polymer films at a high substrate temperature of 350 °C in low-pressure and high-density plasmas employing fluorocarbon gases containing the C-C bond.

4. Conclusion

Behaviors of gas species in ECR plasmas employing low global warming potential fluorocarbon gases of C$_4$F$_8$ and C$_4$F$_8$ with a conventional C$_4$F$_8$ gas were investigated. The spatial distributions of the absolute CF and CF$_2$ radical densities were measured by combining single-path IPIAS and IIF techniques. CF$_2$ radicals have hollow-type distributions in all conditions. The spatial distributions of the CF radical density were changed by plasma conditions. Fluorocarbon films with low dielectric constant of about 3.0 were deposited on the silicon substrate at a high rate of 600 nm/min at the condition of high microwave powers in C$_4$F$_8$ and C$_4$F$_8$ plasmas, whereas the etching reaction was observed in C$_4$F$_8$ plasma. The deposition rates of the film on the substrate showed hill-type distributions and these distributions were quite different from those of CF and CF$_2$ radicals. Behaviors of carbon atoms indicated the similar tendency to those of film deposition. The variation of pressure after the discharge turned on indicated the existence of large molecule polymeric species in C$_4$F$_8$ and C$_4$F$_8$ plasmas. The behaviors of deposition rate of fluorocarbon films could be explained well by those of C atom and polymeric species in the plasmas. C atom and polymeric species are key precursors for the fluorocarbon film deposition at a high rate in low-pressure and high-density fluorocarbon plasmas.

References