Characteristics of SiO$_2$ Etching by Capacitively Coupled Plasma with Different Fluorocarbon Liquids (C$_7$F$_{14}$, C$_7$F$_8$) and Fluorocarbon Gas (C$_4$F$_8$)

Received 25 June, 2021; revised 27 July, 2021; accepted 29 July, 2021

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**ABSTRACT**

Fluorocarbon (C$_7$F$_{14}$, C$_7$F$_8$) plasmas are investigated to verify their etching characteristics as an alternative etchant of SiO$_2$ etch process because C$_7$F$_8$ and C$_7$F$_{14}$ precursors are expected to have low Global warming potentials. Comparing the etch results of C$_4$F$_8$, C$_7$F$_{14}$, and C$_7$F$_8$ plasmas, C$_7$F$_8$ provides the highest selectivity for etching SiO$_2$ at a moderate etching rate of the three fluorocarbons. C$_4$F$_8$ and C$_7$F$_{14}$ plasmas show similar magnitudes of selectivity at the same O$_2$ injection. O$_2$ addition is used to control densities of carbon species and optimize etching conditions. From comparison of the species existing in the C$_7$F$_8$, C$_7$F$_{14}$, and C$_7$F$_8$ plasmas by the electron-emitting source, CF radicals and carbon atoms are important in determining the remarkable selectivity of C$_7$F$_8$ plasma. This understanding is verified using X-ray photoelectron spectroscopy analysis.

**Keywords:** Silicon oxide etching, Liquid fluorocarbon precursor, Global warming potential, Etch selectivity, Capacitively coupled plasma

1. Introduction

In the ultralarge-scaled integrated devices fabrication, as SiO$_2$ etching process for manufacturing 3D semiconductor devices demands high aspect ratio and small feature size, etching characteristics such as high SiO$_2$ etch rate and highly selective etch of SiO$_2$ over Si$_3$N$_4$ or Poly-Si are getting more important. On the other hand, regarding the global warming problems, perfluorinated compounds (PFCs) like C$_2$F$_6$, C$_4$F$_8$, which are used as precursors for SiO$_2$ etching process, generally have high Global Warming Potential (GWP) and been considered to have same potential compared with C$_4$F$_8$ as an alternative fluorocarbon precursor regardless of GWP. As for the reason, from the fact that a portion of parent PFC is known to be effused out of chamber without being dissociated in the plasma, the liquid PFC effused can be condensed and retrieved easily [4,5].

Using the C$_7$F$_{14}$ and C$_7$F$_8$ as liquid fluorocarbon precursors, the etch rate and the etch selectivity of SiO$_2$ over resist are compared with C$_4$F$_8$ in the plasmas. Disassociative characterizations of the precursors were investigated using the quadrupole mass spectrometer (QMS) both in plasma process and plasma-off condition. This analysis method is enable us to interpret the etching characters of the liquid precursor.

2. Experimental details

For verifying etch characteristics of the precursors, a radio frequency (RF, 13.56 MHz) capacitively-coupled plasma (CCP) was used to etch SiO$_2$ layer. The CCP chamber has a diameter of 34 cm and a height of 14.5 cm and the plasma was maintained between two parallel plate electrodes separated by 5 cm. During the etch processes, the RF power was pulsed at 500 Hz with a 50 % duty cycle at 300 W. The process pressure and substrate temperature were maintained at 20 mTorr and room temperature, respectively.

Mixtures of PFC/Ar/O$_2$ were injected to the chamber through the nozzle installed at the top electrode of the chamber. Flow rates of the PFCs were equally 6 sccm during their respective process and flow rate of Ar was kept 6 sccm. It is widely known that oxygen can be used...
to control C\textsubscript{4}F\textsubscript{8} polymer formation and the C\textsubscript{4}F\textsubscript{8} polymer at surface play an important role in the SiO\textsubscript{2} selective etching [6,7]. From this understanding, it is considered that controlling amount of oxygen addition is the primary method to find optimal conditions of each PFCs. In order to optimize the process condition of the precursors, the flow rates of O\textsubscript{2} were changed in range of 0–4 sccm for the experiments of C\textsubscript{4}F\textsubscript{8} and C\textsubscript{7}F\textsubscript{14}. C\textsubscript{4}F\textsubscript{8} precursors deposit more polymer than other precursors, so SiO\textsubscript{2} was not etched in same condition of other precursors. Therefore, the flow rates of O\textsubscript{2} were changed in range of 6–12 sccm for the experiment of C\textsubscript{7}F\textsubscript{14}. For the etch process, substrate was composed of 1 \textmu m thick SiO\textsubscript{2} layer masked with a 200 nm thick poly-Si, which layers were deposited on silicon wafer.

To measure the radical species in the plasmas, the ordinary quadrupole mass spectrometer system (SRS-200) was installed at the chamber. The radical species were extracted from the chamber through metallic tube (3.5 cm in diameter, 2 cm in length) and introduced to the sampling orifice of the QMS, which orifice was 0.1 \textmu m in diameter. Operating pressure of the QMS was maintained below 1 \times 10^{-6} Torr for being free from the collision of gases. Meanwhile, gases decomposed from the precursors using electron emitting source were measured by another QMS (PSM, Hiden Analytical, England) which is capable of appearance potential mass spectroscopy (APMS) analysis.

In order to examine the etch rate and the etch selectivity of SiO\textsubscript{2} over resist, profiles of SiO\textsubscript{2} layer etched in the plasma were examined by field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan). To measure the plasma density, a cut-off probe was used [8,9], which was placed at center of the chamber. And using an oscilloscope installed at bottom electrode, self-bias voltage was measured.

3. Results and discussion

Figure 1(a) shows the etch rates of SiO\textsubscript{2} and Fig. 1(b) shows etch selectivities of SiO\textsubscript{2} over poly-Si as a function of O\textsubscript{2} flow rates in the C\textsubscript{4}F\textsubscript{8}, C\textsubscript{7}F\textsubscript{14}, and C\textsubscript{4}F\textsubscript{8} plasmas.
C₄F₈, C₇F₁₄, and C₇F₈ shown in Fig. 1, it can be analyzed in two aspects. First, the electrical properties of plasma enable to affect etch characteristics can be examined. Flux and density of ions arriving the surface of substrate are related with the electrical property of the plasma such as self-bias voltage of plasma and plasma density. In this regard, electron density and self-bias voltage were analyzed.

In Fig. 2, the plasma density and the self-bias voltage were measured at the same condition of Fig. 1. In Fig. 2(a), plasma density was also not different between the precursors. Therefore, the plasma density is not related with the difference of the etch results in Fig. 1. From the Fig. 2(b), the self-bias voltage is slightly changed with varying precursors, but this variation is not enough to change the etch characteristics for each precursor. Thus, it is considered that self-bias voltage is not related with the difference of the etch results in Fig. 1(a). Therefore, it can be deduced that the differences of etch results between the precursors are not attributed to the change of electrical properties of the plasmas. Meanwhile, despite the oxygen addition, the plasma density and the self-bias voltage were steady. Therefore, it can be also deduced that the electrical properties caused by oxygen addition does not affect etch results of Fig. 1(a).

The differences among the etch properties of the C₄F₈, C₇F₁₄, and C₇F₈ plasmas shown in Fig. 1 can be analyzed in another aspect. Second, plasma species were analyzed by the quadrupole mass spectrometer (QMS). Figure 3 shows (a) C, (b) CF, (c) CF₂, (d) CF₃, and (e) F radical densities measured by QMS under the same conditions used to obtain the data in Fig. 1.

In the C₂F₆ plasma process, both CF and CF₂ radicals were most frequently observed than the other precursor plasma. The C₇F₁₄ plasma has a lower CF₂ radical density than the C₄F₈ plasmas, but larger CF₂ radical density than that of the C₇F₈ plasma. Regarding CF radical, the C₂F₆ and C₇F₁₄ plasmas show the similar magnitude of densities each other. The C₇F₈ plasmas show smaller CF and CF₂ radical densities than those of the other precursor plasmas. In addition, C₇F₈ results show slightly larger fluorine radical density than C₇F₁₄ results. From these facts, it is expected that etch results of C₇F₈ plasmas would show smaller etch selectivity than the C₄F₈ and C₇F₁₄ plasma processes. However, in comparison with the C₄F₈ and C₇F₁₄ etch results,
the selectivities of the C$_2$F$_8$ etch results are larger and the etch rate of C$_2$F$_8$ results are smaller. Meanwhile, it needs to be mentioned that the carbon densities of the C$_2$F$_8$ plasmas were somewhat larger than that of the C$_2$F$_2$ and C$_2$F$_{14}$ plasmas.

The results, like above mentioned, in which tendencies of etch properties were not consistent with changes of C$_2$F$_2$ density measured by QMS are also found in the other report [11]. This is because radical density measured by QMS during plasma process does not represent the information about the species arriving the surface, but represent the species existing in the plasma. Plasma state is normally determined by reactions between species like electron, ion and neutral and by the interaction between the species and solid surface after plasma is initiated by electron impact ionization. Therefore, so as to elucidate plasma state and the etch result accurately, it will be necessary to distinguish the species arriving the surface from the species existing in the plasma.

In order to obtain the information about the species which affects the etching surface, the fluorocarbon films deposited in the C$_2$F$_8$, C$_2$F$_{14}$, and C$_2$F$_8$ plasmas are analyzed by XPS. Figures 4(a)–(c) are the XPS spectra of the fluorocarbon films deposited in the C$_2$F$_8$, C$_2$F$_{14}$, and C$_2$F$_8$ plasmas, respectively. The photoelectron C 1s peaks observed in Fig. 4 are C-C (283.8 eV), C-CF (284.7 eV), CF (286.5 eV), CF$_2$ (289.2 eV), and CF$_3$ (291.5 eV). The pick positions can be shifted due to the charging effect of polymer film [12,13]. In Fig. 4, as the oxygen flow rate increased, decreasing of C 1s peaks were observed for all three precursors. C 1s peaks of C$_2$F$_8$ results were mostly larger than those of the C$_2$F$_2$ and C$_2$F$_{14}$ results. And C 1s peaks of C$_2$F$_{14}$ are larger than those of C$_2$F$_8$ at oxygen flow rate of 2–6 sccm. These results are consistent with the selectivities shown in Fig. 1(b).

For better understanding of the species which affect the etching surface, after C$_2$F$_8$, C$_2$F$_{14}$, and C$_2$F$_8$ are dissociated using electron emitting source, the dissociated species were measured using QMS so that the density of the species decomposed from the precursors (C$_2$F$_8$, C$_2$F$_{14}$, C$_2$F$_8$), which are shown in Fig. 5, would be compared with the species existing in the plasma as shown in Fig. 3.

Figure 5 shows the (a) C, (b) CF, (c) CF$_2$, (d) CF$_3$, and (e) F radical densities measured at various electron impact energies using a QMS after C$_2$F$_8$, C$_2$F$_{14}$, and C$_2$F$_8$ are decomposed by the electron-emitting source of the ionizer in the QMS. For resolution and accuracy of the electron energy, the PSM apparatus was used, allowing APMS analysis.

In Figs. 5(b) and (c), the gases decomposed from the precursors show larger densities of CF than of CF$_2$, while Figs. 3(b) and (c) show no significant differences between CF and CF$_2$. According to the results, CF radicals are considered to be involved in the surface reactions and to have more influence on the etch process than CF$_2$ radicals.

In Figs. 5(b) and (c), the gases decomposed from C$_2$F$_8$ show the highest densities of both CF and CF$_2$, in agreement with Fig. 3. The C$_2$F$_{14}$ plasma shows lower CF$_2$ radical density than the C$_2$F$_8$ plasma, but higher CF$_2$ radical density than the C$_2$F$_8$ plasmas, which also agrees with Fig. 3(c). However, C$_2$F$_8$ plasma shows greater CF radical density than C$_2$F$_{14}$ plasma, which does not match the results of Fig. 3(b). This is considered to be related with the larger C-CF and CF peaks from the C$_2$F$_8$ results compared to those of the other precursor.

It can be deduced that the CF radical is more important in determining the etching characteristics of the C$_2$F$_8$ plasma process than it is with C$_2$F$_{14}$.

On the other hand, in Fig. 5(a), the carbon atom density measured from dissociated C$_2$F$_8$ gas is one order of magnitude higher than that from the other precursors. This result indicates that the C$_2$F$_8$ plasma produces more carbon as carbon atoms, instead of fluorocarbons. It can be also inferred that the carbon atoms and molecules generated by the C$_2$F$_8$ plasma enhance the magnitude of selectivity, accompanying the noticeable formation of C-CF$_3$ bonds shown in Fig. 4(c).

4. Conclusions

Considering the compatibility of C$_2$F$_{14}$ and C$_2$F$_8$ as alternatives for C$_2$F$_8$, C$_2$F$_{14}$ plasma in the SiO$_2$ etch process is expected to show etching characteristics similar to those of C$_2$F$_8$ plasma. The C$_2$F$_8$ plasma process shows a lower etch rate than C$_2$F$_8$ and C$_2$F$_{14}$. However, C$_2$F$_8$ plasma achieves remarkable selectivity with a moderate etch rate by adjusting the amount of carbon produced through applying the appropriate O$_2$ flow rate. C$_2$F$_8$ plasma processing is therefore appropriate for high-aspect-ratio etching processes.

Acknowledgements

This research was supported by a National Research Council of Science & Technology (NST) grant from the Korean government (MSIP)
by the Industrial Strategic Technology Development Program—Next Generation Semiconductor R&D (20010412, Development of Metal Oxide Carbon Layer Strip Process and Commercial Equipment for EUV Mask) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea), by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the MOTIE of the Republic of Korea (No. 20172010105910), by the MOTIE (20009818, 20010420) and KSRC (Korea Semiconductor Research Consortium) support program for the development of future semiconductor devices, by a Korea Institute for Advancement of Technology (KIAT) grant funded by the Korean government (MOTIE) (P0008458, The Competency Development Program for Industry Specialist), and by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2020R1A6A1A03047771).

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