Characteristics of SiO₂ Etching by Capacitively Coupled Plasma with Different Fluorocarbon Liquids (C₇F₁₄, C₇F₈) and Fluorocarbon Gas (C₄F₈)

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ABSTRACT

Fluorocarbon (C₇F₁₄, C₇F₈) plasmas are investigated to verify their etching characteristics as an alternative etchant of SiO₂ etch process because C₇F₈ and C₇F₁₄ precursors are expected to have low Global warming potentials. Comparing the etch results of C₄F₈, C₇F₁₄, and C₇F₈ plasmas, C₇F₈ provides the highest selectivity for etching SiO₂ at a moderate etching rate of the three fluorocarbons. C₄F₈ and C₇F₁₄ plasmas show similar magnitudes of selectivity at the same O₂ injection. O₂ addition is used to control densities of carbon species and optimize etching conditions. From comparison of the species existing in the C₄F₈, C₇F₁₄, and C₇F₈ plasmas by the electron-emitting source, CF radicals and carbon atoms are important in determining the remarkable selectivity of C₇F₈ 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 SiO₂ etching process for manufacturing 3D semiconductor devices demands high aspect ratio and small feature size, etching characteristics such as high SiO₂ etch rate and highly selective etch of SiO₂ over Si₃N₄ or Poly-Si are getting more important. On the other hand, regarding the global warming problems, perfluorinated compounds (PFCs) like C₂F₆, C₄F₈, which are used as precursors for SiO₂ etching process, generally have high Global Warming Potential (GWP) and been considered to raise greenhouse effect [1]. Therefore, it is important to develop an alternative etching process using low GWP precursor and showing competent etching properties compared with conventional SiO₂ etch process.

In an effort to develop an alternative etchant with low GWP, C₅F₈ had been investigated to evaluate its etching performances as an alternative precursor for the SiO₂ etch process [2, 3]. Because C₅F₈ has a double bond in its a cyclic-structure so that C₅F₈ shows shorter atmospheric lifetime and low GWP. Therefore, if C₅F₈ is effused from reactor without being dissociated in plasma, the C₅F₈ effused will not worsen global warming.

Considering the issues, C₇F₈ (octafluorotoluene) and C₇F₁₄ (perfluoro-methylcyclohexane) are investigated in this study as an alternative fluorocarbon precursor for C₄F₈ which is used conventionally in the industry. Although the values of GWPs of C₇F₈ and C₇F₁₄ are not calculated and are unknown, the C₇F₈ and C₇F₁₄ liquid precursors

are considered to have same potential compared with C₅F₈ 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 C₇F₁₄ and C₇F₈ as liquid fluorocarbon precursors, the etch rate and the etch selectivity of SiO₂ over resist are compared with C₄F₈ in the plasmas. Dissociative 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 SiO₂ 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/O₂ 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

Figure 1. (a) Etch rates of SiO₂ and (b) etch selectivities of SiO₂ over poly-Si as a function of O₂ flow rates obtained in the C₄F₈, C₇F₁₄, and C₇F₈ plasmas.

to control C_xF_y polymer formation and The C_xF_y polymer at surface play an important role in the SiO₂ 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 O₂ were changed in range of 0–4 sccm for the experiments of C₄F₈ and C₇F₁₄. C₇F₈ precursors deposit more polymer than other precursors, so SiO₂ was not etched in same condition of other precursors. Therefore, the flow rates of O₂ were changed in range of 6–12 sccm for the experiment of C₇F₈. For the etch process, substrate was composed of 1 μm thick SiO₂ 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 orifices was 0.1 μm in diameter. Operating pressure of the QMS was maintained below 1×10⁻⁶ Torr for being free from the collision of gases. Meanwhile, gases decomposed from the precursors using electron emitting source were measured by the 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 SiO₂ over resist, profiles of SiO₂ 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 SiO₂ and Fig. 1(b) shows etch

Figure 2. (a) Plasma density and (b) self-bias measured as a function of O₂ flow rates in the C₄F₈, C₇F₁₄, and C₇F₈ plasmas.

selectivities of SiO₂ over poly-Si as a function of O₂ flow rate, which are processed in the C₄F₈, C₇F₁₄, and C₇F₈ plasmas. It is known that carbon and fluorine arrived at etching surface form fluorocarbon film and etch SiO₂ film by reacting with Si and oxygen of the surface, but, if the carbon and fluorine arrive to the surface with so large flux and form a thick film, etch rate will be decreased and etch reaction can be stopped [7]. Therefore, controlling the thickness of fluorocarbon on surface is a main method to optimize etch processes [10]. On this understanding, the etch rate and the etch selectivity were investigated at various oxygen flow rates for comparison between the optimal conditions of the C₄F₈, C₇F₁₄, and C₇F₈ plasmas.

As the oxygen flow rate is increased from 0 to 6 sccm for the experiments of C₄F₈ and C₇F₁₄ and increased from 6 to 12 sccm for the experiment of C₇F₈, all the etch rates of the precursors are increased. In the range of oxygen flow rate from 0 to 6 sccm, C₄F₈ and C₇F₁₄ show similar values of selectivities, but the etching rates of the C₄F₈ plasmas were higher than that of the C₇F₁₄ results except for the oxygen flow rate of 2 sccm. At the oxygen flow rate of 2 sccm, selectivity of the C₇F₁₄ results show slightly larger value than that of the C₄F₈ results.

In the C₇F₈ plasma process, oxygen was injected to the chamber with the flow rates of 6–12 sccm. Because, at the oxygen flow rate under 6 sccm, deposition of C_xF_y polymer on the wafer was so large that etching of SiO₂ layer was not progressed. Etch rates of C₇F₈ for oxygen flow rate of 6–12 sccm were lower than those of other precursor for oxygen flow rates of 0–6 sccm, in contrast, etch selectivities of C₇F₈ plasma are larger than those of C₄F₈ and C₇F₁₄ results. Especially, at the oxygen flow rates of 8 and 10 sccm, etch selectivities were significantly larger than those of C₄F₈ and C₇F₁₄ plasma.

In order to explain the differences between the etch properties of

Figure 3. (a) C, (b) CF, (c) CF₂, (d) CF₃, and (e) F radical densities measured by a QMS(SRS-200) in the C₄F₈, C₇F₁₄, and C₇F₈ 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 plasma 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 C₄F₈ 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 plasmas. Regarding CF radical, the C₄F₈ 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,

Figure 4. XPS spectra of photoelectron C 1s peaks of the fluorocarbon film deposited in the (a) C₄F₈, (b) C₇F₁₄, and (c) C₇F₈ plasmas.

Figure 5. (a) C, (b) CF, (c) CF₂, (d) CF₃, and (e) F radical densities measured as a function of electron impact energy using a QMS (PSM) after C₄F₈, C₇F₁₄, and C₇F₈ are decomposed by the electron-emitting source.

the selectivities of the C₇F₈ etch results are larger and the etch rate of C₇F₈ results are smaller. Meanwhile, it needs to be mentioned that the carbon densities of the C₇F₈ plasmas were somewhat larger than that of the C₄F₈ and C₇F₁₄ plasmas.

The results, like above mentioned, in which tendencies of etch properties were not consistent with changes of C_xF_y 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 C₄F₈, C₇F₁₄, and C₇F₈ plasmas are analyzed by XPS. Figures 4(a)–(c) are the XPS spectra of the fluorocarbon films deposited in the C₄F₈, C₇F₁₄ and C₇F₈ 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), CF₂ (289.2 eV), and CF₃ (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 C₇F₈ results were mostly larger than those of the C₄F₈ and C₇F₁₄ results. And C 1s peaks of C₇F₁₄ are larger than those of C₄F₈ 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 C₄F₈, C₇F₁₄, and C₇F₈ are dissociated using electron emitting source, the dissociated species were measured using QMS so that the density of the species decomposed from the precursors (C₄F₈, C₇F₁₄, C₇F₈), which are shown in Fig. 5, would be compared with the species existing in the plasmas as shown in Fig. 3.

Figure 5 shows the (a) C, (b) CF, (c) CF₂, (d) CF₃, and (e) F radical densities measured at various electron impact energies using a QMS after C₄F₈, C₇F₁₄, and C₇F₈ are dissociated using an electron-emitting source [14, 15]. In this study, because the filament is used only for gas dissociation, the angle of the electron beam is not considered and the gas is 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 CF₂, while Figs. 3(b) and (c) show no significant differences between CF and CF₂. 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 CF₂ radicals.

In Figs. 5(b) and (c), the gases decomposed from C₄F₈ show the highest densities of both CF and CF₂, in agreement with Fig. 3. The C₇F₁₄ plasma shows lower CF₂ radical density than the C₄F₈ plasma, but higher CF₂ radical density than the C₇F₈ plasmas, which also agrees with Fig. 3(c). However, C₇F₈ plasma shows greater CF radical density than C₇F₁₄ 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 C₇F₈ 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 C₇F₈ plasma process than it is with C₇F₁₄.

On the other hand, in Fig. 5(a), the carbon atom density measured from dissociated C₇F₈ gas is one order of magnitude higher than that from the other precursors. This result indicates that the C₇F₈ plasma produces more carbon as carbon atoms, instead of fluorocarbons. It can be also inferred that the carbon atoms and molecules generated by the C₇F₈ plasma enhance the magnitude of selectivity, accompanying the noticeable formation of C–CF_x bonds shown in Fig. 4(c).

4. Conclusions

Considering the compatibility of C₇F₁₄ and C₇F₈ as alternatives for C₄F₈, C₇F₁₄ plasma in the SiO₂ etch process is expected to show etching characteristics similar to those of C₄F₈ plasma. The C₇F₈ plasma process shows a lower etch rate than C₄F₈ and C₇F₁₄. However, C₇F₈ plasma achieves remarkable selectivity with a moderate etch rate by adjusting the amount of carbon produced through applying the appropriate O₂ flow rate. C₇F₈ plasma processing is therefore appropriate for high-aspect-ratio etching processes.

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