Full Length Article

Effect of hydrofluorocarbon structure of $\text{C}_3\text{H}_3\text{F}_6$ isomers on high aspect ratio etching of silicon oxide

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ABSTRACT

In this study, using three isomers ($1,1,1,3,3,3$-hexafluoropropane (HFC-236fa), $1,1,2,2,3,3$-hexafluoropropane (HFC-236ca), $1,1,2,2,3,3$-hexafluoropropane (HFC-236ea)) having the same chemical composition of $\text{C}_3\text{H}_3\text{F}_6$, effects of chemical branch structure of three $\text{C}_3\text{H}_3\text{F}_6$ isomers on the plasma characteristics and etch characteristics of high aspect ratio ACL patterned $\text{SiO}_2$ were investigated. During the etching of $\text{SiO}_2$ and amorphous carbon layer (ACL) using the three isomers mixed with oxygen, different etch characteristics and plasma characteristics were observed. In the plasmas, more $\text{CF}_2$ and $\text{H}$ but, less $\text{F}$ were related to the formation of a fluorocarbon polymer layer on the surface, while lower high mass ion species such as $\text{C}_4\text{H}_4$, $\text{C}_3\text{H}_2\text{F}_2$, and $\text{C}_3\text{H}_2\text{F}_2$ were related to the ion bombardment in the order of HFC-236fa, HFC-236ca, and HFC-236ea respectively leading to a lower $\text{SiO}_2$ etch rate. Therefore, when $\text{C}_3\text{H}_3\text{F}_6$ was used, even with the same chemical composition, the chemical branch structure of the compound affected the plasma properties and etch characteristics significantly depending on chemical branches in the compound. We believe that, for other hydrofluorocarbon compounds mixed with a critical oxygen flow rate, plasma properties and $\text{SiO}_2$ etch characteristics can be estimated through properties of chemical branches attached in these compounds.

1. Introduction

Nowadays, as the density of a semiconductor devices is increased and as the critical dimension (CD) size of the device is scaled down to a few nanometers, the device structure is changing from a two-dimensional (2D) device structure to a three-dimensional (3D) device structure because the CD size has reached the limit of reduction. One of the most difficult issues for the fabrication of a 3D device structure is the etching of a high aspect ratio material. Especially, high aspect ratio contact (HARC) hole etching for dynamic random-access memory (DRAM) devices and channel hole etching recently for high aspect ratio contact (HARC) hole etching, a multifrequency capacitively coupled plasma etching equipment installed with a very high frequency (VHF) radio frequency (RF) power for gas dissociation and low frequency RF powers for high energy ion bombardment is generally used to control the gas dissociation and to increase the ion bombardment energy, respectively, for vertical etching of high aspect ratio holes. In addition, to decrease gas dissociation, increase gas recombination for high etch selectivity over ACL mask, and reduce conductance and charging issues related to dielectric hole etching, pulsed plasma etching is actively investigated and applied to HARC etching recently.

For HARC etching, perfluorocarbon (PFC) or hydrofluorocarbon (HFC) gas is generally used as the main etch gas. For channel hole...
etching of 3D NAND, HFC gas is used as the main etch gas. To improve the etch selectivity over ACL mask, a PFC gas with a lower F/C ratio and a HFC gas with a low (F-H)/C ratio are used for the formation of highly polymeric layers on the material’s surface [20–27]. Among PFC and HFC gases used for HARC etching, many fluorocarbon gases such as CF<sub>4</sub>, C<sub>4</sub>F<sub>8</sub> (F/C = 4), C<sub>4</sub>F<sub>8</sub> (F/C = 2), and CHF<sub>3</sub> (F-H/C = 2) are materials with high global warming potentials (GWP) by showing GWP value of 9,540, 12,400, and 6,630, respectively [28]. Therefore, PFCs and HFCs having low GWP values are currently investigated to replace PFCs and HFCs with high GWP values in HARC etching for carbon neutrality. In addition, as a method of carbon retrieval from PFC and HFC exhausted from the etching chamber, liquid fluorocarbons, that is, PFCs and HFCs with a boiling point higher than 0 °C are also investigated as replacements for PFCs and HFCs with low boiling points (b. p. > 0 °C) to collect exhausted PFCs and HFCs easily at a low temperature pump exhaust line without combustion [29].

Recently, it has been reported that, even though ratios of (F-H)/C or F/C are the same, for example, for isomers having the same C<sub>3</sub>H<sub>6</sub>F<sub>4</sub> composition, characteristics of HARC etching can be different depending on the structure of HFCs or PFCs [30–32]. However, detailed analysis and etching mechanism have not been reported yet. Also, it has been found that, due to differences in boiling points of isomers (some of them can have b. p. < 0 °C while others have b. p. > 0 °C), if fluorocarbons are collected at the exhaust line, their recovery properties which can have a global warming effect can also be different depending on isomers.

Therefore, in this study, using three different isomers having the same chemical composition of C<sub>3</sub>H<sub>6</sub>F<sub>4</sub> but with different chemical structures and different boiling points, ACL masked SiO<sub>2</sub> was etched, and their relationships to plasma characteristics and the surface characteristics were investigated. It was found that etching characteristics were affected not only by the F/C ratio or (F-H)/C ratio but also by different structures of isomers due to differently dissociated species in plasmas.

2. Experimental details

A dual frequency capacitively coupled plasma (DF-CCP) system used for this study is shown in Fig. 1. To control plasma density, a 60 MHz rf power (Pearl, CF-3000-60 M) was connected to the top electrode with a matching network. To control ion energy to the substrate, a 2 MHz rf power (ENI, Nova-50A) was connected to the bottom electrode with a matching network. A silicon showerhead was installed at the top electrode to spread the process gas uniformly through shower head holes. A silicon bare wafer attached with coupon sample using a thermal conductive silicone paste was located at the bottom electrode for the processing. The distance between the two electrodes was kept at 30 mm. Both electrodes were cooled to room temperature with a chiller. To maintain the vacuum, a turbo molecular pump (3200 l/s) backed by a dry pump was used.

For dielectric etching evaluation, 1.5 µm thick blank SiO<sub>2</sub> formed by wet oxidation (O<sub>2</sub>/H<sub>2</sub>, 1050 °C, E1200, Centrotherm) on silicon wafers and 300 nm thick Si<sub>3</sub>N<sub>4</sub> deposited by low pressure chemical vapor deposition (SiH<sub>2</sub>Cl<sub>2</sub>/NH<sub>3</sub>, 770 °C, 250 mTorr, PF-D82, P&Tech) on silicon wafers were used. For mask etching evaluation, a 500 nm thick blank ACL deposited by plasma enhanced chemical vapor deposition (He/Ar/N<sub>2</sub>/C<sub>2</sub>H<sub>2</sub>, 400°C, 7 Torr, 700 W RF power, P5000, AMAT) on silicon wafers was used. Patterned SiO<sub>2</sub> etching was also studied using 2.4 µm thick tetraethyl orthosilicate (TEOS) SiO<sub>2</sub> masked by a hardmask composed of 1.4 µm thick ACL/50 nm SiON (supplementary information Figure S1). For the etching, the operating pressure was maintained at 30 mTorr with a gas mixture of Ar (150 sccm)/C<sub>3</sub>H<sub>6</sub>F<sub>4</sub> (50 sccm)/O<sub>2</sub>. The oxygen gas flow rate was varied from 10 to 50 sccm while keeping the same VHF and bias powers. Three different isomers having the same chemical composition of C<sub>3</sub>H<sub>6</sub>F<sub>4</sub> but with different chemical structures, different boiling points, and different global warming effects as shown in Table 1 were used for the etching of SiO<sub>2</sub>

Etch rates were measured with a step profilometer (Alpha step, Alpha-step 500 surface profiler, Tenkor instruments) and a field emission scanning electron microscope (FE-SEM, Hitachi S-4700). The FE-SEM was also used for measuring etch depth/etch selectivity and observing etch profiles for patterned samples. Dissociated species in plasmas were observed with an optical emission spectroscopy (OES, Isoplane SCT 3200; 150 ~ 1000 nm of wavelength, the blaze wavelength of 300 nm and grating of 1200 g/mm) installed at one of the sidewall quartz windows as shown in Fig. 1. Also, a quadrupole mass spectrometer (QMS, PSM003, Hiden Analytical) attached at the chamber sidewall

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Fig. 1. Schematic diagram of a DF-CCP etch system used in this study. QMS and OES were attached at the center of the etch system for plasma analysis.
as shown in Fig. 1 was used to detect dissociated positive ion species in plasmas.

Surface analysis was conducted after etching blank samples of SiO$_2$, Si$_3$N$_4$, and ACL used for estimating blank etch characteristics. As fluorocarbon polymers were formed on the surfaces during the etching process, chemical binding states of fluorocarbon polymers deposited on the etched blank SiO$_2$, Si$_3$N$_4$, and ACL were investigated by X-ray photoelectron spectroscopy (XPS, VG Microtech Inc. ECA2000; Twin Anode X-Ray Gun, Al 180 W (12 kV, 15 mA)). Peak shift was corrected based on C$_{1s}$ (~295 eV) after measurements of surfaces using XPS.

### Table 1

<table>
<thead>
<tr>
<th>Acronym, chemical name of C$_3$H$_2$F$<em>6$ isomers (GWP$</em>{100yr}$) and lifetime values are from the Fifth Assessment Report (AR5) of the United Nations Intergovernmental Panel on Climate Change (IPCC) [28].</th>
<th>Structural formula</th>
<th>CAS</th>
<th>Boiling point (C)</th>
<th>GWP$_{100yr}$</th>
<th>Lifetime (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1,1,3,3,3-hexafluoropropane (HFC-236fa)</td>
<td>CF$_3$CH$_2$CF$_3$</td>
<td>690–39-1</td>
<td>– 1.1</td>
<td>8060</td>
<td>242</td>
</tr>
<tr>
<td>1,1,1,2,3,3-hexafluoropropane (HFC-236ea)</td>
<td>CF$_3$CHFCHF$_2$</td>
<td>431–63-0</td>
<td>6.5</td>
<td>1330</td>
<td>11</td>
</tr>
<tr>
<td>1,1,2,2,3,3-hexafluoropropane (HFC-236ca)</td>
<td>CHF$_2$CF$_2$CF$_2$</td>
<td>680–00-2</td>
<td>5</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Fig. 2.** Etch rates of blank SiO$_2$, Si$_3$N$_4$, and ACL and the etch selectivities of SiO$_2$/ACL and Si$_3$N$_4$/SiO$_2$ for the three C$_3$H$_2$F$_6$ isomers ((a) and (b) for HFC-236fa, (c) and (d) for HFC-236ea, and (e) and (f) for HFC-236ca) measured as a function of oxygen flow rate. The operating pressure was maintained at 30 mTorr with a gas mixture of Ar (150 sccm)/C$_3$H$_2$F$_6$ (50 sccm)/O$_2$. The oxygen gas flow rate was varied from 10 to 50 sccm while keeping the same 60 MHz VHF power of 400 W to the top electrode and −1,700 Volts of dc self-bias voltage with 2 MHz RF power to the substrate.
Surface concentration was estimated by measuring peak areas of Si$_2$p (~103.3 eV), N$_1$s (~398.1 eV), F$_1$s (~684.9 eV), O$_1$s (~531.0 eV), and C$_1$s (~285 eV). For detailed binding states of fluorocarbon polymers formed on the surfaces, peak data of C$_1$s were deconvoluted using an automated peak separation analysis software (PeakFit) after removing background of C$_1$s (~285 eV) narrow scan data in the range from ~ 281 to ~ 296 eV, which gave graph fitting over ~ 99.5 % accuracy.

3. Results and discussion

Blank SiO$_2$, Si$_3$N$_4$, and ACL wafers were etched using the three different isomers having the same chemical composition of C$_3$H$_2$F$_6$ but with different chemical structures (1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), and 1,1,2,2,3,3-hexafluoropropane (HFC-236ca)) as a function of oxygen flow rate. Results are shown in Fig. 2(a) ~ 2(f) for etch rates of blank SiO$_2$, Si$_3$N$_4$, and ACL, and for etch selectivities of SiO$_2$/ACL and Si$_3$N$_4$/SiO$_2$. For the etching, the operating pressure was maintained at 30 mTorr of Ar (50 sccm)/C$_3$H$_2$F$_6$ isomer (50 sccm)/O$_2$ (20 sccm). A 400 W of 60 MHz RF power was applied to the top electrode as the source power and a 2 MHz RF power was applied to the substrate to maintain ~ 1700 V of bias voltage. (a) and (b) are for HFC-236fa, (c) and (d) for HFC-236ea, and (e) and (f) for HFC-236ca.

Fig. 3. Etch depth/etch rate and SEM etch profiles measured for 100 nm ACL hole patterned SiO$_2$ as a function of etch time for three different C$_3$H$_2$F$_6$ isomers with 30 mTorr of Ar (50 sccm)/C$_3$H$_2$F$_6$ isomer (50 sccm)/O$_2$ (20 sccm). A 400 W of 60 MHz RF power was applied to the top electrode as the source power and a 2 MHz RF power was applied to the substrate to maintain ~ 1700 V of bias voltage. (a) and (b) are for HFC-236fa, (c) and (d) for HFC-236ea, and (e) and (f) for HFC-236ca.
mTorr with a gas mixture of Ar (150 sccm)/C₂H₆F₆ (50 sccm)/O₂. The oxygen gas flow rate was varied from 10 to 50 sccm while keeping the same 60 MHz VHF power of 400 W to the top electrode and ~1,700 Volts of dc self-bias voltage with 2 MHz RF power to the substrate. As shown in Fig. 2(a), 2(c), and 2(e), for the oxygen flow rate from 20 to 50 sccm, the SIO₂ etch rate was slightly increased or nearly saturated at ~ 400 nm/ min while etch rates of Si₃N₄ and ACL were increased almost linearly from ~ 200 to ~ 600 nm/min for Si₃N₄ and from ~ 0 to ~ 140 nm/min for ACL similarly for all three C₂H₆F₆ isomers. Therefore, no significant differences in the etch characteristics among the three isomers were observed for oxygen flow rate higher than 20 sccm. Also, as shown in Fig. 2(b), 2(d), and 2(f), when the oxygen flow rate was increased from 20 to 50 sccm, due to the increase of etch rates of Si₃N₄ and ACL while showing nearly saturated SIO₂ etch rate, the etch selectivity of SIO₂ over ACL was continuously decreased from ~ 0.7 to ~ 1.5. However, when the oxygen flow rate was decreased from 20 to 10 sccm, even though the Si₃N₄ etch rate was similarly decreased to ~ 200 nm/min for all three isomers, etch rates of SIO₂ and ACL were decreased differently depending on the isomers, by decreasing etch rates further in the order of HFC-236fa, HFC-236ea, and HFC-236ca from ~ 350, ~ 0, to ~ 100 nm/min for SIO₂ and from ~ 40, to ~ 100 nm/min for ACL. Therefore, the etch rate of blank SiO₂, Si₃N₄, and ACL showed that, even though etch characteristics were similar under high O₂ flow rate conditions (possibly due to more dissociation of the molecular structure of C₂H₆F₆ at higher O₂ flow rates), there were some differences in the etching characteristics among the three isomers especially under low O₂ flow rate conditions. Therefore, very high etch selectivity of SIO₂/ACL close to ∞ could be observed at the oxygen gas flow rate of 20 sccm for all three isomers while keeping the etch selectivity of Si₃N₄/SIO₂ close to ~ 0.8, which is a potential process condition for HARC processing [33]. To investigate etch characteristics of the three C₂H₆F₆ isomers further, SIO₂ patterned with ACL was etched with an oxygen flow rate of 20 sccm while other process conditions were kept the same as those shown in Fig. 2.

Fig. 3(a) ~ 3(f) show etch depths/etch rates and etch profiles of 100 nm hole ACL patterned SIO₂ measured as a function of etch time for the three C₂H₆F₆ isomers with 20 sccm O₂, where 3(a) and 3(b) are for HFC-236fa, 3(c) and 3(d) are for HFC-236ea, and 3(e) and 3(f) are for HFC-236ca. For HFC-236fa, as shown in Fig. 3(a) and 3(b), the SIO₂ etch depth was almost increased linearly with etch time and the SIO₂ etch rate was decreased slightly from ~ 185 to ~ 165 nm/min with the increase of etch depth to ~ 2.4 µm. In the case of HFC-236ea, as shown in Fig. 3(c) and 3(d), the SIO₂ etch depth was increased less linearly with etch time and the SIO₂ etch rate was decreased further with etch depth by showing ~ 180 to ~ 145 nm/min (at ~ 2.4 µm). Therefore, more significant aspect ratio dependent etching (ARDE) effect could be observed. For HFC-236ca, as shown in Fig. 3(e) and 3(f), the increase of SIO₂ etch depth with etch time was the lowest. Therefore, the etch rate with etch depth was decreased the fastest by showing from ~ 160 to ~ 90 nm/min (at ~ 850 nm). The decrease of initial SIO₂ etch rate and the fastest decrease of SIO₂ etch rate with the increase of etch depth of HFC-236ca compared to those of other isomers were related to the deposition of a fluorocarbon layer on the ACL which clogged the ACL hole as shown in the SEM etch profile of Fig. 3 (f). Therefore, even with the ACL patterned SIO₂, the differences in the etch rates of SIO₂ and ACL among the three isomers similar to the blank samples etched between 10 and 20 sccm oxygen flow rate as shown in Fig. 2 could be observed even though the SIO₂ etch rates of the 100 nm ACL hole patterned SIO₂ were lower than those of blank SIO₂ for all three isomers possibly due to the consumption of oxygen by ACL, which made the condition of a lower oxygen flow rate. When the 100 nm ACL hole patterned SIO₂ was etched with a mixture of two isomers, the etch properties averaged over the properties of two isomers were observed (Supplementary Information Figure S2).

In addition to ACL hole patterns, using ACL line patterns, SIO₂ was etched using the three C₂H₆F₆ isomers. SIO₂ etch depths and SEM images of SIO₂ etched for 9 min (etch time for ~ 2.2 µm SiO₂ etching for 100 nm ACL line pattern width) with the ACL line pattern width of 60 ~ 100 nm are shown in Fig. 4(a) and 4(b) for HFC-236fa, 4(c) and 4(d) for HFC-236ea, and 4(e) and 4(f) for HFC-236ca. In Fig. 4(b), 4(d), and 4(f), only SEM images of SIO₂ etched with 60, 80, and 100 nm ACL line patterns are shown. SEM images of SIO₂ etched for the series of ACL line patterns from 60 to 100 nm with 5 nm of pattern distance are shown in Supplementary Information Figure S3. As shown in Fig. 4, the difference in SIO₂ etch depth between 60 and 100 nm line widths was ~ 15.5 % for HFC-236fa, ~ 17.1 % for HFC-236ea, and ~ 43.1 % for HFC-236ca (calculated by ARDE % ARDE % %100,(etch depth of 60 nm line pattern)/(etch depth of 100 nm line pattern)) x100 (%). Therefore, the most severe ARDE effect was observed for HFC-236ca possibly due to more clogging of the ACL line pattern with a smaller line width by a fluorocarbon layer formation as shown in Fig. 4(f), similar to the ACL hole pattern etched with HFC-236ca shown in Fig. 3(b).

To understand the reason for the different etching characteristics among the three C₂H₆F₆ isomers, dissociated species from C₂H₆F₆ plasmas were observed using OES for conditions in Fig. 3. Results are shown in Fig. 5. Fig. 5(a) shows OES spectra for a wide wavelength range (from 150 to 1000 nm) for the three C₂H₆F₆ isomers. Peaks related to CF₂ (251.9 nm), CO (330.6 nm), H (656.5 nm), F (703.7 nm), Ar (750.4 nm), O (844.7 nm), and so on could be observed for the three isomers. Fig. 5(b) ~ 5(e) show peaks in the narrow wavelength range: (b) from 220 to 340 nm for CF₂ and CO, (c) from 648 to 666 nm for H, (d) from 698 to 710 nm for F, and (e) from 842 to 848 nm for O. Peak intensities of CF₂, H, F, and O in Fig. 5(b) ~ 5(e) were normalized with the Ar peak intensity (750.4 nm) of HFC-236ca. Their normalized intensities are shown in Fig. 5(f) (OES peak intensities without normalization and after normalization by its own Ar peak intensity at 750.4 nm are shown in supplementary information Figure S4). No significant differences were found. As shown in Fig. 5(f), higher CF₂, higher H, but lower F in the sequence of HFC-236fa, HFC-236ea, and HFC-236ca could be observed in the plasma. However, no significant differences were observed for O. The higher concentration of CF₂ and H in the plasma were related to the increased polymerization while the higher F concentration was related to the increased etching of SiO₂ and ACL during the etching of ACL masked SIO₂. Therefore, the more polymerization on ACL mask surfaces and low SIO₂ etch rates observed for the ACL patterned SIO₂ in the sequence of HFC-236fa, HFC-236ea, and HFC-236ca in Figs. 3 and 4 were related to the differences in isomer dissociation in the plasma.

In addition to OES, dissociated species in plasmas for different C₂H₆F₆ isomers were observed using QMS under the same conditions shown in Fig. 3. Positive reactive ion species observed in the plasmas are shown in Fig. 6(a) for HFC-236fa, 6(b) for HFC-236ea, 6(c) HFC-236ca, and 6(d) for some mass peaks in 6(a) ~ 6(c). To remove the problem related to the fragmentation of the radical species during the measurement by QMS due to ionization by the ionizer in the QMS, positive reactive ions in the plasmas were directly observed without ionization in the QMS. As shown in Fig. 6(a) ~ 6(c), positive ion peaks such as C₂H₅F₂⁺ and H⁺ dissociated from C₂H₆F₆ and recombinated positive ion peaks such as HF⁺ and CO⁺ could be observed. Differently from OES, no noticeable positive ion peaks related to fluorine or oxygen could be observed possibly due to the difficulty in forming positive ions compared to hydrofluorocarbon radicals. Fig. 6(d) shows comparison of high intensity fluorocarbon related mass peaks such as H¹, CF₂, CHF₂, CF₃, C₂H₅F₂, CH₂F₂, C₂H₄F₂, and the three C₂H₆F₆ isomers shown in Fig. 6 (d), the increase of H⁺, CF₂, and CHF₂ related to the polymerization could also be observed in the sequence of HFC-236fa, HFC-236ea, and HFC-236ca, similar to the results of the OES peaks shown in Fig. 5(f). The decrease of high mass ion peaks such as C₂H₅F₂⁺ and C₂H₆F₂⁺ could also be observed in that sequence, which might result in the decreased surface bombardment by heavy ions in that sequence.

The differences of the dissociated species in the plasmas among the three C₂H₆F₆ isomers as observed in Figs. 5 and 6 under the same process
conditions are believed to be related to the differences in the molecular structures of the C₃H₂F₆ isomers. Fig. 7 shows schematic drawing of three C₃H₂F₆ molecular structures. As shown in Fig. 7, HFC-236fa has two CF₃ branches and HFC-236ca has two CHF₂ branches while HFC-236ea has one CF₃ and one CHF₂ branch. Therefore, in the plasma, HFC-236ca tends to have more CF₂ radicals and CHF₂ radicals related to polymerization while HFC-236fa tends to have more CF₃ (and F) which is more related to etching of SiO₂ as can be seen in the OES data shown in Fig. 5 and the QMS data shown in Fig. 6.

Fig. 8(a) ~ 8(c), 8(d) ~ 8(f), and 8(g) ~ 8(i) show the CIs XPS narrow scan data measured on the surfaces of blank SiO₂, Si₃N₄, and ACL etched with three different C₃H₂F₆ isomers of HFC-236fa, HFC-236ea, and HFC-236ca, respectively, under process conditions shown in Fig. 3.

As shown in Fig. 8(a) ~ 8(i), on the etched surfaces of SiO₂, Si₃N₄, and
ACL, carbon bindings related to C-C (~285 eV), C-CF (~287.5 eV), C-F (~289.5 eV), and C-CF$_2$ (~292 eV) could be observed for all three iso-

ers. Similar to the OES data and QMS data shown in Figs. 6 and 7, higher carbon-rich fluorocarbon polymer related peaks such as C-F and C-CF bonding peaks were observed in the sequence of HFC-236fa, HFC-

236ea, and HFC-236ca on the surfaces of etched blank SiO$_2$, Si$_3$N$_4$, and ACL. Among SiO$_2$, Si$_3$N$_4$, and ACL, the most significant changes in the binding peak intensities of C-F and C-CF were observed for SiO$_2$ while the least changes in peak intensities of C-F and C-CF were observed for Si$_3$N$_4$ possibly due to the increase of hydrogen concentration in the plasma in the order of HFC-236fa, HFC-236ea, and HFC-236ca which tended to increase the etching of Si$_3$N$_4$ in fluorocarbon plasmas. In Fig. 8 (j) ~ 8(i), surface compositions of the SiO$_2$, Si$_3$N$_4$, and ACL etched with three C$_3$H$_2$F$_6$ isomers are shown, respectively. As shown in Fig. 8(j) ~ 8 (i), in the order of HFC-236fa, HFC-236ea, and HFC-236ca, significant increases in C and F were observed on etched SiO$_2$ surface with the
increase of F on the ACL surface while no significant changes in C and F were observed on the etched Si$_3$N$_4$ surface. This might be related to the continuous etching of blank Si$_3$N$_4$ at O$_2$ gas flow rates of 10 ~ 20 sccm while etch rates of SiO$_2$ and ACL were decreased at the O$_2$ gas flow rate of 10 ~ 20 sccm in the order of HFC-236fa, HFC-236ea, and HFC-236ca shown in Fig. 2.

4. Conclusion

Using three isomers having the same chemical composition of C$_3$H$_2$F$_6$, effects of chemical structures of hydrofluorocarbon compounds having the same chemical composition on plasma characteristics and etch characteristics of high aspect ratio ACL patterned SiO$_2$ in addition to etch characteristics of blank SiO$_2$, Si$_3$N$_4$, and ACL were investigated.
When the oxygen flow rate mixed with three different C₃H₆F₆ isomers was sufficiently high, no significant differences in the etch characteristics of SiO₂, Si₃N₄, and ACL could be observed. However, when the oxygen flow rate was lower than a certain critical flow rate of 20 sccm, different etch characteristics and plasma characteristics could be observed depending on chemical structures of the isomers. HFC-236fa has two CF₃ branches and HFC-236ca has two CHF₂ branches while HFC-236ea has one CF₃ and one CHF₂ branch. At the critical oxygen flow rate having near infinite etch selectivity of SiO₂/ACL, the SiO₂ etch rate was lower and the ARDE effect was higher in the order of HFC-
236fa, HFC-236ea, and HFC-236ca. OES showed higher CF and H, but lower F which were related to the formation of fluorocarbon polymer layer. QMS showed lower high mass ion species such as C_2HF_4 and C_2H_5F_3 related to ion bombardment in addition to higher H^+, CF_2^−, and CHF_2 in the order of HFC-236fa, HFC-236ea, and HFC-236ca. XPS also showed higher carbon-rich fluorocarbon polymer on etched materials surfaces in the order of HFC-236fa, HFC-236ea, and HFC-236ca. Therefore, even with the same chemical composition of C_2H_5F_3, the chemical structure of the compound affected plasma properties and etch characteristics significantly depending on the chemical branch structure of the compound when critical oxygen flow rates were used. We believe that, for other fluorohydrocarbon compounds, plasma properties and etch characteristics can be estimated through properties of chemical branches attached in these compounds.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apusc.2022.154050.

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