

Low Global Warming Potential Alternative Gases for Plasma Chamber Cleaning

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ABSTRACT

Etch characteristics of SiO₂ and Si₃N₄ using gas mixtures of C₃F₆O (HFA (Hexafluoroacetone) and HFPO (Hexafluoropropylene oxide))/O₂ were investigated as potential cleaning gas mixtures for SiO₂/Si₃N₄ chemical vapor deposition chamber and their etch rates were compared with those using NF₃. The etch rates using 100% HFA and 100% HFPO were significantly lower than those etched with NF₃. However, when oxygen gas was mixed with HFA and HFPO while keeping total gas flow rate same, the etch rates of SiO₂ and Si₃N₄ were increased with the increase of oxygen flow rate and were reached to 53% for Si₃N₄ etching and 46% for SiO₂ etching compared to the etch rates using NF₃ at 70% of oxygen percentage and the further increase of oxygen percentage decreased the etch rates. The highest etch rates at 70% of oxygen percentage were related to the highest atomic F concentration and the highest F/CF_x ratio in the plasma due to the release of F from C₃F₆O by oxygen and also were related to the removal of a fluorocarbon polymer layer formed on the SiO₂ and Si₃N₄ surfaces at higher oxygen gas percentages. At the oxygen percentage higher than 70%, the etch rates were decreased because the atomic F concentration was decreased due to the lower C₃F₆O gas flow rate for the same total flow rate. Even though the etch rates with HFA/O₂ and HFPO/O₂ are about half of those with NF₃, due to the significantly lower global warming potential (GWP) of <100 compared to 16,100 of NF₃, it is believed that, HFA/O₂ and HFPO/O₂ could be utilized as potential environmentally benign chamber cleaning gases.

KEYWORDS: C₃F₆O Plasma, Chamber Cleaning, Global Warming.

1. INTRODUCTION

NF₃, SF₆ and perfluorocarbons (PFCs) such as CF₄, C₂F₆, C₃F₈, C₄F₈, C₅F₈, etc. have been extensively used in the plasma etching of various materials and, some of these gases with high plasma etch rates for silicon, silicon dioxide (SiO₂), silicon nitride (Si₃N₄), etc., have been also applied to the chamber cleaning for plasma enhanced chemical vapor deposition (PECVD) systems.^{1,2} Among these gases, NF₃ has been most widely used for the most of the PECVD systems due to a high plasma etch rate and, due to the growing industries of semiconductor and thin film transistor-liquid crystal displays, the amount of NF₃ consumed for PECVD chamber cleaning applications is growing rapidly.³ Unfortunately, not only SF₆ and PFCs but also NF₃ used in the plasma etching process and PECVD chamber cleaning process is a global warming gas^{4,5} and these gases attract significant concern to the environment because they trap substantially more heat than CO₂.

The lifetimes and the GWPs of various plasma etching gases are listed in Table I.^{6–10} Especially, the GWP of CF₄ (it is also produced as a by-product from C₄F₆ and C₅F₈ plasmas) is 6630 which is based on 100-year projection and has the atmospheric life time of 50,000 years.^{5,7} These gas molecules will remain in the atmosphere for thousands of years after being released. Therefore, it is important to reduce the emission of NF₃, PFCs, and SF₆ from the plasma processing system to the environment. Furthermore, the reduction of global warming gas emissions is an issue after the Kyoto protocol commitment¹¹ and a lot of researches in finding alternative cleaning gases and synthesizing alternative new gases have been carried out.^{12–14}

In this study, as new potential PECVD chamber cleaning gases replacing NF₃, HFA (Hexafluoroacetone) and HFPO (Hexafluoropropylene oxide), which are isomer gases with the same chemical composition of C₃F₆O, are considered because of their lower GWPs than those currently in use and their plasma etch rates of SiO₂ and Si₃N₄ were compared with those by NF₃ and their etch mechanisms were investigated. Especially, oxygen was added to HFA and HFPO at the same total gas flow rates and its effect on

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Table I. Atmospheric life time and global warming potential (GWP) of various gases.

Acronym, chemical name	Chemical formula	Atmospheric		Ref.
		lifetime (years)	GWP ₁₀₀	
Carbon dioxide	CO ₂	50–200	1	[7, 8]
Carbon tetrafluoride (PFC-14)	CF ₄	50,000	6630	[6, 7]
Perfluorocyclobutane (PFC-318)	c-C ₄ F ₈	3200	9540	[6, 7]
Hexafluoropropane (PFC-116)	C ₂ F ₆	10,000	11,100	[7]
Octafluoropropane	C ₃ F ₈	2600	8900	[7]
Sulfur hexafluoride	SF ₆	3200	23,500	[6]
Nitrogen trifluoride	NF ₃	500	16,100	[6, 7]
Hexafluoropropylene oxide (HFPO), Hexafluoroacetone (HFA)	C ₃ F ₆ O	<1	<100	[9, 10]

the etch characteristics of SiO₂ and Si₃N₄ were compared with those etched with NF₃.

2. EXPERIMENTAL DETAILS

Experiments were performed in a 300 mm capacitively coupled plasma system shown in Figure 1. The top electrode was made of silicon and the bottom electrode was made of aluminum. To the top electrode, 60 MHz rf power was connected through a matching network and the bottom electrode was grounded. The temperature of bottom electrode was kept at 50 °C (IKA, HBC 5 control) using an oil heater.

For the etching of SiO₂ and Si₃N₄, 400 nm thick SiO₂ and Si₃N₄ deposited on glass wafer and patterned by 2.0 μm thick photoresist were used. For the etching of the samples located on the bottom electrodes, gas mixtures of HFA (Hexafluoroacetone)/O₂ and HFPO (Hexafluoropropylene oxide)/O₂ were flowed in the chamber and 500 W of 60 MHz rf power was applied to the top electrode while keeping the same total flow rate of 200 sccm. The chamber pressure was varied from 50 to 450 mTorr. HFA and HFPO are the isomers with the same chemical composition of C₃F₆O and their chemical structures are

also shown in Figure 1. As comparison, 200 sccm NF₃ was also used in the etching of SiO₂ and Si₃N₄.

After etching, the etch rates of SiO₂ and Si₃N₄ samples were estimated using field emission scanning electron microscopy (FE-SEM, Hitachi S-4700) by taking cross-sectional images with the photoresist. The optical emission intensities from reactive radicals such as O, F, C_xF_y, etc. were collected through a view port on the chamber sidewall using optical emission spectroscopy (ICCD, Andor iStar 734). By adding about 1% Ar with the process gases as a tracer gas, relative densities of reactive species such as O, F, and CF₂, in HFA/O₂, HFPO/O₂ gas mixtures, and NF₃ were estimated, therefore, by using Ar actinometry.¹⁴ The chemical binding states of the C1s on SiO₂ and Si₃N₄ surfaces were estimated using X-ray photoelectron spectroscopy (XPS, VG Microtech Inc., ESCA 2000) after the partial etching of 500 nm thick blanket SiO₂ and Si₃N₄ on glass substrates.

3. RESULTS AND DISCUSSION

Figure 2 shows the etch rates of SiO₂ and Si₃N₄ measured as a function of oxygen percentage from 60 to 80% in the gas mixtures of HFA/O₂ and HFPO/O₂. The etching was performed at the rf power of 60 MHz 500 W, 200 sccm of total gas flow rate, 50 mTorr of operating pressure, and 50 °C of substrate temperature. As comparison, the etching was performed with NF₃ at the same conditions. The etch rates of SiO₂ and Si₃N₄ with 100% HFA, 100% HFPO, and 100% NF₃ are shown in the inset of Figure 2. As shown in the inset, when no oxygen was added to HFA and HFPO, the etch rates of SiO₂ were close to 0 for both HFA and HFPO while the etch rates of Si₃N₄ were still low at 0.37 nm/sec and 0.40 nm/sec for HFA and HFPO, respectively. In contrast, the etch rates of SiO₂ and Si₃N₄ using 100% NF₃ were about 0.39 nm/sec and 9.35 nm/sec, respectively, therefore, the etch rates between NF₃ and C₃F₆O were significantly different. However, when the oxygen percentage was increased in HFA/O₂ and HFPO/O₂, the etch rates of SiO₂ and Si₃N₄ were increased

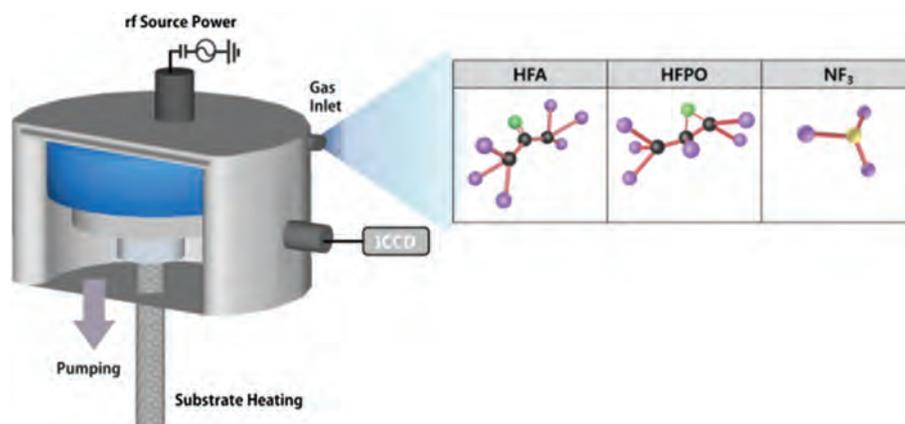


Fig. 1. Schematic diagram of the capacitively coupled plasma system used in the experiment and the molecular structures of HFA, HFPO, and NF₃.

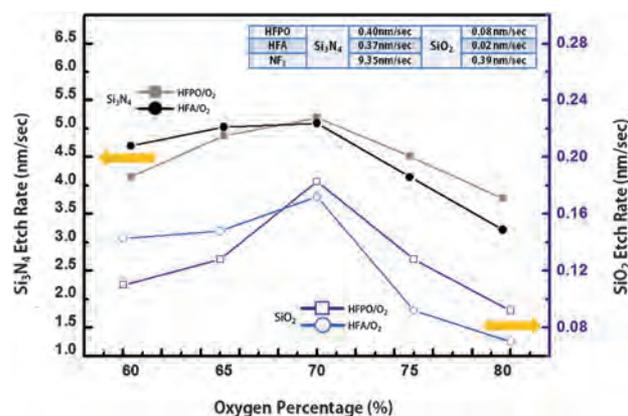


Fig. 2. Etch rate of SiO₂ and Si₃N₄ as a function of O₂ flow percentage while keeping the total gas flow ratio of C₃F₆O/O₂ at 200 sccm. Etch rates of SiO₂ and Si₃N₄ using 100% HFA and 100% HFPO are shown in the inset together with the etch rates using 100% NF₃ as comparison. The rf power was 60 MHz 500 W, the operating pressure was 50 mTorr, and the substrate temperature was kept at 50 °C.

significantly and were reached maximum at 70% oxygen percentage for both HFA/O₂ and HFPO/O₂ and the further increase of oxygen percentage decreased the etch rates. The maximum etch rates of SiO₂ were 0.16 nm/sec and 0.18 nm/sec for HFA/O₂ and HFPO/O₂, respectively, and the maximum etch rates of Si₃N₄ were 5 nm/sec and 5.1 nm/sec for HFA/O₂ and HFPO/O₂. Therefore, the etch rates of SiO₂ and Si₃N₄ with HFA/O₂ and HFPO/O₂ were similar each other and ~53% for Si₃N₄ etching and ~46% for SiO₂ etching compared to the etch rates with NF₃ could

be achieved at 70% of oxygen percentage (C₃F₆O:O₂ = 3:7) with HFA/O₂ or HFPO/O₂.

To understand the etching mechanism during the etching using HFA/O₂ and HFPO/O₂ with the increase of oxygen percentage, the dissociated species in the plasmas were observed using OES for HFA/O₂ and HFPO/O₂ and the results are shown in Figure 3 for (a) 100% HFPO, (b) 100% HFA, (c) 30% HFPO/70% O₂, and (d) 30% HFA/70% O₂. The other operating conditions are as in Figure 2. As shown in Figures 2(a and b), for 100% HFA and 100% HFPO, big emission bands centered at ~300 nm and ~600 nm which are possibly related to the C_xF_y molecular emissions were observed in addition to other optical emission peaks related to F, O, CO, etc. Due to the addition of 1% Ar for Ar actinometry, a small Ar atomic peak was also observed at ~750 nm. However, as shown in Figures 2(c and d), the mixture with oxygen decreased the emission bands possibly related to C_xF_y molecules and increased F and CO peak intensities due to the dissociation of C_xF_y molecules with oxygen. Similar to the etch rates, the OES data for HFA/O₂ and HFPO/O₂ were also similar each other. Therefore, for the further experiments, mostly the properties of HFPO/O₂ were investigated.

For HFPO/O₂, the changes of relative radical densities (I/I_{Ar}) of F, O, CF₂, and CO in the plasma with increasing oxygen percentages were estimated using an Ar actinometry and the results are shown in Figure 4(a). As shown in Figure 4(a), as the oxygen percentage is increased, the densities of fluorocarbon species such as CF₂ were decreased due to reaction with oxygen and

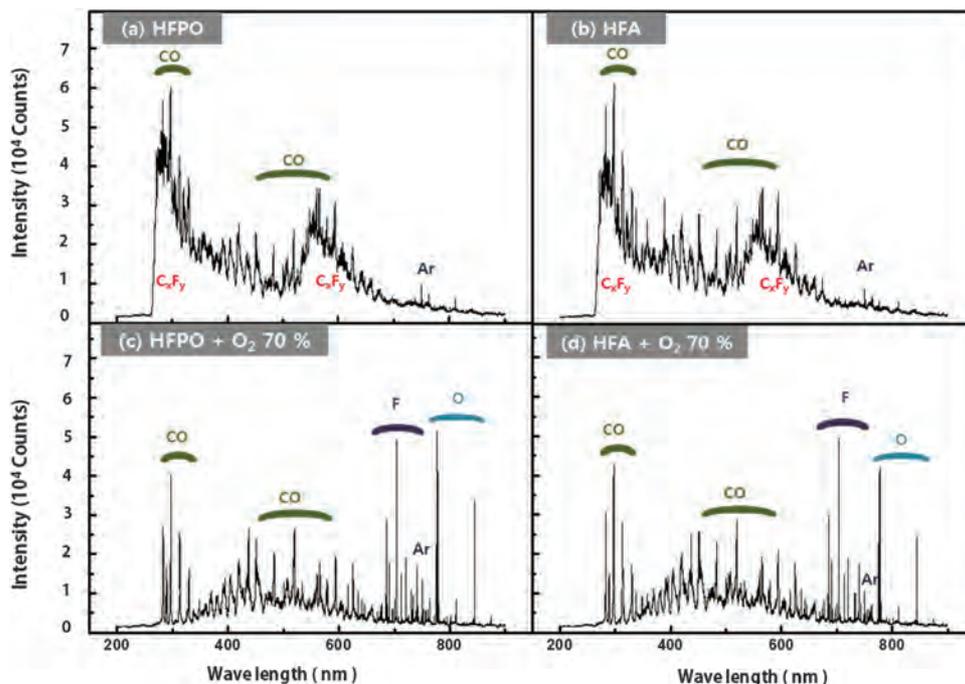


Fig. 3. Optical emission intensities of the plasmas generated with (a) 100% HFPO, (b) 100% HFA, (c) 30% HFPO/70% O₂, and (d) 30% HFA/70% O₂. The optical emission spectra were measured at rf power of 60 MHz 500 W, 50 mTorr of operating pressure, and C₃F₆O/O₂ = 200 sccm. For Ar actinometry, 1% of Ar was added to the plasmas.

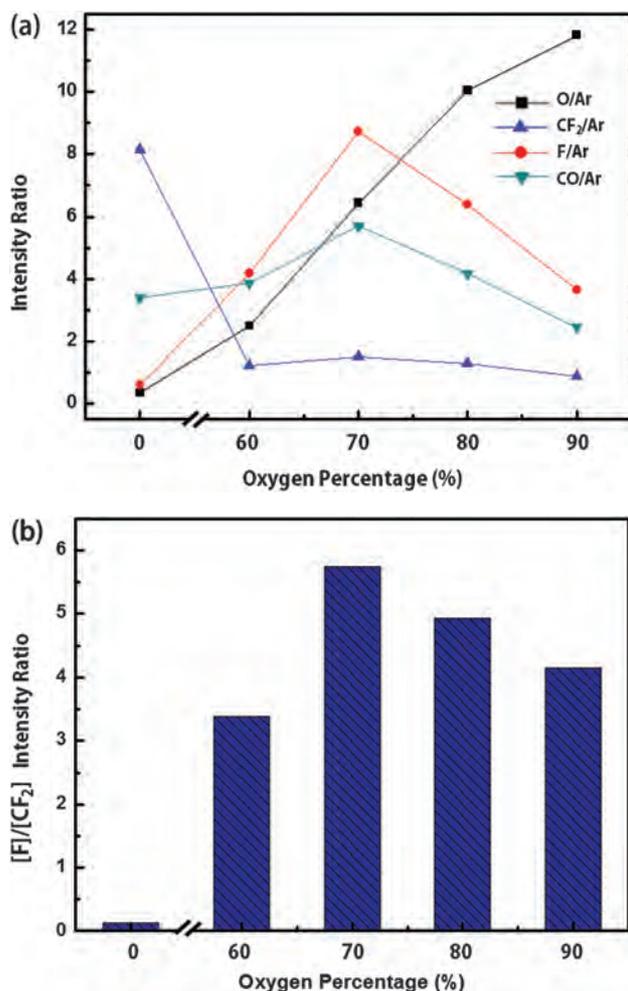


Fig. 4. (a) Variation of relative radical densities of F, O, CF₂, and CO in the HFPO/O₂ plasmas with increasing oxygen percentages estimated using an Ar actinometry. (b) Intensity ratios of [F]/[CF₂] in (a) for different oxygen percentages in HFPO/O₂.

dissociation of C_xF_y in addition to the decrease of C₃F₆O flow rate in the plasma with the increase of oxygen percentage at the same total flow rate. F and CO were also increased with the increase of oxygen percentage up to 70% due to the dissociation of C_xF_y and reaction with oxygen, respectively. However, when the oxygen percentage was higher than 70%, due to the decrease of C₃F₆O flow in the chamber with increasing the oxygen percentage in the HFPO/O₂ gas mixture, the densities of F and CO were eventually decreased. Figure 4(b) shows the intensity ratios of [F]/[CF₂] in Figure 4(a) for different oxygen percentages in HFPO/O₂. In fact, in general, atomic F is related to etching of SiO₂ and Si₃N₄ while CF_x is related to a fluorocarbon layer formed on the SiO₂ and Si₃N₄ surfaces which blocks the etching. As shown in Figure 4(b), the ratio of [F]/[CF₂] increased with the increase of oxygen percentage up to 70% and the further increase of oxygen percentage decreased the ratio. Therefore, the highest etch rates of SiO₂ and Si₃N₄ observed at 70% of oxygen percentage for

HFA/O₂ and HFPO/O₂ are related to the highest F concentration in the plasma and the lowest F/CF₂ ratio, that is, a low fluorocarbon layer formed on the surface during the etching.

As mentioned in Figure 4, the atomic F concentration in the plasma is related to the etching of SiO₂ and Si₃N₄. The relative F densities for different gas mixtures used in the experiment such as 100% HFA, 100% HFPO, 30% HFA/70% O₂, 30% HFPO/70% O₂, and 100% NF₃ were measured using the Ar actinometry, that is, by the intensity ratios of I_F/I_{Ar}, and the results are shown in Figure 5. As shown, in the case of 100% HFA and 100% HFPO, very low F densities in the plasma were observed while the highest F densities in the plasma were observed for NF₃ plasma. By mixing 70% O₂ with HFA and HFPO, significant increase of F density about 66% and 79% of 100% NF₃, respectively, were observed indicating the increase in the SiO₂ and Si₃N₄ etching. However, the intensity ratios of I_F/I_{Ar} were not exactly proportional to the etch rate ratios because, the etch rates are also related to the fluorocarbon layer formed on the surfaces of SiO₂ and Si₃N₄.

The changes of surface characteristics of SiO₂ and Si₃N₄ during the etching with HFPO/O₂ were investigated using XPS by collecting C1s narrow scan data as a function of oxygen percentages and the results are shown in Figure 6 for (a) SiO₂ surface and (b) Si₃N₄ surface. The blank SiO₂ and Si₃N₄ were etched for 10 min before the XPS analysis. The etch conditions are as in Figure 2. For the etching with 100% HFPO, C1s on the surfaces of SiO₂ and Si₃N₄ exhibited complex CF_x bonding peaks indicating a thick fluorocarbon layer on the surfaces which is related to the decrease of etch rates of SiO₂ and Si₃N₄ by blocking the etching by F in addition to a C–C peak caused by air contamination. As the oxygen percentage is increased to 10% (HFPO:O₂ = 9:1) and further to 30% (HFPO:O₂ = 7:3), the peaks related to the fluorocarbon

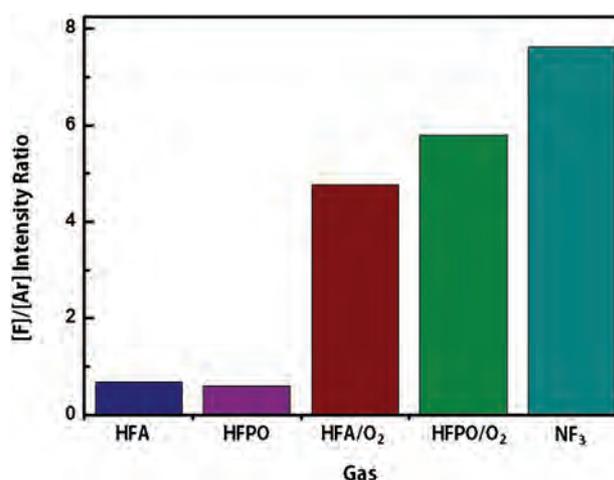


Fig. 5. The F densities for different gas mixtures used in the experiment such as 100% HFA, 100% HFPO, 30% HFA/70% O₂, 30% HFPO/70% O₂, and 100% NF₃ measured using the Ar actinometry.

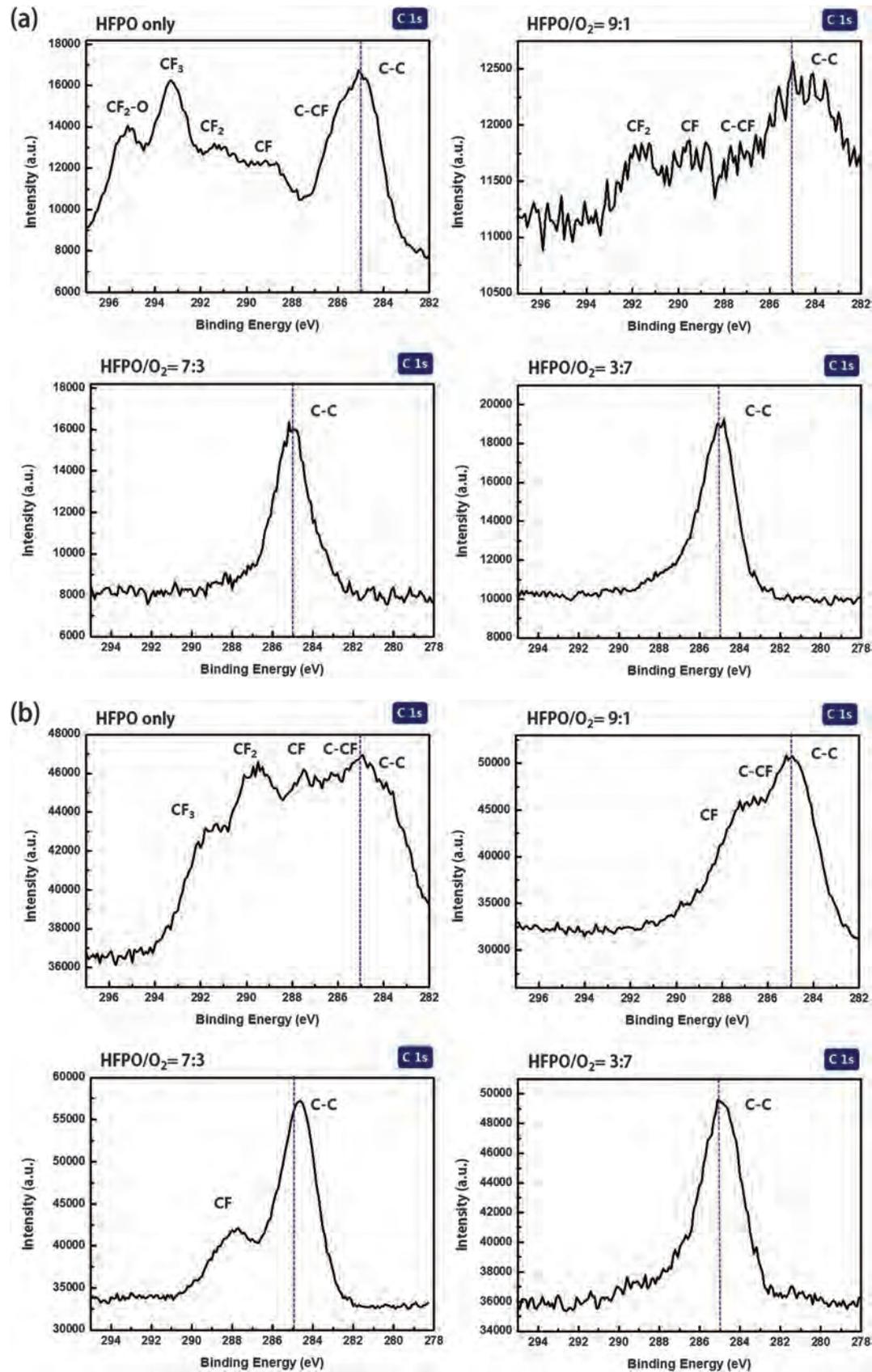


Fig. 6. XPS narrow scan data of C1s obtained after etching of (a) SiO₂ and (b) Si₃N₄ using HFPO/O₂ as a function of O₂ percentage.

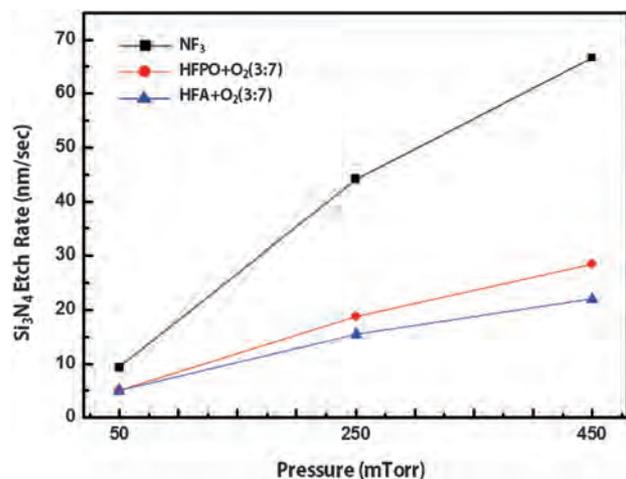


Fig. 7. Etch rates of Si_3N_4 as a function of operating pressure for the etching with 30% HFA/ 70% O_2 , 30% HFPO/70% O_2 , and 100% NF_3 .

layer were decreased indicating the decreased fluorocarbon layer thickness on the surfaces of SiO_2 and Si_3N_4 with increasing oxygen percentage. And, when the oxygen percentage is 70% (HFPO: $\text{O}_2 = 3:7$), the most of peaks related to fluorocarbon layer was removed and only the C–C peak related to the air contamination was observed indicating a negligibly thin fluorocarbon layer on the surfaces of SiO_2 and Si_3N_4 .

For the PECVD chamber cleaning, the chamber pressure is higher than hundreds of mTorr, therefore, the change of etch rates with increasing operating pressure was investigated and the result is shown in Figure 7 for the etching of Si_3N_4 with 30% HFA/ 70% O_2 , 30% HFPO/70% O_2 , and 100% NF_3 . As shown, the etch rates of Si_3N_4 were almost proportional to the operating pressure not only for NF_3 but also for HFA/ O_2 and HFPO/ O_2 , therefore, a similar etch rate ratios between $\text{C}_3\text{F}_6\text{O}/\text{O}_2$ and NF_3 could be observed over a wide range of operating pressure. This results indicate that, even though the etch rates of HFA/ O_2 and HFPO/ O_2 remain similar about half of those of NF_3 over a wide range of operating pressure, due to the very low GWPs of HFA and HFPO, it is believed that these gas mixtures could be used as potential next generation PECVD chamber cleaning gases replacing NF_3 .

4. CONCLUSION

The effects of $\text{C}_3\text{F}_6\text{O}$ isomers (HFA and HFPO) mixed with O_2 on the etch characteristics of SiO_2 and Si_3N_4 were investigated as potential chamber cleaning gases with low GWPs replacing NF_3 . It was found that the etch rates of SiO_2 and Si_3N_4 are strongly enhanced by adding O_2 to the both HFA and HFPO. The SiO_2 etch rates with HFA/ O_2 and HFPO/ O_2 were generally lower than the Si_3N_4 etch rates over the conditions. The change of etch rates with increasing O_2 percentage was related to both atomic fluorine concentration and $[\text{F}]/[\text{CF}_2]$ ratio in the plasma,

and the thickness of fluorocarbon layer thickness on the etched surfaces of SiO_2 and Si_3N_4 . The highest etch rates of SiO_2 and Si_3N_4 , which are $\sim 46\%$ and $\sim 53\%$ of those etched using NF_3 , respectively, were obtained at 70% of oxygen percentage due to the highest F radical density and the highest F/CF_x ratio in the plasma by releasing F from $\text{C}_3\text{F}_6\text{O}$ by oxygen and also by the removal of the fluorocarbon polymer layer formed on the SiO_2 and Si_3N_4 surfaces at higher oxygen gas percentages. Even though the highest etch rates of HFA/ O_2 and HFPO/ O_2 are about half of those of NF_3 , due to the very low GWPs of HFA and HFPO which is <100 compared to 16,100 of NF_3 , it is believed that these gas mixtures could be applied as potential next generation PECVD chamber cleaning gases replacing NF_3 .

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