



Study of Surface Reaction and Gas Phase Chemistries in High Density $C_4F_8/O_2/Ar$ and $C_4F_8/O_2/Ar/CH_2F_2$ Plasma for Contact Hole Etching

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In this study, the characterizations of oxide contact hole etching are investigated with $C_4F_8/O_2/Ar$ and $CH_2F_2/C_4F_8/O_2/Ar$ plasma. As the percent composition of C_4F_8 in a $C_4F_8/O_2/Ar$ mixture increases, the amount of polymer deposited on the etched surface also increases because the C_xF_y polymer layer retards the reaction of oxygen atoms with PR. Adding CH_2F_2 into the $C_4F_8/O_2/Ar$ plasma increases the etch rate of the oxide and the selectivity of oxide to PR. The profile of contact holes was close to 90° , and no visible residue was seen in the SEM image at a $C_4F_8/(C_4F_8+O_2)$ ratio of 58%. The changes of chemical composition in the chamber were analyzed using optical emission spectroscopy, and the chemical reaction on the etched surface was investigated using X-ray photoelectron spectroscopy.

Keywords: Contact hole etching, $C_4F_8/O_2/Ar$ plasma, High density plasma, XPS

1. INTRODUCTION

SiO_2 (oxide) etch processes having high selectivity over photoresist (PR), silicon, and Si_3N_4 (nitride) are required to manufacture ultra-large-scale integrated-circuit devices. Generally, oxide etching is performed by using fluorocarbon gases to deposit a fluoro-polymer on the underlying silicon or mask materials. This deposit enhances the etching selectivity of oxide over silicon or nitride. However, in the patterning of high-aspect-ratio contact holes or self-aligned contacts, these plasmas have serious problems related to the low selectivity of the underlying or mask material, the micro-loading effect, and the etch stop interrupting the etching [1].

Previous studies focused on either the anisotropic etching or selective etching of oxide over silicon, nitride, or PR using conventional low-density plasma sources. Recently, high-density-plasma (HDP) systems have attracted considerable attention,

primarily because HDP sources operate at low pressure and allow independent control of ion flux and ion energy [2-5]. Consequently, the plasma-surface interactions become significant, and surface conditions such as the temperature and cleanliness of the reactor wall play an important role in determining both the gas-phase chemistries and the surface-reaction deposition and etching on the wafer surface.

We studied the fluorocarbon layer formation that appears to dominate the surface reaction in order to understand the etch mechanism for highly selective etching using C_4F_8 and CH_2F_2 additive chemistry in contact hole etching. The relationship between gas chemistry and the fluorocarbon film was systematically investigated. Optical emission spectroscopy (OES) and X-ray photoelectron spectroscopy (XPS) were used to quantitatively analyze the gas chemistry and etched surfaces, respectively.

2. EXPERIMENTAL DETAILS

The HDP etching system is an APTC SELEX200, as shown in Fig. 1. Multi-spiral coils and a bushing, connected to the 12.56-MHz RF power generator, are located above a thick horizontal ceramic window. This plasma source shows characteristics of both traditional sources of inductively coupled plasma (ICP) and

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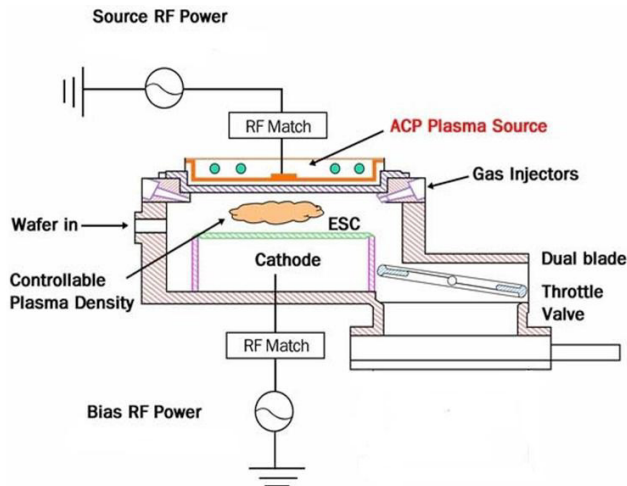


Fig. 1. Schematic diagram of etching system.

capacitively coupled plasma (CCP), as well as its own characteristics. Some of the basic properties and process performances were previously reported [6]. A Semisysco smart-EPD™ system of optical emission spectroscopy was used to observe specific plasma, chemical, and wafer behaviors in the process chamber. Through the extraction of the characteristic behaviors from the optical spectrum, a representative value of a certain process can be obtained.

On a 200-mm wafer, 600-nm-thick TEOS (oxide) was deposited using a low-pressure chemical vapor deposition (LPCVD) and PR films were prepared using a spin-coating system. The etch rates of non-pattern oxide and PR were measured as a function of the C_4F_8/O_2 gas mixing ratio and CH_2F_2 addition into the $C_4F_8/O_2/Ar$ plasma, with the process pressure of 16 Pa, RF power of 100 W, bias power of 1,800 W, and Ar flow rate of 300 sccm. The total flow rate is 331 sccm. The pattern samples were prepared to have contact hole structures by using the KrF photoresist that was used to check the etch profile. The PR thickness for the contact-hole etching mask was 200 nm, and a 58-nm-thick organic bottom anti-reflected coating (OBARC) was used for the photo-mask process.

To analyze the effect of the C_4F_8/O_2 gas mixing ratio and addition of CH_2F_2 gas into the $C_4F_8/O_2/Ar$ plasma, we investigated the chemical species in the gas phase with an optical emission spectroscopy. The surface analysis of polymer on oxide films was etched in various C_4F_8/O_2 gas mixing ratios and was performed using X-ray photoemission spectroscopy (XPS, VG Scientific ESCALAB 200R). Etched contact hole patterns were characterized using field emission scanning electron microscopy (FE-SEM, FEI Sirion 400) for the etch profile.

3. RESULTS AND DISCUSSION

Figure 2 shows the etch rates for both oxide and PR as functions of the C_4F_8/O_2 mixing ratio in the $C_4F_8/O_2/Ar$ plasma. Also, the etch selectivity of oxide over PR is shown. As the C_4F_8 fractional flow rate increases, the oxide etch rate also increases, while the etch rate of PR decreases. Accordingly, higher etch selectivity is obtained for higher C_4F_8 concentration in the $C_4F_8/O_2/Ar$ plasma. The behaviors of etch rates can be simply associated with the behaviors of the corresponding active species that include fluorine atoms and CF_x radicals for the oxide and oxygen atoms for the PR. However, it is reported that the selective etch-

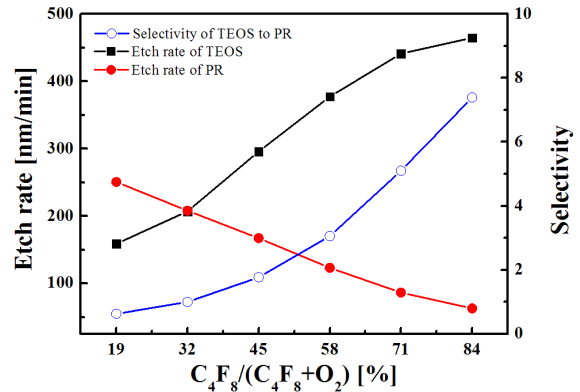


Fig. 2. Etch rates of oxide and PR, and selectivity of oxide to PR as a function of C_4F_8/O_2 gas mixing ratio.

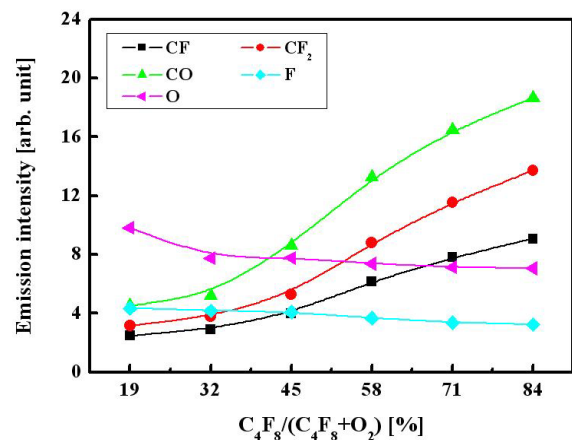


Fig. 3. Optical emission intensities of F, CF, CF_2 , O, and CO radicals as a function of C_4F_8/O_2 gas mixing ratio.

ing of oxide over PR using various fluorocarbon plasmas is influenced not only by the fluxes of active species, but also by the thickness of the fluorocarbon C_xF_y polymer layer formed over the etched structure. Evidently, an increase in the C_4F_8/O_2 mixing ratio increases the thickness of the fluorocarbon C_xF_y polymer layer due to both the increasing deposition rate (through the increasing flux of fluorocarbon radicals) and decreasing destruction rate that is supported by the chemical reaction with oxygen atoms. At the same time, the C_xF_y polymer layer deposited on the oxide can be effectively destroyed by the oxygen released from the oxide. As such, the polymer layer on the PR is expected to be thicker than that for oxide and to play the role of inhibitor for the reaction of oxygen atoms with PR. Together with the decreasing flux of oxygen atoms, the effect of C_xF_y polymer layer also decreases the etch rate of PR and increases the etch selectivity of oxide over PR with increasing C_4F_8/O_2 mixing ratio.

We used OES analysis to investigate the behaviors of the plasma active species. The emission intensities of F (703.7 nm), CF (247.5 nm), CF_2 (251.9 nm), O (844.6 nm), and CO (483.1 nm) radicals were measured as functions of the C_4F_8/O_2 gas mixing ratio [7].

Figure 3 shows that as the C_4F_8/O_2 mixing ratio increases, the emission intensities for both the CF and CF_2 radicals increase, but the intensities of the atomic lines corresponding to the O and F atoms decrease. Assuming that the emission intensities are proportional to the volume densities of the corresponding species in a gas phase, the observed changes in plasma composition

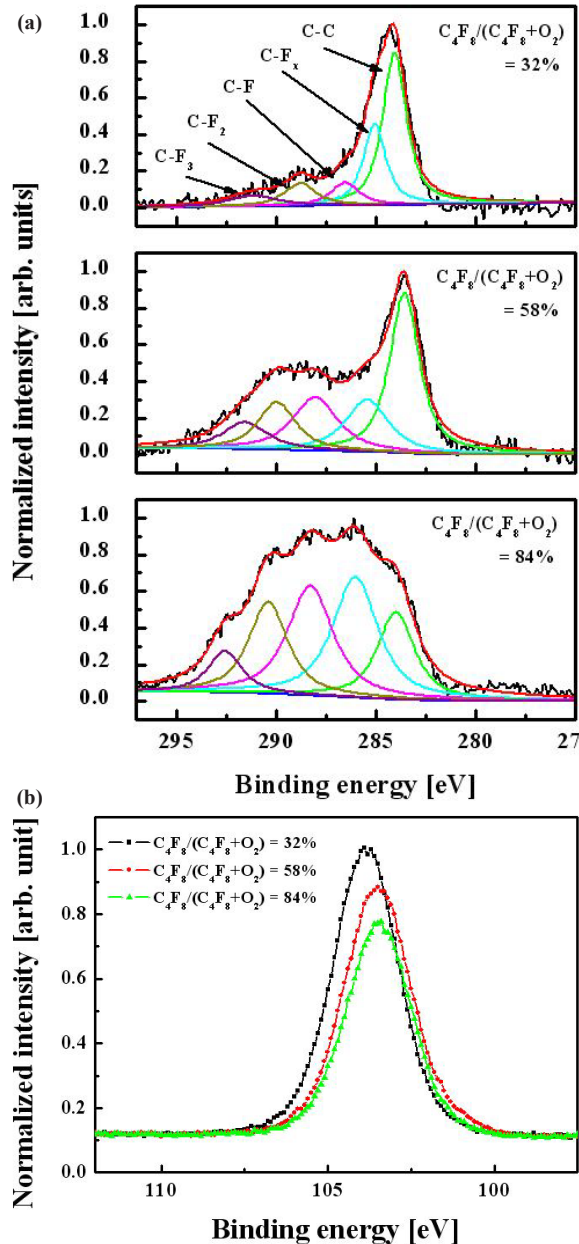


Fig. 4. XPS spectra of (a) C 1s and (b) Si 2p after etching as a function of C_4F_8/O_2 gas mixing ratio.

can result from a combination of several factors. Particularly, increases in both CF and CF_2 densities are potentially caused by two effects: (i) the increasing density of C_4F_8 molecules that are the only source of CF_x radicals in our system and (ii) the decrease in oxygen partial pressure, which lowers the destruction rate for CF_x radicals ($CF_x + O \rightarrow COF_{x-1} + F$) both in bulk plasma and on the etched surface [8]. This also explains the decreasing tendency mentioned for the volume density of F atoms. Finally, comparing the data in Figs. 2 and 3, one can assume that the etching of oxide is controlled more by CF_x radicals than by F atoms.

We used XPS measurements to analyze the chemical composition of the etched surfaces.

Figure 4 shows C 1s and Si 2p XPS narrow-scan spectra for surfaces etched with various gas mixing ratios. A wide C 1s peak can be deconvoluted into five peaks according to well-known data on binding energies for carbon-containing compounds.

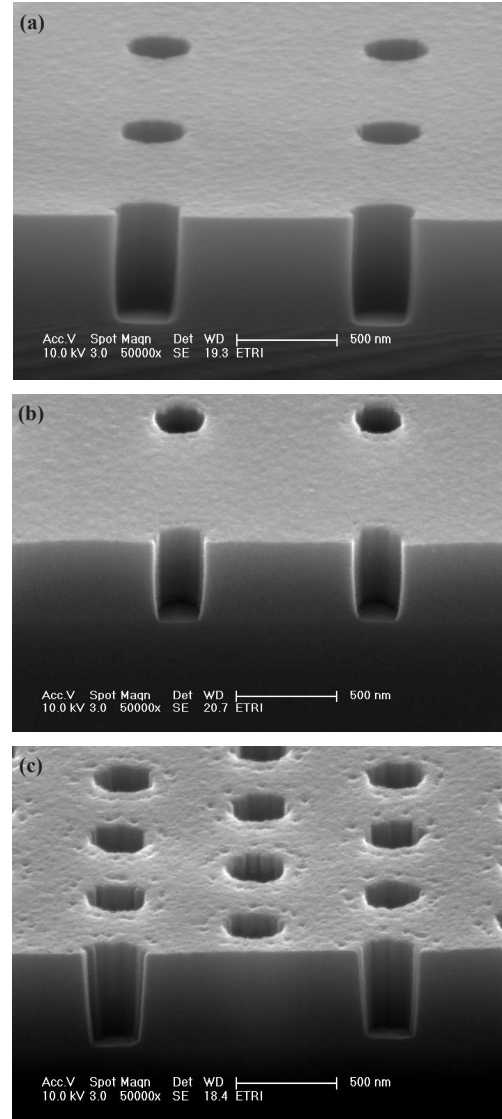


Fig. 5. Cross-sectional images of SEM in the contact hole etching. (a) $C_4F_8/O_2 = 18/13$ sccm (58%), (b) $C_4F_8/O_2 = 22/9$ sccm (71%), and (c) $C_4F_8/O_2 = 26/5$ sccm (84%).

These peaks are 284.3 eV (C-C), 286.6 eV ($C-CF_x$), 288.8 eV (C-F), 290.1 eV ($C-F_2$), and 293.2 eV ($C-F_3$) [9, 10]. Each spectrum shown in Fig. 4(a) shows a similar qualitative composition, except for peak intensities. As the C_4F_8/O_2 ratio increases, the CF_2 and CF_3 bonding increases significantly and their intensities reach the same value as the C-C and C-F peaks. This indicates a growth of the CF_x polymer layer, which has a fluorine-rich and low-carbon composition at high C_4F_8 contents. Figure 4(b) shows that the Si 2p narrow-scan spectra cannot be resolved in the SiO (102.7 eV), SiO_2 (103.6 eV), and SiC (100.7 eV) compounds due to their adjacent binding energies. However, as the C_4F_8/O_2 gas mixing ratio increases, the intensity of Si 2p narrow-scan spectra decreases because the increased CF_x radical obstructs the reaction between the O species and silicon. This phenomenon was related to the change of the etch property.

Figure 5 shows the cross-sectional SEM image of the etched contact holes pattern as a function of the C_4F_8/O_2 mixing ratio in the $C_4F_8/O_2/Ar$ plasma. The profile of holes is close to 90° in Fig. 5(a), and the etch residue is not found at the sidewall. As the C_4F_8 fractional pressure increases, the oxide etch rate and selectiv-

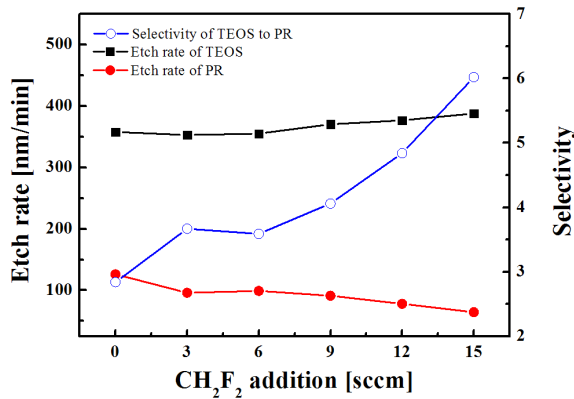


Fig. 6. Etch rates of oxide and PR and selectivity of oxide to PR as a function of CH₂F₂ additive flow ratio into the 58% C₄F₈/O₂ plasma.

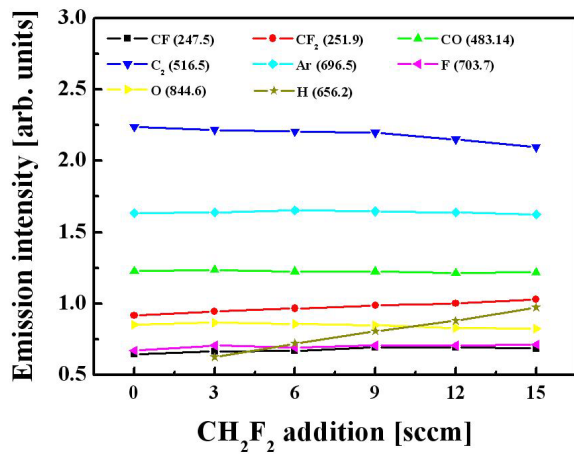


Fig. 7. Optical emission intensities of F, CF, CF₂, O, Ar, C₂, CO, and H radicals as a function of CH₂F₂ additive flow ratio into the 58% C₄F₈/O₂ plasma.

ity of oxide to PR increases, but it has a disadvantage at the etch profile.

Although an adequate etch profile was obtained, a higher etch selectivity is required to make self-aligned contacts and to provide deeper etching. To find the process condition that provides better etch selectivity, we investigated the effect of CH₂F₂ addition in C₄F₈/O₂/Ar (C₄F₈/O₂/Ar=18/13/300) plasma.

Figure 6 shows that the addition of CH₂F₂ results in increasing the etch rate of SiO₂, but in decreasing the etch rate of PR, so that the etch selectivity of oxide over PR increases. These effects may be associated with the role of hydrogen atoms formed in plasma due to the dissociation of CH₂F₂, and at least two mechanisms can be proposed. First, H atoms can attach to atomic fluorine to form HF molecules. This results in decreasing the volume density of F atoms, decreasing the recombination rate of F with CF_x, and thus increasing the density of CF_x, which is the main chemically active species for oxide. This mechanism is in good agreement with the OES data shown in Fig. 7.

From Fig. 7, it can be seen that the addition of CH₂F₂ is accompanied by an increase in the emission intensity of the CF₂ band that can be associated with increasing volume density for these species. Second, hydrogen can assist the chemical etching of oxide by extracting oxygen atoms to form OH radicals.

Figure 8 shows the C 1s and Si 2p XPS narrow-scan spectra of the etched oxide surface with and without an admixture of CH₂F₂

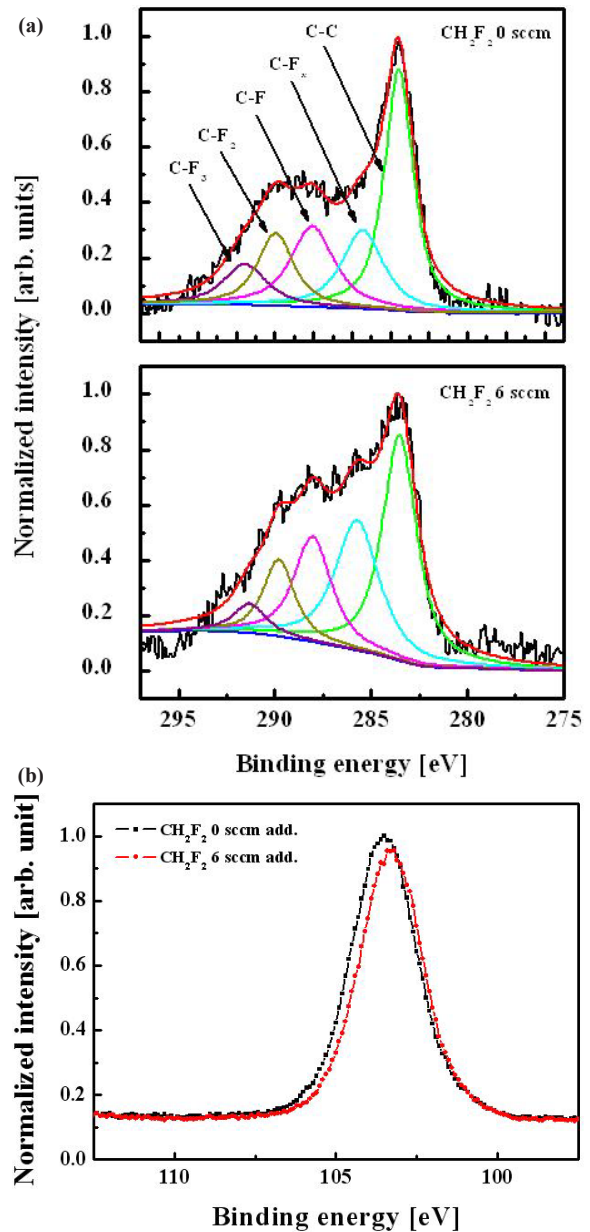


Fig. 8. XPS spectra of (a) C 1s and (b) Si 2p after etching. (a) 0 sccm CH₂F₂ addition and (b) 6 sccm CH₂F₂ addition.

in the C₄F₈/O₂/Ar plasma. The addition of CH₂F₂ increases the density of the CF_x bonds on the surface, which can be associated with the increasing flux of these species coming from bulk plasma. The intensity of the Si 2p XPS narrow-scan spectra is shown in Fig. 8(b). This peak can comprise SiC, SiO, and SiO₂. As mentioned above, in Fig. 4, the intensity change of this peak affects the etch property. Therefore, Fig. 8 demonstrates the increasing volume density of CF_x radicals (as previously mentioned with the OES measurements) and confirms the mechanism proposed to explain the acceleration of the oxide etch rate in the presence of CH₂F₂ molecules.

Figure 9 shows the cross-sectional SEM image of the etched contact holes pattern as a function of CH₂F₂ addition in the C₄F₈/O₂/Ar plasma. When the CH₂F₂ gas was added, a slight bowing profile was shown, but higher selectivity of oxide to PR could be obtained. Moreover, the bowing profile can be removed by changing the gas mixture. However, the excessive CH₂F₂ gas ad-

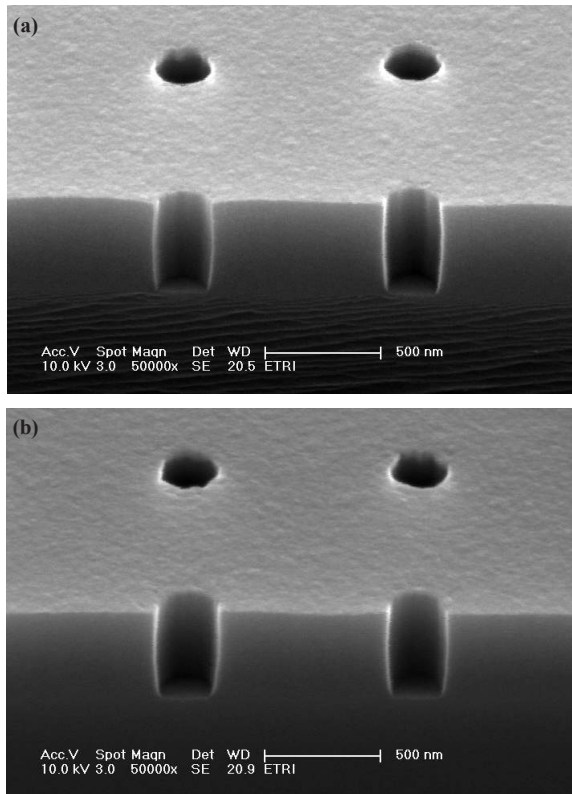


Fig. 9. Cross-sectional images of SEM in the contact hole etching. (a) 6 sccm CH_2F_2 addition and (b) 12 sccm CH_2F_2 addition.

dition induces sidewall roughness of the contact hole, as confirmed in Fig. 9(b).

4. CONCLUSIONS

In this work, we investigated the etching of contact holes through a PR mask using $\text{C}_4\text{F}_8/\text{O}_2/\text{Ar}$ and $\text{CH}_2\text{F}_2/\text{C}_4\text{F}_8/\text{O}_2/\text{Ar}$ gas

mixtures. As the mixing ratio of C_4F_8 on the $\text{C}_4\text{F}_8/\text{O}_2$ increases, the amount of polymer deposited on the etched surface also increases. This leads to an increase in the etch selectivity of oxide over PR because the C_xF_y polymer layer retards the reaction of oxygen atoms with PR. The profile of the contact holes was found to be close to 90° , and the etch residue is not found at the sidewall at a $\text{C}_4\text{F}_8/(\text{C}_4\text{F}_8+\text{O}_2)$ ratio of 58%. We also found that the etch selectivity of oxide over PR can be improved by the addition of CH_2F_2 in the $\text{C}_4\text{F}_8/\text{O}_2/\text{Ar}$ plasma because the CF_x radical volume density is increased.

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