Characteristics of SiO₂ Etching with a C₄F₈/Ar/CHF₃/O₂ Gas Mixture in 60-MHz/2-MHz Dual-frequency Capacitively Coupled Plasmas

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Nanoscale SiO₂ contact holes were etched by using C₄F₈/CHF₃/O₂/Ar gas mixtures in dual-frequency capacitively coupled plasmas (DF-CCPs) where a 60-MHz source power was applied to the top electrode while a 2-MHz bias power was applied to the bottom electrode. The initial increase in the CHF₃ gas flow rate at a fixed CHF₃+O₂ flow rate increased the SiO₂ etch rate as well as SiO₂ etch selectivity over that of the amorphous carbon layer (ACL). When the high-frequency (HF) power was increased both SiO₂ etch rate and the etch selectivity over ACL were increased. For a 300 W/500 W power ratio of 60-MHz HF power/2-MHz low-frequency (LF) and a gas mixture of Ar (140 sccm) /C₄F₈ (30 sccm) /CHF₃ (25 sccm) /O₂ (5 sccm) while maintaining 20 mTorr, an anisotropic etch profile with an SiO₂ etch rate of 3350 Å/min and an etch selectivity of higher than 6 over ACL could be obtained.

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I. INTRODUCTION

As the size of the semiconductor devices is drastically scaled down to nano-scale, the etching of high-aspect-ratio contacts (HARCs) is becoming more difficult [1,2]. To etch nano-patterned HARCs, the multi-layer resist (MLR) structures conventionally composed of a photoresist (PR), SiON layer, and an amorphous carbon layer (ACL), has been developed because it is difficult to etch HARCs directly using a photoresist mask only. However, even though the etching of HARCs tends to show higher etch selectivity and proper etch profile with the MLR structures, for next-generation nano-scale random access memory devices, the etching of nano-scale SiO₂ HARCs using fluorocarbon-based plasmas is becoming more and more important [3,4].

For the etching of HARCs using fluorocarbon plasmas, the dual-frequency capacitively coupled plasma (DF-CCP) has been actively investigated because the typical single-frequency CCP system cannot satisfy the strict requirement of SiO₂ HARCs etching and because controlling the plasma density and the ion bombardment energy separately is difficult [5]. Thus, with the DF-CCP system, improved etch characteristics, such as high etch selectivity and anisotropic etching, have been obtained by adjusting the two frequencies properly. The commonly used frequencies for DF-CCPs are 13.56 MHz (high frequency; HF)/2 MHz (low frequency; LF), 27 MHz/2 MHz, and 60 MHz/2 MHz. Among these frequencies, 60 MHz/2 MHz combined DF-CCP is more effective in the etching of SiO₂ because the gas dissociation progresses more effectively at 60 MHz compared to the lower frequencies of 13.56 MHz and 27 MHz [6–9]. Also, anisotropic etching has been shown to be improved due to a decrease in the sheath thickness and in the number of ion collisions in sheath at the higher frequency [10].

In the etching of SiO₂ HARCs, a C₄F₈-based gas mixture is typically used in order to improve the etch selectivity by depositing a thick fluorocarbon polymer on non-oxide layers, and O₂ gas is added to compensate for the low etch rate due to the fluorocarbon polymer deposition and to adjust the etch profile [11]. However, as the size of the contact hole is reduced to nano-scale, it is difficult to maintain the critical dimension (CD), etch selectivity, anisotropic profile, etc. during the etching of nano patterned HARCs by using the C₄F₈/O₂ gas chemistry alone, so, other fluorocarbon gases may need to be...
added for further adjustment of the etch characteristics.

In this study, CHF$_3$ gas was added to a C$_4$F$_8$/Ar/O$_2$ gas chemistry in the etching of SiO$_2$ HARCs, and the effect of the CHF$_3$/CHF$_3$+O$_2$ ratio in the C$_4$F$_8$/Ar/CHF$_3$/O$_2$ gas mixture on the gas dissociation and surface chemistry, and their relation to the etch characteristics, such as etch rate, etch selectivity, and etch profile, were investigated using a 60 MHz/2 MHz DF-CCP system. In addition, even though DF-CCPs have been investigated for a while, the effect of the frequency ratio of the DF-CCP system on the plasma characteristics and the SiO$_2$ HARC etching characteristics has not been investigated in much detail. Therefore, in this study, in addition to varying CHF$_3$ in the C$_4$F$_8$/Ar/CHF$_3$/O$_2$ gas mixture, we varied the HF/LF ratio and investigated its effects on the plasma and SiO$_2$ etch characteristics.

II. EXPERIMENTAL

The experimental setup of the DF-CCP etch system used in this study is shown in Fig. 1. The chamber was made of anodized aluminum, and the discharge was maintained between two 200-mm-diameter parallel-plate electrodes separated by 30 mm. The top electrode was covered with a perforated silicon plate to flow gases uniformly, and it was connected to a 60-MHz rf power source (HF) to control the plasma density while the bottom electrode was connected to a 2-MHz rf power source (LF) to control the ion bombardment energy. The reactor was evacuated by using turbo molecular pumps (3200 l/s) backed by a booster and rotary pump. The gas was equally distributed through a baffle system from the top electrode. A tight steel mesh block was installed around the bottom electrode to reduce the plasma leakage by the pumping system connected to the bottom chamber. The process pressure was controlled automatically by adjusting a throttle valve.

The 2400-um-thick SiO$_2$ deposited on silicon wafers was masked with a MLR layer composed of patterned photo-resist (PR) layer/70nm SiON layer/550nm ACL. The ACL was used as the hardmask for SiO$_2$ HARC etching to maintain the critical dimension (CD) of the contact hole. Before the etching of SiO$_2$, a SiON layer patterned by using the PR was etched vertically by using a fluorocarbon-based plasma (HF power/LF power = 200 W/200 W, CF$_4$/Ar gas mixture = 80/20 sccm, process pressure 20 mTorr, etch time 35 seconds), followed by ACL etching in a N$_2$/O$_2$ plasma (HF power/LF power = 200 W/200 W, O$_2$/N$_2$ gas mixture = 70/30 sccm, process pressure 20 mTorr, etch time 50 seconds). Finally, the SiO$_2$ layer was etched for various process conditions, such as the HF/LF ratio and the CHF$_3$/CHF$_3$+O$_2$ ratio in C$_4$F$_8$/Ar/CHF$_3$/O$_2$ gas chemistry, while keeping the substrate temperature at room temperature.

The etch characteristics of the SiO$_2$ HARCs layers, such as etch rates and etch profiles obtained using C$_4$F$_8$/Ar/CHF$_3$/O$_2$ gas chemistry, were observed by using field emission scanning electron microscopy (FE-SEM, Hitachi S-4700). The surface chemistry of the etched SiO$_2$ was observed using X-ray photoelectron spectroscopy (XPS, ESCA2000, VG Microtech Inc.) by etching blank SiO$_2$ wafers. Dissociated species in the plasmas, such as F, CF$_2$, etc., in the fluorocarbon plasmas, were observed using optical emission spectroscopy (OES, Avaspec 3648, Avantes).

III. RESULTS AND DISCUSSION

1. Additive Gas Variation

The additive gas ratio of CHF$_3$/CHF$_3$+O$_2$ in the C$_4$F$_8$/Ar/CHF$_3$/O$_2$ plasma of the DF-CCP system can
As shown in Fig. 3(a), for C1s results are shown in Figs. 3(a), (b), and (c), respectively. Functions of the CHF$_3$ densities of the XPS narrow scan spectra were observed as face. The C 1s at 284.6 eV, C-CF at 286.9 eV, CF at 289.3 eV, CF$_2$ at 291.3 eV, and CF$_3$ at 293.7 eV could be identified [17].

Changes in the etch rate and the etch selectivity of SiO$_2$. The plasma characteristics and the etch characteristics of SiO$_2$ were investigated as functions of the ratio of CHF$_3$/CHF$_3$+O$_2$ while keeping the HF source power/LF bias power at 300 W/500 W, the operating pressure at 20 mTorr, the gas flow rates of C$_2$F$_8$/Ar at 20 sccm/150 sccm, and the total gas flow rate of CHF$_3$+O$_2$ at 30 sccm. Figure 2 shows the optical emission peak intensities of Ar, CF, CF$_2$, O, and F and the ratio of CF$_2$/F measured as functions of the CHF$_3$/CHF$_3$+O$_2$ gas ratio by using OES [12–14]. As shown in Fig. 2, an increase in the CHF$_3$/CHF$_3$+O$_2$ gas ratio increased the optical emission peak intensity of CF and CF$_2$ while decreasing the peak intensity of F and O. CHF$_3$ is known to be dissociated through the following reactions by electron impact dissociation [15,16]:

$$CHF_3 + e \rightarrow CF_2 + HF, \Delta H = 2.43 \text{ eV}, \quad (1)$$
$$CHF_3 + e \rightarrow CF_3 + H, \Delta H = 4.52 \text{ eV}, \quad (2)$$
$$CHF_3 + e \rightarrow CHF_2 + F, \Delta H = 4.90 \text{ eV}, \quad (3)$$
$$CHF_3 + e \rightarrow CF_2 + F, \Delta H = 3.83 \text{ eV}, \quad (4)$$
$$CF_2 + e \rightarrow CF + F, \Delta H = 5.35 \text{ eV}, \quad (5)$$

As shown in the above reaction equations, with increasing CHF$_3$ in the gas mixture, increases in CF and CF$_2$ radical densities while decreasing the F radical density because of the decreased reaction of O with C in the CF$_x$ radical. Therefore, an increase in the CHF$_3$/CHF$_3$+O$_2$ gas ratio increased the CF$_2$/F ratio in the plasma.

The increase in the CF and CF$_2$ radical intensities in the plasma caused by an increase in the CHF$_3$/CHF$_3$+O$_2$ gas ratio at given DF-CCP powers (that is, at similar plasma densities and dc-bias voltages by applying the same HF source power and LF bias power) can change the chemistry of the etched SiO$_2$ surface. The C 1s, Si 2p, and O 1s bonding peak intensities of the XPS narrow scan spectra were observed as functions of the CHF$_3$/CHF$_3$+O$_2$ gas ratio, and the results are shown in Figs. 3(a), (b), and (c), respectively. As shown in Fig. 3(a), for C1s, bonding peaks of C-C at 284.6 eV, C-CF at 286.9 eV, CF at 289.3 eV, CF$_2$ at 291.3 eV, and CF$_3$ at 293.7 eV could be identified [17]. When the CHF$_3$ gas flow in the CHF$_3$/CHF$_3$+O$_2$ gas ratio was equal to and lower than 10 sccm, only C-C bonding could be observed. However, with further increases in the CHF$_3$/CHF$_3$+O$_2$ gas ratio, other fluorocarbon bonding peaks, such as C-CF, CF, CF$_2$, and CF$_3$, bonding peaks were observed, and their peak intensities increased with increasing CHF$_3$/CHF$_3$+O$_2$ gas ratio, indicating an increase in the fluorocarbon polymer layer thickness. The Si 2p and O 1s bonding peak intensities shown in Figs. 3(b) and (c) decreased with increasing CHF$_3$/CHF$_3$+O$_2$ gas ratio, indicating an increase in fluorocarbon polymer layer thickness with increasing CHF$_3$/CHF$_3$+O$_2$ gas ratio.
ity of SiO\(_2\)/ACL were also investigated as functions of the CHF\(_3\)/(CHF\(_3\)+O\(_2\)) gas ratio while maintaining the other conditions the same as those in Fig. 2, and the results are shown in Fig. 4. As shown in Fig. 4, an increase in the CHF\(_3\)/(CHF\(_3\)+O\(_2\)) gas ratio increased the SiO\(_2\) etch rate until CHF\(_3\)/O\(_2\) = 20/10; however, further increases in the gas flow ratio decreased the SiO\(_2\) etch rate. However, in the case of the ACL etch rate, an increase in the CHF\(_3\)/(CHF\(_3\)+O\(_2\)) gas ratio decreased the ACL etch rate continuously, so, the etch selectivity increased with increasing CHF\(_3\)/(CHF\(_3\)+O\(_2\)) gas ratio until CHF\(_3\)/O\(_2\) = 25/5, with further increases in the CHF\(_3\)/(CHF\(_3\)+O\(_2\)) gas ratio decreasing the etch selectivity. The decrease in the ACL etch rate with increasing CHF\(_3\)/(CHF\(_3\)+O\(_2\)) gas ratio is believed to be related to the increase in the CF\(_x\)/F ratio, and, therefore, to the increase in the CF and CF\(_x\) flux to the substrate for the formation of a thicker fluorocarbon polymer layer, as observed on the SiO\(_2\) surface. In the case of SiO\(_2\) etching, SiO\(_2\) can be etched even at a high CF\(_x\) flux due to the reaction of carbon in CF\(_x\) with O in SiO\(_2\) when the dc-bias voltage is maintained, so the SiO\(_2\) etch rate appears to increase up to CHF\(_3\)/O\(_2\) = 20/10 even though the CF\(_x\)/F ratio is increased with increasing CHF\(_3\)/(CHF\(_3\)+O\(_2\)) gas ratio. However, when the CHF\(_3\)/(CHF\(_3\)+O\(_2\)) gas ratio is too high, due to the formation of too thick a fluorocarbon polymer layer, the SiO\(_2\) etch rate decreases with increasing CHF\(_3\)/(CHF\(_3\)+O\(_2\)) gas ratio. Therefore, by varying the CHF\(_3\)/(CHF\(_3\)+O\(_2\)) gas ratio, we could obtain a high SiO\(_2\) etch selectivity of about 6 over the ACL at a SiO\(_2\) etch rate of 3350 \(\text{Å}/\text{min}\) for CHF\(_3\)/O\(_2\) = 25/5. Therefore, a further experiment was carried out at an additive gas ratio of CHF\(_3\)/O\(_2\) = 25/5.

2. High-frequency Power Variation

The effects of the HF/LF power ratio of the DF-CCP system on the plasma characteristics and on the etch characteristics have been investigated for a fixed C\(_4\)F\(_8\)/(20)/Ar(150)/CHF\(_3\)(25)/O\(_2\)(5) gas mixture by varying the 60-MHz HF source power while maintaining the 2-MHz LF bias power. Figure 5 shows the optical emission peak intensities of Ar, CF, CF\(_2\), O, and F and the ratio of CF\(_2\)/F measured as functions of the HF source power by using OES [14–16]. The LF bias power was maintained at 500 W, and the operating pressure was kept at 20 mTorr. As shown in Fig. 5, an increase in the HF power while keeping the LF bias power constant increased the dissociated species, such as Ar, CF, CF\(_2\), O, and F, and the ratio of CF\(_2\)/F decreased with increasing HF source power. However, the ratio of CF\(_2\)/F decreased with increasing HF source power, possibly due to further dissociation of CF\(_2\) and to the formation of more F radical at higher HF source powers.

The fluorocarbon polymer formed on the SiO\(_2\) etched using the C\(_4\)F\(_8\)/Ar/CHF\(_3\)/O\(_2\) gas combination as a function of HF source power was investigated by using XPS. Figure 6(a) shows XPS C1s narrow scan data measured on the etched SiO\(_2\) surface as a function of the HF source power. The SiO\(_2\) etch conditions were the same as those in Fig. 5. As shown in the figure, bonding peaks of C-C, C-CF, CF, CF\(_2\), and CF\(_3\) were observed [17]. As shown in the figure, with increasing HF source power, an increase in the bonding peak intensities of C-CF, CF, CF\(_2\),
Fig. 7. Etch rates of SiO$_2$ and ACL and etch selectivity of SiO$_2$ over ACL as functions of the HF power, for a LF power 500 W, a process pressure of 20 mTorr, Ar/C$_4$F$_8$ = 150/20 sccm, an etch time of 2 min.

and CF$_3$ bonding could be observed due to more dissociation of C$_4$F$_8$ and CHF$_3$ into CF$_x$ (x = 1, 2, 3), indicating a thicker fluorocarbon layer formation on the etched SiO$_2$ surface [18]. Figures 6(b) and (c) show the Si 2p peak and the O 1s peak of the XPS narrow scan spectra for the etched SiO$_2$ surface, respectively, measured as functions of the HF source power. As shown in the figures, an increase in the HF source power decreased the peak intensities due to an increase in the polymer thickness. Therefore, the increase in the HF source power increased the fluorocarbon polymer thickness. In general, the decrease in CF$_x$/F in the plasma, as shown in Fig. 5, can decrease the polymer layer thickness due to a decrease in the C/F flux ratio on the surface when other conditions are kept the same. However, in our experiment, with increasing HF source power, the dc-bias voltage, that is, the ion bombardment energy to the substrate, is also decreased due to the increased plasma conductivity at a given LF bias power (not shown). Therefore, the increase in the polymer layer thickness on the SiO$_2$ surface with increasing HF source power appears to be related to the decreased ion bombardment energy to the substrate.

The etch rate of SiO$_2$ was also measured as a function of HF source power for the C$_4$F$_8$/Ar/CHF$_3$/O$_2$ plasma in Fig. 5 and the result is shown in Fig. 7. The ACL etch rate, in addition to the SiO$_2$ etch rate, and the etch selectivity of SiO$_2$ over ACL layer are shown. As shown, the SiO$_2$ etch rate increased from about 2200 to 4240 Å/min with increasing HF source power from 150 to 500 W. An increase in the HF source power slightly increased the ACL etch rate. In the case of the etch selectivity, the increase in the HF source power initially increased the etch selectivity; however, at high HF source power, it appears to be saturated near 6. At a low HF source power of 150 W, due to the low gas dissociation and due to the high ion bombardment energy to the substrate at a low

HF source power, the etch selectivity was low, and the SiO$_2$ etch rate was low due to the low F radical density, as shown in Fig. 5. With increasing HF source power, the SiO$_2$ etch rate was increased due to an increase in the amount of dissociated F in the plasma and an increase in the etch selectivity due to the decreased ion bombardment energy with increasing HF source power. However, due to the increase in the fluorocarbon polymer layer and to the decrease in the ion bombardment energy to the substrate, the etch selectivity appears to be saturated or to remain similar near a value of 6 at high HF source powers. (Also, with increasing HF power, the O$_2$ radical density is increased, and it causes an increase in the ACL etch rate; consequently, the etch selectivity remains similar at high HF source powers.) Therefore, even though the etch selectivity nearly saturates with increasing HF source power, an increase in the SiO$_2$ etch rate with increasing HF source power without a significant decrease in the etch selectivity could be obtained. A high SiO$_2$ etch rate of about 4240 Å/min with an etch selectivity of about 6 over the ACL layer could be obtained at a HF power of 500 W.

3. Etch profiles

Etch profiles of SiO$_2$ masked with a MLR layer composed of PR layer/70-nm SiON layer/550-nm ACL were observed using SEM for various CHF$_3$/O$_2$ ratio and HF source powers while keeping the LF bias power at 500 W, the ratio of Ar/C$_4$F$_8$ at 150 sccm/20 sccm, and the operating pressure at 20 mTorr. The results are shown in Figs. 8 and 9, respectively. The ratio of CHF$_3$/O$_2$ was varied while maintaining the HF source power at 300 W, and the HF source power was varied while keeping the
CHF$_3$/O$_2$ ratio at 25 sccm/5 sccm. The etch time was maintained at 2 min.

Figure 8 shows the SiO$_2$ etch profile observed using a FE-SEM for various CHF$_3$/O$_2$ gas ratios. Figure. 8(a), (b), (c), and (d) are for CHF$_3$ (10 sccm)/O$_2$ (20 sccm), CHF$_3$ (20 sccm)/O$_2$ (10 sccm), CHF$_3$ (25 sccm)/O$_2$ (5 sccm), and CHF$_3$ (30 sccm)/O$_2$ (0 sccm), respectively. With increasing CHF$_3$ ratio, the ACL etched amount decreased, as shown in Fig. 4, possibly due to the thicker fluorocarbon layer formation on the ACL surface. Due to increasing fluorocarbon layer thickness, the width of the etched SiO$_2$ hole decreased with increasing CHF$_3$/O$_2$ gas ratio. Also, at a high CHF$_3$/O$_2$ gas ratio, as shown in Fig. 8(d), the SiO$_2$ etch depth was significantly decreased due to the thick fluorocarbon layer on the SiO$_2$ surface.

Figure 9 shows the SiO$_2$ etch profile observed for various HF source powers from 150 W to 500 W while keeping the LF bias power at 500 W. As shown in the figure, an increase in the HF source power increased the SiO$_2$ etch depth and slightly increased the amount of etched ACL. The width of etched SiO$_2$ hole was not significantly changed by the HF source power; however, at HF source powers higher than 400 W, slight distortions of the SiO$_2$ etch profile could be observed, which were possibly related to the widening of the ACL etch profile with increasing amount of etched ACL.

IV. CONCLUSIONS

Using 60-MHz/2-MHz fluorocarbon DF-CCP, the plasma characteristics and SiO$_2$ etch characteristics applied to HARC etching were investigated as functions of the additive gas ratio of CHF$_3$/(CHF$_3$+O$_2$) in Ar/C$_4$F$_8$/CHF$_3$/O$_2$ and of the HF power/LF power ratio by varying the HF source power while keeping the LF bias power constant. An increase in the CHF$_3$ gas flow rate at a fixed CHF$_3$+O$_2$ flow rate of 30 sccm increased the thickness of the fluorocarbon polymer layer on the substrate surface by increasing the CF$_x$ flux to the substrate and by increasing the CF$_x$/F ratio to the substrate while maintaining the ion bombardment energy. Therefore, the etch SiO$_2$ selectivity over ACL and the SiO$_2$ etch rate were increased with increasing CHF$_3$/(CHF$_3$+O$_2$) ratio, but too high a CHF$_3$/(CHF$_3$+O$_2$) ratio decreased not only the SiO$_2$ etch rate but also the etch selectivity due to the fluorocarbon layer on the SiO$_2$ surface being too thick. An increase in the HF source power while keeping the LF bias power constant at a fixed CHF$_3$/(CHF$_3$+O$_2$) ratio also increased the CF$_x$ flux to substrate by the increasing the fluorocarbon gas dissociation even though the CF$_x$/F flux ratio to the substrate was decreased while decreasing the ion bombardment energy to the substrate. Therefore, the fluorocarbon layer thickness on the substrate also increased with increasing HF power. However, due to the increase in the F density with increasing HF power, not only the SiO$_2$ etch rate but also the ACL etch rate increased with increasing HF power. Therefore, even though the etch selectivity was initially increased with increasing HF power, it was nearly saturated at high HF powers. With increasing CHF$_3$/O$_2$ gas ratio, the etched SiO$_2$ hole width was decreased due to an increase in fluorocarbon layer formation on the ACL surface. A change in the HF power at a fixed CHF$_3$/(CHF$_3$+O$_2$) ratio did not change the SiO$_2$ hole width significantly. However, at high HF powers, even though the SiO$_2$ etch rate was increased without significantly varying the etch selectivity over ACL, due to a widening of the mask profile, a slight distortion of the SiO$_2$ etch profile could be observed. Therefore, an adequate combination of fluorocarbon gas mixture and HF/LF power ratio appears to be required to obtain not only a high SiO$_2$ etch rate and etch selectivity over the mask layer but also a vertical etch profile.

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