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Effect of source frequency and pulsing on the SiO$_2$ etching characteristics of dual-frequency capacitive coupled plasma

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A SiO$_2$ layer masked with an amorphous carbon layer (ACL) has been etched in an Ar/C$_2$F$_6$ gas mixture with dual frequency capacitively coupled plasmas under variable frequency (13.56–60 MHz)/pulsed rf source power and 2 MHz continuous wave (CW) rf bias power, the effects of the frequency and pulsing of the source rf power on the SiO$_2$ etch characteristics were investigated. By pulsing the rf power, an increased SiO$_2$ etch selectivity was observed with decreasing SiO$_2$ etch rate. However, when the rf power frequency was increased, not only a higher SiO$_2$ etch rate but also higher SiO$_2$ etch selectivity was observed for both CW and pulse modes. A higher CF$_2$/F ratio and lower electron temperature were observed for both a higher source frequency mode and a pulsed plasma mode. Therefore, when the C 1s binding states of the etched SiO$_2$ surfaces were investigated using X-ray photoelectron spectroscopy (XPS), the increase of C=–F bonding on the SiO$_2$ surface was observed for a higher source frequency operation similar to a pulsed plasma condition indicating the increase of SiO$_2$ etch selectivity over the ACL. The increase of the SiO$_2$ etch rate with increasing etch selectivity for the higher source frequency operation appears to be related to the increase of the total plasma density with increasing CF$_2$/F ratio in the plasma. The SiO$_2$ etch profile was also improved not only by using the pulsed plasma but also by increasing the source frequency. © 2015 The Japan Society of Applied Physics

1. Introduction

As semiconductor devices are scaled down to nano scale levels for use in ultra scale integrated circuits, the etching of semiconductor devices is has become more difficult to satisfy more stringent requirements of etch characteristics such as etch profile, etch rate, and etch selectivity. In particular, when high-aspect-ratio contacts (HARCs) are etched, plasma-process-induced damage (P2ID), such as pattern distortion and etch stops is observed, which can degrade the electrical performance of semiconductor devices. For the P2ID of HARCs, the electron shading effect caused by the isotropic flux of plasma electrons and the anisotropic flux of plasma ions, which result in negative and positive on the top and bottom of the HARC structure, respectively, is known to be the cause of pattern distortion.

To reduce the electron shading effect, various methods have been investigated and, among these, pulsed plasma techniques have been widely investigated by many research groups. Pulsed plasma is obtained by cyclically turning the radio frequency (rf) power on and off and is known to reduce electron shading by generating low-energy positive plasma ions, which result in negative and positive on the top and bottom of the HARC structure, respectively, is known to be the cause of pattern distortion.

At present, for the etching of HARCs based on fluorocarbon plasmas, dual-frequency capacitive coupled plasmas (DF-CCPs) have also been extensively studied to control the plasma density and ion bombardment energy independently. When the source power of the DF-CCP was operated at a higher frequency, the etch profile was improved by the decreased number of ion collisions in the sheath caused by the decreased sheath thickness.

In this study, a DP-CCP composed of variable-frequency (13.56–60 MHz)/pulsed rf source power and 2 MHz CW rf bias power has been used in the experiment and the effects of the frequency and pulsing of the source rf power on the SiO$_2$ HARC etch characteristics were investigated using a C$_6$F$_{14}$/Ar gas mixture. In particular, we concentrated on the relationship of the SiO$_2$ etch characteristics with the change of reactive radicals such as CF$_2$ and F in the plasma.

2. Experimental procedure

The schematic diagram of the 300-mm-diameter DF-CCP etch system used in this study is shown in Fig. 1. The processing chamber and the bottom electrode were fabricated of anodized aluminum and the top electrode was fabricated of silicon supported by aluminum and a ceramic ring. The top silicon electrode surface was perforated for a uniform reactive gas flow over the substrate surface and the bottom electrode was cooled to room temperature by a chiller. The two electrodes were 20 mm apart. The top silicon electrode was connected to variable- and high-frequency power sources in the range of 13.56–60 MHz to control the plasma characteristics while the bottom electrode was connected to a low-frequency 2 MHz rf power source to control the ion bombardment energy. The chamber was evacuated by a turbomolecular pump (3200 l/s) backed by a dry pump. The process pressure was controlled automatically by adjusting the throttle valve.

A 600-nm-thick amorphous carbon layer (ACL) was used as a hardmask for SiO$_2$ HARC etching to maintain the critical dimension (CD) of the 2-µm-deep contact hole. The SiO$_2$
layer was etched by a CW/pulsed (duty percentage: 50%, 1 kHz) HF source frequency ranging from 13.56 to 60 MHz in an Ar/C4F8 plasma while biasing with 2 MHz CW rf power and while keeping the substrate temperature at room temperature.

The etch rates of SiO2 and the ACL were measured using a step profilometer (Alpha Step 500) and the SiO2 HARC etch profiles masked by the ACL were observed by field-emission scanning electron microscopy (FE-SEM; Hitachi S-4700). The change of the radical intensities of C4F8/Ar gas chemistry such as F, CF2, and Ar was observed by optical emission spectroscopy (OES; Andor™ Shamrock303). The C 1s binding states of the SiO2 surfaces etched under various plasma conditions were observed using X-ray photoelectron spectroscopy (XPS; VG Microtech ESCA2000) by etching blank SiO2 wafers. The characteristics of the substrate bias voltage and electron temperature during the pulse-on and pulse-off conditions for the pulsed plasma mode in addition to the decrease of the ACL etch rate of about 30–50% by pulsing the rf power with a 50% duty cycle. Therefore, when the etch selectivities of SiO2/ACL were measured, as shown in Fig. 2(b), the pulsed condition of a 50% duty cycle showed higher etch selectivity than the CW conditions and the etch selectivity was increased with the increase of source rf frequency for both the pulsed mode and the CW mode. In particular, the improvement of the etch selectivity of SiO2/ACL with the source rf frequency was more significant for the pulsed plasma mode.

To investigate the reason for the differences in SiO2 etch rates and etch selectivities, the radical intensities of Ar/C4F8 plasmas operated under different source rf frequency conditions and pulsed/CW modes were measured using OES. Figure 3 shows the optical emission intensity ratios of CF3 (275.4 nm)/Ar (750.1 nm), F (703 nm)/Ar (750.1 nm),16,17) and CF2/F as a function of source rf frequency for the pulsed/CW modes shown in Fig. 2. As shown in Fig. 3, the intensity ratios of CF3/Ar in the plasma were increased not only with the increase of source frequency but also by pulsing the plasma. The intensity ratios of F/Ar were slightly increased with the increase of source rf frequency; however, the pulsing the plasma decreased the F/Ar ratio at a given source rf frequency. The increase of source rf frequency from 13.56 to 60 MHz increased the intensity ratios of CF2/F but pulsing the plasma with a 50% duty cycle

3. Results and discussion

Figures 2(a) and 2(b) show the etch rates of SiO2 and the ACL and their etch selectivities, respectively, measured for source rf frequencies of 13.56, 27.12, and 60 MHz for the CW mode and pulsed mode (50% duty cycle with a pulsing frequency of 1 kHz). SiO2 and the ACL were etched using a Ar (170 sccm)/C4F8 (40 sccm) gas mixture, an operating pressure of 40-mTorr, and a source rf power/bias rf power of 0.2 kW/1.2 kW. As shown in Fig. 2(a), the SiO2 etch rate increased with the increase of rf frequency from 13.56 to 60 MHz both with and without pulsing even though the SiO2 etch rate with the pulsing of a 50% duty cycle was about 20–30% lower than that etched with the CW mode. In the case of the ACL, the etch rate was not significantly changed with the increase of the source rf frequency. When the pulsing of a 50% duty cycle was used, the ACL etch rate was even decreased with an increase of source rf frequency in addition to the decrease of the ACL etch rate of about 30–50% by pulsing the rf power with a 50% duty cycle.
increased the CF$_2$/F ratio more significantly. In general, the increase of plasma source frequency increases the gas dissociation due to the increased plasma density in the plasma. Hence, the increased number of dissociated radicals such as CF$_2$ and F, observed with the increase of source rf frequency are believed to be related to the increased power consumption of the plasma. However, by pulsing the plasma, the dissociated radicals tend to recombine during the pulse-off period, and F appears to recombine with CF$_2$ to form more CF$_{3+x}$. Therefore, as shown in the figure, by pulsing the plasma, the CF$_2$ radical intensity increased and F radical intensity decreased. The CF$_2$ in the plasma tends to form a polymer layer on the substrate surface, even though SiO$_2$ can be etched by forming CO and SiF$_4$ with CF$_2$, while F in the plasma tends to etch the ACL and SiO$_2$ nonselectively. Therefore, the increased SiO$_2$ etch rate and etch selectivity with the increase of source rf frequency are believed to be related to the increased gas dissociation of C$_4$F$_8$ with the increased CF$_2$/F ratio. The increased etch selectivity of SiO$_2$/ACL with decreasing SiO$_2$ etch rate for the pulsed condition is related to the increase in CF$_2$, radicals with the decrease in F radicals by pulsing the plasmas. By operating at a higher source rf frequency, due to the increased SiO$_2$ etch rate with increased etch selectivity, a higher SiO$_2$/ACL etch selectivity could be observed for the pulsed plasma condition without decreasing the SiO$_2$ etch rate significantly.

Using an emissive probe, the temporal and time-averaged electron temperatures were measured as a function of rf frequency and the results are shown in Figs. 4(a) and 4(b), respectively. For the temporal electron temperature measurement, Ar was used and no bias power was applied. For the plasma conditions, source rf power of 0.2 kW, 170 sccm of Ar at 40 mTorr, 50% duty ratio, and an rf power pulsing source with 1 kHz were used. As shown in Fig. 4(a), during the source power pulse-on time, the bias voltage increased due to the higher plasma density with the higher source rf frequency. The bias voltages during the pulse-off time were the same; however, during the pulse-on time, due to the higher plasma density with the higher source rf frequency, the bias voltage increased due to the decrease of plasma density. The bias voltages during the pulse-off time were the same; however, during the pulse-on time, due to the higher plasma density with the higher source rf frequency, the bias voltage increased due to the decrease of plasma density. Therefore, the time-averaged bias voltage was higher for a lower source rf frequency.

Figures 5(a) and 5(b) show the temporal bias voltage and time-averaged bias voltage, respectively, measured on the substrate as a function of source rf frequency. In Fig. 5(b), the bias voltages measured in the CW mode are also shown. The process conditions were the same as those in Fig. 2 except for the bias power (0.6 kW of 2 MHz CW rf power was used). As shown in Fig. 5(a), during the source power pulse-on time, the bias voltage decreased and, during the source power pulse-off time, the bias voltage increased due to the decrease of plasma density. The bias voltages during the pulse-off time were the same; however, during the pulse-on time, due to the higher plasma density with the higher source rf frequency, the bias voltage was lower for a higher rf frequency. Therefore, the time-averaged bias voltage was higher for a lower source rf frequency condition and for the pulsed mode.

The surfaces of SiO$_2$ etched with Ar/C$_4$F$_8$ plasmas were investigated by XPS. Figures 6(a)–6(c) show the C 1s XPS narrow scan data of a SiO$_2$ surface obtained after the etching of SiO$_2$ for a similar etch depth of 700 nm with the different source rf frequencies of 13.56, 27.12, and 60 MHz, respectively, in the CW mode. As shown in the figure, carbon binding states related to C–C (284.9 eV), C–CF (287.9 eV), CF (289.8 eV), and CF$_2$ (291.5 eV) bonding were observed.
and, as the source rf frequency is increased, the binding peak intensities related to C–CF, CF, and CF2 bondings were increased while the C–C binding peak intensity decreased, possibly indicating the higher CFx/F flux from the plasma as shown in Fig. 3.

Figures 7(a)–7(c) show the C 1s XPS narrow scan data of the SiO2 surface obtained after the etching of SiO2 under the same conditions as those in Fig. 6 with different source rf frequencies of 13.56, 27.12, and 60 MHz, respectively, but in the 50% duty pulse mode. For the pulsed plasma mode, as shown in Figs. 5(a)–5(c), the peak intensities related to C–CF, CF, and CF2 bonding also increased with an increase of rf frequency similar to the CW condition in Fig. 6. In addition, comparison with Fig. 6 shows that pulsing the source power with the 50% duty pulse mode increased the bonding at C–CF, CF, and CF2 on the etched SiO2 surface, indicating increased CFx/F flux from the plasma to the substrate at the same frequency by pulsing the plasma as also shown in Fig. 3.

Using SiO2 wafers patterned with a 100-nm-wide ACL, the etch profiles were observed after the etching of SiO2 as a function of rf source frequency for the CW and pulsed modes. The SiO2 etch time was varied to maintain a similar SiO2 etch depth. To maintain a similar SiO2 etch depth, the etch time was decreased with increasing rf frequency. It was also decreased for the CW mode compared to the pulsed mode due to the decreased SiO2 etch rate with the decreased rf source frequency and with the pulsing as shown in Fig. 2.

Figures 8(a)–8(c) show the SiO2 etch profiles after etching in the CW mode for rf source frequencies of 13.56, 27.12, and 60 MHz. Similar to the results in Fig. 2, due to the increased etch selectivity, the remaining thickness of the ACL was slightly higher for the higher-frequency and pulsed mode conditions. In addition, a reduction of necking near the interface of the ACL and SiO2 was observed with the increase of rf frequency. Figures 9(a)–9(c) show the SiO2 etch profiles after the etching in the 50% duty pulse mode for the source rf frequencies of 13.56, 27.12, and 60 MHz, respectively. As shown in the figures, the pulsing, the profile was improved by decreasing the necking further at the interface of the ACL and SiO2 and it had a more anisotropic etch profile.

4. Conclusions

In this study, SiO2 masked with an ACL has been etched with
Fig. 7. XPS narrow scan C 1s data for SiO₂ surface after etching in the pulse mode (50% duty ratio and 1 kHz pulse frequency): (a) 13.56, (b) 27.12, and (c) 60 MHz. The other conditions are the same as those in Fig. 2.

Fig. 8. (Color online) FE-SEM images of etched SiO₂ contact holes as a function of source frequency in the CW mode. (a) 13.56, (b) 27.12, and (c) 60 MHz. Process conditions: 0.2 kW source rf power, 40 mTorr, and 170/40 sccm Ar/C₄F₈.

Fig. 9. (Color online) FE-SEM images of etched SiO₂ contact holes as a function of source rf frequency under the pulse condition: (a) 13.56, (b) 27.12, and (c) 60 MHz. Process condition: 0.2 kW of source rf power, 40 mTorr, and 170/40 sccm Ar/C₄F₈, 50% duty ratio, and source rf power pulsing with 1 kHz pulse frequency.
increasing rf source frequency from 13.56 to 60 MHz in the CW plasma mode and the pulse plasma mode (50% duty, 1 kHz) while applying 2 MHz CW bias power to the substrate. The effect of increasing source frequency on the SiO$_2$ etch characteristics in the CW and pulse plasma modes was investigated by using a C$_4$F$_8$-based gas in a DF-CCP system. With increasing source rf frequency, the SiO$_2$ etch rate and etch selectivity were increased for both the CW and pulse plasma modes. However, the etch selectivity was more increased in the pulse plasma mode than in the CW plasma mode even though the SiO$_2$ etch rates were decreased by pulsing the plasma. The increased SiO$_2$ etch rates with the increase of rf frequencies for both the CW and pulse modes are believed to be related to the increased ionization and gas dissociation at the higher rf source frequencies. However, the increase of SiO$_2$ etch selectivity over ACL with increasing rf frequencies and by using the pulse mode instead of the CW mode is believed to be related to the increased CF$_x$/F flux to the substrate. OES and XPS results showed the increased CF$_x$/F ratio in the plasma and the CF$_x$ bonding on the etched SiO$_2$ surface, respectively, with the increase of both the source rf frequency and by pulsing the source plasma. An improved SiO$_2$ etch profile was also obtained with the increase of rf source frequency and by pulsing the source plasma. In particular, the significant improvement of the SiO$_2$ etch profile was observed at 60 MHz after the pulsed condition. Therefore, by combining the rf source frequency and pulsing, an anisotropic SiO$_2$ etch profile and high SiO$_2$ etch selectivity over the ACL can be obtained without significantly decreasing the SiO$_2$ etch rate.

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