

Characteristics of SiO₂ etching by using pulse-time modulation in 60 MHz/2 MHz dual-frequency capacitive coupled plasma



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ABSTRACT

60 MHz pulsed radio frequency (rf) source power and 2 MHz continuous wave rf bias power, were used for SiO₂ etching masked with an amorphous carbon layer (ACL) in an Ar/C₄F₈/O₂ gas mixture, and the effects of the frequency and duty ratio of the 60 MHz pulse rf power on the SiO₂ etch characteristics were investigated. With decreasing duty ratio of the 60 MHz pulse rf power, not only the etch rate of SiO₂ but also the etch rate of ACL was decreased, however, the etch selectivity of SiO₂ over ACL was improved with decreasing the duty ratio. On the other hand, when the pulse frequency was varied at a constant duty ratio, no significant change in the etch rate and etch selectivity of both materials could be observed. The variation of the etch characteristics was believed to be related to the change in the gas dissociation characteristics caused by the change in the average electron temperature for different pulsing conditions. The improvement in the etch selectivity with the decrease of duty ratio, therefore, was related to the decreased gas dissociation of C₄F₈ by the decrease of average electron temperature and, which resulted in a change in composition of the fluorocarbon polymer on the etched materials surface from C–C rich to CF₂ rich. With decreasing the duty ratio, not only the etch selectivity but also the improvement in the SiO₂ etch profile could be observed.

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1. Introduction

As the critical dimension (CD) of the semiconductor devices scales down to tens of nanometer for ultra-large scale integrated circuits, the dry etch process is becoming more important due to the difficulty in maintaining the etch rate, etch selectivity, and etch profile for various materials [1–3]. Especially, for the dielectric material etch processing such as SiO₂ contact/via etching, as the aspect ratio increases or as the CD decreases, plasma process induced damages (P2IDs) tend to appear during the etching [4,5]. As one of the methods in reducing the P2IDs, pulsed plasmas have been extensively studied in last few decades [6–9]. A pulsed plasma is generated by periodically turning the rf power on and off. During the rf power off state, the electron temperature is decreased and this decrease, in turn, effectively

decreases the electron energy, and consequently, P2IDs are reduced [10–12].

These days, for the etching of SiO₂ using fluorocarbon plasmas, dual-frequency capacitive coupled plasmas (DF-CCPs) have been widely investigated to control the plasma density and ion bombardment energy, separately [13]. The 60 MHz/2 MHz combined DF-CCP is known to be more effective than other frequency combinations such as 13.56 MHz/2 MHz, 27.12 MHz/2 MHz or 40 MHz/2 MHz in the etching of SiO₂ because the gas dissociation is more effectively progressed at 60 MHz compared to the lower frequencies of 13.56 MHz and 27.12 MHz [14,15]. However, with increasing the source frequency, plasma uniformity tends to be decreased due to the standing wave problem [16,17], and for the improvement of the plasma uniformity at higher frequency operations, pulse plasma has been also investigated [18].

In the etching of SiO₂ with a high aspect ratio contact (HARC), carbon-rich gas mixtures such as Ar/C₄F₈, C₄F₆, etc. are typically used in order to improve the etch selectivity by forming a thick fluorocarbon polymer. However, when 60 MHz/2 MHz combined DF-CCP is used, due to the significant dissociation of those fluorocarbon gases in addition to the standing wave problem of high

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frequency rf power, it is difficult to meet the etching condition of HARC such as CD, etch selectivity, anisotropic profile, etc. especially as the size of contact hole is decreased to low tens of nanometer.

In this study, a pulsed DF-CCP composed of pulsed 60 MHz power on the top electrode as the source power and continuous 2 MHz power on the bottom electrode as the bias power to the substrate was used with a $C_4F_8/Ar/O_2$ gas mixture for the etching of SiO_2 HARC and the effects of 60 MHz source power pulse frequency and duty ratio on the SiO_2 etching characteristics were investigated. Especially, we focused on the etch characteristics such as etch rate, etch selectivity, and etch profile in the 60 MHz/2 MHz DF-CCP system and their relation to the electron temperature and surface chemistry.

2. Experimental

The experimental setup of the DF-CCP etch system used in this study is shown in Fig. 1. This chamber was made of anodized aluminum. The rf discharge was maintained between two 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 (HF) source which can be pulsed to control the plasma characteristics while the bottom electrode was connected to a 2 MHz rf power (LF) to control the ion bombardment energy. The reactor was evacuated by a turbo molecular pumps (3200 l/s) backed by a dry pump. The gas was equally distributed through a baffle system from the top electrode. A tight metal 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 the throttle valve.

The 2.4 μm thick SiO_2 deposited on silicon wafers was masked with a multi layer resist (MLR) structure composed of patterned photoresist layer/70 nm SiON layer/550 nm amorphous carbon layer (ACL). The ACL was used as the hardmask for SiO_2 HARC etching to maintain the CD of the contact hole. Before the etching of SiO_2 , the SiON layer patterned by a photoresist was etched vertically using a fluorocarbon-based continuous wave plasma

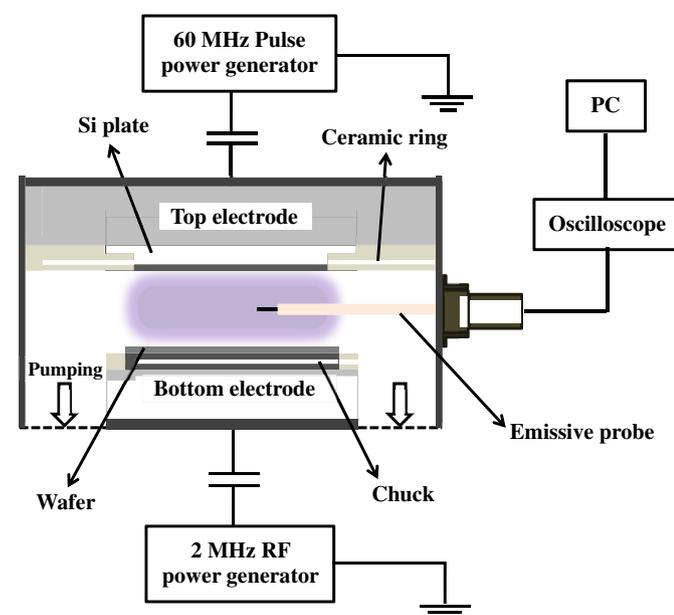


Fig. 1. Schematic diagram of the dual-frequency CCP. 60 MHz rf pulse power was applied to the top electrode to control the plasma characteristics and 2 MHz power was applied to the bottom electrode to control the ion energy to the substrate.

(60 MHz HF power/2 MHz LF power = 200 W/200 W, CF_4/Ar gas mixture = 80/20 sccm, process pressure of 20 mTorr, etch time of 35 s) followed by the ACL etching in a continuous O_2/N_2 plasma (60 MHz HF power/2 MHz LF power = 200 W/200 W, O_2/N_2 gas mixture = 70/30 sccm, process pressure of 20 mTorr, etch time of 50 s). Finally, the SiO_2 layer was etched for various pulse conditions of 60 MHz HF power in a $Ar/C_4F_8/O_2$ gas chemistry (60 MHz HF power/2 MHz LF power = 300 W/500 W, $C_4F_8/Ar/O_2$ = 50/145/5 sccm, process pressure of 20 mTorr) while keeping the substrate temperature at room temperature.

Etch characteristics such as the etch rates of SiO_2 HARC layer/ACL and the etch profiles using the $C_4F_8/Ar/O_2$ gas chemistry were estimated by field emission scanning electron microscopy (FE-SEM, Hitachi S-4700). The instant change of electron temperature for various pulse conditions of 60 MHz HF power in the DF-CCP system was calculated by using an emissive probe. Also, the surface chemistry of the etched SiO_2 for the various pulse conditions was observed using X-ray photoelectron spectroscopy (XPS, ESCA2000, VG Microtech Inc.) by etching blank SiO_2 wafers.

3. Results and discussion

3.1. Etch rate and etch selectivity

The differences in the etch rates of SiO_2 and ACL and their etch selectivities for pulsed and continuous wave plasmas using the DF-CCP system were investigated as functions of pulse duty ratio

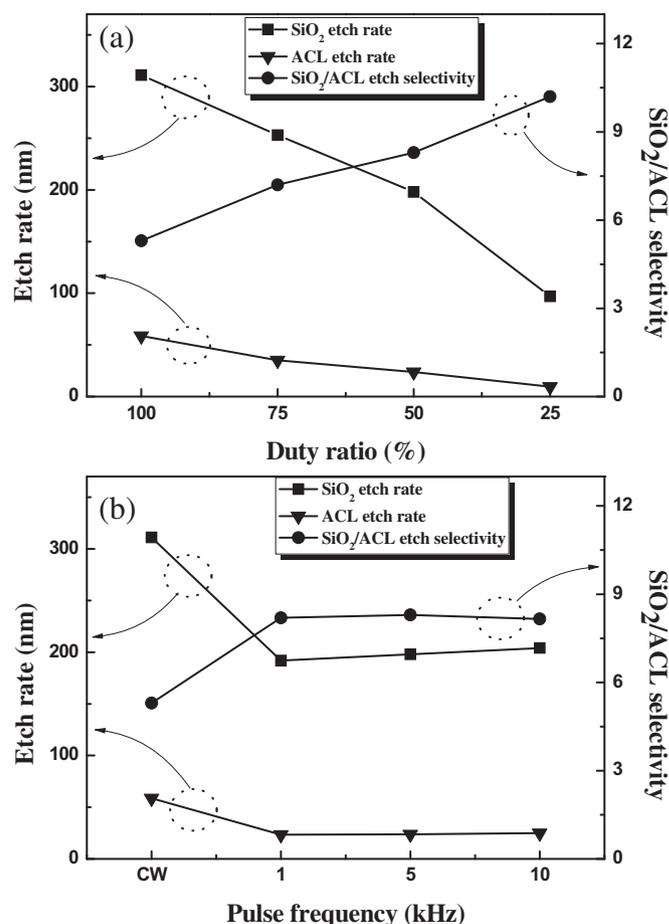


Fig. 2. Etch rates of SiO_2 and ACL and their etch selectivity for the 60 MHz/2 MHz rf power = 300 W/500 W, $Ar/C_4F_8/O_2$ = 150/45/5 sccms, and the process pressure of 20 mTorr as functions of (a) pulse duty ratio and (b) pulse frequency.

(100–25% duty) and pulse frequency (CW ~ 10 kHz) of 60 MHz HF source power and the results are shown in Fig. 2(a) and (b) for the pulse duty ratio and the pulse frequency, respectively. As the SiO₂ pattern etching condition, 300 W of 60 MHz source power, 500 W of 2 MHz bias power, 20 mTorr of operating pressure, and 50/145/5 sccm of C₄F₈/Ar/O₂ gas mixture were used. When the pulse duty ratio was varied, the pulse frequency was fixed at 5 kHz and, when the pulse frequency was varied, the pulse duty ratio was maintained at 50%.

As shown in Fig. 2(a), the etch rates of SiO₂ and ACL were the highest for the CW condition (100% duty percentage) and the decrease of pulse duty ratio decreased the SiO₂ etch rate and ACL etch rate almost linearly due to the decrease in the pulse-on time with the decrease of pulse duty ratio of the 60 MHz HF power. However, as shown in the figure, the etch selectivity of SiO₂ over ACL increased almost linearly with the decrease of pulse duty ratio. On the other hand, when the pulse frequency was varied while keeping the pulse duty ratio at 50%, the etch rates of SiO₂ and ACL were not changed significantly with pulse frequency even though the change from CW to pulse condition decreased the etch rates of SiO₂ and ACL and increased the etch selectivity. To investigate the differences in the etch characteristics on the pulse duty ratio and the pulse frequency, the chemistry of fluorocarbon polymer residue remaining on the etched SiO₂ surface and the instant variation of electron temperature for different pulsing conditions were investigated.

3.2. XPS analysis

Carbon binding states of fluorocarbon polymer remaining on the surface of the etched SiO₂ were investigated using XPS for different

pulse duty ratios including CW of 60 MHz rf power. To analyze the carbon binding states (C_{1s}) of the fluorocarbon polymer on the etched SiO₂, blank SiO₂ wafers were etched about 1 μm with the duty ratio of 100(CW), 75, 50, and 25% and the results are shown in Fig. 3(a)–(d), respectively. As the C_{1s} binding peaks, the peaks related to C–C (284.9 eV), C–CF (287.1 eV), CF (289.4 eV), and CF₂ (293.7 eV) could be observed. As shown, the decrease of the pulse duty ratio increased the bonding peaks related to CF and CF₂, and decreased the bonding peaks related to C–CF and C–C. Therefore, by decreasing the duty ratio, the fluorocarbon polymer residue changed from C–C to CF₂, which is fluorine-rich polymer residue. The change from C–C to CF₂ is believed to be related to the decreased dissociation rate of C₄F₈ with decreasing the pulse duty ratio. When the duty ratio is high and when CW power is used, C₄F₈ is easily dissociated at a high frequency rf power, therefore, a carbon-rich residue tends to form on the etched SiO₂ surface. However, when the pulse duty ratio is low, due to the low dissociation rate of C₄F₈, fluorine-rich polymer residue remains on the SiO₂ surface. Therefore, the lower etch rates of SiO₂ and ACL with the decreasing pulse duty ratio shown in Fig. 2 are related to the low gas dissociation of C₄F₈. However, the higher etch selectivity at the lower pulse duty ratio appears to be related to the different fluorocarbon polymer state remaining on the materials as shown in Fig. 3 which enables the different etch rates between SiO₂ and ACL.

Fig. 4(a)–(d) shows the XPS C_{1s} binding peaks of the fluorocarbon residue remaining on the SiO₂ etched at different pulse frequencies of (b) 1 kHz, (c) 5 kHz, and (d) 10 kHz including (a) CW of 60 MHz rf power. The 60 MHz source power was maintained at 300 W, 2 MHz bias power at 500 W, operating pressure at 20 mTorr, gas mixture of C₄F₈/Ar/O₂ = 50/145/5 sccm, and the pulse duty ratio at 50%. At the different pulse frequencies, the SiO₂ were etched for

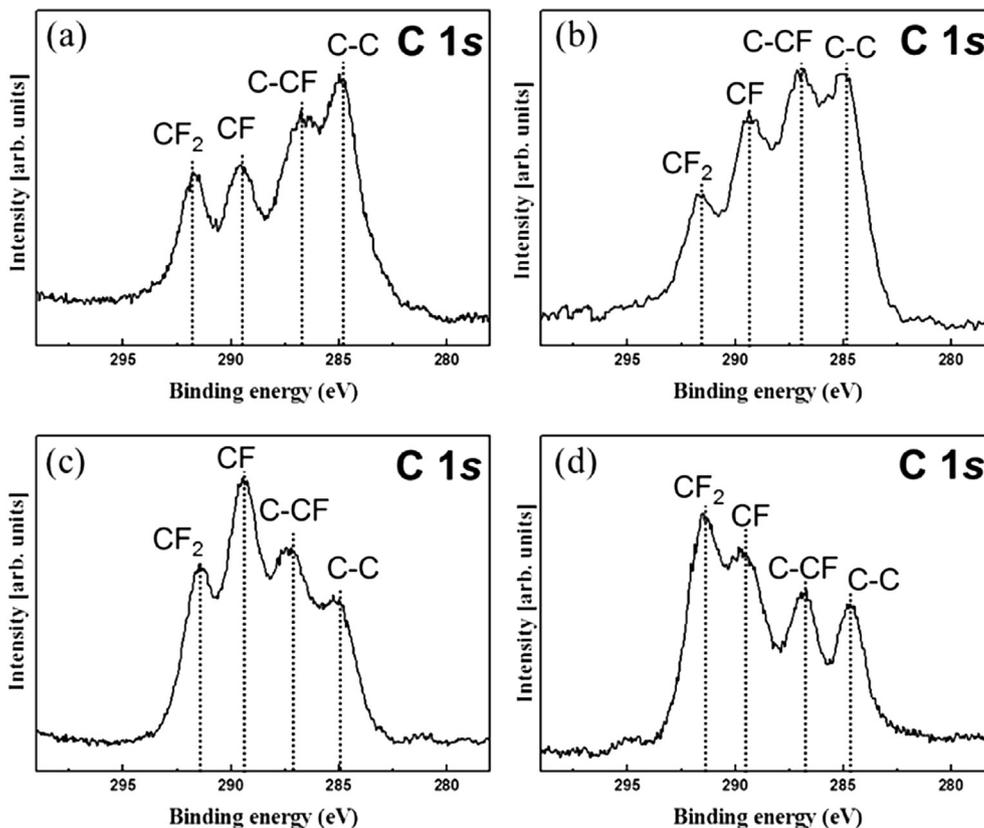


Fig. 3. C_{1s} XPS narrow scan data of the fluorocarbon residue on the SiO₂ surfaces after etching with (a) continuous wave mode, (b) pulse duty ratio of 75%, (c) pulse duty ratio of 50%, and (d) pulse duty ratio of 25%. Pulse frequency was fixed at 5 kHz.

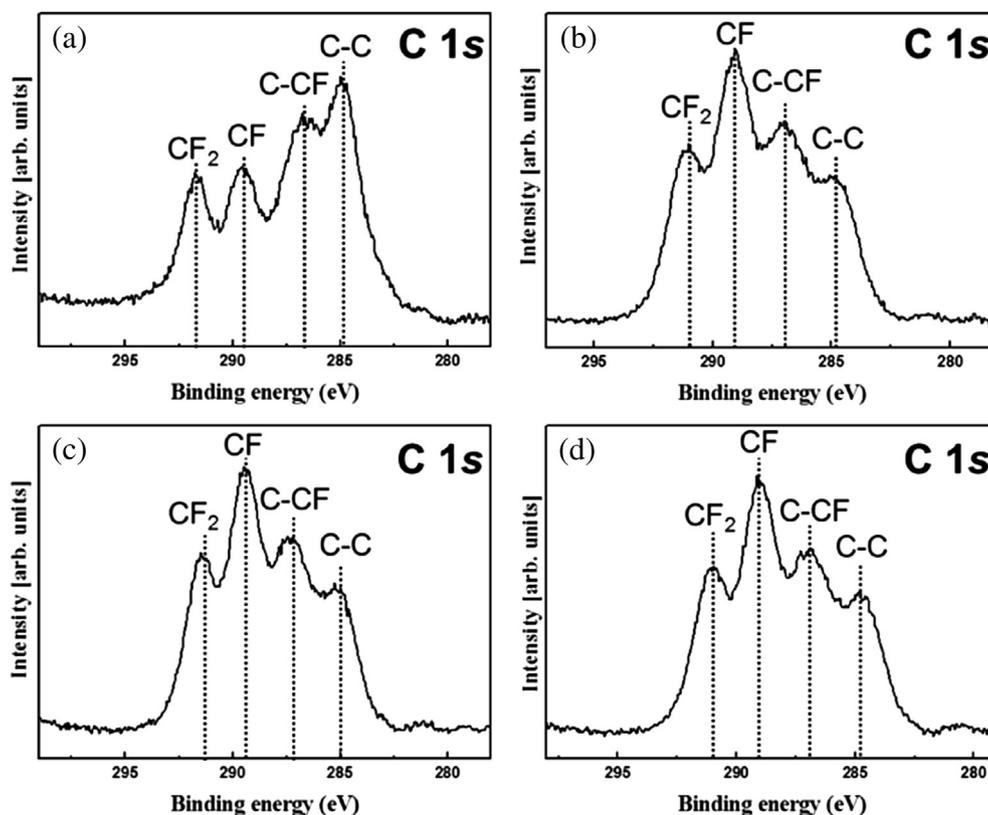


Fig. 4. C_{1s} XPS narrow scan data of the fluorocarbon residue on the SiO_2 surfaces after etching with (a) continuous wave mode, (b) pulse frequency of 1 kHz, (c) pulse frequency of 5 kHz, and (d) the pulse frequency of 10 kHz. Pulse duty ratio was fixed at 50%.

3 min. Compared to the CW plasma, when SiO_2 was etched by pulsed plasmas, the XPS C_{1s} peak showed higher binding peaks related to CF and CF_2 . However, as shown in the figures, the variation of the pulse frequency from 1 to 10 kHz did not change the C_{1s} binding peaks of the fluorocarbon polymer residue, indicating similar gas dissociation characteristics. The XPS results were consistent with the results of etch rates and etch selectivities measured as a function of pulse frequency in Fig. 2(b). The gas

dissociation characteristics in the pulsed plasmas are related to the variation of the plasma characteristics. Therefore, in this study, as one of the important plasma characteristics, the variation of electron temperature in the pulsed plasmas was measured using an emissive probe.

3.3. Electron temperature

When electrons in the plasma have Maxwellian distribution, the electron temperature can be used as the change of electron energy distribution which is related to the gas dissociation characteristics. Due to the deposition characteristics of C_4F_8 , and, due to the noise problem under the pulsing conditions, instead of a typical Langmuir probe, an emissive probe and Ar gas were used and the characteristics of the plasmas were estimated. By heating and floating the probe tip of the emissive probe, instant plasma potential (V_p) and instant floating potential (V_f) during the operation of the pulsed plasma can be measured, respectively, and the instant electron temperature can be estimated using the following formula;

$$V_p - V_f = \frac{kT_e}{2e} \ln\left(\frac{2M}{\pi m}\right)$$

where, k is Boltzmann constant, T_e is electron temperature, m is the electron mass, and M is the atomic mass of the discharge gas [19]. Therefore, using the emissive probe, the effects of rf pulse duty ratio and rf pulse frequency on the change of instant electron temperature were estimated and the results are shown in Figs. 5 and 6, respectively.

Fig. 5 shows the instant change of electron temperature measured as a function of time for the pulse duty ratio of 100(CW),

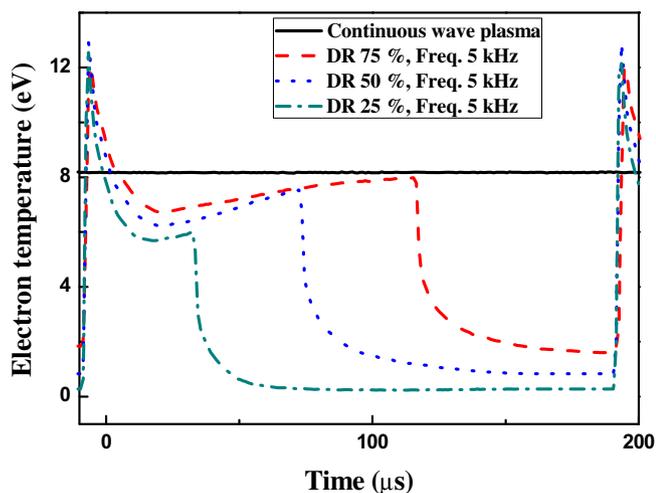


Fig. 5. Instant variation of electron temperature estimated as a function of time for the pulse duty ratio of 100(CW), 75, 50, and 25% at the pulse frequency of 5 kHz. The 60 MHz source power was maintained at 300 W with 150 sccm Ar and at operating pressure of 20 mTorr. No 2 MHz bias power was applied to the substrate.

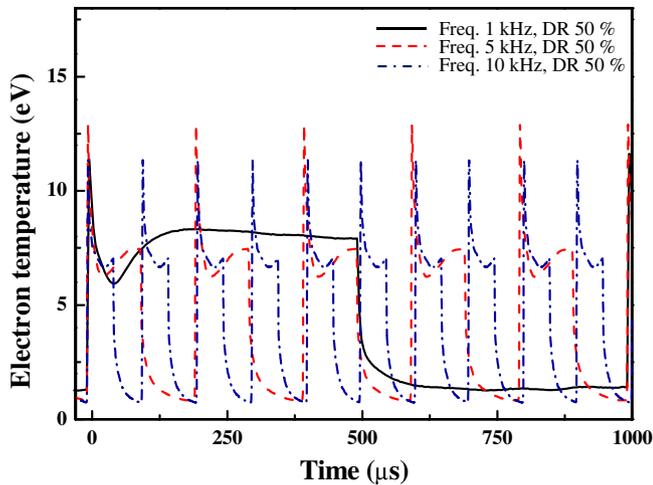


Fig. 6. Instant variation of electron temperature estimated as a function of time for the pulse frequencies of 1, 5, and 10 kHz and at the pulse duty ratio of 50%. Other conditions were maintained same as those in Fig. 5.

75, 50, and 25% and at the pulse frequency of 5 kHz. The 60 MHz source power was maintained at 300 W with 150 sccm Ar and operating pressure of 20 mTorr. No 2 MHz bias power was applied to the substrate. As shown in Fig. 5, for the continuous wave Ar plasma, the electron temperature was measured at about 8.1 eV.

However, as shown in the figure, the decrease of the pulse duty ratio decreased the average electron temperature even though there was an overshoot of instant electron temperature at the initial pulse-on time. Even though the experiment was carried out with an Ar plasma, it is believed that the similar variation of electron temperature can be obtained with reactive fluorocarbon gases such as C_4F_8 . Therefore, a lower average electron temperature obtained with decreasing pulse duty ratio will decrease the dissociation of the fluorocarbon gas in addition to the increased recombination of gas species during the pulse-off time, and which will increase the polymerization on the etched material surface by increasing C_xF_y radical density and decreasing F density in the plasma. Therefore, the higher CF_2 binding of the fluorocarbon residue on the SiO_2 etched with the lower pulse duty percentage shown in Fig. 3 is believed to be related to the decreased dissociation of C_4F_8 gas by decreasing the average electron temperature.

Fig. 6 shows the instant variation of electron temperature measured as a function of time for the pulse frequency of 1, 5, and 10 kHz and at the pulse duty ratio of 50%. Other conditions were maintained same as those in Fig. 5. As shown in the figure, even though the pulse frequency was varied, the instant electron temperature during the pulse-on time was similar at 7–7.5 eV and, after the pulse-off, the electron temperature was rapidly decreased close to 0. Therefore, the average electron temperature was also similar for the pulse frequencies investigated, and which may suggest no significant variation in the dissociation characteristics of fluorocarbon gas for our experimental conditions. No significant

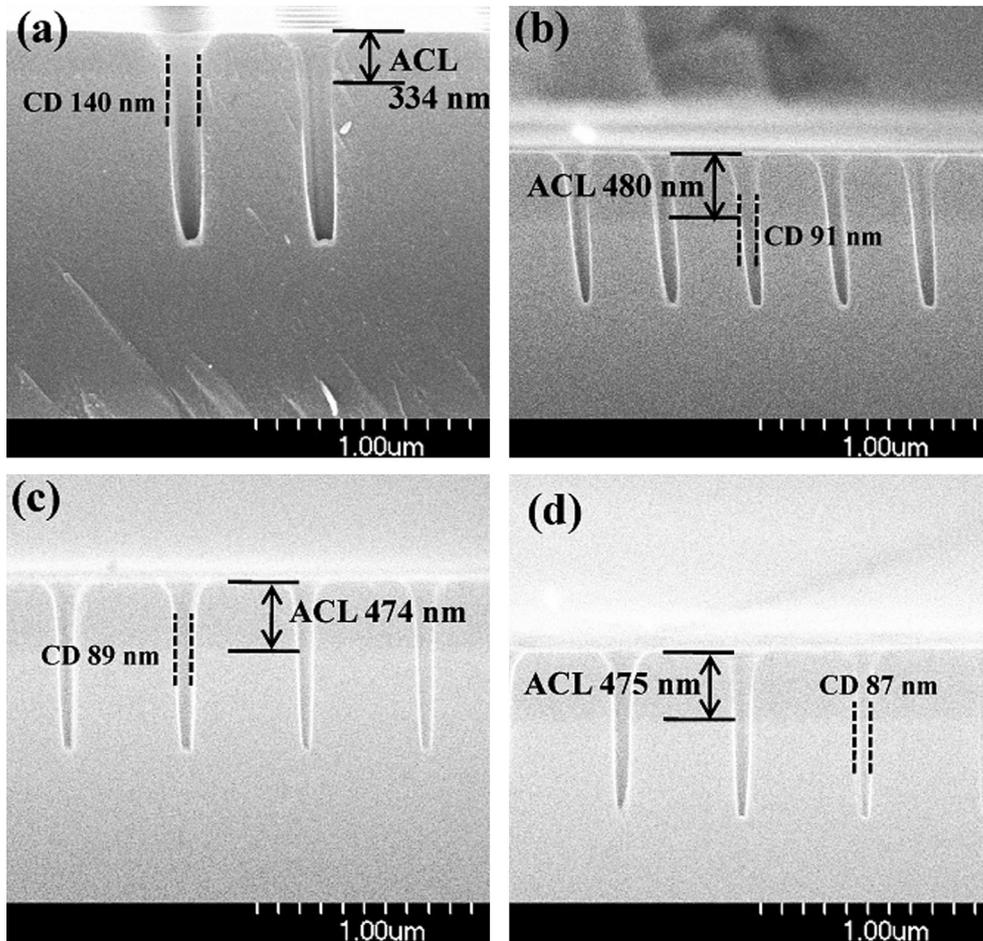


Fig. 7. SiO_2 HARC hole etch profiles observed by FE-SEM after the etching at different pulse frequencies of (b) 1 kHz, (c) 5 kHz, and (d) 10 kHz including (a) CW plasma. The pulse duty ratio was 50% and the etch time was maintained for 3 min. Other etch conditions are the same as those in Fig. 2(b).

change in the etch rates of SiO₂ and ACL and their etch selectivities observed as a function of pulse frequency in our experiment appears to be related to the no significant variation of the fluorocarbon gas dissociation in the plasma.

3.4. Etch profile

Fig. 7(a)–(d) shows the SiO₂ HARC etch profile observed by SEM after the etching at different pulse frequencies of (b) 1 kHz, (c) 5 kHz, and (d) 10 kHz including (a) CW plasma. The pulse duty ratio was 50% and the etch time was maintained for 3 min. Other etch conditions were the same as those in Fig. 2(b). As shown in Fig. 7(a), when SiO₂ contact hole was etched using a CW plasma, even though the etch depths of SiO₂ are higher than those etched by pulsed plasmas, the etch selectivity over ACL was lower and, due to the difficulty in forming sidewall passivation during the etching of SiO₂ contact hole, the SiO₂ contact hole size was increased significantly after the etching. However, by using the pulsed plasmas, due to the formation of C_xF_y radicals in the plasma and due to the formation of

a fluorocarbon residue having more CF_x (x = 1–2) binding on the surface, not only the etch selectivity but also the contact hole size and etch profile were improved due to the formation of enough sidewall passivation during the etching even though the SiO₂ etch rates are lower than that etched using a CW plasma. However, the SiO₂ contact hole etch characteristics measured as a function of pulse frequency from 1 to 10 kHz such as etch depth of SiO₂ contact hole, the contact hole size, etch profile, etc. were similar each other as expected from the results in Figs. 2(b), 4 and 6. It is known that, the SiO₂ contact hole etch profile is easily distorted due to the charging of the contact hole during the etching. In our pulsed plasmas, the 60 MHz power is pulsed and the 2 MHz rf power applied to the substrate is stayed on during the pulse-off period. Therefore, the bias voltage to the substrate is increased during the pulse-off period and it can improve the SiO₂ contact etch profile by increasing the directionality of the incident ion by increasing the ion bombardment energy to the substrate during the pulse-off period.

Fig. 8(a)–(d) shows the SiO₂ contact hole etch profile observed by SEM after the etching of SiO₂ pattern for different pulse duty

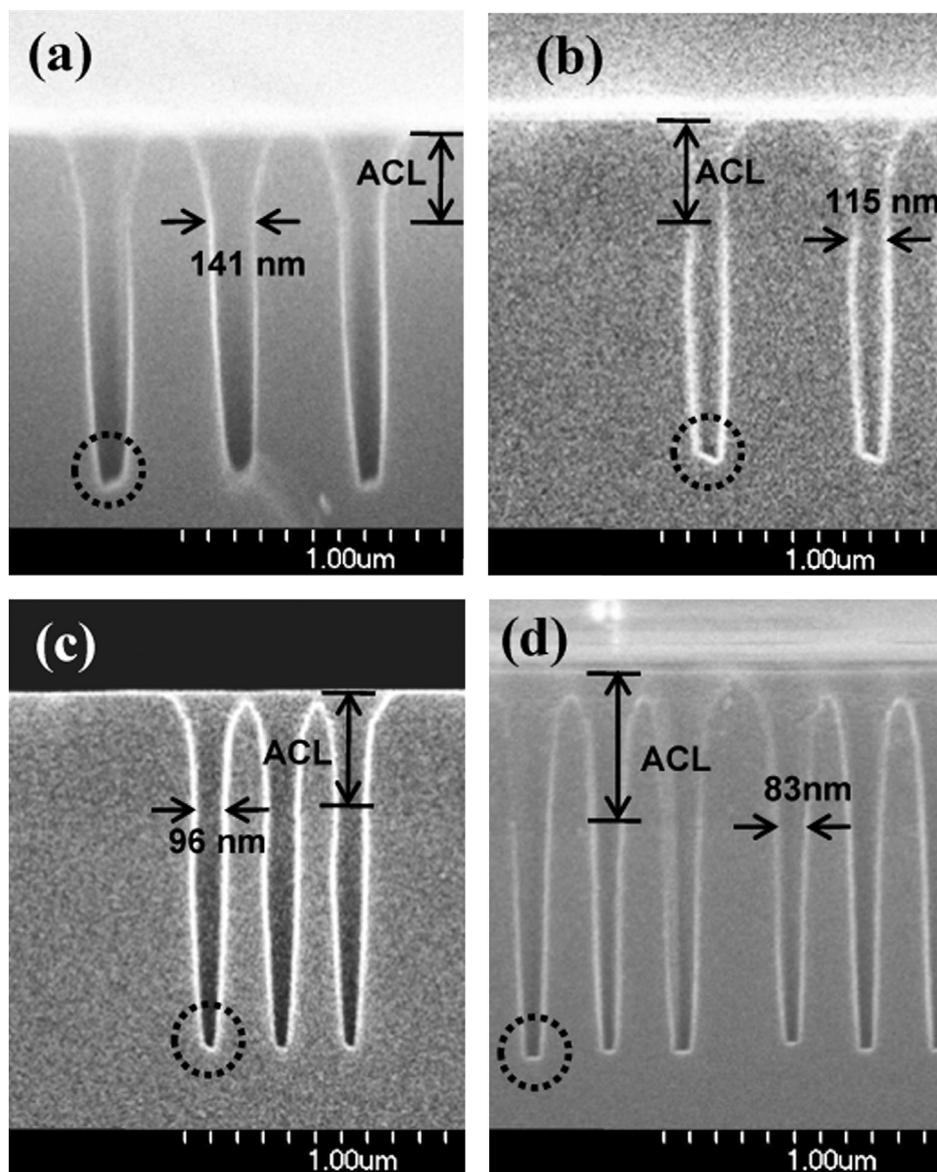


Fig. 8. SiO₂ contact hole etch profiles observed by FE-SEM after the etching of SiO₂ pattern for different pulse duty ratios of (a) 100% (CW), (b) 75%, (c) 50%, and (d) 25% while keeping the pulse frequency at 5 kHz. The etch time was varied to obtain about 1 μm of SiO₂ contact hole etch depth. The other etch conditions are the same as those in Fig. 2(a).

ratios of (a) 100% (CW), (b) 75%, (c) 50%, and (d) 25% while keeping the pulse frequency at 5 kHz. The etch time was varied to obtain about 1 μm of SiO_2 contact hole etch depth. The other etch conditions are the same as those in Fig. 2(a). As shown in the figure, as the pulse duty ratio is decreased from 100% to 25%, the ACL etch rate was decreased and the contact hole size was decreased close to that of ACL mask. The improvement of SiO_2 etch selectivity to ACL and the improvement of contact hole size at the lower pulse duty ratio is believed to be related to the formation of a CF_x -rich ($x = 1-2$) fluorocarbon polymer residue on the surface by the decreased gas dissociation of C_4F_8 gas at the lower average electron energy with the increase of the pulse-off time. In addition, as shown in the figure, the bottom etch profile of SiO_2 contact hole was improved more with the decrease of duty ratio possibly due to the more directional reactive ions due to the increased pulse-off time at the lower pulse duty ratio. However, the use of lower duty ratio of pulsed plasma such as 25% of duty ratio increases the etch time to form a deep SiO_2 contact hole, therefore, too low duty ratio may not be applicable in the actual SiO_2 contact hole etch processing.

4. Conclusions

In this study, 60 MHz/2 MHz DF-CCP, where 60 MHz rf power was applied to the top electrode and 2 MHz rf power was applied to the substrate, was used in the etching of SiO_2 HARC and the effects 60 MHz rf pulsing such as pulse frequency and pulse duty ratio on the SiO_2 etch characteristics have been investigated using C_4F_8 -based gas mixtures. The application of 60 MHz rf power pulsing decreased the etch rate of SiO_2 , however, it improved the etch selectivity of SiO_2 over ACL and also improved the SiO_2 contact etch profile and contact hole size. The decrease of pulse duty ratio of 60 MHz rf power further improved the etch selectivity, the contact etch profile, and the contact hole CD further while decreasing the SiO_2 etch rate, however, the variation of pulse duty frequency at a fixed pulse duty ratio did not change the etch characteristics significantly. XPS C_{1s} narrow scan data of the fluorocarbon polymer layer on the etched SiO_2 surface showed that the decrease of pulse duty ratio increased the binding peaks related to CF_1 and CF_2 bindings, therefore, a CF_x -rich fluorocarbon polymer was formed on the SiO_2 surface during the etching indicating the lower dissociation of C_4F_8 for the decreased pulse duty ratio. The lower dissociation of C_4F_8 for the decreased pulse duty ratio was caused by decreased average electron temperature at the lower pulse duty ratio. However, when the pulse frequency was varied at a fixed duty

ratio, the XPS C_{1s} data showed that carbon binding characteristics of the fluorocarbon residue were not changed significantly due to no significant change in the electron temperature characteristics with the pulse frequency at a fixed pulse duty ratio. The improvement of the SiO_2 contact etch profile with the decrease of pulse duty ratio was also related to more directional reactive ions due to the increased pulse-off time at the lower pulse duty ratio. Even though low pulse duty ratios improves many important etch characteristics, due to the decrease of SiO_2 etch rate, careful study may be required before it is applied to SiO_2 contact hole etch processing.

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