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Angular dependences of SiO_2 etch rates at different bias voltages in CF_4, C_2F_6, and C_4F_8 plasmas

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ABSTRACT

The angular dependences of SiO_2 etch rates at different bias voltages for in CF_4, C_2F_6, and C_4F_8 plasmas were investigated using a Faraday cage system. When the bias voltage was −400 V, the normalized etch yields (NEYs) reached a maximum at 70° in CF_4 and C_2F_6 plasmas, while they decreased monotonically with ion-incident angle in a C_4F_8 plasma. This was because the thickness of the steady-state fluorocarbon film formed on the SiO_2 surface was minimized at an ion incident angle of 70° in CF_4 and C_2F_6 plasmas, while much thicker fluorocarbon films were deposited in a C_4F_8 plasma. When the bias voltage was as high as −1200 V, the thicknesses of the steady-state fluorocarbon films were very thin (less than 2 Å) and nearly unchanged at all ion-incident angles for CF_4 and C_2F_6 plasmas, resulting in nearly the same shape of the NEY curves. In a C_4F_8 plasma, the NEY showed a maximum at an ion-incident angle of 50° because the thickness of the steady-state fluorocarbon film was minimized at this angle.

1. Introduction

Plasma etching of SiO_2 contact holes is one of the key processes in the fabrication of ultra large scale integrated (ULSI) devices [1–4]. In that process, fluorocarbon gases such as CF_4, C_2F_6, and C_4F_8 are widely used as discharge gases [5–7]. As the minimum feature size keeps decreasing, precise control over etch profiles is strongly required during SiO_2 contact hole etching. During plasma etching, the direction of ions incident on the surface of a substrate is not always vertical due to their angular distributions. Therefore, an understanding of the change in etch rate with the angle between the incident ion and the substrate surface is essential to predict and control etch profiles.

The use of a Faraday cage is useful for investigating the angular dependence of etch rates because it allows accurate control over the directions of the ions bombarding the substrate surface [8]. Many studies on the angular dependence of SiO_2 etch rates using Faraday cages have been reported [7–9]. Fluorocarbon plasmas such as CF_4, CHF_3, and C_4F_6 plasmas were used under different process conditions in the cited studies. Discharge chemistry affects etch characteristics such as etch rate. This implies that the angular dependence of SiO_2 etch rates can be affected by discharge chemistry. Therefore, it is necessary to compare the angular dependence of SiO_2 etch rates in various fluorocarbon plasmas under the identical process environments. In addition to discharge chemistry, the bias voltage is also important as it directly determines the energy of ions bombarding the substrate. However, a comprehensive analysis of the effect of discharge chemistry on the angular dependence of SiO_2 etch rates at different bias voltages has not been performed.

In this study, the SiO_2 etch rates at various ion-incident angles in CF_4, C_2F_6, and C_4F_8 plasmas were presented in order to investigate the effect of discharge chemistry on the angular dependences of SiO_2 etch rates. A Faraday cage system was used to control the angle of ions incident on the substrate. The effect of the bias voltage was also investigated by measuring the SiO_2 etch rates at −400 and −1200 V in each fluorocarbon plasma.

2. Experiment

2.1. Inductively coupled plasma system

Etch experiments were performed in an inductively coupled plasma system, as described in a previous study [8]. The inner diameter of the reaction chamber was 200 mm. Separate 13.56 MHz radio-frequency (rf) power generators were used independently to ignite a plasma and bias a sample. The source power was applied to a three-turn coil through a matching box, while the bias power was applied via an electrode with a diameter of 110 mm. A dielectric window (quartz) was located below the induction coil, and the distance between the dielectric window and the electrode was 100 mm.

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2.2. Faraday cage system

A Faraday cage was used to investigate the angular dependence of the etch rates. The Faraday cage was fixed to the electrode in the reaction chamber. The Faraday cage used is a closed box consisting of a cylindrical stainless-steel sidewall (20 mm in height) and a stainless-steel cover grid. The grid diameter and pitch were 0.025 mm and 0.229 mm, respectively. Because the top plane of the Faraday cage was made of a conductive grid, the ions entered the cage perpendicular to the sheath formed along the top plane. The electric potential in the cage was uniform and unaffected by external electric fields. Therefore, the ions travelling inside the cage maintained their initial direction. The utility of a Faraday cage in plasma processing has been reported previously [10–14].

Fig. 1 shows the Faraday cage and substrate arrangement [8]. The ion-incident angle (θ) is defined as the angle between the ion incident direction and the surface normal to the substrate. As the inside of the cage is free of electric fields, the angle of ions incident on a sample substrate could be accurately controlled by varying the angle of the sample holder, which was located inside the cage. In this study, the ion-incident angles were varied in the range 0–90°. The substrates were 500-nm-thick SiO_2 films thermally grown on a p-type Si wafer. Each substrate was cut into a 10 × 5 mm^2 rectangle and placed on the sample holder. The sample holder was fixed on a 3-mm-thick quartz wafer, which was used as the bottom plate.

2.3. Etching of SiO_2

CF_4, C_2F_6, and C_4F_8 were separately used as discharge gases. The following process conditions were maintained for all discharge gases: pressure = 10 mTorr, flow rate = 30 sccm, source power = 250 W, bias voltage = −400 and −1200 V, and electrode temperature = 15 °C. The low (−400 V) and high (−1200 V) values of bias voltage were selected to effectively observe the effect of bias voltage on the angular dependence of the SiO_2 etch rate.

2.4. Measurements of the etch rate

The etch rates (or deposition rates) of the samples were obtained by measuring changes in the thickness of the substrate film with a thickness meter (model SecraThick 2000-Deluxe). In all cases, the thickness was measured at 9 mm from the bottom of the sample holder.

3. Results

Fig. 2 shows the etch rate (ER) and normalized etch rate (NER) of SiO_2 as a function of ion-incident angle at a bias voltage of −400 V in CF_4, C_2F_6, and C_4F_8 plasmas. As seen in Fig. 2(a), the etch rates monotonically decreased with increasing ion-incident angle in all plasmas. When

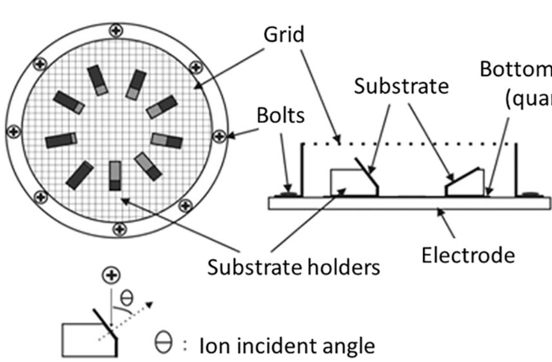

Fig. 1. Schematic diagrams of the Faraday cage and the substrate arrangement in the cage [8]. The ion-incident angle (θ) is defined as the angle between the ion-incident direction and the surface normal to the substrate.

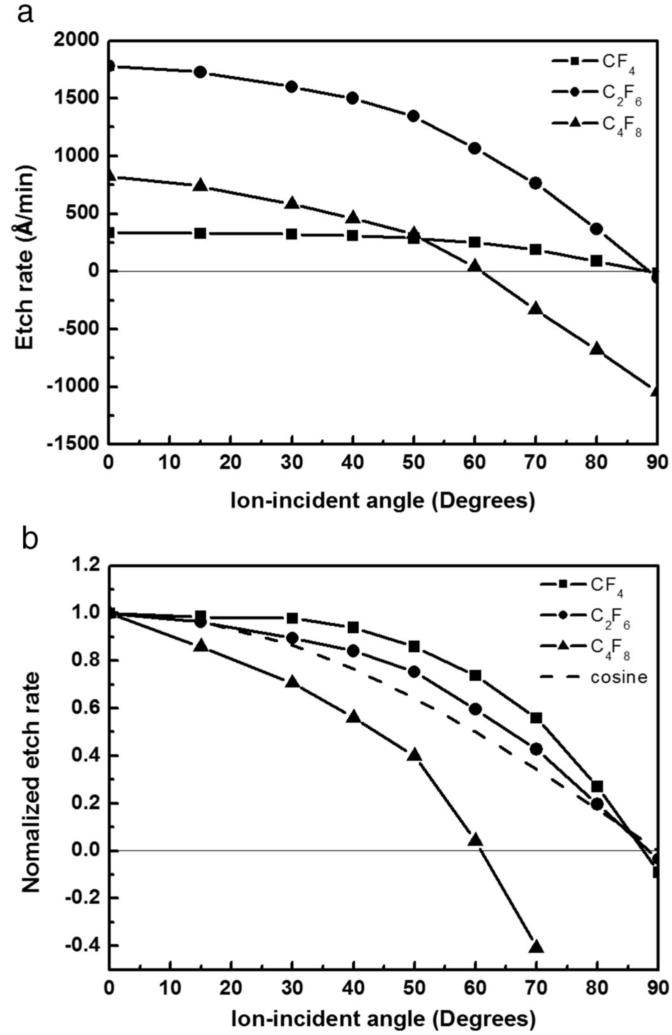

Fig. 2. Angular dependences of (a) etch rates and (b) normalized etch rates of SiO_2 at a bias voltage of −400 V in CF_4, C_2F_6, and C_4F_8 plasmas.

the ion-incident angle was 90°, the etch rates became negative. This indicates that a net deposition occurred at this angle because deposition and etching take place simultaneously in fluorocarbon plasmas. In the C_4F_8 plasma, the etch rate of SiO_2 decreased more rapidly than those in the CF_4 and C_2F_6 plasmas, and the deposition of the fluorocarbon film was observed at a lower ion-incident angle (~60°).

In order to clearly observe the extent to which the etch rate decreases with ion-incident angle, the NER as a function of ion-incident angle is shown in Fig. 2(b). The NER was obtained by normalizing the ER at a specific angle with respect to the ER on the horizontal surface. In the NER curve, the dotted line represents the cosine distribution, which is known to correspond to the changes in the flux of ions incident on the sample [6]. In the CF_4 and C_2F_6 plasmas, the NERs exceeded the cosine values except for 90°. On the other hand, the NERs in the C_4F_8 plasma were below the cosine values at all ion-incident angles. The behavior of the NERs in the various fluorocarbon plasmas implies that etching of SiO_2 is affected by factors additional to the flux of ions incident on the substrate surface.

Fig. 3 shows the ER and NER of SiO_2 as a function of ion-incident angle at a bias voltage of −1200 V in the CF_4, C_2F_6, and C_4F_8 plasmas. As in the case of a low bias voltage (−400 V), the etch rates at a high bias voltage (−1200 V) decreased with increasing ion-incident angle, shown in Fig. 3(a). As expected, the etch rates at −1200 V were higher than those at −400 V at all ion-incident angles in the corresponding plasmas. It is interesting to note that even the deposition rate of

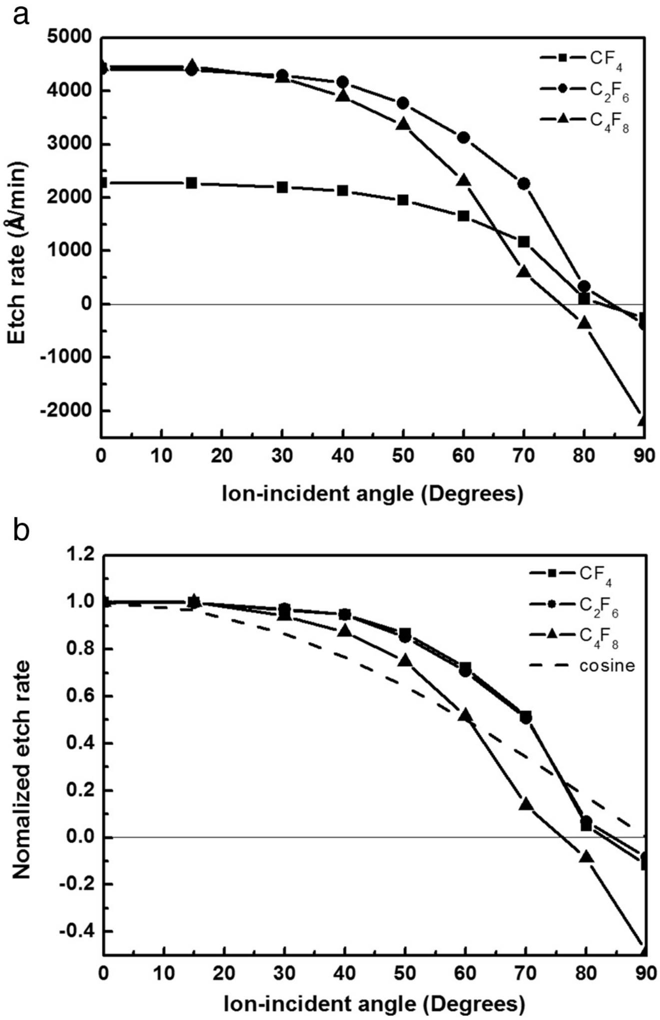

Fig. 3. Angular dependences of (a) etch rates and (b) normalized etch rates of SiO_2 at a bias voltage of −1200 V in CF_4, C_2F_6, and C_4F_8 plasmas.

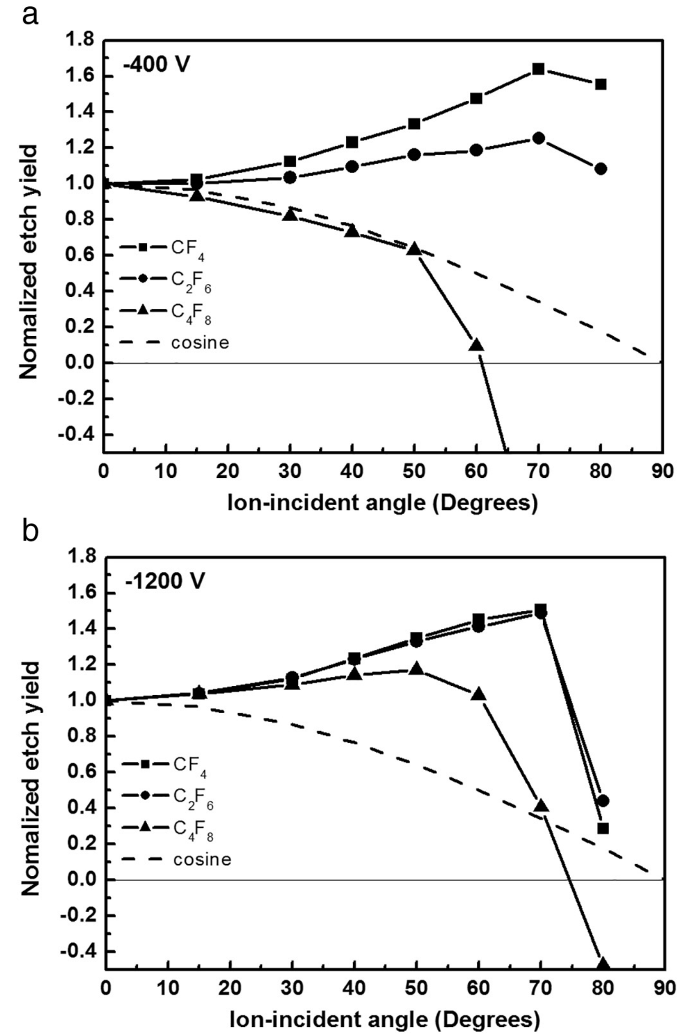

Fig. 4. Angular dependence of normalized etch yields of SiO_2 in CF_4, C_2F_6, and C_4F_8 plasmas. The bias voltages were (a) −400 V and (b) −1200 V.

fluorocarbon films obtained at high ion-incident angles had larger values at −1200 V than at −400 V. It was previously reported that the deposition rates of the fluorocarbon films increased with bias voltage when the ion-incident angles were nearly parallel to the surface of the substrate [9]; these correspond to the high ion-incident angles in our study.

As shown in Fig. 3(b), the NERs of SiO_2 at −1200 V presented a different behavior from those at −400 V. The NERs in the CF_4 and C_2F_6 plasmas were nearly identical to each other. In addition, the NERs were higher than the cosine curve at ion angles up to 70°. In the C_4F_8 plasma, the NERs were lower than the cosine values at ion angles higher than 60°. These results explicitly suggest that the magnitude of bias voltage and the type of fluorocarbon plasma affect the characteristics of SiO_2 etching.

The angular dependences of the ER and NER contain the effect of the change in ion flux with ion-incident angle. Therefore, it is more relevant to use the etch yield (EY), which shows the etch rate per ion flux on the substrate, rather than etch rate for the investigation of ion-surface interactions at various ion-incident angles [7]. The EY is obtained using the following eq. [15]:

$$\mathrm{EY} = \frac{\mathrm{ER}(\theta)}{\Gamma_i \ \cos\theta} \tag{1}$$

where Γ_i is the ion flux normal to the substrate surface.

Fig. 4 shows the angular dependence of the normalized etch yield (NEY) of SiO_2 at bias voltages of −400 and −1200 V in CF_4, C_2F_6, and C_4F_8 plasmas, respectively. The NEY was defined as the etch yield at a specific angle divided by the etch yield on the horizontal surface, EY(θ) / EY(0°). From Eq. (1), it can be calculated that the NEY at an ion-incident angle of θ is equal to NER(θ) / cosθ. At a bias voltage of −400 V, the NEY showed a strong dependence on the type of fluorocarbon plasma [Fig. 4(a)]. The NEYs had a maximum at 70° in CF_4 and C_2F_6 plasmas, and their maximum values were 1.64 and 1.25, respectively. On the other hand, the NEY gradually decreased with ion-incident angle in the C_4F_8 plasma. At a bias voltage of −1200 V, the NEYs of CF_4 and C_2F_6 plasmas showed a maximum at an ion-incident angle of 70°, and the NEY curves were nearly the same even though their maximum values were slightly different (1.46 and 1.42, respectively). In the C_4F_8 plasma, the NEY had a maximum value of 1.17 at an ion–incident angle of 50°.

The NEY curves suggest that etching mechanism of SiO_2 depends on the magnitude of bias voltage and the type of fluorocarbon plasma. It is known that physical sputtering is the main etching mechanism when the etch yield reaches a maximum at angles between 40 and 70° [16]. Therefore, at a bias voltage of −400 V, physical sputtering is a major contributor to the SiO_2 etching while it does not play an important role for a C_4F_8 plasma. However, at a bias voltage of −1200 V, physical sputtering is a major contributor in all the fluorocarbon plasmas used in this study. This is because the bias voltage (thus ion energy) is so high that discharge chemistry barely affects the etching mechanism.

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4. Discussion

During etching in fluorocarbon plasmas, a thin steady-state fluorocarbon film is formed on the substrate surface as a result of the competition between fluorocarbon deposition and substrate etching. The steady-state fluorocarbon film prevents ions from directly colliding with the substrate surface and reduces the diffusion of reactive radicals into the substrate [2,17], which affects the etch yield curve. Therefore, it is necessary to investigate the characteristics of the steady-state fluorocarbon film under the process conditions used in this study.

4.1. Characteristics of steady-state fluorocarbon films formed on the SiO_2 surface at −400 V

Fig. 5 shows the thicknesses of the steady-state fluorocarbon films formed on the SiO_2 surfaces at ion-incident angles of 0, 50, and 70° in CF_4, C_2F_6, and C_4F_8 plasmas at a bias voltage of −400 V. The thickness of the steady-state fluorocarbon film formed on a SiO_2 surface was calculated from the changes in the silicon 2p X-ray photoemission spectra during etching [18]. The steady-state fluorocarbon film at an angle of 70° in C_4F_8 plasma could not be obtained because deposition rather than etching occurred at this angle [see Fig. 2(a)].

In CF_4 and C_2F_6 plasmas, the thickness of the steady-state fluorocarbon film decreased with increasing ion-incident angle from 0 to 70°. This change corresponds to the results that the NEY had maximum values at 70° in CF_4 and C_2F_6 plasmas [see Fig. 4(a)]. In other words, the steady-state fluorocarbon film formed on the SiO_2 surface was more suppressed with increasing ion-incident angle up to 70° because the energy transferred from the ions to the surface reached a maximum at this angle. On the other hand, the thickness of the steady-state film in a C_4F_8 plasma slightly decreased from 8.3 to 8.1 Å with increasing ion-incident angle from 0 to 50°. Moreover, the deposition of fluorocarbon films, rather than SiO_2 etching, was observed at ion-incident angles higher than 70°.

During etching in fluorocarbon plasmas, it is known that CF_2 radicals are the main precursors for the formation of fluorocarbon films on the substrates [19]. Since each fluorocarbon plasma is expected to produce a different amount of reactive fluorocarbon species such as CF_2, optical emission spectroscopy (OES) measurements were performed to investigate the characteristics of the CF_2 radicals produced in the various fluorocarbon plasmas. Fig. 6 shows the optical emission intensity of the CF_2 peak in CF_4, C_2F_6, and C_4F_8 plasmas. The discharge condition for the OES measurements was the same as that for SiO_2 etching except for the zero bias voltage (source power = 250 W, pressure = 10 mTorr, flow rate = 30 sccm, and bias voltage = 0 V). The intensity of the CF_2 peak in the C_4F_8 plasma was about 3–5 times larger than that in the CF_4 and C_2F_6 plasmas, implying that thicker fluorocarbon films are deposited in a C_4F_8 plasma than in CF_4 and C_2F_6 plasmas. This led that the thickness of the steady-state fluorocarbon film in a C_4F_8 plasma decreased slightly (or was nearly unchanged) with increasing ion-incident angle. In this case, it is thought that most of the ion energy transferred to the surface is consumed to suppress the film growth and dissipated in the steady-state fluorocarbon film.

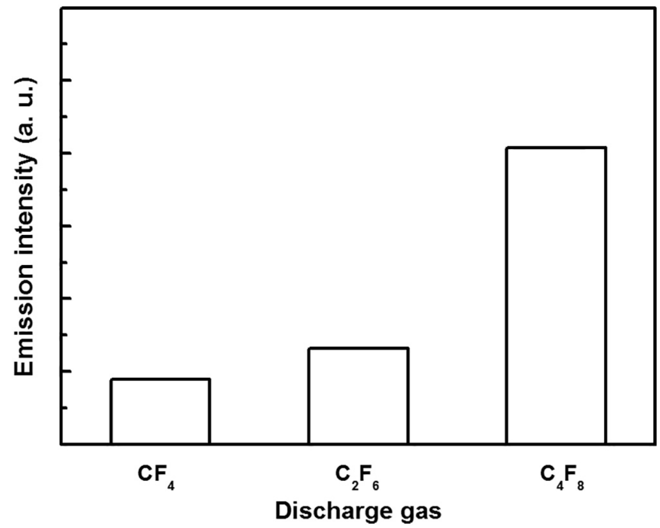

Fig. 6. Optical emission intensity of the CF_2 peak in CF_4, C_2F_6, and C_4F_8 plasmas.

It is worth examining the dependences of the steady-state fluorocarbon film thickness and CF_2 intensity on discharge chemistry. The optical emission intensities of CF_2 radicals (main precursors for the formation of fluorocarbon films) increased in the order of $CF_4 < C_2F_6 < C_4F_8$ plasmas (see Fig. 6) while the thickness of steady-state fluorocarbon films increased in the order of $C_2F_6 < C_4F_8 < CF_4$ plasmas (see Fig. 5). This is because the etch resistance of the fluorocarbon films depends on the type of fluorocarbon plasma. The etch resistance of the fluorocarbon films is characterized with fluorine-to-carbon (F/C) ratio of the film. Fig. 7 shows the F/C ratio of the steady-state fluorocarbon films formed on the horizontal SiO_2 surfaces in CF_4, C_2F_6, and C_4F_8 plasmas at a bias voltage of −400 V. The F/C ratios of the films were calculated from

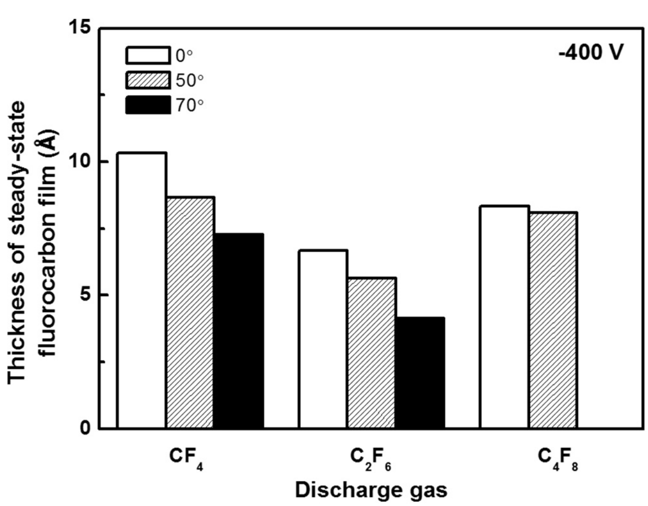

Fig. 5. Thickness of the steady-state fluorocarbon films formed on the SiO_2 surfaces at a bias voltage of −400 V in CF_4, C_2F_6, and C_4F_8 plasmas.

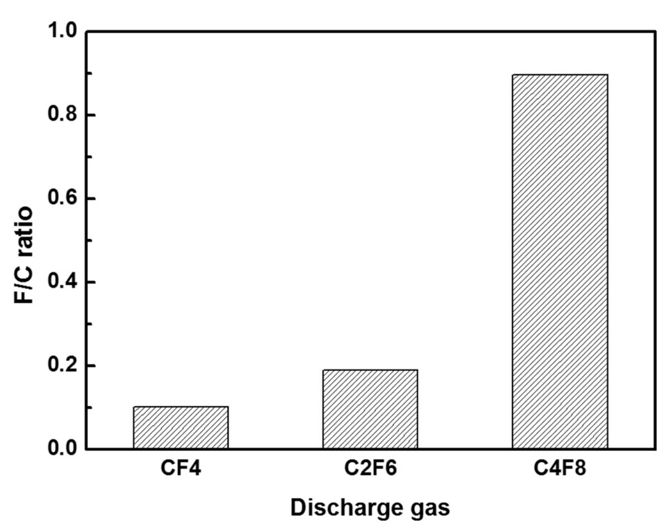

Fig. 7. F/C ratio of the steady-state fluorocarbon films formed on the horizontal SiO_2 surfaces at a bias voltage of −400 V in CF_4, C_2F_6, and C_4F_8 plasmas.

their carbon 1 s X-ray photoemission spectra [20]. It is seen that the F/C ratio of the steady-state fluorocarbon films decreased in the order of C_4F_8 > C_2F_6 > CF_4 plasmas. A fluorocarbon film with a lower F/C ratio is known to be crosslinked more strongly, resulting in enhancement of the etch resistance of this film [21]. For example, the fluorocarbon film deposited in a CF_4 plasma is subject to be etched at the lowest rate due to its lowest F/C ratio. Since the formation of a steady-state fluorocarbon film during etching in fluorocarbon plasmas is a net result from deposition and etching of the fluorocarbon film, the order of the thickness of the steady-state fluorocarbon film is not necessarily the same as that of the CF_2 intensity.

4.2. Characteristics of steady-state fluorocarbon films formed on the SiO_2 surface at −1200 V

Fig. 8 shows the thicknesses of the steady-state fluorocarbon films formed on the SiO_2 surfaces at ion-incident angles of 0, 50, and 70° in CF_4, C_2F_6, and C_4F_8 plasmas when the bias voltage was −1200 V. In CF_4 and C_2F_6 plasmas, the thicknesses of the steady-state fluorocarbon films were very thin (less than 2 Å) at all ion-incident angles. In addition, they decreased very slightly (or nearly unchanged) with increasing ion-incident angle. Considering the atomic radii of carbon (70 pm) and fluorine (40 pm), the thickness of the steady-state fluorocarbon film formed on the SiO_2 surfaces corresponds to a few monolayers. This very thin steady-state fluorocarbon film resulted from a high bias voltage (or high ion energy). When the ion energy is high enough for the ion to pass through the steady-state fluorocarbon film, the underlying SiO_2 surface is directly affected by the bombardment of incident ions so that the steady-state fluorocarbon film becomes thin. The very thin steady-state fluorocarbon films in both CF_4 and C_2F_6 plasmas can also support the NEY curves of CF_4 and C_2F_6 plasmas. As seen in Fig. 4(b), the NEY curves of CF_4 and C_2F_6 plasmas were nearly the same. This implies that the steady-state fluorocarbon films in CF_4 and C_2F_6 plasmas are thin enough so that their performances as etch barriers are negligible.

On the other hand, in a C_4F_8 plasma, the thickness of the steady-state fluorocarbon film formed on the horizontal SiO_2 surface was 3.5 Å, which was higher than that in CF_4 and C_2F_6 plasmas. This may be due to the presence of more CF_2 radicals in a C_4F_8 plasma than in CF_4 and C_2F_6 plasmas. The film thickness slightly decreased to 2.5 Å at an ion-incident angle of 50°. At an ion-incident angle of 70°, the film thickness drastically increased to 26 Å. This characteristic change in the steady-state fluorocarbon film supports the shape of the NEY curve in a C_4F_8 plasma [see Fig. 4(b)]. The NEY showed a maximum at an ion-incident angle of 50° because the thickness of the steady-state fluorocarbon film formed on the SiO_2 surface was minimized at this angle.

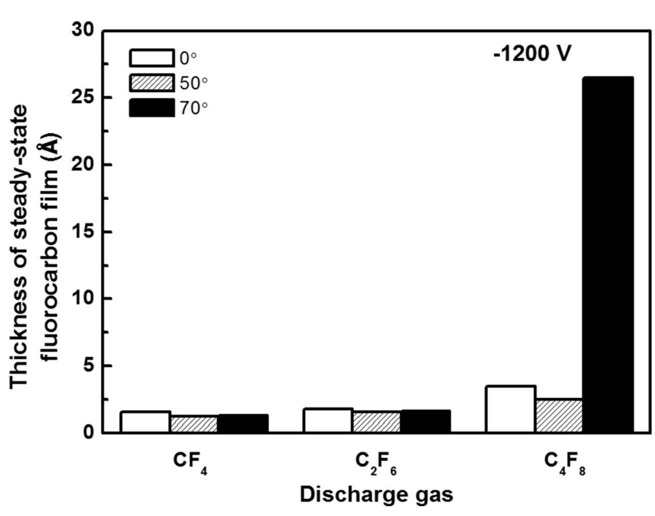

Fig. 8. Thickness of the steady-state fluorocarbon films formed on the SiO_2 surfaces at a bias voltage of −1200 V in CF_4, C_2F_6, and C_4F_8 plasmas.

5. Conclusions

The angular dependence of the SiO_2 etch rate in fluorocarbon plasma such as CF_4, C_2F_6, and C_4F_8 plasmas was investigated at different bias voltages. The etch rates of SiO_2 monotonically decreased with increasing ion-incident angle in all the plasmas studied regardless of bias voltage. However, the angular dependence of the NEY of SiO_2 showed different behaviors depending on the bias voltage.

When the bias voltage was −400 V, the NEY gradually decreased with ion-incident angle in C_4F_8 plasma while they had a maximum at 70° in CF_4 and C_2F_6 plasmas and their corresponding maximum values were 1.64 and 1.25, respectively. The characteristic change in the NEY with ion-incident angle was attributed to the dependence of the steady-state fluorocarbon film thickness on the ion-incident angle. In CF_4 and C_2F_6 plasmas, the thickness of the steady-state fluorocarbon film formed on the SiO_2 surface was minimized at an ion incident angle of 70°, leading to maximum NEY values at this angle. In the C_4F_8 plasma, the thickness of the steady-state fluorocarbon film was barely affected by the ion-incident angle because thicker fluorocarbon films were deposited in this plasma than in CF_4 and C_2F_6 plasmas. This led to a gradual decrease in the NEY with ion-incident angle.

When the bias voltage was −1200 V, the NEYs in CF_4 and C_2F_6 plasmas showed a maximum at an ion–incident angle of 70° and the NEY curves were nearly identical even though their maximum values were slightly different (1.46 and 1.42, respectively). In these plasmas, the thicknesses of the steady-state fluorocarbon films formed on the SiO_2 surface were very thin (less than 2 Å) at all ion-incident angles, and they decreased very slightly (nearly unchanged) with increasing ion-incident angle. This very thin steady-state fluorocarbon film barely performed as an etch barrier, resulting in nearly identical shapes of the NEY curves. In the C_4F_8 plasma, the NEY showed a maximum at an ion-incident angle of 50° because the thickness of the steady-state fluorocarbon film that formed on the SiO_2 surface was minimized at this angle.

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