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Hydrogen effects in hydrofluorocarbon plasma etching of silicon nitride: Beam study with CF^+ , CF_2^+ , CHF_2^+ , and CH_2F^+ ions

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Hydrogen in hydrofluorocarbon plasmas plays an important role in silicon nitride (Si_3N_4) reactive ion etching. This study focuses on the elementary reactions of energetic CHF_2^+ and CH_2F^+ ions with Si_3N_4 surfaces. In the experiments, Si_3N_4 surfaces were irradiated by monoenergetic (500–1500 eV) beams of CHF_2^+ and CH_2F^+ ions as well as hydrogen-free CF_2^+ and CF^+ ions generated by a mass-selected ion beam system and their etching yields and surface properties were examined. It has been found that, when etching takes place, the etching rates of Si_3N_4 by hydrofluorocarbon ions, i.e., CHF_2^+ and CH_2F^+ , are higher than those by the corresponding fluorocarbon ions, i.e., CF_2^+ and CF^+ , respectively. When carbon film deposition takes place, it has been found that hydrogen of incident hydrofluorocarbon ions tends to scavenge fluorine of the deposited film, reducing its fluorine content.

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I. INTRODUCTION

Recently, there have been various needs for highly selective Si_3N_4 etching processes. Selective etching of SiO_2 over Si_3N_4 has been widely used in microelectronics fabrication processes such as contact hole etching in self-aligned processes. Selective etching of Si_3N_4 over SiO_2 and/or Si are also used in processes such as the formation of a dual stress liner and dual/triple hard mask (DHM/THM) etching processes of dual-damascene structures.^{1,2} In such processes, higher selectivity of Si_3N_4 over SiO_2 or Si than what is currently available is more desirable.

In Si_3N_4 etching processes, plasmas based hydrofluorocarbon gases such as CHF_3 and CH_2F_2 are typically used. Etching chemistry by $\text{C}_x\text{H}_y\text{F}_z^+$ ions (with x , y , z being some integers) generated in such plasmas significantly affects etch selectivities among Si_3N_4 , SiO_2 , and Si. For example, it has been known that hydrogen gas added to a fluorocarbon plasma in reactive ion etching (RIE) processes increases Si_3N_4 etch rates,³ which suggests that hydrogen in hydrofluorocarbon plasmas plays a determining role for etching rates of Si_3N_4 .

The goal of this study is to understand etching characteristics of Si_3N_4 in fluorine based plasma etching processes, especially in comparison to those of SiO_2 and Si. A better understanding of Si_3N_4 etching mechanisms is likely to contribute to the development of more selective Si_3N_4 etching processes. In the work presented in this letter, we focus on elementary surface reactions of CHF_2^+ and CH_2F^+ ions with an Si_3N_4 surface. These ions are considered to be abundant in hydrofluorocarbon plasmas generated from CHF_3 or CH_2F_2

gas. Here, a special emphasis is placed on the understanding of the role of hydrogen in Si_3N_4 , SiO_2 , and Si etching processes.

II. EXPERIMENT

To achieve these objectives, we have used a mass-selected ion beam system^{4,5} that can control the injection energy and dose of beam ions with high accuracy. To clarify the effects of hydrogen in Si_3N_4 etching reactions, we performed ion beam etching experiments for Si_3N_4 surfaces by CHF_2^+ and CH_2F^+ ions and compared the results with those by CF_2^+ and CF^+ ions. We also performed similar experiments for Si and SiO_2 substrates and compared the results with those of Si_3N_4 . When the ion beam energy is not sufficiently high, a fluorinated carbon layer is formed on the substrate surface. Surface characteristics of such fluorinated carbon layers were examined by *in situ* x ray photoelectron spectroscopy (XPS).

The mass-selected ion beam system used in this study consists of three parts—an ion source, a mass selecting magnet, and a reaction chamber. Ions are generated by arc discharge in the Freeman-type ion source and are first accelerated up to 25 keV. Ions with a specific mass are selected by the mass selecting magnet. The selected ions are then decelerated to have the desired energy by the deceleration electrode and directed toward a sample surface placed in the reaction chamber. In this beam system, the ion energy range is 0–2000 eV. The ion beam current is evaluated by a Faraday cup that has a pinhole of 1 mm in diameter in its front. When the beam current is evaluated, the Faraday cup is placed at the substrate location. A substrate used in this study is a 1.5 cm × 1.5 cm square wafer chip, on which either a 300 nm thick Si_3N_4 film may be formed by chemical

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vapor deposition (CVD) or a SiO_2 film may be thermally grown. Change in the chemical nature of the substrate surface during the process may be observed with *in situ* XPS, which is installed in the reaction chamber.

In the ion beam system, the reaction chamber is maintained in ultrahigh vacuum conditions at 10^{-8} Pa by three differential pumps placed between the mass selecting magnet and the reaction chamber. The ion dose (which is evaluated from the exposure time and ion current) used in this study is typically in the range of $1.0\text{--}2.0 \times 10^{17}$ ions/cm². Change in thickness of the substrate is measured by an optical interference with a refractive index of 1.465 for SiO_2 and 1.987 for Si_3N_4 . The etching yield is obtained from the loss of surface materials (estimated from the change in film thickness) and the ion beam dose. In the evaluation of an etching yield, the largest possible error could arise from beam current fluctuation. In our experiments, beam current fluctuations are closely monitored and made sure to be limited within $\pm 5\%$. Accordingly, the largest possible errors in our yield evaluation are also limited within $\pm 5\%$.

III. RESULTS AND DISCUSSION

Figure 1 shows etching yields of Si, SiO_2 , and Si_3N_4 by CHF_2^+ and CF_2^+ ion irradiation as functions of the injection energy obtained in this study. The size of possible error for each data point is represented essentially by the size of its symbol given in Fig. 1. The CF_2^+ and CHF_2^+ ion beams were generated from CHF_3 gas. The ion dose for each yield measurement was approximately $1.5\text{--}1.7 \times 10^{17}$ ions/cm². The solid curves denoted as SiO_2 and Si are fitting curves for SiO_2 and Si etching yields by CF_2^+ ion beams obtained in previous experimental studies (some of which are given in Refs. 4 and 6), excluding data obtained in this study (denoted by the open and gray triangles). At least four data points (not shown here) were used to derive each fitting curve shown here. It is seen that etching yield data obtained in this study are in good agreement with the previous data indicated by the solid curves. The solid curve denoted as Si_3N_4 is a fitting curve for Si_3N_4 etching yields by CF_2^+ ion beams obtained in this study, i.e., two data points shown in Fig. 1. The fitting curves are given by the relation

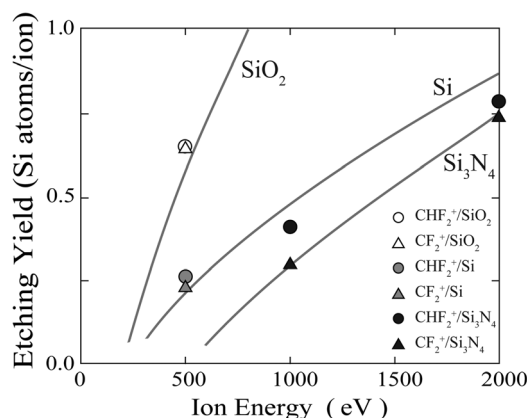


FIG. 1. Etching yields of Si, SiO_2 , and Si_3N_4 by CF_2^+ and CHF_2^+ ion irradiations as functions of ion incident energy.

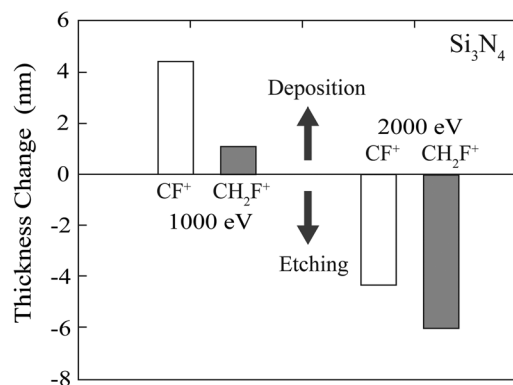


FIG. 2. Changes in film thicknesses of Si_3N_4 substrates due to CF^+ and CHF^+ ion beam irradiations at doses of approximately 1×10^{17} ions/cm².

$$Y = \alpha(E^{1/2} - E_{\text{th}}^{1/2})$$

with Y and E the etching yield and ion energy and α and E_{th} two fitting parameters.⁷

Figure 1 clearly shows that, for SiO_2 or Si, the etching yields by CHF_2^+ and CF_2^+ ions (at 500 eV) are nearly the same, whereas for Si_3N_4 the etching yield by CHF_2^+ ions is higher than that by CF_2^+ ions (at 1000 and 2000 eV). It is seen that, at 2000 eV, the difference of etching yields between CF_2^+ and CHF_2^+ ions is smaller than that at 1000 eV, which suggests that, in the case of Si_3N_4 etching, hydrogen in CHF_2^+ ion enhances the etching yield by some chemical effects and the effects manifest themselves more visibly and profoundly at lower ion incident energy.

Figure 2 shows change in substrate film thicknesses of Si_3N_4 substrates due to CF^+ and CH_2F^+ ion irradiations. In each case, the ion dose was typically $1.5\text{--}1.7 \times 10^{17}$ ions/cm². At 2000 eV, in both cases, steady etching occurs and the film thickness decreases as the ion dose increases. The depletion of Si_3N_4 is larger for CH_2F^+ ions than CF^+ ions, indicating that the etching yield is higher by CH_2F^+ ions than CF^+ ions at this incident energy. On the other hand, at 1000 eV, film deposition occurs in both cases at the center of the beam cross section, i.e., the location of the largest ion dose, and the deposited film is thicker under CF^+ ion irradiation than CH_2F^+ ion irradiation.

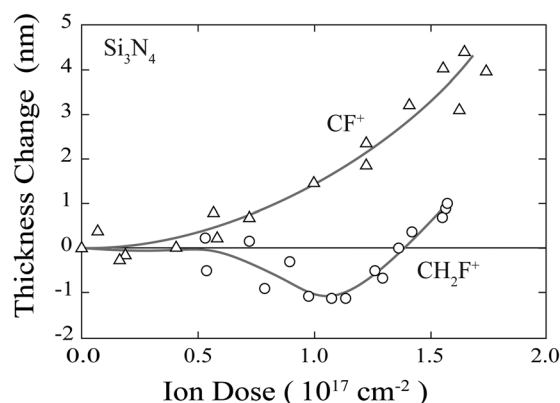


FIG. 3. Changes in film thicknesses of Si_3N_4 substrates due to CF^+ and CHF^+ ion beam irradiations as functions of the ion dose.

Deposition of a thicker film does not necessarily mean that the deposition rate is larger. This may be seen in Fig. 3, where the film thickness changes are shown for Si_3N_4 substrates as functions of the ion dose for CF^+ and CH_2F^+ ion beam irradiations. For CF^+ ion irradiation, the sample thickness increases monotonically with the ion dose. This is most likely caused by the deposition of a fluorinated carbon film. On the other hand, for CH_2F^+ ion irradiation, the substrate is first etched and then deposition takes place at the ion dose slightly larger than 1.0×10^{17} ions/cm². It should be noted that, once the deposition takes place, the rate of increase of film thickness in the case of CH_2F^+ ion irradiation is nearly the same as, or even higher than, that in the case of CF^+ ion irradiation. In the case of CH_2F^+ ion irradiation, the onset of film deposition is shown to be simply delayed. The delay may be caused by some chemical reactions that take place only when a bare Si_3N_4 surface is directly interacting with incident CH_2F^+ ions.

Variations of chemical compositions of deposited carbon films on Si_3N_4 were examined with *in situ* XPS during the ion beam irradiation processes. Figure 4 shows peak intensities of XPS signals from the substrate surfaces for CF^+ [Fig. 4(a)] and CH_2F^+ [Fig. 4(b)] ion irradiation processes as functions of the ion dose. The ion incident energy is 1000 eV in both cases. It is shown that, when the dose is below 5×10^{16} ions/cm², C and F atoms are more rapidly accumulated under CF^+ ion irradiation than CH_2F^+ ion

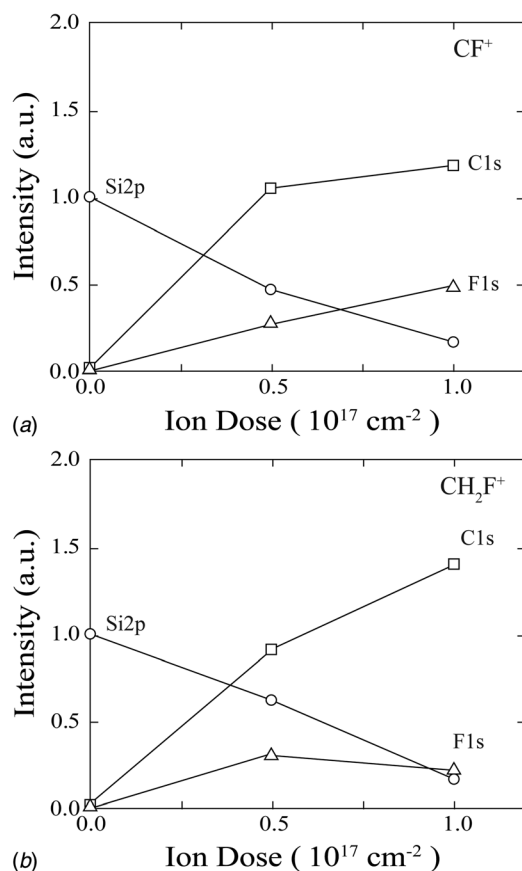


FIG. 4. Peak intensities of XPS signals from Si_3N_4 substrates as functions of the ion dose for 1000 eV (a) CF^+ and (b) CH_2F^+ ion irradiations.

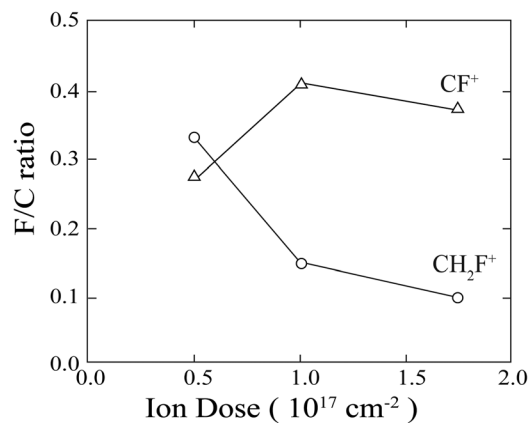


FIG. 5. F/C ratios as functions of the ion dose for 1000 eV CF^+ and CH_2F^+ ion irradiations.

irradiation. When the dose is above 5×10^{16} ions/cm², the rate of C accumulation by CF^+ ion irradiation decreases, whereas that by CH_2F^+ ion irradiation is nearly the same as earlier. However, in the carbon deposited film under CH_2F^+ ion irradiation, the F concentration is almost saturated. Although we have not measured desorbed species during this process yet, we speculate that incident fluorine of CH_2F^+ ions is removed as HF and/or hydrofluorocarbon species by incident hydrogen.

Figure 5 gives the ratios of F content to C content, i.e., the F/C ratio, obtained from *in situ* XPS as functions of the ion dose under CF^+ and CH_2F^+ ion irradiations. The experimental conditions are the same as those for Fig. 4. It is seen that, at a lower dose, the F/C ratios are almost the same in both cases and, as the ion dose increases, they approach two separate values; when sufficiently thick films are deposited, the F/C ratio is higher for CF^+ ion irradiation than CH_2F^+ ion irradiation. Figure 6 shows spectra of C 1s of XPS at an ion dose of 1.0×10^{17} ions/cm² under the same conditions as Figs. 4 and 5. More C–F bonds are observed in the case of CF^+ ion irradiation.

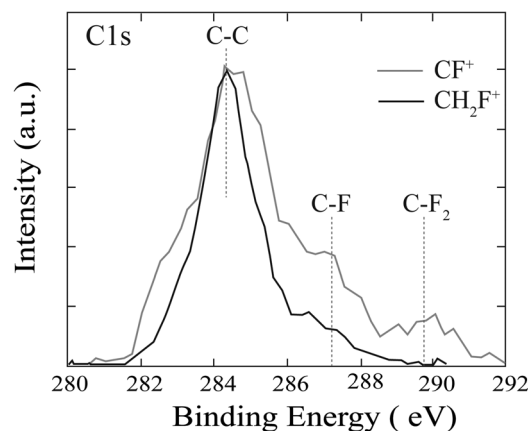


FIG. 6. Profiles of C 1s XPS signals from Si_3N_4 substrates after 1000 eV CF^+ and CH_2F^+ ion irradiations at ion doses of approximately 1×10^{17} ions/cm². The peak locations for the C–C, C–F, and C–F₂ bonds are also indicated.

Figures 4–6 all show that, in the presence of hydrogen in incident ions, the F content of a deposited film is significantly lower. These results indicate that, once a fluorinated carbon film reaches a sufficient thickness, hydrogen in CH_2F^+ incident ions form volatile products with fluorine on the film surface and reduce the F content of the film.^{8–10}

We have also estimated the film thicknesses by Si 2*p* peak intensities, assuming that the escape depth of an Si 2*p* photoelectron is 3 nm (Refs. 10 and 11) and using the data given in Fig. 4. For CF^+ ion irradiation, the fluorinated carbon film thickness varies from 0 to 3.0 to 8.0 nm as the dose increases from 0 to 5.0×10^{16} to 1.0×10^{17} ions/cm². For CH_2F^+ ion irradiation, with the same doses, the film thickness varies from 0 to 2.1 to 9.7 nm. In the early stage of deposition process, the carbon layer grows more slowly in the case of CH_2F^+ ion irradiation. These results are somewhat consistent with the observation shown in Fig. 3, although the thickness change in Fig. 3 may reflect the combined effects of carbon film deposition and Si_3N_4 etching.

Based on the above-given observations, we conjecture the etching reaction mechanism of Si_3N_4 by hydrofluorocarbon ions. First, when a bare surface of Si_3N_4 is exposed to incident hydrofluorocarbon ion beams, the hydrogen of the incident ion beam reacts with nitrogen of Si_3N_4 as well as accumulated carbon on the surface and forms volatile products such as hydrogen cyanide (HCN),^{12–14} facilitating etching of Si_3N_4 caused by reactions between substrate silicon and fluorine of incident ions. The reactions of hydrogen with nitrogen and/or carbon are likely to suppress the deposition of fluorinated carbon and further enhance Si_3N_4 etching reactions. If the beam energy is sufficiently high, etching reactions continue. In such reactions, the etching rate by CH_xF_y^+ ions is higher than that by CF_y^+ ions, as shown in Fig. 1.

If the beam energy is not sufficiently high, then carbon continues to accumulate on the Si_3N_4 surface until the accumulated carbon layer nearly covers up the substrate surface and the incident beam can no longer react directly with Si_3N_4 . Then, hydrogen of the incident ions scavenges fluorine from the deposited fluorinated carbon film, lowering the F content of the carbon film.

In actual plasma etching processes, the effects of charge neutral species can play very important roles. For example, it is known that, in hydrocarbon/fluorocarbon based plasmas, etching selectivity between Si_3N_4 and SiO_2 varies significantly, depending on its hydrogen content.¹⁵ The extent of its variation is by far larger than what we have observed in the hydrofluorocarbon ion beam experiments presented here. Simultaneous irradiation of a substrate surface by energetic ions and thermal charge neutral species could reveal etching properties under conditions more similar to actual plasmas.

However, such a study is beyond the scope of the present work.

IV. SUMMARY AND CONCLUSIONS

In summary, Si_3N_4 etching properties by hydrofluorocarbon (CHF_2^+ , CH_2F^+) and fluorocarbon (CF_2^+ , CF^+) ions have been examined with the use of a mass selected ion beam system. We have evaluated etching yields of Si, SiO_2 , and Si_3N_4 by CHF_2^+ and CF_2^+ ion irradiation. It has been found that hydrogen of incident hydrofluorocarbon ions enhances the Si_3N_4 etching yield if the case is compared with etching by hydrogen-free fluorocarbon ions. This is possibly due to reactions that form volatile species containing both hydrogen and nitrogen, such as HCN. When fluorinated carbon film deposition takes place on Si_3N_4 substrates by CH_2F^+ and CF^+ ion irradiation, XPS analyses of the surfaces indicate that hydrogen scavenges fluorine atoms of the deposited film. In the present study; however, volatile reaction products have not been directly measured yet and such measurements are the subject of future study.

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