

Evidence of Radical-free Etching of SiO₂ by Fluorocarbon Molecule under Ion Bombardment

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Under ion bombardment to SiO₂/Si surface, the additional beam of C₅F₈ gas molecule causes an enhancement of etching reactions, regardless of radical-free condition. Etching yield is measured as a function of C₅F₈/Ar⁺ flux ratio, and the result is compared with the etching yield in selective SiO₂/Si plasma etching. It is found that the contribution of fluorocarbon parent gas to the SiO₂ etching is not negligible in the conventional plasma etching process.

Key words: fluorocarbon molecule, ion bombardment, SiO₂ etching, radical-free, beam experiment

1. INTRODUCTION

Recently, high selective dry etching of SiO₂/Si is achieved in fluorocarbon plasma, for example, using C₄F₈/Ar/O₂ mixture gas. Based on the International Technology Roadmap for Semiconductors, etching technology is required to achieve the thin contact hole of a high aspect ratio with the 32 nm technology node or less in the next generation of ultra-large-scale integrated circuit [1]. Moreover, from a viewpoint of avoiding a greenhouse effect, various kinds of fluorocarbon etching gases have been developed, such as C₅F₈ or C₄F₆ with less global warming potential. Consequently, these alternative gas candidates are requested to attain a good performance for the etching even in an extremely thin hole. Therefore, in order to establish a reproducible minute etching and control precisely particle densities in the alternative etching plasma, it is important to understand the etching mechanism and the chemical reactions occurring on the SiO₂/Si surface. To date, a large number of studies have been reported on the role of ion and neutral radicals on the etching processes in fluorocarbon plasmas, and on a comparison of etch profile or etching selectivity [2–12]. Recently, the researches on the alternative gases are also reported from the same viewpoint [13–17]. However, little is known about the influence of fluorocarbon parent gas on the etching reactions. Because the direct contribution by parent gas to the etching is neglected from the consideration that they are chemically stable unless dissociated. In a previous paper, we have reported the evidence of the enhancement in etching reactions under co-incidence of fluorocarbon molecule and Ar⁺ to the SiO₂ surface [18]. In the present paper, the direct contribution to SiO₂/Si etching by C₅F₈ gas molecule, one of alternative etching gases, is evaluated by beam experiment under a radical-free condition. In other words, the SiO₂ etching yield under co-incidence of C₅F₈ and Ar⁺ is obtained and compared with the results in conventional plasma etching. From this comparison, the direct contribution of C₅F₈ molecule to the SiO₂ etching in fluorocarbon plasma is revealed.

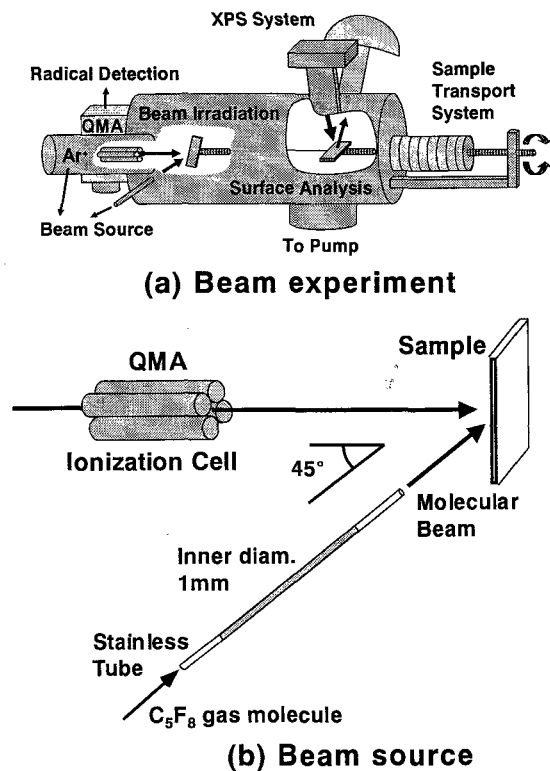


Fig.1. Schematic illustration of (a) the apparatus for beam experiment and (b) setup for co-incidence of C₅F₈ gas and Ar⁺ ion.

2. EXPERIMENTAL

Experiments have been performed in a well-controlled beam apparatus reported previously [10]. Experimental setup is shown in fig. 1. The apparatus is composed of four parts: an ion beam source for Ar⁺ beam production, a monochromated XPS system for the surface analysis, and a quadrupole mass spectrometer

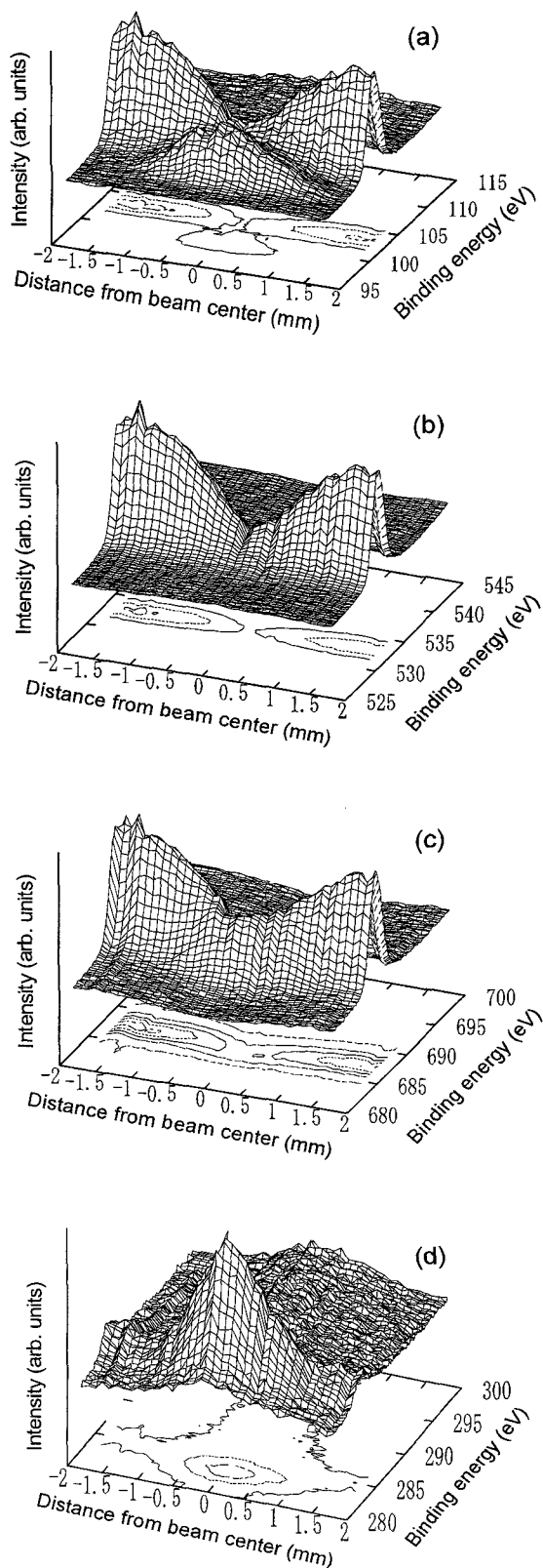


Fig. 2. XPS spectra of (a)Si_{2p}, (b)O_{1s}, (c)F_{1s}, and (d)C_{1s} at the radial position from beam center.

(QMA) for detection of surface-produced species, although the QMA is not used in the present experiment. A base pressure of about 10^{-9} Torr is obtained with use of four turbomolecular pumps at a total pumping speed of about 2000 l/s. Thermally grown 20-nm-thick SiO₂ layer on silicon substrate is employed as test sample. Before the experiment, the surface of sample is cleaned by ultrasonic cleaning in acetone and by pre-irradiation of Ar⁺ in the vacuum. The sample installed at the beam irradiation part is exposed to Ar⁺ beam and C₅F₈ flood simultaneously, in a high vacuum condition. To compare the influence of fluorocarbon co-incidence, CF₂ radical is produced by thermal decomposition of Hexafluoropropylene Oxide (HFPO) and is directed to the sample surface. In the beam source, the Ar⁺ beam is generated by electron-impact ionization of Ar and by mass selection of a singly charged Ar ion with a quadrupole mass filter. The beam energy (E) of Ar⁺ is controlled from 100 to 900 eV by positive and negative as voltages applied to the ion beam source and a sample stage, respectively. The Ar⁺ beam is directed to a sample in parallel to the surface normal. The Ar⁺ flux density is determined by average flux density within an area of 1 mm diameter of the beam. The C₅F₈ beam is directed from an angle of 45° to the sample through a stainless steel tube with a diameter of 1 mm. To produce CF₂ radical by thermal decomposition of HFPO, the tube can be heated up to 600 °C by DC current (a few A) flowing through the tube wall. The flux ratio (R) of C₅F₈ molecule to Ar⁺ is varied from 0.25 to 250. After exposure to the beam, the sample is transferred to the surface analysis station, and the atomic composition of the sample surface is measured by *in situ* x-ray photoelectron spectroscopy (XPS). The etching yield is evaluated from etched depth and etching time.

3. RESULTS AND DISCUSSION

The co-incidence of C₅F₈ gas molecule and Ar⁺ causes chemical etching reaction on the SiO₂ surface, which is similar to that in conventional fluorocarbon plasmas. The surface atomic composition is observed from XPS results, that is, a production of SiF_x layer and a deposition of fluorocarbon layer on the SiO₂ surface by the beam incidence. In this beam device, the Ar⁺ beam has its maximum flux density at the center of the beam, and the flux ratio of C₅F₈ to Ar⁺ increases with increasing the radial distance from the beam center, because the C₅F₈ flux density is almost constant over the area of the Ar⁺ beam. Due to the spatial variation of C₅F₈/Ar⁺ flux ratio, XPS spectra also change with the spatial position. For examples, figs. 2(a), 2(b), 2(c), and 2(d) show spatial variation of XPS Si_{2p}, O_{1s}, F_{1s}, and C_{1s} spectra, respectively, along the radial position from beam center, after the co-incidence of an Ar⁺ beam at $E=400$ eV (fluence: 5×10^{17} cm⁻²) and C₅F₈ beam (fluence: 1.25×10^{18} cm⁻²). In a series of this experiment, we have observed the decrease in the O component and the increase in the F and C components immediately after starting the beam incidence. After then, each atomic composition remains almost constant during the SiO₂ etching. Subsequently, a decrease in the O is observed again with the drastic increase in the C, at Ar⁺ fluence of 0.5×10^{17} cm⁻². These changes mean the complete removal of the SiO₂ at the beam center.

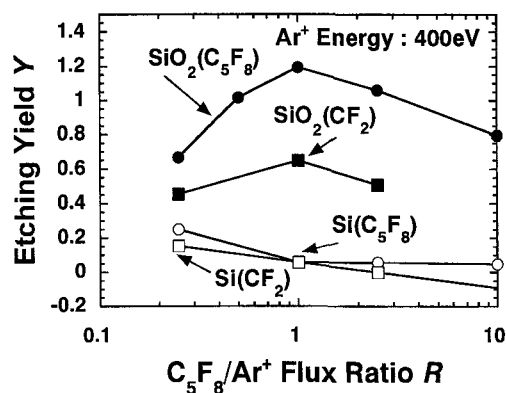


Fig. 3. C_5F_8/Ar^+ flux ratio dependence of etching yield of SiO_2 and Si under co-incidence of C_5F_8/Ar^+ and CF_2/Ar^+ .

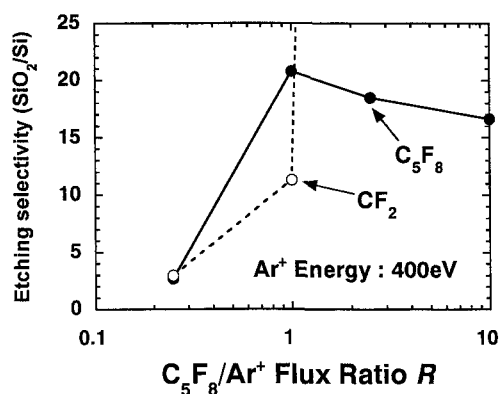


Fig. 4. Variation of etching selectivity of SiO_2/Si as a function of C_5F_8/Ar^+ flux ratio, evaluated from fig. 3.

In the present study, the $Si2p$ peak (fig. 2(a)), $Si-O$ peak (binding energy: 103.3 eV) disappears at the beam center and increase in $Si-Si$ peak (binding energy: 99.3 eV) is observed at the center of the beam. The XPS $O1s$ data (fig. 2(b)) shows the disappearance of the oxygen content at the beam center, which is in good agreement with the $Si2p$ result. Moreover, figs. 2(c) and 2(d) show the spatial variation of fluorocarbon layer on the surface, i.e., increase in the C content and decrease in the F content at the beam center. This means that, after the SiO_2 removal, thick carbon rich layer is deposited at the beam center. In contrast with the beam center, other region shows thin fluorocarbon layer, which indicates that the surface is still under SiO_2 etching. The XPS results clearly demonstrate the surface chemical reactions of C_5F_8 parent gas molecule under co-incidence of Ar^+ , without any kinds of radical incidence.

Based on the XPS measurements, the energy dependence of the SiO_2 etching yield is measured at

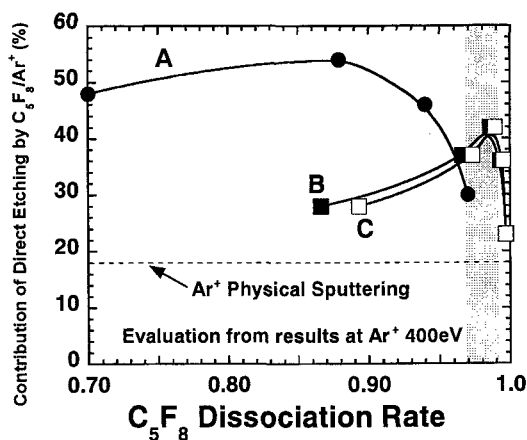


Fig. 5. Direct contribution of C_5F_8/Ar^+ in the $C_5F_8/Ar^+/O_2$ plasmas reported by the literature A [13], B [14], and C [15], according to C_5F_8 dissociation rate in the plasmas.

various Ar^+ energy, where monotonic increase in SiO_2 etching yield is observed. SiO_2 etching yield of 2.5 is obtained in the condition of $E=900$ eV and the flux ratio $R=1$. Next, dependences of SiO_2 and Si etching yields on the C_5F_8/Ar^+ flux ratio are measured as shown in fig. 3. As a reference, the results under co-incidence of CF_2 radical and Ar^+ are also shown in the same figure. In the case of C_5F_8/Ar^+ co-incidence, an etching yield of ~ 1.2 is observed at $R\sim 1$. In the case of CF_2/Ar^+ , the etching yield has a maximum at $R\sim 1$, although, the maximum etching yield is about a half of that for C_5F_8/Ar^+ . In contrast to the SiO_2 etching yield, Si etching yield monotonically decreases with increasing R irrespective of the incident fluorocarbon species. From these results, the flux ratio dependence of the SiO_2/Si etching selectivity is obtained as shown in fig. 4. In the case of C_5F_8/Ar^+ co-incidence, the maximum etching selectivity of ~ 20 is obtained at the condition of $R=1$. In the CF_2 case, the etching selectivity increases with the flux ratio, and becomes infinity at $R>1$, because the Si etch stop appears at this condition with the deposition of fluorocarbon layer on the Si at $R>1$. These results indicate that not only the SiO_2 etching but also the selective etching of SiO_2/Si can be realized by the C_5F_8/Ar^+ co-incidence under the radical-free condition.

From the results obtained by the beam experiment, one can evaluate the contribution of C_5F_8 molecule to the SiO_2 etching in commercially available C_5F_8/Ar plasmas for the SiO_2/Si selective etching. In conventional $C_5F_8/Ar/O_2$ capacitively-coupled plasma for the SiO_2/Si selective etching, the maximum SiO_2/Si etching selectivity is obtained at a pressure of 30 mTorr, an RF bias voltage of 1450 Vp-p, Ar^+ flux density of $10^{16} \text{ cm}^{-2}\text{s}^{-1}$, and a total flow rate of 415 sccm (C_5F_8 : 7 sccm, Ar: 400 sccm, O_2 : 8 sccm) [13]. In this etching condition, the maximum SiO_2 etching rate is 500 nm/min, which corresponds to a SiO_2 etching yield of 2.2. The C_5F_8 flux ($\Gamma_{C_5F_8}$) to the surface is obtained from the following equation,

$$\Gamma_{C_5F_8} = \frac{N}{4} \sqrt{\frac{8\kappa T}{\pi M}} \quad (1)$$

where N is the C₅F₈ number density under the plasma etching condition and T is the gas temperature. If we assume the survival rate of C₅F₈ gas molecule to be a few % in the plasma at the maximum SiO₂/Si etching selectivity, the C₅F₈ flux is calculated to be 2.5×10^{15} cm⁻²s⁻¹, which gives the C₅F₈/Ar⁺ flux ratio of 0.25. On the other hand, the present result in fig. 3 shows an etching yield of 0.67 at $R=0.25$ and $E=400$ eV. Thus, the present beam study suggests that the direct contribution of C₅F₈ molecule to the SiO₂/Si etching is about 30%, according to the estimated etching yield ratio of 0.67/2.2, although Ar⁺ energy for the plasma experiment and the beam experiment are different. Using the same procedure, the direct contribution of C₅F₈ to the total etching yield is plotted by the curve A in fig. 5, as a function of the percentage of the C₅F₈ dissociation in the plasma. Based on the data of M. Ooka, et al. [14] and S. Takagi, et al. [15] in the C₅F₈/Ar/O₂ plasmas, the direct contributions of the C₅F₈ molecule to the SiO₂/Si etching are evaluated in the similar manner, and are plotted in fig. 5 by curves B and C, respectively. Here, we used the ion number density of 1×10^{11} cm⁻³ and ion mass number of C₄F₆⁺ in the evaluation. These results suggest that, in case where 97–99% C₅F₈ is dissociated by the plasma, the direct contribution of SiO₂/Si etching by C₅F₈ parent gas will be roughly 30–40%. However, it should be noted that the contribution of pure Ar⁺ physical sputtering to the total sputtering yield is about 18% as shown in fig. 5.

Physical and chemical processes taking place on the SiO₂ surface under Ar⁺ bombardment with thermal flux of the fluorocarbon molecule are not well understood yet, but can be tentatively considered as follows. For example, C₅F₈ molecules absorbing on the SiO₂ surface may be dissociated into C_xF_y radicals through several processes: (1) direct collision with Ar⁺ ions, (2) vibrational excitation by collision with energetic lattice atoms (Si, O) under Ar⁺-induced collision cascade processes, and (3) collisions with Si and O atoms sputtered by Ar⁺ impact. As a consequence, the resultant C_xF_y and F radicals react with Si and O atoms on the surface, giving rise to etching of SiO₂ and deposition of a fluorocarbon layer. In the case of C₅F₈, there may be an additional process. The C₅F₈ molecule has a ring structure with a double bond and four single bonds. The double bond is broken by dangling bonds on SiO₂ surface, which are continuously produced by Ar⁺ bombardment, and thus the C₅F₈ molecule is chemically bound to the SiO₂ surface. The chemisorbed C₅F₈ is bombarded by Ar⁺ ions, yielding radicals for etching and forming a fluorocarbon layer. Such a unique process of C₅F₈ may cause results different from other fluorocarbon molecules.

4. Conclusion

In the present study, SiO₂ etching by co-incidence of C₅F₈ molecule and Ar⁺ was investigated in a beam apparatus. From the variation of XPS spectra along the radial position from the beam center, the spatial profile of the etched surface was observed. Moreover, the

direct contribution of C₅F₈ to SiO₂/Si etching was discussed, based on a beam experiment under a radical-free condition. The SiO₂ etching yield was obtained under co-incidence of C₅F₈ and Ar⁺, and the result was compared with the reported etching yield from the plasma experiment. The contribution of C₅F₈ molecule to the SiO₂ etching was estimated to be roughly 30–40% under typical plasma condition if we consider the survival C₅F₈ of a few % in plasma.

Acknowledgments

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