Chemical and Physical Roles of Individual Reactive Ions
in Si Dry Etching

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It has been generally recognized that, in dry etching, chemically reactive ion species in a plasma play a major role in directional etching. For high-speed etching with large selectivity, a systematic study of surface chemical reaction of reactive ions is required to select the optimum condition on plasma parameters.

The fact that the physical and chemical sputtering yields of Si by F+ ion bombardment can be determined by "in situ" quartz crystal oscillator microbalance (QCOM) monitoring has already been reported. The present paper extends this technique to observe etching characteristics of F+, CF+, CF2+, and CF3+, i.e., the four major ion species in a CF4 plasma. It also reports the chemical/physical roles of individual reactive ions.

Apparatus used in the experiments is schematically shown in Fig. 1. A high energy reactive ion beam from an ion source was mass-separated and guided into an ultrahigh vacuum (UHV) reaction chamber. It was then decelerated to 100 ~ 3000 eV just in front of QCOM. Ambient pressure during ion beam etching was typically 4 x 10^-8 Torr.

Incident ion energy dependences of the chemical etching and physical sputtering rates of Si by F+ ion bombardment are shown in Fig. 2. These curves were derived from the measured values of chemical \( Y_C \) and physical sputtering yields \( Y_P \). It should be noted that the differences between chemical and physical sputtering rates become small in the low-energy region where the former surpasses the latter near 100 eV. The \( Y_C \) is nearly constant in the whole energy region. Thus, 100 eV ion bombardment is sufficient to enhance the chemical reaction of Si with F+ ion. Furthermore, a large selectivity with a directional etching profile is considered obtainable by low-energy ion beam etching, since the physical sputtering yield does not change appreciably from one material to another. These facts suggested the differences in etching selectivities and speeds between microwave plasma etching and reactive ion etching. The mean kinetic energy of reactive ions in the former is one order smaller than that in the latter. Typical energy values are 10 ~ 20 eV for the former and 100 ~ 1000 eV for the latter. Therefore, it can be assumed that Si is etched chemically rather than physically by ions in microwave plasma etching. This is different from the case of reactive ion etching.

Total sputtering yields \( Y_T \) of Si by CF+ ion bombardment are shown in Fig. 3 as a function of the incident ion energy (solid line). The \( Y_C \) of CF+ ion, also shown as a broken line, is derived from the measured reaction probability. Thus, the difference between both curves represents \( Y_P \). For the CF+ case, carbon or carboneous polymer deposition was found to take place in the 100 ~ 700 eV region, while Si etching was observed in the high energy region. For CF2+, the same phenomenon was observed, though the critical energy became lower (100 eV). For CF3+ ion beam etching, no deposition was observed in the entire energy region measured. The XPS spectra of Si surface etched by F+ (Fig. 4(a)) and CF+ (Fig. 4(b))...
ion beams showed the presence of Si-C and C-F bonds in the CF⁺ case, while Si was hardly covered with carbon in the F⁺ case. These results indicate that surface coverage with carbon and/or related polymer varies with the F/C ratio of incident ion species and their energy.

Energy dependence of total Si sputtering yields in a CF₄ plasma was reported by Coburn et al (4). They stated that it does not follow the conventional physical sputtering theory, especially, in the low-energy region (0 ~ 500 eV), and explained it by the formation of carbon overlayer on Si surface by CF₃⁺ bombardment. However, according to the present results, CF₃⁺ is found not so effective for the carbon accumulation, but Cr⁺ has very large effects on it, which means that the present results disagree with Coburn's explanation.

References
(1) S. Tachi, K. Miyake, and T. Tokuyama, JJAP Letter (in press)

Fig.1 Schematic diagram of mass-selected, ion beam etching machine

Fig.2 Incident ion energy dependences of the chemical etching and physical sputtering rates of Si by F⁺ ion

Fig.3 Incident ion energy dependences of the total and chemical sputtering yields of Si by CF⁺ ion

Fig.4 XPS spectra of Si etched by F⁺ (a) and CF⁺ (b) ion beams