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Reaction of Fluorocarbon Species with Si and SiO₂ Surfaces¹

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Highly-selective high-aspect-ratio etching of SiO₂/Si is an indispensable key issue in the ULSI manufacturing processes. Furthermore, recent etching technology utilizes high density plasmas and requires complex fluorocarbon molecules such as C₄F₆ or C₅F₈ to achieve high etching speed and high etching selectivity. To improve etching performance, precise control of fluorocarbon plasmas based on deep understanding of radical reactions on SiO₂ and Si surfaces is required. Well-defined beam experiments in ultra-high vacuum are powerful for basic study of surface reactions. This paper shows elementary surface processes of fluorocarbon etching process, especially focused on the unique chemical reactivity of C₅F₈ molecule under co-incidence of Ar ion. The device was specially designed so as to enable *in situ* measurements of etching yield and etched surfaces. Namely, Ar⁺ beam at energies from 50 to 400 eV and various kinds of fluorocarbon neutral species (C₅F₈, C₄F₈, CF₂) are co-incident on a clean SiO₂ surface at a controlled flux. Etching yield of beam-incident surface is measured by profilometer while *in-vacuo* X-ray photoelectron spectroscopy (XPS) analysis reveals a time evolution of atomic composition of surface layer during the etching. In the case of C₄F₈/Ar⁺, surface atomic composition after SiO₂ etching was almost similar to that of pure Ar⁺ sputtering except for a small amount of F component. In the case of C₅F₈/Ar⁺, however, formation of fluorocarbon layer after SiO₂ removal was observed as in the case of CF₂/Ar⁺. The SiO₂ etching yield monotonically increased with the Ar⁺ incident energy above 400 eV, and the etching yield of 2.4 was obtained at an Ar⁺ incident energy of 900 eV with C₅F₈ co-incidence, which was about 3 and 1.5 times larger compared with pure Ar⁺ sputtering and CF₂/Ar⁺ co-incidence, respectively. These results suggest that fluorocarbon molecules themselves are important species in fluorocarbon etching plasma.

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