

Highly selective etching of SiO₂ over Si₃N₄ and Si in capacitively coupled plasma employing C₅HF₇ gas

Quadrupole mass-spectroscopic analysis - in the novel C₅HF₇/O₂/Ar plasma - has revealed important neutral and ionic species, such as C_xF_y (X>2), C_xF_y (Y/X<2), and C_xHF_y. Compared with conventional C₅F₈/O₂/Ar plasmas, it was found that plasma etching of SiO₂ films with high selectivity against SiN films was obtained. In accordance with the analytic results, the mechanism involved the formation of thicker C-rich fluorocarbon film on SiN obtained by impinging the C-rich hydrofluorocarbon species, characterised in the novel plasma.

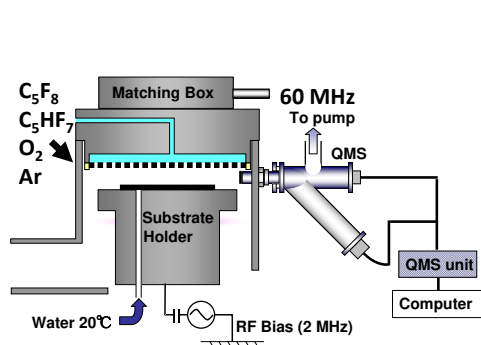
C₅F₈ and C₅HF₇ are mainly fragmented in electro-impact ionization at 70 eV into C₃F₃ and C₃HF₂, respectively. Indeed, the fragmentation pattern for C₅HF₇ clearly detected H-containing species substituting one F atom with one H atom, ie CF₂→CHF, C₂F₂→C₂HF, CF₃→CHF₂ and so on.

In a real plasma for dielectric etching, it is well-known that, dissociation, ionization and attachment occur by collisions with electrons, which typically have a Maxwellian energy of a few eV. Therefore, there was a large difference in gas chemistries between neutral species with and without H atoms for the actual C₅F₈/O₂/Ar and C₅HF₇/O₂/Ar plasma. In addition, combined with quantum chemical calculations, it was concluded that the main dissociation pathway of the cyclic C₅F₈ molecules was C₅F₈→CF₂+C₄F₆ and through further multiple dissociations, smaller fragmentation occurred following reactions; CF₂→CF+F, or C₄F₆→C₃F₃+CF₃. Therefore, large fraction of CF₃, CF₂, CF, C₃F₃ and each related H-substituted species, such as CHF₂, CHF, CH, and C₃HF₂ were detected.

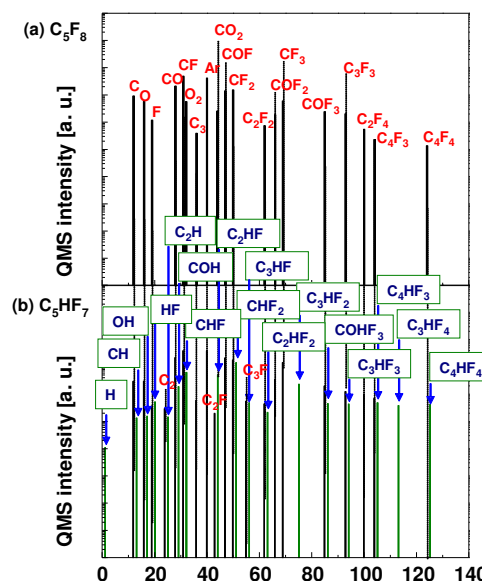
Furthermore, the entrance of the quadrupole mass spectrometer was located at the chamber wall of the commercialized reactor, which unfortunately only provided information about the composition of positive ions at the closed chamber wall excluding the sample surface. The main positive ionic species detected were CF₃⁺, CF₂⁺, CF⁺ in addition to Ar⁺. It is also noteworthy that large molecule ions such as C₃F₃⁺, C₂F₄⁺ and C₄F₄⁺ were detected. The behaviour of large molecule ions – C_xF_y or C_xHF_y coincided with selective etching of SiO₂ films, since selective formation of the C-rich fluorocarbon layer on SiN films was achieved.

The main focus of this research was the characterisation of gas molecules for improved etching. To improve the etching performances such as etch rates, material's selectivity, etched profile control, it is generally recognized that the key factors are surface reactions that obey plasma chemical properties. Hence, feedstock gases are the most important issues. The main gases of selection in the etching of SiO₂ has changed over time – for instance, CF₄, C₂F₆, C₄F₈, C₄F₆, and C₅F₈. Also, H- and O-containing species – CHF₃, CH₂F₂, C₃F₆O, C₅F₁₀O, etc – are helpful as controls, especially with regards to the amount of F atoms involved in the plasma chemistry. We emphasize that information on the relationship between the etching properties and the chemistry of novel gases is

of significant interest for scientific and industrial purposes. Therefore, we concentrate our continuous research in the elucidation of the etching mechanism through the diagnostics of the gas phase and surface analysis.



Schematic diagram of experimental apparatus



Quadrupole mass analytical results
of neutrals in $C_5F_8/O_2/Ar$ or
 $C_5HF_7/O_2/Ar$ plasmas

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