Highly selective etching of SiO_2 over Si_3N_4 and Si in capacitively coupled plasma employing C_5HF_7 gas

Quadrupole mass-spectroscopic analysis - in the novel $C_5HF_7/O_2/Ar$ 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 $C_5F_8/O_2/Ar$ plasmas, it was found that plasma etching of SiO_2 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.

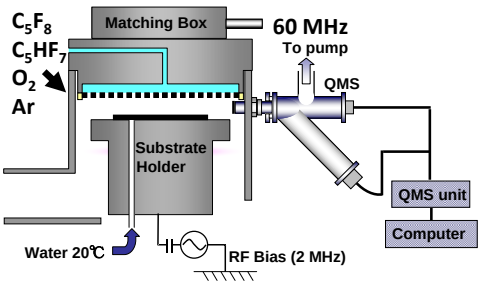
C_5F_8 and C_5HF_7 are mainly fragmented in electro-impact ionization at 70 eV into C_3F_3 and C_3HF_2, respectively. Indeed, the fragmentation pattern for C_5HF_7 clearly detected H-containing species substituting one F atom with one H atom, ie $CF_2 \rightarrow CHF$, $C_2F_2 \rightarrow C_2HF$, $CF_3 \rightarrow CHF_2$ 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 $C_5F_8/O_2/Ar$ and $C_5HF_7/O_2/Ar$ plasma. In addition, combined with quantum chemical calculations, it was concluded that the main dissociation pathway of the cyclic C_5F_8 molecules was $C_5F_8 \rightarrow CF_2 + C_4F_6$ and through further multiple dissociations, smaller fragmentation occurred following reactions; $CF_2 \rightarrow CF + F$, or $C_4F_6 \rightarrow C_3F_3 + CF_3$. Therefore, large fraction of CF_3, CF_2, CF, C_3F_3 and each related H-substituted species, such as CHF_2, CHF, CH, and C_3HF_2 were detected.

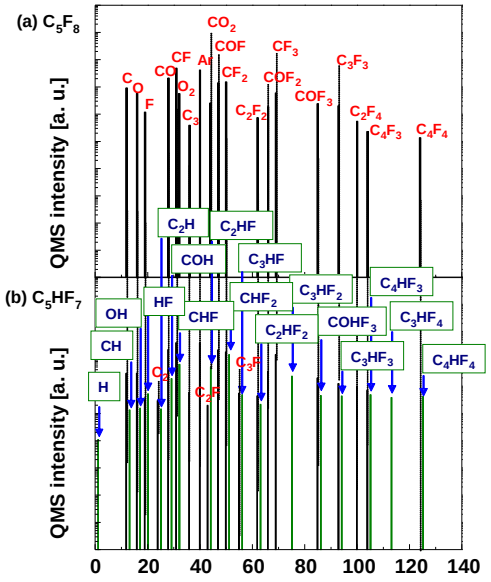
Furthermore, the entrance of the quadrupole mass spectrometer was located at the chamber wall of the commercialized reactor, which unfortunately only provided information about the composition of positive ions at the closed chamber wall excluding the sample surface. The main positive ionic species detected were CF_3^+, CF_2^+, CF^+ in addition to Ar^+. It is also noteworthy that large molecule ions such as $C_3F_3^+$, $C_2F_4^+$ and $C_4F_4^+$ were detected. The behaviour of large molecule ions – C_xF_y or C_xHF_y coincided with selective etching of SiO_2 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 SiO_2 has changed over time – for instance, CF_4, C_2F_6, C_4F_8, C_4F_6, and C_5F_8. Also, H- and O-containing species – CHF_3, CH_2F_2, C_3F_6O, $C_5F_{10}O$, 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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