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Time-resolved measurement of ion composition in a pulse modulated $Ar/C_4F_8/O_2$ dual-frequency capacitively coupled plasma using mass spectrometry

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High-capacity 3D NAND semiconductor storage devices are key devices supporting today's information society. The 3D NAND manufacturing process requires a technology to form high aspect ratio (HAR) holes that penetrate hundreds of layers of SiO/SiN stacked film. Reactive ion etching (RIE) using fluorocarbon gas is used to achieve such structures. Particularly in HAR etching, highly directed ions accelerated by the high electric field in the sheath near the substrate are thought to contribute more to the etching of the hole bottom than radicals. However, it is difficult for electrons to reach the hole bottom, resulting in the accumulation of positive charges at the HAR hole bottom. The increase in voltage inside the holes due to the accumulation of positive charge is thought to prevent ions from entering the hole bottom or to bend their trajectories, resulting in abnormal etch profiles and reduced etch rates. In addition, the continuous discharge can cause excessive polymer deposition on the sidewalls, leading to clogging of the holes.

To overcome these problems, pulse modulation (on-off modulation or high-low modulation) of the power for plasma generation and bias is often used to suppress excessive gas dissociation or to provide charge relaxation through the influx of electrons or negative ions into the holes. However, fluorocarbon gas plasmas (with argon dilution) are known to produce various ion species, and there is concern that pulsing the power may cause changes in the ion composition over time during the etch time (on or high period), resulting in changes in etch properties and causing a decrease in etch rate.

We have experimentally investigated the time evolution of the ion composition during the pulse-on period of an on-off pulse-modulated $Ar/C_4F_8/O_2$ dual-frequency (VHF-LF) capacitively coupled plasma (CCP) at a frequency of 1 kHz with a duty cycle of 50% using a quadrupole mass spectrometer (QMS). The results showed that the composition ratio of Ar^+ ions to fluorocarbon ($C_xF_y^+$) ions was initially large in the early phase of the pulse-on period, but it changed dramatically within a few hundred microseconds, with Ar^+ ions decreasing and $C_2F_4^+$ ions becoming the dominant species. Optical emission spectroscopy (OES) and electron density measurements using a surface wave probe suggested that the electron temperature was initially high in the early pulse-on phase, but decreased rapidly within a few microseconds [1].

To investigate the effect of the electron temperature on the ion composition during the pulse-on period, the time variation of the ion composition was evaluated by varying the pulse-off period. Depending on the residual charged particles during the pulse-off period, the Ar^+ ion composition and the electron temperature immediately after pulse-on became higher as the pulse-off period was longer. This result indicates that the electron energy immediately after pulse-on is an important factor in determining the ratio of ionization rates of Ar^+ and $C_xF_y^+$ ions [2].

Using the experimentally obtained values of the ion composition at the initial stage of pulse-on, the time-varying phenomena of the ion composition were also investigated by numerical analysis based on a particle balance model, taking into account the rates of ion production, loss, ion-ion recombination, and ion-molecule reactions. The numerical results showed that the time evolution of the ion composition can be well explained by using the time constant of ion loss due to ambipolar diffusion [2].

We further investigated and compared the time variation of the ion composition in two different modulation schemes, on-off modulation and high-low modulation, using QMS. Immediately after the power rise (on or high period), Ar^+ ions were dominant in both modulations, but the proportion of Ar^+ ions was larger in the on-off modulation than in the high-low modulation. Over time, Ar^+ ions decreased while $C_xF_y^+$ ions increased on similar time scales for both modulations. At steady state, the ion compositions of both modulations were nearly identical. These results suggest that the mechanism of ion composition change over time is the same for both modulations.

For a more detailed discussion, the ion composition was evaluated from the ion production rate at pulse rise and compared with the experimentally measured ion composition . The total ion production rate was evaluated from the slope of the time variation of the electron density after power rise, based on the zero-dimensional particle conservation equation. The ionization cross section data were used to estimate the effective electron energy so that the sum of the ionization rates for each ion equals the total ion production rate, and the ion composition ratio was evaluated. The good agreement between the experimentally measured ion composition and that evaluated from the ion production rates. It suggests that the initial ion composition is determined by the high ionization rates derived from the high-energy electrons immediately after the pulse rise.

[1] S. Kuboi, et al., Jpn. J. Appl. Phys. **62**, SI1003 (2023).
[2] S. Kuboi, et al., Jpn. J. Appl. Phys. **63**, 016001 (2024).