Influence of pulse-off time on time-varying ion composition in a pulse-operated Ar/C₄F₈/O₂ dual-frequency capacitively coupled plasma

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Abstract: Influence of pulse-off time on time-varying ion composition in a pulse-operated dual-frequency (DF) $Ar/C_4F_8/O_2$ capacitively-coupled plasma (CCP) is investigated. With increasing the pulse-off time period, increase in the Ar^+ composition just after turning on the pulse is observed. Mechanism of the ion composition change by the pulse-off time is discussed.

Keywords: etching plasma, fluorocarbon, ion composition, gas mixture, pulsed plasma.

1. Introduction

In recent years, data amount used in the world has exploded with big data related to the internet of things (IoT), Cloud and AI. Consequently, the memory devices for storing these data are required to rapidly increase their capacity. To meet these requirements, 3D memory structure has developed instead of planar 2D structure, where multiple layers are used to increase the density of memory cells [1]. One of the most important technologies in 3D memory is etching technology of the high aspect ratio (HAR) features in silicon dielectric films. In many cases, the reactive ion etching (RIE) with pulse-modulated dual-frequency capacitively-coupled plasma (DF-CCP) is used in this technique [2].

In general, the RIE process is influenced by neutral and ion flux, neutral and ion composition, as well as ion energy. In the case of HAR etching, however, neutral radicals have large incident angle as well as high surface reaction probability, and these characteristics make radical transport to the hole bottom difficult. As a result, molecular ions are expected to be one of alternative chemical precursors to proceed the etching reaction [3]. Therefore, understanding of ion behaviour, such as ion energy and ion composition, is important to improve the etching performance in the HAR features etching process.

To give an insight into the ion behavior in pulseoperated $Ar/C_4F_8/O_2$ DF-CCP, we have measured timeresolved mass spectrometry taking account for ion energy distribution due to fluctuating plasma potential, and have revealed that the ion composition shows drastic time dependence. We also have discussed a mechanism why ion composition change is induced in the pulsed plasma [4]. In this study, to confirm the mechanism we proposed, timedependent measurement of ionic composition is carried out by changing pulse-off time, *i.e.*, by changing residual afterglow plasma at a moment of next pulse-plasma production.

2. Experiment

Figure 1 shows experimental setup. A plasma is produced by applying a superimposed dual frequency (2/40 MHz) to a CCP-type RF electrode that is installed in a 160 mm cylindrical vacuum chamber. The diameter of the groundand RF-electrode is 110 mm with an electrode spacing of 30 mm. A grounded liner is installed around the electrode to confine the plasma within the electrode gap space [4]. The supplied 40 MHz VHF power and 2 MHz LF power are each less than 400 W and both powers are pulse-modulated with a pulse-on time of 0.5 ms and changing pulse off time from 0.2 to 1.0 ms. $Ar/C_4F_8/O_2$ gases are supplied into the chamber from the gas manifold behind the grounded electrode through small holes using a mass flow controller at flow rates of 34/4/2 sccm, respectively. Total pressure in the chamber is maintained at 4.0 Pa.

Ar and fluorocarbon ions in the plasma are extracted to a differentially-pumped quadrupole mass spectrometer (QMS) equipped with an energy analyzer through a 0.1 mm diameter orifice. Timing pulses for the plasma modulation are also introduced into the QMS for time-resolved measurement of ions. From mass spectrum measurement, it revealed that Ar^+ , O_2^+ , CF^+ , CF_2^+ , CF_3^+ , $C_2F_4^+$, $C_3F_5^+$ and $C_4F_7^+$ ions are most dominant ones in the plasma.

To evaluate ion composition, *i.e.*, ion flux component to the wall by the QMS, one must be careful to consider the ion energy distributions (IEDs) of each ion, because the QMS ion signal is energy-separated and ions have energy spread due to plasma potential oscillation. To solve this, all IEDs of dominant ions are measured in every 20 μ s. Then, total ion flux for each ion at each timing is obtained by integrating the IEDs for each ion at each timing.

In order to measure the time-resolved ion composition



Fig.1. Schematic of experimental apparatus.

by the QMS, signal delay of the QMS depending on ion mass must be also considered because of the long transit distance of ions from the orifice to the detector (secondary electron multiplier). To evaluate the signal delay time and its dependence on ion mass, a linear relationship was confirmed between the signal delay time and the inverse square root of the mass, from light (CF⁺) to heavy (C₃F₅⁺) ions. Then, delay time of each ion in the QMS is carefully calibrated and, hereafter, time after the pulse is turning on is denoted as T_C .

3. Influence of pulse-off time on ion composition

We measured time-variation of ion composition during the pulse-on period, changing the pulse-off time from 0.2 to 1.0 ms. Figure 2 shows ion compositions of Ar^+ and $C_3F_5^+$ as a representative of fluorocarbon ions at pulse-off time of 0.2 and 1.0 ms. When a pulse-off time of 0.2 ms, Ar^+ and $C_3F_5^+$ compositions just after turning on the pulse ($T_C=20 \mu s$) are ~37 % and ~13%, respectively. After then, Ar^+ composition decreases monotonically to ~20 % with the time. In a pulse-off time of 1.0 ms, Ar^+ and $C_3F_5^+$ compositions at $T_C=20 \mu s$ drastically changes with higher Ar^+ composition and lower $C_3F_5^+$ composition.

Figure 3 schematically explains time-dependent ion composition in Ar/C_4F_8 pulsed plasma. It is known that, in pulsed plasmas, electron temperature T_e (or mean electron energy) becomes high immediately after turning on the pulse and decreases with time, as shown in Fig. 3(a). Considering that electron energy after turning on the pulse is influenced by charged particles in the afterglow plasma, electron energy at the pulse-on timing tends to be lower when the afterglow plasma density is high. The result in fig. 2 suggests that the change in the ion composition just after turning on the plasma is influenced by electron temperature at the pulse-on timing. Ionization coefficient k_{iz} is a function of T_e and, due to difference between ionization cross sections of Ar and C₄F₈,[5] k_{iz} of Ar becomes larger than that of C_4F_8 at higher T_e . Fig. 3(b) schematically shows ionization rates, *i.e.*, product of k_{iz} and parent gas density, of Ar^+ and $C_2F_4^+$. This means that Ar^+ is preferentially produced to increase the plasma density at the plasma ignition phase. Fig. 3(c) schematically shows electron density after turning on the plasma and we have confirmed that the electron density reaches almost a half of its steady-state density at $T_{\rm C}=10\sim20$ µs. This means that the ion composition of the plasma at the initial stage of the pulse-on is almost dominated by the ionization coefficients at high T_e . Charged particles, however, are always replaced by newly-produced ion-electron pairs and the ion composition changes to its steady-state which is determined by ionization coefficients at steady-state T_e (Fig. 3(c)). Decrease of pulse-on stage Ar⁺ composition at a pulse-off time of 0.2 ms, clearly indicates decrease in the initial T_e by reducing the pulse-off time.

4. References

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Fig.2. Ion compositions of Ar^+ and $C_3F_5^+$ during pulse-on period, at pulse-off periods of 0.2 and 1.0 ms.



Fig. 3. Schematically-shown $T_{\rm C}$ dependences of (a) electron temperature, (b) ionization rates of Ar⁺ and C₂F₄⁺, (c) electron density, and (d) ion intensities of Ar⁺ and C₂F₄⁺.