EFFECTS OF He ADDITIVE IN CH4 AND CF4 RF PLASMAS

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ABSTRACT
Plasma diagnostics and plasma processings in 13.56 MHz rf plasmas of CH4 and CF4 gases mixed with He, were carried out. In the plasma diagnostics, the density of ion flux reaching electrode, and both ion sheath thickness and dc self-bias voltage at powered electrode were measured. The results were utilized in the mechanistic studies on the plasma processings; the deposition of hydrogenated hard carbon film in the CH4 plasma and the etching of Si in the CF4 plasma. The He additive can produce additional positive ions by deexcitation process in CH4 and CF4 plasmas, and they considerably affect the results in both plasma processings.

1. INTRODUCTION
Radio-frequency (rf) discharges with planar parallel electrodes are of quite important tools in materials processings such as film deposition and etching. In most applications for these processings, a substrate is located at one of parallel electrodes, normally a cathode (powered) electrode. Hence, the results in the plasma processings are often related to the motions of ions produced in the plasma volume, which are accelerated towards the electrode with a potential drop across the plasma sheath. Indeed, the ions having relatively large kinetic energy induce the generation of hard carbon film in the CH4 plasma [1], and influence the etching anisotropy in the CF4 plasma [2]. The He additive in CH4 and CF4 plasmas, therefore, may greatly affect the plasma processings, because the excitation energy of metastable He atom (He(2^3S) : 19.8 eV) and the ionization energy of He atom (24.5 eV), are larger than the ionization potentials of both CH4 (12.6 eV) [3] and CF4 (16.3 eV) [4] molecules.

This paper describes the role of the He additive on the carbon film deposition in CH4 plasma and the etching of Si in CF4 plasma. The mechanistic studies on these processings have also been carried out using results on plasma diagnostics.

2. EXPERIMENTAL
A schematic diagram of an experimental apparatus for diagnostics and plasma processings is shown in Fig.1. A power supply used to generate the plasma is a 13.56 MHz rf oscillator. Parallel cathode (powered) and anode (grounded) electrodes in a plasma reactor consist of stainless-steel disks 153 mm in diameter with a spacing of 60 mm. The lower cathode electrode is covered with a ground shield set. CH4 and CF4 gases mixed with He were used in the plasma processings. Gas pressure in the reactor was measured with a capacitance manometer, and was regulated with a vari-
able conductance valve. In the measurement of ion flux density, a quadrupole mass spectrometer was attached to upper anode electrode, and ions reaching the electrode were extracted through a orifice (200μm in diameter) formed at the center of the electrode. Plasma sheath thickness at the cathode electrode was estimated with an optical emission profile (OEP) between both electrodes, which was measured using a CCD image sensor in combination with a microcomputer [5]. The dc self-bias voltage at the cathode electrode was also measured.

3. RESULTS AND DISCUSSION
3.1 Plasma processings in CH4 + He plasma

In order to know how the character of CH4 plasma changes when He gas is added, the plasma sheath thickness and the dc self-bias voltage at the cathode electrode were measured. The results are indicated in Figs. 2 and 3, respectively. The sheath thickness increases with the increase of He composition rate and then indicate a maximum value. The condition giving this maximum value is lied at lower He composition rate for lower gas pressures. The behavior of dc self-bias voltage is essentially similar to the sheath thickness, as shown in Fig.3. These anomalous behaviors are thought to be associated with the variations in the plasma characteristics. They can also be easily distinguished through the state of the discharge and/or the OEP. The OEP changes from CH4 plasma-like to He plasma-like when the He composition rate increases. The critical composition rate showing this drastic change in the OEP exists around the condition at where the dc self-bias voltage becomes maximum (for an example, 30 % CH4 at 100 mTorr). At this composition rate, the deposition rate of carbon film decreased abruptly, and then no film deposition occurred for further addition of He, as shown in Fig.4. The composition rate at where the film deposition just goes to zero, exists at lower CH4 composition rate for higher gas pressure.

The mass spectrometry measurements were also carried out in order to know a reason why no film deposition occurred in He rich CH4 + He mixture plasma. Figure 5 shows mass spectra of He, CH4 and CH4 + He (two kinds of composition rates) plasmas at 100 mTorr of gas pressure. In the CH4 plasma, higher hydrocarbon ions (CnHm+) in addition to predominant CH3+, CH4+, CH5+, C2H5+ ions, are observed. In the He plasma, major He+ ion and cluster ions Hen+ with n up to 17 are obtained. On the other hand, in the CH4 + He plasma of which the carbon film deposition occurred (for an example, 50 % CH4 composition rate), it is quite surprising that the mass spectrum is very similar to that in pure CH4 plasma, and a weak He+ ion intensity is obtained. In the He rich CH4 + He plasma with no film deposition (for an example 20 % CH4 composition rate), several kinds of HenHm+ ions and also no hydrocarbon ions are observed in addition to major He+ ion. The HenHm+ ions are thought to be formed by the following reaction;

\[\text{Hen}^+ + \text{CH}_4 \rightarrow \text{HenHm}^+ + \text{CH}_4-m\]

because the neutral CHn molecules can also be measured in the plasma, which was carried out by electron impact ionization of neutral species.

Figure 6 shows the variations in mass intensities of several kinds of ions in CH4 +
He plasmas at 100 mTorr. All of the ions indicate drastic changes at the condition where the deposition rate indicates the abrupt decrease, with the increase of He composition rate: HenHm+ ions greatly increase whereas CnHm+ ions decrease. The results suggest that for He rich composition rate the plasma is maintained with He-contained ions, and in CH4 rich plasma hydrocarbon ions contribute to maintain the plasma. In the mechanistic study about the film deposition, it can be also concluded that the ionic hydrocarbons play a major role in the hard carbon film formation.

3.2 Plasma processings in CF4 + He plasma

A small amount of He additive in CF4 plasma scarcely affects the character of CF4 plasma, as can be understood by the results in Figs.7 and 8: the sheath thickness and the dc self-bias voltage indicate only a small increase with increasing the He composition rate, and the state of the plasma is almost similar to that of pure CF4 plasma. Several percent of CF4 volume in CF4 + He plasma rather changes considerably the plasma character, that is, the sheath thickness indicates the great increase, and the self-bias voltage shows the abrupt decrease. These behaviors are quite different from those in the CH4 + He plasmas.

Such variations in the plasma character can also be recognized from the results in mass spectrometry measurements. Figure 9 shows the behaviors of predominant positive ions in CF4 + He plasmas when the CF4 composition rate is varied. The CF3+ ion increases in spite of the decrease of CF4 volume, while ions containing He decrease with the decrease of He in CF4 + He plasma. The increase in the CF3+ ion will be due to the penning ionization with the excited He atoms.

As generally the etching rate and the etching anisotropy depend strongly on the ion flux density at the electrode, the He additive in the CF4 plasma affects the Si etching process. Figure 10 shows the Si etching rates in CF4 + He plasmas at several kinds of gas pressures. At lower pressures less than 100 mTorr, the etching rate decreases gradually when the He volume increase, and at He composition rates more than 80% it decreases remarkably. At higher pressure conditions the etching rate increases and then indicates a maximum value at around 80% He composition rate. In order to investigate the origin on the increase of etching rate, the pressure dependence on CF3+ ion flux reaching the electrode was measured for the different CF4 composition rate. The results are shown in Fig.11. For He rich (lower CF4 composition rate) plasma, CF3+ ions can reach the electrode even at high pressure conditions, which may be due to the increase in diffusion length of CF3+ ions in CF4 + He mixture plasma. This causes the increase in etching rate, and simultaneously makes the etching profile being anisotropic.

4. CONCLUSION

Plasma diagnostics using the ion sheath thickness, the dc self-bias voltage and also the mass spectrometry, and plasma processings on carbon film deposition in CH4 + He plasma and on Si etching in CF4 + He plasma, were examined. The effects of the He additive in both CH4 and CF4 plasmas are quite different. In the CH4 + He plasma, a large amount of He volume in the plasma decreases remarkably the deposition rate of carbon film, and at lower pressure conditions no film deposition occurred.
On the other hand, in the CF\textsubscript{4} + He plasmas at higher pressure conditions the He additive increases Si etching rate and causes the etching profile to be anisotropic. These results are associated with the variation of positive ions, and thus the He additive affects the composition of ions in the plasma.

REFERENCES
Fig. 4: Deposition rate of hard carbon film in CH$_4$+He plasma as a function of CH$_4$ composition rate.

Fig. 5: Mass spectra of positive ions in He, CH$_4$ and CH$_4$+He plasmas at 100 mTorr.

Fig. 6: Mass intensities of positive ions in CH$_4$+He plasmas at 100 mTorr as a function of CH$_4$ composition rate.
Fig. 7 The sheath thickness at cathode electrode in CF$_4$ + He plasma as a function of CF$_4$ composition rate.

Fig. 8 The dc self-bias voltage at cathode electrode in CF$_4$ + He plasma as a function of CF$_4$ composition rate.

Fig. 9 Mass intensities of positive ions in CF$_4$ + He plasma at 100 mTorr as a function of CF$_4$ composition rate.

Fig. 10 Etching rate of Si in CF$_4$ + He plasma as a function of CF$_4$ composition rate.

Fig. 11 Mass intensity of CF$_3^+$ ion in CF$_4$ + He plasma as a function of gas pressure.