Effect of inelastic collision reactions of SF$_6$ on electron energy distribution in Ar ambient capacitively coupled plasma


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Abstract: Investigation on electron energy distribution of SF$_6$/Ar capacitively coupled plasma was done with measured electron energy distribution function (EEDF) and reaction rates of inelastic collision reactions of SF$_6$. It is revealed that electron attachment mainly decreases density of electrons whose energy is below 6 eV and dissociation mainly decreases density of electrons whose energy is over 10 eV.

Keywords: plasma diagnostics, OES, EEDF, CCP

1. Introduction

SF$_6$ plasma is commonly used for plasma assisted material processes such as dry etching of silicon in semiconductor industry. [1,2] Many researchers have studied about the process of plasma etching with SF$_6$ plasma by developing model based on chemical kinetics. [3~5] However little is known about property of electron energy distribution with electro-negative gases like SF$_6$.

In plasma assisted material processes, electron energy distribution is essential to understand how plasma works in the processes and furthermore to control the processes because it determines gas phase reactions such as attachment, dissociation and ionization. Usually electron temperature is used to represent electron energy distribution with an assumption that the shape of the electron energy distribution is Maxwellian. This assumption is guaranteed only when elastic electron collision is enough. However, in process plasma, non-Maxwellian EEDF is frequently reported [6~8] and in these cases electron temperature is not proper to reflect electron energy distribution of the plasma. Therefore measurement of EEDF shape in addition to electron temperature is important and could be very useful for monitoring how the process is proceeding and detecting problems of the process.

In this study, variation of electron energy distribution is observed and analysed as an electro-negative gas, SF$_6$, is added to Ar ambient plasma. When SF$_6$ is added to Ar ambient plasma, the inelastic collision reactions such as electron attachment, dissociation and ionization would affect EEDF of Ar ambient plasma. Langmuir probe signals and optical emission spectroscopy (OES) signals are used to measure electron density, electron temperature and the shape factor of EEDF. The wavelength and intensity of an OES signal are representing which and how often certain reaction is occurring in the plasma. We applied a corona-equilibrium (CE) based analysis model with combination of some OES signals to measure effective electron temperature and the shape factor of EEDF. [9] EEDF was obtained by combining electron density measured from Langmuir probe signals and effective electron temperature and the shape factor of EEDF measured from OES signals. The result corresponds with previous studies on reactions of SF$_6$ plasma.

2. Experimental Setup

Figure 1 shows a schematic diagram of our experimental setup. Experiments were performed in a capacitively coupled plasma which has a narrow gap (25 mm) and asymmetric electrodes. The area ratio of top electrode to bottom electrode is 1.67. The top electrode is anodized and encircled with an alumina ring for insulating it from the chamber. On the bottom electrode, a blank silicon wafer of 300mm diameter is laid with electrostatic chuck. The top electrode is powered by 100 MHz radio-frequency (RF) generator through 100 MHz RF power matcher. 100 MHz power on top electrode was set to 500W. Gases are inserted with radial uniformity through a silicon showerhead, placed under the top electrode. Gas flow rate is controlled by mass flow controller calibrated for Ar and SF$_6$. Operating pressure was 20 mTorr of Ar ambient gas and SF$_6$ was added to change the molar fraction of SF$_6$ to Ar, from 0% to 7.14%. The molar fraction of SF$_6$ to Ar is low because we aimed to see the effect of a little change of SF$_6$ on electron energy distribution in actual process plasma.

A single Langmuir probe was used to measure positive ion density, electron density and electron temperature. The properties were measured by fitting the I-V curve to a model. The probe was driven by a high voltage op-amp (APEX PA107) between -100V and 60V and the current was measured using a 1 kΩ shunt resistor with an isolated op-amp (AD210AN). The probe has a 0.1φ×3mm cylindrical tungsten tip to draw current. RF compensation for the probe signal was done by using 9.6φ×11.5mm reference tip and RF chokes.

The OES signals were measured by a CCD spectrometer (SM 245, Spectral Products Inc., wavelength range of 200 ~ 1050 nm, resolution of 0.25nm). The optical fiber was set toward the radial center of the chamber and the signals were relatively calibrated by
using a tungsten-halogen lamp. Several OES signals were used to measure effective electron temperature and the shape factor of the EEDF with a CE based analysis model. [9] The CE based analysis is valid in this experiment because the operating pressure was 20mTorr, low enough to apply the analysis.

3. Results and Discussions

Figure 2 shows variation of electron saturation current and ion saturation current from Langmuir probe as SF\(_6\) was added to 20mTorr Ar ambient plasma. As the molar fraction of SF\(_6\) to Ar increases electron saturation current decreases and ion saturation current increases. The increase of ion saturation current comes from dissociative ionization of SF\(_6\) which increases positive ion density. According to previous studies on SF\(_6\) plasma [3–5, 10], dissociative ionization is one of the key reactions because the rate coefficient of dissociative ionization with electrons whose energy is over 10 eV is a few orders of magnitude larger than those of other reactions except dissociation.

The decrease of electron saturation currents results from electron attachment. Electron attachment to SF\(_6\) and SF\(_5\) by electrons, whose energy is almost 0 eV, has cross section several orders of magnitude larger than any other reactions. [11] Also, dissociative electron attachment and electron attachment to F have large cross section with electrons which has energy from 4 eV to 13 eV. Therefore, electrons which can be easily attached to SF\(_6\), SF\(_5\) or F are abundant and this makes electron attachment significant compared to other inelastic collision reactions. Plentiful electron attachment leads to decrease of electron density and increase of negative ion density. This is the reason why electron saturation current decreases as the molar fraction of SF\(_6\) to Ar increases, while ion saturation current increases.

To get effective electron temperature and the shape factor of the EEDF, OES signals should be analysed. Figure 3 illustrates how electron temperature and the shape factor of the EEDF changes when the molar fraction of SF\(_6\) to Ar increases. Figure 3 (a) shows that the effective electron temperature, which is obtained from both Langmuir probe analysis and OES signal analysis, increases as SF\(_6\) is added to Ar plasma. The error between two methods to measure effective electron temperature is below 1 eV and they show same tendency as the molar fraction of SF\(_6\) to Ar increases. The rise of effective electron temperature can be explained by electron attachment. The threshold energy of electron attachment to SF\(_6\) and SF\(_5\) is almost 0 eV while dissociation and dissociative ionization have threshold energy over 9.6 eV. Most electrons have energy lower than effective electron temperature, 3–4 eV, in low temperature plasma. The energy distribution of electrons and the threshold energies of certain reactions make electron attachment serious. Furthermore the heating power of 100MHz was set to 500W which means no addition of heating source. Thus the addition of SF\(_6\) to Ar ambient plasma makes attachment of low energy electrons considerable and this leads to increase of effective electron temperature without additional heating. Also, decrease of electron density measured from Langmuir probe analysis supports this result.

Fig. 1. Schematic diagram of experimental setup.

Fig. 2. (a) Ion saturation current and (b) electron saturation current from Langmuir probe signal analysis as SF\(_6\) is added to Ar ambient plasma.
Increase of the molar fraction of SF₆ to Ar results in increase of the shape factor according to Fig. 3 (b). The shape factor is the exponential part of the generalized EEDF with the isotropic velocity space assumption and it determines whether the EEDF is bi-Maxwellian, Maxwellian or Druvesteyn. [12]

\[ g(\varepsilon) = \varepsilon^{-1/2} f(\varepsilon) = c_1 \exp(-c_2 \varepsilon^2) \] (1)

If the shape factor is 1, the EEDF is Maxwellian. If the shape factor is lower than 1, it means that the EEDF is bi-Maxwellian like. In case of the shape factor of the EEDF over 1, the EEDF is Druvesteyn like. [12] Therefore the Ar ambient plasma in our experiment has bi-Maxwellian EEDF and as the addition of SF₆ increases the EEDF of the plasma gradually changes to Maxwellian EEDF. However effective electron temperature and the shape factor of the EEDF should be considered together because effective electron temperature shows only integrated property and the shape factor of the EEDF is not able to represent averaged energy of electrons. Variation of effective electron temperature and the shape factor can be analysed by gas phase reactions caused by the addition of SF₆. Detailed explanation is done with measured EEDFs.

Figure 4 illustrates the EEDFs which are obtained from the combination of electron density from Langmuir probe signals and electron temperature and the shape factor of the EEDF from OES signals. Normalized EEDF is obtained from measured electron temperature and the shape factor and electron density is multiplied to get EEDFs. Decrease of electrons which have energy below 6 eV is conspicuous as SF₆ is added to Ar ambient plasma. Decrease of low energy electrons corresponds with the explanation on rise of effective electron temperature. In Fig. 4, the EEDF when SF₆ is not added to Ar ambient plasma has much more electrons which have energy lower than 6 eV compared to other cases. The addition of SF₆ to Ar ambient plasma brings serious number of low energy electron attachment because the threshold energy of electron attachment to SF₆ and SF₅ is almost 0 eV and cross section of electron attachment with electrons which has energy around 0 eV is several orders of magnitude larger than other reactions such as dissociation and ionization. Also, electron attachment to F has large cross section with electrons which has energy from 4 eV to 13 eV. [11] It was already shown in Fig. 2 (b) that significant number of electron attachment occurs as SF₆ is added to Ar ambient plasma. The decrease of electron is obviously shown in variation of measured EEDFs.

Moreover decrease of electrons which have energy over 10 eV is observed when the molar fraction of SF₆ to Ar changes from 2% to 7%, though it is not as serious as the decrease of low energy electrons. Decrease of high energy electrons is due to dissociation and dissociative ionization of SF₆. Both electron impact inelastic collision reactions
have high threshold energy over 9.6 eV and higher rate coefficient than that of other inelastic collision reactions with electrons whose energy is over 10 eV. [11] Thus many electrons which have energy above the threshold energy of dissociation or dissociative ionization loss their energy by those reactions. This result corresponds with previous studies on SF$_6$ plasma. It was expected or modelled by many previous studies that dissociation and dissociative ionization are dominant reactions compared to other reactions in SF$_6$ plasma because of their high rate coefficients. [3~5]

4. Conclusion

It is shown that addition of SF$_6$ gas in Ar ambient plasma changes Maxwellian EEDF of Ar ambient plasma to bi-Maxwellian EEDF, even if the portion of SF$_6$ to Ar is low (< 8%). From the variation of EEDF and gas phase reaction rates of SF$_6$, it is revealed that electron attachment and dissociation mainly affect change in the shape of EEDF when SF$_6$ is added to Ar ambient plasma. As more SF$_6$ gas is added, the tail of the EEDF decreases by dissociation and dissociative ionization of SF$_6$. More importantly electron attachment to SF$_6$, SF$_5$ or F leads to serious decrease of low energy electrons which have energy below 6 eV. Therefore this study draws a conclusion that assumption of Maxwellian EEDF in SF$_6$/Ar plasma is not guaranteed and the effect of inelastic collision reactions on EEDF by SF$_6$ should be concerned. Further discussions about experimental results will be done at the conference.

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6. References