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Investigation of electronegativity in a radio-frequency Xe/SF$_6$ inductively coupled plasma using a Langmuir probe

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The ratio of negative ion to electron densities (electronegativity) has been investigated using a Langmuir probe technique in a radio-frequency Xe/SF$_6$ inductively coupled plasma, where the electron density is in the order of $10^{16}$ m$^{-3}$ and the electron and negative ion temperatures are about 3.5–5 and 0.4 eV, respectively, which are weakly dependent on SF$_6$ content and power injected into plasma. The electronegativity, which is between 5 and 10, does not strongly depend on SF$_6$ content, while it decreases gradually with the increase of electron density. © 2001 American Institute of Physics. [DOI: 10.1063/1.1414297]

Plasmas using fluorinated gas plasma such as CF$_4$ and SF$_6$, which are widely utilized in material processing, are mainly produced by capacitively and inductively coupled radio-frequency (rf) helicon and microwave discharges. Chabert et al. obtained the ratio of negative ion density $n_-$ to electron density $n_e$ (electronegativity $\alpha = n_- / n_e$) in a SF$_6$ helicon plasma using a probe method, while St-Onge, Margot, and Chaker detected $\alpha$ in a SF$_6$ electron cyclotron resonance plasma using ion acoustic waves and laser-induced photodetachment techniques. On the other hand, Nagaseki et al. measured the mass spectra of negative ions in a SF$_6$ capacitively coupled discharge, observing that $\alpha$ is dominant with smaller amounts of SF$_5$ and SF$_4$.

In the present letter, we investigate the SF$_6$ content and the injected power $P_{abs}$ dependences of $\alpha$, $n_e$, and the effective electron temperature $T_e$ in a rf Xe/SF$_6$ inductively coupled plasma (ICP), with keeping the total pressure for discharge-off at 2.5 mTorr. We use the two ways to estimate $\alpha$: one is to use the detected peak of the second derivative $i_p''$ of the probe current $i_p$ with respect to the probe bias voltage $V_p$, and the other is to use the ratio of the negative saturation current to the positive ion one measured for negative bias of −30 to −50 V far from plasma potential $V_G$.

The Xe/SF$_6$ ICP, which was produced by the azimuthal electric field induced by a planar five-turn coil connected with an L-type capacitive matching network through a power source, was sustained in a cylindrical stainless-steel chamber with 15 cm inner diameter and 10 cm length. A cylindrical probe with 3.5 mm length and 0.25 mm diameter was installed at the center of the chamber. The flow rates of Xe and SF$_6$ were controlled using two mass-flow controllers, and the total flow rate corresponding to the sum of each flow rate was maintained at 10 sccm. The details of the experimental apparatus and probe detection system have been described in a previous paper.

Typical SF$_6$ content and $P_{abs}$ dependences of $i_p''$ are shown in Figs. 1(a) and 1(b), respectively. Since the electrons with energy lower than 2 eV are assumed to be depleted due to attachment collisions with SF$_6$ and F (F$_2$), the sharp peak of $i_p''$ at about 0.4 eV may be caused by the negative ions. As shown in Fig. 1(a), the electron energy distribution function (EEDF) measured in a Xe plasma can be approximated as a Maxwellian below the ionization threshold energy. Thus, a bi-Maxwellian structure in the bulk of the EEDF cannot be formed in a Xe/SF$_6$ ICP. The second derivative $i_p''$ for electronegative gas can be given as

$$ i_p'' = \frac{A q^2}{4} \left[ \frac{2 q}{m_e} \frac{1}{\sqrt{V}} F(e) + \frac{2 q}{m_-} \frac{1}{\sqrt{V}} F_-(e) \right], $$

where $A = 1$ for electronegative gas.

FIG. 1. (a) SF$_6$ content dependence of $i_p''$ with $P_{abs} = 80$ W, where $i_p''$ for pure Xe at $P_{abs} = 20$ W is also included for comparison; (b) $P_{abs}$ dependence of $i_p''$ for 20% SF$_6$ content.
where \( A \) is the probe area, \( q \) the electron charge, \( m_e \) the electron mass, \( m_- \) the negative ion mass, \( V (= V_p - V_e) \) the difference between \( V_p \) and \( V_e \), and \( F(\varepsilon) \) and \( F_- (\varepsilon) \) are the EEDF and the negative ion energy distribution function (NEDF), respectively. The extrapolated lines shown by the dotted lines in Fig. 1 are used to distinguish the NEDF from \( i_-'' \). Density \( n_e \) is given as \( n_e = (2q)^{3/2}(m_e)^{1/2} \left| A \right| \int_0^\infty V^2 i_-'' dV \), where the extrapolated line is used as \( i_-'' \) below 2 eV, and the effective temperature \( T_- \) is determined from the slope at \( \varepsilon \) around 4–8 eV. On the other hand, the NEDF can be estimated by subtracting the line from the measured \( i_-'' \), resulting in the negative ion temperature \( T_- \) of about 0.4 eV. The value of \( T_- \) is close to that in the SF\(_6\) helicon plasma. If the dominant negative ions can be identified, the value of \( \alpha \) can be determined using the maximum peak heights \( i_m \) and \( i_-'' \) of \( i_-'' \) and \( i_-'' \) from the following equation:

\[
\alpha = \frac{i_-''}{i_m - i_-''} \left( \frac{T_-}{m_+} \right)^{3/2} \left( \frac{m_-}{m_e} \right)^{1/2},
\]

where \( i_-'' \), which is given by subtracting the extrapolated line from the measured \( i_-'' \), is the second derivative of negative ion current and \( i_m \) is that of the electron current.

The value of \( \alpha \) estimated from Eq. (2) has some ambiguities due to the difficulty in precisely determining \( m_- \) and \( T_- \). Thus, it is necessary to estimate \( \alpha \) using an alternate method, and to compare that obtained from Eq. (2). Here, we can estimate the value of \( \alpha \) from the ratio of the electron saturation current and the positive ion current, referring to the radial motion theory described in a previous paper. Boltzmann distributions are assumed for electrons and negative ions, and positive ion density \( n_i \) is assumed to be expressed as

\[
n_i(V) = \frac{I_i}{2\pi r_l q (2qV/m_i)^{1/2}},
\]

where \( r \) is the radial position, \( I_p \) the probe length, \( I_i \) the ion current collected by the probe, and \( m_i \) the positive ion mass. By introducing the following dimensionless parameters \( \eta = qV/T_e \), \( \xi = r/\lambda_D \), \( \lambda_D = (e_0 T_e/n_e q_0^2)^{1/2} \), and \( \gamma = T_e/T_- \), the distribution of the potential in a cylindrical case, which is described by the Poisson equation, can be given as

\[
\frac{\partial^2 \eta}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial \eta}{\partial \xi} = \frac{I_i/I_L}{\eta} = \frac{1}{1+\alpha} [\exp(-\eta) + \alpha \exp(-\eta \gamma)],
\]

where \( I_L \) is a normalized factor given by \( I_L = 2\pi r l q \lambda_D \sqrt{2T_e/m_i} \). In the quasineutral region we can assume that \( \partial^2 \eta/\partial \xi^2 = \partial \eta/\partial \xi = 0 \), so that Eq. (4) becomes

\[
\sqrt{\eta} \frac{1}{1+\alpha} [\exp(-\eta) + \alpha \exp(-\eta \gamma)] = (I_i/I_L) \xi^{-1},
\]

in which the differentiation \( \partial \eta / \partial \xi \) provides the initial value necessary to solve Eq. (4). The potential distribution \( \eta(\xi) \) is obtained for various \( I_i/I_L \) by numerically solving Eq. (4) using a Runge–Kutta method. Then, \( I_i/I_L \) is estimated from \( \eta(\xi) \) for a given probe radius \( r_p \), which \( \eta(\xi) = r_p/\lambda_D \). With notation of the ratio \( g(\alpha) \) of \( I_i/\eta_p=10 \) to \( I_h \), the current \( I_i/\eta_p=10 \) for various \( \alpha \) is given by

\[
I_i/\eta_p=10 = g(\alpha)/(q n A \sqrt{2 T_e/m_i}).
\]

In the case of \( \alpha \) lower than 20–30, the negative charge current \( I_n \) at \( V_p = V_e \) can be regarded as the electron current

\[
I_n = q n A \sqrt{2 T_e/m_e}.
\]

Then, the ratio \( R_c \) of \( I_i/\eta_p=10 \) to \( I_n \) is given as

\[
R_c = g(\alpha)((1+\alpha)/\xi_p) \sqrt{4 \pi m_e/m_i}.
\]

The value of \( \alpha \) can be obtained from Eq. (8) using measured \( R_c \).

The SF\(_6\) content dependences of \( n_e \) and \( T_e \) in (a) and \( \alpha \) in (b) at \( P_{abs} = 80 \text{ W} \).

**Fig. 2.** SF\(_6\) content dependences of \( n_e \) and \( T_e \) in (a) and \( \alpha \) in (b) at \( P_{abs} = 80 \text{ W} \).

**Fig. 3.** \( P_{abs} \) dependences of \( n_e \) and \( T_e \) in (a) and \( \alpha \) in (b) for 20% SF\(_6\) content.
the increase of the SF$_6$ content, while $T_e$ and $\alpha$ increase gradually for content lower than 20% and may be independent of content higher than 20%. As shown in Fig. 3, density $n_e$ is approximately proportional to $P_{abs}$, while $T_e$ and $\alpha$ decrease gradually with $P_{abs}$. There still remains significant problems in the $\alpha$ estimation using the two techniques. In the $\alpha$ estimation from Eq. (2), overestimation in $T_\perp$, which comes from the inaccuracy of the extrapolation of $i_e^2$ and the limitation of the energy resolution, may cause overestimation in $\alpha$ of about 20%–30%. On the other hand, density $n_e$ estimated from Eq. (6) is about 1.3–1.4 times larger than $n_e$ in a pure Xe ICP. When the correction factor, which is determined so as to satisfy the ratio of $n_i$ to $n_e$ is equal to unity in pure Xe, is introduced into Eq. (6), the values of $\alpha$ from Eq. (8) are about 20% smaller than those without the factor. After all, there still remains the difference in $\alpha$ estimated from Eqs. (2) and (8) by a factor of about 2. However, both SF$_6$ content and $P_{abs}$ dependences of $\alpha$ obtained from Eqs. (2) and (8) are similar and the value of $\alpha$ was between 5 and 10. These dependences may be explained from the comparison of the recombination loss and the detachment loss with the species dissociated from SF$_6$.

In conclusion, electronegativity $\alpha$ has been investigated using a Langmuir probe technique in a rf Xe/SF$_6$ inductively coupled plasma, where $n_e$ is in the order of $10^{16}$ m$^{-3}$ and $T_e$ and $T_\perp$ are about 3.5–5 and 0.4 eV, respectively, by changing the SF$_6$ content and power injected into the plasma. Electronegativity $\alpha$ may be independent of SF$_6$ content for content higher than 20%, while it decreases gradually with $P_{abs}$. The estimated value of $\alpha$ is between 5 and 10.

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