Radial Diffusion of Negative Ions Produced by Magnetized String-Type CF₄ Plasma

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Fluorine negative ions (F⁻) produced by a column-type magnetized plasma with CF₄ gas diffuse radially and accumulate around the plasma column. To explain the features of this accumulation, the radial profiles of the negative-ion density n_- as functions of discharge parameters are measured using a hot-wire-type Langmuir probe. The modified Bohm theory is applied to evaluate n_- as $n_-/n_e > 2$ and the negative ions are well confined between two end plates. n_- around the plasma column decreases with increasing magnetic field from 0.01 to 0.15 T. With increasing pressure from 0.25 to 1.1 Pa, n_- around the plasma column gradually decreases.

KEYWORDS: magnetized string plasma, fluorine negative ion, Langmuir probe, radial diffusion, carbon tetra fluoride, ion source

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In conventional plasma etching methods, charging in microscopic etching holes would break insulation layers.¹⁾ Notching (local sidewall etching) due to the charging effect obstructs precise silicon etching.^{2,3)} To avoid these problems, silicon etching using negative ions has been investigated.^{4,5)} A negative-ion beam with a considerably high ion flux applicable to silicon etching is a strong candidate for the superior production of ultralarge-scale integrated circuits (ULSIs) to avoid charge accumulation in 10-nm-scale etching holes. For this purpose, a column-plasma-type negative-ion source has been proposed and developed,^{6,7)} by which halogen negative ions can be produced and alkali-metal impurities can be excluded. In these sources, negative ions are more likely to accumulate around the plasma column⁸⁾ because of sufficient confinement along a magnetic field. In a hollow-type electron cyclotron resonance (ECR) plasma, high-density negative ions have accumulated in the central region along a magnetic field. By utilizing a multistring-type plasma, a large volume negative-ion source has been developed.⁹⁾

Here, to obtain the optimum conditions for accumulating negative ions, the diffusion features of negative ions and electrons across the magnetic field have been investigated experimentally. Fluorine negative ions (F^-) have been produced using a magnetized CF_4 plasma by injecting a string-type electron beam along a magnetic field, and their properties as functions of magnetic field, gas pressure and beam current have been investigated.

A simple density model of CF_4 plasma is considered, where there are three dominant charged species: CF_3^+ (created by electron impact ionization, $e + CF_4 \rightarrow CF_3^+ + F + 2e$), F^- (created by dissociative attachment, $e + CF_4 \rightarrow CF_3 + F^-$), and electrons. Thermal electrons in the plasma are produced by injecting an electron beam along the magnetic field with 100 eV of energy, part of which is lost at the end electrodes after diffusing along the magnetic field, and attach to CF_4 molecules. On the other hand, the produced negative ions (F^-) are confined well along the magnetic field by sheath potentials at the end plates, and are partially lost by recombining with positive ions. Around the column-type plasma, the radial diffusion speeds of electrons and negative ions

are very different, which causes the production of ion-ion plasmas. The perpendicular diffusion coefficient of an electron is much smaller ($\sim 1/10$ times) than that of a negative ion.

In this model, electrons are produced only in the electron beam region, and therefore become extinct at the end plates with an absorption probability or diffuse across the magnetic field. In a steady-state plasma, the continuity equation for electrons can be written as

$$K_{iz}n_{EB}n_0 + D_{\perp e}\nabla^2 n_e - \alpha n_e = 0, \quad (1)$$

where K_{iz} is the ionization reaction rate constant, n_{EB} is the beam electron density, n_0 is the neutral molecule density, $D_{\perp e}$ is the radial diffusion coefficient for an electron, α is the electron absorption coefficient, which shows sum of the time-averaged absorption probability at the end plates and the probability by the ion-ion attachment, and n_e is the thermal electron density. From ref. 10, $K_{iz} = 2.98 \times 10^{-13} \text{ m}^3/\text{s}$. Equation (1) is solved in a cylindrical coordinate system using *Mathematica* software (Wolfram Research Inc., ver. 5.2), and thus a radial profile of the electron density is obtained.

Negative ions, in this model, are assumed to be produced through the dissociative attachment, bounce at the end plates, diffuse across the magnetic field and therefore become extinct partly by recombination with positive ions. The continuity equation for negative ions in a steady-state plasma can be written as

$$K_{att}n_en_0 + D_{\perp -}\nabla^2 n_- - K_{rec}n_-n_+ = 0, \quad (2)$$

where K_{att} is the dissociative attachment coefficient of F^- ions production, K_{rec} is the ion-ion recombination coefficient, $D_{\perp -}$ is the radial diffusion coefficient of negative ions, and n_+ is the positive-ion density. From ref. 11 and 12, $K_{att} = 7.57 \times 10^{-17} \text{ m}^3/\text{s}$ and $K_{rec} = 5.0 \times 10^{-13} \text{ m}^3/\text{s}$. This equation is also solved using *Mathematica* software and the radial profile of the negative-ion density is obtained.

In the Langmuir probe measurement, the presheath potential $\Delta\phi_{ps}$ in front of an electrode is reduced owing to negative ions, and a fraction of the negative ions is reflected in the presheath re-

gion. This condition is referred to as “the modified Bohm condition”.¹³⁾ The effect of negative ions on the generation of a presheath ($n_-/n_e \geq 2$) and $n_{eb} + n_- = n_{+b}$ (n_{eb} : electron density in the bulk plasma, n_- , n_{+b} : negative-ion density and positive-ion density in the bulk plasma) is considered. At the reference position, the charge neutrality condition $n_{e0} = n_{+0}$ is assumed, where n_{e0} , n_{+0} are the electron density and positive-ion density, respectively, and the negative-ion density is much smaller. The density ratio of negative-ion density to electron density in the bulk plasma is written as^{7, 13)}

$$\frac{n_-}{n_{eb}} \approx \frac{J_{+s}/n_{eb}}{J_{+s0}/n_{e0}} \exp\left(\frac{e\gamma\Delta\phi_{ps}}{\kappa T_{eb}} - \frac{1}{2}\right) \sqrt{\frac{\kappa T_{e0}}{2e\Delta\phi_{ps}}} - \exp\left\{\frac{e\Delta\phi_{ps}(\gamma-1)}{\kappa T_{eb}}\right\}, \quad (3)$$

where $\gamma = T_{eb}/T_-$ (ratio of electron temperature to negative-ion temperature in the bulk plasma). J_{+s0}/n_{e0} (ratio of positive-ion saturation current of the probe to electron density) and T_{e0} (electron temperature) are measured at a reference position in the radial center, where $n_-/n_{eb} \ll 1$. n_-/n_{eb} is obtained using eq. 6 and Fig. 3 of ref. 7, where the asymptotic method using the graph is utilized. In this experiment, the effect of positive-ion temperature can be neglected in the evaluation of n_-/n_{eb} because the ion flow to the probe with $\kappa T_- \sim 0.1$ eV^{14, 15)} has little influence on sheath generation.

Figure 1 shows a schematic diagram of the experimental setup. A metal chamber of 2.0 m length and 21 cm diameter is set across eight solenoid coils producing a magnetic field of 0 – 0.15 T. An electron beam of 10 mm diameter is injected by an electron beam source (placed at the axial center about 85 cm from the chamber end), which has a beam energy of $\Psi_{BE} = 100$ eV and a current of $I_{BE} = 0 - 0.05$ A. The anode of the beam source (20 cm in diameter) with a gridded hole of 10 mm diameter is grounded. At about 77 cm from the beam source, an electrically grounded end plate, 20 cm in diameter, is placed. Hot-wire-type Langmuir probes, made of Ta wire of 0.2 mm diameter, shaped as half-circles of 1.5 mm diameter are used for the diagnosis of the plasma. Here, results are obtained using the probe placed 21 cm from the anode plate.

The radial density profiles of electrons, n_e , and negative ions, n_- , obtained experimentally and using the model calculations with eqs. (1) and (2) are shown in Fig. 2. In this case, $B = 0.03$ T, $p = 0.6$ Pa, $\Psi_{BE} = 100$ eV and $I_{BE} = 0.05$ A. In the calculation of eq. (1), $D_{\perp e} = 0.040$ m²/s (ref. 16) and $\alpha = 2.0 \times 10^3$ m²/s are utilized, and adequate boundary conditions are used. The first term of eq. (1) can be omitted as it is assumed that no electrons are produced outside the beam radius ($r = 5$ mm). In the calculation of eq. (2), $D_{\perp -} = 0.50$ m²/s (ref. 16), $K_{rec} = 5.0 \times 10^{-13}$ m³/s (ref. 12) and $n_- \approx n_+$ are utilized. As zero production of negative ions outside the beam diameter is assumed, the first term of eq. (2) can be omitted.

It can be confirmed that the electrons become extinct significantly outside the beam diameter, whereas the negative-ion density radially decreases gradually due to radial diffusion and axial confinement at the end plates. Therefore, around the string plasma, ion-ion plasmas with high n_- have been generated. However, there is a discrepancy between the experiment and the calculation of the radial profiles of n_- . It is conjectured that the potential structure or some instabilities suppress the radial diffusion.

The radial profiles of the plasma potential ϕ_p and the floating potential ϕ_f at $p = 0.6$ Pa and $B = 0.03$ T are shown in Fig. 3. The plasma potential throughout the radial distribution is positive, which confines the negative ions at the end plates.

The magnetic field dependences of n_- and n_e at $r = 0, +5$, and -5 cm are shown in Fig. 4, where p (CF₄) = 0.6 Pa, $\Psi_{BE} = 100$ eV and $I_{BE} = 0.05$ A. It is found that n_- decreases with an increase in B at $r = +5$ and -5 cm. By increasing the magnetic field, n_e at $r = 0$ increases gradually, whereas at $r = +5$ and -5 cm, n_e remains almost constant.

The pressure dependences of n_- and n_e at $r = 0, +5$, and -5 cm are shown in Fig. 5. n_- gradually decreases at $r = +5$ and -5 cm, with an increase in p (CF₄), where $B = 0.03$ T, $\Psi_{BE} = 100$

eV and $I_{BE} = 0.05$ A. n_e at $r = 0$ slowly decreases with increasing p (CF_4). n_e at $r = +5$ and -5 cm remains almost constant with increasing p .

Fluorine negative ions, F^- , produced by the string-type magnetized plasma with CF_4 gas diffuse radially and are confined in the magnetic field. The radial diffusion of electrons is consistent with the model calculation, whereas the radial diffusion of F^- is not well clarified by the model calculation, for which a study is underway. The electron beam current, magnetic field and gas pressure are the controlling parameters for negative-ion production. In this experiment, by decreasing B and decreasing p , a higher accumulation of F^- ions is obtained.

In order to obtain a large-diameter negative-ion source, a multistring-type plasma can be used⁹⁾, where negative ions accumulate among the string-type-plasma columns. By using a specially designed grid with an acceleration electric potential and a converging magnetic field, only negative ions can be extracted for a large-diameter negative-ion beam, which will be reported in the future after further study.

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Figure captions

Fig. 1. Schematic diagram of DC plasma experiment.

Fig. 2. Radial profiles of n_e (a) and n_- (b) obtained by experiments and using model calculations. $B = 0.03$ T and $p = 0.6$ Pa, measured at $z = 21$ cm from the anode.

Fig. 3. Radial distributions of $\mathcal{O}_p$ and $\mathcal{O}_f$. $B = 0.03$ T and $p = 0.6$ Pa.

Fig. 4. B dependences of n_- (a) and n_e (b) at $r = 0, +5$, and -5 cm. $p = 0.6$ Pa. $z = 21$ cm from the anode.

Fig. 5. p dependences of n_- (a) and n_e (b) at $r = 0, +5$, and -5 cm. $B = 0.03$ T. $z = 21$ cm from the anode.

Fig. 1. Schematic diagram of DC plasma experiment.

(a)

(b)

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(a)

(b)

Fig. 5. p dependences of n_- (a) and n_e (b) at $r = 0, +5$, and -5 cm. $B = 0.03$ T. $z = 21$ cm from the anode.