Radial Density Profiles of Fluorine Negative Ions and Electrons around a Magnetized String Plasma in CF₄ Gas

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Radial density profiles of electrons and fluorine negative ions around a string-type CF₄ plasma across a magnetic field are measured using a wire-type Langmuir probe. Modified Bohm theory is applied to evaluate negative-ion density, and it is confirmed that negative ions are well confined between two end plates. Parameter dependences of the density profiles are also measured. Simple density models for electrons and negative ions are proposed, and their radial density profiles are obtained by solving the equations of continuity. The experimental and theoretical results are in good agreement for electrons, whereas there are some discrepancies for negative ions. An unexpected small recombination rate coefficient of negative ions and radial electric field might be the reason for this discrepancy.

KEYWORDS: fluorine negative ion, ion source, string-type plasma, radial diffusion, Langmuir probe, magnetized plasma, plasma etching, carbon tetrafluoride

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1. Introduction

Ultra-fine etching using electronegative plasmas is a likely candidate to improve the plasma etching process for the production of higher quality ultra-large-scale integrations (ULSIs). Plasma etching with negative ions has been shown to be effective to reduce ^{1,2)} the damage ^{3–6)} that eventually occurs during conventional plasma etching. Therefore, clear knowledge about the production, diffusion, and extinction characteristics of negative ions, as well as positive ions and electrons, produced by electronegative gas discharge is vital to ensure efficient industrial application of negative-ion plasmas.

A column-type magnetized plasma with electronegative gas produces negative ions, where negative ions accumulate around the plasma column⁷⁾ because they are confined sufficiently along the magnetic field. Using this property, column-type negative ion sources have been developed.^{8, 9)} Separative diffusion of fluorine negative ions is realized around a multistring-type plasma made by a multihole-type obstacle plate, and a large-diameter negative-ion source can be produced.¹⁰⁾

In this study, in order to clarify the process of accumulation of negative ions and to improve negative-ion density, careful measurement of negative-ion density (F^-) and electron density around a simple string-type plasma is carried out. The radial density profiles of negative ions and electrons under different gas pressures and magnetic fields are measured. Theoretical models of the production, diffusion, and extinction of electrons and F^- ions in the magnetized CF_4 plasma are proposed.

Calculations using the continuity equations of electrons and negative ions according to the model have been carried out to know whether the models support the experimental results.

2. Theory

The proposed model of a string-type magnetized plasma is shown in Fig. 1, where production, diffusion, and extinction characteristics of fluorine negative ions (F^-) produced by a column-type magnetized plasma with CF_4 gas have been investigated. Initially the plasma is produced by electron-beam injection along the magnetic field. In this model, the dominant charged species are electrons, F^- ions and CF_3^+ ions, and the later two species are produced by dissociative attachment ($e + CF_4 \rightarrow CF_3^+ + F^-$) and electron impact ionization ($e + CF_4 \rightarrow CF_3^+ + F + 2e$), respectively. The F^- ions produced diffuse radially and accumulate around the plasma column. In addition to the experimental investigation, calculations using continuity equations for F^- ions and electrons, as they appear in the proposed model, have been carried out.

In the DC-discharge plasma, thermal electrons in the plasma are produced by injecting an electron beam along the magnetic field with 100 eV of energy. Some of the thermal electrons are lost at the end electrodes after diffusing along the magnetic field or by attaching to CF_4 molecules. On the other hand, the negative ions produced are well-confined along the magnetic field by sheath potentials at the end plates and are partially lost by recombining with positive ions. Around the

string-type plasma, the radial-diffusion speeds of electrons and negative ions are very different, which produces the ion-ion plasma. Moreover, the bipolar-type diffusion in the magnetic field establishes a substantial radial electric field such that the radial diffusions of negative ions are decelerated.

2.1 The model equations

We consider the proposed model illustrated in Fig. 1. Taking into account the perpendicular mobility ($\mu_{\perp}$) of the species and the radial electric field ($E_{\perp}$), the continuity equations for electrons and negative ions can be written as

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

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

respectively. In these equations, K_{iz} , K_{att} , and K_{rec} symbolize the ionization rate constant of the electron beam, dissociative attachment coefficient of F^- ion production, and ion-ion recombination coefficient, respectively. $D_{\perp e}$ and $D_{\perp -}$ are the radial diffusion coefficients for electrons and negative ions, respectively. n_e and n_- are the densities in the bulk plasma region of electrons and negative ions, respectively. n_{EB} and n_0 are the beam electron density and neutral molecule density, respectively. A constant, α , is introduced in this model to show an averaged electron absorption coefficient in eq. (1), which includes both the time-averaged absorption probability at the end plates and the probability of electron-ion attachment. The equations of continuity are solved in a cylindrical coordinate system using MATHEMATICA

version 5.2 (Wolfram Research) software adopting adequate boundary conditions.

2.2. Solution to the continuity equations

In order to solve the continuity equation for electrons [eq. (1)], it is assumed that thermal electrons are mainly produced by the collisions of beam electrons with the neutrals within the electron-beam diameter region ($\varnothing_{EB} = 10$ mm) and are lost by axial diffusion and absorption at the ends. Therefore, in the region outside the beam diameter, $r \geq 0.005$ m, production of electrons can be neglected, i.e., the first term in eq. (1) can be taken as equal to zero. At the periphery of the electron beam, electron density is assumed from the experimental measurement to be $n_e|_{0.005} = 3 \times 10^{15} \text{ m}^{-3}$. Moreover, the gradient of electron density at the inner walls of the vessel (at $r = 0.1$ m from the axial center) is considered to be zero, i.e., $\partial n_e / \partial r|_{0.1} = 0$. $D_{\perp e} \approx 0.04 \text{ m}^2 \text{ s}^{-1}$ is used for a typical value of an applied magnetic field of 0.03 T ¹¹⁾ and an electron temperature of 2 eV . The probability of absorption of electrons is assumed to be $\alpha = 2.0 \times 10^3 \text{ s}^{-1}$ from the experimental results.

For negative ions, it is assumed that F^- ions are produced mainly by electron attachment processes within the electron beam diameter region and are diffused radially and lost by recombination with positive ions. Therefore, outside the electron beam region, production of F^- ions can be neglected. This assumption leads to the first term in eq. (2) at $r \geq 0.005$ m being set as zero. At the edge of the beam, the negative-ion density and gradient of negative-ion density are taken to be $n_-|_{0.005} = 3 \times 10^{16} \text{ m}^{-3}$ and $\partial n_- / \partial r|_{0.005} = -6.3 \times 10^{18} \text{ m}^{-4}$, respectively, according to the

experiment. The perpendicular diffusion coefficient of negative ions $D_{\perp-} \approx 0.5 \text{ m}^2 \text{ s}^{-1}$ for an applied magnetic field of 0.03 T and a negative-ion temperature $T_- = 0.1 \text{ eV}$ is used.^{12,13)} The recombination rate coefficient of negative ions with positive ions is set according to the reference, $K_{\text{rec}} = 5 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$.¹⁴⁾

3. Experimental Procedure

An illustration of the experimental setup is shown in Fig. 2. A 2.0 m long vacuum vessel 21 cm in diameter made of stainless steel is set across eight solenoid coils producing a magnetic field $B = 0\text{--}0.15 \text{ T}$ along the z -axis. An electron beam 10 mm in diameter with a beam energy $\psi_{\text{BE}} = 100 \text{ eV}$ is injected by an electron beam source placed at the axial center. An electrically grounded anode plate with a gridded orifice 10 mm in diameter forms the shape of the electron beam. The beam current of this source is as high as 0.05 A. An end plate of 20 cm diameter at ground potential is set 77 cm from the beam source. Hot-wire-type Langmuir probes made of Ta wire of 0.2 mm diameter and shaped into half-circle of 1.5 mm diameter are used to diagnose the plasma. Results reported in this article are obtained using the probe placed 21 cm from the anode plate.

The modified Bohm method is used to evaluate negative-ion density from the Langmuir probe data of the negative-ion-rich plasma. For a weak electronegative plasma, where $n_-/n_e < 2$, the normal Bohm condition can be used at the sheath region of the plasma boundary, and n_- can be estimated from the Langmuir probe

measurement.⁷⁾ On the other hand, in the presence of many negative ions ($n_-/n_e \geq 2$), the magnitude of presheath potential $\Delta\phi_{ps}$ is reduced, and this potential reflects a quantity of negative ions in the presheath region. In this article, this condition is called “the modified Bohm condition”. In this condition, the ion saturation current density flowing to the probe is given by^{8,15)}

$$J_{is} \approx e \left[n_{eb} \exp\left(-\frac{e\Delta\phi_{ps}}{\kappa T_{eb}}\right) + n_{-b} \exp\left(-\frac{e\gamma\Delta\phi_{ps}}{\kappa T_{eb}}\right) \right] \times \sqrt{\frac{2e\Delta\phi_{ps}}{M_+}}, \quad (3)$$

where n_{eb} and n_{-b} are the electron density and negative-ion density in the bulk plasma, respectively, and $\gamma = T_{eb}/T_{-b}$ (the ratio of electron temperature to negative-ion temperature in the bulk plasma).⁸⁾

According to the calculation method described in ref. 7, we can evaluate n_{-b}/n_{eb} from the probe data, where the charge neutrality condition in the bulk plasma, $n_{eb} + n_{-b} = n_{ib}$ (n_{ib} : positive-ion density in bulk plasma) is used. Probe data at a reference point are used where negative-ion density is negligible and charge neutrality, $n_{e0} = n_{i0}$ (n_{e0} and n_{i0} : electron density and positive-ion density at the reference point, respectively) is satisfied. Then, eq. (3) is modified to be

$$\frac{n_{-b}}{n_{eb}} \approx \frac{J_{is}/n_{eb}}{J_{is0}/n_{e0}} \exp\left(\frac{e\gamma\Delta\phi_{ps}}{\kappa T_{eb}} - \frac{1}{2}\right) \sqrt{\frac{\kappa T_{e0}}{2e\Delta\phi_{ps}}} - \exp\left(\frac{e\Delta\phi_{ps}(\gamma-1)}{\kappa T_{eb}}\right), \quad (4)$$

where J_{is0} and T_{e0} stand for the positive ion current density and electron temperature at the reference point, respectively. The presheath potential $e\Delta\phi_{ps}/\kappa T_{eb}$ as a function of n_{-b}/n_{eb} can be evaluated for different values of γ from the modified Bohm method, as

stated in equations (6.4.9) and (6.4.10) in ref. 15. Therefore, n_{-b}/n_{eb} can be obtained by measuring $(J_{is}/n_{eb})/(J_{is0}/n_{e0})$, T_{eb} , and T_{e0} , and using eq. (3) and Fig. 3 of ref. 8, in which the asymptotic method in the graph is utilized.

When $e\Delta\phi_{ps}$ is smaller than the positive-ion temperature in the bulk plasma, κT_{+b} , the ion saturation current to the probe is influenced by the thermal ion flow.⁸⁾ In this experiment, both κT_{+b} and the negative-ion temperature κT_{-b} are assumed to be 0.1 eV, which is suitable for usual low-pressure laboratory plasmas,^{12,13)} and the effect of positive-ion temperature on the n_{-b}/n_{eb} evaluation can be neglected.

4. Results and Discussion

Radial density profiles of negative ions and electrons from the experiment and from the calculation are compared. In considering the polarity of the radial electric field, the field decelerates the negative ions and electrons, and accelerates the positive ions. However, the effect of $E_{\perp}$ on n_e is very small. As the perpendicular mobility of electrons and $E_{\perp}$ do not have much influence on the electron density distribution, the experimental results of radial distributions of n_e are in good agreement with the results obtained by solving the model equation for electrons as shown in Fig. 3(a).

The radial density distribution of negative ions changes owing to the effects of $E_{\perp}$, which could cause the discrepancies between the theoretical evaluation and experimental measurements of n_{-} shown in Fig. 3(b). With the assumption in the diffusion equation that no negative ions are produced in the bulk plasma region, the effect of production of negative ions at the beam edge region might have been

underestimated. Moreover, the recombination coefficient cited in ref. 14 and used in the calculations may be too large to be used under the present condition, which strongly modifies the radial density profile. Nonetheless, in this collisional plasma, $\mathbf{E} \times \mathbf{B}$ drift and diamagnetic drift can also be important, as they would produce instabilities resulting in a greater diffusion, which would increase the density of negative ions in the bulk plasma region.

Radial distributions of n_e and n_- , and their dependences on magnetic fields at a typical gas pressure of 0.6 Pa are measured and shown in Fig. 4. Both n_e and n_- decrease with an increase in B from 0.013 to 0.15 T. The higher magnetic field leads to a lower electron temperature and higher-density electron distribution within the beam region because electrons are confined for a longer time in the plasma and lose energy due to multiple collisions. On the other hand, the electron density increases because more ionizing collisions take place. A decrease in negative-ion density in the bulk plasma region with an increase in magnetic fields can be understood in terms of the diffusion coefficient of negative ions that decreases with increasing B .

Magnetic-field dependences of the density profiles of electrons and negative ions obtained by the calculations are shown in Fig. 5. As the perpendicular diffusion coefficients of the species decrease with B , radial profiles of n_e and n_- tend to decrease with B .

Radial distributions of n_e and n_- , and their dependences on pressures are shown in Fig. 6. In the edge plasma region, n_e tends to increase with pressure as T_e

decreases, whereas in the source region ($r \approx 0\text{--}0.5\text{ cm}$) n_e tends to decrease with pressure. The electron-retarding field, which is inversely proportional to T_e , increases as the pressure increases. The electron collision mean-free-path, λ , decreases with pressure, and the electron temperature decreases. This increase of collision frequency creates more thermal electrons, and hence lowers the density distribution of energetic electrons in the source region, eventually increasing the density distribution of thermal electrons in the bulk plasma. However, it is conjectured that higher collision frequencies among electrons and CF_4 molecules would reduce the production rate of F^- ions via dissociation of excited molecules and cause n_- to decrease with pressure.

Pressure dependences of the density profiles of electrons and negative ions were also calculated and the results are shown in Fig. 7. As the perpendicular diffusion coefficients of the species increase with p (as collision frequency increases), radial profiles of n_e , n_- tend to increase with p as shown in Fig. 7. As the pressure-dependent variations are not large, the experimental results do not show strong pressure dependence of the density distributions.

The density profile of negative ions, n_- , obtained experimentally is not quite consistent with the calculated results as shown in Fig. 3(b). Therefore, calculation of negative-ion density by changing the recombination coefficient was carried out and the results are shown in Fig. 8, where $B = 0.01\text{ T}$. A coefficient smaller than the value from ref. 14 tends to move to the calculated values closer to the experimental results, which suggests that the recombination rate coefficient is much smaller than the value

presented in the reference.

The perpendicular mobilities $\mu_{\perp}$ of electrons and F^{-} are 0.14 and 38.5 $m^2 V^{-1} s^{-1}$, respectively, as calculated for $B = 0.01$ T, $T_e = 1.0$ eV, and $T_- = 0.1$ eV. When $E_{\perp} = 2.9, 5.0,$ and 10 V/m, the calculated results of the radial profiles of n_e and n_- are shown in Fig. 9. The radial electric field retards negative-ion diffusion, and the average positive radial electric field of 29 V/m in the experiment causes a negative effect on the theoretical consistency. Therefore, the diffusion caused by the radial electric field is not very important in this experiment.

5. Conclusions

Thermal electrons are confined axially by a magnetic field, and radial expansion is very small for $B = 0.03$ T. Before radial diffusion, the electrons tend to disappear at the axial boundary. Fluorine negative ions, F^{-} , produced in the plasma diffuse radially and are well-confined along the magnetic field, bouncing at the boundary sheath. The radial density profile of electrons is consistent with the model calculation, whereas the radial density profile of F^{-} is not well clarified by the model calculation. By using a smaller recombination rate coefficient for F^{-} ions, the calculated values approach the experimental results, which we suggest, is the reason of this discrepancy. The $\mathbf{E} \times \mathbf{B}$ drift caused by the radial electric fields and some instability assists the diffusion, but further study is necessary to clarify these effects. The electron-beam current, magnetic field, and gas pressure are the controlling parameters for negative-ion production.

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Figure captions

Fig. 1. Model figure of negative-ion accumulation around a string-type magnetized plasma. The plasma is produced by electron beam injection.

Fig. 2. Illustration of experimental setup for string-type plasma.

Fig. 3. Radial profiles of (a) n_e and (b) n_- obtained by experiment and using model calculations. $D_{\perp e} = 0.04 \text{ m}^2 \text{ s}^{-1}$ and $\mu_{\perp e} = 0.14 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. $D_{\perp -} = 4.7 \text{ m}^2 \text{ s}^{-1}$ and $\mu_{\perp -} = 38.5 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. $B = 0.03 \text{ T}$ and $p = 0.6 \text{ Pa}$ are measured at $z = 21 \text{ cm}$ from the anode.

Fig. 4. Radial profiles of (a) n_e and (b) n_- for four magnetic fields obtained experimentally at a pressure $p = 0.6 \text{ Pa}$. $z = 21 \text{ cm}$ from the anode.

Fig. 5. Magnetic field dependences of radial profiles of (a) n_e and (b) n_- calculated using the model equations. $p = 0.6 \text{ Pa}$.

Fig. 6. Radial profiles of (a) n_e and (b) n_- for four gas pressures obtained experimentally in a magnetic field of $B = 0.03 \text{ T}$. $z = 21 \text{ cm}$ from the anode.

Fig. 7. Dependence of radial profiles of (a) n_e and (b) n_- on gas pressure calculated using the model equations. $B = 0.03 \text{ T}$.

Fig. 8. Dependence of radial profiles of (a) n_- and (b) n_+ on recombination coefficient calculated using the model equations. $D_{\perp -} = 0.5 \text{ m}^2 \text{ s}^{-1}$.

Fig. 9. Radial profiles of (a) n_e and (b) n_- calculated using the model equations for $E_{\perp} = 2.9, 5.0, \text{ and } 10 \text{ Vm}^{-1}$. $B = 0.03 \text{ T}$, $T_e = 1.0 \text{ eV}$ and $T_- = 0.1 \text{ eV}$.

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