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Temporal behavior of the electron and negative ion densities in a pulsed radio-frequency CF$_4$ plasma

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Electron and negative ion densities in the afterglow and in the plasma initiation phase of a 13.56 MHz rf discharge in CF$_4$ were measured by using a microwave cavity method and a laser photodetachment technique. Measurements were carried out at low rf powers ($\lesssim 10$ W) and in the pressure range from 100 to 300 mTorr. The electron density in the afterglow showed an enhanced decay rate due to the presence of negative ions. Electrons originating from negative ions through associative collisional detachment with neutral radicals were also detected in the afterglow. Decay curve analysis of the negative ion density gave an ion–ion (presumably CF$_3^+ - F^-$) recombination rate constant of $(5 \pm 2) \times 10^{-13}$ m$^3$s$^{-1}$, and showed that, in the active plasma, the negative ion loss rates by associative detachment and ion–ion recombination are of the same order of magnitude. The behavior of the electron and negative ion densities in the plasma initiation phase indicates that molecules and radicals that slowly accumulate in the plasma do not play a significant role in the production of negative ions.

I. INTRODUCTION

Radio-frequency plasmas in halogen-containing electronegative gases are widely used for dry etching of materials in the fabrication of microelectronic devices. Large amounts of negative ions can exist in such plasmas and investigation of their role in the physics and chemistry of the plasmas is of particular importance. Detection of negative ions in halogen-containing rf plasmas has been reported for such gases as Cl$_2$, BC1$_3$, F$_2$/He, SF$_6$, CF$_4$, C$_2$F$_6$, C$_3$F$_6$, and CHF$_3$. For Cl$_2$ and BC1$_3$ rf plasmas Gottcho and Gaebe have investigated the identities of negative ions, their effects on the local fields, and their formation and loss kinetics.

Recently the authors and others have developed a quantitative and highly sensitive method for detecting negative ions by utilizing a microwave cavity method to measure electrons generated by laser photodetachment. By use of this technique, negative ion densities in a 13.56 MHz discharge of fluorocarbon gases (CF$_4$, C$_2$F$_6$, C$_3$F$_6$, and CHF$_3$) have been measured as a function of pressure and rf power. Generally, it was found that the negative ion density was about one order of magnitude higher than the electron density. For CF$_4$ and C$_2$F$_6$ plasmas, the identity of the negative ions was also investigated in wavelength-dependent photodetachment measurements using a dye laser. In the case of the CF$_4$ plasma it was found that the great majority of the negative ions consists of F$^-$, while in the case of C$_2$F$_6$ a significant amount of negative ions other than F$^-$ (e.g. CF$_3^-$) exist. The results confirm mass spectrometry data in a pulsed rf CF$_4$ plasma and are consistent with the relative yields of different negative ions in electron attachment to CF$_4$ and C$_2$F$_6$.

The purpose of the present work has been to extend the study of a CF$_4$ plasma to transient measurements, in order to obtain information about the formation and loss processes of negative ions in the plasma.

In CF$_4$ plasmas, F$^-$ is produced by dissociative electron attachment to CF$_4$ and removed by recombination with positive ions. Besides these processes, radicals and stable molecules like CF$_2$ and C$_2$F$_6$ which accumulate in the plasma with relatively high densities may contribute significantly to the production and loss of negative ions. The electron attachment rate constant for C$_2$F$_6$ is one to two orders of magnitude larger than that for CF$_4$ at the usual electron temperatures in low pressure plasmas and thus may produce a significant amount of negative ions. The CF$_3^-(x = 1-3)$ radicals may effectively remove F$^-$ by associative detachment collision

$$F^- + CF_x \rightarrow CF_{x+1} + e^-,$$ (1)

since the reaction is exothermic and the cross sections for such reactions can be very large at low energies. In order to elucidate these points, we have measured the negative ion density together with the electron density in the afterglow and in the plasma initiation phase of a pulsed rf discharge in CF$_4$. Charged particle decay in a negative-ion containing afterglow is quite different from that in the absence of negative ions and to our knowledge this phenomenon has hardly been studied experimentally. Therefore we will also discuss the decay phenomena itself in some detail.

II. EXPERIMENT

The experimental apparatus and the method of determining electron and negative ion densities are basically the same as reported previously and only the essential features are described here. A plasma was generated in a cylindrical microwave cavity made of aluminum, which at the same
The inner diameter of the cavity is 17.5 cm and its height, or the separation between the rf electrodes, is 2 cm. In the bottom of the cavity a disc of 12 cm diameter is electrically separated from the rest of the cavity to be rf powered, whereas the rest is held at the ground potential. This configuration minimizes the deterioration of the quality factor $Q$ for the used $TM_{020}$ mode. The CF$_4$ gas was introduced into the cavity through holes in the rf powered electrode at a flow rate of 20 sccm in all measurements.

Radio-frequency power at 13.56 MHz was amplitude modulated to form a rectangular pulse. The repetition frequency of the pulse was 10 Hz and its duty ratio was (mostly) 50%. At the falling edge of the rf power, the rf voltage between the electrodes disappeared in about 1 μs. However, since the rf power was fed through a matching network which contained a blocking capacitor, a dc bias voltage, amounting from a few tens of volts to more than 100 V in the steady state, remained for a few tens of microseconds after the fall of the rf voltage. To avoid possible effects of this bias voltage on afterglow measurements, some of the measurements were carried out by using a short circuit; it consists of conventional switching transistors and makes a short circuit between the electrodes immediately after the fall of the rf power. The use of the short circuit reduced the duration of the dc bias voltage to a few microseconds, but the measurements were limited to low rf powers by the maximum applicable voltage of the transistors employed. The short circuit with its cabling consumed part of the rf power, as was detected by the decrease of the electron density with the output level of the rf power supply unchanged. We therefore assumed that the rf power actually given to the plasma was equal to the power that gave the same electron density without using the short circuit.

The electron density of the plasma was determined from the shift of the microwave resonance frequency (at about 3 GHz using the $TM_{020}$ mode) from the empty-cavity value to the plasma-containing value. A weak microwave signal at a certain fixed frequency was introduced into the cavity through a small loop antenna and the transmitted signal was detected by another antenna. The detected signal was rectified, recorded by a fast digitizing oscilloscope, and stored in the memory of a personal computer (PC). The measurement was repeated at some 100 different microwave frequencies taken at intervals of (mostly) 0.2 MHz. From the entire set of recorded signals, the PC can reconstruct a cavity resonance curve at each instant of time, thus determining the electron density from the shift of the resonance frequency. The time resolution of the measurements was only limited by the $Q$ factor of the cavity ($\sim 2000$) and was about a few hundred nanoseconds. The PC also controlled the entire measurement sequence described above.

To determine the negative ion density, the plasma was irradiated by a frequency-quadrupled (266 nm) pulsed Nd:YAG laser (Quanta Ray, DCR 11). The laser beam was introduced into the cavity through a slot made in its side wall and let out through another slot in the opposite side; the beam axis was parallel to and through the center between the rf electrodes. The power density of the laser beam was sufficiently high to cause photodetachment of electrons from all the negative ions in its path. Thus the negative ion density can be determined from the increase of the electron density just after the irradiation of the plasma, knowing the irradiated plasma volume. To measure the temporal variation of the negative ion density, the plasma was irradiated by a laser pulse at various delay times with respect to the rise or fall of the modulated rf power. If the negative ion density is very low, the shift of the resonance frequency caused by the photodetached electrons can be much smaller than the width of the resonance curve. In such cases, if the microwave frequency is appropriately fixed at a slightly off-resonant position, the jump in the detected microwave signal at the instant of laser irradiation should be linearly proportional to the negative ion density. Therefore, the temporal variation of the relative negative ion density can be studied by using only one microwave frequency, significantly to reduce the measurement time. Measurements of the negative ion density in the late-afterglow plasma were carried out on such a relative scale and were put on an absolute scale by actually measuring the resonance-frequency shift for one of the data points.

### III. AMBIPOLAR DIFFUSION

Ambipolar diffusion phenomena in the presence of negative ions has been formulated by a number of authors and most thoroughly by Rogoff. To an extent helpful for later discussion we briefly summarize the theory. Assuming that the charged particles in a weakly ionized plasma are only one type of positive ion, one type of negative ion, and electrons, their fluxes are given by

\begin{align}
\Gamma_+ &= -D_+ \nabla n_+ + \mu_+ n_+ E, \\
\Gamma_- &= -D_- \nabla n_- - \mu_- n_- E, \\
\Gamma_e &= -D_e \nabla n_e - \mu_e n_e E,
\end{align}

where $E$ is the space-charge electric field, $D$ the diffusion coefficient, $\mu$ the mobility, and $n$ the particle density, with subscripts $+$, $-$, and $e$ standing for the positive ion, negative ion, and electron, respectively. On the assumption of quasineutrality $n_+ = n_- + n_e$ which also implies $\Gamma_+ = \Gamma_- + \Gamma_e$, we can eliminate $E$ from Eqs. (2)-(4). The resulting expressions are rather complicated, but can be simplified under certain conditions. Let us write

$$\alpha = n_- / n_e,$$

$$\gamma = (D_e / \mu_e) / (D_+ / \mu_+),$$

where $\gamma$ is the ratio between the electron and ion temperatures if the particle energy distribution functions are Maxwellian (we also assume equal positive and negative ion temperatures). When $\alpha$ is small or moderately large so that $\alpha \ll \mu_e / (\mu_+ + \mu_-) \sim 10^{-2} - 10^{-3}$, and if $\alpha$ is constant over space, Eqs. (2)-(4) can be approximated as

$$\Gamma_+ \approx -D_+ (1 + \gamma) \nabla n_+,$$

(5)
\[
\Gamma_\pm = - \left[ D_\pm (1 - \gamma) + D_\mp (1 + \alpha) \left( 2 \mu_- / \mu_\alpha \right) \right] \nabla n_\mp ,
\]

Equation (5) has the same form as the well-known ambipolar flux in the absence of negative ions. In Eq. (6) the second term in the square brackets is only important when the first term nearly vanishes with \( \gamma \approx 1 \); in other words, the effective diffusivity for negative ions is much smaller than free ion diffusivities under isothermal conditions (\( \gamma \approx 1 \)) and can be negative when \( \gamma > 1 \). Equation (7) shows that the effective electron diffusivity is approximately proportional to \( \alpha \) and thus can be much larger than the ambipolar diffusivity in the absence of negative ions. The increase of the electron diffusivity with increasing \( \alpha \) saturates when \( \alpha \) becomes large enough that \( \alpha > \mu_\alpha / (\mu_+ + \mu_-) \); under this condition the electron flux is given by (also on the assumption of constant \( \alpha \) over space)

\[
\Gamma_\mp = - D_\mp \left[ 1 + (\mu_+ - \mu_-) / \gamma (\mu_+ + \mu_-) \right] \nabla n_\mp ,
\]

that is, the effective electron diffusivity is close to the free electron diffusivity. Further when \( \alpha > \gamma \mu_\alpha / (\mu_+ + \mu_-) \), the ion fluxes reduce to

\[
\Gamma_+ \approx \Gamma_- \approx - D_{al} \nabla n_+ ,
\]

where \( D_{al} = (\mu_- D_+ + \mu_+ D_-) / (\mu_+ + \mu_-) \) is the ambipolar diffusion coefficient for the ion-ion system.

The electron densities measured in this work are in the range of \( 10^{15} - 10^{11} \text{ m}^{-3} \) and at low densities the assumption of quasineutrality might be no longer valid. To get ideas about the phenomena at low electron densities, as well as to see the variation of \( \alpha \) over space, a numerical simulation of the afterglow plasma was carried out. The results are presented in the appendix.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Electron density in the afterglow

Figures 1 and 2 show the decay of the electron and negative ion densities after termination of the discharge for different conditions. In general, the electron density decay curves show that the relatively rapid decay rate in the early afterglow (\( t \leq 0.3 \text{ ms} \)) slows down in the late afterglow, approaching the negative ion decay rate. Mainly referring to the result in Fig. 1(a) for convenience, the behavior of the electron density is interpreted as follows.

First we estimate the diffusion loss rate of electrons in the afterglow. We note that the high electron temperature in the active plasma cools down to thermal values in the afterglow almost immediately on the time scale shown in the figures; on the basis of reported cross sections for rotational excitation of CF\(_4\) by electron impact, \( \text{CF}_4^+ \), and therefore, from the measured mobility of CF\(_4^+\), in CF\(_4\), \( \text{CF}_4^+ \), together with the assumption of approximate equality of the mobilities of CF\(_3^+\) and CF\(_4^+\), an estimate of \( D_+ \) at 100 mTorr (\( T_i = 0.03 \text{ eV} \)) is obtained to be \( 0.023 \text{ m}^2 \text{s}^{-1} \). Thus the electron diffusion loss rate given by

\[ 2(\alpha + 1) \Lambda / 2, \]

where \( \Lambda = (2/\pi) \text{ cm} \), is found to be \( 1.2 \times 10^4 \text{ s}^{-1} \) for \( \alpha = 10 \). If the electron density decays faster than the negative ion density, the value of \( \alpha \), and accordingly the electron loss rate, increase rapidly as the time goes on. This means that electrons should disappear almost completely in about 100 \( \mu \text{s} \), as is observed in the simulation shown in the Appendix [Fig. 5(a), curve \( a_1 \)]. The behavior of the experimental electron density in Fig. 1(a), in its early-afterglow part, shows features just described above and therefore can be explained as an ambipolar diffusion phenomenon with the diffusivity enhanced by the presence of negative ions.

Some volume loss processes of electrons may also contribute significantly to the decay of the electron density in the early afterglow. Recombination of thermonized electrons with molecular ions can take place with a rate constant as large as \( 10^{-12} \text{ m}^3 \text{s}^{-1} \) (Ref. 19); with \( n_+ = 10^{16} \text{ m}^{-3} \), this rate constant gives an electron loss rate of \( 10^4 \text{ s}^{-1} \), which is comparable to the diffusion loss rate at the
FIG. 2. Decay of the electron \( n_e \) and negative ion \( n_\text{–} \) densities in the afterglow of a CF4 plasma generated at a pressure of 200 mTorr and rf powers of (a) 3.5 W and (b) 9 W; only the 3.5-W measurements were made by using a short circuit. The solid lines through the measured negative ion densities (□) are the result of a simulation with parameters shown in Table I.

beginning of the decay. Nondissociative attachment of thermalized electrons to molecules and radicals in the CF4 plasma could safely be neglected if we use typical rate constants for ternary and radiative attachment processes. Dissociative attachment of thermalized electrons to CF\( _x \) (\( x = 1 - 4 \)) and C\( _2F_6 \) is energetically not possible. However, dissociative attachment to F\( _2 \) has a large rate constant \( (\sim 10^{-14} \text{ m}^3\text{s}^{-1}) \), and may well be a significant electron loss process depending on the F\( _2 \) density in the plasma; if the F\( _2 \) density is \( \sim 10^{18} \text{ m}^{-3} \), the electron loss rate due to this process is comparable to the diffusion loss rate at the beginning of the decay. The decay rate of the electron density in Fig. 1(a) gradually increases as the time increases in the early afterglow part. Thus, even if the above mentioned processes are important at the beginning of the decay, the diffusion loss process soon outweighs them as \( \alpha \) increases.

It is clear from the above discussion that the observed persistence of the electron density in the late afterglow should be ascribed to some electron generation process, probably to the collisional detachment reaction given by Eq. (1). Thus the apparent slow electron-density decay rate in the late afterglow should be due to the slow negative ion decay rate. The actual electron loss rate in the late afterglow is much faster, as is demonstrated by the fact that the excess electrons generated by laser induced photodetachment in the late afterglow disappeared with a time constant of about 1 \( \mu \text{s} \).

It may be of interest to note the effect of the short circuit on the electron density decay. Among the results shown in Figs. 1 and 2, only the result in Fig. 2(b) was measured without short circuit. The electron density in Fig. 2(b) shows a rapid decrease for a period of a few tens of microseconds immediately after termination of the discharge. The length of this period coincides with the duration of the dc bias voltage in the afterglow, and it is likely that the dc bias voltage accelerates the electron escape to the wall.

B. Negative ion density in the afterglow

The temporal variation of the negative ion density was measured up to about \( t = 3 \text{ ms} \) after termination of the discharge. However, the detected excess-electron signals for measurements with \( t \geq 2 \text{ ms} \) were almost constant and showed no spatial dependence when the laser beam was scanned in the axial direction of the cylindrical cavity; this makes a marked contrast with the measurements at \( t = 0.5 \text{ ms} \), in which the negative ion density showed a sine-like distribution between the electrodes. Moreover, some signal was also detected without igniting the plasma. Therefore we have judged that the signal in the very late afterglow does not come from electrons detached from negative ions, but comes from some kind of photoelectrons, possibly generated on the walls by stray laser photons. In the results shown in Figs. 1 and 2, the nominal density obtained from the very late afterglow has been subtracted from all the data points. This correction is only a few percent in the early afterglow, but becomes large in the late afterglow.

The negative ion density in Figs. 1 and 2 shows a decrease of more than two orders of magnitude in the displayed 2-ms period. The assumption that the initial decay rate is caused entirely by ion–ion recombination leads to a conclusion that the decrease of the density should be only one order of magnitude in the same time period because of the rapidly decreasing recombination loss rate with decreasing ion density. Diffusion is not expected to be important as a negative ion loss process as is suggested by Eq. (6) with \( \gamma = 1 \) as well as by the simulation in the appendix. We therefore reach the conclusion that the negative ions are lost significantly by collisional detachment, confirming the conclusion in the previous section.

To analyze the behavior of the negative ion density more quantitatively, we have employed the following model:

\[
\frac{dn_\text{–}}{dt} = -k_{\text{ri}}n_e n_\text{–} - K_{\text{d}} n_\text{–} \exp(-Rt). \tag{10}
\]

Here, \( k_{\text{ri}} \) is the ion–ion recombination rate constant and \( K_{\text{d}} \) is the collisional detachment rate given by the product of the rate constant \( k_d \) and \( n_0 \), the density of the species (in the active plasma) that cause collisional detachment; \( n_0 \) is assumed to decrease exponentially at a rate \( R \) in the after-

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TABLE I. Collisional detachment rate $K_d$ and its decreasing rate $R$ deduced from the fit of the solution of Eq. (10) to the experimental results. The recombination rate constant $k_3$ was fixed at $5 \times 10^{-13}$ m$^3$ s$^{-1}$ in the fit. Estimated errors in $K_d$ and $R$ are 20%.

<table>
<thead>
<tr>
<th>Pressure (mTorr)</th>
<th>Power (W)</th>
<th>$K_d$ ($10^3$ s$^{-1}$)</th>
<th>$R$ ($10^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>3.5</td>
<td>4.0</td>
<td>0.42</td>
</tr>
<tr>
<td>200</td>
<td>3.5</td>
<td>5.5</td>
<td>0.46</td>
</tr>
<tr>
<td>300</td>
<td>3.5</td>
<td>6.6</td>
<td>1.1</td>
</tr>
<tr>
<td>500</td>
<td>9</td>
<td>5.8</td>
<td>0.86</td>
</tr>
</tbody>
</table>

The recombination rate constant $k_3$ was fixed at $5 \times 10^{-13}$ m$^3$ s$^{-1}$ in the fit. Estimated errors in $K_d$ and $R$ are 20%.

The reason why the model could not give a good fit for the full time span may be explained as follows. Electrons generated by collisional detachment can have much higher energy ($\sim 1$ eV) than the thermal energy. As the effective electron diffusivity increases with increasing $\alpha_e$, generated hot electrons do not have sufficient cooling time before escaping to the wall and thus the average electron energy becomes higher than the thermal energy. This will cause negative equivalent diffusivity of the negative ions, as is suggested by Eq. (6) and the simulation in the appendix, resulting in slowing down of the negative ion decay rate. We expect the effect to be largest shortly after the beginning of the decay, when initial thermalized electrons largely disappear while the generation rate of hot electrons is still relatively high. For the result in Fig. 1(b) the effect should be small because of a relatively small diffusivity at 300 mTorr; it should also be small for the result in Fig. 2(b) because a relatively large amount of initial thermalized electrons takes a longer time to disappear.

The results in Table I indicate that in the active plasma collisional detachment and ion-ion recombination are comparable negative ion loss processes under the present low-power conditions. As $K_d$ appears relatively insensitive to the rf power, so does the density of the species that cause collisional detachment. This might not be surprising if we note that $R$, the loss rate of those species, increases with increasing rf power.

Because of the reasons mentioned in Sec. I, the associative detachment reaction in Eq. (1) is believed to be most responsible for the collisional electron detachment from F$^-$. Booth et al. investigated the CF$_2$ and CF radical densities in the afterglow and in the plasma initiation phase of a 100-W rf CF$_4$ discharge, and concluded that the dominant loss mechanism of these radicals is a wall process. They found that for CF$_2$ the density decay rate in the afterglow was around 140 s$^{-1}$ at 50 mTorr, which decreased by a factor of 2 when pressure was increased up to 500 mTorr; for CF the decay rate was around 600 s$^{-1}$ at 50 mTorr, which also decreased by a factor of 3 at 500 mTorr. In contrast to these results, the value of $R$ in Table I increases with increasing pressure. This suggests that the dominant species that causes associative collisional detachment from F$^-$ is neither CF$_2$ nor CF, but likely to be CF$_3$. Adopting a value of $k_d = 5 \times 10^{-16}$ m$^3$ s$^{-1}$ as the detachment collision rate constant, the density of the species that perform associative detachment is estimated to be $K_d/k_d \sim 10^{19}$ m$^{-3}$. In the simulation of a CF$_4$ plasma (500 mTorr and $n_e = 6 \times 10^{16}$ m$^{-3}$) by Rya and Plumb, the CF$_3$ density accumulated to a few times $10^{19}$ m$^{-3}$. Thus if we assume that $K_d$ depends weakly on the rf power also in the higher power region, the assumption that CF$_3$ is mainly responsible for the detachment collision does not contradict with the simulation by Ryan and Plumb.

C. Plasma initiation

Figure 3 shows the variation of the electron density in the initiation period of a 100-mTorr 12-W discharge. After a transient overshoot for a period of a few hundred microseconds, the electron density only shows a slow and small increase toward a steady-state value. The negative ion density was also measured at $t=0.5$ ms and $t=3$ ms after the plasma initiation, as well as in the steady-state plasma; the results indicate that for $t>0.5$ ms the negative ion density slightly ($\sim 15\%$) decreases toward a steady-state value.
The C₂F₆ molecules are known to have a much larger electron attachment cross section than CF₄, and they are expected to build up in the plasma with a time scale much longer than 0.5 ms. Thus, if electron attachment to C₂F₆ (also to any other species that slowly accumulate in the plasma) produces a significant amount of negative ions in the discharge, the steady-state negative ion density should be significantly larger than the density measured at \( t = 0.5 \) ms after the plasma initiation, contrary to the observed fact. We may therefore conclude that the electron attachment to CF₄ is by far the dominant process that produces negative ions. Similar measurements were made for a 300-mTorr 12-W plasma and led to the same conclusion.

Some information about the building up of the species that cause collisional detachment can be obtained also from the afterglow measurements. Figure 4 shows the electron density decay in the early afterglow after the discharge was run for 1, 3, and 50 ms. Since no short circuit was employed, the electron density first shows a rapid decay due to the remaining dc bias voltage. Subsequently the decay rate slows down with a disappearing bias voltage and after that it again begins to increase as \( \alpha \) increases, causing a shoulder in the decay curve as can be seen in the figure. Throughout the decaying process, electrons are being generated by collisional detachment. Therefore, the more electrons are generated, the longer it should take for the electron density to decay, that is, the shoulder should become broader as the electron generation rate \( k_d n_- \) increases. Since we expect that \( n_- \) in the early afterglow does not depend significantly on the rf pulse width, we may correlate the "width" of the shoulder with \( k_d \) or the density of the species that cause collisional detachment.

In Fig. 4 the width of the shoulder is the largest for curve 2. This means that the density of the species that causes collisional detachment peaks and then decreases toward the steady-state value when the plasma is initiated. In the experiments by Booth et al., the CF₂ and CF densities increased monotonically after the plasma initiation. In the simulation of Ryan and Plumb, only the CF₂ density showed such peaking, which was probably caused by a slow building up of fluorine atoms which remove CF₂ by association. Thus although the plasma conditions are somewhat different, the above facts accord with the assumption that CF₃ is mainly responsible for the detachment collision.

V. CONCLUSIONS

Temporal behavior of the electron and negative ion densities in a low-power (\( \lesssim 10 \) W) pulsed rf plasma in CF₄ was investigated in the pressure range from 100 to 300 mTorr. Enhancement of electron diffusivity in the presence of negative ions was directly demonstrated from the fast decay of the electron density in the afterglow. The behavior of the electron density in the afterglow also revealed the existence of detachment collisions in the plasma. By analyzing the decay of the negative ion density in the afterglow, an ion-ion recombination rate constant and a collisional detachment rate could be estimated. The results indicate that in the active plasma the negative ion removal rates due to the two processes have the same order of magnitude. The estimated collisional detachment rate and accordingly the density of the species that cause collisional detachment increase with increasing pressure and are relatively insensitive to the variation of the rf power under the present experimental conditions. It is also shown that the density of the species that causes collisional detachment peaks and then decreases toward the steady-state value when the plasma is initiated. These observations together with some reported facts about the CF₃ radical densities in CF₄ plasmas are in agreement with the assumption that the collisional detachment is mainly caused by CF₃ through an associative detachment reaction. From the behavior of the measured electron and negative ion densities in the plasma initiation phase, it is confirmed that electron attachment to CF₄ is the predominant process to produce negative ions in the plasma.

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APPENDIX

To support the discussion given in the text, we show in this appendix some numerical solutions of time-dependent transport equations coupled with Poisson's equation. Specifically they are

\[
\frac{\partial n_+}{\partial t} = D \frac{\partial^2 n_+}{\partial x^2} - \mu \frac{\partial}{\partial x} (\varphi n_+),
\]  
(A1)
$P^+ = 0.76 \text{ m}^2\text{s}^{-1}\text{V}^{-1}$, $\mu^- = 1.14 \text{ m}^2\text{s}^{-1}\text{V}^{-1}$, and $\text{positive ion (}n_+\text{), and negative ion (}n_-\text{) densities in the presence}$

Boeuf.26 The 2-cm electrode spacing was divided into 100

DeaslongasD,%D+,D- andn,PZ 10$^3\text{m}^{-3})$. For curves $D+/P^- = 0.03 \text{ eV}$.

In Fig. 5 (a), the simulated decay of the average values of the electron ($n_e$),

positive ion ($n_+$), and negative ion ($n_-$) densities in the presence (curves $a_1, a_2, a_3$) and absence (curves $b_1, b_2$) of negative ions; diffusion is assumed to be the only loss process. For clarity, the negative ion density is multiplied by 0.8 for curve $a_2$. (b) Simulated behavior of the electron density ($n_e$; mean value) and the negative ion density ($n_-; \text{mean value; } n_-; \text{value at the center of space}$) when collisional detachment exists; the electron temperature is assumed to be 0.3 eV (curves $a_1, a_2$) or to be equal to the ion temperature of 0.03 eV (curves $b_1, b_2$).

$$\frac{\partial n_-}{\partial t} = D_- \frac{\partial^2 n_-}{\partial x^2} + \mu_- \frac{\partial}{\partial x} (E n_-),$$  \hspace{1cm} (A2)

$$\frac{\partial n_+}{\partial t} = D_+ \frac{\partial^2 n_+}{\partial x^2} + \mu_+ \frac{\partial}{\partial x} (E n_+),$$  \hspace{1cm} (A3)

$$\frac{\partial E}{\partial x} = \epsilon_0 (n_+ - n_- - n_e),$$  \hspace{1cm} (A4)

where $\epsilon$ is the elementary charge, $\epsilon_0$ is the permittivity of free space, and the other notations are the same as in Eqs. (2)–(4). The method of solution and the boundary conditions employed are essentially the same as described by Boeuf.26 The 2-cm electrode spacing was divided into 100 cells and the time step of the integration was 2 ns. A half-cycle sine function, with its zeros at the boundary, was used as the initial distribution of the particle densities. Based on Ref. 16, the following values were used for the mobility and diffusion coefficient of ions at 100 mTorr: $\mu_+ = 0.76 \text{ m}^2\text{s}^{-1}\text{V}^{-1}$, $\mu_- = 1.14 \text{ m}^2\text{s}^{-1}\text{V}^{-1}$, and $D_+/\mu_+ = D_-/\mu_- = 0.03 \text{ eV}$.

In Fig. 5 (a), the simulated decay of the particle densities in the presence of negative ions is compared with that in the absence of negative ions. The afterglow plasma was assumed to be isothermal ($D_+/\mu_+ = 0.03 \text{ eV}$) and the value of $D_e$ was somewhat arbitrarily chosen to be 90 m$^2$s$^{-1}$ (the results were not very sensitive to a specific value of $D_e$ as long as $D_e > D_+, D_-$ and $n_e \approx 10^{13} \text{ m}^{-3}$). For curves $a_1, a_2,$ and $a_3$ the initial peak particle densities were taken to be $n_e = 10^{15} \text{ m}^{-3}$, $n_+ = 10 \times n_e$, and $n_- = 11 \times n_e$. For curves $b_1$ and $b_2$, $n_e = n_+ = 10^{15} \text{ m}^{-3}$. Although the figure is presented for a pressure of 100 mTorr, it can represent the results at a pressure of $x$ times 100 mTorr if the time scale is multiplied by $x$. Comparison of curves $a_1$ and $b_1$ demonstrates that the presence of negative ions can greatly enhance the electron escape (note the different time scales used for display). Though not clear from curves $a_1 - a_3$, the average value of the net-space-charge density $n_+ - n_- - n_e$ becomes comparable to average $n_e$ when it decreases to $\sim 10^{12} \text{ m}^{-3}$; however, the net space charge is concentrated in the region near the wall, and its density is always less than $10^{11} \text{ m}^{-3}$ at the center of space. The net charge flux to the wall, $\Gamma_+ - \Gamma_- - \Gamma_e$ becomes comparable to $\Gamma_e$ at $n_e \approx 10^{11} \text{ m}^{-3}$. For curve $a_1$, the electron decay rate is close to that of free electrons at $n_e \sim 10^{11} \text{ m}^{-3}$, while for curve $b_1$ the electron decay is much slower at the corresponding electron density. Thus, although the breakdown of the quasineutrality is considerable at $n_e \sim 10^{11} \text{ m}^{-3}$, the existence of large amounts of positive and negative ions still has a notable effect on the electron diffusivity around this electron density. As can be seen from curve $a_2$, the loss of negative ions by diffusion is strongly suppressed until most electrons have disappeared. While the quasineutrality is valid, suppression of the negative-ion diffusion necessarily means that the ratio between the slopes of curve $a_2$ and curve $a_3$ is equal to $\alpha + 1$, as Eqs. (5) and (7) (with $\gamma = 1$) predict. The density ratio $\alpha$ is found to be a weak function of position, its variation over space being at most a factor of three throughout the decay process. (This is only true under the isothermal condition; for $\gamma > 1$, the ratio $\alpha$ can be orders of magnitude smaller near the wall than in the center of space.)

In the late-afterglow part of Figs. 1 and 2, the electron density is low, but electrons are continuously generated by collisional detachment and escaping to the wall rapidly. To estimate the effect of such electrons on the diffusion of negative ions, the following simulation was carried out. Introducing a negative ion loss term $-K_{\mu_-e}$ and an electron generation term $+K_{\mu_+e}$ into Eqs. (A2) and (A3), respectively, Eqs. (A1)–(A4) were integrated with initial densities (peak values) $n_+ = n_- = 10^{15} \text{ m}^{-3}$ and $n_e = 0$. The collisional detachment rate $K_\gamma$ was assumed to be time- and space-independent and was set at 2000 s$^{-1}$, which roughly corresponds to the late-afterglow value for the results in Fig. 1(a). Figure 5(b) shows the results of the integration with $D_+/\mu_+ = 0.3 \text{ eV}$ (curves $a_1, a_2, a_3$) and $D_+/\mu_+ = 0.03 \text{ eV}$ (curves $b_1, b_2$); $D_e$ was fixed at 90 m$^2$s$^{-1}$. The calculated electron density (curves $a_1, b_1$) first increases to $\sim 10^{12} \text{ m}^{-3}$ within 1 $\mu$s, where generation nearly balances with diffusion loss, and subsequently varies relatively slowly because of the slow variation of the generation rate and the effective diffusion loss rate. When the electron temperature is assumed to be 0.03 eV (curve $b_1$), the electron density gradually increases to reach a magnitude comparable to the negative ion density; calculations with a 10 times as large value of $D_e$ led to a similar result. Since such a large electron density relative to the ion density is not observed in the experimental results in Figs. 1 and 2, it is suggested that the actual electron temperature in the late afterglow is somewhat higher than the thermal value. The slope of the average negative ion density decay curve (curve $a_2$) almost coincides with the assumed detachment rate of 2000 s$^{-1}$. This means that the detached $a_1$ and $b_1$ demonstrate...
electrons, despite their low density, prevent negative ions from escaping to the wall. As seen from curve $a_3$, the negative ion density in the center of space, when calculated with an electron temperature of 0.3 eV, decays somewhat more slowly than 2000 s$^{-1}$ in the early stage of the decay. This indicates that electrons at low densities can still cause diffusion of negative ions with a negative equivalent diffusivity.