Numerical study of Ar/CF$_4$/N$_2$ discharges in single- and dual-frequency capacitively coupled plasma reactors

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A one-dimensional particle-in-cell/Monte Carlo model is developed to study capacitively coupled (cc) radio-frequency discharges in a gas mixture of Ar, CF$_4$, and N$_2$. The charged species, which are followed in the model, are: Electrons and Ar$^+$, CF$_3^+$, N$_2^+$, F$^-$, and CF$_3^-$ ions. The simulation considers electron – neutral (Ar, CF$_4$, and N$_2$) collisions, various kinds of collisions of ions with neutrals, positive–negative ion recombination, and electron–ion recombination. The model yields results for electron and ion densities, fluxes and energy distributions, collision rates and electric field, and potential distributions. The simulations are performed for a 0.8/0.1/0.1 ratio of Ar/CF$_4$/N$_2$ mixture at a pressure of 30 mTorr in single (13.56 MHz) and dual frequency (27/2 MHz) cc reactors and a comparison between the two frequency regimes is made. Results show that the structure of the discharges is electronegative in both cases. F$^-$ and CF$_3^-$ ions are the main negative charge carriers in the single and dual frequency regime, respectively. In the presence of low-frequency (2 MHz) and a strong electric field, the light F$^-$ ions are no longer confined in the bulk plasma and they partially respond to the instantaneous electric field. The calculated electron energy probability function profiles can be approximated to a Druyvesteyn and bi-Maxwellian distribution with high-energy tails in the single- and dual-frequency regime, respectively. The ion energy distribution is narrow with one outstanding peak in the single-frequency scheme, whereas it is wide and bimodal in the dual-frequency scheme. © 2003 American Institute of Physics.

I. INTRODUCTION

Radio-frequency (rf) plasma etching is well recognized for its anisotropy, which is a critical process parameter in integrated circuit manufacturing. Conventional capacitively coupled (cc) reactors powered by 13.56 MHz rf sources meet many plasma processing requirements. However, the scaling evolution of semiconductor devices needs more and more accurate transfer patterns with minimum damage on the substrate, which can be achieved by the precise control of both the ion bombardment energy and the ion flux. Single-frequency systems face difficulties providing an independent control of ion energy. For that purpose, dual-frequency systems have been introduced and studied. The dual rf excitation setup allows the plasma density to be determined by one high-frequency (HF), e.g., 13.56 or 27 MHz, or very high-frequency (VHF) source, e.g., 100 MHz, while the substrate self-bias voltage is controlled by the secondary low-frequency (LF), e.g., in the order of 1 MHz. In addition, the LF–(V)HF scheme provides a significantly wider ion bombardment energy range in comparison with a single-HF configuration. Therefore, the study of this plasma processing is of great importance for further improvement of its performance. In the early 90’s, Goto et al. introduced the cc HF–VHF (13.56 – 100 MHz) setup and demonstrated its advantages in low ion energy etching. The discharge was maintained between two electrodes, one of them was driven by a VHF power supply and the other biased by HF. The wafer was placed on the biased electrode. Later on, other dual-frequency schemes, like LF–(V)HF and commensurate frequencies, were applied. Tsai et al. experimentally investigated etching of SiO$_2$ structures in a dual-frequency (27/2 MHz) Ar/CO/CF$_4$ discharge. The dependence of plasma parameters on the substrate frequency and power has also been numerically studied by particle-in-cell (PIC) and fluid models. It was shown that the plasma density is predominantly determined by the primary power source while self-bias and ion bombardment energy are determined by the substrate power source. The experimental study of Ar and Ar/CF$_4$ plasma structures in LF–(V)HF reactors demonstrated that LF biasing and HF plasma production could be functionally separated by increasing the sustaining frequency from 13.56 MHz (HF) to 100 MHz (VHF). However, if the source frequencies are close to each other (e.g., 6.78 and 13.56 MHz) the nonlinear interaction effects can be strong and the resulting plasma characteristics cannot be independently controlled. Recently, an Ar/CF$_4$ discharge has been numerically investigated in a pulsed LF–VHF reactor. The reduction of the local charging by allowing negative ions to reach the electrodes during the off phase has been discussed. The simulation results of the present work show that the same effect can be achieved by applying a different dual-frequency configuration. In the present reactor, the two power supplies are both applied to one of the electrodes and the other electrode is grounded. The wafer is placed on the driven electrode. The purpose of the present work is to study...
Numerically, the discharge structure and properties, and to compare the simulation results of the plasma parameters in a conventional cc single-frequency (13.56 MHz) and dual-frequency (2 + 27 MHz) reactor by means of a one-dimensional PIC/Monte Carlo (MC) method. The influence of the second LF on the discharge parameters, such as charged particle densities and energy distributions, is discussed.

Plasma chemical issues are as much important in the further optimization of etching processes as plasma processing units. Feedgas mixes are usually complex because of the conflicting requirements on the etch rate, selectivity to mask, and anisotropy. Carbon tetrafluoride (CF4) is a basic component in gas mixtures for plasma etching of silicon and silicon dioxide and, therefore, is the most well-studied etch system. Feedgas mixes are usually complex because of the conflicting requirements on the etch rate, selectivity to mask, and anisotropy. Carbon tetrafluoride (CF4) is a basic component in gas mixtures for plasma etching of silicon and silicon dioxide and, therefore, is the most well-studied etch system.

In our previous paper, we presented a one-dimensional PIC/MC model and clarified the plasma structure and parameters in electropositive Ar, electronegative CF4, and Ar/CF4 discharges at different ratios. 

A rapid decrease in electron density is observed with the addition of even a small amount of CF4 to Ar, i.e., the dominant negative charge carriers are the negative ions, and this profoundly influences the sheath dynamics. In the present article, the model is extended to examine the discharge structure in a mixture of Ar and CF4, which is often used for etching, provides insight into the process.

In Sec. II, the input parameters, the outline of the model, and the collisions included in the simulation are given. In Sec. III, the results of the simulation, such as the electric field and potential distributions, charged particle densities, and energy distributions, are presented and discussed. Finally, in Sec. IV, a summary is given.

II. DESCRIPTION OF THE MODEL

A schematic diagram of the dual-frequency cc reactor considered in this study is shown in Fig. 1. The plasma is sustained between two parallel plates, each is 20 cm in diameter and separated from the other by 2 cm. One of the electrodes is driven by a single-frequency (13.56 MHz) power source. The amplitude of the applied voltage is 700 V. The other electrode is grounded. The simulation is carried out at a pressure of 30 mTorr. It should, however, be mentioned that the model presented here, can also be applied to other discharge conditions. The computation is based on a one-dimensional coordinate space and three-dimensional velocity space PIC/MC algorithm. The motion of the charged particles is simulated by the PIC method using the standard explicit “leap frog” finite difference scheme. A PIC simulation treats the charged particles in a kinetic way. It is attractive because the fields and the energy distributions are obtained self-consistently from first principles.

The collisions between the charged particles are added by combining the PIC model with a MC procedure. In the case of modeling of electron-neutralic discharges, the major disadvantage of this method is that it requires a long computational time to reach convergence. The negative charges are confined in the bulk plasma and the only loss mechanism, i.e., ion–ion recombination, has a relatively low reaction frequency. Kawamura et al. point out many physical and numerical methods of speeding up the PIC calculations. Some of the methods, such as longer ion time steps, different weights for electrons and ions, and improved initial density profiles, are applied in this simulation. A more detailed description of the PIC technique can be found in Birdsall and Langdon. Electrons are absorbed and ions are neutralized on the electrodes. Secondary electron emission is included here because the rf discharge is assumed to be in the y-regime at the conditions under study.

The initial densities of the charged species in the model are based on experimental and simulation data. The initial velocities are calculated from the Maxwellian distribution at an average electron temperature of 2 eV and an average ion temperature of 0.043 eV (500 K). The charged species, which are followed in the model, are: Electrons, Ar+, CF3+, N2+, F+, and CF3 ions. Simulation results in a pure cc rf CF4 discharge show that the dominant positive ions are CF3+, with a density exceeding those of CF3+, CF+, C+, and F+ by more than 2 to 3 orders of magnitude, and NCF3+ ≈ N+ + NCF3+ + Ne, where N denotes the number densities in the bulk plasma. For that reason, CF3+ is the only type of positive ions of CF4 followed in the model.

The interactions between the particles are treated by the MC method, which is basically a probabilistic approach. To calculate collision probabilities, it is necessary to have the corresponding collision cross section data, which are not always available. Hence, the present model uses several techniques to define the collision probabilities even when the collision cross sections are unknown.

The electron–neutral collision probability is determined by the null collision method based on cross section data. In the present model, however, the expression for determining the electron scattering angle differs from the one proposed in Ref. 19, as is explained in Ref. 20. The Ar+ – Ar, Ar+ – N2, N2+ – N2, and N2+ – Ar collision probabilities are calculated in the same way. The other ion – neutral elastic and reactive collisions, included in the model, are calculated by an ion–molecule collision model for endothermic reactions. The positive–negative ion recombination probability is determined from a recombination rate constant. The outlines of all techniques are given in our previous paper. In this article, the electron – positive ion...
and at low pressure, a fluid model is more suitable to follow the radicals, such as the electrons. In addition, in comparison with the PIC/MC technique, the concentration and the collision frequency of the other neutrals with the electrons are expected to be much smaller than the concentration and the collision frequency of the background gas. Thus, the influence of the background gas on the radicals is accounted for.

The collisions of electrons with other neutrals, like CF$_4$, nitrogen, and argon, can significantly influence the ion and electron densities, and electron temperature, depending on the power, pressure, and gas composition. Therefore, the concentration and the collision frequency of these collisions taken into account the null-collision technique. Let us express the electron–neutral reaction rate constant, as proposed by Nanbu and Denpoh.

The positive–negative ion and electron–ion recombination reactions considered in the model and the corresponding recombination rate coefficients are presented in Table II. The positive–negative ion and electron–ion recombination reactions, the corresponding rate constants, and the references, are presented in Table II. The ion–ion and electron–ion recombination cross sections and, hence, the probabilities are determined from a given expression for the corresponding threshold energies. The ion–ion and electron–ion recombination rate constants on the electron temperature $T_e$ and ion temperature $T_i$ make the model more complicated. The electron–ion recombination is treated using the null-collision technique. Let us express the electron–ion rate constants as $k_{e-i} = a(T_e)^{1/2}$, where $a$ is equal to $3.95 \times 10^{-13}/T_i$ and $7.72 \times 10^{-14}$ for electron–CF$_4^+$ and electron–N$_2^+$ recombination, respectively. The electron temperature is calculated from $T_e = m_e \nu_e^2/3e$, where $m_e$ and $\nu_e$ are the mass and velocity of the electron, respectively, and $e$ is the electron charge. The probability that an electron with velocity $\nu_e$ combines with a positive ion in time step $\Delta t$ is given by

$$P_{e-i} = W_i N_i \frac{a}{V_e \sqrt{m_e/3e}} \nu_e \Delta t,$$

where $W_i$ and $N_i$ are the ion weight (representing the real number of ions in one simulated superparticle) and the number of the simulated ions, respectively, in a cell with a volume $V_e$. Since Eq. (1) has a singularity at $\nu_e = 0$, a cutoff parameter ($\nu_e_{\text{cutoff}}$) is introduced to obtain the maximum recombination probability.
combination probability. The cutoff parameter is chosen to be 1/5 of the mean electron velocity in each cell so that the probability that a randomly sampled electron has a velocity less than \( (v_e)_{\text{min}} \) is only 1.1% in equilibrium. If the number of the simulated electrons in a cell is \( N_e \), the maximum number of the simulated electrons \( N_{\text{re}} \) that can recombine is calculated from

\[
(N_{\text{re}})_{\text{max}} = \frac{N_e N_i}{V_c} \frac{a}{\sqrt{m_e/3e}} \frac{\Delta t}{(v_e)_{\text{min}}}. \tag{2}
\]

The colliding electrons \( (N_{\text{re}})_{\text{max}} \) are chosen randomly. Then it is checked for each electron with velocity \( v_e \) whether it recombines with an ion, i.e., if a random number \( R \) is less than \( (v_e)_{\text{min}}/v_e \). If \( R \geq (v_e)_{\text{min}}/v_e \), the recombination is null.

It should be kept in mind that in the case of different weights for ions \( W_i \) and electrons \( W_e \), as in the present simulation, the maximum number of simulated ions that can recombine \( (N_{ri})_{\text{max}} \) is not equal to \( (N_{re})_{\text{max}} \) and is given by

\[
(N_{ri})_{\text{max}} = (N_{re})_{\text{max}} \frac{W_e}{W_i}.
\]

For the electron – \( \text{CF}_3^+ \) recombination model, the ion temperature is determined as the mean energy in each cell, i.e., \( T_i = m_i <v_i^2>/3e \), where \( m_i \) and \( v_i \) are the mass and velocity of the ion, respectively.

In the simulation, the recombination time step is taken to be \( 10^5 \) times longer than the electron time step; the probability for recombination is, indeed, low because of the much lower ion densities in comparison with the neutral gas density.

III. RESULTS AND DISCUSSION

The calculations are performed for an \( \text{Ar/CF}_4/\text{N}_2 \) mixture at a ratio of 0.8/0.1/0.1. In Figs. 2-8, the rf powered electrode is at position 0 and the grounded electrode is at position 2 cm. The gas temperature is set to 300 K. The simulation grid is uniform and it consists of 100 cells. The electron time step is 3.7 \( \times 10^{-11} \) s. To speed up the calculation, the ion time step is set to be 25 times longer than the electron time step. The choice of the grid spacing and the time steps is defined by the accuracy criteria for PIC/MC
codes with explicit mover. Typical results of this model are electron and ion densities, fluxes and energy distributions, collision rates and electric field, and potential distributions. The calculated discharge quantities in the dual-frequency regime are saved at different phases in 2 LF and 27 HF cycles since one LF cycle does not contain an integer number of HF cycles. The discharge quantities in the single-frequency regime are saved at different phases in one cycle.

A. Potential and electric-field distributions

Figures 2 and 3 present the simulation results of the potential and electric-field distribution in the single- and dual-frequency regime, respectively. The results are given as a function of distance from the driven electrode and as a function of time in one HF (13.56 MHz) cycle in the conventional cc rf reactor, and in 2 LF (2 MHz) cycles in the dual-frequency (2 + 27 MHz) reactor. The behavior as a function of time and distance looks the same for both frequency regimes, but the difference is found in the absolute values. Indeed, the maximum and minimum values of the potential at the driven electrode in the dual-frequency regime are almost twice as large as those in the one-frequency regime, for the same applied voltage amplitude (700 V), and consequently, the electric field in the sheaths is also much stronger [cf. Figs. 2(a), 2(b), 3(a), and 3(b)].

The discharge structure is electronegative in both investigated schemes. A close look at the electric field in the bulk...
plasma [Figs. 2(c) and 3(c)] shows the appearance of double-layer structures (i.e., the local maxima or minima of the electric field) and field reversal near the bulk–sheath interface (cf. with the results for a pure CF₄ discharge, presented in Ref. 12). The electric field in the bulk plasma is substantial [up to 2000 V/m and 6000 V/m, Figs. 2(c) and 3(c), respectively] since the potential in the bulk is not constant in space. The sheaths are wide due to the narrow gap and the strong electric fields. The electric-field distribution is related to the charged particle density distributions.

B. Electron density distribution

The electron density distribution in both frequency regimes is shown in Fig. 4. In the single frequency reactor [Fig. 4(a)] the electrons move toward one of the electrodes depending on the phase of the applied voltage, i.e., toward the grounded electrode at phase $\pi$/2, and toward the powered electrode at phase $3\pi$/2. The electron density profile in the bulk is significantly different from the flat profile observed in computational and experimental investigations of an Ar/CF₄ discharge at 10% concentration of CF₄, applied voltage amplitude 200 or 240 V, and at a pressure range from 50 to 200 mTorr. Substantial [up to 2000 V/m and 6000 V/m, Figs. 2(c) and 3(c), respectively] since the potential in the bulk is not constant in space. The sheaths are wide due to the narrow gap and the strong electric fields. The electric-field distribution is related to the charged particle density distributions.

C. Ion density distributions

Figure 5 presents the ion density distributions for the single- and dual-frequency reactors. In the single-frequency reactor, the ion density profiles are constant in time throughout the HF cycle [Fig. 5(a)]. The dominant negatively charged species are negative ions, mainly F⁻ (1.2 × 10¹⁵ m⁻³) and to a lesser extent CF₃ ions (6 × 10¹³ m⁻³). This is indeed clearly higher than the electron density. Since the diffusive flux of the negative ions is very low and the electric field is always directed outward, the negative ions are confined in the bulk plasma and are almost
absent in the sheath [Fig. 5(a)]. In the sheath, mainly positive ions and electrons are found [Figs. 5(a) and 4(a)]. The main positive ion is Ar$^+$ and its density in the bulk is $1.8 \times 10^{16}$ m$^{-3}$. CF$_3^+$ and N$_2^+$ ions have densities, which are in the order of $1.0 \times 10^{15}$ and $0.8 \times 10^{15}$ m$^{-3}$, respectively, hence, more than an order of magnitude lower than the density of the Ar$^+$ ions.

For the dual-frequency reactor CF$_3^+$ ions are the dominant negatively charged species with a density of $1.3 \times 10^{16}$ m$^{-3}$ [Fig. 5(b)], whereas the density of the F$^-$ ions is rather small, i.e., only $5 \times 10^{14}$ m$^{-3}$ [Fig. 5(c)]. This is in contrast to investigations for cc single HF pure CF$_4$, Ar/CF$_4$, and Ar/CF$_4$/N$_2$ discharges (see Refs. 8–13). In the presence of LF (2 MHz) and the high electric-field acceleration, the light F$^-$ ions are not confined in the bulk plasma as in HF discharges. They have enough time to move toward the electrodes. The much heavier CF$_3^+$ ions cannot respond to the LF and they remain in the bulk plasma [cf. Figs. 5(b) and 5(c)], where the only loss mechanism is the positive–negative ion recombination with extremely low reaction probability. This explains the higher CF$_3^+$ density compared to the F$^-$ density. The F$^-$ density profile is greatly modulated by the LF and F$^-$ ions are detected at the powered electrode at phase $\pi/2$ of the LF cycle [Fig. 5(c) and see next for the F$^-$ ion energy distribution function (IEDF) at the powered electrode]. From the electric-field distribution, one could expect that F$^-$ ions are able to reach the powered electrode at phase $3\pi/2$, when the electric field is almost 0, like the electrons [Figs. 3 and 4(b)]. However, at that time, F$^-$ ions are detected at the grounded electrode [Fig. 5(c)]. Indeed, the F$^-$ ions are inert in comparison with the electrons and 2 MHz is not low enough for F$^-$ to respond instantaneously to the electric field. This explains the time delay (phase shift of half of a period, $\pi$). We have also carried out simulations for a dual-frequency ($1 \pm 27$ MHz) reactor (not presented here), and they show that F$^-$ ions reach the electrodes at a phase shifted with $\pi/2$ in comparison with the phase when the electric field is close to 0. Hence, a lower LF (1 MHz compared to 2 MHz) results in a smaller phase shift ($\pi/2$ versus $\pi$).

The positive ion density distributions, at phase 0 of the LF cycle in the dual-frequency reactor are presented in Fig. 5(b). The positive ions, can respond to the LF to some extent because the ion plasma frequency $\omega_{pi}$ (calculated to be $2.5 \times 10^7$ s$^{-1}$, $5.3 \times 10^7$ s$^{-1}$, and $5.8 \times 10^7$ s$^{-1}$ for Ar$^+$, CF$_3^+$, and N$_2^+$ ions, respectively) and the applied LF $\omega_{LF}=1.3 \times 10^7$ s$^{-1}$ have comparable values. The main positive ion is again Ar$^+$ and its density in the bulk is $1.4 \times 10^{16}$ m$^{-3}$. CF$_3^+$ and N$_2^+$ ions have densities of about $1.1 \times 10^{15}$ and $0.6 \times 10^{15}$ m$^{-3}$, respectively [Fig 5(b)]. The Ar$^+$ density as a function of time in two LF cycles is given in Fig. 5(d). The density profile depends on time although the dependence is weak.

D. Electron energy distribution

The main advantage of the PIC/MC method is that it does not require any assumption for the electron energy distribution function (EEDF), which is a crucial parameter in the discharge behavior. The EEDF is an output from the calculation. Figure 6 shows the EEPF $f_e(\varepsilon)$ [$= F_e(\varepsilon) e^{-\varepsilon/2}$, where $F_e(\varepsilon)$ is the EEDF and $\varepsilon$ is the electron energy] at the center of the discharge and averaged for one HF cycle in the single-frequency reactor and for 2 LF cycles in the dual-frequency reactor. In the conventional HF reactor, the profile of the EEDF is complicated and can be approximated by a Maxwellian distribution in its low-energy part (i.e., until about 2 eV), and by a Druyvesteyn distribution in the higher-energy part (Fig. 6—solid line). A low-energy electron group is formed with average energy of 1.5 eV. The electron–neutral (mainly Ar because of the highest concentration in the gas mixture) collision frequency of this group ($\approx 7 \times 10^6$ s$^{-1}$) is smaller than the applied frequency ($\approx 9 \times 10^7$ s$^{-1}$), and the low-energy electrons oscillate without collisions in the bulk.$^{32}$

In the dual-frequency reactor, the profile can be approximated by a bi-Maxwellian distribution (Fig. 6—dashed line). The two electron energy groups have energies of 3.5 and 7.5 eV. In the presence of the LF ($\omega_{LF}=10^7$ s$^{-1}$), the two groups effectively interact with the neutrals. The calculated reaction rates show that all electron–neutral collisions in the dual-frequency regime have reaction rates from two to five times higher than the reaction rates in the single-frequency regime. The high-energy tails in both cases are due to the comparatively strong electric field in the bulk, which is a characteristic feature of electronegative discharges. The averaged electron energy determined by the EEDF is calculated to be 7.5 eV and 7.3 eV in the single- and dual-frequency regime, respectively.

E. Ion energy distributions

Figure 7 presents the normalized F$^-$ IEDF at the driven electrode, where the wafer is placed in the dual-frequency reactor. Highly energetic F$^-$ ions (with energy up to 400 eV) are detected at phase $\pi/2$ of the LF cycle [cf. also Fig. 5(c)]. The incident negative ion flux on the wafer reduces the local charging, which is an important issue in improving the performance of the anisotropic etching processes. The negative F$^-$ ion injection was numerically observed also in an Ar/CF$_4$ discharge sustained in a pulsed two-frequency reactor during the off phase.$^7$ In the single-frequency reactor, the electron and positive ion fluxes on the wafer have the same magnitude for a short time during the anodic part of the rf cycle. During the cathodic part of the rf cycle, only positive ions reach the wafer. In the dual-frequency reactor, the electron flux on the wafer is substantial for a longer time during the anodic part of the LF cycle and is replaced by the negative F$^-$ ion flux for a short time of the cathodic part of the LF cycle, reducing the accumulated charge in this way.

The Ar$^+$, CF$_3^+$, and N$_2^+$ IEDFs at the powered electrode, averaged over one HF cycle in the conventional cc rf reactor are presented in Figs. 8(a) and 8(b). The Ar$^+$, CF$_3^+$, and N$_2^+$ IEDFs at the powered electrode, averaged over 2 LF cycles in the dual-frequency reactor are presented in Figs. 8(c) and 8(d). The IEDFs in the single-frequency regime are narrow with one outstanding peak, whereas the IEDFs in the dual-
frequency regime are broad and bimodal as is expected in the presence of the LF.\textsuperscript{33,34}

The parameter determining the shape of the IEDF is the relation $\tau_{\text{ion}}/\tau_{\text{rf}}$, where $\tau_{\text{ion}}$ is the ion transit time and $\tau_{\text{rf}} = 2\pi/\omega_{\text{rf}}$ is the rf period.\textsuperscript{33}

In the HF regime, $\tau_{\text{ion}}/\tau_{\text{rf}} > 1$, i.e., the ions take many rf cycles to cross the sheath, and they respond only to the average sheath potential drop. In a collisionless sheath, this results in a narrow IEDF with one or two peaks, depending on the value of $\tau_{\text{ion}}/\tau_{\text{rf}}$.\textsuperscript{33,34} The IEDF width $\Delta E$ is defined as $\Delta E = E_2 - E_1$, where $E_1$ and $E_2$ are the energies at which the peaks are observed. The width $\Delta E$ decreases with increasing $\tau_{\text{ion}}/\tau_{\text{rf}}$ until, at some point, the two peaks can no longer be resolved. Analytical calculations and experiments in the HF regime show that the width $\Delta E$ is centered at $e\bar{V}_s$, where $\bar{V}_s$ is the mean sheath voltage drop, and it depends on the ion mass ($\Delta E \sim m_i^{1/2}$).\textsuperscript{33,34}

However, the sheaths in the etching reactors, at the conditions under study, cannot be considered collisionless. Elastic and charge exchange collisions broaden the IEDF profile and shift it toward lower energies. Charge exchange collisions lead to the formation of secondary peaks, which are placed at energies lower than $E_1$ and $E_2$.\textsuperscript{33,34}

In the present simulation, for the single-frequency reactor, the two peaks coincide at energies lower than $e\bar{V}_s$ ($\bar{V}_s$ is calculated to be 282 V) [Figs. 8(a) and 8(b)]. The number of secondary peaks in the Ar$^+$ and N$_2^+$ IEDFs are due to the frequent resonant and nonresonant charge transfer collisions between Ar$^+$ or N$_2^+$ and Ar or N$_2$. The charge transfer reaction, CF$_3^+ - CF_3$, is not considered in the model since the density of the CF$_3$ radicals is much lower in comparison with the CF$_4$ density, with a value in the order of 10$^{16}$ m$^{-3}$.\textsuperscript{9,10} The elastic collisions CF$_3^+ - CF_4$ shift the position of the primary peak to an energy of 270 eV (cf. with the calculated $\bar{V}_s$ above). The Ar$^+$ and N$_2^+$ peaks are placed at energies of 240 eV and 260 eV, respectively, due to the influence of both types of collisions. The dependence on the ion mass is also observed. Indeed, the heaviest CF$_3^+$ ion has a narrow IEDF maximum compared to the wider Ar$^+$ and N$_2^+$ primary peaks.

In the LF regime, the ion transit time $\tau_{\text{ion}}$ is less than the rf period $\tau_{\text{rf}}$, i.e., the ions cross the sheath in a small fraction of the rf cycle and they reach the electrode with an energy equal to the instantaneous sheath potential drop.\textsuperscript{33,34} In this simulation $\tau_{\text{ion}}/\tau_{\text{LF}}$, where $\tau_{\text{LF}}$ is the LF period ($f = 2$ MHz), is calculated to be 0.9, 1.2, and 0.7 for Ar$^+$, CF$_3^+$, and N$_2^+$ ions, respectively. The two outstanding peaks in the profile correspond to the averaged minimum and maximum sheath potential drop. In collisionless LF sheaths, the distribution is independent of the ion mass.\textsuperscript{33} However, in the present dual-frequency regime, the influence of the applied HF (27 MHz) is observed and the IEDF width depends on the ion mass $m_i$, i.e., as $m_i$ is increased, $\Delta E$ is reduced (cf. the IEDF width for the three positive ions in Figs. 8(c) and 8(d), considering that $m_{N_2^+} < m_{Ar^+} < m_{CF_3^+}$). The influence of the collisions is the same as in the single-HF regime.

IV. SUMMARY

A one-dimensional PIC/MC model has been developed to describe the structure of a cc rf discharge in a gas mixture of Ar, CF$_4$, and N$_2$. The model follows electrons, Ar$^+$, CF$_3^+$, F$^-$, CF$_3^-$, and N$_2^+$ ions. The collisions treated by the MC method include electron – neutral (Ar, CF$_4$, and N$_2$) collisions, various kinds of collisions of Ar$^+$, CF$_3^+$, F$^-$, CF$_3^-$, or N$_2^+$ with neutrals, positive – negative ion recombination, and electron – ion recombination.

The simulations are performed for 0.8/0.1/0.1 ratios of Ar/CF$_4$/N$_2$ mixture at a pressure of 30 mTorr in single-(13.56 MHz) and dual-frequency (2 + 27 MHz) cc reactors and a comparison between the two frequency regimes is made. The model yields results for the electron and various ion densities, their fluxes and energy distributions, the collision rates and the electric field, and potential distributions. The results are presented as a function of distance to the driven electrode and as function of time in one HF cycle in the single-frequency reactor, and in two LF cycles in the dual-frequency reactor.

The results show that the structure of the discharge is electronegative in both investigated regimes, i.e. double-layer structure and electron density maxima at the bulk – sheath interface are observed, and the main negative carriers are the negative ions. The electron densities in the bulk have similar values in the two regimes. In the dual-frequency regime, the electrons oscillate in one of the sheaths for half of a LF (2 MHz) period with the applied HF (27 MHz). The main negative ion in the single-frequency regime is F$^-$, whereas it is CF$_3^-$ in the dual-frequency regime. Indeed, in the presence of LF (2 MHz) and the strong electric-field acceleration, the light F$^-$ ions are not confined in the bulk plasma as in single-HF discharges and they have enough time to move toward the electrodes. Highly energetic F$^-$ ions (with energy up to 400 eV) are detected at phase $\pi/2$ of the LF cycle at the driven electrode and at phase $3\pi/2$ of the LF cycle at the grounded electrode. The much heavier CF$_3^-$ ions cannot respond to the LF and they remain in the bulk plasma. The positive ion densities do not depend on the phase in the single-frequency reactor. However, in the dual-frequency reactor, the positive ions respond slightly to the LF. The main positive ion is Ar$^+$. The densities of each of the positive ions have similar values in the two regimes.

The calculated EEPF profiles can be approximated to a Druyvesteyn and bi-Maxwellian distribution with high-energy tails in the single- and dual-frequency regime, respectively. The IEDF in the single-frequency regime is narrow with one outstanding peak, whereas the IEDF in the dual-frequency regime is broad and bimodal. The IEDF energy width depends on the ion mass.

In conclusion, the present simulations show that the dual-frequency regime improves the following plasma parameters, which are very important in the etching processes:

1. It provides a significantly wider ion bombardment energy range in comparison with the single-HF configuration.

2. It reduces the charge accumulation by F$^-$ injection to the electrodes.
(3) It randomizes the electron energy by a higher electron–neutral collision frequency in comparison with the single-HF regime at the same pressure. This results in an EEDF distribution, close to the bi-Maxwellian, which can significantly simplify further calculations of plasma quantities determined by the EEDF.

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