Effects of fast atoms and energy-dependent secondary electron emission yields in PIC/MCC simulations of capacitively coupled plasmas

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Abstract. In most PIC/MCC simulations of radio frequency capacitively coupled plasmas (CCPs) several simplifications are made: (i) fast neutrals are not traced, (ii) heavy particle induced excitation and ionization are neglected, (iii) secondary electron emission from boundary surfaces due to neutral particle impact is not taken into account, and (iv) the secondary electron emission coefficient is assumed to be constant, i.e. independent of the incident particle energy and the surface conditions. Here we question the validity of these simplifications under conditions typical for plasma processing applications. We study the effects of including fast neutrals and using realistic energy-dependent secondary electron emission coefficients for ions and fast neutrals in simulations of CCPs operated in argon at 13.56 MHz and at neutral gas pressures between 3 Pa and 100 Pa. We find a strong increase of the plasma density and the ion flux to the electrodes under most conditions, if these processes are included realistically in the simulation. The sheath widths are found to be significantly smaller and the simulation is found to diverge at high pressures for high voltage amplitudes in qualitative agreement with experimental findings. By switching individual processes on and off in the simulation we identify their individual effects on the ionization dynamics and plasma parameters. We conclude that fast neutrals and energy-dependent secondary electron emission coefficients must be included in simulations of CCPs in order to yield realistic results.

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1. Introduction

Low pressure capacitively coupled plasmas (CCP) are widely used for plasma processing: they are basic tools in applications such as plasma-enhanced chemical vapor deposition and plasma etching in the semiconductor industry, as well as in applications aimed at surface treatment in bio-engineering and medicine [1–3]. Their manifold applications
as well as their complex physics have been motivating extensive research in this field via modern experimental methods, analytical modeling, and computer simulation techniques.

The Particle-in-Cell (PIC) approach [4, 5] combined with Monte Carlo (MC) type treatment of collision processes (known as PIC/MCC [6]) has become the prevailing self-consistent numerical method for the kinetic description of low-pressure CCPs [7–9]. In this approach “superparticles”, representing a large number of real plasma particles, are traced, and their interaction is handled via the electric field calculated at points of a computational grid. This efficient simulation technique makes it possible to follow the spatio-temporal evolution of discharge characteristics and to obtain information about various plasma parameters, e.g. densities and fluxes of different plasma species, particle heating rates, rates of different collision processes, etc.

In most of the PIC/MCC studies of CCPs the plasma species that are included in the model are the electrons and the ions formed from the background gas. For instance, in case of CCPs in argon, which is perhaps the most studied gas by PIC/MCC simulations, electrons and (singly charged) argon ions are traced in the discharge gap. Other plasma species, such as metastables and fast neutrals created in ion-atom collisions are usually not taken into account in the models.

Regarding the description of the secondary electron emission processes taking place at the boundary surfaces, further simplifications are also customary. In several studies secondary electron emission from the electrodes has simply been neglected. While CCPs can be sustained in their α-mode of operation without secondary electrons [10–17], this assumption is not always justified. In most studies that consider secondary electron emission (i) a constant value for the secondary electron yield, $\gamma$, is used, that is independent of the discharge conditions (e.g. the energy of impacting ions), (ii) only the ion-induced secondary electron emission is taken into account, neglecting the contributions of other plasma species, (iii) the effect of the surface conditions is not accounted for. In contrast to the α-mode, beyond the mode transition to γ-mode, secondary electron emission plays an essential role in the ionization dynamics [10,18–23]. It is known that besides positive ions the fast neutrals, metastable atoms and VUV photons can as well contribute to secondary electron emission and that the importance of these species depends to a great extent on the discharge conditions (incident particle energies) and electrode surface properties (see [24]). The effect of these “other” species can implicitly be included in a discharge model via definition of an “apparent” or “effective” secondary electron emission coefficient, as the ratio of the secondary electron flux to the ion flux at the electrode. The apparent yield, $\gamma^*$, has been obtained by Phelps and Petrović [24] for the case of a homogeneous electric field (breakdown / Townsend discharge conditions) and by Donkó [25,26] and Marić et al. [27] for cathode fall conditions in abnormal DC glow discharges in argon.

The effects of including fast neutrals and realistic secondary electron yields in the calculations have already been addressed in several previous studies for specific geometries and discharge conditions, but are widely ignored in most current simulations.
of low pressure CCPs under conditions relevant for plasma processing applications. A series of simulation studies by Bogaerts et al. [28–32] on low-pressure DC and radio frequency (RF) analytical glow discharges in argon have demonstrated the importance of electrode surface conditions and fast neutrals contributing to ionization in the gas phase and to sputtering of the electrodes. Braginsky et al. [33] have found the contribution of fast atoms to the secondary electron emission to be comparable to the secondary electron emission due to ion impact in a low-frequency (1.76 MHz) CCP. Bojarov et al. [34] have recently studied the effects of energy dependent $\gamma$-coefficients and fast atoms in CCPs and the effects of different surface conditions at the powered and grounded electrodes. Secondary electrons also significantly affect the realization of the separate control of the ion flux and the mean ion energy at the electrodes in dual-frequency capacitive RF discharges such as found in [18,19]. An asymmetry effect induced by the different electron emission properties of the two electrodes of CCPs (having unequal $\gamma$-coefficients at both electrodes), reported by Lafleur et al. in [35], was found to significantly influence the electrical generation of a DC self-bias and the independent tuning of ion properties in electrically asymmetric discharges [36,37].

These previous observations show that special attention must be paid to the set of plasma particles traced in PIC/MCC models of CCPs and to the precise description of the processes (taking place both in the discharge volume and at the boundary surfaces) that are implemented in the model, in order to realize a realistic description of capacitive RF discharges.

Here we perform a systematic investigation of the effects of fast neutrals and realistic energy-dependent secondary electron emission coefficients on the calculated discharge characteristics resulting from PIC/MCC simulations of CCPs under conditions relevant for plasma processing applications. We focus on single-frequency discharges driven at $f=13.56$ MHz and at three different pressures of 3 Pa, 20 Pa and 100 Pa to probe a non-local collisionless, an intermediate, and a collisional regime. At each of these pressures, simulations are carried out for a wide range of voltage amplitudes. The tracing of fast neutrals is switched on and off and different implementations of secondary electron emission from the electrodes due to heavy particle impact are included in the model. Simulations with constant as well as energy-dependent emission coefficients are performed and secondary electron emission is switched on and off. In this way gas phase and surface effects of heavy particles on the discharge characteristics are identified and separated. We find a dramatic effect of taking into account fast neutrals and realistic secondary electron emission coefficients on process relevant plasma parameters such as the plasma density and ion fluxes to the electrodes. Based on these results, we propose that such processes should be included in PIC/MCC simulations to yield more realistic results.

In section 2 we describe the discharge conditions and specify different physical models that allow the identification of the above effects. The results are presented in section 3, which is split into 3 parts according to the 3 different pressures investigated (3 Pa, 20 Pa, and 100 Pa). In each of these three subsections the effect of including fast neutrals
in the model and the effect of using energy-dependent secondary electron emission yields are separately discussed. Conclusions are drawn in section 4.

2. Physical models and simulation method

![Graph](image), Figure 1. (a): Cross sections of elementary processes used in the simulation [38–40]. The solid lines indicate electron collisions (1: elastic, 2: excitation, 3: ionization), the dashed lines indicate Ar⁺ cross sections (4: isotropic part of elastic scattering, 5: backward elastic scattering, 6: excitation, 7: ionization), and the dotted lines indicate fast Ar atom cross sections (8: isotropic elastic scattering, 9: excitation, 10: ionization). (b): Energy dependence of secondary-electron yields due to Ar⁺ and fast Ar atom (Ar⁺) impact onto a copper electrode under typical laboratory conditions (termed as “dirty” surfaces in [24]).

The calculations are based on our electrostatic 1d3v bounded plasma Particle-in-Cell code complemented with Monte Carlo treatment of collision processes (PIC/MCC) [41, 42], which is extended to handle additional processes to be discussed later on. The discharges investigated are geometrically symmetric. The plane, parallel, and infinite electrodes, separated by a distance of 2.5 cm, are assumed to be made of the same material with identical surface conditions, hence characterized by the same electron
emission and particle reflection properties. We cover neutral gas pressures of 3 Pa (low pressure), 20 Pa (intermediate pressure), and 100 Pa (high pressure). The neutral gas temperature is constant, taken to be 350 K. A voltage waveform of \( V(t) = V_0 \cos(2\pi ft) \) with \( f = 13.56 \) MHz is applied to one electrode located at \( x = 0 \) cm, while the other electrode is grounded. At the electrodes, electrons are reflected with a probability of 0.2 [43].

**Table 1.** Characteristics of the different models used in this work. \( \gamma^* \) is the effective electron yield calculated according to equation (1). \( \text{Ar}^f \) denotes fast atoms.

<table>
<thead>
<tr>
<th>Model</th>
<th>Secondary yield</th>
<th>PIC species</th>
<th>Collisions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( \gamma = 0 )</td>
<td>( e^- ), ( \text{Ar}^+ )</td>
<td>( e^-+\text{Ar}, \text{Ar}^++\text{Ar} ) (elastic, excitation, ionization)</td>
</tr>
<tr>
<td>B</td>
<td>( \gamma = 0.1 )</td>
<td>( e^- ), ( \text{Ar}^+ )</td>
<td>( e^-+\text{Ar}, \text{Ar}^++\text{Ar}, \text{Ar}^f+\text{Ar} ) (elastic, excitation, ionization)</td>
</tr>
<tr>
<td>C</td>
<td>( \gamma = \gamma^* )</td>
<td>( e^- ), ( \text{Ar}^+ ), ( \text{Ar}^f )</td>
<td>( e^-+\text{Ar}, \text{Ar}^++\text{Ar}, \text{Ar}^f+\text{Ar} ) (elastic, excitation, ionization)</td>
</tr>
<tr>
<td>D</td>
<td>( \gamma = 0 )</td>
<td>( e^- ), ( \text{Ar}^+ )</td>
<td>( e^-+\text{Ar}, \text{Ar}^++\text{Ar}, \text{Ar}^f+\text{Ar} ) (elastic, excitation, ionization)</td>
</tr>
<tr>
<td>E</td>
<td>( \gamma = \gamma^* )</td>
<td>( e^- ), ( \text{Ar}^+ ), ( \text{Ar}^f )</td>
<td>( e^-+\text{Ar}, \text{Ar}^++\text{Ar}, \text{Ar}^f+\text{Ar} ) (elastic, excitation, ionization)</td>
</tr>
</tbody>
</table>

The different models used here are listed in Table 1. In the first set of the models, A, B, and C, the “active” species of the PIC/MCC simulations are electrons and \( \text{Ar}^+ \) ions. The MC collision routine handles collisions of these species with the atoms of the background gas. In these models different approaches are used for the secondary emission: model A neglects this process by setting \( \gamma = 0 \), model B uses \( \gamma = 0.1 \), a value often adopted in discharge simulations, while model C calculates the effective secondary yield based on the energies and corresponding yields of the individual positive ions impacting the electrodes.

In the second set of the models, D and E, tracing of fast Ar atoms (\( \text{Ar}^f \)) is also included. The fast neutrals are created mainly in the sheaths, as a result of elastic ion - thermal atom and subsequent fast atom - thermal atom collisions. Neutrals with energies above 23 eV, which are able to generate excitation of the background gas, are treated as fast atoms and are traced in the gap until their energy drops below this threshold value, or until they arrive at the electrodes.

For the conditions covered here ions and fast neutrals contribute dominantly to secondary electron emission [24, 25], thus we disregard the contributions of metastable atoms and UV/VUV photons. The effective secondary yield is calculated as:

\[
\gamma^* = \frac{\sum_{k=1}^{N_i} \gamma_i(\epsilon_k) + \sum_{k=1}^{N_a} \gamma_a(\epsilon_k)}{N_i},
\]

where \( \epsilon_k \) is the energy of the ion or atom (upon arrival at the electrode) noted by \( k \), \( N_i \) and \( N_a \) are the total number of ions and fast atoms reaching a given electrode during a RF period. The energy-dependent secondary yields for ions and fast atoms, \( \gamma_i \) and \( \gamma_a \), respectively, used in this calculation are given as [24, 44]:

\[
\gamma_i(\epsilon) = \frac{0.006\epsilon}{1 + (\epsilon/10)} + \frac{1.05 \times 10^{-4}(\epsilon - 80)^{1.2}}{(1 + \epsilon/8000)^{1.5}},
\]

(1)
Note that a correction to (2), which appeared originally in [24], was given subsequently in [44] and that we use coefficients that characterize surfaces typical for laboratory conditions (termed as “dirty surfaces” in [24]). In the models when fast neutrals are not considered, the calculation of the apparent yield according to (1) uses only the first term of the right-hand side of the equation.

The cross sections for electron-neutral and ion-neutral collision processes are taken from [38–40], while for Ar$^+\text{+Ar}$ and Ar$^+\text{+Ar}$ collisions (elastic scattering, ionization, and the dominant excitation processes) the source of cross section data is [38]. The set of cross sections is plotted in figure 1(a), while the secondary electron emission coefficients for ion and atom impact are plotted as a function of the incident particle energy is displayed in figure 1(b).

At each of the pressures covered, the effect of fast atoms and that of using energy-dependent secondary electron yields in the simulations are investigated. In order to clarify the effect of fast neutrals in the gas phase, simulation results obtained by (i) tracing only ions and (ii) tracing both ions and fast atoms are compared, while the secondary electron emission is neglected ($\gamma = 0$) - models A and D. To study the effect of considering energy-dependent secondary yields in the model, simulations are carried out and the results are confronted for the following conditions: (i) only ions are traced and a constant secondary electron emission coefficient, $\gamma = 0.1$, is used - model B; (ii) only ions are traced and energy-dependent secondary yield for ions is used - model C; and (iii) both ions and fast neutrals are traced and energy-dependent secondary yields for these species are used - model E. The last setting represents the most complete model that includes both the gas-phase and surface effects of the heavy particles, Ar$^+$ ions and fast neutral atoms, in a realistic way, by calculating $\gamma^*$ based on elementary data on energy-dependent electron yields of these two species. Including these additional processes results in a marginal increase of the computation time by only 3% - 5%.

3. Results

3.1. Low pressure (3 Pa)

Gas phase effects of fast atoms

In Figure 2, simulation results for the ion density in the center of the discharge, the ion flux and the mean energy of ions at the electrodes are plotted as a function of the driving voltage amplitude at 3 Pa, based on models A and D, i.e. for the following conditions: (i) as heavy particles, only ions are traced in the model (black lines and squares) and (ii) both ions and fast neutrals are traced (red lines and circles). The secondary electron emission coefficient is $\gamma = 0$ for all cases, i.e. it is assumed that no secondary electron emission is induced by the heavy particles hitting the electrodes. In this way the gas
phase effects of tracing fast neutrals are isolated and can be understood separately from the surface effects.

If only ions are traced, tuning the driving voltage amplitude from 200 V to 1000 V results in an increase of the ion density at the discharge center from $2 \times 10^{14}$ m$^{-3}$ to $5 \times 10^{14}$ m$^{-3}$ [Figure 2(a)]. However, if fast atoms are also traced, increasing the voltage amplitude has a dramatic effect on the calculated plasma density: it increases by about an order of magnitude, from $2.7 \times 10^{14}$ m$^{-3}$ to $2.7 \times 10^{15}$ m$^{-3}$, by changing the voltage amplitude from 200 V to 1000 V.

While at the low voltage amplitude of 200 V, we observe only a slight difference between the ion densities obtained by running the simulations with and without tracing of fast neutrals (the ion density is slightly higher when both ions and fast atoms are traced), the large influence of fast atoms via the $\text{Ar}^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{Ar} + e^-$ process becomes evident at high voltages. For instance, at 1000 V, including fast atoms in the model results in an increase of the ion density at the discharge center by a factor of about 5.4.

The time averaged density distributions of electrons and ions obtained from the simulation including fast neutrals are shown in figure 3 as a function of the distance from the powered electrode for three different voltage amplitudes (300 V, 600 V, and 900 V). Here and everywhere below, the powered electrode is located at $x = 0$ cm and the grounded electrode is located at $x = 2.5$ cm. Figure 3(a) also includes the density profiles obtained from the simulation that traces only ions for comparison. It is noted that at this low pressure of 3 Pa no regular sheath-bulk plasma structure will be obtained for any driving voltage amplitude, if only ions are traced in the model. The development of a quasi-neutral plasma bulk is only observed at high voltage amplitudes.
(above 600 V), when fast atoms are also included in the model. This means that tracing fast neutrals and including ionization by neutral particles results in significantly smaller sheath widths. We note that in experiments significantly smaller sheaths are indeed observed compared to the results of simulations that do not trace fast neutrals [42, 46]. Based on our results presented here, the lack of a realistic treatment of fast neutrals is found to be a reason for these previous differences between the results of simulations and experiments.

For all voltage amplitudes investigated, the calculated charged particle densities are higher if fast atoms are taken into account in the model. The higher densities can be explained by the effect of fast neutrals on the ionization dynamics such as shown in figures 4 and 5. Figure 4 shows spatio-temporal plots of the total ionization rate (a) and the individual contributions of electrons (b), ions (c), and neutrals (d) for a voltage amplitude of 600 V as resulting from model D (including fast neutrals, γ = 0) as an example. Under these conditions, the discharge operates in the α-mode, i.e. the ionization is dominated by electrons heated by sheath expansion. We find the ionization by neutrals and ions to be maximum at the electrodes and the ionization by neutrals to be about one order of magnitude stronger compared to that of the ions. The ionization rate induced by ions is maximum at the electrodes, since ions are accelerated towards the electrodes by the sheath electric field resulting in higher probabilities for an ionizing collision with the neutral background gas close to the electrodes. Fast neutrals are mainly produced by charge exchange collisions of ions with thermal neutrals. Due to the acceleration of positive ions towards the electrode this results in faster neutrals in close vicinity to the electrode and, therefore, more ionization by neutrals at the
Figure 4. Spatio-temporal plot of the total ionization rate (a) and the contribution of electrons (b), ions (c) and fast neutrals (d) to the ionization, obtained from PIC/MCC simulations based on model D, i.e. by tracing both ions and fast neutrals in the model. Discharge conditions: 3 Pa, 13.56 MHz, 2.5 cm electrode gap, $V_0=600$ V, $\gamma = 0$. The color scales are given in m$^{-3}$s$^{-1}$.

Electrode compared to further away from boundary surfaces. Fast neutrals also have an indirect, but important effect on the electron impact ionization rate such as shown in figure 5 for 1000 V as an example. Fast neutrals cause ionization inside the sheaths, i.e. they generate electrons inside the sheaths. Similarly to secondary electrons generated at boundary surfaces, these electrons are accelerated towards the plasma bulk by the sheath electric field and can be multiplied by collisions. In this way ionization by fast neutrals increases the electron impact ionization rate (we note that a similar effect takes place in the sheath of cold-cathode DC discharges [26]). At the low pressures of 3 Pa the collisional multiplication of electrons inside the sheaths is inefficient and the effect of the ionization by fast neutrals on the ionization rate of electrons is weak, but present. This effect is more important at higher pressures (as will be discussed further below). The difference between the densities obtained when only ions are traced and when both ions and fast atoms are traced in the simulation increases with increasing the voltage amplitude. This is related to the more pronounced importance of the process of fast atom impact ionization at high driving voltages due to the higher particle energies. The
difference between the direct contribution of fast atoms and ions to the total ionization in the gap increases as a function of the driving voltage amplitude: the contribution of fast atoms is about 16 times higher than that of ions at 200 V (16% versus 1%), while at 1000 V this factor is about 105 (5% versus 0.05%).

In Figure 2, the flux and the mean energy of ions reaching the electrodes, $\Gamma_i$ and $\langle E_i \rangle$, respectively, are also shown [plots (b) and (c)]. These plasma parameters are most relevant for various plasma processing applications and are, therefore, discussed in detail here. $\Gamma_i$ is higher for all voltage amplitudes when fast atoms are also traced in the model. This can be explained by the higher plasma density as a result of efficient fast atom impact ionization and an enhancement of the electron impact ionization rate due to ionization by ions and fast neutrals inside the sheaths. The difference between the ion fluxes obtained with and without tracing neutrals increases with increasing the voltage amplitude: a slight change of $\Gamma_i$ by a factor of 1.1 is obtained at 200 V, while at 1000 V the ion flux increases by a factor of 1.35 when fast atoms are included in the simulation [Figure 2(b)]. This is explained by the stronger effect of fast neutrals on the total ionization rate at higher voltage amplitudes. The mean energy of ions at the
electrodes is not influenced significantly by including fast atoms [Figure 2(c)]. Similarly to $\Gamma_i$, the flux of fast atoms at the electrodes also increases with increasing the driving voltage amplitude. The flux of fast atoms (above 23 eV) is about the same as that of ions at all voltage amplitudes investigated at 3 Pa. At low voltages, the mean energy of fast atoms at the electrodes is close to that of ions. At high voltages, the mean energy of ions largely exceeds that of fast atoms.

Already at this point our results show that including fast neutrals is essential and must not be neglected in PIC/MCC simulations of CCPs at low pressures in order to ensure more realistic results.

*Effects of using energy-dependent $\gamma$*

In Figure 6, simulation results for the plasma density, the flux and mean energy of ions at the electrodes are plotted as a function of the driving voltage amplitude at 3 Pa. These results are obtained by switching on and off the tracing of fast atoms in the simulation and using energy-dependent secondary electron yields for heavy particles, as well as a constant $\gamma$-coefficient to describe the secondary electron emission at the electrodes, in the following combinations: (i) as heavy particles, only ions are traced and an energy-dependent secondary electron yield for ions hitting the electrodes is implemented in the simulation (black lines and squares - model C), (ii) as heavy particles, ions and fast atoms are traced, and energy-dependent secondary electron yields for these species are used in the simulation (red lines and circles - model E), and (iii) as heavy particles, only ions are traced in the simulation and a constant secondary electron emission coefficient, $\gamma = 0.1$, is used (blue lines and triangles - model B), which represents simulation settings typically used in PIC/MCC simulations of CCPs. This approach allows to study the effect using realistic energy-dependent $\gamma$-coefficients for ions only and the consequences of fast neutrals on surface processes in addition to volume processes (already identified in the previous section) in comparison to usual PIC/MCC simulations, where both processes are neglected.

When only ions are traced in the model, using an energy-dependent secondary electron yield for ions, results in plasma densities slightly lower than those obtained by using a constant secondary electron emission coefficient, $\gamma = 0.1$, for all voltage amplitudes between 200 V and 1000 V [Figure 6(a)]. The lower plasma densities can be explained by analyzing the values of the effective secondary electron emission coefficient, $\gamma^*$, calculated in the model according to equation (1). $\gamma^*$ increases by a factor of 2 by increasing the voltage amplitude from 200 V to 1000 V (see Figure 7). However, $\gamma^*$ remains below 0.1 for all voltage amplitudes if only ions are traced in the model. The deviation of $\gamma^*$ from 0.1 is the origin of the difference observed in the plasma densities. When fast atoms are also traced in the model, $\gamma^*$ increases by a factor of 2.8 by increasing the voltage amplitude from 200 V to 1000 V and it is higher than 0.1 at voltages above 800 V (Figure 7). Besides the additional ionization caused by gas phase effects of fast atoms (discussed in the previous section), the secondary electrons
Figure 6. Ion density in the center of the discharge (a), ion flux (b), $\Gamma_1$, and mean ion energy ($\langle E_i \rangle$), at the electrodes as a function of the driving voltage amplitude, obtained from PIC/MCC simulations using an effective energy-dependent secondary electron emission coefficient, $\gamma^*$, and tracing only ions (line with open squares - model C) and both ions and fast neutrals (line with open circles - model E) in the model. Simulation results obtained by using a constant secondary electron emission coefficient, $\gamma = 0.1$, and tracing only ions in the model are also shown (line with filled triangles - model B). Discharge conditions: 3 Pa, 13.56 MHz, 2.5 cm electrode gap.

Figure 7. Effective secondary electron emission coefficient as a function of the driving voltage amplitude obtained from PIC/MCC simulations using energy-dependent secondary electron emission coefficients and tracing only ions (line with open squares) and both ions and fast neutrals (line with open circles) in the model. Discharge conditions: 3 Pa, 13.56 MHz, 2.5 cm electrode gap.

generated by fast neutral impact lead to even more ionization, resulting in higher plasma
densities compared to the results obtained when $\gamma = 0.1$ is used and only ions are traced [Figure 6(a)]: at 200 V the ion densities at the discharge center are approximately equal $(3.3 \times 10^{14} \text{m}^{-3})$, while at 1000 V a change by a factor of 11 $(7.8 \times 10^{15} \text{m}^{-3}$ versus $7 \times 10^{14} \text{m}^{-3}$) is obtained. Generally, including secondary electron generation due to ion and fast neutral impact results in significantly higher plasma densities compared to the simulation results shown in figure 2, where secondary electron emission is completely switched off. At 1000 V driving voltage amplitude switching on the (energy-dependent) generation of secondary electrons by ions and fast atoms results in a density increase by a factor of about 3.

Tracing only ions and implementing an energy-dependent secondary electron yield for them has only a minor effect on the flux of ions at the electrodes compared to the results obtained by tracing only ions and using $\gamma = 0.1$ [figure 6(b)]. When fast atoms are also traced, the flux of ions at the electrodes is higher for all voltage amplitudes than those obtained for typical settings of PIC/MCC simulations [figure 6(b)]: at the highest voltage amplitude studied here, an increase of $\Gamma_i$ by a factor of 1.6 is obtained $(1.27 \times 10^{19} \text{m}^{-2}\text{s}^{-1}$ versus $7.8 \times 10^{18} \text{m}^{-2}\text{s}^{-1}$). Again, this is explained by the higher plasma densities, when fast neutrals are included. The mean energy of ions is slightly influenced only at high voltage amplitudes by including fast atoms in the model [figure 6(c)]. This can be explained by a decrease of the sheath lengths at high voltage amplitudes, if fast neutrals are included, due to higher ion densities compared to the results of simulations, where only ions are traced.

These results show that PIC/MCC simulations of CCPs performed by using a constant $\gamma$-coefficient (with values around 0.1), or by considering the energy dependence of the secondary electron yield on heavy particle impact but tracing only ions in the model, can largely underestimate the real plasma density. Thus, we conclude that energy-dependent surface coefficients should be used in addition to tracing fast neutrals in simulations of CCPs at low pressures in order to obtain realistic results.

3.2. *Intermediate pressure (20 Pa)*

*Gas phase effects of fast atoms*

The gas phase effects of including fast atoms in the simulation on the calculated discharge characteristics are investigated at an intermediate pressure of 20 Pa. A study similar to that performed at 3 Pa is carried out: simulations are run for different values of the driving voltage amplitude (i) by tracing only ions in the model (model A) and (ii) by tracing both ions and fast atoms in the model (model D). The secondary electron emission is neglected in all cases by setting $\gamma = 0$ in order to isolate the gas phase effects of including fast neutrals from the surface effects. When only ions are traced in the model the voltage amplitude is varied between 100 V and 1000 V. When fast atoms are also included in the model, convergence of the simulations could only be achieved for voltage amplitudes up to 500 V.
In figure 8, the ion density at the center of the discharge as well as the flux and mean energy of ions reaching the electrodes are shown as a function of the driving voltage amplitude for the two different conditions specified above. Here, a strong effect of tracing fast atoms on all three discharge characteristics can be observed. If only ions are traced, the central plasma density increases by a factor of about 19.5 by tuning the voltage amplitude from 100 V to 1000 V (1.97 × 10^{15} \text{m}^{-3} \text{ versus} \ 38.5 \times 10^{15} \text{m}^{-3}) \ [\text{figure 8(a)}]. When both ions and fast atoms are traced, the plasma density exhibits an increase by a factor of 138 by increasing the voltage amplitude from 100 V to the maximum value possible of 500 V at 20 Pa (1.91 \times 10^{15} \text{m}^{-3} \text{ versus} 2.64 \times 10^{17} \text{m}^{-3}). A comparison of these results shows that fast atoms have a great impact on the calculated plasma density especially at high voltage amplitudes (above 200 V): e.g. while at 300 V the plasma density is about 2.26 times higher when fast neutrals are also traced in the model (9.17 \times 10^{15} \text{m}^{-3} \text{ versus} 20.8 \times 10^{17} \text{m}^{-3}), at 500 V an increase by a factor of about 15 is obtained (1.73 \times 10^{16} \text{m}^{-3} \text{ versus} 2.64 \times 10^{17} \text{m}^{-3}).

The effect of fast atoms on the calculated plasma density can also be observed in figure 9, where the time-averaged charged particle densities are presented for 300 V and 500 V. Figure 9 reveals the impact of fast neutrals on the length of the sheath as well: tracing fast neutrals in the model results in a considerable decrease of the sheath widths. These effects can be explained based on the ionization dynamics. As it can be seen in figure 10, tracing of fast neutrals results in significant ionization close to the electrodes. This ionization is mainly induced by fast atoms. Under these conditions, the effect of ionization by fast neutrals on the electron impact ionization rate is much stronger compared to the low pressure scenario discussed in the previous section for two reasons: (i) more electrons are generated inside the sheath by ionization induced
Fast atoms have a large impact on the flux of ions at the electrodes [figure 8(b)]; these electrons are effectively multiplied in the sheath. These electrons are accelerated to high energies in the sheath and generate ionization in the bulk, which finally leads to the increase of the plasma density and decrease of the length of the sheath. This is illustrated in figure 10, where strong ionization (due to electron impact) is observed at times of high sheath voltage. This effect is stronger at higher driving voltage amplitudes due to more ionization by fast neutrals inside the sheaths and a more effective acceleration and multiplication of electrons generated inside the sheaths by heavy particle ionization at higher driving voltages.

Fast atoms have a large impact on the flux of ions at the electrodes [figure 8(b)]: for all voltage amplitudes between 100 V and 500 V the ion flux is higher if fast atoms are included in the model. Compared to the case when only ions are traced, a maximum increase by a factor of about 15 is obtained at 500 V (6.3 × 10^{18} m^{-2}s^{-1} versus 9.5 × 10^{19} m^{-2}s^{-1}). The higher fluxes of ions can be explained by the higher plasma densities obtained when fast atoms are traced in the model due to ionization caused by fast atoms. The mean energy of ions at the electrodes is also affected by fast atoms. Higher values for the mean ion energy are obtained by tracing fast atoms in the model compared to the scenario of tracing only ions as heavy particles [figure 8(c)]. This is due to the effect of fast atoms on the length of the sheath (figure 9): when fast atoms are traced, higher plasma densities and shorter sheath lengths are obtained.

The decrease of the sheath length leads to less collisions involving ions in the sheath. Therefore, ions reach the electrodes at higher energies.

A remarkable effect of tracing fast neutrals is the fact that the simulation diverges for driving voltage amplitudes above 500 V under these conditions, while the simulation converges for all voltage amplitudes studied here (up to 1000 V), if fast atoms are not

Figure 9. Time averaged charged particle density distributions for different voltage amplitudes, (a) V_0=300 V and (b) V_0=500 V, obtained from PIC/MCC simulations by tracing only ions (continuous lines - model A) and both ions and fast neutrals (dashed lines - model D). Discharge conditions: 20 Pa, 13.56 MHz, 2.5 cm electrode gap, γ = 0.
Figure 10. Spatio-temporal plots of the ionization rate for different voltage amplitudes, $V_0=300$ V (a and c) and $V_0=500$ V (b and d), obtained from PIC/MCC simulations by tracing only ions (a and d - model A) and both ions and fast neutrals (c and d - model D). Discharge conditions: 20 Pa, 13.56 MHz, 2.5 cm electrode gap, $\gamma = 0$. The color scales are given in m$^{-3}$s$^{-1}$.

Effects of using energy-dependent $\gamma$

Figure 11 shows the central ion density, ion flux, and the mean ion energy at the electrodes as a function of the driving voltage waveform at 20 Pa based on the models C, E, and B, i.e. for simulations that (i) trace only ions as heavy particle species and
using $\gamma = 0.1$ (blue lines and triangles), (ii) trace only ions as heavy particles, but include an effective $\gamma$-coefficient (black lines and squares), and (iii) trace ions as well as fast atoms and include energy-dependent $\gamma$-coefficients for both heavy particle species (red lines and circles). The first scenario (only ions and $\gamma = 0.1$) corresponds to the conditions typically used in simulations of CCPs.

For the models, where only ions are traced, increasing the secondary electron emission coefficient from 0 (see figure 8) to 0.1 results in a significant increase of the central ion density, the ion flux, and the mean ion energy at the electrodes due to additional ionization by secondary electrons. These increases are more pronounced at higher driving voltage amplitudes, since ionization by secondary electrons is more effective at higher sheath voltages. For the same reason the simulation will diverge at the highest voltage amplitudes above 600 V, if $\gamma = 0.1$ is used instead of $\gamma = 0$. The mean ion energy increases due to shorter and less collisional sheaths due to higher plasma densities at a given voltage for $\gamma = 0.1$ compared to $\gamma = 0$. Generally, the effect of secondary electrons is stronger compared to the 3 Pa cases due to more collisional sheaths and a more effective multiplication of secondary electrons inside the sheaths under otherwise identical conditions.

Tracing only ions in the simulation with an energy-dependent $\gamma$-coefficient results in a lower ion density, flux, and mean ion energy compared to using $\gamma = 0.1$, because $\gamma^*$ is lower than 0.1 for the driving voltage amplitudes used here (figure 12). This shows that a realistic treatment of secondary electron emission results in a less important
Figure 12. Effective electron emission coefficient, \( \gamma^* \), as a function of the driving voltage amplitude obtained from PIC/MCC simulations using energy-dependent secondary electron emission coefficients and tracing only ions (line with open squares - model C) and both ions and fast neutrals (line with open circles - model E) in the model. Discharge conditions: 20 Pa, 13.56 MHz, 2.5 cm electrode gap.

The contribution of \( \gamma \)-electrons to the ionization dynamics compared to assuming a constant emission coefficient of 0.1 under these conditions. \( \gamma^* \) increases as a function of the driving voltage amplitude due to higher values of the incident heavy particle energies at the electrodes.

Tracing fast neutrals in addition to ions and including realistic energy-dependent \( \gamma \)-coefficients results in the highest central ion density, flux, and mean ion energy, because of the gas phase effects of fast neutrals on the ionization dynamics discussed before and the additional generation of secondary electrons at the electrodes by fast neutral particle impact. Therefore, \( \gamma^* \) is generally higher, if fast neutrals are included compared to simulations only tracing ions (figure 12). For the same reason the simulation will diverge for driving voltage amplitudes above 400 V, if energy-dependent \( \gamma \)-coefficients are included and fast neutrals are traced, while it will converge up to 500 V, if secondary electron emission is neglected (\( \gamma = 0 \), figure 8).

Figure 13 shows the time averaged ion and electron density profiles obtained from the simulation at 20 Pa and 300 V driving voltage amplitude for models B and E, i.e. for tracing only ions and using \( \gamma = 0.1 \) such as done in most PIC/MCC simulations of CCPs (solid lines) and for tracing both ions as well as fast neutrals and using an effective secondary yield (dashed lines). The latter approach corresponds to the most realistic model used in this work. The comparison of the density profiles obtained based on the different models demonstrates how important a realistic description of heavy particle dynamics and secondary electron emission at boundary surfaces is under these conditions.
conditions. The density profile obtained from the realistic simulation differs strongly from the one obtained from classical simulation settings, i.e. the central plasma density is higher by a factor of about 3 and the sheaths are smaller by a factor of about 2 in the more realistic simulation.

3.3. High pressure (100 Pa)

Gas phase effects of fast atoms

Figure 14 shows the central ion density as well as the flux and mean energy of ions reaching the electrodes as a function of the driving voltage amplitude at 100 Pa for models A and D, i.e. resulting from simulations, where only ions are traced (black lines and squares) and where both ions and fast neutrals are traced (red lines and circles), while secondary electron emission from the boundary surfaces is deactivated. In this way a collisional regime is investigated, while collisionless and intermediate regimes were studied in the previous sections. In both models, the highest driving voltage amplitudes, for which the simulation converges, are significantly lower compared to the lower pressure scenarios. This is in agreement with experiments, where the current increases with increasing driving power, while the voltage remains low [47, 48].

At this high pressure, the gas phase effects of tracing fast neutrals in the simulation are much weaker compared to the lower pressure conditions discussed before. This is caused by the more collisional sheaths, that reduce the heavy particle energies inside the sheaths strongly. Therefore, the additional ionization by fast neutrals inside the sheaths and its enhancement of the electron impact ionization rate are low particularly at low driving.
These results show that neglecting fast neutrals is justified at high pressures and low neutrals at energies above the threshold for ionization are not generated efficiently due high driving voltage amplitudes. Thus, the central ion density, the ion flux, and mean energy at the electrodes will remain essentially unchanged, if fast neutrals are included, up to about 200 V. At higher driving voltages, the electric field inside the sheaths is high enough to accelerate ions to energies above the threshold for ionization of the background gas by fast neutrals within one mean free path. Thus, neutrals with high enough energies to ionize will be generated more efficiently via charge-exchange collisions and including fast neutrals in the simulation has a stronger effect on the discharge characteristics at high driving voltage amplitudes.

Figure 15 shows exemplary time averaged density profiles for electrons and ions resulting from models A and D (with and without fast neutrals) at 200 V. The density profiles are similar with respect to the central plasma density and the sheath widths, since fast neutrals at energies above the threshold for ionization are not generated efficiently due to the high collisionality of the boundary sheaths at this high pressure. These results show that neglecting fast neutrals is justified at high pressures and low driving voltage amplitudes.

Effects of using energy-dependent $\gamma$

Figure 16 illustrates the effects of using energy-dependent $\gamma$-coefficients on the central ion density as well as the ion flux and mean energy at the electrodes. Results obtained from models C, E, and B are compared, i.e. (i) only ions are traced, but energy-dependent $\gamma$-coefficients are used (black lines and squares - model C), (ii) ions as well as fast neutrals are traced and energy-dependent $\gamma$-coefficients are used (red lines and circles - model E), and (iii) only ions are traced and $\gamma = 0.1$ is used (blue lines and
Figure 15. Time averaged charged particle density distributions obtained from PIC/MCC simulations by tracing only ions (continuous lines - model A) and both ions and fast neutrals (dashed lines - model D) in the simulation. Discharge conditions: 100 Pa, 13.56 MHz, 200 V voltage amplitude, 2.5 cm electrode gap, $\gamma = 0$.

Figure 16. Ion density in the center of the discharge (a), ion flux (b), $\Gamma_i$, and mean ion energy (c), $\langle E_i \rangle$, at the electrodes as a function of the driving voltage amplitude, obtained from PIC/MCC simulations using the effective secondary electron emission coefficient, $\gamma^*$, and tracing only ions (line with open squares - model C) and both ions and fast neutrals (line with open circles - model E) in the simulation. Simulation results obtained by using a constant secondary electron emission coefficient, $\gamma = 0.1$, and including only ions in the model are also shown (line with filled triangles - model B). Discharge conditions: 100 Pa, 13.56 MHz, 2.5 cm electrode gap.

Generally, including secondary electrons enhances the central ion density, the ion flux, and the mean ion energy due to additional ionization by secondary electrons and smaller sheaths, respectively.
In contrast to the lower pressure scenarios discussed in the previous sections, model B (only ions, $\gamma = 0.1$) yields the highest central density, flux and mean ion energy of all three models. This is caused by a significant overestimation of the secondary electron emission coefficient by assuming $\gamma = 0.1$ under these high pressure collisional conditions. In fact, the emission coefficient is much smaller than 0.1 such as shown in figure 17. $\gamma^*$ is between 0.01 and 0.03 depending on the driving voltage amplitude. It is slightly higher for simulations including ions and fast atoms compared to simulations, where only ions are traced. Its low value is caused by the low energies of the heavy particles at the electrodes due to the collisional sheaths. The ion density, flux, and mean energy are slightly higher for simulations, where fast neutrals are included in addition to ions, since additional secondary electrons are generated at the electrodes by fast neutrals.

These results show that the role of secondary electrons at high pressure collisional conditions is significantly less important compared to classical assumptions of $\gamma = 0.1$. Figure 18 shows the time averaged profiles of the electron and ion densities resulting from model B (tracing only ions and assuming $\gamma = 0.1$) and model E (tracing both ions as well as fast neutrals and using energy-dependent emission coefficients) at 200 V and 100 Pa. Due to the collisional sheaths and the low heavy particle energies at the electrodes, the resulting density profiles are similar, but the assumption of $\gamma = 0.1$ results in higher central plasma densities compared to using energy-dependent emission coefficients. The opposite effect is observed at lower pressures (see figure 13).

These results demonstrate that at high pressures (collisional regime) the secondary
The effects of including processes induced by fast neutrals and using realistic energy-dependent secondary electron emission coefficients due to ion and fast neutral impact at the electrodes on the spatio-temporal ionization dynamics, plasma density, ion flux, and mean ion energy obtained from PIC/MCC simulations of CCPs have been investigated systematically under conditions relevant for plasma processing applications. By studying single frequency CCPs operated in argon and driven at 13.56 MHz at 3 Pa, 20 Pa, and 100 Pa, we probe a collisionless, an intermediate, and a highly collisional regime. A systematic variation of the driving voltage amplitude is performed at each pressure and individual processes such as tracing fast neutrals, the presence of secondary electron emission from boundary surfaces, and the energy-dependence of the corresponding $\gamma$-coefficients for ions and fast neutrals are mutually switched on and off to separate gas phase and surface effects of heavy particles on the discharge characteristics.

4. Conclusions

The effects of including processes induced by fast neutrals and using realistic energy-dependent secondary electron emission coefficients due to ion and fast neutral impact at the electrodes on the spatio-temporal ionization dynamics, plasma density, ion flux, and mean ion energy obtained from PIC/MCC simulations of CCPs have been investigated systematically under conditions relevant for plasma processing applications.

Figure 18. Time averaged charged particle density distributions obtained from PIC/MCC simulations using energy-dependent secondary electron emission coefficients and tracing both ions and fast neutrals in the model (dashed lines - model E), and using a constant secondary electron emission coefficient, $\gamma = 0.1$, and tracing only ions in the model (continuous lines - model B). Discharge conditions: 100 Pa, 13.56 MHz, 200 V voltage amplitude, 2.5 cm electrode gap.
Compared to classical simulations, where $\gamma \approx 0.1$ is typically assumed, independently of the incident particle energy, as well as the surface conditions and only ions are traced, we find dramatic effects of tracing fast neutrals and including realistic energy-dependent $\gamma$-coefficients on the discharge characteristics. Under most conditions the plasma density and the ion flux at the electrodes will be drastically increased by a factor of up to 10, if more realistic simulations are performed. This is found to result in shorter and less collisional sheaths and, therefore, in higher mean ion energies at a given driving voltage amplitude. Moreover, the simulation is found to diverge at voltage amplitudes, for which classical simulations still converge. These results are explained by the gas phase and surface effects of heavy particles on the ionization dynamics using realistic energy-dependent secondary electron emission coefficients and are in qualitative agreement with experimental findings. It is found that fast neutrals induce significant ionization inside the sheaths. In this way electrons are generated inside the sheaths at times of high sheath voltage within the RF period. This results in an acceleration of these electrons to high energies and towards the plasma bulk, as well as their multiplication by collisions inside the sheaths. Depending on the collisionality of the sheaths the ionization by fast neutrals can enhance the electron impact ionization significantly in this way. Fast neutrals are also found to contribute strongly to the generation of secondary electrons at the electrodes and enhance the ionization, as well as the plasma density and ion flux additionally in this way. In contrast to the assumption of a constant $\gamma$-coefficient made in most prior PIC/MCC simulations of CCPs, the effective secondary electron emission coefficient is found to be a strong function of the driving voltage amplitude and pressure due its dependence on the incident heavy particle energies. At high pressures its value is always much lower than 0.1, i.e. the role of secondary electrons is overestimated in classical simulations at high pressures, while it can be underestimated at lower pressures, where the effective emission coefficient is found to be higher than 0.1 for high driving voltage amplitudes.

Generally, our results show that classical PIC/MCC simulations of CCPs that do not trace fast neutrals and do not include realistic energy-dependent secondary electron emission coefficients yield unrealistic results under many discharge conditions relevant for low pressure plasma processing applications. As these simulation tools are used for process optimization and important fundamental physical effects are neglected, we propose to include fast neutrals and energy-dependent surface coefficients in simulations of CCPs in order to yield more realistic results. Such more realistic simulations require only marginally longer computation times (3 % - 5 %) compared to simulations that trace only ions and use constant $\gamma$-coefficients under the conditions investigated here.

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