The role of fast argon ions and atoms in the ionization of argon in a direct-current glow discharge: A mathematical simulation

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A model is developed for a direct-current glow discharge in argon by a combination of a hybrid Monte Carlo fluid model of electrons and ions in the entire discharge and a Monte Carlo model of ions and fast atoms in the cathode dark space, in which fast ion and atom impact ionization are incorporated. The relative importance of these processes, compared to electron impact ionization is investigated, as a function of distance from the cathode and at different discharge conditions. It is found that they are dominant close to the cathode, and that they gain importance with increasing voltages. With the incorporation of these processes it was possible to predict current–voltage relations which are in excellent agreement with experiment. Also, the length of the cathode dark space, as a function of pressure and voltage, is calculated; the results agree with Aston's empirical formula. © *1995 American Institute of Physics.*

I. INTRODUCTION

Glow discharges are used for plasma etching and deposition[1] and also in analytical chemistry as spectroscopic sources for mass spectrometry and optical emission spectrometry.[2,3] To improve the results in these application fields, a good insight in the glow discharge is desirable. We try to obtain this by mathematical modeling. Different kinds of models can be used to describe glow discharges, i.e., fluid models, Boltzmann models, and Monte Carlo simulations. Recently, some hybrid models were developed by a combination of a Boltzmann or Monte Carlo model with a fluid model.[4–9] In a previous article[9] we presented a hybrid Monte Carlo fluid model for the electrons and ions in the glow discharge. With this model it was possible to calculate the electrical current when voltage and pressure were given. Comparison of these calculated currents as a function of voltage and pressure with experimentally obtained values indicated that at low voltages the current–voltage relations were correctly predicted (increasing current with increasing voltage) but at voltages above 600 V the calculated current remained constant with increasing voltage. Also the calculated cathode dark space length increased with voltage, whereas the reverse tendency is generally accepted.[10] Collision processes taken into account in this model were electron impact excitation and ionization and elastic collisions. It appears that these processes are the dominant ones at low voltages but that at higher voltages other processes come into play. Indeed, electron impact ionization is responsible for the increasing current with increasing voltage at low voltages ($V<600$ V) since the electrons have mean energies below the maximum in the electron impact ionization cross section curve (at about 100 eV)[11] and higher voltages therefore yield higher electron energies which causes more ionization and hence higher currents. At voltages above about 600 V, however, the mean energies lie beyond the maximum of this cross section curve and electron impact ionization can therefore not be responsible for the increasing currents with increasing voltages. It was suggested[9,12] that fast ion and atom impact ionization [reactions (1) and (2), respectively] could start playing a role,

$$\mathrm{Ar}_f^+ + \mathrm{Ar}^0 \rightarrow \mathrm{Ar}_f^+ + \mathrm{Ar}^+ + e^-, \quad (1)$$

$$\mathrm{Ar}_f^0 + \mathrm{Ar}^0 \rightarrow \mathrm{Ar}_f^0 + \mathrm{Ar}^+ + e^-. \quad (2)$$

Indeed these processes are expected to become relatively more important at high voltages, since their cross sections rise from about 10^{-21}–4×10^{-20} cm^2 below 15 eV to about 4×10^{-17} cm^2 at 35 eV and further to about 5×10^{-16} cm^2 at 1000 eV.[13] These processes are generally not considered when modeling glow discharges; most of these models are, indeed, meant to describe glow discharges used for etching and deposition which typically operate at low voltages (~300 V). Glow discharges used as spectroscopic sources in analytical chemistry, which we tend to describe, operate at voltages of about 1 kV and fast ion and atom impact ionization can become important. In Ref. 14 these processes were incorporated in the modeling of electrical discharges at very high ratios of electric field to gas density ($\mathcal{E}/n$) and at low gas densities, and it was indeed found that they become more important than electron impact ionization at $\mathcal{E}/n>1.5\times10^{-13}$ V cm^2.

In this work, we extend our previous model[9] and include fast ion and atom impact ionization as collision processes. Investigation is made about their relative importance compared to electron impact ionization, as a function of distance from the cathode and at different discharge voltages and pressures. By this extension, we are able to obtain the correct current–voltage relations and the correct behavior of the cathode dark space length as a function of voltage and pressure.

II. DESCRIPTION OF THE MODEL

In the model it is assumed that the plasma consists of argon atoms at rest, fast argon atoms, argon ions, and elec-

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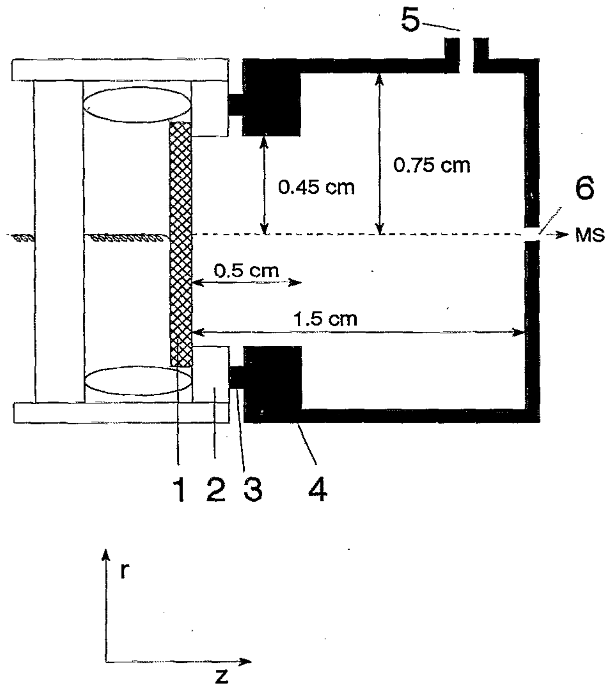

FIG. 1. Standard glow discharge cell in the VG 9000 glow discharge mass spectrometer (Fisons): (1) sample (cathode); (2) mask; (3) insulator; (4) cell body (anode); (5) gas inlet (argon); (6) exit slit.

trons. The model is a combination of the hybrid Monte Carlo fluid model of electrons and ions in the entire discharge, described in Ref. 9, and the ion and fast atom Monte Carlo model of Ref. 15 for the cathode dark space (CDS). A detailed description of the physics and mathematics of these models can be found in these articles. The fluid model is only one dimensional. In the Monte Carlo simulations, three-dimensional motion of the particles is already incorporated, although the species feel only the influence of an axial electric field, since this follows from the fluid model. The discharge geometry to which the Monte Carlo simulations are applied is that of a standard discharge cell of the Fisons VG 9000 mass spectrometer for analyzing flat samples (see Fig. 1).

The ion and fast atom Monte Carlo model described in Ref. 15 takes only charge-transfer and elastic collisions into account. In the present model, also fast ion and atom impact ionization and excitation are incorporated. Ionization cross sections by electron impact and by ion/atom impact are taken from Ref. 11 and from Refs. 13 and 14, respectively. Since small variations in the values of the cross sections (for example 30%) result in large variations in the calculated currents (i.e., a factor of 4), we have adjusted them in order to achieve calculated currents in agreement with experimental values. In practice, they were lowered by 50%. This approach seems reasonable, since the cross sections vary over many orders of magnitude in the entire energy range (0–1400 eV). Moreover, as is shown later, the calculated currents do not only agree with experiment at one voltage value but the correct current–voltage behavior is predicted in the entire voltage range, which seems to warrant our adjustment. The reason that this adjustment has to be carried out is not completely understood yet. Maybe the experimental cross sections are subject to such large errors. This can be true for the ion and atom impact ionization cross sections, since they were not yet studied very extensively by many authors. In Ref. 13 the authors report a systematic uncertainty of ~30% for their cross sections. However, the electron impact ionization cross sections are studied much more extensively and the corresponding errors will be much lower. Nevertheless, relative differences of about 30% can occur between various experimental values, as is shown in Ref. 16. A more plausible explanation is the effect of gas heating. In our model, we use a constant gas temperature of 298 K, but at the higher voltages under consideration this temperature is probably higher, resulting in a lower gas density and hence less collisions, which would yield lower currents. Another candidate is electron–ion recombination, which is normally considered unimportant in the glow discharge and has therefore been neglected, but which possibly should have been taken into account. The most reasonable explanation is, however, the one-dimensional approach of the fluid model. Indeed, in the three-dimensional geometry, electrons and ions can be lost by radial diffusion to the walls, which results in lowering of the current. This reasoning is based on previous work concerning the diffusion of sputtered material.[17,18] In the one-dimensional model[17] a fitting parameter (i.e., for the distance between anode and cathode) was needed to achieve agreement between calculated and experimental etching rates, whereas in the two-dimensional model[18] (cylindrical symmetry) good agreement was reached without this fitting parameter. The adjustment of the cross sections can therefore be interpreted as a correction factor for the one-dimensional character of the fluid model. In future work, we extend the model to two dimensions, in order to test the latter assumption.

The Monte Carlo models of the electrons and of the argon ions and fast atoms are combined with each other through these ionization processes. The model starts with the electron Monte Carlo simulation, with an initial guess of the total electrical current and electric field. The electron flux at the cathode is determined by $j_e(0)=j_{tot}\gamma/(1+\gamma)$, where γ is the secondary electron emission coefficient due to ion bombardment (i.e., 0.083 for Cu/Ar). In this electron Monte Carlo simulation the ionization rate by electron impact is calculated. This ionization rate (creation rate of ions) is used as input in the ion and fast atom Monte Carlo simulation. The ion flux at the interface between cathode dark space (CDS) and negative glow (NG) is determined by $j_i(l)=j_{tot}+j_e(l)$, where $j_e(l)$ is the electron flux at the CDS/NG interface, computed in the electron Monte Carlo simulation. In the ion and fast atom Monte Carlo simulation, the ionization rate by fast ion and atom impact is calculated. This ionization rate (creation rate of electrons) is again put into the electron Monte Carlo simulation, and this procedure is repeated until convergence is reached (i.e., when the ionization rates and the ion and electron fluxes do not change anymore from one iteration loop to another). The total ionization rates due to electrons, ions and fast atoms, together with the slow electron creation rate, are used as input in the

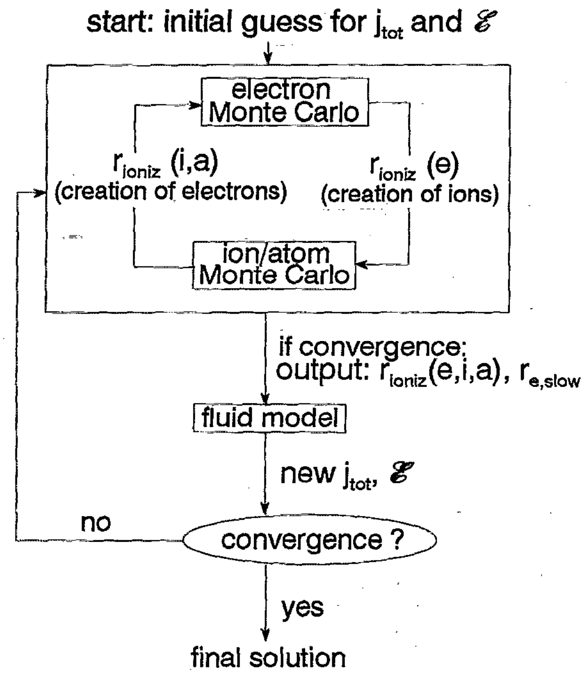

FIG. 2. Flowchart of the model.

fluid model, as described in Ref. 9. The fluid model yields a new electric field and total electrical current. These new values are again used in the electron and ion/fast atom Monte Carlo simulations, which gives new ion and slow electron creation rates for the fluid model. The total procedure is repeated until final convergence is reached. A flowchart of the entire model is illustrated in Fig. 2.

III. RESULTS AND DISCUSSION

Since the cross sections of electron impact and fast ion/atom impact ionization are of the same order of magnitude (i.e., $\sim 3\times 10^{-16}$ cm^2 at the maximum (about 100 eV) for electrons and about the same value at 500 eV for ions/atoms), one can expect that these processes will be of comparable importance at sufficiently high voltages. Figure 3 shows the efficiencies of these processes for electrons, ions, and fast atoms in the CDS at 100 Pa Ar and 1000 V; i.e., the number of ionization processes per electron/ion/fast atom and per cm. The efficiency of electron impact ionization is clearly higher than those of ion and fast atom impact ionization; the electrons have, indeed, energies which yield more efficient ionization than the ions and fast atoms, i.e., the electron mean energies are of the order of 400–600 eV, while the ion and fast atom mean energies are less than 120 and 6 eV at these discharge conditions, respectively.[15] Moreover, the efficiency of electron impact ionization is nearly constant throughout the CDS (and also in the NG), whereas the efficiency of fast ion and atom impact ionization decreases linearly towards the NG, to become virtually zero at about 0.12 cm from the cathode.

In Fig. 4 the ionization rates of these processes are illustrated at 100 Pa Ar and 1000 V, for electrons, ions, and fast atoms in the CDS. The rates are the efficiencies multiplied

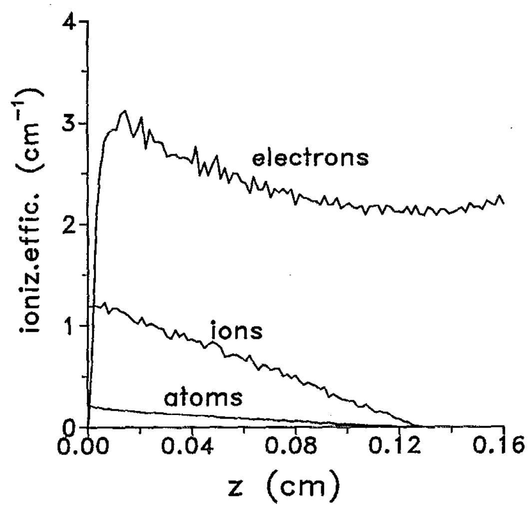

FIG. 3. Efficiency of impact ionization by electrons, ions, and fast atoms in the CDS, as a function of distance from the cathode, at 100 Pa and 1000 V, expressed as number of ionization processes per electron/ion/atom and per cm.

by the fluxes of particles at each position. We see that the ionization rates by ion impact and especially by atom impact gain in importance, due to the higher fluxes.[15] Close to the cathode, most of the ionization occurs by fast atom impact and also by ion impact. Further in the CDS, the ionization by atom and ion impact decreases while the contribution of the electrons increases. Close to the CDS/NG interface, all the ionization is caused by electrons. When integrating the ionization rates over the total one-dimensional distance, we obtain the relative importance of each of the different processes at 100 Pa and 1000 V. About 5.6% and 13.2% of the total ionization in the discharge is due to ion and fast atom impact in the CDS, respectively. About 11% is caused by electron impact in the CDS and the remaining 70.2% is ascribed to electron impact in the NG. Hence, since the NG covers in general the larger part of the discharge, electron impact ion-

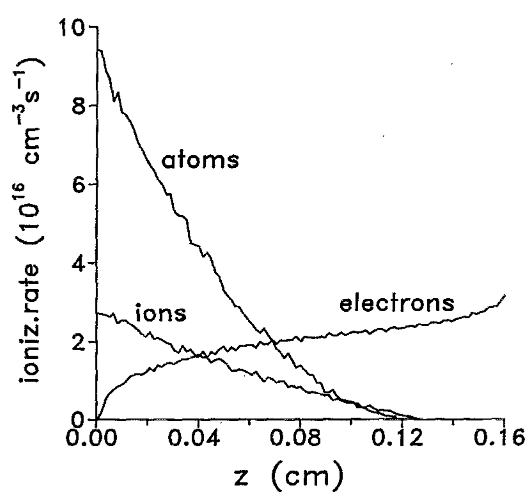

FIG. 4. Rate of impact ionization by electrons, ions, and fast atoms in the CDS, as a function of distance from the cathode, at 100 Pa and 1000 V.

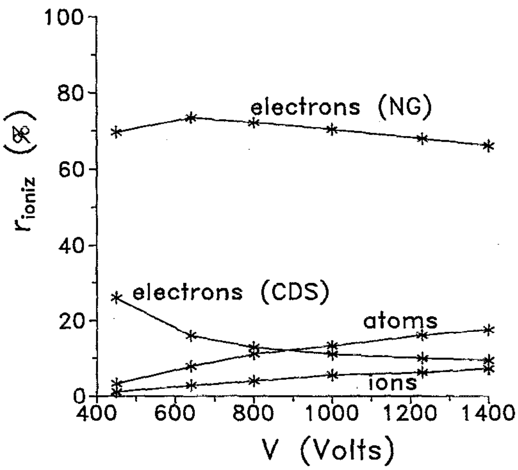

FIG. 5. Relative contribution of impact ionization by electrons, ions, and atoms, as a function of voltage, at 100 Pa, integrated over the whole discharge.

ization in this region is still the most important ionization process, but ion and fast atom impact ionization in the CDS clearly cannot be neglected.

Figure 5 shows the relative importance of ionization due to fast ion and atom impact in the CDS and electron impact in the CDS and NG, as a function of discharge voltage at 100 Pa Ar. Although electron impact ionization in the NG remains the predominant process at all voltages, ion and especially fast atom impact ionization are gaining increasing importance at higher voltages, due to the higher energies of the particles. The relative contribution of ion and fast atom impact ionization increases also slightly with decreasing pressure.

Figure 6 represents the current–voltage relations at different pressures, obtained from this model. The current increases with voltage at constant pressure and also increases with pressure at constant voltage. Moreover, the slope of the

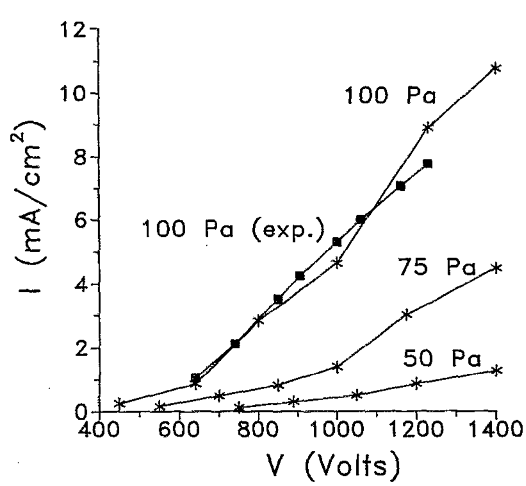

FIG. 6. Calculated currents (*) as a function of voltage at three pressures. With the previous hybrid model these calculated currents were constant at voltages above 600 V. Experimental data obtained at ~100 Pa are also shown (■).

current–voltage curve is steeper at high pressures. Experimental values measured with the VG9000 glow discharge mass spectrometer (Fisons) for Cu in Ar at 100 Pa (Ref. 19) are also included for comparison. The excellent agreement between experiment and theory in the entire voltage range suggests that the present model is realistic. It should be noted, however, that the exact influence of the pressure cannot easily be checked, since it is difficult to accurately measure the pressure inside the discharge cell of the VG 9000 mass spectrometer.

In Ref. 20 an empirical formula for the current–voltage relation in a direct-current (dc) glow discharge was given as

$$V=V'+RI, \tag{3}$$

where V' is the breakdown voltage beyond which current begins to flow and R is the resistance of the discharge. This resistance can be considered to a first approximation as being only a function of the distance between cathode and anode, of the cathode area and of the pressure in the cell. More accurately, the resistance also increases linearly with current density, since the increased charge density inhibits either charge creation or charge mobility.[21] Writing the resistance more explicitly yielded the following current–voltage relation:[20]

$$V=V'+\frac{4k'}{\pi D^m}\frac{I^r}{p^s}, \tag{4}$$

where $4k'/\pi D^m$ expresses the dependence of the resistance on the geometry of the cell (k' is a function of the length and πD^m represents the cathode area). Applied to our current–voltage relations, r can be taken equal to 1 (i.e., linear current–voltage relation, resistance independent of current), and s takes a value of about 3. Comparing this with the fitted values of s in Ref. 20 (i.e., 2.34–2.99), our calculated pressure dependence seems correctly described.

Finally, we were able to calculate the length of the CDS as a function of voltage and pressure, illustrated in Fig. 7(a). The CDS length increases with decreasing voltage and pressure, which is necessary in order to sustain the discharge. At extremely low pressures and voltages, the CDS would take up the entire discharge region. Indeed, the glow discharge can be maintained without NG, but the CDS is an essential zone. By further lowering the pressure and voltage, the discharge would stop. The pressure effect is clearly more pronounced than the voltage effect, and the latter is generally larger at low voltages. We evaluated our calculated results with an empirical relation proposed by Aston[22] between the CDS length d_{cds} and pressure and current density in the discharge,

$$d_{cds}=\frac{A}{p}+\frac{B}{j^{1/2}}, \tag{5}$$

where A and B are constants. In Fig. 7(b) it is indeed seen that there is a linear relationship between d_{cds} and $j^{-1/2}$ at constant pressure. The inverse proportionality between d_{cds} and pressure at constant current is also more or less observed, although the CDS length seems to vary somewhat

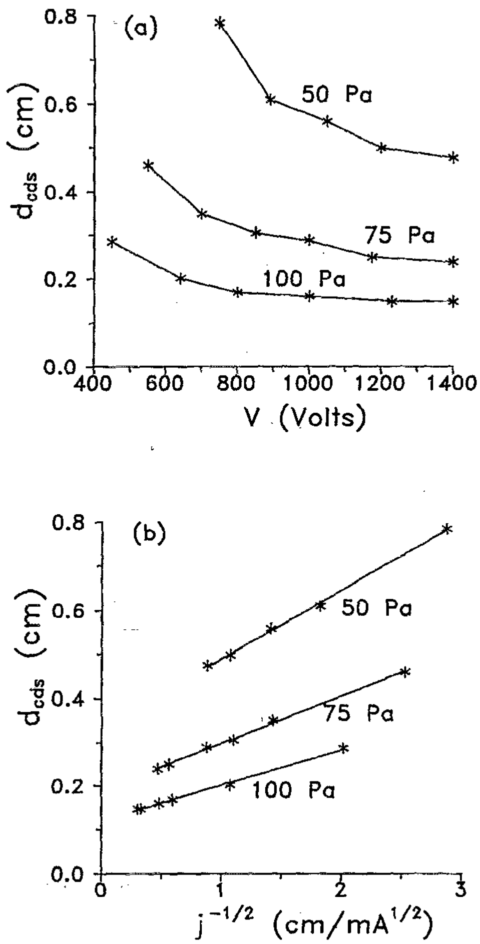

FIG. 7. Cathode dark space lengths d_{cds} at three pressures, (a) as a function of voltage, and (b) as a function of $j^{-1/2}$ (verification of Aston's empirical formula; j is the total electrical current density). With the previous model, these calculated CDS lengths increased with voltage.

more than the pressure. In general, a satisfactory agreement between our calculated results and the empirical formula is found, which validates our present model.

IV. CONCLUSION

We combined a hybrid Monte Carlo fluid model of electrons and ions in the entire glow discharge with a Monte Carlo model of ions and fast atoms in the CDS, in which ion and atom impact ionization have been incorporated. The relative importance of these processes compared to electron impact ionization is investigated, as a function of distance from the cathode and at different voltages and pressures. It is found that these processes become increasingly important at higher voltages due to their higher energies, while pressure seems to have no significant influence. After slight adjustment of the ionization cross sections found in the literature, probably in order to account for the radial losses of ions and electrons in the one-dimensional fluid model, we were able to predict correct current–voltage relations in the entire voltage range, which was not possible with the previous hybrid Monte Carlo fluid model, where ion and fast atom impact ionization were neglected. Finally, the lengths of the CDS were calculated at different voltages and pressures. These lengths were found to increase with decreasing pressure and voltage, which is also an improvement compared to the previous hybrid model where the lengths increased with increasing voltage. Moreover, the present lengths are in good agreement with Aston's empirical formula.

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