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Three-dimensional modeling of a direct current glow discharge in argon: is it better than one-dimensional modeling?

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Abstract To obtain a better insight in the glow discharge, one-dimensional and three-dimensional models were developed for describing the behavior of the different species present in the discharge. In general, three-dimensional models are more complex and consume more computer time than one-dimensional models. To test whether it is really necessary to develop three-dimensional models or whether the one-dimensional approximation yields already a satisfactory description of the glow discharge, the results of both approaches have been compared. For the investigated cell geometry, the results are more or less comparable. Hence, one-dimensional models are in a first approximation sufficient to obtain a better insight in the glow discharge. However, three-dimensional models can give additional information (e.g., crater profiles at the cathode) and are therefore a progress when a more complete description of the discharge is intended.

Introduction

For good analytical practice of glow discharge techniques (mass spectrometry and optical emission spectrometry), a clear insight in the glow discharge is desirable. We try to obtain this by mathematical modeling. We have developed a set of models (fluid models and Monte Carlo simulations) to describe the behavior of the different species present in a direct current glow discharge in argon [1–10]. The models were originally developed in one dimension [1–6], and were later extended to three dimensions, and applied to the standard cell for analyzing flat samples of the VG9000 glow discharge mass spectrometer (VG Elemental, Thermo Instruments) [7–10]. Due to the cylindrical symmetry of this cell, the three dimensions could be reduced to two dimensions in the fluid models. The Monte Carlo simulations (i.e., describing the trajectory and collision processes of the particles) are, however, carried out entirely in three dimensions. Due to limited space, a complete description of the modeling network is not possible here. Table 1 presents an overview of the species assumed to be present in the plasma, and the different models used to describe these species. The fast electrons are treated with a Monte Carlo model; collision processes incorporated are elastic collisions with argon atoms, electron impact excitation and ionization from the argon ground state and from the metastable level, and ionization of sputtered copper atoms. The behavior of the slow electrons and the argon ions is calculated in a fluid model; the continuity and transport equations are coupled with the Poisson equation to obtain a self-consistent electric field distribution. Moreover, the argon ions are described with a Monte Carlo model in the cathode dark space (CDS), as well as the fast argon atoms which are created by charge transfer and elastic collisions from the argon ions. The collision processes taken into account are symmetric charge transfer for the argon ions, elastic collisions with argon atoms for both argon ions and fast atoms, and fast argon ion and atom impact ionization and excitation of argon atoms. The argon metastable atoms are handled with a fluid model, consisting of a balance equation with different production and loss processes. The atoms of the cathode material (copper is taken as an example), which are sputtered away from the cathode due to the bombardment by argon ions and fast argon atoms, enter the plasma with energies of a few eV. They lose these energies almost immediately by collisions with the argon gas atoms, until they are thermalized. This thermalization process of the sputtered copper atoms is described with a Monte Carlo model. The subsequent diffusion, the creation of copper ions and the transport of these copper ions, are

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Table 1 Overview of the different models used to describe the plasma species

Plasma species	Model
Fast electrons	Monte Carlo (entire discharge)
Slow electrons	Fluid (entire discharge)
Ar^+ ions	Fluid (entire discharge)
Ar^+ ions	Monte Carlo (CDS)
Ar_f^0 atoms	Monte Carlo (CDS)
Ar_m^* metastable atoms	Fluid (entire discharge)
M^0 atoms (thermalization)	Monte Carlo (entire discharge)
M^0 atoms + M^+ ions (diffusion, ionization)	Fluid (entire discharge)
M^+ ions	Monte Carlo (CDS)

handled in a fluid model. Finally, the behavior of the copper ions in the CDS is also treated with a Monte Carlo model. All these models are combined into a comprehensive modeling network, and solved iteratively until final convergence is reached, to obtain an overall picture of the glow discharge. For more information about the models, see [1–10].

Modeling of a glow discharge in three dimensions is clearly more complicated than modeling in one dimension. Indeed, three-dimensional scattering of the particles has to be taken into account, and the solution algorithms and boundary conditions of the models become more intricate. Moreover, the three-dimensional models require considerably more calculation time, i.e. the particles in the Monte Carlo models have to be followed for a longer time in the plasma due to back and forth scattering, and the solution algorithms in the fluid models require an additional loop for the radial direction. On the other hand, three-dimensional models present, in principle, a more realistic picture of the glow discharge cell.

Typical results of both our one-dimensional and three-dimensional models have been presented in a number of previous papers (i.e., refs. [1–6] and [7–10], respectively), and they will therefore not be shown here again. In the present paper, we want to investigate whether one-dimensional models also yield a satisfactory description of the reality or, in other words, whether it is worthwhile to incorporate three-dimensional effects in the models. Therefore, the results of the three-dimensional simulations will be compared with results of one-dimensional models. Two kinds of "one-dimensional" models will be examined. The first one is a combination of one-dimensional fluid models and three-dimensional Monte Carlo simulations. In the fluid models, cathode and anode are represented by two infinitely wide parallel plates without side-walls, so that the quantities in the plasma vary only with axial distance from the cathode. In the Monte Carlo models the exact three-dimensional cell geometry is already included and three-dimensional scattering of the particles is taken into account. However, the particles feel only the influence of an axial electric field, since this is what follows from the one-dimensional fluid approach. This kind of model can be expected to be more or less realistic if the length of the cell is smaller than its diameter, so that the side-walls have a minor effect anyhow. In the second kind of one-dimensional model, three-dimensional scattering of the particles is also neglected in the Monte Carlo calculations and it is assumed that the particles move only in one direction.

The results of our three-dimensional models will be compared with results of both kinds of one-dimensional models considered above. For simplicity, the three-dimensional simulation is designated as 3D model, the combination of three-dimensional Monte Carlo and one-dimensional fluid models is specified as 3D1D model, whereas the complete one-dimensional approach is indicated as 1D model.

Results of the comparison and discussion

Figure 1 shows a schematic picture of the VG9000 glow discharge cell to which the models are applied. However, the cell used for the modeling work is approximated by a closed configuration, without gas inlet and exit slit to the mass spectrometer. This implies that there is no gas flow and that the argon gas is more or less at rest, uniformly distributed throughout the cell. This approximation seems to be more or less justified, as argued in ref. [9]. The one-dimensional models apply to a cell consisting of two parallel electrodes,

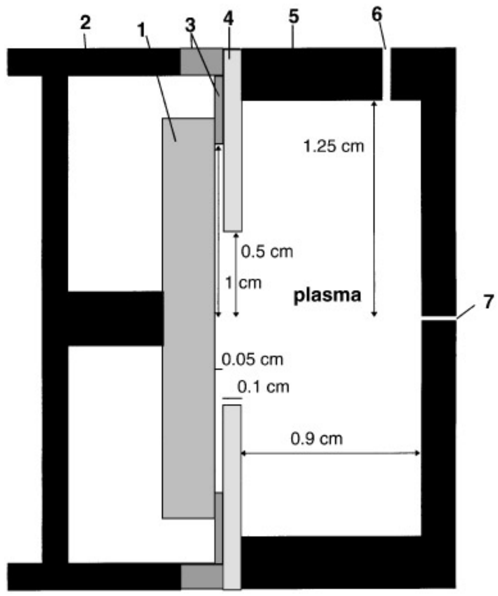

Fig. 1 Schematic representation of the glow discharge cell to which the models are applied (VG9000 standard cell for analyzing flat samples; VG Elemental, Thermo Group). *1*: Sample (cathode); *2*: sample holder (at cathode potential); *3*: insulator; *4*: front plate (at anode potential); *5*: cell house (anode); *6*: argon gas inlet; *7*: exit slit to the mass spectrometer

placed at a distance of 1.05 cm from each other, which is exactly equal to the distance between cathode and anode backplate in the VG9000 glow discharge cell.

With the models, the total electrical current can be calculated in a self-consistent way, when pressure, voltage and gas temperature are given. The calculated current can then be compared with experimental values, to test the validity of the models. For a gas temperature of 360 K, the 3D model yielded a current of 3.4 mA at 1000 V and 75 Pa (see ref. [8]). When assuming the same gas temperature, the 3D1D model resulted in a current of 5.7 mA at the same voltage and pressure conditions. Indeed, in the one-dimensional argon ion-slow electron fluid model, the argon ions and slow electrons cannot get lost at the sidewalls. Hence there are more current carriers in the plasma, which manifests itself in a higher electrical current. A current of 3.4 mA could be obtained by increasing the gas temperature to 410 K. Indeed, at a higher gas temperature, the gas atom number density is lower, which results in less ionization collisions and hence in a lower current. The 1D model calculated an electrical current of 1.8 mA at 360 K, 1000 V and 75 Pa, which is lower than in the 3D model. Indeed, in the one-dimensional Monte Carlo approximation, the electrons and ions move only in the forward direction, causing thereby less ionization collisions than in a three-dimensional Monte Carlo model where they can scatter back and forth and have a longer residence time in the plasma. Hence, in spite of the fact that the one-dimensional fluid model yields more current carriers (see above), the net effect is a lower electrical current than in the 3D model. When lowering the gas temperature to 330 K, the same electrical current of 3.4 mA could be obtained.

Since the exact gas temperature in the glow discharge is not known, it is used as a kind of fitting parameter in the models, i.e., it is chosen in order to obtain realistic values for the electrical current. The values of 330 K, 360 K and 410 K all seem reasonable. Therefore, as long as the exact gas temperature is not known, it must be concluded that the three kinds of models yield realistic results for the electrical current. In order to make the best comparison between the three models, the 3D1D model and the 1D model were calculated at 410 K and at 330 K, respectively, so that the three kinds of models present results at the same voltage-pressure-current conditions.

Figure 2 shows the one-dimensional argon ion density profiles, calculated with the three different models. The results of the 3D model are taken at the cell axis (r = 0). The slow electron density has almost the same profile, except that it is zero in the cathode dark space (CDS) and at the anode wall (see ref. [8]). The argon ion density calculated with the 3D model is a factor of about 2 lower than the results of the one-dimensional models. Indeed, as explained before, in the one-dimensional fluid model the argon ions and slow electrons do not get lost at the side walls, giving rise to a higher

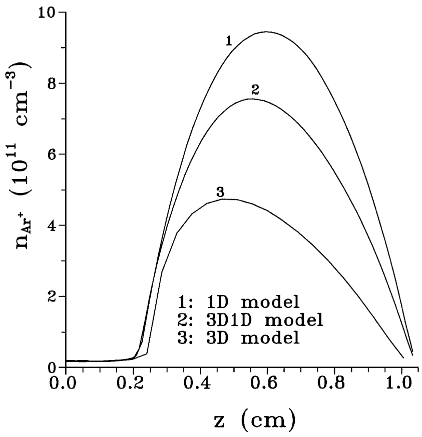

Fig. 2 One-dimensional density profiles of the argon ions, calculated with the 3D model and two 1D models (at 75 Pa, 1000 V, 3.4 mA, copper cathode in argon)

density in the plasma. The argon ion density resulting from the 1D model is still a little higher than the one obtained with the 3D1D model, due to the slightly lower gas temperature which yields lower diffusion coefficients and hence somewhat higher densities.

The fast electron density feels the influence of the three dimensions in a different way, as appears from Fig. 3. Indeed, the densities calculated with the 3D and the 3D1D model (i.e. three-dimensional Monte Carlo models) are a factor of about 2 higher than the 1D results. This is attributed to the back and forth scattering of the electrons in the three-dimensional Monte Carlo models, giving rise to a higher residence time in the plasma and hence a higher density. The fact that the density obtained with the 3D model is somewhat higher than the 3D1D result is again ascribed to the slightly lower gas temperature, yielding a higher argon gas atom density and therefore more ionization collisions and more electron multiplication. The same trend

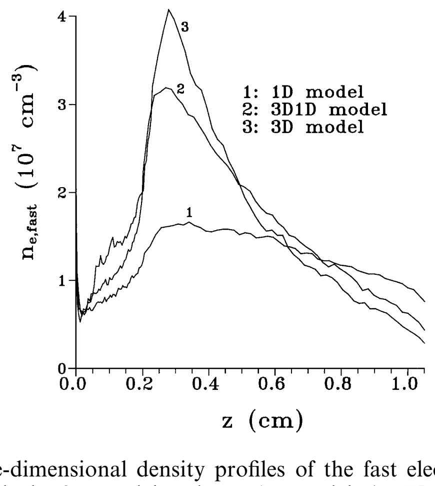

Fig. 3 One-dimensional density profiles of the fast electrons, calculated with the 3D model and two 1D models (at 75 Pa, 1000 V, 3.4 mA, copper cathode in argon)

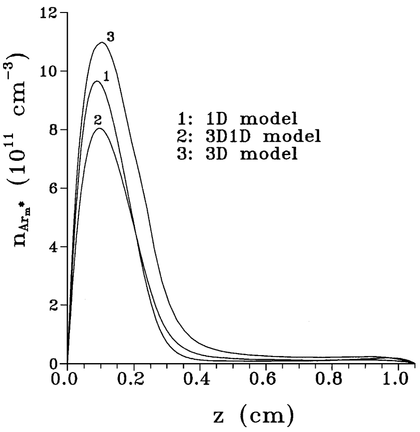

Fig. 4 One-dimensional density profiles of the argon metastable atoms, calculated with the 3D model and two 1D models (at 75 Pa, 1000 V, 3.4 mA, copper cathode in argon)

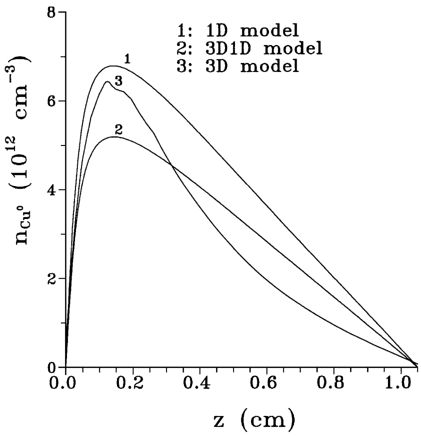

Fig. 5 One-dimensional density profiles of the sputtered copper atoms, calculated with the 3D model and two 1D models (at 75 Pa, 1000 V, 3.4 mA, copper cathode in argon)

as for the fast electron density was also observed for the fast argon atom density.

The argon metastable atom density does not show much variation among the different models, as can be seen from Fig. 4. The 3D result was found to be slightly higher than both one-dimensional densities. This is at first sight surprising, since one would expect a lower density due to deexcitation-losses at the sidewalls. However, another loss process (electron collisional transfer to the nearby energy levels) comes into play with the opposite effect. Indeed, this loss process is lower for the 3D model, due to a lower slow electron density (see above). The effect of the deexcitation-loss at the sidewalls seems to be of minor importance compared to the loss by electron collisional transfer, giving rise to a slightly higher density in the 3D model. The fact that the density computed from the 1D model is somewhat higher than the one obtained with the 3D1D model, in again attributed to the difference in gas temperature (see above).

Also the sputtered copper atom density is only little affected by the three dimensions, as appears from Fig. 5. The main effect of the 3D approach is the somewhat faster drop in the copper atom density after its maximum compared to the one-dimensional fluid models. Indeed, in the one-dimensional models the density spreads out by diffusion along the cell axis only, whereas in the 3D model it can spread also in the radial direction, yielding a lower density at the cell axis. The small difference in the absolute values of the copper atom density calculated in the three models, is owing to the variations in the gas temperature: a higher gas temperature yields a higher diffusion coefficient and hence a lower density.

Figure 6 illustrates the effect of the three dimensions on the copper ion density. The density calculated with the 3D model is a factor of 3 lower than the 3D1D model and a factor of 5 lower compared to the 1D

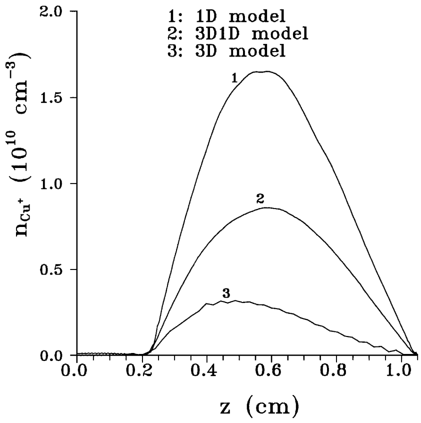

Fig. 6 One-dimensional density profiles of the copper ions, calculated with the 3D model and two 1D models (at 75 Pa, 1000 V, 3.4 mA, copper cathode in argon)

model. The copper ion density is calculated from the copper atom density and the amount of ionization. The latter is given by electron impact ionization, Penning ionization and asymmetric charge transfer. The copper atom density varies only slightly among the different models (see above). Electron impact ionization is of minor importance (see refs. [3, 5, 9]) and the amount of Penning ionization (determined by the argon metastable atom density) is also barely influenced by the three-dimensional effects (see above). The amount of asymmetric charge transfer ionization (determined by the argon ion density), however, varies more clearly among the different models. The latter effect is responsible for the increase in copper ion number density in the order of 3D, 3D1D, 1D model. From Fig. 5 and 6 follows that the calculated degree of ionization of copper is also slightly different among the three approaches: the 3D model yielded a value of 0.1%, the 3D1D model 0.14%, and the 1D model 0.2%. In general, it can be concluded that the number densities resulting from the three kinds of models vary only slightly. The shapes of the profiles are barely influenced and the absolute values of the densities stay in the same order of magnitude.

The densities of the charged particles (electrons, ions) give rise to a certain electric field and potential distribution throughout the discharge, determined by the Poisson equation. Since the densities of the charged particles, calculated with the three kinds of models do not show large difference, it follows that the axial electric field and the potential distributions are also quite similar for the three models. Since these distributions, both in one dimension and in two dimensions, were presented already in previous papers (i.e., refs. [2] and [8], resp.), they are not repeated here. The computed length of the CDS (defined as the position where the potential goes through zero) was only slightly smaller in the 1D and 3D1D models than in the 3D models (i.e. 0.2 cm compared to 0.24 cm). The most significant difference is, of course, the absence of a radial electric field in the 1D and 3D1D models, but the latter does not seem to have a large effect on the behavior of the species in the plasma.

Since the electric field distributions of the three models are barely different, the energies of the plasma species are quite similar to each other too. The largest difference was found for the electron energies, which are shown in Fig. 7. The average energy calculated with the 1D model is somewhat higher, since the electrons move only in the forward direction and they do not lose so much energy as when they would scatter back and forth. The 3D and 1D3D results are almost identical. The energies of the argon ions, fast argon atoms and copper ions calculated with the three kinds of models nearly coincide.

The relative contributions of argon ions, fast argon atoms and copper ions to the sputtering at the cathode are comparable for the three models: the contributions amount to about 72–73 % for the fast argon atoms and about 25–26 % for the argon ions. The contribution of the copper ions (i.e. the amount of self-sputtering) rises slightly from the 3D model (ca. 1 %) over the 3D1D model (ca. 1.7 %) to the 1D model (ca. 2.4 %), as could be expected from the increased copper ion density (see figure 6).

Figure 8 presents the one-dimensional profiles of the electron impact excitation rates, calculated with the three models. This figure can be seen as a representative example for the other electron collision rates, which behave in the same manner. The excitation rate obtained with the 3D model is somewhat higher than the 3D1D result. This is attributed to the slightly lower gas temperature adopted as input parameter, yielding a higher argon gas atom density and hence more collisions. The 1D model computed the lowest excitation rate, in spite of the lower gas temperature used. The reason for this lies in the fact that the electrons cannot scatter back and forth in the one-dimensional Monte Carlo model, giving rise to less excitation in the beginning of the NG. However, in the one-dimensional Monte Carlo model, a larger number of electrons can reach the backplate of the cell since they cannot get lost at the sidewalls. This results in a slightly higher excitation rate at the end of the cell. Since it is known from optical emission profiles [11] that the excitation rate is characterized by a peak in the beginning of the NG, it can be concluded that the three-dimensional Monte Carlo models yield more realistic results.

The collision rates of the argon ions are not significantly influenced by the three-dimensional effects. Indeed, the most frequent collision processes for the argon ions are symmetric charge transfer collisions. Each time an argon ion undergoes a charge transfer

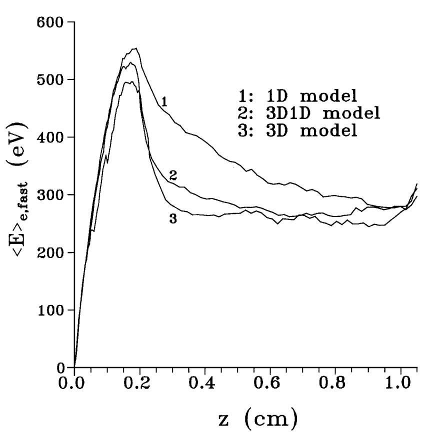

Fig. 7 One-dimensional density profiles of the electron mean energies, calculated with the 3D model and two 1D models (at 75 Pa, 1000 V, 3.4 mA, copper cathode in argon)

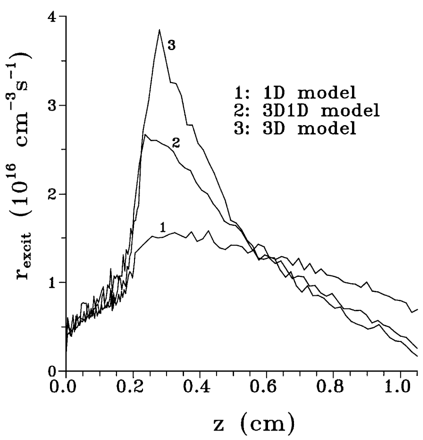

Fig. 8 One-dimensional electron impact excitation rates of argon, calculated with the 3D model and two 1D models (at 75 Pa, 1000 V, 3.4 mA, copper cathode in argon)

Table 2 Relative contributions of the three ionization mechanisms for copper, calculated with the three models

	3D	3D1D	1D
Penning ionization	59%	41%	40%
Asymmetric charge transfer	37%	55%	58%
Electron impact ionization	4%	4%	2%

collision, it starts again from rest in a direction parallel to the electric field. Hence, even in the three-dimensional Monte Carlo models, the argon ions move mainly in the forward direction. Therefore, the difference between the three-dimensional and one-dimensional models is only small. The same is true for the fast argon atoms, since they are created by charge transfer collisions from the argon ions. It was found that they undergo slightly more collisions in the 3D model, compared to the 3D1D model, due to the lower gas temperature which was selected, giving rise to more collisions; and the latter model calculates in turn slightly more collisions than the 1D model, due to the possibilities of back and forth scattering. However, the effects are almost negligible.

The relative contributions of electron impact, fast argon ion impact and fast argon atom impact ionization to the ionization of argon atoms, are nearly the same for the three kinds of models. Concerning the ionization of the sputtered copper atoms, it was mentioned before that asymmetric charge transfer becomes more important in the 3D1D model and especially in the 1D model, due to the higher argon ion density (see above). The importance of Penning ionization and electron impact ionization remains more or less the same. Hence, the relative contribution of asymmetric charge transfer becomes more important in both one-dimensional models, as can be seen from Table 2.

Also the relative roles of the different production and loss processes for the argon metastable atoms change slightly in the three models, as is illustrated in Table 3. The main difference is that electron collisional transfer to the nearby energy levels gains importance in both one-dimensional models, at the expense of diffusion and deexcitation at the walls. Indeed, electron collisional transfer is more significant due to the higher slow electron densities in the one-dimensional models (see above), and diffusion followed by deexcitation at the walls is of minor importance due to the absence of sidewalls. Moreover, electron impact excitation is a little more important in both one-dimensional models, at the expense of argon ion and atom impact excitation. However, the qualitative trends in the roles of the different production and loss processes remain more or less the same in the three kinds of models.

One of the main trumps of the three-dimensional model compared to both one-dimensional models is the possibility to calculate crater profiles. The calculation of these crater profiles, and some typical results, are shown and discussed in detail in ref. [10]. Since the one-dimensional models yield no information about variations in the radial direction, they are not able to calculate crater profiles. From the total flux of sputtered copper atoms and the flux of copper atoms redepositing on the cathode, the net flux of sputtered atoms (i.e. the erosion rate) can however still be calculated. In both one-dimensional models, a value of 1.4 μm/h was obtained. This is significantly lower than the three-dimensional result at the same discharge conditions (i.e. about 8 μm/h at the center of the crater, see ref. [10]). The reason for this can be attributed to the much higher redeposition flux of copper atoms on the cathode in the one-dimensional models. Indeed, the latter was calculated to be about 94 % of the total sputtered flux in both one-dimensional models, whereas the three-dimensional model computed a value of 57%. It was found that the erosion rate calculated with the three-dimensional model is in better agreement with experiment [12] than the values obtained with the one-dimensional model. This was also observed by van Straaten et al. [13]. The erosion rates calculated with their one-dimensional model were too low compared to experiment, due to the high redeposition flux to the cathode. The authors introduced a fitting parameter (i.e. an effective sink distance from the cathode at which

Table 3 Relative contributions of the different production and loss processes for the argon metastable atoms, calculated with the three models

	3D	3D1D	1D
Prod: electron impact excitation	12%	32%	23%
Prod: argon ion impact excitation	17%	15%	16%
Prod: argon atom impact excitation	71%	53%	61%
Prod: radiative recombination	~ 0.005%	~ 0.05%	~ 0.09%
Loss: diffusion	82%	53%	58%
Loss: electron collisional transfer	11%	40%	33%
Loss: Penning ionization of copper atoms	3.7%	3.7%	5.4%
Loss: metastable-metastable collisions	3.0%	2.4%	3.3%
Loss: electron impact excitation	~ 0.3%	~ 0.8%	~ 0.1%
Loss: electron impact ionization	~ 0.02%	~ 0.02%	~ 0.002%
Loss: two-body collisions with argon atoms	~ 0.1%	~ 0.1%	~ 0.2%
Loss: three-body collisions with argon atoms	~ 0.01%	~ 0.01%	~ 0.02%

the same amount of sputtered material is removed from the plasma, as the combined effects of the side walls), in order to reach agreement with experiment. In their two-dimensional description of the diffusion process, the fitting parameter was not necessary anymore [14]. Hence, it can indeed be concluded that the three-dimensional model calculates more realistic values for the erosion rate than the one-dimensional models.

Conclusion

In general, the differences among the three approaches are rather small for the discharge geometry investigated. The qualitative trends are similar in the three models; only some minor quantitative variations are observed. The electrical current calculated for a given pressure, voltage and gas temperature stayed within a factor of three. A value of 3.4 mA could be obtained in the three models at 1000 V and 75 Pa, when selecting the gas temperature between 330 K and 410 K. Since the actual value of the gas temperature is unknown, it must be concluded that the three models calculate realistic discharge characteristics.

The number densities of the plasma species are computed to be in the same order of magnitude in the three models. The main difference is found for the copper ion density, which is somewhat higher in the one-dimensional models compared to the three-dimensional model. This also results in a slightly higher ionization degree of copper, and a somewhat higher contribution of self-sputtering in the one-dimensional models. The electrical field and potential distributions are similar in the three models. Also the particles' energies and the collision rates deviate only slightly from each other. The differences in the calculated etching rates are, however, somewhat larger, and it was found that the results of the three-dimensional model are in better agreement with the experiment than the one-dimensional results. Moreover, the three-dimensional model is able to calculate the crater profiles at the cathode. The latter can easily be compared with experiment, to test the validity of the model.

Summarized, the one-dimensional models present already a realistic picture of the glow discharge, for the discharge geometry investigated. In a first approximation, they are sufficient to obtain better insight in the discharge processes. However, the three-dimensional models can give additional information, like the behavior of the calculated quantities throughout the whole three-dimensional discharge volume, and can therefore be seen as a progress in order to obtain a more complete description of the glow discharge. Moreover, it should be borne in mind that the results of this comparison are characteristic for the VG9000 glow discharge cell, and may not necessarily be generalized to other cell geometries.

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References

1. Bogaerts A, van Straaten M, Gijbels R (1995) Spectrochim Acta 50B:179–196
2. Bogaerts A, Gijbels R, Goedheer WJ (1995) J Appl Phys 78: 2233–2241
3. Bogaerts A, Gijbels R (1995) Phys Rev A 52:3743–3751
4. Bogaerts A, Gijbels R (1995) J Appl Phys 78:6427–6431
5. Bogaerts A, Gijbels R (1996) J Appl Phys 79:1279–1286
6. Bogaerts A, Gijbels R (1996) Fresenius J Anal Chem 355:853–857
7. Bogaerts A, van Straaten M, Gijbels R (1995) J Appl Phys 77: 1868–1874
8. Bogaerts A, Gijbels R, Goedheer WJ (1996) Anal Chem 68:2296–2303
9. Bogaerts A, Gijbels R (1996) Anal Chem 68:2676–2685
10. Bogaerts A, Gijbels R (1997) Spectrochim Acta B (in press)
11. Surendra M, Graves DB, Jellum GM (1990) Phys Rev A 41:1112–1125
12. Jonkers C, Ph.D. Dissertation (1995) University of Antwerp
13. van Straaten M, Vertes A, Gijbels R (1991) Spectrochim Acta 46B:283–290
14. van Straaten M, Gijbels R, Vertes A (1993) Anal Chem 64: 1855–1863