Role of sputtered Cu atoms and ions in a direct current glow discharge: Combined fluid and Monte Carlo model

A. Bogaerts[a] and R. Gijbels
Department of Chemistry, University of Antwerp (UIA), Universiteitsplein 1, B-2610 Wilrijk-Antwerp, Belgium

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The Cu atoms sputtered from the cathode and the corresponding Cu ions in an argon direct current glow discharge are described by a combination of two models: a fluid model for their overall behavior (diffusion and migration) in the entire discharge and a Monte Carlo model for the explicit transport of the Cu ions in the cathode dark space. The models are combined with other models described previously for the electrons, Ar ions, fast Ar atoms, and Ar metastables, in order to obtain an overall picture of the glow discharge. Results of the fluid model are the densities and fluxes of the Cu atoms and ions. At 100 Pa and 1000 V the Cu atom and ion densities are of the order of 10^{12}–10^{13} and 10^{10}–10^{11} cm^{-3}, respectively. The ionization degree is hence about 1%, which is much higher than for Ar. The Cu ion to Ar ion density is about 6% and the Cu ion to Ar ion flux is about 5%. The energy distribution of the Cu ions bombarding the cathode is calculated with the Monte Carlo model and shows good agreement with experiment. It is characterized by a peak at maximum energy, in contrast to the energy distribution of Ar ions and fast atoms. Since sputtering increases with the bombarding energy, the amount of self-sputtering is significant, although still clearly lower than the contribution of Ar ions and fast atoms. The influence of pressure, voltage, and current on all these quantities is investigated. © *1996 American Institute of Physics.* [S0021-8979(96)04503-9]

I. INTRODUCTION

Glow discharges are used for etching and deposition purposes[1] and also as a spectroscopic source for analytical techniques like mass spectrometry and optical emission spectrometry.[2,3] To acquire better results in these application fields, a good insight into the glow discharge is desirable. We try to obtain this by mathematical modeling. In glow discharges used as an ion source for mass spectrometry, like we tend to describe, the cathode is made of the material to be analyzed. It is bombarded by ions and fast atoms of the glow discharge plasma which causes the sputtering of cathode atoms. These atoms can be ionized in the plasma, and the subsequent ions are analyzed in the mass spectrometer. Therefore, we pay special attention to the atoms sputtered from the cathode and to the ions formed out of them.

The densities of these species can be determined both experimentally and theoretically. In Ref. 4 a model was developed to calculate the density profile of sputtered atoms by a simple one-dimensional diffusion equation, after these sputtered atoms have been thermalized in the plasma. This model was used in Ref. 5 for an Ar/Mo system to calculate etching rates, which were compared with experimental values. The latter model was extended to two dimensions in Ref. 6; two-dimensional density distributions of sputtered atoms and crater profiles for the Ar/Mo system were calculated at different discharge conditions and for slightly modified cell types. A similar diffusion model was also developed in Ref. 7. In the latter work, calculated sputtered atom density profiles were compared with results obtained by atomic absorption measurements for a Cu–Cr cathode (99:1) in Ar. Comparison between theoretical and experimental sputtered atom density profiles was also performed in Ref. 8 for a Li cathode in Ar. Furthermore, the spatial distribution of sputtered atoms in the glow discharge has been measured, for example, by laser fluorescence for Na atoms in Ar in Ref. 9, by atomic absorption and atomic emission in Ref. 10 for Cu and Fe atoms in Ar respectively, and by atomic absorption for Cu atoms in a radio-frequency discharge in Ref. 11. In Ref. 12 the absolute density of Cu atoms was determined in a Ne–Cu hollow cathode laser. In all these works only the sputtered atoms are concerned. Only a few papers, describing glow discharges used as metal-vapor hollow cathode lasers, also treat the ions of the cathode material. In Refs. 13 and 14 a Ne–Cu hollow cathode is modeled by solving a set of three coupled differential equations (for Ne^+, Cu^0, and Cu^+, respectively) and the results are compared with experimental values.

In the present work a model is developed to compute the densities of sputtered Cu atoms and Cu ions in a dc glow discharge by solving two coupled differential equations. Moreover the behavior of the Cu ions in the cathode dark space (CDS) is calculated explicitly in a Monte Carlo model. The models are combined with other models described earlier[15–18] for the electrons, Ar ions, fast Ar atoms, and Ar metastables, in order to obtain an overall picture of the glow discharge. Results of the fluid model include the densities and fluxes of the Cu atoms and ions and the ionization degree of Cu. By comparison of the Cu ion densities and fluxes with the ones for Ar ions, the relative importance of the Cu ions in the discharge can be investigated. The Monte Carlo model yields the energy distribution of the Cu ions bombarding the cathode. By comparison with the energy distributions

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[a] Author to whom correspondence should be addressed; Electronic mail: bogaerts@uia.ua.ac.be

of the Ar ions and fast Ar atoms at the cathode, the relative contribution of self-sputtering can be calculated. The influence of voltage, pressure, and current on these quantities is investigated.

II. DESCRIPTION OF THE MODEL

A. Fluid model for Cu^0 and Cu^+

The fluid model is one dimensional, i.e., it applies to a discharge between two infinitely wide electrodes (anode and cathode) so that quantities vary only with distance from the electrodes. The cathode is bombarded by Ar ions, fast Ar atoms (and Cu ions, see below) which causes the sputtering of cathode (Cu) atoms. In principle also Cu ions can be sputtered from the cathode, but they will return instantaneously toward the cathode because of the strong electric field in front of it. The sputtered Cu atoms arrive in the plasma and lose their initial energy of a few eV almost immediately by collisions with the gas particles. After they have been thermalized, the further transport is diffusion dominated, i.e., starting from an initial distribution of thermalized particles (thermalization profile) they can diffuse further into the plasma or back toward the cathode. The sputtered Cu atoms can also be ionized in the glow discharge plasma, leading to the formation of Cu ions. The three most important ionization mechanisms include Penning ionization by Ar metastables, charge transfer by Ar ions, and electron impact ionization. The transport of the Cu ions created in this way is controlled by diffusion and by migration in the electric field. The loss of Cu ions could be caused by an electron–ion recombination. However, since in Ref. 13 it is demonstrated that this processes is negligible, it is omitted in the present model.

The above described behavior of Cu atoms and ions is expressed in the following equations:

$$\frac{\partial n_{\mathrm{Cu}}(x)}{\partial t}+\frac{\partial j_{\mathrm{Cu}}(x)}{\partial x}=r_{\mathrm{prod,Cu}}(x)-r_{\mathrm{loss,Cu}}(x), \tag{1}$$

$$\frac{\partial n_{\mathrm{Cu}^+}(x)}{\partial t}+\frac{\partial j_{\mathrm{Cu}^+}(x)}{\partial x}=r_{\mathrm{prod,Cu}^+}(x), \tag{2}$$

$$j_{\mathrm{Cu}}(x)=-D_{\mathrm{Cu}}\,\frac{\partial n_{\mathrm{Cu}}(x)}{\partial x}, \tag{3}$$

$$j_{\mathrm{Cu}^+}(x)=-D_{\mathrm{Cu}^+}\,\frac{\partial n_{\mathrm{Cu}^+}(x)}{\partial x}+\mu_{\mathrm{Cu}^+}n_{\mathrm{Cu}^+}(x)\mathscr{E}(x), \tag{4}$$

$$r_{\mathrm{prod,Cu}}(x)=J_0F_T(x), \tag{5}$$

$$\begin{aligned} r_{\mathrm{loss,Cu}}(x)&=r_{\mathrm{prod,Cu}^+}(x)\\ &=n_{\mathrm{Cu}}(x)[r_{\mathrm{EI}}(x)+k_{\mathrm{PI}}n_{\mathrm{Ar}_m^*}(x)+k_{\mathrm{CT}}n_{\mathrm{Ar}^+}(x)]. \end{aligned} \tag{6}$$

n_{Cu} and n_{Cu^+} are the densities of the Cu atoms and ions, respectively; j_{Cu} and j_{Cu^+} are their respective fluxes {diffusion controlled for the atoms [eq. (3)] and diffusion and migration controlled for the ions [eq. (4)]}. The diffusion coefficient of the Cu atoms in argon (D_{Cu}) is calculated with a formula of the rigid-sphere model for a mixture of two chemical species.[19] Since it can be assumed in a first approximation that diffusion is not determined by the charge of a particle, the diffusion coefficient of the Cu ions (D_{Cu^+}) is taken to be equal to that of the Cu atoms, i.e., $D_{\mathrm{Cu}} = D_{\mathrm{Cu}^+}=144.6\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ at 1 Torr Ar and room temperature. The mobility of the Cu ions (μ_{Cu^+}) is adapted from Ref. 20 where a graph of the mobility as a function of the ion mass in Ar, Ne, and He was presented. It was taken to be $1837.4\ \mathrm{cm}^2\ \mathrm{s}^{-1}\ \mathrm{V}^{-1}$ at 1 Torr Ar. $\mathscr{E}(x)$ represents the electric field distribution throughout the discharge, calculated in the hybrid Monte Carlo fluid model[16] (see below).

The production rate of the Cu atoms [$r_{\mathrm{prod,Cu}}$; Eq. (5)] is given by the sputtered flux from the cathode (J_0) multiplied by the thermalization profile [$F_T(x)$]. It is indeed assumed that thermalization of the atoms is a much faster process than diffusion and that it is already finished when diffusion starts.[4] $F_T(x)$ is computed by a Monte Carlo model.[21] J_0 is calculated from an empirical formula of the sputtering yield[22] and the flux energy distribution of the particles bombarding the cathode [i.e., the Ar ions and fast atoms, and also the Cu ions (see below)].

The loss rate of the Cu atoms ($r_{\mathrm{loss,Cu}}$) is equal to the production rate of the Cu ions ($r_{\mathrm{prod,Cu}^+}$) and expresses the ionization of Cu atoms by electron impact ionization, Penning ionization, and charge transfer [Eq. (6)]. $r_{\mathrm{EI}}(x)$ is the electron impact ionization rate, which is calculated in the electron Monte Carlo model (see below) with the cross section of electron impact ionization taken from Ref. 23. k_{PI} and k_{CT} are the rate coefficients of Penning ionization and charge transfer, respectively. To calculate the cross section of Penning ionization, an empirical formula[24] was used which was fitted to some experimentally obtained cross sections[24,25] in order to arrive at approximate values for other elements. The Penning ionization cross section of Cu at thermal energies was in this way computed to be $4.87\times10^{-15}\ \mathrm{cm}^2$ which corresponds to a k_{PI} of $2.36\times10^{-10}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. Cross-section values for the charge transfer between Ar^+/Cu are very difficult to find in the literature. It is generally known[26–28] that the charge transfer process is most likely when the energy difference between levels of the bombarding ion and the created ion is sufficiently small, and that the probability of charge transfer decreases rapidly with increasing energy difference. Based on this knowledge, a method to estimate the charge transfer rate constants was proposed in Ref. 29 and a value of $1.75\times10^{-10}\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ was suggested for k_{CT} between Ar^+/Cu. This is only an approximated value, but since we did not find more accurate data, we will have to be satisfied with this solution, keeping in mind that the obtained results will be subject to uncertainties. Also, the conclusions of these calculations are not necessarily true for other cathode materials. Finally, $n_{\mathrm{Ar}_m^*}$ and n_{Ar^+} are the Ar metastable density and the Ar ion density.

These continuity equations for the Cu atoms and ions [Eqs. (1) and (2)] are coupled to each other through $r_{\mathrm{loss,Cu}}(x) = r_{\mathrm{prod,Cu}^+}(x)$. Boundary conditions for this system are chosen as $n_{\mathrm{Cu}}=0$ and $n_{\mathrm{Cu}^+} = 0$ at both the cathode and the anode. The coupled equations are discretized to finite difference equations and the resulting bi-tridiagonal system is solved with the extended Thomas algorithm described in the appendix of Ref. 30.

B. Monte Carlo model for Cu^+ in the CDS

In order to obtain information about the energy distribution of the Cu ions at the cathode, which is of importance for the calculation of sputtering by Cu ions, the behavior of the Cu ions in the electric field of the CDS was described explicitly by a Monte Carlo model. This model is actually three dimensional (three-dimensional trajectories and scattering), but the results are integrated over the entire radial distance, so that they are given as output in only one dimension.

From the fluid model, we know the flux of Cu ions that enter the CDS from the negative glow (NG) and the number of Cu ions that are formed in the CDS itself. The ions are followed in the Monte Carlo model in this exact proportion. The only collision processes that are incorporated are elastic collisions with Ar gas atoms. The numerical value of the cross section for this process is taken to be 6×10^{-16} cm^2, independent of the energy; this order of magnitude was deduced from cross-section curves found in Ref. 31. We also tested other values and it was found that the results did not vary much so that the choice of the value for this cross section is not so critical. We took this value since the energy distribution of Cu ions at the cathode calculated with this cross section, especially the peak height at maximum energy, showed the best agreement with experimentally measured energy distributions of Cu ions at the cathode[32] (see below). Other possible collisions are estimated to be negligible: asymmetrical charge transfer with Ar atoms would have a considerably lower cross section, and collisions with other plasma particles (Cu atoms, Ar ions, Ar metastables, electrons) are unimportant due to the much lower densities of these species compared to the Ar atom density.

The ions are followed one after the other during successive time steps. During each time step the trajectory is calculated by Newton's laws and the probability of collision is computed. This probability is compared with a random number between 0 and 1. If the probability is lower, no collision takes place and the ion is followed during the next time step. If the probability is higher, a collision takes place. The new energy and direction after collision are determined in complete analogy to the procedure explained in Ref. 15 for elastic collisions of Ar ions in Ar, with the only difference being that the masses of the two colliding particles are not equal to each other. In these collisions, fast Ar atoms can be formed, which are also treated in a Monte Carlo model, exactly in the same way as described in Ref. 15. Hence, for all details about the physics and mathematics of the Monte Carlo model (Newton's laws, collision probability, new energy and direction, etc.) we refer to Ref. 15.

C. Combination of the models

The two models described above, together with the models for the other plasma species described earlier,[15–18] are combined in order to obtain an overall picture of the glow discharge. The flow chart of the coupling is presented in Fig. 1. The details of how the models described earlier are connected to each other, are not included here, since this was discussed in previous papers[15–18] and it would make the present flow chart too complicated. Only the way these models are combined with the present models is explained.

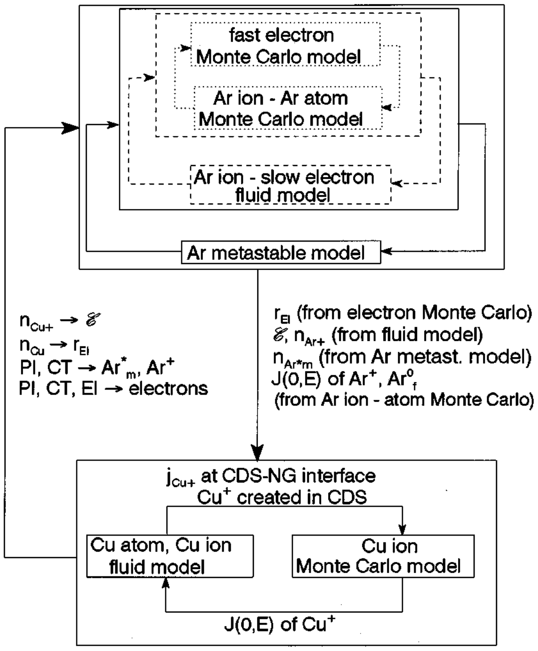

FIG. 1. Flow chart of the model.

First the electron Monte Carlo, the Ar ion, and fast Ar atom Monte Carlo, the Ar ion–electron fluid model, and the Ar metastable model are calculated, until convergence is reached, with an initial guess for the Cu atom density and assuming that there are no Cu ions in the plasma. Results of these models which are of importance for the Cu atom and ion models include (i) the Cu electron impact ionization rate calculated in the electron Monte Carlo model (extension of Refs. 15 and 16 by the incorporation of this process), (ii) the electric field distribution (used to determine the Cu ion migration) and the Ar ion density (needed for the charge transfer ionization of Cu) calculated in the Ar ion–electron fluid model,[16] (iii) the Ar metastable density (needed for the Penning ionization of Cu) calculated in the Ar metastable model,[17] and (iv) the flux energy distribution of the Ar ions and fast atoms bombarding the cathode (required to calculate the sputtering flux of Cu atoms) computed in the Ar ion and fast Ar atom Monte Carlo model.[15,18]

With these results, the fluid model of Cu atoms and ions is calculated. This yields, among others, (i) the flux of Cu ions that enter the CDS from the NG and (ii) the number of Cu ions formed in the CDS, which are used as input data in the Cu ion Monte Carlo model. The latter model leads to the flux energy distribution of the Cu ions bombarding the cathode, which is used again in the Cu atom and ion fluid model, together with the flux energy distribution of Ar ions and atoms, to calculate the amount of sputtering. The Cu atom and ion fluid model and the Cu ion Monte Carlo model are solved iteratively until the results remain unchanged (i.e., already after a few cycles).

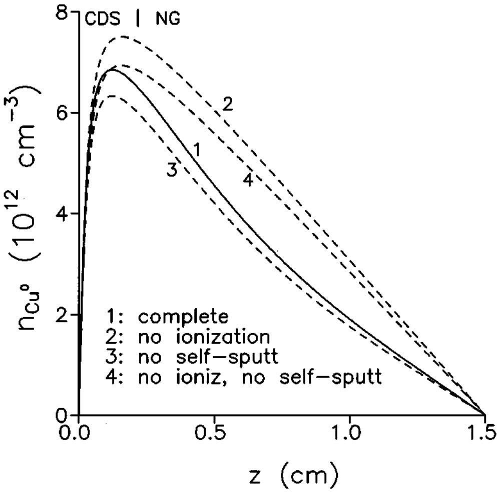

FIG. 2. Density profile of the Cu atoms (Cu cathode in Ar—100 Pa, 1000 V).

The latter two models can influence the models described earlier in the following ways: (i) the Cu ion density also determines the electric field distribution calculated in the Ar ion–electron fluid model, (ii) the Cu atom density fixes the new electron impact ionization rate of Cu, computed in the electron Monte Carlo model, (iii) the Penning ionization and charge transfer processes cause a decrease in the Ar metastable and Ar ion densities, respectively, and (iv) the three ionization processes of Cu lead to an increase in the electron density. The complete system is solved iteratively until convergence is reached.

III. RESULTS AND DISCUSSION

Calculations were carried out for a Cu cathode in an Ar discharge at 100 Pa gas pressure and 1000 V discharge voltage. The discharge cell is assumed to be 1.5 cm long and infinitely wide.

Figure 2 shows the calculated Cu atom density distribution throughout the discharge. This density profile shows a maximum relatively close to the cathode and then gradually decreases towards the anode, which is in agreement with results found in literature, both experimentally and theoretically.[4–11] The density is of the order of 10^{12}–7×10^{12} cm^{-3} which is about four orders of magnitude lower than the Ar atom density (n_{Ar} is about 2.43×10^{16} cm^{-3} at 100 Pa). We compared the Cu atom density calculated in this model with Cu atom densities calculated by neglecting self-sputtering by Cu ions and/or loss by ionization, as is indicated in Fig. 2. Both effects are rather small but not completely negligible.

The density profile gives rise to a diffusion flux which goes through zero relatively close to the cathode; the flux is slightly positive toward the anode but extremely negative at the cathode, indicating that backdiffusion is exceedingly important. At 100 Pa and 1000 V the sputtering flux amounts to about 4.53×10^{16} cm^{-2} s^{-1} whereas the flux of Cu atoms back to the cathode was calculated to be about 4.24×10^{16} cm^{-2} s^{-1}, leading to a net sputtering flux of about 2.94×10^{15} cm^{-2} s^{-1} (only about 6.5% of the entire sputtering flux).

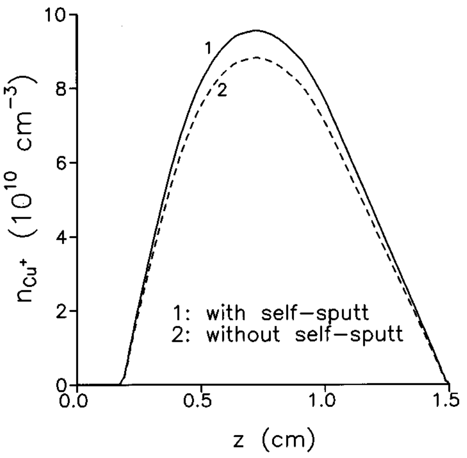

FIG. 3. Density profile of the Cu ions (Cu cathode in Ar—100 Pa, 1000 V).

In Fig. 3 the calculated Cu ion density profile is illustrated, both with and without the incorporation of self-sputtering. Like the Ar ion density,[16] the Cu ion density is small but nearly constant in the CDS and reaches a maximum (of nearly 10^{11} cm^{-3}) halfway through the discharge. Knowing that the Ar ion density has a maximum of about 1.6×10^{12} cm^{-3} at these discharge conditions, the Cu ion density corresponds to about 6% of the Ar ion density. Comparing this value with the Cu atom to Ar atom density ratio, we conclude that the sputtered Cu atoms are much more efficiently ionized. It was indeed found in Ref. 17 that electron impact ionization, which is the major ionization process for the Ar atoms, is only of minor importance for the sputtered atoms, since Penning ionization and charge transfer are much more effective processes. The presently calculated Cu ion to Ar ion density ratio is in rather good agreement with the results found in Ref. 13 for a Cu/Ne hollow cathode discharge. By comparing the Cu ion density with the Cu atom density, the ionization degree of Cu in the glow discharge was calculated to be about 1.6% at the typical discharge conditions of 100 Pa and 1000 V. This agrees with the general statement in glow discharge mass spectrometry literature where ionization degrees of about 1% are usually mentioned.[2]

The Cu ion flux follows the same course as the Ar ion flux,[16] i.e., it is negative (directed toward the cathode) in the first part of the discharge, changes sign halfway through the cell and then takes positive values (directed toward the anode). The value at the cathode is about -1.19×10^{15} cm^{-2} s^{-1} (i.e., 5.2% of the Ar ion flux at the cathode), whereas the anode, which contains the exit slit toward the mass spectrometer, is bombarded by a Cu ion flux of 3.69×10^{14} cm^{-2} s^{-1} (i.e., 4.9% of the Ar ion flux). In observations with the VG 9000 mass spectrometer slightly higher values are generally obtained at these discharge conditions (i.e., ~5–20%), but in view of the approximate way of calculating the ionization rate of Cu, and knowing that this value is calculated from the Cu atom to Ar atom density ratio of four orders of magnitude, the presently obtained value in

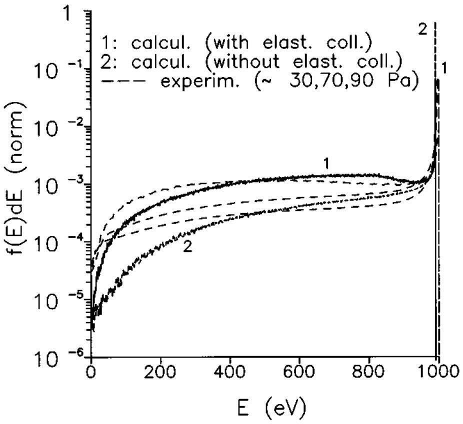

FIG. 4. Normalized flux energy distributions of the Cu ions bombarding the cathode: comparison between calculated and experimental results (Cu cathode in Ar—100 Pa, 1000 V).

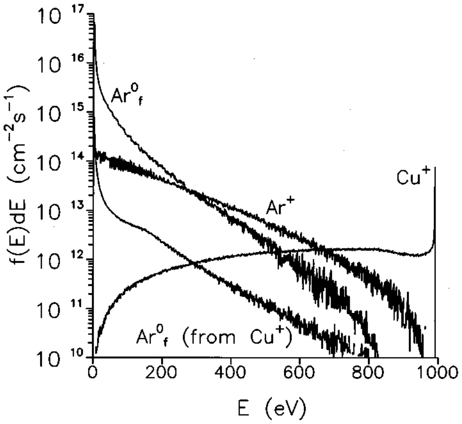

FIG. 5. Flux energy distributions of the Ar ions, fast Ar atoms, Cu ions, and fast Ar atoms formed by Cu ion collisions, bombarding the cathode (Cu cathode in Ar—100 Pa, 1000 V).

the percent order is certainly in satisfactory agreement with experiment.

Figure 4 presents the normalized flux energy distribution of the Cu ions arriving at the cathode, calculated in the Monte Carlo model. The distribution has a pronounced peak at maximum energy (note the logarithmic scale), which means that most of the Cu ions bombarding the cathode, originate from the NG and pass the CDS without collisions. We compared this calculated distribution with energy distributions measured experimentally for Cu ions bombarding the cathode of the VG 9000 mass spectrometer at 1000 V discharge voltage,[32] presented by the dashed lines in Fig. 4. Since it was impossible to measure the exact pressure inside the glow discharge chamber, only approximate values are given. The calculated energy distribution shows a rather good agreement with the experimental ones. For comparison, also the energy distribution calculated without elastic collisions is included, presented by curve 2 in Fig. 4. The peak at maximum energy calculated in this way is still an order of magnitude higher than both the experimental values and the calculations including elastic collisions; this indicates that elastic collisions are important enough to have effect on the energy distribution.

In contrast to the energy distribution of the Cu ions at the cathode, the energy distributions of the Ar ions and fast atoms do not show a peak at maximum energy but, on the contrary, are characterized by a rapidly decreasing curve, as is illustrated in Fig. 5. This figure shows the flux energy distributions of the Ar ions, fast Ar atoms, and Cu ions bombarding the cathode. Also included is the flux energy distribution of the fast Ar atoms that are formed by elastic collisions of Cu ions. This flux energy distribution has nearly the same course as the one for the fast Ar atoms formed by collisions of Ar ions, but is about three orders of magnitude lower. It should be noticed that the terminology of ‘‘fast Ar atoms’’ is used to be able to distinguish with the thermalized ‘‘bulk’’ Ar atoms, and that all Ar atoms which possess energies above 1 eV belong to this group. From Fig. 5 it is seen that the cathode is predominantly bombarded by fast Ar atoms with very low energies. Also the Ar ions that bombard the cathode have rather low energies. However, almost all Cu ions that arrive at the cathode have the maximum energy corresponding to the total voltage drop.

Taking into account that the efficiency of sputtering (the sputtering yield) increases with the energy of the bombarding particles (see Fig. 6, which is obtained by using the formula described in Ref. 22), it is expected that the contribution of the Cu ions to the sputtering process of the cathode (self-sputtering) is non-negligible, in spite of their lower flux. Moreover, Fig. 6 illustrates that the sputtering yield for Cu ions on a Cu cathode is slightly higher than the one for Ar ions of the same energy, due to their higher masses. In Fig. 7 the contribution of the different species in the total sputtering as a function of their energy is presented. In spite of the lower sputtering yield at low energies, the major contribution is still accomplished by the fast Ar atoms at low energies. The Ar ions also have a large contribution at low and intermediate energies, whereas the Cu ions are especially effective at maximum energy. The contribution of fast Ar atoms formed by Cu ion elastic collisions remains negligible at all energies, as was expected from Fig. 5. Summed over all

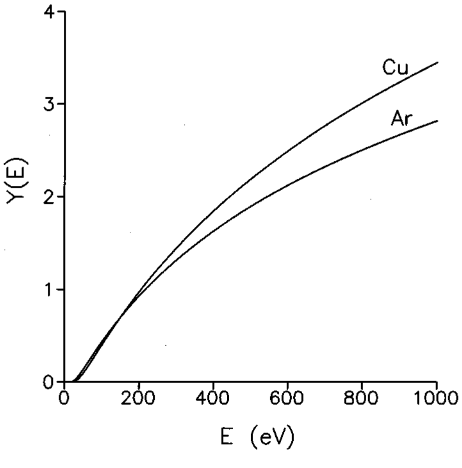

FIG. 6. Sputtering yield as a function of the incident energy for Cu and Ar.

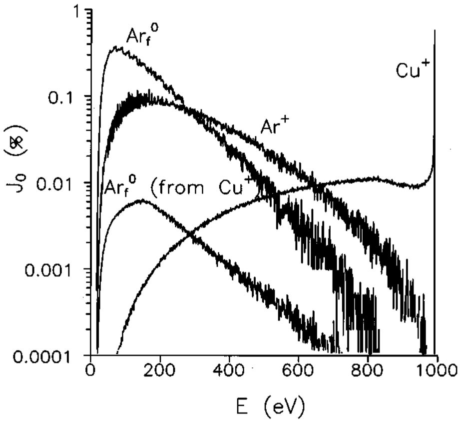

FIG. 7. Relative contribution to sputtering as a function of incident energy, for the Ar ions, fast Ar atoms, Cu ions, and fast Ar atoms formed by Cu ion collisions (Cu cathode in Ar—100 Pa, 1000 V).

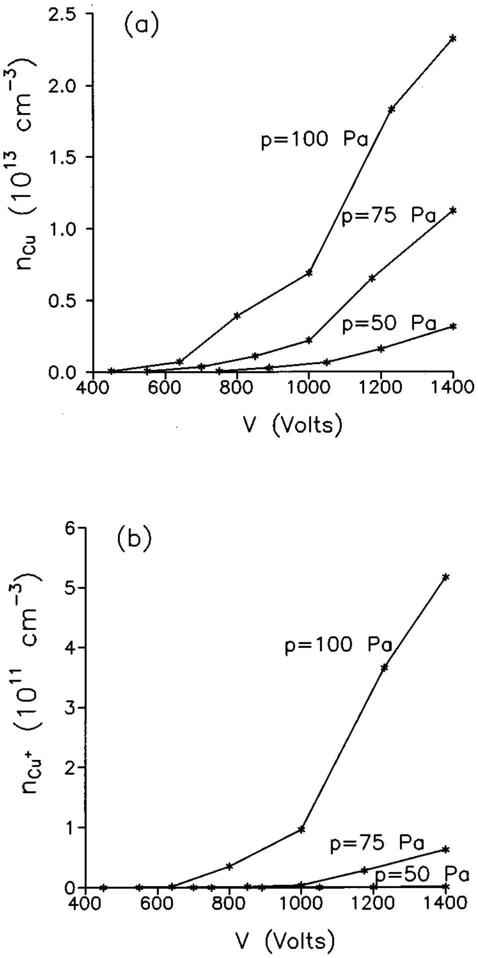

FIG. 8. Density at the maximum of the profile for Cu atoms (a) and Cu ions (b) as a function of voltage at three pressures (Cu cathode in Ar).

energies, the contributions of the different bombarding species at 100 Pa and 1000 V amount to about 61.0%, 31.0%, 6.55%, and 1.45% for the fast Ar atoms, Ar ions, Cu ions, and fast Ar atoms formed by Cu ion collisions, respectively. It should be noticed that the contribution of Cu ions can still be somewhat underestimated, since the experimentally obtained ratio of Cu ion flux to Ar ion flux at the cathode[32] is slightly higher than the calculated one (i.e., about 18.8% compared to about 5.2%). Hence, although the fast Ar atoms and also the Ar ions account for the majority of sputtering, the role of Cu ions (self-sputtering) cannot be neglected.

The fact that self-sputtering could be important was also suggested in other papers. In Refs. 13 and 14 the sputtering contribution of Cu ions was found to be larger than the one of Ne ions, which was ascribed to the higher energy and of course also to the fact that Ne ions are not very effective in sputtering due to their low masses. In Ref. 32 the amount of self-sputtering was estimated by comparing the measured energy distributions of Ar ions and Cu ions, and a value of 42% was found for Cu in Ar at 1000 V. This value does not consider the contribution of fast Ar atoms, and will therefore be clearly too high. Nevertheless it indicates that self-sputtering can be quite significant.

In order to investigate the influence of pressure, voltage, and current on the behavior of the Cu atoms and ions, calculations were performed for a range of voltages, pressures, and currents (V=450–1400 V, p=50–100 Pa, I=0.2–10 mA/cm^2). These are typical discharge conditions used with the VG 9000 glow discharge mass spectrometer (Fisons) for a Cu cathode in Ar.

Figure 8(a) shows the Cu atom density at the maximum of its profile as a function of voltage at three pressures. The density clearly increases with voltage and pressure. Indeed higher pressures and voltages yield higher currents and hence higher fluxes of particles bombarding the cathode. This results in more sputtering and hence a higher sputtered Cu atom density. Moreover, at higher voltages, the bombarding particles have higher energies, and since sputtering increases with the energy of the bombarding species, this will also cause more sputtering and hence a higher sputtered Cu atom density. The maximum Cu density is situated between 0.1 and 0.22 cm from the cathode at all discharge conditions investigated. The position shifts slightly away from the cathode with decreasing pressure since the Cu atoms can diffuse further into the plasma at lower pressures. The position shifts slightly toward the cathode with increasing voltage which is attributed to the fact that at higher voltages the ionization rate of Cu atoms increases (see below) and the resulting depletion in the density profile leads to a slight shift of the position of the maximum toward the cathode (see Fig. 2). The voltage effect on the position is however still smaller than the pressure effect.

In Fig. 8(b) the Cu ion density at the maximum of its profile is presented as a function of voltage at three pressures. The Cu$^+$ density also increases with voltage and pressure and the effect is even more pronounced than for the Cu atom density. This can be easily understood because the Cu ion density is the product of the Cu atom density and the amount of ionization which depends on the density of Ar ions, Ar metastables, and electrons. Since both the Cu atom density and the Ar ion, Ar metastable, and electron densities increase with voltage and pressure, the Cu ion density will also increase and even more rapidly, with voltage and pres-

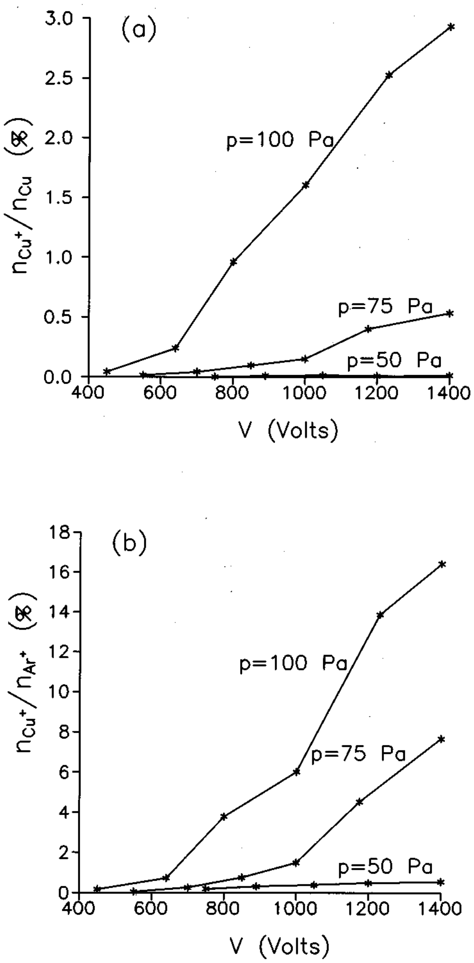

FIG. 9. Ratio of Cu ion to Cu atom density (a) and of Cu ion to Ar ion density (b) as a function of voltage at three pressures (Cu cathode in Ar).

sure. This indicates that higher voltages and pressures will give higher Cu ion signals in the mass spectrometer, which results in a better analytical sensitivity. In the VG 9000 mass spectrometer however, the voltage will seldom exceed 1.5 kV to avoid short-circuiting, and the pressure increase is limited by the coupling with the low pressure mass spectrometer (till $\sim 10^{-8}$ Torr). The position of the maximum of the Cu ion density does not change considerably with voltage and pressure and lies nearly halfway through the discharge cell.

Due to the more rapid increase of the Cu ions with pressure and voltage compared to the Cu atoms, the ionization degree of Cu will increase with pressure and voltage. This is illustrated in Fig. 9(a). At 50 Pa the ionization degree was calculated to be about 0.01%. At 75 Pa it rises from about 0.01% at low voltages to about 0.5% at high voltages. At 100 Pa the amount of Cu that will be ionized increases to about 3% at 1400 V. It is clear that high voltages and pressures yield a better ionization efficiency. Moreover the ratio of Cu ion density to Ar ion density increases with voltage and pressure, as is reflected in Fig. 9(b). At 50 Pa this ratio remains below 1%, at 75 Pa it reaches 6% at 1400 V, whereas at 100 Pa it exceeds 16% at 1400 V. This is quite considerable, in view of the much lower Cu atom to Ar atom density ratio (see previous text). Also the ratio of Cu ion flux to Ar ion flux rises with voltage and pressure. Figure 10 shows this ratio of fluxes at the cathode, but the ratio at the anode is comparable. In general this flux ratio is calculated to vary between 1% and 10%, depending on discharge conditions, which is slightly lower than, but still in satisfactory agreement with mass spectrometric observations.

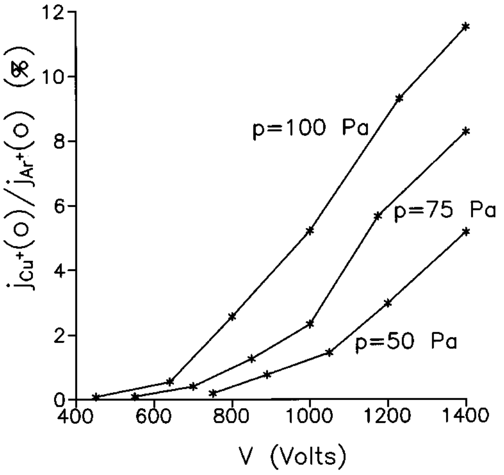

FIG. 10. Ratio of Cu ion to Ar ion flux at the cathode as a function of voltage at three pressures (Cu cathode in Ar).

The increasing Cu ion flux compared to the Ar ion flux at the cathode at higher voltages and pressures is also reflected in the relative contribution of self-sputtering, presented in Fig. 11. The contribution of fast Ar atoms to the sputtering is dominant at all voltages and pressures but decreases with increasing voltage and pressure. The contribution of Ar ions takes the second place, increasing with pressure but nearly independent of voltage. The contribution of Cu ions increases with pressure and voltage, as was expected from Fig. 10. Self-sputtering is therefore non-negligible, especially at high voltages and pressures.

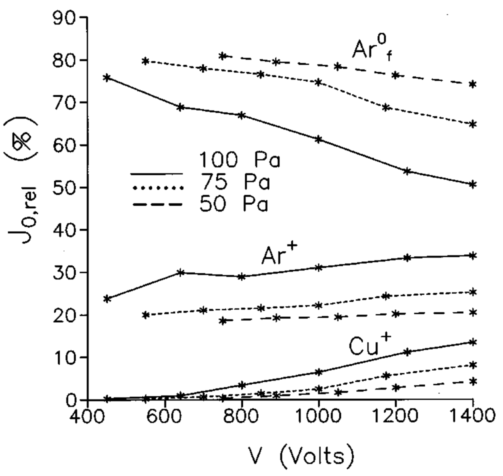

FIG. 11. Relative contribution to sputtering by the fast Ar atoms, Ar ions, and Cu ions, as a function of voltage at three pressures (Cu cathode in Ar).

IV. CONCLUSION

A model is developed to describe the sputtered Cu atoms and the Cu ions in a dc argon glow discharge. A fluid model handles the Cu atoms and ions in the discharge, whereas a Monte Carlo model explicitly treats the Cu ions in the CDS. These models are combined with other models previously described for the other plasma species to obtain an overall picture of the glow discharge.

Results of the fluid model are the density profiles and fluxes of the Cu atoms and ions. The Cu atom density reaches values of 10^{12}–10^{13} cm^{-3} whereas the Cu ion density is of the order of 10^{10}–10^{11} cm^{-3} at 100 Pa and 1000 V, yielding an ionization degree of about 1%. This is much higher than the ionization degree of Ar, indicating that Cu is much more efficiently ionized than Ar. This is also reflected in the much higher Cu ion to Ar ion density ratio (~6% at 100 Pa and 1000 V) than the Cu atom to Ar atom density ratio (~four orders of magnitude). The energy distribution of the Cu ions bombarding the cathode was calculated with the Monte Carlo model and good agreement with experiment was reached. The energy distribution is characterized by a high peak at maximum energy, in contrast to the energy distributions of Ar ions and atoms bombarding the cathode. Since the sputtering yield increases with the energy of the bombarding species, it was expected that the sputtering by Cu ions (self-sputtering) could become significant. This was indeed observed, although the fast Ar atoms and to a lesser extent the Ar ions are still more important for the sputtering process.

The influence of pressure, voltage, and current on the role of Cu atoms and ions was also investigated. The Cu atom and Cu ion densities both clearly increase with voltage and pressure, the effect being more obvious for the Cu ions. The ratio of Cu ion to Cu atom density (i.e., the ionization degree of Cu) increases with pressure and voltage. This is also true for the ratio of Cu ion to Ar ion densities and fluxes, indicating that the Cu ions gain importance toward higher voltages and pressures. The latter is also reflected in the amount of self-sputtering which increases with voltage and pressure, although the contribution of Ar ions and particularly of fast Ar atoms remain clearly dominant.

It should be noticed however that the present results are based on a one-dimensional model and do therefore not necessarily reflect completely the three-dimensional reality.

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