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LECTURE

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Mathematical description of a direct current glow discharge in argon

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Abstract In order to achieve a better understanding of the glow discharge, different models have been developed for the different species present in the plasma. An overview of the models is given and some typical results are presented. These results include, among others, the densities and energy distributions of the plasma species, the electric field and potential distribution, the contribution of different ionization mechanisms to the ionization of argon and sputtered atoms, the relative contribution of different plasma species to the sputtering process, and the variation of the cathode dark space length and the electrical current as functions of voltage and pressure. The validity of the present models is supported by the good agreement of the calculated current-voltage curves with experiment.

I Introduction

In recent decades, glow discharges have gained increasing interest as sources for analytical techniques, like mass spectrometry, optical emission spectrometry and atomic absorption spectrometry. To improve the results in these application fields, a good insight into the glow discharge is required. One way to reach this goal is by mathematical modelling. Three major approaches to modelling can be found in the literature. The first one is to deal with the glow discharge plasma as a fluid [1–4]. The species are assumed to be in hydrodynamic equilibrium and are described with the continuity equations and flux equations based on diffusion and migration. This kind of model is only an approximation, especially for the fast electrons which are far from hydrodynamic equilibrium. The second approach is a kinetic (Boltzmann) model [5] which copes with the non-equilibrium situation of the various species by describing them with the Boltzmann transport equation. The third way is via Monte Carlo simulations [6]. The species are simulated one after the other. Their trajectory is described by Newton's laws and their collisions are treated with random numbers. This model is the most accurate one, because it deals with the particles on the lowest microscopical level. However, in order to reach satisfactory statistics, a large number of particles have to be simulated, which requires a long calculation time. Hence, each model has its advantages and disadvantages. Therefore, it is desirable, in practice, to use a combination of different models for describing the glow discharge. Species that are not in hydrodynamic equilibrium, like the electrons, must be treated with a Monte Carlo model, whereas species that are more or less in equilibrium, can be described with a fluid model. In this paper, modelling work for a direct current glow discharge in argon is presented, by using different models for different kinds of species and results obtained with this model.

II Description of the models

The models presented are one-dimensional, i.e. they apply to a discharge between two infinitely wide parallel plates so that the quantities vary only with distance from the electrodes. In the Monte Carlo simulations, however, three-dimensional motion of the species is already incorporated. The species that are assumed to be present in the plasma include argon atoms at rest, uniformly distributed throughout the discharge, singly charged positive argon ions, fast argon atoms, argon metastable atoms, fast and slow electrons, and atoms and ions of the cathode material. Table 1 summarizes the different models used to describe these species and gives appropriate references for a full description of the models.

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

Plasma species	Model	Ref.
Electrons: fast	Monte Carlo (entire discharge)	[7, 8]
Electrons: slow	Fluid (entire discharge)	[8]
Ar^+ ions	Fluid (entire discharge)	[8]
	Monte Carlo (CDS)	[7,9]
Ar_f^0 atoms	Monte Carlo (CDS)	[7,9]
Ar_m^* metastable atoms	Fluid (entire discharge)	[10]
M^0 (thermalization)	Monte Carlo (entire discharge)	[11]
M^0, M^+ (diffusion, ionization)	Fluid (entire discharge)	[12]
M^+	Monte Carlo (CDS)	[12]

All the models are coupled to each other by the interaction processes between the plasma species. The combined models are solved iteratively until final convergence is reached, in order to obtain an overall picture of the glow discharge.

a) Fast electrons. These are simulated by a Monte Carlo model in the entire discharge [7, 8]. Collision processes taken into account are electron impact excitation, ionization and elastic collisions. The electrons start at the cathode and are simulated during successive timesteps, based on Newton's laws and random numbers, until they collide at the walls or until they are slowed down by collisions. Indeed, when their energies become lower than the excitation threshold of argon (ca. 12 eV), they are transferred to the slow electron group.

b) Slow electrons and argon ions. The behaviour of these species is described with a fluid approach in the entire discharge. The equations are the continuity equations and flux equations based on diffusion and migration in the electric field, both for electrons and argon ions, together with the Poisson equation to obtain a self-consistent electric field. Due to the strong coupling and the severe nonlinearity of these equations, solving this fluid model is a difficult numerical problem and special solution methods have to be used [8].

c) Argon ions and fast argon atoms. Since the argon ions are not completely in hydrodynamic equilibrium in the cathode dark space (CDS) where a strong electric field is present, they are described in this region with a Monte Carlo model, together with the fast argon atoms that are created from the ions by symmetric charge transfer [7, 9]. The collision processes incorporated in this model comprise charge transfer (for the ions) and elastic collisions, ion and atom impact ionization and excitation (for the ions and fast atoms).

d) Argon metastable atoms. These species are described with a fluid model in the entire discharge [10]. A balance equation is constructed, taking into account all known production and loss processes. The production processes include electron, argon ion and fast argon atom impact excitation, and argon ion-electron radiative recombination. The loss processes comprise electron impact ionization and excitation from the metastable level, electron quenching to the nearby resonant levels, metastable-metastable collisions, Penning ionization of sputtered atoms, two-body and three-body collisions with argon ground state atoms, and diffusion and subsequent deexcitation at the walls.

e) Atoms and ions of the cathode material. When the atoms are sputtered from the cathode, they lose their initial energy of a few eV almost immediately by collisions with the gas particles. This thermalization process is simulated with a Monte Carlo model [11]. The further transport of the sputtered atoms is diffusion dominated. The transport of the sputtered atoms, their ionization and the transport of the created ions (by diffusion and migration in the electric field) are described with a fluid model in the entire discharge [12]. The ionization processes considered in this model are Penning ionization, asymmetric charge transfer and electron impact ionization. Moreover, since the ions of the cathode material are not in hydrodynamic equilibrium in the CDS, they are also treated in this region with a Monte Carlo model [12].

III Results and discussion

Results are shown for a direct current glow discharge in argon with a copper cathode, at a gas pressure of 100 Pa, a discharge voltage of 1000 V and an electrical current of 3 mA, which are typical discharge conditions for the VG 9000 glow discharge mass spectrometer (VG Elemental, Fisons).

Figure 1a, b shows the densities of the different plasma species. The argon ion density is nearly constant in the CDS, increases rapidly at the beginning of the negative glow (NG), reaches a maximum halfway the discharge, whereafter it decreases again. The slow electron density is almost zero in the CDS but is slightly higher than the argon ion density in the NG. It is nearly equal to the sum of the argon ion and copper ion densities in this region. This results in a net positive space charge in the CDS and nearly charge neutrality in the NG. The fast electron density was calculated to be in the order of 10^7 cm^{-3}; hence it does not contribute to the space charge. The argon metastable atom density is of the same order of magnitude as the argon ion and slow electron densities at these discharge conditions, but reaches a maximum relatively close to the cathode. The copper atom density is somewhat higher, but still of the same order of magnitude. It also reaches a maximum close to the cathode whereafter it decreases almost linearly towards the anode. In Fig. 1b, the copper ion

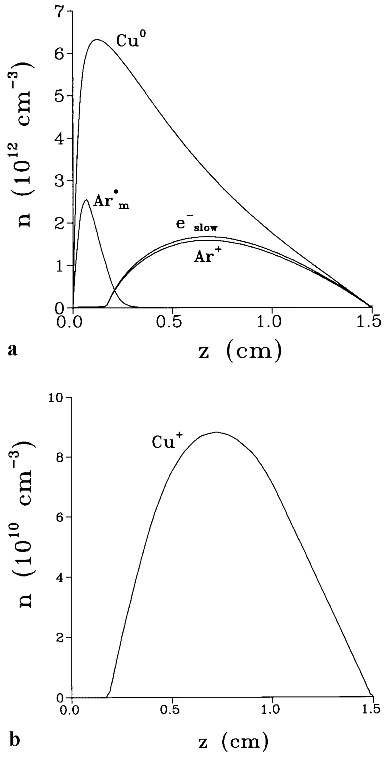


Fig. 1a, b Density profiles of the argon ions (Ar^+), slow electrons (e^-_{slow}), argon metastable atoms (Ar^*_m) and sputtered copper atoms (Cu^0) (**a**) and of the copper ions (Cu^+) (**b**), at 100 Pa and 1000 V (copper cathode in argon)

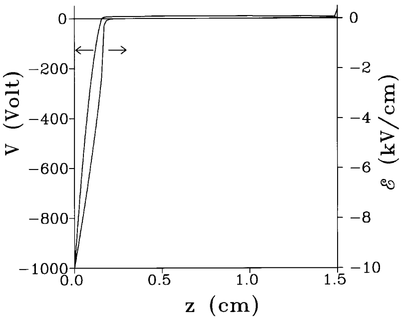
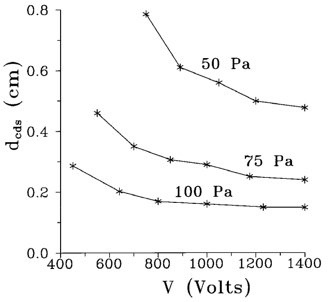


Fig. 2 Electric field and potential distributions throughout the discharge, at 100 Pa and 1000 V

density is presented. It has the same profile as the argon ion density and is of the order of 10^{10}–10^{11} cm^{-3}. Comparing this with the copper atom density yields the ionization degree of copper (i.e. the copper ion density to copper atom density ratio), which is calculated to be about 1% at these discharge conditions. The copper ion to argon ion density ratio is a few percent. Comparing this with the copper atom to argon atom density ratio of about 10^{-4} (n_{Ar} is ca. 10^{16} cm^{-3}), it can be concluded that the copper atoms are much more efficiently ionized than the argon atoms.

In Fig. 2, the potential and electric field distributions throughout the discharge are illustrated. The potential

Fig. 3 Length of the cathode dark space (d_{cds}) as a function of voltage at different pressures



shows a large increase in the CDS and goes through zero at about 0.15 cm from the cathode. This position is defined as the interface between CDS and NG. The potential reaches a small positive value in the NG (ca. 8–10 V, which is called the plasma potential) and returns to zero at the anode backplate. The electric field also shows a large increase in the CDS, it is small in the NG, it changes sign nearly halfway the discharge and increases to about 500 V/cm at the anode backplate. Figure 3 presents the length of the CDS as a function of voltage at different pressures. The CDS length increases with decreasing voltage and pressure, which is necessary to sustain the discharge. At very low pressures, 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. At still lower pressures, the glow discharge would be no longer self-sustained.

Figure 4a, b shows the ionization rates throughout the discharge of the argon atoms and sputtered copper atoms, respectively. The majority of argon ions (Fig. 4a) are formed by direct electron impact ionization of ground state atoms, although ion and especially atom impact ionization becomes increasingly important close to the cathode. The contribution of metastable-metastable collisions leading to ionization of one of the atoms is only small, and that of electron impact ionization from the metastable levels is completely negligible at these discharge conditions. Integrated over the entire one-dimensional distance, the relative contributions of the different processes amount to about 74% for electron impact, about 6.3% and 16.7% for ion and atom impact, and about 3% for metastable-metastable collisions. The argon metastable atoms, however, play an important role in the ionization of copper atoms (see Fig. 4b). Both Penning ionization by argon metastables and asymmetric charge transfer by argon ions seem to be the dominant mechanisms. The exact relative contribution of asymmetric charge transfer is difficult to predict, since the cross sections of this process are not easily available in the literature. The efficiency of this process depends on the availability of energy levels of the element ion which lie close to the argon ion ground or metastable levels. It is however known from literature [13, 14] that if the element ion possesses such energy levels, the cross section

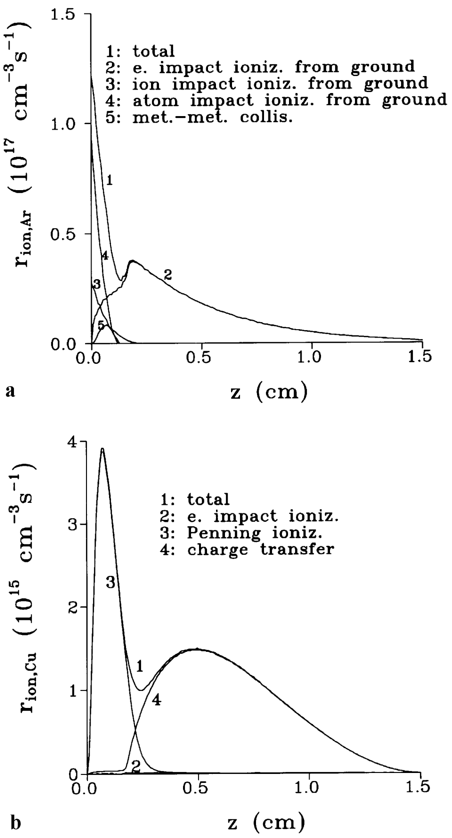


Fig. 4a, b Relative contribution of different ionization processes to the ionization of argon (**a**) and of copper (**b**), at 100 Pa and 1000 V

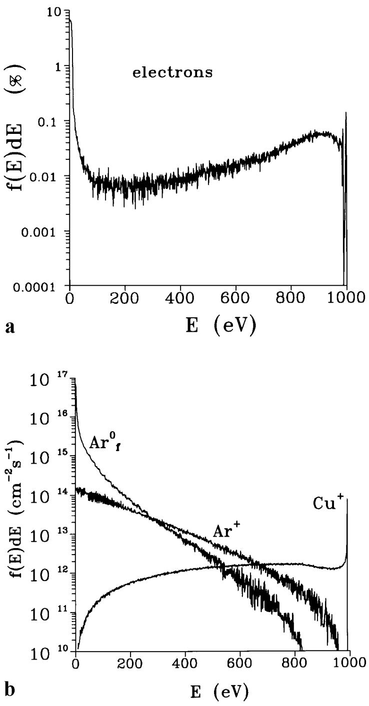


Fig. 5a, b Energy distribution of the electrons bombarding the anode backplate (**a**) and of the argon ions (Ar^+), fast argon atoms (Ar_f^0) and copper ions (Cu^+) bombarding the copper cathode (**b**), at 100 Pa and 1000 V

of asymmetric charge transfer is comparable to the cross section of Penning ionization. Steers et al. [15] have demonstrated the occurrence of charge transfer between argon and copper, therefore we assumed that the cross sections of asymmetric charge transfer and Penning ionization are comparable. This assumption is only an approximation, and the results of Fig. 4b have therefore to be considered with caution. It is however clear from Fig. 4b that electron impact ionization is only of minor importance for the ionization of copper atoms (of the order of 1%). Due to the much more efficient Penning ionization (and probably charge transfer) the copper atoms are much more efficiently ionized than the argon atoms, which was also demonstrated with Figs. 1a and 1b.

In Fig. 5a, the energy distribution of the electrons bombarding the anode backplate is presented. Most of the electrons have low energies. However, electrons of all energies are present in the plasma. A small peak is even observed at maximum energy, which represents the electrons that have traversed the entire discharge without any collisions. Figure 5b shows the energy distribution of the species bombarding the cathode plate. The energy distributions of the argon ions and fast argon atoms are characterized by a rapidly decreasing curve towards higher energies. This means that these species lose much energy by collisions (especially symmetric charge transfer for the argon ions). The mean energy of the argon ions at the copper cathode is about 160 eV, compared to a mean energy of the electrons in the CDS of about 600–700 eV at these discharge conditions [7]. In contrast to the energy distribution of the argon ions and fast argon atoms, the energy distribution of the copper ions at the cathode is characterized by a pronounced peak at maximum energy. Indeed, due to the relatively low number density of copper atoms, symmetric charge transfer of copper ions and atoms does not play a significant role, and the copper ions will therefore not lose so much energy. The energy distribution of the argon ions and copper ions bombarding the cathode is in good agreement with experimental measurements at the VG 9000 mass spectrometer [16]. Since the efficiency of sputtering increases with the energy of the bombarding particles, it is expected that the contribution of the copper ions to the sputtering process (self-sputtering) is non-negligible, in spite of the lower flux compared to the argon ion and fast argon atom fluxes. The relative contribution to sputtering of the different bombarding species was calculated, and it was found that at 100 Pa and 1000 V the relative contributions of fast argon atoms, argon ions and copper ions amount to about 62%, 31% and 7%, respectively. Hence, although the fast argon atoms and also the argon ions account for the

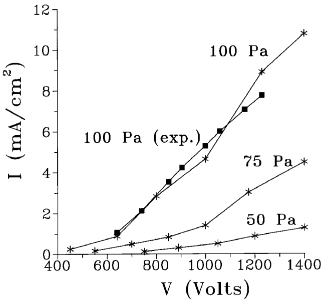


Fig. 6 Calculated electrical currents as a function of voltage at three pressures, and comparison with experiment at 100 Pa

majority of sputtering, the role of copper ions (self-sputtering) cannot be neglected.

Finally, when pressure and voltage are given, it is possible to calculate the resulting electrical current with our models. This is illustrated in Fig. 6 for the typical discharge conditions of the VG 9000 glow discharge mass spectrometer. Comparison is also made with experiment at one pressure, and the excellent agreement demonstrates that the present models are more or less realistic.

IV Conclusion

A combination of different mathematical models for different plasma species is presented to give an overall description of the direct current glow discharge. Some typical results of the models are illustrated, like the density profiles of the plasma species, the electric field and potential distribution throughout the discharge, the length of the CDS as a function of discharge conditions, the different ionization mechanisms in the plasma, the energy distributions of the different plasma species and the relative contribution to sputtering. More details and more results can be found in the cited papers. When pressure and voltage are given, the resulting electrical current could be calculated and showed good agreement with experiment. This strongly supports the validity of the present models.

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