Modelling of glow discharge ion sources for mass spectrometry: potentials and limitations

R. Gijbels and A. Bogaerts

Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium.

Introduction

A glow discharge is a kind of plasma, i.e. a partially ionised gas consisting of different species (a large number of neutrals and nearly equal concentrations of positive and negative charges) which can all interact with each other. The glow discharge is created when a voltage of about 1 kV is applied between two electrodes, inserted into a cell filled with gas at low pressure (e.g. argon at about 100 Pa). The applied voltage causes the formation of positive ions and electrons in the plasma. The ions are accelerated towards the negative electrode (cathode) where they can release electrons upon bombardment. The electrons can give rise to ionisation and excitation collisions in the plasma. The ionisation collisions create new electrons and ions; the latter can again release electrons at the cathode etc. These processes make the glow discharge a self-sustaining plasma. The excitation collisions and subsequent de-excitations, with emission of radiation, are responsible for the characteristic name of the "glow" discharge (it emits a glow of light; the most well-known glow discharges are neon lamps).

Besides applications in the lighting industry (neon lamps, fluorescent lamps,...), glow discharges are also utilised for plasma etching and thin film deposition in the microelectronics industry, as plasma displays, as hollow cathode metal-vapour ion lasers and in analytical spectroscopy as sources for mass spectrometry (GDMS) and optical spectrometric techniques [glow discharge optical emission spectrometry (GD-OES), atomic absorption spectrometry (GD-AAS) and atomic fluorescence spectrometry (GD-AFS)], for the analysis of solid materials. The latter application is based on the phenomenon of cathode sputtering. The material to be analysed is used as the cathode of the glow discharge, which is sputter-bombarded by ions and atoms from the plasma. Atoms of the cathode material are released (or "sputtered") from the cathode and enter the plasma where they can be ionised or excited, thereby creating ions and excited atoms (and characteristic photons) of the cathode material (i.e. material to be analysed). Coupling of the glow discharge to a mass spectrometer or an optical spectrometric detector makes this technique, therefore, useful for the direct elemental analysis of solid materials. Moreover, since the concept of sputtering implies that the sample is eroded "layer after layer", it is possible to determine the elemental composition of successive layers as a function of depth (i.e. depth-profiling). For more information about the analytical applications of glow discharges see Reference 1.

For good analytical practice of glow discharges, a clear insight into the fundamental processes taking place in the plasma is desirable. This can be obtained by mathematical modelling (simulation of the interactions among the plasma species) or by plasma diagnostics (measuring the characteristic plasma quantities). In this paper, we present the state-of-the-art of our modelling work for direct current glow discharges, used as ion sources for mass spectrometry (GDMS). Some typical results of the models will be shown and discussed, in comparison with experimental data, to test the validity of the models.

Brief overview of the modelling work

In the past few years, we have developed a set of three-dimensional models describing the behaviour of the different species present in an argon glow discharge, used as the ion source for mass spectrometry. The species, assumed to be present in the plasma, are argon gas atoms at rest, argon ions, fast argon atoms, excited argon atoms in the metastable level, atoms and ions of the cathode material (material to be analysed) and electrons. These species are described either with Monte Carlo simulations (i.e. for the "fast" plasma species, which are not in equilibrium with the strong electric field in certain parts of the discharge, like electrons) or with fluid approaches (for the "slow" plasma species, which can be considered in thermal equilibrium with the electric field, like the atoms). All these models for the different species are coupled due to the interaction processes among the particles and they are solved iteratively, until final convergence is reached, to obtain an overall picture of the glow discharge. More information about these models can be found, for example, in References 2 and 3 and in the references cited in these papers.

Typical results of the models

The typical results that can be obtained with our models are summarised in Table 1. Some of these results will be presented here at typical discharge conditions of GDMS and in the standard cell for analysing flat samples with the VG9000 glow discharge mass spectrometer (VG Elemental, Thermo-group). Copper is taken as an example of the cathode material. A schematic diagram of this (cylindrically symmetrical) cell is depicted in Figure 1.

Important quantities that can be calculated are the number densities of the different species present in the glow discharge plasma. Figure 2 shows the sputtered copper atom density profile at 75 Pa, 1000 V and 3 mA. It reaches a maximum at a few mm from the cathode and decreases gradually towards the cell walls. The density at the maximum is about 3–5 orders of magnitude lower than the argon gas atom density (at 75 Pa and nearly room temperature, the argon gas atom density is about 2.5×10^{16} cm^{-3}). To check the modelling

Table 1. Overview of the typical results that can be obtained with the models.

- Electrical current as a function of voltage and pressure.
- 3D number density profiles and fluxes of: thermalised argon atoms, argon ions, fast argon atoms, argon metastable atoms, fast and thermalised electrons, atoms and ions of the cathode material.
- 3D potential distributions and (axial and radial) electric field distributions.
- Energy distributions and mean energies as a function of position from the cathode, of: electrons, argon ions and fast argon atoms, cathode ions.
- 3D collision rates of the different collision processes taken into account and relative importance of these collision processes.
  - *Electrons:* Rates of elastic collisions, ionisation of argon ground state and metastable atoms, and of sputtered cathode atoms, excitation of argon ground state and metastable atoms.
  - *Argon ions in the CDS:* Rates of symmetric charge transfer, elastic collisions, ion impact ionisation and excitation of argon ground state atoms.
  - *Fast argon atoms in the CDS:* Rates of elastic collisions, atom impact ionisation and excitation of argon ground state atoms.
  - Rates of *Penning ionisation and asymmetric charge transfer* of sputtered atoms.
  - Rates of the different *production and loss processes* of the metastable argon atoms.
- Sputtering (erosion) rates at the cathode. Thermalisation profiles of the sputtered atoms. Amount of redeposition on the cathode by backscattering or backdiffusion. Relative contributions of argon ions, fast argon atoms and cathode ions to the sputtering process.
- 2D crater profiles due to sputtering at the cathode.
- Ionisation degrees of argon and cathode atoms.
- Ion fluxes at the exit slit of the glow discharge cell to the mass spectrometer.

results, we have measured three-dimensional sputtered atom density profiles with laser-induced fluorescence (LIF) spectrometry and good agreement was reached between calculated and experimental results.[4] The density profile of the copper ions formed by ionisation from the copper atoms is illustrated in Figure 3, for the same discharge conditions. The density is nearly constant close to the cathode and reaches a maximum at the centre of the discharge. It decreases again to low values at the cell walls. From the copper atom and copper ion densities, the ionisation degree of copper can be deduced. At the present discharge conditions, a value of 0.1% was calculated but it should be mentioned that this value depends strongly on the discharge conditions (pressure, current, voltage), on the cell geometry and on the type of cathode material. According to our calculations, it can range from 0.001% at low pressures and voltages and small cells, to about 10% at higher pressures and voltages and larger cells. The sputtered ion density profiles were also measured in three dimensions by LIF spectrometry,[4] and it was found that the calculated profile was in excellent qualitative agreement with the experimental results but the absolute values were still somewhat too low, which is probably due to uncertainties in the rate constants for the different ionisation processes incorporated in the model.[4]

Energy distributions of the plasma species can also be computed by the models. Figure 4 presents the calculated flux energy distribution of the copper ions at different positions from the cathode. The electric field in the glow discharge is very high in the first few mm in front of the cathode (called "cathode dark space"), but the larger part of the discharge ("negative glow") is nearly field-free. Therefore, the copper ions have thermal energies in the negative glow region and they gain energy on their way towards the cathode. They can, however, also lose energy by collisions and are, therefore, characterised by a complete energy distribution ranging from thermal to maximum (i.e. 1000 eV) energies. As can be seen from the pronounced peak at maximum energy in Figure 4, most copper ions bombard the cathode with maximum energy and only a few lose energy by collisions. This calculated energy distribution is in very good agreement with measured energy distributions of the copper ions bombarding the cathode.[5,6] Since the efficiency of cathode sputtering increases with the

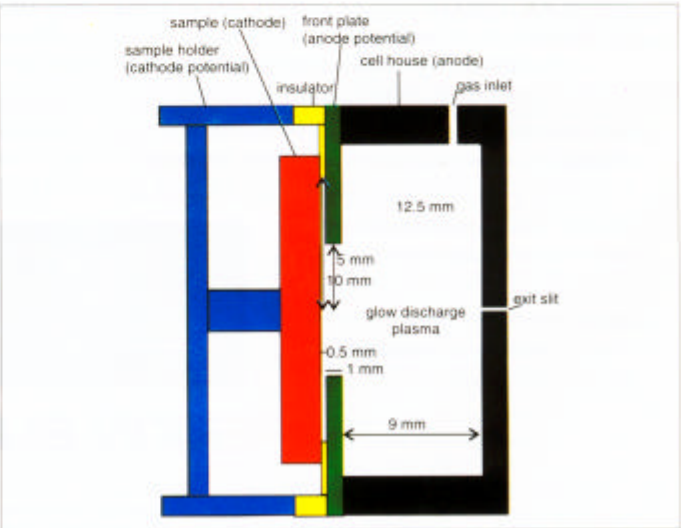

Figure 1. Schematic representation of the standard cell for analysing flat samples in the VG9000 glow discharge mass spectrometer.

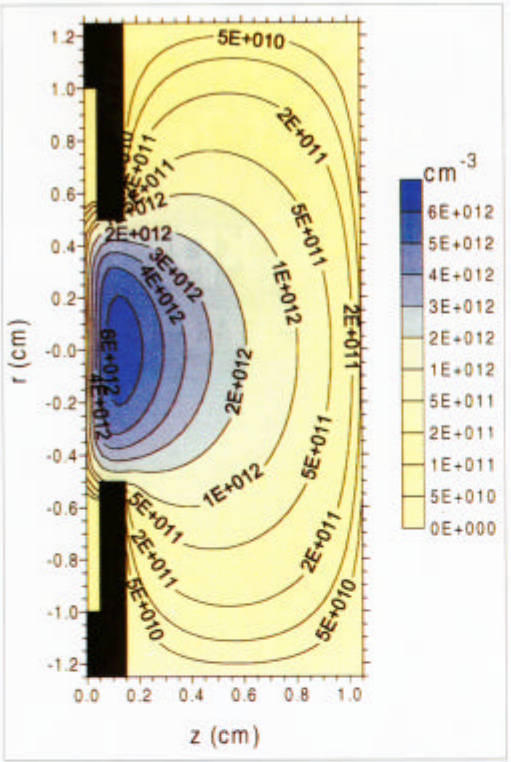

Figure 2. Calculated number density profile of the sputtered copper atoms at 75 Pa, 1000 V and 3 mA.

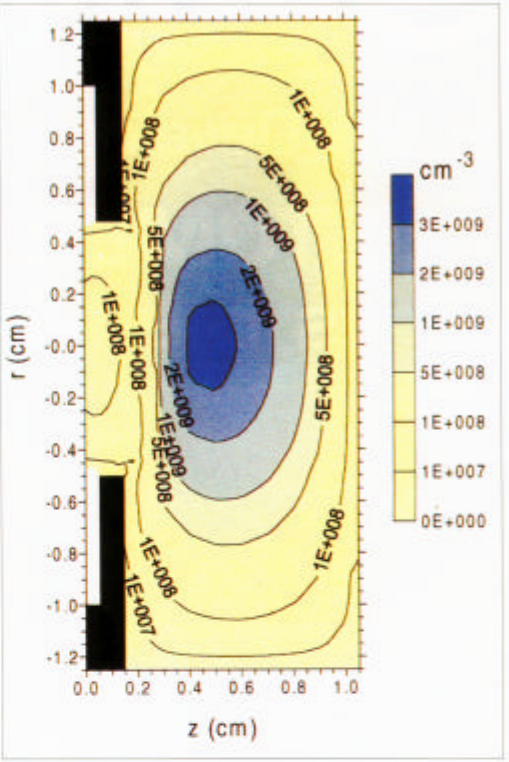

Figure 3. Calculated number density profile of the copper ions at 75 Pa, 1000 V and 3 mA.

energy of the bombarding species, it can be expected that the copper ions have a non-negligible role in the sputtering (called "self-sputtering"), in spite of their lower fluxes compared to the argon ions and fast argon atoms.[3,5] It was calculated that at 1000 V, 75 Pa and 3 mA, the fast argon atoms, argon ions and copper ions contribute to about 73%, 26% and 1% to the sputtering, respectively. However, the contribution of self-sputtering increases with voltage and pressure.

From the models, information can also be obtained about the collision processes of the plasma species. An example is presented in Figure 5, which shows the collision rate of electron impact excitation. The excitation processes, and the subsequent de-excitations, are responsible for the emission of light in the glow discharge. The calculated excitation rate is in good agreement with experimental observations: it is low close to the cathode, in the region called "cathode dark space", and it reaches its maximum after a few mm in the "negative glow", which is indeed known as the brightest part of the discharge.

Moreover, the crater profiles and etching rates due to sputtering at the cathode can be calculated. Figure 6 illustrates a typical calculated crater profile. It reproduces, at least qualitatively, the typical crater profiles often found experimentally:[7] (i) the crater is much deeper at the sides than in the centre; (ii) the crater bottom is not completely flat; (iii) the crater walls are not perfectly steep and (iv) there is a small rim outside the crater profile. Also, the absolute values (i.e. the etching rates) are in reasonable agreement with experimental results.[7] It can be understood that this crater profile is not favourable for depth-profiling because it deteriorates the depth-resolution. When changing the voltage, pressure and current, or when using another cell geometry, it is possible to obtain crater profiles more suitable for depth profiling. Experimental optimisation of the craters occurs often by trial-and-error and this is rather time-consuming. With the models, we are able to study trends in the crater profiles as a function of pressure, voltage, current and cell geometry and we can predict at which conditions optimum crater profiles can be obtained.

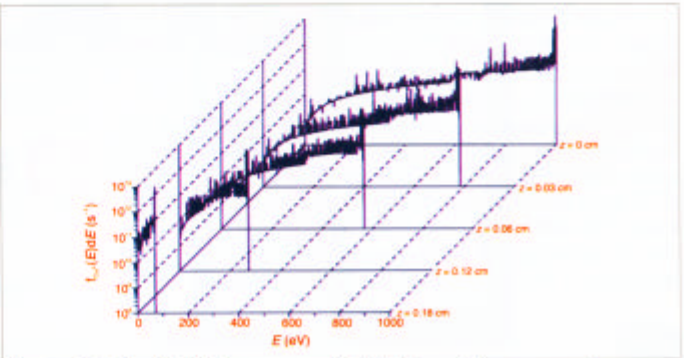

Figure 4. Calculated flux energy distribution of the copper ions, as a function of distance from the cathode, at 75 Pa, 1000 V and 3 mA

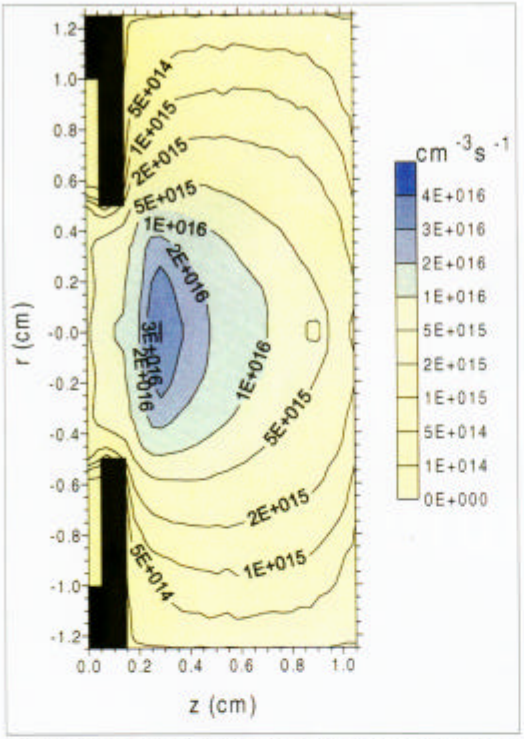

Figure 5. Calculated rate of electron impact excitation collisions throughout the discharge at 75 Pa, 1000 V and 3 mA.

Finally, when the glow discharge is used as the ion source for mass spectrometry, special interest goes to the ion intensities in the mass spectrum. The present models can calculate the ion fluxes at the position of the exit slit to the mass spectrometer, which can give an idea of the ion intensities in the mass spectrum. When applying the models to different cell geometries, they can predict the corresponding ion intensities in the mass spectra and they can, therefore, be useful for cell optimisation and new cell design.

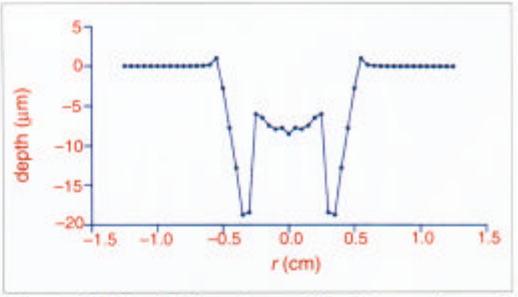

Figure 6. Calculated crater profile after one hour of sputtering at the copper cathode at 75 Pa, 1000 V and 3 mA.

Conclusion

Some typical examples of what can be calculated with our models are presented. The satisfactory accordance with experimental data illustrates that the models give already a realistic picture of the glow discharge. Generally, it can be concluded that mathematical modelling is a useful tool to obtain better insight into the fundamental aspects of the glow discharge which is desirable for improving the analytical performance of glow discharge spectroscopy.

References

1. R.K. Marcus, *Glow Discharge Spectroscopies*. Plenum Press, New York (1993).
2. A. Bogaerts, R. Gijbels and W.J. Goedheer, *Anal. Chem.* **68,** 2296 (1996).
3. A. Bogaerts and R. Gijbels, *Anal. Chem.* **68,** 2676 (1996).
4. A. Bogaerts, E. Wagner, B.W. Smith, J.D. Winefordner, D. Pollmann, W.W. Harrison and R. Gijbels, *Spectrochim. Acta* **52B,** 205 (1997).
5. A. Bogaerts and R. Gijbels, *J. Appl. Phys.* **79,** 1279 (1996).
6. M. van Straaten, A. Bogaerts and R. Gijbels, *Spectrochim. Acta* **50B,** 583 (1995).
7. A. Bogaerts and R. Gijbels, *Spectrochim. Acta* **52B,** in press (1997).