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Comparison of modeling calculations with experimental results for rf glow discharge optical emission spectrometry

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Abstract

A model developed recently for a radio-frequency glow discharge, is applied to experimental Grimm-type discharge conditions, to check the validity of the model calculations. The calculated electrical characteristics (rf voltage, d.c. bias voltage, electrical power, peak-to-peak current, as well as the time-profiles of voltage and current), and the calculated erosion rates are compared with the measured values for an rf frequency of 3.5 MHz. The electrical characteristics are found to be in fairly good agreement. The calculated and measured erosion rates show larger discrepancies. Compared to the d.c. Grimm-type glow discharge, where similar quantities were compared and were found in excellent agreement, the agreement is less satisfactory in the rf discharge. This illustrates that the rf discharge is much more complicated than a d.c. discharge, and that more fundamental studies are required. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In previous years, a set of 2D models has been developed by Bogaerts et al. to describe direct current (d.c.) glow discharges. These d.c. glow discharge models can be considered as being thoroughly validated. Indeed, comparison with experiment has been carried out for several different calculation results. In a very recent paper in this journal [1], the results are reported from a comparison between modeling calculations and experimental results in a d.c. Grimm-type glow

discharge, for the electrical characteristics, the erosion rates and the optical emission intensities of various ArI, CuI and CuII lines, and in general, very good agreement between model and experiment was obtained [1]. Moreover, some other comparisons with experiment have been carried out for the d.c. glow discharge models, e.g. for the two-dimensional sputtered tantalum atom and ion density profiles [with laser-induced fluorescence (LIF) spectrometry] [2], for the two-dimensional argon metastable atom density profiles (with LIF) [3], for the one-dimensional sputtered lithium atom density profiles (with concentration-modulated atomic spectrometry; COMAS) [4], for the electron densities (with Langmuir probe measure-

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ments) [5], for the crater profiles and erosion rates in the VG9000 glow discharge mass spectrometer [6], for argon and copper ion energy distributions at the cathode [7], and for optical emission intensities as a function of distance from the cathode [8]. In all these examples, the agreement between calculated and measured values was indeed found to be fairly good.

The radio-frequency (rf) discharge, on the other hand, has appeared to be much more complicated to be theoretically described. A few modeling attempts have been presented by Bogaerts et al. in the past few years for analytical rf Grimm-type glow discharges [9–11]. The major problem appeared to be the correct treatment of slow electrons, which can be heated by the fluctuating bulk electric field, and the corresponding ionization by these electrons (so-called α -ionization). In a recently published paper [11] all electrons are treated with the Monte Carlo method, and this approach is believed to give a correct picture of ionization in the rf Grimm-type glow discharge [11].

Beside this, a discrepancy has also been observed between the rf models of Bogaerts et al. and the rf model of Belenguer et al. [12]. Indeed, in Belenguer et al. [12] it was reported that the calculated current and voltage were out of phase by $\pi/2$ at typical Grimm-type rf-GD-OES conditions, whereas the models of Bogaerts et al. predict that current and voltage are roughly in phase at the same operating conditions. The reason for this discrepancy is that Belenguer et al. found that the displacement current, which is indeed always out of phase with the voltage, was two orders of magnitude higher than the ion and electron conduction currents [12], whereas Bogaerts et al. calculated that the displacement current was lower than or at maximum equal to the ion and electron conduction currents [11].

To elucidate the problem of this discrepancy and to check the validity of the rf modeling results, it is necessary to compare the calculated results with experimental data. In the present paper such a comparison is carried out for typical Grimm-type rf-GD-OES conditions. The rf frequency used in the experimental set-up (see below) was 3.5 MHz, instead of the more commonly used value of 13.56

MHz. This has, however, only a minor effect on the obtained modeling results. Indeed, in the past we have also carried out calculations at 13.56 MHz, and the same conclusions could be drawn as from the present calculations. The main emphasis in the comparison carried out here is on the electrical characteristics, i.e. voltage and current as a function of time in the rf-cycle, as well as the d.c.-bias voltage, the peak-to-peak current and the electrical power, because this has been the subject of major concern in previous studies [9–12], and the electrical characteristics should first be correctly predicted before the other calculation results (densities, collision rates, sputtering, optical emission intensities,...) can be trusted.

2. Description of the model

The model network is very similar to the d.c. model network [1], except for some basic differences, inherent to rf discharges (see [9–11,13–15]). The species assumed to be present in the plasma are the argon gas atoms, the electrons, argon ions, fast argon atoms, argon atoms in various excited levels, sputtered copper atoms and copper ions, both in the ground state and in various excited levels. These species are described with a combination of Monte Carlo, fluid and collisional–radiative models, as is explained in the literature [9–11,13–15]. Since this modeling network is also briefly overviewed in Bogaerts et al. [1], albeit for the d.c. discharge, it will not be repeated here. Because the present paper focuses mainly on the electrical characteristics, it is, however, worthwhile to mention that the argon ions and electrons, which determine the electrical characteristics, are described with the improved hybrid Monte Carlo fluid model, for which more information can be found in Bogaerts et al. [11]. Finally, it should be mentioned that the calculations in the rf case are much more time-consuming than in the d.c. case. Indeed, (i) all electrons, including the slow ones, are described with the Monte Carlo method; (ii) the time-step in the fluid model should be small to avoid numerical instabilities (i.e. divergence instead of convergence of the calculations); and (iii) a large number of rf-cycles have to be followed, both in the Monte Carlo and the fluid

model, to ensure that periodic steady state is reached. A typical calculation takes longer than 1 week on a professional workstation.

3. Experimental set-up

The experiments were carried out with a Spectrumat 1000 S (Spectrums). The optical signals were only used to check the vacuum tightness and the stability of the discharge. The glow discharge source used for this study is based on the Grimm-type [16]. It has an anode diameter of 4 mm, an integrated water cooling from the backside of the sample and can be used in d.c. and rf operation modes. Voltage and current probes are integrated in the source body [17]. The source is electrically shielded and the sample is surrounded by rf voltage. Sample size and position have no influence on the voltage and current measurement. The capacitive voltage divider has a conversion factor of 1/2000 V/V. The current converter is placed close to the plasma, which leads to a small ‘external’ displacement current. The equivalent remaining capacity is approximately 3 pF. The current probe has a nearly frequency independent current to voltage conversion of 2 V/A in the frequency range between 1 and 200 MHz. The current signal is not disturbed by the leak current of the water cooling. The bias voltage of the plasma is measured with a high voltage probe (GE 3121 1/100 V/V) inside the power cable between the GD source and the coupling capacitor. The analog signals are digitized with an oscilloscope (LeCroy LC584A, bandwidth 1 GHz), with bandwidth limited to 200 MHz. Voltage and current signals are sampled at 2 Gs s⁻¹ and averaged 15 times. Using conducting samples the plasma voltage U_{pl} is equal to the measured voltage U_m . With the help of the measured current I_m the plasma current is calculated by $I_{pl}(t) = I_m(t) - C_r dU_{pl}(t)/dt$, whereas C_r is the remaining capacity determined by a zero measurement. The latter means a measurement without plasma (no gas pressure), to ensure that the measured value does not originate from the plasma, but from the external circuit (capacitor). The estimated error for the amplitude of voltage and current is approximately 5%. The power is calculated by:

$$P = \frac{1}{T_p} \int_0^{2\pi} U_{pl}(t) I_{pl}(t) dt$$

for one period with the periodic time T_p . The estimated error is in the range of 7%.

For the measurements we used a self-built free running rf generator [18] with a working frequency of 3.5 MHz. In principle it is a LC parallel resonance circuit driven by a tube. A high voltage power supply is used to power the generator. The amplitude of the rf voltage is proportional to the d.c. voltage and has a maximal amplitude of 2500 V. The GD source is connected with a coaxial cable. The plasma is part of the resonance circuit. By changing the plasma impedance the resonance frequency changes in the range of 20 kHz in a few periods. Therefore, after the ignition the voltage is very quickly stabilized. It is known that the harmonics distribution of the driving rf voltage has an influence on the spectral emission of the plasma. To reduce the influence on the plasma and to invest less effort into the voltage and current measurement, a driving voltage with as little harmonics as possible is needed. Our generator has a high quality resonance circuit, which causes a harmonic suppression of greater than 50 dBc. This means that the ratio of the amplitude of the first harmonic to the amplitude of the fundamental is smaller than 1/316.

A mass flow controller (Tylan FC-260) steers the argon gas flow (gas purity 99.998%). It is given in standard cubic centimeters per minute (sccm = cm³ min⁻¹ at 1013 mbar and 273 K). The argon pressure is calculated with the formula:

$$p/\text{mbar} = 0.632 + 17.56 \text{ flow/sccm} - 2.597 (\text{flow/sccm})^2.$$

The calibration constants are measured. For this purpose we fixed a vacuum adapter to the plane of the sample, which is connected to a vacuum meter (MKS Baratron Type 127; range 0–100 mbar).

We use a massive Cu-sample ($\varnothing = 300$ mm, $h = 10$ mm). To get the same plasma conditions, the distance between the anode and the Cu sample must be the same for each measurement. For this purpose we pressed the samples with constant pressure to the cathode plate. After each measure-

ment, the GD source is cleaned with a special drilling tool. Nevertheless, small differences of the surface of the anode cannot be excluded. Additionally, the redeposition of sputtered material at the crater edge causes little difference in the gas flow and temperature differences of sample, source and discharge gas exist. All these facts may lead to small differences in the plasma conditions (between 5 and 10%) even if the same discharge conditions are applied.

4. Results and discussion

The calculations and measurements were performed at three different pressures, which are the same as in the d.c. comparison [1], and for each pressure at three different electrical conditions. The rf-frequency was 3.5 MHz for all conditions investigated. The rf amplitude of the voltage, the gas pressure and the temperature are used as input in the model, and the d.c.-bias voltage, the current and the electrical power are calculated. It should be mentioned that this approach is different from our previous rf model, where the electrical power was used as input value, and the rf amplitude voltage was calculated (based on power dissipation) [9–11].

Fig. 1 shows the calculated (solid lines) and measured (dashed lines) voltage at the rf-electrode as a function of time in one rf-cycle, at all conditions investigated here. The voltage is negative during most of the rf-cycle, due to the highly negative d.c.-bias (see thin solid and dashed lines, for the calculated and experimental values, respectively). The voltage is only positive at approximately $\omega t = \pi/2$. It appears that excellent agreement is reached between calculated and measured voltages as a function of time. The absolute values of the experimental d.c.-bias voltage are somewhat higher than the calculated values. Hence, because of the negative values of the d.c.-bias voltage, the experimental voltage as a function of time lies slightly below the calculated data. The d.c. bias voltage is calculated in the model based on the condition that the computed electron and ion currents at the rf-electrode, integrated over one rf-cycle, should be equal to each other. If the time-integrated electron current is calculated to be

higher, the d.c.-bias voltage is made more negative to attract ions and repel electrons, until the electron and ion currents are equal to each other, and vice versa. It should be mentioned that it is not straightforward to reach such a good agreement between calculated and measured d.c.-bias voltages. Indeed, in previous work, the discrepancy was somewhat larger (of the order of 100 V). In order to reach better agreement, we adapted the ion and electron mobilities and diffusion coefficients, compared to our previous work. The electron mobility (μ_e) and diffusion coefficient (D_e) were assumed to be $4 \times 10^6 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ and $4 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$ at 1 torr and 300 K, respectively. This corresponds to a mean electron temperature of 0.1 eV ($kT_e = D_e/\mu_e$) in the bulk plasma, which appears to be low. However, recent measurements have indeed confirmed this value [19–21]. The ion diffusion coefficient (D_i) is assumed to be $40 \text{ cm}^2 \text{ s}^{-1}$ at 1 torr and 300 K, in correspondence to our previous model; this value appeared to be not very critical. The major difference is found in the value of the ion mobility (μ_i) which was previously approximated by a constant value, and is now treated more correctly as a function of the electric field (E) [22]:

$$\mu_i = \frac{\mu_{i0}}{(1 + (0.02181E/p)^{1.5})^{0.33}}$$

where p is the pressure in torr, E is the electric field in V cm^{-1} , and $\mu_{i0} = 1246 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ at 1 torr and 300 K.

The absolute values of the calculated and measured d.c.-bias voltages are plotted as a function of rf-amplitude voltage in Fig. 2 (represented by solid and dashed lines, respectively). It appears that the d.c.-bias voltage is in absolute value only approximately 50–100 V lower than the rf-amplitude, at all conditions investigated. The difference between $U_{\text{d.c.-bias}}$ and U_{rf} is somewhat larger at rising pressure, and the calculated differences were also somewhat larger than the experimental data (see also Fig. 1). However, in general the agreement between calculated and experimental results is fairly good.

Fig. 3 shows the calculated (solid lines) and measured (dashed lines) electrical currents at the

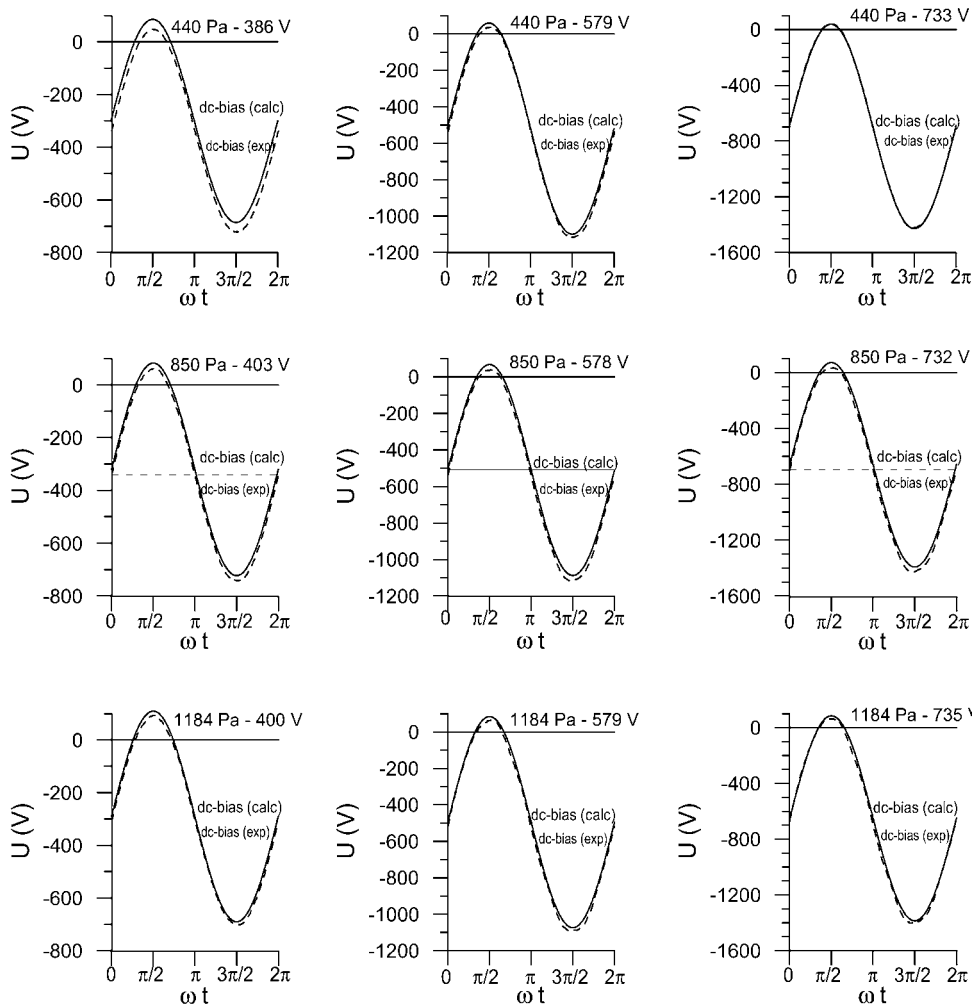


Fig. 1. Calculated (solid lines) and measured (dashed lines) voltages as a function of time in one rf-cycle, at several conditions of pressure and amplitude of the voltage. Also shown are the calculated and measured d.c.-bias voltages (solid and dashed thin lines, respectively).

rf-electrode, as a function of time in the rf-cycle, at all conditions investigated. The agreement between theory and experiment is not perfect but it is satisfactory. In order to reach this reasonable agreement between model and experiment, we slightly adapted the gas temperature in the same range as for the d.c. conditions [1]. We call the agreement satisfactory, because at least the same time-behavior is found, with a pronounced positive peak at approximately $\omega t = \pi/2$ (due to electrons bombarding the rf-electrode) and a negative value

in the rest of the rf-cycle (mainly determined by the ion flux bombarding the rf-electrode; indeed, the latter is positioned at the left, hence the ions move in the negative z -direction).

It should be mentioned that the total electrical current in an rf discharge is not only composed by ion and electron conduction currents, but it contains a third term, i.e. the displacement current, which arises from the movement (i.e. expansion and collapse) of the rf-sheath as a function of time. Indeed, this yields a change in the positive

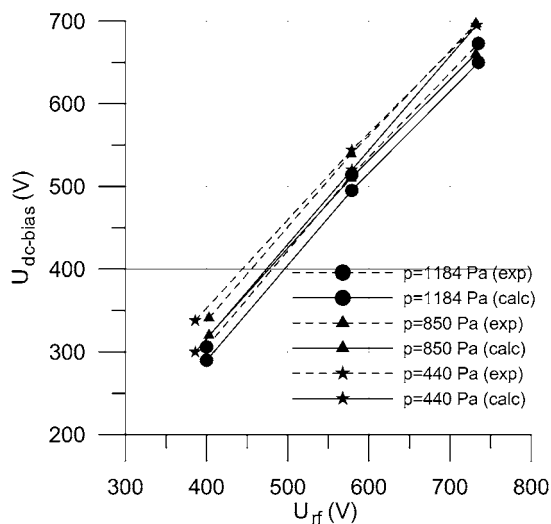


Fig. 2. Calculated (solid lines) and measured (dashed lines) d.c.-bias voltages as a function of rf amplitude voltage, at three different pressures.

charge density in the rf-sheath as a function of time, and hence in a current, since $I = dq/dt$ (where I , q and t are the symbols for current, charge and time). It is important to note that the displacement current is always out of phase by $\pi/2$ with respect to the voltage. More explanation of the displacement current is given in Bogaerts et al. [11].

By comparing Figs. 1 and 3, it appears that both calculated and measured voltage and current are in phase with each other. This was indeed predicted in our previous work as well [9–11], but the opposite was reported in Belenguer et al. [12]. The reason is that the model of Belenguer et al. [12] predicted that the displacement current was two orders of magnitude higher than the ion and electron conduction currents. The present, fairly good agreement between our model results and the experimental data, clearly demonstrates that the displacement current is not dominant at typical Grimm-type rf-GD-OES conditions. The reason for this is clear [11]. Grimm-type glow discharges are characterized by a small rf-powered electrode whereas the grounded electrode (i.e. the cell walls) is large. This big difference between the sizes of both electrodes is responsible for the large d.c.-

bias (see above). The latter gives rise to a small sheath in front of the rf-electrode, which does not change considerably in length as a function of time, hence yielding a small displacement current. It should be mentioned that not all capacitively coupled rf discharges are characterized by a small displacement current. Indeed, this type of current is typical for rf discharges with electrodes of comparable size, where the rf sheaths change considerably. In the case of two electrodes of comparable size, and at lower gas pressures and lower d.c. bias voltages, such as typically used for the plasma enhanced chemical vapor deposition of thin films, the displacement current is, at least in the rf-sheath, of comparable magnitude or even higher than the ion or electron currents [23,24].

At this point it is important to realize that both the results obtained by the model and by the measurements apply only to the plasma current; hence, the capacitive current of the measuring circuit is subtracted in the experiment, to obtain the pure plasma current (see also above). Probably, the high value of the displacement current calculated in Belenguer et al. [12], is not only related to the plasma, because the authors calculated even a high current in the absence of a plasma (see the discussion in [11]).

However, the displacement current calculated in our model did not appear to be completely negligible. It was at maximum equal to the ion conduction current. It appears that some discrepancies between the calculated and experimental current (e.g. at 440 Pa and 733 V, between $\omega t = \pi$ and $3\pi/2$) are caused by the contribution of the displacement current in the calculations. Hence, this suggests that the calculated displacement current is still somewhat too high, compared to the experimental data. On the other hand, it also appears that the calculated current in the beginning and at the end of the rf-cycle is somewhat too high compared to the experimental data, at almost all conditions investigated. This has probably nothing to do with the displacement current, but it is attributed to the ion flux which appears too high around $\omega t = 2\pi$, compared to the experimental results. The model predicts indeed that the ion fluxes are at maximum at $\omega t = 2\pi$ [13], because the ions are supposed not to be able to follow the

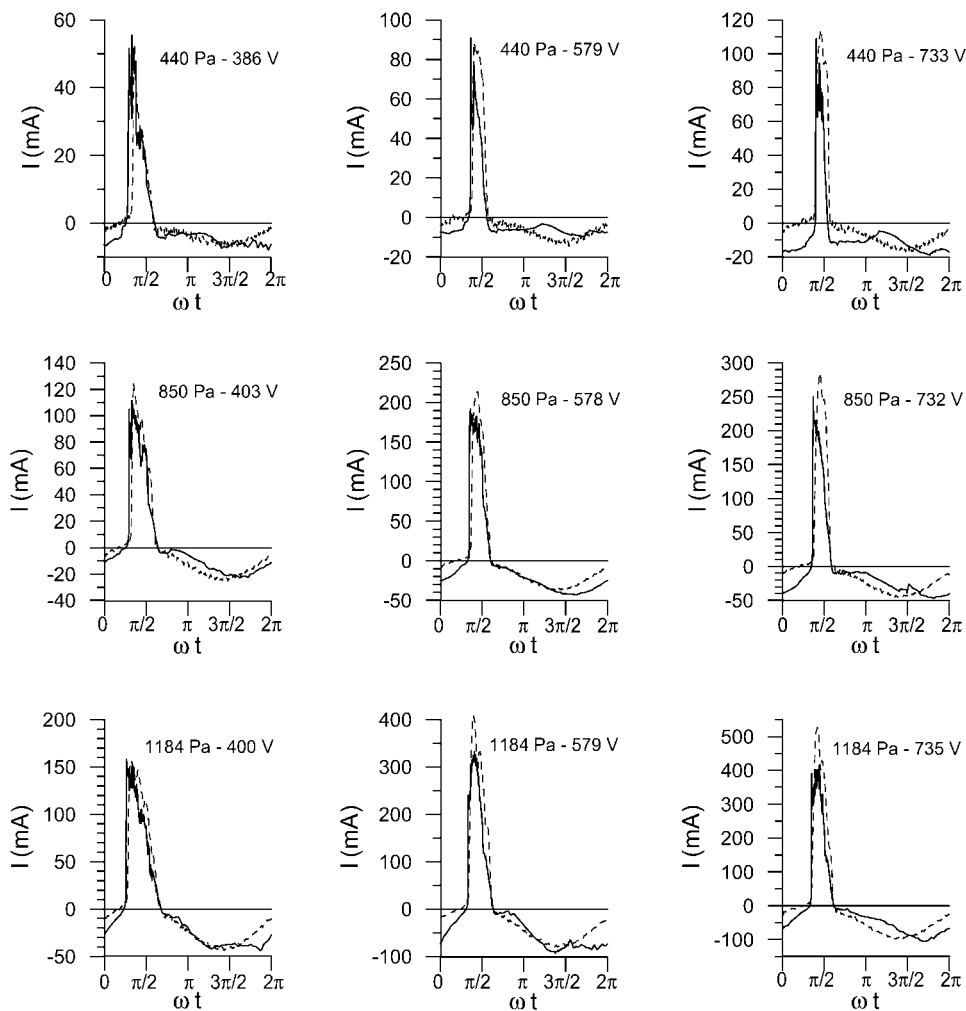


Fig. 3. Calculated (solid lines) and measured (dashed lines) electrical currents as a function of time in one rf-cycle, at several conditions of pressure and amplitude of the voltage.

time-varying electric fields. Hence, in the model they move in a so-called effective electric field, which actually lags somewhat behind the real electric field [9]. This approximation in the model does not seem to be the most appropriate one, because experimentally the current reaches its most negative value at $\omega t = 3\pi/2$, which seems to be determined by the maximum ion flux at this time in the rf-cycle. Indeed, at the frequency of 3.5 MHz, the ions can probably follow the real electric field, reaching a maximum at $\omega t = 3\pi/2$.

Summarizing, it appears that experimentally, the electrical current is characterized by a sinusoidal current profile, in phase with the voltage, with a superimposed peak current at $\omega t = \pi/2$. This sinusoidal current profile is not exactly found back in the calculations, and this is attributed to (i) the ion flux reaching a maximum value somewhat later in time than in the experiment; and (ii) the calculated displacement current which appears somewhat too high compared to the experiment. Finally, the calculated pronounced peak at $\omega t = \pi/2$, due to

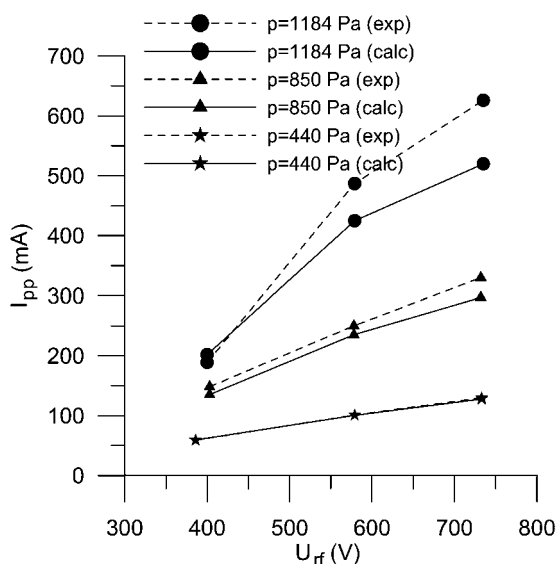


Fig. 4. Calculated (solid lines) and measured (dashed lines) peak-to-peak currents as a function of rf amplitude voltage, at three different pressures.

the electron flux bombarding the rf-electrode, does not exactly coincide with the measured peak, i.e. at some conditions it drops a bit too early or it reaches a lower absolute value. Nevertheless, after all we consider the present agreement fairly satisfactory, especially in view of the controversy, which existed between different modeling results (i.e. current in or out of phase with voltage). Figs. 1 and 3 clearly indicate that the current and voltage are in phase with each other, and this result on its own, was the most important for us at this stage. The fine-structure of the exact current behavior needs further investigation in the future.

Fig. 4 presents the calculated (solid lines) and measured (dashed lines) peak-to-peak currents as a function of rf-amplitude voltage. As can also be seen in Fig. 3, the calculated peak-to-peak currents are somewhat lower than the experimental data, especially at the highest pressure investigated, which is mainly attributed to the somewhat lower positive peak values (see above). Nevertheless, the same tendency as a function of voltage and pressure is observed, which is already satisfactory for us, at this stage.

The calculated and measured electrical power values as a function of rf-amplitude and pressure, are depicted in Fig. 5 (solid and dashed lines, respectively). It should be mentioned that the power is calculated in the rf model in two distinct ways. (i) The easiest way is to calculate it from the product of voltage and current as a function of time [11], similar as in the experiment:

$$P_{\text{IU}} = \frac{1}{T} \int_0^{2\pi} U(t)I(t)dt$$

where T is the time of the rf-period. $U(t)$ and $I(t)$ are both calculated in the fluid model:

$$U(t) = U_{\text{rf}} \sin(\omega_{\text{rf}} t) + U_{\text{d.c.-bias}}$$

$$I(t) = e(j_{\text{ion,rf}}(t) - j_{\text{elec,rf}}(t)) + J_{\text{d,rf}}(t)$$

where $j_{\text{ion,rf}}$ and $j_{\text{elec,rf}}$ are the ion and electron fluxes bombarding the rf-electrode, and $J_{\text{d,rf}}$ is the displacement current at the rf-electrode (see above).

(ii) To check the above calculation method (which is the most simple one, but might give unrealistic results if the time behavior of voltage and current are not 100% correctly calculated; see above), the electrical power is also calculated from the power dissipation in the discharge by ions and electrons (i.e. the energy gain of ions and electrons due to the electric field, by Ohmic heating, integrated over the entire discharge region and rf-cycle) [9].

It appears from Fig. 5 that both calculation methods yield slightly different results, which might be attributed to the calculated current time-profile which is not completely correct, as well as to some approximations in the calculation of Ohmic heating (i.e. calculated in the fluid code, which is an approximation for fast electrons). Hence, the observed differences illustrate the typical errors expected in the model calculations. Nevertheless, the calculation results differ by not more than 20%, and they are also comparable to the experimental data. Moreover, they exhibit the same trend as a function of voltage and pressure, so that they are, at this stage, satisfactory for us.

Up to now, we have focused our comparison to the electrical characteristics of the rf glow discharge. Apart from some minor differences, mainly

in the fine-structure of the calculated current time-profiles, the agreement was found to be fairly reasonable. In analogy to a previous paper [1], where we compared model and experiments for a d.c. Grimm-type glow discharge, we have now also compared the calculated and measured erosion rates and optical emission intensities for the rf case. Fig. 6 shows the erosion rates, calculated by the model (solid lines) and measured (dashed lines), as a function of rf-voltage and pressure. In the model for the sputtering, we used a sticking coefficient of 0.1, in analogy to the d.c. case [1]. It appears from Fig. 6 that the absolute values of the calculated and measured erosion rates are in reasonable agreement, but the comparison for the tendency as a function of voltage is less convincing than for the d.c. calculations. The reason is that the calculated ion fluxes were not yet 100% correct (see Fig. 3 above), and these errors are reflected (and are amplified) in the calculated erosion rates.

The correlation between calculated and measured optical emission intensities for ArI, CuI and CuII lines as a function of voltage and pressure was worse than for the erosion rates (and is

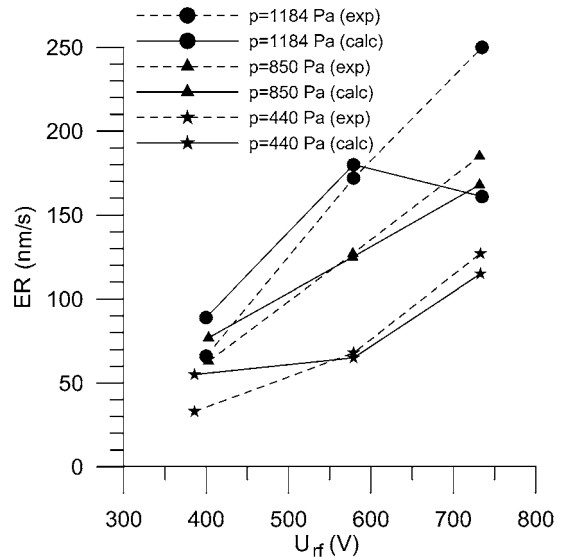


Fig. 6. Calculated (solid lines) and measured (dashed lines) erosion rates due to sputtering at the cathode, as a function of rf amplitude voltage, at three different pressures.

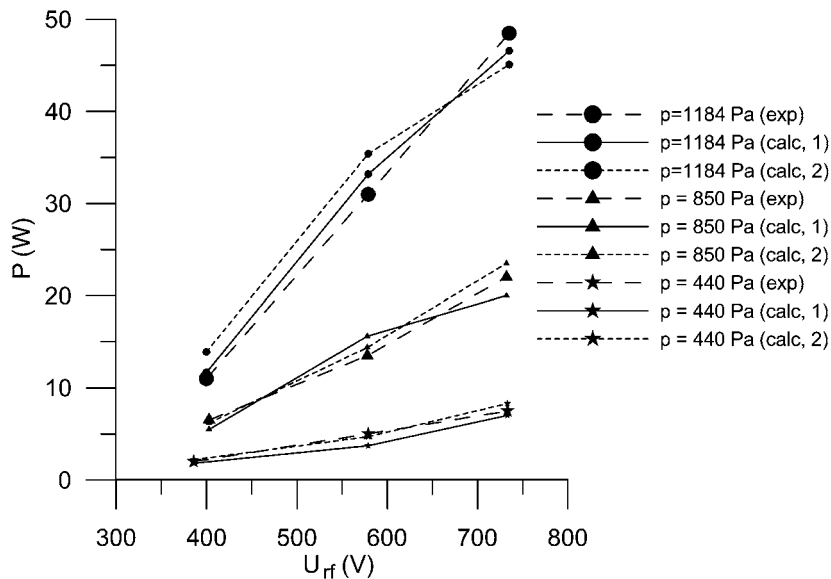


Fig. 5. Calculated and measured electrical power values as a function of rf amplitude voltage, at three different pressures. The experimental data are illustrated by wide dashed lines and large symbols. The calculated data (smaller symbols) are represented in two ways, according to the calculation method: solid lines: method 1 (product of voltage and current); small dashed lines: method 2 (power dissipated by ions and electrons).

therefore not presented here). The reason is that the optical emission intensities are the final results of the calculations, and they depend on a combination of many calculated quantities. Hence, the errors in the different steps of the calculations will be enlarged in the optical emission intensities. Since even the calculated electrical characteristics (more specifically the fine-structure in the current time-profiles) were not yet in exact agreement with the experimental data, it is indeed to be expected that the optical emission intensities are subject to errors. It is clear that in a first step we have to solve the differences in the fine-structure of the electrical characteristics, before we will be able to present a reasonable comparison between the calculated and measured optical emission intensities. In the d.c. glow discharge, on the other hand, the electrical characteristics are much simpler, and excellent agreement was reached between model and experiment. Consequently, the calculated and measured d.c. erosion rates and optical emission intensities, were already in satisfactory agreement.

5. Conclusion

A comparison is made between model calculations and experimental measurements for an rf Grimm-type glow discharge, at three different pressures and three different electrical conditions per pressure. The main emphasis was on the electrical characteristics, i.e. voltage and current as a function of time in the rf-cycle, as well as the d.c. bias voltage, the peak-to-peak current and the electrical power. The most important result of this paper is that both calculations and experiments revealed that voltage and current are in phase with each other, at typical Grimm-type rf-GD-OES conditions. Apart from some discrepancies, mainly in the fine-structure of the electrical current as a function of time in the rf-cycle, the overall agreement between measured and calculated electrical characteristics was fairly good. In analogy to a comparison previously carried out for the d.c. discharge, we have also compared calculated and experimental erosion rates and optical emission intensities. The correlation for the erosion rates was still reasonable but less convincing than for

the d.c. comparison, and it was not satisfactory for the optical emission intensities. The reason is that these quantities appear at the end of the calculated results, and hence depend on a combination of many other calculated quantities (and their corresponding errors). It is clear that in a first step exact agreement should be obtained for the electrical characteristics, before good agreement can be expected for the other quantities. In the d.c. case, the agreement between theory and experiment was found to be much better. This demonstrates that the rf discharge is more complicated than its d.c. counterpart, from a numerical modeling point of view, and that further fundamental studies are required.

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