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Spectrochimica Acta Part B 50 (1995) 1337–1349

SPECTROCHIMICA
ACTA
PART B

Plasma diagnostics of an analytical Grimm-type glow discharge in argon and in neon: Langmuir probe and optical emission spectrometry measurements

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Received 13 January 1995; accepted 9 May 1995

Abstract

Comparative investigations were performed on a Grimm-type glow discharge source by Langmuir probe measurements and by optical emission spectrometry. The Langmuir probe measurements yielded electron temperatures and number densities of electrons, whereas the optical emission spectrometry measurements resulted in data for excitation and ionization temperatures of different species. The results confirm that there is no local thermal equilibrium in the discharge plasma. The operating conditions of the glow discharge source and also the working gas and the cathode material were varied to investigate their influence on the plasma parameters. The outcome of the plasma diagnostics will be used to improve the modelling of relevant excitation and ionization processes by computer simulation. The major physical processes in the low pressure glow discharge plasma should be better understood if the analytical capability of this spectrochemical excitation and ionization source has to be further enhanced.

Keywords:

1. Introduction

Low pressure gas discharges are well known spectrochemical excitation and ionization sources. Operated with a plane or pin-type cathode, gas discharges have found widespread applications for the quantitative analysis of solid samples by optical emission spectrometry (OES) [1–6] and mass spectrometry [6–10]. In most cases, argon is used as the working gas, which sustains the discharge at pressures of about 50–500 Pa and with typically 1 kV voltage between the electrodes. The nature of the plasma is determined by the working conditions of the discharge (gas pressure, voltage, current) and by the properties of the cathode material (erosion rate, electrical conductivity, emissivity of secondary electrons). To achieve high accuracy of the analytical results and optimum detection power, the fundamental excitation and

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ionization processes of the glow discharge as a function of the working conditions and cathode properties have to be understood. This knowledge can be acquired by theoretical modelling [11-15] and by experimental plasma diagnostics [16-36]. A simulation of the major processes in the glow discharge is possible by mathematical modelling. Results for certain plasma parameters that are very difficult to measure experimentally can be obtained in this way. However, the models are simplified and possibly they do not fully reflect the real situation. It is clear that the reliability of the computer simulation can be improved by additional information from plasma diagnostics concerning experimentally accessible plasma parameters.

The most important plasma diagnostic techniques are (i) Langmuir probe measurements [18-21] yielding electron and positive ion number densities, electron temperatures, the electron energy distribution and the plasma potential; (ii) optical emission spectrometry measurements [22-31] which can give information on electron number densities and on different temperatures (gas, electron, excitation and ionization temperatures); (iii) atomic absorption and fluorescence measurements mostly using lasers to measure densities of different plasma species [32-34]; and (iv) mass spectrometry in order to study ionization processes in the plasma [35].

In general, the interpretation of results derived by plasma diagnostics or by theoretical modelling is complicated by the known fact that there is no local thermal equilibrium (LTE) in the discharge plasma due to the strong electric field gradient. Consequently the plasma cannot be described by a unique temperature; on the contrary different species indicate different temperatures (i.e. gas temperature, electron temperature, excitation and ionization temperature, etc.). The temperature data derived under non-LTE actually have no real physical meaning; nevertheless they indicate whether the varying working conditions of the glow discharge influence the plasma parameters and thus the analytical outcome.

In the present work, Langmuir probe and OES measurements are described, which have been performed on two individual Grimm-type glow discharge (GD) sources (one used in GDMS, the other used in GD-OES), each of them equipped with an anode tube of 8 mm diameter (see Fig. 1(a) and 1(b), respectively). The discharge conditions used in both glow discharge sources were nearly the same, in order to make a reliable comparison between the two experiments possible. The Langmuir probe measurements yielded electron temperatures and densities whereas with OES excitation and ionization temperatures were measured. The results are compared with relevant literature data [19-31]. The temperatures obtained from the Langmuir probe measurements are compared with the spectroscopical data in order to look

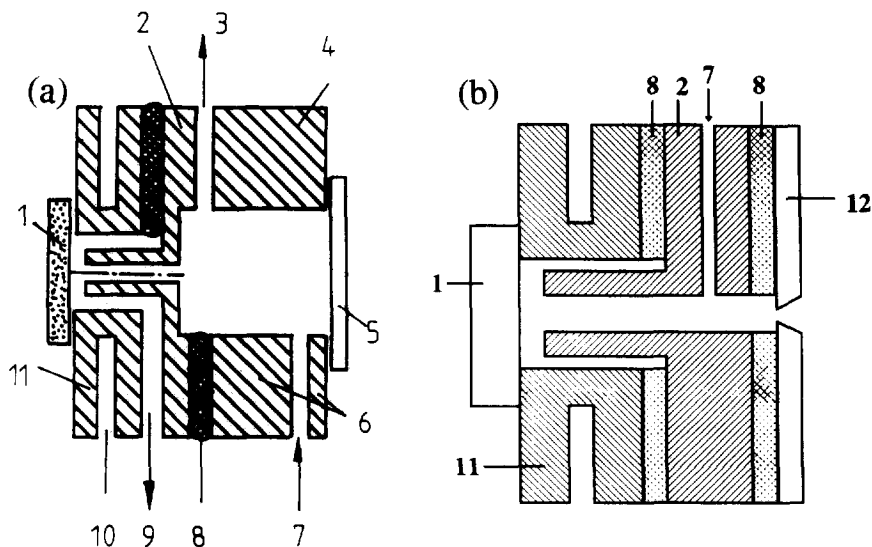


Fig. 1. Schematic view of the Grimm-type glow discharge cell, used for OES (a) and for MS (b): 1, sample; 2, anode tube; 3, pump 1; 4, anode block; 5, quartz window; 6, anode block; 7, gas inlet; 8, Teflon insulation; 9, pump 2; 10, cooling; 11, cathode; 12, exit aperture (to MS).

for the possible existence of LTE. By studying the influence of different gases (Ar and Ne), working conditions (pressure, voltage and current) and cathode materials a better insight into the complexity and diversity of processes in the glow discharge can be acquired.

2. Experimental

2.1. Langmuir probe measurements

The Langmuir probe measurements are the oldest and most widely used of all plasma diagnostic techniques [18]. The technique consists of inserting a small electrode (usually a thin metal wire) into the plasma and applying a voltage to it, with respect to a reference electrode. By changing the voltage at the probe and recording the corresponding current, the current–voltage (I – V) characteristic of the probe is obtained. From this I – V characteristic, the main plasma properties can be deduced. The I – V curve can be divided into three regions (see Fig. 2). (a) When the probe is biased positively with respect to the local plasma potential, the flux of all the negative particles to the probe is collected and current saturation occurs. This region is called the electron saturation region. (b) When the applied potential is lower than the local plasma potential, the probe acts as an energy selector, collecting only those electrons which have energies large enough to overcome the retarding potential. This is the electron retardation region. (c) If the applied potential is further negatively biased, none of the plasma electrons has enough energy to overcome the retarding potential and all the current measured is due to the positive ions. This region is the ion saturation region.

Although the construction of the Langmuir probe and the recording of the I – V characteristic are relatively straightforward, the data analysis for recovering the actual plasma properties is very complex. One has to be very careful that the Langmuir probe does not disturb the plasma, otherwise the real plasma is not observed but only the disturbed region around the probe. A general theory valid for all plasma parameters and probe shapes does not exist. Instead there are different sets of approximate equations, corresponding to different limiting regions of plasma parameters. The most important parameters defining the different regions are the shape of the probe (cylindrical, spherical or plane), the ratio of ion temperature to electron temperature

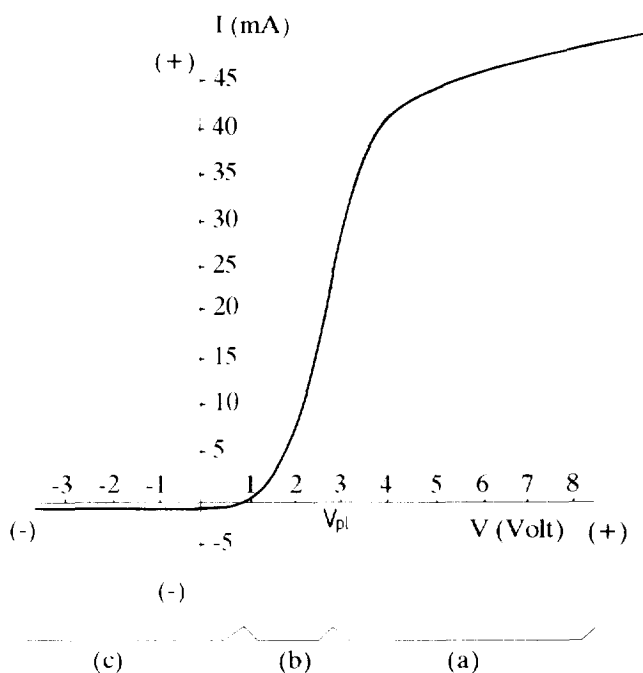


Fig. 2. Typical I – V characteristic of Langmuir probe measurements: (a) electron saturation region; (b) electron retardation region; (c) ion saturation region. V_{pl} , plasma potential.

(T_i/T_e), the energy distribution of the electrons (Maxwellian or not), and the relative values of the probe radius r , the mean free path of the electrons λ , and the Debye length λ_D [19]. In our case, the pressure is low enough for $\lambda \gg r$ to be true (i.e. a collision-free plasma) and we also have $r \gg \lambda_D$ so that we are in the limiting case of a thin plasma sheath. We used a cylindrical probe and assumed that the electrons have a Maxwellian energy distribution and that T_i/T_e is equal to zero. With these assumptions, the plasma properties can be calculated from the I - V characteristic.

As already mentioned, Langmuir probe measurements yield, in theory, electron temperatures, electron and positive ion number densities, the electron energy distribution and the plasma potential. In practice however, we could only calculate electron temperatures and electron densities. The electron temperature is determined based on the assumption that the electron energy distribution in the plasma is Maxwellian

$$I_e = A \exp\left(-\frac{eV_p}{kT}\right) \quad \ln I_e = A' - \frac{eV_p}{kT} \quad (1)$$

The electron temperature is derived from the slope of a semi-log plot ($\ln I_e$ versus V_p , where V_p is the probe potential and I_e is the electron current; it is found after subtracting the saturated ion current from the total current). This method of determination gives two different electron temperatures, belonging to two different electron groups. The electron temperature determined from the slope in region (b) (in the order of 0.4 eV) belongs to the so-called thermalized electrons, whereas the electron temperature found in region (c) (in the order of 4 eV) corresponds to the so-called secondary electrons (electrons which are created in ionizational collisions but are not yet thermalized). The electron number density is determined from the saturated ion current at a well defined potential [19,20]

$$I_i = en_e r l \left(\frac{2\pi k T_e}{m_i}\right)^{0.5} i_i \quad (2)$$

The fitting parameter i_i is first set equal to unity and n_e is calculated from Eq. (2). Next the Debye length (λ_D) is determined from [37]

$$\lambda_D = 740 \sqrt{\frac{T_e}{n_e}} \quad (3)$$

Using the Laframboise curves for the case of a thin plasma sheath, a cylindrical probe and T_i/T_e equal to zero, i_i is derived for the specific values of V_p and r/λ_D . Inserting this i_i again into Eq. (2), the calculation is repeated until convergence is achieved (i.e. typically after three approximations).

The plasma potential can in principle be derived from the intersection of the straight lines in regions (a) and (b) of the semi-log plot ($\ln I_e$ versus V_p). Another approach to determine the plasma potential is the second derivative method. The plasma potential is the potential where d^2I/dV^2 is equal to zero, which is also situated near region (a). However, region (a) of the I - V characteristic could not be used in practice, because the electron saturation current is about two orders of magnitude higher than the ion saturation current; hence the large currents which are drawn to the probe often seriously disturb the plasma, making accurate measurements impossible. Therefore the plasma potential could not accurately be defined. Consequently, the electron energy distribution and the ion number density, which are normally derived from the plasma potential, have not been determined either.

To determine the electron temperatures and density, a single tungsten Langmuir probe with a cylindrical geometry was used. The probe has to be small in order to minimize the plasma perturbation. In our case its length is 0.5 mm and its diameter is 0.1 mm. The tungsten wire is electrically shielded by a ceramic tube of 0.2 mm inner diameter and 0.5 mm outer diameter. The cathode-to-probe distance is held constant at 7 mm, which is the region from where ions are sampled if the glow discharge is used as ion source. The probe is connected to a ± 30 V

dual d.c. power supply. The applied potential is measured between the probe and the anode (used as reference electrode). The voltage over a resistor R of $100\ \Omega$ gives the current drawn to the probe. An x - y recorder yields the I - V curve. The measurements were made for two different gases (Ar and Ne) and two different sample materials (Fe and Cu), at three different pressures and a range of current-voltage values.

2.2. Optical emission spectrometry measurements

OES measurements were performed to define excitation temperatures of different species (Ar and Ne as working gas, and Fe and Ni as cathode material). In addition the ionization temperature of Ar was estimated.

The method for determining the excitation temperatures is based on the assumption that the glow discharge plasma is in LTE, i.e. the populations of atoms, ions or molecules of the species at the different energy levels follow a Boltzmann distribution [38]. The absolute intensity of a spectral line involved in the transition from an upper level q to a lower level p , in the absence of selfabsorption, can be written as

$$I_{qp} = \frac{d}{4\pi} A_{qp} \frac{hc}{\lambda_{qp}} n \frac{g_q \exp\left(-\frac{\epsilon_q}{kT}\right)}{Z} \quad (4)$$

where I_{qp} is the intensity, d is the depth of the source, A_{qp} is the Einstein transition probability, λ_{qp} is the wavelength corresponding to this transition, h is Planck's constant, c is the velocity of light, n is the particle number density, g_q and ϵ_q are the statistical weight and the energy of the upper level respectively, k is Boltzmann's constant, T is the absolute temperature and Z is the partition function. Taking logarithms and rearranging, we have

$$\ln \frac{I_{qp} \lambda_{qp}}{g_q A_{qp}} = \ln \frac{d h c}{4\pi} + \ln \frac{n}{Z} - \frac{\epsilon_q}{kT} \quad (5)$$

When applying Eq. (5) to a group of spectral lines emitted by atoms, ions or molecules of the same species, we see that $\ln(I_{qp} \lambda_{qp} / g_q A_{qp})$ is a linear function of ϵ_q , because $dh/4\pi$ and n/Z are constants, i.e. they have the same values for all the lines involved. Consequently, if $\ln(I_{qp} \lambda_{qp} / g_q A_{qp})$ is plotted against ϵ_q (a so-called Boltzmann plot), a straight line will result, the slope of which yields the excitation temperature.

The ionization temperature can be determined by the following two equations, provided that the plasma is nearly in LTE [22,38]

(a) The Saha-equation

$$\log \frac{\alpha}{1-\alpha} = -\log n_e + \frac{3}{2} \log T - \frac{5040}{T} V_i + \log \frac{Z_i^+}{Z_a} + 21.683 \quad (6)$$

where α is the degree of ionization, n_e is the electron density, T is the ionization temperature, V_i is the ionization potential, and Z_i^+ and Z_a are the partition functions of the ion and the atom, respectively.

(b) The equation for the degree of ionization as a function of the intensity ratio of an atom line and an ion line

$$\log \frac{\alpha}{1-\alpha} = \log \frac{I_{qp}^+}{I_{qp}} - \log \frac{g_q^+ A_{qp}^+ \nu_{qp}^+}{g_q A_{qp} \nu_{qp}} - \frac{5040}{T} (V_q^+ - V_q) + \log \frac{Z_i^+}{Z_a} \quad (7)$$

where I_{qp}^+ and I_{qp} are the intensities of the ion and the atom line, g_q^+ and g_q are the statistical weights of the upper levels of the ion and the atom, A_{qp}^+ and A_{qp} are the transition probabilities

of the ion and the atom line, ν_{qp}^+ and ν_{qp} are the corresponding frequencies, and V_q^+ and V_q are the energies of the upper level of the ion and of the atom.

Combining these equations, one obtains

$$\log n_c = \frac{3}{2} \log T + 21.683 - \frac{5040}{T} (V_i^+ \nu_q^+ + V_q) - \log \frac{I_{qp}^+}{I_{qp}} + \log \frac{g_q^+ A_{qp}^+ \nu_{qp}^+}{g_q A_{qp} \nu_{qp}} \quad (8)$$

Measuring the intensities of the spectral lines of an atom and ion of the same element yields the ionization temperature when the electron density is known (i.e. from Langmuir probe measurements).

To determine the ionization and excitation temperatures, the line intensities of atoms and ions were measured sequentially by means of a monochromator, which was illuminated by the glow discharge source in end-on configuration via optical quartz fibres. Relevant data of the monochromator are: Czerny–Turner mounting, 450 mm focal length of the collimator, holographic grating with 1180 grooves mm^{-1} and with 1 μm blaze wavelength, 1:6 aperture ratio and 1.8 nm mm^{-1} reciprocal linear dispersion at 500 nm. The radiant intensities were recorded by a side-on type photomultiplier tube R928 from Hamamatsu. To correct for the sensitivity of the focusing optics–spectrometer–photomultiplier system, the whole system was calibrated with a 100 W tungsten-halogen lamp of which the spectral irradiance data are certified. The excitation temperatures were measured with either Ar or Ne as working gas using Al as the cathode material. In order to investigate how the erosion rate, and hence the number density of sample atoms, influences the plasma parameters, the excitation temperatures were estimated for different analyte atoms (Fe and Ni) using the corresponding sample materials. The discharge was operated at three different gas pressures and for different voltages. The ionization temperature was determined by measurements of Ar (I) and Ar (II) line intensities. The spectral lines of the different elements used in the investigation are listed in Table 1. The intensities of the spectral lines were integrated over a time interval of 1 s and the mean of ten successive measurements was calculated. It is well known [23] that the slope of the Boltzmann plot and hence the derived excitation temperature is influenced by the selection of spectral lines. Special attention was paid so that the spectral lines corresponded to a rather narrow wavelength range. Furthermore, the accuracy of the results determined by the slope method is limited mainly by the uncertainties of the transition probability data [23–25]. Other factors which have to be considered are discussed in Ref. [23]. The transition probability data for Ar (I), Ar (II) and Ne (I) are taken from Ref. [39], the data for Fe (I) and Ni (I) are taken from Ref. [40].

3. Results and discussion

3.1. Langmuir probe measurements

Fig. 3 shows the electron temperature of the thermalized electron group at three different pressures as a function of cell voltage, for Cu in Ar. At these voltages and pressures, discharge

Table 1

Spectral lines used in this work for plasma diagnostics of analytical glow discharges by optical emission spectroscopy

Element	Spectral lines used/nm
Ar (I)	549.587, 555.87, 560.673, 592.881, 687.129, 693.767, 703.026, 720.699, 727.294, 738.398, 750.387, 751.465, 800.616, 801.479
Ar (II)	378.08, 386.85, 407.201, 413.173, 427.753, 442.601, 457.935, 458.99, 460.96, 465.789, 472.686, 476.486, 480.601, 484.782, 487.99, 496.507, 500.93
Ni (I)	534.109, 540.056, 626.65, 633.443, 638.299, 650.653, 653.288, 659.895, 667.828, 671.704, 692.947, 702.405, 703.241, 705.911, 724.517, 743.89, 748.887, 753.577, 837.761, 849.536
Fe (I)	358.12, 371.994, 372.256, 373.487, 374.556, 374.949, 375.824, 382.043, 385.637
Ni (I)	338.057, 341.477, 342.371, 344.626, 345.847, 346.165, 349.296, 351.034, 351.505, 352.454, 356.637, 361.046, 361.939, 385.83

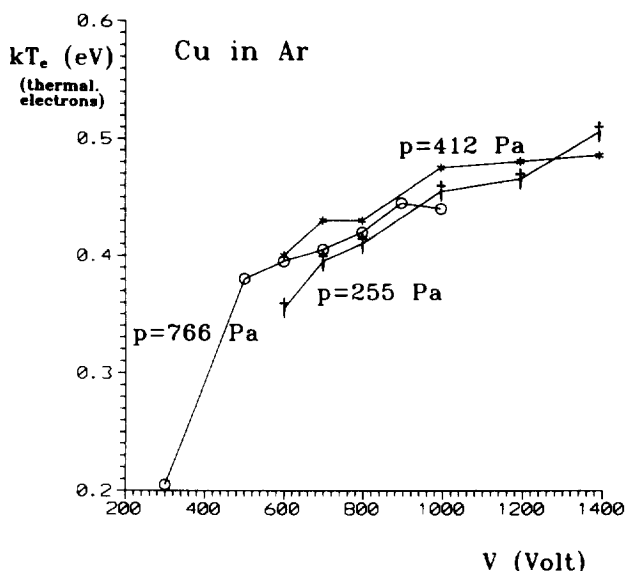


Fig. 3. Electron temperature of the thermalized electron group, as a function of voltage at different pressures, obtained from Langmuir probe measurements (Cu cathode in Ar).

currents ranging from 1 to 50 mA were obtained. The electron temperature varies between 0.2 and 0.6 eV, in agreement with Refs. [19–21]. The electron temperature slightly increases for higher voltages, although the effect is not always very clear. At higher voltages, the electrons are accelerated to higher energies, and the thermalization is then not always complete at the measuring position. The electron temperature does not seem to be much influenced by the pressure. The results were very similar for Fe as sample material and for Ne as discharge gas, when comparable I - V discharge conditions were used. Hence at the same I - V values, the sample material and the discharge gas did not seem to have any influence either.

In Fig. 4 the electron temperature of the secondary electron group is illustrated for Cu in Ar. These secondary electrons are created by ionizational collisions but they have not experienced enough collisions to be thermalized yet. Generally their energy lies between 3.5 and 6.5 eV. We do not see any clear effect of the pressure and the voltage, nor is there any significant difference between the gases and the cathode materials. The observed fluctuations are probably due to the impossibility of accurately evaluating this electron temperature.

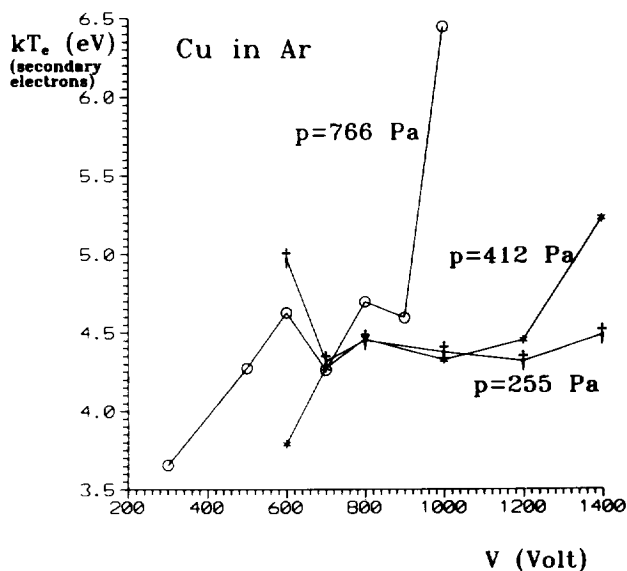


Fig. 4. Electron temperature of the secondary electron group, as a function of voltage at different pressures, obtained from Langmuir probe measurements (Cu cathode in Ar).

The electron density as a function of cell voltage is given in Fig. 5 for Cu in Ar at three different pressures. We did not observe any clear influence of the gas and the cathode material, but the effects of gas pressure and cell voltage seem to be rather large. Higher voltages and higher pressures both yield higher electron densities. The electron density can range from 10^{12} cm^{-3} at low pressures and low voltages to $4 \times 10^{14} \text{ cm}^{-3}$ at high pressures and voltages. These values are higher than the ones found in Refs [20,21], but when taking into account the higher pressures and voltages used here, this difference is understandable. The obtained electron density is also in agreement with results found in the literature for optical emission measurements [26–29]. These values of the electron density will be used to define the ionization temperature with Eq. (8) (see below).

3.2. Optical emission spectrometry measurements

The excitation temperatures were determined by the slope method for the different gaseous and metallic species mentioned above. In the case of Ar (I), Ar (II) and Ne (I) the measurement was performed on samples of pure Al in order to obtain a simple line spectrum of the metallic species and to avoid spectral interferences with the relevant lines of the gaseous components. Moreover, the relatively low erosion rate observed for Al ensured that the discharge plasma was not seriously affected by the variation of the working parameters.

The results obtained for Ar (I) at different gas pressures and discharge voltages are shown in Fig. 6. The temperature values found are in the range from 0.6 to 0.85 eV (i.e. 6900–9800 K) and agree rather well with other data [25,27–30] if the respective discharge conditions are taken into account. The data are somewhat higher but still in the same order of magnitude as the thermalized electron temperature derived from the Langmuir probe measurements. This indicates that partial LTE (PLTE) was established between the thermalized electrons and the neutral Ar atoms, as is expected from the measured electron number density which is in the same order of magnitude as the validity criterion for the PLTE assumption (i.e. 10^{14} cm^{-3} [27]). The increase of the excitation temperature of Ar (I) with increasing voltage and pressure as shown in Fig. 6 indicates that the excitation of neutral Ar atoms is predominantly caused by electron impact processes. Indeed, higher voltages yield electrons with higher energies (cf. Fig. 3) which are more able to cause excitation. Higher pressures result in higher electron number densities (cf. Fig. 5) and consequently more electron impact excitation collisions.

The excitation temperatures obtained for Ne (I) in the discharge plasma are represented in Fig. 7. The values range from 0.5 to 0.9 eV (i.e. 5700–10400 K) and are hence comparable

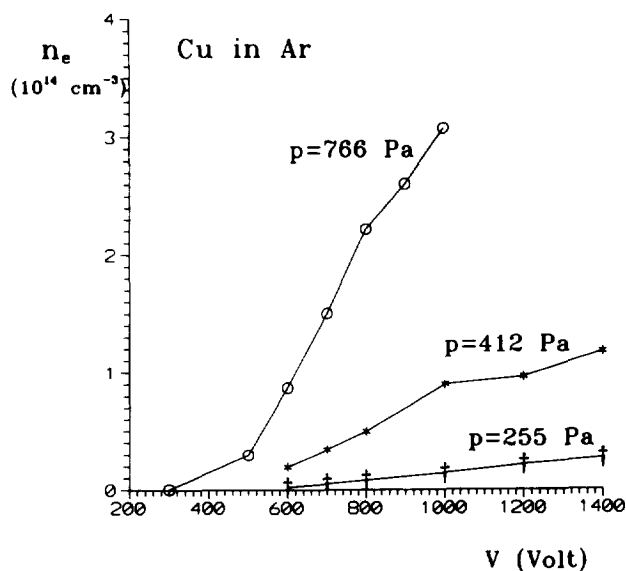


Fig. 5. Electron density, as a function of voltage at different pressures, obtained from Langmuir probe measurements (Cu cathode in Ar).

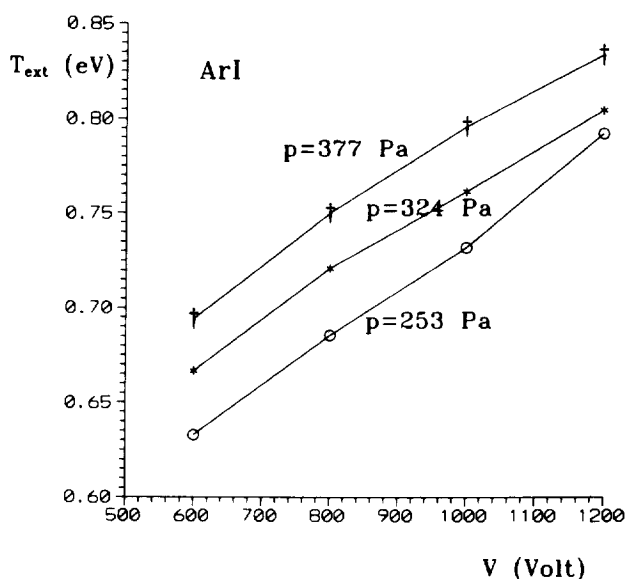


Fig. 6. Excitation temperature of Ar (I), as a function of voltage at different pressures, obtained from OES measurements (Al cathode in Ar).

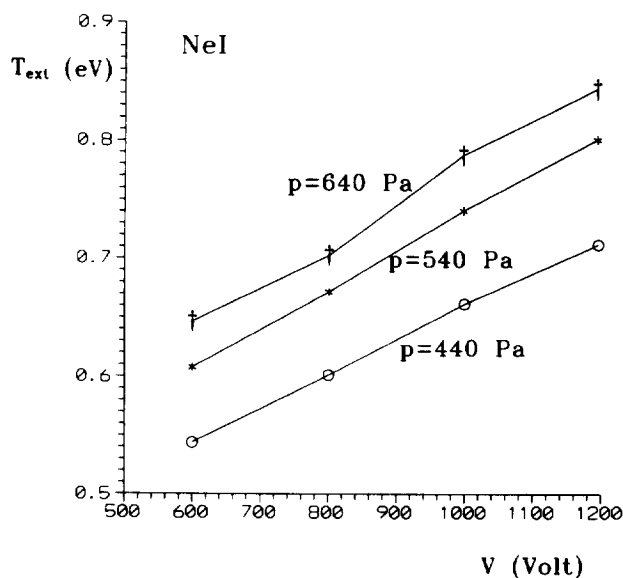


Fig. 7. Excitation temperature of Ne (I), as a function of voltage at different pressures, obtained from OES measurements (Al cathode in Ne).

to the values observed for Ar (I). Moreover, the excitation temperatures of Ne (I) and of Ar (I) follow the same course with increasing voltage and pressure.

The measured excitation temperatures of Ar (II) are about 3.5–4.4 eV (i.e. 40200–50600 K) and do not reflect a marked dependence on gas pressure or voltage. These values are comparable to the data reported in Ref. [27,29,30]. Compared with Ar (I) the excitation temperatures derived for Ar (II) are clearly higher. This indicates the existence of at least two distinguishable electron groups. Generally three groups of electrons are assumed to exist in a glow discharge [14]: (i) a highly energetic primary group that has not undergone many collisions, with energies nearly corresponding to the total discharge voltage; (ii) a group of secondary electrons possibly existing as many sub-groups, having lower energies due to many collisions but not yet thermalized; and finally (iii) a thermalized electron group. The thermalized and one secondary electron group are defined in the Langmuir probe measurements of this work as having an average energy of about 0.5 and 4.5 eV, respectively (cf. Figs. 3 and 4). The first group

(primary electrons) and other secondary electron groups with higher energies could not be observed with the Langmuir probe measurements. The thermalized electron group is assumed to have a Maxwellian distribution that peaks at about 0.5 eV which is much too low for excitation (the excitation energy of Ar (I) is about 12 eV). However electrons in the tail of the Maxwellian distribution with energies exceeding 12 eV can be responsible for the excitation of Ar (I) lines, resulting in nearly equal values of excitation and electron temperatures and hence in an approximated LTE. The energy of this group, however, is not sufficient to ionize and excite argon atoms simultaneously so that the primary or secondary electron groups have to be responsible for the creation of excited argon ions. These electrons have enough energy for excitation at all voltages and pressures, resulting in a higher excitation temperature which is moreover independent of the working conditions.

In order to investigate the influence of working conditions on the excitation of analyte atoms, which is of importance for the analytical application of the glow discharge techniques, the excitation temperatures of Fe (I) and Ni (I) were measured by means of the spectral lines of these elements listed in Table 1. For this purpose metallic samples of pure iron and nickel were used with Ar or Ne as the working gas.

The excitation temperatures of Fe (I) in Ar are shown in Fig. 8. The results in Ne (not shown) are comparable. Compared to Ar (I) and Ne (I) the excitation temperatures derived for Fe (I) are much lower, ranging from 0.26 to 0.3 eV (i.e. 3000–3500 K). The reason for this can be found in the choice of spectral lines. Due to the limited availability of spectral lines free of interferences lying in the suitable wavelength range, we could only use spectral lines for Fe (I) corresponding to a specific group of energy levels, lying close to each other (i.e. from 3.2 to 4.4 eV). The excitation temperature is then probably only related to these energy levels. In Ref. [30], the authors have illustrated that the Boltzmann plot is not always a straight line but can be a more or less exponentially decreasing curve, hence resulting in a steep slope (and thus a low excitation temperature) for the lower energy levels and a less steep slope (a higher excitation temperature) for the higher energy levels. Comparing our results with the literature [23,25,30,31], satisfactory agreement is found if minor differences in the discharge conditions are taken into account. These references all used nearly the same spectral lines belonging to this small group of energy levels. In Ref. [31] values ranging from 3000 to 5000 K are obtained, depending on the spectral lines used. The influence of voltage and pressure on the excitation temperature is rather small and not clear.

The excitation temperatures of Ni (I) in both the argon and the neon discharges are very similar to those derived for Fe (I) and are not explicitly shown here. The corresponding values are between 0.22 and 0.25 eV (i.e. 2500–2900 K) in argon and slightly higher (between 0.24

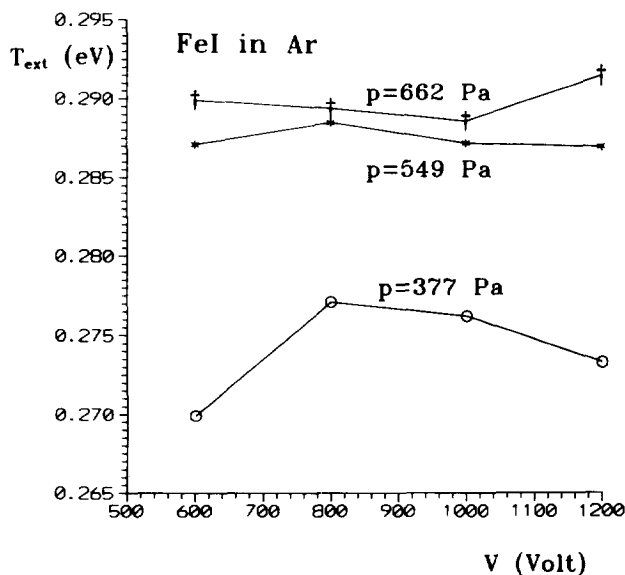


Fig. 8. Excitation temperature of Fe (I), as a function of voltage at different pressures, obtained from OES measurements (Fe cathode in Ar).

and 0.32 eV, i.e. 2800–3700 K) for neon as discharge gas. The agreement with the values obtained for Fe (I) is not surprising because Fe and Ni have nearly the same electronic structure and similar energy levels were used for both elements (ranging from 3 to 4.5 eV); moreover, both solids have approximately the same erosion rate. Also the influence of discharge voltage and gas pressure on the Ni (I) excitation temperatures resembles that of Fe (I). It seems that neither voltage nor pressure have much influence on the obtained excitation temperatures of Fe (I) and Ni (I) because the energy levels lie close to each other and all experience nearly the same influence from pressure and voltage. The fact that voltage and pressure do not have such a clear influence on the excitation temperatures of Fe (I) and Ni (I) can also be attributed to the occurrence of other excitation processes (Penning excitation, charge transfer, etc.), illustrating the complex nature of the glow discharge.

As has already been mentioned above, the ionization temperature can be derived from spectroscopic measurements if the electron density of the plasma is known. The Langmuir probe measurements yielded electron densities in the range from 10^{12} to 4×10^{14} cm^{-3} , depending on the actual discharge conditions (Fig. 5). Using Eq. (8) approximate values of the ionization temperature of Ar were calculated with different combinations of atom–ion spectral line pairs. The estimated data range from 2600 to 6000 K corresponding to the electron density of 10^{12} cm^{-3} and from 3400 to 7900 K corresponding to the higher electron density of 4×10^{14} cm^{-3} . From the large range of values obtained, we conclude that the glow discharge plasma is not really in LTE, otherwise only one ionization temperature would be found, which would also be equal to the measured excitation temperatures. Nevertheless, the calculated excitation and ionization temperatures are in the same order of magnitude.

4. Conclusions

Measurements by Langmuir probe and OES were performed in order to determine the physical plasma parameters which are relevant with respect to the analytical applications of the GD–OES and GDMS techniques. The Langmuir probe measurements gave information about the electron temperatures and electron number density. The electron temperatures were determined for two clearly distinguishable electron groups. The results for the so-called secondary electron group are in the range from 3.5 to 6.5 eV, corresponding to 40000–75000 K. The thermalized electron group yielded values between 0.2 and 0.6 eV, corresponding to 2300–7000 K. The temperature of the thermalized electrons was found to increase with increasing discharge voltage, whereas the gas pressure had no significant influence. The electron densities obtained by the Langmuir probe measurements varied in the range from 10^{12} to 4×10^{14} cm^{-3} , increasing with voltage and pressure. The nature of the gas and cathode material did not seem to have a large effect on the temperatures and density. Although Langmuir probe measurements, as such, are fast and easy to perform, the calculation of the plasma properties is complicated and the results are actually only semi-quantitative. Quantitative information is indeed very difficult to obtain, due to the approximate nature of calculating the plasma properties and due to the possible disturbance of the plasma by the probe. Moreover coating of the probe (tip and ceramic) occurred after a few hours of sputtering; this changed the surface area of the probe necessitating regular replacement of the ceramic sleeve.

OES measurements were performed to obtain excitation temperatures of different gases and analyte atoms in the discharge based on the construction of the corresponding Boltzmann plots. Using Al as a cathode material with low sputtering rate, the excitation temperatures are in the range from 6900 to 9800 K for Ar (I) (argon as discharge gas), and from 5700 to 10400 K for Ne (I) (neon as discharge gas). The observed increase of the excitation temperatures with increasing discharge voltage and pressure indicates that electron impact is the favoured excitation process. The excitation temperatures obtained for Ar (II) are much higher (about 40200–50600 K) than for Ar (I) indicating that the glow discharge plasma is not in complete LTE. Moreover the excitation temperature of Ar (II) is not affected by voltage and pressure variations. The excitation temperatures of Fe (I) and Ni (I) analyte atoms were measured by using the corresponding cathode materials for either argon or neon as discharge gas. The values obtained for Fe (I) and Ni (I) (about 3000 K) are very similar and rather independent of the

discharge parameters. Finally, the ionization temperature of Ar was estimated from spectral lines of Ar (I) and Ar (II). Values ranging from 2600 to 7900 K were obtained. The OES measurements which were carried out are relatively easy to perform, although defining the excitation temperature can be a time-consuming undertaking because a large number of spectral lines have to be measured. Care has to be taken that the spectral lines are not subject to interferences. An important advantage compared to the Langmuir probe measurements is the non-disturbing character of this technique.

Comparison was made between the Langmuir probe and optical emission spectrometry measurements. The two experiments were performed on two individual sources at different positions in the plasma; the Langmuir probe data correspond to a distance of 7 mm from the cathode whereas the OES measurements were performed in end-on configuration which yielded integrated values, predominantly originating at 3 mm from the cathode where the light intensity is the highest. When comparing the two experiments, we have to be aware of these differences.

Comparison of the electron temperatures obtained from the Langmuir probe measurements with the excitation temperatures of the different species and with the ionization temperature of Ar acquired by the OES measurements, can give us information about (non) LTE in the glow discharge. We found that the electron temperature of the thermalized electrons, the excitation temperatures of the different atoms and the ionization temperature of Ar are all in the same order of magnitude (i.e. between 2500 and 10000 K, for the whole range of pressures and voltages). This suggests that the thermalized electrons are nearly in equilibrium with the excited states of atoms and with the degree of ionization of Ar, which we can call a partial LTE (PLTE). However the occurrence of a second and even a third electron group (of which the temperature could not be obtained by Langmuir probe measurements), and the large differences between the excitation temperatures of Ar (I) and Ar (II), indicate that a general LTE in the glow discharge is certainly not reached.

The experimental data presented so far reveal useful information about the fundamental processes in the glow discharge and can be useful for the computer modelling. In order to acquire a more detailed knowledge of the complex excitation and de-excitation mechanisms which are relevant in the analytical glow discharge, further investigations are necessary, in particular side-on measurements in order to achieve a radial and lateral distribution of the actual plasma parameters and laser absorption spectrometry measurements which yield densities of species in different excited states.

Acknowledgements

A. Bogaerts is indebted to the National Science Foundation (NFWO) for financial support. The authors wish to thank M. Schüth-Bregiel and B. Böbersen for their help in carrying out the measurements. A. Bogaerts and R. Gijbels acknowledge financial support from the Federal Services for Scientific, Technical and Cultural Affairs (DWTC/SSTC) of the Prime Minister's Office through IUAP-III (Conv.49).

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