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Argon and copper optical emission spectra in a Grimm glow discharge source: mathematical simulations and comparison with experiment

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The spectral line intensities of 605 argon atom lines and 103 copper atom and ion lines were calculated for a Grimm-type glow discharge source under typical conditions of glow discharge optical emission spectrometry. The calculations were based on the Einstein transition probabilities for radiative decay and on the level populations of excited levels of the argon atoms and copper atoms and ions, which were computed previously in a comprehensive self-consistent modeling network for the behavior of the various species present in a glow discharge (argon atoms and ions, sputtered atoms and ions, in various levels, and electrons). To the authors' knowledge, the optical emission spectra of argon atoms and of copper atoms and ions have been calculated in this explicit way for the first time. The spectra were integrated over the entire cell axis, to simulate end-on observation. Moreover, the spatial dependence of some spectral lines along the cell axis was elucidated. Finally, the effects of voltage and pressure on the calculated spectral line intensities were investigated and comparisons were made with experimental data. The agreement between theory and experiment was satisfactory for argon; for copper there was still some discrepancy, indicating that the model, in spite of its comprehensive nature, still has some shortcomings.

Keywords: *Modeling; glow discharge; optical emission spectrometry; Grimm*

Glow discharges are used in analytical chemistry, mainly as spectroscopic sources for mass spectrometry (GDMS) and optical emission spectrometry (GD-OES).[1,2] In recent years, we have developed a set of models for analytical glow discharges[3–11] in order to obtain a better understanding of the plasma processes, with the final goal of improving the analytical results. Most attention has been paid to glow discharges used as ion sources for mass spectrometry, *e.g.*, the calculation of the degree of ionization, the density profiles and fluxes of sputtered atoms and the corresponding ions,[8,10] the study of the effect of the cell geometry on these quantities[12,13] and the prediction of relative sensitivity factors.[14] Recently, however, the set of models has also been applied to the Grimm source, which is the standard source for GD-OES.[15] Moreover, two additional models have been developed, for describing the behavior of the various excited levels of argon atoms[16] and of sputtered copper atoms and ions.[17] Since the excited levels can decay to lower levels by emission of radiation, these models are of direct interest for GD-OES. In a previous paper,[18] the optical emission spectrum of argon atoms resulting from the modeling calculations was presented for a simple one-dimensional geometry. However, as mentioned above, most GD-OES analyses occur in the Grimm source. Therefore, in this work, the argon atomic spectrum was calculated for the Grimm source under typical GD-OES conditions; in a similar way, the spectrum was computed for copper atoms and ions. To our knowledge, this is the first time that a spectrum has been calculated in such an explicit way, with only the gas pressure and temperature, discharge voltage, cell geometry and cross-sections for the various plasma processes as input values. Moreover, the spatial dependence of some spectral lines of argon atoms and copper atoms and ions are presented, and the influence of discharge conditions (pressure, voltage, current) on the spectral line intensities is considered.

CALCULATION PROCEDURE

A comprehensive three-dimensional modeling network has been developed before,[3–17] consisting of different sub-models for the various species present in an argon dc glow discharge, *i.e.*, electrons, argon gas atoms, argon ions, fast argon atoms created from collisions with fast argon ions, argon atoms in excited levels, sputtered copper atoms and the corresponding ions, also in various excited levels. The behavior of all these species (transport mechanisms, all possible collision processes in the plasma, interaction with the cell walls, *etc.*) is calculated explicitly. Moreover, Poisson's equation is solved to obtain the electric field distribution throughout the discharge. The only input values are gas pressure and temperature, discharge voltage, cell geometry and various cross-section data, transport coefficients, *etc.* Typical results consist of the density profiles, fluxes and energy distributions of the various species throughout the discharge, the macroscopic electrical current, which is the sum of the microscopic fluxes of the charged plasma species (and which is in good correspondence with experimental data), information about the various collision processes in the plasma and about the sputtering at the cathode (erosion rates, crater profiles, *etc.*) and the potential and electric field distribution throughout the discharge, *etc.* In general, reasonable agreement is achieved between the calculated results and experimental values, which indicates that the model presents a realistic picture of the glow discharge.

For the present purpose, the level populations of various excited levels of argon atoms and sputtered copper atoms and copper ions, calculated in previous work,[16,17] were used to compute the optical emission spectrum. Sixty-five argon atom levels, eight copper atom levels and seven copper ion levels were considered in the models. The plasma processes taken into account included electron, fast argon ion, fast and slow argon atom impact excitation, de-excitation and ionization from all levels, radiative decay between the levels, electron–ion radiative recombination and three-body recombination, and also Penning ionization, asymmetric charge transfer, metastable atom–metastable atom collisions and two- and three-body collisions with argon atoms. Some of the levels considered in the model were effective levels, *i.e.*, a group of levels consisting of a number of individual levels. The level populations of the individual levels were calculated from the effective level populations, based on the ratio of the statistical weights.

When multiplying these individual level populations with the Einstein transition probabilities for radiative decay to the lower levels, the intensities of several spectral lines can be calculated. For the argon atoms, 605 transitions were considered (see a recent paper[18] for more details), whereas for the copper atoms and ions 103 spectral line intensities were computed. The Einstein transition probabilities were adopted

from refs. 19 and 20 for the argon atoms and from refs. 21–24 for the copper atoms and ions.

RESULTS AND DISCUSSION

The calculations were performed in a standard Grimm-type glow discharge cell under typical GD-OES conditions. The cell is more or less cylindrically symmetrical; hence the calculations could be performed in two dimensions (axial and radial directions).

Optical emission spectrum

Fig. 1 shows the spectrum of the argon atom lines on a logarithmic scale, calculated by integration over the entire cell axis, to simulate 'end-on' observation. Typical conditions of 800 V discharge voltage and 500 Pa argon gas pressure were assumed, which yielded an electrical current of 28 mA. The latter is calculated by our model as a final result, *i.e.*, as the sum of the microscopic fluxes of the charged plasma species. It corresponds reasonably well with typical experimental currents, which indicates that the model presents a more or less realistic picture of the discharge. Fig. 1 shows that the argon atom spectrum is fairly complex. However, on a linear scale, only some lines between 700 and 1000 nm are visible, which correspond to the 4p–4s transitions (the so-called 'red lines'; see also ref. 18). Apart from the red lines, of which the 811.53 nm line is particularly intense, also some lines between 400 and 450 nm are of reasonable intensity. The latter correspond to the 5p–4s transitions and are called the 'blue lines'. They are responsible for the characteristic blue light of the argon glow discharge. This spectrum agrees reasonably well with experimental spectra found in the literature[25] and it is also very similar to the spectrum calculated before with the one-dimensional model for discharge conditions of 1000 V, 1 Torr and 2 mA. This indicates that the spectrum will not change too drastically with varying discharge conditions and cell geometry, as was expected already from the satisfactory agreement in previous work[18] between our calculated spectrum and experimental spectra under different discharge conditions.

The calculated spectrum of the copper atoms and ions is illustrated in Fig. 2, for the same discharge conditions as in Fig. 1. It should be mentioned that this spectrum is probably not complete, *i.e.*, only those lines are given which correspond to transitions between the levels that are taken into account in our model.[17] For example, the 402.3 and 406.3 nm lines, which are also observed experimentally, are absent in the calculated spectrum, since they originate from the $3d^{10}5d$ levels, which were not included in the earlier model[17] (*i.e.*, only the levels up till $3d^{10}4d$ were incorporated). However, apart from these two lines, most lines which are experimentally encountered are also seen in Fig. 2. It is apparent from Fig. 2 that most copper atomic and ionic lines are situated between 200 and 400 nm, whereas there are only a few lines in the higher wavelength region where the most intense argon atom lines (the red lines) are found. The latter suggests that spectral interferences from argon atom lines on the sputtered (and therefore analytically important) copper lines are only minimal.

Fig. 3 presents a detail of the calculated copper atom and ion spectrum in the region 200–400 nm. The 324.7 and 327.4 nm lines clearly dominate the spectrum, as is also the case in the experimental spectrum. In general, it can be seen from Figs. 2 and 3 that the copper atom lines are more intense than the copper ion lines, which is as expected, because the copper atom level populations are also higher than the corresponding level populations of copper ions. However, the copper ion lines originating from the $3d^94p^3P_2$ level, especially the 224.7 nm line, seem to form an exception to this, because they are even more intense than most copper atom lines. This is in excellent agreement with experiment: it was demonstrated by Steers and Fielding[26] that this level is selectively excited by asymmetric charge transfer with argon ions, and that spectral lines originating from this level are, therefore, selectively enhanced.

Spatial dependences of some spectral lines

The above spectra are the result of integrating along the axial direction at the cell axis. Information about the axial dependence of some selected spectral lines is given in Fig. 4 (for the argon atom lines) and Fig. 5 (for the copper atom and ion lines), for 800 V, 500 Pa and 28 mA. It is seen in Fig. 4 that the argon atom lines corresponding to 4p–4s transitions are characterized by two peaks, one adjacent to the cathode (corresponding to the cathode glow) and a second one at about 0.1 cm from the cathode (which is in the beginning of the negative glow). The first peak is due to fast argon ion and atom impact excitation, whereas the second peak is attributed to electron impact excitation. For the 811.53 nm line, the first

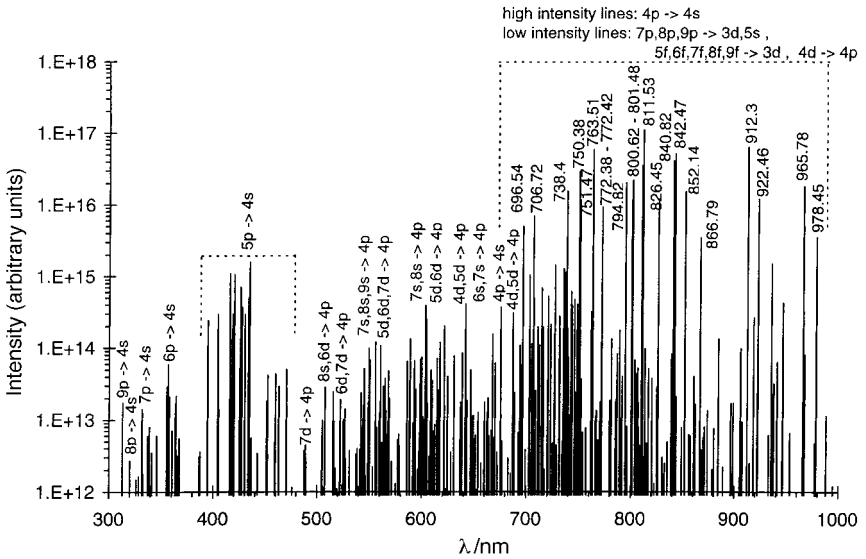

Fig. 1 Calculated spectrum of the argon atom lines in a Grimm-type glow discharge cell, integrated over the entire cell axis, to simulate end-on observation (at 800 V, 500 Pa, 28 mA).

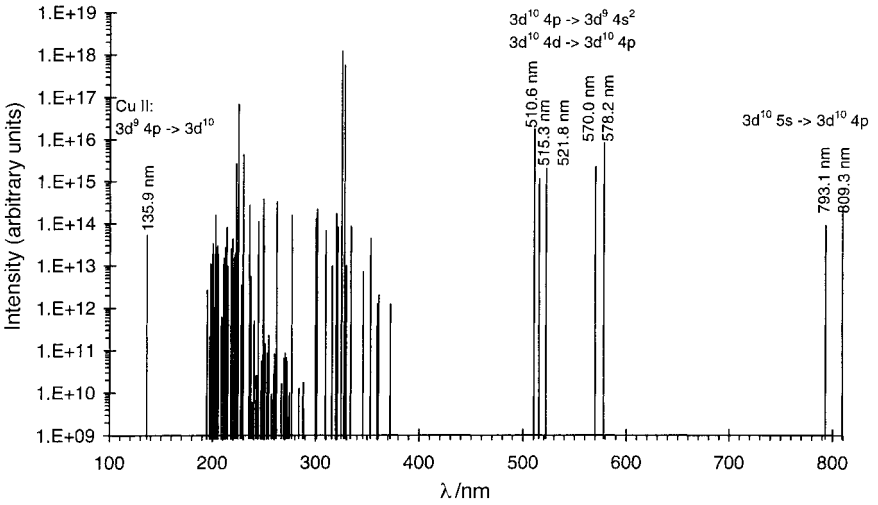

Fig. 2 Calculated spectrum of the copper atom and ion lines in a Grimm-type glow discharge cell, integrated over the entire cell axis, to simulate end-on observation (at 800 V, 500 Pa, 28 mA).

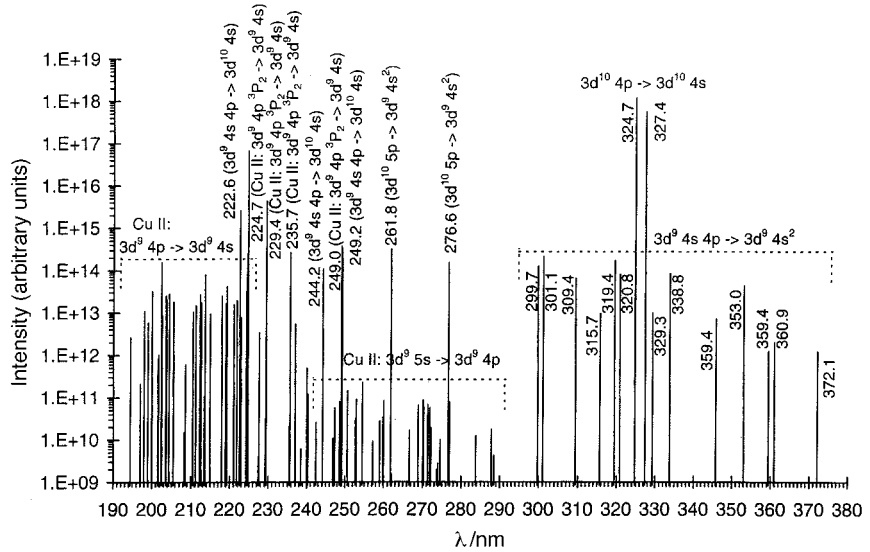

Fig. 3 Calculated spectrum of the copper atom and ion lines in a Grimm-type glow discharge cell, integrated over the entire cell axis, to simulate end-on observation (at 800 V, 500 Pa, 28 mA): detail of the 200–400 nm range.

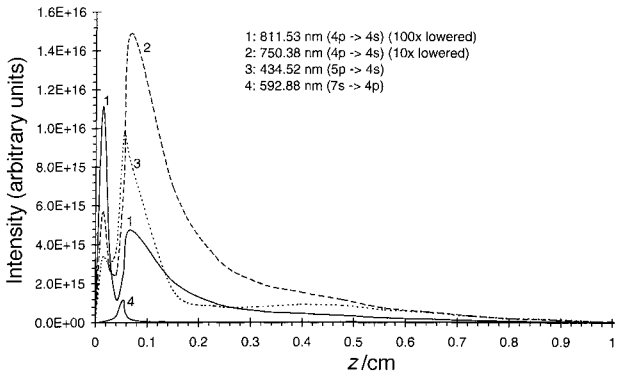

Fig. 4 Calculated spectral line intensities of some argon atom lines in a Grimm-type glow discharge cell at the cell axis, as a function of distance from the cathode (at 800 V, 500 Pa, 28 mA).

peak seems to be clearly dominant over the second peak, whereas the reverse is true for the 750.38 nm line. This is in excellent agreement with the experimental spatial dependences presented by Rozsa *et al.*[27] Argon ion and atom impact excitation are only important for the low levels, because the high levels require too much excitation energy, and the 811.53 nm line corresponds to a low 4p level, whereas the 750.38 nm line originates from a high 4p level. This explains also why the lines coming from higher argon atom levels do not (or almost not) exhibit a peak near the cathode, but show only a peak in the beginning of the negative glow. More information about the spatial dependence of the argon atom lines is given elsewhere.[18]

The copper atom lines also have their highest intensity at about 0.1 cm from the cathode, as shown in Fig. 5 for the 324.7 and 327.4 nm lines. This profile is characteristic for all copper atom lines, and is the result of the sputtered copper atom density profile which peaks also at about 0.1 cm from the cathode.[15] The copper ion lines, on the other hand, show a broader maximum between 0.1 and 0.2 cm from the cathode, as illustrated in Fig. 5 for the 224.7 nm line. This profile corresponds again to the copper ion density profile[15] and is characteristic for all copper ion spectral lines. It follows from Figs. 4 and 5 that the intensities of argon atom, copper atom and copper ion lines are only significant in the first 1 cm from the cathode. Hence, although the Grimm source is typically

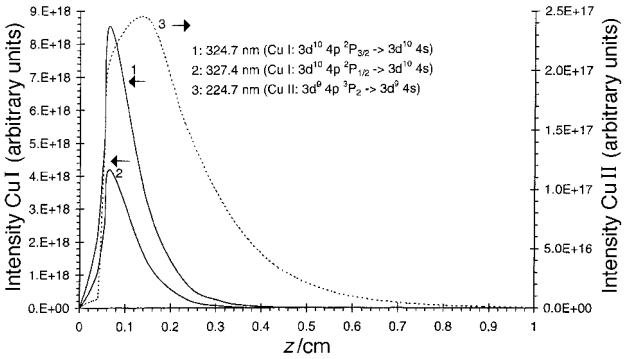

Fig. 5 Calculated spectral line intensities of some copper atom and ion lines in a Grimm-type glow discharge cell at the cell axis, as a function of distance from the cathode (at 800 V, 500 Pa, 28 mA).

several centimeters long (in the model, a total cell length of about 8 cm was assumed), the majority of the end-on measured (integrated) intensity comes from the first 1 cm.

Influence of discharge conditions

We also investigated the effect of discharge conditions (voltage, pressure, current) on the calculated spectral line intensities. Figs. 6(a)–(c) present the spectral line intensities as a function of voltage at three pressures, for three representative argon atom lines, *i.e.*, the 750.39 nm line originating from a 4p level (a), the 427.22 nm line coming from a 5p level (b) and the 592.88 nm line which corresponds to one of the higher levels (*i.e.*, a 7s level) (c). All three lines become more intense with increase in voltage and pressure. These calculated line intensity variations (solid lines, left axis) were compared with experimental data, which are also shown (dashed lines, right axis).[28] The effect of the pressure cannot exactly be compared, because the measurements were performed in an argon discharge with an aluminum cathode, which operates in a different pressure regime. However, the same trend of increasing intensity with increase in pressure is observed. The effect of the voltage, on the other hand, can be compared more directly, and appears to be excellent for the 427.22 nm line and also for the 592.88 nm line, but it is less satisfactory for the 750.39 nm line. This behavior is representative for all other argon atom lines, *i.e.*, the agreement between the calculated and experimental voltage dependences is almost perfect for all lines, except for the 4p–4s lines, which rise too much with increasing voltage. This indicates that our model describing the behavior of the various excited argon atom levels has some shortcomings for the low 4p levels, but it gives a fairly good prediction for the higher levels. The reason for the disagreement for the 4p levels is probably due to some weakness in the description of fast argon ion and atom impact excitation. These processes become, in general, more important at higher voltages, which yield higher ion and atom energies, and it has been demonstrated in several papers that they can have a significant contribution.[27,29,30] Nevertheless, the too rapid increase with voltage indicates that the contribution of these processes is probably overestimated, which is not unreasonable since the cross-sections are subject to large uncertainties. For the higher levels, these fast argon ion and atom impact processes are of only minor importance or completely negligible, which explains why these levels are better described by the model.

The absolute values of the calculated spectral line intensities cannot directly be checked with the experimental values, because the model calculates emission intensities as the number of photons emitted per second, whereas the experimental intensities are the result of instrumental sensitivities also. However, the variation of relative intensities among the various

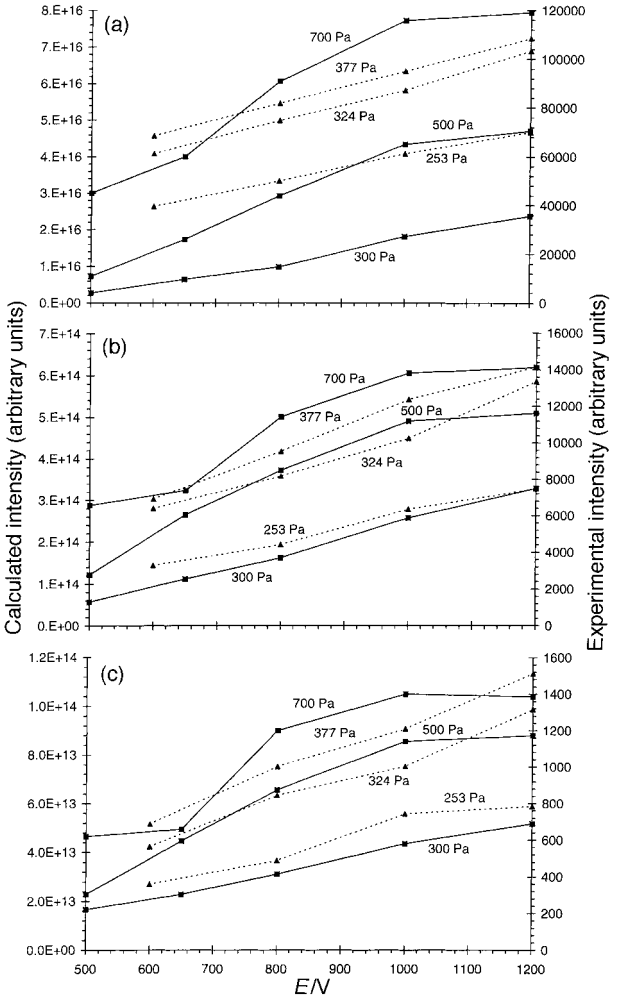

Fig. 6 Calculated spectral line intensities of some argon atom lines in a Grimm-type glow discharge cell, integrated over the entire cell axis, as a function of voltage for three pressures (solid lines, left axis), and comparison with experimental data[28] (dashed lines, right axis). (a) $\lambda = 750.39$ nm (originating from a 4p level); (b) $\lambda = 427.22$ nm (originating from a 5p level); and (c) $\lambda = 592.88$ nm (originating from a 7s level).

spectral lines can be checked. Looking at the absolute values of the left and right ordinate axes in Figs. 6(a)–(c) illustrates that the relative intensities of the argon atom spectral lines are more or less correctly predicted. The 750.39 nm line, originating from a 4p level, is clearly higher, both experimentally and as a result of the calculations, than the 427.22 nm line coming from a 5p level, and the latter is again clearly higher than the 592.88 nm line originating from a high (7s) level. Exact correspondence is, however, not yet reached, *e.g.*, the 750.39 nm line intensity is higher in the calculations than in the experiment. This may be attributed to some incorrect description of the levels in the model, *e.g.*, uncertainties in cross-sections, the populations of the 4p levels may be overestimated owing to fast argon ion and atom impact excitation. However, looking at the other lines investigated, it was found that all lines lying in the high wavelength range were lower in the experiment, also those originating from high levels which are not populated by ion and atom impact excitation (*e.g.*, the 720.7 nm line, coming from a 6s level). This suggests that the slight discrepancy is probably also due to variations in the spectral sensitivity of the measured lines over the entire wavelength range. Nevertheless, the relative intensities of the various lines are in qualitative agreement (*i.e.*, high intensity in the model corresponds to high intensity in the experiment), and this was also

true for all other argon atom lines investigated, which are not presented here.

The effect of voltage and pressure on the copper atom line intensities is presented in Fig. 7(a)–(d) for four characteristic lines. The modeling results are again given by the solid lines (left axis), whereas the experimental data are represented by the dashed lines (right axis).[28] It should be mentioned that no copper ion lines are shown, because the spectral line intensities were found to vary in the same manner with voltage and pressure as the copper atom lines, and we have no experimental data available, because the spectral line intensities in the region which is generally measured (> 300 nm) are low and are difficult to distinguish from copper atom lines.

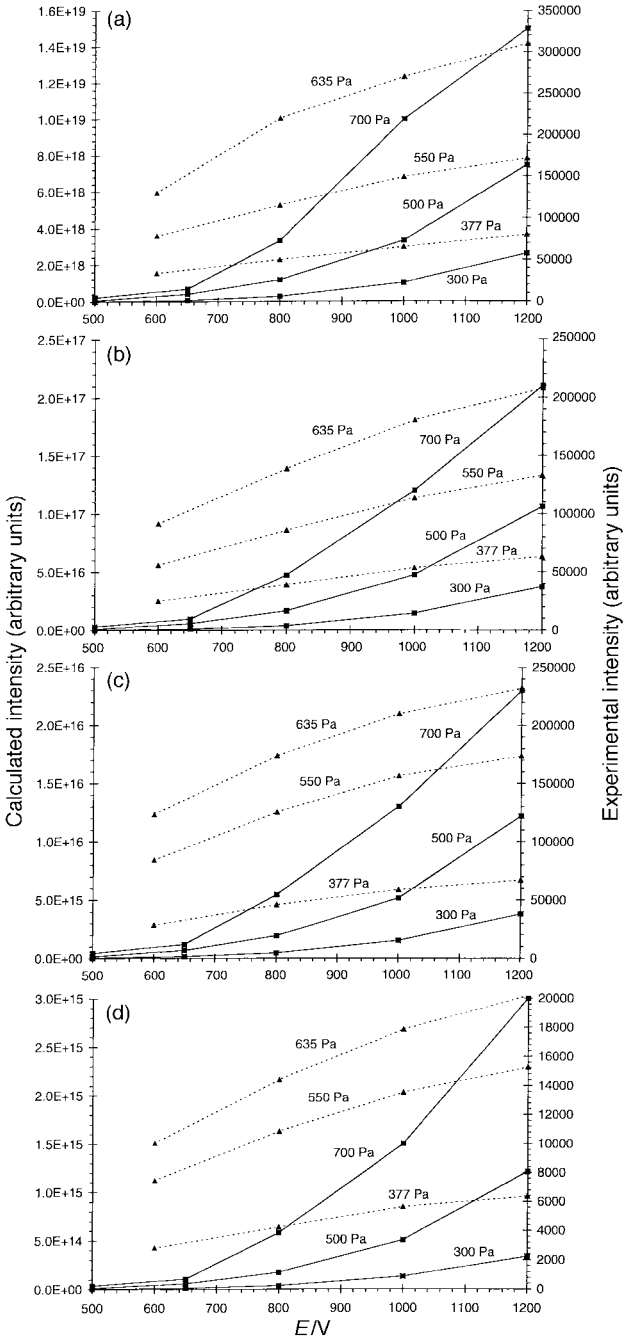

Fig. 7 Calculated spectral line intensities of some copper atom lines in a Grimm-type glow discharge cell, integrated over the entire cell axis, as a function of voltage for three pressures (solid lines, left axis), and comparison with experimental data[28] (dashed lines, right axis). (a) $\lambda = 324.7$ nm (decay from a 4p level to the ground state); (b) $\lambda = 510.55$ nm (originating from a 4p level); (c) $\lambda = 521.82$ nm (originating from a 4d level); and (d) $\lambda = 809.26$ nm (originating from a 5s level).

It is observed that in the case of the copper atom lines, the pressures are more or less comparable, because both the modeling calculations and the experiments were carried out for a discharge with copper cathode. The pressure effect is in good qualitative agreement, but this is not true for the voltage effect. Indeed, the model predicts a too rapid increase of the line intensities with voltage. Since excitation of the copper atoms is primarily due to electron impact excitation, and since the latter is comparable to electron impact excitation of the argon atoms, which seems to be correctly described by the model (see above), we would have expected excitation of the copper atoms also to be correctly predicted. Therefore, this suggests that the sputtering is not correctly calculated. In a previous paper[15] we presented the calculated etching rates (both as depth per unit time and as mass per unit time), and the absolute values were found to be in good agreement with experimental values found in the literature. However, this is no guarantee of the correct prediction of the voltage effect. Therefore, it would be of great interest to check whether the calculated sputtering rate rises correctly with voltage or not. On the other hand, the cross-sections for electron impact excitation of copper atoms are not as well known as for argon atoms. In most cases, they were the result of quantum mechanical calculations up to electron energies of 20 eV,[31] and we had to extrapolate the cross-section curves to values as high as about 1000 eV. Hence the variation of these cross-sections as a function of electron energy is subject to large uncertainties, and this may also explain the incorrect prediction of the voltage effect.

Looking again at the absolute values of the left and right ordinate axes, it seems that the relative intensities of the various copper atom lines are not completely correctly predicted by the model either. The 324.7 nm line is extremely intense in the model: for example, it is a factor 60 higher than the 510.55 nm line, whereas the experimental intensities differ by a factor of only 1.5. Both lines originate from a $3d^{10}4p$ level; therefore, the reason for this discrepancy must be sought elsewhere than in an incorrect description of the upper level. It is well known that the 324.7 nm line, which decays to the copper atom ground state, is subject to self-absorption. This is accounted for in the model by the means of escape factors, *i.e.*, a substantial fraction of the emitted radiation is again reabsorbed by the lower level, so that only a small fraction of the photons can escape.[17] However, it appears that the effect of self-absorption is still underestimated in the model. Comparing the other three lines presented in Fig. 7(b)–(d), it follows that the 510.55 nm line was calculated to be a factor of 10 higher in the model than the 521.82 nm line, although the measured line intensities were of comparable magnitude. Since both lines lie close to each other, this cannot be attributed to variations in spectral sensitivity. On the other hand, the 521.82 and 809.26 nm lines show fairly good agreement between model and experiment, *i.e.*, the 521.82 nm line is a factor of about 10 higher than the 809.26 nm line, both theoretically and experimentally. This suggests that the model either overestimates the population of the $3d^{10}4p$ level or underestimates the population of the higher levels ($3d^{10}5s$ and $3d^{10}4d$). It is true that the model describing the copper excited levels takes into account only a limited number of levels, and that maybe the effects of higher levels cannot be neglected. Moreover, as mentioned above, the cross-sections for copper excited levels were very difficult to find in the literature, and they may be subject to large uncertainties. Hence it is not unexpected that there is still some disagreement with the experimental data. After all, the model calculates everything (*i.e.*, level populations, spectral line intensities, *etc.*) starting only from gas pressure and temperature, discharge voltage and cell geometry as input values, with the use of transition probabilities, cross-sections,

etc., which are all subject to considerable uncertainties. Therefore, we find the present agreement satisfactory.

Finally, comparing the intensities of argon and copper atom lines [Figs. 6(a)–(c) and 7(a)–(d)], we can see that the model has in general calculated lower intensities for the argon lines than for the copper lines, and this is also observed experimentally. This is unexpected, since the sputtered copper atom ground state density is lower than the argon atom ground state density.[15] However, the excited atom levels of both copper and argon were calculated to be of comparable magnitude[16,17] and, moreover, the Einstein transition probabilities for copper lines were found to be generally higher than those for argon lines.[19–22] For some lines, the agreement between experiment and theory is fairly good, *e.g*., the argon 592.88 nm line is calculated to be about a factor of 25 lower than the copper 809.26 nm line and the experimental intensities differ by a factor of 13; also, the difference in intensity of the argon 750.39 nm and the copper 510.55 nm lines is comparable in both the model (*i.e*., a factor of 3) and the experiment (*i.e*., a factor of 2). Some other lines show a larger discrepancy but, in general, the correct qualitative trend is observed for all lines, and also for the other lines which were investigated but which are not presented here.

CONCLUSION

The level populations of excited argon atom and copper atom and ion levels, calculated in two previous papers,[16,17] were used to calculate the optical emission spectra of both argon and copper in a Grimm-type glow discharge under typical GD-OES conditions. The argon spectrum shows the most dominant peaks in the 700–1000 nm region (*i.e*., the red lines), whereas the copper spectrum has the main peaks in the lower wavelength region between 200 and 400 nm. This is in qualitative agreement with experiment. The spatial dependence of some argon and copper lines was investigated, and it was found that the argon and copper atom lines show a maximum at about 0.1 cm from the cathode (*i.e*., in the beginning of the negative glow), although the argon lines originating from low 4p levels also exhibit a peak adjacent to the cathode, attributed to fast argon ion and atom impact excitation. The copper ion lines are characterized by a broader maximum between 0.1 and 0.2 cm from the cathode. In general, the spectral intensities of all the lines investigated become negligible after about 1 cm from the cathode. Finally, the effect of pressure and voltage on the calculated intensities of argon and copper lines was studied and compared with experiment. For the argon lines, the agreement was satisfactory, regarding both the effect of voltage and pressure and the relative intensity variations among the different lines. For the copper lines, a larger discrepancy was observed, which shows that our model is not yet able to give a complete description of the reality. This is not completely unexpected, however, in view of the uncertainties in some input data (*e.g*., variation of the cross-sections as a function of electron energy) and the limited number of excited copper levels incorporated in the model. Nevertheless, when one takes into account that the model calculates all quantities using only the gas pressure and temperature, discharge voltage and cell geometry as input values, and that for the first time a spectrum has been calculated in this explicit way, the present calculation results are considered satisfactory.

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