Application of argon collisional-radiative model for inductive RF discharge research

Azamat R Gizzatullin\textsuperscript{1,2}, Y O Zhelonkin\textsuperscript{1,3}, E F Voznesencky\textsuperscript{3}, Azat R Gizzatullin\textsuperscript{1,2}

\textsuperscript{1} PVS LLC, 82, Tukaya street, Kazan, 420022, Russia
\textsuperscript{2} Bauman Moscow State Technical University, 5/1, Baumanskaya 2-ya, Moscow, 105005, Russia
\textsuperscript{3} Kazan National Research Technological University, 68, Karla Marksa street, Kazan, 420015, Russia

E-mail: zhelonkin.ya@gmail.com

Abstract. The technique of optical emission spectroscopy (OES) in combination with plasma emission models for determining the parameters of a gas discharge is presented. Measurements of charge carrier concentration and electron temperature in an inductively coupled RF plasma of argon are carried out under low pressure. The concentration and temperature of electrons were determined by selecting the ratio of the intensities of the spectral lines calculated with the collision-radiative model (CRM) to the intensities of the lines obtained in the experiment. The model describes the kinetics of the first 30 excited states of argon and takes into account the following processes: direct electron impact excitation / relaxation, spontaneous emission, radiation trapping, electron impact ionization and charge loss due to diffusion on the walls. The obtained OES results were compared with the results of Langmuir probe measurements of plasma parameters.

1. Introduction

Optical emission spectroscopy (OES) and the relative intensity method are widely used to diagnose low-temperature plasma [1-6], providing a contactless and accurate definition of the main parameters of a gas discharge, such as electron temperature and density. Each line of the discharge spectrum corresponds to an optical transition between two quantum levels of an atom / molecule, and the concentration of gas particles in the excited state determines the intensity of the spectral line. In turn, concentration is a function of electron temperature and density (pressure). Having determined the concentrations of particles in different states, one can calculate the dependence of the different ratios of the intensities of the spectral lines on the electron temperature and concentration and compare these parameters with the experiment.

The model should take into account two main processes in the case of low-temperature plasma: electron impact excitation and optical transition with radiation. In general, such models are called collisional-radiative, and the simplest of them is called the corona model, which takes into account
only the excitation and optical transition from the one level [7]. For argon plasma, there are metastable states that play an important role in kinetics; therefore, the corona model is unacceptable in most cases. An overview of the use of collisional radiation models (CRM) for determining plasma parameters can be found in [4].

The purpose of this work is to study the parameters of an inductive plasma discharge using an argon CRM model. The plasma emission spectra were measured in a laboratory setup, and the temperatures and densities of electrons were determined. The characteristics of the discharge were compared with the results obtained using the Langmuir probe.

2. Experiment
An experimental vacuum setup is shown in Figure 1. An inductive discharge is ignited in a quartz flask with a diameter of 154 mm and a height of 236 mm using a flat geometry inductor, which is supplied with RF power (13.56 MHz) from the AE Cesar 1330 generator with automatic matching device (MD) AE VarioMatch 5000. Pumping means (VP) - a vacuum unit AVR-150, consisting of an AVZ-20D forvacuum pump and a booster pump DVN-150. Vacuum measurement - capacitance sensor MKS 627B. The flow of working gas (GS), argon, is carried out through the mass flow regulator RRG-10-360. The range of operating pressures in the experiment is 1–20 Pa.

We use in studies the Ocean Optics USB4000-VIS-NIR (SM) spectrometer with Plasus PL-25-12-00 (CO) collimator optics, the spectral range of measurements is 345 - 1041 nm with a resolution of 1.5 nm. Probe measurements are carried out using a Langmuir probe (LP) with cylindrical tips made of tungsten 23.4 mm long and 0.5 mm in diameter, the distance between the tips is 3 mm. The probe has a filter against RF interference.

![Figure 1. Experimental setup](image)

3. Argon CRM
The CRM model proposed in [8], which takes into account the recombination of electrons on the walls of the vacuum chamber [3], was implemented. CRM describes a homogeneous plasma, and spatial non-uniformity is taken into account by introducing the characteristic plasma dimensions, which determine self-absorption and diffusion. The model considers stationary low-temperature and low-density argon plasma and describes the kinetics of the ground state and the first 30 excited states of the Ar atom. Figure 2 shows all the states and transitions considered in the model under consideration.

The CRM model proposed in [8], which takes into account the recombination of electrons on the walls of the vacuum chamber [3], was implemented. CRM describes a homogeneous plasma, and spatial non-uniformity is taken into account by introducing the characteristic plasma dimension, which determine self-absorption and diffusion. The model considers stationary low-temperature and low-density argon plasma and describes the kinetics of the ground state and the first 30 excited states of the Ar atom. Figure 2 shows all the states and transitions considered in the model.
Table 1. Explanations and references to the processes included in the model

| Process                      | Variable | Dependence | Reference |
|------------------------------|----------|------------|-----------|
| Diffusion                    | $\tau$   | $T_g, p$   | [3,9]     |
| Heavy particle ionization    | $\alpha$ | $T_g$      | [3,10,11] |
| Electron impact (de-)ioniztion | $Q$      | $T_e, EEDF$ | [12,13,14] |
| Spontaneous emission         | $Q_{ion}$| $T_e, EEDF$ | [15]      |
| Radiation trapping           | $A$      | -          | [16,17]   |

Energy balance equations are compiled for each energy level and include the processes listed above. Some of the processes play a large role on ones levels, others on others. Without giving any explanations, let us give an example of a balance equation for metastable levels of 4s states:

$$Q_{gs\rightarrow 4s} n_e n_{gs} + \sum_k Q_{k\rightarrow 4s} n_en_k = [(Q_{4s\rightarrow gs} + \sum_k Q_{4s\rightarrow k} + Q_{4s\rightarrow ion}) n_e + \sum_l=4s_1 \alpha_{4s, l} n_l (1 + \delta_{4s, l}) + + \tau^{-1}_{4s}] n_{4s}$$

(1)

where $k$ denotes all other excited states, the Kronecker delta covers the case when two resonant atoms of the same kind collides.

Metastable states are especially important for plasma, because spontaneous emission is forbidden for them, this leads to a long lifetime of these particles. As a result, various collisional mechanisms play an important role in the de-excitation rate.

4. Determination of the plasma parameters

In the numerical calculation of plasma parameters, the method of minimizing the error function was used, which was proposed [6] and is widely used in [8, 21, 22]. It is distinguished by a higher accuracy
and a wide range of applicability for pressure, in contrast to the “cross-point” method proposed by Jordanova et al. [3].

Having calculated the population of the excited states $n_e$, we can estimate the intensity of the spectral line corresponding to the optical transition $i \rightarrow j$, as follows

$$I_{ij}^{CRM} = C \frac{hc}{\lambda_{ij}} n_{ij} A_{ij} \eta_{ij}$$

(2)

where the coefficient $C$ is the same for all lines, the indices pass through all the values corresponding to the spectral lines in the considered wavelength range.

The error function $\Delta$, that describes the difference between the relative theoretical and experimental spectra, can be introduced as follows:

$$\Delta = \sqrt{\sum_{ij} (I_{ij}^{CRM} - I_{ij}^{EXP})^2}$$

(3)

where the summation is performed on the selected 20 spectral lines in the range of 660–930 nm belonging to the 2p → 1s series with an Einstein coefficient greater than $10^6$ s$^{-1}$. For the given experimental spectrum, $\Delta$ is a function of $T_e$, $n_e$. Minimization of the $\Delta$ function gives the values of the $T_e$, $n_e$ variables. It can also give an argon density in the chamber at the outlet, if it is not taken as the initial parameters, however, this significantly increases the calculation time and sometimes leads to singularity.

5. Results

The results of the calculation of the CRM system of equations and the subsequent minimization of the error function performed by the Maple code are presented in Fig. 3. In this figure, black (CRM) denotes intensity values whose correspond to the minimum deviation from the experimental intensities for given $n_e$ and $T_e$. This pair of $n_e$ and $T_e$ is considered as the output value of the calculation. Their values under various experimental conditions are listed in Table 2.

Figure 3. Normalized experimental and calculated spectra at $P = 1$ Pa, $W = 120$ W
Table 2. Results of plasma parameters calculation using CRM and measurements obtained from the Langmuir probe (R is the distance from the axis of the quartz bulb)

| Pressure (Pa) | R (cm) | $T_e^{\text{OES}}$ (eV) | $T_e^{\text{probe}}$ (eV) | $n_e^{\text{OES}}$ ($\text{m}^{-3}$) | $n_e^{\text{probe}}$ ($\text{m}^{-3}$) |
|--------------|--------|-------------------------|---------------------------|---------------------------------|---------------------------------|
| 1            | 0      | 4.1                     | 3.9                       | $3 \cdot 10^{15}$               | $2.1 \cdot 10^{15}$             |
| 1            | 5      | 3.9                     | 3.9                       | $1.6 \cdot 10^{15}$             | $1.1 \cdot 10^{15}$             |
| 5            | 0      | 4.0                     | 4.0                       | $5.2 \cdot 10^{15}$             | $4.1 \cdot 10^{15}$             |
| 5            | 5      | 3.8                     | 3.9                       | $2.8 \cdot 10^{15}$             | $2.3 \cdot 10^{15}$             |
| 20           | 0      | 3.7                     | 3.8                       | $6.0 \cdot 10^{16}$             | $5.7 \cdot 10^{16}$             |
| 20           | 5      | 3.7                     | 3.8                       | $3.5 \cdot 10^{16}$             | $2.1 \cdot 10^{16}$             |

6. Conclusion

The method of determining the temperature and density of electrons in a plasma based on minimizing the difference between the relative intensities of the spectral lines of Ar, given by experiment and calculated by CRM, implemented on the example of an ICP discharge with a flat inductor, allows one to obtain numerical values of the main parameters of various types of gas discharge. The technique is convenient because there is no need for manual processing of both input and output data, but it requires writing a complex calculation code and large computational powers. Comparison of OES plasma parameters with the results of double probe diagnostics showed that the electron concentration determined by the optical method is, on average, lower by 24% than the density determined by the probe. Both methods give similar values of electron temperature with a maximum error not exceeding 10%.

References

[1] Boffard J B, Lin C C, DeJoseph C A 2004 Application of excitation cross sections to optical plasma diagnostics J. Phys. D 37 R143–R161
[2] Donelly V M 2004 Plasma electron temperatures and electron energy distributions measured by trace rare gases optical emission spectroscopy, J. Phys. D 37 R217–R236
[3] Iordanova S and Koleva I 2007 Optical emission spectroscopy diagnostics of inductively-driven plasmas in argon gas at low pressures Spectrochim. Acta B 62 344–56
[4] Zhu X-M and Pu Y-K 2010 Optical emission spectroscopy in low-temperature plasmas containing argon and nitrogen: determination of the electron temperature and density by the line-ratio method J. Phys. D: Appl. Phys. 43 403001
[5] Boffard J B, Jung R O, Lin C C and Wendt A E 2010 Optical emission measurements of electron energy distributions in low-pressure argon inductively coupled plasmas Plasma Sources Sci. Technol. 19 065001
[6] Zhu X-M, Pu Y-K, Celik Y, Siepa S, Schungel E, Luggenh¨olscher D and Czarnetzki U 2012, Possibilities of determining non-Maxwellian EEDFs from the OES line-ratios in low-pressure capacitive and inductive plasmas containing argon and krypton, Plasma Sources Sci. Technol. 21 024003
[7] Huddlestone R H and Leonard S L 1965 Plasma Diagnostic Techniques (New York: Academic Press)
[8] Siepa S L 2017 Global Collisional-Radiative Model for Optical Emission Spectroscopy of Argon and Argon-Containing Plasmas Dissertation for a doctorate degree (Ruhr-Universität Bochum)
[9] Crintea D L, Czarnetzki U, Iordanova S, Koleva I and Luggenh’olscher D 2009 Plasma diagnostics by optical emission spectroscopy on argon and comparison with Thomson scattering J. Phys. D: Appl. Phys. 42 045208
[10] Ferreira C M, Loureiro J and Ricard A 1985 Populations in the metastable and the resonance levels of argon and stepwise ionization effects in a low-pressure argon positive column J. Appl. Phys. 57 82–90

[11] Zhiglinsky A G (ed) 1994 Handbook of Constants of Elementary Processes with Atoms, Ions, Electrons and Photons (St Petersburg: St Petersburg State University)

[12] Zatsarinny O and Bartschat K 2013 The B–spline R–matrix method for atomic processes: application to atomic structure, electron collisions and photoionization. Journal of Physics B: Atomic, Molecular and Optical Physics 46 112001

[13] Chilton J E, Boffard J B, Schappe R S and Lin C C 1998 Measurement of electron–impact excitation into the 3p54p levels of argon using Fourier–transform spectroscopy. Phys. Rev. A, 57 267–277

[14] Zhu X-M, Cheng Z-W, Carbone E, Pu Y-K, and Czarnetzki U 2016 Determination of state–to–state electron-impact rate coefficients between Ar excited states: a review of combined diagnostic experiments in afterglow plasmas. Plasma Sources Science and Technology 25 043003

[15] Vriens L and Smeets A H M 1980 Cross–section and rate formulas for electron–impact ionization, excitation, deexcitation, and total depopulation of excited atoms Phys. Rev. A 22 940–951

[16] Kramida A,Ralchenko Yu, Reader J and NIST ASD Team. NIST Atomic Spectra Database (ver. 5.3), [Online]. Available: http://physics.nist.gov/asd [2016, August 9]. National Institute of Standards and Technology, Gaithersburg, MD., 2015

[17] Zatsarinny O and Bartschat K 2006 B–spline calculations of oscillator strengths in neutral argon. Journal of Physics B: Atomic, Molecular and Optical Physics 39 2145

[18] Bhatia A K and Kastner S O 1997 Doppler–profile escape factors and escape probabilities for the cylinder and hemisphere. Journal of Quantitative Spectroscopy and Radiative Transfer 58 347 – 354

[19] Bhatia A K and Kastner S O 2000 Global and local Doppler-profile escape factors for plane–parallel geometry. Journal of Quantitative Spectroscopy and Radiative Transfer 67 55 – 63

[20] Kastner S O and A. K. Bhatia A K 1997 Half–widths, escape probabilities and intensity factors of opacity–broadened Doppler– and Voigt–profile lines. Journal of Quantitative Spectroscopy and Radiative Transfer 58 217 – 231

[21] Evdokimov K E, Konischev M E, Pichugin V F, Sun Z 2017 Study of argon ions density and electron temperature and density in magnetron plasma by optical emission spectroscopy and collisional-radiative model Resource-Efficient Technologies 3 187-193

[22] Siepa S L, Danko S, Tsankov T V, Mussenbrock T and Czarnetzki U 2014 On the OES line-ratio technique in argon and argon-containing plasmas, J. Phys. D. Appl. Phys. 47 445201