PECULIARITIES OF ATOMIC OXYGEN CONCENTRATION MEASUREMENT BY MEANS OF ACTINOMETRY IN NEGATIVE GLOW PLASMA OF LOW PRESSURE DISCHARGE IN OXYGEN

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This proceeding presents results of investigations of an influence of dissociative excitation and cascading processes on precision of oxygen dissociation degree measurement in negative glow plasma of low pressure discharge by means of actinometry based on emission of O (844.6 nm) and Ar (750.4 nm) with the use of different model and calculated shapes of electron energy distribution function.

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INTRODUCTION

Recently oxygen plasma is widely used in different technological processes [1, 2]. For such plasma it is important to know atomic oxygen concentration [O], since namely this species plays dominant role in many practical applications. The most widely used method of [O] measurement is actinometry [3] which is simpler in the use and does not require expensive equipment in comparison with other plasma optical diagnostics methods, such as LIF or TALIF. The essence of actinometry is adding of small amount of pre-determined gas-actinometer (rare gases are the most often used ones) to working gas (oxygen in our case), and determining ratio of their concentrations using ratio of emission intensities of certain spectrum lines of actinometer gas and the component of interest for us. In case of [O] measurement, the most popular is the use of argon emission line with wavelength λ = 750.4 nm ($2p_1 \rightarrow 1s_2$ transition) and oxygen line with λ= 844.6 nm ($3p^3P \rightarrow 3s^3S$ transition). Rate of populating the levels by electron hits is

$$K = \sqrt{\frac{2e}{m_e}} \int_{E_{th}}^{\infty} \sigma(\varepsilon) \cdot \varepsilon \cdot f(\varepsilon) \cdot d\varepsilon ,$$

where E_{th} is threshold energy of the process, $\sigma(\varepsilon)$ is the process cross section, $f(\varepsilon)$ is electron energy distribution function (EEDF) with normalizing condition

$$\int_0^{\infty} \sqrt{\varepsilon} f(\varepsilon) d\varepsilon = 1 .$$

Thus we see that the precision of [O] measurements by actinometry method is defined by proper selections of both excitation cross sections of the processes, and the EEDF shape. Populating Ar level ($2p_1$) can be done both by the only direct electron hits with cross section σ_e^{dir} (Ar, $2p_1$), and by combined action of electron hits and cascading processes from upper levels with apparent cross section σ_e^{app} (Ar, $2p_1$). In case of populating the level O($3p^3P$) the situation is somewhat more complex. Excitation of this state can be performed both by direct electron hit excitation of oxygen atoms (cross section σ_e^{dir} (O, $3p^3P$)), and due to dissociative excitation with cross section σ_{de}^{dir} (O, $3p^3P$). Similarly to excitation of Ar atoms, taking into account cascading processes results in the increase of excitation cross section values for O($3p^3P$) state up to σ_e^{app} (O, $3p^3P$) and σ_{de}^{app} (O, $3p^3P$), respectively.

In case of positive column of direct current discharges and plasma of low pressure high-frequency capacitive discharges, the EEDF "tail", as compared to Maxwellian distribution, is depleted by fast electrons (such EEDF in many cases can be expressed as $f(\varepsilon) \sim \exp(-k\varepsilon/T_e)$, where $k \approx 1.2$–1.4). In this case main role in populating the levels is performed by direct excitation by electrons with energy of about the excitation threshold. Cascading processes of the populating from upper levels play minor role since their excitation threshold values are in a range where electron quantity is essentially less. The same considerations essentially regard contribution of the cascading at dissociative excitation of O($3p^3P$) level.

The situation becomes considerably more complex in case of negative glow plasma (and in some cases plasma of low pressure inductively coupled discharges). EEDF in the plasmas of such discharges differs by the presence of high-energy EEDF "tail" with mean electron energy being several times higher than mean energy of major portion of the electrons. In this case processes of dissociative excitation and cascading can play considerably more significant role in populating O and Ar levels under study.

In Fig. 1 one can clearly see such difference in the excitation processes of O and Ar levels at different EEDF shapes. Model bi-Maxwellian EEDF with different values of high-energy electron temperature T2 were built following from the results of experimental measurements of plasma parameters of the hollow cathode discharge, and calculated EEDF was obtained using 0-D model of such discharge [4].

From this figure one can clearly see that, for correct determining of [O] in the plasmas of discharges with enhanced (relatively to Maxwellian distribution) content of high-energy electrons in EEDF, one should take into consideration all excitation processes for O and Ar levels used in the actinometry.

Purpose of our work was an investigation of the influence of populating O($3p^3P$) and Ar(2p1) levels by dissociative excitation and cascading processes on the precision of O_2 dissociation degree measurement in negative glow plasma with different used model and calculated EEDF.

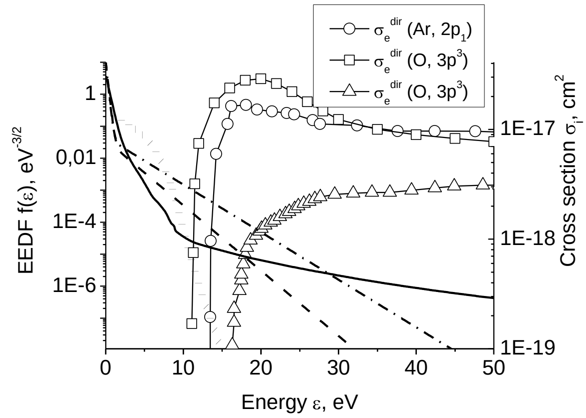

Fig. 1. Model bi-Maxwellian EEDF f(ε): -·- T2 = 2.9 eV; - - T2 = 2.1 eV; calculated EEDF with T2 ≈ 14 eV [4]; ●●● calculated EEDF of positive column (PC) plasma in low pressure discharge [5] Direct excitation cross sections of Ar(2p1) and O(3p^{3}P) states

1. METHODS AND TECHNIQUES

Ratio of emission intensities $I_{Ar(2p1)}$ and $I_{O(3P)}$ of spectrum lines Ar(2p1) and O(3p^{3}P) enables determining relative concentration of atomic oxygen [5]:

$$\frac{[O]}{[O_2]} = C_{3P}^{2p1}\frac{I_{O(3P)}}{I_{Ar(2p1)}} - \frac{K_{de}^{3P}}{K_e^{3P}} \quad , \qquad (1)$$

where

$$C_{3P}^{2p1} = \frac{[Ar]}{[O_2]}\frac{h\nu 750}{h\nu 844}\frac{A^{2p1}}{A^{3P}}\frac{k_e^{2p1}}{k_e^{3P}}\frac{\sum_j A_{ij}^{3P} + \sum_q K_q^{3P}[O_2]}{\sum_j A_{ij}^{2p1} + \sum_q K_q^{2p1}[O_2]}, \qquad (2)$$

and K_e, K_{de} are rates of populating by direct electron hits and dissociative populating, respectively; $h\nu_{ij}$ is energy of actinometry line emission quantum; A_{ij} is Einstein coefficient for respective transition; K_Q is rate of collisional quenching of excited states.

An analysis of existing up to now literature on the cross section values was accomplished, and selection of actual and recommended excitation cross sections of Ar(2p$_1$) and O(3p^{3}P) levels was done which are presented in Fig. 2 [6-10].

Apparent cross section of dissociative excitation of O(3p^{3}P) level by electron hit was taken from [7]. Direct cross section of dissociative excitation of O(3p^{3}P) level by electron hit was estimated by subtracting the cross sections of upper state from apparent cross section value at 100 eV energy using the method described and applied for O(3p^{5}P) level in mentioned work.

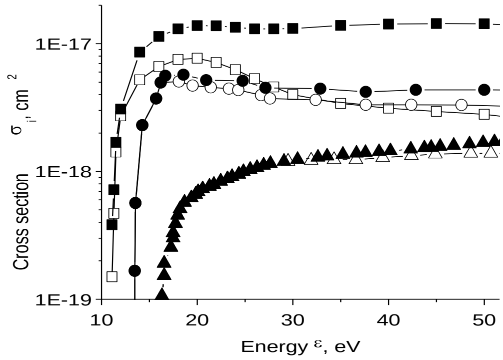

Fig. 2. Excitation cross sections: -○- σ_e (Ar 2p$_1$), -□- σ_e (O, 3p^{3}P),- Δ- σ_{de} (O, 3p^{3}P). Open points – direct cross section, close points – apparent one

Direct and apparent cross sections of excitation by electron hits for Ar(2p$_1$) level were taken from [8]. Contribution of cascading to Ar(2p$_1$) level population is minimum one, as compared to the other Ar(2p$_x$) levels, that is why it is most often used in OES methods.

Direct cross section of O(3p^{3}P) excitation by electron hit of oxygen atom was taken from [9]. Apparent cross section of excitation of this level was obtained by summing its direct excitation cross sections and direct electron hit excitation cross sections of upper levels using approach described in [7].

The quenching rates K_q^{2p1} and K_q^{3P} were taken from [5].

Model EEDF used in the calculations were created on a basis of experimental EEDF in energy range 0…12 eV [4]. As it has been shown there, EEDF of hollow cathode discharge plasma has bi-Maxwellian behavior, at that temperature of “hot” (ε ≥ 2 eV) electrons T2 significantly exceeds that of “cold” electrons T1. At 4 Pa T2 temperature increases towards the chamber center from ≈ 2.3 eV up to ≈ 3.0 eV, and, on the contrary, at 12 Pa decreases towards the center from ≈ 2.1 eV down to ≈ 1.7 eV. Since it is difficult to obtain the data on T2 at energy ≥ 12 eV by probe technique, model EEDF were obtained by approximation of high-energy “tails” of experimental EEDF for T2 temperature up to 50 eV energy.

Calculated EEDF for both pressure values had similar profiles, and temperature of electrons with energies higher than excitation thresholds of used argon and atomic oxygen levels T2 ≈ 14 eV.

2. RESULTS AND DISCUSSIONS

From Fig.3 one can see, that ratios of rates K_e^{2p1}/K_e^{3P} and K_{de}^{3P} /K_e^{3P} grow up monotonously with T2 temperature increase at the use of both direct and apparent cross section. It should be also noted that, due to the difference in absolute values of cross sections, the growth of K_e^{2p1}/K_e^{3P} ratio does not exceed ≈ (1.5…2), whereas K_{de}^{3P} /K_e^{3P} increases by about 10 times. At that, use of apparent cross section decreases these ratios by about 1.5…2 times in the whole range of T2 variations. (Smaller values of these ratios in case of use of apparent cross sections is due to fact that σ_e^{app} (O,

$3p^3P$) is ≈ (2…3) times larger than σ_e^{dir} (O, $3p^3P$) practically in the whole range of energy ε, whereas the difference between σ_e^{dir} (Ar, $2p_1$) and σ_e^{app} (Ar $2p_1$), as well as σ_{de}^{dir} (O, $3p^3P$) and σ_{de}^{app} (O, $3p^3P$), is practically absent).

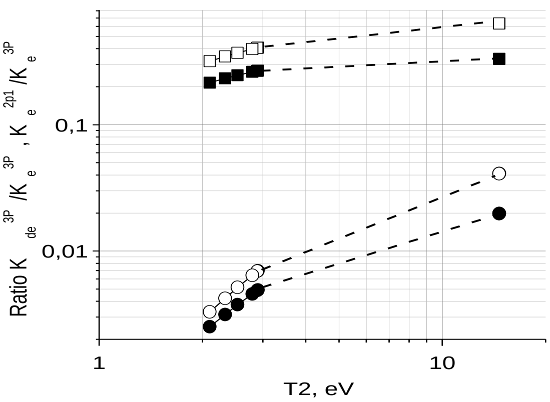

Fig. 3. Dependencies of ratios K_e^{2p1}/K_e^{3P}(-□-) and K_{de}^{3P}/K_e^{3} (-○-) on temperature T2 at the use of direct (open points) and apparent (close points) cross sections

In calculations of dissociation degree $[O]/[O_2]$ the dependencies of intensity ratio $I_{O(3P)}/I_{Ar(2p1)}$ experimentally measured in [4] were used (Fig. 4). One can see that at working gas pressure P = 4 Pa ratio of spectrum line intensities $I_{O(3P)}/I_{Ar(2p1)}$ is higher than that at 12 Pa pressure and slightly (about 1.3 times) decreases with radius R increase, whereas at 12 Pa pressure this ratio is practically independent on R.

Calculation of dissociation degree by formulas (1,2) has shown, that at the use of model EEDF taking into account process of dissociative excitation of O($3p^3P$) state results in variation of dissociation degree by no more than 5 %, and in case of calculated EEDF – no more than ≈ 20 %. The results of $[O]/[O_2]$ calculations presented below are obtained without taking mentioned process into account.

Results of oxygen dissociation degree calculations are presented in form of $[O]/[O_2]$ dependency on the system radius in Figs. 5,a,b. In case of model EEDF, each R value was corresponded by certain T2 value used in the calculations of rates of the processes and $I_{O(3P)}/I_{Ar(2p1)}$ ratio. In case of calculated EEDF, T2 radial dependence was absent because of the use of 0-D model, due to that $[O]/[O_2]$ dependencies on R are approximate ones.

From Figs. 5a,b one can see that with the use of model EEDF, $[O]/[O_2]$ dependencies on R for both P values well correlate with $I_{O(3P)}/I_{Ar(2p1)}$ behavior at the use in calculation of both direct, and apparent cross sections. In other words, in our case T2 radial dependencies weakly influence the $[O]/[O_2]$ dependence on R.

More interesting is an influence of used cross sections of the processses on $[O]/[O_2]$ value. Comparison of Fig. 5,a and Fig. 5,b shows that substitution of direct cross section by apparent one decreases $[O]/[O_2]$ value by about 1.5 times. Besides, difference between $[O]/[O_2]$ values, obtained with the use of model and calculated EEDF essentially decreases at that. As it follows from expression (2) and figure 3, main role in this effect is performed by essential (in comparison with the other

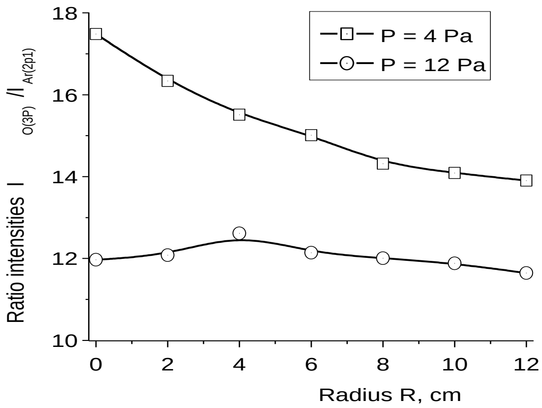

Fig. 4. Experimentally obtained dependencies of emission intensity ratio $I_{O(3P)}/I_{Ar(2p1)}$ on the system radius for two oxygen pressure values

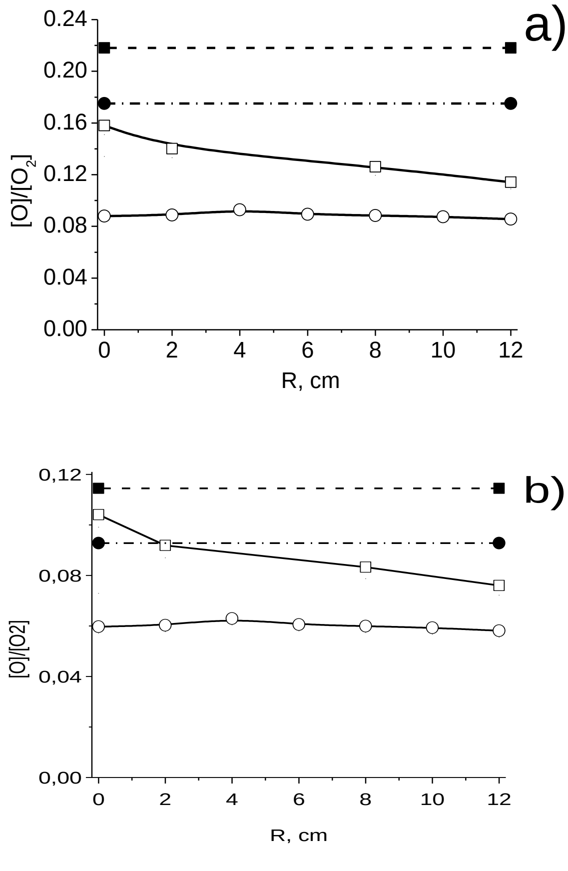

Fig. 5 . Dependencies of oxygen dissociation degree $[O]/[O_2]$ on radius R for two O_2 pressure values with different EEDF. a – with the use of direct cross-section; b – with the use of apparent cross section. (-□-) – model EEDF with T2 = (2.3…2.9) eV, corresponding to P = 4 Pa; (-○-) – model EEDF with T2 = 2.1 eV, corresponding to P = 12 Pa; (-■-) – calculated EEDF for P = 4 Pa; (-● -) – calculated EEDF for P = 12 Pa

processes) difference in the values of direct and apparent excitation cross sections of O($3p^3P$) state.

For refining the influence of EEDF shape and used excitation cross sections on the precision of dissociation degree [O]/[O_2] measurement in the plasma of hollow cathode discharge, in subsequent it is planned to perform similar researches with the use of another pair of lines involving Ar($2p_1$) and O($3p^5P$) states.

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ОСОБЕННОСТИ ИЗМЕРЕНИЯ КОНЦЕНТРАЦИИ АТОМАРНОГО КИСЛОРОДА В ПЛАЗМЕ ОТРИЦАТЕЛЬНОГО СВЕЧЕНИЯ РАЗРЯДА НИЗКОГО ДАВЛЕНИЯ В КИСЛОРОДЕ МЕТОДОМ АКТИНОМЕТРИИ

Ю.В. Лаврукевич, С.В. Мацевич, В.Ю. Баженов, В.В. Циолко

Представлены результаты исследования влияния процессов диссоциативного возбуждения и каскадирования при различных формах модельных и расчетных функций распределений электронов по энергиям на точность определения степени диссоциации кислорода в плазме отрицательного свечения разряда низкого давления методом актинометрии с использованием излучения линий O (844,6 нм) и Ar (750,4 нм).

ОСОБЛИВОСТІ ВИМІРЮВАННЯ КОНЦЕНТРАЦІЇ АТОМАРНОГО КИСНЮ В ПЛАЗМІ НЕГАТИВНОГО СВІТІННЯ РОЗРЯДУ НИЗЬКОГО ТИСКУ В КИСНІ МЕТОДОМ АКТИНОМЕТРІЇ

Ю.В. Лаврукевич, С.В. Мацевич, В.Ю. Баженов, В.В. Ціолко

Представлено результати досліджень впливу процесів дисоціативного збудження та каскадування при різних формах модельних та розрахункових функцій розподілу електронів за енергіями на точність визначення дисоціації кисню в плазмі негативного світіння розряду низького тиску методом актинометрії з використанням випромінювання ліній O (844,6 нм) та Ar (750,4 нм).