INFLUENCE OF COMPONENT CONTENT OF Ar/O_2 MIXTURE ON OXYGEN DISSOCIATION DEGREE IN PLASMA OF LOW PRESSURE DISCHARGE WITH HOLLOW CATHODE

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Influence of argon content in Ar/O_2 mixture on O_2 dissociation degree and atomic oxygen concentration in the plasma of low pressure glow discharge with hollow cathode is determined experimentally and theoretically. It is found that atomic oxygen concentration dependence on argon content in the mixture exhibits non-monotonous behavior with a minimum at $Ar/(Ar+O_2) \approx 50\%$. Results of calculation and experiment are in a good agreement.

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INTRODUCTION

Oxygen discharges are widely used in plasma technologies, particularly, for photoresist etching, modification of surface features of materials, deposition of thin oxide films, etc. [1 - 3]. For all those applications it is important to know the density of active particles, as well as its dependence on the plasma parameters (i.e. pressure, power, gas mixture composition, etc.). Most often, technological applications are realized using the discharges in mixtures of oxygen and inert gases, rather than those in pure oxygen. Inert gas adding to ixygen can essentially increase the rates of plasma-chemical processes. Particularly, in [4] it has been shown that photoresist etching rate by the plasma of discharge in 50% Ar/O_2 mixture is twice higher than that in case of use of the discharge in pure oxygen.

Purpose of our work is an investigation of the influence of argon adding in working gas mixture on oxygen dissociation degree, as well as the dependence of atomic oxygen concentration value in the negative glow plasma of low pressure discharge on argon content in the gas mixture.

1. THEORETICAL MODEL

For calculations of dependencies of plasma component concentrations on the gas mixture content, averaged model of plasma-chemical processes in hollow cathode discharge was built. The model was mainly analogous to one considered in [1]. We assumed that the component concentrations are uniformly spread over the whole volume of the chamber represented by cylinder with diameter D = 38 cm and length L = 42 cm.

In the kinetics calculations we considered 18 components. For oxygen, the following species were considered: molecular oxygen in both ground state $O_2(X^3\Sigma_g)$, and in excited metastable states $O_2(a^1D_g)$, $O_2(b^1\Sigma_g^+)$ and $O_2(A^3\Sigma_u^+$, $A^3\Delta_u$, $c^1\Sigma_u^-)$; atomic oxygen ground state $O(^3P)$ and at metastable level $O(^1D)$; ozone O_3, as well as positive ions O^+ and O_2^+, and negative ions O^-, O_2^- and O_3^-. Argon atoms were considered as the following species: the ground state $Ar(3s^23p^6)$, metastable levels Ar^m (mixture of $1s_5$ and $1s_3$ levels with fixed ratio of 5:1), radiation-bounded levels Ar^r ($1s_2$ and $1s_4$ levels), all levels Ar(4p), as well as Ar^+ ions. Totally, in the calculations 131 elementary processes were taken into consideration. Rate constants for all reactions were taken the same as in [5], excluding reactions of oxygen dissociation and ionization, argon ionization in ground and metastable states, as well as reactions of excitation of electron levels of molecular oxygen and argon.

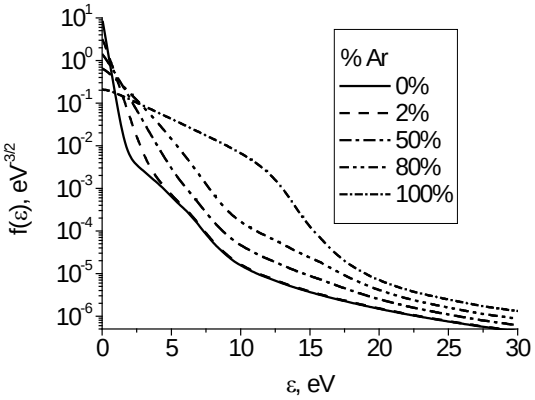

Fig. 1. Electron energy distribution function in Ar/O_2 mixture for different argon content. Total pressure is 4 Pa, electric field strength is 20 mV/cm, power introduced into the discharge is 250 W

Mentioned constants were determined from electron energy distribution function (EEDF) which was obtained by solving Boltzman equation, which was solved together with the system of kinetic equations. The EEDF $f(\varepsilon)$ was normalized as follows:

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

At solving this equation, electron energy losses to ionization of molecular oxygen and argon, oxygen dissociation, excitation of the first seven electron levels of molecular oxygen, argon levels 1s and 2p (including stepwise excitation 1s → 2p), and oxygen oscillation levels were taken into account. Electron heating was done by electric field with a strength assumed to be 20 mV/cm, as well as at the expense of "secondary" electrons formed at the gas ionization by electrons accelerated in the near-cathode layer. The dependence of energy distribution of these "secondary" electrons was considered to be proportional to $1/(\varepsilon^2 + \varepsilon_0^2)$, where ε_0 is ionization energy, and the formation density was determined following from power density introduced into the discharge, and the energy spent to ionization, excitation of the atoms and the molecules, and dissociation. Cross section values for electron processes used for calculations of rate constants, as well as EEDF calculation, were taken from [6 - 11].

Fig. 1 exhibits EEDF appearance for different content of the mixture. One can see that argon adding results in the increase of portion of electrons having energy higher than 12 eV, which in turn results in the increase of the rate constant of oxygen dissociation by electron hits (Fig. 2).

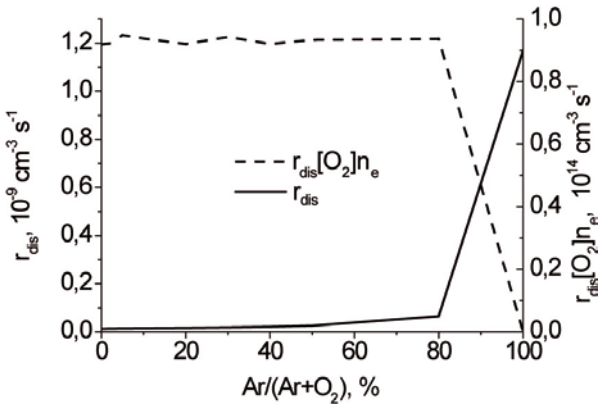

Fig. 2. Dependencies of constant of molecular oxygen dissociation by electron hits (solid curve, left axis) and the rate of dissociation by electron hits (dashed curve, right axis) on argon content in the discharge mixture. The discharge parameters are the same, as in Fig. 1

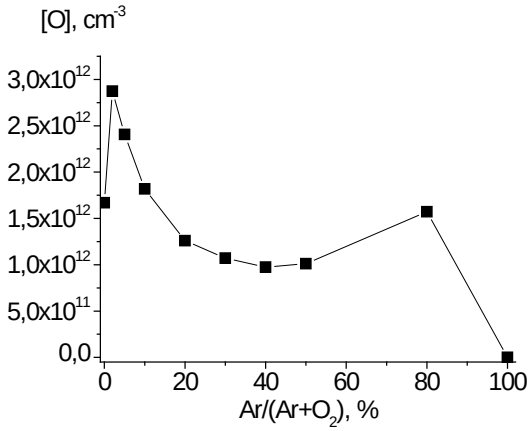

Fig. 3. Dependence of calculated atomic oxygen concentration in the discharge on argon content in the mixture. The discharge parameters are the same as in Fig. 1

However, a multiple of this constant and molecular oxygen concentration is practically independent on oxygen content in the discharge mixture up to 10% value. Thus, if the dissociation would be the only channel of atomic oxygen formation, its concentration should be unchanged for all mixtures, and should abruptly drop at molecular oxygen content approach to zero value. Exactly such behavior is observed in RF discharges. However, as one can see from Fig. 3, calculated dependence of atomic oxygen concentration has non-monotonous appearance. That is, in hollow cathode discharge the dissociation is not the single channel of atomic oxygen formation. As it is shown by both calculations and experiment, large amount of oxygen negative ions should be present in such discharge, so that a native assumption can be made regarding an influence of these ions on the processes of atomic oxygen formation. However, clarification of particular mechanism of influence of the ions on atomic oxygen concentration requires further investigations.

2. EXPERIMENTAL SETUP AND METHODS

The schematic diagram of the experimental setup with diagnostic system [TRG-OES] (trace rare gases optical emission spectroscopy) is shown in Fig. 4. Hollow cathode discharge plasma was created in cylindrical working chamber 3 made of stainless steel with 38 cm diameter and 42 cm length, which served as the discharge cathode. The discharge anode 2 was a disk made of copper with 30 cm diameter located near one of the chamber end walls. Another end wall of the chamber was elaborated from usual glass, and was used for spectrum measurements of the discharge plasma emission.

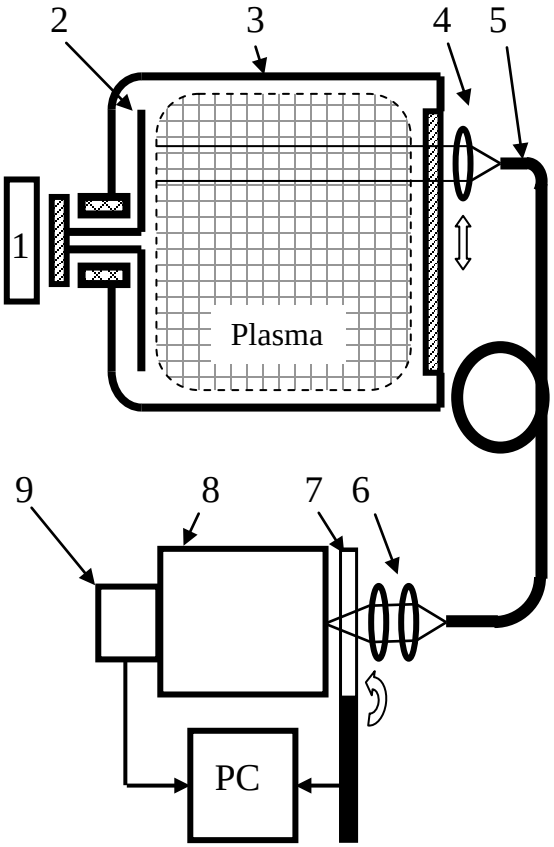

Fig. 4. Schematic diagram of the experimental setup: 1 – illuminator based on incandescent lamp; 2 – discharge anode; 3 – discharge cathode; 4 – lens; 5 – light guide; 6 – collimator; 7 – light flux chopper; 8 – monochromator MDR-23; 9 – liquid nitrogen cooled PMT FEU-62

Chamber evacuation was done by means of diffusion pump down to residual gas pressure of about $5 \cdot 10^{-3}$ Pa, and after that working gas mixture was supplied till the pressure of 4 Pa. To avoid oil vapor coming into working chamber, the diffusion pump was equipped by a trap cooled by liquid nitrogen. Argon content in working mixture was varied from 1 to 70% with maintaining of the gas filling pressure of 4 Pa. The discharge electgric power supply was performed by means of DC source with controlled voltage and discharge current. At variation of gas mixture parameters, power introduced into the discharge was maintained at unchanged value of 230 W.

Spectrum measurements in the experiment were performed by means of optical system based on the use of

monochromator MDR-23 (diffraction grating had spatial frequency of 1200 lines per millimeter). Spatial selection of the plasma emission from small (about 2 cm diameter) part of the discharge was done by lens 4, which could be moved in radial direction. Input end of fiber-optic light guide 5 was located in focal plane of the lens 4. The light guide length was 10 m. Radiation from its output end was delivered to input slit of the monochromator by means of collimator 6. Light flux was modulated by means of chopper 7 with 120 ms period. For detection of the radiation, photomultiplier tube (PMT) of FEU-62 type (9), cooled by liquid nitrogen with the use of specially developed cryostat, was used. Studied spectrum range was limited by the light guide transmission, and comprised 550…1000 nm. Calibration of spectrum sensitivity of the system was accomplished with the use of incandescent lamp of OP-33-03 type, at that the lamp emission spectrum was measured with the lens 4 placement in a center of the discharge chamber window.

PMT signal was digitized by 16-bit ADC and processed by means of specially developed software for obtaining desired signal-to-noise ratio. The processing was based on dark signal subtraction synchronously with chopper 7 operation, data averaging (acquisition time for spectrum interval of 3 nm was about 5 minutes) and determining intensities of atomic lines using a value of the square under spectrum dependence of the emission interpolated accordingly to response function of the monochromator. For efficiency enhancement of the last stage of processing, triangle shape of response function was used, which was created by means of setting wide enough equal widths (0.4 mm) of input and output slits of the monochromator.

In optical measurements emission of oxygen atoms at 844.6 nm wavelength, corresponding to 3p3P → 3s3S transition, and those of argon atoms at 750.4 and 751.4 nm wavelengths, corresponding to 2p1 → 1s2 and 2p5 → 1s4 transitions (Paschen notation) were used.

For determining oxygen dissociation degree actinometry method [12] was used taking into account dissociative populating of oxygen level (O, 3p3P) [13], in accordance to which

$$\frac{[O]}{[O_2]} = C_{3P}^{2p1}\frac{I_{844}}{I_{750}} - \frac{K_{de}^{3P}}{K_e^{3P}},$$

where

$$C_{3P}^{2p1} = \frac{h\nu_{750}}{h\nu_{844}}\frac{A_{ij}^{2p1}}{A_{ij}^{3P}}\frac{\sum A_{ij}^{3P} + k_Q^{3P}[O_2]}{\sum A_{ij}^{2p1} + k_Q^{2p1}[O_2]}\frac{K_e^{2p1}}{K_e^{3P}}\frac{[Ar]}{[O_2]},$$

I_{844}, I_{750} are intensities of emission lines of oxygen at 844 nm wavelength and argon at 750 nm wavelength, respectively, K_{de}^{3P}, K_e^{3P}, K_e^{2p1} are rates of dissociative populating of oxygen level, and populating the levels of oxygen and argon by electron hits, respectively, A_{ij}^{2p1}, A_{ij}^{3P} are Einstein coefficients for argon and oxygen levels, $\sum A_{ij}^{2p1}$, $\sum A_{ij}^{3P}$ are sums of Einstein coefficients for argon and oxygen levels in case of branching, $k_Q^{3P}[O_2]$, $k_Q^{2p1}[O_2]$ are rates of quenching excited levels of oxygen and argon. At that, it should be noted that the rates of reactions

$$K = \sqrt{\frac{2e}{m_e}}\int_0^\infty \varepsilon \cdot f(\varepsilon)\cdot\sigma(\varepsilon)\cdot d\varepsilon,$$

were calculated taking into consideration total cross sections (σe(Ar, 2p1) for argon level 2p1 populating by electron hits, σe(O, 3p^{3}P) for oxygen level 3p^{3}P populating by electron hits, and σde(O, 3p^{3}P) for dissociative populating of oxygen level 3p^{3}P), which take into account cascading in the populating of considered actinometry levels [14]. Corresponding spectroscopic data for the lines used in calculations were taken from NIST database [15].

Fig. 5 presents excitation cross sections of the states [16 - 18] used by us in determination of molecular oxygen dissociation degree, and examples of calculated f(ε) for two values of argon concentration in the mixture.

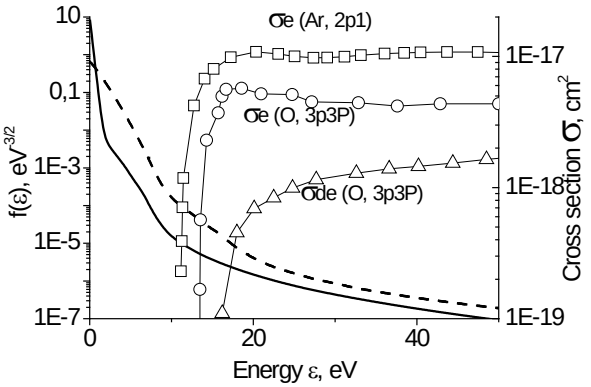

Fig. 5. Calculated f(ε): solid line – 0% argon fraction; dashed line – 80% argon fraction in gas mixture. Apparent excitation cross sections of Ar(2p1) and O(3p^{3}P) states

3. RESULTS AND DISCUSSIONS

One can see from Fig. 6,a,b that with Ar concentration increase in the mixture, argon emission intensity I_{750} grows up essentially faster in comparison with emission of oxygen line I_{844} decrease. It in turn results in abrupt decrease of intensity ratio I_{844}/I_{750} with Ar content increase in the mixture.

In Fig. 7,a dependence of molecular oxygen dissociation degree [O]/[O_2] on argon content in the mixture obtained with the use of intensity ratio I_{844}/I_{750} from Fig.6 is presented. One can see from the figure that argon adding to oxygen results in abrupt decrease of the dissociation degree – [O]/[O_2] decreases from ≈12% at Ar/(Ar+O_2) = 0% down to ≈ 2.5% at Ar/(Ar+O_2) ~20…30 %. At subsequent argon content increase, the dissociation degree increases and reaches ~15% at Ar/(Ar+O_2) = 80%.

From Fig. 7,b one can see that, at first, [O] concentration value monotonously decreases with argon content increase in working mixture, and reaches a value of ~10^{13} cm^{-3} at Ar/(Ar+O_2) being higher than about 10…15%, and subsequently increases up to ~ $3\cdot10^{13}$ cm^{-3} at 80% argon content in the mixture.

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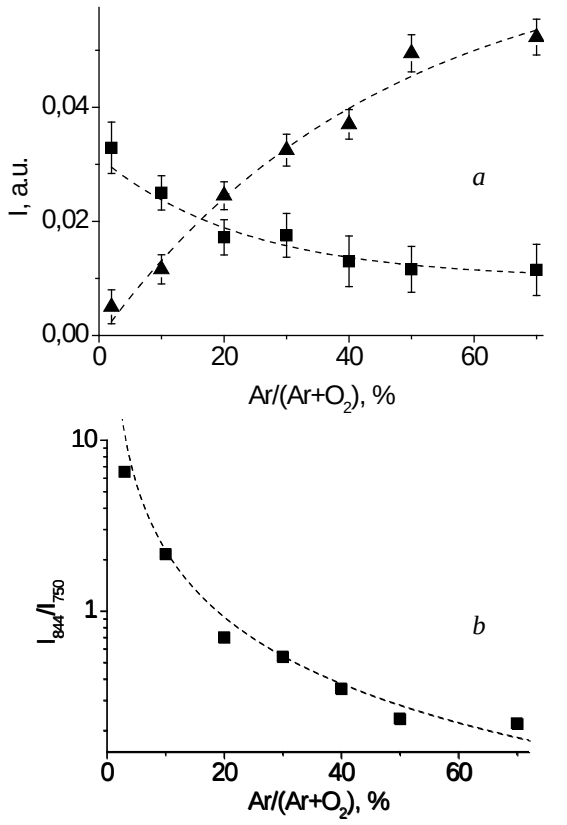

Fig. 6. Experimental measured dependencies of emission intensities I_{844} – (■) and I_{750} – (▲) on percentage of argon content in plasma generating mixture (a), and dependence of the ratio I_{844}/I_{750} (b)

Experimental obtained [O] dependence on argon content in the mixture is generally in agreement with calculated one (see Figs. 7,b and 3). Both of them exhibit non-monotonous dependence of [O] on argon content in the mixture at $Ar/(Ar+O_2)$ variation from several to 80%. Certain discrepancy exists al small argon content – in the calculation we observe local maximum of [O] at argon content of about 2%, while experimental obtained dependence possesses even behavior. It is due to fact that in the experiment argon concentration increments were too large for observation of this maximum. In subsequent, we plan to accomplish [O] value measurements in Ar concentration range ~0.5…5% with smaller increments of the last value.

Besides, numeric modeling gives [O] values lower by about an order of magnitude, as compared to experimental data, which can be explained by peculiarities of the used model and inaccuracies of the values of cross sections and rates for the processes considered in the calculations (see section 2).

[O] value growth at argon concentration increase from ~50 to 80% looks somewhat unclear, both in the calculation, and in the experiment.

In general, it should be noted that the behavior of atomic oxygen concentration dependence on argon content in the mixture Ar/O_2 essentially depends on both the type of used discharge, and its parameters. In already mentioned article [4] the authors state that that maximum concentration [O] is achieved at 1:1 quantitative ratio in Ar/O_2 mixture.

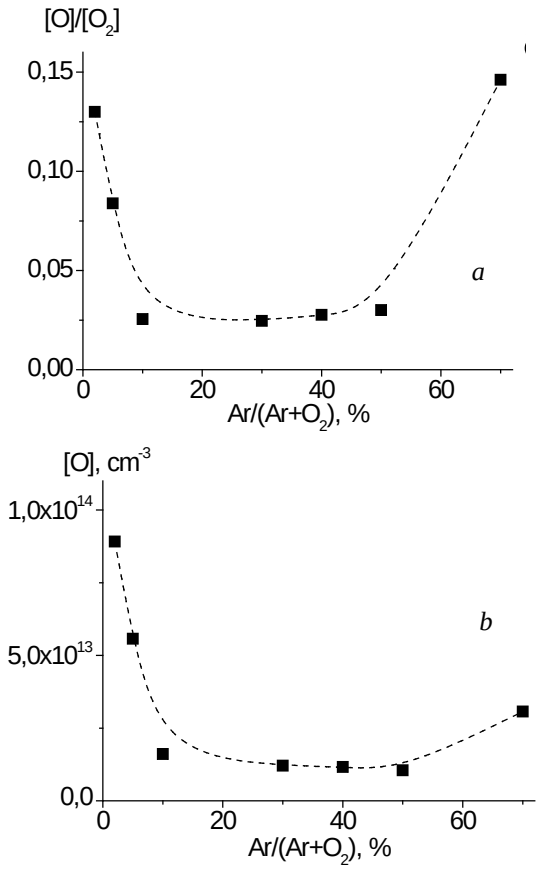

Fig. 7. Dependencies of oxygen dissociation degree $[O]/[O_2]$ with calculated EEDF versus Ar percentage in working gas mixture (a), and atomic oxygen concentration dependencies (b)

In [19] the authors also note an increase of atomic oxygen amount in Ar/O_2 mixture, and it occurs already at 20% argon adding to the mixture. In [5] an extremum in behavior of atomic oxygen amount in Ar/O_2 mixture was not observed and a drop of [O] value occurred at Ar content in the mixture > 90%. Authors of [20] used different plasma generating mixture Ar/N_2, and noted atomic nitrogen concentration maximum at 20…25% of Ar content in the mixture.

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ВЛИЯНИЕ КОМПОНЕНТНОГО СОСТАВА СМЕСИ Ar/O_2 НА СТЕПЕНЬ ДИССОЦИАЦИИ КИСЛОРОДА В ПЛАЗМЕ РАЗРЯДА НИЗКОГО ДАВЛЕНИЯ С ПОЛЫМ КАТОДОМ

В.Ю. Баженов, Ю.В. Лаврукевич, В.М. Пиун, А.В. Рябцев, В.В. Циолко

Экспериментально и теоретически установлено влияние содержания аргона в смеси Ar/O_2 на степень диссоциации O_2 и концентрацию атомарного кислорода в плазме тлеющего разряда низкого давления с полым катодом. Установлено, что зависимость концентрации атомарного кислорода от содержания аргона в смеси носит немонотонный характер с минимумом при $Ar/(Ar+O_2)$ ~50%. Результаты расчета и эксперимента находятся в хорошем согласии.

ВПЛИВ КОМПОНЕНТНОГО СКЛАДУ СУМІШІ Ar/O_2 НА СТУПІНЬ ДИСОЦІАЦІЇ КИСНЮ В ПЛАЗМІ РОЗРЯДУ НИЗЬКОГО ТИСКУ З ПОРОЖНИСТИМ КАТОДОМ

В.Ю. Баженов, Ю.В. Лаврукевич, В.М. Піун, А.В. Рябцев, В.В. Ціолко

Експериментально та теоретично встановлено вплив вмісту аргону в суміші Ar/O_2 на ступінь дисоціації O_2 та концентрацію атомарного кисню в плазмі жевріючого розряду низького тиску з порожнистим катодом. Встановлено, що залежність концентрації атомарного кисню від вмісту аргону в суміші має немонотонний характер з мінімумом при $Ar/(Ar+O_2)$ ~50%. Результати розрахунку та експерименту достатньо гарно узгоджуються.