KINETICS OF Ar_2^+, Ar_2^* AND Ar^* IN VOLUME BARRIER DISCHARGE IN ARGON

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By means of computer simulation it is shown that Ar_2^+, Ar_2^* and Ar^* species possess maximum concentration in volume barrier discharge in argon. Dependencies of concentrations of these species on the discharge parameters are obtained. Dependencies of characteristics of Ar_2^+ ion flows from the discharge plasma are determined experimentally.

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1. INTRODUCTION

In the last decade plasma of low pressure discharges is widely used for modification of functional properties of surfaces of different materials. Particularly, treatment of polyimide films by ion streams from low pressure discharge plasma allows obtaining good alignment of liquid crystals. At the same time, necessity of use of high-vacuum pumping tools in technological setups essentially complicates processes of surface treatment and rises up their cost. An alternative to such discharges is represented by atmospheric pressure discharges, first of all, corona and barrier ones. Besides simplification and lowering cost of technological devices, use of atmospheric pressure discharges enables creation of dense streams of different active species (first of all, excited molecules, atoms and radicals), which in turn results in shortening treatment time of the substrates. The first attempt in this direction was recently made in [1]. It was found that nematic liquid crystal can be aligned on the homeotropic polyimide substrate exposed to flux of active species from Ar volume barrier discharge. In [2,3] dependencies of the pretilt angle on parameters of treatment of the substrates (electric power introduced into barrier discharge, volume rate of argon purge through the discharge gap, duration of the treatment) were determined. However, up to now mechanism of formation of the aligning layers is not clear. It is essentially due to fact that characteristics of a flow of species blown out of barrier discharge are not known.

Due to that, purpose of the present work consists in experimental and theoretical study of the component content of species, both immediately in the barrier discharge plasma, and in the area of placement of treated substrate.

2. CALCULATION

As it is known, volume barrier discharge represents a set of short-living microdischarges which are stochastically spread over the surface of electrodes. In a number of cases, for instance, at consideration of the component content of electrically neutral species in a barrier discharge in [4], power introduced into the discharge can be averaged over the discharge chamber volume. In the present case such approach can not be used since in a majority of reactions electrons are involved which exist only in channels of the microdischarges, and typical duration of other processes with participation of excited levels of argon are essentially less than a time of diffusion of these species outside the microdischarge channel.

The time evolution of the gas components in the discharge was calculated using the model proposed in [5] that considers a DBD as a sequence of electric current pulses – 'micropulses'. Each micropulse simulating a set of microdischarges was supposed to have a rectangular form with duration τ. The number of simultaneously proceeding microdischarges that contribute to one micropulse in the external circuit is determined by their surface density σ. Thus, the effective gas volume excited by microdischarges of a single micropulse is equal to $\sigma S\pi r^2 d$, where r is the average microdischarge radius, d is the width of the gas gap, and S is the electrode area. Assuming that the number of micropulses per unit time is equal to fm, where f is the frequency of the applied electric field and m is the average number of pulses per cycle, the specific power deposition per pulse can be expressed in the form

$$w = \frac{W}{(\sigma S\pi r^2 d)(fm\tau)}, \qquad (1)$$

where W is the discharge power. The calculations were performed at the same values of the parameters of microdischarges as in [5].

Concentrations of the species during the microdischarge occurrence were calculated with the use of kinetic equations

$$\frac{dN_i}{dt} = S_{ei} + \sum_{ij} k_{ij} N_j + \sum_{ijl} k_{ijl} N_j N_l + \ldots, \qquad (2)$$

where N_i are concentrations of argon atoms in ground and excited states, respectively, and k_j, k_{jl} are rates of kinetic processes. Term S_{ei} represents the rate of formation of the products of electronic-atomic reactions, and is determined from relation

$$S_{ei} = \frac{w}{\varepsilon_{ei}} \frac{W_{ei}}{\sum_j W_{ej} + W_t}. \qquad (3)$$

Here w is power introduced into a volume unit of the microdischarge determined by expression (1), W_{ei} is specific power spent for electron non-elastic process with threshold energy ε_{ei}:

$$W_{ei} = \sqrt{\frac{2q}{m}} n_e N_i \varepsilon_{ei} \int_0^\infty \varepsilon Q_{ei}(\varepsilon) f(\varepsilon) d\varepsilon, \qquad (4)$$

where $q = 1.602 \cdot 10^{-12}$ Erg/eV, m and n_e are electron mass and concentration, Q_{ei} is cross section of respective non-elastic process, and $f(\varepsilon)$ is electron energy distribution function. W_t corresponds to specific power spent for gas heating:

$$W_t = \frac{2m}{M} \sqrt{\frac{2q}{m}} n_e N \int_0^\infty \varepsilon^2 Q_t(\varepsilon) f(\varepsilon) d\varepsilon, \qquad (5)$$

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where Q_t is cross section of transport scattering of electrons on argon atoms, M and N are their mass and concentration.

For a time interval between two microdischarges, the kinetics was calculated without taking electron processes in consideration ($S_{ei}=0$).

After a time interval equal to the diffusion time t_{diff}, the obtained concentrations were averaged over the volume of the discharge chamber with regard for the process of gas escape due to its circulation. Thus, the concentrations of the gas components in the discharge volume after the k-th averaging were calculated as

$$N_i^k = \frac{N_{mdi} V_{md}}{V} + N_i^{k-1} - N_i^{k-1} \frac{t_{diff}}{T_r} \quad , \quad (6)$$

where N_{mdi} are concentrations of species of type i in the microdischarge volume prior to a time point of averaging, V_{md} is volume occupied by the microdischarges, V is the discharge chamber volume, T_r is residence time of the gas in the discharge gap. At that neutral species diffuse into the volume for a time of время t_{diff}, and charged ones – for a time of ambipolar diffusion t_{da}. Their values differ by about one order of magnitude, so that positive ions are accumulated in the discharge volume much faster than electrically neutral species.

Stationary concentration of species of type i is determined as

$$N_i = \frac{N_{mdi} V_{md}}{V} \frac{T_r}{t_{diff}} . \quad (7)$$

Thus, concentration of the species in the discharge is determined by a value of volume occupied by the microdischarges, and a ratio between transient time of the mixture in the microdischarge and a time of diffusion of the species out of the microdischrge.

System of kinetic equations (1) was solved together with Boltzman equation for electron energy distribution function (EEDF). Kinetic model took into consideration 14 excited argon levels – 4 levels of $3p^5 4s$ configuration (metastable states $1s_5$ and $1s_3$ ($^3P_2$ and $^3P_0$) and resonant $1s_4$ and $1s_2$ ($^3P_1$ and $^1P_1$)), and 10 levels of $3p^5 4p$ configuration ($2p_{10}…2p_1$). Values of cross sections and rates of kinetic reactions for these states were taken from [6-9]. As well, kinetics of Ar^+ и Ar_2^+ ions, and excited dimers Ar_2*(1), Ar_2*(3) и Ar_2** [10] were taken into account.

Electron processes occurring during a microdischarge included reactions of direct excitation of levels of s- and p- configurations by electron impact, direct ionization of argon, and also consecutive excitation of metastable states $1s_5$ и $1s_3$ to levels $2p_{10}…2p_1$, and consecutive ionization of argon from excited states of s- and p- configurations.

Generated excited argon atoms and ions participate in a three-piece conversion processes resulting in creation of excited dimers Ar_2*(1), Ar_2*(3) and Ar_2**, and Ar_2^+ ions. In subsequent, excited dimers either form Ar_2^+ ions, or decompose in a result of spontaneous emission. At that, lifetime of Ar_2*(3) triplet state of 1.6 μs essentially exceeds lifetime of Ar_2*(1) singlet level (7 ns). Decomposition of highly excited dimers Ar_2** occurs under collisions with argon atoms, whereas loss of Ar_2^+ ions happens in processes of dissociative recombination.

Calculations have shown that at experimental parameters the highest concentration in the discharge volume is exhibited by Ar_2^+ ions, excited dimers $Ar_2^*(3)$, $Ar_2^*(1)$ and Ar^* atoms. However, whereas ion concentration value could reach $\approx 5*10^{10}$ cm^{-3}, dencities of other species were essentially less – $\approx 10^8$ cm^{-3}, $5*10^5$ cm^{-3} and 10^7 cm^{-3} respectively. Temporal evolutions of Ar_2^+, $Ar_2^*(3)$, $Ar^*(1s_5)$ and $Ar_2^*(1)$ concentrations at different residence time T_r are presented in Fig.1. One can see from the figure that residence time decrease (or, in other words, increase of volume rate of argon purge through the discharge volume) results in decrease of concentrations of these species. At the same time, behavior of dependencies of concentrations of electrically neutral species and ions, as a whole, are somewhat different. Particularly, whereas concentrations of electrically neutral species reach their quasistationary values at $t \approx 0.3$ s ($T_r = 0.12$ s) and $t = 0.03$ s ($T_r = 0.013$ s), these time values for Ar_2^+ ions are shorter by a factor of almost 2-3.

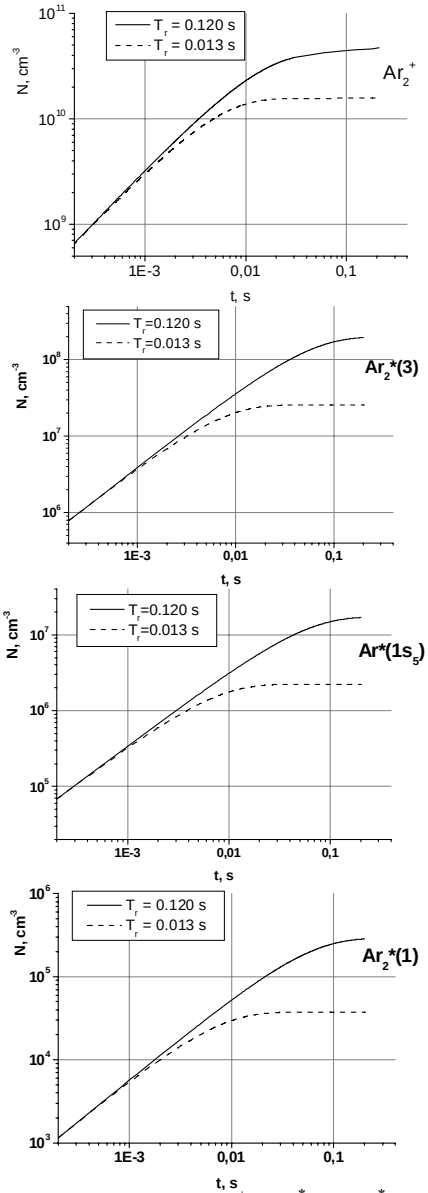

Fig.1. Dependencies of Ar_2^+, $Ar_2^*(3)$, $Ar^*(1s_5)$ and $Ar_2^*(1)$ concentrations averaged over the discharge volume on the discharge glow time t at different residence time T_r and W_d = 1 W/cc

For estimation of a flow of electrically neutral species onto the substrate surface the following approach was used. After reaching stationary values of concentrations of the species in the discharge volume in calculation, the discharge was "turned off" and after that temporal evolution of concentrations of the same species was calculated again. Results of such calculation are presented in Fig.2. One can see from the figure that concentrations of the species already at ~ 10^{-5} s after turning off the discharge are just about 10^2 cm^{-3}. Since carrying-out the species from the discharge volume onto treated substrate occurs only due to argon purge with a rate ~ 10^2 cm/s, travel time of the species from the discharge volume to the substrate (≈ 0.5 cm spacing) is about $5 \cdot 10^{-3}$ s. Comparison of these time values shows that electrically neutral species from the discharge plasma practically can not reach treated substrate.

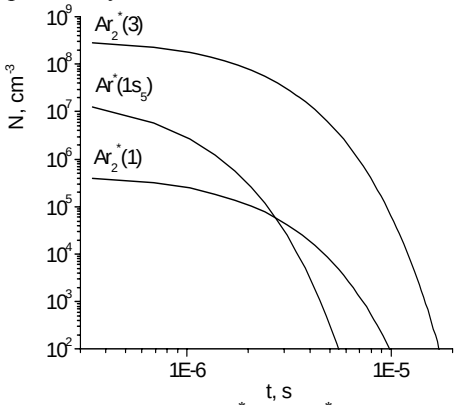

Fig.2. Dependencies of Ar_2^* (3), $Ar^*(1s_5)$ and Ar_2^*(1) concentrations averaged over the discharge volume on time after "turning off" the discharge. T_r = 0.12 s W_d = 1 W/cc

One can not estimate concentration of Ar_2^+ ion flow onto the substrate in such way, because their carrying-out from the discharge volume is determined by ion drift in electric field, rather than argon purge.

3. EXPERIMENTAL

3.1. EXPERIMENTAL SETUP

Schematic diagram of the experimental setup is presented in Fig.3. Barrier discharge 1 glowed in the gap with 1 mm thickness between the electrodes with 40×50 mm dimensions. The discharge was oriented by its wide side towards treated substrate 3. Volume rate υ of argon purge through the discharge gap was varied in a range of 1…10 l/min. It corresponded to the average residence time of species in the discharge gap $T_r \approx (0.01…0.1)$ s and mean linear velocities of gas particles ≈ $(0.3…3) \cdot 10^2$ cm/s. The discharge was powered by AC voltage of 0…15 kV with 3 kHz frequency. Specific power in the discharge W_d was varied in a range of 0.2…1.5 W/cm^3. By means of moving system 4, treated substrate 3 was translated forward and backward perpendicularly to the band shape particle stream from the discharge with a speed of 1.3 mm/s. The distance between output slit of the discharge and the substrate was about 4 mm and the angle between the substrate's normal and the particle stream was about 60°.

Measurements of parameters of the flows of charged species onto the substrate were performed by means of collector with 1 mm width and 30 mm length placed on moving system 4 parallel to output slit of the discharge system. Potential of the collector was measured by means of electrostatic voltmeters of C50 type. Use of special module for data acquisition enabled obtaining real-time dependencies of current onto the collector on the discharge parameters.

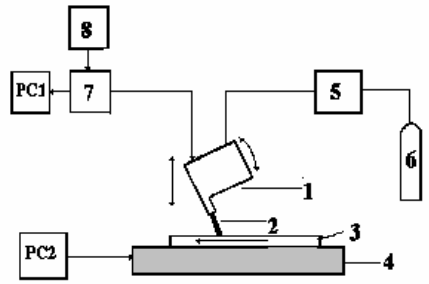

Fig.3. Schematic diagram of atmospheric plasma processing setup. 1 - barrier discharge block; 2 - flow of active particles; 3 – substrate; 4 - moving system; 5 - gas feed regulation system; 6 - gas cylinder; 7 – module for measuring the discharge parameters; 8 - power supply

3.2. EXPERIMENTAL RESULTS

Fig.4 exhibits the dependencies of transverse distribution of band shaped ion stream density on residence time T_r (in assumption of uniform longitudinal distribution of ion stream current density). one can see from the figure that:

- in a drift process cross section of ion flow increases approximately twice;
- increase of residence time T_r from 0.013 s to 0.12 s results in the current density increase approximately twice, which is in a good correlation with the calculated dependencies of Ar_2^+ concentrations on T_r (see Fig.1).

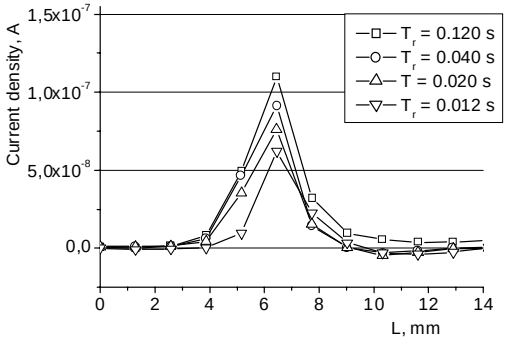

Fig.4. Dependencies ofion current density distributions over the substrate surface on residence time T_r at W_d = 0.9 W/cc

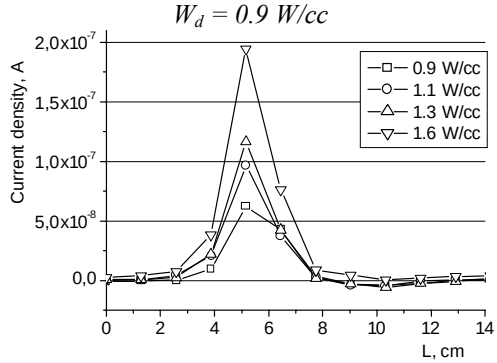

Fig.5. Dependencies of ion current density distributions over the substrate surface on specific power W_d at residence time T_r = 0.013 s

The measurements have also shown that ion current density increases practically linearly with a growth of specific power in the discharge, at that half-width of the current density distribution remains practically the same (see Figs.5,6).

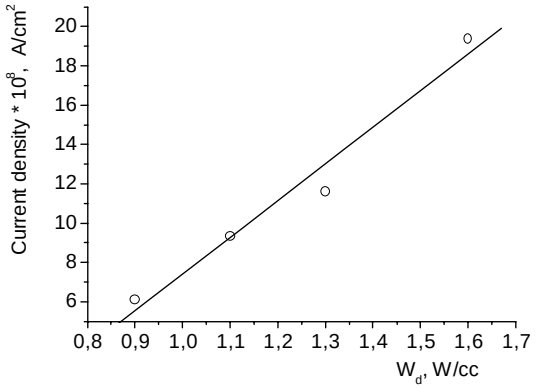

Fig.6. Dependence of maximum ion current density onto the substrate on specific power in the discharge W_d at T_r = 0.013 s

For estimation of density of ions coming to the substrate, measurements of potentials in a space between output slit of the discharge and the substrate have been accomplished. It is determined that, depending on the discharge parameters (specific power, purge rate), potential fall in a gap between the discharge and the substarte varies in a range of ≈ (200…400) V. Then, with the following assumptions: 1) main mechanism of carryiong-out the ions from the discharge onto the substrate is a drift in electric field; 2) mobility of Ar_2^+ ions exceeds that of Ar^+ ions approximately twice (analogously to the difference in mobility of molecular ions He_2^+, Ne_2^+ and atomic ions He^+, Ne^+), that is $\mu_I \approx 4$ cm^2·atm/V·s [11,12], we obtain ion density of order of 10^8 cm^{-3}.

Thus, the results of both calculations and experimental investigations show that the main role in modification of polyimide substrates, resulting in liquid crystal alignment, is performed by molecular ions Ar_2^+.

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КИНЕТИКА Ar_2^+, Ar_2^*И Ar^* В ОБЪЕМНОМ БАРЬЕРНОМ РАЗРЯДЕ НА АРГОНЕ

В.В. Циолко, В.Ю. Баженов, Л.В. Дяченко, А.И. Щедрин, А.Г. Калюжная

При помощи компьютерного моделирования показано, что наибольшую концентрацию в объемном барьерном разряде на аргоне имеют частицы Ar_2^+, Ar_2^* и Ar^*. Найдены зависимости концентраций этих частиц от параметров разряда. Экспериментально установлены характеристики потоков ионов Ar_2^+ из плазмы разряда.

КІНЕТИКА Ar_2^+, Ar_2^* ТА Ar^* В ОБ'ЄМНОМУ БАР'ЄРНОМУ РОЗРЯДІ НА АРГОНІ

В.В. Ціолко, В.Ю. Баженов, Л.В. Дяченко, А.І. Щедрін, Г.Г. Калюжна

За допомогою комп'ютерного моделювання показано, що найбільшу концентрацію в об'ємному бар'єрному розряді на аргоні мають частки Ar_2^+, Ar_2^* та Ar^*. Знайдено залежності концентрацій цих часток від параметрів розряду. Експериментально встановлено характеристики потоків іонів Ar_2^+ з плазми розряду.