A DIFFUSION MODE OF THE HOMOGENEOUS DISCHARGE AT PRESENCE OF TWO KINDS OF THE BASIC IONS

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Abstract
The electric field strength, the total ion fluxes, and gas and wall temperatures were measured in the positive column of a d.c. discharge at a pressure $P = 200$ Pa and a discharge current $I_d = 50$ mA for $x$Ar-$H_2$ mixture ($x = 0$-$100$ %). The approach for description of kinetic model, which takes into account a presence of two kinds of the basics ions, was offered. This model was verified on an example of $x$Ar-$H_2$ plasma. It was revealed that the reactions of associative ionization play a key role in the mechanism of ionization. According to the model the basic ions were the $^+$ and $^+$ ones.

1. Introduction

The plasma systems are widely used for realization of processes of plasma chemical etching and modification. The development of a priori methods for simulation of fluxes of particles onto a processable surface and external plasma parameters (pressure, discharge current, gas composition) is very current and interest. Such model for an Ar-$H_2$ mixture is presented here.

2. Experimental details

The discharge was generated in a glass (molybdenum sealing) cylindrical reactor with 15-mm inner diameter at gas pressure $p = 200$ Pa, flow rate $Q \sim 1.7$ cm$^3$/s (STP) and discharge current $I_d = 50$ mA. An initial composition of Ar-$H_2$ mixture was set by the changing of the gas flow velocity balance under the fixed pressure. Such parameters as electric field strength, gas temperatures and wall temperatures were measured.

The flux density of positive ions on a wall was derived from volt-ampere characteristic (VAC) of a flat probe. The treatment of an ion part of the probe characteristic was carried out as follows. The dependence of an ion current $i_+^*$ on probe potential $V$ looks like [1]:

$$i_+ = \frac{1}{4} n_e e V S \frac{2}{\sqrt{\pi}} (1-\eta)^n,$$

(1)
where \( V_i = \left( \frac{k \cdot T_e}{M_+} \right)^{\frac{1}{2}}, \eta = \frac{e \cdot V}{k \cdot T_i} \); \( T_e, T_i \) are electron and ion temperatures accordingly; \( S \) is a probe surface area; \( n \) is an exponent, which, according to the various theories of an ion current, can be within from 0.5 to 1.5. The VAC was measured up to large negative potentials versus plasma one (= 100). In this case its form was depended on ion current only. The VAC was fitted by expression (1) with subsequent extrapolation to floating potential (a wall potential) \( V_f \). The \( \Gamma_e \) flux density of positive ions was as \( \Gamma_e = \frac{i_+(V_f)}{S \cdot e} \). The casual error \( \Gamma_e \) did not exceed \( \pm 20\% \) (3 measurements, fiducial probability 0.9).

3. Setting of a problem

Let plasma consists of electrons and two kinds of ions. A mode of the discharge is diffusive. Geometry is cylindrical. The fluxes of electrons and ions are described by the following equations:

\[
\begin{align*}
\Gamma_e &= -D_e \nabla n_e - \mu_e n_e E_r, \\
\Gamma_i^+ &= -D_i^+ \nabla n_i^+ + \mu_i^+ n_i^+ E_r, \\
\Gamma_2^+ &= -D_2^+ \nabla n_2^+ + \mu_2^+ n_2^+ E_r,
\end{align*}
\]

where \( D_e, D_i^+, D_2^+ \) - diffusion coefficients; \( n_e, n_i^+, n_2^+ \) - concentrations; \( \mu_e, \mu_i^+, \mu_2^+ \) - mobility of electrons and ions; \( E_r \) - an electrical field strength of volume charge.

From a condition that these fluxes are equal it possible to obtain the \( E_x \) value. Taking into account that \( n_2^+ = n_e - n_i^+ \) we obtain:

\[
\Gamma_e \left( \frac{\mu_i^+ - \mu_2^+}{\mu_e} \right) \nabla n_e + \left( \frac{\mu_i^+}{\mu_e} D_e \nabla n_e - (D_2^+ - D_e) \nabla n_i^+ + \left( D_1^+ - D_2^+ \right) \nabla \alpha n_e,
\]

where \( \alpha = \frac{n_i^+}{n_e} \). Using definitions \( \epsilon_x = D_e / \mu_e, \varphi = \mu_2^+ / \mu_i^+ \), \( D_\alpha = \mu_i^+ \epsilon_x \) and taking into account that \( \mu_i^+, \mu_2^+ \ll \mu_e \) and \( D_1^+, D_2^+ \ll D_e \) we obtain that:

\[
\lambda_e = \left( 1 - \varphi \right) \epsilon_x \nabla \alpha, \quad \lambda_e = \frac{i_+(V_f)}{S \cdot e}.
\]
Doing the same for ions of the 1st sort we obtain:

$$\Gamma_1^+ = -D_\lambda^+ \alpha \nabla n_e.$$  \hspace{1cm} (4)

4. Numeric calculation details

As an example we shall consider a Ar-H2 plasma (x = 0-99 %). The basic ions of this plasma are the $^+\text{H}$ and $^3\text{H}$ ions. Let $\mu_1^+$ is mobility of the $^+\text{H}$ ion, $\mu_3^+$ is mobility of the $^3\text{H}$ ion, $\alpha = [H^+)/n_e]$. Thus we have the (3), (4) equations for fluxes of electrons and ions and list of reactions which are represented in the table 1.

The continuity equation for flux density of electrons neglecting an electron-ion recombination and other bulk processes of electron charge neutralization can be write as the following:

$$\frac{1}{r} \frac{d}{dr} \left[ r \left[ (1 - \Psi) \alpha \phi \right] \dot{\Gamma}_\lambda^e \right] + \frac{d n_e}{dr} + \left[ k_1 \text{H} + k_2 \text{H}^+ + k_3 \text{Ar} + k_4 \text{Ar}^+ + k_5 \text{H}_2 + k_6 \text{H}^+ \text{H}_2 + k_7 \text{Ar}^+ \right] n_e + k_8 \text{H}^+ \text{H}_2 + k_9 \text{Ar}^+ = 0$$

where $k_i$ is rate coefficient for $i$th reaction, $i$ is a number of reaction from the list (table 1).

Table I. Reactions of formation and conversion of the charged particles [2]

| For $\text{e}$ | 1. $e + \text{H} \rightarrow \text{H}^+ + e + e$ | $k = f(E/N_0)$ |
| 2. $e + \text{H}^+ \rightarrow \text{H}^+ + e + e$ | $k = f(E/N_0)$ |
| 3. $e + \text{H}_2 \rightarrow \text{H}_2^+ + e + e$ | $k = f(E/N_0)$ |
| 4. $e + \text{Ar} \rightarrow \text{Ar}^+ + e + e$ | $k = f(E/N_0)$ |
| 5. $e + \text{Ar}^+ \rightarrow \text{Ar}^+ + e + e$ | $k = f(E/N_0)$ |
| 6. $\text{H}^+ + \text{H}_2 \rightarrow \text{H}_2^+ + e$ | $\sigma_{pe} = 5 \times 10^{-15} \text{ cm}^2$ |
| 7. $\text{Ar}^+ + \text{Ar}^+ \rightarrow \text{Ar}^+ + \text{Ar} + e$ | $k = 1 \times 10^9 \text{ cm}^3/\text{s}$ |

| For $\text{H}^+$ | 1. $e + \text{H} \rightarrow \text{H}^+ + e + e$ | $k = f(E/N_0)$ |
| 2. $e + \text{H}^+ \rightarrow \text{H}^+ + e + e$ | $k = f(E/N_0)$ |
| 8. $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_2^+ + \text{H} + \text{H}_2$ | $k = (1-20) \times 10^{-10} \text{ cm}^3/\text{s}$ |
| 9. $\text{H}^+ + \text{H}_2 + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}_2$ | $k = 3.1 \times 10^{-9} \text{ cm}^6/\text{s}$ |
| 3. $e + \text{H}_2 \rightarrow \text{H}_2^+ + e + e$ | $k = f(E/N_0)$ |

| For $\text{H}_2^+$ | 8. $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_2^+ + \text{H} + \text{H}_2$ | $k = (1-20) \times 10^{-10} \text{ cm}^3/\text{s}$ |
| 10. $\text{H}_2 + \text{Ar}^+ \rightarrow \text{H}_2^+ + \text{Ar}$ | $k = 3 \times 10^{-10} \text{ cm}^3/\text{s}$ |
| 11. $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ | $k = (2-20) \times 10^{-10} \text{ cm}^3/\text{s}$ |
| 12. $\text{H}_2^+ + \text{Ar} \rightarrow \text{H} + \text{ArH}^+$ | $k = (5-30) \times 10^{-10} \text{ cm}^3/\text{s}$ |

| For $\text{Ar}^+$ | 4. $e + \text{Ar} \rightarrow \text{Ar}^+ + e + e$ | $k = f(E/N_0)$ |
| 5. $e + \text{Ar}^+ \rightarrow \text{Ar}^+ + e + e$ | $k = f(E/N_0)$ |
| 7. $\text{Ar}^+ + \text{Ar}^+ \rightarrow \text{Ar}^+ + \text{Ar} + e$ | $k = 1 \times 10^9 \text{ cm}^3/\text{s}$ |
| 10. $\text{H}_2 + \text{Ar}^+ \rightarrow \text{H}_2^+ + \text{Ar}$ | $k = 3 \times 10^{-10} \text{ cm}^3/\text{s}$ |

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\[ 13. \quad \text{Ar}^+ + \text{Ar} + \text{Ar} \rightarrow \text{Ar}_2^+ + \text{Ar}^+ \quad k = (8.39) \times 10^{-32} \text{cm}^6/\text{s} \]

\[ 14. \quad \text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} \quad k = 7.4 \times 10^{-10} \text{cm}^3/\text{s} \]

where \( \text{H}^+, \text{Ar}^+ \) - exited states of atoms of hydrogen \( \text{H}(2S, 2P) \) and of argon \( \text{Ar}(3P_2, 3P_1, 3P_0, 3P_1) \).

Inputting the following variables and definitions \( n_e/n_{e_0} = g_e \); \( r/R = x ; \ y_{e_0} = \frac{[\text{H}]}{N_0} \)

(and in the same way for each of components); \( y_{e_0} = n_{e_0}/N_0 \); \( \mu_{10}^+ = \mu_{10}^+ N_0 \);

\[ \lambda = \left[ k_1 y_{e_0} + k_2 y_{e_0} + k_3 y_{e_0} + k_4 y_{\text{Ar}_2} + k_5 y_{\text{Ar}} \right] \frac{(N_0 R)^2}{\varepsilon_x \mu_{10}}; \]

\[ P = \frac{k_6 y_{e_0} y_{e_0} + k_7 \left( y_{\text{Ar}_2} \right)^2}{y_{e_0}} \frac{(N_0 R)^2}{\varepsilon_x \mu_{10}}, \]

we obtain

\[ \frac{1}{x} \frac{d}{dx} x \left[ (1 - \varphi) \alpha + \varphi \right] \frac{dg_e}{dx} + \lambda g_e + P = 0. \]

In such a manner it is possible to obtain the continuity equation for \( \text{H}^+ \) ion flux density

\[ \frac{1}{x} \frac{d}{dx} x \alpha \frac{dg_e}{dx} + Q g_e + P_1 = 0, \]

where \( Q = QQ \frac{(N_0 R)^2}{\varepsilon_x \mu_{10}} \), and \( P_1 = PP \frac{(N_0 R)^2}{y_{e_0} \varepsilon_x \mu_{10}} \), QQ is total factor of ionization in reactions with participation of electrons and PP is total factor of ionization in reaction without participation of electrons. As the result we have system of the equations:

\[ \begin{cases} 
\frac{1}{x} \frac{d}{dx} x \left[ (1 - \varphi) \alpha + \varphi \right] \frac{dg_e}{dx} + \lambda g_e + P = 0 \\
\frac{1}{x} \frac{d}{dx} x \alpha \frac{dg_e}{dx} + Q g_e + P_1 = 0 \times (1 - \varphi) 
\end{cases} \]

Subtracting the second equation from the first one we obtain:

\[ \frac{a^2 g_e}{dx^2} + \frac{1}{x} \frac{dg_e}{dx} + \left[ \frac{\lambda - Q (1 - \varphi)}{\varphi} \right] g_e + \left[ \frac{P - P_1 (1 - \varphi)}{\varphi} \right] = 0 \]

or inputting the definition \( \lambda^2 = \frac{\lambda - Q (1 - \varphi)}{\varphi} \):

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\[
\frac{d^2 g_e}{dz^2} + \frac{1}{z} \frac{dg_e}{dz} + g_e + \frac{[P - Pl(1 - \varphi)]}{\lambda^2 \varphi} = 0.
\]

Solution of this equation with \( g'_e(0) = 0, \ g_e(0) = 1, \) and \( g_e(1) = 0 \) boundary conditions is

\[
g_e(x) = \left( \frac{P - Pl(1 - \varphi)}{\lambda^2 \varphi} + 1 \right) J_0(\lambda, x) - \frac{P - Pl(1 - \varphi)}{\lambda^2 \varphi},
\]

where the \( \lambda_* \) (eigenvalue) has to satisfy to a condition:

\[
\frac{P - Pl(1 - \varphi)}{\lambda^2 \varphi} = \left( \frac{P - Pl(1 - \varphi)}{\lambda^2 \varphi} + 1 \right) J_0(\lambda_*).
\]

For the Schottky diffusion theory when \( 1 \to 0 \) \( \lambda_* \) is equal 2.405. In such a manner it is possible to solve the equations for the each of ion sorts.

Last expression actually defines the stationary value of the reduced electrical field \( E/N_0 \) in an implicit form, which is necessary for maintenance of the discharge. This value can be obtained by means the combine solution the Boltzmann equation and equations of chemical kinetics for atoms and molecules. The appropriate data on cross-sections of elastic and inelastic processes were taken from [3, 4] for hydrogen from [5] for argon and the rate coefficients were taken from [6-11].

5. Main results

The values of the reduced electric field and of the ion density fluxes calculated according to the model and experimentally obtained are presented in figure 1.
Figure 1. The reduced electric field strength (a) and the ion density flux on a wall (b) as a function of Ar-H$_2$ plasma composition. Pressure is 200 Pa, discharge current is 50 mA, R = 0.75 cm. The points are experimental data, the curves are calculated data.

With increasing the Ar percentage the electric field strength is reduced (fig. 1a). For maintenance of a discharge current the increase of the electron density or of the drift velocity is necessary. Notice that the drift velocity is actually reduced. The increase of the electron density is possible as a result of increase of ionization rate (for example, at our conditions we have $n_e(x\text{Ar})$: 0%-2.2×10$^{10}$, 20%-2.5×10$^{10}$, 40%-2.7×10$^{10}$, 60%-3.0×10$^{10}$, 80%-4.0×10$^{10}$, 90%-5.6×10$^{10}$, 99%-1.2×10$^{11}$ cm$^{-3}$). However according to our calculations the increase of the argon content in the mixture results in a depletion of the eedf by fast electrons and hence in a reduction of high-threshold process rates, in particular, of electron-impact ionization rate. Partially, the decrease of ionization rate is compensated by reduction of ion mobilities (fig.1b). However when the argon content is more than 20 % according to experiment, the total ionization rate is increased. This increase can be explained only by existence of additional channels of ionization namely associative ionization (reaction 6 in table. 1). The rate of this reaction is limited to formation rate of the exited hydrogen atoms. In H$_2$ plasma or in xAr-H$_2$ plasma where x is up to 20 %, for the reasons mentioned before, the formation rate of the exited atoms is not great and the ionization rate is decreased. However, as the argon...
content is increased the formation rate grows as a result of additional reaction $H + Ar^* \rightarrow H^* + Ar$ [2]. As result the total ionization rate is increased.

The offered approach allows to calculate both fluxes of ions and fluxes of another particles onto a surface to estimate a possibility of ion-chemical processes occurring on plasma – wall boundary.

References


