MODELLING OF THE PROCESSES INVOLVED IN THE TEMPORAL EVOLUTION OF THE AR METAStABLE ATOMS DENSITY IN THE AFTERGLOW OF HIGH VOLTAGE PULSED DISCHARGES*

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The temporal distribution of the concentration of argon metastable atoms in the afterglow of a high voltage pulsed hollow cathode discharge plasma is determined by numerical modeling using the drift diffusion approximation method. The main metastable – metastable collision process considered in this simulations is ArM + ArM → Ar+ + Ar + e with the reaction rate k = 6.4 × 10^-16 m^3/s. The concentration of argon metastables in the 2–36 µs temporal afterglow is in the range of 1.87–0.33 × 10^19 1/m^3.

The numerical results are in good agreement with the experimental one obtained by absorption spectroscopy in the afterglow of neon voltage pulsed hollow cathode discharges.

1. INTRODUCTION

The temporal variation of the ArM density distribution in the afterglow of the pulsed discharges can be very useful in the analytical investigation systems like GD-OES and GD-MS, in which the energy transfers of the various active species present in the plasma, electrons, ions and neutrals are central for the excitation and ionization of the analyte species. In this context, it is very important to know the processes involved in the afterglow plasmas and to estimate its temporal distribution.

In this paper, using the numerical simulation of the plasma processes we predicted the temporal evolution of the ArM atoms density in the afterglow of a pulsed hollow cathode discharge. We used the CFD-ACE+ software developed by ESI Group. The numerical results are based on the solution of the 3 moment equations derived from Boltzmann equation with the assumption of Maxwellian energy distribution for electron and heavy (ions and neutrals) particle transport, in conjunction with the electric field solved from the Poisson equation. The electrons


and ions number densities are solved using the drift-diffusion approximation for electrons and ions fluxes derived from electron respectively ions momentum equations. The mass and momentum equations solved for neutral and excited species are used for the calculation of the argon and metastable argon atoms densities.

2. RESULTS AND DISCUSSIONS

2.1. THE DRIFT-DIFFUSION APPROXIMATION EQUATIONS

The drift-diffusion equations are “reduced” equations derived from the well-known fluid equations (i.e., mass and momentum conservation laws) for ions and electrons under the assumption of high collision frequencies with the neutrals. The momentum-conservation law for electrons may be written as

\[
m_e n_e \left( \frac{\partial \tilde{v}_e}{\partial t} + \tilde{v}_e \cdot \nabla \tilde{v}_e \right) = -\nabla p_e - en_e \tilde{E} - m_e n_e \nu_e \tilde{v}_e
\]

where \( m_e \) is the electron mass, \( n_e \) is the electron density, \( \nu_e \) is the electron “fluid” (drift) velocity, \( p_e \) is the electron fluid pressure, \( \tilde{E} \) is the electric field, and \( \nu_e \) is the electron collision frequency at which the plasma electrons collide with the neutral gas molecules. Electron-ion collisions are negligible compared with electron-neutral collisions. If the left-hand side term (i.e., the inertia term) of Equation (1) is negligibly small, we obtain

\[
\tilde{v}_e = \frac{-\nabla p_e}{m_e n_e \nu_e} - \frac{e \tilde{E}}{m_e \nu_e}
\]

Equation (2) states that \( \tilde{v}_e \) is determined by the balance among the pressure force, electrostatic force, and the drag force.

The electron flux \( \tilde{\Gamma}_e = n_e \tilde{v}_e \) is given by

\[
\tilde{\Gamma}_e = -n_e \mu_e \tilde{E} - \nabla (D_e n_e)
\]

where \( \mu_e = e/m_e \nu_e \) is the electron mobility and \( D_e = k_B T_e/m_e \nu_e \) is the electron diffusivity. The equation of state \( p_e = n_e k_B T_e \) and the Einstein relation \( D_e/\mu_e = k_B T_e/e \) are also used. Similarly, the ion drift velocity \( \tilde{v}_i \) and ion flux \( \tilde{\Gamma}_i = n_i \tilde{v}_i \) can be expressed as

\[
\tilde{\Gamma}_i = -n_i \mu_i \tilde{E} - \nabla (D_i n_i)
\]

where \( \mu_i = Z_i e/m_i \nu_i \) is the ion mobility, \( Z_i e \) and \( \nu_i \) are the ion charge and ion-neutral collision frequencies and \( D_i = k_B T_i/m_i \nu_i \) is the ion diffusivity.
The equations for the electron and ion densities, \( n_e \) and \( n_i \) and the electric field \( \vec{E} \) are given by the mass conservation equations and Poisson’s equation:

\[
\frac{\partial n_e}{\partial t} + \nabla \cdot \vec{\Gamma}_e = S_e, \quad \frac{\partial n_i}{\partial t} + \nabla \cdot \vec{\Gamma}_i = S_i
\]

\[
\Delta \Phi = -\frac{e}{\epsilon_0} \left( Z_n \left( n_i - n_e \right) \right)
\]

In above equations, \( S_e \) and \( S_i \) denote the source terms for the electrons and ions produced or consumed in chemical reactions. Sources and sinks of electrons and ions in the bulk plasma are usually due to ionization, recombination, electron attachment, and charge exchange. In the case of electropositive discharges with single-ion species, we may write \( S_e = S_i = k_i n_e n_u - k_r n_i n_e \), where \( k_i \) and \( k_r \) are ionization and recombination rate coefficients.

In Poisson’s equation (6), \( \Phi \) denotes the electrostatic potential, \( \vec{E} = -\nabla \Phi \). Equations (3)-(5) represent the drift-diffusion equations for the system. They are solved together with Poisson equation.

These equations are coupled with the mass and momentum equations written for neutral and excited species and solved together by the CFD-ACE+ multi-component software code [1, 2].

The rate coefficients are given by the Arrhenius relation, i.e. [1, 2]:

\[
k_i = A_i \exp \left( -\frac{E}{k_B T} \right), \quad \text{where } A_i \text{ is a constant, } E \text{ is the threshold energy}
\]

and \( T \) the process temperature. For argon, \( A_i = 1 \times 10^{-14} \text{ m}^3/\text{s} \).

At low pressure, the kinetic processes for the afterglow of the Ar pulsed discharges are mainly those of \( \text{Ar}^M \) atoms destruction. The list of processes with the specific reaction rates considered in these calculations is given in Table 1.

### 2.2. Boundary Conditions

The potential \( \Phi \) at the cathode and wall boundaries is set to zero, and the applied DC voltage at the anode is about 30 V. The boundary conditions for electron and ion fluxes can be written as

\[
\Gamma_{e,a} = \frac{1}{4} n_e v_{e,th} - \gamma \sum (q_i \Gamma_{i,a}) \quad \Gamma_{e,a} = n_e \mu_e E
\]

where \( v_{e,th} = (8 k_B T_e / \pi m_e)^{1/2} \)

is the electron thermal velocity, \( \gamma \) is the secondary electron emission coefficient. For these simulations we set \( \gamma = 0 \). The electron and ion fluxes \( \Gamma_{e,a}, \Gamma_{i,a} \) are normal and directed toward the walls. The total surface charge density on the dielectric
surface is zero. The reactions considered at the surfaces are: $\text{Ar}^+ \rightarrow \text{Ar}$, $\text{Ar}^M \rightarrow \text{Ar}$, and $\text{Ar}^* \rightarrow \text{Ar}$.

### 2.3. INITIAL CONDITIONS

In the CFD-ACE$^+$ software it is necessary to define the initial conditions: the temperature ($T = 300$ K) the gas pressure ($p = 500$ Pa) the electric potential ($V = 0$ V) and the electron temperature ($T_e = 0.4$ eV). The gas components were defined function of the considered temporal afterglow moment as can be observed in Table 2.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ar} + e = \text{Ar} + e$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ar}^M + e = \text{Ar}^* + e$</td>
<td>$k = 2 \times 10^{-13} \text{ m}^3/\text{s}$</td>
</tr>
<tr>
<td>$\text{Ar}^* + e = \text{Ar} + e$</td>
<td>$k = 1 \times 10^{-13} \text{ m}^3/\text{s}$</td>
</tr>
<tr>
<td>$\text{Ar}^M + \text{Ar} = \text{Ar}^* + \text{Ar}$</td>
<td>$k = 3 \times 10^{-13} \text{ m}^3/\text{s}$</td>
</tr>
<tr>
<td>$\text{Ar}^M + \text{Ar}^M = \text{Ar}^+ + \text{Ar} + e$</td>
<td>$k = 6.4 \times 10^{-16} \text{ m}^3/\text{s}$</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Table 2</th>
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<tbody>
<tr>
<td>Ar (%)</td>
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<td>----------------</td>
</tr>
<tr>
<td>99.983</td>
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<td>99.9835</td>
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### 2.4. GEOMETRICAL MODEL DESCRIPTION

Figure 1a depicts the computational domain of the hollow cathode discharge. A scheme of a similar discharge tube is presented in [3]. In the axysimetrical model presented here are considered only the walls in contact with plasma, Fig. 1b, the x axis being the symmetry axis (i-j-k-l). Due to symmetry, only half of the geometry is simulated. The boundary a-b-c-d is the metallic surface with a 30 V applied potential, e-f and g-h represent the metallic grounded electrode and d-e and a-h domains represent dielectric walls. The length of the boundary a-d is about 10 mm and of a-i boundary is about 4 mm. The f-g line represents a hole of 2 mm in the grounded electrode.
2.5. NUMERICAL SCHEME

The finite volume numerical scheme (CFD-ACE⁺) is used to obtain the discretized equations based on a upwind scheme. The main variables such as species densities, electrons density, and potential are obtained iteratively. Implicit time marching scheme is used with time step size equal to $1 \times 10^{-8}$s. The time marching calculations are continued until the variation of that plasma variables is within $1 \times 10^{-5}$% of the value of that plasma variable from the previous time step. The solutions are then considered to be steady. For the geometry shown in Fig. 1, 130 × 60 meshes are placed in x and y directions. It is a symmetric model with a structured grid.

2.6. SIMULATIONS RESULTS

In figure below is presented the spatial distribution of the Ar$^M$ and Ar$^+$ density inside the hollow cathode. The temporal evolution of the Ar$^M$ density distribution in the hollow cathode obtained in the afterglow plasma is presented in Fig 3. Using the experimental set-up presented in [3], with a conventional pulsed spectral source and an original experimental supply and detection system has been estimated the temporal distribution density of Ne$^M$ atoms (measured for $^{3}\text{P}_2 - 2\text{P}_3$ transition at 597.4 nm) in a hollow cathode pulsed discharge afterglow plasma. The simulation results are in good agreement with the experimental one with an error around ±10 %.

Experimentally, the similarities between the Ar$^M$ and Ne$^M$ density distribution in the afterglow of pulsed discharges have already been investigated in [4]. The implication of Ne for GD-MS technique was also emphasised in [5]. We compared the simulation results for Ar with the experimental results for Ne in order to evidence the similarities between them and the possibility of using the neon as working gas for GD-MS technique.
Fig. 2 – Spatial distribution of the ArM, Ar\(^+\) densities inside the hollow cathode at \(t = 24 \mu s\).

Fig. 3 – The temporal distribution of the ArM and NeM in the afterglow plasma.
3. CONCLUSIONS

In this paper, by numerical modeling using the drift-diffusion approximation method we established the temporal and spatial distribution of Ar$^M$ density in the afterglow of a high voltage pulsed hollow cathode discharge. These numerical results are in good agreement with experimental results obtained for neon.

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4. REFERENCES