Influence of small additives of nitrogen in 1D-modeling of non-uniform microwave discharge of low pressure in hydrogen

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Abstract. A one-dimensional simulation for studying the influence of small additives of nitrogen to the parameters and structure of non-uniform microwave discharge in hydrogen at pressure of 1 Torr has been performed. It is shown that the profiles of the electron density and microwave field are affected by changes both in the EEDF and in the ionic constituent of the plasma. The EEDF influences in a spherical region of the discharge (away from the central electrode). The addition of nitrogen increases the mobility of electrons and leads to reduction of size of the plasma formation. The change in the ion components of plasma (N$_2$H$^+$ becomes the main ion) affects the structure of the plasma near the surface of the electrode.

1. Introduction
It has been shown in a number of works that even a small amount of gas additives to the plasma-forming gas can greatly change the properties of plasma. In particular, the gas additives may influence the processes of ionization and excitation of particles and therefore the electric field, which in the self-sustained plasma is determined by the balance of charged particles. In works [1, 2] both experimentally (by means of optical emission spectroscopy) and numerical 1D and 2D modeling the effect of small additions of hydrogen on the electrode microwave discharge at low pressure in nitrogen has been investigated. It is shown that the non-uniformity of discharge leads to the fact that the nature of the influence of hydrogen additives (0-30% of the flow rate) on the intensity of the radiation bands of nitrogen is different in different parts of the discharge. There is also a different influence of hydrogen on the vibrational distribution of nitrogen molecules in $^2\Sigma_u^+$ state in different parts of the discharge. Raising the level of hydrogen addition changes the ion composition of plasma: the main ion $N_2^+$ in the spherical region is replaced by a lighter ion $N_2H^+$. This, according to quasi-static one-dimensional modeling, leads to an increase of the microwave field in the spherical part of the discharge and change of the emission intensity of second positive system of nitrogen. Results of 2D modeling [1] basically coincide with the results of the 1D simulation [2]. Thus, it is shown that the main effect of hydrogen additives on parameters of the nitrogen discharge is associated with changes in the ion composition of plasma. In this work we investigated the influence of small additives of nitrogen in the hydrogen discharge. A similar problem has been solved in [3], where the authors on the basis of 0-dimensional simulation studied the influence of changes of the EEDF on the parameters of the hydrogen discharge due to the addition of nitrogen. In this paper, in the framework of 1D model of inhomogeneous electrode microwave discharge in hydrogen, along with the impact of changes in the
EEDF we examine the influence of changes in ion composition due to the introduction of small amount of nitrogen (up to 5 vol.%).

2. Model
Here we use a self-consistent quasi-static model of the microwave discharge in the electrode system with spherical symmetry, which was previously described in detail in [4]. The model includes the equation for the electric field strength in the quasi-static approximation, Poisson equation and balance equations for charged and neutral particles. The contribution of processes involving vibrationally excited molecules in the ground state is carried out, using the well-known analytical expression for the vibrational distribution of the molecules, obtained in the diffusion approximation [5]. The EEDF is determined from the solution of the homogeneous stationary Boltzmann equation.

The processes of direct, stepwise and associative ionization, dissociation, recombination of charged and neutral particles in the bulk and on the wall, ion-molecular reactions, excitation and de-excitation of molecules are taken into account. The balance equations for nitrogen plasma describe the kinetics of charged (e, H⁺, H₂⁺, N⁺, N₂⁺, N⁺, N₂⁺, NH⁺), and neutral (H, H(2S,2P), H(3S,3P,3D), N(3Σ_u), N₂(B'Π_g), N₂(C'Π_u), N₂(a'Σ_u), N(4S), N(3D), N(3P), NH) particles. We use the kinetic schemes for hydrogen and nitrogen, developed in our earlier works [4, 6, 7]. The processes, which include interaction of particles of both gases, are shown in Table 1. The kinetic model includes the processes of quenching of metastables of nitrogen molecules by hydrogen and the reaction of conversion of hydrogen ions into the ion N₂H⁺. The plasma is simulated at a gas pressure of 1 Torr, the microwave frequency of 2.45 GHz and gas temperature of 600 K.

Table 1 Processes, which include interaction of particles of both gases.

| Processes | K, см³·сек⁻¹ |
|-----------|-------------|
| 1 \( N_2^+ + H_2 \Rightarrow N_2H^+ + H \) | \( K = 1.7 \cdot 10^{-9} \) [8] |
| 2 \( N_4^+ + H_2 \Rightarrow N_2H^+ + H + N_2 \) | \( K = 1.1 \cdot 10^{-8} \) [8] |
| 3 \( N_2H^+ + e \Rightarrow H + N_2 + e \) | \( K = 3.7 \cdot 10^{-8} \) [9, 10] |
| 4 \( H_2^+ + N_2 \Rightarrow N_2H^+ + H \) | \( K = 1.95 \cdot 10^{-9} \) [8, 11] |
| 5 \( H_2^+ + N_2 \Rightarrow N_2H^+ + H_2 \) | \( K = 1.8 \cdot 10^{-9} \) [9, 12] |
| 6 \( N_2(3Σ_u^+) + H \Rightarrow N_2 + H \) | \( K = 5.0 \cdot 10^{-11} \) [9, 13] |
| 7 \( N_2(3Σ_u^+) + H_2 \Rightarrow N_2 + H + H \) | \( K = 2.0 \cdot 10^{-10} \exp(-3500/T_g) \) [14] |
| 8 \( N_2(B'Π_g) + H_2 \Rightarrow N_2(3Σ_u^+) + H_2 \) | \( K = 2.5 \cdot 10^{-11} \) [8, 15] |
| 9 \( N_2(a'Σ_u^-) + H \Rightarrow N_2 + H \) | \( K = 1.5 \cdot 10^{-11} \) [9] |
| 10 \( N_2(a'Σ_u^-) + H_2 \Rightarrow N_2 + H + H \) | \( K = 2.6 \cdot 10^{-11} \) [9] |
| 11 \( N(3D) + H_2 \Rightarrow H + NH \) | \( K = 2.3 \cdot 10^{-12} \) [9, 15] |
| 12 \( N(2P) + H_2 \Rightarrow H + NH \) | \( K = 2.5 \cdot 10^{-14} \) [9, 16] |
| 13 \( H + NH \Rightarrow H + N_2 \) | \( K = 5.0 \cdot 10^{-11} \) [9, 17] |

3. Results
The results of the calculations are presented in figures 1-3. Figure 1 shows profiles of the electron density and microwave fields for different percentage of additives of nitrogen.

In the near-electrode region with a strong microwave field one finds small (~0.5%) increase in the values of \( n_e \) for cases with nitrogen additives compared to \( n_e \) for pure hydrogen. In a spherical plasma
region (i.e. extended region adjacent to the narrow near-electrode region of strong microwave field, where the value of the microwave field is about 100 V/cm, see Fig.1b) the values of \( n_e \) for cases with nitrogen additives on the contrary are lower than \( n_e \) for pure hydrogen plasma. As for the microwave field, it is growing in the whole region of the plasma in the case of additives of nitrogen (Fig.1 b).

Several computational tests have been performed to investigate changes in discharge characteristics, dealt with the introduction of additives of nitrogen.

When making nitrogen additions to the hydrogen discharge, the ion \( \text{N}_2\text{H}^+ \) becomes the main ion (Fig. 2). This ion is much heavier and thus less mobile than the ion \( \text{H}_3^+ \), which is the main ion in the discharge in pure \( \text{H}_2 \). This can cause a profile change of the electron density and also change of other plasma properties.

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**Fig. 1.** Radial profiles of the electron density \( n_e \) (a) and microwave field (b). Blue lines – discharge of pure hydrogen; red lines – with 5% nitrogen added; green lines – with 20% nitrogen added. I – region of strong microwave field, II – spherical region of the discharge, \( n_e = 7 \times 10^{10} \text{ cm}^{-3} \) – critical value of plasma density. The inset A in Fig.1b shows the region of strong microwave field in an enlarged scale.

**Fig. 2.** Radial profiles of ion density for a discharge in hydrogen with 5% nitrogen added: blue line - ion \( \text{N}_2\text{H}^+ \); the dark green line is the ion \( \text{H}_3^+ \); blue line - ion \( \text{H}_2^+ \); pink line - ion \( \text{N}_4^+ \).
To confirm this hypothesis, we made calculations for the mixture with the addition of 5% nitrogen, but with a kinetic scheme which excludes the appearance of the ion N$_2$H$^+$. The corresponding profile is shown by the horizontal orange ellipses in figure 3. In the region of strong fields the electron density profile coincides with the profile of a $n_e$ for pure hydrogen discharge, while the rest of the profile coincides with the profile calculated for a 5% additive without changes in the kinetic scheme. This test shows that the presence of the ion N$_2$H$^+$ has an effect only in the region of strong microwave fields near the surface of the electrode-antenna.

To determine the effect of changes in the EEDF we made the calculation for the mixture of H$_2$ with 5% of nitrogen additive, but with the EEDF calculated for the pure hydrogen discharge. As a result, the electron density profile outside the near-electrode region of strong microwave fields almost everywhere coincides with the $n_e$ profile for a discharge in pure H$_2$ (Fig.3, the vertical purple ellipses). This means that the change in the EEDF due to addition of nitrogen affects the characteristics of plasma in the spherical region, where the magnitude of the microwave field is small.

Fig. 3. Radial profiles of the electron density of discharge: blue line - pure hydrogen; red line - with 5% nitrogen added; violet vertical ellipses – with the addition of 5% nitrogen, but with the EEDF, calculated for a discharge of pure hydrogen; horizontal orange ellipses - with the addition of 5% nitrogen, but with a kinetic scheme, which excludes the appearance of ion N$_2$H$^+$. I – region of strong microwave field, II - spherical region of the discharge.

Obviously, a change in the EEDF can affect the reaction rates of mechanisms with the electron impact and transport properties of the electron motion in a DC field due to charge separation, namely the diffusion and mobility coefficients. Our analysis has shown that the change in the EEDF affects mainly the electron mobility. Calculated DC fields of charge separation in plasma are found to be about 1-3 V/cm. For these values of the field the coefficients $\mu_e$ for the case with 5% of nitrogen additive are higher (~0.1-0.3%) than the coefficients $\mu_e$ for a pure hydrogen discharge. Because the field of charge separation is always directed from the center of the chamber to the electrodes, the electrons drift in this field towards the center of the discharge. Drift flow of electrons to the center of the plasma reduces the diffusion flux of electrons to the electrodes, which leads to a squeeze of the electron profile in comparison with the profile of $n_e$ in pure hydrogen discharge (Fig. 1 a).

4. Summary
It is shown that in conditions of strongly inhomogeneous plasma, in case when small additives of nitrogen are added into the hydrogen discharge, the inclusion of processes of ion conversion, along
with a change of the EEDF, leads to a more complex picture of the influence of additives on the plasma parameters than those described in [3]. Changes in the EEDF, in the ion composition of plasma and in transport properties of electrons affect the profile of the electron density and microwave field already at 5% addition of nitrogen. The EEDF influences in a spherical region of the discharge away from the electrode. The addition of nitrogen increases the mobility of electrons and leads to reduction of size of the plasma formation. The change in the ion components of plasma (N₂H⁺ becomes the main ion) affects the structure of the plasma near the surface of the electrode.

5. References

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