Numerical analysis of the effect of surface recombination on N-atom in discharge and post-discharge region

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ABSTRACT

In this paper, the effect of surface recombination on N-atom production is discussed through a one-dimensional simulation of Townsend dielectric barrier discharge in pure N₂ based on a fluid model. By comparison of the experimental results, the recommended value of the sticking coefficient of N–N surface recombination is 0.5–1. The spatial-temporal distribution of N-atom of simulation results in discharge and post-discharge agree with experimental results. When the sticking coefficient is 0.5, the primary active species include N, N₂(A), and N₂(a'). N₄⁺ is the densest positive ion, which can reach $4.77 \times 10^9 \text{ cm}^{-3}$. N-atom can reach the saturation level within about 30 ms. The highest number density is $3.14 \times 10^{14} \text{ cm}^{-3}$ at the position 0.25 mm away from the surface. The numerical simulation results are very consistent with the experimental results. The contribution of surface recombination and three-body recombination for the decay of N-atom are roughly equal in the post-discharge region.

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I. INTRODUCTION

It is well known that the dielectric barrier discharge (DBD) has some advantages, such as a low working temperature and a straightforward structure and low cost. Therefore, DBDs have been used more and more in ozone generation, pollutant removal, biological application, and large-scale surface treatment, and so on.¹

DBDs have discharge regimes: filamentary and homogeneous.² In the filamentary regime, the discharge consists of a multitude of micro discharges. The electron and ion density are concentrated in the filaments. The inhomogeneity of filamentary plasma leads to difficulty in indirect measurement. On the other hand, in the homogeneous regime, also called Townsend DBD (TDBD), there is a uniform positive space charge and an electric field between two electrodes. Moreover, the density of charged particles is relatively low.

It is difficult to measure the plasma directly because of its high reaction speed and high parameters. There are a few studies that present direct measurements of the discharge area. Dilecce *et al.*³

measured the N₂(A) metastable state density in a DBD in nitrogen and nitrogen with a small admixture of oxygen operating in TDBD by optical-optical double resonance laser-induced fluorescence (LIF). Es-Sebbar *et al.*⁴ determined the absolute density of ground-state nitrogen atoms N in TDBD in pure nitrogen by two-photon absorption laser-induced fluorescence (TALIF) spectroscopy. The experimental results indicated that the vital physical parameter which governs the N atom density is the energy dissipated in the gas at the measurement position. The N atom number density reaches an approximate value of around $3 \times 10^{14} \text{ cm}^{-3}$. The analyses of these measurements show that the nitrogen–nitrogen volumetric recombination is not the only loss mechanism of atomic nitrogen. The surface recombination processes also play a significant role. Based on the experimental results, Tsyganov and Pancheshnyi⁵ developed a zero-dimensional plasma-chemical model considering a set of detailed kinetic schemes to simulate the production of the N-atom in TDBD in pure nitrogen at atmospheric pressure. In Tsyganov's model, the

surface reaction cannot be discussed in depth. To keep the simulation results consistent with the experimental results, Tsyganov *et al.* directly multiplied the N_2 dissociative cross section by a factor 1/2, which does not seem like a reasonable approach.

Another mechanism that plays an essential role in the generation and loss of atoms in plasma reactions is the nonequilibrium vibration kinetics.⁶ On the one hand, when atoms recombine on the surface, they usually produce molecules in vibrational excited states. These surface reactions can modify the vibrational distribution function (VDF) of molecules in the gas phase.^{7,8} On the other hand, the vibrational kinetics of N_2 in the gas phase can alter the dissociation rates either from the plateau of VDF formed by the recombination of atoms as well as by the VDF formed in the gas phase or from the variation of the electron energy distribution function (EEDF).^{6,9,10} In more recent studies, the non-equilibrium vibrational distribution was found to dramatically increase the global rates of dissociation and ionization processes.⁶ However, the energy levels of the molecules are very complicated. The vibrational cross sections have not been especially well measured or calculated for most molecules.¹¹ The nonequilibrium vibrational kinetics in nitrogen plasma are largely progressing. Laporta *et al.*,¹² Armenise *et al.*,¹³ and Capitelli *et al.*¹⁴ calculated complete sets of e - V (electron-vibration) and V - T (vibration-translation) energy transfer cross sections and rates, the latter involving both atomic and molecular species. Despite these efforts, until now, the presence of excited states in plasma kinetics is not correctly accounted for, in general limiting the action of excited states to superelastic terms connecting vibrational and electronic excited states to the ground vibrational one ($v=0$) of the molecule.

In this paper, we developed a one-dimensional fluid model of plasma to simulate the discharge process in TDBD in pure N_2 . In this simulation, we employed a detailed nitrogen kinetic scheme. The influence of the surface recombination reaction of the N atom is discussed. In this 1-dimensional simulation, the spatial distribution of active species at a different time or different position can be obtained. Through comparison of the simulation results with the experimental results, we recommend that the value of the sticking coefficient of N-N surface recombination should be 0.5–1. The numerical simulation results are consistent with the experimental results. The parameters recommended in this paper can be referenced in similar applications.

II. NUMERICAL MODEL

The 1D fluid model of plasma is used to analyze the discharge process and the production of the N-atom in the discharge and post-discharge. In the fluid model, all the plasma species, including electrons, are treated as a continuum. This model involves, for all plasma species, the continuity equations, momentum equations, and energy equations (usually only for electrons), which are velocity moments of the kinetic Boltzmann equation. The Poisson equation completes the system for the self-consistent electric field. In fluid models of glow discharge, momentum equations are usually reduced to the drift-diffusion equation, and “local field approximation” (LFA) for transport and rate coefficients is employed. The details of these equations and the computational process can be found in Ref. 15–18.

A. Plasma simulation model

In this model, a plasma is divided into two types of fluids: electrons and heavy particles. Here, the electron is described using the drift-diffusion approximation as follows:

$$\frac{\partial n_e}{\partial t} + \nabla \cdot \Gamma_e = R_e, \quad (1)$$

$$\frac{\partial n_e}{\partial t} + \nabla \cdot \Gamma_e + \mathbf{E} \cdot \Gamma_e = R_e, \quad (2)$$

$$\Gamma_{e,e} = -n_{e,e}(\mu_{e,e} \cdot \mathbf{E}) - n_{e,e}(D_{e,e} \cdot \nabla n_{e,e}), \quad (3)$$

where n_e and n_e are the electron number density and the electron energy density, respectively, $n_e = 2/3n_e T_e$, T_e is the electron temperature (eV), $\mathbf{E}$ is the electric field strength, μ_e is the electron mobility, μ_e is the electron energy mobility, D_e is the diffusion coefficient of the electron, D_e is the electron energy diffusivity, R_e is the electron rate expression, R_e is the energy loss/gain due to inelastic collisions, and Γ_e and Γ_e are the flux of the electron and electron energy.

The source terms of Eqs. (1) and (2) are determined by the plasma chemistry using the rate coefficients given by

$$R_e = \sum_{j=1}^M c_j k_{ej} N_n n_e, \quad (4)$$

$$R_e = \sum_{j=1}^M c_j k_{ej} N_n n_e \Delta e_j, \quad (5)$$

where c_j is the mole fraction of the target species for the j th reaction, k_{ej} and Δe_j are the rate coefficient and energy loss for the j th reaction, respectively, and N_n is the total neutral particle number density. The electron transport properties (μ_e , D_e , $\mu_{e,e}$, and $D_{e,e}$) and the rate coefficient (k_{ej}) are calculated using a Boltzmann equation solver, as shown in Sec. II B.¹⁹

The heavy particles, such as ions, atoms, and metastable molecules, are also described using the drift-diffusion approximation as follows:

$$\rho \frac{\partial w_k}{\partial t} = \nabla \cdot \mathbf{j}_k + R_k, \quad (6)$$

$$\mathbf{j}_k = -\rho w_k (Z_k \mu_k \cdot \mathbf{E}) - \rho D_{km} \cdot \nabla w_k, \quad (7)$$

where $\mathbf{j}_k$ is the diffusive flux, D_{km} is the effective binary diffusivity, R_k is the rate expression, Z_k is the charge number for species k , ρ is the density of the mixture, and w_k is the mass fraction of each species,

$$R_k = MW_k \sum_{j=1}^M \left(k_j \prod_{i=1}^Q c_i \right), \quad (8)$$

where MW_k is the molar mass of species k (kg mol^{-1}), c_i is the mole fraction of i th species in the j th reaction, and k_j is the rate coefficient of the j th reaction. If the j th reaction is an electron collision reaction such as reactions No. 1–No. 13 in Table I, $k_j = k_{ej} N_A^{-1}$, where N_A is Avogadro's constant.

Substituting Eq. (7) into Eq. (6), the total mass flux of the ions and metastable atoms can be expressed as follows:

$$\Gamma_k = \rho w_k (Z_k \mu_k \cdot \mathbf{E}) + \rho D_{km} \cdot \nabla w_k. \quad (9)$$

TABLE I. Reaction mechanisms of N₂ plasma in this model.

No.	Reaction	Rate ^{a,b,c}	$\Delta\epsilon^d$	References
1	$e + N_2 \Rightarrow e + N_2(A)$	k_{e1}	7.00	22
2	$e + N_2 \Rightarrow e + N_2(B)$	k_{e2}	7.35	22
3	$e + N_2 \Rightarrow e + N_2(a')$	k_{e3}	8.40	22
4	$e + N_2 \Rightarrow e + N_2(C)$	k_{e4}	11.03	22
5	$e + N_2 \Rightarrow e + N + N$	k_{e5}	13.00	22
6	$e + N_2 \Rightarrow 2e + N_2^+$	k_{e6}	15.6	22
7	$e + N_2 \Rightarrow 2e + N + N^+$	2.4×10^{-27}		5,14
8	$e + N_2 + N^+ \Rightarrow N + N_2$	$6.0 \times 10^{-27} (300/T_e)^{1.5}$		5,14
9	$e + N_2^+ \Rightarrow N + N$	$9.0 \times 10^{-8} (300/T_e)^{0.39}$		5,14
10	$e + N_2^+ \Rightarrow N + N(^2D)$	$8.1 \times 10^{-8} (300/T_e)^{0.39}$		5,14
11	$e + N_2^+ \Rightarrow N + N(^2P)$	$9.0 \times 10^{-9} (300/T_e)^{0.39}$		5,14
12	$e + N_3^+ \Rightarrow N + N_2$	$2.0 \times 10^{-7} (300/T_e)^{0.5}$		5,14
13	$e + N_4^+ \Rightarrow N_2 + N_2$	$2.3 \times 10^{-6} (300/T_e)^{0.53}$		5,14
14	$N_2(A) + N_2(a') \Rightarrow e + N_4^+$	4.0×10^{-12}		5,14
15	$N_2(a) + N_2(a') \Rightarrow e + N_4^+$	1.0×10^{-11}		5,14
16	$N^+ + N_2 + N \Rightarrow N_2^+ + N_2$	1.7×10^{-29}		5,14
17	$N^+ + N_2 + N_2 \Rightarrow N_3^+ + N_2$	$1.7 \times 10^{-29} (300/T_{eff})^{2.1}$		5,14
18	$N_2^+ + N \Rightarrow N^+ + N_2$	$7.2 \times 10^{-13} (T_{eff}/300)$		5,14
19	$N_2^+ + N_2(A) \Rightarrow N_3^+ + N$	3.0×10^{-10}		5,23
20	$N_2^+ + N_2 + N \Rightarrow N_3^+ + N_2$	$9.0 \times 10^{-30} \exp(400/T_{eff})$		5,14
21	$N_2^+ + N_2 + N_2 \Rightarrow N_4^+ + N_2$	$5.2 \times 10^{-29} (300/T_{eff})^{2.2}$		5,14
22	$N_3^+ + N \Rightarrow N_2^+ + N_2$	6.6×10^{-11}		5,14
23	$N_4^+ + N \Rightarrow N^+ + N_2 + N_2$	1.0×10^{-11}		5,14
24	$N_4^+ + N_2 \Rightarrow N_2^+ + N_2 + N_2$	$2.1 \times 10^{-16} \exp(T_{eff}/121)$		5,14
25	$N_2(B) \Rightarrow N_2(A) + h\nu$	1.3×10^5		5,14
26	$N_2(C) \Rightarrow N_2(B) + h\nu$	2.5×10^7		5,14
27	$N_2(a') \Rightarrow N_2 + h\nu$	1.0×10^2		5,14
28	$N_2(A) + N \Rightarrow N_2 + N$	2.0×10^{-12}		5,14
29	$N_2(A) + N \Rightarrow N_2 + N(^2P)$	$4.0 \times 10^{-11} (300/T_{gas})^{2/3}$		5,14
30	$N_2(A) + N_2 \Rightarrow N_2 + N_2$	3.0×10^{-16}		5,14
31	$N_2(A) + N_2(A) \Rightarrow N_2 + N_2(B)$	3.0×10^{-10}		5,14
32	$N_2(A) + N_2(A) \Rightarrow N_2 + N_2(C)$	1.5×10^{-10}		5,14
33	$N_2(B) + N_2 \Rightarrow N_2 + N_2$	2.0×10^{-12}		5,14
34	$N_2(B) + N_2 \Rightarrow N_2(A) + N_2$	3.0×10^{-11}		5,14
35	$N_2(C) + N_2 \Rightarrow N_2(a') + N_2$	1.0×10^{-11}		5,14
36	$N_2(a') + N_2 \Rightarrow N_2(B) + N_2$	1.9×10^{-13}		5,14
37	$N(^2D) + N_2 \Rightarrow N_2 + N$	$2.3 \times 10^{-14} \exp(510/T_{gas})^{2/3}$		5,24
38	$N(^2P) + N_2 \Rightarrow N_2 + N$	6.0×10^{-14}		5,24
39	$N(^2P) + N \Rightarrow N(^2D) + N$	6.0×10^{-13}		5,24
40	$N(^2P) + N \Rightarrow N + N$	1.8×10^{-12}		5,24
41	$N + N + N_2 \Rightarrow N_2 + N_2(A)$	1.7×10^{-33}		5,14
42	$N + N + N_2 \Rightarrow N_2 + N_2(B)$	2.4×10^{-33}		5,14

^aRate coefficients k_{e1} – k_{e6} are computed from the cross section σ and the electron energy distribution function.^{20,22}^bRate coefficients of reactions No. 7–42 have units of s⁻¹, cm³ s⁻¹, and cm⁶ s⁻¹.^c $T_{eff} = T_{gas} + \frac{\pi}{6k} \frac{m_i m_n}{m_i + m_n} v^2$, here, T_{gas} is the gas temperature, k is the Boltzmann constant, m_i and m_n are the mass of ions and neutral species, respectively, v is the mean ion velocity.⁵^d $\Delta\epsilon$ indicates the electron energy loss in the reaction, and the unit is eV.

The electrostatic field is computed using the Poisson equation for space charge as follows:

$$-\nabla \cdot \epsilon_0 \epsilon_r \nabla V = q_e(n_+ - n_-), \quad (10)$$

where n_+ is the total number density of all positive ions such as N_2^+ , N_3^+ , and N_4^+ , n_- is the total number density of all negative ions and electrons, ϵ_0 is the permittivity of the vacuum, and ϵ_r is the dielectric constant of the spatial material.

The electron diffusivity, energy diffusivity, and energy mobility can be computed from the electron mobility using the following relationship:

$$D_e = \mu_e T_e, \quad D_\epsilon = \mu_e T_e, \quad \mu_e = (5/3)\mu_e. \quad (11)$$

Here, the electron mobility can be computed from cross section data by the following integral:

$$\mu_e N = -\frac{1}{3} \left(\frac{2q_e}{m_e} \right)^{\frac{1}{2}} \int_0^\infty \frac{\epsilon}{\tilde{\sigma}_m(\epsilon)} \frac{\partial f(\epsilon)}{\partial \epsilon} d\epsilon, \quad (12)$$

where ϵ is the energy (SI unit: Joule), $\tilde{\sigma}_m(\epsilon)$ is the effective momentum transfer cross section defined in Ref. 20, and $f(\epsilon)$ is the electron energy distribution function (EEDF).

The rate coefficients of Eqs. (4) and (5) can be computed from cross section data by the following integral:

$$k_e = -\frac{1}{3} \left(\frac{2q_e}{m_e} \right)^{\frac{1}{2}} \int_0^\infty \epsilon \sigma(\epsilon) f(\epsilon) d\epsilon, \quad (13)$$

where $\sigma(\epsilon)$ is the collision cross section.

Here, we focus on the surface reactions of this fluid model. As discussed above, we neglect the movement of species toward the surface induced by the flow. However, the thermal diffusion toward the surface will lead to surface reactions. As shown in Table II, the surface reactions in this simulation are irreversible processes. The law of mass action governs the rate of progress of the i th reaction with K reactants

$$q_i = k_{f,i} \prod_{j=1}^K c_j, \quad (14)$$

TABLE II. Surface reactions in N_2 plasma.

No.	Surface reaction	Sticking coefficient γ_i
1	$N^+ \Rightarrow N$	1
2	$N_2^+ \Rightarrow N_2$	1
3	$N_3^+ \Rightarrow N + N_2$	1
4	$N_4^+ \Rightarrow N_2 + N_2$	1
5	$N(^2D) \Rightarrow N$	1
6	$N(^2P) \Rightarrow N$	1
7	$N_2(A) \Rightarrow N_2$	1
8	$N_2(B) \Rightarrow N_2$	1
9	$N_2(C) \Rightarrow N_2$	1
10	$N_2(a') \Rightarrow N_2$	1
11	$N + N \Rightarrow N_2$	Undetermined

where c_j is the concentration of the j th species. $k_{f,i}$ is the forward rate constant which is related to the sticking coefficient γ_i and the thermal velocity at a wall via

$$k_{f,i} = \left(\frac{\gamma_i}{1 - \gamma_i/2} \right) \sqrt{\frac{RT}{2\pi M}}, \quad (15)$$

where R is the gas constant and M is the mean molecular mass. The sticking coefficient γ_i changes from 0 to 1. Moreover, a higher coefficient means more intense surface reactions. The neutralization of ions and deexcitation of metastable molecules and atoms is very fast.¹¹ Thus, the Sticking coefficient γ_i is chosen as 1 in No. 1–No. 10 surface reactions. Concerning the recombination of N–N, the sticking coefficient γ_{11} will be discussed in the simulations.

B. N_2 plasma reaction mechanism

The reaction mechanisms of N_2 plasma are very complex. Pitchford and Phelps *et al.*²¹ compiled cross sections for electron collisions with N_2 molecules. They identified 25 electron collision reactions, including elastic scattering, vibrational excitations, rotational excitations, dissociative electron attachment, ionization, and dissociation. This reaction system contains many molecules and atoms, such as N, $N(^2D)$, $N(^2P)$, N_2^+ , $N_2(\text{rot})$, $N_2(\text{vib})$, $N_2(A)$, $N_2(B)$, $N_2(C)$, and $N_2(a')$. Besides, the detailed information is still lacking in the existing literature about the ionization cross section of excited molecules and the Penning ionization. Therefore, it is complicated to completely clarify the reaction mechanism of N_2 plasma based on experiments.

Fortunately, in this paper, we are mostly concerned about how many atom N are produced in N_2 plasma. Other complex reactants are not the focus of this paper. In this simulation, a set of 42 chemical reactions⁵ and 11 surface reactions with 13 species are considered (shown in Table I). The species include electrons (e), positive ions (N^+ , N_2^+ , N_3^+ , N_4^+), neutral atoms [N, $N(^2D)$, $N(^2P)$], and molecular species [N_2 , $N_2(A)$, $N_2(B)$, $N_2(C)$, $N_2(a')$]. The reactions include excitation and ionization by electron impact, associative ionization, ion-electron recombination, ion conversion, and excited species conversion. The details of this set of kinetic schemes can be found in Ref. 5 and 14. Figure 1 shows the electron collision cross section sets used in this simulation.

In our simulation, the electronically excited states formed by electron collisions are considered. Still, the vibrationally excited states are not considered, because this paper focuses on the effect of the recombination on the wall on the N-atom through a relatively simple reaction mechanism. It is complicated to calculate the complete nonequilibrium vibration kinetics. For example, Capitelli *et al.*,⁶ Armenise and Capitelli,⁸ and Colonna *et al.*¹⁰ considered 68 vibrational energy levels of the N_2 ground state. The collision transition between these energy levels and the reaction of vibrational molecules will make our one-dimensional model too complicated. Of course, this is also a deficiency of this study. After further improvement of the calculation method, the perfect reaction mechanism should be simulated as much as possible. Based on the existing research results, the vibrational energy kinetics can enhance the formation of the N-atom. In other words, the creation of the N-atom in our model is underestimated. Therefore, the conclusion of this paper is a little conservative when we analyze the surface effect later.

FIG. 1. Cross section sets of electron collision reactions: (a) reactions with larger collision cross section and (b) reactions with larger collision cross section.

In Eqs. (12) and (13), the transport coefficients and rate coefficients may be somewhat specific to the discharge conditions. These coefficients concerning electrons depend on the EEDF. In weakly ionized gases in uniform electric fields and collisional low-temperature plasmas, the EEDF is non-Maxwellian and determined by an equilibrium between electric acceleration and momentum and energy losses in collisions with neutral gas particles.²⁵ The free and user-friendly computer program BOLSIG+ has been developed for the numerical solution of the Boltzmann equation for electrons in weakly ionized gases.²² In this paper, we use BOLSIG+ 11/2019 to obtain electron transport properties and rate coefficients from cross section data, as shown in Fig. 1. Figures 2 and 3 shows the results for μ_e and k_e . Generally, the electron temperature of corona discharge that we calculate should be between 1 and 2 eV. By trial calculation, we determined a corresponding mobility of $2 \times 10^{24} \text{ m}^{-1} \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ when the electron temperature is equal to 1.5 eV.

FIG. 2. Electron mobility vs electron temperature.

FIG. 3. Rate coefficients of electron collision reactions vs electron temperature.

In solving the Boltzmann equation, the superelastic collisions of the excited states are considered. However, the superelastic collision processes of vibrationally excited states are not introduced. According to the research of Capitelli *et al.*,⁹ the vibrational kinetics can affect the distribution of electronic EEDF. Figure 4 shows the EEDF for different reduced electric fields E/N with temperature $T_{\text{gas}} = 300 \text{ K}$, pressure $p = 1 \text{ atm}$, and fixed electron molar fraction $\chi_e = 10^{-10}$ in our mechanisms. Compared with Ref. 9, the distribution of electrons with $T_e < 2 \text{ eV}$ in Fig. 4 is lower, and the distribution of electrons with $T_e > 2 \text{ eV}$ in the high energy state is higher. These differences can be mainly ascribed to the role of inelastic collisions from vibrationally excited states, which deplete the EEDF. Such EEDF has two effects. On the one hand, the dissociation process of vibrational energy level is not considered, and the reaction of the N-atom generated by the vibrational energy level will be reduced. On the other hand, the direct dissociation process can be strengthened due to the high-energy electrons,

FIG. 4. The EEDF of N_2 as a function of reduced electric field E/N , at $p = 1 \text{ atm}$ and $T_{\text{gas}} = 300 \text{ K}$.

which are not consumed by the vibration dynamics. Therefore, in the current plasma simulation process, a complete and reliable reaction mechanism is essential.

The surface reactions considered in this simulation, as listed in Table II, are discussed here. The charge accumulation on the dielectric surface is involved in our simulation. There are three types of surface reactions. The first is the surface neutralization process of positive ions, as No. 1–4 reactions shown in Table II. Because the walls of the discharge are the surface of the glass plates, the secondary electron emission on the surface can be ignored. The second type is the de-excitation process of excited molecules and atoms on the surface, as No. 5–11 reactions shown in Table II. The third critical reaction is the N–N recombination reaction. This reaction was also emphasized in both the experiment analysis⁴ and the 0D simulation.⁵ The reaction rate is challenging to determine. In this paper, we will compare the simulation results with the experimental results to determine the parameters of γ_{11} . In the following computation, if $\gamma_{11} = 1$, it means that the reaction rate of the N–N recombination reaction is high-speed, and the N atom is very easy to recombine on the surface. However, in the actual process, the recombination rate is more complex and will be affected by the surface characteristics.

C. Simulation condition

In this paper, the discharge processes of Ref. 4 are simulated. Here, the nitrogen flow passes through a plate–plate DBD discharger that operates in the Townsend (homogenous) regime. In this series of calculations, the discharger is simplified as a one-dimensional structure shown in Fig. 5. The pressure is 1 atm and the temperature T_{gas} is 300 K. The discharge gap is 2 mm, and two dielectric plates of 1 mm are covered with the metallic electrodes. The dielectric permittivity constant of the dielectric plates and nitrogen is 8.75 and 1, respectively. A sinusoidal AC power supply with a 17 kV peak-to-peak voltage and a 2 kHz frequency is used. The finite element method is employed for the plasma simulation, and the specific calculation method is shown in Refs. 16 and 26. Figure 6 shows the 1D mesh used in this finite element simulation. In the region near the surfaces of the glass plates, an excellent resolution is used to resolve the plasma sheath. However, away from the surfaces, a coarser mesh is used to make the calculation efficient. The number of degrees of freedom in this mesh is 2168. The type of hardware used in the simulation is an Intel Core i7–6700 K central processing unit (CPU) (4.00 GHz and 32 GB of RAM).

In the cited experiment,⁴ the gas flow rate varied from 0.8 to 4 l/min, which corresponds to a maximum residence time at the end of the discharge length ranging from 62.5 to 12.5 ms. The

FIG. 5. Schematic diagram of the DBD plasma discharger.

FIG. 6. One-dimensional mesh used for the simulation of the plasma.

mean gas velocity varied from 36 to 145 cm/s. The deduced Péclet number changes between 12 and 50, which means that the radical convection prevails over their diffusion. In other words, the velocity toward the surface can be neglected. Meanwhile, it can be assumed that the change of velocity can also be ignored since the velocity is low enough. These two assumptions indicate that the impact of gas flow on plasma can be neglected. As a result, the discharge condition of the gas flow at different positions is just dependent on the residence time. Furthermore, the simulation results with varying times will correspond to the discharge in an experiment at a different position. We will analyze and compare the distribution of the N-atom with the cited work.

III. RESULTS AND DISCUSSION

A. The discharge characteristics

Figure 7 shows the typical voltage and current density traces of the simulation results with the Sticking coefficient γ_{11} chosen as 0.5. Here, V_{app} is the applied voltage of the external power supply. V_{gap} is the voltage on the discharge gap during discharge, with the maximum

FIG. 7. The voltage and current density of the simulation results.

value of about 4 kV. i_{DBD} is the current density of discharge space, reaching the maximum value on the rising edge of V_{app} . The maximum value of i_{DBD} is about $0.2 \text{ mA} \cdot \text{cm}^{-2}$. The reduced electric field in this simulation is only about 74 Td. The relationship between the applied voltage and the current density is very consistent with the experimental results.⁴

In our simulation model, the computation of V_{gap} and i_{DBD} is different from the capacitance method introduced in Refs. 4 and 5. In this simulation, the Poisson equation is solved coupling with the continuity equations of charged particles. The distributions of positive ions and the surface charge accumulation are calculated. Thus, the gap voltage is lower than that estimated by Tsyganov and Pancheshnyi.⁵

B. Spatial-temporal distribution of the N-atom

Figure 8 shows the spatial-temporal distribution of the N-atom with different γ_{11} . There are two regions in Fig. 8: a discharge region corresponding to the time interval 0–65 ms and a post-discharge

FIG. 8. The spatial-temporal distribution of the N-atom of simulation results with different γ_{11} , (a) $\gamma_{11} = 1$, (b) $\gamma_{11} = 0.5$, (c) $\gamma_{11} = 0.1$, and (d) $\gamma_{11} = 0.01$.

region corresponding to the following time. In these four conditions, the number density of the N-atom reaches the maximum value at about 30 ms. Moreover, in the post-discharge region, the number density of N drops down rapidly after stopping of the discharge. The number density in the area close to the dielectric surface is higher than that in the central area. With $\gamma_{11} = 1$ or 0.5, the surface recombination of N is faster. The highest number density is 2.53×10^{14} and $3.14 \times 10^{14} \text{ cm}^{-3}$ at the position 0.25 and 0.75 mm, respectively. Since the positions of 0.25 mm and 0.75 mm are symmetrical, and the values are the same, only the numerical results of 0.25 mm are discussed in the following description. Moreover, the N number density in the central area is about 2×10^{14} and $2.68 \times 10^{14} \text{ cm}^{-3}$, respectively. When $\gamma_{11} = 0.1$ or 0.01, the surface recombination is relatively weak. The maximum number density appearing near the surface is about 4.61×10^{14} and $5.80 \times 10^{14} \text{ cm}^{-3}$, and in the central area it is about 2.7×10^{14} and $3.2 \times 10^{14} \text{ cm}^{-3}$, respectively. The higher the sticking coefficient, the smaller the number density of the N-atom is. In the post-discharge region, the N number density is smaller with the higher sticking coefficient, too.

Figure 9 shows the number density of the N-atom in the central area with different sticking coefficients varying with the residence time. When the discharge is stable (30 ms later), the N number density decreases with the increase in γ_{11} . When $\gamma_{11} = 1$, the N number density is about $2 \times 10^{14} \text{ cm}^{-3}$. When γ_{11} is 0.01, the N number density is about $3 \times 10^{14} \text{ cm}^{-3}$, about 1.5 times that of the former. The simulation results follow the experiment well when the sticking coefficient was chosen as 0.5, as shown in Figs. 10 and 11.

Figure 10 shows the number density of the N-atom at a different position in the discharge region and also shows the TALIF measurement results.⁴ In the first 25 ms, the number density of N atoms increases rapidly. When the discharge is stable, the number density at position 0.25 mm is higher than that at position 1 mm. When γ_{11} is 0.1 and 0.01, the results are much higher than those of the two groups and they are not shown in Fig. 10. As shown in Fig. 10, in the first 25 ms, the simulation result at the position of 1 mm with $\gamma_{11} = 1$ is very consistent with the experimental results. In the time after 25 ms, when

FIG. 9. The number density of the N-atom in the central area with different sticking coefficients varying with the residence time.

FIG. 10. Profile of the N-atom number density at different positions in the discharge region with $\gamma_{11} = 1$ and 0.5.

$\gamma_{11} = 0.5$, the simulation result at the position 0.25 mm is very consistent with the experimental results. Obviously, in the actual process, the concentration distribution of the N atom is related to the spatial position. However, due to the narrow discharge space, it is challenging to measure the point by point plasma data in the experiment. Thus, Ref. 4 only gives the data of one test point, which may be the result between the high-density area and low-density area. However, our simulation data shows the distribution data. Therefore, from the comparison of the results in Fig. 10, we can roughly confirm that when γ_{11} is between 0.5 and 1, the numerical simulation results are very consistent with the experimental results.

Figure 11 shows the decay process of the N-atom in the post-discharge region with $\gamma_{11} = 1$ and 0.5. The primary decay processes include the surface recombination and the three-body bulk recombination in the gas phase, $N+N+M \rightarrow N_2+M$. Ref. 4 pointed out that the decay speed of the N atom will not be as fast as the experimental results if only considering the three-body recombination reaction. So

FIG. 11. The profile of N-atom number density at a different position in the post-discharge region with $\gamma_{11} = 1$ and 0.5.

the surface recombination process is essential in the actual discharge. When γ_{11} is 0.1 and 0.01, the results are much higher than those of the two groups and they are not shown in Fig. 11, also. As shown in Fig. 11, The experimental data are almost all in the maximum and minimum range of the numerical simulation with $\gamma_{11} = 0.5$. As discussed above, since the vibration kinetics are not considered in this model, in fact, the generation of the N-atom is underestimated. Therefore, the sticking coefficient of N-N surface recombination is recommended to be 0.5 or 0.5–1 in the simulation under the same working conditions.

C. Main components and reactions

Figure 12 shows the typical distributions of main components at $t = 40$ ms with $\gamma_{11} = 0.5$. At this time, the discharge is stable, and the applied voltage $V_{app} = 0$ V. Inspection of these curves shows that the DBD is an efficient source of active species, such as N and $N_2(A)$, which reaches a high number density as $3.05 \times 10^{14} \text{ cm}^{-3}$ and $1.63 \times 10^{13} \text{ cm}^{-3}$. The other active species, such as $N_2(a')$, can reach 10^{11} cm^{-3} . $N_2(B)$ and $N_2(C)$ have the same profile, and the value is about 10^9 cm^{-3} . N_4^+ is the densest positive ion, which can reach $4.77 \times 10^9 \text{ cm}^{-3}$. The number density of other positive ions N^+ , N_2^+ , and N_3^+ is much smaller than the N_4^+ number density. The maximum of the electron number density changes around $2 \times 10^8 \text{ cm}^{-3}$.

Through comparing the rate of each reaction, the following four reactions have the most significant effect on the production and decay of the N-atom: dissociation $e+N_2 \rightarrow e+N+N$, ion conversion $N_4^++N \rightarrow N^++N_2+N_2$, and the three-body recombination $N+N+N_2 \rightarrow N_2+N_2(A)$ and $N+N+N_2 \rightarrow N_2+N_2(B)$. Figure 13 shows the reaction rates of these four reactions. The dissociation of $e+N_2$, which is the production of the N-atom, can reach the highest reaction rate of about $1.1 \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ near the surface as well as it is minimal in the central area of discharge space. This reaction will stop simultaneously at the beginning of the post-discharge region. The distributions of the reaction rate of the two three-body recombinations are the same as the different rates, as shown in Figs. 13(c) and 13(d). Compared to Figs. 13(b)–13(d), the contribution of ion N_4^+ to the

FIG. 12. The profile of the number of density of primary components at $t = 40$ ms with $\gamma_{11} = 0.5$.

FIG. 13. The spatial-temporal distribution of reaction rates, (a) dissociation $e + N_2 \Rightarrow e + N + N$, (b) ion conversion $N_4^+ + N \Rightarrow N^+ + N_2 + N_2$, (c) the three-body recombination $N + N + N_2 \Rightarrow N_2 + N_2(A)$, and (d) $N + N + N_2 \Rightarrow N_2 + N_2(B)$.

decay of the N-atom is more significant than that of three-body recombination by about two orders of magnitude. As a consequence, the ions have little effect on the decay of the N-atom. Figure 14 shows the profile of the surface recombination rate in the post-discharge region with $\gamma_{11} = 0.5$ and the rate decrease from 1.73×10^{-5} to $1.75 \times 10^{-4} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. Compared with Figs. 13(c) and 13(d), it can be concluded that the contribution of surface recombination and three-body recombination for the decay of the N-atom are roughly equal when the discharge gap is 2 mm through a simple calculation.

D. Other plasma properties

For readers to understand more about this plasma discharge, we draw a few more relevant plasma properties in the following figures (Figs. 15–17). In this simulation, the surface reaction processes have a significant influence on the N-atom in the N_2 TBD, but not on the other plasma characteristics. Thus, we only draw the electron temperature, electron number density, and total ion density with $\gamma_{11} = 0.5$. In

FIG. 14. The profile of the surface recombination rate in the post-discharge region with $\gamma_{11} = 0.5$.

these figures, to see clearly, we draw the parameter distribution between 39 and 41 ms. Figure 18 shows the change of electric potential with $\gamma_{11} = 0.5$ in 39–41 ms. On the whole, the TBD is plasma with weak ionization. During the discharge, the electron temperature can reach 2.95 eV. When the number density of electrons is too low during post-discharge, the significance of electron temperature is not significant. The electron density can reach $1.96 \times 10^8 \text{ cm}^{-3}$ during the discharge, and the ion density is about $2.32 \times 10^{10} \text{ cm}^{-3}$. Compared with Fig. 12, the number density of the N-atom and the excited state $N_2(A)$ is much higher than that of the ion.

IV. CONCLUSIONS

In this paper, a 1-dimensional fluid model of plasma is developed to simulate the discharge process in TBD in pure N_2 by considering a set of 42 chemical reactions and 11 surface reactions with 13 species. The production and decay of the N-atom are the primary study objects. Through comparison with the experimental results, the

FIG. 15. The spatial-temporal distribution of electron temperature with $\gamma_{11} = 0.5$.

FIG. 16. The spatial-temporal distribution of electron number density with $\gamma_{11} = 0.5$.

FIG. 17. The spatial-temporal distribution of ion temperature with $\gamma_{11} = 0.5$.

FIG. 18. The spatial-temporal distribution of electric potential with $\gamma_{11} = 0.5$ during 39–41 ms.

sticking coefficient of N–N surface recombination is recommended to be 0.5–1 in the simulation under the same working conditions. Under this condition, the spatial-temporal distribution of the N-atom of simulation results in the discharge region and post-discharge region agrees well with the experimental results.

The simulation results indicate that TDBD is an efficient source of active species. The primary active species include N, $N_2(A)$, and $N_2(a')$. The N atom can reach the maximum value within about 30 ms. The highest number density is at the position 0.25 mm. The dissociation, three-body reactions, and surface recombination have a significant effect on the production and decay of the N-atom. For the reactors with a discharge gap of about 2 mm, the contribution of surface recombination and three-body recombination for the deterioration of the N-atom is roughly equal in the post-discharge region.

Finally, the distribution of the N-atom discussed in this simulation can be referred to in applications with a similar condition. The recommended value for the sticking coefficient of surface reaction can be used in the same simulation.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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