Nitrogen atoms in a travelling wave sustained N$_2$ discharge

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Abstract

The influence of the discharge operation conditions, including wall conditions, on the N($^4$S) atom production and loss mechanisms in a discharge sustained by a travelling surface wave has been investigated. By means of an actinometry technique the relative density of N($^4$S) atoms has been detected. The axial distribution of the relative number of the nitrogen atoms and its dependence on the wall temperature are obtained.

1. Introduction

The understanding of the processes of surface modification by N atoms motivated the investigation of travelling wave sustained N$_2$ discharges as N atom sources. Nitrogen discharges are often operated at low pressure conditions in order to provide atoms in the spatial afterglow where, due to their long lifetime, atoms are present due to axial transport. Moreover, the interaction of atomic species with the wall can influence their volume density as far as wall reactions determine the probabilities for atomic reassociation [1]. This work presents an experimental and theoretical investigation on the influence of the discharge operation conditions (including wall conditions) on the N($^4$S) atom production and loss mechanisms in a discharge sustained by a travelling surface wave. By means of optical emission spectroscopy the relative density of N($^4$S) atoms has been detected. Since the relation between the intensity of the emission lines and the densities of the species is not straightforward a comparison with predictions of a theoretical model is also done.

2. Experimental conditions and procedures

The experiments have been performed in a microwave discharge sustained by an azimuthally symmetric surface wave (TM mode) of frequency $\omega/2\pi = 2.45$ GHz excited by a waveguide-surfatron device. The plasma column is created in N$_2$ at a constant pressure $p = 0.5$ Torr, in a quartz tube with inner radius $a = 0.75$ cm. The gas is introduced with a flow rate in the range $Q = 19 - 53$ sccm. Photons emitted by the plasma are collected via an optical fiber into the entrance slit of a SPEX 1250M spectrometer (2400 gr/mm grating) equipped with a Hamamatsu R928 photomultiplier.

An actinometry technique (argon was used as an actinometer) has been performed to detect the ground state N($^4$S) atoms [2]. The intensity ratios $I_N/I_{Ar}$ of the $\lambda = 744.23$ nm and the $\lambda = 746.83$ nm nitrogen atomic lines (transition 3p $^4$S$_0 \rightarrow$ 3s $^4$P) to the $\lambda = 750.39$ nm argon line (transition 2p$_1 \rightarrow$1s$_2$) have been detected as a measure of the relative number of N($^4$S) atoms in the discharge volume (see the emission spectrum of the discharge in Fig. 1). At a
fixed axial position along the discharge the relative number of nitrogen atoms [N]/[N₂] can be correlated with the intensity ratio of the lines [2] i.e.,

\[
\frac{[N]}{[N₂]} \propto \frac{Iₙ}{I_{Ar}}
\]

The constant depends on the ratio of the rate constants for excitation of Ar(2p₁) and N(3p \(^4\)S₀) states. Since the threshold for the excitation of 2p₁ Ar level is 13.47 eV, a value which is close to the excitation threshold for the 3p \(^4\)S₀ level of N, which is 13.80 eV, this ratio keeps approximately constant although the reduced electric field (E/N, N is the neutral density) and consequently the electron energy distribution function change along the discharge length [3]. The addition of the actinometer (small amount of Ar) does not disturb the discharge operation.

The gas temperature \(T_g\) has been determined by measuring the rotational distribution of the second positive system of nitrogen \(N₂(C^2Π_u, v') \rightarrow N₂(B^2Π_g, v'')\) in the 375.5 – 379 nm wavelength range assuming that the translational and rotational modes are in equilibrium [4]. An infrared sensitive measurement using an electrooptical thermometer provides experimental data for the axial variation of the wall temperature during the discharge operation (the wall is cooled by natural convection only).

2. Theoretical model

The theoretical investigation is based on a model accounting in a self-consistent way for discharge (electron and heavy particle) kinetics, gas thermal balance and wave electrodynamics [5]. The steady-state electron Boltzmann equation is solved taking into account momentum transfer collisions, electron-electron collisions, electron impact excitation of electronic levels of N₂ and inelastic and superelastic collisions of electrons with vibrationally excited nitrogen molecules. Furthermore, this equation is coupled to a system of rate balance equations describing the kinetics of vibrationally excited \(N₂(X^1Σ^+_g, ν)\) molecules, the most important electronic states \(N₂(A^3Σ_u^+, B^3Π_g^+, C^3Π_u, a^1Σ_u^-, a^1Π_u, wΔν)\), and ground state \(N(4S)\) nitrogen atoms. The continuity equations for the electrons and the main positive ions \((N₂^+, N₄^+)\) are further coupled to the above system in order to determine the field strength maintaining the discharge. The total rate of ionisation accounts for direct ionisation by electron impact on \(N₂(X^1Σ^+_g)\) molecules, stepwise electron ionisation from metastable states and associative ionisation as a result of collisions between \(N₂(A^3Σ_u^+)\) and \(N₂(a^1Σ_u^-)\) metastable species. The system of rate balance equations further takes into account the processes of dissociation and atomic re-association. A number of gas heating sources such as V-V and V-T vibrational relaxation mechanisms of \(N₂\) molecules in different types of \(N-N₂\) and \(N₂-N\) collisions, pooling reactions between \(N₂(A^3Σ_u^+)\) metastables, deactivation of metastable states on the wall, ion heating etc., are included in the gas thermal balance equation. Under steady state conditions, the spatial rate of wave power change is due to the power absorbed by the electrons per unit discharge length. Thus, the local power balance equation, linking the wave
power flux with the electron power losses provides the axial description of the discharge structure \cite{3,4}.

Numerous volume and wall processes involving atoms strongly influence the discharge operation. In the present model, the kinetics of nitrogen atoms in the ground $N^4S$ and metastable $N^2D^2P$ states is taken into account by considering a number of source and loss channels. The main source of ground state $N^4S$ nitrogen atoms is electron impact dissociation 

$$e + N^4S \rightarrow e + N^4S + N^2D.$$

One of the loss channels of $N^4S$ atoms is atomic re-association on the wall. The probability $\xi = 5 \times 10^{-4}$ (silica wall) has been assumed for this process.

$$N^4S + \text{wall} \rightarrow \frac{1}{2} N^4S + N^2D,$$

The other channel is associated with effective destruction by electron impact as a result of the two-step reaction

$$e + N^4S \rightarrow e + N^2D^2P,$$

$$N^2D^2P \rightarrow \frac{1}{2} N^4S + \frac{3}{2} N^2D,$$

It is assumed that most of the metastable atoms are converted to the ground state, i.e. through collisions with the wall and quenching in collision with heavy particles, with total effective probability $\gamma$.

$$N^2D^2P \rightarrow \frac{1}{2} N^4S,$$

The most excited metastable atoms are converted to the ground state and $\gamma$ is, in fact, close to one ($\gamma = 0.85$ is assumed in the calculations).

An effective quenching with the metastable $N^4S + N^2D^2P$ by the two step reaction

$$N^4S + N^2D^2P \rightarrow \frac{1}{2} N^4S + \frac{3}{2} N^2D,$$

constitutes another loss channel.

4. Results and discussion

The variation of the ratio of the atomic lines intensities to the Ar line intensity, as a measure of the relative number of nitrogen atoms along the plasma column length, is shown in Fig. 2. The measurements have been performed at two different gas flow rates and constant gas pressure $p = 0.5$ Torr. The variation of the gas temperature (see Fig. 3) as a result of inhomogeneous wave power transfer (under nearly isobaric conditions for the present experiment) results in a variation of the gas velocity which decreases towards the end of the discharge. In order to unify the results the distance towards the plasma column end $\Delta z$ is normalised to the total discharge length $L_t$. The gas velocity corresponding to the two flow
rates (19 and 53 sccm) ranges between (7 – 11) m/s and (18 – 29) m/s respectively. The variation of gas flow rate does not influence the axial distribution of nitrogen atom relative density as the experimental results show. Due to the low gas velocities (much smaller than the sound speed) the residence time of the atoms in the volume is much greater than the characteristic times of the other creation and loss processes of the ground state \( N(4S) \) atoms. Thus, the axial transport of the nitrogen atoms does not have significant influence on the local particle balance under the conditions considered.

The smooth variation of the relative number density of \( N(4S) \) atoms along the main part of the plasma column length is followed by a sharp drop close to the end. Since direct electron impact dissociation is the main source channel of \( N(4S) \) ground state atoms for the present conditions, the decrease in electron density causes decreasing dissociation degree of \( N_2 \) molecules towards the plasma column end, as theoretical and experimental demonstrate (Fig. 4). The observed deviation of the theoretically predicted profile (for \( \Delta z/L_e = 0.5 – 0.1 \)) and measured one may be attributed to the variation of the wall reassociation probability due to the drop in the wall temperature close to the end (see Fig.3). The temperature dependence of wall reassociation probability \( \xi \) has not been accounted for in the calculations.

Fig. 5 shows the percentage contribution of the different loss processes of \( N(4S) \) atoms along the discharge. Due to the high ionisation degrees \( (10^{-4} – 10^{-7}) \) the channel associated with electron impact destruction is the dominant loss channel along the main part of the discharge column length. The axial variation of the electron density, \( N_2(A^3\Sigma_u^+) \) metastable molecule density and wall temperature results in a different axial variation of the percentage contribution of the corresponding channels. Due to the sharp drop in the electron density close to the plasma column end the contribution of the electron impact destruction to the total losses decreases while the percentage contribution of the other two channels increases. Close to the end (\( \Delta z/L_e < 0.1 \)) the losses due to the quenching of \( N_2(A^3\Sigma_u^+) \) by \( N(4S) \) start to be comparable with the losses due to electron impact destruction. It should be stressed however that the present result is to be regarded as merely indicative due to the large uncertainties in input data. Particularly, this concerns the values of the probability for wall reassociation of ground state atoms \( \xi \) and the total effective probability for destruction of metastable \( N(2D,2P) \) atoms \( \gamma \).
To investigate the sensitivity of the processes for creation and loss of ground state N(4S) atoms to wall conditions an externally forced change of the wall temperature (in the limits 400<T<460K) has been performed. By external heating of the wall, T_w has been changed locally, in the region corresponding to axial distances (0<Δz/L<0.1), i.e. at the end of the discharge. The corresponding variation of the ratio \( \frac{I^*_N}{I^*_Ar} \) for the λ=746.83 nm nitrogen atomic line, as a measure of relative number of nitrogen atoms, when T_w changes is depicted in Fig. 6. The intensity of the λ=744.23 nm atomic line is beneath the background noise close to the end and has not been used for the measurements. Increasing the “local” wall temperature results in increasing values of the ratio \( \frac{I^*_N}{I^*_Ar} \). The theoretical results when the temperature dependence [5] of the wall reassociation probability \( \xi \) (T_w) is taken into account also show an increase in relative number of atoms as T_w increases. Different mechanisms can influence the degree of dissociation at the conditions considered. Changing of the wall temperature can result in changes of \( \xi \) (decreasing in the considered temperature interval) as well as in the local gas thermal balance and reduced electric field which strongly influences the processes of N_2 dissociation.
The theoretical results demonstrate a crucial influence of the metastable \( \text{N}(^2\text{D}, ^2\text{P}) \) kinetics on the \( \text{N}(^2\text{S}) \) density. However, the large uncertainties in the value of wall reassociation probability \( \xi \) should be also kept in mind because at higher values of \( \xi \) the contribution of the wall reassociation to the total atomic losses can be comparable or even to dominate. For this reason it is of great importance to get reliable experimental data on the nitrogen atoms kinetics.

References