

Nitrogen ion dynamics in low-pressure nitrogen plasma and plasma sheath

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Laser-induced fluorescence (LIF) excitation and time-resolved LIF spectroscopy have been used to explore the interaction of a nitrogen plasma with a metal surface. The rotational temperature, the concentration of N_2^+ , and the lifetime of $N_2^+(B^2\Sigma_u^+)v=0$ were measured as a function of distance from the metal surface. It was observed that the lifetime of the excited ion decreases sharply in the plasma sheath which is created in front of the metal surface. The concentration of $N_2^+(X^2\Sigma_g^+)$, which was measured simultaneously with the lifetime of excited N_2^+ , indicates a quasilinear decrease from the cathode to the grounded surface. T_{rot} undergoes a gradual reduction from the bulk plasma up to the surface where its value is a good approximation of the surface temperature. An interpretation of these phenomena including a numerical simulation of the lifetime decrease is proposed here. The calculated values are in good agreement with experimental results. The dependence of lifetime decrease on the sheath potential as well as on other important parameters (cross section, profile of the electric field) is further discussed.

I. INTRODUCTION

Low-pressure glow discharges are used in various applications concerning surface modification (etching, film deposition, coating, etc.). These applications involve a variety of physical (energy transfer, ion neutralization) and chemical (catalysis, atom recombination) interactions of plasma with solids.

The behavior of the different species in the plasma sheath, which is created in front of a metal surface during the interaction of the metal with plasma, is important for understanding the physical and chemical phenomena that take place.

We have studied the system N_2^+ /metal (metal:W, Mo, Fe) in an rf nitrogen plasma. The rotational temperature of the plasma, $N_2^+(X^2\Sigma_g^+)$ concentration and lifetime of $N_2^+(B^2\Sigma_u^+)v=0$ have been measured using laser-induced fluorescence (LIF). This very sensitive, nonintrusive, *in situ* diagnostic method has been used for investigating the transfer of internal energy of molecules scattered at surfaces¹⁻³ and for the determination of the lifetime of excited molecules.^{4,5} It is also considered that LIF is nearly ideal for measuring internal energy distributions of ions and radicals in rf plasmas.⁶⁻⁸ LIF, in contrast to optical emission spectroscopy, allows spatially resolved measurements with a high accuracy at any position inside the discharge, even at the area close to the electrodes or to a floating surface placed into the plasma.

The lifetime of $N_2^+(B^2\Sigma_u^+)v=0$, and also the concentration of N_2^+ and the T_{rot} have been measured at different distances from a metal plate placed in the plasma between the electrodes and for different values of plasma parameters (pressure, input power).

In order to explain the results concerning the N_2^+ , lifetime measurements of excited $Ar(3p_6)$ and $N_2(C^3\Pi_u)v=0$ were performed under similar conditions.

In the second part of this work a model simulating the lifetime decrease is presented. This model is based on the

indications of the experimental results; the lifetime diminution is due to the electric field and the attractive forces that accelerate the positive charged species. This results in an enhanced collision frequency and subsequently higher deactivation probability.

The experimental apparatus and the LIF technique are briefly described in Sec. II, while the results on lifetime, concentration, and rotational temperature of the nitrogen ion are discussed in Sec. III. In Sec. IV we include the description of the model and the reasons imposing the Monte Carlo technique together with the results and discussion on the effect of the main parameters. Finally, conclusions are presented in Sec. V.

II. EXPERIMENT

The experimental setup is shown in Fig. 1. Nitrogen plasma is created in a pyrex tube (3.5 cm diameter, 10 cm length) by a rf 13.50 MHz generator (Fig. 2). The rf and the ground electrodes (5×5 cm) surround the tube and their curvature matches the external surface of the reactor. The grounded metal surface ($5\text{ cm}\times 1.5\text{ cm}$) is placed between the two electrodes.

The reactor is pumped down to 10^{-3} mbar with a mechanical two stages pump. The flow rates of the gases are controlled by mass flow meters and the pressure is measured by capacitance manometer.

$N_2^+(X^2\Sigma_g^+)$ is selectively excited to $N_2^+(B^2\Sigma_u^+)v=0$ electronic state by a commercial available tunable laser pumped by a nitrogen laser. The average energy is about $30\ \mu\text{J}/\text{pulse}$ (BBQ dye) with 4 ns duration and a bandwidth greater than $0.4\ \text{\AA}$. The fluorescence is collected by a fused silica lens (f:100 mm) at a direction normal to the laser beam and focused to the entrance slit of a Jobin Yvon 1-m monochromator. The detector is a Hamamatsu PMT (R955) (2 ns rise time). A boxcar averager triggered by the laser, a digital oscilloscope, and a personal computer are used for signal processing and recording.

For the spatial scanning experiments, the reactor is translated with an accuracy of 0.2 mm while the laser beam and the fluorescence collection system are fixed. The $N_2^+(B^2\Sigma_u^+)v=0$ lifetime can be measured by pumping the band head 3914 Å and by tuning the monochromator either at 3914 Å (0,0) or at 4278 Å (0,1). In the first case (pumping and collecting 3914 Å), two different base line substractions are needed: one of the laser beam reflexions and another for the continuous light emitted from the discharge. The laser reflexions can be abstracted by using a pulse discharge with a half the laser frequency, which is 10 pulses/s, and automatically subtraction by the boxcar. In the second case (pumping 3914 Å, collecting 4278 Å) only the continuous emission is subtracted. For rotational temperature measurements the laser was scanned from 3885 to 3914 Å and the monochromator was tuned at 3914 or 4278 Å. In both cases the spectra are similar.

III. EXPERIMENTAL RESULTS: DISCUSSION

A. Lifetime of $N_2^+(B^2\Sigma_u^+)v=0$

The lifetime of excited nitrogen ions was measured as a function of distance from the metal surface, for various pressures. In the bulk plasma this value varies between 30 and 60 ns depending on the pressure and is in good agreement with that reported in the literature.⁹ The results in Figs. 3 and 4 indicate that the lifetime remains constant in the bulk plasma and decreases near the metal surface where the sheath is created. This decrease was observed for all pressures tested (between 0.1 and 1 Torr) and for distances up to 4–5 mm from the surface. The lifetime variation of $N_2^+(B^2\Sigma_u^+)v=0$ is independent of the nature of the metal (Fig. 5); thus this phenomenon cannot be related to physical or chemical properties of the metal.

A similar phenomenon has been observed experimentally^{10–12} and has been simulated¹³ for distances of some tenths of Angstroms away from the surface. It was attributed to

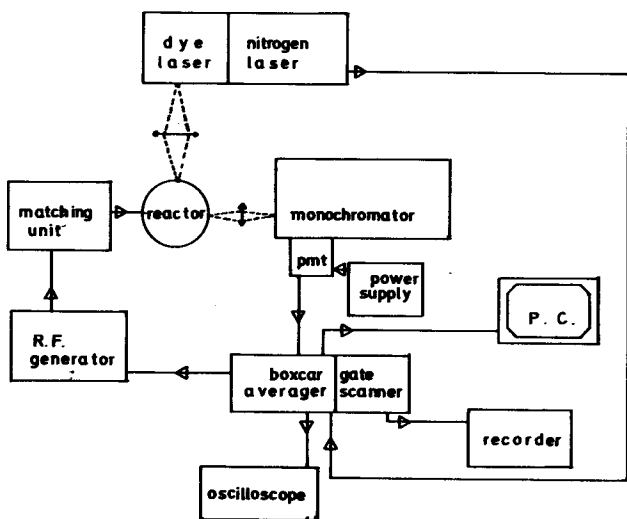


FIG. 1. Experimental apparatus for optical emission and laser-induced fluorescence spectroscopy.

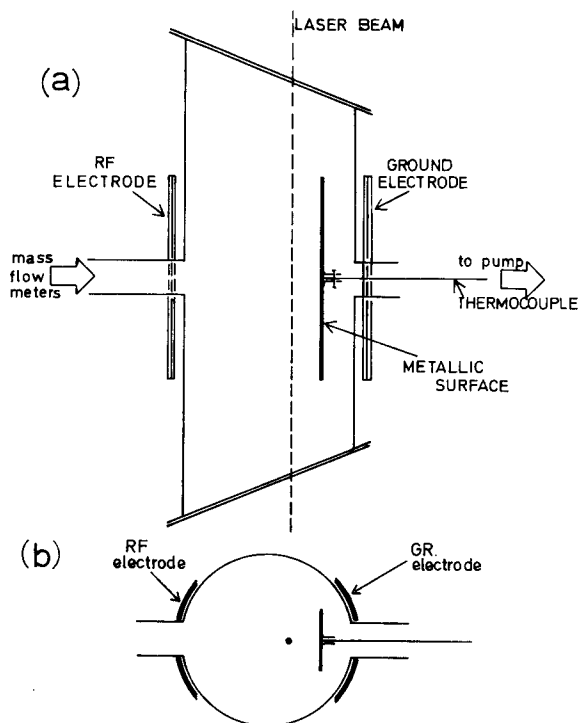


FIG. 2. (a) Vertical and (b) horizontal cross-sectional view of reactor. (Pyrex tube diam: 3.5 cm with external electrodes.)

forces which have no action at distances of some mm, which is the case of the present experiment.

We have found only one case of lifetime decrease in the literature¹⁴ where the lifetime of excited Cl_2^+ was about 30%

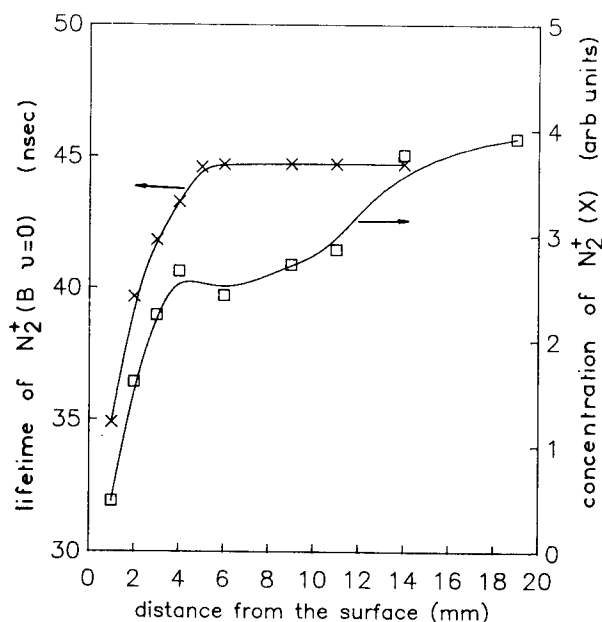


FIG. 3. Profile $N_2^+(B^2\Sigma_u^+)v=0$ lifetime and $N_2^+(X^2\Sigma_g^+)$ concentration [pressure 0.3 Torr, input power 90 W ($V_{rf} = 200$ V), surface temperature 480 K, $T_{gas} = 520$ K].

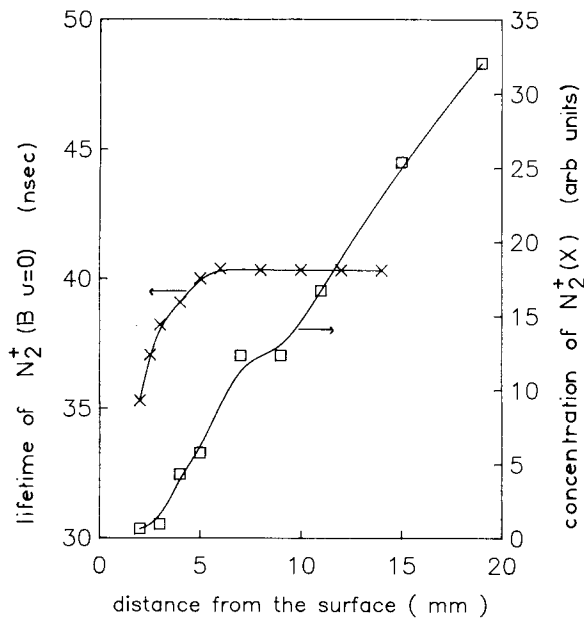


FIG. 4. Profile of $N_2^+(B^2\Sigma_u^+)v=0$ lifetime and $N_2^+(X^2\Sigma_g^+)$ concentration [pressure 0.5 Torr, input power 60 W ($V_{rf} = 140$ V), $T_{surf} = 420$ K, $T_{gas} = 480$ K].

lower at distance 3 mm away from the electrode; that is in good agreement with our experimental results.

In order to examine if the lifetime decrease is limited only to the ions or if it is also observable in neutral species, lifetime measurements of neutral excited species (atomic or molecular) have been performed. The species probed are $N_2(C^3\Pi_u)$ and $Ar(3p_6)$. The results show that the lifetime for Ar in the bulk plasma and in the sheath is almost constant (Fig. 6) (there is a light increase in the vicinity of the surface). The lifetime of $N_2(C^3\Pi_u)$ follows a similar trend.

A possible explanation for the lifetime variation could be the interaction of the excited molecules with particles

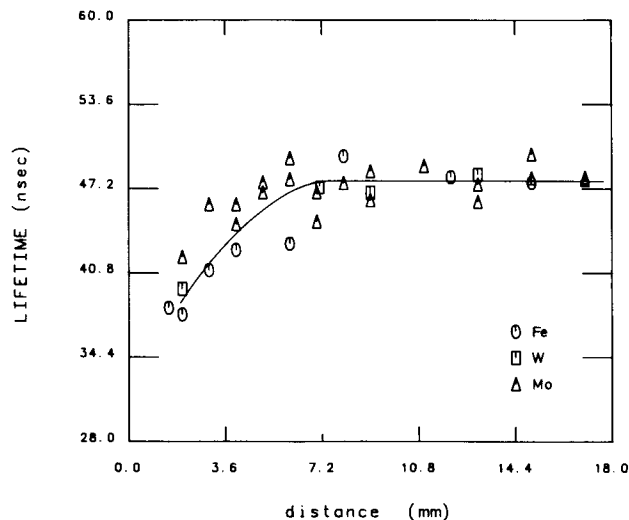


FIG. 5. Lifetime of $N_2^+(B^2\Sigma_u^+)v=0$ vs the distance from the metallic surface for different metals (pressures 0.35 mbar, input power 90 W).

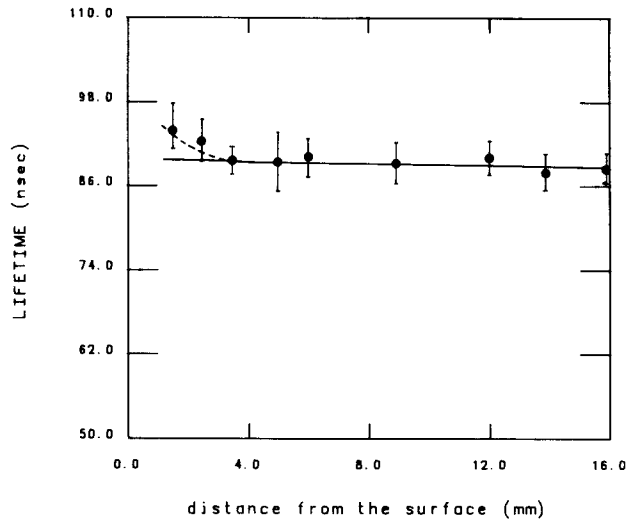


FIG. 6. Lifetime of excited Ar ($1s_5 - 3p_6$) vs the distance from a W surface. ($T_{surf} = 337$ K; pressure: 0.1 mbar; input power: 15 W).

ejected from the metal by sputtering. Indeed the experiments for Ar and N_2^+ were performed for different input power (10 and 100 W, and the surface temperatures were 340 and 500 K, respectively). Under these conditions, particularly in the second case (100 W, $T_{surf} = 500$ K), metal particles created by sputtering could increase the local density number and consequently the collision number, resulting in a local lifetime decrease. However it must be noticed that neither optical emission spectroscopy nor LIF experiment confirmed the presence of metallic atoms in the sheath. Also, phenomena which usually accompany sputtering, like particle deposition on the reactor walls or windows, were not observed. Hence this hypothesis must be excluded as an explanation for the lifetime decrease.

From the preceding it results that the decrease of the lifetime is a specific ionic phenomenon. In that case another possible explanation could be that secondary electrons ejected from the metal surface by Auger-type processes neutralize the ions arriving in the sheath. This enhanced neutralization rate reduces the fluorescence intensity of $N_2^+(B^2\Sigma_u^+)v=0$. Normally a similar neutralization action is expected also for the ground-state ions and as a result a noticeable reduction of $N_2^+(X^2\Sigma_g^+)$ concentration should also appear, but as we can see (Figs. 3 and 4) this does not happen.

The most probable explanation is that the lifetime decreases due to the enhanced acceleration of the nitrogen ions in the sheath region. The electric field becomes stronger closer to the surface, thus ions become faster and the collision frequency increases leading to a lifetime diminution.

This explanation also gives an answer concerning the different behavior of excited Ar atoms and nitrogen excited molecules. As they conserve their velocity in the sheath area, lifetime reduction is not observed. A simulation based on the above considerations is proposed in the second part of this work.

B. Rotational temperature in the sheath

The rotational temperature calculation based on the first negative system of N_2 is widely used for the determination of the gas temperature (see Ref. 15, and references therein). The rotational temperature was measured on the R branch of $N_2^+(B^2\Sigma_u^+)v=0 \rightarrow N_2^+(X^2\Sigma_g^+)v=0$ transition from LIF excitation spectra (Fig. 7).

The resolution of this spectrum is not sufficient for accurate measurement of the rotational temperature by the usual Boltzmann plot. This is due to the bandwidth limit of the laser which is greater than 0.4 \AA . To overcome this problem an R branch simulation was developed considering a Boltzmann distribution over the rotational levels; each of the peaks follows a Gaussian distribution with a standard deviation depending on the bandwidth. The bandwidth is calculated by trial and error method and then is confirmed experimentally with an atomic line at an adjacent wavelength and the same scan parameters. T_{rot} measured by this method, for a bandwidth depending on the scanning parameters, has an accuracy of about 20 K.

Using this method T_{rot} was measured at different distances from a Fe surface. This profile, as well as the concentration of $N_2^+(X^2\Sigma_g^+)$ measured by the intensity of 3914 \AA band head, are presented in Fig. 8. T_{rot} has a nearly constant value ($570 \pm 20 \text{ K}$) in the bulk plasma and decreases in the sheath area. The intercept of T_{rot} line gives a rotational temperature of about $480 \pm 20 \text{ K}$ at the surface. The surface temperature (T_{surf}) measured at the same time by a thermocouple is 485 K . This observation confirms that the surface temperature is in equilibrium (within the accuracy of measurements) with the T_{rot} of N_2^+ .

The additional translation energy of the ions in the sheath has no effect on their rotational temperature. The rotational temperature of ions continues to be in equilibrium with the neutral gas temperature and not with their kinetic

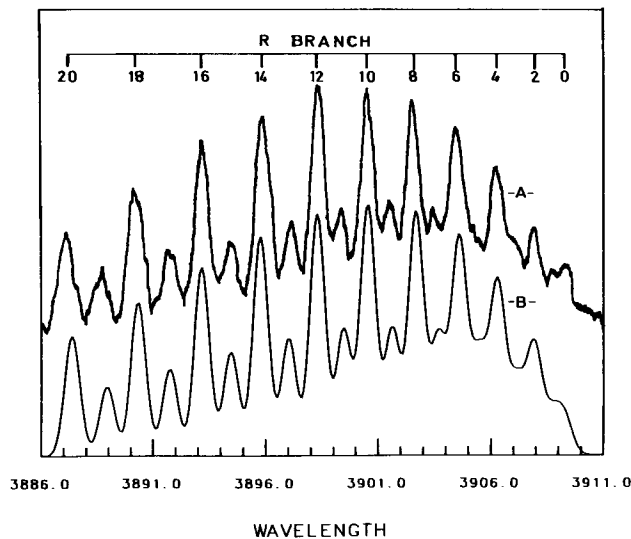


FIG. 7. A: LIF excitation spectrum for the R branch of $N_2^+(B^2\Sigma_u^+)v=0 \rightarrow N_2^+(X^2\Sigma_g^+)v=0$. B: Computer simulation of the above spectrum for rotational temperature measurement.

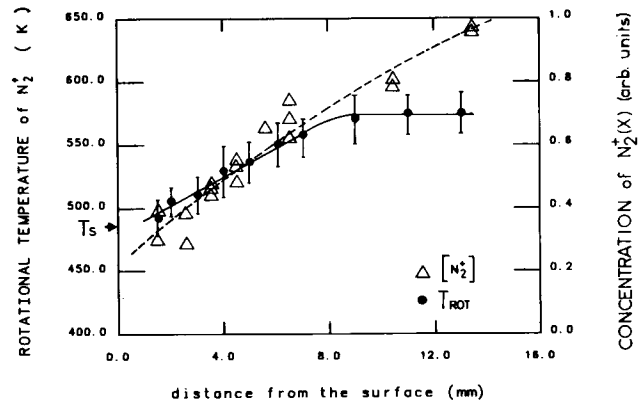


FIG. 8. Rotational temperature measured by LIF spectroscopy and concentration of $N_2^+(X^2\Sigma_g^+)$ measured by time resolved LIF spectrum vs the distance from an Fe surface (pressure 0.5 mbar, input power 90 W, surface temperature 485 K).

temperature at the same point. The charge exchange collision is the dominant process in the sheath because its cross section is large compared to the cross section of other processes (elastic or inelastic collision). After a charge exchange collision the created ion conserves the rotational energy of the molecule. Thus the measured rotational energy (LIF spectrum gives the image of the pumped initial state, and we measure the rotational temperature of the ground-state ion) must have almost the same value as the rotational energy of the parent molecules.

Margoulis and Jolly¹⁶ have measured the ion rotational temperature in the negative glow of a nitrogen discharge and also in the region near the cathode. They found that T_{rot} of the ions is equal to the T_{rot} of the neutral gas in the bulk plasma, but in the sheath area the ion acceleration perturbs this equilibrium and the ionic T_{rot} becomes higher than the gas temperature. The difference in this case is that there is a large electric field in the cathode region (3000 V/cm). It is possible that for much higher ion kinetic energies the cross section for inelastic collisions becomes important and the rotational temperature of the ions is influenced by the ion acceleration in the sheath. In our case the electric field is much weaker ($100\text{--}300 \text{ V/cm}$).

Petitjean and Ricard¹⁷ have also measured the N_2^+ rotational temperature near a metal surface (cathode). They used emission spectroscopy for measuring the rotational temperature of the excited state. Their results indicate that the ion rotational temperature is in equilibrium with the surface temperature which is in equilibrium with the neutral gas temperature.¹⁸

C. Ground-state concentration of N_2^+

Time-resolved LIF spectra have been used for the determination of the relative concentration of ground-state ions. These measurements have been obtained by pumping the band head of $v'=0, v=0$ transition (3914 \AA). The results show a quasilinear decrease of the $N_2^+(X^2\Sigma_g^+)$ concentration with increasing distance from the rf electrode (Figs. 3

and 4). The highest concentration of N_2^+ ($X^2\Sigma_g^+$) was measured near the cathode and the lowest one near the grounded surface. For the concentration measurements the lifetime diminution was not taken into account. Thus in the sheath area the concentration of the ground-state ions presents a lower value than the real one. The observed axial distribution can be explained by the fact that the N_2^+ ions are created by collisions with energetic electrons located mainly near the rf electrode, and then are destroyed by the reaction $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$, or by neutralization.¹⁹

The decrease of the ion concentration becomes more sharp in the sheath area (Fig. 3) when the input power increases. On the contrary, in the bulk plasma the decrease is steeper as the input power is lower (Fig. 4). The ion concentration profile reflects the profile of the energetic electrons able to create ions in the plasma. For high input power [90 W and rf voltage (V_{rf}) is about 200 V] the sheath area is strictly delimited (Fig. 3), whereas for lower input power the sheath limits are not clearly defined from the ion concentration profile (Fig. 4). This is because the concentration is very low near the metal as well as in the bulk plasma, while the electric field is weak and the signal decreases smoothly as one approaches the surface.

For high input power the profile has a local maximum near the sheath region. The maximum is due to the enhanced ionization caused by the secondary electrons emitted from the metal and accelerated through the sheath to the boundaries of the bulk plasma. The energy of these electrons exceeds the ionization threshold when the input power is high enough and the electric field strong. This maximum is present only in the case when the acceleration in the anode sheath permits the electrons to acquire the necessary energy for ionization. This is why for lower input power the decrease of the ion concentration does not present any local extrema.

The number of secondary electrons depends on the number of the incident ions while their energy depends on the ionization potential of the incident ions and mainly on the created field. The two parameters (ion flux and field intensity) depend on the input power and become significant for sheath voltages of about 100 V.

IV. SIMULATION

The experimentally observed lifetime decrease of the excited ions in the plasma sheath could be used for the determination of the parameters that are responsible for this behavior. For this reason a model simulating the above phenomenon becomes necessary.

A. Description of the model

This model, in what it concerns the ion trajectories, is based on a stochastic analysis whereas the calculation of sheath potential is based on a parametric model.

The energy distribution of the ions across the sheath is a problem which has been studied by many authors (see Ref. 20 and references therein). A representative case, with conditions similar to ours, is that of Davis and Vanderslisse.²¹ They have proposed an analytical expression for the ion energy distribution which has been confirmed by other authors

as it is referred by Chapman.²² The main assumptions for this model are as follows: (1) Little or no ionization in the sheath. The ion flux remains constant across the sheath. (2) The dominant collision process is of symmetrical charge transfer ($N_2^+ + N_2 \rightarrow N_2 + N_2^+$). (3) The charge exchange cross section is independent of energy. (4) The electric field decreases linearly to zero at the dark space–glow interface. The first assumption is considered to be valid in our conditions whereas this is not true for the second and third assumptions. The deactivation of an excited nitrogen ion does not proceed through symmetrical charge transfer; the cross section for this process is very low or negligible.⁹ For an excited ion the symmetrical charge transfer involves the transfer not only of a valence electron but also of electronic excitation. Hence the dominant process is that of the elastic collision.^{23,24}

Since in our case the analytical expression does not apply, a stochastic approach based on the Monte Carlo technique was chosen. This technique has the disadvantage of consuming much CPU time, but it has the advantage of easy access and modification of the initial assumptions (type of collisions process, model of the electric field, etc.). The Monte Carlo technique has been previously used^{20,25} for the determination of ion energy distribution. This choice gives us the possibility of including the excited ions which are not detectable. This category includes excited ions, which although are deactivated by radiation (when their radiative lifetime is over), their drift displacement is greater than the focused area, or they are deactivated reaching the surface.

The stochastic technique for the calculation of excited ion trajectories can be described by the following steps.

A ground state ion begins its trajectory after a charge exchange collision with a velocity randomly chosen from a Maxwellian distribution and a random angle. Its velocity at a specific time t is the vector addition of its initial velocity and the velocity due to the electric field (function of time and space). Its trajectory is calculated as a function of time from the expression

$$s = \int_0^t v dt, \quad (1)$$

while its drift displacement is calculated in the same way taking into account the drift velocity.

The mean free path between two collisions is defined by

$$\lambda = \frac{1}{\sigma_{col} N} \quad (2)$$

where σ_{col} is the collision cross section, and N the density of collision partners.

Let $\Delta s = -\lambda \ln(r)$ ($r \in (0,1]$) be the distance until the first collision of the ground-state ion, and $\Delta s_1 = (r)\Delta s$ be the distance that it had transversed until the time it was excited by the laser beam (and Δs_2 is the rest of the free path). Let $t_{RLT} = -60 \ln(r)$ be the excited ion lifetime in a noncollisional environment. The time needed for the excited ion to reach the first collision partner is t_1 .

If $t_1 < t_{RLT}$ this collision will take place between an excited ion and a molecule. The energy of the excited ion at the moment of collision is $(\frac{1}{2})mv^2$ and the deactivation cross section σ_d is calculated as a function of the above energy. σ_d

is considered to be proportional to $E^{-0.41}$ where E is its kinetic energy.²⁴ Then $\lambda_d = (\sigma_d N)^{-1}$ and $\Delta s_d = \lambda_d \ln(r)$. If $\Delta s_d < \Delta s_2$ the ion will be deactivated by a nonradiative process. In all other cases the collision is considered to be elastic and the excited ion has a new lifetime $t_{\text{RLT}} = t_{\text{RLT}} - t_1$ to undergo a new collision.

After each collision the excited ion is either deactivated if $\Delta s_d \leq \Delta s_{\text{tot}}$ (and the trajectory of a new ion is studied) or remains in its excited state if $\Delta s_d > \Delta s_{\text{tot}}$. The latter spends its radiative lifetime and loses its excess energy emitting a photon, which will be detected if the total drift displacement is shorter than the detection area.

The sheath parameters were calculated using analytical expressions.²⁶ The discharge is considered to be a capacitively coupled rf electropositive discharge with two equal area electrodes. It is established by applying a voltage $V(t) = V_{\text{rf}} \sin(\omega t)$.

Then the time-dependent value of the plasma potential will be

$$V_p(t) = \bar{V}_p + \Delta V_p \sin(\omega t), \quad (3)$$

where

$$\bar{V}_p = (1/2) V_{\text{rf}} \quad \text{and} \quad \Delta V_p = [c_i / (c_i + c_\omega)] V_{\text{rf}}. \quad (4)$$

c_i and c_ω are the time average sheath capacitances. For a grounded surface the sheath potential (V_{sh}) is equal to the plasma potential (V_p).

The sheath thickness can be calculated from the formula

$$l(t) = l_{\text{dc}} + l_{\text{rf}} \sin(\omega t + \phi),$$

where ω is the rf frequency and ϕ the phase shift between the oscillation of sheath thickness and the plasma potential. The sheath thickness is considered to be independent of time.

For the electric field we use the parametric formula proposed by Kushner²⁰:

$$E(x,t) = E_0 (l_{\text{sh}} - x)^a, \quad E_0 = V_{\text{sh}}(t) [(a+1)/l_{\text{sh}}^{a+1}], \quad (5)$$

where a is a positive constant usually equal to unity, but in this model the value $a = 1.2$ was also tested.

B. Simulation results and discussion

The lifetime of an excited ion in the bulk plasma is a function of pressure and temperature. The ion velocities are approximately equal to the molecular velocities and the excited state lifetime depends only on the local temperature which determines a local number density. An additional force is acting in the sheath, namely the electric field. The local velocity depends not only on the local temperature but also on the local electric field, which is able to increase the ion velocities many times. The electric field has a dominant role on the excited ion lifetime.

The method used in this model requires a lot of CPU time. The minimum number of ions for a precise calculation of the lifetime is about 6000. Thus we need 6000 excited ions that will be deactivated by radiation process before they leave the detected area. This means that we need to examine the trajectory of at least 10 000 ions for 1 mm distance from the surface, because the probability of detection is about 0.6

or 60%; while in the bulk plasma (for 46 ns lifetime) this probability is about 0.92.

The deactivation cross section is related to the value of the electric field through the relation $\sigma_d \propto E^{-0.41}$. This relation indicates that the lifetime decreases as the velocity (or the temperature) increases, because the rate of decrease of σ_d is lower than the rate of increase of the collision frequency. Actually, a simple analytical model which takes into account the dependence of σ_d upon the mean kinetic energy ($E_x \times \lambda \times e$) gives a lifetime decrease which does not agree with the experimental data (Fig. 9). The calculated lifetime decrease is important in the sheath boundary and is lower as the distance from the surface is shorter, having a limit where the velocity increase has a negligible effect on the lifetime.

Our model demonstrates that the lifetime decreases as a result of a higher collision frequency and the greater drift velocity (the elastic collisions permit the excited ions to acquire higher velocities compared to the ground state ions that undergo charge exchange collisions). The higher velocities allow the excited ions to move in a nondetected area or to reach the surface before their radiative deactivation. For the bulk region the probability for an excited ion to radiate away from the point of its creation is lower than of 1% but for a distance 1 mm from the surface this probability is about 20% (for an electric field 360 V/cm). This means that this effect is negligible for the bulk plasma but is important for the sheath region, and its role becomes more significant as the distance from the surface decreases. This means that the measured lifetime does not correspond to the real lifetime as the electric field becomes stronger.

The good agreement between the calculated and the experimental data (Figs. 10 and 11), confirms that the main considerations (trajectory, type of collision) and the assumptions (collision cross section, profile of the electric field) are correct or are very near to reality. A discussion on the effect of the main parameters is presented below.

The sheath voltage drop is the main parameter responsible for the lifetime decrease. We used the plasma potential as sheath potential because our experimental data concern a grounded surface and not the cathode electrode. The de-

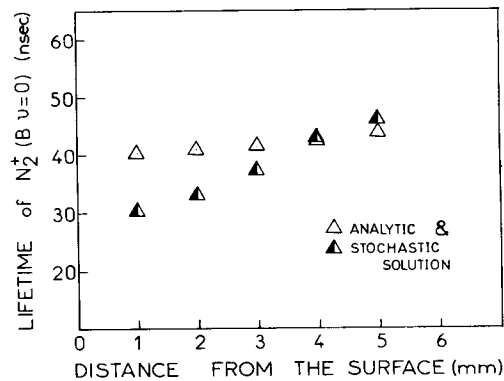


FIG. 9. Comparison between a simple analytic solution and a stochastic model. In the first case the lifetime decrease is important only in the sheath boundary but the value of the lifetime tends to a limit as the electric field increases. The results from the stochastic solution shows an almost linear lifetime decrease. ($T_{\text{gas}} = 540$ K, $T_{\text{surr}} = 480$ K, pressure = 0.3 Torr, $l_{\text{sh}} = 5$ mm, $a = 1.2$, $V_{\text{sh}} = 100$ V).

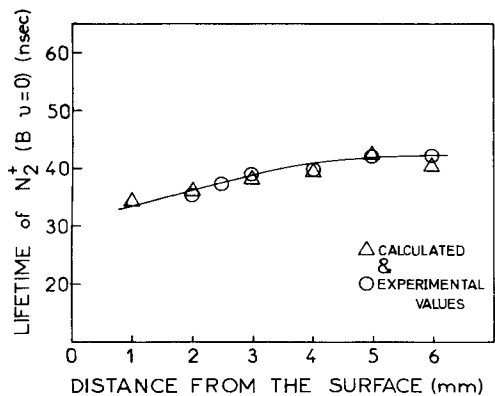


FIG. 10. Comparison between experimental and calculated results. The calculated point for distance 6 mm was calculated from the analytical expression $1/\tau = 1/\tau_0 + k[N]$. Thus this is the expected result for the point of 5 mm as well, where the electric field has the same mean value of 0 V. ($T_{\text{gas}} = 480$ K, $T_s = 420$ K, pressure = 0.5 Torr, $l_{\text{sh}} = 5$ mm, $a = 1.2$, $V_{\text{sh}} = 70$ V).

pendence of the lifetime decrease on the sheath potential is shown in Fig. 12. For a sheath potential of 100 V the lifetime at a distance of 1 mm from the surface is 67% of the lifetime in the bulk; for 200 V this percentage becomes 63%, and for $V_{\text{sh}} = 20$ V it becomes 83%. The dependence of the lifetime on the sheath potential gets stronger when its value is low. For the same ΔV_{sh} the lifetime presents a lower variation as the sheath potential is higher. The change of the sheath potential does not only influence the lifetime in the sheath, but also in the bulk plasma where the mean electric field is zero but the nitrogen ions are subject to the action of the sinusoidal plasma potential. In real experimental conditions these changes of lifetime in the bulk plasma are balanced by the different plasma temperature which has the opposite result of the lifetime.

Besides the value of the voltage drop another important parameter is the profile of the electric across the sheath. As it has been referred the parametric formula

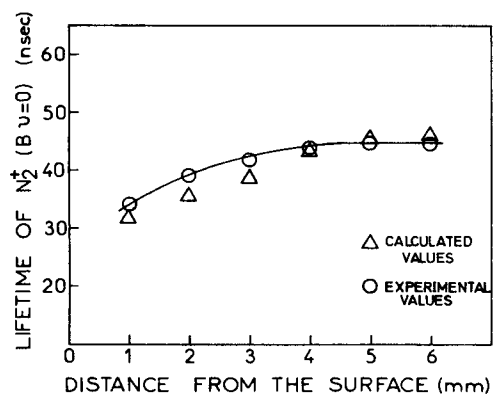


FIG. 11. Comparison between experimental and calculated results. The calculated point for distance 6 mm was calculated from the analytical expression $1/\tau = 1/\tau_0 + k[N]$. Thus this is the expected result for the point of 5 mm as well, where the electric field has the same mean value of 0 V. ($T_{\text{gas}} = 540$ K, $T_{\text{surr}} = 480$ K, pressure = 0.3 Torr, $l_{\text{sh}} = 5$ mm, $a = 1.2$, $V_{\text{sh}} = 100$ V).

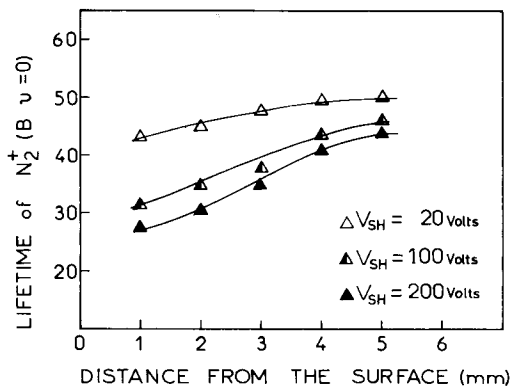


FIG. 12. Influence of the sheath voltage of the lifetime decrease. The gas temperature remains constant for all the steps from the bulk plasma to the surface and the only reason for the lifetime decrease is the electric field. The different plasma potential results in a different lifetime in the bulk plasma where the mean electric field is zero ($T_{\text{gas}} = 450$ K, $T_{\text{surr}} = 450$ K, pressure = 0.3 Torr, $l_{\text{sh}} = 5$ mm, $a = 1.2$).

$$E(x,t) = V_{\text{sh}}(t) [(a+1)/l_{\text{sh}}^{a+1}] (l_{\text{sh}} - x)^a,$$

has been used. For $a = 1$ the field is linear. Considering a linear electric field the lifetime also has a linear decrease from the sheath boundary up to the surface (Fig. 13). For $a > 1$ it becomes convex and for $a < 1$ it is concave. The profile of the electric field was measured by Moore *et al.*²⁷ and was found to be linear at any moment in the rf cycle. The sheath width is not equal at any time in the rf cycle but its value is $l_{\text{dc}} + l_{\text{rf}} \sin(\omega t)$. This means that for a part of the rf cycle in a region of width l_{rf} near the sheath boundary there is no electric field, or the mean electric field is weaker than the time average of the electric field. In our case the l_{rf} is not known and the only information for the sheath width was the distance where the lifetime appears to be lower. To overcome this problem we have used for the simulation $a = 1.2$. This value of a is an alternative way to consider the existence of a region near the bulk where the field is weaker. For a sheath width of 5 mm the value of the electric field at a

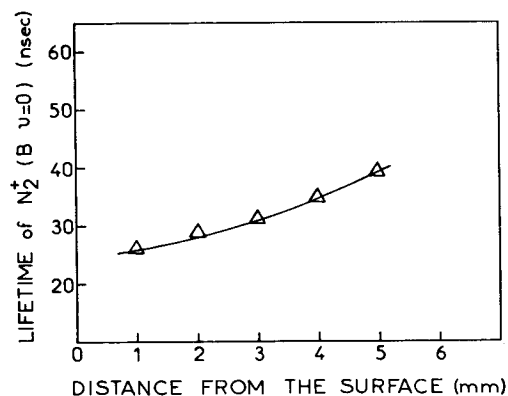


FIG. 13. Profile of the lifetime when the electric field increases linearly ($a = 1$). The decrease is greater near the sheath boundary ($T_{\text{gas}} = 580$ K, $T_s = 500$ K, pressure = 0.5 Torr, $l_{\text{sh}} = 5$ mm, $a = 1$, $V_{\text{sh}} = 200$ V).

distance of 4 mm is $0.8V_{sh}$ for $a = 1$, and $0.63V_{sh}$ for $a = 1.2$. For a distance of 1 mm it is $3.2V_{sh}$ and $3.36V_{sh}$, respectively. The difference is significant near the bulk and becomes negligible as the distance from the surface becomes shorter. This value of a gives a lifetime decrease closer to the experimental data and at the same time the field linearity is valid in the main region of the sheath. This value was used for the majority of cases.

Finally, other important parameters for the simulation are the values of the cross sections, namely the deactivation and the elastic collision cross section. The equation of Comes and Speier²⁴ gives the dependence of the deactivation cross section on the ion translation energy. The value of σ_d for temperatures between 300 and 500 K calculated by this relation is a little lower than that calculated from our experimental data, which is in agreement with the value obtained by Jolly.⁹ This results in a little higher lifetime value in the bulk region where the lifetime is calculated in the same way as in the sheath (for zero mean electric field). The other important cross section is the elastic collision cross section. Its value is not known and we have used the value of 43 \AA^2 , which is equal to the collision cross section of nitrogen. The real value is expected to be larger, because electric attractive forces caused by polarization play an important role. The effect of σ on the lifetime is shown in Fig. 14 where the results for two different values of σ (43 and 200 \AA^2) are presented. A higher value of σ results in a lower lifetime in the sheath and in the bulk region, because it enhances the collision frequency and at the same time the kinetic energy at the moment of collision is lower; this results in higher deactivation probability and lower lifetime. The dependence of σ on the ion kinetic energy is not known and was considered to be constant. The exact value of σ is important for our calculations. A five times increase of its value has as a result a lifetime decrease similar to that provoked by an increase of the sheath voltage from 70 to 100 V.

IV. CONCLUSION

In this paper T_{rot} , N_2^+ concentration, and $N_2^+(B^2\Sigma_u^+)v=0$ lifetime have been measured by LIF in a

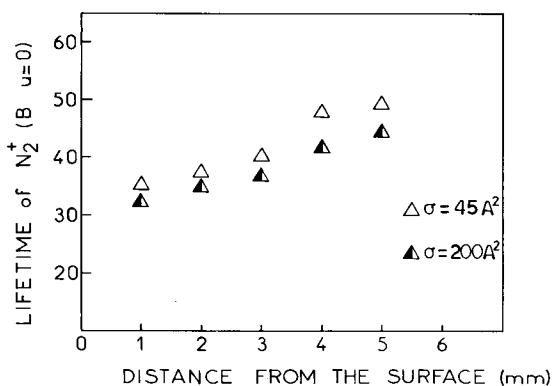


FIG. 14. Lifetime profile for two different values of the elastic cross section. The dependence of the lifetime on σ is almost the same for all the values of the electric field ($T_{gas} = 480 \text{ K}$, $T_{surf} = 420 \text{ K}$, pressure = 0.3 Torr, $l_{sh} = 5 \text{ mm}$, $a = 1.2$, $V_{sh} = 70 \text{ V}$).

nitrogen plasma and plasma sheath. A model simulating the experimentally observed lifetime decrease in the plasma sheath was also presented. The lifetime decrease of $N_2^+(B)$ at distances up to 4–5 mm from the metal surface is reported for the first time. This phenomenon is characteristic for the ions and can be attributed to their acceleration in the sheath which increases the collision frequency and reduces their lifetime.

The results for the N_2^+ concentration present a quasilinear decrease from the rf electrode to the metal surface with no observable perturbations near the surface. The rotational temperature of N_2^+ measured by LIF shows a continuous decrease from the bulk plasma up to the surface. The T_{rot} close the surface is equal to surface temperature, indicating an equilibrium of the plasma with the surface.

The presented model is based on a Monte Carlo analysis of the excited ion trajectories and the results are in good agreement with the experimental values. Small changes of the electric field have small effect on the lifetime decrease. This means that very precise values of the experimental measurements are necessary for accurate estimation of the local electric field.

The precise values of two other parameters, namely the electric field profile and the cross sections for all the possible reactions of $N_2^+(B)$ are of great importance. Their exact determination will have significant effect on the lifetime estimation.

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