DETERMINATION OF N_2 ATOM DENSITY IN N_2 AND IN N_2-CH_4 H.F. FLOWING POST-DISCHARGES

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Abstract

N-atom density has been determined in N_2 and N_2 - (10^{-5}-10^{-3})CH_4 flowing microwave post-discharge by NO titration and emission spectroscopy.
The NO titration clearly gives accurate results in the late afterglow where the N+N recombination is the dominant reaction. The proposed spectroscopic method extends the diagnostic of N atoms density from the late to the early (pink) afterglow. The effect of a few CH_4 addition into N_2 on the N-atom density is reported.

1) Introduction

Production of active species in flowing post-discharges is studied in connection with plasma reactions for surface treatments. With N_2 H.F. flowing discharges, the N atom flux in the post-discharge has been previously determined by NO titration and it has been correlated to the growing of iron nitrided layers [1]. The N_2 post-discharge is characterized by specific afterglows, named pink afterglow at shorter times (10^{-3}s-10^{-2}s) and late afterglow at longer times (10^{-2}s-10^{-1}s). It is shown in [2] how to separate the pink and the late afterglow from the N_2 1st positive vibrational distribution and how to determine the N atom relative density from the 1st positive intensity.

It is the purpose of the present paper to compare the diagnostics of N atoms density by optical spectroscopy and by NO titration in the whole time period of the pink and of the late afterglows.

The effect of a few CH_4 into N_2 on the N atom production is then reported.

2) The experimental set-up

The experimental set-up of the H.F. 2.45 GHz flowing discharge and post-discharge is reproduced in Fig. 1. A microwave generator (Raytek, power up to 2kW) is connected to a resonant cavity. The plasma is produced via a coupling antenna in a quartz tube (12 mm o.d., 10 mm i.d.) crossing the microwave cavity. The gas pressure and the flow rate are measured by means of a baratron gauge and a mass flowmeter.

Optical emission is analysed by a quartz optical fiber connected to a monochromator (HRS 1, Jobin-Yvon, 1220 gr./mn) with a photomultiplier (Hamamatsu R928) and a chart recorder. The optical spectra are recorded along the z axial distance (cf Fig. 1) from discharge end (1) to the pink afterglow (2) and to the late afterglow (3). The N atom density is measured by NO titration with a pipe tube of diameter 4mm which can move along the post-discharge from the end of the late afterglow to the pink afterglow (cf Fig. 1). An Ar-5%NO gas mixture has been used, the N titration by NO being umperturbed with the Ar gas. The mixing of N atoms with NO has been improved by ending the Ar-NO pipe tube with three small slots of width about 1 mm.

3) N atom density in the N_2 post-discharge

The N atom density is obtained by NO titration at the extinction point between emissions of the NOβ violet bands and of the NO_2^* green continuum (cf [1] for more details). Then, the N and NO flow rates are equal in quantity. The N atom density versus the post-discharge time is reproduced in Fig. 2 for 180 W N_2 discharges at gas pressures from 10 to 100 mbars and flow rates from 0.2 to 1 Slm^{-1}.

The post-discharge time is calculated from the z distance measurements by taking into account the gas temperature variations along the post-discharge tube [3]. It can be deduced from Fig. 2 that the N atom density is slowly decreasing in the afterglow until $3\ 10^{-2}$ s in the gas pressure range 10-100 mbar.

Now, it is discussed how to obtain the N atom density from the N_2 1st positive emission.

The late afterglow is produced by the following reaction :

$$N + N + N_2 \rightarrow N_2(B, v') + N_2 \qquad a)$$

$$N_2(B, v') \rightarrow N_2(A, v'') + h\upsilon,$$

with a strong enhancement of $N_2(B, v'=11)$ which is the signature of N atoms in the post-discharge.

At N_2 gas pressure higher than 1 Torr, the $N_2(B, v')$ levels are mainly destroyed by N_2 quenching :

$$N_2(B, v') + N_2 \rightarrow \text{products} \qquad b)$$

so that the 1st positive intensity is related to the N atom density as it follows :

$$I_{N_2}(1^{st}\text{ pos.}) = K(\lambda)\cdot \frac{hc}{\lambda} A_r\,[B, v'] \qquad (1)$$

$$\text{with } [B, v'] = [N]^2 \frac{k_a}{k_b}$$

In equation (1), $K(\lambda)$ is the spectral response at the wavelenght λ of the optical system, A_r is the radiative emission probability, k_a and k_b are the rate coefficients of reactions a) and b), respectively. It results from eq. (1) that I_{N_2} (1^{st} pos.) is proportional to $[N]^2$.

In the pink afterglow, the N_2 1st positive emission is produced by other kinetics reactions that reaction a) where the $N_2(X, v)$ vibrational density plays an important part [2]. As a consequence, the $N_2(B, v')$ vibrational is continously decreasing with v' without the v'=11 enhancement as observed in the late afterglow. In situations where the pink and the late afterglow are not clearly separated, it is necessary to employ the method given in [2] to separate reaction a) and to determine the relative N atom density from the N_2, 1^{st} positive spectrum. The normalized $r_{B,v'}$ distribution of $N_2(B, v')$ populations with :

$$r_{B,v'} = \frac{[N_2(B, v')]}{\sum_{v'=7}^{12}[N_2(B, v')]}$$ is the addition of $r_{B,v'}$ (N+N) as given by eq. (1)

and

of $r_{B,v'}$ (pink) with :

$$r_{B,v'} = A\ r_{B,v'}(N+N) + B\ r_{B,v'}(\text{pink}) \qquad (2)$$

Choosing the $I(\lambda = 580.4$ nm) intensity of the N_2(B, 11-A, 7) transition, it results from eq. (1) and (2) that :

$$[N] = \sqrt{A\ I(\lambda = 580.4\ \text{nm})},$$

in relative units. (3)

The relative N atom density given by eq. (3) is reproduced in Fig. 3 versus the post-discharge time in experimental conditions as in Fig. 2. It can be observed in Fig. 3 that the slow N atom decrease with time is more clearly extended in the pink afterglow than in Fig. 2 for NO titration.

The results reported in Fig. 3 in the pink afterglow are for a value of A (cf eq. (2)) higher than 0.4. The results of relative N atom densities in Fig. 3 are well correlated to that of N atoms density obtained by NO titration method except in the pink afterglow. In the pink afterglow, the NO molecules can react with other active nitrogen species than the N atoms contrary to what happens in the late afterglow. It is then necessary to increase the NO flow rate to obtain the extinction point of the N atom titration and then the N atom density is surestimated in the pink afterglow.

4) N atom density in N_2 - (10^{-5} - 10^{-3}) CH_4 post-discharges

The interest of N_2 with small additives of CH_4 has been recently demonstrated to improve the iron nitriding process [4]. With a CH_4/N_2 ratio of 5 10^{-4} in a 40 Torr - 120 W H.F. post-discharge with 90% Ar gas, it has been obtained thick $\varepsilon + \gamma'$ iron nitride layers of thickness 20-22 µm, without oxides, for treatment times of 4 hours at 840 K of diameter 1cm Fe substrates. The N atom relative density has been determined from the N_2 1^{st} positive vibrational distribution by applying eq. (2) and (3). With N_2/CH_4 gas mixtures, the NO titration of N atoms cannot be applied as NO can react with the CH_4 products in the post-discharge.

The results are reproduced in Fig. 4 for N_2-xCH_4 with x = 0 - 10^{-3} and two post-discharge times Δt=1.6 and 2.1 10^{-2} s with a 180 W H.F. discharge at 50 mbar and Q=1Slm^{-1}.

From the N_2 1^{st} pos. vibrational distribution, it has been found A = 0.3 (cf eq. (2)) in pure N_2 indicating a strong contribution of the pink afterglow. With x > 5 10^{-5} of CH_4, it is obtained A= 0.5 - 0.6 showing a decrease of the pink afterglow part. The N atoms density is increasing with CH_4 by a factor of about 2 for x ≈ 10^{-4} corresponding to a maximum value.

For $x > 10^{-4}$, the N atom density decreases slowly until values about 2 times lower than in pure N_2 for $x = 7.5\ 10^{-4}$. The maximum value of N atoms density at $x \approx 10^{-4}$ is well related to the improvement of the nitriding process found in [4].

5) Conclusion

A spectroscopic method from the N_2, 1st pos. vibrational intensities has been applied to determine the N atom densities in N_2 and N_2-(10^{-5}-10^{-3})CH_4 H.F. post-discharges.

Quantitative results are obtained by NO titration in conditions of late afterglow where the N + N recombination is the dominant reaction.

The present spectroscopic method can be extended to short time afterglows (pink) and to N_2 with addition of reactive gas where the NO titration is questionable. A maximum of N atoms with a factor 2 increase has then been determined in the present N_2-10^{-4} CH_4 H.F. post-discharge for 50 mbar. For pressure lower than 50 mbar, the methane addition leads to a decrease of N density in the pink afterglow but an increase is still observed in the late afterglow.

References :
[1] A. RICARD, J. OSEGUERA, L. FALK, H. MICHEL and M. GANTOIS *I.E.E.E. Trans. Plasma. Sci.* 18 (1990) 940
[2] S. BOCKEL, A.M. DIAMY and A. RICARD
P.S.E. Garmish (1994)
[3] J. ALANDARI, A. M. DIAMY, L. HOCHARD, J.C. LEGRAND, A. RICARD *I.S.P.C. - 11 Loughborough* (1993)
[4] A. RICARD
Surf. Coatings Techn. 59 (1993) 67

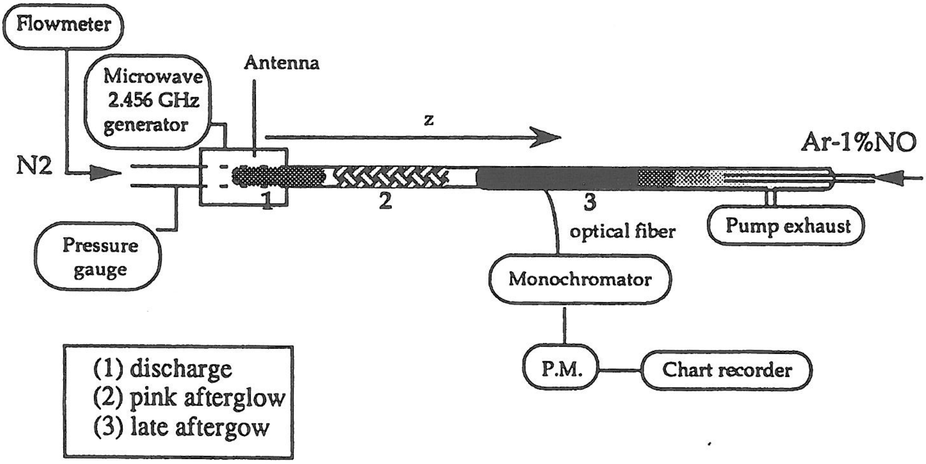

Fig. 1 : Experimental set-up

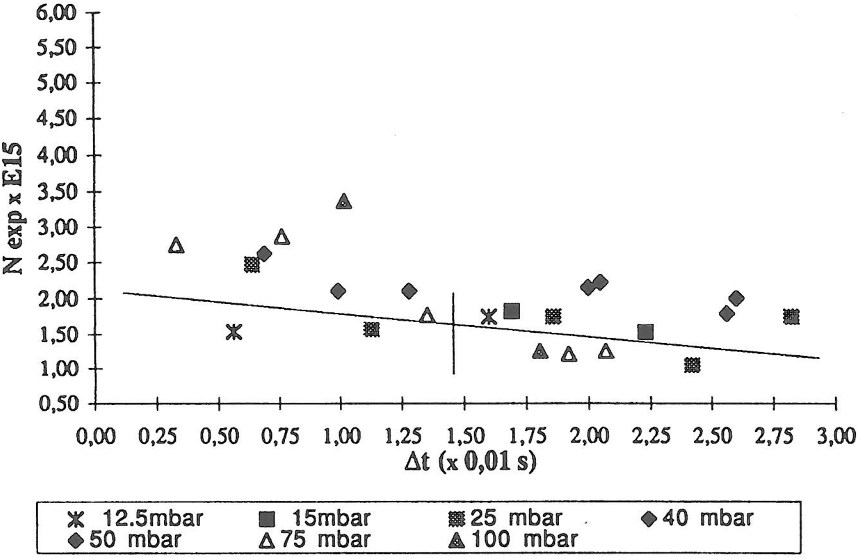

Fig. 2 : N atom density versus the post-discharge time for 180 W N_2 discharges at flow rates from 0.2 to 1 $Sl.min^{-1}$

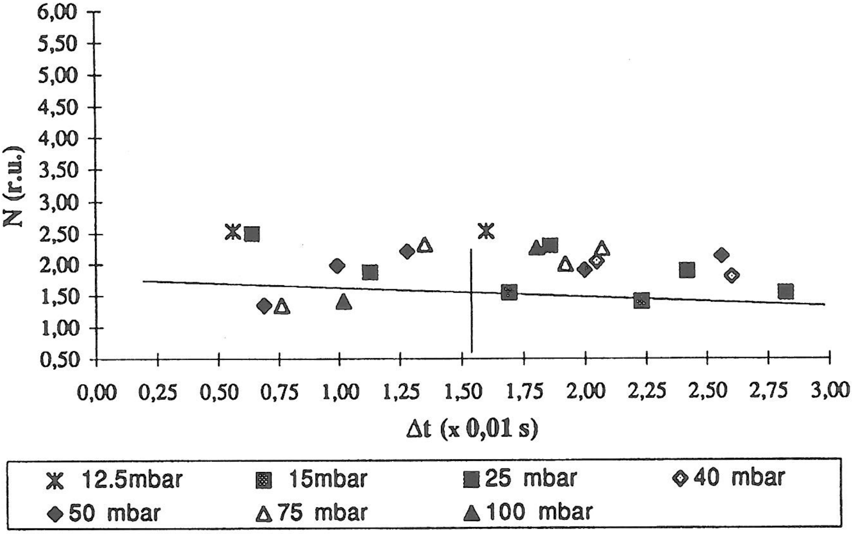

Fig. 3 : Relative N atom density given by [N]= (a I (λ=580.4 nm)$^{1/2}$ versus the post-discharge time for 180W N_2 discharges at flow rates from 0.2 to 1 $Sl.mn^{-1}$.

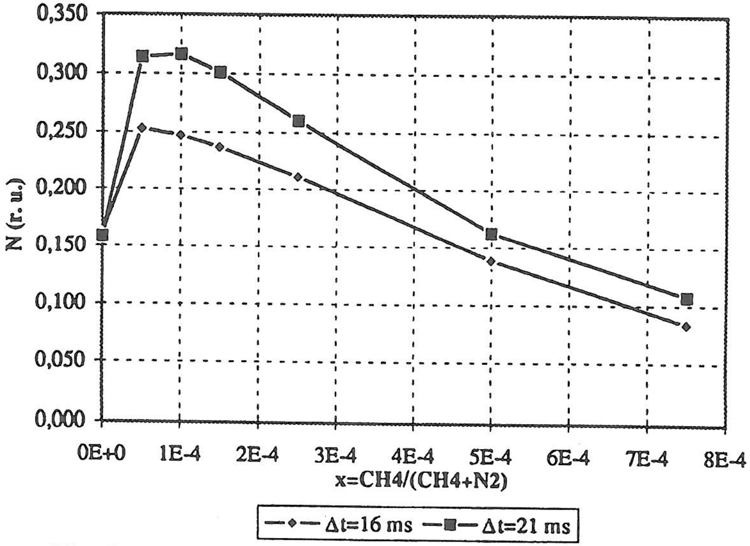

Fig. 4 : Effect of CH_4 on N atom relative density given by eq. (3) with a 180 W H.F. discharge at 50 mbar and Q=1Sl.mn^{-1}
[N](x=0) = 1.5 E15 cm^{-3}