

Electrical and optical characterization of pulsed plasma of N₂–H₂

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Abstract. This paper considers the electrical and optical characterization of glow discharge pulsed plasma in N₂/H₂ gas mixtures at a pressures range between 0.5 and 4.0 Torr and discharge current between 0.2 and 0.6 A. Electron temperature and ion density measurements were performed employing a double Langmuir probe. They were found to increase rapidly as the H₂ percentage in the mixture was increased up to 20%. This increase slows down as the H₂ percentage in the gas mixture was increased above 20% at the same pressure. Emission spectroscopy was employed to observe emission from the pulsed plasma of a steady-state electric discharge. The discharge mainly emits within the range 280–500 nm. The emission consists of N₂ (*C – X*) 316, 336, 358 nm narrow peaks and a broad band with a maximum at $\lambda_{max} = 427$ nm. Also lines of N₂, N₂⁺ and NH excited states were observed. All lines and bands have their maximum intensity at the discharge current of 0.417 A. The intensities of the main bands and spectral lines are determined as functions of the total pressure and discharge current. Agreement with other theoretical and experimental groups was established.

PACS. 52.80.-s Electric discharges – 52.70.Kz Optical (ultraviolet, visible, infrared) measurements – 51.70.+f Optical and dielectric properties – 51.50.+v Electrical properties

1 Introduction

The plasma of the glow discharge in N₂–H₂ mixture have been studied in metallic surface nitriding for purpose of improving surface properties such as resistance to corrosion, wear or fatigue by the development of a thin surface layers having high resistance properties [1–4]. However, the active species that are produced during the pulse and the behavior of these species during or after [5,6] the discharge have scarcely been studied. Petitjean and Ricard [5] have studied the emission spectroscopy of a N₂–H₂ glow discharge for metallic surface nitriding at low pressure (1–3 Torr) and low current density (1–6 mA cm⁻²). They detected excited states of the species N₂, N₂⁺, N, N⁺, H, NH, as well as those of metal atoms. Also, Brühl et al. [6] studied the optical emission of N₂ and N₂⁺ radiative states in the negative glow of N₂, DC pulsed discharges, at pressures 1–4 Torr and current densities 1–6 mA cm⁻². They found strong intensities of the N₂ second positive system (especially from $v = 1$).

However, since, there are no systematic studies undertaken to monitor the active species generated in the glow discharge by plasma emission spectroscopy, therefore, it is the aim of the present work to perform analysis of glow

discharge by electrical and optical characterization employing pulsed plasma at discharge pressures between 0.5 and 4.0 Torr and discharge currents of 0.2 to 0.6 A, at N₂–H₂ discharge gas mixture of N₂ percentage varying from 0 and 100%.

2 Experimental set-up

AC glow discharge plasma in N₂–H₂ gas mixture was generated in a 60 Hz AC pulsed plasma apparatus shown in Figure 1 [7]. The reactor consisted of two stainless steel circular plane electrodes, 3 mm thick and 30 mm in diameter, located inside the cavity of a quartz tube of 400 mm in length and 320 mm in diameter, which was fixed in the center of the reaction chamber. The electrodes were completely covered by the quartz tube, avoiding the generation of plasma along its surface and ensuring that the discharge is being generated only around the surface of the cathode's planar disc (9 cm²). The lateral flange held the gas inlets, vacuum connection and pressure sensor. The left lateral flange was a quartz window, used to monitor the active species generated in the glow discharge by plasma emission spectroscopy; this was performed using a Jovin-Yvon Spec 0.270 m monochromator equipped with a 1200 lines-mm⁻¹ holographic grating with a platinum

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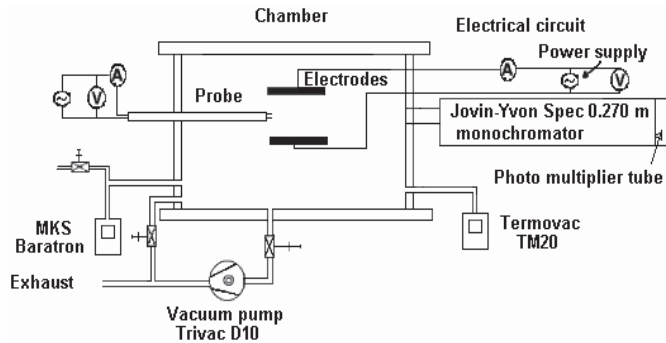


Fig. 1. Experimental apparatus.

coating. The spectrum (200–600 nm) of the emission cell was recorded with a photo multiplier tube (PMT) and sodium Saliglate Scintillator. The PMT used has a spectral response in the range of 185–680 nm with peak efficiency at about 400 nm. The wavelength scan interval was 1 nm and the dwell time was 500 ms. Signal was recorded by a PMT with a stand-alone high voltage power supply (−800 V) and an acquisition controller. The data were obtained in a single accumulation with a 0.5 s integration time. The environment of a N_2 – H_2 mixture was kept at a total pressure between 0.5 and 4.0 Torr. The adjustable power supply maintained an output between 300 and 400 V AC, and a discharge current range of 0.2 to 0.6 A. The gases were ultrahigh pure (Praxair 99.999%). The plasma chamber was initially evacuated to a base pressure of 1.0×10^{-6} Torr with a turbo-molecular pump and purged with the working gas at a pressure of 4.0 Torr.

Langmuir probes are commonly used as a diagnostic tool for the determination of plasma parameters. Basically the Langmuir probe consists of one or two electrodes inserted into the plasma. In the double probe configuration, the current collected by the electrodes is measured as a function of the voltage applied between the two electrodes. From the current-voltage characteristics of the probe, electron temperature (T_e) and ion density (n_i) can be derived. The double Langmuir probe employed in this work consists of a 0.0635-mm-radius tungsten wire (W-WI-005, Kimball Physics Inc.). The probe was located inside a glass capillary, having a hole of 0.7 mm inside diameter; inside. Both wires were shielded separately with plastic insulating cylinders. The wire tips were extended 1.0 mm beyond the glass capillary to form the probe. The inside bore of the glass capillary was enlarged at the probe end, to form a cavity in order to prevent metal deposits on the glass, thus increasing the probe area [8]. The probe was aligned parallel to the cylindrical axis of the discharge tube and could be moved only in the forwards and backwards directions in the center of the plasma by using a manual micrometer motion feed through.

The voltage difference applied to the probe was manually scanned from +30 V to −30 V and vice versa by a regulated dc power supply (EXTECH, Model 382213). The probe current was monitored by an Electrometer (EM, Model E16). The scanning time for each I – V curve was 5–10 min. Owing to sputtering or contamination of the

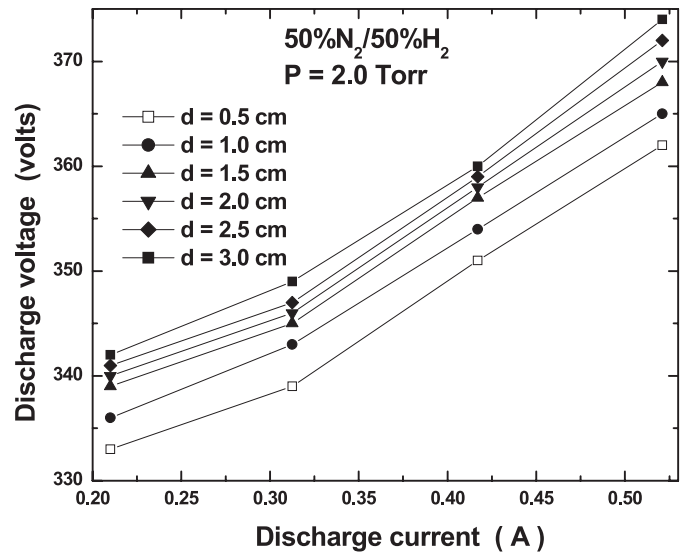


Fig. 2. Electrical characteristics of planar-cathode glow discharge.

probe tips, the total measurement time for one probe was restricted to approximately 5–6 h. The final I – V curves obtained were the results of an average of 6 data scans at each probe voltage.

3 Results and discussion

3.1 Electrical measurements

The AC glow discharge electrical characteristics in 50% N_2 /50% H_2 mixture at 2.0 Torr, with electrodes spacing between 0.5 and 3.0 cm were investigated and the results are shown in Figure 2. Similar curves were obtained at different mixtures of N_2 – H_2 .

The data in Figure 2 confirm that the plasma is operating in the abnormal glow mode, characterized by increases in the operating voltage when the current is raised under given electrodes spacing. In such mode, discharge voltage (V) increased from 333 to 343 V as the electrodes spacing was increased from 0.5 to 3.0 cm, similar trends of voltage-current were observed by Fang and Marcus [9]. This may be explained by the fact that as the current is increased, the discharge glow will eventually cover the entire cathode surface; at this point any increase in discharge current will result in an increase in the discharge voltage. While the voltage response (increase) to electrodes spacing variations as seen in Figure 2, is attributed to high secondary electron energies that are needed to maintain the plasma at higher electrodes spacing, due in turn to more efficient collisional processes [10]. As seen, within the entire current range of 0.2–0.6 A, and at all electrodes spacing (0.5 to 3.0 cm), the plasma is operating at abnormal discharge mode that is required for atomic spectroscopy and for analytical glow discharge devices [11]. The data of Figure 2 were used at 0.21 A, in plotting the discharge voltage against Pd with P taken to be 2.0 Torr, and the

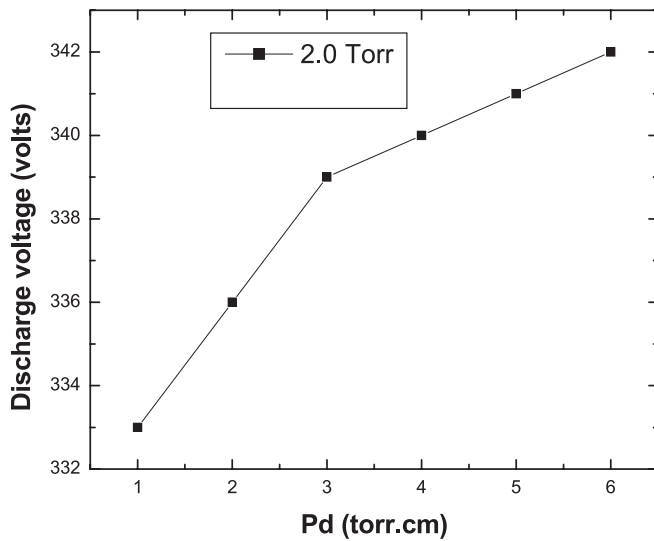


Fig. 3. Discharge voltage as a function of Pd with P taken as 2 Torr.

results are presented in Figure 3. These results show the discharge voltage to be dependent on the gap between the two electrodes at the same pressure. Similar results were obtained by Garamoon et al. [12].

In order to examine the influence of hydrogen presence on the plasma, the electrodes separation was set to 15 mm and discharge voltage to 350 V. Under these conditions, the plasma current was measured as a function of N₂ percentage at pressures of 1, 2, 3, and 4 Torr. The results are plotted in Figure 4, and they show an increase in the discharge current as the percentage of N₂ in the gas mixture was increased reaching a maximum value at discharge gas mixture of 75%N₂-25%H₂, followed by a decline as the H₂ percentage reached values lower than 20%. Similar result were obtained [13] in which the discharge current increased due to the addition of less than 10% H₂, that was followed by an increase in cathode temperature. This behavior is explained as a cathode surface effect, in which an increase in cathode temperature leads to a rise in the secondary electronic emission coefficient [14] due to reducing surface oxides [15] by hydrogen or by ion mobility change in the cathode dark space, caused by hydrogen producing a larger nitrogen-hydrogen molecular ion flux [16].

The evaluation algorithm for obtaining the electron temperature was run in the following manner. First the probe characteristic curve is differentiated two times and then smoothed. Smoothing was performed following the procedure described by Savitzky and Golay [17]. For each of the obtained current-voltage characteristic curve at each percentage of H₂, the electron temperature is calculated using the equation given in [18]. Following that, a theoretical curve is fitted to the entire measured experimental current-voltage characteristic data curve as given by [19,20] by adjusting only the ion density (n_i).

Figure 5 shows the electron temperature measured at different percentage values of N₂ in the gas mixture. It shows a decreasing pattern. This decreasing pattern is rather slow starting at 3.4 eV electron temperature at

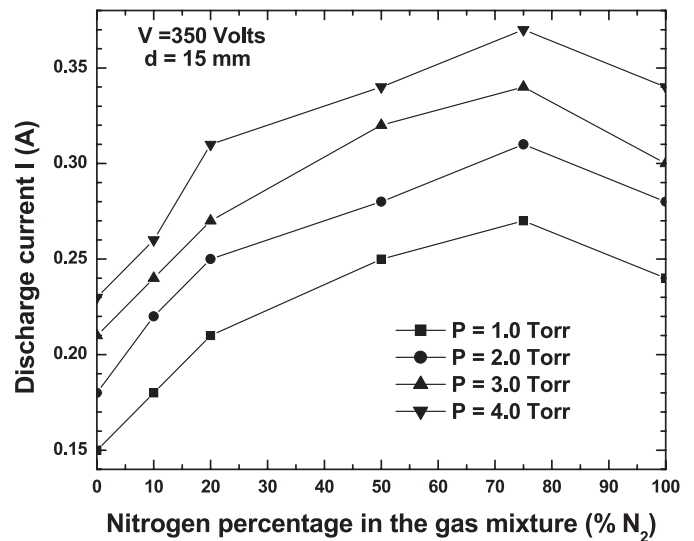


Fig. 4. Discharge current as a function of N₂ percentage in N₂-H₂ gas mixture at 350 volts discharge voltage and 15 mm electrodes separation at pressures between 1 and 4 Torr.

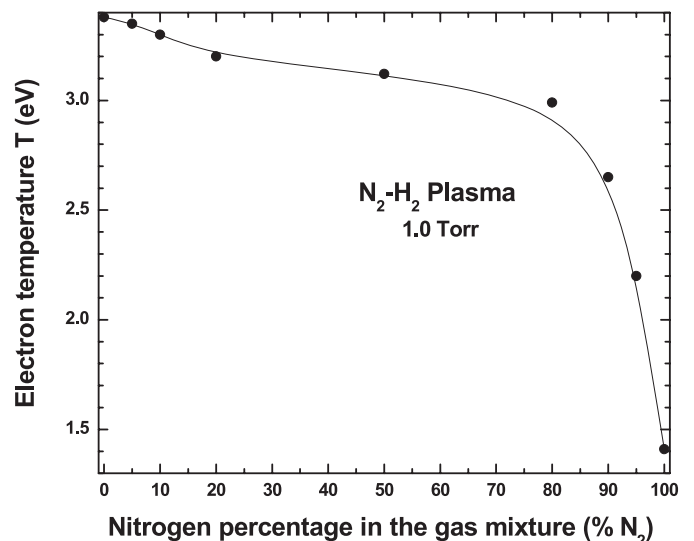


Fig. 5. Electron temperature as a function of N₂ percentage.

100% N₂ reaching 3.0 eV at 80% of N₂ in the mixture. This decrease in electron temperature becomes very rapid as the N₂ percentage is increased reaching a value of 1.4 eV at 100% N₂.

The correlation between the variation of the electron temperature and the relative number of nitrogen atoms should be pointed out. Electron impact dissociation is the main source channel for ground state nitrogen atoms for the present conditions. Increasing the H₂ amount results in an increase of T_e , thus in the high-energy part of the electron distribution function and, consequently, in the rate of molecular dissociation.

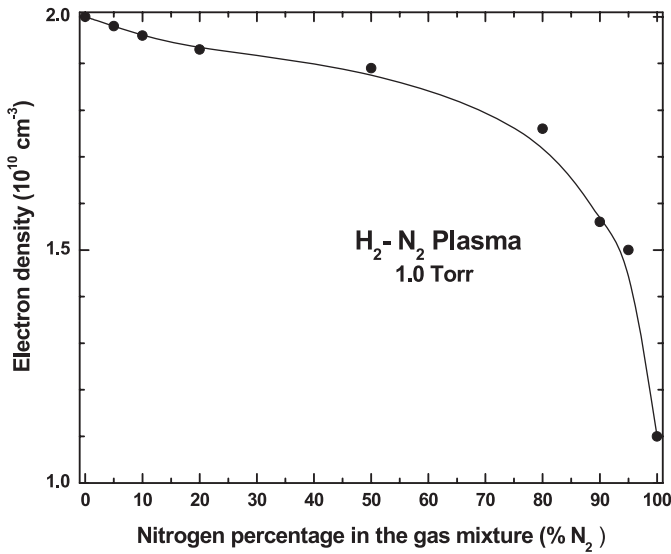


Fig. 6. Electron density as a function of N_2 percentage.

The above mentioned evolution procedure resulted as well as with electron densities that are displayed as a function of N_2 percentage in the mixture in Figure 6.

3.2 Emission spectrometry measurements

Emission spectroscopy measurements for 50% N_2 /50% H_2 glow discharge plasma at a pressure of 3.0 Torr and electrodes spacing of 1.0 cm were made at discharge currents of 0.21, 0.3125, 0.417, and 0.54 A. A typical sample at 0.3125 A discharge current is shown in Figure 7. This allowed analysis of the most luminous area, which corresponds to the negative glow near the cathode dark space. Identified species in Figure 7 are reported in Table 1.

Only the most intense and well resolved spectral lines in the ultraviolet (UV) region corresponding to N_2 , N_2^+ and NH are quoted [21]. The observed narrow peaks centered at 316, 336, 358 nm corresponds to the most intense peaks of the N_2 ($C - X$) transitions, while that at 427 nm corresponds to N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) transition.

The broad maximum between 350 and 500 nm is most probably due to the overlap of the N_2 and N_2^+ emission peaks. This was verified during the experimental work by decreasing the N_2 percentage in the mixture from 100% to 10%. A steady decline of the broad maximum was observed, and practically disappearing at 10% N_2 and 90% hydrogen.

The observed peak at 336 nm may also be identified with the NH ($A - X$) transition. Finally, narrow peaks at 358, and 391 nm and that at 427 nm correspond to spectral lines of N_2^+ ($B - X$).

The effect of the discharge current on emission line intensities of several spectral lines is shown in Figure 8 for 3.0 Torr pressure and 1.0 cm electrodes spacing. The emission lines are 316 nm, 358 nm and 427 nm for N_2 ; 358 nm and 427 nm for N_2^+ and 336 nm for NH . Near linearity of this dependence is observed in the range of 0.2

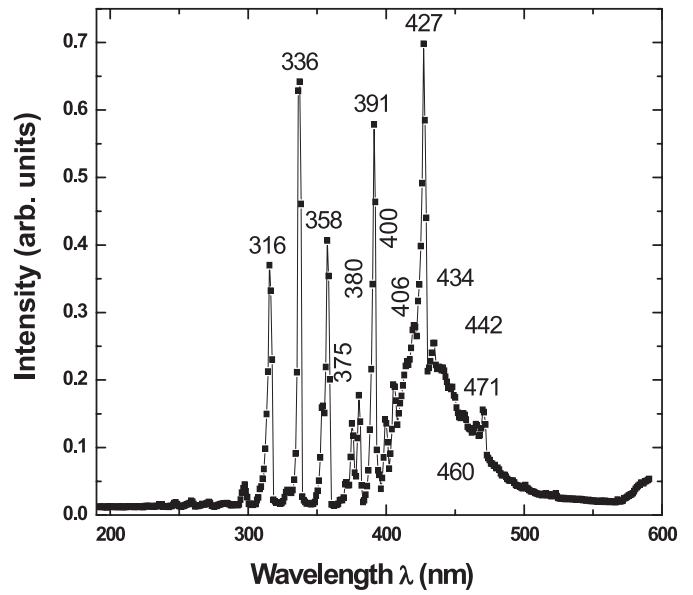


Fig. 7. Emission spectroscopy measurements at 3.0 Torr and 1.0 cm electrodes separation and for several discharge currents in 50% N_2 /50% H_2 plasma gas mixture.

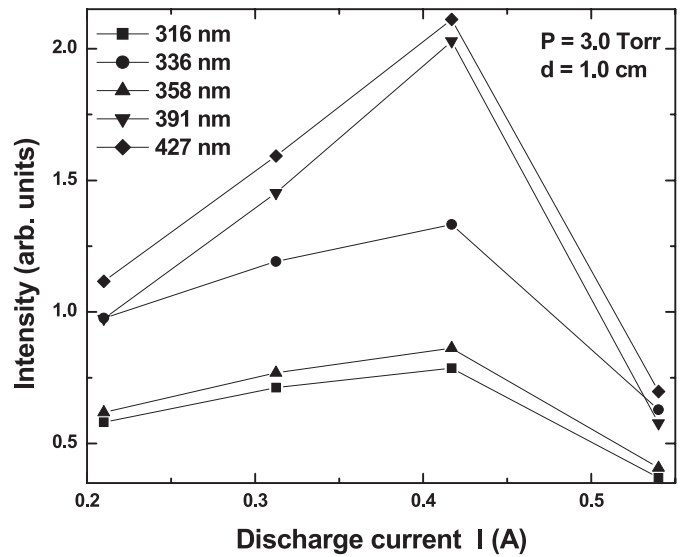


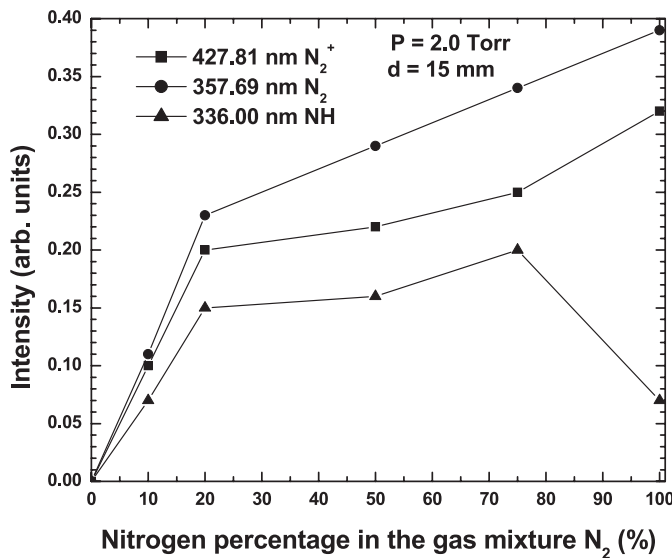
Fig. 8. The intensities of the five main emission lines (316, 336, 358, 391 and 427 nm) at 3.0 Torr and 1.0 cm electrodes separation as a function of discharge currents.

to 0.42 A discharge currents, while a decreasing behavior occurs at currents higher than 0.42 A.

Emission spectra were recorded at 2 Torr discharge gas pressure and 15 mm electrodes spacing for N_2 percentage in the gas mixture between 0 and 100%. From these spectra, the intensities for the most intense emission lines at 336.00, 357.69, and 427.81 nm corresponding to NH ($A^3\Pi \rightarrow X^3\Sigma^-$), N_2 ($C^3\Pi_u \rightarrow XB^3\Pi_g$), and N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) were plotted as a function of N_2 percentage in the discharge gas mixture and the results are shown in Figure 9.

Table 1. Most intense spectral lines observed in 50%N₂/50%H₂ negative glow discharges.

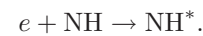
Species	Transition	ν'	ν''	Spectral line (nm)	Spectral line (nm)
				From reference 11	measured
N ₂	$C^3\Pi_u \rightarrow XB^3\Pi_g$	1	0	315.93	316
NH	$A^3\Pi \rightarrow X^3\Sigma^-$	0	0	336.01	336
N ₂	$C^3\Pi_u \rightarrow XB^3\Pi_g$	0	0	337.13	
N ₂	$C^3\Pi_u \rightarrow XB^3\Pi_g$	0	1	357.69	358
N ₂ ⁺	$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	1	0	358.21	
N ₂	$C^3\Pi_u \rightarrow XB^3\Pi_g$	1	3	375.54	375
N ₂	$C^3\Pi_u \rightarrow XB^3\Pi_g$	0	2	380.49	380
N ₂ ⁺	$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	0	0	391.44	391
N ₂	$C^3\Pi_u \rightarrow XB^3\Pi_g$	1	4	399.84	400
N ₂	$C^3\Pi_u \rightarrow XB^3\Pi_g$	0	3	405.94	406
N ₂ ⁺	$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	1	2	423.65	424
N ₂	$C^3\Pi_u \rightarrow B^3\Pi_g$	1	5	426.97	427
N ₂ ⁺	$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	0	1	427.81	
N ₂	$C^3\Pi_u \rightarrow XB^3\Pi_g$	0	4	434.46	434
N ₂	$C^3\Pi_u \rightarrow XB^3\Pi_g$	3	8	441.77	442
N ₂ ⁺	$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	2	4	459.97	460
N ₂ ⁺	$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	0	2	470.92	471

**Fig. 9.** Intensities of the most intense emission lines at 31600, 336.00, 357.69, and 427.81 nm corresponding to NH ($A^3\Pi \rightarrow X^3\Sigma^-$), N₂ ($C^3\Pi_u \rightarrow XB^3\Pi_g$), and N₂⁺ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) as a function of N₂ percentage at 2 Torr pressure and 15 mm electrodes separation.

These data point to the fact that the upper excited states of each of the three states reach nearly its maximum population (equilibrium) at 20% N₂. Further increase in N₂ percentage seem to contribute to slower increase in the population of the $C^3\Pi_u$ and $B^2\Sigma_u^+$ upper excited states, hence resulting in a slower increase in the intensities of the N₂ ($C^3\Pi_u \rightarrow XB^3\Pi_g$), and N₂⁺ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) emission lines. While the population of the upper excited state of $A^3\Pi$ seem to decrease as the N₂ percentage is increased above 75%, hence resulting in a decrease in the intensity of the NH ($A^3\Pi \rightarrow X^3\Sigma^-$) emission line. Calculated N₂ ($C^3\Pi_u$) and NH ($A^3\Pi$) concentration versus

N₂ percentage [22] was shown to increase rapidly as the N₂ percentage was increased to about 10%, the increase in the N₂ ($C^3\Pi_u$) population slows down as the N₂ percentage continues to increase up to about 100% as it was observed in the present work. While the calculated NH concentration [22] was shown to increase rapidly as the N₂ percentage was increased up to 10%. Further increase in the N₂ percentage resulted in a constant population of the NH ($A^3\Pi$) excited state for N₂ percentage between 10 and 75%. This was followed by a decline in the population of the NH ($A^3\Pi$) for N₂ percentage above 75% as it was observed in this work resulting in lower intensities for the NH ($A^3\Pi \rightarrow X^3\Sigma^-$) emission line.

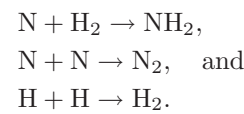
Since the radiative level of NH ($A^3\Pi$) is low (3.7 eV), therefore it is easily accessible through direct electron excitation



That is followed by the decay to the NH ($X^3\Sigma^-$), resulting in the 336.01 nm emission line.

This spectral line has been observed in glow discharge from metallic surface nitriding [5].

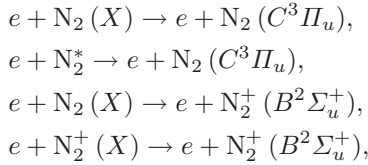
As a result, the lower intensity of the 336 nm line measured in this work would imply that NH radicals are mainly formed in the region surrounding the cathode (cathode dark space) [5]. From the parent gases N₂ and H₂, the primary radicals N, H and NH are generated during each pulse by electron impact, and are rapidly consumed by reactions such as:



They (the primary radicals N, H and NH) are, however generated during the next pulse. Positive and negative ions (N⁺, N₂⁺, N₃⁺, N₄⁺, H⁺, H₂⁺, H₃⁺, NH⁺ and H⁻) are also produced and in turn, they initiate other processes, such

as recombination, detachment, charge transfer and ion conversion.

Considering the population of N_2 and/or N_2^+ (391 nm and 427 nm emission lines) to be the most abundant, this would imply that the main process for the production of N_2 and/or N_2^+ is the electron impact excitation or electron impact ionization and excitation, that is

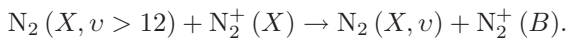


with radiative transfer as the main depopulation process of these species via:

$C^3\Pi_u \rightarrow B^3\Pi_g$ (the second negative system of N_2) and

$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ (the first negative system of N_2^+).

Equally, collisions of $N_2^+(X)$ with $N_2(X, v)$ molecules as given by the following reaction can be of relevance:



Therefore, the strong intensity of $N_2(C^3\Pi_u \rightarrow XB^3\Pi_g)$, and of $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ observed in the negative glow within the pressure range of the present study can be related to the presence of high electron density and/or high vibrational excitation of the $N_2(X)$ ground state. The spectral line at 391 nm has been observed in pulsed DC discharge [6] and glow discharge for metallic surface nitriding [5].

4 Conclusions

The experimental study mainly focused on measurements of electron temperature and ion density as a function of N_2 percentage in the N_2 - H_2 gas mixture. Electron temperature and ion density were found to rise rapidly as the H_2 percentage in the gas mixture was increased up to 20%, followed by slow increase as the H_2 percentage was further increased. The plasma was found to be operating in the abnormal glow mode.

The emission from the pulsed plasma was mainly within the range 280–500 nm. It was found to consist of $N_2(C-X)$ 316 nm, 336 nm, 358 nm narrow peaks and a broad band with a maximum at $\lambda_{max} = 427$ nm. Also lines of N_2 , N_2^+ and NH excited states were observed. All lines have their maximum intensity at discharge current of 0.417 A.

Maximum population (at equilibrium) of the excited molecules and molecular ions resulting in the emission lines at 336.00, 357.69, and 427.81 nm corresponding to NH ($A^3\Pi \rightarrow X^3\Sigma^-$), $N_2(C^3\Pi_u \rightarrow XB^3\Pi_g)$, and $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ is reached at 20% N_2 and 80% H_2 . The strong intensity of $N_2(C^3\Pi_u \rightarrow XB^3\Pi_g)$, and of $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ observed in the negative glow within the pressure range of the present study can be

related to the existence of a high electron density and/or high vibrational excitation of the $N_2(X)$ ground state. The lower intensity of the 336 nm line would imply that NH radicals are mainly formed in the region surrounding the cathode (cathode dark space).

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