Discharge conditions and emission spectroscopy of \( \text{N}_2 \) and \( \text{N}_2^+ \) active species in a variable power \( dc \) pulsed plasma used for steel nitriding

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The variations of stainless steel cathode temperature \( (T_c) \) as a function of nominal plasma power (driven by discharge frequency) and duty cycle at different pressures (0.6-3.2 torr) in nitrogen plasma are reported in conditions favourable for plasma nitriding. Above power at 200 kHz, it is found that increase in power does not have any significant effect on \( T_c \). Corresponding optical emission spectroscopy (OES) study near the cathode surface shows that the presence of vibrational bands of second positive system of \( \text{N}_2 (\Delta v = 0, -1, -2, -3) \) and first negative system of \( \text{N}_2^+ (\Delta v = 0, -1, -2) \) are dominant. The variation of intensity of those nitrogen molecular bands as a function of discharge power at various pressures has been studied. At 2 torr, the vibrational temperature of \( \text{N}_2 \) molecule is calculated from \( \text{N}_2 \) vibrational spectra at different discharge power regime as frequency is varied from 100 to 500 kHz. The variation of power in this frequency range 50-500 kHz has a similar effect on \( T_c \) and optical emission intensity. Floating potential in variable power conditions has been measured by Langmuir probe which shows a plateau after 3.2 Watt/cm\(^2\) (at 200 kHz) plasma power density.

**Keywords**: Plasma power, Discharge frequency, Optical emission spectroscopy, Vibrational bands, Floating potential

1 Introduction

Optical emission spectroscopy (OES) has been extensively used to identify and characterize the excited and ionized species in glow discharge plasma. Some advantages of using OES diagnostics are that information can be acquired without perturbing the plasma and this method is also applicable to that part of plasma where conventional diagnostic cannot be placed. In abnormal glow discharge, nitrogen plasma has applications towards improving the surface properties of a material. This process of surface modification is widely known as plasma nitriding, is usually done between 1-10 torr pressure, 400-800 V discharge voltage and above 1 mA/cm\(^2\) current density, by which surface properties like hardness, corrosion resistance, frictional wear resistance, fatigue strength etc. of a material can be improved. For stainless steel (SS) nitriding, substrate temperature is kept at around 810 K in a \( \text{N}_2/\text{N}_2-\text{H}_2 \) \( dc \) pulsed discharge. Surface hardness of 800-1200 HV, case depth of 50-200 micron etc. have been achieved by forming the nitrided layer of \( \text{Fe}_{2-4}\text{N} \), \( \text{CrN} \), \( \text{Cr}_2\text{N} \) etc over the SS surface\(^1\).

Heating of cathode in a \( dc \) pulsed nitriding system is generally done by varying discharge voltage, duty cycle and gas pressure. The variation of frequency of the discharge can also be effectively used to achieve the heat of reaction. The \( dc \) pulsed nitriding of steel sample is reported at 793 K by varying discharge frequency\(^2\) between 10-60 kHz. The variation of duty cycle is another interesting factor because by decreasing its value arcing formation can be minimized. By doing so, a better uniformity in current density and cathode temperature have been achieved. Therefore, in case of variable frequency and variable duty cycle biased heating, discharge power variation needs to be looked into to understand and optimize the nitriding process. This nitriding plasma emits radiation corresponding to various excited and ionized state of molecular nitrogen. Energetic neutrals and ions heat up the cathode and make possible the nitride forming reaction over the surface. Using OES, rotational temperature \( (T_r) \) of nitrogen molecular ion at the nitriding conditions is found to be in equilibrium with the cathode temperature\(^3\) while \( \text{N}_2 \) vibrational temperature \( (T_v) \) range goes to 2000-20000 K, higher than \( T_r \). A comparative study has been reported between theoretically and experimentally found \( T_v \) in \( \text{N}_2 \) plasma, which shows a good agreement with a 17% discrepancy\(^4\). The researchers in Ref. 5 have studied rotational and vibrational
temperature in inductively coupled CF$_4$ plasma by OES. Therefore, in a frequency biased heating, the role of $T_c$ is also a subject of attention.

In this paper, we have reported the effect of discharge power and duty cycle of a dc pulsed discharge on cathode temperature ($T_c$) of stainless steel and studied the corresponding emission spectroscopy in conditions favourable for plasma nitriding. Langmuir probe measurement is done in order to find the floating potential variations at various power levels related to different frequencies and to find electron temperature near the surface of the cathode. The time averaged vibrational spectra of nitrogen molecule are used to study the vibrational temperature variation in the variable power discharge driven by discharge frequency.

2 Experimental Details

The experimental set-up has been described elsewhere. The glow discharge plasma is powered by a rectangular negative pulse applied to the cathode. The discharge parameters viz. voltage, duty cycle and frequency are variable in the range 100-1000 V, 20-80% and 20-500 kHz, respectively. The power supply can detect arcing produced inside the chamber and stops its operation while heavy arcing goes on. The number of arcing at which the power will go off automatically in a certain time can be set manually. Lowering of duty cycle of discharge and gas pressure (0.1-0.5 torr) reduces arcing at the initial stage of plasma production or when the cathode material is new, thereby, stabilizing the plasma current. Running in low duty cycle and low-pressure condition is, thus, essential to avoid arcing. Discharge parameters-voltage, frequency and duty cycle have been measured by a Tektronix made TDS 320 oscilloscope and P 6015 A high voltage probe. Discharge current is measured by an inbuilt ammeter of the dc pulsed power supply which is a time averaged value. The nominal average power is calculated by multiplying the average voltage, duty cycle obtained from the oscilloscope with average current obtained from the power supply meter. Langmuir probe is biased by a $-45$ V to $+45$ V dc power supply. Probe bias voltage and corresponding current across a 1 K resistance are recorded in the oscilloscope.

Prior to taking data, the system has been operated for 2-3 h so that all the parameters like pressure, discharge voltage, discharge current and more importantly $T_c$, get stabilized. $T_c$ does not come to a stable value very fast compared to rest of the parameters. The time taken to achieve a stable value for $T_c$ on changing frequency, duty cycle/voltage is different at different pressure and also depend upon step size between two readings. Observing all these, we have operated the plasma for a maximum 45 min to obtain a value for $T_c$.

OES study has been done by a CVI Laser Corporation make DK 480 ½ meter monochromator and an AD 110 photomultiplier detection unit. Wavelength calibration is done by a He-Ne Laser at 633 nm. The profile shows a 2.2 nm instrumental shift and a FWHM of about 0.2-0.3 nm at 10 micron slit width. Slit width is adjusted at 150 microns so that distinct peaks as well as good resolution (comparable to the maximum resolution at minimum 10 micron slit width) are obtained. The focused region of plasma is the negative glow of the discharge. The radiation is carried out to the monochromator slit by lens, fiber and fiber-slit coupler.

3 Results and Discussion

3.1. Discharge frequency and nominal power density

Nominal power density in the plasma is observed to be strongly dependent on discharge frequency of dc pulsed power supply. Power has a sharp rise between 50-200 kHz at 2 torr pressure. After 200-300 kHz, the increase in power is slow and overall fluctuation up to 500 kHz is 20% of significant increase in power density during 50-200 kHz variation (Fig. 1). This region may be considered as the power plateau region of the discharge and the role of discharge, plasma parameters and N$_2$ species has to be understood.

3.2. Measurement by Langmuir probe

Floating potential ($V_f$) in the plasma 2 cm away from the cathode and at 2 torr pressure, 620 V is...
measured by a cylindrical Langmuir probe of 4 mm in length and 1.6 mm diameter from probe current-voltage (i-v) characteristic or by oscilloscope (when no i-v found). At different power levels corresponding to each frequency floating potentials are noted. During power density variation of 2.9-3.2 watt/cm² (50-200 kHz) floating potential has a decrease from 108 V to 79 V (in magnitude). At power levels between 200-500 kHz, floating potential remain almost constant (Fig. 2). Discharge between probe tip and cathode during biasing prevent taking current-voltage (i-v) characteristic at 2 torr. However, probe characteristic (Fig. 3) taken at 0.2 torr pressure shows that floating potential and electron temperature follow almost the same pattern at different frequencies. Electron temperature measured at 0.2 torr between 50-500 kHz (670 V, 110 mA, no power change observed) reveal that during frequency variation electron temperature does not vary significantly (1.09 eV-1.48 eV while floating potential variation is in the range 11.5 -14.2 V). This result shows that pressure indeed play a role in discharge frequency variation in glow discharge, which is effective in case of high pressure (2 torr) as compared to low pressure (0.2 torr). Decrease in floating potential at 2 torr implies a decrease in electron temperature between 50-200 kHz and possibly electron density should have an enhancement in this region while in the plateau region, electron temperature and density become stagnant.

3.3. Discharge parameters and cathode temperature ($T_c$)

At 1.6 and 3.2 torr pressures and 790 V discharge voltage, the nominal discharge power is increased by biasing discharge frequency and the heating of cathode has a response like Fig. 4(a-b). After 3.8 watt/cm² (at 200 kHz), $T_c$ reaches saturation and remains so up to power at 500 kHz. At 3.2 torr pressure, high nitriding temperature can be attained and the flatness in the temperature curve starts at comparatively elevated value.

Fig. 5(a)/5(b) show the variation in current density ($J_d$) and $T_c$ as a function of duty cycle variation from 20 to 80% at 0.66, 1.60 and 3.2 torr pressures, respectively in N₂ plasma, keeping discharge frequency and discharge voltage fixed at 22 kHz and 790 V. In this case, when duty cycle is varied from 20 to 80%, it is observed that rate of increase of $T_c$ with respect to duty cycle is faster at high pressure above 50% duty cycle.

Discharge voltage versus $J_d$ variation at 1.3 and 1.9 torr keeping discharge frequency fixed at 22 kHz is made [Fig. 6], the variation of $T_c$ with respect to discharge voltage is also has a straight line variation (not shown). Unlike discharge frequency and duty cycle variations, the effect of discharge voltage on $T_c$ is almost linear. This is quite obvious from the linear discharge voltage versus current characteristics in abnormal glow region of glow discharge plasma.

3.4 Emission spectrum

With the resolution of our spectrometer, emission vibrational states of N₂ and N₂⁺ appear distinctly [Fig. 7(a-c)]. The first negative system of N₂⁺ and second positive system of N₂ considerably dominate the spectrum from 330 to 480 nm. N₂ (0,0), N₂ (1,2), N₂
intensities are the prominent bands in this range of the emission spectrum. In the 660-790 nm wavelength range, three strong emissions are observed. Strongest of them is close to \( \text{N}_2 \) (2,2) of Herman’s infrared system. This is the second intense band of this system. Although \( \text{N}_2 \) (0,0) is the most intense band, its wavelength is out of range of the detection capacity of our monochromator. Moreover, since \( \text{N}_2 \) (2,2) is detected itself as a weak band and intensities of \( \text{N}_2 \) (2,0) (706.17 nm) and \( \text{N}_2 \) (2,1) (743.50 nm) bands are comparatively weaker, their presence could not be found with our existing spectrometer. Identification of 674.102 nm and 715.502 nm emission could not been done so far with available references. Different species identified along with relevant information are presented in Table 1.

3.5 Band intensities

Figs 8-9 show the intensity variations of \( \text{N}_2 \) (0,0) of second positive system at 2.0, 3.0, 4.3 torr and \( \text{N}_2^+ \) (1,2) of first negative system at 4.3 torr as a function of discharge power driven by discharge frequency between 50-500 kHz (80 % duty cycle) with 630 V cathode bias voltages. It is observed that band intensities of \( \text{N}_2 \) (0,0) state (\( \text{N}_2 \) second positive) increase with increasing discharge power up to 3.81 watt/cm\(^2\) and have a small fluctuation above this level. The power at 3.81 watt/cm\(^2\) is driven by 200 kHz frequency. The power above this point has not
significantly rise as we have seen from the frequency-power plot and this small increase in power is unable to make good amount of excitation of N$_2$ (0,0) state. At higher pressure, the emission intensity is high and the plateau occurs at higher values of emission. This may be due to electron impact excitation of the vibrational state N$_2$ (0,0) which rises at high pressure. In case of N$_2^+$ (1,2) emission with respect to discharge power at 4.3 torr, intensity has a sharp fall after 3.83 watt/cm$^2$ at 300 kHz driving frequency. At high frequencies above 100 kHz, ion energy has a sharp

Fig. 6—Change of current density with discharge voltage at 1.3 torr (square) and 1.9 torr (up triangle) (with discharge frequency and duty cycle fixed at 22 kHz and 80%)

Fig. 7(a)—Vibrational bands of molecular nitrogen in nitrogen plasma between 325-384 nm at 1.6 torr pressure (with 200 kHz discharge frequency, 80% fixed duty cycle, and 790 V discharge voltage)

Fig. 7(b)—Vibrational bands of molecular nitrogen ion in nitrogen plasma between 380-430 nm at 1.6 torr pressure (with 22 kHz discharge frequency, 80% fixed duty cycle and 790 V discharge voltage)

Fig. 7(c)—Observation of N$_2$ (2,2) emission of Herman’s infrared system with wavelength scanned between 660-790 nm at 1.6 torr pressure (with 200 kHz discharge frequency, 80% fixed duty cycle and 790 V discharge voltage)
decrease and ion molecule collisions are becoming less significant. Discharge power versus intensity variations of $N_2$ and $N_2^+$ bands are analogous to discharge power versus $T_c$ variation. This result reveals that $N_2^+$ molecular ion is responsible for heating of cathode. It can also be concluded that in addition to $N_2^+$, neutral $N_2$ also takes part in heating of the cathode.

3.6 Vibrational temperature

For non-thermal excitation like electron molecule collision, an effective vibrational temperature can be determined from the sum rule if the sequence is well developed. Vibrational temperature ($T_v$) can be determined from the relative integrated band intensity relation given as follows:

$$I_{\nu'\nu''} \propto S_{\nu'\nu''} \nu^{\frac{4}{\nu'}} \exp(-E_{\nu'}/T_v) \quad \ldots \ (1)$$

where $E_{\nu'}$ is energy of excited state, $\nu$ the frequency of light emitted, $k$ is Boltzmann constant and $S_{\nu'\nu''}$ is the band strength for the transition.

The band origin is used as a frequency while Franck-Condon factors are used instead of band strength, relative values of band strength agree within a few per cent.

Vibrational temperature of nitrogen molecule is calculated as a function of discharge power driven by discharge frequency from the vibrational distribution's Eq. (1). Relative intensity ratio of $N_2 (1,3)$ and $N_2 (0,2)$ bands ($\Delta \nu = -2$) of $N_2$ second positive system are used to find the vibrational temperature of nitrogen molecule at different frequency regime at 2 torr. In determining vibrational temperature by ratio of relative intensities of two bands, integrated intensities and Franck-Condon factors are used.

Franck-Condon factors of $N_2 (1,3)$ state is 0.20027 while that of $N_2 (0,2)$ is 0.14691. The variation of vibrational temperature as a function of discharge frequency is presented in Table 2. A minimum vibrational temperature of 4207± 599 K at 4.99 watt/cm$^2$ (100 kHz) and a maximum of 9717 ± 2273 at 5.06 watt/cm$^2$ (500 kHz) has been found. $T_v$ has a decrease of 1476 K after 5.06 watt/cm$^2$ (200 kHz), except this level it increases with increasing frequency. During the 100-500 kHz frequency variation at 2 torr pressure, the $T_v$ increment is 182 K.

Which means vibrational temperature may play an important role in the variation of cathode temperature. An increase in Ti substrate temperature is reported by the researchers as the $N_2$ vibrational temperature increases. They claimed that the effect of vibrational temperature is the most essential temperature for nitriding, whereas the effect of electron temperature, density and rotational temperature are less.

![Graph 8: Intensity variations of $N_2 (0,0)$ state of second positive system at 2.0, 3.0 and 4.3 torr as a function of discharge power driven by discharge frequency between 50-500 kHz (80% duty cycle) with 630 V cathode bias voltage.](image8)

![Graph 9: Intensity variation of $N_2^+ (1,2)$ state of first negative system at 4.3 torr as a function of discharge power driven by discharge frequency between 50-500 kHz (80% duty cycle) with 630 V cathode bias voltage.](image9)

<table>
<thead>
<tr>
<th>Discharge Frequency (kHz)</th>
<th>Power Density (watt/cm$^2$)</th>
<th>$T_v$ of $N_2$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4.99</td>
<td>4207 ± 599</td>
</tr>
<tr>
<td>200</td>
<td>5.06</td>
<td>7532 ± 30</td>
</tr>
<tr>
<td>300</td>
<td>5.34</td>
<td>6056 ± 1927</td>
</tr>
<tr>
<td>400</td>
<td>5.25</td>
<td>8549 ± 1758</td>
</tr>
<tr>
<td>500</td>
<td>5.06</td>
<td>9717 ± 2273</td>
</tr>
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</table>
remarkable. With electron temperature \( (T_e) \) of \( \sim 1 \) eV as measured by Langmuir probe while the gas at room temperature \( (T_g) \) the glow discharge will deviate from equilibrium. The temperature difference \( T_e - T_g \) is proportional to square of ratio of energy acquired by electrons from the electric field \( (E) \) and pressure \( (E/p) \). At higher values of \( E/p \), electron temperature deviates largely from gas temperature and the plasma will be in non-equilibrium rather in a local thermodynamic equilibrium (LTE). However, vibrational and rotational excitation temperatures of molecules \( (T_v, T_g) \) also do not approach \( T_e \) and \( T_g \) in a non-thermal plasma and in our case \( T_v > T_g > T_e \). Vibrational excitation rate coefficients of \( N_2 \) by electron impact are very high of the order of \( 10^{10} \) as compared to vibrational VT relaxation rate coefficients. As a result, most of the electron energy of non-thermal glow discharge utilized for vibrational excitations and so value of \( T_v \) is higher than gas temperature\(^{12} \).

**4 Conclusions**

(1) In this paper, it has been shown that in a \( dc \) pulsed \( N_2 \) plasma that discharge power (driven by discharge frequency) variation has a significant effect on \( T_e, N_2/N_2^+ \) intensities and vibrational temperature of \( N_2 \) molecule. Intensity variation of (0,0) band of \( N_2 \) and (1,2) band of \( N_2^+ \) at different power levels (50-500 kHz) is found to be similar with the variation of \( T_e \). This proves that high energetic neutrals and molecular ions are responsible for heating the nitried surface. (2) At comparatively high pressure, emission intensity level is greater as can be seen from intensity plot of \( N_2(0,0) \) at 2.0, 3.0 and 4.3 torr pressure. At a fixed pressure, increase in discharge power as discharge frequency is increased is which is due to decrease in electrical impedance of the discharge\(^{13} \).

(3) The region of \( T_e, N_2 \) and \( N_2^+ \) intensity variation after power at 200 kHz can be attributed to reduction of ratio between maximum ion energy and operating voltage\(^{14,15} \) at high frequencies (above 100 kHz). As a result, discharge power does not increase very rapidly as discharge frequency is increased after 200 kHz. At frequency lower than 200 kHz, ions cross the sheath in times shorter compared to time period of discharge and thus, they are accelerated by the instantaneous sheath fields. Consequently, ion bombardment energy will be more at low frequency regime. At higher frequencies above 200 kHz, ions require many cycles of discharge to cross the sheath\(^{16} \), which is \( < 3 \) mm in our situation. As a result, ions cross the sheath slowly compared to time period of discharge and accelerated by a time averaged sheath potential. Thus, the effect of discharge frequency will be negligible at higher frequencies. Floating potential has also a decrease from 108 to 79 V (in magnitude) up to power at 200 kHz after which it does not increase which means electron temperature and density (considering small variation in ion saturation current) in the power plateau region becomes stagnant and unable to excite \( N_2 \) and \( N_2^+ \) more to have a rise in intensity. While in the power increasing region electron density must have a sharp increase.

(4) The second intense band of Herman’s infrared system i.e \( N_2 \) (2,2) has been observed. In nitriding plasma, we are not aware of reporting the detection of \( N_2 \) (2,2) so far by any researcher.

(5) Between 100-500 kHz, discharge frequency variation at 2 torr and corresponding power levels, it has been found from \( N_2 \) vibrational distribution that vibrational temperature of nitrogen molecule has 4207 ± 599 K to 9717 ± 2273 K variation.

Our study of discharge phenomena and related spectroscopy will help in optimizing as well as understanding the plasma assisted nitriding process.

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**References**