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Diagnostics of $He+N_2+CO_2$ Plasmas in Non-segmented Cylindrical Cathode Magnetron by DC Supply

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Abstract. We measured plasma parameters (excitation temperature, electron density, rotational and vibrational temperature) in non-segmented cylindrical cathode magnetron by optical emission spectroscopy (OES). Admixture of $He+N_2+CO_2$ gases in ratios of 3:2:1 is deployed for plasma study by means of OES diagnostics in a regime of the magnetic field. The objective of study is to understand effect of the gas mixture $He+N_2+CO_2$ on plasma parameters. The rotational temperature (T_{rot}), vibrational temperature (T_{vib}), and electron density (n_e) were calculated using spectral lines which were obtained through OES. This work also aims to investigate the validity of the excitation temperature (T_{exc}) by OES as an alternative to the electron temperature (T_e). The whole results of emission spectroscopy in a mixture of $He+N_2+CO_2$ are analyzed by changing magnetic field (in Tesla), current (in mA), pressure (Pa), keeping flow rate (sccm) constant.

Introduction

Low temperature [*Adamovich et al.*, 2017], low-pressure [*Fantz,* 2006] plasma in glow discharge [*Bogaerts,* 1999] has been investigated for decades due to their interest in technological applications. Helium is one of those gas that has been extensively used for technological study purposes with admixture of various molecular gases. The main reason for such studies are active species produced in such processes which are very important for multiple applications, such as biological sterilization [*Sakudo et al.,* 2019], plasma-assisted ignition and combustion [*Starikovskiy et al*., 2013], surface treatment [*Leahy et al.*, 2006], and various other studies. These studies are based on the assumption that mixing helium with a gas of higher molecular weight, using neon, nitrogen, carbon dioxide, or else change the spectral characteristics of the glow discharge substantially. The degree and trend of these changes typically depend on the discharge conditions, such as the sort of noble gas, percentage of the admixture, pressure, magnetic field, and so on.

In this article admixture of $He+N_2+CO_2$ gases in ratios of 3:2:1 is deployed for plasma study using optical emission spectroscopy The motivation for admixture study of $He+N_2+CO_2$ plasmas is to explore plasma parameter behavior of $He+N_2+CO_2$ in different discharge parameter.

In nitride synthesis or surface treatment, atomic nitrogen plays an important role due to its high chemical reactivity, therefore, the concentration of atomic nitrogen becomes significant in the discharge. In addition at higher N_2 concentrations, the admixture of N_2+He begins to appreciably affect the electron energy balance in the plasma providing an increase in the electron energy losses which is caused by the excitation of the vibrational and lower electronic levels [*Flores et al.,* 2014].

The CO_2 in admixture of $He+CO_2$ concentration can lead to an additional ionization mechanism, which is directly related to the molecules, without involving the metastable atoms of the noble gas [*Reyes et al*., 2008].

Since most changes in the discharge parameters influence both the density of the plasma species and the electron energy distribution function (EEDF). If any modification is made in the discharge parameters such as input power, filling pressure, and gas composition, the intensity of the emission lines cannot be assumed proportional to the density of the ground-state species. These can affect the plasma parameter results. These measuring techniques constitute an active field of research and are particularly suitable for low-pressure discharges.

In this paper, we report the measurement of plasma parameters (electron temperature, electron density, rotational and vibrational temperature) as a function of discharge parameters such as changing input current, pressure, and magnetic field keeping flow rate constant as it is not reported yet.

Experimental setup

The non-segmented cylindrical magnetron consists of a cylindrical cathode mounted coaxially inside the anode configuration as shown in Fig. 1. The discharge volume is axially limited utilizing two disc-shaped limiters, which are connected to the cathode potential. The schematic consist of the electrodes configuration is shown in Fig. 1. The diameters of the cathode and anode are 10 mm and 60 mm, respectively. The length of the discharge volume is 120 mm. The homogeneous magnetic field is created by two coils and is parallel with the common axis of the system. To prevent overheating the coils and cathode, the system is cooled by water. The pumping unit consists of a combination of turbomolecular and rotary pumps. The ultimate pressure is with the order of 10^{-3} Pa. The typical flow rate is 2 sccm and is adjusted utilizing the MKS flow controller to keep the pressure in the discharge volume constant. The pressure is 6 Pa, 12 Pa, and 18 Pa while current change is 0.1 A, 0.2 A, 0.3 A, 0.4 A and magnetic field is 20 mT and 40 mT respectively.

The spectroscopic apparatus consists of TRIAX550 system with a Czerny–Turner mounting grating monochromator with 1200 grooves/mm grating and grating size is 76 mm × 76 mm. TRIAX550 system with having a focal length of 0.55 meters plane grating delivers near-perfect spectral imaging over on 27 mm wide and 7 mm high Peltier couple cooled CCD detector. The wavelength positioning accuracy is ± 0.3 nm, and the spectral resolution of 0.025 nm. The slit width can be varied in steps of 12.5 microns, having a dispersion of 1.55 nm/mm, respectively. The CCD detector has matrix of 1024 × 256. The TRIAX550 spectrometer together with CCD 3000 interface are controlled by the SynerJY software. The system is intensity calibrated using tungsten halogen lamp.

Theory for plasma parameter study from optical emission spectroscopy

N_2 SPS and various line positions

The second positive system (SPS) [*Lebedev et al.*, 2006] of nitrogen molecule ($C\,^3\Pi_u \rightarrow B\,^3\Pi_g$) consists of the upper and lower electronic states both are $^3\Pi$ states having three sub-states each, $^3\Pi_0$, $^3\Pi_1$, and $^3\Pi_2$. The increase in the rotation number (J) causes the sub-states to evolve according to the Hund rule keeping Λ-doubling of rotation levels. The transition contains 27 branches and 9 of them are the principal ones with $\Delta\Omega = 0$ (Ω is the sum of orbital quantum number Λ).

Vibrational temperature

Vibrational temperature [*Zhang et al.,* 2015] of molecular nitrogen can be determined based on the second positive system of a nitrogen emission spectrum. This implies the radiation transition: $N_2\,(C^3\Pi_u) \rightarrow N_2\,(B^3\Pi_g) + h\nu$. In order to calculate the vibrational temperature (T_v) we assumed the Boltzmann distribution of the spectral line intensity (I).

$$I = CAv\,(v')\,e^{-G\,(v')\,hc/k_b t_v}, \quad (1)$$

where C is a fitted constant, A is the Frank Condon factor, v (v') is defined as

$$v\,(v') = 2\pi C / \lambda, \quad (2)$$

and, G (v') is defined as $G\,(v') = w_e\,(v'+1/2) - w_e x_e\,(v'+1/2)^2$.

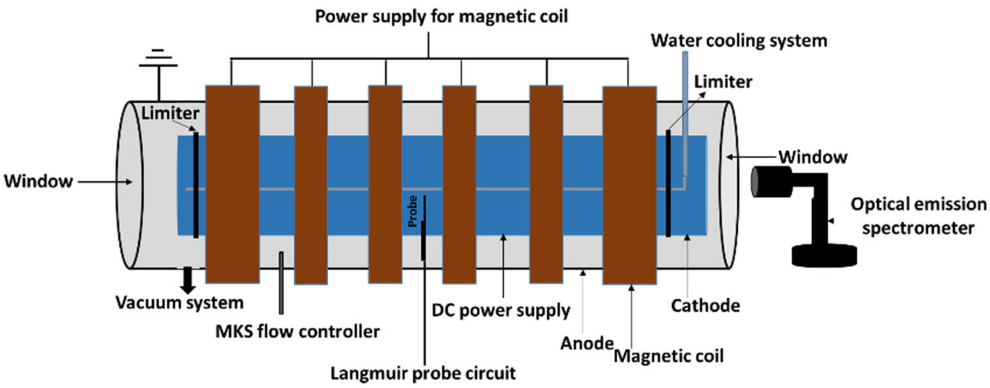

Figure 1. Non-segmented cylindrical cathode magnetron set up.

Here, c is the speed of light that is 3×10^8 ms^{-1}, h is Planck's constant, w_e and w_ex_e are Herzberg's vibrational constant. The intensity ratio of two bands belonging to the SPS N_2 ($C^3\Pi_u \rightarrow B^3\Pi_u$) ($\Delta v = 2$ vibrational system) at the wavelength 371 nm and 380.5 nm are used to determine the vibrational temperature via a line-ratio method.

Rotational temperature

Rotational temperature (T_{rot}) [*Zhang et al.,* 2015] is the substitute to the gas-kinetic temperature, which is the quantity needed to characterize the thermal motion of the bulk, ground state neutrals. Simply, the T_{rot} describes the Boltzmann distribution by which the different rotational states of the molecule are populated. Gas temperature measurements in non-equilibrium plasmas are indeed often obtained by emission spectroscopy from the population distribution in rotational levels of excited states of diatomic molecules (rotational temperature). The T_{rot} of the plasma can be obtained by measurement of the relative intensities of the doublets derived from the rotational R branch. The unwritten rule is that the rotational temperature of molecules in the discharge is equivalent to the gas temperature if the molecular excited states are produced by direct electron excitation from the ground state. We have chosen to use the N_2 ($C^3\prod_u$) $\rightarrow$ N_2 ($B^3\prod_g$) SPS as mentioned in 3.2.1, since it can easily be identified in an emission spectrum and it has a large oscillator strength. The N_2 (C $^3\prod_u$) $\rightarrow$ N_2 (B $^3\prod_g$) SPS consists of triple-headed bands, all degraded to shorter wavelengths. The rotational spectrum consists of three branches: P, Q, and R. Further, the P and R branches are split into three sub-branches, and the Q branch is split into two. The equation for rotational temperature calculations is shown below;

$$Log(I/(J' + J'' + 1)) = Log\ C - (B_v' hc/kT)J'(J' + 1) \quad (3)$$

previously, J' = J''+1 for the R-branch and J' = J''– 1 for the P-branch. Note that, if the left-hand term is plotted with respect to J' (J'+1), the slope of the resulting linear distribution will be equal to $(B_v' hc/kT)$, yielding the rotational temperature of the molecule. We have taken only J > 6 because for lower values the line intensities could not be accurately measured.

Excitation temperature

The excitation temperature (T_{exc}) describes population of excited energy levels by means of Boltzmann distribution. The T_{exc} [*Jamroz et al.,* 2010; *Abrar et al.,* 2013] of plasma can be estimated by the intensity ratio of the emission spectral lines When the thermal equilibrium is satisfied, the number of particles in the two energy states of an atom satisfies the Boltzmann distribution. Thus, ratio of the intensity values of two spectral lines is used in this method.

$$K_BT_{exc} = (E_2 – E_1)/Log\ (I_1\lambda_1g_2A_2/ I_2\lambda_2g_1A_1) \quad (4)$$

Here I_1 and the I_2 are the intensity of the selected bands from the second positive and the first positive systems at wavelengths 375.4 nm, and 391.44 nm, respectively, λ is the wavelength, E is excitation energy, g is statistical weight, and A is transition probability. The error consideration was 5 %.

Electron density

Electron density (n_e) is one of the most important plasma parameters because it determines the Debye length, the plasma frequency, the electrical conductivity and the probability of electron-induced processes such as excitation or chemical reactions. We determined the n_e using the concept of line ratios [*Devia et al.*, 2015].

$$n_e = ((I_{391.4}/I_{380.5}) – 0.0108) \times 10^{17}\ m^{-3}/1.048 \quad (5)$$

The distribution is Maxwellian where the dominant species and primary ions are ground state N_2 molecules and N_2^+ respectively. The population of the excited state N_2^+ ($B^2\sum^+ u$) is created from the ionization of neutral N_2 molecules due to the hot electrons and the corresponding radiative decay emits photons at 391.4 nm. The error consideration was 10 %.

Reactions of helium and carbon dioxide with nitrogen in DC discharge

The understanding of the reactions pathway in which N_2 is present can be of great interest for the understanding processes which occur in plasma. For the nitrogen, the main part of the observed spectra belongs to the SPS, which results from the transition N_2 ($C^3\Pi_u \rightarrow B^3\Pi_u$) where $C^3\Pi_u$ is the upper state and has higher energy than $B^3\Pi_u$ (lower state). The main reaction pathway involving the electron impact excitation from the ground state N_2(X, v = 0) to the excited state N_2 (C, v′) is as follows [*Flores et al.*, 2014]

$$e + N_2(X, v = 0) \rightarrow e + N_2(C, v') \quad (E_{th} = 11.1 \text{ eV}),$$

$$N_2(C, v') \rightarrow N_2(B, v'') + h\nu .$$

For the specific (C, v ′) → (B, v ″) transition, the emission intensity of the second positive system is stated as follows;

$$I_{CB}(v', v'') = C(\lambda) n_{n_2} n_e X_X^C(Te) \frac{A_{CB}(v',v'')}{\sum_{v''} A_{CB}(v',v'')} , \quad (6)$$

where n_{n_2} represent the number density of N_2(X, v = 0), the n_e is the number density of electrons, X_S^C (Te) is the excitation rate coefficients for electron impact excitation, A_{CB} is the Einstein coefficient and C(λ) is the spectral response of spectrometer at specific wavelength λ.

The other major part of nitrogen spectra is the first negative system. The positive ion of nitrogen N_2^+ (B, v') can also be produced through electron impact ionization either by direct or step-wise [*Flores et al.*, 2014]

$$e + N_2(X, v = 0) \rightarrow N_2^+(X, v') + 2e \quad (E_{th} > 15.6 \text{ eV}),$$

$$e + N_2^+(X, v = 0) \rightarrow N_2^+(B, v') + e \quad (E_{th} > 3.3 \text{ eV}).$$

The pathway of radiative de-excitation of N_2^+(B,v') state is described as follows;

$$N_2^+(B, v') \rightarrow N_2^+(X, v = 0) + h\nu$$

The resulting emission intensity of N_2^+ ($B^2\Sigma u \rightarrow X^2\Sigma_g^+$) band is stated as

$$I_{BX}^+(v', v'') = C(\lambda)[(n_{n_2} n_e X_X^{B^+}(Te)) + (n_e^2 X_X^{B^+}(T_e))] \frac{A_{BX}^+(v',v'')}{\sum_{v''} A_{BX}^+(v',v'')} . \quad (7)$$

The threshold excitation energy of the N_2 ($C^3\prod_u$) radiative state is 11.1 eV, which is less than the helium metastable state of 3 S (19.8 eV). Therefore, the N_2 ($C^3\prod_u$) radiative state can be depopulated by the inelastic collisions of helium metastable atoms through Penning ionization, as follows:

$$He^* + N_2(C^3\prod_u) \rightarrow He + N_2^+ + e^- .$$

Furthermore, the energy of the helium metastable atoms having $2^3 S_1$ (19.8 eV) and $2^1 S_1$ (20.6 eV) states is higher than the threshold ionization energy of the N_2 molecule (15.57 eV). Therefore, the ionization mechanism of N_2 is influenced by helium considerably.

The most important processes in the generation of electrical discharges in N_2–He mixture are primarily the electron impact excitation, ionization, and dissociation. Therefore, considering the low density non-segmented cylindrical magnetron, the important processes are the inelastic electron–atom, electron–molecule, and subsequent emission transitions from excited states [*Flores et al.*, 2014] as depicted below,

$$N_2(X^2\Sigma_g^+) + e \rightarrow N_2(C^3\prod_U) + e \rightarrow N_2(B^3\prod_g) + h\nu + e$$

$$N_2(X^2\Sigma_g^+) + e \rightarrow N_2^+(B^2\Sigma_u^+) + e \rightarrow N_2^+(X^2\Sigma_g^+) + h\nu + e$$

$$He(1^1S) + e \rightarrow He(3^1P_1) + e$$

$$He(1^1S) + e \rightarrow He(3^3D_{1,2,3}) + e$$

$$He(1^1S) + e \rightarrow He(3^1D_2) + e$$

The excitation energy of the emitting state $N_2(C^3\prod_U)$ at 337.13 nm is 11.03 eV, and the emission cross-sections for electron impact excitation of the nitrogen molecule are in the order of 10^{-22} to 10^{-23} m^2 [*Flores et al.*, 2014].

Several possible reactions can result from the electron interaction with N_2 and CO_2 molecules. The collisions of an electron and vibrational excitation of N_2 and CO_2 molecules are the fastest electron-impact processes [*Reyes et al*., 2008]. In this we consider the most important reaction for the generation of electrical discharges in N_2/CO_2 mixture [*Reyes et al*., 2008].

$$C_2O + NO \rightarrow NCO + CO$$

$$C_2O + NO \rightarrow CN + CO_2$$

$$C_2O + NO_2 \rightarrow NCO + CO_2$$

$$C_2O + N \rightarrow CN + CO$$

Species such as N, O, O_2, C, C^{-2}, CO_2, CN, NO_2, NCO, C_2O, and N_2O and their excited electronic states are certainly present in small amounts in emission spectrum. But, nevertheless these all species play an important role in the formation of several other vital species.

Result and Discussion

A typical spectroscopic emission measurement of He+N_2+CO_2 glow discharge plasma in the pressure range for 6, 12, and 18 Pa is displayed in Fig. 2. Only the most intense spectral lines and bands of the plasma in the range of 200–1100 nm are processed. The principal species observed were: at 337.13 and 357.69 nm for N_2 second positive system (SPS); at 391.44 and 427.81 nm for N_2 first negative system (FNS); at 501.57, 587.56, and 667.82 nm for He.

Considering among the population of O_2, CO, and CO_2 emission bands to be the most abundant, this would imply that the main process for the production of these species is the electron impact dissociation or ionization excitation. The species observed were O_2 ($b^1\ \Sigma g + - X^3 \sum g -$) at 400 nm; CO ($a'^3\ \Sigma - a^3\ \Pi$) at 483 nm; CO_2 ($A^2\ \Pi - X^2\ \Pi$) at 353.2 nm.

The excitation temperature versus the current plot is shown in Fig. 3. It can easily be interpreted that with increasing current the overall behavior of T_{exc} increases. The increment behavior can be explained by abnormal heating in terms of the bounce resonant motion of low energy electrons in the bulk plasma at the low pressure. Adding a small amount of N_2 to He lowers T_{exe} sharply. This is because rate constant for ionization of N_2 is more than ten times larger than that of He. However, the presence of CO_2 can be the factor for vital increment in excitation temperature as the rate constant for ionization in CO_2 and N_2 is near same respect to He. The error range taken in to considerations is 10 %.

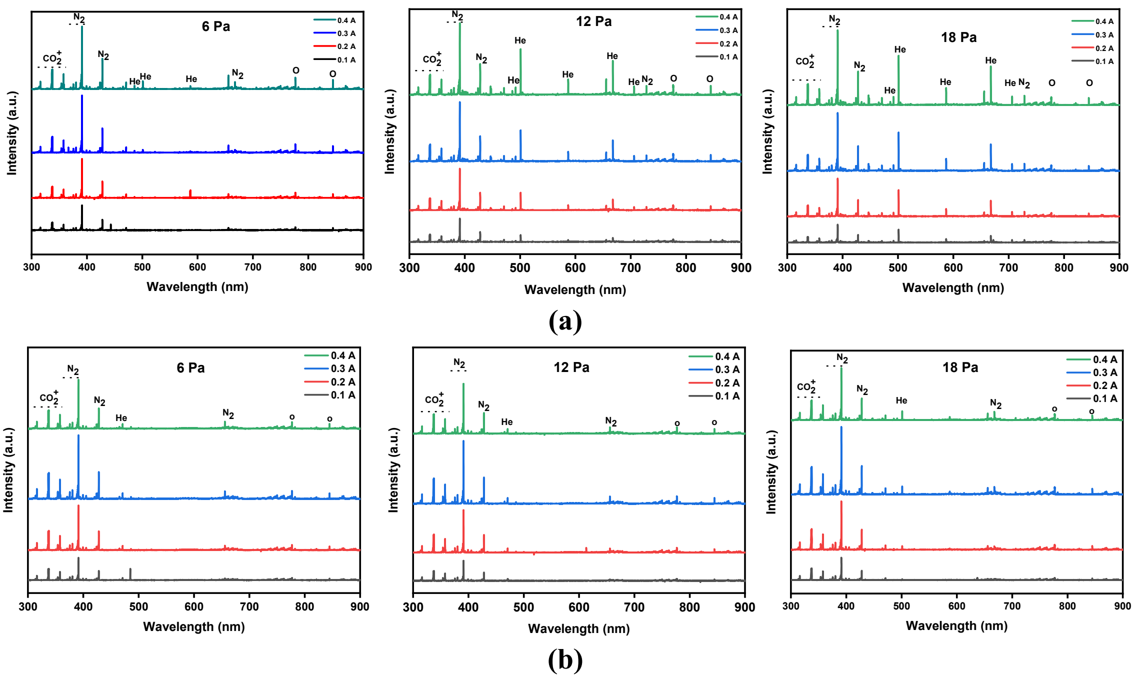

Figure 2. Optical emission spectra for magnetic field (a) 20 mT, (b) 40 mT, for pressure range of 6 Pa, 12 Pa and 18 Pa.

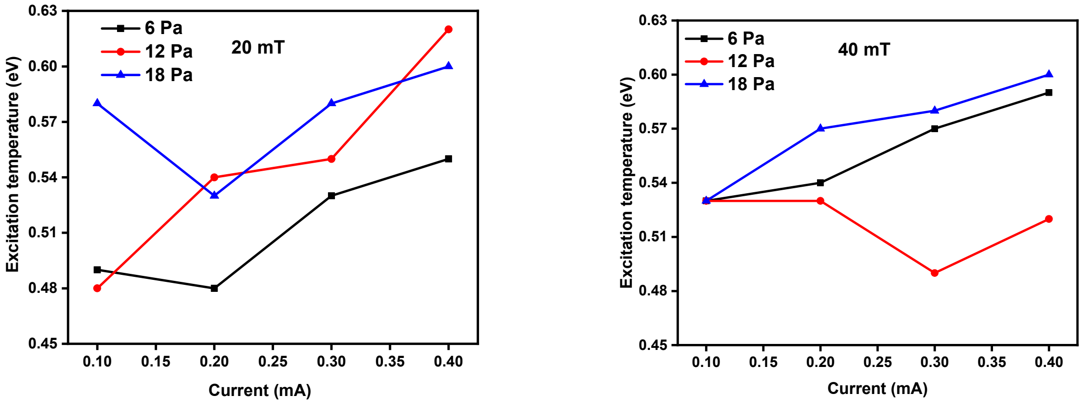

Figure 3. Excitation temperature measurement through intensity ratio of the emission spectral lines.

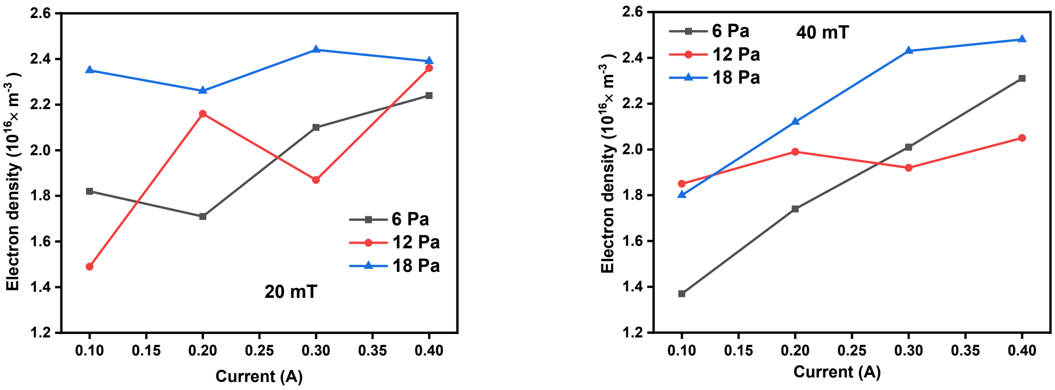

Figure 4. Electron density measurement through intensity ratio of the emission spectral lines.

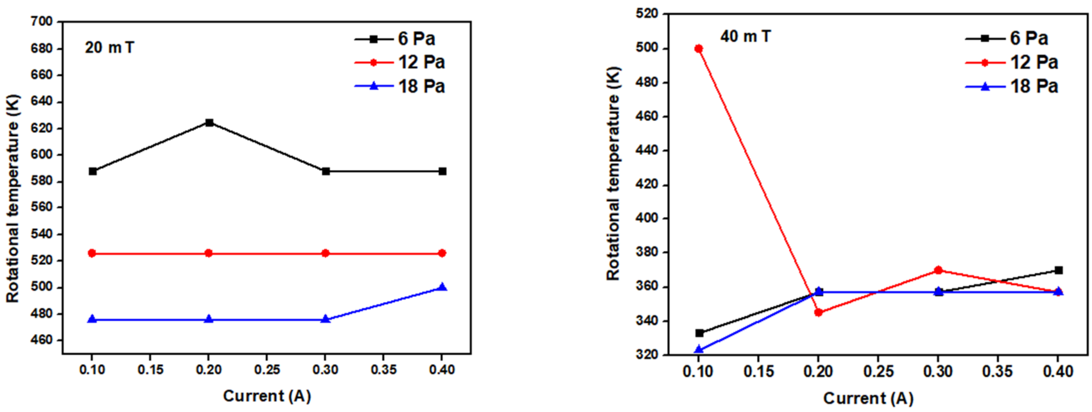

Figure 5. Rotational temperature measurement through the measurement of the relative intensities of the doublets derived from the rotational R branch.

Figure 4 shows the electron density as a function of the current. Here we can see that with increasing current the n_e increases. The increase of discharge current leads to an increase in the number of electrons emitted from the cathode, hence the increase of the ionization processes leads to the increasing density of electrons. The error range taken in to considerations is 5%.

The results of rotational or translational temperature measurements in the cylindrical magnetron discharge are presented in Figs. 5 and 6. From the results, we can see that T_{rot} has essentially different values with the 20 mT (470–650 K) than those with the 40 mT (320–500 K) which reflects the fact that kinetic temperature in 20 mT mode is higher. It can be seen that the T_{rot} shows almost no changes for any value of admixture in the discharge and grouping near 520 K in the 20 mT mode and near 320 K in the 40 mT mode case.

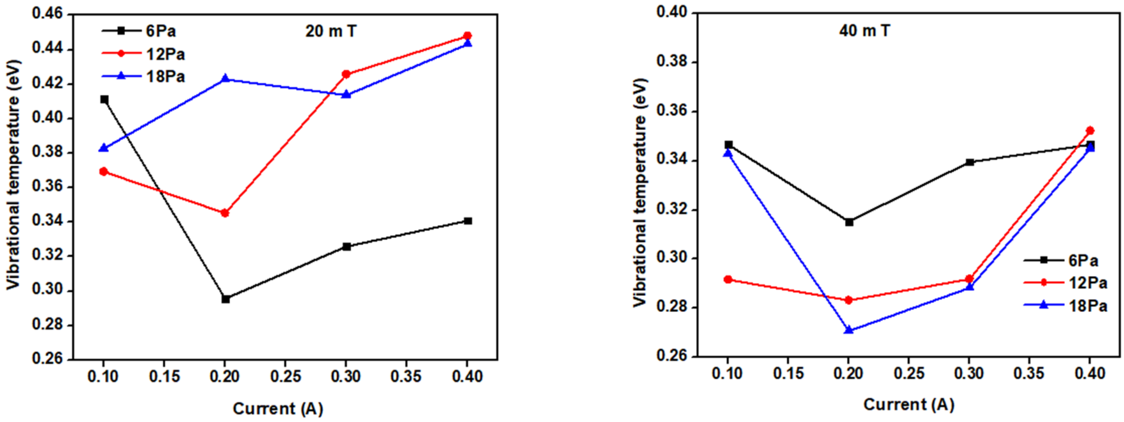

Figure 6. Vibrational temperature is determined based on the second positive system of a nitrogen emission spectrum.

In He+N_2+CO_2 gas mixtures, the N_2 (C, Δv = 2) states are enhanced by reaction (4) as was discussed in section 3. The results in Fig. 6 indicate that all these factors contribute to the increase in T_{vib} for He + N_2 + CO_2 gas mixtures at 25 percent of nitrogen with increasing current values. As such, an increase in the T_{vib} is governed by a rise in plasma density which causes an increase in the production rate of vibrational excited nitrogen molecules. The high T_{vib} suggests that the plasma is under non-equilibrium conditions, i.e., a vast difference between rotational (gas) temperature and vibrational temperature.

Conclusion

We presented our results on series of Langmuir-probe and OES measurements, which were carried out for the non-segmented cylindrical cathode system. We measured electron densities, electron temperature, excitation temperature, rotational temperature, and vibrational temperature in He+N_2+CO_2 plasmas.

The electronic excitation temperature was determined by using the two-line intensity ratio method of 375.4 nm, and 391.44 nm. The vibrational temperature T_{vib} was calculated with minimization procedure for the sequence (Δv = 2) of the N_2 second positive system ($C^3\Pi u-B^3\Pi g$) from 372 nm to 382 nm by comparing the measured optical emission spectroscopy (OES). The rotational temperature (T_{rot}) of the plasma can be obtained by the measurement of the relative intensities of the doublets derived from the rotational R branch. The electron density was determined using the concept of line ratios of 391.4 nm and 380.5 nm. The relations between the measured temperatures are as follows: T_{exc}>T_{vib}> T_{rot}.

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