Determination of Electron Excitation Temperature in an RF-DC Hollow Cathode Nitrogen Plasma

J M Windajanti¹, D J D H Santjojo¹, M A Pamungkas¹, and Abdurrouf¹

¹ Physics Department, Brawijaya University, Malang-Indonesia

Email: abdurrouf@ub.ac.id or windajanti_jm@student.ub.ac.id

Abstract. An RF-DC nitrogen glow discharge generated inside a rectangular hollow cathode was investigated as a source of nitrogen atoms. The plasma was produced at a frequency of 2 MHz at a low-pressure condition at the range of 30 to 100 Pa. The power generator was controlled at the RF voltage of 150 V and DC bias voltage of -500 V. The atomic nitrogen species have been detected by employing an optical emission spectroscopy technique. The use of a rectangular hollow cathode proves that the increase of nitrogen atoms species at a wavelength range of 700-900 nm was produced from the dissociation process of molecular nitrogen species. The present work aims to determine the electron excitation temperature based on the OES spectra. The excitation temperature was calculated by using the Boltzmann plot method. The result is the excitation temperature determined at the range of 0.59 to 0.71 eV. The excitation temperature in the hollow cathode was decreased with the increasing pressure.

1. Introduction
Plasma nitriding is the clean and energy saving of thermo-chemical surface treatments based on the diffusion of nitrogen atoms in the metal [1]–[3]. In the nitriding process, when the nitrogen particles are accelerated and hit the cathode, they were dissociated into radicals or ionic species for subsequent reactions, and then atomic reacted nitrogen atoms adsorbed and diffused into interstitial sites of metal [1]. One of the essential parameters of a plasma is the degree of ionization required to produce and sustain a plasma. The balance of electrons and ions in the plasma is regulated by excitation, dissociation, recombination, and diffusion or convection to the boundary [4]. The occurrence of ionization and dissociation of nitrogen molecules, and the way each species reacted in the plasma significantly affect the process [5]. That mechanism should be controlled by the selection of optimum parameters in the plasma nitriding process such as the gas pressure, temperature, gas mixture, and nitriding time [6].

The glow discharge plasma was produced and sustained by the electric fields from either alternating current (AC) and direct current (DC) power supplies. The plasma contain charged particles, i.e., molecules, atoms, and radicals [7]. Recently, a new generation of low-pressure, high-density plasma has led to the enhanced plasma-assisted nitriding concept to meet the possibility to overcome some disadvantages of conventional nitriding [8]. A characteristic feature of this high-density source is the uncoupling of the plasma generated from the hollow cathode devices as a section of the reactor loaded with the substrates. A high density plasma can be achieved by considerably enlarge the mean free path of species by using the low-pressure chamber condition [2].

Research on plasma nitrogen is exciting because nitrogen is a complex medium. The nitrogen species plasma behaviour is vital for the plasma treatment process, but it was not fully understood.
This paper constitutes the fundamental aspects of low-pressure nitrogen plasma glow discharges that contain the existence of strong coupling in the kinetics of the process, such as electron kinetics, molecular vibrations, surface interactions, and chemical reactions [9], [10]. In this work, we restrict our investigation to determine the excitation temperature of the electron in RF-DC nitrogen plasma operated at a frequency around 2 MHz by using the Boltzmann plot method based on the recorded spectrum by optical emission spectroscopy (OES).

2. Experimental Method

The material, instrument and primary operating parameter used in this study are described in our previous publications [11], [12]. In this work, three hollow cathodes with the length of 60, 80 and 100 mm and a gap height of 15 mm were chosen. The chamber pressure was varied from 30 Pa to 100 Pa with a 10 Pa step. The pressure variation was intended to determine the optimum conditions of working plasma pressure for each hollow tube length variation. An optical emission spectrometry (OES) was utilized to characterize the nitrogen plasma condition. The spectrometer was Aurora4000 Fibre Optic Spectrometer used to record photon emissions produced from the nitrogen plasma. The radiation was picked up through an optically transparent silica window in front side of the chamber. A 5 μm slit and a tiny lens were utilized to locate measurement position at approximately 100 mm from the centre of the plasma. The nitrogen emission intensity was measured in the wavelength range from 200 nm to 1100 nm by using a photosensor amplifier with an optical resolution of <0.75 nm FWHM. The data was stored in a computer and analyzed using spectral analysis software. The software was utilized to determine peaks of nitrogen species in the wavelength range of 700 to 900 nm. After that, each peak was matched to the nitrogen atom spectrum database in the NIST Atomic Spectrum Line Database to get the nitrogen atom peak (N I) along with data on energy levels, transition probabilities, and statistical weights of each N I peak. The Boltzmann plot method was used to determine the plasma excitation temperature, which is related to the energy needed by electrons to excite an atom from its ground state to its excitation state. In this experiment, it is assumed that there is a local thermal equilibrium in the plasma for the calculation of the electron excitation temperature.

Using the wavelength of emitted light (\( \lambda_{ij} \)) and intensity (\( I_{ij} \)), we use the Boltzmann equation as follow.

\[
\ln \frac{I_{ij}}{A_{ij}\beta_i} = -\frac{E_i}{kT} + C
\]  

where \( A_{ij} \) is the transition probability, \( \beta_i \) are the statistical weights of upper states, \( E_i \) is the upper energy levels, \( k \) is the Boltzmann constant \( (1.38 \times 10^{-23} \text{ J/K}) \), \( T \) is the temperature in kelvin (K), and \( C \) is a constant. Using the plotting of Eq. (1) with \( E_i \) in the horizontal axis and \( \ln \frac{I_{ij}}{A_{ij}\beta_i} \) in the vertical axis will result in a straight line, and the electron temperature can be determined from the slope of the straight line.

3. Result and Discussion

A process of increasing the intensity of plasma glow discharge is carried out using a rectangular hollow cathode. With a nitrogen gas flow rate of 100 ml/min, the plasma was generated using an RF voltage of 150 V and a DC bias voltage of -500 V. When the plasma is turned on at a pressure of 100 Pa, the plasma has not been trapped inside the hollow cavity. However, the plasma was trapped in the cavity in lower pressure. In this investigation, the ability of three different lengths rectangular hollow cathode to trap electrons were compared. The intensifying of plasma intensity occurs due to the trapping of electrons in the hollow cavity so that plasma discharge appears brighter, as shown in Fig. 1.

It can be seen in the figure; the emission intensity was increased when the plasma is trapped in the cavity for a given voltage due to the hollow cathode effect [13]. The negative glow region inside the hollow cathode cavity is a thin sheath around the inner cathode surface. When the electron mean free
path exceeds the plasma size, the trapped electrons make it possible to sustain the discharge at low gas pressures. Since the secondary electrons are formed, they are accelerated through the sheath and bounce back and forth between the opposite sheaths known as the pendulum effect [14].

![Figure 1](image1.jpg)  
**Figure 1.** Plasma condition inside the rectangular hollow cathode (a) H=15 mm, L=100 mm, p=100 Pa and (b) H=15 mm, L=100 mm, p=30 Pa.

The occurrence of secondary electron emissions is very important to increase the gas ionization in the plasma discharge, which will later be accelerated to the cathode. The effect is generally considered essential for the hollow cathode discharge operation due to the electrons ionize the working gas in their path and increase the intensity of the plasma species. This happens because electrons trapped in the hollow cavity will ionize the gas and lose a lot of energy there without having time to move out, marked by the high concentration glow discharge in the cavity. Also, the presence of axial magnets formed in the hollow cathode can trigger the formation of electron beams which increase the ionization process [15].

![Figure 2](image2.jpg)  
**Figure 2.** The OES spectra of RF-DC pure nitrogen discharge inside the rectangular hollow cathode with gap height of 15 mm and tube length of 100 mm at pressure 30 Pa and 90 Pa in the wavelength range of (a) 300 to 900 nm and (b) 700 to 900 nm.
On the other hand, the determination of pressure also influences the process. If the pressure used is too high, the mean free path value of the electron will get smaller, so that the electron collides with other particles before getting enough energy to ionize the gas. However, if the pressure is too low, the electrons will not be trapped in the hollow cavity, so the effect of the hollow cathode to increase plasma intensity does not occur. It can be concluded that ion density is more influential on the success of the nitriding process than the energy value of the ion [16].

The OES spectra show the formation of four bands in our RF-DC nitrogen plasma discharge inside the rectangular hollow cathode, as shown in Fig. 2 (a). There were three bands of neutral N\(_2\) molecules and N\(_2^+\) molecule ions, i.e. the second positive system of N\(_2\) molecule at a wavelength range of 300-360 nm, the first negative system of N\(_2^+\) molecular ions at the wavelength range of 390-475 nm, and the weak peak intensity of the first positive system of N\(_2\) molecule at the wavelength range >600 nm. In Fig. 2 (b), we can observe the formation of the fourth band which stated the line emission of atomic N (N I) and ion N\(^{+}\) (N II) overlapped with the first positive system of N\(_2\) at the wavelength range of 700-900 nm [17]. The nonequilibrium characteristic of the nitrogen excited-state species always shown by low-pressure plasma.

In low-pressure nitrogen discharge, there was a high density of long-lived, stable, and active species found as the ground state molecules and atoms and the excited molecules in metastable states and vibrational states. The electron impact inelastic collision plays a vital role in the formation of active species. In this collision, the accelerate electrons spend their energy to the collided particles. Several reactions were occurred and accompanied by the excitation of electrons from the collided atoms where the photons will be emitted during relaxation.

Actually, in most cases, it was hard to acquire a high dissociation rate (>2%) when the plasma is generated by pure molecular nitrogen [10], [18]. It is due to the stable bonding of N\(_2\). Herein the addition of rectangular hollow cathode device has been succeeded to enhance the dissociation rate of pure N\(_2\) in RF-DC plasma. The molecules dissociation take place through the vibrational and electronic excitation. The slow electron mostly induced the dissociation of the molecule by the electron excitation [5]. Nitrogen atom occurs due to the N\(_2\) excitation through dissociation and dissociative ionization by electron impact [17]. Nitrogen plasma accommodates the atomic N and N\(^+\) species through the electronic excitation. This process needs the energy about several electron volts above their ground states [3]. The reaction kinetic of nitrogen atom according to the formation of the ground state atom N(\(^4\)S) and the metastable state N (\(^2\)D, \(^2\)P) through the electron impact dissociation.

Next, we will discuss the plasma temperature. Accurate determination of the gas kinetic temperature in reactive glow discharges is fundamental to the understanding of plasma processes, especially the nitriding process [5]. The nitrogen atoms (N I) and nitrogen ions (N II), especially the nitrogen atom N(\(^4\)S) is the most important species in the metal hardening process [10], [19]. The temperature of plasma formed with molecular gas, such as nitrogen gas was determined by different temperatures such as rotational (T\(_r\)), vibrational (T\(_v\)), and excitation (T\(_e\)) temperature, in addition to electron and gas temperatures. In this investigation, we focus on determining the temperature of excitation due to the formation of nitrogen atomic species that occurs through electronic excitation. The excitation temperature can be determined by a reasonably simple method by using the Boltzmann plot through analysis of the nitrogen atom species formed in the plasma. Through the wavelength and intensity data of nitrogen atoms in the 700-900 nm wavelength, the excitation temperature value will be determined [20].

We have solved the electron excitation temperature using the Boltzmann equation for nitrogen atom species in a ground state and metastable state (S, P, D) formed in our RF-DC plasma in the pressure range of 30 to 90 Pa. The results of the excitation temperature are explained in Fig. 3. For the RF-DC plasma inside the rectangular hollow cathode with the length of 100 mm at pressure 30 Pa, the excitation temperature is 0.657 eV. The range of excitation temperature values obtained from calculations for hollow cathodes with a length of 80 mm between 0.590 to 0.657 eV. And in the hollow with a length of 60 mm, the excitation temperature can reach the value of 0.713 eV. The
discharges in the 60 mm length tube tend to be unstable, and sometimes plasma suddenly comes out of the hollow cavity.

Our calculations showed that the excitation temperature tends to decrease at the pressure of 30 to 90 Pa for hollow cathode with a gap height. The results obtained for each size of the hollow cathode tube length of 60, 80, and 100 mm are shown in Fig. 4.

![Figure 3](image3.png)

**Figure 3.** The calculation of excitation temperature of RF-DC plasma inside the rectangular hollow cathode with a gap height of 15 mm and tube length of 100 mm at pressure 30 Pa.

![Figure 4](image4.png)

**Figure 4.** Excitation temperature as a function of pressure for the three types of hollow cathode tube length of 100, 80, and 60 mm, respectively, determined by the Boltzmann plot from the RF-DC plasma inside the rectangular hollow cathode with gap height of 15 mm.

The electrons emitted by the cathode surface are trapped by the electric field produced by the cathode cavity. In the hollow cathode, it is possible that there is a multiplication of electrons. The formation of fast electrons is responsible for the ionization process and the increase of plasma density. The ionization process takes place in the sheath region, and for electrons with a long mean free path, the electrons can be reflected repeatedly and generate secondary electrons there [13]. The most important aspect of pressure is to control whether, in the plasma species interaction, the mean free path is larger or smaller than the discharge dimension [20]. At low pressure, electrons have a long mean free path, undergo acceleration in the sheath, and are reflected back and forth by the surface of the cathode. When the electrons collide with the gas molecules, the electrons will lose energy gradually. With the long trajectory, the electrons are understood to generate a large number of secondary electron and gain high-density plasma.

4. **Conclusion**

The result of this investigation allows us to conclude that the use of the rectangular hollow cathode obtains the enhancing plasma density of pure nitrogen plasma generated by the RF-DC generator inside the cavity. The formation of nitrogen atoms (N I) and nitrogen ions (N II) in the wavelength range of 700 to 900 nm of the nitrogen spectra prove that trapped electron in the hollow cavity causes the dissociation process of the neutral molecules (N₂) and molecular ions of nitrogen (N₂⁺). By using the Boltzmann Plot of atomic nitrogen species, the excitation temperature for this RF-DC plasma inside the rectangular hollow cathode with the gap height of 15 mm and tube length of 100 mm is 0.657 eV at pressure 30 Pa. The highest excitation temperature for each size of the cathode hollow reaches its highest value at its optimum working pressure at the lowest pressure where electrons can
still be trapped in hollow cavities. The difference in the height of the hollow cathode plays the role of optimal working pressure where for smaller hollow gap sizes the working pressure increases. The range of excitation temperature in the hollow cathode with a gap height of 15 mm and a length of 100 mm was between 0.590 to 0.657 eV. It was found that if the chamber pressure is increased, the excitation temperature tends to decrease. Its due in higher pressure, the electrons mean free path became shorter so that the electrons lose energy more quickly due to the increase of the collisions frequency with the particles in the plasma without the ionization and dissociation process which results in a decrease in the intensity of the plasma species.

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