The Influence of Hollow Cathode Geometry and N$_2$-H$_2$ Gas Mixture on the 2 MHz RF-DC Plasma Species and Density

J M Windajanti$^1$, Abdurrouf$^1$, D Joko H Santjojo$^1$ and M A Pamungkas$^1$

$^1$Physics Department, Faculty of Mathematics and Sciences, Brawijaya University, Jalan Veteran Malang, East Java, Indonesia

*Corresponding author: abdurrouf@ub.ac.id

Abstract. RF-DC plasma combined with the hollow cathode effect is used to generate plasma inside a hollow cavity. A high-density plasma was formed inside a vacuum chamber using a 2 MHz RF generator. A hollow cathode was utilized to focus the power at the voltage of 150 V with DC bias of -500 V. The plasma system was specially designed for titanium nitriding process at low temperature using N$_2$-H$_2$ gas mixture. The N$_2$-H$_2$ gas with a flow rate of 90-10 mL/minute was conducted at pressure 20 to 150 Pa. The cylindrical and rectangular hollow cathodes are used to make the discharge containing attractive atoms or molecules inside the hollow cavity. The trapped electrons could trigger the secondary electron emission that induced high-density plasma. The geometry components such as gap size, diameter, and cavity depth combined with variations of chamber pressure have been studied to produce high-density plasma. The species inside of N$_2$-H$_2$ plasma were detected by OES based on light emission. The high-intensity peaks of N$_2^*$ molecules from the second positive system and N$_2^+$ ions from the first negative system at the wavelength range of 300 to 500 nm were detected to obtain effective plasma species for the nitriding process.

1. Introduction
The plasma glow discharge consists of largely neutral atoms and molecules. Although the positive charge is equally the same as the negative charge, some ionized gas may exist in the plasma [1]. The plasma discharge is generated from a low pressure gas contained in a vacuum chamber. When a potential difference is given between the two electrodes, plasma discharge will be formed after a 'gas breakdown' so that the gas ionization process occurs to release electrons and positive ions. When positive ions are forced to the cathode, a bombardment of positive ions with the cathode can trigger the release of advanced electrons called 'secondary electron emission'. Moreover, when these electrons collide with gas particles in the plasma, it will cause excitation and ionization of the gas particles. Excitation of gas atoms or molecules will be followed by the radiative decay to a lower level while it is emitting light with special characteristics (i.e. the appearance of violet colors on nitrogen plasma). The collision events that occur in the ionization process create new ion and electron pairs that make self-sustained on plasma glow discharge [2]. In radio frequency (RF) discharges, the power and the electrons are coupled so the discharges have more efficient ionization than the DC discharge. The current in an RF discharge is generally a displacement current, results from the oscillatory motion of the electrons when they comply with the electric field [3]. An addition of DC bias voltage could attract the positive ions onto the cathode table to obtain the high-density plasma [4].

A plasma glow discharge is used in various fields of application, such as in the process of surface hardening, thin film deposition, and etching in materials technology, in the microelectronics industry,
and also as a laser and lighting [5], [6]. The nitriding process using plasma glow discharge is a common method for increasing wear and corrosion resistance in surface hardening processes without affecting bulk material and also avoiding fatigue in the material due to high temperature processes. The advantage of this process is energy savings and no anti-pollution equipment requirements [7]. In the nitriding process, the bombardment of positive ions onto nitrided specimens placed on the cathode plate is a cathodic process that requires a high rate of nitrogen ionization. Plasma nitriding is faster than conventional nitriding because the surface of the specimen is saturated with nitrogen. Plasma process parameters, i.e. chamber pressure, DC bias and the RF Power control the composition and the depth of the nitride layer [4]. The effectiveness of plasma nitriding is always being developed by reducing the temperature and processing time [5].

With the cathode geometry like a cavity, a hollow cathode discharge will be formed where the plasma is trapped by the electrode wall. The loss of electrons in the plasma will decrease because the electrons are trapped by the cathode geometry, and result in the higher plasma density (10^{11} to >10^{13} cm^{-3}) inside the hollow tube. The decrease is due to the occurrence of the pendulum effect which makes electrons to be reflected by the sheath on both sides of the cathode wall which induces a long electron trajectory to produce a large number of high-energy secondary electrons. Also, the electrons have only one direction to escape from the plasma, which is along the axis of the hollow cathode [8]. The negative glow of the plasma can expand to occupy the interior volume of the cathode using an appropriate combination of a given hollow cathode diameter or separation of the cathode surface with the chamber gas pressure under the applied power. The increasing of the discharge current depends on the hollow cathode geometry. An inter-cathode distance of the rectangular hollow or diameter of the cylindrical hollow is the important parameter that influences the discharge behavior. The decreased of the inter-cathode distance or the diameter could increase plasma density due to the emission of high energy electrons by the hollow cathode and then enhance the gas ionization [9].

The present work aims to investigate the influence of both pressure and hollow cathode geometry on the luminous intensity emitted by the plasma. The emission is originated from the positive column of glow discharge plasma that generated using pure N\textsubscript{2} gas and N\textsubscript{2}-H\textsubscript{2} gas mixture for constants discharge voltage of RF and DC bias generator.

2. Experimental Method

2.1. High-density RF-DC plasma system
A high-density RF-DC plasma nitriding system is utilized to generate a plasma of N\textsubscript{2}-H\textsubscript{2} gas. In this plasma system there is no need for a mechanical matching box, but rather by adjusting the frequency of 2 MHz. The input and output power are automatically matched with the response time limited to only one millisecond. This fast power control provides full use of plasma with a pressure range of more than 50 Pa. With a neutral electric condition of the vacuum chamber, the RF and DC power can be controlled independently. The RF plasma is produced by the dipole electrodes, and then the DC bias is directly applied to attract the ions towards the cathode.

The RF-DC plasma system composed by a vacuum chamber which equipped with the RF and DC bias plasma generator, vacuum pump, and gas supply system. In the vacuum chamber interior, the main part components are a pair of RF dipole rod electrodes and a stainless steels cathode plate. An addition of a hollow cathode device was placed on the cathode plate. The gas pressure was controlled by Pirani vacuum gauge control (Ulvac GP-2G) and the RF and DC bias voltage by the voltmeter. The nitrogen and hydrogen gas was injected into the chamber via a flowmeter through an inlet at the top side of the chamber. The schematic design of the RF-DC plasma system is depicted in Figure 1.

In this investigation process, the hollow cathode device is first placed on the cathode plate, followed by a vacuum process until it reaches a bottom pressure of 4 Pa. After that, nitrogen gas is introduced into the chamber as a plasma carrier gas until the pressure rises up to 100 Pa, and then the plasma was ignited. On the use of the N\textsubscript{2}-H\textsubscript{2} gas mixture, the hydrogen gas would be entered after the plasma was generated by using pure nitrogen gas. Table 1 shows the processing parameter.
Figure 1. The schematic design of the RF-DC plasma system, consist of: (1) vacuum chamber; (2) 2 MHz RF generator; (3) DC bias generator; (4) N$_2$-H$_2$ gas inlet with flowmeter; (5) vacuum pump; (6) anode dipole rod; (7) cathode plate; and (8) hollow cathode device.

Table 1. The operating conditions of the high-density plasma system.

| Processing Parameter                  | Set-up Value                      |
|--------------------------------------|-----------------------------------|
| Base pressure vacuum of chamber      | 4 Pa                              |
| RF frequency                         | 2 MHz                             |
| RF voltage                           | 150 V                             |
| DC bias voltage                      | -500 V                            |
| Gas flow rate                        | N$_2$ gas: 100 mL/min; N$_2$-H$_2$ gas: 90-10 mL/min |
| Pressure of gas mixture              | Variance at 20-150 Pa             |

2.2. Quantitative plasma diagnosis

An identification of ion density of N$_2$-H$_2$ plasma inside the hollow cathode device in the high-density RF-DC plasma nitriding system was carried out using a quantitative plasma diagnosis. The various plasma species and their characteristics were identified by the optical emission spectroscopy (OES Aurora-4000 GE UV-NIR) with the typical setup as illustrated in Figure 2.

Figure 2. A typical setup of optical emission spectroscopy (OES).
The existence of plasma reactive species strongly depends on the control parameters such as applied voltage and gas flow rate. The emission spectra of N$_2$-H$_2$ gas were recorded in the wavelength range from 200 nm to 1100 nm. The emission light is detected through the optically transparent silica window located in front of the chamber by a photosensor amplifier. Knowing the nitrogen plasma species is important for the adjustment of process parameters in order to the optimization process of the specific applications using the plasma treatment.

2.3. Hollow cathode geometry
A device of the hollow cathode is inserted into the chamber and placed on the cathode plate. There are two models of hollow tube used in this study, i.e. hollow cathode with a cylindrical and rectangular cross-section. The 80 mm length of cylindrical hollow has two kinds of a diameter of 50.8 and 38.1 mm, respectively. The same length of rectangular hollow has a gap height of 25 and 20 mm, respectively. A photograph of the hollow cathode depicted in Figure 3.

![Figure 3. The geometry of hollow cathode tube.](image)

3. Result and Discussion
Photons emitted by radiative decay after the electron boost the plasma species into upper electronic states can be obtained and analyzed by recording the OES spectrum because it has a characteristic wavelength in the optical region of V-UV spectra. The density of plasma ions can be measured by this measurement technique, by analogy that the specific wavelength of the light emission intensity from excited states of a specific wavelength is proportional to the species concentration in that excited states [10].

![Figure 4. OES Spectra of N$_2$ Plasma and N$_2$-H$_2$ Plasma generated without hollow cathode chamber at 100 Pa.](image)
The glow discharge was generated by using the RF- DC plasma generator with the power of 100 W and the RF frequency of 2 MHz. At the time of observation, the voltage used to generate plasma was 150 V and -500 V for each RF and DC bias generator. The reactive species of the nitrogen molecules and hydrogen atoms spectra were identified in the wavelength range from 300 to 700 nm on the recorded optical emission spectra from 200 to 1100 nm. The result of nitrogen peaks was determined from the glow discharge from pure nitrogen gas with the flow rate of 100 mL/min in comparison with those from the N2-H2 gas mixture with the flowrate of each one of 90-10 mL/min as seen in Figure 4. From the recorded of OES spectra, it showed that there were several strong nitrogen molecular lines of N2+ (activated nitrogen molecules) and N2++(nitrogen ion molecules) [4]. There were three peaks with a high-intensity line of N2+ that come from the transition of C3Πu → B3Πg at the second positive system. There were also three peaks with a high intensity of N2+ in which the strongest emission is the lines of nitrogen ion at first negative system (1NS) with the wavelength of 391.4 nm from the transition of B3Σu+ → X3Σg+ electronic state [11], [12]. Several dominant peaks of nitrogen molecule obtained from the recording of OES on discharge generated by this RF-DC generator can be observed in Table 2. It was also observed the hydrogen peak at a wavelength of 656.5 nm which is the Balmer series transition from the 3rd to 2nd energy level called H. peak.

### Table 2. The nitrogen gas species in glow discharge RF-DC plasma.

| Nitrogen Species | Wavelength (nm) | Upper Energy Level | Lower Energy Level |
|------------------|-----------------|--------------------|--------------------|
| N2∗ | 315.9 | C3Π [1] | B3Π [0] |
| N2× | 337.1 | C3Π [0] | B3Π [0] |
| N2+ | 357.7 | C3Π [1] | B3Π [1] |
| N2++ | 391.4 | B3Σ [0] | X3Σ [0] |
| N2+++ | 427.7 | B3Σ [0] | X3Σ [1] |
| N2++ | 470.9 | B3Σ [0] | X3Σ [2] |
| H | 656.5 | Balmer series (n = 3 to n = 2) |

Without a hollow cathode, the plasma OES spectra of N2+ ions at 391.4 and 427.7 nm produced with a mixture of N2-H2 gas has a higher intensity than the pure N2 gas as shown in Figure 4. There is also an obtained of higher peak of H species at 656.5 nm. The other peak intensity is almost the same. Further investigation on the effect of mixing the hydrogen gas to nitrogen gas with varying concentrations of both gases is still needed. It is necessary to increase the concentration of nitrogen ions because the presence of these ions greatly affect the effectiveness of plasma nitriding process used.

When the chamber pressure was increased from 20 to 150 Pa, it was obtained that the peak intensity of each species of nitrogen molecules was sensitive to these changes as illustrated in Figure 5. In the plasma generated from pure N2 gas, peak intensity reaches a maximum value at a pressure of 80 Pa processes, whereas in the plasma of N2-H2 gas mixture at a pressure of 100 Pa. Even with a small concentration, mixing of H2 gas in N2 gas is very influential on plasma generation. Plasma becomes very dim at chamber pressures below 60 Pa, while in the use of pure N2 gas plasma still appears to hold up to a pressure of 15 Pa even though the peak intensity of the plasma species decreases.

In theory, the glow discharge structure depends on the gas used, the chamber gas pressure, and the material and geometric shape of the electrodes [13]. In this investigation, the effect of the addition of the hollow cathode device to the plasma structure formed was obtained. Based on the OES spectrum, the addition of hollow cathode will not affect the type of plasma species are formed. The difference in shape and size of the hollow cathode geometry affects only the intensity of each molecule peak of nitrogen and hydrogen species, as well as the effect on the optimum pressure that was produced the highest intensity.
Figure 5. Effect of chamber pressure to the intensity of nitrogen plasma species in pure nitrogen (a) and nitrogen-hydrogen gas mixture (b) plasma.

The use of cylindrical hollow cathode did not increase the intensity of nitrogen ions in the plasma. However, in the use of rectangular hollow cathodes, there appears to be an increase in the intensity of nitrogen ions. The uses of cylindrical hollow cathode slightly decreased the intensity the peak intensity of N$_2^+$ at 391.4 and 427.7 nm but it increased the N$_2^*$ peak at 337.1 and 357.7 nm. In the cylindrical hollow cathode, the adding of hydrogen gas slightly reduced the intensity of N$_2^+$ peak at 391.4 and 427.7 nm and also the N$_2^*$ peak at 315.9, 337.1 and 357.7 nm. However, there was a significant increase in the peak intensity of H, species at 656.5 nm, as seen in Figure 6.

Figure 6. OES spectra of N$_2$ plasma and N$_2$-H$_2$ plasma at cylindrical hollow cathode at 30 Pa.

Meanwhile, the use of rectangular hollow cathodes can increase the intensity of nitrogen ions in the plasma. Compare to plasma without hollow cathode, the uses of rectangular hollow cathode increase the intensity of almost all nitrogen species. The N$_2^*$ peak at 315.9, 337.1 and 357.7 nm are enhanced, but the key point was the increase of N$_2^+$ peak intensity at 391.4 and 427.7 nm. On the other hand, the intensity of N$_2^*$ peak and N$_2^+$ peak was almost the same for the adding of hydrogen gas with the slight increase of the peak intensity of H, species at 656.5 nm.
An interesting result in the use of hollow cathodes with different cross-sections is the enormous effect on the optimum pressure of the process. In Figure 8, it can be observed that the optimum pressure for the process by using a mixture of N$_2$-H$_2$ gas with a flow rate of 90-10 mL/min is 30 Pa and 100 Pa, respectively, for cylindrical hollow cathode and rectangular hollow cathode.

**Figure 7.** OES spectra of N$_2$ plasma and N$_2$-H$_2$ plasma at rectangular hollow cathode at 100 Pa.

Figure 8. Effect of chamber pressure to the plasma species intensity of N$_2$-H$_2$ gas mixture in the cylindrical hollow cathode (a) and in the rectangular hollow cathode (b).

4. **Conclusion**

In conclusion, the plasma glows discharge structure is influenced by the type of gas used to generate plasma, the amount of pressure in the chamber, and also the geometrical shape of the additional hollow cathode device. The addition of hydrogen gas as an N$_2$-H$_2$ gas mixture with a flow rate of 90-10 mL/min could change the intensity of nitrogen species inside the glow discharge plasma. The use of a rectangular
hollow cathode increases the intensity of nitrogen ion species at the high-pressure process. The plasma species peak intensity was increased when the hollow gap reduces. On the other hand, the cylindrical hollow cathode is effective for plasma processing at low pressure. And, reducing the hollow diameter could increase the plasma species intensity.

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