Pulse-periodic abnormal glow discharge in nitrogen, argon, hydrogen and their mixtures

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Abstract. Abnormal glow discharge in the pulse-periodic mode in Ar, H₂, N₂, Ar+N₂, and N₂+H₂ was investigated. Current-voltage characteristics, Langmuire probe and optical spectroscopy data were analysed. The electron temperature of 2-5 eV and concentration of 1-3 × 10¹⁰ cm⁻³ have been measured. Lines of N₂ N₂⁺, N, N⁺, NHₓ, Ar⁺, Ar, Ti, Fe, H, and OH have been detected by optical spectrometry. Dependences of intensities of spectral lines of N₂, N₂⁺, N, and N⁺ on Ar and H₂ content in gas mixtures were measured.

1. Introduction
Plasma nitriding and film deposition are widely used in industry for surface modification [1,2], and glow discharge is often used for this purpose. Therefore, investigations of the discharge are performed to choose optimum processing parameters [3,4]. Well-known drawback of the classical glow discharge at elevated pressures is its sudden transition in the arc mode. Nevertheless, if to operate the discharge at high frequency, the arc has no time to develop [5], which makes this regime attractive for technological applications.

Mixtures of gases are often used to optimise technological treatment; particularly during plasma nitriding, argon and hydrogen are often added to nitrogen to activate its penetration into the material. Though the pulsed-periodic abnormal glow discharge is widely used in industry, there are few works devoted to its properties. The discharge in N₂+H₂ mixture was investigated in [6], and a sharp increase of the intensity of the spectral lines was observed after adding up to 20% of hydrogen to nitrogen. The discharge in N₂+Ar mixture was investigated in [7], and it was found, that the intensity of N₂⁺ decreased, while the intensity of N₂ increased with increasing argon fraction above 20%.

This work describes some results of emission-spectroscopic investigations, probe diagnostics, and the discharge current–voltage characteristic measurements in nitrogen, argon, hydrogen, and their mixtures in a wide range of compositions.

2. Experimental
The glow discharge installation is described in [8]. In brief, it consists of a vacuum chamber with pressure sensors, a dual-channel pumping system, a gas inlet system, and a power supplier. The cathode was a rod 100 mm in length coaxially installed inside a cylindrical anode 180 mm in diameter and 420 mm in length. The cathode was made either of russian stainless steel 12X18H10T (analogue

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AISI 321) or Russian titanium alloy BT-6 (analogue Ti-6Al-4V). Diameters were 12 mm and 10 mm, respectively. Coaxial thermal screen made of several layers of stainless steel sheets 0.5 mm thick was the anode.

The discharge was powered by a generator of rectangular pulses with the amplitude of 400-650 V, pulse repetition frequency variable from 1 to 100 kHz, and a duty cycle variable from 10 to 80%. The discharge voltage and current were measured by a four-channel digital oscilloscope Tektronix TPC 2024B using a voltage divider and a shunt.

Discharges in Ar, N\textsubscript{2}, H\textsubscript{2}, Ar+N\textsubscript{2}, and N\textsubscript{2}+H\textsubscript{2} at a pressure of 1 torr and 1.5 torr were investigated.

Optical radiation from plasma was measured through a quartz glass window by a 3-channel spectrometer AvaSpec-ULS2048L-USB2-RM in the wavelength range from 200 to 810 nm with an optical resolution of 0.12 nm to 0.18 depending on the channel. The signal was analyzed by a standard software package Avantes and identified using data bases [9-11].

The Langmuir probe was made from a W wire 0.5 mm in diameter and had the working length of 8.5 mm (working surface 13.5 mm\textsuperscript{2}). The probe was placed about 5-8 mm from the cylindrical surface of the cathode. The decreasing voltage pulses with the amplitude of 50 V and duration of 35 ms were applied to the probe. The plasma concentration and the electron temperature were determined according classic theory in the collisionless regime [12-14].

3. Experiment results

Typical dependencies of the discharge voltage and current are shown in Figure 1. This example is given for the voltage of power supply of 500 V, frequency of 3 kHz, and the duty cycle of 30%. One can see that the discharge reaches about the steady state regime at this frequency and duty cycle. The mean discharge power increased with the duty cycle.

![Figure 1](image_url) An example of the time dependencies of the discharge voltage and current for the discharge with SS cathode ignited in N\textsubscript{2} at 1 Torr, 500 V, 3 kHz, and the duty cycle of 30%.

Figure 2 and 3 shows the current-voltage characteristics for the cathode made of steel and titanium alloy. One can see that the current rises with the voltage, and this is the signature of the abnormal glow discharge [5, 13]. The average discharge power increases with gas pressure, and this was also observed in [15]. The discharge in the gas mixture Ar+N\textsubscript{2} is more powerful than discharges in pure argon and pure nitrogen, and the same result was found from comparison of discharges in Ar+N\textsubscript{2} and in pure N\textsubscript{2} in [16]. The discharge current depends on the cathode material used: it is higher for SS cathode. This difference can be connected with the difference of secondary electron emission efficiency from SS and Ti.

Figure 4 shows a typical current-voltage characteristics of the Langmuir probe. Typical values of the electron temperature and the plasma concentration were 2-5 eV and \(\sim1-3\times10^{10}\) cm\textsuperscript{-3}, respectively, both for Ar and for N\textsubscript{2} in experiments with steel cathode at a pressure of 1 torr, discharge voltage of 600 V, frequency 3 kHz, and the duty cycle of 80%. The temperature and concentration increased with increase of voltage, and duty cycle.
The temperature and the concentration obtained in other works are lower. For example, 0.1-0.3 eV and $10^9$ cm$^{-3}$ were obtained in [17] in N$_2$-H$_2$ mixture at 1 kHz and a duty cycle of 60%.

**Figure 2.** The current-voltage characteristics with the SS cathode at frequency 3 kHz; 30% duty cycle, and pressures (a) 1 torr and (b) 1.5 torr.

**Figure 3.** The current-voltage characteristics of the discharge. The cathode - titanium alloy. Frequency 3 kHz, duty cycle 30%.

**Figure 4.** The current-voltage characteristic of the probe. Cathode - SS, gas - nitrogen, pressure 1 torr.

Figure 5 shows examples of optical spectra from the discharges in Ar, N$_2$, Ar+N$_2$ (1:1), and N$_2$+H$_2$ (1:1), obtained at a pressure of 1.0 torr, voltage of 480-650V, pulse frequency of 3 kHz, and a duty cycle of 60-80%.

A comparison of the experimental spectra with reference spectra indicates the presence of the following lines in the discharge in argon: Ar$^+$, Ar, Ti, Ti$^+$, Fe, H, OH. Lines in nitrogen were N$_2$, N$_2^+$, N, N$^+$, Fe, H, and OH. Similar results were observed in [17]. The intensity of radiation depends on the pressure and the applied voltage. The energy of electrons mainly depends on the applied potential and on the gas pressure. Optical emission increases with the gas pressure due to increase of the probability of inelastic collisions [18].

It is known that the nitriding process is activated by N$_2^+$, N, N$^+$, and NH$_x$ species in plasma as they easily penetrate through the surface. One can see that all these components exist in the optical spectra. Lines OH and H in nitrogen plasma appear due to water vapor, while lines Fe, Fe$^+$, Ti, Ti$^+$ appear due to sputtering of the cathode and structural elements. The absence of twice ionized atoms and molecules indicates that the electron temperature is relatively low.

One can roughly estimate the electron temperature from optical spectra with an error of about 50% [19]. This estimation gives 1.5 eV for a glow discharge in argon and nitrogen, which is in a good agreement with the data from probe measurements.
Figure 5. Emission spectra of an abnormal glow discharge in: a) Ar, b) N₂, c) Ar+N₂, d) N₂+H₂.

Figure 6 shows dependencies of intensities of several optical lines on gas composition. The analyzed lines were N₂(C^3Π_u→B^3Π_g), N₂^(+) (B^3Σ_u^+→X^3Σ_g^+), NH (A^3Π→X^3Σ), N (2p3s→2p3s), N^(+) (2p3s→2p3p), and H_α.

The intensities of ion lines have a maximum if about 10-20% of argon is added to nitrogen, and the maximum intensity is roughly 1.5 times the intensity in pure nitrogen. Further increase of argon concentration leads to gradual decrease of nitrogen ion line intensities down to the background level at 100% Ar, mainly due to decrease of the nitrogen amount in mixture.

Intensities of lines of neutrals N₂ and N increase with increase of Ar concentration. At 90% Ar, a sharp decrease is observed, but the intensities do not drop to zero at 100% Ar. This effect may be
explained by release of nitrogen from the cathode due to argon ion impact. The maximum intensity of lines of neutrals, which is observed at low concentration of nitrogen, is about 2.5 times their intensity in pure nitrogen. Qualitatively similar behavior of neutral and ion lines was observed in [7] in the classic glow discharge. The explanation was based on comparison of the energies for reactions in plasma. Increase of argon content leads to increase of the number of excited argon atoms in plasma. These argon atoms can transit to the metastable state, and this needs 11.55 eV for transition to $^3P_2$ and 11.72 eV to $^3P_0$. The alternative process is so-called Penning excitation where excited argon transfers its energy to nitrogen molecule in inelastic collision and excites it ($\text{Ar}^*+\text{N}_2=\text{N}_2^*+\text{Ar}$). The threshold excitation energy of $\text{N}_2$ is 11.1 eV, which is smaller than the energy necessary for excitation of metastable argon atoms. Therefore, increase of $\text{N}_2$ radiative states with increase of the argon concentration is observed due to Penning excitation. The Penning excitation is possible also with participation of nitrogen molecular ions $\text{Ar}^*+\text{N}_2^+=\text{N}_2^++\text{Ar}$, but this reaction needs a higher energy of about 18.7 eV, and experimentally the rate of this reaction even decreases with increase of argon concentration. There are two other reactions $\text{Ar}^*+\text{N}_2=\text{N}_2^++\text{Ar}$ (15.57 eV) and $\text{Ar}^*+\text{N}_2^+=\text{N}_2^++\text{Ar}^+$ (15.75 eV), which have also a higher energy. Therefore excited neutral molecules are preferentially produced with adding argon to nitrogen. The intensities of ion lines become less at large argon content just because the content of nitrogen in the mixture decreases.

Though the energy of electrons increases with argon addition, and the ionization of $\text{N}_2$ is more sensitive to high-energy electrons than excitation of ($^3\text{P}_u$) state, the concentration of exited ions decreases with argon content due to prevailed Penning excitation of $\text{N}_2$ molecules by metastable argon atoms.

Figure 6 shows also variations of intensities of lines in mixture of nitrogen and hydrogen. Intensities of all ion and neutral lines have maxima if 10-20% of hydrogen is added to nitrogen. Increase of nitrogen excitation at about 20% of hydrogen was observed also in [6]. The increase of intensity of nitrogen lines with the addition of small quantities of hydrogen can be connected with increase of the secondary electron emission coefficient. The decrease at high hydrogen concentrations may be connected with decrease of the nitrogen content in plasma.

4. Conclusion
Glow discharge powered with the frequency of 3 kHz in Ar, $\text{H}_2$, $\text{N}_2$, $\text{Ar}+\text{N}_2$, and $\text{N}_2+\text{H}_2$ have been investigated at pressures of 1.0 - 1.5 torr. The discharges has increasing current-voltage characteristics typical for abnormal glow discharge. The discharge current in the gas mixtures was higher than that in pure gases. The current increased with the gas pressure. The discharge was almost in the steady state regime during the pulse, and the mean discharge power increased with the duty cycle.
The probe measurements gave the electron temperature of 2-5 eV, and the plasma density of $10^{10}$ cm$^{-3}$.

All main lines $\text{N}_2$, $\text{N}_2^+$, $\text{N}$, and $\text{N}^+$ are found in optical spectra, and NH$^+_x$ was additionally found in presence of hydrogen. These species are active in nitriding of steels and alloys. In the mixture of $\text{N}_2^+$-Ar, the maximum concentration of nitrogen ions was at about 80-90% of $\text{N}_2$, while the maximum concentration of excited neutrals is at about 10% of $\text{N}_2$. In the mixture of $\text{N}_2$+$\text{H}_2$, the maximum concentration of both nitrogen ions and neutrals is at about 80-90% of $\text{N}_2$.

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References
[1] Kashaev N, Stock H-R and Mayr P 2005 J. Surf. Coat. Technol. 200 502–506
[2] Ramazanov K N, Ishmukhametov D Z and Sadkova N S 2011 Vestnik UGATU 15 3 (43) 67-71
[3] Kumar S and Ghosh P K 1993 J. Phys. D: Appl. Phys 26 1419-1426
[4] Garcia-Cosio G, Martinez H, Calixto-Rodriguez M and Gomez A 2011 J. Quant. Spectrosc. Radiat. Transfer 112 2787–2793
[5] Granovsky V D 1974 Electric current in gases. The steady current (Moscow: Nauka)
[6] Kim Y.M., Kim J.U., Han J.G. Investigation on the pulsed DC plasma nitriding with optical emission spectroscopy. 2002 Surf. Coat. Technol. 151-152 227-232
[7] Qayyum A, Shaista Zeb, Naveed M A, Rehman N U, Ghauri S A and Zakaullah M 2007 J. Quant. Spectrosc. Radiat. Transfer 107 361–371
[8] Borisyuk Yu V, Oreshnikova N M, Berdnikova M A, Tumarkin A V, Khodachenko G V and Pisarev A A 2015 Phys. Procedia 71 105-109
[9] Zaidel A N, Prokofiev V K and Raisk S M 1962 Tables of Spectral Lines (Moscow).
[10] Pearse R W B and Gaydon A G 1975 The indentification of molrecular spectra (London, New York: Chapman and Hall)
[11] Ochkin V N 2009 Spectroscopy of low temperature plasma (Wiley-VCH)
[12] Lebedev U A Electrical probe in low-pressure plasmas (URL: http: // plasma. karelia.ru > pub / ftpn / Lebedev)
[13] Raizer Yu P 1991 Gas Discharge Physics (Springer, Berlin, New York)
[14] Demidov V I, Kolokolov N B and Kudryavtsev A A 1996 Probe Methods of Diagnostics of Low Temperature Plasma (Moscow: Energoatomizdat)
[15] Sharma M K and Saikia B K 2008 Indian J. Pure Appl. Phys. 46 463-470
[16] Sharma M K, Saikia B K and Bujarbaruah S 2008 Surf. Coat. Technol. 203 229–233
[17] Hannemann M, Hamann S, Burlacov I, Börner K, Spies H-J and Röpcke J 2013 Surf. Coat. Technol. 235 561–569
[18] Saeed A, Khan A W, Jan F, Waqar M, Abrar M, Zaka-Ul-Islam M, Hussnain A and Zakaullah M 2014 Pulsed dc discharge in the presence of active screen for nitriding of high carbon steel Mat. Res. 17
[19] Kolesnikov V N 2007 Spectroscopic diagnostics of plasma (Moscow: MEPhI)