Low-frequency ferromagnetic enhanced inductively coupled plasma for plasma-assisted nitriding

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Abstract. Experimental investigation of low-frequency (100 kHz) nitrogen inductively coupled plasma with magnetic coupling enhanced by ferrite cores has been carried out, for nitrogen pressures of 50–200 mTorr. Discharge electric field strength and ion density were measured for various discharge currents. Plasma-assisted nitriding of titanium test samples was performed for sample bias of -1200 V and sample current density of 1 mA/cm². Formation of hexagonal $\omega$-Ti and tetragonal TiN phases was revealed.

1. Introduction
At present, plasma-assisted nitriding with the use of “external” sources of dense ($10^{10}–10^{12}$ cm$^{-3}$) low pressure (<0.1 Torr) non-equilibrium plasma is increasingly used to improve surface hardness, corrosion and wear resistance of various metals and alloys, instead of a conventional DC glow discharge nitriding at intermediate pressures of 1−10 Torr [1]. The use of an “external” plasma source allows us to regulate the substrate bias and the substrate current independently, and control both the ion energy and the ion flux density on the nitriding surface. The high flux density of ions and radicals enhances the process of plasma nitriding, while the low pressure of plasma-forming gas leads to high ion energy values (due to the collisionless ion motion in a plasma sheath near the surface), cleans out a thin surface oxide layer decreasing the nitrogen diffusion rate [2].

The development of plasma-assisted nitriding technology requires new plasma sources with high ion and radical densities at low gas pressures and long service life of the plasma source. Inductive discharges with enhancement of magnetic coupling between the induction coil and plasma by ferromagnetic cores are of particular interest for this purpose, as they allow an effective generation of electrodeless plasma in a low frequency radio range (~100 kHz) [3]. The electrodeless (inductive) principle of discharge generation makes it possible to overcome the limitations caused by sputtering of electrodes at high discharge current densities and low pressures of the plasma-forming gas. The use of ferromagnetic cores to enhance the magnetic coupling between the induction coil and plasma makes it possible to improve the power supply matching, and reduce the frequency of inductively coupled plasma generation from 1–10 MHz down to 10–100 kHz range [3]. In turn, the low frequency of inductive discharge generation allows the use of the cheap and mass-produced power supplies for induction heating with a frequency of 10–100 kHz, instead of expensive radio frequency (RF) power supplies.

Therefore, the low-frequency ferromagnetic enhanced inductively coupled plasma (FMICP) is of interest to develop new various plasma processing devices, including the plasma sources for plasma-
assisted nitriding. The aim of this work is experimental investigation of a low-pressure nitrogen FMICP to develop the new method of plasma-assisted nitriding.

2. Experimental setup
A scheme of experimental setup is shown in figure 1. Gas discharge chamber 1 is made of stainless steel water cooled sections with the inner diameter of 23 cm and total length of 100 cm. The sections are sealed and dielectrically separated with silicon rubber gaskets. A narrow (internal diameter of 4 cm) U-shaped chamber 2 with total length of 84 cm, together with the main discharge chamber 1, forms a closed current path of the FMICP. Ferrite cores 3 enhance the magnetic coupling between the discharge and inductor 4. A power supply of 500 V, 50–100 kHz 5 is used for discharge generation. The power supply is connected to the inductor through a matching network 6 (variable LC circuit). Discharge current is measured with a current transformer 7. To determine a vortex electric field strength \( E \) that drives the FMICP, a RMS value of AC voltage \( U_k \) is measured with a voltmeter 8 between two neighbor sections of the gas discharge chamber. The total sum of all voltage drops between the chamber sections is determined by Faraday’s law:

\[
\sum U_k = \int_E Edl = -\frac{\partial \Phi}{\partial t},
\]

where \( \Phi \) is an alternate magnetic flux in the core, \( L \) is a total discharge path. A characteristic value of the vortex electric field strength \( E \) is estimated as a ratio of \( U_k/L_k \) where \( L_k \) is the discharge path between two neighbor sections (\( \sum L_k = L \)).

Nitrogen is used as a plasma-forming gas. The flow rate of nitrogen is regulated with a leak valve (not shown). Nitrogen pressure is measured with a MKS baratron 626a 9. Double Langmuir probe 10 made of 200 μm tungsten wire is used to measure ion density. Titanium test samples 11 with the size of 40x30x5 mm were placed inside the discharge chamber to test the process of plasma-assisted nitriding in the FMICP. The sample temperature was measured with a thermocouple of type K 12. Sample bias was regulated with a DC power supply 13. To pump out the discharge chamber, a fore pump 14 is used.

3. Results and discussion
In figure 2, dependencies of electric field strength \( E \) on discharge current \( I \) are shown for the gas discharge chambers 1 and 2, for various nitrogen pressures. The observed negative voltage-current characteristics are typical of the positive column of glow discharges (PC); the similarity of the FMICP with PC is discussed in [4]. However, unlike the classic PC in a cylindrical tube, or a toroidal FMICP

![Figure 1. Experimental setup:](image-url)
[4], our experimental setup has a complex geometry with variable cross-section of the gas discharge chamber. It leads to a non-uniform distribution of electric field strength $E$ along the discharge path $L$. Nevertheless, the abovementioned measurements of intersection voltages $U_k$ allow us to evaluate the characteristic values of electric field strength in the discharge chamber $1$ and the U-shaped chamber $2$ ($E_k = U_k / L_k$). The value of electric field strength determines the value of discharge power density $P = E J$ (where $J$ is a current density) that is why it is necessary to determine the values of electric field strength for the main chamber and the U-shaped chamber separately.

The values of electric field strength in the main discharge chamber with internal diameter of 23 cm are almost two times smaller than those for the U-shaped part with ID of 4 cm. It is the well-known effect caused by decreasing of the charged particles lifetime $\tau$ and the consequent increasing of the diffusion losses:

$$\frac{1}{\tau} = \frac{D_a}{\Lambda_f^2},$$

where $D_a$ is the ambipolar diffusion coefficient (cm$^2$ s$^{-1}$) and $\Lambda_f = R/2.94$ is the characteristic diffusion length ($R$ is the discharge chamber radius, cm). The higher the diffusion losses of charged particles, the higher the electric field strength needed to maintain ionization balance of the discharge.

In figure 3, a dependence of ion density on the FMICP current is shown for the main discharge chamber $1$. Optical emission spectroscopy measurements of a nitrogen RF inductively coupled discharge for comparable conditions (nitrogen pressure of 75 mTorr) indicate that only $N_2^+$ ions are present in plasma [5], therefore only $N_2^+$ ions are considered to be responsible for the ion current to the Langmuir probe or the test samples. The typical $N_2^+$ densities achieved in the main discharge chamber with internal diameter of 23 cm are $(2–7) \times 10^{10}$ cm$^{-3}$, for the FMICP current of 1.5–6 A and the FMICP power density of $5–15$ mW/cm$^3$. Comparing the FMICP with other methods of producing the dense nitrogen plasma at low pressures, a high value of nitrogen ion density of $10^{12}$ cm$^{-3}$ is reported in [6] for a pulsed non-self-sustained glow discharge with a large-area (2 m$^2$) hollow cathode, at the nitrogen pressure of 7.5 mTorr and the average discharge power density of 150 mW/cm$^3$. Taking into account a linear dependence of ion density on the FMICP current (figure 3), we should enlarge the discharge current up to 80 A to achieve the same ion density of $10^{12}$ cm$^{-3}$. Considering the weak dependence of electric field strength at high discharge currents (figure 2), the FMICP power density would be about 190 mW/cm$^3$, i.e. close to that of reported in [6]. As the principle of FMICP generation does not
require electrodes, the discharge current is not limited with the process of electrode sputtering, and depends only on the capability of the power supply.

To test the process of plasma-assisted nitriding in the FMICP, titanium samples were treated under the nitrogen pressure of 200 mTorr, negative sample bias of -1200 V, the sample temperature of 510 °C and ion current density on the sample surface of 1 mA/cm$^2$. X-ray diffraction analysis of the sample surface was carried out before and after the treatment. Before the plasma-assisted treatment, X-ray diffraction pattern had the peaks related to hexagonal $\alpha$-Ti phase with $c/a$ ratio of 1.587. After 1 hour of the FMICP nitriding, the peaks related to hexagonal $\omega$-Ti phase with $c/a$ ratio of ~0.61 were detected. The formation of $\omega$-Ti phase is also reported in [7], for titanium nitriding in RF (2 MHz) discharge under the pressure of N$_2$/H$_2$ mixture of 225–560 mTorr, negative sample bias of -500 V and -600 V and the sample temperature of 450 °C. The authors of [7] suppose the $\alpha$-Ti to $\omega$-Ti transformation to be the factor enhancing the speed of nitrogen diffusion into the lattice. Three hours of the FMICP nitriding resulted in the formation of a layer with 75% $\alpha$-Ti, 23% $\omega$-Ti and 2% tetragonal TiN. The authors [7] report the formation of a layer with TiN phase concentration of up to ~9% for 4 hours nitriding process; therefore, the issue of the optimization of the FMICP nitriding process has not been solved yet. Moreover, the process of plasma nitriding is a complex process and still is not fully understood. For example, it is shown [8, 9] that plasma nitriding of titanium using nitrogen hollow cathode glow discharge occurs even in the case of the absence of nitrogen ions, and determined by atomic nitrogen. However, the aim of the paper is not to investigate the plasma assisted nitriding of titanium, but to show the possibilities of the FMICP as the source of nitrogen ions and active particles for plasma assisted nitriding technology.

4. Conclusion
The enhancement of magnetic coupling between inductor and inductive discharge with ferromagnetic materials allows generation of the large volumes of “dense” (ion density of $10^{10}–10^{12}$ cm$^{-3}$) nitrogen plasma at low (<0.1 Torr) pressures, which can be used for the plasma-assisted nitriding technology. The key advantage in comparison with thermionic arc or hollow cathode direct current plasma sources is the absence of electrodes and the increased lifetime of the plasma source. In comparison with RF inductively coupled plasma sources, which are widely used in plasma processing, the FMICP has the lowest frequency range of discharge generation (<100 kHz) and the best matching between the power supply and plasma, which significantly simplify the development of plasma processing devices.

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