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Gas-discharge plasma application for ion-beam treatment of the holes' inner surfaces

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Abstract. The possibility to modify the holes and pipes' inner surface with focused high-intensity low-energy ion beams was first shown in this work. The studies were carried out using an axially symmetric single-grid system for the ions' extraction from a free plasma boundary with subsequent ballistic focusing of the ion beam. Ion implantation of the inner surface was carried out in the region of the ion beam defocusing. The studies considered the effect of a nitrogen ions' beam with energy of 1.4 keV on the inner surface of a tube with a diameter of 20 mm made of stainless steel AISI 321. The beams were formed with a repetition rate of 40 kHz and pulse durations of 5, 7.5 and 10 µs. It is shown that the mutual deposition of the sputtered material on the tube' opposite sides partly compensates for ion sputtering. As a result of implantation of the inner surface of a pipe made of stainless steel AISI 321, the nitride layers with a thickness of more than 15 microns with a nitrogen dopant content of 22-30 at.% were obtained.

1. Introduction

Modification of materials and coatings' properties by radiation impacts of various natures is applied in science and technology [1-12]. Ion implantation is widely used on an industrial scale for ion doping of semiconductor materials. Using ion implantation to modify metals and coatings' properties is limited by the small projective range of ions in the substance. The team of the Scientific Laboratory for High-Intensity Ion Implantation of the National Research Tomsk Polytechnic University have recently proposed and tested the implantation method using high-intensity repetitively-pulsed ion beams of gases, metals and semiconductors [13-16]. Developing the method of low-energy high-intensity implantation of gas and metal ions into various materials has shown the possibility to form ion-doped layers with thicknesses of tens and hundreds of micrometers [14, 17, 18].

It is known that modification of the properties and structure of the holes' inner surface is a special problem in the technologies of ion-plasma treatment of odd-shaped parts. Even plasma-immersion ion implantation [4], providing uniform ion doping of odd-shaped parts, does not bring about modification of extended holes' inner surfaces.

In this paper, the regularities and features of the modification of holes' inner surfaces in ANSI 321 steel by focused low-energy high-intensity beams of nitrogen ions are first investigated.

2. The experimental setup and methodology of the research

Research on nitrogen ion implantation into the holes' inner surfaces was carried out using a complex technological installation to implement combined modes of ion-beam and ion-plasma treatment of materials, the general scheme of which is shown in figure 1.

A source of continuous gas-discharge plasma with a heated cathode "PINK" [19] was used as a gas plasma generator. The plasma source operated at a nitrogen pressure in the working chamber of 0.6 Pa. The discharge current in the experiments was set at 30 A.

The operation principle of the system to form repetitively-pulsed high-intensity beams of gas ions is based on the ion extraction from the free plasma boundary, using a grid electrode, and their subsequent ballistic focusing in the equipotential drift space [15, 16, 20]. The grid electrode is made in the form of a part of a sphere with a diameter of 200 mm and a cell size of 0.5×0.5 mm^2 and a transparency of about 50%. It is the implementation of the grid electrode in the form of a second-order surface that allows ballistic focusing of the accelerated ion flux. The high-intensity beams' formation system was installed at a distance of 150 mm from the plasma source output.

To study the features and patterns of high-intensity implantation of low-energy ions into the holes' inner surfaces, a model version of a closed hexagonal hole, shown in figure 2, was used. This system was collapsible and made it possible to replace a pipe or a hole in experiments. In general, it made it possible to compensate for the substantial ion sputtering of the surface during high-intensity implantation due to ion-sputtered material deposition on opposing elements. The hexagonal cylinder was fixed on a special insulated holder. Besides, using the replaceable flat samples greatly simplified the study of various properties of the modified layers. Plates made of AISI 321 alloy with dimensions of 65×13×3 mm^3 were used as face-samples. The distance between the opposite plates fixed in the holder was 20 mm.

In most experiments, the hexagonal cylinder was installed in such a way that the focus of the beam was at the entrance to the cylinder, that is, at a distance of 130 mm from the grid electrode. To study the influence of the beam focus location relative to the hexagonal cylinder on the dopant accumulation patterns, the experiments were carried out with the cylinder installed at a distance of 100 mm from the grid electrode. In this case, the ion beam focus is located inside the workpiece.

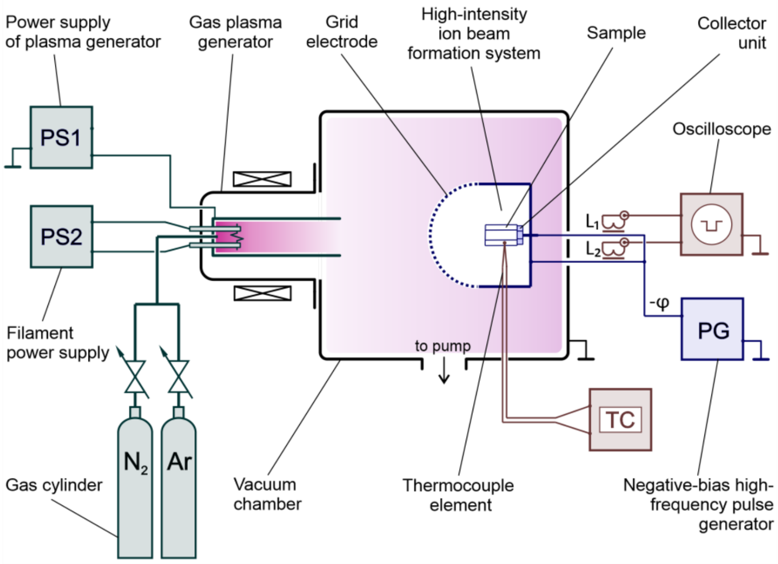


Figure 1. Diagrams of the experimental setup.

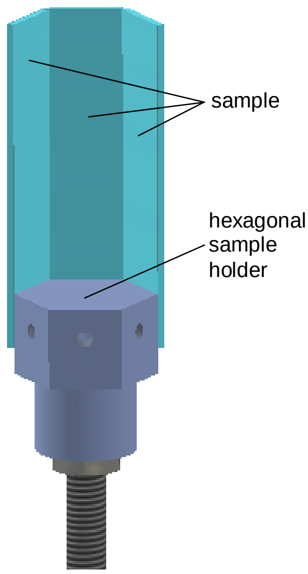


Figure 2. Diagram of the manifold assembly for hole modeling.

The grid electrode and irradiated samples were connected to a high-frequency pulsed generator of a bias voltage of negative polarity. The generator provided the formation of pulses of negative bias potential with amplitude of 1.4 kV, at a pulse repetition rate of 40 kHz and durations of 5, 7.5 and 10 μs. To ensure the same irradiation fluence in different regimes, with a change in the pulse duration of the bias potential (5, 7.5, and 10 μs), the treatment time was proportionally reduced (120, 80 and 60 min, respectively).

The samples' temperature during the high-intensity implantation of nitrogen ions was measured with an isolated thermocouple installed on the back side of one of the faces.

Surface morphology was investigated using an optical non-contact three-dimensional profilometer "STIL 3D Micromesure". The modified near-surface layer's elemental composition and the distribution of nitrogen dopant over depth in the samples' transverse sections were analyzed using the X-ray spectral method with an energy-dispersive attachment "Bruker XFlash 4010" to an electron microscope "Hitachi S-3400 N". Concentration profiles were obtained at various distances from the input of the hexagonal cylinder to the maximum depth of the investigated hole of 40 mm with a step of 5 mm.

3. Results and discussion

The first stage included high-intensity implantation of nitrogen ions under conditions of significant ion sputtering of the sample's surface. The experiments were carried out using only two elements of a hexagonal cylinder. In this case, due to the small angle of ions' incidence on the target surface, the ion sputtering was significant, and the possibility of compensating for ion sputtering due to the sputtering products' deposition from other elements was excluded.

High-intensity nitrogen ion implantation was carried out for 120 min with a high-intensity repetitively-pulsed beam of nitrogen ions with energy of 1.4 keV at a pulse duration of 5 μs and a frequency of 40 kHz. The surface morphology study using a profilometer showed the presence of significant sputtering of the near-surface layer to a depth of approximately 90 μm. At the same time, the nitrogen dopant distribution along the depth, presented in figure 3, showed the formation of a very thin ion-modified layer with a thickness of slightly more than 1 μm. Thus, in contrast to normal ion implantation variants investigated in [18], an increase in ion sputtering of the surface due to a change in the angle of ions' incidence led to a significant decrease in the doped layer thickness. This result clearly proves the influence of ion sputtering on the ion-doped layer formation under conditions of high-intensity ion implantation.

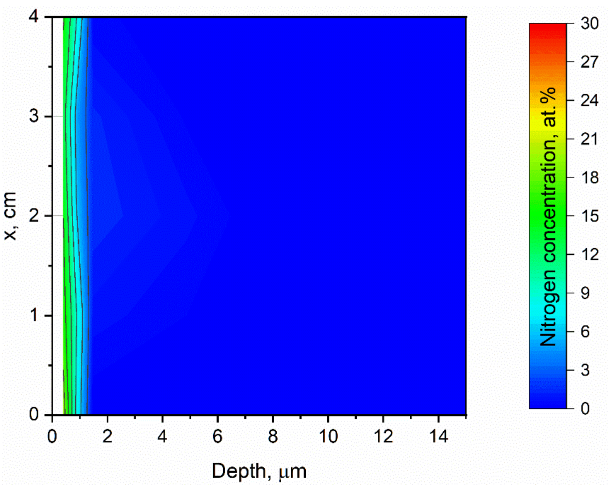


Figure 3. Depth distribution of nitrogen concentration in ANSI 321 steel target for the case of irradiation of only two plates of a hexagonal cylinder with a high-intensity nitrogen ion beam with energy of 1.4 keV at a pulse duration of 5 μs and a frequency of 40 kHz.

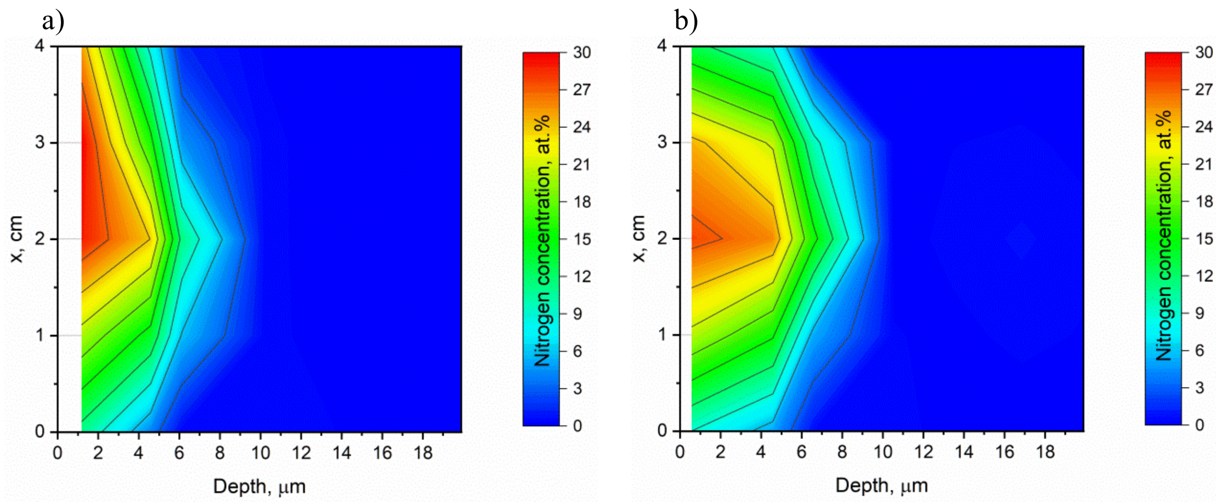
The second stage included high-intensity ion implantation into a hexagonal closed system modeling a hole. It was assumed that an axially symmetric system should significantly reduce ion sputtering of the irradiated surface due to compensating for sputtering by sputtering products' deposition from other parts of the cylinder, improving the conditions for diffusion saturation of the implanted surface with nitrogen.

The studies were carried out at fixed ion energy in the beam of 1.4 keV and a bias potential pulse frequency of 40 kHz. The temperature of the samples during ion implantation was determined by the duration of the bias potential pulses. The main parameters of four different regimes of high-intensity nitrogen ion implantation are shown in table 1.

Table 1. Regimes of high-intensity nitrogen ion implantation.

Specimen No	Bias potential parameters: Pulse duration (μs)	Bias potential parameters: Amplitude (kV)	Bias potential parameters: Frequency (kHz)	Amplitude of the beam current (A)	Processing time (min)	Discharge current (A)	Sample temperature (°C)
1	5			0.9	120		400
2	7.5	1.4	40		80	30	515
3	10				60		570
4	10			1.2	50	50	615

According to table 1, varying the pulse duration of the bias potential and the discharge current of the plasma source makes it possible to change the irradiated targets' temperature from 400 to 615°C.



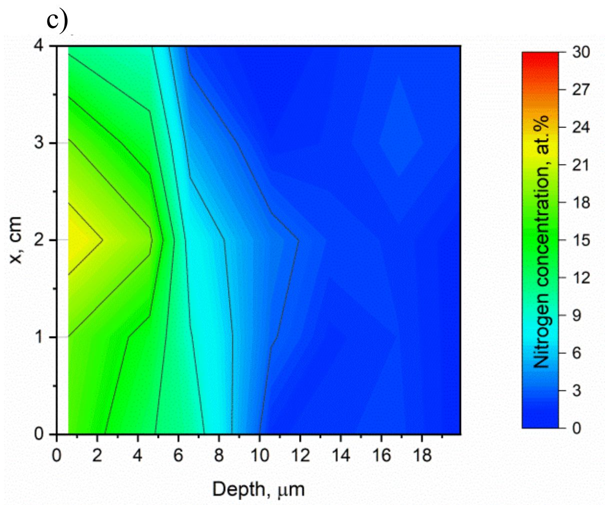


Figure 4. Nitrogen concentration distribution over the doped layer's depth in the samples depending on the bias potential's pulse duration and the target temperature: a) – 5 μs, 400°C; b) – 7.5 μs, 515°C; c) – 10 μs, 570°C.

Figure 4 shows the nitrogen concentration distributions over the depth of the sample's doped layer depending on the bias potential's pulse duration (5, 7.5 and 10 μs). Data was obtained over a length of 40 mm with a step of 5 mm.

The maximum depth of nitrogen distribution in experiments with constant irradiation fluence was achieved with a bias potential pulse duration of 10 μs and a target temperature of 570°C and was about 8 μm (figure 4c). The minimum ion-doped layer's thickness occurred at a duration of 5 μs and a target temperature of 400°C and was approximately 6 μm (figure 4a). Obviously, the formation of deeply ion-doped layers is influenced by the target's temperature, on which the diffusion of nitrogen depends. With an increase in the target's temperature from 400 to 515°C, an increase in the nitrogen penetration depth is observed, while the treatment time is halved (table 1).

It is typical for all treatment regimes, that the modified layer is observed over the entire length of the treated hole. A characteristic feature of the obtained experimental results is associated with the fact that the largest penetration depth of nitrogen dopants in the samples' near-surface layer has a certain maximum depending on the distance to the hole's output. For treatment regimes 1 and 2 presented in table 1 and figure 4a, b, the maximum penetration depth of nitrogen dopants is observed at a distance of approximately 20 mm from the hole's output. This distribution of nitrogen dopants is primarily associated with the choice of the workpiece position relative to the grid electrode focus.

According to the data presented in figure 4, it can be seen that the maximum nitrogen concentration near the target surface for treatment options with bias potential durations of 5 and 7.5 μs and, respectively, treatment times of 120 and 80 min is approximately 30 at.% (figures 4a and 4b). In the case of treatment for 60 min (figure 4c) with a pulse duration of 10 μs and a temperature of 570°C, the maximum concentration was only 22 at.%.

Noteworthy is the result of high-intensity nitrogen implantation in regime 3. According to the data in figure 4c, in this case, there is a nitrogen distribution along the hole length with a fairly high homogeneity. In general, the results presented in figure 4 convincingly prove that nitrogen saturation of the near-surface layer of ANSI 321 steel is achieved due to high-intensity implantation of low-energy nitrogen ions. Obviously, in any of the irradiation regimes, the sample is heated to a high temperature along its entire length. However, diffusion saturation of the doped layer takes place in the ion beam region.

Experiments were carried out on modification with a high-intensity nitrogen beam when the hexagonal cylinder was displaced relative to the beam focus by 30 mm along the axis of the system so that the beam focus was located inside the workpiece. Figure 5 shows the concentration distribution of nitrogen dopants over the doped layer depth at various distances from the output to the hexagonal cylinder after exposure to a nitrogen ion beam obtained in irradiation regime 4 (table 1).

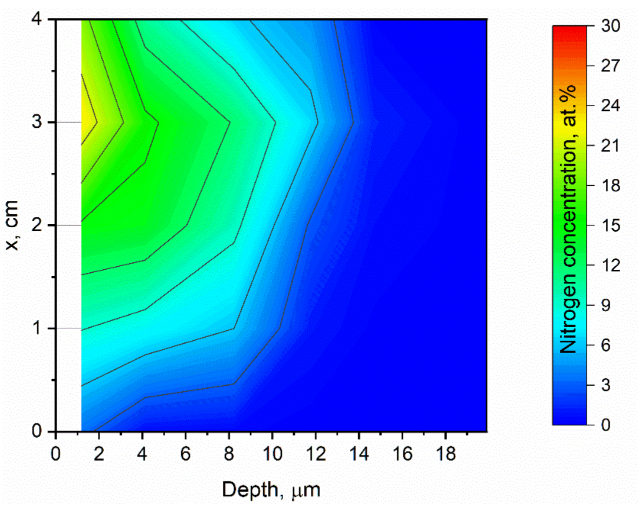


Figure 5. Nitrogen dopant concentration distribution over the doped layer depth when the hexagonal cylinder is shifted relative to the beam focus by 30 mm.

Obviously, the shift of the hexagonal cylinder shifted the position of the maximum in the nitrogen distribution over the modified layer depth by about 10 mm into the hole. At the same time, the maximum itself practically did not change. This result can be explained by the fact that although in this regime the ion current amplitude was increased due to an increase in the gas discharge current, when the focus was shifted into the depth of the workpiece, part of the ion beam fell on the outer surface of the hexagonal cylinder.

In general, the approach associated with the dynamic movement of the workpiece relative to the ion beam focus during one technological cycle can make it possible to form deeply ion-doped layers uniform along the length.

The study of the surface's ion sputtering by a high-intensity ion beam of a closed hexagonal cylinder showed a significant ion sputtering suppression.

Figure 6 shows the sputtering profile of a sample made of AISI 321 steel as a result of exposure to a focused beam of nitrogen ions in regime 3 (table 1). The three-dimensional image shows that the ion sputtering region is located at a distance of about 20 mm from the sample's edge. Maximum ion sputtering depth does not exceed 14 μm.

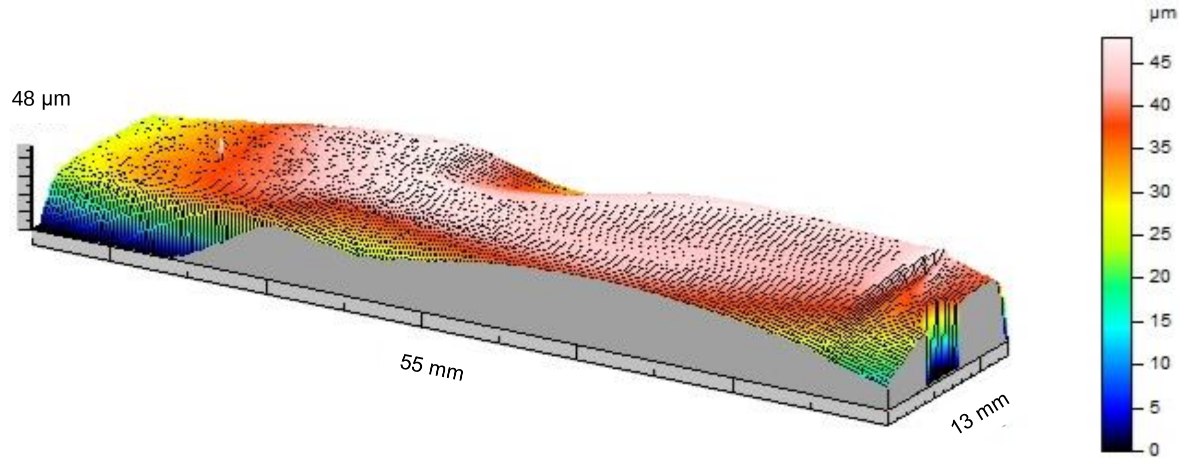


Figure 6. 3D image of the sample's surface modified by a high-intensity repetitively-pulsed nitrogen ion beam with energy of 1.4 keV, a pulse duration of 10 μs, and a frequency of 40 kHz.

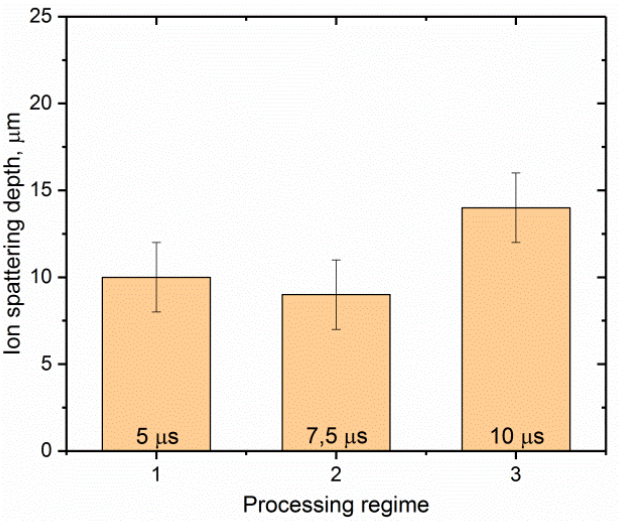


Figure 7. Maximum depth of ion sputtering after ion implantation in various irradiation regimes.

The data of measurements of surface's ion sputtering depth in different ion implantation regimes in accordance with table 1 are shown in figure 7. According to the presented data, in a series of experiments with constant irradiation fluence at different pulse durations of the accelerating voltage, the depths of ion sputtering are from 9 to 14 μm. The tendency of an increase in the sputtering depth with an increase in the bias pulse duration, as shown in an early work [17], is associated with an increase in the samples' temperature during ion implantation.

Thus, as a result of the performed studies, it has been shown that several competing processes take place during high-intensity ion implantation. It is obvious that the formation of deep ion-doped layers is influenced by the target's temperature, on which the radiation-enhanced diffusion of nitrogen depends. As shown in [16], deep ion doping is also influenced by the ion current density. Ion sputtering is a competing process. In the experiment with a hole part, the sputtered layer depth significantly exceeded the ion-modified layer's thickness. In the case of experiments with a full hole during the treatment in the same regimes, the formation of an ion-doped layer with a significant thickness is realized, which confirms the significant influence of self-compensation of ion sputtering in axially symmetric holes.

4. Conclusion

In this work, the possibility of modifying the inner surface of deep holes with focused high-intensity low-energy ion beams is first shown. The ion beam was exposed to a sample with a hole near the beam formation system focus in the beam's defocusing region.

High-intensity nitrogen ion implantation was studied at a fixed energy of 1.4 keV and a bias potential pulse frequency of 40 kHz, but at different pulse durations (5, 7.5 and 10 μs) and at different temperatures of 400, 515 and 570°C, respectively. It was found that the ion-modified layer thickness in ANSI 321 steel depends on both the implantation temperature regime and the surface's ion sputtering conditions. The maximum thickness of the ion-doped layer was about 9 μm at a target's treatment temperature of 570°C at an irradiation time of 60 min.

It has been experimentally shown that the mutual deposition of the sputtered material on opposite sides of the holes' surface elements leads to a significant ion sputtering compensation and an increase in the ion-modified layer's thickness.

The paper has shown the possibility of uniform ion doping of the hole's inner surface both due to the selection of the optimal irradiation regime and due to the dynamic movement of the irradiated workpiece relative to the ion beam focus.

Acknowledgments

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