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TOF-SIMS study on surface modification of reed switch blades by pulsing nitrogen plasma

K.A. Arushanov^a, M.N. Drozdov^b, S.M. Karabanov^a, I.A. Zeltser^c, A. Tolstogouзов^{d,*}

^a Department of Electronic Engineering and Technology, Ryazan State University of Radio Engineering, Gagarina Str. 59/1, 390005 Ryazan, Russian Federation

^b Institute for Physics of Microstructures of the Russian Academy of Sciences (IPM RAS), 603950 Nizhni Novgorod, Russian Federation

^c Ryazan Metal Ceramics Instrumentation Plant Joint Stock Company (RMCI PJSC), Novaya Str. 51B, 390027 Ryazan, Russian Federation

^d Centre for Physics and Technological Research (CeFITec), Dept. de Física da Faculdade de Ciências e Tecnologia (FCT), Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

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ABSTRACT

A TOF-SIMS-5 by ION-TOF operating with pulsed 25 keV Bi⁺ for analysis and 2 keV Cs⁺ for sputtering was used to study depth compositional changes in near-surface layers of permalloy (iron–nickel) blades after treatment by pulsed nitrogen plasma directly in sealed reed switches. The formation of 350 nm-thick oxy-nitride coating in the contacting region of the blades was observed. It was found that the origin of this coating cannot be explained just by nitrogen and oxygen diffusion inside the treated material. Rather, cathode sputtering and re-deposition of sputtered products, thermal decomposition of nitrides and oxides along with sputter-induced surface roughening can also contribute in the formation of the modified layers.

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1. Introduction

A reed switch (RS) is a small electromechanical device having two ferromagnetic blades (reeds) that are hermetically sealed inside a glass envelope. When the device is exposed to a magnetic field, the reeds pull together and the switch closes. Reed switches were invented at Bell Telephone Laboratories in 1936 and are still widely used today in switchgear.

One of the main technological processes of RS production is the deposition of protective coatings on the contacting surface of reeds. To fabricate such coatings, electroplating of noble metals (gold, palladium, rhodium, ruthenium, etc.) is generally employed [1]. However, this technique has several disadvantages: first of all, it results expensive in view of the electrical energy and the materials required. Furthermore, electrodeposition baths are polluting and expensive to dispose of. Finally, it is difficult to deposit complex coatings with well-defined composition and structure.

Plasma processing is a well-established method for improving corrosion and erosion resistance of metal surfaces [2]. As an alternative to the deposition of high-priced metals, we proposed to produce protective nitride coatings on the surface of permalloy

(nickel–iron) blades by ion-plasma treatment (IPT) directly in sealed reed switches. Our developments and research in this field are summarized in [3,4]. It was shown that the electrical resistance of modified reed switches remains stable and does not exceed 0.1 Ohm after 10⁷ switching cycles, and the breakdown voltage is not inferior to that of standard devices with electroplated coatings.

Topographical features and the local distributions of electrostatic potential on the surface of blades before and after IPT were studied with atomic force and metallurgical microscopy. The development of surface pores, cones and nanosized asperities with specific conducting properties was observed, and the formation of iron and nickel nitrides was confirmed by Auger electron and X-ray photoelectron spectroscopy [3,4].

Here, we report on a study by time-of-flight secondary ion mass spectrometry (TOF-SIMS) aimed at obtaining more detailed information about the reed surfaces. By means of this technique, sputter depth profiles of the working (contacting) and nonworking regions of RS blades before and after ion-plasma treatment were obtained. Since IPT is a very complex process including several reactions taking place simultaneously in the plasma and on the surface and near-surface layers of treated materials, theoretical prediction and computer modeling of the depth distributions of nitrogen-containing species and impurities is a hardly feasible task [5]. Only an experimental approach enables monitoring of in-depth compositional changes and on the basis of these results to choose

* Corresponding author. Tel.: +351 21 294 8576; fax: +351 21 294 8549.

E-mail address: a.tolstogouзов@fct.unl.pt (A. Tolstogouзов).

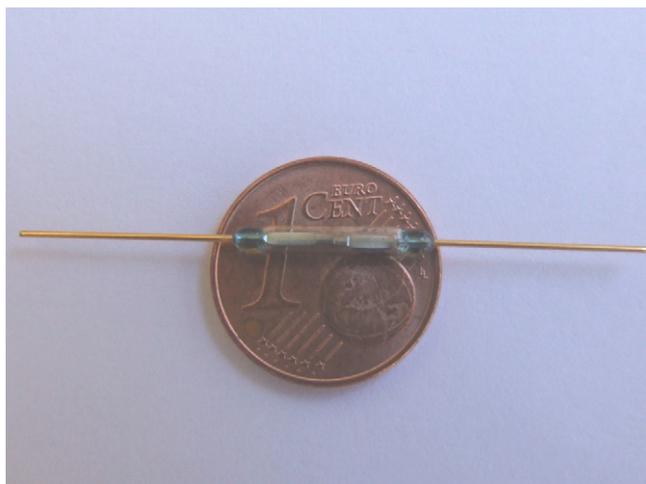


Fig. 1. External view of a reed switch MKA-14701.

optimal IPT conditions for the production of high-quality nitride coatings.

2. Experimental

We studied pilot samples MKA-14701 (Fig. 1) manufactured at RMCIP JSC (Ryazan, Russian Federation) on the basis of commercially produced reed switches MKA-14103. For both types of reed switches, the blades were pressed of vacuum-melt permalloy (Ni 52%, Fe 48%) wires by Dilaton™, degreased and annealed in hydrogen atmosphere. When sealing reed switches, pure (99.99%) nitrogen with the pressure in the range of $(33\text{--}40) \times 10^3$ Pa was used as a filling gas.

The manufacturing route of the MKA-14701 was described elsewhere [3,4]. As against the standard technology, the operation *Electroplating* was replaced by *Ion-Plasma Treatment*. For that, a pulsed DC potential (up to 2 kV) was applied between open contact blades with a gap of 27–30 μm . The polarity of the potential was changed with a frequency of 50 Hz. The glass envelope plays the role of working vacuum chamber and the blades operate sequentially as anode and cathode. The duration of a single IPT cycle was chosen to be 30 s.

TOF-SIMS measurements were carried out at IPM RAS (Nizhni Novgorod, Russian Federation) using TOF.SIMS-5 by ION-TOF (Muenster, Germany). The instrument operates in dual beam mode with pulsed 25 keV Bi^+ ions for analysis and 2 keV Cs^+ ions in DC mode for sputtering. The angle of incidence was 45° for both ion beams. The sputter beam with a 120 nA sample current was scanned over an area of $200 \mu\text{m} \times 200 \mu\text{m}$, and the analysis zone was ca. 4% around the center of sputter crater. Different atomic and molecular negatively charged secondary ions were registered. The crater depths were measured by an optical profiler Taly-surf CCI-2000 by AMETEK Taylor Hobson (Leicester, UK). Detailed description of the experimental TOF-SIMS conditions can be found in [6].

Before the analysis, glass envelopes of reed switches were mechanically cracked, and the blades were pulled out. No special cleaning of the blades has been performed, except for the removing of residual small glass pieces from the blade's surface by air jet.

3. Results

Two characteristic regions of different color were observed on the blade's surface after thirty cycles of IPT. One can recognize these areas in the image obtained by optical microscopy (Fig. 2). The area

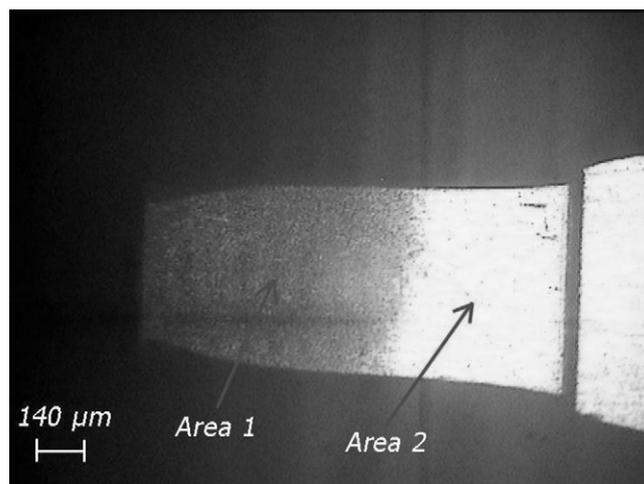


Fig. 2. Optical image of the reed switch blade after thirty cycles of ion-plasma treatment.

1 is the working region, the contacting area of blades, where gas discharge was initiated by high-voltage pulses. This region turned dark after ion-plasma treatment.

The depth profiles of negative secondary ions measured for a MKA-14701 reed switch after IPT were shown in Figs. 3 and 4 for the working (reg. 1) and nonworking (reg. 2) regions of blades, respectively. According our numeration, this sample was designated as the sample #8. Fig. 5 shows similar depth distributions for the blade of an unprocessed RS (the sample #5). For this sample, only the working (contacting) region was measured.

All profiles are presented in a semi-logarithmic scale, and the sputter time was converted into the depth of sputtering assuming a constant sputter rate of 70 nm min^{-1} estimated via the measurements of the final crater depth after the ending of the experiments. It has been shown [7] that for plasma-nitrided iron alloys, the sputter rate is approximately constant both within the treated layer and across the boundary (interface) between this layer and bulk material, and a single profilometer measurement at the end of a depth profile is sufficient to calibrate the depth scale over the whole profile.

As characteristic ions for the nitride coatings, we selected intense molecular ions FeN^- , NiN^- , CN^- and NO^* , their depth distributions are shown in panel (a) of each figure. Depth profiles of atomic oxygen and oxygen-containing ions FeO^- and NiO^- are presented in panel (b), the distributions of the most intense impurities C^- , S^- , Cl^- are shown in panel (c). The intensities of FeN^- and FeO^- profiles were normalized with respect to the Fe_2^- intensity; other data were normalized with respect to the Ni_2^- intensity. The ratio of intensities $\text{Fe}_2^-/\text{Ni}_2^-$ was found to be constant over the whole sputter depth for every region of the RS blades studied in this work.

It is worth noting that the ion yield of atomic and molecular nitrogen ions is very low (their depth profiles are not shown here). Concerning other secondary ion species, whose depth distributions are shown in Figs. 3–5, it is very likely that FeN^- and NiN^- ions are the fragments of Fe_nN and Ni_nN ($n = 2\text{--}4$) molecules dissociated under heating, cathode sputtering of blades and ion-beam bombardment during TOF-SIMS analysis. Iron and nickel oxide ions, as well as atomic oxygen and nitric oxide ions, can originate from natural oxide films, existing on the surface of blades. Carbon is mainly a residual contamination from lubricants used in the technological operation of jet drawing of permalloy wires. Carbon nitride is a product of the interaction between carbon and nitrogen on the surface and in the plasma; these elements tend forming strong chemical bonds including single ones [8]. Chlorine is a common surface contamination with very high negative ion yield; in our

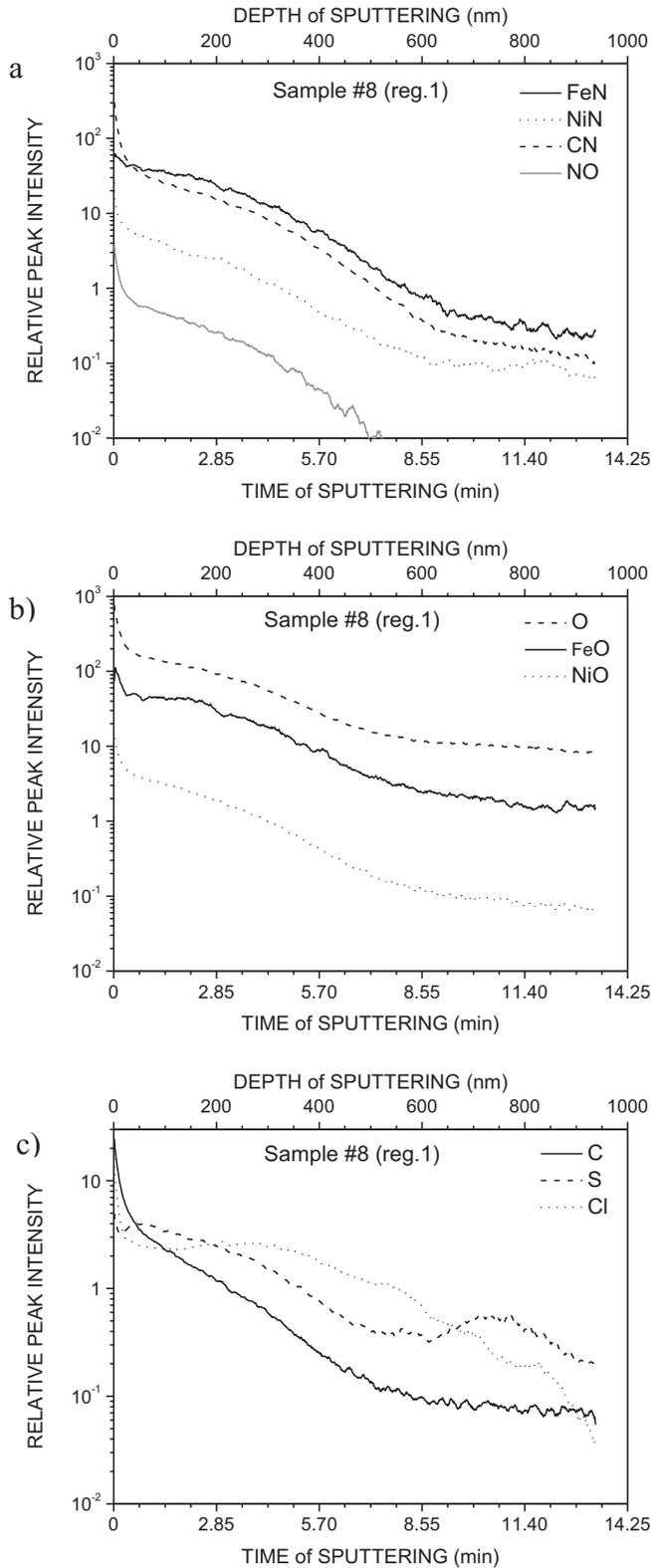


Fig. 3. Depth profiles of negative secondary ions of the working region of the sample #8 (after ion-plasma treatment): (a) nitrogen- and (b) oxygen-containing ions, (c) impurities. The intensities of FeN^- and FeO^- profiles were normalized with respect to the Fe_2^- intensity. The other data were normalized with respect to the Ni_2^- intensities.

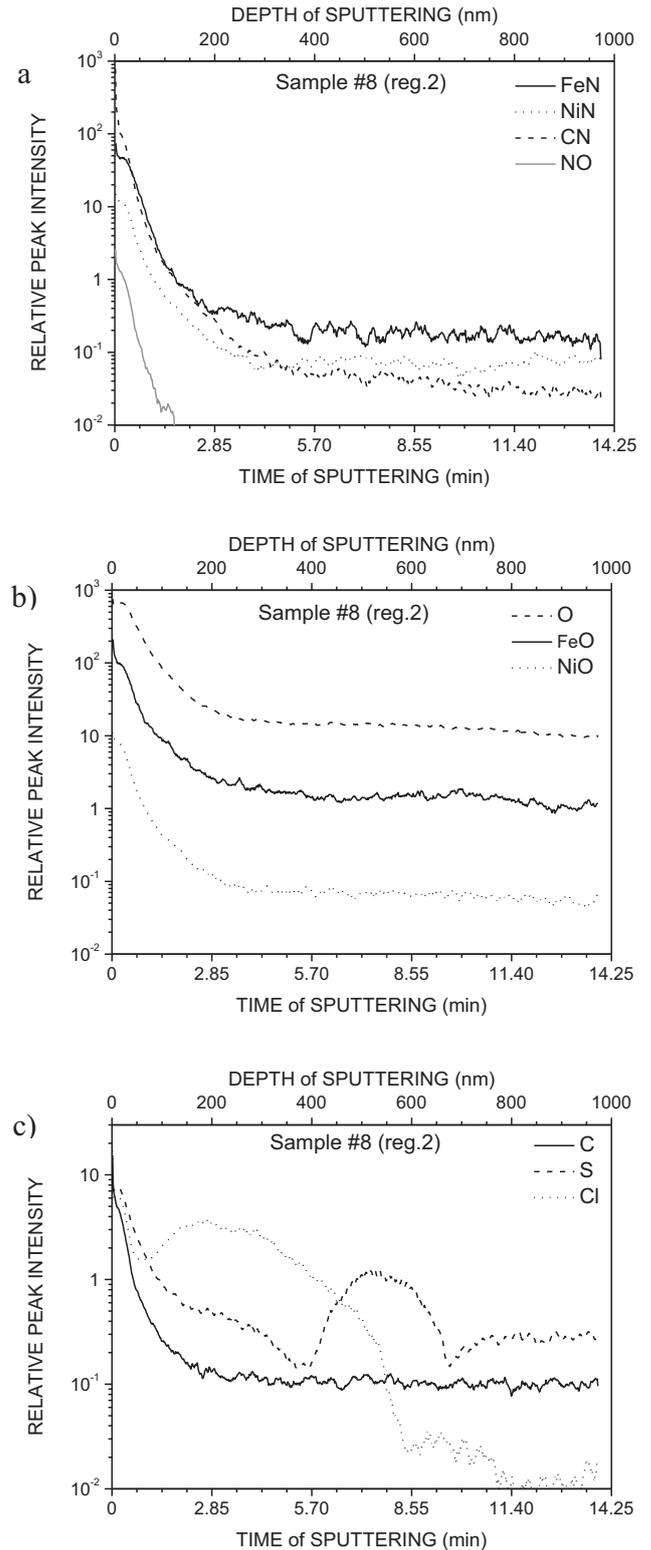


Fig. 4. Depth profiles of negative secondary ions of the nonworking region of the sample #8 (after ion-plasma treatment): (a) nitrogen- and (b) oxygen-containing ions, (c) impurities. The intensities of FeN^- and FeO^- profiles were normalized with respect to the Fe_2^- intensity. The other data were normalized with respect to the Ni_2^- intensities.

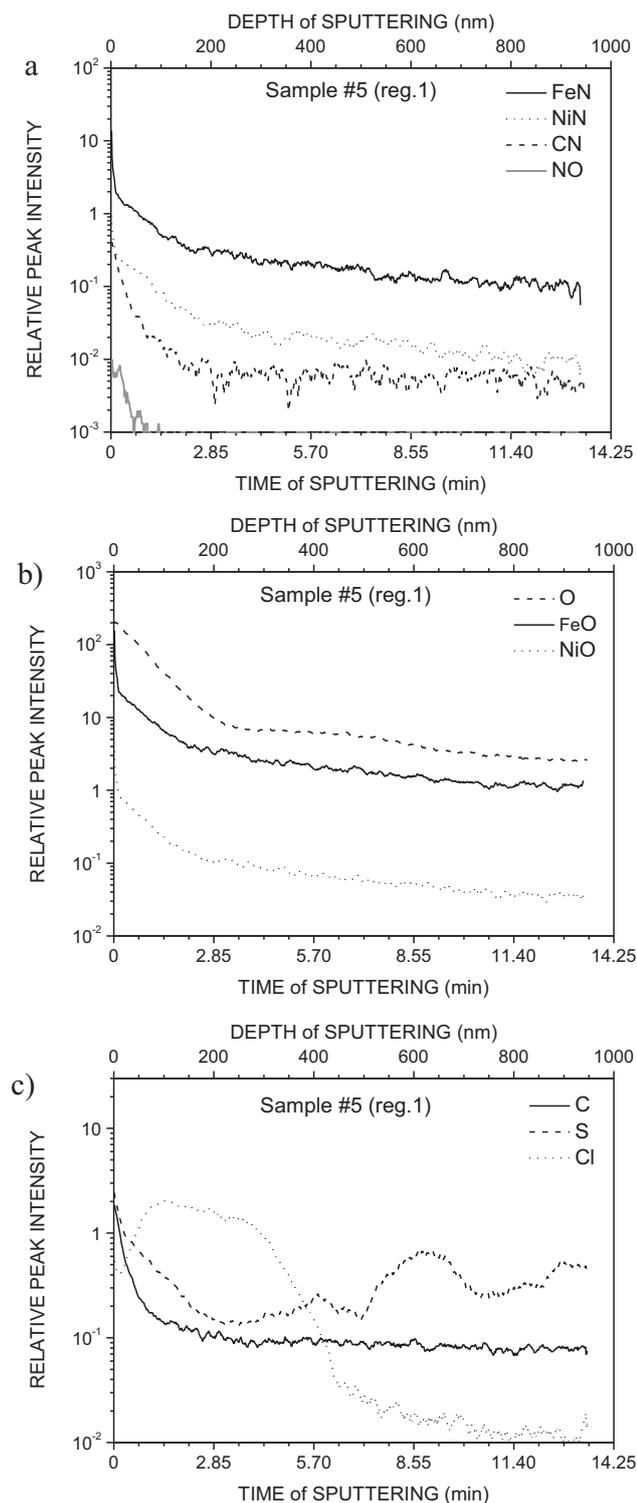


Fig. 5. Depth profiles of negative secondary ions measured of the working region of the sample #5 (without ion-plasma treatment): (a) nitrogen- and (b) oxygen-containing ions, (c) impurities. The intensities of FeN^- and FeO^- profiles were normalized with respect to the Fe_2^- intensities. The other data were normalized with respect to the Ni_2^- intensities.

case, it could be mainly result of chlorine-containing solvents used for the cleaning of permalloy wires. Sulfur, which is also a strong electronegative element, is a bulk impurity in permalloy.

At present, we cannot quantify the samples composition on the base of TOF-SIMS data since we have no information about the secondary ion yield of atoms and molecules produced via

Bi^+ bombardment of nitrides on the surface of blades. However, with proper normalization we are able to compare the results presented in Figs. 3–5 and estimate the thickness of the coatings at the working and nonworking regions of blades.

4. Discussion

Glow discharge or ion nitriding is the oldest plasma-assisted method for the surface treatment of metals [9]. Although its application in industry is already well developed and established, there is today no universal theory explaining the physical–chemical processes underlying this method. According to the simplified models [5,10], during ion nitriding the active nitrogen species (atoms, excited molecules and various radicals generating in the plasma) are chemisorbed on the surface and diffused into the bulk of treated sample (in our case, an iron-nickel blade). The nitrogen ions and fast molecules continuously bombard the sample surface, and a great part of their energies is spent on heating of the sample. This bombardment erodes the sample surface via sputtering of surface atoms and molecules – Fe, Ni, nitrides and oxides, C, O, S, Cl, and other impurities. Other processes like ion and neutral scattering, electron and ion emission, ion implantation also occur. Sputtered and scattered particles collide and react with gas molecules forming nitride compounds, which are deposited at the surface of blades and on the walls of glass envelope. Some authors [11] maintain that cathode sputtering of iron-based alloys in the nitrogen plasma is an inefficient process due to the low value of the N/Fe (N/Ni) atomic mass ratio, i.e. the small portion of the energy transferred from nitrogen ions to surface atoms in elastic collisions. At high temperatures on the surface, more than 400–500 °C, nitrides can dissociate and the released nitrogen diffuses into the bulk of the sample while also evaporating in the plasma. In the low temperature area (<300 °C) a shallow (nanometric scale) implantation of nitrogen ions can affect the density, phase composition and microstructure of nitride layers, accelerating their formation [11].

Usually, glow discharge plasma nitriding is carried out at 10–10³ Pa pressure with 0.3–1 kV potential difference between cathode and anode [10]. The electric-field strength, E , is set within the range from 10 to 50 V cm⁻¹. In our case, ion-plasma treatment of RS blades was performed at $p \sim 3 \times 10^4$ Pa and $E \sim 0.5 \times 10^6$ V cm⁻¹, which are much higher than typical IPT operating conditions. As a consequence, the processes occurring on the surface and near-surface layers of blades and in the plasma are more complex than discussed above. For example, with an increase in the nitrogen pressure, the number of sputtered particles which return the surface of blades due to the collisions with gas molecules becomes considerably bigger. According to [12], at $pd \geq 0.1$, where d is the distance between cathode and anode (a gap between open reeds) more than 90% of the sputtered particles are re-deposited on the surface of cathode (in our case, $pd = 0.5$ –0.7).

Also, the contacting surface of blades (reg. 1 in Fig. 2) is intensively eroded by cathode sputtering. Using an atomic force microscope NTEGRA by NT-MDT (Zelenograd, Russian Federation), we estimated an average roughness, R_a , in this area in the range of 90–115 nm, whereas in the nonworking region (reg. 2 in Fig. 2) R_a does not exceed 25 nm. Similar results were obtained in [13], where after 1 h ion nitriding at 400 °C with a current density of 1 mA cm⁻¹ surface roughness of an austenitic stainless steel increased by a factor of ten and reached 100 nm. We did not measure the temperature of blades in the course of IPT. However, we can estimate it as rather high, especially, in the working region but lower than 550 °C, which is the softening temperature of soda-lime-silica glass used for the production of RS envelopes.

In the past twenty years, many articles devoted to the theoretical modeling and computer simulation of ion nitriding of different

iron alloys were published (e.g., [5,11,14,15]) and a rather good agreement with experimental data has been obtained. State-of-the-art models consider competing processes like nitrogen transport inwards treated material and simultaneous decreasing of the thickness of nitrogen-containing layer by cathode sputtering. However, these models operate with ideal flat surfaces and homogeneous sputtering. In actual processes, the sputter yield of nitrides forming on the surface of treated samples is considerably lower than of pure metals and alloys. It results in selective sputtering producing specific surface topography, especially, in case of our IPT conditions (high nitrogen pressure, current density and electric-field strength). The deposition of nitrides from the plasma on the contacting surface of blades and thermal decomposition of these compounds should be taken into account as well.

With the above considerations in mind, we can now discuss the experimental depth profiles presented in Figs. 3–5. All distributions of the nitrogen-containing ions collected from the working region of blades after IPT (Fig. 3a) exhibit similar shapes with a slow decrease from the surface inwards the sample. The character of decreasing is non-diffusive. Similar results were obtained in [13] by nuclear reaction analysis and were shown in [5] as actual N-profile of plasma-nitrided low alloy steels. In the nonworking region of the sample #8 (Fig. 4a), the initial intensities of all profiles are about the same as in the working region. However, decreasing of the profiles is more rapid and the shape is characteristic of a classical diffusion process. For the sample #5 (without IPT), we observed only a surface increase of ion intensities (Fig. 5a), mainly due to increasing of secondary ion yields in the near-surface layers. The level of the residual signals depends on the type of secondary ions but, at same time, does not depend on the regions where the measurements were carried out, and on the treatment of the samples. This level corresponds to bulk nitrogen contamination of permalloy wires.

Fig. 6 shows the depth profiles of FeN^- and NiN^- ions for both samples in a linear scale. From these data, we can estimate the thickness of nitride coating at the level of 10% of maximum within the range of 320–380 nm in the working and less than 75 nm in the nonworking regions of the sample #8 (with IPT). The slow decrease of FeN^- and NiN^- depth distributions in the working region of the treated blades can be explained by the combined influence of several factors: nitrogen diffusion, cathode sputtering and re-deposition of sputtered products, thermal decomposition of nitrides and the development of sputter-induced topographical relief in this region. The last process is of a great importance for sputter depth profiling by SIMS and other analytical techniques (see, e.g., [16]) since surface roughness (in our case, $R_a \sim 100$ nm) distorts actual depth distributions resulting in the broadening of the interface between nitride coating and substrate. In our opinion, the topographical relief in the contacting region of blades after IPT is one of the main reasons for the change in color of this region (Fig. 2).

In the nonworking region of treated blades, the contribution of cathode sputtering, surface roughness and thermal decomposition of nitride compounds are weaker, while the nitrogen diffusion becomes dominant process. Using the SRIM-2008.04 code [17] we estimated the average penetration depth of nitrogen ions in permalloy. Even for 2 keV ions, it is only 3.2 nm and in the case of ion-plasma treatment of RS blades ion implantation has insignificant impact on the depth distributions of nitrogen-containing species.

The depth distributions of atomic oxygen and oxide ions are shown in panels (b) of Figs. 3–5. These distributions are very similar to the profiles of nitrogen-containing ions discussed above. It means that the ion-plasma treatment of reed switch blades under our experimental conditions should be considered as oxy-nitriding process. The source of oxygen is likely to be the iron and nickel

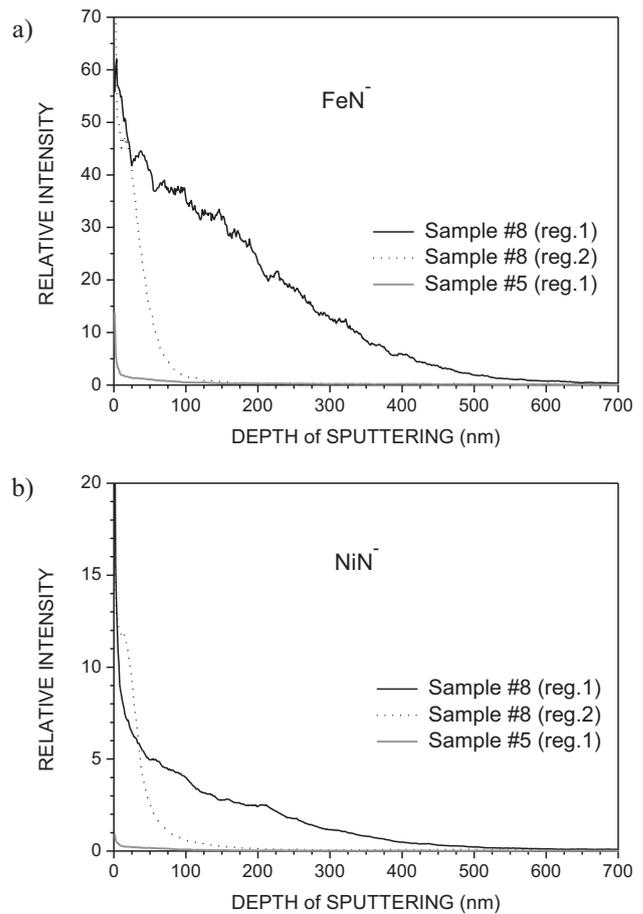


Fig. 6. Scaled depth distributions of FeN^- (a) and NiN^- (b) secondary ions measured for the samples #5 (without ion-plasma treatment) and sample #8 (after ion-plasma treatment).

oxides existing on the surface of blades, although it may also derive from the products of outgassing of the walls of glass envelopes in the course of plasma processing.

The carbon profile obtained in the working region of treated blades (Fig. 3c) is extended inwards the sample with diffusion-like behavior. It differs from the C-profiles measured in the nonworking region of the same sample (Fig. 4c) and for the unprocessed sample #5 (Fig. 5c). The last profiles reflect only the presence of carbon or hydrocarbon surface contaminations. The depth distributions of sulfur and chlorine negative secondary ions, also presenting in panels (c) of Figs. 3–5, show irregularities, especially, in the nonworking region of the treated sample #8 (Fig. 4c) and for the unprocessed sample #5 (Fig. 5c). In our opinion, these bumps were caused by segregation processes in the permalloy wires during its fabrication. The detailed discussion of these processes is beyond the scope of the present paper. However, it should be noted that ion-plasma treatment made these distributions more regular (Fig. 3c). Due to very high negative ion yields of sulfur and chlorine, its actual concentrations can be small enough, probably, lower than 10^{18} at cm^{-3} , and, in our opinion, these impurities have negligible influence on the properties of nitride coating on the surface of RS blades.

5. Conclusion

The results of the present study provide a detailed TOF-SIMS characterization of the surface layers on reed switch blades before and after treatment in pulsing nitrogen plasma. Our focus is on the Cs^+ sputter depth profiling, which revealed the formation

of approximately 350 nm-thick nitride coating in the contacting region of blades. It was found that the origin of this coating cannot be explained only by nitrogen diffusion inwards treated material. Cathode sputtering and re-deposition of sputtered products, thermal decomposition of nitrides and sputter-induced surface roughening can also contribute in the formation of the modified layers. The depth profiles of atomic oxygen and oxide ions obtained for this coating indicate that we deal with not only ion nitriding but with an oxy-nitriding process. In the nonworking region of the treated blades, the oxy-nitride coating is also produced but thinner, of 75 nm in thick, and of the diffusive behavior.

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