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# Plasma Immersion Ion Implantation for Surface Treatment of Complex Branched Structures

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**Abstract.** The paper presents experimental results demonstrating the capabilities of plasma immersion ion implantation of silicon (Si) for surface treatment of complex branched structures such are self-expanding intravascular nickel-titanium (NiTi) stents. Using NiTi stents of diameter 4 and 8 mm, it is shown that plasma immersion ion implantation can provide rather homogeneous doping of their outer and inner surfaces with Si atoms. Also presented are research data on the processes that determine the thickness, composition, and structure of surface layers subjected to this type of treatment.

## INTRODUCTION

One of the ways to increase the biocompatibility of medical implants is their surface modification by plasma immersion ion treatment. However, the shape of medical implants is often very complex and branched, which can result in nonuniform surface treatment. This concerns, in particular, intravascular stents of cylindrical grid shape used to recover the lumen of narrowed blood vessels. When a stent is implanted into a vessel, its outer surface contacts the interior wall of the vessel and its inner surface contacts the blood. Therefore, for increasing the biocompatibility of stents, they require surface modification on both sides. The paper presents research data on the elemental composition of outer and inner surface layers in self-expanding NiTi stents doped with Si by plasma immersion ion implantation. Our previous studies show that surface doping of NiTi specimens with Si atoms speeds up the formation of an endothelial monolayer on the specimen surface, thus increasing their biocompatibility [1]. Despite numerous papers on the use of plasma immersion ion implantation for surface modification of stents, e.g., [2–5], the issues related to modification of their inner surface is left untouched. At the same time, due to the specific formation of an electric field around a stent under applied bias, the possibility of modifying its inner surface is not so apparent.

## MATERIALS AND METHODS

In our study, we used stents of two dimension types: (1) stents of diameter 4 mm and length 30 mm for implantation into common carotid arteries and (2) stents of diameter 4 mm and length 30 mm for implantation into infrarenal abdominal aortas.

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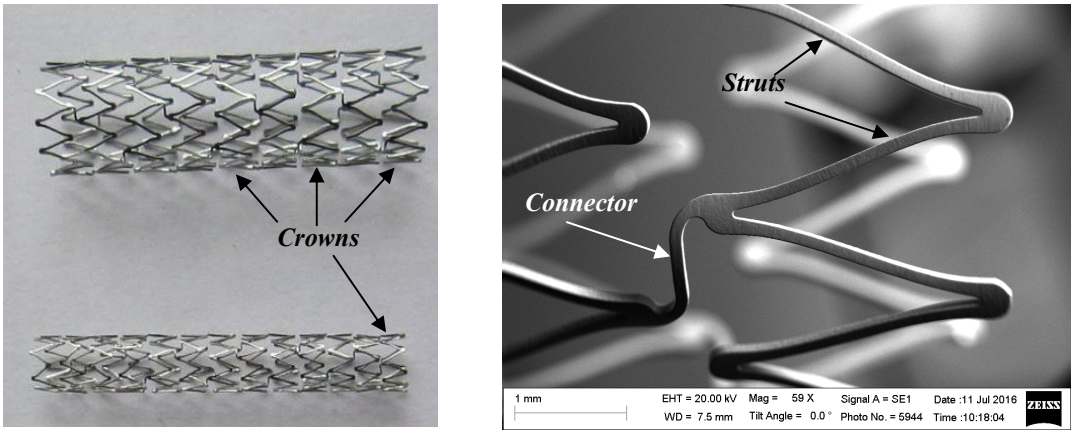



(a) (b)

**FIGURE 1.** Stent design (a) and its elements (b)

The stents were laser cut from a nitinol tube with subsequent annealing on a mandrel to a specified diameter. The stent design represented crowns comprising V-shaped elements with connectors (Fig. 1).

The stent surface was modified by plasma immersion ion implantation on a SPRUT technological vacuum complex developed at Tomsk State University (Tomsk, Russia). The design of the complex and its technological capabilities are described elsewhere [6]. The technological mode of surface modification included magnetron sputtering of a Si target in argon plasma. The stents were suspended in special holders along the perimeter of a round working table such that the longitudinal axis of the stents was kept vertical. The vacuum chamber allowed an arrangement of up to 27 stents at a time. The working table and the holders rotated about their axes with a rate of 2 rpm. For treatment, we used one magnetron with a power of 0.2 kW. The frequency and the amplitude of negative bias applied to the stents were 30 kHz and 1000 V, respectively. The treatment time was 60 min.

The plasma composition and the content of ionized elements in the plasma were estimated with the use of a COLIBRI-2 multichannel atomic emission spectrometer by comparing the intensities of selected lines with their intensities in reference spectra.

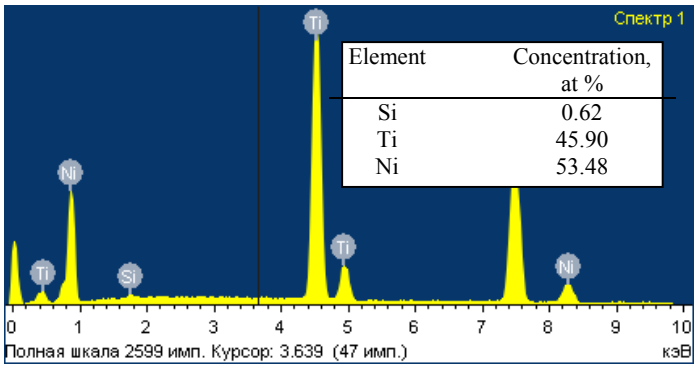
The element distributions in depth from the stent surface was analyzed on stent segments cut out from different sites of the crown using a Shkhuna-2 Auger electron spectrometer available at the Center for Collective Use of Tomsk Polytechnic University. Because the surface of the stent elements was not planar and their size was small (100–150 μm in width), the ion beam diameter was ~1 μm to provide more accurate measurements.

The chemical composition of the outer and inner surface layers of the stents was studied on an EVO 50 scanning electron microscope (Zeiss, Germany) with a Wave 500 wavelength dispersive spectrometer (Oxford Instruments) available at the Nanotekh Shared Use Center of ISPMS SB RAS. Because the material in X-ray spectroscopy is excited to a depth of up to 3 μm and the penetration depth of Si atoms in the treatment mode used is no more than 100 nm [1], the method gives only comparative element concentrations in different surface regions.

## RESULTS AND DISCUSSION

For technological control, a 1-mm thick NiTi plate of dimensions 10×10 mm was subjected to surface modification simultaneously with the stents. The composition of the plate was the same as that of the stents. Figure 2 shows the Si distribution over the surface of the NiTi plate. The NiTi plate was broken into nine fragments and the average Si concentration in each fragment was determined from measurements at nine points. As can be seen, the Si distribution is rather uniform, suggesting that the technological mode provides homogeneous plasma immersion ion implantation. Figure 3 shows the distribution of chemical elements in depth from the outer and inner surfaces of the NiTi stents modified by plasma immersion ion implantation. It is seen that on both sides, there is a Se-doped layer of thickness 10–70 nm.

Figure 4 shows the distribution of Si atoms lengthwise the outer and inner surfaces of the stents of two dimension types. It is seen that the spread in values from crown to crown is rather small and can be explained, among other things, by inhomogeneity of the initial nitinol composition. The average Si concentration lengthwise the stents of both dimension types is somewhat higher at their inner surface.




(a)

| | | |
|---|---|---|
| 0.44 | 0.52 | 0.40 |
| 0.45 | 0.42 | 0.40 |
| 0.55 | 0.34 | 0.45 |

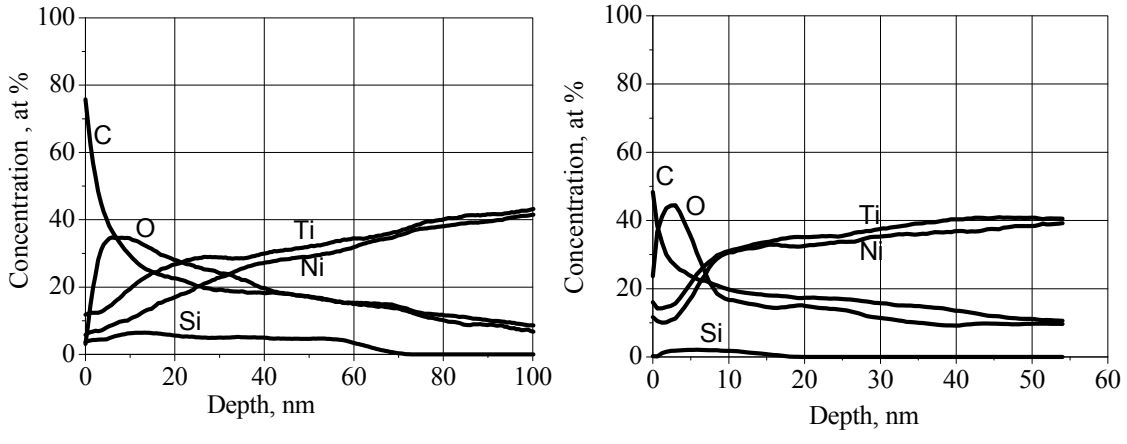
(b)

**FIGURE 2.** Spectrum of elements (a) and distribution of Si atoms over the plate surface (b)

The research results allow the following assumptions on the formation of a modified surface layer in the stents. In plasma immersion ion implantation, the stents are insulated from the chamber walls and are neutral till bias is applied. On all sides, the stents are surrounded by plasma, i.e., immersed into it. Our measurements show that in the technological mode used, the plasma consists of Ar and Si ions and also of excited Ar and Si neutrals the concentration of which is much higher than that of Ar and Si ions. Upon applying a negative bias, a positive space charge layer is formed around the stents. The thickness of the space charge layer $d$ and the plasma density $j$ are related by the Child–Langmuir equation (assuming that the charge number of ions is 1):

$$j = \frac{4\varepsilon_0}{9}\sqrt{\frac{2e}{M}}\frac{U^{3/2}}{d^2}, \qquad (1)$$

where $\varepsilon_0$ is the vacuum permittivity, $e$ is the electron charge, $U$ is the potential (voltage) of a treated object (stent) with respect to the plasma, $M$ is the mass of an ion of plasma-forming gas. Estimates show that in the technological mode used, the thickness of the positive space charge layer is about 2 cm. The arising electric field causes bombardment of the stent by accelerated ions moving perpendicular to its outer surface. Because the stent is a hollow grid cylinder, part of the accelerated ions penetrates inside the stent where they move by inertia with no electric field and bombard the inner surface of the stent. Although the elements of the stents are a barrier to the penetration of ions, their area in the stent makes up a mere 15–20% such that the stent "transparency" for ions is rather high. Additionally, the transparency is increased due to rotations of the working table and respective equipment during treatment. If the energy of ions is sufficient, they are implanted into the crystal lattice with subsequent diffusion deep into the stent material; otherwise the ions are likely deposited on the stent surface.




(a) (b)

**FIGURE 3.** Distribution of chemical elements in depth from the outer surface of stents sized to 8×60 mm (a) and from the inner surface of stents sized to 4×30 mm (b)

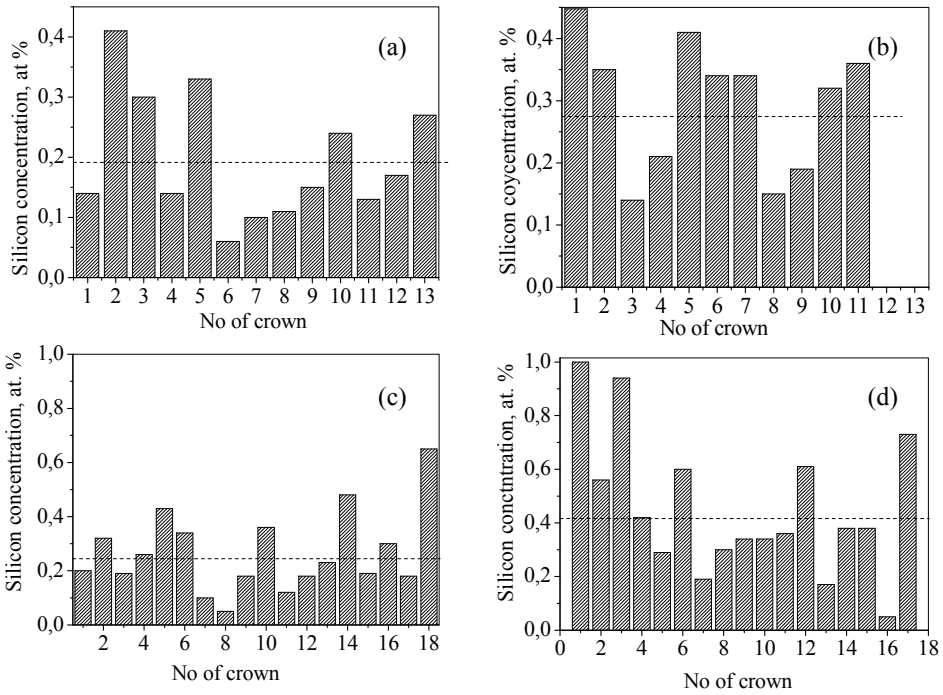



**FIGURE 4.** Distribution of Si atoms lengthwise the outer (a, c) and inner surfaces (b, d) for stents sized to 4×30 mm (a, b) and to 8×60 mm (c, d). The dashed lines correspond to the average Si concentration

This is true only for dopant ions (in our case, Si ions), because ions of inert gases (argon) are hardly implanted or deposited on the substrate. The Si neutrals present in the plasma are apparently also deposited on the stent surface on either side, forming a coating. The accelerated Ar ions bombarding the Si-coated stent knock part of the Si atoms into the NiTi lattice, and part of the coating is sputtered. The rates of the above processes and their ratio determine the thickness, composition, and structure of the modified layer. From general considerations, it can be assumed that the sputtering rate at the outer surface of the stents is higher. This assumption explains the higher average Si concentration at their inner surface (Fig. 4).

## CONCLUSION

Thus, our study suggests that plasma immersion ion implantation allows surface modification of complex branched objects. During plasma immersion ion implantation, the treated object is involved in several processes at a time: implantation of dopant ions and atoms, diffusion, and coating deposition and sputtering. The rates of these processes and their ratio determine the mechanism for the formation of a modified layer. It is shown that plasma immersion ion implantation provides rather homogenous Si doping of both the outer and the inner surface of peripheral stents shaped as hollow grid cylinders. Reasoning from our previous studies, it can be concluded that the Si concentration at the stent surface is sufficient for increasing their biocompatibility.

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