Sigma Aldrich silicon plates polished on one side (⟨1 0 0⟩) of the N-type with an oxide layer of ~ 2 nm, medical orthopedic titanium and steel implants.

2.2. Characterization methods and instrumentation

The surface roughness was investigated by atomic force microscopy ('NT-MDT'). The scan was done at a frequency of 0.8–1.01 Hz, with resolutions of 156 × 156 and 256 × 256 points. Image processing and statistical processing of the results were performed using Microsoft Excel and Origin.

Dry film thickness was determined using the spectral ellipsometer 'Ellipse 1891 SAG. Measurements of spectral dependences of the Ψ and Δ ellipsometric angles carried out in wavelength at 250–1100 nm. The spectral resolution of the instrument is 2 nm, the recording time of one spectrum did not exceed 20 s, the angle of incidence of the light beam on the sample was 70 °C. A four-zone measurement technique was used, followed by averaging across all four zones.

The wetting angle was determined by a lying drop method using the 'DSA100-KRUSS GmbH' apparatus at ambient temperature and pressure. The average drop diameter averaged 2–5 mm. The wetting angle was determined after 30, 60 and 120 s. A picture of the surface of the implants was taken in at least three areas due to irregularities.

SEM pictures were obtained using two scanning electron microscopes (Quanta 3D 200i (FEI company) and Hitachi S-3400 N (USA)).

2.3. Method of obtaining multiple layers

The silicon plates were pretreated with ethyl alcohol, then with concentrated sulfuric acid (H_2SO_4 conc), followed by washing with distilled water until pH reached to neutral. Part of the silicon plates was also treated with a solution of sulfuric acid and hydrogen peroxide ('piranha') for 1 h and washed with a large amount of distilled water.

Medical orthopedic titanium and steel implants were also treated with two methods: mechanical cleaning followed by exposure to an ultrasonic bath for 1 h, and further sequential treatment with solutions of acetone (1 h) and ethyl alcohol (1 h) or a solution of 'piranha'. The process completed with exposure in an ultrasonic bath (15 min).

The preparation of multiple layers on the surface of the substrates was carried out by a semi-automatic dip-coating method. After activation, one layer based on polyethyleneimine is applied to the surface in order to create a bridge between the film and the solid substrate. Polyelectrolyte solutions with a concentration of 0.01 M were used and the loading and removal rate was 0.001 m/s. The production of thin films was started by immersing the substrates in a chitosan pH 3 solution followed by drying to secure the adsorbed polymer particles and washing with a buffer solution at the same pH to remove the non-adsorbed particles. The polyanion was then applied at pH 6 to the chitosan-containing surface in a similar sequence. In this way, the desired amount of bilayers was obtained. Crosslinking with glutaraldehyde was carried out in order to eliminate peeling of the coating from the surface from the solid substrate during long-term storage. The concentration of glutaraldehyde that was used is 2%.

3. Results and discussion

To obtain antibacterial coatings for a particular medical product, an important requirement is to obtain a developed surface that provides good 'clinging' of chemical reagents to the base of the material. Therefore, controlling the morphology and wetting angle of the surface before and after activation is an important step in the process of producing nano coatings. As a result of the analysis of various methods of etching the surfaces of titanium and steel implants, which are most often used in practical medicine, we have chosen solvents based on inorganic ('piranha' solution) and organic substances. Coatings were obtained using the semi-automatic immersion method, during which the substrates are immersed and removed at a given speed and kept in solution for a certain time. In this method, an important point is the choice of the rate of immersion and removal of the substrate, since at high speeds (>0.001 m / s), the solution quickly drains from the surface of the substrate and subsequent drying will lead to uneven distribution of the polyelectrolyte layer and unevenness on the surface. When the rates of removal and immersion are less than < 0.001 m / s along the edges of the solid substrate, solution droplets solidify, which upon further layering leads to a rough coating at the edges of the substrate. Treatment with organic solvents includes polishing with sandpaper followed by washing successively with acetone and ethyl alcohol. From Fig. 1 (a, b), it can be seen that after machining and etching with organic solvents, no significant changes are observed on the surface of the steel substrates, and in the case of etching with a piranha solution (Fig. 1 (c, d), the formation of micro-cracks is visible, which will create favourable conditions for adsorption of hydrophilic polymers on the surface of the substrate.

The change in the physical and chemical characteristics of the surface was monitored by measuring the wetting angle of the surface, after each treatment with solutions, by a lying drop method. As shown by the experimental data, Fig. 2 (a), before etching, the wetting angle of the steel implants was in the range 89–93.7°. Etching the implant surface with organic solvents and piranha solution (Fig. 2 b and c) reduced the wetting angle to 70–80, 6° and ~ 62°, respectively.

The wetting angle for all silicon plates after cleaning with the 'piranha' solution was 27, 0°, and etching with one sulfuric acid reduced the wetting angle to 33, 7°, which may result from incomplete removal of organic fats.

Therefore, surface preparation is one of the essential and major steps in producing an active surface to produce uniform nanolayers in the form of multilayers. For titanium, steel and silicon samples, treatment with the sulfuric acid solution with the addition of hydrogen peroxide is most suitable. The multiple microcracks produced by the treatment are active centers and, according to Taylor's theory, contribute to good and uniform adsorption of the fungal groups of polyelectrolytes.

Polyelectrolytes are promising polymer matrixes for producing bioactive protective coatings. Chitosan, sodium carboxymethyl cellulose, and polyacrylic acid were chosen as polyelectrolyte owing to their biocompatibility, acid-basic properties and they can potentially be used to produce multilayers with the desired chemical-biological characteristics. Nanolayers were carried chitosan at pH 3 and polyanions at pH 6, both polyelectrolytes have a high degree of ionization. Thus, when chitosan is adsorbed on carboxymethyl cellulose, the polycation fully compensates polyanion. Depending on the pH of the medium, the coating can grow linearly or exponentially, thereby forming a thick or thin coating. Also, the pH of the solution affects not only the thickness but also the morphology of the films. A study of the dependence of the thickness on the number of bilayers made it possible to establish that the coating thickness linearly depends on the number of bilayers. The pH value of the solution affects not only the thickness but also the roughness of the coating. Earlier, we found that with an increase in pH to 5, the average roughness first increases and then decreases. Also, with a change in pH, a change in the morphology of multilayer films is observed.