

# Atomic force microscopy study of the morphology of copper sulfide layers formed on polyamide film surface

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The morphology of polyamide PA6 films modified by copper sulfide layers was studied by the atomic force microscopy method. Copper sulfide,  $\text{Cu}_x\text{S}$ , layers on the surface of PA6 film were formed by treating PA film samples in dodecathionic acid,  $\text{H}_2\text{S}_{12}\text{O}_6$ ,  $0.002 \text{ mol} \cdot \text{dm}^{-3}$  solution and then with  $\text{Cu(II/I)}$  salt solution. Formation of copper sulfide layers was found to proceed unevenly, in the form of islands which later grew into agglomerates. The surface of the layers was relatively uneven and rather rough. The thickness of  $\text{Cu}_x\text{S}$  layers increased with increasing the duration and temperature of polymer treatment in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution. The same tendency was observed in the change of surface roughness: it increased with prolonging polymer treatment in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and with increasing in the solution temperature.

**Key words:** polyamide, dodecathionic acid, copper sulfide layer, morphology

## INTRODUCTION

Over the last decades, researchers of various fields of science have been involved in studies of copper chalcogenides  $\text{Cu}_x\text{Y}$  ( $\text{Y} = \text{S}, \text{Se}, \text{Te}$ ) – their synthesis, physical and chemical properties and modification of dielectrics by these compounds. Interest in  $\text{Cu}_x\text{Y}$  and their thin layers deposited on various dielectric substances, including polymeric ones, was focused first of all on their possible use in the production of solar energy elements [1–5]. In the last years, more attention is given to thin layers of these compounds as transparent and electrically conductive coatings on glass and polymers [6], for production of various sensors [7–9], electronic and optical devices [10, 11], thermoelectric converters [12].

Polymer films modified by electrically conductive layers of copper chalcogenides may be used in practice only when they meet certain requirements. For example, for the metallization of plastics, coatings of low electrical resistance and highly adhesive with the polymer are needed; the production of electronic materials requires coatings with a precise and stable electrical resistance; for adhesive joinings, coarse coatings strongly adhesive with the polymer are necessary.

$\text{Cu}_x\text{S}$  layers deposited on polyethylene and silicon are sensitive to ammonia gas, but the value of  $x$ , which is determined by the conditions of technology, must be 0.75–2 [8, 13].

Modifying polymers with layers of copper chalcogenides, it is important not only to determine the phase composition of the coatings formed, but also to study its morphology, since in many cases the latter determines the properties and possible use of dielectrics modified by thin  $\text{Cu}_x\text{S}$  layers.

For the characterization of  $\text{Cu}_x\text{S}$  layer morphology and roughness estimation we applied the method of atomic force microscopy.

Over the last decade, the sorption–diffusion method for the formation of thin copper sulfide layers on the surface of polyamide 6 (PA) based on the initial treatment of a polymer with the solutions containing anions of polythionates,  $\text{S}_n\text{O}_6^{2-}$ , has been under extensive investigation [14–18]. The polythionate ions containing chains of divalent sulfur atoms of low oxidation state,  $^-\text{O}_3\text{S}-\text{S}_x-\text{SO}_3^-$  [12–14], are sorbed by a polymer. Upon treating the sulfurized polymer with a solution of copper(II/I) salt, layers of copper sulfide,  $\text{Cu}_x\text{S}$ , on the surface of a polymer are formed [14–18].

In our last works, we have shown that using solutions of dodecathionic acid,  $\text{H}_2\text{S}_{12}\text{O}_6$ , as sulfurization agents of PA, semi-conducting and electrically conductive  $\text{Cu}_x\text{S}$  layers are formed on the surface of this polymer; the phase composition of these layers was studied by X-ray diffraction analysis [18, 19].

The aim of the present work was to study the morphology of  $\text{Cu}_x\text{S}$  layers formed on the surface of polyamide 6 film, using a solutions of dodecathionic acid by the method of atomic force microscopy (AFM).

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## EXPERIMENTAL

Layers of copper sulfide were deposited on polyamide 6 (PA) (manufacturer TY 6-05-1775-76, grade PK-4,  $15 \times 70$  mm,  $70 \mu\text{m}$ ). The PA films were boiled in distilled water for 2 h to remove the monomer residues. They were dried with filter paper and then over anhydrous  $\text{CaCl}_2$  for 24 h.

The PA films were sulfurized in a thermostatic vessel, using a continually stirred  $0.002 \text{ mol/dm}^3$  solution of polythionic acid  $\text{H}_2\text{S}_{12}\text{O}_6$  at 20, 30, 40 and  $50^\circ\text{C}$  for 6 h. At certain time intervals the samples were withdrawn, rinsed with distilled water, dried with filter paper, left over anhydrous  $\text{CaCl}_2$  for 24 h and then used in the analysis and further experiments.

Solutions of dodecathionic acid were prepared and the average number of sulfur atoms ( $n$ ) in the  $\text{H}_2\text{S}_n\text{O}_6$  molecule was determined by the methods described in Ref. [20].

Samples of sulfurized PA were treated with a solution of Cu(II/I) salts at  $80^\circ\text{C}$  for 10 min. A Cu(II/I) salt solution was made from crystalline  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and hydroquinone as described in Ref [18]. It is a mixture of Cu salts, containing  $0.34 \text{ mol/dm}^3$  of Cu(II) and  $0.06 \text{ mol/dm}^3$  of Cu(I) [21]. After treatment with a solution of Cu(II/I) salts, samples of PA were rinsed with distilled water, dried over anhydrous  $\text{CaCl}_2$  and used in further experiments.

The morphology of the surface of  $\text{Tl}_x\text{S}$  layers, the quantitative microscopy of the roughness of precipitated layers on the surface of PA were studied by employing an atomic NT-206 force microscope in a contact regime with high resolution probes with the force constant  $k = 3 \text{ N/m}$ . Characteristics of the atomic force microscope: the maximum scan field area up to  $12 \times 12$  microns, the measurement matrix up to  $512 \times 512$  points and more, the maximum range of measured thickness 2.5 microns, vertical resolution 0.1–0.2 nm. An AFM cantilever produced by Silicon-MDT in cooperation with MikroMasch (Estonia); type – NONCONTACT silicon cantilever NSC11/15; characteristics of the cantilever: curva-

ture radius less than 10 nm; tip thickness  $15 \dots 20 \mu\text{m}$ ; full tip cone angle less than  $20^\circ$ . Lateral force microscopy studies are useful for imaging variations in surface friction that can arise from inhomogeneity in surface material.

## RESULTS AND DISCUSSION

Results of earlier studies [16, 18, 19] showed that under PA film treatment in acidified water solutions of potassium pentathionate,  $\text{K}_2\text{S}_5\text{O}_6$ , or dodecathionic acid, the anionic particles containing sulfur atoms of low oxidation state,  $^-\text{O}_3\text{S}-\text{S}-\text{S}-\text{SO}_3^-$  or  $^-\text{O}_3\text{S}-\text{S}_{10}-\text{SO}_3^-$ , respectively sorb or diffuse into the polymer. While treating the sulfurized PA films with solutions of Cu(II/I) salts, exactly these central divalent sulfur atoms of a low oxidation state react with Cu(II/I) ions and form layers of copper sulfides on the surface of semihydrophilic PA [16, 18, 19].

To characterize the morphology and roughness of the  $\text{Cu}_x\text{S}$  layers, we applied the method of atomic force microscopy.

A morphological study by atomic force microscopy of PA modified with  $\text{Cu}_x\text{S}$  layers revealed the coatings to be essentially different. Fields of  $12 \times 12$  microns were investigated; for the quantitative estimation of the surface, the standard programs of the view treatment were used.

The views of  $\text{Cu}_x\text{S}$  layer surface obtained by AFM are shown in Figs. 2–9 and 12–17. A view of the initial PA surface is presented in Fig. 1. We have determined that the thickness and surface morphology of the sulfide layers formed on PA depends on the conditions of polymer sulfurization.

Profile sections of  $\text{Cu}_x\text{S}$  coatings formed on PA surface when the polymer had been sulfurized for 0.5, 2.0, 4.0, 6.0 h at a temperature of  $40^\circ\text{C}$  with  $0.002 \text{ mol} \cdot \text{dm}^{-3} \text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated for 10 min with Cu(II/I) salts solution allowed to estimate quantitatively the thickness and diameter of separate crystallites (Figs. 2–5, the crystallinity of  $\text{Cu}_x\text{S}$  layers was shown in earlier studies [18, 19] by X-ray diffrac-

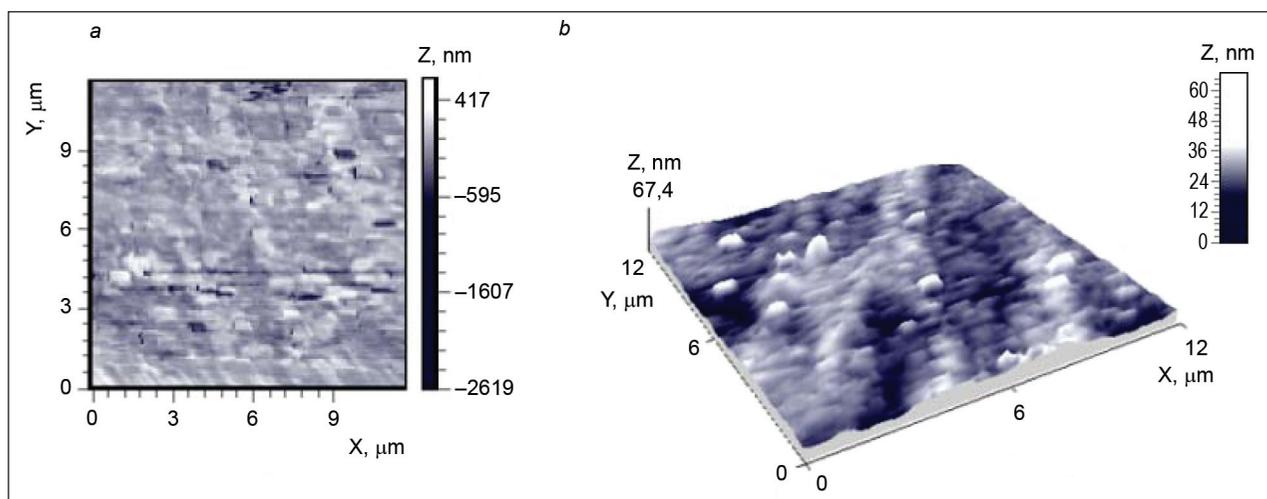


Fig. 1. Atomic force microscopy view of initial (not sulfurized) PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). Scan field area  $12 \times 12$  microns. Interval of unevenness thickness up to 67.4 nm

tion). When the polymer was sulfurized for 0.5 h at a temperature of 40 °C in  $H_2S_{12}O_6$  solution, the thickness of the bigger crystallite was ~310 nm (diameter ~1,5  $\mu m$ ) and of the smaller crystallite ~217 nm (diameter ~1,5  $\mu m$ ) (Fig. 2). On prolonging the sulfurization to 2.0 h, the thickness of bigger crystallites increased to ~590 nm and of smaller crystallites to ~472 nm (Fig. 3). When the polymer was sulfurized for 4.0 h, the thickness of crystallites was ~230 nm (Fig. 4), i. e. decreased, but the evenness of the surface increased. Thus, on prolonging PA sulfurization in  $H_2S_{12}O_6$  solution from 0.5 to 2.0 h (in the same conditions of sulfurized PA “copperizing”), the thickness of crystallites increased about twice (Figs. 2, 3). The same tendency was observed in the change of coating roughness: because of the different thickness and form of crystallites it increased. However, upon increasing

the duration of PA sulfurization to 4.0 h, the thickness and roughness of crystallites decreased. The thickness of separate crystallites reached ~230 nm and the diameter 0.95–1.5  $\mu m$ . On the further prolongation of sulfurization (to 6.0 h, Fig. 5) the thickness of crystallites again increased to ~450 nm, but their diameter of crystallites reduced to ~0.73  $\mu m$ .

Copper sulfide coatings on PA surface, when the polymer was sulfurized for 0.5, 2.0, 4.0 and 6.0 h at a temperature of 40 °C in  $H_2S_{12}O_6$  solution and then treated with Cu(II/I) salt solution, are shown in Figs. 6–9. One can see that upon a short (0.5 h) PA treatment in  $H_2S_{12}O_6$  solution, the growth of copper sulfide coating begins from the formation of small islands (Fig. 6). The lightest places in separate areas of the surface show the peaks of crystallites. The crystallites here are of different thickness and diameter. Prolongation of sulfurization

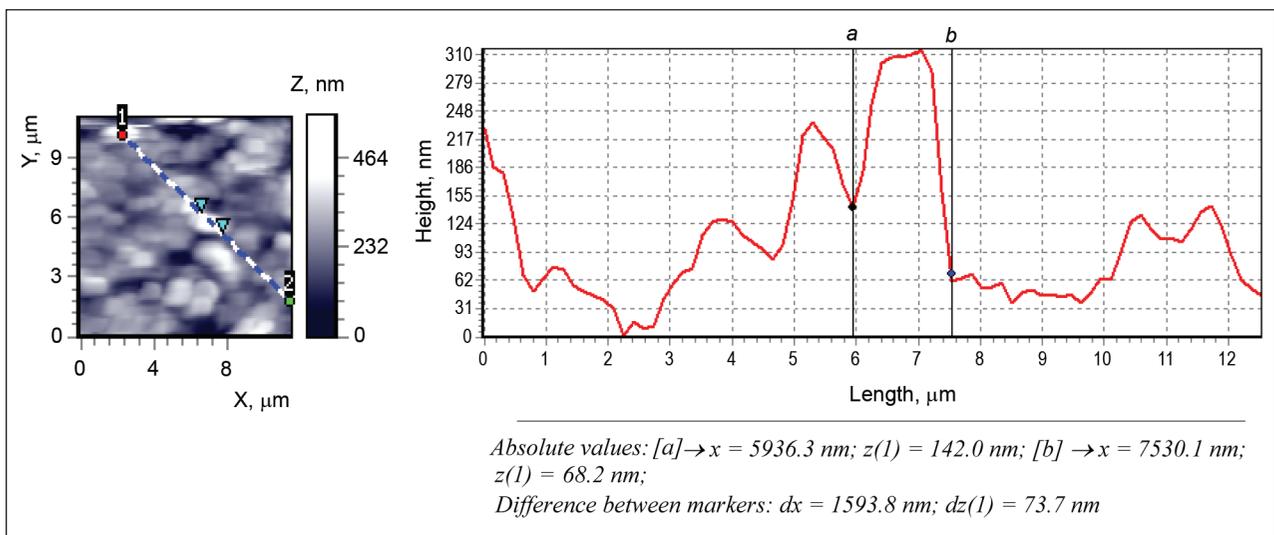


Fig. 2. Topographic image and line profile of sulfide coating formed on PA surface. PA was sulfurized for 0.5 h at 40 °C in  $H_2S_{12}O_6$  solution and then treated with Cu(II/I) salt solution

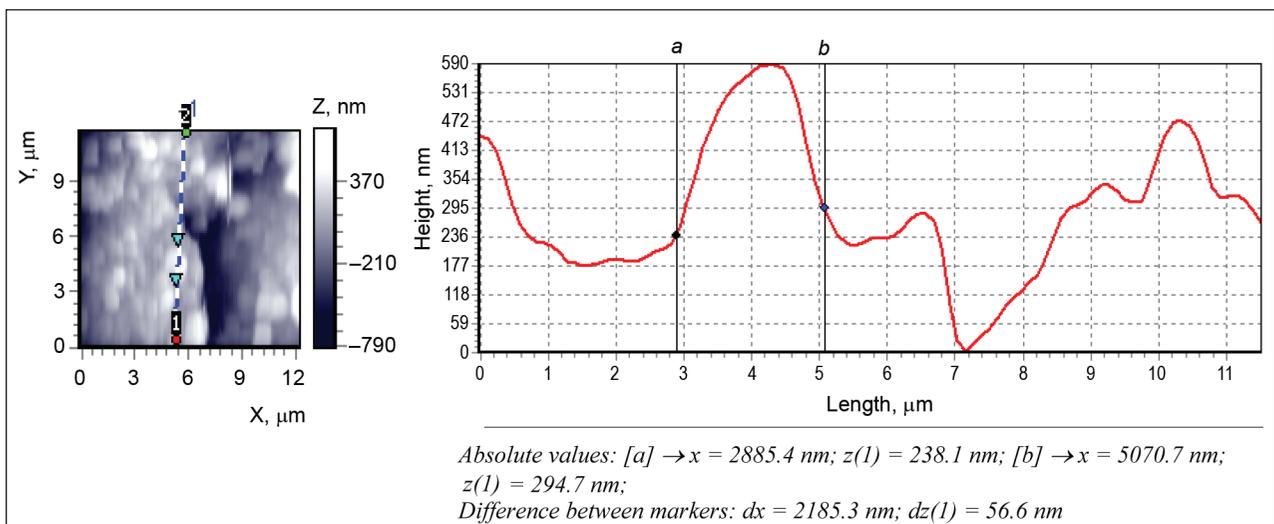


Fig. 3. Topographic image and line profile of sulfide coating formed on PA surface. PA was sulfurized for 2.0 h at 40 °C in  $H_2S_{12}O_6$  solution and then treated with Cu(II/I) salt solution

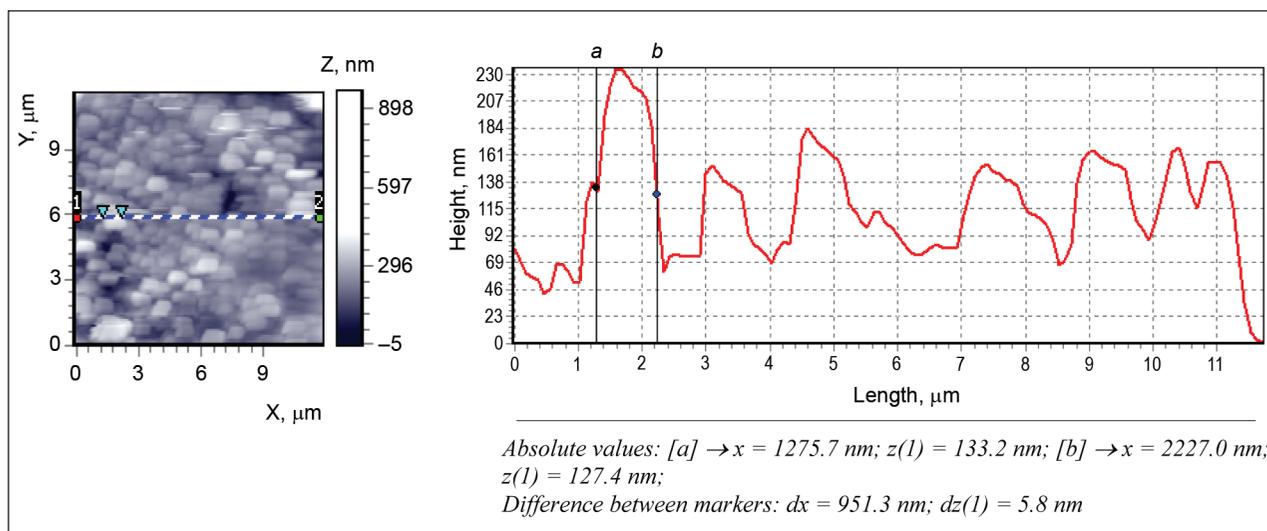


Fig. 4. Topographic image and line profile of sulfide coating formed on PA surface. PA was sulfurized for 4.0 h at 40 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with Cu(II/I) salt solution

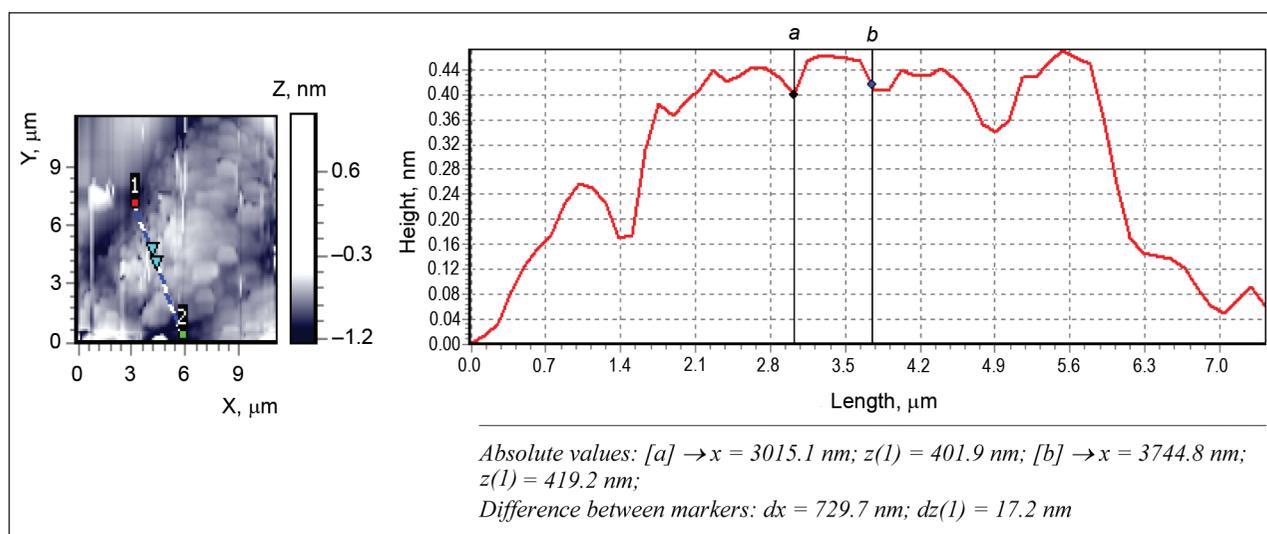


Fig. 5. Topographic image and line profile of sulfide coating formed on PA surface. PA was sulfurized for 6.0 h at 40 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with Cu(II/I) salt solution

to 2.0 h caused the beginning of clusterization: crystallites of various diameter and thickness begin slowly joining into agglomerates (Fig. 7), and a thicker  $\text{Cu}_x\text{S}$  coating is formed. On the further prolongation of PA sulfurization in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution at 40 °C to 4.0 and 6.0 h in the same conditions of sulfurized PA “copperizing”, bigger agglomerates composed of crystallites having a different diameter, thickness and, shape were formed (Figs. 8, 9). As is shown in Fig. 10, the thickness of the coating increased on prolonging PA treatment in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution from 0.5 to 6.0 h.

Formation of islands at separate places of the surface and their integration into agglomerates composed of crystallites of different thickness and diameter increases the roughness of the surface. This is shown by the roughness parameter (Fig. 11). Figure 11 shows that the average roughness increas-

es on prolonging PA treatment with  $\text{H}_2\text{S}_{12}\text{O}_6$  solution from 0.5 to 2.0 h. However, upon the prolongation of PA sulfurization to 4.0 h, the average roughness of the surface decreased (the coating became more homogeneous), i. e. crystallites joining into agglomerates more evenly covered the surface, resulting in a decrease of the coating’s thickness (Fig. 10). With the further prolongation of sulfurization (to 6.0 h), the roughness and thickness of the coating increased (Figs. 10, 11).

In the further studies of the formation of  $\text{Cu}_x\text{S}$  layers on PA surface, coatings were formed by sulfurizing PA for 4.0 h at a temperature of 20, 30, 40 and 50 °C with  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treating with Cu(II/I) salt solution (Figs. 8, 12–14). In Fig. 12 one can see that the formation of a coating, because of the low temperature of PA treatment with  $\text{H}_2\text{S}_{12}\text{O}_6$  solution, proceeded slowly and an uneven covering was obtained.

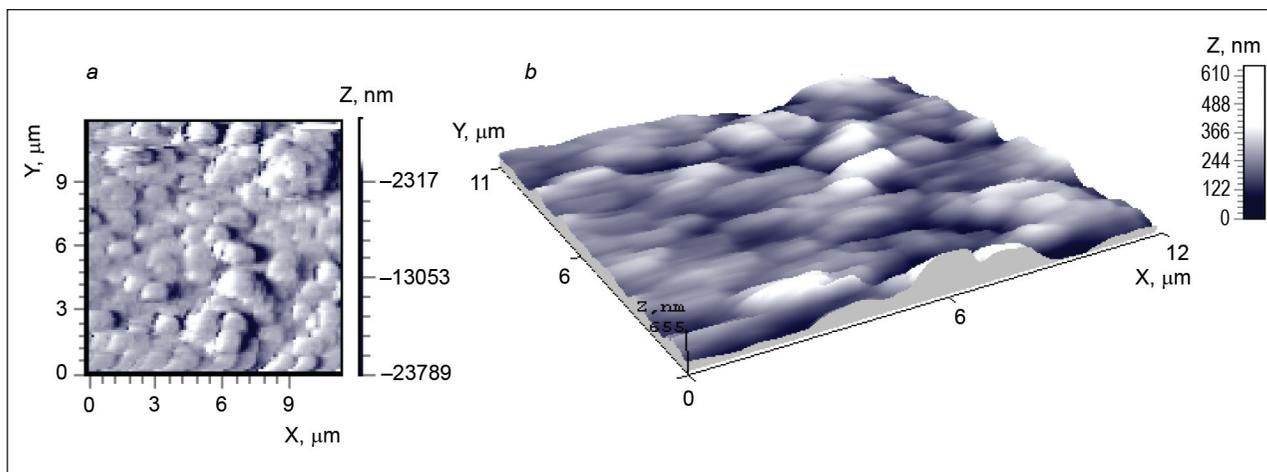


Fig. 6. Atomic force microscopy view of thin  $\text{Cu}_x\text{S}$  layers formed on PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). PA was sulfurized for 0.5 h at 40 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with  $\text{Cu}(\text{II}/\text{I})$  solution

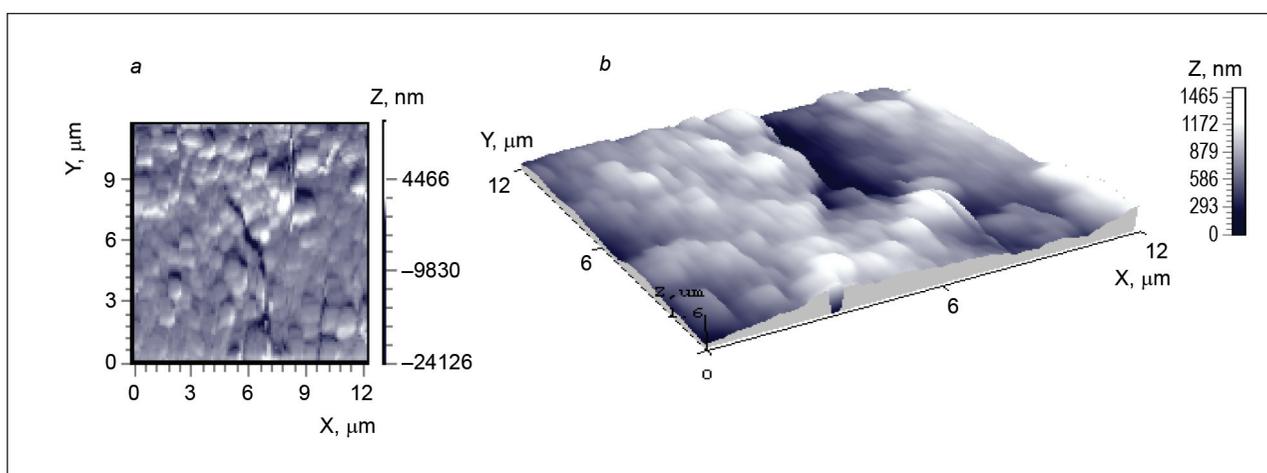


Fig. 7. Atomic force microscopy view of thin  $\text{Cu}_x\text{S}$  layers formed on PA surface: 2D view of lateral forces microscopy (a) and 3D topography view (b). PA was sulfurized for 2.0 h at 40 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with  $\text{Cu}(\text{II}/\text{I})$  solution

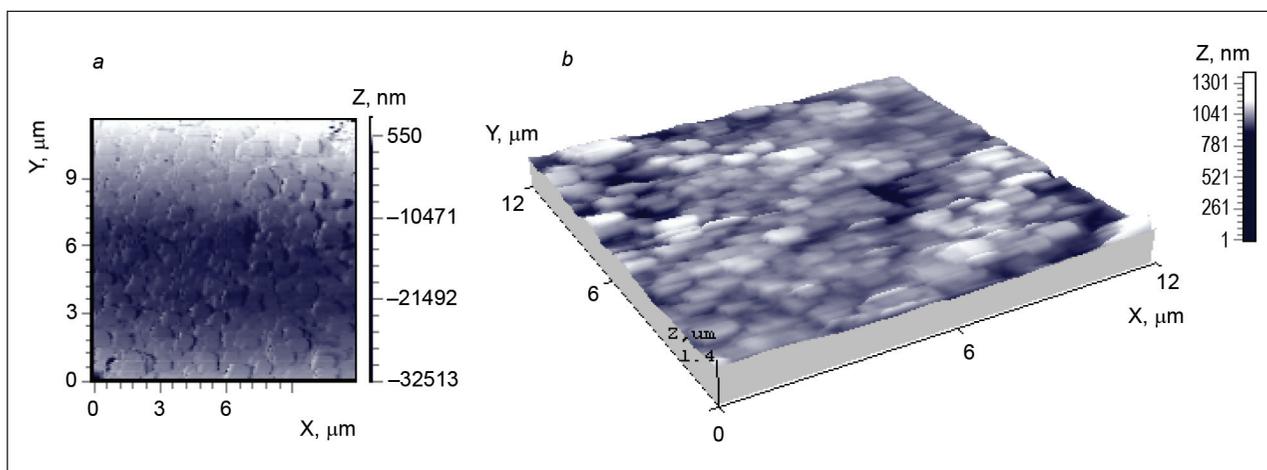
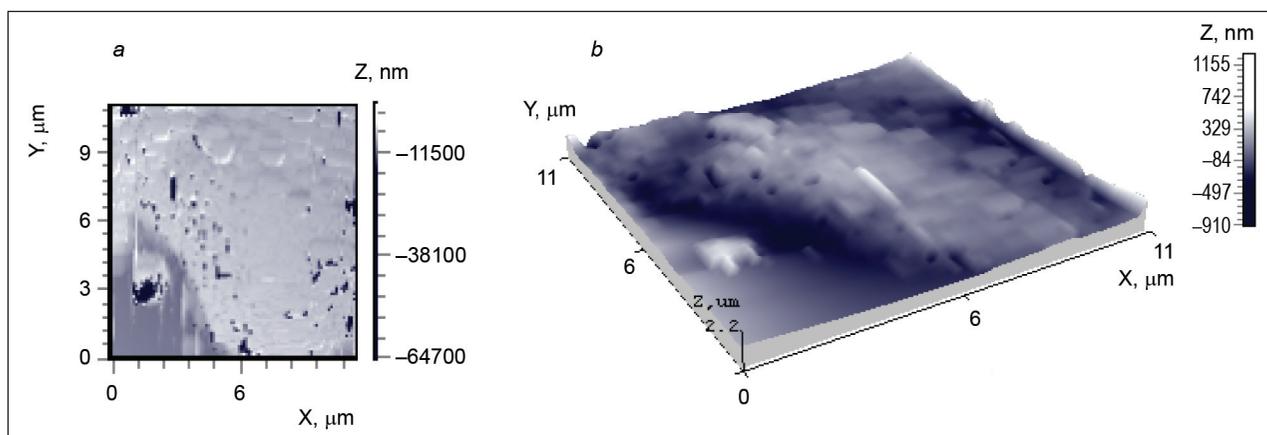


Fig. 8. Atomic force microscopy view of thin  $\text{Cu}_x\text{S}$  layers formed on PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). PA was sulfurized for 4.0 h at 40 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with  $\text{Cu}(\text{II}/\text{I})$  solution

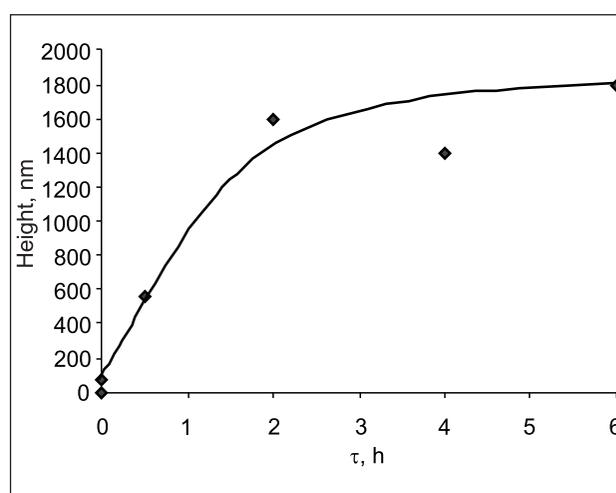


**Fig. 9.** Atomic force microscopy view of thin  $\text{Cu}_x\text{S}$  layers formed on PA surface: 2D view of lateral forces microscopy (a) and 3D topography view (b). PA was sulfurized for 6.0 h at 40 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with  $\text{Cu}(\text{II}/\text{I})$  solution

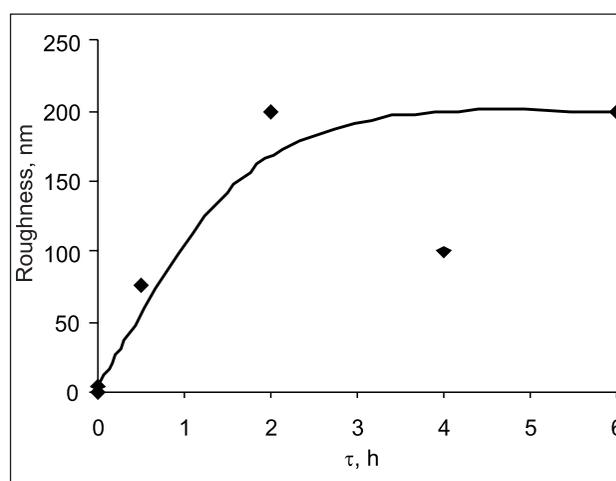
Only in separate places formation of small islands begins; the thickness of the coating is  $\sim 937$  nm. On the further growing of the coating (increasing the temperature of PA sulfurization in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution to 30 °C), the number of islands increases, some of them are single and in some places are grown together into relatively large agglomerates formed of the crystallites of various diameter (Fig. 13). The thickness of the coating slightly increased – from 937 to 965 nm (compare with Fig. 12). Upon increasing the temperature of the sulfurization solution to 40 °C, the presence of even larger agglomerates is observed (Fig. 8) and the thickness of the coating increases to 1.4  $\mu\text{m}$ . On further increasing sulfurization temperature to 50 °C, even larger agglomerates are formed, and their thickness increases to 1.8  $\mu\text{m}$  (Fig. 14). Thus, the increase of sulfurization temperature from 20 to 50 °C results in a double increase of the coating's thickness.

The profile sections of these coatings showed their surfaces to be rather uneven (Figs. 4, 15–17). The roughness increases because crystallite surfaces (Figs. 8, 12–14) and profiles (Fig. 4, 15–17) show their different thickness, diameter and form. Change of the roughness is shown by the roughness parameter (Fig. 18). The thickness of crystallites decreases with increasing the temperature of  $\text{H}_2\text{S}_{12}\text{O}_6$  solution, but the thickness of the coating increases (Fig. 19).

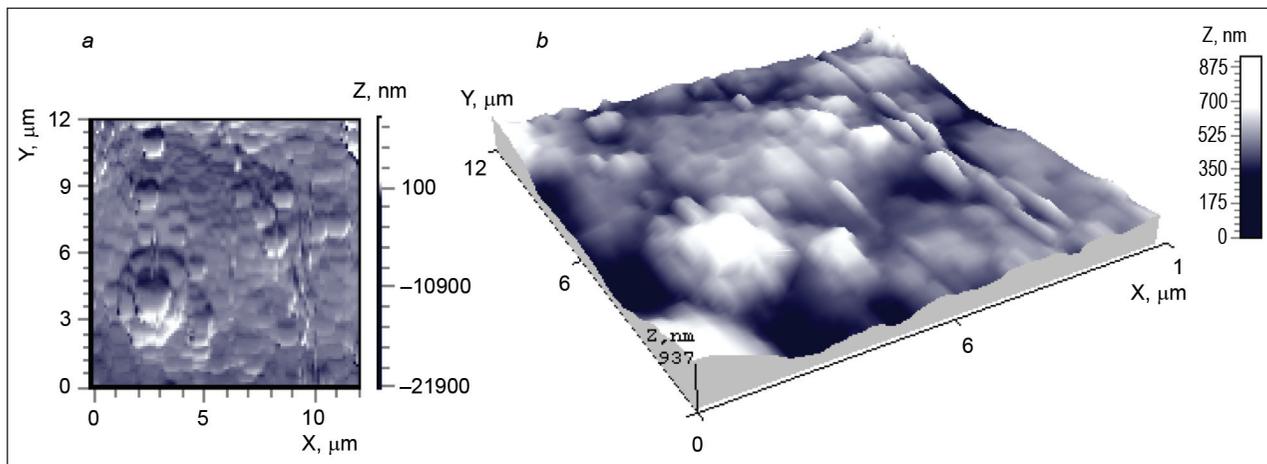
Summarizing the results of  $\text{Cu}_x\text{S}$  layer morphological studies, it is possible to state that, depending on the duration and temperature of initial PA sulfurization in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution (in the same conditions of sulfurized PA “copperizing”), formation of copper sulfide layers proceeds unevenly as islands which later grow together into bigger agglomerates. The surface of the formed coatings is uneven, rather rough. The thickness of the coating increases with prolonging PA sulfurization in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and increasing the temperature (Fig. 19). An analogous tendency is observed also in the average roughness of coating surface (Fig. 18): it increases with increasing the duration of PA treatment with  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and the temperature of this solution.



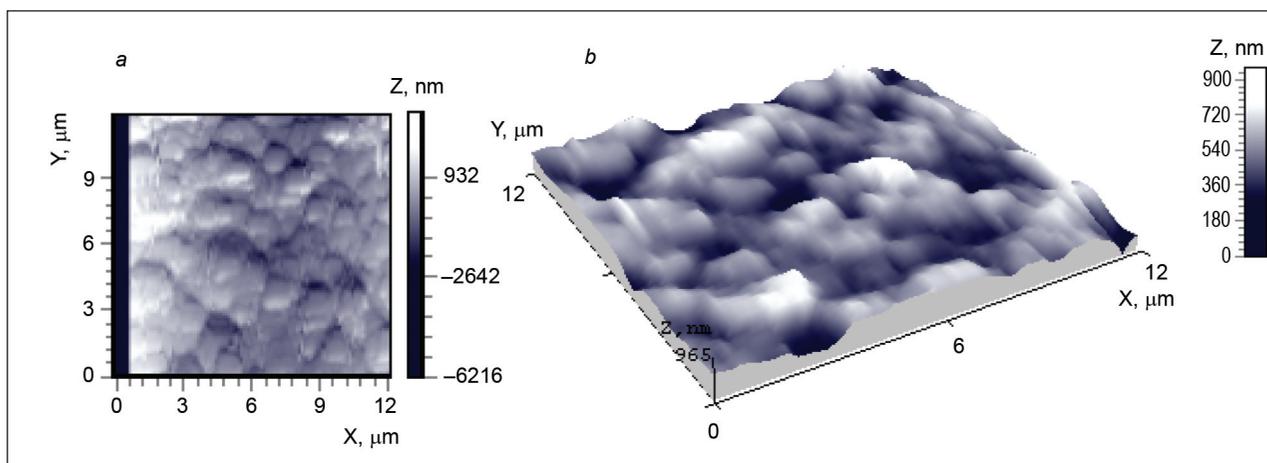
**Fig. 10.** Dependence of the thickness of  $\text{Cu}_x\text{S}$  coating on the duration of PA treatment with  $\text{H}_2\text{S}_{12}\text{O}_6$  solution at 40 °C



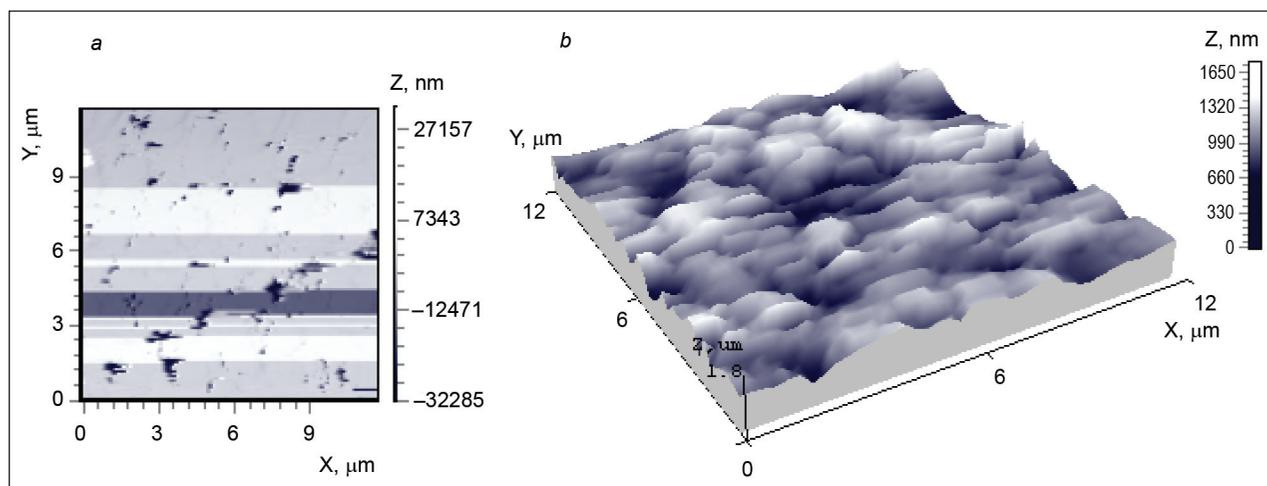
**Fig. 11.** Dependence of average roughness of  $\text{Cu}_x\text{S}$  coating on the duration of PA treatment with  $\text{H}_2\text{S}_{12}\text{O}_6$  solution at 40 °C



**Fig. 12.** Atomic force microscopy view of thin  $\text{Cu}_x\text{S}$  layers formed on PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). PA was sulfurized for 4.0 h at 20 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with alkalified  $\text{Cu}(\text{II}/\text{I})$  salt solution



**Fig. 13.** Atomic force microscopy view of thin  $\text{Cu}_x\text{S}$  layers formed on PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). PA was sulfurized for 4.0 h at 30 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with alkalified  $\text{Cu}(\text{II}/\text{I})$  salt solution



**Fig. 14.** Atomic force microscopy view of thin  $\text{Cu}_x\text{S}$  layers formed on PA surface: 2D view of lateral forces microscopy (a) and 3D topography view (b). PA was sulfurized for 4.0 h at 50 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with alkalified  $\text{Cu}(\text{II}/\text{I})$  salt solution

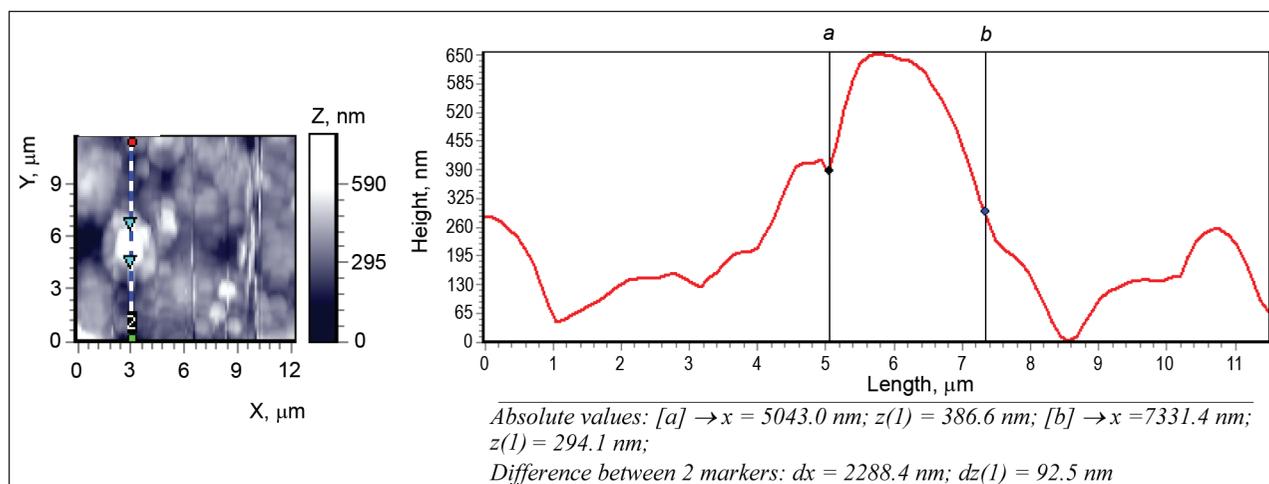


Fig. 15. Topographic image and line profile of sulfide coating formed on PA surface. PA was sulfurized for 4.0 h at 20 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with Cu(II/I) salt solution

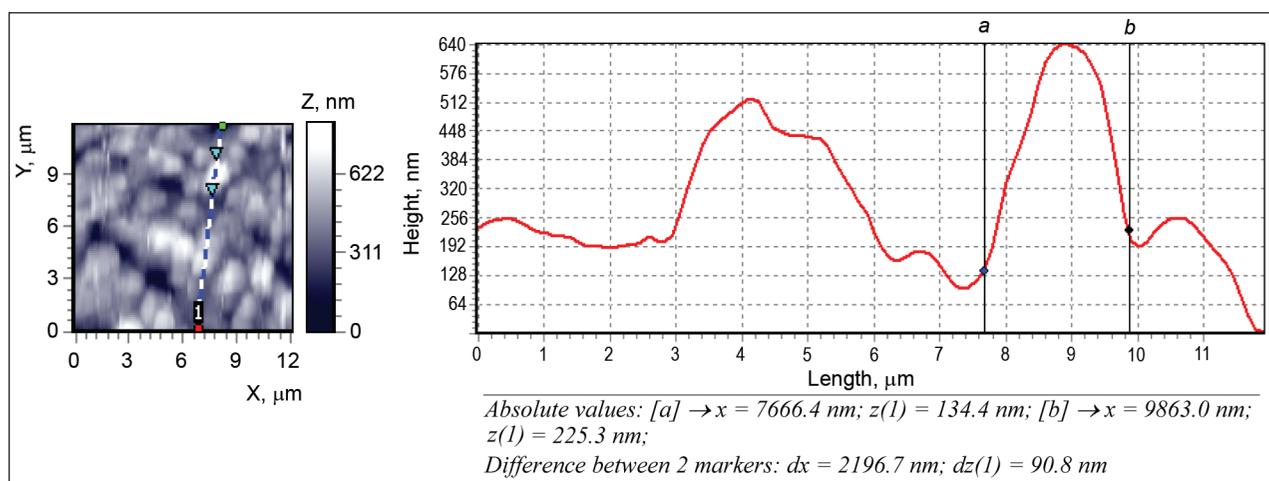


Fig. 16. Topographic image and line profile of sulfide coating formed on PA surface. PA was sulfurized for 4.0 h at 30 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with Cu(II/I) salt solution

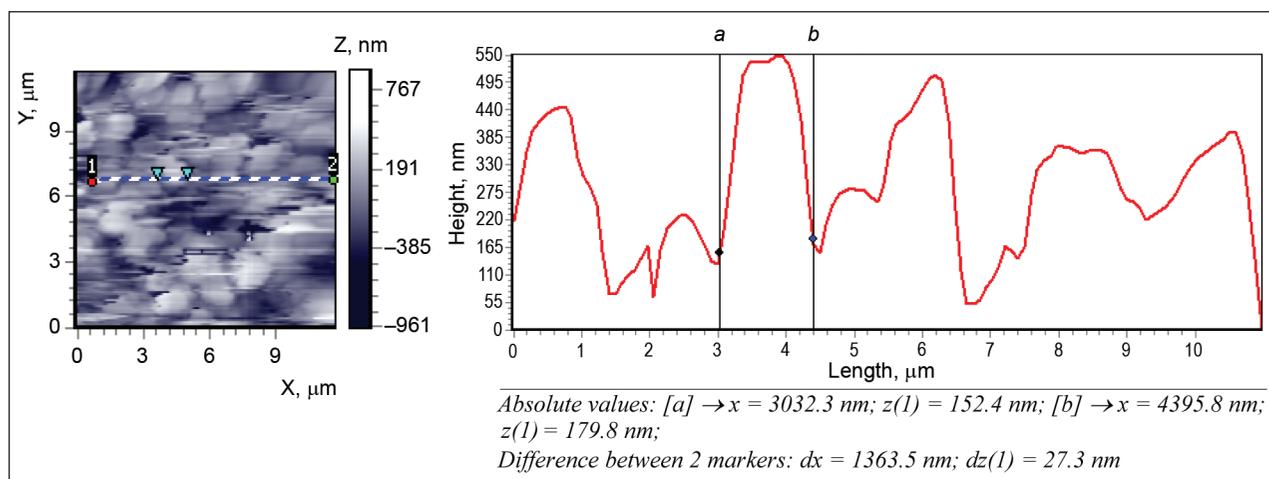


Fig. 17. Topographic image and line profile of sulfide coating formed on PA surface. PA was sulfurized for 4.0 h at 50 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with Cu(II/I) salt solution

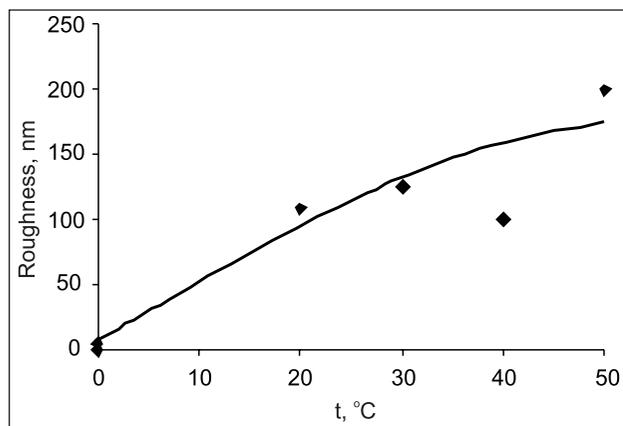


Fig. 18. Dependence of coating average roughness on the temperature of PA treatment for 4.0 h in  $H_2S_{12}O_6$  solution

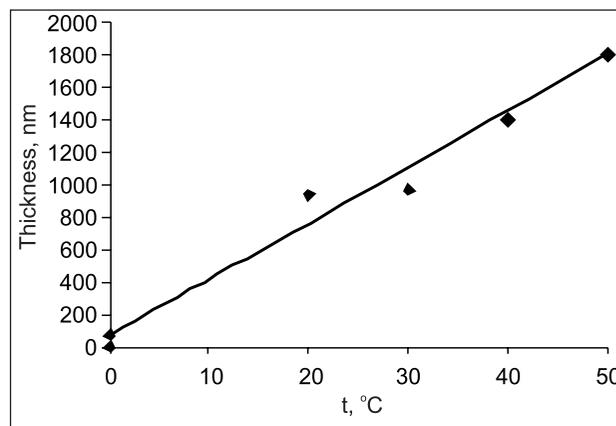


Fig. 19. Dependence of the thickness of  $Cu_xS$  coating on temperature when PA was sulfurized for 4.0 h in  $H_2S_{12}O_6$  solution and then treated with  $Cu(II/I)$  salt solution

## CONCLUSIONS

1. The morphology of  $Cu_xS$  layers formed on polyamide 6 film surface employing solutions of dodecathionic acid,  $H_2S_{12}O_6$ , was studied by the atomic force microscopy method. Copper sulfide layers were found to form unevenly as islands which grew into bigger agglomerates.

2. The morphology and roughness of  $Cu_xS$  layers depend significantly on the conditions of initial polymer sulfurization with  $H_2S_{12}O_6$  solution if the same conditions of sulfurized polyamide treatment in copper(II/I) salt solution have been used.

3. The thickness of a sulfide layer increases with increasing the duration and temperature of polyamide sulfurization. The same tendency is observed in the change of the average roughness of  $Cu_xS$  layers: it increases with increasing the duration and temperature of polymer sulfurization.

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## VARIO SULFIDŲ SLUOKSNIŲ, SUDARYTŲ POLIAMIDO 6 PLĖVELĖS PAVIRŠIUJE, MORFOLOGIJOS TYRIMAS ATOMINĖS JĖGOS SPEKTROSKOPIJA

### Santrauka

Atominių jėgų mikroskopijos (AJM) metodu ištirta vario sulfidinių,  $Cu_xS$ , sluoksnių, sudarytų poliamido 6 plėvelių paviršiuje naudojant dodekationato rūgšties,  $H_2S_{12}O_6$ ,  $0,002 \text{ mol} \cdot \text{dm}^{-3}$  koncentracijos tirpalus, morfologija. Vario sulfidiniai sluoksniai PA paviršiuje sudaryti, apdorojant plėveles dodekationato rūgšties tirpalais ir po to jas veikiant  $Cu(II/I)$  druskų tirpalu. Nustatyta, kad dėl poliamido 6 sierinimo  $H_2S_{12}O_6$  tirpale trukmės ir temperatūros (esant vienodoms sierinto PA „variavimo“ sąlygoms) vario sulfidų sluoksniai formuojasi netolygiai, salelėmis, kurios suauga į didesnius aglomeratus. Susidariusios dangos paviršius nelygus, gana šiurkštus. Nustatytas  $Cu_xS$  dangos aukštis didėja ilginant polimero apdorojimo  $H_2S_{12}O_6$  tirpale trukmę ir didinant temperatūrą. Analogiškai kinta ir vario sulfidinių sluoksnių paviršiaus šiurkštumas: jis didėja ilginant PA apdorojimo  $H_2S_{12}O_6$  tirpale trukmę ir didinant temperatūrą.