

# Thallium sulfides and their layers on polyamide surface

Vitalijus Janickis\*,

Rūta Stokienė

*Kaunas University of Technology,  
Radvilėnų 19, LT-50254 Kaunas,  
Lithuania*

When polyamide 6 (PA) films are exposed for different time to acidified solutions of sodium trithionate,  $\text{Na}_2\text{S}_3\text{O}_6$ , and sodium tetrathionate,  $\text{Na}_2\text{S}_4\text{O}_6$ , and later to alkalified solution of  $\text{Tl}_2\text{SO}_4$ ,  $\text{Tl}_x\text{S}$  layers on PA films are formed. A study of IR and UV absorption spectra has shown that pentathionate,  $\text{S}_5\text{O}_6^{2-}$ , ions are sorbed from acidified water solutions of potassium pentathionate,  $\text{K}_2\text{S}_5\text{O}_6$ , by PA films. The concentration of pentathionate ions sorbed into a polymer increases with increasing the concentration of  $\text{K}_2\text{S}_5\text{O}_6$  solution, as well as the temperature and duration of treatment. A layer of nonstoichiometric thallium sulfide,  $\text{Tl}_x\text{S}$ , was obtained after treating sulfurized PA with a solution of  $\text{Tl}_2\text{SO}_4$ . The concentration of thallium increased when the concentration and temperature of the pentathionate solution had been increased. Supposedly, a compact  $\text{Tl}_x\text{S}$  layer forms on the PA film, which terminates the further diffusion of  $\text{Tl}^+$  ions from  $\text{Tl}(\text{I})$  salt solution. The water solution of dodecathionic acid,  $\text{H}_2\text{S}_{12}\text{O}_6$ , acts effectively as a sulfurization agent of PA. The values of sulfur concentration in PA increase with increasing the duration of treatment and the temperature of  $\text{H}_2\text{S}_{12}\text{O}_6$  solution.  $\text{Tl}_x\text{S}$  layers are formed on the surface of PA film if a polymer sulfurized in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution is treated with alkalified solution of  $\text{Tl}_2\text{SO}_4$ . The concentration of thallium in the polyamide film increases with increasing the duration and temperature of initial sulfurization. Four thallium sulfide phases,  $\text{TlS}$ ,  $\text{Tl}_2\text{S}_2$ ,  $\text{Tl}_4\text{S}_3$  and  $\text{Tl}_2\text{S}_5$ , were identified in the composition of the layers by X-ray diffraction. The determined regularities enable formation by the sorption–diffusion method of thallium sulfide layers of a desirable composition, using dodecathionic acid as a PA sulfurization agent. The XPS analysis of  $\text{Tl}_x\text{S}$  layers, formed by using  $\text{H}_2\text{S}_{12}\text{O}_6$  solution as a precursor, showed various thallium, sulfur and oxygen compounds:  $\text{Tl}_2\text{O}_3$ ,  $\text{Tl}_2\text{S}_3$ ,  $\text{Tl}_2\text{S}$ ,  $\text{S}_8$ ,  $\text{Tl}_2\text{SO}_4$  and  $\text{Tl}(\text{OH})_3$ . Studies of  $\text{Tl}_x\text{S}$  layer surface morphology by the AFM method have shown that, depending on the temperature of the initial polyamide sulfurization in  $\text{K}_2\text{S}_5\text{O}_6$  or  $\text{H}_2\text{S}_{12}\text{O}_6$  solution (in the same “thalliumizing” conditions of sulfurized PA), thallium sulfide layers are formed unevenly as islands which grow into bigger agglomerates. The surface of the coatings is rather uneven and rough.

**Key words:** review, polythionates, polyamide, thallium sulfide layer

## INTRODUCTION

Nano-structured composite materials are intensively studied during the last decade as new possibilities for advanced devices.

Binary thallium chalcogenides possess unique physical properties important for advanced science and technology; for example, they are used in solar batteries, while  $\text{TlS}$  and  $\text{Tl}_2\text{S}$  are photoconductors; thus, layers of thallium chalcogenides formed on the surface of polymeric materials can be useful for the specific photonic applications [1–3]. Layers of

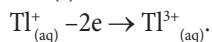
thallium sulfides show a great variety of stoichiometry, valuable physical properties and find applications in photoconductive devices and solar batteries [4–6].

The great number of these compounds and thus the large variety of their physical properties are determined by possible different oxidation states (+1 and +3) of thallium atoms in the compounds. In the thallium–sulfur system, many types of sulfides have been reported:  $\text{Tl}_2\text{S}$ ,  $\text{Tl}_4\text{S}_3$ ,  $\text{TlS}$ ,  $\text{TlS}_2$ ,  $\text{Tl}_2\text{S}_5$ ,  $\text{Tl}_2\text{S}_9$ . Here,  $\text{TlS}$  and  $\text{Tl}_4\text{S}_3$  are double sulfides:  $\text{Tl}^{\text{I}}[\text{Tl}^{\text{III}}\text{S}_2]$  and  $\text{Tl}^{\text{I}}_3[\text{Tl}^{\text{III}}\text{S}_3]$ , respectively, whereas  $\text{TlS}_2$ ,  $\text{Tl}_2\text{S}_5$ ,  $\text{Tl}_2\text{S}_9$  may be considered as polysulfides  $\text{Tl}_x\text{SS}_n$  (for example,  $\text{Tl}_2\text{SS}_8$  with elemental composition:  $\text{Tl}_2\text{S}_9$ ). It is known, as mentioned above, that  $\text{TlS}$ ,  $\text{Tl}_2\text{S}$  and  $\text{Tl}_4\text{S}_3$  are photoconductors [4, 6, 7].

\* Corresponding author. E-mail: vitalijus.janickis@ktu.lt

Thallium sulfides are usually coloured substances, most often of brown, red and black colour, insoluble in water, hydroxide solutions and in the majority of organic solvents [8].

It is known [9] that Tl(I) compounds in neutral solutions are more stable than Tl(III) compounds, but in alkaline solutions Tl(I) ions undertake oxidation into Tl(III) [10–12]:



The methods of formation of electrically conductive *p*- and *d*-metal sulfide layers on the surface of dielectrics, which have been and still are studied at Lithuanian scientific institutions (Vilnius University, Institute of Chemistry, Kaunas University of Technology), according to their mechanism may be divided into two main groups. The chemical methods when layer forms as a result of precipitation reaction in a solution containing metal ions and a chalcogenation agent are ascribed to the first group. Sorptive methods when the surface of dielectric does sorb compounds of poor solubility which later are converted into electrically conductive metal chalcogenides are ascribed to the second group [13].

The chemical bath deposition (CBD) method is most often used in the deposition of electrically conductive layers of gallium, indium and thallium sulfides on various substrates. Nair with coworkers and other researchers [14–18] for a number of years have been studying the mechanism of formation of electrically conductive layers by the CBD method and the optical and electrical properties of the layers obtained. Thin semiconductive coatings of GaS, In<sub>2</sub>S<sub>3</sub>, Tl<sub>2</sub>S, Tl<sub>4</sub>S<sub>3</sub> were deposited on various dielectrics. Polycrystalline layers are obtained by this method and, for the layer to acquire properties specific to a certain sulfide, the obtained coatings must be treated thermally at a certain temperature in the air or in the nitrogen atmosphere.

Thin thallium sulfide layers on glass, covered with a thin layer of ZnS as an activator, are deposited from a mixture of thallium citrate complex and thiocarbamide at a temperature of 25–50 °C [15]. X-ray diffraction analysis has shown that Tl<sub>2</sub>S and Tl<sub>4</sub>S<sub>3</sub> phases prevail in the obtained coating, and on a glass sulfide a coating 0.1–0.75 μm thick is deposited. Almost amorphous layers of Tl<sub>4</sub>S<sub>3</sub> or Tl<sub>2</sub>S composition were photoconductors. The electrical conductance of the heated and then cooled layer was  $7.5 \cdot 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$  and the photoconductivity  $5 \cdot 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$  which are typical of such cases.

From the mixture of thallium(I) nitrate, ammonia and thiocarbamide (sulfurization agent), dark brown and black homogeneous Tl<sub>x</sub>S coatings on glass were obtained [19]. The phase composition of the coating studied by X-ray diffraction showed the domination of TlS phase. The morphology of the coating was studied with a scanning electron microscope: the thickness was about 0.5 μm. According to authors of the study [19], this coating has a *p*-type conductivity.

Thin Tl<sub>2</sub>S (0.05–1 μm) layers of Tl<sub>2</sub>S were obtained on the glass surface of using a precipitation mixture composed of thallium(I) nitrate and thiocarbamide solutions [14].

Sulfide layers of galium subgroup metals may be of various phase composition and photoconductive.

Summarizing the reviewed literature concerning the chemical deposition method, we may state that this method has some advantages but also disadvantages such as a large number of stages, complicated preparation of the surface, the use of expensive catalysts and the unstability of solutions.

The sorption–diffusion method for obtaining thallium sulfide layers is simple and promising. In this method, after sorption of the sulfurization agent, the polymer substance is treated with a thallium salt aqueous solution. The solutions of polythionic acids, H<sub>2</sub>S<sub>n</sub>O<sub>6</sub> (n = 3–45), are suitable for sulfurization of the majority of polymers [20]. Recently, it has been reported [21] that thallium sulfide layers on polyethylene (PE) surface can be deposited using a solution of higher polythionic acids.

Studies carried out at the Department of Inorganic Chemistry of the Kaunas University of Technology [22, 23] have shown that polythionates are suitable for the sulfurization of polymeric substances and are used to form on polymer surface semiconducting and electrically conducting copper sulfide layers which are important for advanced technology (the results of the studies were patented) [24, 25].

On continuation of studies on the use of polythionates as sulfurization agents for the modification of polymers, in a number of works for the polycapromide polyamide 6 sulfurization and formation on its surface of thallium sulfide (Tl<sub>x</sub>S) layers we used acidified solutions of lower polythionates (trithionate, S<sub>3</sub>O<sub>6</sub><sup>2-</sup>, tetrathionate, S<sub>4</sub>O<sub>6</sub><sup>2-</sup>, pentathionate, S<sub>5</sub>O<sub>6</sub><sup>2-</sup>) and a solution of dodecathionic acid, H<sub>2</sub>S<sub>12</sub>O<sub>6</sub>.

The aim of the present work was to summarize, review and discuss the results obtained by us during systematic studies of the processes of interaction of the sulfurization agent, H<sub>2</sub>S<sub>n</sub>O<sub>6</sub>, with the semi-hydrophilic polymeric material – polyamide 6 film (PA), as well as of sulfurized polymer treatment with a thallium(I) salt solution on the formation of thallium sulfide layers [26–37]. The chemical and phase composition of Tl<sub>x</sub>S layers was studied by the methods of atomic absorption spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy (XPS). Atomic Force (AFM) microscopies were used to characterize the surface morphology of thallium sulfide layers.

## EXPERIMENTAL

A PA 6 film (specification TY 6-05-1775-76, grade PK–4, 70 μm thick) produced in Russia was used. Prior to the experiments, pieces of the film 15 × 70 mm in size had been boiled in distilled water for 2 h to remove the remainder of the monomer. Then they were dried with filter paper and kept in a desiccator over CaCl<sub>2</sub> for 24 h.

Distilled water, chemically and analytically pure reagents were used to produce solutions.

The salts of polythionates – sodium trithionate monohydrate, Na<sub>2</sub>S<sub>3</sub>O<sub>6</sub> · H<sub>2</sub>O, sodium tetrathionate dihydrate, Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> · 2H<sub>2</sub>O, and potassium pentathionate hemihydrate, K<sub>2</sub>S<sub>5</sub>O<sub>6</sub> · 1.5H<sub>2</sub>O, – were prepared employing methods

described in classical literature [38–40]. The prepared salts were kept in the dark, in a desiccator over concentrated sulfuric acid.

For polymer sulfurization, 0.1 and 0.2 mol · dm<sup>-3</sup> acidified with HCl (0.1 mol · dm<sup>-3</sup>) Na<sub>2</sub>S<sub>3</sub>O<sub>6</sub> and Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> solutions at a temperature of 30 and 50 °C, and 0.025–0.2 mol · dm<sup>-3</sup> acidified with HCl (0.1 mol · dm<sup>-3</sup> HCl, pH ~1.5) solutions of K<sub>2</sub>S<sub>5</sub>O<sub>6</sub> at a temperature 0–20 °C were used.

0.002 mol · dm<sup>-3</sup> solution of dodecathionic acid was prepared and the average number of sulfur atoms in the polythionic acid molecule was determined by the methods developed by J. Janickis with coworkers [41]. For PA sulfurization, H<sub>2</sub>S<sub>12</sub>O<sub>6</sub> solutions at a temperature of 20–50 °C were used.

For the formation of Tl<sub>x</sub>S layers, sulfurized PA film samples were treated with unstirred 0.1 mol/dm<sup>3</sup> Tl<sub>2</sub>SO<sub>4</sub> (pH 2.8) solution containing KOH (0.015 mol · dm<sup>-3</sup>) [42, 43] during 10 min at a temperature of 80 °C. When using alkalified Tl(I) salt solution, thallium sulfide layers on the surface of PA were obtained. After treatment with the solution of Tl(I) salt, PA samples were rinsed with distilled water, dried over anhydrous CaCl<sub>2</sub> and used in further experiments.

Sulfur concentrations (C<sub>s</sub>) in PA film samples were determined potentiometrically [44]. First, a sample of a sulfurized PA film was treated under heating with 10–15 ml of 10 mol · dm<sup>-3</sup> KOH solution and diluted with the same amount of distilled water. Standard calomel and platinum electrodes were used for the potentiometric titration of the solution obtained in KOH with 0.05 N solution of iodine under stirring. For potentiometric measurements, a pH-meter (pH–673 M millivoltmeter) was used.

The concentrations of thallium (C<sub>Tl</sub>, mg · g<sup>-1</sup>) in PA films were determined by the atomic absorption spectroscopy method using a Perkin–Elmer 503 atomic absorption spectrophotometer [45]. PA films modified by Tl<sub>x</sub>S layers were dissolved in 2 cm<sup>3</sup> of concentrated HNO<sub>3</sub>, diluted with distilled water and boiled for 30 min (complete degradation of PA film). Then the solution was diluted up to 25 cm<sup>3</sup> and analysed.

The UV, VIS (200–400 nm) and IR (400–1400 cm<sup>-1</sup>) spectra were obtained with the aid of Spectronic<sup>R</sup> Genesys<sup>TM</sup> and Perkin–Elmer GX spectrometers, system FT–IR.

X-ray diffraction analysis of thallium sulfide layers was performed employing a ДПОH-6 X-ray diffractometer (Russia) (supply unit ПYP 5.50), radiation CuK<sub>α</sub> Ni filter, monochromator angular, stream in a tube 30 μA, working voltage 30 kV). X-ray diffraction data were analysed with Search Match, Xfit, ConvX and Excel computer programs.

XPS spectra of thallium sulfide layers were recorded with an ESCALAB MKII spectrometer (VG Scientific, radiation Mg K<sub>α</sub> 1253.6 eV, output 300 W). Vacuum in the analysing chamber was kept at a level of 1.33 · 10<sup>-8</sup> Pa, the distribution of elements in the depth was determined by sputtering with an Ar<sup>+</sup> gun with the ion energy of about 1.0 keV. The samples were etched in a preparation chamber with the vacuum 9.3 · 10<sup>-3</sup> Pa and current 20 μA; the rate of etching was 1 nm / 30 s. The maximum accuracy of the method was ± 0.1 at. %. To inves-

tigate the layers obtained by the XPS method, the photoelectron spectra of Tl4f7, O1s and S2p were recorded. Empirical sensitivity factors for these elements were taken from the literature [46], and the spectra obtained were compared with the standard ones [47].

The morphology of the surface of Tl<sub>x</sub>S layers, the quantitative microscopy of the roughness of precipitated layers on the surface of PA were studied employing an NT-206 atomic force microscope, in contact regime with high resolution probes with the force constant k = 3 N/m. The characteristics of the atomic force microscope: the maximum scan field area up to 15 × 15 microns, the measurement matrix up to 512 × 512 points and more, the maximum range of measured heights 2.5 microns, lateral resolution 2 nm, vertical resolution 0.1–0.2 nm. Lateral force microscopy studies are useful for imaging variations in surface friction that can arise from inhomogeneity in surface material, and also for obtaining edge-enhanced images of any surface.

## RESULTS AND DISCUSSION

The modification of PA film by creating on its surface layers of thallium sulfides was performed in two stages. The first stage of this process is the interaction of PA film with a polythionate solution when the sulfurization of PA film occurs, i. e. anions containing sulfur atoms sorb-diffuse into the matrix of the PA surface.

In the second stage, the sulfurized PA film is treated with Tl(I) sulfate water solution. As a result of the interaction of thallium ions with the polythionate ions sorbed-diffused in the PA film containing sulfur atoms of low oxidation state, layers of thallium sulfides of variable composition are formed on the polymer surface.

### Modification of PA films with layers of thallium sulfides by lower polythionates – sodium trithionate monohydrate, Na<sub>2</sub>S<sub>3</sub>O<sub>6</sub> · H<sub>2</sub>O, and sodium tetrathionate dihydrate, Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> · 2H<sub>2</sub>O

Earlier it has been determined [48] that the rate of sorption by PA of S<sub>3</sub>O<sub>6</sub><sup>2-</sup> and S<sub>4</sub>O<sub>6</sub><sup>2-</sup> ions from water solutions of its salts increases with an increase in solution concentration and that it proceeds faster from acidified solutions since amorphization of the polymer under the action of H<sup>+</sup> and polythionate ions occurs, and it lasts shorter to penetrate in-between the macromolecules of the polymer [49]. The saturation of the polymer with sulfur in Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> solutions of both used concentrations proceeds in the same manner (Fig. 1, curves 1 and 2): the concentration of sulfur in PA during the first hour increases and later gradually decreases. The decrease of sulfur concentration after 1 h of sulfurization may be explained by the known S<sub>4</sub>O<sub>6</sub><sup>2-</sup> ion decomposition forming elemental sulfur, SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> ions, with the latter two withdrawing from the polymer.

In the second stage of PA film modification, after samples of the polymer sulfurized in Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> solution had been

treated for 10 min with an alkalified  $Tl_2SO_4$  solution at a temperature of 80 °C, layers of thallium sulfides,  $Tl_xS$ , were formed on its surface: the colourless PA films became brown with a metallic tint.

Thallium concentration in PA films sulfurized for up to 2 h increases (Fig. 1, curves 3 and 4). With the further prolongation of the initial PA film sulfurization, the concentration of thallium in PA gradually decreases. Also, contrary to sulfur, the concentration of thallium is higher in the polymer which was sulfurized in a  $Na_2S_4O_6$  solution of a lower concentration (Fig. 1, curve 3). The decrease of thallium concentration in the polymer after it has reached the highest value, and the higher thallium concentration in the polymer sulfurized in a  $Na_2S_4O_6$  solution of a lower concentration may be explained by the reduction of  $S_4O_6^{2-}$  ion stability with time in the solution of a higher concentration, since in the polymer after decomposition only the elemental sulfur remains, which is slower than polythionate ions to react with  $Tl^+$  ions.

The saturation of the polymer with sulfur in  $Na_2S_3O_6$  solution at a temperature of 50 °C is reached after 3 h, and in the solution of a lower temperature the concentration of sulfur increases throughout the whole experimental time (Fig. 2, curve 2). The faster increase in sulfur concentration during PA film sulfurization at a higher temperature may be explained by the fact that the swelling of PA at a higher temperature proceeds at a higher rate, the distance between the PA macromolecules increases, and this accelerates the diffusion of  $S_3O_6^{2-}$  ions. The concentration of thallium, depending on the duration of the initial sulfurization and the temperature of  $Na_2S_3O_6$  solution, increases in PA films sulfurized for 0.5 and 2 h (Fig. 2, curves 3 and 4), and later it does not change or slightly reduces. The decrease of thallium concentration with an increase in the duration of sulfurization with  $Na_2S_3O_6$  solution and the higher thallium concentrations while sulfurizing with the solution of a lower temperature may be explained by the lower stability of  $S_3O_6^{2-}$  ions at a higher temperature. The values of  $Tl : S$  molar ratios in the PA film with the prolongation of sulfurization time and an increase in the temperature of  $Na_2S_3O_6$  solution increase in the interval 1 : 2–1 : 20.

The above results indicate that using acidified solutions of sodium trithionate and tetrathionate, on PA surface it is possible to form thallium sulfide layers of various composition. However, the  $Tl_xS$  layers were too thin to allow studying their phase composition by X-ray diffraction. Therefore, in the further studies, for the formation of  $Tl_xS$  layers on PA surface, polythionates of higher sulfurity (containing more sulfur atoms in the molecule) – potassium pentathionate ( $K_2S_5O_6 \cdot 1.5H_2O$ ) and dodecathionic acid ( $H_2S_{12}O_6$ ) – solutions were used as precursors.

#### Formation of thallium sulfide layers on PA surface sulfurized in potassium pentathionate solution

The nature of sulfur-containing particles sorbed by a PA film was studied by means of IR and UV absorption spectra of polymer films treated in a potassium pentathionate solution.

It was found that the peaks of most intensive bands in the IR spectra of PA samples sulfurized in a  $K_2S_5O_6$  solution, recorded by the compensation method (PA absorption eliminated), were in the intervals 418–484, 523–568, 609–737, 985–1079, 1111–1284  $cm^{-1}$  (Fig. 3), and on the basis of results on IR spectra of polythionates reviewed in the work [50] they were assigned to the  $\nu_{S-S}$ ,  $\delta_{as}(O-S-O)$ ,  $\delta_s(O-S-O)$ ,  $\nu_s(S-O)$  and  $\nu_{as}(S-O)$  vibrations, respectively.

These results have confirmed that the sorption of pentathionate ions by PA occurs during polymer treatment with an acidified  $K_2S_5O_6$  solution. The UV absorption spectra of PA

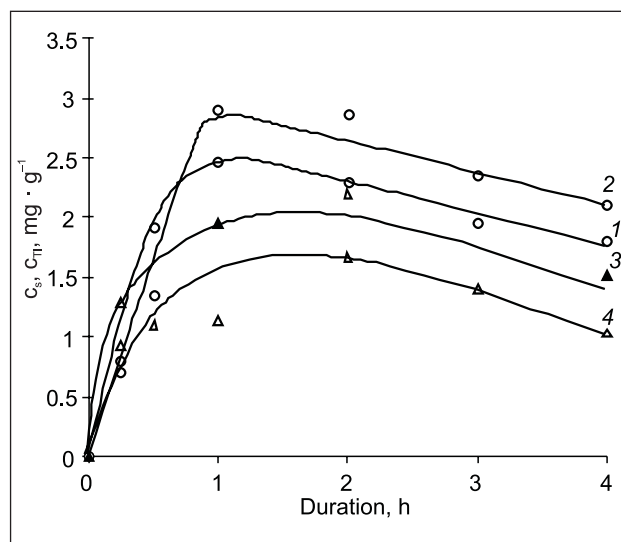


Fig. 1. Time-related changes of sulfur ( $c_s$ ) and thallium ( $c_{Tl}$ ) concentration in PA films sulfurized with  $Na_2S_4O_6$  at a temperature of 50 °C and treated with  $Tl_2SO_4$  solutions. Concentration of  $Na_2S_4O_6$ ,  $mol \cdot dm^{-3}$ : 1 ( $c_s$ ) – 0.1; 2 ( $c_s$ ) – 0.2; 3 ( $c_{Tl}$ ) – 0.1; 4 ( $c_{Tl}$ ) – 0.2

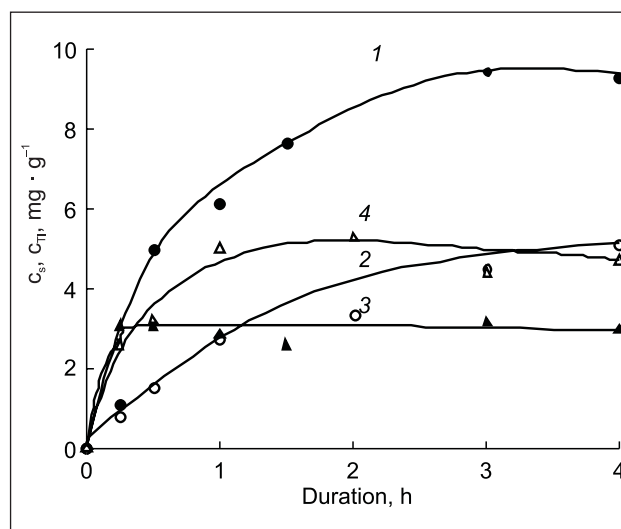
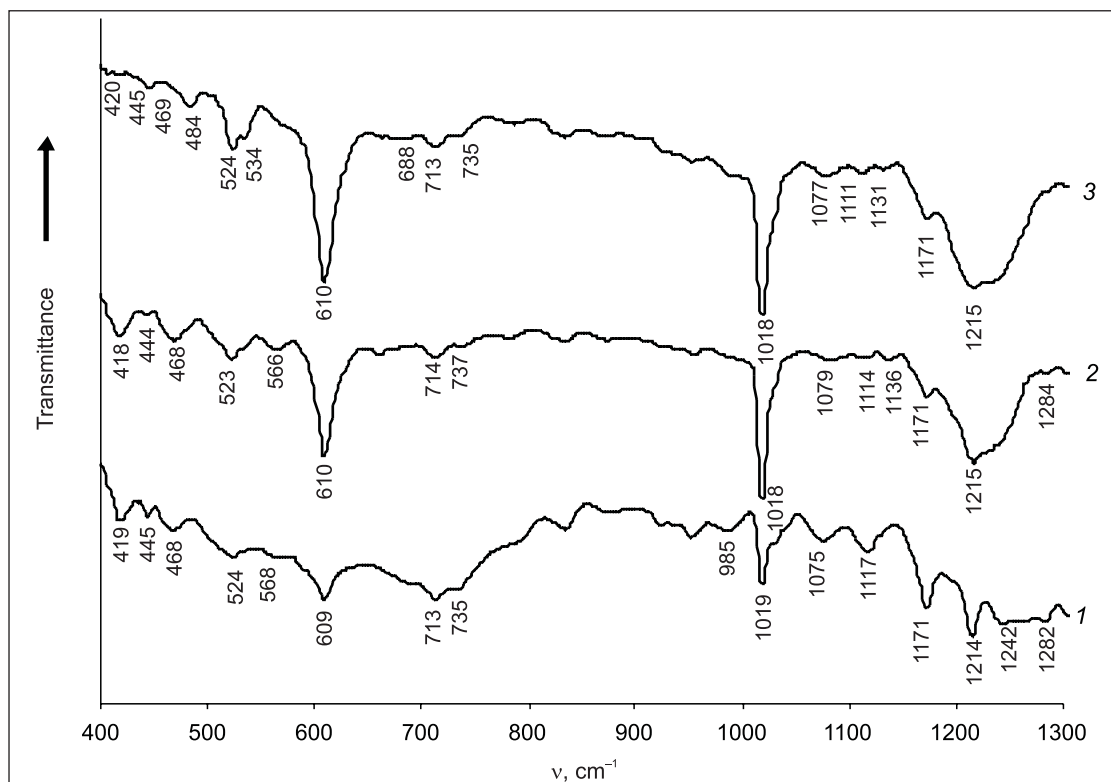
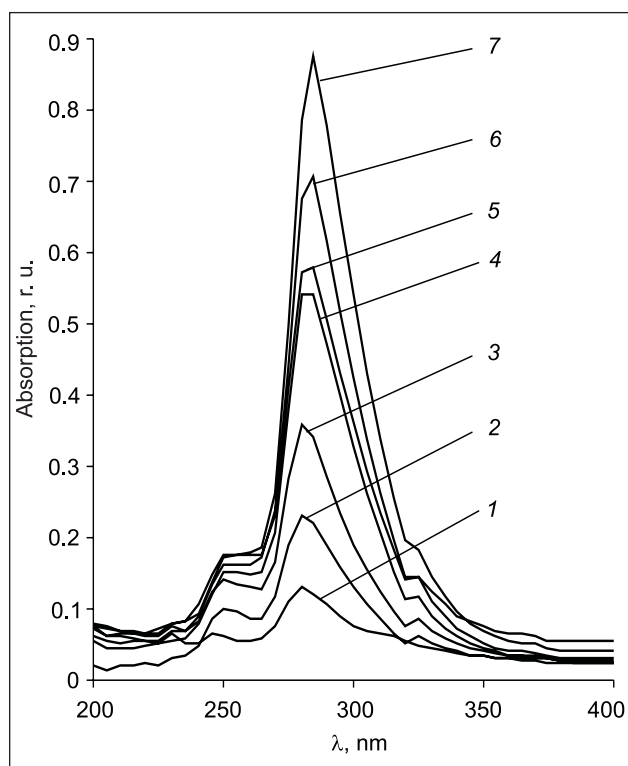


Fig. 2. Time-related changes of sulfur and thallium concentration in PA films sulfurized with 0.2  $mol \cdot dm^{-3}$  solution of  $Na_2S_3O_6$  at a temperature, °C: 1 – 50 ( $c_s$ ); 2 – 30 ( $c_s$ ); 3 – 50 ( $c_{Tl}$ ); 4 – 30 ( $c_{Tl}$ )





**Fig. 3.** IR absorption spectra of PA films sulfurized in acidified ( $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$ ,  $\text{pH} \sim 1.5$ )  $0.2 \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2\text{S}_5\text{O}_6$  solution at a temperature of  $10^\circ\text{C}$  for different periods of time. Duration of PA sulfuration, h: 1 – 1, 2 – 2, 3 – 5



**Fig. 4.** UV absorption spectra of PA films sulfurized in acidified  $0.05 \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2\text{S}_5\text{O}_6$  solution at a temperature of  $10^\circ\text{C}$  for different periods of time. Duration of PA sulfuration, h: 1 – 0.25, 2 – 1, 3 – 2, 4 – 3, 5 – 4, 6 – 5, 7 – 6

samples sulfurized for different periods of time in a  $\text{K}_2\text{S}_5\text{O}_6$  solution are observed at 250, 285 and 325 nm (Fig. 4).

According to data of a study of UV absorption spectra of lower potassium polythionates [50], the absorption maxima of pentathionate ions are most intensive at 256 and 295 nm. Thus, UV absorption spectra recorded by us have again confirmed that sulfur is sorbed by PA films in the form of pentathionate ions.

Chemical analysis of PA samples sulfurized in a  $\text{K}_2\text{S}_5\text{O}_6$  solution showed that the concentration of sulfur sorbed by a polymer increased with increasing the temperature of the sulfuration solution (Fig. 5). The concentration of sorbed sulfur increased with an increase of the temperature of  $\text{K}_2\text{S}_5\text{O}_6$  solution. The values of sulfur concentration obtained in PA (up to  $\sim 7.5 \text{ mg} \cdot \text{g}^{-1}$ ) were significantly higher than those obtained in the study in which the sorption of lower polythionates – trithionate,  $\text{S}_3\text{O}_6^{2-}$ , and tetrathionate,  $\text{S}_4\text{O}_6^{2-}$  – by PA films had been studied. Thus, the results obtained in the present work provided conditions for the formation of thallium sulfide,  $\text{Tl}_x\text{S}$ , layers on PA surface.

The layers of thallium sulfides,  $\text{Tl}_x\text{S}$ , were formed on the surface of PA samples sulfurized in  $\text{K}_2\text{S}_5\text{O}_6$  solution after their treatment with alkalinized  $\text{Tl}_2\text{SO}_4$  solution. The concentration of thallium increased when the concentration and temperature (Fig. 6) of the pentathionate solutions were increased, but its increase was observed only when the duration of the initial polymer treatment was prolonged until 1 h, although

the sulfur concentration was increasing during 6 h of sulfuration. The dependence of thallium concentration in PA films on the duration of PA initial sulfuration in  $K_2S_5O_6$  solution in all conditions of this process (temperature 1–20 °C, the concentration of solution 0.025–0.2 mol · dm<sup>-3</sup>) is the same. The values of thallium concentrations in the polymer lie in a rather narrow interval of 1.2–2.6 mg · g<sup>-1</sup>. It has been proposed that a compact  $Tl_xS$  layer forms on the PA film and terminates the further diffusion of  $Tl^+$  ions from the solution of  $Tl(I)$  salt, and these ions cannot get into contact with the compounds containing sulfur atoms of a low oxidation state, sorbed–diffused in the initial stage. As a result, the values of  $Tl/S$  molar ratios in the  $Tl_xS$  layers decrease with increasing the duration of the initial stage, sulfuration solution concentration and temperature.

#### Modification of PA films by thallium sulfide layers using dodecathionic acid solutions

The results of the above studies have shown that increasing the number of sulfur atoms in the molecule of polythionate, which serves as a precursor in the formation of thallium sulfide layers on PA surface, leads to higher concentrations of sulfur sorbed–diffused by the polymer, and sulfide layers of a higher thickness are formed. Therefore, dodecathionic acid solutions as precursors of PA sulfuration were studied.

The nature of sulfur-containing particles sorbed by a PA film was studied by means of IR and UV absorption spectra of the polymer films treated in a dodecathionic acid solution.

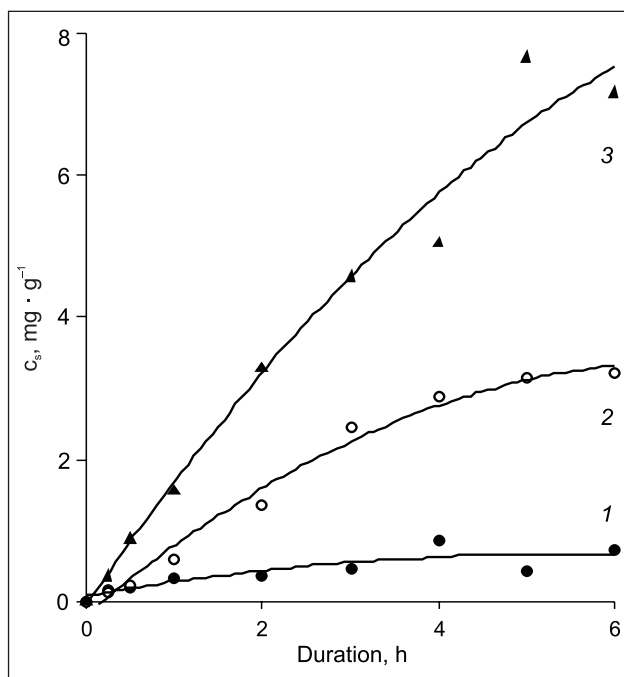


Fig. 5. Time-dependent changes of sulfur concentration in PA films with time during their treatment with acidified 0.1 mol · dm<sup>-3</sup>  $K_2S_5O_6$  solution at a different temperature. Temperature, °C: 1 – 1; 2 – 10; 3 – 20

It was found that the peaks of most intensive bands in the IR spectra of PA samples sulfurized in a  $H_2S_{12}O_6$  solution, recorded by the compensation method (PA absorption eliminated), were in the intervals 420–473 ( $\nu_{s-s}$ ), 503–558 ( $\delta_{as}(O-S-O)$ ), 612–724 ( $\delta_s(O-S-O)$ ), 838–1100 ( $\nu_s(S-O)$ ), 1144–1293 ( $\nu_{as}(S-O)$ ) cm<sup>-1</sup>. Assignment of the absorption

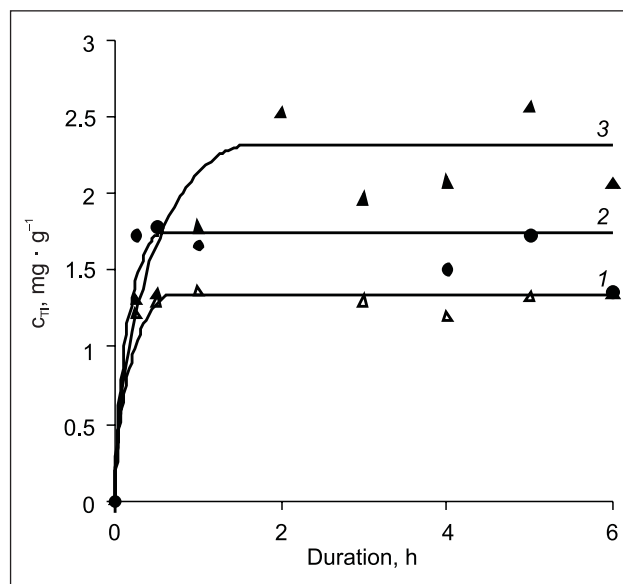


Fig. 6. Time-related changes of thallium concentration in PA films first treated with acidified 0.05 mol · dm<sup>-3</sup> solution of  $K_2S_5O_6$  and then with  $Tl(I)$  salt solution. Temperature of  $K_2S_5O_6$  solution, °C: 1 ( $\Delta$ ) – 1; 2 ( $\bullet$ ) – 10; 3 ( $\blacktriangle$ ) – 20

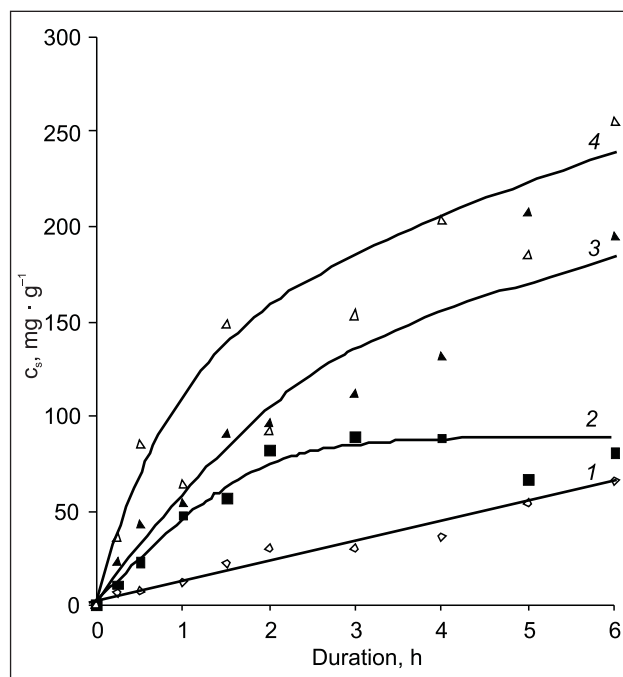
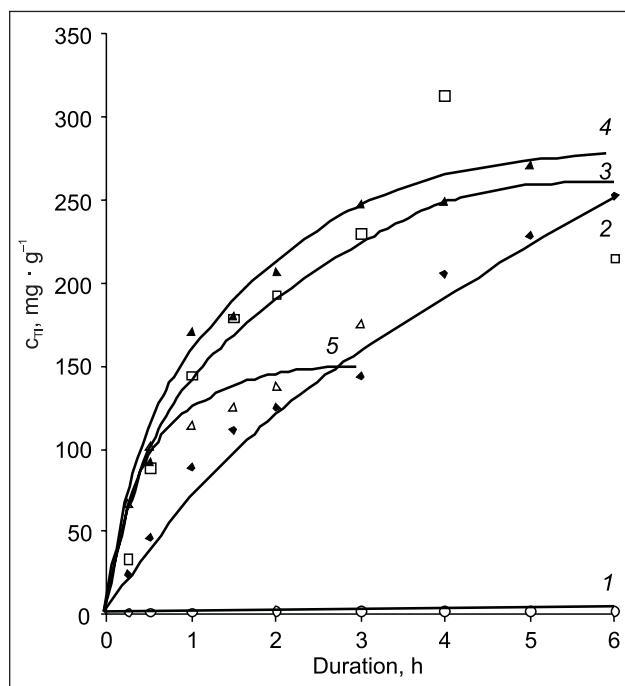


Fig. 7. Time-dependent changes of sulfur concentration in PA films during their treatment with  $H_2S_{12}O_6$  solution at different temperatures. Temperature, °C: 1 – 20, 2 – 30, 3 – 40, 4 – 50



**Fig. 8.** Dependence of the concentration of thallium in sulfide layer on PA film on sulfurization duration when treating it with acidified ( $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$ )  $0.05 \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2\text{S}_2\text{O}_8$  solution at  $20 \text{ }^\circ\text{C}$  (1) and with  $0.002 \text{ mol} \cdot \text{dm}^{-3}$  solution of  $\text{H}_2\text{S}_{12}\text{O}_6$  at different temperatures. The temperature ( $^\circ\text{C}$ ) of  $\text{H}_2\text{S}_{12}\text{O}_6$  solution: 2 – 20, 3 – 30, 4 – 40, 5 – 50

peaks was done on the basis of literature data [20, 50]. These results have confirmed that the sorption of dodecathionate ions by PA occurs during polymer treatment with  $\text{H}_2\text{S}_{12}\text{O}_6$  solution.

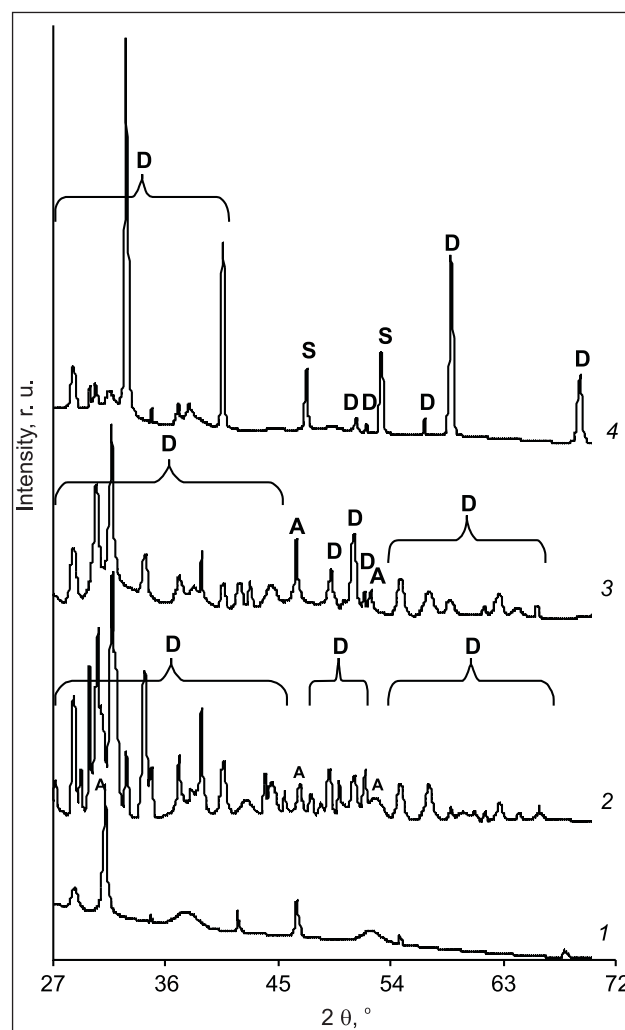
Absorption maxima in the UV absorption spectra of PA samples sulfurized for different periods of time in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution are at  $\sim 225$ ,  $\sim 250$ ,  $\sim 290$  and  $\sim 322$ – $332 \text{ nm}$ . According to data of a study of UV absorption spectra of polythionates [50–53], the absorption maxima of polythionate ions as shoulders and peaks are at  $\sim 215$ ,  $\sim 250$ ,  $\sim 290$  and  $\sim 340 \text{ nm}$ . Thus, UV absorption spectra recorded by us have confirmed again that sulfur is sorbed by PA films in the form of polythionate ions.

The concentration of sulfur in the samples during exposure in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution increased continuously with time (Fig. 7). Sulfur concentrations in the range  $\sim 10$ – $240 \text{ mg} \cdot \text{g}^{-1}$  might be obtained by varying the temperature of  $\text{H}_2\text{S}_{12}\text{O}_6$  solution: a higher sulfur concentration was obtained at a higher temperature.

In order to form  $\text{Tl}_x\text{S}$  layers on the surface of sulfurized PA films, they were treated with an alkalinized  $\text{Tl}_2\text{SO}_4$  solution. The concentration of thallium in the sulfide layer increased with the time of PA sulfurization at all temperatures studied, and a different concentration of thallium at each temperature was reached ( $\sim 150$ – $270 \text{ mg} \cdot \text{g}^{-1}$ ).

The concentration of thallium in PA increases with an increase in the sulfur concentration obtained at a sulfurization

temperature of  $20$ – $40 \text{ }^\circ\text{C}$  (Fig. 8). This is quite understandable since with a higher concentration of sulfur sorbed–diffused into the PA, a larger amount of  $\text{Tl}^+$  ions may be involved in the reaction with the sulfur species. The molar  $\text{Tl/S}$  ratio in thallium sulfide layers on PA surface was calculated from their content measured in PA films. We have found that the  $\text{Tl/S}$  ratio does not depend much on the time of initial PA sulfurization, but in all cases it decreases with increasing the temperature of  $\text{H}_2\text{S}_{12}\text{O}_6$  solution. By changing the conditions of sulfurization, it was possible to obtain thallium sulfide layers on the surface matrix layer of PA of stoichiometrical composition varying from  $\sim \text{Tl}_{0.15}\text{S}$  to  $\text{Tl}_{1.2}\text{S}$ . The decrease of the  $\text{Tl/S}$  molar ratio with an increase in the temperature of the sulfurization solution may be explained by the fact that the concentration of sulfur sorbed–diffused into PA grows with an increase of the sulfurization temperature to a significantly higher extent as compared to the thallium content increase



**Fig. 9.** X-ray diffraction patterns of thallium sulfide layers in the surface of PA. PA was initially treated with a solution of  $\text{H}_2\text{S}_{12}\text{O}_6$  for 3 h at a different temperature and then with a  $\text{Tl(I)}$  salt solution. Temperature,  $^\circ\text{C}$ : 1 – 20, 2 – 30, 3 – 40, 4 – 50. A –  $\alpha$ - $\text{TlS}$ , B – tetragonal  $\text{Tl}_2\text{S}_2$ , C – monoclinic  $\text{TlS}$ , D – orthorhombic  $\text{Tl}_2\text{S}$ , S – elemental sulfur S

with the  $H_2S_{12}O_6$  solution temperature. It seems that the reaction product – thallium sulfides – hinders the further diffusion of  $Tl^+$  ions into the polymer.

Four phases,  $TlS$ ,  $Tl_2S_2$ ,  $Tl_2S_5$  and  $Tl_4S_3$ , were identified by X-ray diffraction analysis in thallium sulfide layers on PA surface. If the duration of the initial PA sulfurization was short (0.5–1.0 h) and the temperature was relatively low (20 °C), the  $\alpha$ - $TlS$  and orthorhombic  $Tl_2S_5$  phases prevailed in the diffractograms of the  $Tl_xS_y$  layers. The phase composition of these layers approached the composition of the orthorhombic  $Tl_2S_5$  phase, if the duration and temperature of the initial polymer sulfurization had been increased. From these data we have concluded that changing the conditions of PA sulfurization leads to the formation of thallium sulfide layers of different composition.

#### X-ray photoelectron spectroscopic investigation of thallium sulfide layers on PA surface formed with the use of dodecathionic acid solutions

The processes of PA film sulfurization and sulfide layer formation take place in a natural environment; therefore, it is impossible to prevent its influence. PA, on its surface, absorbs oxygen, moisture and other compounds. XPS data of sulfurized samples show that rather a large part of the surface absorbs oxygen: the latter and water were absorbed from the environment. PA during sulfurization absorbs polythionate ions which later gradually decompose. The products of

decomposition are detected in sulfurized samples. The S 2p spectra show that sulfur exists in two forms. The surface of a sample and the surface of an etched sample contain more elemental sulfur, since its maximum at 163.5–163.8 eV is more intensive.

The metal sulfides formed in the polymer surface matrix by the sorption–diffusion method are formed in the form of dendrites, therefore, in-between the dendrites there may remain absorbed oxygen, water and others compounds. For this and others reasons, the microstructure of a metal sulfide layer may significantly differ from the macrostructure and chemical composition of all layers.

The coating surface was first studied by the XPS method, and then the coatings were etched with  $Ar^+$  ions and their composition in the deeper layer was studied. The analysis was restricted to a very thin layer composition. From the obtained data, i. e. the element atomic percentages, binding energies and individual elements Tl 4f7, S 2p and O 1s spectra, it is possible to predict the composition of the layer.

The maxima in S 2p spectra, corresponding to the binding energy values of ~161–162 eV, show the presence of sulfide sulfur; the maxima corresponding to the binding energy values of ~163–164 eV indicate the presence of elemental sulfur, and the maxima corresponding to the binding energy of ~168 eV imply the presence of sulfate sulfur.

Analysing the XPS data (Fig. 10, Table) and comparing the distribution of Tl, S and O on the surface of the samples,

Table. Data of X-ray photoelectron spectroscopic study of  $Tl_xS_y$  layers on PA surface

Etching conditions	Element	Amount, at. %	Binding energy, eV	Possible composition	Tl : S
<b>No. 1 (PA sulfurized 3 h at 20 °C)</b>					
Surface	Tl	3.03; 10.47	117.8; 118.8	$Tl_2O_3$ , $Tl_2S_3$	
	S	8.2; 5.93	161.4; 167.6	$Tl_2S_7$ , $Tl_2SO_4$	
	O	7.62; 10.87; 4.34	530.4; 531.0; 531.8	$Tl(OH)_3$	0.96
	C	49.54	284.6; 286.9		
Etched 15 s – 30 $\mu$ A	Tl	25.13	118.7	$Tl_2S_3$ , $Tl_2S_7$	
	S	19.83; 4.19	162.2; 168.8	$Tl_2SO_4$	
	O	7.54; 6.18; 3.82	531.3; 532.0; 533.1	$Tl(OH)_3$	1.05
	C	33.32	284.8; 285.8		
Etched 60 s – 30 $\mu$ A	Tl	35.01; 6.37	118.4; 118.9	$Tl_2S_3$ , $Tl_2S$	
	S	25.95	162.2		
	O	–	–		1.59
	C	32.66	287.0		
<b>No. 2 (PA sulfurized 3 h at 40 °C)</b>					
Surface	Tl	3.44; 7.07	119.1; 119.7	$Tl_2SO_4$ , $Tl_2O_3$	
	S	8.02; 3.98	162.2; 168.2	$Tl(OH)_3$	
	O	16.49; 2.73	530.8; 532.1	$Tl_2S_3$ , $Tl_2S$	0.87
	C	58.27	284.6; 287.1		
Etched 15 s – 30 $\mu$ A	Tl	12.57; 9.64	118.0; 118.5	$Tl_2S$ , $Tl_2S_3$	
	S	21.78; 2.68	161.5; 168.0	$Tl_2SO_4$	
	O	12.68; 0.74	531.1; 533.5	$Tl(OH)_3$	0.91
	C	39.91	284.6; 285.1		
Etched 60 s – 30 $\mu$ A	Tl	17.17; 17.58	118.0; 118.8	$Tl_2S$ , $Tl_2S_3$ , $S_8$	
	S	28.36; 5.03	161.4; 164.0		
	O	–	–		1.04
	C	31.87	284.5		



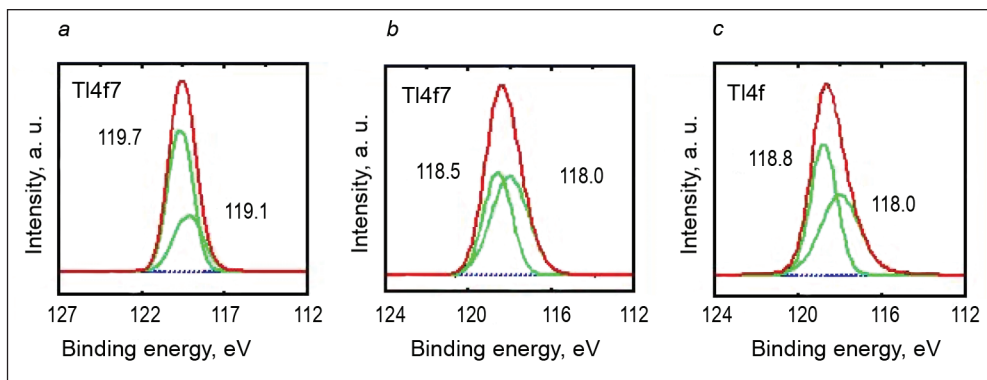


Fig. 10. XPS spectra of sample 2 (PA sulfurized 3 h at 40 °C): *a* – surface, *b* – etched for 15 s, *c* – etched for 60 s

we have found that oxygen takes the bulk of a sample surface. Such a high content of oxygen may be explained by its chemical absorption, by a low-soluble  $\text{Tl}_2\text{SO}_4$  absorption on the layer surface and by insoluble thallium(III) hydroxide formation on the coating surface.

The obtained data show that on the layer surface and in the etched layer, various thallium, sulfur and oxygen compounds are present. The following compounds have been identified:  $\text{Tl}_2\text{O}_3$ ,  $\text{Tl}_2\text{S}_3$ ,  $\text{Tl}_2\text{S}$ ,  $\text{S}_8$ ,  $\text{Tl}_2\text{SO}_4$ ,  $\text{Tl}(\text{OH})_3$ . The highest content of  $\text{Tl}_2\text{SO}_4$  and  $\text{Tl}(\text{OH})_3$  was found on the coating surface. Thallium sulfides, like copper sulfides, take the form of dendrites. Thus, some absorbed thallium sulfate remains in-between the dendrites. During the redox reaction between thallium(I) ions and elemental sulfur, formed during the decomposition of polythionic acid, thallium(III) ions appear, which with the  $\text{HO}^-$  ions present in the alkalinized  $\text{Tl}_2\text{SO}_4$  solution form insoluble  $\text{Tl}(\text{OH})_3$ . The oxygen may be joined into  $\text{Tl}_2\text{O}_3$ . Oxygen was not detected in samples etched for 60 s; there thallium ions were joined with the sulfide sulfur into thallium sulfides. At a higher sulfurization temperature, more sulfur was detected. The reason may be the bigger amount of sorbed polythionate ions and of elemental sulfur as a product of their decomposition. Elemental sulfur was present in a deeper layer. The content of thallium in deeper layers increased; for example, the content of thallium in a sample sulfurized for 3 h at 40 °C increased from 10.51 (surface) to 34.75 (etched for 60 s) at. %.

#### Study of the morphology of thallium sulfide layers formed on PA surface using $\text{H}_2\text{S}_{12}\text{O}_6$ solutions

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

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

A morphological study of PA modified with  $\text{Tl}_x\text{S}$  layers by atomic force microscopy revealed the coatings to be es-

entially different. Fields from  $4 \times 4$  to  $12 \times 12$  microns were investigated; for the quantitative estimation of the surface, the standard programs of the view treatment were used. We have determined that the thickness and surface morphology of sulfide layers formed on PA do depend on the conditions of polymer sulfurization. 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 “thalliumizing”) the formation of thallium sulfide layers proceeds unevenly, in the form of islands which later grow into larger agglomerates. The surface of the layers formed is relatively uneven and rather rough.

Having done the profile sections of  $\text{Tl}_x\text{S}$  coatings formed on PA surface when the polymer had been sulfurized 0.5, 1.0, 3.0, 6.0 h at the temperature of 30 °C with  $0.002 \text{ mol} \cdot \text{dm}^{-3}$   $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated 10 min with  $\text{Tl}(\text{I})$  salt solution, it was possible to estimate the height and diameter of separate crystallites. When the polymer was sulfurized 0.5 h at a temperature of 30 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution, the height of the bigger crystallite was ~440 nm (diameter ~1.3  $\mu\text{m}$ ) and of the smaller crystallite ~250 nm (diameter ~0.8  $\mu\text{m}$ ). On prolongation of sulfurization to 1.0 h, the height of crystallites remained similar. The height of the bigger crystallite when the polymer had been sulfurized for 1.0 h was ~420 nm and when sulfurized for 3 h ~880 nm.

Thus, it followed that on prolongation of PA sulfurization in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution from 0.5 to 3.0 h (in the same conditions of sulfurized PA “thalliumizing”), the height of crystallites increases about twice. The same tendency was observed in the change of coating roughness: because of the different height and form of crystallites it increased. However, when the duration of PA sulfurization was increased to 6.0 h, the height of crystallites decreased and the roughness did not change. The height of separate crystallites reached ~830 nm and their diameter 3.2  $\mu\text{m}$ .

The views of thallium sulfide coatings on PA surface when the polymer had been sulfurized for 0.5, 1.0, 3.0 and 6.0 h at a temperature of 30 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with  $\text{Tl}(\text{I})$  salt solution are shown in Figs. 11–14. One can see that upon a short duration (0.5 h) of PA treatment

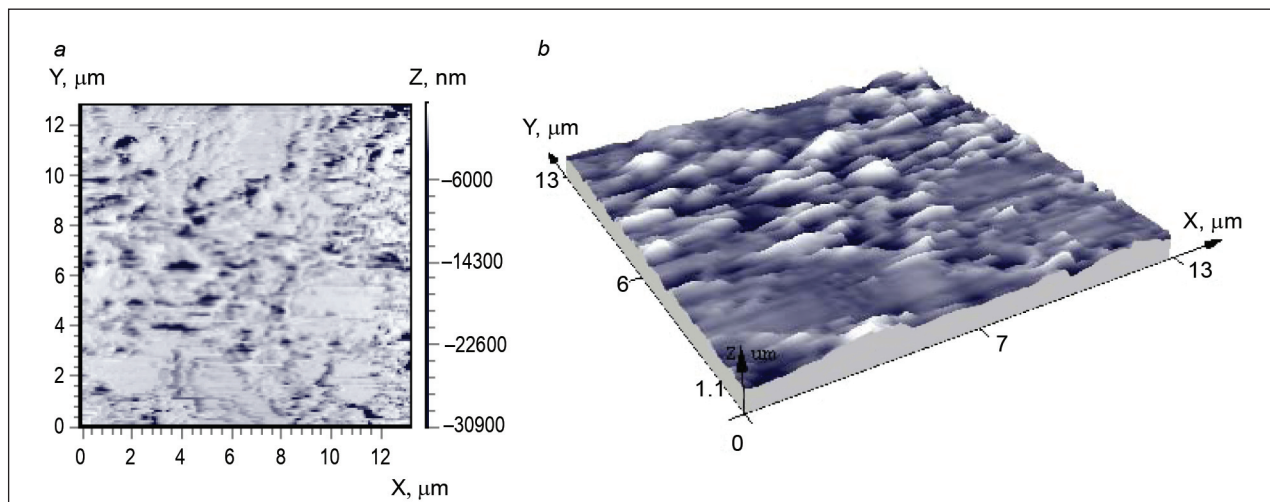


Fig. 11. Atomic force microscopy view of thin  $Tl_xS$  layers formed on PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). PA was sulfurized for 0.5 h at a temperature of 30 °C in  $H_2S_{12}O_6$  solution and then treated with alkalified  $Tl_2SO_4$  solution

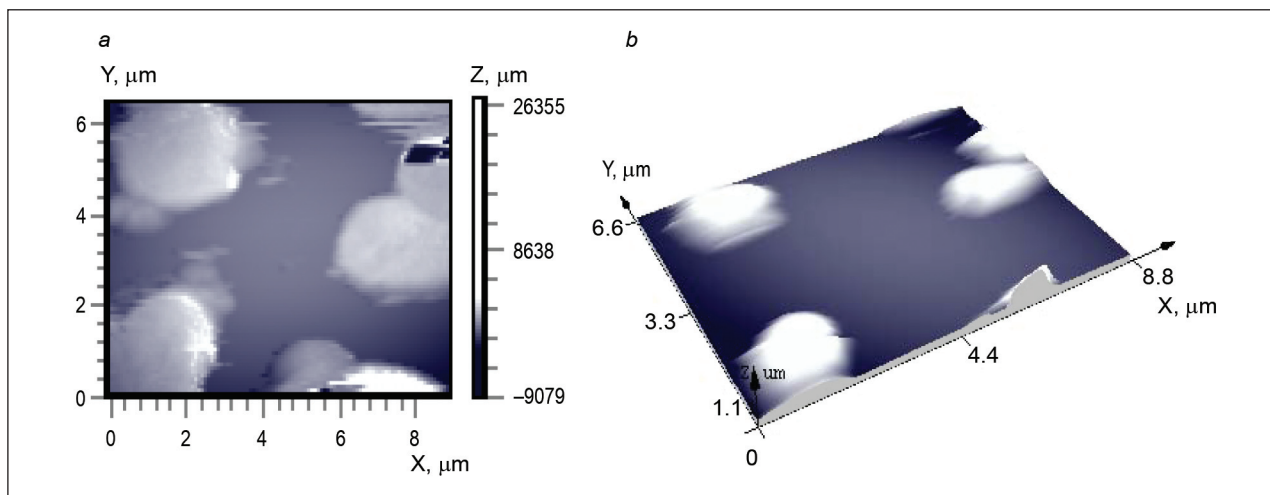


Fig. 12. Atomic force microscopy view of thin  $Tl_xS$  layers formed on PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). PA was sulfurized 1.0 h at a temperature of 30 °C in  $H_2S_{12}O_6$  solution and then treated with alkalified  $Tl_2SO_4$  solution

in  $H_2S_{12}O_6$  solution, the growth of thallium sulfide coating begins from the formation of small islands (Fig. 11). The lightest places in separate areas of the surface show that there are the peaks of crystallites. The crystallites here are of different height and diameter. Prolongation of sulfurization to 1.0 h causes the beginning of clusterization: crystallites of various diameter and height begin slowly to join into agglomerates (Fig. 12), and a thicker  $Tl_xS$  coating is formed. Upon the further prolongation of PA sulfurization in  $H_2S_{12}O_6$  solution at a temperature of 30 °C (to 3.0 and 6.0 h) in the same conditions of sulfurized PA “thalliumizing”, bigger agglomerates composed of crystallites of different diameter, height and form are growing (Figs. 13 and 14). As is shown in Fig. 15, the preliminary determined thickness of the coating increases about twice upon prolonging PA treatment in  $H_2S_{12}O_6$  solution from 0.5 to 6.0 h.

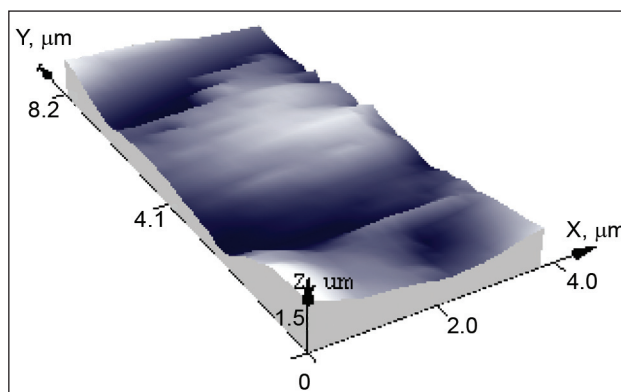


Fig. 13. Atomic force microscopy view of thin  $Tl_xS$  layers formed on PA surface: AFM 3D topography view. PA was sulfurized for 3.0 h at a temperature of 30 °C in  $H_2S_{12}O_6$  solution and then treated with alkalified  $Tl_2SO_4$  solution

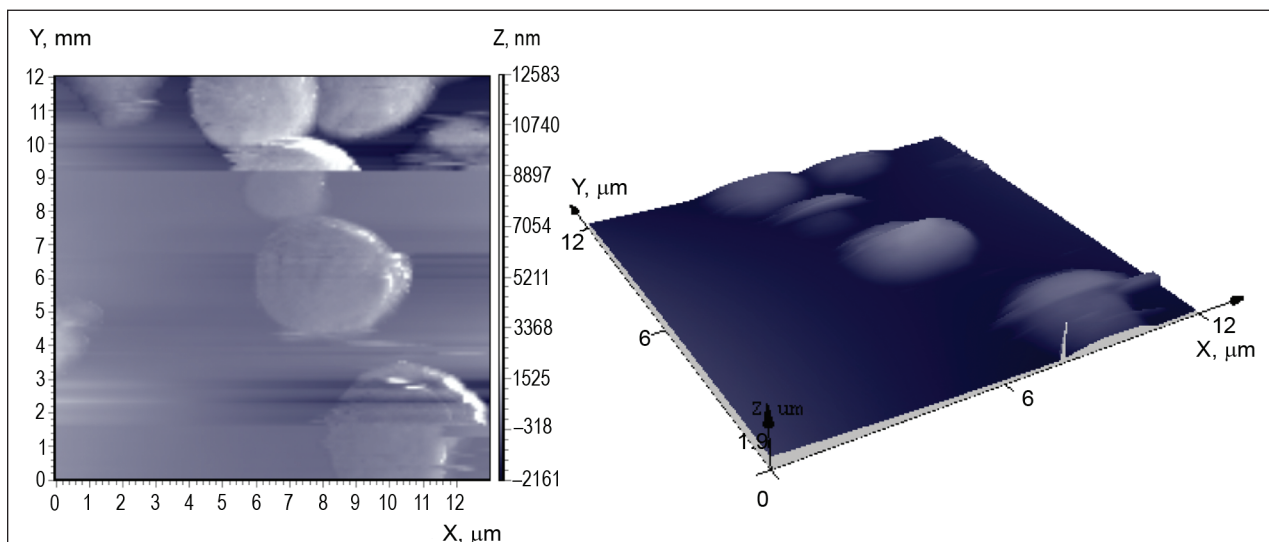


Fig. 14. Atomic force microscopy view of thin  $Tl_xS$  layers formed on PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). PA was sulfurized for 6.0 h at a temperature of 30 °C in  $H_2S_{12}O_6$  solution and then treated with alkalinized  $Tl_2SO_4$  solution

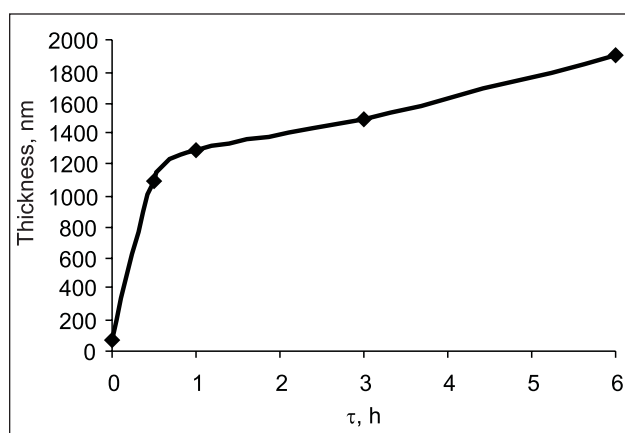


Fig. 15. Dependence of preliminary determined thickness of  $Tl_xS$  coating on the duration of PA treatment with  $H_2S_{12}O_6$  solution at a temperature of 30 °C

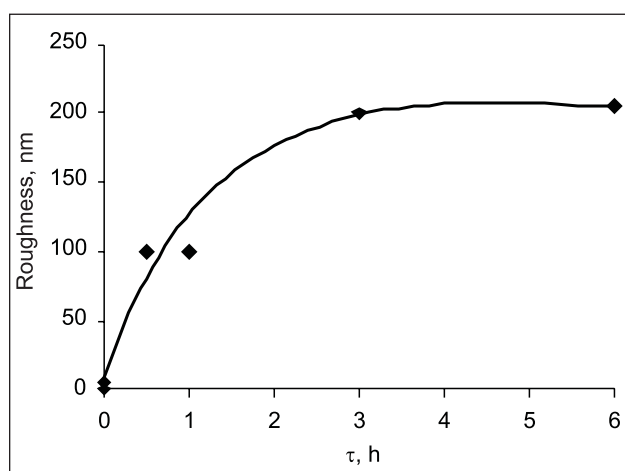


Fig. 16. Dependence of the average roughness of  $Tl_xS$  coating on the duration of PA treatment with  $H_2S_{12}O_6$  solution at a temperature of 30 °C

Formation of islands at separate places of the surface and its integration into agglomerates composed of crystallites of different height and diameter increase the roughness of the surface. This is shown by the roughness parameters (Fig. 16). As follows from the graph presented in Fig. 16, the average roughness increases on the prolongation of PA treatment with  $H_2S_{12}O_6$  solution from 0.5 to 3.0 h. However, upon the further prolongation of PA sulfurization (to 6.0 h) the average roughness of the surface does not change. Thus, the crystallites joining the agglomerates more evenly cover the surface and increase the coating's thickness (Fig. 15).

While further studying formation of  $Tl_xS$  layers on PA surface, the coatings were formed by sulfurizing PA for 3.0 h at a temperature of 20, 30, 40 and 50 °C with  $H_2S_{12}O_6$  solution and then treating with  $Tl_2SO_4$  solution. These coatings are shown in Figs. 13, 17–19. In Fig. 17 one can see that formation of a coating, because of the low temperature of PA treatment with  $H_2S_{12}O_6$  solution, proceeds slowly and the covering is uneven. The thickness of the coating is ~623 nm. On further growing the coating (increasing the temperature of PA sulfurization in  $H_2S_{12}O_6$  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 crystallites of various diameter (Fig. 13). The thickness of the coating increases ~2.5 times (compare with Fig. 17). Upon increasing the temperature of sulfurization solution to 40 °C, the presence of even larger agglomerates is observed (Fig. 18) and the thickness of the coating increases about 3 times (to ~1.9  $\mu m$ ). On the further increase of sulfurization temperature to 50 °C, formation of even larger agglomerates is observed, but the thickness of the coating remains unchanged (Fig. 19), possibly because it is impossible to obtain accurate data on the thickness of layers obtained by atomic forces microscopy, and the thickness shown in the topographic view is only very preliminar.

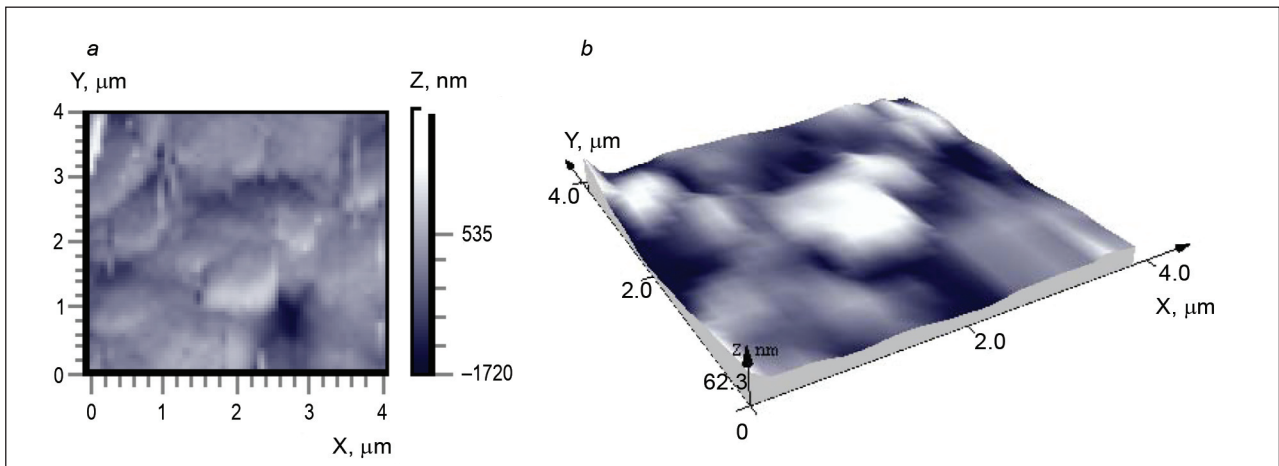


Fig. 17. Atomic force microscopy view of thin  $Ti_xS$  layers formed on PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). PA was sulfurized for 3.0 h at a temperature of 20 °C in  $H_2S_{12}O_6$  solution and then treated with alkalified  $Ti_2SO_4$  solution

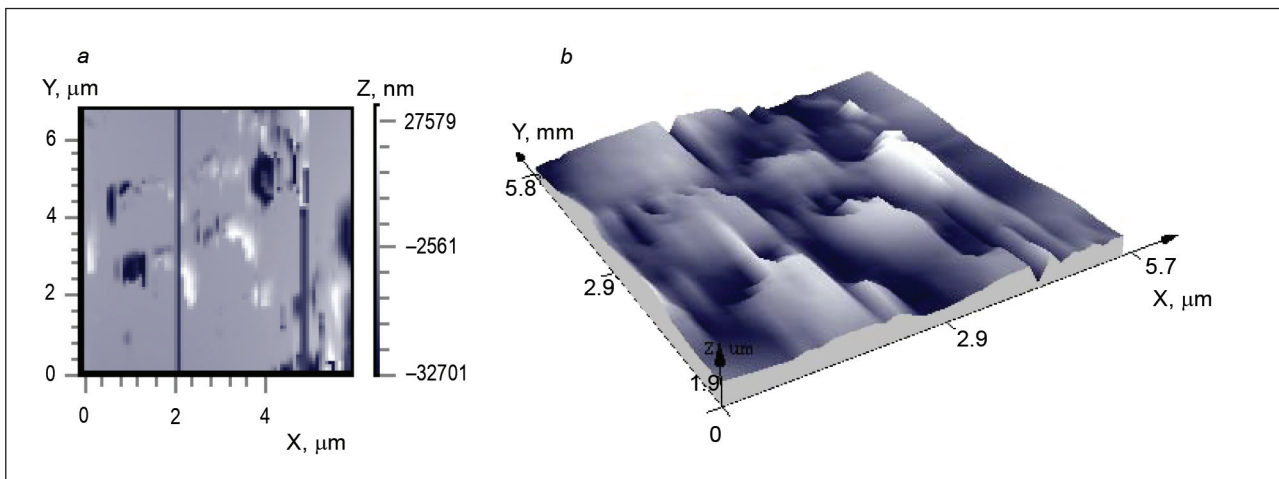


Fig. 18. Atomic force microscopy view of thin  $Ti_xS$  layers formed on PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). PA was sulfurized for 3.0 h at a temperature of 40 °C in  $H_2S_{12}O_6$  solution and then treated with alkalified  $Ti_2SO_4$  solution

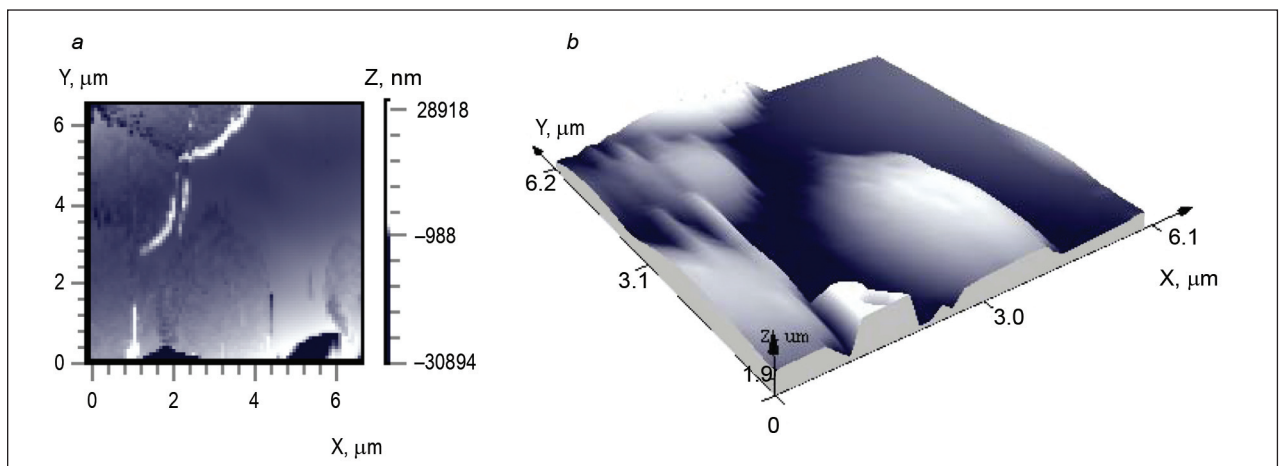


Fig. 19. Atomic force microscopy view of thin  $Ti_xS$  layers formed on PA surface: 2D view of lateral force microscopy (a) and 3D topography view (b). PA was sulfurized for 3.0 h at a temperature of 50 °C in  $H_2S_{12}O_6$  solution and then treated with alkalified  $Ti_2SO_4$  solution



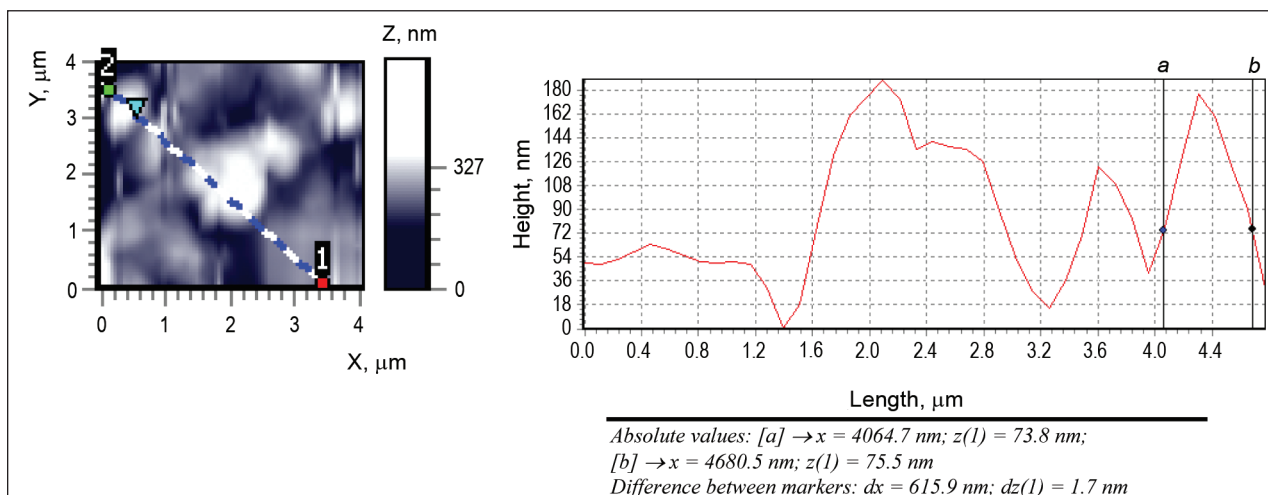


Fig. 20. View of topographic image and line profile of sulfide coating formed on PA surface. PA was sulfurized for 3.0 h at 20 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with alkalified  $\text{Ti}_2\text{SO}_4$  solution

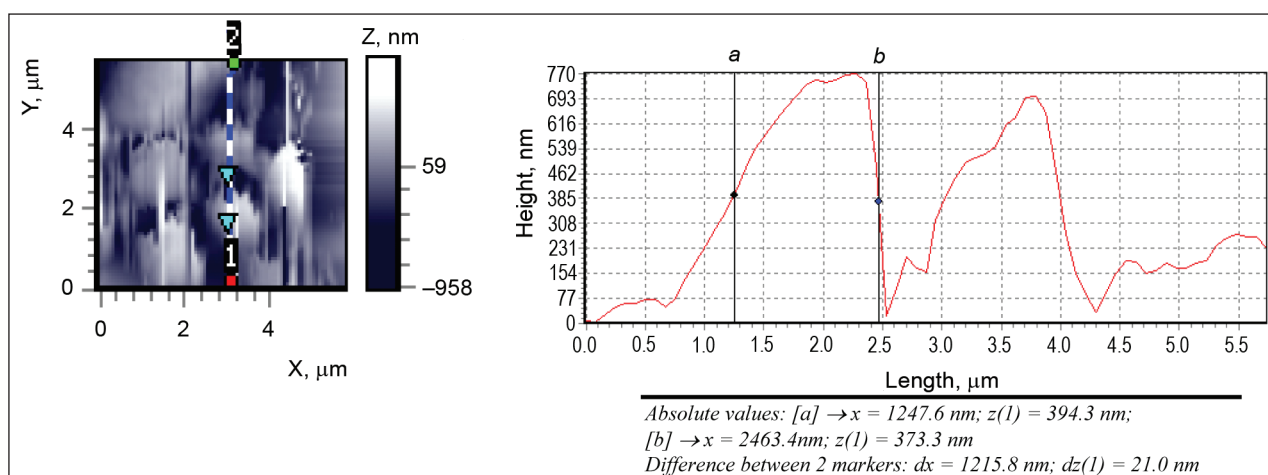


Fig. 21. View of topographic image and line profile of sulfide coating formed on PA surface. PA was sulfurized for 3.0 h at 40 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with alkalified  $\text{Ti}_2\text{SO}_4$  solution

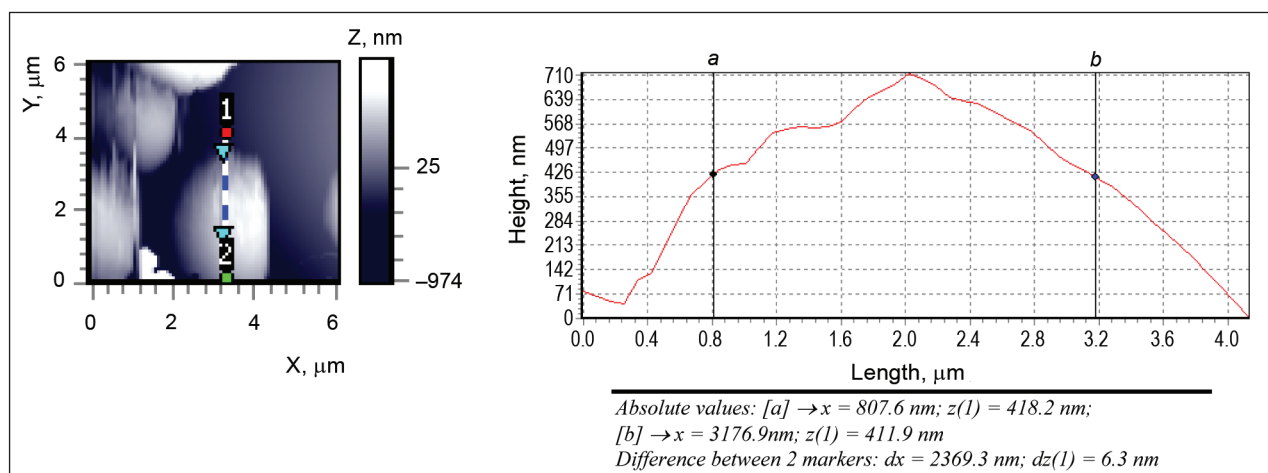


Fig. 22. View of topographic image and line profile of sulfide coating formed on PA surface. PA was sulfurized for 3.0 h at 50 °C in  $\text{H}_2\text{S}_{12}\text{O}_6$  solution and then treated with alkalified  $\text{Ti}_2\text{SO}_4$  solution



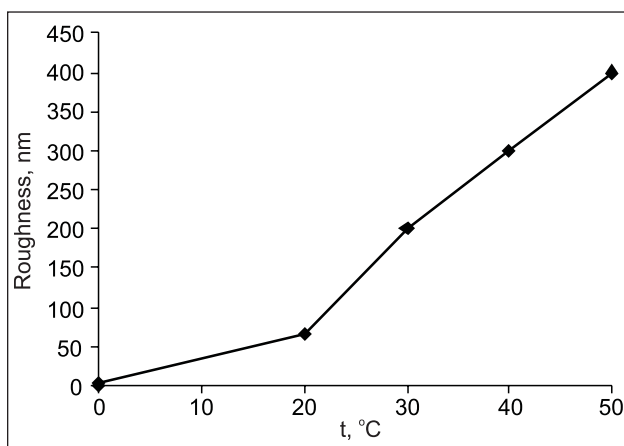


Fig. 23. Dependence of the coating average roughness on the temperature of PA treatment for 3.0 h in  $H_2S_{12}O_6$  solution

The profile sections of these coatings have shown that their surface is rather uneven (Figs. 20–22). The roughness increases and, as shown in Figs. 13, 17–19 and Figs. 20–22, the crystallites are of different height, diameter and form. The change of the roughness is caused by the roughness parameters (Fig. 23).

To summarize, it is possible to state that depending on the duration and temperature of initial PA sulfurization in  $H_2S_{12}O_6$  solution (in the same conditions of sulfurized PA “thalliumization”), the formation of thallium sulfide layers proceeds unevenly as islands which later grow together into bigger agglomerates. The surface of the formed coating is uneven, rather rough. The preliminarily determined thickness of the coating increases with the prolongation of PA sulfurization in  $H_2S_{12}O_6$  solution and rising the temperature from 20 to 30 °C (Fig. 24). An analogous tendency is observed also in the average roughness of coating surface (Fig. 23), but it regularly increases in the whole interval of the temperature used (20–50 °C).

## CONCLUSIONS

1. When polyamide 6 (PA) films are exposed for different time (up to 4 h) to acidified (0.1 mol  $dm^{-3}$  HCl) 0.1 and 0.2 mol  $dm^{-3}$  solutions of  $Na_2S_3O_6$  and  $Na_2S_4O_6$  at 30 or 50 °C and later for 10 min to alkalinized 0.1 mol  $dm^{-3}$  solution of  $Tl_2SO_4$ ,  $Tl_xS$  layers on PA films are formed. The molar Tl : S ratio in  $Tl_xS$  layers formed on PA sulfurized with acidified 0.2 mol  $dm^{-3}$  solution of  $Na_2S_3O_6$ , depends on the temperature of  $Na_2S_3O_6$  solution and sulfurization duration and varies from 1 : 2 to 1 : 20.

2. A study of IR and UV absorption spectra has shown that pentathionate,  $S_5O_6^{2-}$ , ions are sorbed from acidified water solutions of potassium pentathionate,  $K_2S_5O_6$ , by PA films. The concentration of pentathionate ions sorbed into a polymer increases with increasing the concentration of  $K_2S_5O_6$  solution, as well as the temperature and duration of treatment.

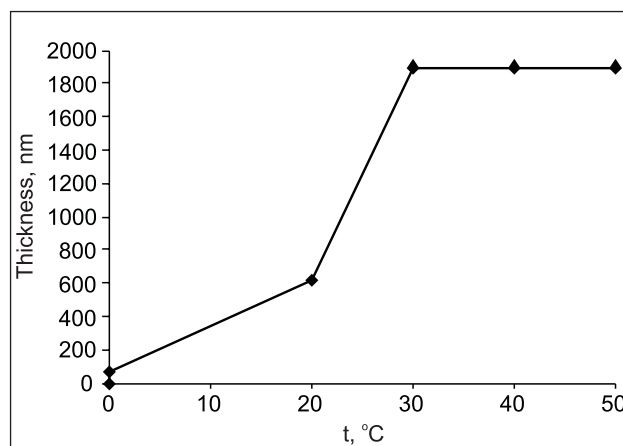


Fig. 24. Dependence of preliminary determined thickness of  $Tl_xS$  coating on the temperature when PA was sulfurized for 3.0 h in  $H_2S_{12}O_6$  solution and then treated with alkalinized  $Tl_2SO_4$  solution

The values of sulfur concentration, depending on sulfurization conditions, vary from 0.07 to 7.16  $mg \cdot g^{-1}$ , allowing modification of PA surface by layers of thallium sulfides.

3. A layer of nonstoichiometric thallium sulphide,  $Tl_xS$ , was obtained after treating sulfurized PA with an alkalinized solution of  $Tl_2SO_4$ . The concentration of thallium increased when the concentration and temperature of the pentathionate solutions had been increased, but the increase was observed only when the duration of the initial polymer treatment had been prolonged until 1 h. Supposedly, a compact  $Tl_xS$  layer forms on the PA film, which terminates the further diffusion of  $Tl^+$  ions from  $Tl(I)$  salt solution, and these ions cannot get into contact with the compounds sorbed–diffused in the initial stage and containing sulfur atoms of low oxidation state. The concentration of thallium in PA varied from 1.2 to 2.6  $mg \cdot g^{-1}$ .

4. The water solution of dodecathionic acid,  $H_2S_{12}O_6$ , acts effectively as a sulfurization agent of PA. The values of sulfur concentration obtained in PA (up to  $\sim 255 mg \cdot g^{-1}$ ) increase with increasing the duration of treatment and the temperature of  $H_2S_{12}O_6$  solution.

5.  $Tl_xS$  layers are formed in the surface of PA film if a polymer sulfurized in  $H_2S_{12}O_6$  solution is treated with alkalinized solution of  $Tl_2SO_4$ . The concentration of thallium in the polyamide film increases with increasing the duration and temperature of initial sulfurization, and varies from  $\sim 25$  to  $\sim 250 mg \cdot g^{-1}$ ; the stoichiometrical composition of  $Tl_xS$  layers varies from  $\sim Tl_{0.15}S$  to  $Tl_{1.2}S$ . Four thallium sulfide phases,  $TlS$ ,  $Tl_2S_2$ ,  $Tl_4S_3$  and  $Tl_2S_5$ , were identified in the composition of the layers by X-ray diffraction, but the maxima of  $TlS$  and  $Tl_2S_5$  phases prevailed in the diffractograms. The determined regularities enable formation by the sorption–diffusion method of thallium sulfide layers of a desirable composition, using dodecathionic acid as a PA sulfurization agent.

6. The XPS analysis of  $Tl_xS$  layers on the PA surface, formed by using  $H_2S_{12}O_6$  solution as a precursor, showed

that various thallium, sulfur and oxygen compounds –  $Tl_2O_3$ ,  $Tl_2S_3$ ,  $Tl_2S$ ,  $S_8$ ,  $Tl_2SO_4$  and  $Tl(OH)_3$  – are present on the layer's surface and in the etched layer. The content of thallium and sulfur increases in the etched layers.

7. Studies of  $Tl_xS$  layer surface morphology by the AFM method have shown that, depending on the temperature of the initial polyamide sulfurization in  $K_2S_5O_6$  or  $H_2S_{12}O_6$  solution (in the same "thalliumizing" conditions of sulfurized PA), thallium sulfide layers are formed unevenly as islands which grow into bigger agglomerates. The surface of the coatings is rather uneven and rough. The preliminarily determined thickness of the sulfide layer increases with increasing the PA sulfurization temperature. The same tendency was observed in the change of the average roughness: it increased with the PA sulfurization temperature.

Received 24 September 2009

Accepted 6 October 2009

## References

- R. S. Mane, C. D. Lokhande, *Mater. Chem. Phys.*, **65**, 1 (2000).
- I. M. Ashraf, H. Elshaikh, A. M. Badr, *Cryst. Res. Technol.*, **39**(1), 63 (2004).
- V. Estrella, R. Mejia, M. T. S. Nair, P. K. Nair, *Mod. Phys. Lett. B*, **15**(17–19), 737 (2001).
- Y. Ni, M. Shao, Z. Wu, F. Gao, X. Wei, *Solid State Commun.*, **130**(5), 297 (2004).
- H. A. Elshaikh, I. M. Ashraf, A. M. Badr, *Physica Status Solidi (B)*, **241**(4), 885 (2004).
- H. A. Elshaikh, I. M. Ashraf, A. M. Badr, *Phys. Chem. B*, **108**(31), 11327 (2004).
- A. Mondal, P. Pramanik, *Thin Solid Films*, **110**, 65 (1983).
- G. Nickless, *Inorganic Sulphur Chemistry*, Elsevier Publishing Company, Amsterdam–London–New York (1968).
- A. G. Lee, *The Chemistry of Thallium*, Amsterdam (1971).
- G. Remi, *Kurs neorganicheskoi khimii*, Mir, Moskva (1972).
- N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford–New York–Toronto–Sydney–Paris–Frankfurt (1978).
- I. A. Ugai, *Neorganicheskaya khimiya*, Moskva (1989).
- A. Žebrauskas, *Chem. technol.*, **1**(3), 39 (1996).
- V. Estrella, R. Mejia, M. T. S. Nair, P. K. Nair, *Mod. Phys. Lett. B*, **15**(17–19), 737 (2001).
- V. Estrella, M. T. S. Nair, P. K. Nair, *Thin Solid Films*, **414**, 289 (2002).
- A. M. Mancini, G. Micocci, A. Rizzo, *Mater. Chem. Phys.*, **9**(1–3), 29 (1983).
- C. D. Lokhande, A. Ennaoui, P. S. Patil, M. Giersig, K. Diesner, M. Muller, H. Tributsch, *Thin Solid Films*, **340**(1), 18 (1999).
- K. Yamaguchi, T. Yoshida, H. Minoura, *Thin Solid Films*, **431–432**, 354 (2003).
- Y. Ni, M. Shao, Z. Wu, F. Gao, X. Wei, *Solid State Commun.*, **130**(5), 297 (2004).
- V. Janickis, *Polythionates*, Technologija, Kaunas (2006).
- I. Bruzaite, V. Janickis, I. Ancutiene, *Solid State Phenomena*, **106**, 133 (2005).
- R. Maciulevičius, Ph. D. Thesis, Kaunas, Lithuania (1995).
- I. Ancutienė, Ph. D. Thesis, Kaunas, Lithuania (1995).
- Pat. Lithuania 4402 B (1998).
- Pat. Lithuania 4111 B (1997).
- R. Ivanauskas, N. Kreivėnienė, V. Janickis, R. Stokienė, *Chem. Technol.*, **3**(29), 40 (2003).
- R. Ivanauskas, R. Stokienė, V. Janickis, N. Kreivėnienė, *Proceedings of Baltic Polymer Symposium 2004, November 24–26 in Kaunas*, Kaunas, (2004).
- R. Ivanauskas, V. Janickis, R. Stokienė, N. Kreivėnienė, *Chem. technol.*, **1**(35), 20 (2005).
- V. Janickis, R. Ivanauskas, R. Stokienė, N. Kreivėnienė, *Chem. technol.*, **3**(37), 32 (2005).
- R. Ivanauskas, V. Janickis, R. Stokienė, *Chem. Technol.*, **1**(39), 29 (2006).
- V. Janickis, R. Ivanauskas, R. Stokienė, N. Kreivėnienė, *Materials Science*, **12**(4), 311 (2006).
- V. Janickis, R. Ivanauskas, R. Stokienė, *Chemija*, **17**(4), 7 (2006).
- I. Ancutienė, V. Janickis, R. Ivanauskas, R. Stokienė, N. Kreivėnienė, *Polish J. Chem.*, **81**, 381 (2007).
- V. Janickis, R. Ivanauskas, R. Stokienė, *Proceedings of Baltic Polymer Symposium 2007*, Druskininkai, 187 (2007).
- V. Janickis, R. Ivanauskas, R. Stokienė, *Chemija*, **19**(1), 32 (2008).
- V. Janickis, R. Ivanauskas, R. Stokienė, M. Andrulevičius, *Chemija*, **20**(1), 45 (2009).
- I. Ancutienė, V. Janickis, R. Stokienė, *Chemija*, **20**(1), 38 (2009).
- R. Willstätter, *Chem. Ges.*, **36**, 1831 (1903).
- K. Daukšas, E. Ramanauskas, *Inorganic Synthesis*, Mintis, Vilnius (1970).
- G. Brauer (ed.), *Rukovodstvo po preparativnoi neorganicheskoi khimii*, Izdatelstvo inostrannoi literatury, Moskva (1956).
- J. V. Janickis, J. N. Valančiūnas, V. J. Zelionkaitė, V. J. Janickis, S. A. Grevys, *Lietuvos TSR Mokslų akademijos darbai. B ser.*, **3**(88), 83 (1975).
- V. Janickis, I. Ancutienė, I. Bružaitė, *Chem. technol.*, **2**(23), 35 (2002).
- I. Bružaitė, Ph. D. Thesis, Kaunas, Lithuania (2005).
- V. I. Alekseev, *Kolichestvennyi analiz*, Khimiya, Moskva (1972).
- Analytical Methods for Atomic Absorption Spectrometry*, Perkin–Elmer Corp., Norwalk, Conn. (1973).
- D. Briggs, M. P. Sich (eds.), *Analiz poverkhnosti metodom ozhe- i rentgenovskoi fotoelektronnoi spektroskopii*, Mir, Moskva (1987).
- C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder et al., *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin–Elmer Corporation, Minnesota (1978).
- R. Ivanauskas, R. Rumša, V. Janickis, *Chem. technol.*, **3**(20), 4 (2001).
- R. Ivanauskas, V. Janickis, R. Maciulevičius, *Chem. technol.*, **3**(12), 71 (1999).

50. V. J. Janickis, Doctoral Diss., Kaunas (1983).
51. L. Lorenz, R. Samuel, *Z. Physik. Chem. (B)*, **14**, 219 (1931).
52. M. Schmidt, T. Sand, *J. Inorg. Nucl. Chem.*, **26**, 1173 (1964).
53. V. Janickis, S. Grevys, *Chem. technol.*, **3(41)**, 5 (2006).

Vitalijus Janickis, Rūta Stokienė

## TALIO SULFIDAI IR JŲ SLUOKSNIAI DIELEKTRIKŲ PAVIRŠIUJE

### *Santrauka*

Talio sulfidų,  $Tl_xS$ , sluoksniai susidaro poliamido 6 (PA) plėvelių paviršiuje, jeigu PA paveikiamas skirtingą laiką parūgštintais natrio tritionato,  $Na_2S_3O_6$ , arba natrio tetrionato,  $Na_2S_4O_6$ , tirpalais ir po to pašarmintu  $Tl_2SO_4$  tirpalu. IR ir UV absorbcijos spektrais parodyta, kad pentationato jonai,  $S_5O_6^{2-}$ , yra sorbuojami PA iš parūgštintų vandeninių kalio pentationato,  $K_2S_5O_6$ , tirpalų. Polimeru sorbuotų pentationato jonų koncentracija didėja, didinant  $K_2S_5O_6$  tirpalo koncentraciją, temperatūrą ir PA apdorojimo trukmę. Paveikus sierintą PA pašarmintu  $Tl_2SO_4$  tirpalu, PA paviršiuje gauti nestecheometrinio talio sulfido,  $Tl_xS$ , sluoksniai. Talio koncentracija PA didėja, kai didinama pentationato tirpalo koncentracija ir

temperatūra. Manoma, kad PA paviršiuje susidaro kompaktinis  $Tl_xS$  sluoksnis, trukdantis tolesnę  $Tl^+$  jonų difuziją iš  $Tl(I)$  druskos tirpalo. Dodekationato rūgštis,  $H_2S_{12}O_6$ , tirpalas veikia efektyviai kaip PA sierinimo agentas. PA gautos sieros koncentracijos didėja, didinant apdorojimo  $H_2S_{12}O_6$  tirpale trukmę ir šio tirpalo temperatūrą.  $Tl_xS$  sluoksniai susidaro PA plėvelių paviršiuje, jeigu  $H_2S_{12}O_6$  tirpale sierintas polimeras apdorojamas pašarmintu  $Tl_2SO_4$  tirpalu. Talio koncentracija PA plėvelėje didėja, didinant pradinio sierinimo trukmę ir temperatūrą. Keturių talio sulfidų fazės –  $TlS$ ,  $Tl_2S_2$ ,  $Tl_4S_3$  ir  $Tl_2S_5$  – identifikuotos gautų sluoksnių sudėtyje rentgeno difrakcine analize. Nustatyti dėsningumai įgalina sorbciniu-difuziniu metodu, naudojant  $H_2S_{12}O_6$  tirpalą kaip PA sierinimo agentą, sudaryti norimos sudėties talio sulfidų sluoksnius. Rentgeno fotoelektroninė  $Tl_xS$  sluoksnių, sudarytų kaip prekursorių naudojant  $H_2S_{12}O_6$  tirpalą, analizė parodė, kad šių sluoksnių sudėtyje yra įvairūs talio, sieros ir deguonies junginiai:  $Tl_2S_3$ ,  $Tl_2S$ ,  $S_8$ ,  $Tl_2SO_4$  ir  $Tl(OH)_3$ .  $Tl_xS$  sluoksnių paviršiaus morfologijos tyrimas atominės jėgos mikroskopija parodė, kad dėl PA pradinio sierinimo  $K_2S_5O_6$  ar  $H_2S_{12}O_6$  tirpale temperatūros (naudojant tokias pačias PA „taliavimo“ sąlygas) talio sulfidų sluoksniai formuojasi netolygiai salelėmis, kurios suauga į didesnius aglomeratus; dangų paviršius gana nelygus ir šiurkštus.