

X-ray photoelectron spectroscopy investigation of Cu_xS and Tl_xS layers on the polyamide film surface formed with the use of dodecathionic acid

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The phase composition of polyamide 6 (PA) films modified by layers of copper sulfides, Cu_xS , and thallium sulfides, Tl_xS , was studied by the X-ray photoelectron spectroscopy method. Copper sulfide and thallium sulfide layers on the surface of PA film were formed by treating PA film samples in a $0.002 \text{ mol} \cdot \text{dm}^{-3}$ solution of dodecathionic acid, $\text{H}_2\text{S}_{12}\text{O}_6$, at a temperature of 20 and 40 °C and then with Cu(II / I) salts or Tl_2SO_4 solution. It was determined that in the surface of PA samples modified by copper sulfides, various copper, sulfur and oxygen compounds (CuS , Cu_2S , CuO , S_8 , CuSO_4 and Cu(OH)_2) and in the PA surface modified by thallium sulfides, various thallium, sulfur and oxygen compounds (Tl_2O_3 , Tl_2S_3 , Tl_2S , S_8 , Tl_2SO_4 and Tl(OH)_3) were present. The content of copper and thallium sulfides in deeper chalcogenide layers was higher than on the surface of the layers.

Key words: Cu_xS and Tl_xS layers, polyamide, X-ray photoelectron spectroscopy

INTRODUCTION

Over the last decades, researchers of various fields of science have been involved in studies of copper chalcogenides Cu_xY ($\text{Y} = \text{S}, \text{Se}, \text{Te}$) – their synthesis, physical and chemical properties and modification of dielectrics by these compounds. Interest in Cu_xY and their thin layers deposited on various dielectric substances, including polymeric ones, was focused first of all on their possible use in production of solar energy elements [1–7] since these layers have characteristic physical properties: good transmittance in the visible (20–50%) and poor in the infrared (10–20%) spectral region, low (<10%) absorbance of visible light, also a relatively large (>15%) reflectance in the infrared region of spectra [8]. In the last years, more attention is given to thin layers of these compounds as transparent and electrically conductive coatings on glass and polymers [9], for production of various sensors [10–12], electronic and optical devices [13, 14], thermoelectric converters [15].

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.

Cu_xS 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 [11, 12]. Thus, while modifying polymers with copper chalcogenide layers, it is very important to establish the phase composition of the coatings, which in most cases predetermines the properties and possible use of modified polymers.

Electrical conductance is one of the most important properties of copper chalcogenides, because of which these compounds are widely used. Copper atoms in copper chalcogenide phases may be in various oxidation state: Cu^+ , Cu^{2+} , or even Cu^+ and Cu^{2+} in one phase. Depending on the stoichiometric composition of copper chalcogenides, these compounds have different electrophysical and optical properties: they may be insulators, semiconductors, electrical conductors and some of them even superconductors. At room temperature, copper with sulfur forms two stoichiometric phases – Cu_2S (chalcocite) and CuS (coveline) – and three nonstoichiometric phases – $\text{Cu}_{1.75}\text{S}$ (anilite), $\text{Cu}_{1.8}\text{S}$ (digenite) and $\text{Cu}_{1.96}\text{S}$ (djurleite). This variety of copper sulfide phases presents some difficulty while studying the phase composition of polymers modified with copper chalcogenide layers.

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The binary chalcogenides of thallium, Tl_xY, because of their unique physical properties, are also important for advanced technology and science [16–21]. For example, they are used in solar batteries [18, 21]; Tl₅Te₃ is a superconductor at a low temperature [22, 23], TlS and Tl₂S are photoconductors [24, 25].

Analysing the phase composition of polymers modified with copper chalcogenide layers, the method of X-ray photoelectron spectroscopy (XPS) is often used [26–34]. This method of the determination of surface atomic composition is based on the analysis of bonds formed in various compounds. In this case, the surface of a sample is studied first and then, the coating surface being etched by Ar⁺ ions up to one or a few nanometres deep, the coating's composition is studied in a deeper layer. This analysis is restricted only by a study of the chemical composition of a very thin surface layer when the thickness of the whole layer may reach a few tenths of a micrometre.

From the data gained by the XPS method, i. e. from the atomic percentage of elements, binding energies and the spectra of individual elements, it is possible to determine the layer surface composition.

The aim of the present work was to study by the X-ray photoelectron spectroscopy method and compare the composition of PA film surface modified with copper sulfides and thallium sulfides.

EXPERIMENTAL

Layers of copper sulfides and thallium sulfides were deposited on polyamide 6 (PA) films produced in Russia, Yekaterinburg “Uralplastik” enterprise (manufacturer's TY 6-05-1775-76, grade PK-4, 15 × 70 mm, 70 μm). 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 CaCl₂ for 24 h.

PA films were sulfured in a thermostatic vessel for up to 4.5 h at a temperature of 20 and 40 °C using a continually stirred 0.002 mol · dm⁻³ solution of H₂S₁₂O₆ prepared by the method presented in [35]. At certain time intervals, PA film samples were removed from H₂S₁₂O₆ solution, rinsed with distilled water, dried with filter paper, left over CaCl₂ for 24 h and then used in further experiments and analysis. By the XPS method we studied Cu_xS layers formed by treating sulfurized PA films for 10 min with Cu(II / I) salt solution at a

temperature of 78 °C [36] and Tl_xS layers formed by treating sulfurized PA films for 10 min with alkalified Tl₂SO₄ [37] solution at a temperature of 80 °C.

XPS spectra of Cu_xS and Tl_xS layers were recorded with an ESCALAB MKII spectrometer (VG Scientific, radiation Mg K_α 1253.6 eV, output 300 W). Vacuum in the analysing chamber was kept at a level of 1.33 · 10⁻⁸ Pa, and the distribution of elements in the depth was determined by sputtering with an Ar⁺ gun with the ion energy of about 1.0 keV. The samples were etched in a preparation chamber with the vacuum 9.3 · 10⁻³ Pa and current 20 μA; the duration of etching was 15–60 s. The maximum accuracy of the method was ± 0.1 at. %. To investigate the layers obtained by the XPS method, the photoelectron spectra of Cu 2p_{3/2}, Tl f_{7/2} and S 2p were recorded. Empirical sensitivity factors for these elements were taken from the literature [38], and the spectra obtained were compared with the standard ones [39].

RESULTS AND DISCUSSION

The processes of PA film sulfurization and sulfide layer formation take place in a natural environment; therefore, it is impossible to prevent its influence. Semihydrophilic polymer PA, under the action of the environment, absorbs on its surface oxygen, moisture and other compounds. Sulfurized samples were first investigated by X-ray photoelectron spectroscopy. From data presented in Table 1 it follows that a rather large part of the surface is taken by oxygen. We suppose that oxygen and water were absorbed from the environment. PA during sulfurization absorbs polythionate ions which with time gradually decompose. The products of decomposition are detected in sulfurized samples. The S 2p spectra presented in Fig. 1 show that sulfur exists in two forms. On the surface of the sample (Fig. 1, a) and in the surface of the etched sample (Fig. 1, b) there is more elemental sulfur, since the maximum at 163.5–163.8 eV is more intensive.

The metal sulfides forming layers in the polymer surface matrix by the sorption–diffusion method take the form of dendrites [40], therefore, among the dendrites there may remain absorbed oxygen, water and other compounds. For this and other reasons, the microstructure of a metal sulfide layer may significantly differ from the macrostructure and chemical composition of all layers.

Table 1. XPS data on PA film sulfurized for 4 h at a temperature of 20 °C

| Etching conditions | Element | Amount, at. % | Binding energy, eV | Composition |
|------------------------|---------|---------------|---------------------|---|
| Surface | S | 2.38; 1.37 | 163.3; 168.3 | S ₈ (–S–), SO ₄ ²⁻ |
| | O | 12.85; 5.1 | 531.1; 532.6 | H ₂ O, O _{2abs} |
| | C | 69.07 | 284.5; 285.6; 287.6 | |
| | N | 9.23 | 399.5; 401.1 | |
| Etched 15 s – 30 μA | S | 8.43; 0.19 | 163.5; 167.9 | S ₈ (–S–), SO ₄ ²⁻ |
| | O | 10.18; 0.35 | 531.7; 534.2 | H ₂ O, O _{2abs} |
| | C | 75.49 | 284.4; 286.2; 287.6 | |
| | N | 5.36 | 399.2 | |

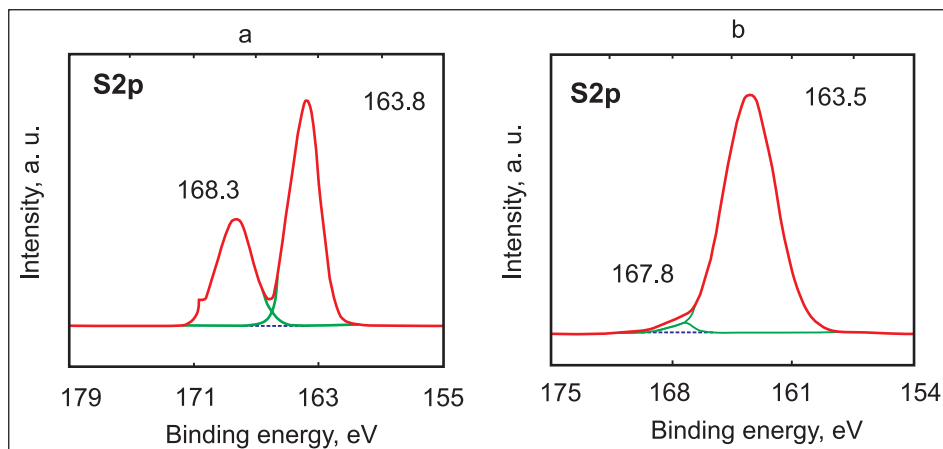


Fig. 1. PA sulfurized at 20 °C for 4 h: a) surface, b) etched

The coating surface was first studied by the XPS method, and then the coatings were etched by Ar^+ ions and their composition in a deeper layer was studied. The analysis was restricted by a very thin layer. From the obtained data, i. e. the atomic percentage of element binding energies and individual elements Cu 2p3, Tl 4f7, S 2p and O 1s spectra, it is possible to predict the composition of a layer. The maxima in S 2p spectra, corresponding to the binding energy values of $\sim 161\text{--}162$ eV, show the presence of sulfide sulphur; the maxima corresponding to the binding energy values of $\sim 163\text{--}164$ eV indicate the presence of elemental sulfur, and the maxima corresponding to the binding energy of ~ 168 eV hint to the presence of sulfate sulfur.

Copper sulfide and thallium sulfide layers formed by PA film sulfurization in $\text{H}_2\text{S}_{12}\text{O}_6$ solution at a temperature of 20 and 40 °C and then treated in Cu(II / I) salts or Tl_2SO_4 solution were studied by the XPS method.

Analysis of the data presented in Table 2 (samples 1–4) and a comparison of the distribution of Cu, S and O in the surface of the samples have shown that oxygen takes the biggest part of the surface of all samples. Such a large oxygen amount may be explained by its chemical absorption and also by copper sulfate absorption on the layer surface, as well as by insoluble copper(II) hydroxide formation on the surface; $\text{Cu}(\text{OH})_2$ may be formed while washing coatings with water.

Data in Table 2 show that on the layer's surface and in the etched surface various compounds of copper, sulfur and oxygen are present. The following compounds have been identified: CuS , Cu_2S , CuO , S_8 , CuSO_4 , $\text{Cu}(\text{OH})_2$. Analysis has shown that on the surface of all copper sulfide layers studied, there was only a small amount of copper sulfides, while the absorbed oxygen, copper sulfate, hydroxide and oxide take the largest part. We have mentioned that the metal sulfides take the form of dendrites, therefore, the absorbed copper sulfate and copper hydroxide remain in-between them.

When the layer's surface is etched by Ar^+ ions, the content of oxygen significantly decreases, or it disappears at all. This indicates that oxygen in the composition of the compounds is present on the surface only. Significantly more copper sulfides are found in the etched layers. This is shown also by the values of copper and sulfur ratios calculated from their atomic percentages.

From the data of analysis it follows that the composition of the layers formed in different conditions is similar (Table 2). This confirms also the similarity of the elements' spectra, therefore, here only very characteristic spectra are presented (Fig. 2). From a comparison of the Cu and S atomic percentages of samples No 1 and 2 it is obvious that more sulfur and copper are present in samples sulfurized at a higher tempera-

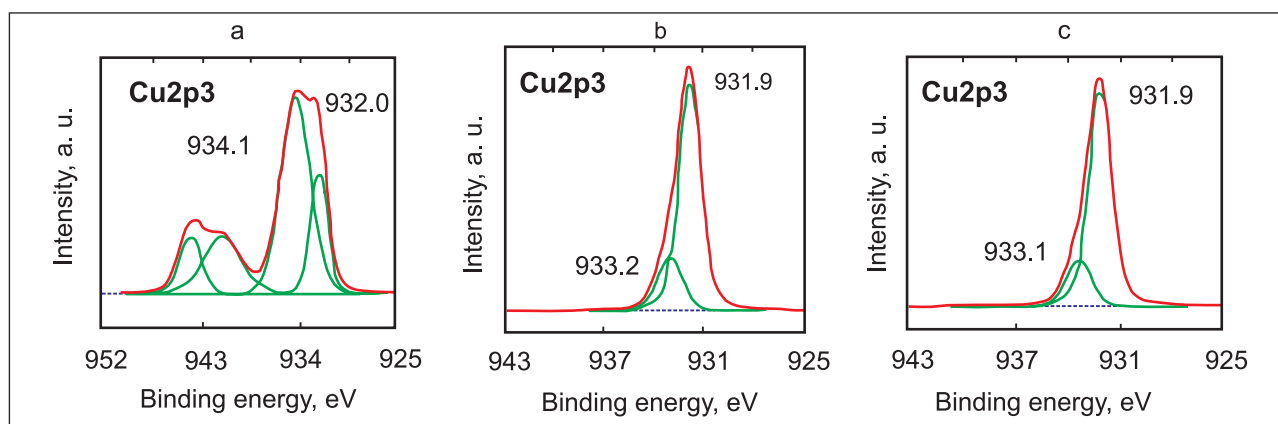


Fig. 2. Sample No. 4 (PA sulfurized for 6 h at a temperature of 40 °C): a – surface, b – etched for 15 s, c – etched for 60 s

Table 2. XPS data on Cu_xS layers formed on PA surface

| Etching conditions | Element | Amount, at. % | Binding energy, eV | Possible composition | Cu : S |
|---|---------|---------------|---------------------|------------------------------|--------|
| <i>Sample No. 1 (PA sulfurized at 20 °C, 4 h)</i> | | | | | |
| Surface | Cu | 2.75; 1.93 | 932.3; 934.3 | CuS, Cu ₂ S, CuO, | 1.04 |
| | S | 3.89; 0.62 | 161.3; 167.8 | CuSO ₄ | |
| | O | 23.76; 1.15 | 531.1; 532.5 | Cu(OH) ₂ | |
| | C | 65.9 | 284.4; 285.7; 287.9 | | |
| Etched for 15 s – 30 μA | Cu | 29.89; 15.53 | 932.1; 932.8 | CuS, Cu ₂ S, | 1.75 |
| | S | 22.07; 3.83 | 161.3; 163.3 | S ₂ | |
| | O | 2.92 | 531.5 | Cu(OH) ₂ | |
| | C | 25.76 | 284.3; 285.7 | | |
| <i>Sample No. 3 (PA sulfurized at 40 °C, 2 h)</i> | | | | | |
| Surface | Cu | 1.79; 2.7 | 932.4; 934.2 | CuS, Cu ₂ S, CuO, | 1.12 |
| | S | 3.18; 0.82 | 161.9; 167.8 | CuSO ₄ | |
| | O | 20.89; 2.07 | 531.2; 533.2 | Cu(OH) ₂ | |
| | C | 66.77 | 284.5; 285.6; 288.0 | | |
| Etched for 15 s – 30 μA | Cu | 32.63; 7.56 | 931.9; 933.1 | CuS, Cu ₂ S | 1.44 |
| | S | 27.84 | 161.2 | | |
| | O | 3.07 | 531.3 | Cu(OH) ₂ | |
| | C | 28.9 | 284.2; 285.7 | | |
| Etched for 60 s – 30 μA | Cu | 44.35; 9.7 | 932.0; 933.2 | CuS, Cu ₂ S | 1.73 |
| | S | 31.31 | 161.2 | | |
| | O | – | – | | |
| | C | 14.64 | 284.2; 285.6 | | |
| <i>Sample No. 2 (PA sulfurized at 40 °C, 4 h)</i> | | | | | |
| Surface | Cu | 2.14; 3.24 | 932.5; 934.4 | CuS, Cu ₂ S, CuO, | 1.05 |
| | S | 4.24; 0.87 | 161.7; 168.2 | CuSO ₄ | |
| | O | 22.56; 0.64 | 531.2; 533.2 | Cu(OH) ₂ | |
| | C | 64.26 | 284.6; 285.9; 288.2 | | |
| Etched for 15 s – 30 μA | Cu | 40.14; 8.43 | 931.9; 933.2 | CuS, Cu ₂ S | 1.54 |
| | S | 31.53 | 161.3 | | |
| | O | – | – | | |
| | C | 19.9 | 284.1; 286.1 | | |
| <i>Sample No. 4 (PA sulfurized at 40 °C, 6 h)</i> | | | | | |
| Surface | Cu | 1.41; 3.87 | 932.0; 934.1 | CuS, Cu ₂ S, CuO, | 0.76 |
| | S | 5.22; 1.7 | 161.7; 167.9 | CuSO ₄ | |
| | O | 23.15; 3.38 | 531.2; 532.8 | Cu(OH) ₂ | |
| | C | 58.83 | 284.4; 285.8; 287.9 | | |
| Etched for 15 s – 30 μA | Cu | 22.24; 4.8 | 931.9; 933.2 | CuS, Cu ₂ S | 1.21 |
| | S | 22.27 | 161.2 | | |
| | O | 4.03 | 532.2 | Cu(OH) ₂ | |
| | C | 46.66 | 284.0; 284.9; 285.7 | | |
| Etched for 60 s – 30 μA | Cu | 32.38; 8.04 | 931.9; 933.1 | CuS, Cu ₂ S | 1.39 |
| | S | 29.01 | 161.2 | | |
| | O | 3.37 | 532.0 | Cu(OH) ₂ | |
| | C | 27.16 | 283.8; 285.1 | | |

ture. In the samples sulfurized at a higher temperature for the same time (15 s), the content of sulfur was higher by 5.6 at. %.

Analysing XPS data of samples Nos. 2, 3 and 4 we see that the content of sulfur increases while increasing the time of sulfurization: 2 h – 4 at. %, 4 h – 5.11 at. %, 6 h – 6.92 at. %.

Comparison of data on surface and etched samples shows that the amount of sulfide sulfur increases very much; for example, the amount of sulfide sulfur in samples sulfurized for 2 h increases from 3.18 (surface) to 31.31 (etched for 60 s) at. %.

The copper content increases analogously (Fig. 2, Table 2). For example, the content of copper in sample No. 4 increased from 5.28 (surface) to 40.42 (etched for 60 s) at. %. Thus, when the content of sulfur in PA film is higher, more copper ions react and more copper sulfides are formed. This is shown also by the increasing value of the copper and sulfur ratio.

Upon analysing data presented in Table 3 (samples No. 1 and 2) and comparing the distribution of elements Tl, S and O on the surface of these samples, we have concluded that

Table 3. XPS data on Tl_xS layers formed on PA surface

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

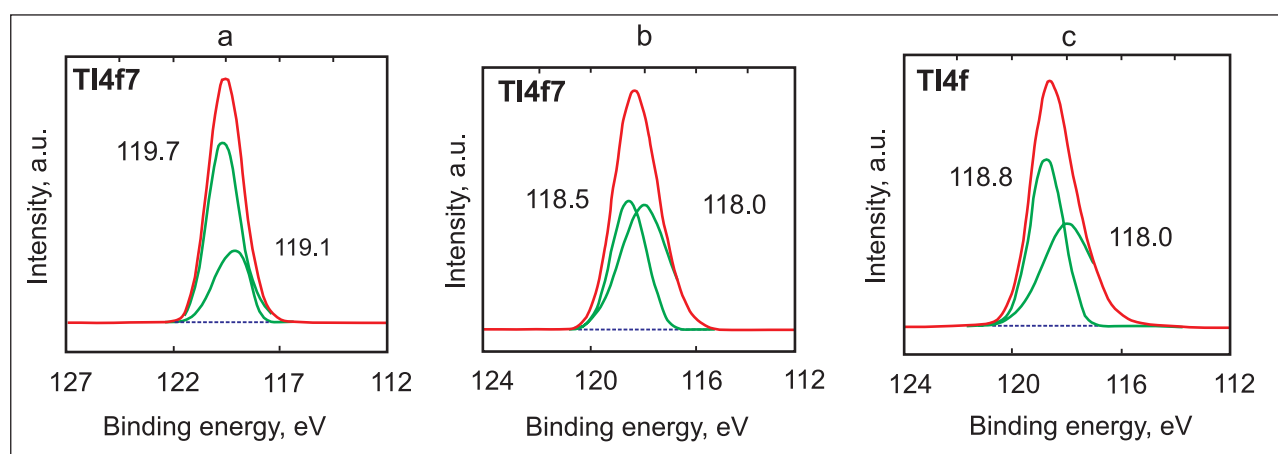


Fig. 3. Sample No 2 (PA sulfurized at 40 °C, 3 h): a – surface, b – etched for 15 s, c – etched for 60 s

oxygen takes the main part on a sample surface. As was mentioned above, such a high content of oxygen may be explained by its chemical absorption and by a low-soluble thallium(I) sulfate absorption on the layer surface and of insoluble thallium(III) hydroxide formation on the coating surface.

From data presented in Table 3 it follows that on the layer's surface and in the etched layer various thallium, sulfur and oxygen compounds are present. The following compounds have been identified: Tl_2O_3 , Tl_2S_3 , Tl_2S , S_8 , Tl_2SO_4 ,

$Tl(OH)_3$. The biggest amounts of Tl_2SO_4 and $Tl(OH)_3$ were present on the coating's 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 decomposition of polythionic acid, thallium(III) ions appear, which with the HO^- ions present in the alkalified Tl_2SO_4 solution form insoluble $Tl(OH)_3$. Oxygen may be joined into Tl_2O_3 . Oxygen was not detected

in samples etched for 60 s; there, thallium ions were joined with sulfide sulfur into thallium sulfides. At a higher sulfurization temperature, more sulfur was detected, possibly because of the bigger amount of sorbed polythionate ions and elemental sulfur, the product of their decomposition. Elemental sulfur was present in a deeper layer (Table 3, sample No. 2). The content of thallium in deeper layers increased; for example, in sample No. 2 (Table 3 and Fig. 3) it increased from 10.51 (surface) to 34.75 (etched for 60 s) at. %. More thallium and sulfur were present in the deeper layer: this is shown by the value of their ratio.

CONCLUSIONS

1. The phase composition of polyamide 6 films modified by copper sulfide, Cu_xS, and thallium sulfide, Tl_xS, layers was studied by the X-ray photoelectron spectroscopy method. Copper sulfide and thallium sulfide layers on the surface of polyamide films were formed by treating polyamide 6 films with the 0.002 mol · dm⁻³ solution of dodecathionic acid at a temperature of 20 and 40 °C and then with Cu(II / I) salts or Tl₂SO₄ solution.

2. On the surface of polyamide samples modified with copper sulfides, there are various copper, sulfur and oxygen compounds – CuS, Cu₂S, CuO, S₈, CuSO₄ and Cu(OH)₂, and on the surface of polyamide modified with thallium sulfides various thallium, sulfur and oxygen compounds – Tl₂O₃, Tl₂S₃, Tl₂S, S₈, Tl₂SO₄ and Tl(OH)₃ – were present.

3. The content of copper and thallium sulfides in the deeper layers of chalcogenides was higher than on the layer surface.

Received 17 December 2008

Accepted 24 December 2008

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**Cu_xS IR Tl_xS SLUOKSNIŲ POLIAMIDO PLĖVELIŲ
PAVIRŠIUJE, SUDARYTŲ NAUDOJANT DODEKA-
TIONATO RŪGŠTĮ, TYRIMAS RENTGENO
FOTOELEKTRONINE SPEKTROSKOPIJA**

S a n t r a u k a

Fazinė poliamido 6 (PA) plėvelių, modifikuotų vario sulfidų, Cu_xS, ir talio sulfidų, Tl_xS, sluoksniais, sudėtis tirta rentgeno fotoelektroninės spektroskopijos metodu. Vario sulfidų ir talio sulfidų

sluoksniai PA plėvelių paviršiuje sudaryti, apdorojant PA plėveles 0,002 mol · dm⁻³ koncentracijos dodekationato rūgšties, H₂S₁₂O₆, tirpalu 20 ir 40 °C temperatūroje ir po to Cu(II / I) druskų arba Tl₂SO₄ tirpalu. Nustatyta, kad PA bandinių, modifikuotų vario sulfidais, paviršiuje yra įvairių vario, sieros ir deguonies junginių – CuS, Cu₂S, CuO, S₈, CuSO₄ ir Cu(OH)₂, o PA paviršiuje, modifikuotame talio sulfidais, yra įvairių talio, sieros ir deguonies junginių – Tl₂O₃, Tl₂S₃, Tl₂S, S₈, Tl₂SO₄ ir Tl(OH)₃. Vario ir talio sulfidų kiekiai gilesniuose chalkogenidų sluoksniuose yra didesni, nei jų kiekiai sluoksnių paviršiuje.