Chalcopentathionic compounds as precursors for the formation of semiconductive and conductive copper chalcogenide layers on polyamide surface

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Kaunas University of Technology, Radvilėnų 19, LT-50254 Kaunas, Lithuania Semiconductive and electrically conductive layers of copper chalcogenides - copper sulfides, Cu S, mixed copper sulfides - copper selenides, Cu S-Cu Se, and mixed copper sulfides - copper tellurides, Cu_S-Cu_Te, - on the polyamide 6 (PA) surface were formed using the sorption-diffusion method and water solutions of potassium pentathionate, K₂S₂O₂ potassium selenopentathionate, K, SeS₄O₆ and potassium telluropentathionate, K, TeS₄O₆, as the precursors of polymer chalcogenization. Chalcopentathionate anions containing chains of divalent chalcogen atoms of low oxidation state, $O_3S-S-S-S-SO_3$, $O_3S-S-Se-S-SO_3$ and $O_3S-S-Te-S-SO_3$, are sorbed-diffused into PA films if they are treated with chalcopentathionic compound solutions. The concentrations of sorbed chalcogens increase with an increase of the temperature and concentration of the precursor solution and the duration of PA treatment. Cu,S, Cu,S-Cu,Se or Cu,S-Cu, Te layers are formed on the surface of PA film when a chalcogenized polymer is treated with a water solution of copper(II / I) salt: the anions of chalcopentathionates react with copper ions. The concentration of copper increases with increasing the concentration and temperature of precursor solution and the duration of PA initial chalcogenization. XPS and XRD results confirmed the formation of copper chalcogenide layers on PA surface. The phase composition of Cu_S, Cu_S-Cu_Se and Cu S-Cu Te layers depends on the conditions of PA chalcogenization, i. e. the concentration and temperature of chalcopentathionate solution and on the duration of initial treatment in the precursor solution. Cu_sS Layers formed using K₂S₅O₆ solutions are composed of the low-conductive tetragonal chalcocite, Cu₁₉₆S, monoclinic djurleite, Cu₁₉₃₇₅S, electrically conductive rhomhedral *digenite*, Cu₂S₅, orthorhombic *anilite*, Cu₂S₄, and cubic CuS₂; layers of Cu₂S-Cu₂Se formed using K₂SeS₄O₆ solutions – of low conductive *chalcocite*, Cu₂S, electrically conductive *digenite*, Cu₁₈S, djurleite, Cu, 9275S, anilite, Cu, 75S, and of copper selenides – bellidoite, Cu, Se, umangite, Cu, Se, klockmannite, CuSe, krutaite, CuSe, and Cu,Se; layers of Cu,S-Cu,Te formed using K,TeS406 solutions – of *chalcocite*, Cu₂S, *djurleite*, Cu_{1.9375}S, *anilite*, Cu_{1.75}S, *digenite*, Cu_{1.8}S, copper sulfide CuS2, copper tellurides Cu272 Te2, Cu4Te3, Cu185 Te, vulcanite, CuTe, Cu180 Te. The phase composition determines the electrical characteristics of the obtained layers: the sheet resistance of Cu_S layers varies from 0.104 to $1.52 \cdot 10^3$ K Ω/\Box , of Cu_xS-Cu_ySe layers from 12.2 Ω/\Box to 4.8 M Ω/\Box , of Cu S-Cu Te layers from ~1.0 k Ω / \Box to 4 · 10³ k Ω / \Box . The established regularities enable formation of Cu_xS, Cu_xS–Cu_ySe and Cu_xS–Cu_yTe layers of a desirable composition and conductivity.

Key words: review, chalcopentathionates, polyamide, copper chalcogenide layer

INTRODUCTION

Copper sulfide, copper selenide and copper telluride belong to chalcogenides – binary compounds of elements (mainly metals) with chalcogens, $Cu_x Y$ (Y = S, Se, Te). These compounds are of great interest owing to their variations in stoichiometric composition, nanocrystal morphology, complex structure, valence states, unique properties, and their potential applications in numerous fields [1–7]. Copper chalcogenides are semiconductors with thermoelectric properties and ionic conductivity. They have attracted considerable interest

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because of their wide range of applications in various fields of science and technology, in various devices such as solar cells, optical data storage, etc. [8–10].

Copper chalcogenide, $Cu_x Y$, thin layers have a number of applications, too: they are used in various devices such as solar cells, super ionic conductors, photo-detectors, photothermal conversion, electroconductive electrodes, microwave shielding coating, gas sensors [11–29], etc.

Various methods such asvacuum evaporation, activated reactive evaporation, spray pyrolysis, electroless deposition, successive ionic layer adsorption and reaction (SILAR), chemical bath deposition were used for the formation of copper chalcogenide layers on various dielectrics and on polymers [30–38].

Over the last decade, the use of the sorption-diffusion method for the formation of thin copper chalcogenide layers on the surface of polyamide 6 (PA) based on the initial treatment of a polymer with the solutions containing anions of polythionates, $S_n O_6^{2-}$, selenopolythionates, $SeS_n O_6^{2-}$ (n = 2, 4), and telluropentathionates, $TeS_4O_6^{2-}$, has been under extensive investigation [24, 25, 28, 29, 39–95]: the polythionic compound anions containing chains of divalent chalcogen atoms of low oxidation state [96–98] – polythionates, ⁻O₂S–S₂–SO₂, selenotrithionate, ⁻O₃S-Se-SO₃, selenopentathionate, ⁻O₃S-S-Se-S-SO₃, telluropentathionate, -O₃S-S-Te-S-SO₃, - are sorbed by a polymer. Upon treating chalcogenized polyamide with a solution of copper(II / I) salt, the copper sulfide, Cu S, [24, 41-46, 48-63], copper selenide, Cu Se, [25, 65-69], mixed copper sulfide-copper selenide, Cu_S-Cu_Se, [28, 71-77, 79-85] or mixed copper sulfide-copper telluride, Cu_S-Cu_Te, [29, 55, 79, 81, 83, 86–95] layers on the surface of a polymer are formed.

The aim of the present work was to integrate and to discuss the results obtained by us during studies of the sorption of chalcopentathionic compounds ions (pentathionate, $S_5O_6^{2-}$, selenopentathionate, $SeS_4O_6^{2-}$, telluropentathionate, $TeS_4O_6^{2-}$) into PA, as well as the formation and characterization of copper sulfide and mixed copper chalcogenide layers, since only separate fragments of these studies have been described in our previous publications [28, 29, 43, 47, 48, 50, 54–57, 59, 61, 62, 70–95].

EXPERIMENTAL

A PA 6 film (specification TY 6-05-1775-76, grade PK–4, 70 μ m 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 dessicator over CaCl₂ for 24 h.

Potassium pentathionate hemitrihydrate, $K_2S_5O_6 \cdot 1.5H_2O_5$, was produced by the method of Kurtenacker [99]; potassium selenopentathionate hemitrihydrate, $K_2SeS_4O_6 \cdot 1.5H_2O_5$, was prepared and chemically analyzed according to published procedures [100]; potassium telluropentationate hemitrihydrate, $K_2TeS_4O_6 \cdot 1.5H_2O_5$, was prepared and chemically analysed according to procedures published by O. Foss [101, 102]. The prepared salts were kept in the dark, in a desiccator over concentrated sulfuric acid.

PA films were sulfurized in a thermostatic vessel, using a continually stirred acidified (0.1 mol \cdot dm⁻³ HCl, pH ~1.5) 0.025–0.2 mol \cdot dm⁻³ K₂S₅O₆ solutions for up to 6 h at a temperature of 1–20 °C. Such interval of concentration was chosen because of the stability of potassium pentathionate in a solution. Preliminary experiments had shown that the sorption from the solutions of a lower concentration was too slow and insufficient, and at a higher concentration the stability of K₂S₅O₆ decreased significantly. The stability of pentathionate solution at temperatures higher than 20 °C was insufficient, either.

The samples of PA film were chalcogenized in the 0.025, 0.05, 0.1 and 0.2 mol \cdot dm⁻³ solutions of K₂SeS₄O₆ acidified with the addition of HCl (0.1 mol \cdot dm⁻³ HCl, pH ~1.5) at a temperature of 30, 40 and 50 °C. The total duration of experiments was 4.5 h.

The chalcogenization solution of potassium telluropentathionate was prepared at a concentration of 0.025-0.05-0.1 mol/ dm³ in 0.2 mol/dm³ solution of HCl (pH ~1.5); PA film samples were chalcogenized in K₂TeS₄O₆ solutions at a temperature of 1, 10 and 20 °C. At certain time intervals, PA film samples were removed from the chalcogenization solution, rinsed with distilled water, dried with filtration paper, left over CaCl₂ for 24 h and then used in further experiments and analysis.

Samples of chalcogenized PA were treated with a solution of Cu(II / I) salts at 78 °C for 10 min. A solution of Cu(II / I) salts was made from crystalline $CuSO_4 \cdot 5H_2O$ and hydroquinone as described in [103]. It is a mixture of Cu salts, containing 0.34 mol/dm³ of Cu(II) and 0.06 mol/dm³ of Cu(I) [104]. After treatment with a solution of Cu(II / I) salts, PA samples were rinsed with distilled water, dried over anhydrous CaCl₂ and used in further experiments.

Sulfur concentration (Cs) in PA film samples sulfurized in $K_2S_5O_6$ solution was determined potentiometrically [105]. First, a sample of a sulfurized PA film was treated under heating with 10–15 ml of 10 mol \cdot dm⁻³ KOH 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 concentration of sulfur in PA chalcogenized in $K_2SeS_4O_6$ solution was determined nephelometrically as described in [106]. The concentration of sulfur in PA chalcogenized in $K_2TeS_4O_6$ solutions, in the form of sulfates, was determined turbidimetrically [90, 107]. Before analysis, samples of PA with tellurium and sulfur containing films had been mineralized. Samples were treated with concentrated HNO₃ to destroy PA and to oxidize tellurium and sulfur compounds to tellurites and sulfates. Heating with concentrated hydrochloric acid removed the excess of nitric acid. Sulfate ion in the concentration range of 1–15 mg/dm³ may be easily determined by utilizing the reaction with barium chloride in a solution slightly acidified with hydrochloric acid to give barium

sulfate. The intensity of the transmitted light as a function of the concentration of the dispersed phase of BaSO₄ was measured photometrically with a KFK-4 photoelectric colorimeter (Russia) at $\lambda = 400$ nm. The standard deviation in the range of concentrations 5–10 mg/dm³ was 8%.

The concentrations of selenium, tellurium and copper in a PA sample were determined using a Perkin-Elmer 503 atomic absorption spectrometer [108]. Before analysis, samples of PA with copper chalcogenide films had been mineralized as desribed in determination of sulfur concentration. For the conditions described above, the sensitivity of the AAS method is 1 µg/ml tellurium for the 1% absorption.

UV spectra were recorded on a Spectronic^R Genesis 8 UV / Visible spectrophotometer with a compensation of PA absorption; the range of 200–800 nm. IR spectra were recorded with a Perkin Elmer FTIR Spectrum GX spectrophotometer by averaging 64 scans with 0.3 cm⁻¹ resolution at room temperature for each sample, the range 400–1 400 cm⁻¹.

The phase composition of copper chalcogenide layers on PA surface was investigated by X-ray diffraction techniques with a DRON-6 diffractometer equipped with a special device for beam limitation at low and medium diffraction angles using a graphite-monochromatized Cu–K α radiation source ($\lambda = 1.54178$ Å) under a voltage of 30 kV and a current of 30 mA. The XRD patterns were recorded with a step of 0.05° from 2 θ = 30° to 70°. X-ray diffractograms of PA samples with layers of copper chalcogenides were treated using Search Match, ConvX, Xfit, Dplot 95 and Photo Styler programs to eliminate PA maxima.

The resistance of copper sulfide films formed employing $K_2S_5O_6$ was measured using an E7-8 numerical measuring instrument with special electrodes. The electrodes were produced from two nickel-plated copper plates. The plates were fixed with a 1 cm spacing, and the dielectric material was placed between them. We measured sheet resistance (R) of Cu_xS layers on polymers. The concept of sheet resistance is used to characterize thin deposited layers. Sheet resistance was specified as "ohms per square" (Ω / \Box , ohms / square).

The resistance of $Cu_x S-Cu_y Te$ and $Cu_x S-Cu_y Se$ layers of a different composition to the constant current was measured with an MS8205F constant current numerical measuring device with special electrodes. The electrodes were produced from two nickel-plated copper plates. The plates were fixed with 1 cm, spacing and the dielectric material was placed between them.

XPS spectra of Cu_xS, Cu_xS–Cu_ySe and Cu_xS–Cu_yTe layers were recorded with an spectrometer ESCALAB MKII (VG Scientific, radiation Mg K_a – 1253.6 eV, output 300 W). Vacuum in the analysing chamber was kept at a level of $1.33 \cdot 10^{-8}$ Pa, 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 $9.3 \cdot 10^{-3}$ Pa and current 20 µA; the duration of etching was 10-180 s and the rate 1 nm / 30 s. The maximum accuracy of the method is ± 0.1 at. %. To investigate the layers obtained by the XPS method, the photo-

electron spectra of Cu $2p_{3/2}$, Se $3d_{5/2}$, Te $3d_{5/2}$ and S 2p were recorded. Empirical sensitivity factors for these elements were taken from the literature [109], and the obtained spectra were compared with the standard ones [110].

The morphology of the surface of Cu₂S and Cu₂S-Cu₂Te layers, the quantitative microscopy of the roughness of layers formed on the surface of PA were studied with the NT-206 atomic force microscope in the 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 from 10×10 up to 35×35 microns, the measurement matrix up to 512×512 points and more, the maximum range of measured heights 4 microns, lateral resolution 2 nm, vertical resolution 0.1-0.2 nm. Lateral force microscopy studies are useful for imaging the variations in surface friction that can arise from inhomogeneity in surface material, and also for obtaining edge-enhanced images. Microscopic investigations of the morphology and roughness of Cu_xS-Cu_ySe layers were performed also using a QUESANT QScope-250 (Quesant Corporation, USA) atomic force microscope in the contact regime with ultra high resolution probes (Micromash Corp.). The data of measurements were analysed using the Scan Atomic[™], SPIP (Scanning Probe Image Processor) programs. Areas of 10×10 microns were investigated; standard microscope program equipment of image maintenance as well as specialized SPIP package (Image Metrology Corp.) were applied for the quantitative evaluation of the surface.

RESULTS AND DISCUSSION

The modification of PA film by depositing layers of copper chalcogenides on its surface in our studies was performed in two stages. The first stage of this process was the interaction of PA film with a chalcopentathionic compound (pentathionate, $S_5O_6^{2-}$, selenopentathionate, $SeS_4O_6^{2-}$, telluropentathionate, $TeS_4O_6^{2-}$) solution when the chalcogenization of PA film occurs, i.e. anions containing three divalent chalcogen atoms of low oxidation state sorb-diffuse into the matrix of the PA surface.

In the second stage, the chalcogenized PA film was treated with Cu(II / I) salt water solution. As a result of the interaction of copper ions with the chalcopentathionate ions sorbeddiffused in the PA film, the layers of copper chalcogenides of variable composition were formed on the polymer surface. For example, as a result of redox reactions of Cu(II / I) solution with the surface of PA sulfurized with the solution of potassium pentathionate, $K_2S_5O_6$, electrical conductive layers of copper sulfides were formed:

$$S_5O_6^{2-} + 2Cu^+ + 2H_2O \rightarrow Cu_2S + 2S + 2H_2SO_4$$
, (1)

$$S_5O_6^{2-} + Cu^{2+} + 2H_2O \rightarrow CuS + 2S + 2H_2SO_4$$
, (2)

$$1/nS_n + 2xCu^+ \to Cu_xS + xCu^{2+}.$$
(3)

Cu(II) ions did not react with the elemental sulfur.



Fig. 1. IR spectra of PA treated in 0.2 mol/dm³ K₂S₅O₆ solution at 10 °C for different time. Sulfurization time, h: 1 - 1, 2 - 2, 3 - 5

Formation of copper sulfide layers on polyamide 6 surface using potassium pentathionate solutions

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.

We found that the peaks of most intensive bands in the IR spectra of PA samples sulfurized in K₂S₅O₆ solution, recorded by the compensation method (PA absorption eliminated), were in the intervals 418-484, 523-568, 609-737, 985-1079 and 1111-1284 cm⁻¹ (Fig. 1). On the grounds of the literature data [111, 112], the peaks in the first interval were assigned to the valence vibrations in the S–S bond (v_{s_s}) , in the second interval – to the asymmetric deformation O–S–O vibrations, δ_{as} (O–S–O), in the third interval - to the symmetric deformation O-S-O vibrations, δ_1 (O-S-O), in the fourth interval – to the symmetric valence S–O vibrations, v_s (S–O), and in the fifth interval – to the asymmetric valence S–O vibrations, v_{as} (S–O). These results have confirmed that the sorption of pentathionate ions by PA occurs during polymer treatment with an acidified $K_2S_5O_4$ solution.

The UV absorption spectra of PA samples sulfurized for different periods of time in $K_2S_5O_6$ solution are shown in Fig. 2. Three absorption maxima are observed in these spectra: at 250 nm as an obvious shoulder, at 285 nm as a peak, and at 325 nm as an unclearly defined shoulder.

According to data of a study of the UV absorption spectra of lower potassium polythionates [113, 114], the absorption maxima of pentathionate ions are most intensive at 256 and 295 nm. Thus, UV absorption spectra recorded by us have confirmed again that sulfur is sorbed by PA films in the form of pentathionate ions. The intensity of absorption maxima in the spectra, as expected, increased with an increase in the duration of a polymer treatment with potassium pentathionate solution.



Fig. 2. UV absorption spectra of PA films sulfurized in 0.05 mol \cdot dm⁻³ K₂S₅O₆ solution at a temperature of 10 °C for different period of time. Duration of PA sulfurization, h: 1 - 0.25, 2 - 1, 3 - 2, 4 - 3, 5 - 4, 6 - 5, 7 - 6

Formation of copper sulfide layers on the surface of polyamide 6 chalcogenized in $K_2S_5O_6$ solution

The concentration of sulfur sorbed by a polymer during its treatment in a $K_2S_5O_6$ solution increased with increasing the temperature (Fig. 3) and concentration (Fig. 4) of the sulfurization solution.

Then the chalcogenized PA samples were treated with a water solution of Cu(II / I) salts. Changes of a PA tape appearance after its treatment with Cu(II / I) solution indicated formation of copper chalcogenide layers on the surface of the



Fig. 3. Change of sulfur concentration in PA with time during its treatment with 0.05 mol \cdot dm⁻³ K₂S₅O₆ solution at different temperature. T, °C: 1 - 1; 2 - 10; 3 - 20



Fig. 4. Change of sulfur concentration in PA with time during its treatment with $K_2S_5O_6$ solution of different concentration at a temperature of 10 °C. Concentration of K,S₅O₆ solution, mol \cdot dm⁻³: 1 – 0.025, 2 – 0.05, 3 – 0.1, 4 – 0.2

polymer. The tapes from colourless transformed into yellow, then into brown and acquired a metallic lustre. Electrical measurements finally confirmed that PA surface from the dielectric became a semiconductor or an electrical conductor.

The conditions of initial chalcogenization determined the concentration of copper and the chemical and phase composition of the chalcogenide layer formed: the concentration of copper increased (up to ~40 mg \cdot g⁻¹) with increasing the temperature and concentration of PA sulfurization precursor solution (Figs. 5, 6).



Fig. 5. Dependence of copper concentration in PA on the period of initial PA treatment with 0.05 mol \cdot dm⁻³ K₂S₅O₆ solution at different temperature. Sulfurized PA was treated with a Cu(II / I) salt solution. T, °C: 1 - 1, 2 - 10, 3 - 20



Fig. 6. Dependence of copper concentration in PA on the period of initial PA treatment with $K_2S_5O_6$ solution of different concentration at a temperature of 10 °C. Concentration of $K_1S_2O_6$ solution, mol \cdot dm⁻³: 1 – 0.05, 2 – 0.1, 3 – 0.2

X-ray photoelectron spectroscopy analysis of $Cu_x S$ layers formed on the surface of polyamide 6 using $K_2S_5O_6$ solutions

The study of the phase composition of Cu_xS layers by the method of X-ray photoelectron spectroscopy (XPS) was restricted to studying the chemical and phase composition of the Cu_xS surface layer.

By the XPS method were studied copper sulfide layers formed on PA 6 films which had been sulfurized for different time (0.5, 4.0 and 6.0 h) in acidified solutions of $K_2S_5O_6$ of different concentration (0.025, 0.05, 0.10 and 0.20 mol \cdot dm⁻³) and temperature (1, 10 and 20 °C). Then the sulfurized films were treated with a Cu(II / I) salt solution. The results are shown in Figs. 7–10.

The values of Cu $2p_{3/2}$ spectra bond energies of not etched Cu_xS layers, presented in Figs. 7 and 8, indicate the presence of CuO, Cu₂O, CuS, Cu₂S, Cu and CuSO₄ in the composition of these layers. It is also obvious that the composition of these compounds does not depend on the conditions of sulfurization. From the S 2p spectra of the same layers one can see

that, besides CuS and $CuSO_4$, also K_2SO_4 and elemental sulfur are present in the composition of the layer. Sulfate ions and elemental sulfur form during the interaction of sulfurized PA films with the copper salt solution [115]:

$$S_n O_6^{2-} + 2Cu^+ + 2H_2 O \rightarrow Cu_2 S + (n-3)S + 2H_2 SO_4.$$
 (4)

 K_2SO_4 and sulfur are found in the spectra of copper sulfides on the surface of PA 6 films formed by its sulfurization at a temperature of 1 and 10 °C. It is possible that not all $CuSO_4$, K_2SO_4 and elemental sulfur had been removed from the surface of copper sulfide layers during their washing with distilled water after treatment with a copper salt solution. It is also impossible to prevent the formation of CuO and Cu₂O in the polymer surface since all processes of copper sulfide layer formation proceed in an oxygen-containing environment.

From data of Cu, S, O and C distribution in copper sulfide layers it follows that the biggest part of the unetched surface is taken by carbon and oxygen, their content depending on sulfurization conditions changing within 69.2–81.1 at. % for



Fig. 7. XPS Cu $2p_{3/2}$ spectra of not etched copper sulfide layers on PA 6 films formed by sulfurization for 4 h in 0.1 mol·dm⁻³ solutions of $K_2S_5O_6$ of different temperature and then treated with Cu(II / I) salt solution



Fig. 8. XPS Cu $2p_{3/2}$ spectra of not etched copper sulfide layers on PA 6 films formed by sulfurization for 4 h at a temperature of 10 °C by $K_2S_3O_6$ solutions of different concentration and then treated with Cu(II / I) salt solution



Fig. 9. XPS S 2p spectra of not etched copper sulfide layers on PA 6 films formed by sulfurization for 4 h in 0.1 mol \cdot dm⁻³ solutions of K₂S₅O₆ of different temperature and then treated with Cu(II / I) salt solution

Fig. 10. XPS S 2p spectra of not etched copper sulfide layers on PA 6 films formed by sulfurization for 4 h in the $K_2S_5O_6$ solution of different concentration at s temperature of 10 °C and then treated with Cu(II / I) salt solution

C and 16.0–25.9 at. % for O. The bulk of carbon must be attributed to the matrix of the polymer and some part to gases containing carbon adsorbed on the surface from the atmosphere. Oxygen is present in the composition of copper oxides and salts mentioned above (Figs. 7–10), possibly because of the physical adsorbtion of water and oxides present in the air.

After a copper sulfide layer had been etched by Ar⁺ ions for 90 s, the content of carbon remained similar (62.3–87.1 at.%), but the content of oxygen decreased (6.8–19.7 at.%), indicating that the bulk of carbon belongs to the polymer matrix, whereas the content of oxygen in the deeper layers decreases and does not influence much the composition of these layers. This indication was confirmed by results of X-ray diffraction, since no copper oxides were detected in the composition of copper sulfide layers. The content of copper and sulfur on the surface of Cu_xS layers, depending on the conditions of sulfurization, changed within 0.9–2.1 at.% and 0.8–2.6 at.%, respectively. The concentrations of these elements in the layers

after etching with Ar^+ ions for 90 s increased to 2.3–12.9 at. % and 2.4–9.9 at. %, respectively, indicating a higher concentration of copper sulfides in the layers as compared with that on the layer surface. The values of the Cu : S atomic ratio, depending on the sulfurization conditions, changed on the surface of the layers and after their etching from 0.69 to 1.93.

Summarising the results obtained by the XPS method, we could state that copper sulfide layers form on PA 6 film surface when films are sulfurized in different conditions and then treated with a Cu(II / I) salt solution. The following compounds were detected on the surface of the layers: CuO, Cu₂O, CuS, Cu₂S, Cu, CuSO₄, K₂SO₄ and elemental sulfur. It is known that the value of *x* in Cu₂S sulfides may change from 1 to 2, forming non-stoichiometric sulfides. But the XPS analysis according to the literature data and the values of bonding energies give a possibility to determine only stoichiometric sulfides (CuS and Cu₂S). Thus, an XPS study gives only additional information concerning the composition of copper

sulfide layers formed on PA 6 film surface. More comprehensive data were obtained by X-ray diffraction analysis of Cu_xS layers formed by us.

X-ray diffraction studies and electrical sheet resistance of copper sulfide layers formed on the surface of polyamide 6 films using K₂S₅O₆ solutions

Cu_xS layers of various composition are formed on the surface of the polymer and in its bulk after treating PA samples containing sorbed polythionate ions with copper (II / I) solution. The phase composition of the formed layer was established by comparing its X-ray diffraction patterns with those of known copper sulfides [116–119]. The chemical composition and crystal structure of the majority of Cu_xS minerals such as *chalcocite*, Cu₂S, *djurleite*, Cu_{1.95}S, *yarrowite*, Cu_{1.12}S and *covellite*, CuS were investigated. The crystal structure of Cu_xS depends on the chemical composition and the conditions of synthesis. The composition of Cu_xS deposited by the sorption–diffusion methods was scarcely investigated.

Structural studies of the copper chalcogenide, $Cu_x Y (Y = S, Se, Te)$ layers formed by the sorption–diffusion method are limited by the polycrystallinity of the obtained layers, as well as by the existence of $Cu_x Y$ phases of various composition and structure, and by the crystallinity of PA. The intensity of the polymer peaks at $\theta < 13^\circ$ exceeds the intensity of copper chalcogenide peaks several times. Therefore, the area of $2 \theta \ge 26.0^\circ$ was investigated in more detail.

After treatment of PA samples with sorbed polythionate anions for a different time in a copper salt solution at 78 °C, Cu_xS films of different composition were obtained. The X-ray diffraction patterns of the films showed peaks of various copper sulfide phases coexisting in a film (Figs. 11, 12).

The X-ray diffraction patterns of Cu_sS layers formed on PA after its sulfurization in K₂S₅O₆ solutions of different concentration for 4 h at 10 °C are shown in Fig. 11. When the 0.025 and 0.05 mol · l⁻¹ solutions of potassium pentathionate had been used for polymer sulfurization, the peaks of orthorhombic *anilite*, $Cu_{1.75}$ S, at 2 θ = 41.10, 48.50, 53.60, 58.40, 60.90 ° [116] and monoclinic *djurleite*, Cu_{1.9375}S, at 2 θ = 34.40 and 38.20 ° [117] were detected (Fig. 11, curves 1 and 2). The peak of an additional phase of CuS₂ at $2\theta = 59.80^{\circ}$ [118] was detected in Cu_sS layers formed on PA initially sulfurized with $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{K}_2 \text{S}_5 \text{O}_5$ solution (Fig. 11, curve 3). We noted that the number of more conductive anilite peaks and their intensity increased with increasing the concentration of $K_2S_5O_6$ solution used for PA sulfurization: only one peak of djurleite at 2 θ = 38.20 ° [117] and the peaks of *anilite* at 2 θ = 37.60, 46.50 and 49.60 ° [116] were found in the diffraction pattern of Cu₂S layer on PA, sulfurized with 0.20 mol · dm⁻³ solution of $K_2 S_5 O_4$ (Fig. 11, curve 4).

Analysis of X-ray diffraction patterns of Cu_xS layers formed on PA sulfurized for 4 h with 0.1 mol \cdot dm⁻³ K₂S₅O₆ solution at different temperatures showed that their phase composition changed (Fig. 12). On treating PA samples with K₂S₅O₆ solution at 1 °C, phases of poorly conductive *djurleite*,



Fig. 11. X-ray diffraction patterns of Cu_xS layers on PA (peaks of *djurleite* $(Cu_{1.9375}S) - Dj$, *anilite* $(Cu_7S_4) - A$, copper sulfide $(CuS_2) - S$). PA was treated with $K_2S_5O_6$ solution of different concentration for 4 h at 10 °C. Sulfurized PA was treated with Cu(II / I) salt solution. The concentration of $K_2S_5O_6$ solution, mol \cdot dm⁻³: 1 - 0.025, 2 - 0.05, 3 - 0.10, 4 - 0.20



Fig. 12. X-ray diffraction patterns of Cu_xS layers on PA (peaks of *djurleite* (Cu_{1.9375}S) – Dj, *chalcocite* (Cu_{1.96}S) – Ch, *anilite* (Cu₂S₄) – A, *digenite* (Cu₃S₅) – D, copper sulphide CuS₂₇ – S). PA was initially treated with 0.1 mol \cdot dm⁻³ of K₂S₅O₆ solution for 4 h at different temperature. Sulfurized PA was treated with Cu(II / I) salt solution. The temperature of K₂S₅O₆ solution, °C: *1* – 1, *2* – 10, *3* – 20

Cu_{1.9375}S (peak at 2 θ = 38.2 °), and tetragonal *chalcocite*, Cu_{1.96}S, [119] (peak at 2 θ = 48.8 °) were detected (Fig. 12, curve 1). When the temperature of K₂S₅O₆ solution was raised up to 10 °C, the Cu_xS layer consisted of three phases: monoclinic *djurleite*, Cu_{1.9375}S (2 θ = 38.2 °), more conductive orthorhombic *anilite*, Cu₇S₄, (peaks at 2 θ = 49.4 and 64.7 °) and conductive cubic copper sulfide CuS₂ (peak at 2 θ = 59.8 °) (Fig. 12, curve 2). The further increase of the PA film sulfurization temperature to 20 °C resulted in the formation of a Cu_xS layer consisting of four phases: monoclinic *djurleite*, Cu_{1.9375}S (peak at 2 θ = 38.2 °), orthorhombic *anilite*, Cu₇S₄ (peaks at 2 θ = 49.4, 50.5, 59.6 and 61.5 °), tetragonic *chalcocite*, Cu_{1.96}S (2 θ = 45.02 °) and more conductive rhombohedral *digenite*, Cu₉S₅ (peak at 2 θ = 60.1 °) (Fig. 12, curve 3).

Changes of the phase composition of copper sulfide layers determine the electrical conductivity of these layers. The sheet resistance depends greatly on the conditions of PA initial sulfurization (Table 1). When the duration of PA initial chalcogenization was prolonged and the concentration of chalcogenization solution was increased, the conductivity of Cu_xS layers increased, too. It is known [120] that the electrical resistance of Cu_xS decreases 10⁶ times when the value of *x* changes from 2 to 1. In these conditions, the stoichiometrical composition of Cu_xS changes in the direction of decreasing *x*, resulting in the formation of copper sulfide layers of low electrical resistance (~100 Ω / \Box).

Thus, the established regularities enable formation on PA surface of $Cu_x S$ layers of a desirable composition and conductivity.

X-ray studies have also shown that if the sulfurization time of PA is prolonged, the concentration of the low-conductive *chalcocite* (Cu_{1.96}S) and *djurleite* (Cu_{1.9375}S) phases decrease, but of the more conductive *anilite* and rhombohedral *digenite* (Cu₉S₅) increased. If the duration of PA sulfurization is increased to four hours (but the concentration of K₂S₅O₆ solution and temperature are unchanged), the phase of the more conductive orthorhombic *anilite* (Cu₇S₄) dominates in the Cu_xS layer formed; besides, the phase of rhombohedral *digenite* (Cu₉S₅) was formed. Thus, the stoichiometrical composition of copper sulfides change in the direction of *x* decrease, resulting in the formation of Cu_xS layers with a very low electrical resistance. Study of the morphology of $Cu_x S$ layers formed on PA surface using $K_2S_5O_6$ solutions

Modifying polymers with layers of copper 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 Cu_vS layers.

For the morphology and roughness characterization of $Cu_x S$ layers we applied the method of atomic force microscopy. A morphological study of PA modified with $Cu_x S$ layers revealed the layers to be essentially different. The aim of this study was to find the predominant mechanism of $Cu_x S$ layer formation on PA surface, the conditions of layer homogenity and growth evenness. Fields of 35×35 microns were investigated; for the quantitative estimation of the surface, the standard programs of the view treatment were used. It has been determined that the surface morphology of copper chalcogenide layers formed on PA surface depends on the conditions of polymer sulfurization. The surface views of $Cu_x S$ layers obtained by AFM are shown in Fig. 14–16, and a view of initial PA surface is presented in Fig. 13.

Studying the formation of Cu₂S layers on PA surface, formation of coatings was carried out by sulfurizing PA for 4.0 h at a temperature of 1, 10 and 20 °C with 0.1 mol \cdot dm⁻³K₂S₅O₆ solution and then treating with Cu(II / I) salt solution. Views of these coatings are shown in Figs. 14, 15 and 16. In a view presented in Fig. 14, one can see that formation of a coating, because of a low temperature of PA treatment with K₂S₂O₆ solution, proceeds slowly, an uneven covering is observed. Only in separate places the formation of small islands begins; the height of the coatingis - ~203 nm. With the further growth of the coating (increasing the temperature of PA sulfurization in $K_2S_2O_4$ solution to 10 °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. 15). The height of the coating increased to 314 nm. Upon increasing the temperature of sulfurization solution to 20 °C, the presence of even larger agglomerates is observed (Fig. 16), and the height of the coating increased to 776 nm. Thus, increasing the temperature of sulfurization from 1 to 20 °C results in an increasing of coating height ~3.8 times.

Solution of $K_2S_5O_6$		Duration of sulfurization, h								
Concentration, mol · dm ⁻³ Temperature, °		0.25	0.50	1.00	2.00	3.00	4.00	5.00	6.00	
0.025	1	-	-	-	-	$1.52 \cdot 10^{3}$	55.4	13.3	8.05	
	10	-	-		2.44	1.35	0.98	0.50	0.39	
0.05	1	-	-	-	-	-	-	0.93	0.81	
	10	-	-	-	-	3.03	2.67	1.11	1.05	
	20	-	-	-	0.283	0.236	0.194	0.161	0.119	
0.10	1	-	-	-	-	-	56.13	36.00	2.07	
	10	-	-	-	21.78	1.63	1.12	0.58	0.35	
	20	-	4.5 · 10 ²	2.2	0.457	0.227	0.127	0.122	0.104	
0.20	10	_	_	985	2.34	0.80	0.391	0.273	0.298	

Table 1. Sheet resistance (k Ω/\Box) of Cu₂S layers on PA first treated with K₂S₂Solution and then with Cu(II / I) salt solution at 78 °C for 10 min

Profile sections of $Cu_x S$ coatings has shown that the coating surface is rather uneven. The roughness increases and, as is seen from the views of surfaces (Figs. 14–16) and from line profiles, the crystallites are of different height, diameter and

form. Changes of the roughness are shown by the roughness parameters (Fig. 17). The height of the crystallites increases with increasing the temperature of $K_2S_5O_6$ solution; the height of the coating has increased ~4 times (Fig. 18).



Fig. 13. Atomic force microscopy view of initial (not sulfurized) PA surface: 2D view of lateral forces microscopy (*a*) and 3D topography view (*b*). Scan field area 12×12 microns. Interval of uneveness height up to 67.4 nm





Fig. 14. Atomic force microscopy view of thin Cu_xS 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 1 °C in 0.1 mol \cdot dm⁻³ K₂S₅O₆ solution and then treated with Cu(II / I) solution

Fig. 15. Atomic force microscopy view of thin Cu_xS 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 10 °C in 0.1 mol \cdot dm⁻³ K₂S₅O₆ solution and then treated with Cu(II / I) solution



Fig. 16. Atomic force microscopy view of thin Cu_xS 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 0.1 mol \cdot dm⁻³ K₂S₅O₆ solution and then treated with Cu(II / I) solution



Fig. 17. Dependence of $Cu_x S$ layer mean square roughness on the temperature of PA sulfurization. PA was treated for 4 h in 0.1 mol/dm³ K₂S₂O₂ solution

Summarizing the results of the morphological studies of Cu_xS layers it is possible to state that, depending on the temperature of initial PA sulfurization in $K_2S_5O_6$ solution (in the same conditions of sulfurized PA "copperizing"), the formation of copper sulfide layers proceeds unevenly as islands, which later grow together into bigger agglomerates. The surface of the coating is uneven, rather rough. The height of the coating increases with increasing the temperature of PA sulfurization in $K_2S_5O_6$ (Fig. 18). An analogous tendency was observed also in changes the average roughness of coating surface (Fig. 17): it increases with increasing the temperature of sulfurization.

Formation of copper sulfide – copper selenide layers on polyamide 6 surface using potassium selenopentathionate solutions

To investigate sulfur and selenium sorption into PA from potassium selenopentathionate solutions, it was relevant to ascertain in what form (as elemental chalcogens, its radicals or selenopentathionate ion $\text{SeS}_4\text{O}_6^{2-}$) chalcogens sorb on PA.

Our investigations showed that the semi-hydrophilic polymer PA sorbs selenopentathionate ions from these solutions. The sorption of selenopentathionate ions, $SeS_4O_6^{2-}$, from 0.025–0.20 mol/dm³ solutions of K₂SeS₄O₆ by PA has been studied by IR (400–1 300 cm⁻¹) and UV (200–450 nm) absorption spectroscopy. The peaks in the IR spectra (Fig. 19) were found in the ranges 449–466, 534–535, 608–725, 830–1017 and 1095–1226 cm⁻¹and have been assigned to the v (S–S), δ_{as} (O–S–O), δ_s (O–S–O), v_s (S–O) and v_{as} (S–O), respectively. This data confirmed that the ions of selenopentathionate are sorbed into PA, because of similarity of the peaks of the former with the peaks in IR spectra of chalcopolythionates and K₂SeS₄O₆, respectively, at 421–452, 536, 618–637, 1027–1036, 1226 cm⁻¹ [97, 98, 112, 121–123].



Fig. 18. Dependence of Cu_xS layer height on the temperature of PA sulfurization. PA was treated for 4 h in 0.1 mol/dm³ K₁S₂O_x solution



Fig. 19. IR spectra of PA treated with 0.05 mol/dm³ solution of $K_2SeS_4O_6$ at 50 °C for different time. Chalcogenization time, min: 1 - 10, 2 - 30, 3 - 90

In the UV absorption spectra, three absorption maxima are observed: at 240–250 nm as a strong peak, at 280 nm as weakly expressed shoulder (this peak is observed only in the spectra of PA samples chalcogenized longer than 20 min in the $K_2SeS_4O_6$ solution) and at 280–320 nm as a clear shoulder (Fig. 20). The position of the peaks at 280–320 nm and at 240–250 nm depends on the duration of PA chalcogenization and moves towards lower frequencies with an increase of treatment time. UV absorption spectra of chalcogenized PA are analogous to the UV spectrum of chalcopolythionates and $K_2SeS_4O_6$ solution [97, 98, 123–126], but all peaks in the chalcogenized polymer spectra are moved towards lower frequencies because of sorbed selenopentathionate bonds with the chelating groups of the polymer. Thus, UV and IR absorption spectra confirmed that sulfur and selenium are sorbed into PA in the form of selenopentathionate ions.

Formation of copper sulfide – copper selenide layers on the surface of polyamide 6 chalcogenized in $K_2SeS_4O_6$ solution

Chemical analysis of chalcogenized samples has shown that the concentration of sulfur and selenium sorbed into PA depends on the temperature and concentration of selenopentathionate solution and the time of the polymers treatment (Fig. 21, 22). With an increase in these parameters, the concentration of sulfur and selenium in the PA increases as well. Our data have also shown that the increase of the temperature of the $K_2Ses_4O_6$ solution depending on the concentration



Fig. 20. UV absorption spectra of PA treated with 0.05 mol/dm³ solution of $K_2SeS_4O_6$ at 50 °C for different time. Chalcogenization time, min: 1 - 10, 2 - 20, 3 - 30, 4 - 90, 5 - 120, 6 - 150, 7 - 210, 8 - 270

of sulfur sorbed in the polymer is much more pronounced than the increase of the concentration of the selenopentathionate solution.

Upon summarizing the results of the first stage of PA modification – chalcogenization – we may conclude that potassium selenopentathionate is a suitable precursor for the formation of copper chalcogenide layers on PA surface.

Then, the interaction of PA chalcogenized in the potassium selenopentathionate solutions with a solution of Cu(II / I) salts was studied. Brown or even black semiconductive or conductive copper sulfide – copper selenide layers were formed. The copper chalcogenide layers were found to form as a result of heterogeneous redox reactions among Cu⁺, Cu²⁺ and SeS₄O₆²⁻ ions. The formation of a Cu_xS–Cu_ySe layer depends on the concentrations of sulfur and selenium in the chalcogenized PA.

The concentration of copper in the layer was found to be directly and strongly dependent on the concentrations of sulfur and selenium in PA (Fig. 23). PA treated longer with $K_2SeS_4O_6$ requires more copper for the formation of a solid copper chalcogenide layer. A continuous chalcogenide layer decelerates the further increase of copper concentration in the polymer. The concentration of copper in the chalcogenide layer on PA chalcogenized in selenopentathionate solutions changes uniformly until the saturation is reached (Fig. 23).

Summarizing the results of PA film modification at the second stage, we have concluded that the concentration of copper is dependent on the conditions of the initial phase – chalcogenization, i. e. on the concentration and temperature of precursor solution, and on the duration of treatment.

Electrical sheet resistance and X-ray diffraction studies of copper sulfide – copper selenide layers formed on the surface of polyamide 6 films using $K_2SeS_4O_6$ solutions

The microscopic analysis of PA surface modified with copper chalcogenides showed an irregular formation of Cu_xS-Cu_ySe layers with the formation of islands. This unevenness increases the probability of the layer's interaction with the impurities and cause some difficulties in measuring



Fig. 21. Kinetics of sulfur (curves 2 and 4) and selenium (curves 1 and 3) sorption on PA at 50 °C at different precursor K,SeS₄O₂ concentrations: 1 and 2 – 0.025 mol/dm³, 3 and 4 – 0.2 mol/dm³



Fig. 22. Kinetics of sulfur (curves 2 and 4) and selenium (curves 1 and 3) sorption on PA treated with 0.05 mol/dm³ solution of K₂Ses₄O₆ at different temperatures °C: 1 and 2 – 30, 3 and 4 – 50



Fig. 23. Kinetics of copper concentration in the layer of copper chalcogenides on PA vs the time of initial PA treatment with $K_2SS_4O_6$ solutions at different temperatures: 1 - 0.025 mol/dm³ at 50 °C, 2 - 0.05 mol/dm³ at 50 °C, 3 - 0.2 mol/dm³ at 50 °C, 4 - 0.05 mol/dm³ at 30 °C

	Electrical sheet resistance, Ω/\Box								
Duration, h	Initial concentration of of $K_2 SeS_4 O_6$ solution, mol / dm ³								
	0.025	0.05	0.05*	0.1	0.2				
0.5	178.0	88.0	145.8	48.6	60.0				
1.0	99.7	70.4	84.5	71.0	32.7				
1.5	72.0	63.8	54.3	48.0	19.8				
2.0	68.7	61.7	44.2	52.5	14.4				
2.5	61.5	51.8	47.9	47.0	13.6				
3.5	53.6	42.9	42.8	32.5	12.3				
4.5	18.8	60.5	42.7	20.8	13.0				

Table 2. Electrical sheet resistance of copper chalcogenide layers on PA depending on the initial concentration of $K_2SeS_4O_6$ solution and the duration of chalcogenization at 50 °C

* The temperature 30 °C.

the surface electrical resistance. A detailed study of the resistance of PA modified with Cu_xS-Cu_ySe layers was complicated; therefore, we measured the electrical resistance of the external layer of the chalcogenide surface only.

The results presented in Table 2 show that under conditions of our experiments it was possible to form layers of copper sulfides and selenides with the electrical sheet resistance varying from less than $\sim 200 \Omega / \Box$ to even $\sim 10 \Omega / \Box$.

A tendency of a decrease of electrical resistance with increasing the concentration of precursor solution was observed: increasing the concentration by one tenth reduced the value of electrical resistance of the chalcogenide layer, depending on the duration of chalcogenization, three to five times. A direct dependence of the chalcogenide layer resistance on copper concentration in the layer was observed not in all cases, since copper chalcogenides of various stoichiometry and electrical conductivity and in different amounts could be formed. The increased number of phases and the intensity of their maxima reflects an increased concentration of copper sulfides and copper selenides on PA surface. The decrease of electrical resistance of these layers may be explained not only by the increased concentration of copper chalcogenide phases, but also by its qualitative changes.

The phase composition of the formed layers was established by comparing teir X-ray diffraction patterns with those of known copper chalcogenides [116–119, 127–132]. The chemical composition and crystal structure of the majority of Cu_xS and Cu_ySe minerals such as *chalcocite*, Cu₂S, *djurleite*, Cu_{1.95}S, *yarrowite*, Cu_{1.12}S, *covellite*, CuS, monoclinic Cu₂Se, orthorhombic CuSe₂ and cubic Cu_{2-x}Se, *berzellianite*, are well investigated [116–119, 127–132]. The crystal structure of Cu_xS and Cu_ySe depends on the chemical composition and the conditions of synthesis. The composition of Cu_xS and Cu_ySe deposited by sorption methods was scarcely investigated.

XRD spectra of PA chalcogenized at a different temperature in $K_2SeS_4O_6$ solutions of different concentration and for a different period of time showed peaks of various copper chalcogenide phases coexisting in the film (Figs. 24, 25).

The phases of *monoclinic djurleite*, $Cu_{1.9375}S$, (maxima at 2 θ = 32.7, and 38.08 °C), *cubic digenite*, $Cu_{1.8}S$, (maxima at 2 θ = 29.7, 36.3 and 49.1 °C), *orthorhombic chalcocite*, Cu₂S

(maxima at 2 θ = 40.9 °C), and *tetragonal bellidoite*, Cu₂Se (maxima at 2 θ = 38.6 and 45.5 °C) were determined on the surface of PA chalcogenized at a lower temperature (30 °C, Fig. 24, curve 1).

On the surface of PA chalcogenized at a higher temperature (50 °C), besides the phases mentioned above, the phases of *orthorhombic anilite*, $Cu_{1.75}S$, (maxima at 2 θ = 34.1 and 40.8 °C), *tetragonal umangite*, $Cu_{3}Se_{2}$, (maxima at 2 θ = 49.2 °C), and *orthorhombic klockmannite*, CuSe (maxima



Fig. 24. X-ray diffraction patterns of chalcogenide layers on PA (peak of $Cu_2S - C$, $Cu_{1.9375}S - J$, $Cu_{1.8}S - D$, $Cu_{1.75}S - A$, $Cu_2Se - B$, $Cu_3Se_2 - U$, CuSe - K, $CuSe_2 - L$, $Cu_2Se_x - X$) treated first for 270 min with $K_2SeS_4O_6$ solutions at a different temperature and then with Cu(II / I) salt solution: 1 - 0.05 mol/dm³ at 30 °C, 2 - 0.05 mol/dm³ at 50 °C, 3 - 0.2 mol/dm³ at 50 °C



Fig. 25. X-ray diffraction patterns of chalcogenide layers on PA (peaks: $Cu_2S - C$, $Cu_{1.9375}S - J$, $Cu_{1.8}S - D$, $Cu_{1.75}S - A$, $Cu_2Se - B$, $Cu_3Se_2 - U$, CuSe - K) treated first with 0.05 mol/dm³ K₂SeS₄O₆ solution at 50 °C for different time and then with Cu(II / I) salt solution. Treatment time, min: 1 - 10, 2 - 60, 3 - 150, 4 - 270

at 2 θ = 41.9 °C) were found, and the less conductive phase of *chalcocite*, Cu₂S, disappeared (Fig. 24, curve 2).

With increasing the concentration of precursor solution, the concentration of more conductive phases of $Cu_{1.9375}$ S, $Cu_{1.8}$ S and Cu_2 Se increased and the phases of *anilite*, $Cu_{1.75}$ S, and *klockmannite*, CuSe, disappeared, but the new phases of *orthorhombic copper selenides*, $CuSe_2$ (maxima at 2 θ = 31.4 °C), and Cu_2Se_x , (maxima at 2 θ = 39.1 °C) appeared (Fig. 24, curve 3).

The phase composition of Cu_xS-Cu_ySe layers with increasing the duration of PA chalcogenization at the same temperature and concentration remained almost unchanged, but the concentration of less conductive *chalcocite* decreased and that of electrically conductive copper sulfides and selenides increased (Fig. 25). For example, only one new phase of *orthorhombic klockmannite*, CuSe, appeared after 60 min (Fig. 25, curve 2) and the less conductive phase of *chalcocite*, Cu₂S, dissapeared (Fig. 25, curve 4).

With increasing of the concentration and temperature of precursor solution and the duration of PA treatment, the highest concentration of conductive copper selenides was attaned and the composition of $Cu_x S$ phases changed in the direction of a decrease of *x*.

The determined formation regularities of Cu_xS-Cu_ySe layers enable to select conditions under which semiconductive and electrically conductive mixed Cu_xS-Cu_ySe layers of a desirable chemical and phase composition and of predicted electrical resistance may be formed on polyamide surface.

X-ray photoelectron spectroscopy analysis of $Cu_x S-Cu_y Se$ layers formed on the surface of polyamide 6 using $K_2 SeS_4O_6$ solutions

The phase composition of Cu_xS-Cu_ySe layers studied by the method of X-ray photoelectron spectroscopy (XPS) was limited to a study of the chemical and phase composition of a very thin (up to 1 nm) Cu_xS-Cu_ySe surface layer as compared with the thickness of the whole chalcogenide layer (a few tenths of μ m).

When the PA film samples treated in a chalcogenization solution for different periods of time were exposed to a solution of Cu(II / I) salts, formation of a layer composed of different copper, sulfur and selenium compounds took place in the surface of the polymer. The following compounds were identified: Cu,S, CuS, Cu,O, CuO, CuSe, Cu,Se and Se.

As mentioned above, the values of x and y in the Cu_xS - Cu_ySe layers changed from 1 to 2, i. e. nonstoichiometric copper sulfides and selenides were formed. It was impossible from the data of XPS analysis to determine accurately the values of x and y compared with the data obtained by the method of X-ray diffraction, which enables a direct identification of various intermediate copper sulfides and selenides.

A study of Cu, S, Se and O distribution in a Cu S-Cu Se layer has shown that oxygen takes the largest part (49-61 at. %) on the surface of all PA film samples. All processes of the copper chalcogenide layer formation proceed in a natural environment. Therefore, it is impossible to prevent the influence of the environment on the chemical composition of the layers. This is the reason for oxygen presence in the surface of a chalcogenide layer. The presence of water joined by physical and chemical adsorption is also possible. Oxygen in a deeper layer is undoubtedly bound into Cu₂O and CuO oxides. Therefore, the chalcogenide layers in the surface of the polymer are formed in the form of islands which enable an easy contact of the atmospheric oxygen with the ions of copper and chalcogens. The amount of oxygen significantly decreased (1-9 at.%) when the surface of the sulfide layer was etched with Ar⁺ ions, showing that oxygen was present only on the surface of the chalcogenide layer. The content of O in the deeper layers was very small, and its presence should not influence the chemical composition of the layer and its properties.

Data of the XPS analysis have shown that the composition of Cu_xS–Cu_ySe layers formed in different experimental conditions is rather similar. For example, oxygen takes 56.89 at. % on the surface of the chalcogenide layer when the PA has been initially chalcogenized in 0.05 mol \cdot dm⁻³ K₂SeS₄O₆ solution for 10 min at a temperature of 50 °C. The bond energy values of $E_b = 530.1$ and 531.5 eV in the spectra of O 1 s showed that part of oxygen should be joined into the Cu(I) oxide, Cu₂O, and the bond energy $E_b = 533.5$ eV indicated the presence of HO⁻ groups. These groups may be present in the composition of Cu(OH)₂, which may be formed while washing the chalcogenide layer with water. The bond energy of 161.3 eV in the spectra of S 2p showed the presence of Cu(I) and Cu(II) sulfides in the surface. The values of $E_b = 53.8, 54.2, 55.3, eV$ in the spectra of Se $3d_{5/2}$ indicated the presence of elemental selenium. The spectra of Cu $2p_{3/2}$ confirmed the presence of the mentioned copper sulfides and of Cu(I) oxide, Cu₂O ($E_b = 932.1$ eV), and of Cu(II) oxide, CuO ($E_b = 933.9$ eV). Changes of the chemical composition and of the element amounts occured when the chalcogenide layer had been etched with Ar⁺ ions.

The content of oxygen decreased six times (to 9.38 at. %), but the content of Cu, S and Se increased significantly. The S 2p spectra indicated formation of copper sulfides in the layer: the bond energy $E_b = 161.5$ eV showed Cu₂S, and $E_b = 162.5$ eV indicated CuS. The bond energy $E_r = 932.2$ eV in the spectra of Cu 2p_{3/2} confirmed the presence of copper sulfides and of Cu(I) oxide, Cu₂O, in the chalcogenide layer.

Studies of Cu $_x$ S–Cu $_y$ Se layers on the surface of PA initially chalcogenized for 1–4.5 h showed that the chemical composition was similar to the composition of layers formed when the polymer chalgenization stage was shorter. Again, a high content of oxygen was found on the surface of the copper chalcogenide layer. This content decreased to a minimum after the surface etching with Ar⁺ ions. Traces of elemental selenium were found in all samples studied, because the chalcogenization solution gradually decomposed with time.

These results confirmed the results obtained by the X-ray diffraction analysis of the layers: the composition of a layer on prolonging the polymer initial chalcogenization stage in a solution of the same concentration and temperature to 4.5 h remained almost the same.

Summarizing the results of our studies, we could state that potassium selenopentathionate solution is a suitable agent of polyamide chalcogenization for the formation on its surface of electrically conductive Cu_xS-Cu_ySe layers. This agent of chalcogenization, because of a unique structure of the anion $-O_3S-S-Se-S-SO_3^-$ comprising sulfur and selenium atoms of low oxidation state, enabled to insert into the PA surface a matrix layer of the anionic S and Se particles. Treatment of a polymer modified in such a way with the solution of Cu(II / I) salts resulted in the formation of a mixed copper sulfide – copper selenide layer of a desirable chemical composition and electrical resistance. This chalcogenization agent has enabled forming mixed chalcogenide layers for the first time. These coatings may have properties peculiar to both copper sulfides and copper selenides.

Formation of copper sulfide – copper telluride layers on polyamide 6 surface, using potassium telluropentathionate solutions

To investigate sulfur and tellurium sorption into PA from potassium telluropentathionate solutions, it was relevant to ascertain in what form (as elemental chalcogens, their radicals or teluropentathionate ion, $\text{TeS}_4O_6^{2-}$) chalcogens are sorbed on PA.

Our investigations have showed that the polyamide sorbs telluropentathionate ions from these solutions. The sorption of telluropentathionate ions, $\text{TeS}_4 O_6^{2-}$, like the sorption of pentathionate ions, $\text{S}_5 O_6^{2-}$, and selenopentathionate ions, $\text{SeS}_4 O_6^{2-}$, from 0.025–0.10 mol/dm³ solutions of K₂TeS₄O₆ by PA was studied by IR (400–1 300 cm⁻¹) (Fig. 26) and UV (200–400 nm) (Fig. 27) absorption spectroscopy. The peaks in the IR spectra were found in the intervals 412–483, 506–525, 575–730, 845–1101 and 1136–1290 cm⁻¹and were assigned to the



Fig. 26. IR spectra of PA treated in 0.1 mol/dm³ K₂TeS₄O₆ solution at 20 °C for different time. Chalcogenization time, h: 1 - 0.25, 2 - 0.5, 3 - 2.0, 4 - 4.0

ν (S–S), $δ_{as}$ (O–S–O), $δ_{s}$ (O–S–O), $ν_{s}$ (S–O) and $ν_{as}$ (S–O), respectively. These data confirmed telluropentathionate ions to be sorbed into PA because of the similarity of the peaks of the former to the peaks in IR spectra of chalcopolythionates and K₂YS₄O₆ (Y = S, Se, Te), [97, 98, 112, 121–123] respectively, at 404–450, 510–550, 580–730, ~1010, ~1210 cm⁻¹.

In the UV absorption spectra, PA samples sulfurized for different periods of time in $K_2 TeS_4O_6$ solutions contain four absorption maxima: at ~228 nm, ~256 and ~284 nm as peaks and at ~354 and ~428 nm as weakly expressed shoulders (Fig. 27). According to the UV absorption spectra of chalcopolythionates [97, 98, 123–126], the absorption maxima of polythionate and selenopolythionate ions as shoulders and peaks occur at ~215, ~250, ~290 and ~340 nm. Thus, UV absorption spectra recorded by us have again confirmed that chalcogens are sorbed by PA films in the form of telluropentathionate ions.

The inflence of the concentration and temperature of $K_2 TeS_4O_6$ solution on the sorption–diffusion of $TeS_4O_6^{2-}$ ions into PA film was studied. The increase of sorbed tellurium and sulfur concentration at a temperature of 1, 10 and 20 °C with increasing the concentration of potassium telluropentathionate solution was not obvious (Fig. 28). For example, with increasing the duration of the polymer treatment in $K_2 TeS_4O_6$ solution at a temperature of 10 °C to 24 h, the concentration of sorbed–diffused tellurium increased from 14.60 to 18.40 mg/cm³ and of sulfur from 0.542 to 0.916 mg/cm³ (Fig. 28, curves 1 and 3).

Tellurium and sulfur concentrations in the polymer increased with increasing the temperature of chalcogenization solution (Fig. 29). This was more obvious when PA samples were chalcogenized in a solution of a higher concentration. For example, while increasing the duration of polymer treatment in 0.025 mol/dm³ K₂TeS₄O₆ solution to 8 h, tellurium concentraton increased from 2.265 to 13.640 mg/cm3 and of sulfur from 0.207 to 1.058 mg/cm³. When the concentration of K₂TeS₄O₆ solution was four times higher, tellurium concentration increased from 4.38 to 16.45 mg/cm3 and sulfur from 0.185 to 1.219 mg/cm³. On prolonging chalcogenation to 24 h, changes of tellurium and sulfur concentrations were not pronounced.

Chemical analysis of chalcogenized samples has showed that the concentration of



Fig. 27. UV absorption spectra of PA treated in 0.1 mol/dm³ K₂TeS₄0₆ solution at 20 °C for different time. Chalcogenization time, h: 1 - 0.25, 2 - 0.5, 3 - 2.0, 4 - 4.0



Fig. 28. Changes of sulfur (*a*) and tellurium (*b*) concentrations in PA films chalcogenized in $K_2 \text{TeS}_4 0_6$ solution at 10 °C. The concentration of $K_2 \text{TeS}_4 0_6$ solution, mol \cdot dm⁻³: 1 – 0.025, 2 – 0.05, 3 – 0.1



Fig. 29. Changes of sulfur (*a*) and tellurium (*b*) concentrations in PA films chalcogenized in 0.05 mol \cdot dm⁻³ solution of K, TeS₄O₆ at different temperature, °C: 1 – 1, 2 – 10, 3 – 20



Fig. 30. Changes of copper concentration in PA films chalcogenized in $K_2 \text{TeS}_4 0_6$ solutions at 10 °C. The concentration of $K_3 \text{TeS}_4 0_c$ solution, mol \cdot dm⁻³: 1 – 0.025, 2 – 0.05, 3 – 0.1



Fig. 31. Changes of copper concentration in PA films chalcogenized in 0.05 mol \cdot dm⁻³ K₂TeS₄O₆ solutions at different temperature, °C: 1 - 1, 2 - 10, 3 - 20

sulfur and tellurium sorbed into PA with increasing the temperature and concentration of chalcogenization solution and the time of the polymer treatment increases as well. Our data also showed that increasing the temperature of $K_2SeS_4O_6$ solution is much more effective for the concentration of sulfur sorbed in the polymer for increasing the concentration of telluropentathionate solution.

Summarizing the results of the first stage of PA modification – chalcogenization, – we could conclude that potassium telluropentathionate is a suitable precursor for the formation of copper chalcogenide layers on PA surface.

Then, the interaction of PA chalcogenized in potassium telluropentathionate solutions with a solution of Cu(II / I) salts was studied. Brown or even black semiconductive or electrically conductive copper sulfide – copper telluride layers were formed. Copper chalcogenide layers were formed as a result of heterogeneous redox reactions among Cu⁺, Cu²⁺ and TeS₄O₆²⁻ ions. Formation of a Cu_xS–Cu_yTe layer depended on the initial sulfur and tellurium concentrations in chalcogenized PA.

The concentration of copper in the layer was strongly dependent on sulfur and tellurium concentrations in PA (Figs. 30, 31). PA treated with $K_2 TeS_4 O_6$ for a longer time requires more copper for the formation of a solid copper chalcogenide layer. A continuous chalcogenide layer decelerates the further increase of copper concentration in the polymer. The concentration of copper in the chalcogenide layer on PA chalcogenized in telluropentathionate solutions changed uniformly until the saturation was reached.

Summarizing the results of PA film modification at the second stage, we could conclude that the concentration of copper is dependent on the conditions of the initial phase, i. e. on the concentration and temperature of the precursor solution and the duration of treatment.

Electrical sheet resistance and X-ray diffraction studies of copper sulfide – copper telluride layers formed on the surface of polyamide 6 films, using $K_2 TeS_4 O_6$ solutions The microscopic analysis of PA surface modified with copper chalcogenides showed an irregular formation of Cu_xS-Cu_yTe layers: they formed islands. This unevenness increased the probability of the layer's interactions with the impurities and caused some difficulties while

T, °C	Concentration of solution, mol/dm³	Duration of PA chalcogenization, h								
		0.25	0.5	1	2	3	4	8	12	24
1	0.025	-	-	-	-	-	-	30.7	8.9	4.0
	0.05	-	-	-	-	-	180	17.3	6.2	5.2
	0.1	-	-	-	-	-	-	11.3	15.8	4.2
10	0.025	1.0 · 103	110.6	153	40.5	13.9	8.9	3.1	2.3	1.6
	0.05	-	-	-	1.1 · 10 ³	31.4	29.0	10.1	7.0	2.1
	0.1	-	-	-	24.6	13.7	4.3	2.9	2.8	1.5
20	0.025	-	-	1.0 · 10 ³	113.8	109.7	-	7.7	4.9	2.2
	0.05	-	-	23.3	13.2	10.3	4.4	2.1	1.7	2.2
	0.1	-	256.4	41.4	9.9	9.9	5.0	1.6	1.6	2.9

Table 3. Electrical sheet resistance ($k\Omega/\Box$) of Cu₂S–Cu₂Te layers on PA first treated in K₂TeS₄O₆ solution and then with Cu(II / I) salt solution

measuring the surface electrical resistance. A detailed study of the resistance of PA modified with Cu_xS-Cu_yTe layers was complicated; therefore, we limited ourselves to measuring the electrical resistance of the external layer of the chalcogenide surface.

The results presented in Table 3 show that under conditions of our experiments it is possible to form layers of copper sulfides and tellurides with the electrical sheet resistance varying from less than $\sim 1.0 \cdot 10^3 \text{ k}\Omega / \Box$ to even $\sim 1.5 \text{ k}\Omega / \Box$. The value of resistance decreased with increasing the duration of chalcogenization and the concentration and temperature of chalcogenization solution, and this value was greatly dependent on the chalcogenization conditions (Table 3).

A tendency of electrical resistance decrease with increasing the concentration of precursor solution was observed. However, the dependence of the chalcogenide layer resistance on copper concentration in the layer was direct not in all cases since copper chalcogenides of various stoichiometry and electrical conductivity and in different amounts may be formed. The increased number of phases and the intensity of their maxima reflected an increased concentration of copper sulfides and copper tellurides on PA surface. The decrease of the electrical resistance of these layers may be explained not only by the increased concentration of copper chalcogenide phases, but also by their qualitative changes. Therefore, a decrease of electrical sheet resistance implied that a larger amount of electrically conductive copper sulfide and copper telluride phases was formed in the layers on PA surface, increasing the duration of chalcogenization, the concentration and temperature of chalcogenization solution.

The phase composition of the formed layers was established by comparing their X-ray diffraction patterns with those of known copper chalcogenides [116–119, 127–136]. The chemical composition and crystal structure of the majority of Cu_xS and Cu_yTe minerals such as *chalcocite* Cu₂S, *djurleite* Cu_{1.95}S, Cu₄Te₃, Cu_{1.80}Te, Cu_{1.85}Te and *vulcanite*, CuTe were investigated. The crystal structure of Cu_xS and Cu_yTe was found to depend on the chemical composition and synthesis conditions. The composition of Cu_xS and Cu_yTe deposited by sorption methods was scarcely investigated.

The XRD spectra of PA films treated for different time with 0.025 mol/dm³ K₂TeS₄O₆ solution at 10 °C and then with Cu(II / I) salt solution are presented in Fig. 32. The maxima characteristic of the copper sulfide and copper telluride



Fig. 32. X-ray diffractograms of PA films first treated in 0.025 mol/dm³ K₂TeS₄O₆ solution at a temperature of 10 °C and then in Cu(II / I) salt solution. Duration of chalcogenization, h: 1 – 0.25, 2 – 2, 3 – 12, 4 – 24. A – Cu₇S₄, Dj – Cu_{1.9375}S; Ch – Cu₂S; C₁ – Cu₄Te₃; C₁₁ – Cu_{1.85}Te; Vu – CuTe; C₁₂ – Cu_{1.80}Te; Vi – CuS₂, S – S

phases and of the elemental sulfur were detected in almost all spectra. The value of electrical sheet resistance of Cu $_x$ S–Cu $_y$ Te layers was found to decrease (from $1.0 \cdot 10^3$ –40.5 k Ω / \Box to -3.1-1.6 k Ω / \Box) with the initial PA chalcogenization duration (from 0.25–2.0 to 8–24 h). The lowest value was observed for PA treated for 24 h in K₂TeS₄O₆ solution. The maxima of more conductive phases of *anilite*, Cu₇S₄, and copper tellurides CuTe, Cu₄Te₃, were detected in XRD spectra of PA chalcogenized for a longer period of time. They were almost absent in the spectra of PA films chalcogenized for a shorter period of time. The value of electrical sheet resistance of Cu _xS–Cu _yTe layers decreased also (7.7–2.1–1.6 k Ω / \Box) with increasing the concentration of chalcogenization (K₂TeS₄O₆) solution (0.025–0.05–0.1 mol/dm³).

The spectra of PA films chalcogenized in the telluropentathionate solution of different concentration (Fig. 33) have showed that the maxima of phases of good electrical conductance CuS₂ and Cu₄Te₃ already dominate when 0.05 mol/dm³ chalcogenization solution has been used for the formation of copper chalcogenide layers. A study of XRD spectra of PA films with Cu_xS–Cu_yTe layers formed using the chalcogenization solution at a temperature of 1–20 °C has revealed that the same highly conductive phases are detected also in copper chalcogenide layer formed by using the K₂TeS₄O₆ solution of a higher temperature (20 °C). This is in accordance with data of electrical sheet resistance measurements of these films: its value decreased (17.3–10.1–2.1 k Ω / \Box) with increasing the temperature (1–10–20 °C) of chalcogenization solution.

Summarizing the results presented above, it was possible to state that the phase composition and electrical sheet resistance of mixed copper sulfide-copper telluride layers on PA surface, formed using potassium telluropentathionate solution as a polymer chalcogenization agent, depended on chalcogenization conditions, i. e. on its duration and on the concentration and temperature of solution. With increasing the values of these factors, electrical sheet resistance of the layers decreased. This fact was reflected by XRD spectra of these layers: the maxima of higher electrical conductance phases appeared in the spectra.

X-ray photoelectron spectroscopy analysis of Cu_xS-Cu_yTe layers formed on the surface of polyamide 6, using $K_2TeS_4O_6$ solutions

The composition of the copper chalcogenide layer in deeper layers (up to 1 nm) after its surface had been etched (bombardment with Ar⁺ ions) was studied. From data gained by the XPS method, i. e. from the amount of elements (atomic percentages), the values of binding energies and the spectra of individual elements (S2p, Te3d5, Cu2p3 and O1s), it was possible to reveal the composition of the obtained layer. The analysis was restricted to a study of the chemical composition of a very thin surface layer. In the present work, the dependence of the layer composition on the concentration of chalcogenization agent solution, temperature and treating duration in this solution was studied.

The maxima in S 2p spectra, corresponding to the binding energy values of ~161–162 eV, showed the presence of sulfide sulfur; the maxima corresponding to the binding energy values of ~163–164 eV indicated the presence of elemental sulfur [109, 110]. The maxima in Te 3d5 spectra, corresponding to the binding energy values of ~572–573 eV, showed the presence of a telluride ion, and the maxima corresponding to the binding energy value of ~575.8 eV indicated the presence of TeO₂ or Te(IV) [109, 110, 137]. The maxima in Cu2p3 corresponding to the binding energy values of ~932 eV showed the presence of Cu⁺ and Cu²⁺.

The data of analysis showed that the composition of layers obtained in different conditions was similar; this was confirmed by the similarity of spectra. In the etched surface, various compounds of copper, sulfur and tellurium (Cu₂S, CuS, S₈, Cu_xS, Cu_yTe) were present. We analysed only the layer's surface etched by Ar⁺ ions, and oxygen in the deeper layer was not detected. The atomic percentage of the elements showed



Fig. 33. X-ray diffractograms of PA films first treated for 8 h in K₂TeS₄O₆ solution at a temperature of 20 C and then in Cu(II / I) salt solution. Concentration of K₂TeS₄O₆ solution, mol/dm³: 1 - 0.025, 2 - 0.05, 3 - 0.1. A $- Cu_{2}S_{4}$, D $j - Cu_{1.9375}$ S, Vi $- CuS_{2}$, C₁ $- Cu_{4}Te_{2}$, C₂ $- Cu_{2}S$, C₁ $- Cu_{1.85}Te$

that copper sulfides and tellurides took the major part in the layers. Also, the content of copper sulfides in the composition of a layer was higher since the amount of sulfide sulfur in the layers studied was about three times higher than that of the telluride tellurium. These data are in agreement with the equation according to which telluropentathionate ions react with copper(I) ions [90]:

$${\rm TeS}_{4} {\rm O}_{6}^{2-} + 6{\rm Cu}^{+} + 2{\rm H}_{2}{\rm O} \rightarrow \rightarrow {\rm Cu}_{2}{\rm Te} + 2{\rm CuS} + 2{\rm Cu}^{2+} + 4{\rm H}^{+} + 2{\rm SO}_{4}^{2-}.$$
 (5)

From the above equation it follows that more copper sulfide compared with copper telluride is formed. The atomic percentages of the elements (Cu, S, Te) increasing the concentration of $K_2 \text{TeS}_4 O_6$ solution changed insignificantly. Therefore, we could state that an increase in chalcogenization agent solution concentration almost did not change the composition of the layer.

Upon calculating from atomic percentages the copper and sulfur-tellurium ratios, we found that their values decreased with increasing the K₂TeS₄O₆ solution concentration. These data are in good agreement with the results of electrical sheet resistance measurements of the samples, i. e. the samples were more conductive at a lower value of the copper and sulfur-tellurium ratio. When the Cu: (S + Te) ratio was equal to 1.69, the value of sheet resistance was 7.7 k Ω / \Box ; when the former was 1.51, the value of sheet resistance was 2.08 k Ω / \Box , and at the ratio value of 1.41 it was 1.63 k Ω / \Box .

Comparison of element atomic percentages showed that more copper was present in samples chalcogenized at a higher temperature: at 1 °°C – 54.1 at. %, at 10 °C – 57.29 at. %, at 20 °C – 60.13 at. %, but the highest content of sulfide sulfur was found in a sample chalcogenized at the lowest (1 °C) temperature; the largest content of tellurium in the telluride form was present in a sample chalcogenized in K₂TeS₄O₆ solution at a temperature of 10 °C.

We have calculated that the ratio of copper with sulfur-tellurium increases with increasing the temperature of $K_2 \text{TeS}_4 O_6$ solution. The increase of this ratio may be dependent on several reasons, for example, on the fact that a telluropentathionate ion at a higher temperature decomposes:

$$\operatorname{TeS}_{4}O_{6}^{2-} \to \operatorname{Te} + S_{4}O_{6}^{2-} \tag{6}$$

or
$$\operatorname{TeS}_{4}O_{6}^{2-} \to \operatorname{Te} + 2S + SO_{2} + SO_{4}^{2-}, \tag{7}$$

Therefore, copper ions may react not only with $\text{TeS}_4 O_6^{2-}$ ions according to the above equation, but also with the products of this ion decomposition [90, 139]. The following processes are possible:

$$Cu_{2}Te - 2e \rightarrow CuTe + Cu^{2+}$$
(8),

$$2\mathrm{Te} + 2\mathrm{e} \to \mathrm{Te}_2^{2-} \tag{9},$$

$$Cu^{2+} + Te_2^{2-} \rightarrow CuTe + Te.$$
(10)

The decrease in the content of sulfur may be explained by formation and liberation of SO₂.

In the etched layer, not only the copper sulfide and copper telluride, but also a copper hydroxide is present. The metal sulfides forming layers in the polymer surface matrix by the sorption-diffusion method take the form of dendrites [34, 120]; therefore, among the dendrites, there may remain adsorbed compounds. In our case, insoluble copper hydroxide formed during washing the layer's surface with water remained among the dendrites. The highest content of oxygen (34.19 at. %) was detected in samples chalcogenized for a very short time (only 0.25 h), possibly significantly smaller amounts of sulfur and tellurium in the samples; therefore, a chalcogenide layer forms separate islands, and more copper hydroxide is adsorbed inbetween the islands or dendrites. The presence of separate islands determines the low electrical conductivity of a sample (the value of sheet resistance was 1.04 $10^3 k\Omega / \Box$); this is confirmed by the value of the copper to sulfur-tellurium ratio calculated from the percentages of these elements and equal to 2.61.

Analysing the XPS data, we have concluded that the copper and sulfur-tellurium ratio decreases with increasing the duration of chalcogenization; this is in accordance with the results of the sample sheet resistance measurements since samples with a lower value of this ratio were more conductive.

In a PA film chalcogenized for a very long time (24 h), a small amount of Te(IV) (2.05 at. %) was detected. It could be TeO₂ [137, 138] or TeO₃^{2–} [90]:

 $2\text{Te} + 2\text{CuO} + 2\text{HO}^{-} \rightarrow \text{Cu}_{2}\text{Te} + \text{TeO}_{2}^{2-} + \text{H}_{2}\text{O}, \quad (11)$

$$Cu_{2}Te + 6CuO + 2HO^{-} \rightarrow 4Cu_{2}O + TeO_{3}^{2-} + H_{2}O.$$
(12)

Summarizing XPS data, we have stated that copper sulfides and copper tellurides take the largest part of the layers in PA film samples.

Study of the morphology of Cu_xS-Cu_yTe layers formed on PA surface, using K₂TeS₄O₆ solutions

A morphological study by atomic force microscopy of PA modified with Cu_xS-Cu_yTe layers revealed the layers to be essentially different. The aim of this study was to find the predominant mechanism of Cu_xS-Cu_yTe layer formation on PA surface, i. e. the layer homogenity and growth evenness. Fields of 12×12 microns were investigated; for the quantitative estimation of the surface, standard programs of the view treatment were used. It has been determined that the surface morphology of the copper chalcogenide layers formed on PA surface depends on the conditions of polymer chalcogenization.

From the cross-sections of Cu_xS-Cu_yTe layers formed on PA surface when the polymer was chalcogenized in 0.025 mol/dm³ K₂TeS₄O₆ solution for 0.25, 2 and 24 h at a temperature of 10 °C, it was possible to determine the average height and diameter of the crystallites (Figs. 34–36). When the polymer was chalcogenized for 0.25 h in $K_2 \text{TeS}_4 O_6$ solution, the height of crystallites reached 88 nm and the diameter ~0.1–1.0 µm, the maximum and mean height of the layer being 103 nm and 61 nm, respectively (Figs. 34, 37). On prolonging the chalcogenization to 2 h, the height of the crystallites decreased to 66 nm and the diameter remained unchanged (~0.4–1.0 µm); the maximum and mean height of the layer increased to 144 nm and 228 nm, respectively (Figs. 35, 37).

However, under a 24-h chalcogenization, the mean and maximum height of the layer decreased to 56 nm and 166 nm, respectively (Figs. 36, 37).

At a short duration of polymer treatment in $K_2 TeS_4 O_6$ solution (0.25 h), the growth of chalcogenide layer began from the formation of separate small islands (Fig. 34). On prolonging chalcogenization to 2 h, the growth of the chalcogenide layer proceeded more intensively, and after chalcogenization for 24 h clusterization begins; as a result, crystallites of various diameter and height slowly begin joining into agglomerates (Figs. 35, 36). The mean roughness slightly decreases; this means that crystallites joining into agglomerates more evenly cover the surface, and the layer becomes more homogeneous.

Studying the formation of Cu_xS-Cu_yTe layers on PA surface, chalcogenide layers were formed also by changing the temperature, i. e. PA was chalcogenized for 8 h in 0.05 mol/dm³ K₂TeS₄O₆ solution at a temperature of 1, 10, 20 °C and then treated with a Cu(II / I) salt solution.

The cross-sections of these layers showed that their surface was rather uneven. The roughness changed irregularly, and crystallites were of different height, diameter and form. The change of roughness was shown by the roughness parameters. The height of crystallites, like the roughness of the layer, with increasing the temperature of PA chalcogenization in K_2 TeS₄O₆ solution was changing irregularly. At a low temperature of treating PA in K, TeS4O6 solution, the formation of the layer was slow and irregular. The maximum height of the layer was ~160 nm. On increasing the temperature of chalcogenization solution to 10 °C, the height of the layer decreased to ~90 nm, but at a temperature of 20 °C it increased again to ~149 nm. Thus, with increasing the chalcogenization temperature from 1 to 20 °C, the height of the layer changes irregularly. The reason may be differences in the phase composition of Cu_vS-Cu_vTe layers obtained at a different temperature.



Fig. 34. Atomic force microscopy view of $Cu_x S-Cu_y Te$ layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized 0.25 h a the temperature of 10 °C in 0.025 mol/dm³ K₃TeS₄O₄ solution and then treated with Cu(II / I) solution



Fig. 35. Atomic force microscopy view of $Cu_x S - Cu_y Te$ layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 2 h at a temperature of 10 °C in 0.025 mol/dm³ K₃TeS₄O₄ solution and then treated with Cu(II / I) solution



Fig. 36. Atomic force microscopy view of $Cu_x S-Cu_y Te$ layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 24 h at a temperature of 10 °C in 0.025 mol/dm³ K, TeS $_{a}O_{a}$ solution and then treated with Cu(II / I) solution



Fig. 37. Dependence of the mean square roughness (*a*) and maximum and mean height (*b*) of a layer on the duration of PA treatment in 0.025 mol/dm³ K, TeS₄O₆ solution at a temperature of 10 °C



Fig. 38. Dependence of layer mean square roughness (*a*) and height (*b*) on the concentration of K, TeS, 0_c solution while treating PA for 8 h at a temperature of 20 °C

Thus, the above-listed AFM results have shown that, depending on the conditions of PA initial chalcogenization in $K_2 \text{TeS}_4 O_6$ solution (in the same "copperizing" conditions), the formation of copper chalcogenide layers proceeds irregularly in the form of islands which grow into larger agglomerates. The surface of the layer is uneven, rather rough. The maximum height of the layer slightly reduced with prolonging PA treatment in $K_2 \text{TeS}_4 O_6$ solution (Fig. 37). The reduction of layer height was more significant while increasing the concentration of chalcogenization solution; the same tendency was observed in the change of the layer roughness (Fig. 38).

CONCLUSIONS

1. Investigation of the sorption of sulfur-, selenium- and tellurium-containing particles into polyamide 6 (PA) from acidified solutions of potassium chalcopentathionates ($K_2S_5O_6$, $K_2Se_4O_6$ and $K_2TeS_4O_6$) has confirmed that pentathionate, selenopentathionate and telluropentathionate anions containing chains of three divalent chalcogen atoms of low oxidation state $-O_3S-S-Y-S-SO_3$ (Y = S, Se, Te) sorb-diffuse into PA treated with solutions of potassium chalcopentathionates. The concentration of sulfur, selenium and tellurium in PA sorbed from $K_2S_5O_6$, $K_2SeS_4O_6$ and $K_2TeS_4O_6$ solutions increases with increasing the duration of treatment and the concentration and temperature of the precursor solution.

2. Copper sulfide, Cu_xS , copper sulfide–copper selenide, Cu_xS-Cu_ySe , and copper sulfide–copper telluride, Cu_xS-Cu_yTe , layers of various composition are formed on PA surface when a polymer chalcogenized in $K_2S_5O_6$, $K_2SeS_4O_6$ and $K_2TeS_4O_6$ solutions has been treated with Cu(II / I) salt solution: anionic particles containing chalcogen atoms of low oxidation state react with copper ions. Copper concentration in copper chalcogenide layers depends on chalcogen concentrations in PA and increases with increasing the latter values.

3. The phase composition of the layers depends on the concentration and temperature of the precursor solution and on the duration of treatment in it. X-ray diffraction studies of Cu_xS layers revealed five phases: *djurleite*, Cu_{1.9375}S, *chalcocite*, Cu_{1.96}S, *anilite*, Cu₇S₄, *digenite*, Cu₉S₅, and copper sulfide CuS₂. Cu_xS-Cu_ySe layers are composed of low-conductive *chalcocite*, Cu_{1.9375}S, *anilite*, Cu_{1.75}S, and of copper selenides – *bellidoite*, Cu₂Se, *umangite*, Cu₃Se₂, *klockmannite*, CuSe, *krutaite*, CuSe₂ and Cu₂Se_x. Cu_xS-Cu_yTe layers formed using K₂TeS₄O₆ solutions are composed of copper sulfides – *chalcocite*, Cu₂S, *djurleite*, Cu_{1.9375}S, *anilite*, Cu_{1.75}S, *villamanite*, CuS₂ and of copper tellurides – *vulcanite*, CuTe, Cu₄Te₃, Cu_{1.80}Te and Cu_{1.85}Te.

4. The use of potassium chalcopentathionate solutions as precursors enables the formation on the surface of a polymer of semiconductive and electrically conductive layers of copper chalcogenides: the electrical resistance of $\operatorname{Cu}_x S$ layers varies from $104 \Omega / \Box$ to $1.52 M\Omega / \Box$, of $\operatorname{Cu}_x S$ -Cu_ySe layers from $12.3 \Omega / \Box$) to $465.8 \Omega / \Box$, and $\operatorname{Cu}_x S$ -Cu_yTe layers have the resistance in the range $1.5 \text{ k}\Omega / \Box \text{ t} - 1.1 \cdot 10^3 \text{ k}\Omega / \Box$; the value of resistance depends greatly on the conditions of PA initial interaction with potassium chalcopentathionate solution.

5. The analysis of the chemical composition of Cu_xS , Cu_xS-Cu_ySe and Cu_xS-Cu_yTe layers studied by the method of X-ray photoelectron spectroscopy confirmed the formation of copper sulfides, selenides and tellurides of various phases in the polyamide surface.

6. A morphological study (by atomic force microscopy) of PA modified with Cu_xS and Cu_xS-Cu_yTe layers has revealed the layers to be essentially different. The surface morphology of copper chalcogenide layers formed on PA surface depends on the conditions of polymer chalcogenization: the formation of layers proceeds irregularly in the form of islands which grow into larger agglomerates. The surface of the layer is uneven, rather rough.

7. The obtained results and determined regularities enable formation on PA surface by the sorption–diffusion method of copper chalcogenide layers of desirable composition and conductivity, using solutions of potassium chalcopentathionates as polyamide 6 chalcogenization agents.

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CHALKOPENTATIONINIAI JUNGINIAI – PUSLAIDININKINIŲ IR LAIDŽIŲ ELEKTRAI VARIO CHALKOGENIDŲ SLUOKSNIŲ SUDARYMO POLIAMIDO PAVIRŠIUJE PIRMTAKAI

Santrauka

Puslaidininkiniai ir laidūs elektrai vario chalkogenidų – vario sulfidų, Cu_xS, mišriųjų vario sulfidų–vario selenidų, Cu_xS–Cu_ySe, ir mišriųjų vario sulfidų–vario telūridų, Cu_xS–Cu_yTe, sluoksniai poliamido 6 (PA) paviršiuje sudaryti taikant sorbcinį-difuzinį metodą ir vandeninius kalio pentationato, K₂S₅O₆, kalio selenopentationato, K₂SeS₄O₆, ir kalio telūropentationato, K₂TeS₄O₆, tirpalus, kaip polimero chalkogeninimo pirmtakus. Chalkopentationatų anijonai, turintys dvivalenčių, mažo oksidacijos laipsnio chalkogenų atomų grandines, $^{-}O_3S-S-S-SO_3^{-}$, $^{-}O_3S-S-S-Se-S-SO_3^{-}$, $^{-}O_3S-S-Te-S-SO_3^{-}$, sorbuoja-difunduoja į PA plėveles, jei jos apdorojamos chalkopentationinių junginių tirpalais. Sorbuotų chalkogenų koncentracijos didėja, didėjant pirmtako tirpalo koncentracijai, temperatūrai ir PA apdorojimo trukmei. Cu_xS, Cu_xS-Cu_ySe ar Cu_xS-Cu_y Fe sluoksniai susidaro PA plėvelės paviršiuje, kai chalkogenintas polimeras apdorojamas vandeniniu vario (II / I) druskos

tirpalu: chalkopentationatų anijonai reaguoja su vario jonais. Vario koncentracija PA didėja, didinant pirmtako tirpalo koncentraciją, temperatūrą ir PA chalkogeninimo trukmę. XPS ir XRD tyrimai patvirtino vario chalkogenidų sluoksnių PA paviršiuje susidarymą. Cu_xS, Cu_xS–Cu_ySe ir Cu_xS–Cu_yTe sluoksnių fazinė sudėtis priklauso nuo chalkopentationato tirpalo koncentracijos, temperatūros ir pradinio apdorojimo pirmtako tirpale trukmės. Cu_xS sluoksniai sudaryti iš mažai laidaus tetragoninio chalkocito, Cu, of S, monoklininio jurlito, Cu₁₉₃₇₅S, laidaus elektrai rombinio digenito, Cu₉S₅, ortorombinio anilito, Cu₂S₄, ir kūbinio CuS₂; Cu₂S-Cu₂Se sluoksniai - iš mažai laidaus chalkocito, Cu₂S, laidaus elektrai digenito, Cu_{1.8}S, jurlito, Cu_{1.9375}S, anilito, Cu_{1.75}S, ir vario selenidų – bellidoito, Cu₂Se, umangito, Cu₃Se₂, klokmanito, CuSe, krutaito, CuSe₂ ir Cu₂Se_x; Cu_xS-Cu_yTe sluoksniai – iš *chalkocito*, Cu₂S, *jurlito*, Cu_{1,9375}S, anilito, Cu_{1.75}S, digenito, Cu_{1.8}S, vario sulfido, CuS₂, vario telūridų, Cu_{2,72}Te₂, Cu₄Te₃, Cu₁₈₅Te, vulkanito, CuTe, Cu_{1.80}Te. Fazinė sudėtis sąlygoja gautų sluoksnių elektrines charakteristikas: Cu_S sluoksnių elektrinė kvadrato varža kinta nuo 0,104 iki 1,52 \cdot 10³ K Ω / \Box , Cu_S-Cu_Se sluoksnių – nuo 12,2 Ω / \Box iki 4,8 M Ω / \Box , Cu_S-Cu_Te sluoksnių – nuo ~1,0 k Ω/ □ iki 4·103 k Ω/ □. Nustatyti dėsningumai leidžia sudaryti norimos sudėties ir laidumo elektrai Cu_s, Cu_xS-Cu_ySe ir Cu_xS-Cu_yTe sluoksnius.