

Formation and study of electrically conductive layers of copper sulfides formed on the polyamide surface by the use of potassium pentathionate

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Semiconductive and electrically conductive layers of copper sulfides on the polyamide 6 (PA) surface were formed using the sorption–diffusion method and a water solution of potassium pentathionate, $K_2S_5O_6$, as a precursor of polymer sulfurization. Pentathionate anions containing chains of divalent sulfur atoms of low oxidation state, $^-O_3S-S-S-SO_3^-$, are sorbed–diffused into PA films if they are treated with $K_2S_5O_6$ solution. The concentration of sorbed sulfur increases with an increase of the temperature and concentration of the precursor solution and the duration of PA treatment. Cu_xS layers are formed on the surface of PA film when a sulfurized polymer is treated with the water solution of copper(II / I) salt: pentathionate anions react with copper ions. The concentration of copper increases (up to $\sim 40 \text{ mg} \cdot \text{g}^{-1}$) with increasing the concentration and temperature of the precursor solution. XRD results confirmed the formation of Cu_xS layers on the surface of PA. The phase composition of Cu_xS layer depends on the concentration and temperature of potassium pentathionate solution and on the duration of initial treatment in the $K_2S_5O_6$ solution. The layers are composed of the low-conductive tetragonal chalcocite, $Cu_{1.96}S$, monoclinic djurleite, $Cu_{1.9375}S$, electrically conductive rhombohedral digenite, Cu_9S_5 , orthorhombic anilite, Cu_7S_4 , and cubic CuS_2 . The phase composition determines the electrical characteristics of the layers obtained: the sheet resistance varies from 0.104 to $1.52 \cdot 10^3 \text{ K}\Omega / \square$. X-ray photoelectron spectroscopy confirmed formation of copper sulfides of various phases. The regularities established in the present work enable formation of Cu_xS layers of a desirable composition and conductivity.

Key words: potassium pentathionate, polyamide, copper sulfide layer

INTRODUCTION

Dielectrics (including polymers) with layers of copper chalcogenides have attracted the interest of researchers first of all because of their importance for solar energy elements and converters [1, 2]. In this line of investigation, we explore the possibility to associate at the nanometric scale layered solids such as copper sulfides with functional semihydrophilic polymers, mainly isolators. Various polymers modified with copper sulfide films on their surface represent a new class of materials – composites with novel combinations of properties. Copper sulfide is an interesting material for its metal-like electrical conductivity [3] and ideal characteristics for

solar energy absorption [4]. Therefore, films of copper sulfide on polymers are used as conductive substrates for metal deposition [5, 6] and semiconductors [7], as polarizers of infrared radiation [8], as active absorbers of radio waves [9]. Due their optical properties, Cu_xS thin films find use in many photovoltaic and photothermal applications [10].

Hydrophilic and semi-hydrophilic polymers are capable of absorbing ions of various electrolytes from aqueous solutions [11]. Over the last decade, the sorption–diffusion method for the formation of thin copper sulfide layers on the surface of polyamide 6 (PA), based on the initial treatment of a polymer with the solutions containing anions of polythionates, $S_nO_6^{2-}$, has been under extensive investigation at the Department of Inorganic Chemistry of the Kaunas University of Technology. It was assumed that during treatment

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the polythionate ions containing chains of divalent sulfur atoms of low oxidation state, $^{-}O_3S-S_x-SO_3^{-}$ [12–14], are sorbed by a polymer.

Thin layers of copper sulfides are formed on PA surface if a sulfurized polymer is later treated with a solution of copper(II / I) salts [15–17].

In earlier studies using this method, a PA film had been first treated with a water solution of higher polythionic acid, $H_2S_nO_6$ ($n = 9–33$) [15–18]. A disadvantage of this method, however, is that the synthesis of highly sulfurized polythionic acids from the hydrogen sulfide, H_2S , sulfurous, H_2SO_3 , and thiosulfuric, $H_2S_2O_3$, acids is rather complicated and lasts up to two days [19]. Besides, a gradual spontaneous decomposition of these acids with the liberation of elemental sulfur occurs with time [20]; also, acid solutions exert a specific effect on the structure of PA [21].

The aim of the present work was to summarize, review and discuss the results obtained by us while studying the process of pentathionate ions sorption–diffusion into PA, also processes of the formation of copper sulfide layers in the surface of PA films, and to characterize the copper sulfide layers obtained, since only separate fragments of these studies were described in our previous publications [22–25]. The chemical and phase composition of Cu_xS layers, their electrical conductance were studied by the methods of atomic absorption spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and by measuring electrical sheet resistance.

EXPERIMENTAL

A PA 6 film (specification TY 6-05-1775-76, grade PK-4, 70 μm thick), produced in Russia, was used. Prior to the experiments, pieces of the film 15 \times 70 mm in size had been boiled in distilled water for 2 h to remove the remainder of the monomer. Then they were dried with filter paper and kept in a desiccator over $CaCl_2$ for 24 h.

Potassium pentathionate hemitrihydrate, $K_2S_5O_6 \cdot 1.5H_2O$, was produced by the method of Kurtenacker [26].

PA films were sulfurized in a thermostatic vessel, using a continually stirred acidified (0.1 mol \cdot dm $^{-3}$ HCl, pH \sim 1.5) 0.025–0.2 mol \cdot dm $^{-3}$ $K_2S_5O_6$ solutions for up to 6 h at a temperature of 1–20 $^{\circ}C$. 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 $K_2S_5O_6$ decreased significantly. The stability of pentathionate solution at temperatures higher than 20 $^{\circ}C$ was insufficient, either.

At certain time intervals, the PA film samples were removed from $K_2S_5O_6$ solution, rinsed with distilled water, dried with filtration paper, left over $CaCl_2$ for 24 h and then used in further experiments and analysis.

Sulfur concentration (Cs) in PA film samples was determined potentiometrically [27]. First, a sample of a sul-

furized 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.

After immersion in $K_2S_5O_6$ solution, a sample was treated with Cu(II / I) solution, then rinsed with distilled water, dried over $CaCl_2$, and used for analysis and subsequent experiments. 0.4 mol \cdot dm $^{-3}$ Cu(II / I) salt solution was made from crystalline $CuSO_4 \cdot 5H_2O$ and 0.1 mol hydroquinone as a reducing agent. In this mixture, a ratio of univalent and divalent copper salts, independently of temperature, at 0.34 mol \cdot dm $^{-3}$ Cu(II) salt and 0.06 mol \cdot dm $^{-3}$ Cu(I) salt is present [28]. The concentration of copper in PA samples was determined using an atomic absorption Perkin–Elmer spectrometer 503 ($\lambda = 325$ nm) [29].

The conductivity of copper sulfide films at the constant current was measured using an E7-8 numerical measuring instrument with special electrodes.

The UV, VIS (200–400 nm) and IR (400–1400 cm^{-1}) spectra were obtained with the aid of Spectronic^R GenesysTM and Perkin–Elmer GX spectrometers, system FT–IR.

The phase composition of the copper sulfide layer was investigated by X-ray diffraction, using a DRON-6 diffractometer (radiation $Cu-K_{\alpha}$). X-ray diffractograms of PA samples with Cu_xS layers were treated using the Search Match, ConvX, Xfit, and Microsoft Excel programs. XPS spectra of Cu_xS layers were recorded with a ESCALAB MKII spectrometer (VG Scientific, radiation $Mg K_{\alpha} - 1253.6$ eV, output 300 W). The 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 30–180 s. The rate of etching was 1 nm / 30 s. The maximum accuracy of the method is ± 0.1 at. %. To investigate layers obtained by the XPS method, the photoelectron spectra of Cu 2p $_{3/2}$ and S 2p were recorded. Empirical sensitivity factors for these elements were taken from the literature [30], and the spectra obtained were compared with the standard ones [31].

RESULTS AND DISCUSSION

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 $K_2S_5O_6$ solution, recorded by the compensation method (PA absorption eliminated), were in the intervals 418–484, 523–568, 609–737, 985–1079 and 1111–1284 cm^{-1} . On the grounds of the literature data [14, 32], the peaks in the first interval were assigned to the

valence vibrations in the S-S bond (ν_{s-s}), in the second interval to the asymmetric deformation O-S-O vibrations $\delta_{as}(O-S-O)$, in the third interval to the symmetric deformation O-S-O vibrations, $\delta_s(O-S-O)$, in the fourth interval to the symmetric valence S-O vibrations, $\nu_s(S-O)$, and in the fifth interval to the asymmetric valence S-O vibrations, $\nu_{as}(S-O)$. These results confirm that the sorption of pentathionate ions by PA occurs during polymer treatment with an acidified solution of $K_2S_5O_6$.

The UV absorption spectra of PA samples sulfurized for different periods of time in $K_2S_5O_6$ solution are shown in Fig. 1. 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 [33, 34], the absorption maxima of pentathionate ions are most intensive at 256 and 295 nm. Thus, UV absorption spectra recorded by us confirm again that sulfur is sorbed by PA films in the form of pentathionate ions. The intensity of absorption maxima in the spectra, as expected, increases with an increase in the duration of a polymer treatment with potassium pentathionate solution.

Chemical analysis of PA samples sulfurized in a $K_2S_5O_6$ solution showed that the concentration of sulfur sorbed by a polymer increases with increasing the temperature (Fig. 2) and concentration (Fig. 3) of the sulfurization solution.

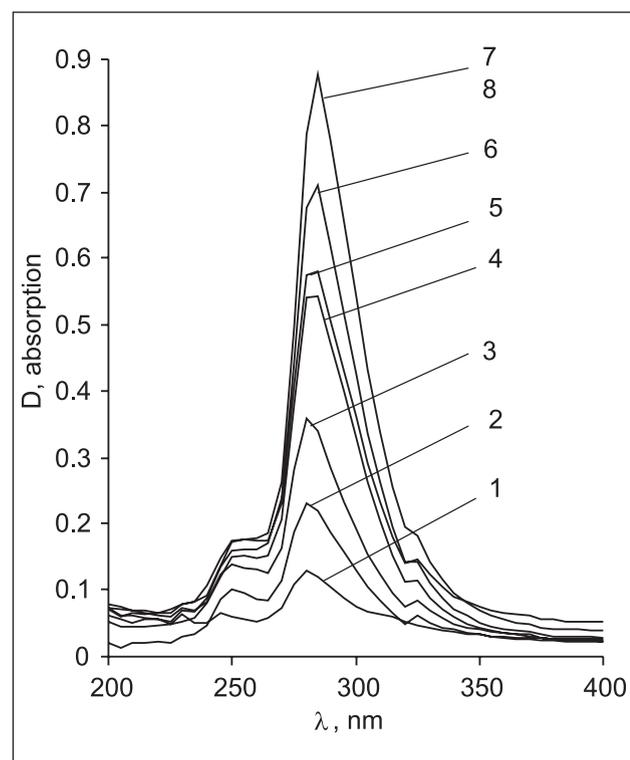


Fig. 1. UV absorption spectra of PA films sulfurized in acidified $0.05 \text{ mol} \cdot \text{dm}^{-3}$ $K_2S_5O_6$ solution at a temperature of $10 \text{ }^\circ\text{C}$ for different periods of time. Duration of PA sulfurization, h: 1 – 0.25, 2 – 1, 3 – 2, 4 – 3, 5 – 4, 6 – 5, 7 – 6

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 polymer. The tapes from colourless transform into yellow, then into brown and acquire a metallic lustre. Electrical

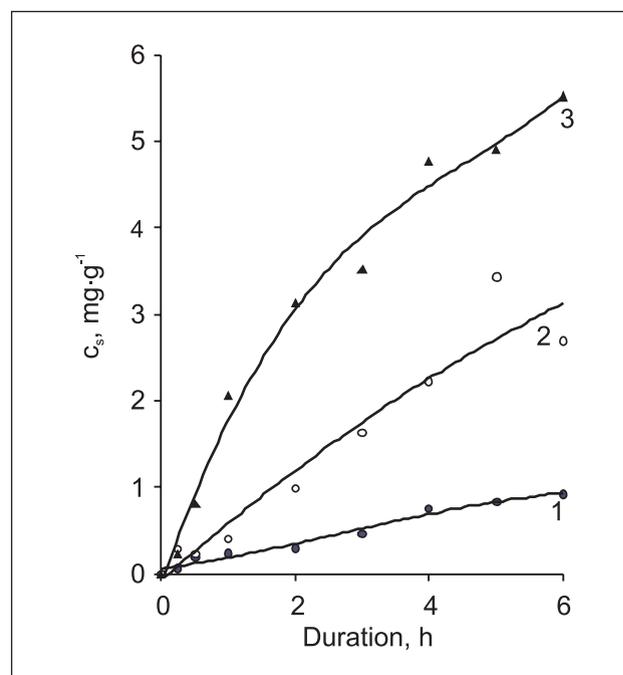


Fig. 2. Change of sulfur concentration in PA with time during its treatment with acidified $0.05 \text{ mol} \cdot \text{dm}^{-3}$ $K_2S_5O_6$ solution at different temperature. $T, \text{ }^\circ\text{C}$: 1 – 1; 2 – 10; 3 – 20

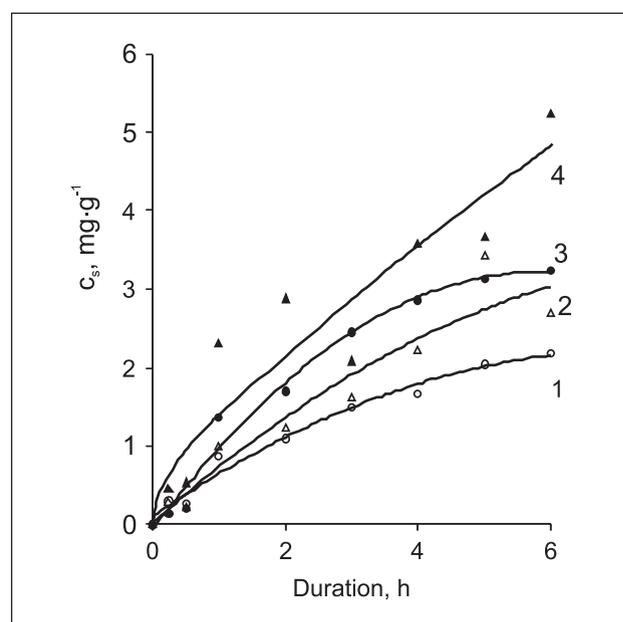


Fig. 3. Change of sulfur concentration in PA with time during its treatment with acidified $K_2S_5O_6$ solution of different concentration at a temperature of $10 \text{ }^\circ\text{C}$. Concentration of $K_2S_5O_6$ solution, $\text{mol} \cdot \text{dm}^{-3}$: 1 – 0.025; 2 – 0.05; 3 – 0.1; 4 – 0.2

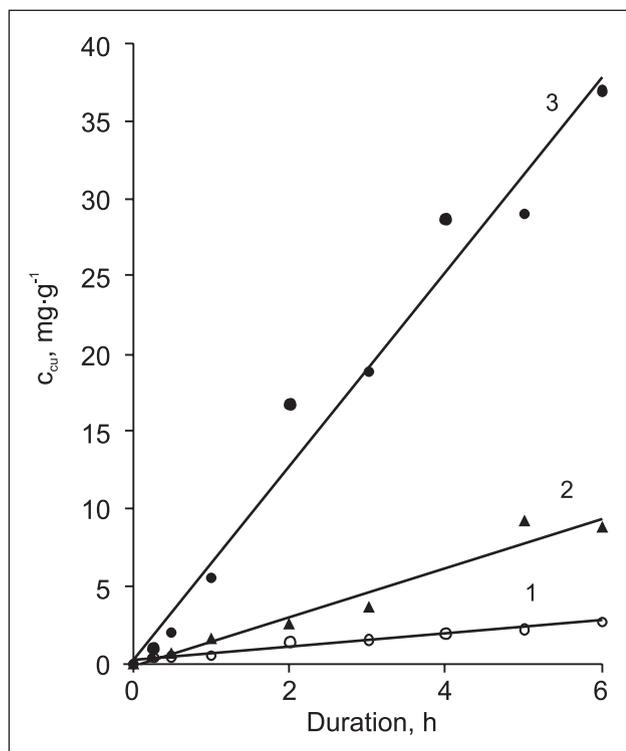


Fig. 4. Dependence of copper concentration in PA on the period of initial PA treatment with acidified $0.05 \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2\text{S}_5\text{O}_6$ solution at different temperature. Sulfurized PA was treated with a $\text{Cu}(\text{II} / \text{I})$ salt solution at 80°C for 10 min. $T, ^\circ\text{C}$: 1 – 1; 2 – 10; 3 – 20

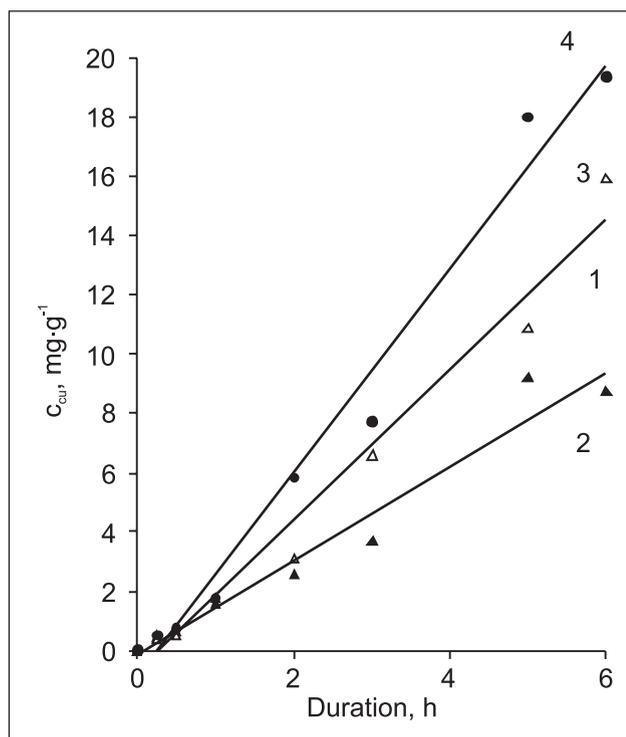


Fig. 5. Dependence of copper concentration in PA on the period of initial PA treatment with acidified $\text{K}_2\text{S}_5\text{O}_6$ solution of different concentration at a temperature of 10°C . Concentration of $\text{K}_2\text{S}_5\text{O}_6$ solution, $\text{mol} \cdot \text{dm}^{-3}$: 1 – 0.5; 2 – 0.1; 3 – 0.2

measurements finally confirmed that PA surface from the dielectric became a semiconductor or an electrical conductor.

The conditions of initial chalcogenation determine the concentration of copper and the chemical and phase composition of the chalcogenide layer formed: the concentration of copper increases (up to $\sim 40 \text{ mg} \cdot \text{g}^{-1}$) with increasing the temperature and concentration of PA sulfurization precursor solution (Figs. 4, 5).

Cu_xS layers of various composition are formed on the surface of the polymer and in its bulk after treatment of PA samples with 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 [35–38]. The chemical composition and crystal structure of the majority of Cu_xS minerals such as chalcocite Cu_2S , djurleite $\text{Cu}_{1.95}\text{S}$, yarrowite $\text{Cu}_{1.12}\text{S}$ 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 method was scarcely investigated.

Structural studies of Cu_xS layers formed by the sorption–diffusion method are limited by the polycrystallinity of the layers obtained, as well as by the existence of Cu_xS phases with various compositions and structures, and by the crystallinity of PA. The intensity of the polymer peaks at $\theta < 13^\circ$ exceeds the intensity of copper sulfide peaks a few times. Therefore, the area of $2\theta \geq 26.0^\circ$ was investigated in more detail.

After treatment of PA samples with sorbed polythionate anions for a different time in a copper salt solution at 80°C , Cu_xS films of different composition were obtained. X-ray diffraction patterns of the films showed peaks of various copper sulfide phases coexisting in a film (Figs. 6, 7).

The X-ray diffraction patterns of Cu_xS layers formed on PA after its sulfurization in $\text{K}_2\text{S}_5\text{O}_6$ solutions of different concentration during 4 h at 10°C are shown in Fig. 6. When the 0.025 and $0.05 \text{ mol} \cdot \text{l}^{-1}$ solutions of potassium pentathionate had been used for polymer sulfurization, the peaks of orthorhombic anilite, $\text{Cu}_{1.75}\text{S}$, ($72\text{--}617$) at $2\theta = 41.10, 48.50, 53.60, 58.40, 60.90^\circ$ [35] and monoclinic djurleite, $\text{Cu}_{1.9375}\text{S}$, ($71\text{--}1383$) at $2\theta = 34.40$ and 38.20° [36] were detected (Fig. 6, curves 1 and 2). The peak of an additional phase of CuS_2 ($83\text{--}1619$) at $2\theta = 59.80^\circ$ [37] was detected in Cu_xS layers formed on PA initially sulfured with $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2\text{S}_5\text{O}_6$ solution (Fig. 6, curve 3). We noted that the number of more conductive anilite peaks and their intensity increased with increasing the concentration of the $\text{K}_2\text{S}_5\text{O}_6$ solution used for PA sulfurization: only one peak of djurleite at $2\theta = 38.20^\circ$ [36] and three peaks of anilite at $2\theta = 37.60, 46.50$ and 49.60° [35] were found in the diffraction pattern of the Cu_xS layer on PA sulfured with $0.20 \text{ mol} \cdot \text{dm}^{-3}$ solution of $\text{K}_2\text{S}_5\text{O}_6$ (Fig. 6, curve 4).

Analysis of X-ray diffraction patterns of Cu_xS layers formed on PA sulfured for 4 h with $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2\text{S}_5\text{O}_6$

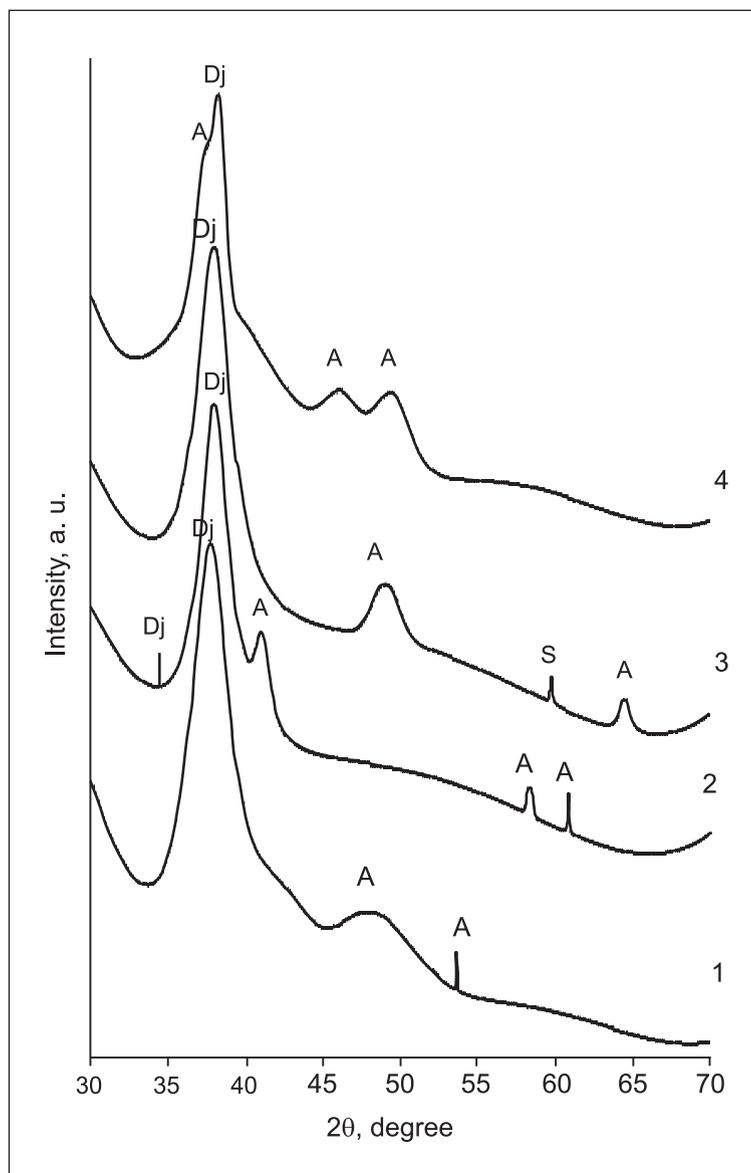


Fig. 6. X-ray diffraction patterns of Cu_xS layers on PA (peaks of djurleite ($\text{Cu}_{1.9375}\text{S}$) – Dj, anilite (Cu_7S_4) – A, copper sulfide (CuS_2) – S). PA was treated with $\text{K}_2\text{S}_5\text{O}_6$ solution of different concentration for 4 h at 10 °C. Sulfurized PA was treated with $\text{Cu}(\text{II}/\text{I})$ salt solution at 80 °C for 10 min. The concentration of $\text{K}_2\text{S}_5\text{O}_6$ solution, $\text{mol} \cdot \text{dm}^{-3}$: 1 – 0.025; 2 – 0.05; 3 – 0.10; 4 – 0.20

solution at different temperatures showed that their phase composition had changed (Fig. 7). On treating PA samples with $\text{K}_2\text{S}_5\text{O}_6$ solution at 1 °C, phases of poorly conductive djurleite, $\text{Cu}_{1.9375}\text{S}$ (peak at $2\theta = 38.2^\circ$), and tetragonal chalcocite, $\text{Cu}_{1.96}\text{S}$ (29–578) [38] (peak at $2\theta = 48.8^\circ$) were detected (Fig. 7, curve 1). When the temperature of $\text{K}_2\text{S}_5\text{O}_6$ solution was raised up to 10 °C, the Cu_xS layer consisted of three phases: monoclinic djurleite, $\text{Cu}_{1.9375}\text{S}$ ($2\theta = 38.2^\circ$), more conductive orthorhombic anilite, Cu_7S_4 , (peaks at $2\theta = 49.4$ and 64.7°) and conductive cubic copper sulfide CuS_2 (peak at $2\theta = 59.8^\circ$) (Fig. 7, 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, $\text{Cu}_{1.9375}\text{S}$ (peak at $2\theta = 38.2^\circ$), orthorhombic anilite, Cu_7S_4 (peaks at $2\theta = 49.4, 50.5, 59.6$ and 61.5°), tetragonal chalcocite, $\text{Cu}_{1.96}\text{S}$ ($2\theta = 45.02^\circ$) and of more conductive rhombohedral digenite, Cu_9S_5 (peak at $2\theta = 60.1^\circ$) (Fig. 7, 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 is prolonged and the concentration of chalcogenation solution is increased, the conductivity of Cu_xS layers increases, too. It is known [39] that the electrical resistance of Cu_xS decreases 10^6 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 x decreases, resulting in the formation of copper sulfide layers of low electrical resistance ($\sim 100 \Omega / \square$).

Table 1. Sheet resistance ($\text{k}\Omega / \square$) of Cu_xS layers on PA films first treated with $\text{K}_2\text{S}_5\text{O}_6$ solution and then with $\text{Cu}(\text{I}/\text{II})$ salt solution at 80 °C for 10 min

$\text{K}_2\text{S}_5\text{O}_6$ solution		Duration of sulfurization, h							
Concentration, $\text{mol} \cdot \text{dm}^{-3}$	Temperature, °C	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	–	$4.5 \cdot 10^2$	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

Thus, the established regularities enable formation on PA surface of Cu_xS 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 ($\text{Cu}_{1.96}\text{S}$) and djurleite ($\text{Cu}_{1.9375}\text{S}$) phases decreases, but of the more conductive anilite and rhombohedral digenite (Cu_9S_5) increases. If the duration of PA sulfuration is increased to four hours (but the concentration of $\text{K}_2\text{S}_5\text{O}_6$ solution and temperature are unchanged), the phase of the more conductive orthorhombic anilite (Cu_7S_4) prevail dominates in the Cu_xS layer formed; besides, the phase of rhombohedral digenite (Cu_9S_5) is formed. Thus, the stoichiometrical composition of copper sulfides changes in the direction of x decrease, resulting in the formation of Cu_xS layers with a very low electrical resistance.

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 $\text{K}_2\text{S}_5\text{O}_6$ solutions of different concentration (0.025, 0.05, 0.10 and $0.20 \text{ mol} \cdot \text{dm}^{-3}$) and temperature (1, 10 and 20°C). Then the sulfurized films were treated for 10 min with a $\text{Cu}(\text{II} / \text{I})$ salt solution at a temperature of 78°C . The results are shown in Figs. 8–11 and presented in Tables 2–4.

The values of $\text{Cu } 2p_{3/2}$ spectra bond energies of not etched Cu_xS layers, presented in Figs. 8 and 9, indicate the presence of CuO , Cu_2O , CuS , Cu_2S , Cu and CuSO_4 in the composition of these layers. It is also obvious that the composition of these compounds does not depend on the conditions of sulfurization.

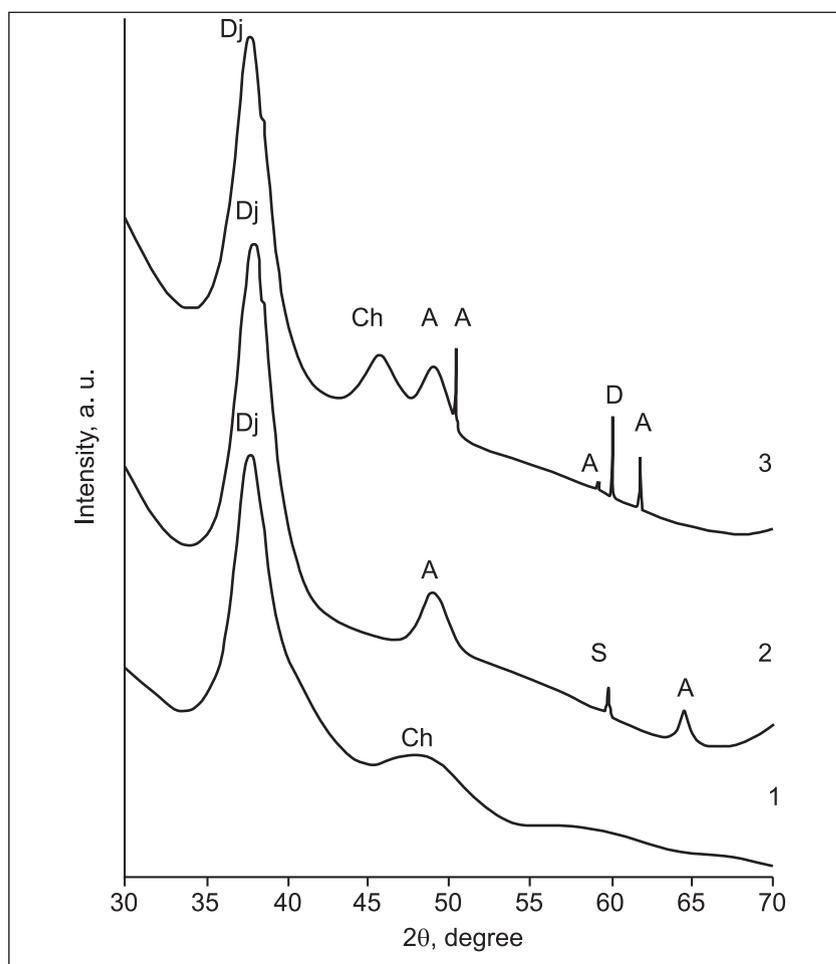


Fig. 7. X-ray diffraction patterns of Cu_xS layers on PA (peaks of djurleite ($\text{Cu}_{1.9375}\text{S}$) – Dj, chalcocite ($\text{Cu}_{1.96}\text{S}$) – Ch, anilite (Cu_7S_4) – A, digenite (Cu_9S_5) – D, copper sulphide (CuS_2) – S). PA had been initially treated with $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{K}_2\text{S}_5\text{O}_6$ solution for 4 h at different temperature. Sulfurized PA was treated with $\text{Cu}(\text{II} / \text{I})$ salt solution at 80°C for 10 min. The temperature of $\text{K}_2\text{S}_5\text{O}_6$ solution, $^\circ\text{C}$: 1 – 1; 2 – 10; 3 – 20

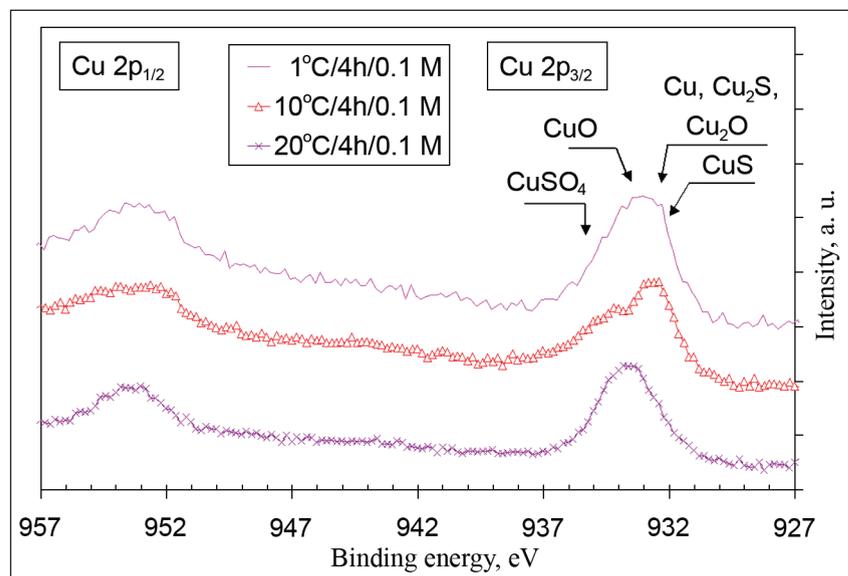


Fig. 8. XPS $\text{Cu } 2p_{3/2}$ spectra of unetched copper sulfide layers on PA 6 films formed by their sulfurization for 4 h in $0.1 \text{ mol} \cdot \text{dm}^{-3}$ acidified $\text{K}_2\text{S}_5\text{O}_6$ solutions of different temperature and then treated with $\text{Cu}(\text{II} / \text{I})$ salt solution

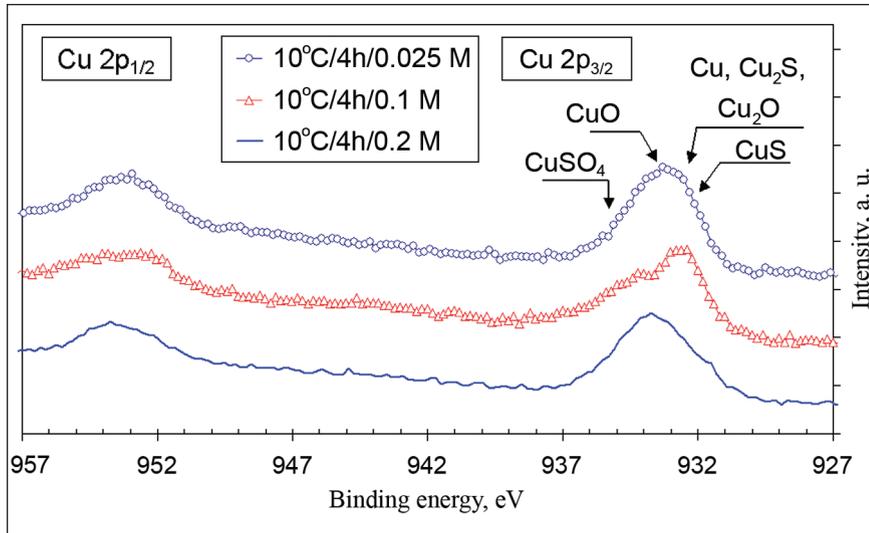


Fig. 9. XPS $2p_{3/2}$ spectra of unetched copper sulfide layers on PA 6 films, formed by their sulfuration for 4 h at a temperature of $10^\circ C$ with acidified $K_2S_5O_6$ solutions of different concentration and then treated with $Cu(II/I)$ salt solution

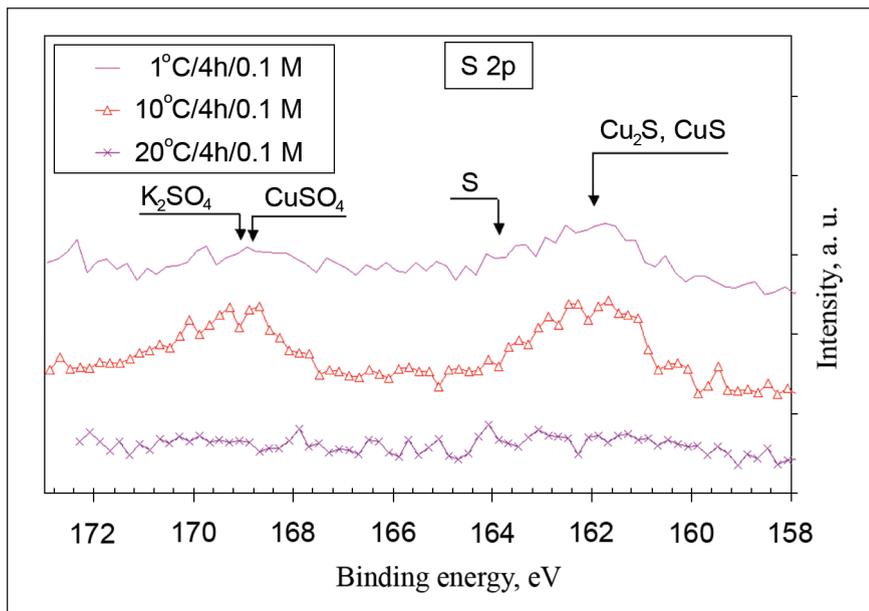


Fig. 10. XPS $S 2p$ spectra of unetched copper sulfide layers on PA 6 films, formed by their sulfuration for 4 h in $0.1 \text{ mol} \cdot \text{dm}^{-3}$ acidified $K_2S_5O_6$ solutions of different temperature and then treated with the $Cu(II/I)$ salt solution

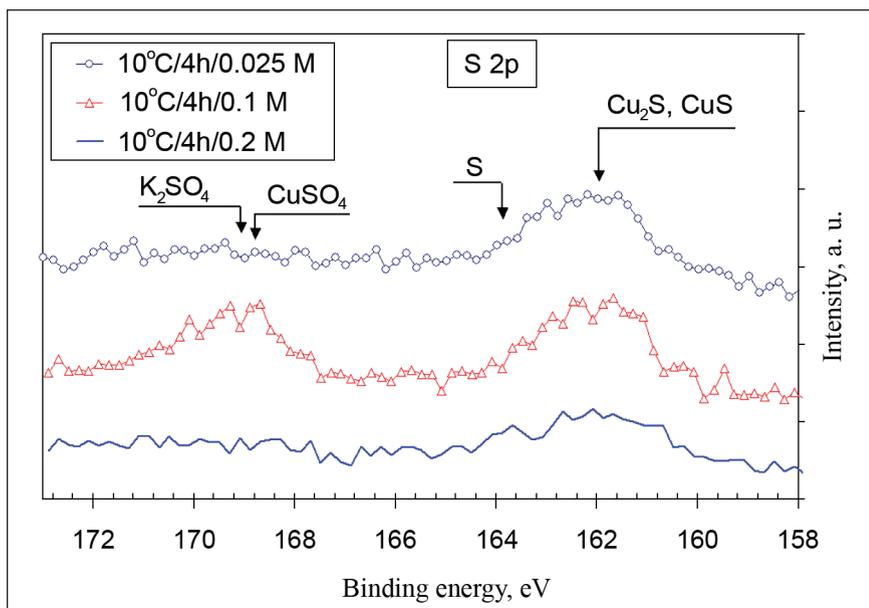
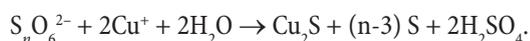


Fig. 11. XPS $S 2p$ spectra of unetched copper sulfide layers on PA 6 films, formed by their sulfuration for 4 h in $K_2S_5O_6$ solutions of different concentration at a temperature of $10^\circ C$ and then treated with $Cu(II/I)$ salt solution

From the S 2p spectra of the same layers one can see that, besides CuS and CuSO₄, also K₂SO₄ 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 [40]:



K₂SO₄ 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 CuSO₄, K₂SO₄ and elemental sulfur had been removed from the surface of copper sulfides 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 on 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 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. 8–11) possibly because of the physical adsorption of water and oxides present in the air.

After a copper sulfide layer had been etched by Ar⁺ ions during 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 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. This indicates 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 may 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 lay-

Table 2. Data of XPS analysis of Cu_xS layers on PA 6 films formed by their sulfurization in acidified 0.1 mol · dm⁻³ K₂S₂O₈ solution for 4 h at different temperature and then treated with Cu(II / I) salt solution

Sulfurization temperature	Etching conditions	Element	Content, at %	Atomic Cu : S ratio	Electrical sheet resistance of the layer, kΩ / □
1	Before etching	Cu	1.6	1.33	56.13
		S	1.2		
		O	19.1		
		C	78.1		
	Etched for 30 s	Cu	3.8	1.15	
		S	3.3		
		O	26.9		
		C	66.1		
	Etched for 90 s	Cu	9.2	1.74	
		S	5.3		
		O	13.3		
		C	72.1		
10	Before etching	Cu	1.8	0.69	1.12
		S	2.6		
		O	24.4		
		C	71.1		
	Etched for 30 s	Cu	6.3	1.02	
		S	6.2		
		O	16.3		
		C	71.3		
	Etched for 90 s	Cu	8.9	1.16	
		S	7.7		
		O	19.7		
		C	63.7		
20	Before etching	Cu	1.3	1.44	0.13
		S	0.9		
		O	20.7		
		C	77.0		
	Etched for 30 s	Cu	2.8	1.65	
		S	1.7		
		O	21.2		
		C	74.3		
	Etched for 90 s	Cu	4.1	1.32	
		S	3.1		
		O	14.0		
		C	78.7		

ers: CuO, Cu₂O, CuS, Cu₂S, Cu, CuSO₄, K₂SO₄ and elemental sulfur. It is known that the value of *x* in Cu_xS sulfides may change from 1 to 2, forming non-stoichiometric sulfides. But 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, as shown above.

Table 3. Data of XPS analysis of Cu_xS layers on PA 6 films, formed by their sulfurization in acidified $\text{K}_2\text{S}_5\text{O}_6$ solution of different concentration for 4 h at a temperature of 10 °C and then treated with $\text{Cu}(\text{II} / \text{I})$ salt solution

The concentration of sulfurization solution, $\text{mol} \cdot \text{dm}^{-3}$	Etching conditions	Element	Content, at %	Atomic Cu : S ratio	Electrical sheet resistance of the layer, $\text{k}\Omega / \square$
0.025	Before etching	Cu	0.9	0.69	6.56
		S	1.3		
		O	19.8		
		C	78.0		
	Etched for 30 s	Cu	2.3	1.28	
		S	1.8		
		O	20.3		
		C	75.6		
	Etched for 90 s	Cu	4.3	1.79	
		S	2.4		
		O	10.5		
		C	82.8		
Etched for 180 s	Cu	7.2	1.53		
	S	4.7			
	O	14.8			
	C	73.3			
0.05	Before etching	Cu	1.6	1.23	2.67
		S	1.3		
		O	17.3		
		C	79.8		
	Etched for 30 s	Cu	7.1	1.15	
		S	6.2		
		O	14.4		
		C	72.3		
	Etched for 90 s	Cu	12.9	1.30	
		S	9.9		
		O	14.8		
		C	62.3		
0.1	Before etching	Cu	1.8	0.69	1.12
		S	2.6		
		O	24.4		
		C	71.1		
	Etched for 30 s	Cu	6.3	1.02	
		S	6.2		
		O	16.3		
		C	71.3		
	Etched for 90 s	Cu	8.9	1.16	
		S	7.7		
		O	19.7		
		C	63.7		
0.2	Before etching	Cu	1.0	1.25	0.39
		S	0.8		
		O	17.1		
		C	81.1		
	Etched for 30 s	Cu	1.9	1.19	
		S	1.6		
		O	34.5		
		C	62.0		
	Etched for 90 s	Cu	4.9	1.40	
		S	3.5		
		O	12.0		
		C	79.6		

Table 4. Data of XPS analysis of Cu_xS layers on PA 6 films, formed by their sulfurization in acidified $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{K}_2\text{S}_5\text{O}_6$ solution at a temperature of 20 °C for different periods of time and then treated with $\text{Cu}(\text{II} / \text{I})$ salt solution

The duration of sulfurization, h	Etching conditions	Element	Content, at %	Atomic Cu : S ratio	Electrical sheet resistance of the layer, $\text{k}\Omega / \square$
0.5	Before etching	Cu	2.1	0.75	450.0
		S	2.8		
		O	25.9		
		C	69.2		
4.0	Before etching	Cu	1.3	1.44	0.127
		S	0.9		
		O	20.7		
		C	77.0		
	Etched for 30 s	Cu	2.8	1.65	
		S	1.7		
		O	21.2		
		C	74.3		
	Etched for 90 s	Cu	4.1	1.32	
		S	3.1		
		O	14.0		
		C	78.7		
6.0	Before etching	Cu	1.5	1.25	0.104
		S	1.2		
		O	16.0		
		C	81.2		
	Etched for 30 s	Cu	4.1	1.78	
		S	2.3		
		O	9.6		
		C	84.0		
	Etched for 90 s	Cu	2.3	1.32	
		S	3.8		
		O	6.8		
		C	87.1		
Etched for 180 s	Cu	5.5	0.85		
	S	6.5			
	O	12.5			
	C	75.5			

CONCLUSIONS

1. The sorption of pentathionate ions from acidified $0.025\text{--}0.20 \text{ mol} \cdot \text{dm}^{-3}$ water solutions of potassium pentathionate, $\text{K}_2\text{S}_5\text{O}_6$, by polyamide 6 films has been studied by IR ($400\text{--}1300 \text{ cm}^{-1}$), UV ($200\text{--}400 \text{ nm}$) absorption spectra and chemical methods. Peaks in the IR spectra of pentathionate anions sorbed into a polyamide were found in the intervals $418\text{--}484$, $523\text{--}568$, $609\text{--}737$, $985\text{--}1079$, $1111\text{--}1284 \text{ cm}^{-1}$ and assigned to the $\nu_{\text{S-S}}$, $\delta_{\text{as}}(\text{O-S-O})$, $\delta_{\text{s}}(\text{O-S-O})$, $\nu_{\text{s}}(\text{S-O})$ and $\nu_{\text{as}}(\text{S-O})$, respectively. Three absorption maxima were observed in the UV absorption spectra: at 250 nm as a clear shoulder, at 285 nm as a peak, and at 325 nm as an unclearly defined shoulder. These spectral data have confirmed that sulfur is sorbed by PA films in the form of pentathionate ions.

2. The concentration of sulfur sorbed by a polymer increases with increasing the temperature, the concentration of the potassium pentathionate solution and the duration of polymer treatment.

The concentration of copper in a polymer film is strongly dependent on the concentration of sulfur in the PA, i. e. the amount of copper varies in proportion to sulfur concentration in the samples.

3. Copper sulfide, Cu_xS , layers on the surface of polyamide, formed by the use of potassium pentathionate as a precursor of a polymer chalcogenization, were studied by the methods of chemical analysis, X-ray diffraction and by atomic force microscopy. X-ray diffraction studies of Cu_xS layers revealed five phases: djurleite ($\text{Cu}_{1.9375}\text{S}$), chalcocite ($\text{Cu}_{1.96}\text{S}$), anilite (Cu_7S_4), digenite (Cu_9S_5) and copper sulphide (CuS_2). The phase composition depended on the conditions of PA sulfurization and the subsequent treatment of the sulfurized polymer with a Cu(II/I) salt solution.

4. The formation regularities of Cu_xS layers and the chemical and phase composition of the formed layers enable obtaining electrically conductive or semi-conductive copper sulfide films. The sheet resistance of the samples varied from $104 \Omega / \square$ to $1.52 \text{ M}\Omega / \square$ and depended on the conditions of PA interaction with $\text{K}_2\text{S}_5\text{O}_6$ solution. The obtained results and the established regularities enable formation on polyamide film surface of Cu_xS layers of a desirable composition and conductivity.

5. The X-ray photoelectron spectroscopic determination of the chemical composition of Cu_xS layers up to 1 nm deep confirmed formation of copper sulfides of various phases in the surface of a polyamide.

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References

1. S. T. Lakshmikumar, *Mater. Sol. Cells*, **32**, 7 (1994).
2. V. M. Garcia, P. K. Nair, M. T. Nair, *J. Cryst. Growth*, **203**(1–2), 113 (1999).
3. R. S. Mane, C. D. Lokhande, *Mater. Chem. Phys.*, **65**, 1 (2000).
4. X.-H. Liao, N.-Y. Chen, S. Xu, S.-B. Yang, J. Zhu, *J. Cryst. Growth*, **252**, 593 (2003).
5. R. N. Bhattacharya, H. Wiesner, T. A. Berens, R. J. Matson, J. Keane, R. K. Ramanathan, A. Swartzlander, A. Mason, R. Noufi, *J. Electrochem. Soc.*, **4**, 1376 (1997).
6. J. Cardoso, O. Gomezdaza, L. Ixthilco, M. T. S. Nair, P. K. Nair, *Semicond. Sci. Technol.*, **16**, 123 (2001).
7. A. Žebrauskas, A. Mikalauskiene, *Chemistry*, **3**, 84 (1993).
8. Pat. USSR 1331291 (1986).
9. Pat. USSR 268525 (1986).
10. J. Johansson, J. Kostamo, M. Karppinen, L. Niinistö, *J. Mater. Chem.*, **12**, 1022 (2002).
11. G. E. Zaikov, A. L. Yordanskiy, V. S. Markin, *Diffusion of Electrolytes into the Polymers*, Moscow (1984).
12. O. Foss, in: H. J. Emeleus, A. G. Sharpe (eds.), *Advances in Inorganic Chemistry and Radiochemistry*, New York, Academic Press, **2**, 237 (1960).
13. K. Maroy, *Crystal structures of penta-, selenopenta-, telluropenta- and hexathionates*, PhD thesis, Bergen, Norway (1975).
14. V. J. Janickis, S. A. Grevys, *Rus. J. Inorg. Chem.*, **22**, 411 (1977).
15. R. Maciulevičius, *Formation of copper sulfide layers on polyamide using polythionic acids*, PhD thesis, Kaunas, Lithuania (1995).
16. Pat. 4402 B, Lithuania (1998).
17. V. Janickis, R. Maciulevičius, R. Ivanauskas, I. Ancutienė, *Coll. Polym. Sci.*, **281**, 84 (2003).
18. R. Maciulevičius, V. Janickis, R. Ivanauskas, *Chemistry* **4**, 141 (2000).
19. J. Janickis, J. Valančiūnas, V. Zelionkaitė, V. Janickis, S. Grevys, *Trans. Lithuanian Acad. Sci. Ser. B*, **3**(88), 83 (1975).
20. S. Grevys, V. Janickis, *Chem. Technol.*, **2**(36), 95 (2005).
21. R. Ivanauskas, V. Janickis, R. Maciulevičius, *Chem. Technol.*, **4**(13), 71 (1999).
22. R. Ivanauskas, R. Stokienė, V. Janickis, N. Kreivėnienė, *Chem. Technol.*, **1**(35), 20 (2005).
23. V. Janickis, R. Ivanauskas, R. Stokienė, N. Kreivėnienė, *Chem. Technol.*, **3**(37), 32 (2005).
24. V. Janickis, R. Ivanauskas, R. Stokienė, *Chem. Technol.*, **3**(39), 29 (2006).
25. I. Ancutienė, V. Janickis, R. Ivanauskas, R. Stokienė, N. Kreivėnienė, *Polish J. Chem.*, **81**, 381 (2007).
26. A. Kurtenacker, W. Fluss, *Z. Allgem. Anorg. Chemie*, **210**, 125 (1933).
27. P. K. Norkus, G. S. Šimkevičiūtė, *Rus. J. Analyt. Chem.*, **26**, 39 (1971).
28. I. Ancutienė, V. Janickis, V. Grevys, *Chemistry*, **2**, 3 (1997).
29. *Analytical Methods for Atomic Absorption Spectrometry*, Perkin-Elmer Corp., Norwalk, Conn. (1973).
30. D. Briggs, in: M. P. Seah (ed.), *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, Mir, Moscow (1987).
31. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder et al., *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corp., Minnesota (1978).
32. V. J. Janickis, J. V. Janickis, *Trans. Lithuanian Acad. Sci. Ser. B*, **6**(157), 43 (1986).
33. L. Lorenz, R. Samuel, *Z. Physik. Chem. (B)*, **14**, 219 (1931).
34. M. Schmidt, T. Sand, *J. Inorg. Nucl. Chem.*, **26**, 1173 (1964).
35. K. Koto, N. Morimoto, *Acta Crystallogr. Sec. B*, **26**, 915 (1970).
36. Jr. Howard, *Science*, **203**, 356 (1979).
37. Jr. H. E. King, C. T. Prewitt, *Am. Mineral.*, **64**, 1265 (1979).
38. A. Janosi, *Acta Crystallogr.*, **17**, 311 (1964).
39. A. Žebrauskas, *Chem. Technol.*, **1**(3), 39 (1996).
40. V. Janickis, *Chem. Technol.*, **4**(30), 5 (2003).

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ELEKTRAI LAIDŽIŲ VARIO SULFIDŲ SLUOKSNIŲ POLIAMIDO PAVIRŠIUJE SUDARYMAS NAUDOJANT KALIO PENTATIONATĄ IR JŲ TYRIMAS

Santrauka

Puslaidininkiniai ir elektrai laidūs vario sulfidų sluoksniai sudaryti poliamido 6 (PA) paviršiuje sorbciniu-difuziniu metodu, naudojant vandeninį kalio pentationato, $K_2S_5O_6$, tirpalą, kaip polimero sierinimo prekursorių. Pentationato jonai, turintys divalenčių mažo oksidacijos laipsnio sieros atomų grandinę $^-O_3S-S-S-SO_3^-$, yra sorbuojami-įdifunduoja į PA plėveles, jeigu jos apdorojamos $K_2S_5O_6$ tirpalu. Sorbuotos sieros koncentracija didėja, didinant prekursoriaus tirpalo koncentraciją, temperatūrą ir PA apdorojimo trukmę. Cu_xS sluoksniai susidaro PA plėvelių paviršiuje, kai sierintas polimeras apdorojamas vandeniniu vario(II / I) druskų tirpalu:

pentationato anijonai reaguoja su vario jonais. Vario koncentracija didėja (iki $40 \text{ mg} \cdot \text{g}^{-1}$), didėjant prekursoriaus tirpalo koncentracijai ir temperatūrai.

Rentgeno difrakcinės analizės rezultatai patvirtino Cu_xS sluoksnių susidarymą PA paviršiuje. Fazinė Cu_xS sluoksnio sudėtis priklauso nuo kalio pentationato tirpalo koncentracijos ir temperatūros bei nuo pradinio apdorojimo $K_2S_5O_6$ tirpale trukmės. Šie sluoksniai sudaryti iš mažai laidaus tetragoninio chalkocito, $Cu_{1.96}S$, monoclinio djurleito, $Cu_{1.9375}S$, elektrai laidaus romboedrinio digenito, Cu_9S_5 , ortorombinio anilito, Cu_7S_4 , ir kubinio CuS_2 . Fazinė sudėtis lemia elektrines sudarytų sluoksnių savybes: elektrinė kvadrato varža kinta nuo $0,104$ iki $1,52 \cdot 10^3 \text{ K}\Omega / \square$. Sluoksnių sudėtis nustatymas rentgeno fotoelektroninės spektroskopijos metodu patvirtino įvairių fazių vario sulfidų susidarymą. Nustatyti dėsnin-gumai įgalina sudaryti PA paviršiuje norimos sudėties ir laidumo elektrai Cu_xS sluoksnius.