Formation of conducting copper sulfide layers on polyamide 6 using polythionates and analysis of these layers

Vitalijus Janickis*,

Remigijus Ivanauskas,

Rūta Stokienė

Department of Inorganic Chemistry, Kaunas University of Technology, Radvilėnų 19, LT-50254 Kaunas, Lithuania

The formation of semiconductive and electrically conductive layers of copper sulfides, Cu_xS, by sorption–diffusion on the surface of polyamide 6 (PA) using solutions of potassium polythionates–trithionate, $K_2S_3O_6$, tetrathionate, $K_2S_4O_6$, pentathionate, $K_2S_5O_6$, and dodecathionic acid, $H_2S_{12}O_6$, has been investigated. The measurement of IR and UV absorption spectra has shown that sulfur is sorbed on – it is diffused in the PA films in the form of polythionate anions. The concentration of sulfur in PA increases with the increase in the sulfurization time, the sulfur content in the polythionate molecules and the temperature of the sulfur precursor solution. The concentrations of sulfur obtained in the polymer treated with a solution of dodecathionic acid (up to ~8 mmol/cm³) are significantly higher than those obtained in the PA films treated with the solutions of lower potassium polythionates (up to ~0.07–0.22 mmol/cm³). Copper sulfide layers are formed on the surface of the PA film if the sulfurized polymer is treated with a solution of copper(II / I) salts. The conditions of polymer initial sulfurization determine the concentration of copper in PA, the stoichiometric composition of Cu_xS layers and the variation of the electrical sheet resistance of Cu_xS layers. The concentration of copper in PA increases with the increase in the sulfurization time, the sulfur content in the polythionate anion and the temperature of the precursor solution, and varies from 0.0035 to ~8 mmol/cm³. Ten Cu_xS phases – chalcocite (Cu_2S and $Cu_{1.96}S$), anilite (Cu_7S_4 and Cu_7S_5), djurleite ($Cu_{31}S_{16}$ and $Cu_{19375}S$), copper sulfide (CuS_2), digenite (Cu_9S_5), yarrowite (Cu_9S_8) and covelline (CuS) – were identified on copper sulfide layers on the polymer surface by X-ray diffraction analysis. The electrical sheet resistance of Cu_xS layers obtained decreases with the increase in the sulfurization duration and temperature, and the number of sulfur atoms in the polythionate anion.

Key words: polythionates, polyamide, copper sulfide layers, composition

INTRODUCTION

Semiconductive and electrically conductive composites are widely studied and used in various fields of modern technology. Semihydrophilic polyamide 6 (PA) with layers of copper sulfides belong to this group of composites. Modified polymers might be used as conductive substrates for electrodeposition of metal [1] and as semiconductors [2] or gas sensors functioning at temperatures near to room temperature [3, 4], as polarizers of infrared radiation [5] or as solar absorber coatings [6]. Due to the optical properties of copper sulfide, Cu_xS, thin films find their uses in many photovoltaic and photothermal applications [7].

Various methods were used to form copper sulfide layers on various dielectrics and on polymers: vacuum evaporation [8], activated reactive evaporation [9], spray pyrolysis [10], electrodeless deposition [11], successive ionic layer adsorption and reaction (SILAR) [12], chemical bath deposition [13, 14].

In this study, the layers of copper sulfide on PA were obtained by a sorption–diffusion method elaborated by us [15].

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

The method consists of two stages. In the first stage – sulfurization of the polymer – PA films are treated with a solution of higher polythionic acid ($H_2S_nO_6$, n = 15–33), the molecules of which contain chains of divalent sulfur atoms, $^-O_3S–S_{n-2}–SO_3^-$. In the second stage, the sulfurized polymer is treated with a solution of Cu(II / I) salts, and thin layers of semiconductive and electrically conductive copper sulfides form on the surface of polymer [15].

The aim of present work was to study and compare the formation, chemical and phase composition, and electrical properties of Cu_xS layers on PA, formed by the sorption–diffusion method using solutions of potassium polythionates, $K_2S_nO_6$, n = 3–5, and dodecathionic acid, $H_2S_{12}O_6$; to find out the variations of electrical sheet resistance due to the nature of the precursor of sulfur and to the conditions of PA sulfurization.

EXPERIMENTAL

The layers of copper sulfide were deposited on polyamide 6 (PA) (TY 6-05-1775-76, grade PK–4, 15 × 70 mm, 70 μm). The PA films were boiled in distilled water for 2 h to remove the mono-

mer residues. They were dried with filter paper and then over anhydrous CaCl$_2$ for 24 h.

The PA films were sulfurized in a thermostatic vessel using a continually stirred 0.1 mol/dm^3 solution of potassium polythionates in HCl (c = 0.1 mol/dm^3) at 10, 20 and 50 °C or 0.002 mol/dm^3 solution of polythionic acid H$_2$S$_{12}$O$_6$ at 20, 40 and 50 °C for 6 h.

At certain time intervals, the samples were withdrawn, rinsed with distilled water, dried with filter paper, left over anhydrous CaCl$_2$ for 24 h and then used in the analysis and further experiments.

Potassium trithionate monohydrate, K$_2$S$_3$O$_6$, potassium tetrathionate, K$_2$S$_4$O$_6$, and potassium pentathionate hemitrihydrate, K$_2$S$_5$O$_6$ · 1.5H$_2$O, were prepared employing the methods described in [16–18].

Solutions of dodecathionic acid were prepared and the average number of sulfur atoms (*n*) in the H$_2$S$_n$O$_6$ molecule was determined by the methods described in [19].

The samples of the sulfurized PA were treated with a solution of Cu(II / I) salts at 80 °C for 10 min. The Cu(II / I) salt solution was made from crystalline CuSO$_4$ · 5H$_2$O and hydroquinone as described in [20]. It was a mixture of Cu salts, containing 0.34 mol/dm^3 of Cu(II) and 0.06 mol/dm^3 of Cu(I) [21]. After the treatment with the solution of Cu(II / I) salts, the samples of PA were rinsed with distilled water, dried over anhydrous CaCl$_2$ and used in the further experiments.

The concentration of sulfur (c$_s$) in the PA films was determined potentiometrically [22]. A sample of the sulfurized PA film was treated under heating with 10–15 ml of 10 mol/dm^3 KOH solution and diluted with the same amount of distilled water. Standard calomel and platinum electrodes were used in potentiometric titration of KOH solution with 0.05 mol/dm^3 solution of iodine under stirring. A pH-meter – pH-673 M millivoltmeter was used for the potentiometric measurements.

The concentration of copper in the PA films after dissolving in concentrated nitric acid was determined using a Perkin–Elmer atomic absorption spectrometer (λ = 450 nm) [23].

The UV and Visible (200–400 nm) and IR (400–1400 cm^{-1}) spectra were obtained on Spectronic^R Genesys^{TM} and Perkin–Elmer GX spectrophotometers.

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

The phase composition of copper sulfide layers was investigated by X-ray diffraction (XRD) using a DRON-6 diffractometer (Cu K$_\alpha$ radiation). X-ray diffractograms of the PA samples with copper sulfide layers were treated using programs Search Match, ConvX, Xfit and Microsoft Excel.

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 the polymer films treated in potassium pentathionate and the dodecathionic acid solutions.

It was found that the peaks of the most intensive bands in the IR spectra of the PA samples sulfurized in a K$_2$S$_5$O$_6$ solution, recorded by the compensation method (PA absorption eliminated) were in intervals of 419–484, 524–568, 610–735, 985–1075, 1111–1282 cm^{-1} (Fig. 1 a). When the PA samples were sulfurized in a H$_2$S$_{12}$O$_6$ solution, the peaks of the most intensive bands in the IR spectra in intervals of 420–473, 503–558, 612–724, 838–1100, 1144–1293 cm^{-1} were found (Fig. 1 b). According to the literature data [24], 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_s(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 confirm the fact that the sorption of pentathionate and dodecathionate ions by PA occurs during the polymer treatment with the solutions of K$_2$S$_5$O$_6$ and of H$_2$S$_{12}$O$_6$.

The UV absorption spectra of the PA samples sulfurized for different periods of time in the solutions of K$_2$S$_5$O$_6$ and of H$_2$S$_{12}$O$_6$ are shown in Fig. 2. Three absorption maxima are observed in the spectra of the PA treated with the K$_2$S$_5$O$_6$ solution (Fig. 2 a): at ~250 nm as a weak peak – shoulder, at 285 nm as a very intensive peak, and at ~325 nm as a not intensive peak – shoulder. Three absorption maxima are observed in the
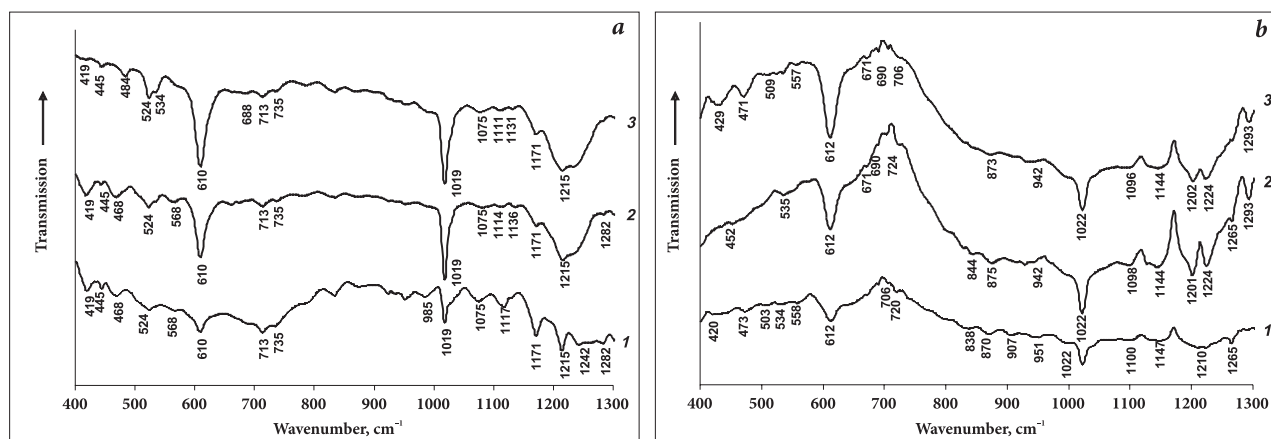

Fig. 1. IR absorption spectra of PA films with different sulfurization times with: *a)* 0.1 mol/dm^3 K$_2$S$_5$O$_6$ solution at a temperature of 20 °C. Sulfurization time, h: *1* – 1, *2* – 2, *3* – 5; *b)* 0.002 mol/dm^3 solution of H$_2$S$_{12}$O$_6$ at 20 °C. Sulfurization time, h: *1* – 0.25, *2* – 0.5, *3* – 2.0

spectra of the PA treated with the $H_2S_{12}O_6$ solution (Fig. 2 b): at ~250 nm as a strong peak, at ~290 nm as a broad shoulder and at ~322–332 nm as shoulders or peaks. According to the data of studies of the UV absorption spectra of polythionates [25–27], the absorption maxima of polythionate ions are at ~250, ~290 and ~340 nm. Thus, the UV absorption spectra recorded by us confirmed once again that sulfur is sorbed by the PA films in the form of $S_nO_6^{2-}$ ions. The intensity of the absorption peaks in the spectra, as expected, increases with an increase in the duration of the polymer treatment with the solutions of potassium pentathionate and dodecathionic acid.

In this work the kinetics of sorption-on–diffusion-in of sulfur from the solutions of polythionates and of dodecathionic acid into PA film was investigated (Figs. 3 and 4). The sulfur concentration in the PA film greatly depends on the sulfur content (number of sulfur atoms in the molecule) in the sulfuriza-
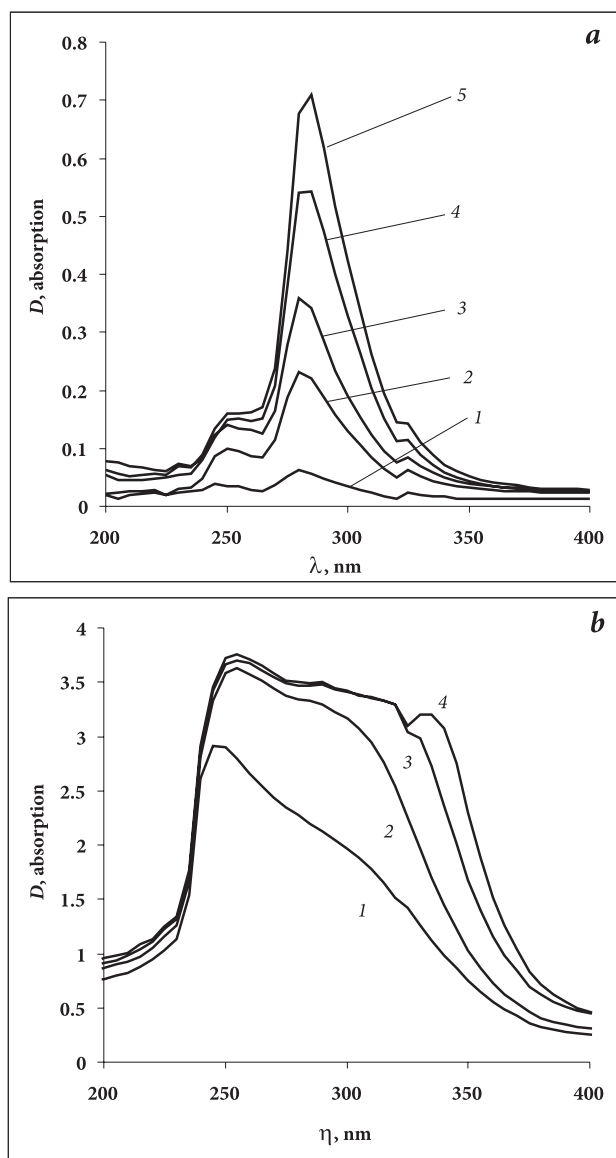
tion agent (Fig. 3). A significant difference – ca ~30 times and ca ~110 times – was found in the concentration of sulfur in the PA films using different precursors – $K_2S_3O_6$ or $H_2S_{12}O_6$ solutions after sulfurization for 0.25 h and 6 h, respectively, despite the the fact that the molar concentration of $H_2S_{12}O_6$ solution was 50 times lower than that of $K_2S_3O_6$ solution. The concentration of sulfur in the PA film, sulfurized in $K_2S_5O_6$ and $H_2S_{12}O_6$ solutions (Fig. 3, curves 3 and 4), show a sharp increase of up to 6 h of sulfurization, while in the PA sulfurized in the solutions of $K_2S_3O_6$ and $K_2S_4O_6$, which contains a lower number of sulfur atoms in the molecule, (Fig. 3, curves 1 and 2), the saturation of the polymer is reached already after ~2 h.

It was found that the concentration of sulfur in the samples (c_s, mmol/cm³) during the exposure in the solution of $H_2S_{12}O_6$ at 20, 40 and 50 °C and in the solution of $K_2S_5O_6$ at 10 and 20 °C increases continuously with time. Sulfur concentration in the range of ~0.010–8 mmol/cm³ might be obtained by varying the sulfurity of polythionate ion and the temperature of the solution (Fig. 4). These results show that a higher concentration of sulfur was obtained at a higher temperature and a higher sulfurity of the precursor.
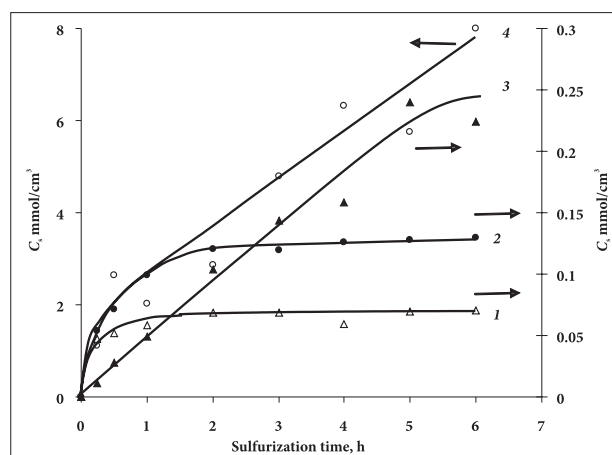

Fig. 2. UV absorption spectra of PA films with different sulfurization times with: *a)* 0.1 mol/dm³ $K_2S_5O_6$ solution at a temperature of 20 °C. Sulfurization time, h: *1* – 0.25, *2* – 1, *3* – 2, *4* – 4, *5* – 6; *b)* 0.002 mol/dm³ solution of $H_2S_{12}O_6$ at 20 °C. Sulfurization time, h: *1* – 0.25, *2* – 0.5, *3* – 1.0, *4* – 2.0

Fig. 3. Change of the sulfur concentration in the PA films sulfurized in solutions of polythionates of different sulfurity with time at 50 °C. Sulfurization agent: *1* – $K_2S_3O_6$, *2* – $K_2S_4O_6$, *3* – $K_2S_5O_6$ (20 °C), *4* – $H_2S_{12}O_6$
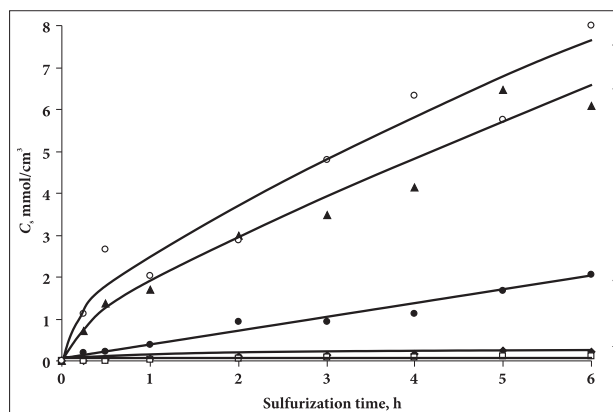
Fig. 4. Change of sulfur concentration in PA films sulfurized in $K_2S_5O_6$ and $H_2S_{12}O_6$ solutions at different temperatures. Sulfurization temperature, °C: *1* – 10 ($K_2S_5O_6$), *2* – 20 ($K_2S_5O_6$), *3* – 20 ($H_2S_{12}O_6$), *4* – 40 ($H_2S_{12}O_6$), *5* – 50 ($H_2S_{12}O_6$)

In order to form copper sulfide layers on the surface of the sulfurized PA films, they were treated with a Cu(II / I) salt solution. As a result of the redox reactions of polythionates anions, $S_nO_6^{2-}$, sorbed-on–diffused-into a polymer and sulfur formed during the decomposition of the sorbed polythionates with Cu(II / I) solutions, the layers of copper sulfides on the surface of PA were formed:

$$S_nO_6^{2-} + 2Cu^+ + 2H_2O \rightarrow Cu_2S + (n-3)S + 2H_2SO_4, \qquad (1)$$

$$1/nS_n + 2xCu^+ \rightarrow Cu_xS + xCu^{2+}. \qquad (2)$$
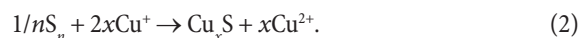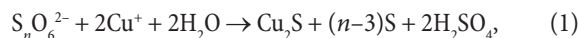
The concentration of copper (C_{Cu}) in PA, sulfurized in the $K_2S_5O_6$ solution (Fig. 5, curve 3), shows a gradual increase during all the sulfurization time, while using the solutions of $K_2S_3O_6$, $K_2S_4O_6$ and $H_2S_{12}O_6$ (Fig. 5, curves 1, 2 and 4), the values of C_{Cu} increase only up to a sulfurization time of 1–2 h, when the saturation of PA is reached.

The concentration of copper (C_{Cu}, mmol/cm³) in PA increases also with the increase in the polythionate solution temperature, and different copper concentrations in PA at each temperature are reached (Fig. 6). That is completely understandable since with the higher concentration of sulfur sorbed-on–diffused-in the PA a larger amount of copper ions may be involved in the reaction with the sulfur species.

Depending on the sulfurization time of PA films, brown or even black semi-conductive or electrically conductive copper sulfide layers were obtained. The values of electrical sheet resistance of the layers formed vary with the exposure time in the sulfurization solution in a large interval exibiting a minimum at the maximum duration of treatment (Table). For the Cu_xS layers formed after the exposure of the polymer to the solution of $K_2S_5O_6$ during 6 h, the value of electrical sheet resistance decreased from $4.5 \cdot 10^5$ to 104 $\Omega/\square$ – approximately by 5000 times. These values also depend on the degree of $S_nO_6^{2-}$ sulfurity (number of sulfur atoms n in the polythionate anion) and the temperature of the polythionate solution. The sheet resistance of the Cu_xS layers could be measured only after 2 h of sulfurization when the solution of $K_2S_3O_6$ or $K_2S_4O_6$ was used. Nevertheless, the values of electrical sheet resistance were still rather high – $(2.55–1.05) \cdot 10^3$ $\Omega/\square$. The data presented in Table show that the value of electrical resistance of the formed Cu_xS layer in all cases decreases significantly with the increase in the temperature of the PA sulfurization solution even reaching values of only a few $\Omega/\square$.

The overall decrease in the resistance value of Cu_xS layers with an increase in the sulfurization time and temperature of polythionate solution might be explained by the growth of the thickness of the layers (a continuous increase in the sulfur and copper concentration with an increase in the time and temperature of PA sulfurization (Figs. 3–6)).

The value of electrical sheet resistance of the copper sulfides layer greatly depends on the sulfur content (the number of sulfur atoms in the molecule) in the sulfurization agent. A significant difference – ca ~4000 times and ca ~20 times – was found in the electric resistance of the layers of Cu_xS on the PA formed using different precursors – $K_2S_5O_6$ or $H_2S_{12}O_6$ solutions at 20 °C after sulfurization for 0.25 h and 6 h, respectively, despite the fact that
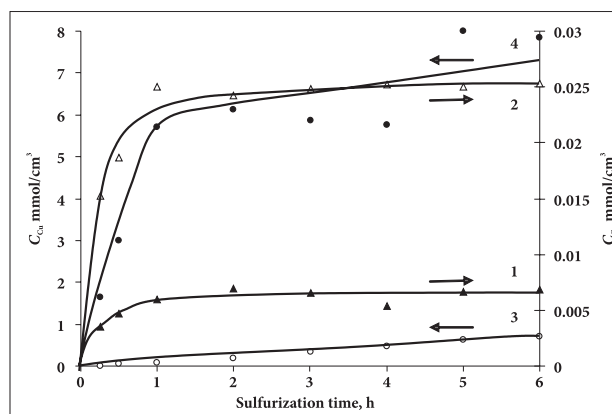

Fig. 5. Change of copper concentration in the PA films sulfurized in different precursor solutions with time at 50 °C. Sulfurization agent: 1 – $K_2S_3O_6$, 2 – $K_2S_4O_6$, 3 – $K_2S_5O_6$ (20 °C), 4 – $H_2S_{12}O_6$
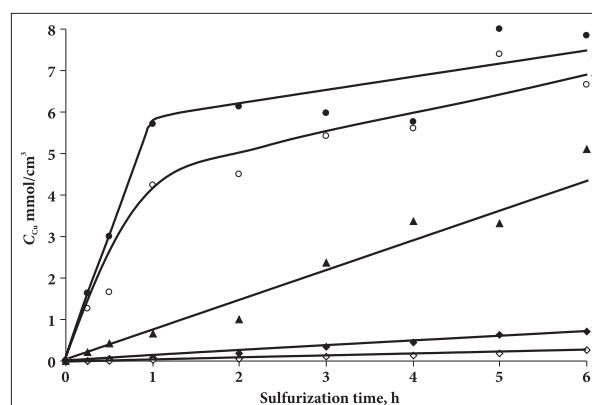

Fig. 6. Change of copper concentration in PA films sulfurized in $K_2S_5O_6$ and $H_2S_{12}O_6$ solutions at different temperatures. Sulfurization temperature, °C: 1 – 10 ($K_2S_5O_6$), 2 – 20 ($K_2S_5O_6$), 3 – 20 ($H_2S_{12}O_6$), 4 – 40 ($H_2S_{12}O_6$), 5 – 50 ($H_2S_{12}O_6$)
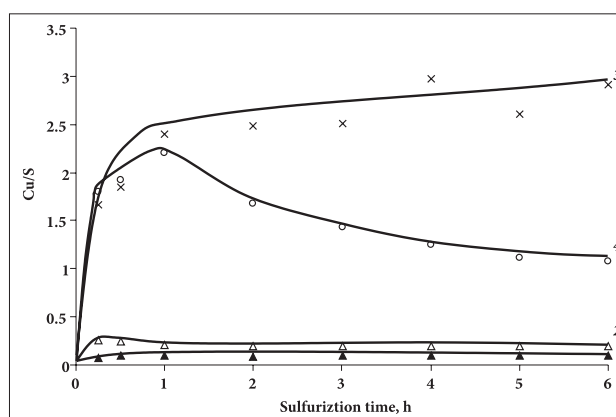
Fig. 7. Change of the molar ratio of Cu / S in the Cu_xS layers on PA with initial sulfurization time. Sulfurization agent: 1 – $K_2S_3O_6$ (50 °C), 2 – $K_2S_4O_6$ (50 °C), 3 – $K_2S_5O_6$ (20 °C), 4 – $H_2S_{12}O_6$ (40 °C)

the molar concentration of $H_2S_{12}O_6$ solution was by 50 times lower than that of $K_2S_5O_6$ solution. These data reveal that a significant contribution of the sulfur content in the precursor molecule lists, most probably due to the chemical composition of the latter, i. e. for three divalent sulfur atoms of in the $K_2S_5O_6$ molecule, there are ten divalent sulfur atoms in the $H_2S_{12}O_6$ molecule.

The electrical sheet resistance of the copper sulfide layers depends on their phase composition. As pointed out in [13], a change of the stoichiometry from Cu_2S to CuS leads to an extreme decrease in the electrical resistance (by a million of times).

It was found (Fig. 7) that the value of x in the Cu_xS layers formed may be very different. It can be explained by the mechanism of copper sulfide layer formation. The copper sulfide layer forms as a result of heterogeneous redox reactions between Cu^+, Cu^{2+}, $S_nO_6^{2-}$ and S (equations 1 and 2), and this layer separates the reacting particles. When this layer is compact, copper ions and polythionate react owing to their diffusion through the film of the reaction product – the film of Cu_xS. The transference of charge occurs because of good electrical conductivity of Cu_xS and it increases when x becomes smaller [13]. The Cu^+ and Cu^{2+} ions diffuse from the solution side through the copper sulfide layer formed in the surface matrix of the PA, and the polythionate ions and sulfur diffuse from the deeper layers of the PA through the sulfide film towards the surface of the polymer.

When $H_2S_{12}O_6$ solution was used for the PA sulfurization, a higher concentration of sulfur particles was reached in PA (Figs. 3 and 4). Therefore, a more compact Cu_xS layer forms and the copper ions more easily diffuse through it into the polymer depth and react with the sulfur containing particles. As a result, the concentration of copper in the PA increases too (Figs. 5 and 6). But when the solution of trithionate and tetrathionate is used for sulfurization, low concentrations of sulfur and later of copper are reached in the PA. In the case of $K_2S_5O_6$ used for the initial PA sulfurization, the sorbed pentationate ions completely react with the copper ions and the increase of in the Cu / S ratio values (the increase in x value in the Cu_xS layer) may be due the formation of others copper compounds (CuO, Cu_2O, $Cu(OH)_2$) adsorbed on the Cu_xS layer surface.

X-ray diffraction analysis gives rather an accurate identification of copper sulfides formed on the surface of PA. The results of this analysis are presented in Figs. 8 and 9.

The phase composition of the deposited film was established by comparing its X-ray images with those of known minerals. The chemical composition and crystal structure of the majority of Cu_xS minerals such as chalcocites – $Cu_{1.96}S$ (29–578) and Cu_2S (2–1289), anilites – Cu_7S_5 ($Cu_{1.4}S$) (72–617) and Cu_7S_4 ($Cu_{1.75}S$) (33–489), copper sulfide – CuS_2 (83–1619), djurleites – $Cu_{1.9375}S$ (71–1383) and $Cu_{31}S_{16}$ ($Cu_{1.9375}S$) (34–660), digenite – Cu_9S_5 ($Cu_{1.8}S$) (26–476), copper sulfide – CuS_2 (83–1619), yarrowite – Cu_9S_8 ($Cu_{1.125}S$) (36–379) and covelline – CuS (76–1725) was investigated [28–37]. The crystal structure of Cu_xS depends on the chemical composition and conditions of the synthesis. The composition of Cu_xS deposited by chemical methods has been little investigated.

Structural studies of the Cu_xS layers deposited by 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 the PA film itself. The intensities of its maximum at $\theta < 24°$ a few times exceeds the intensity of the copper sulfide maximum. Therefore, the area of $2\theta \geq 26.0°$ was investigated in detail.

The analysis of the X-ray diffraction patterns showed that after 30 min of sulfurization in the solution of $K_2S_5O_6$
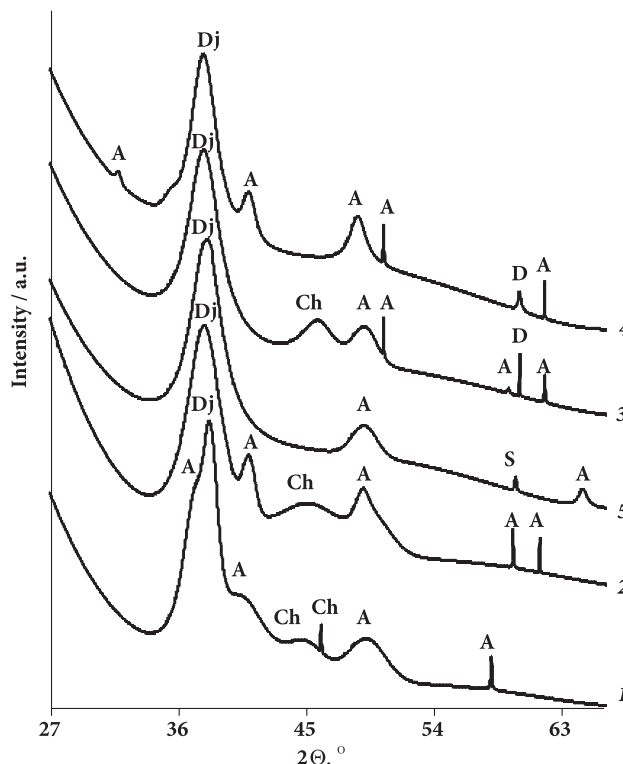

Fig. 8. X-ray diffraction patterns of Cu_xS layers on PA (peaks of djurleite, $Cu_{1.9375}S$, – Dj, chalcocite, $Cu_{1.96}S$, – Ch, anilite, Cu_7S_5, – A, digenite, Cu_9S_5, – D, copper sulfide, CuS_2, – S). PA was treated with the solution of $K_2S_5O_6$ at 10 and 20 °C. Sulfurization time, h: *1* – 0.5, *2* – 2, *3 – 4*, *4* – 6 (10 °C), *5* – 4 (10 °C)

at 20 °C, the peaks of orthorhombic anilite (Cu_7S_5 (72–617)) (at $2\theta = 37.2$, 40.76, 49.4, 58.06°), tetragonal chalcocite ($Cu_{1.96}S$ (29–578)) (at $2\theta = 45.02$, 46.04°) and monoclinic djurleite ($Cu_{1.9375}S$ (71–1383)) (at $2\theta = 38.2°$) are detected (Fig. 8 curve 1). When the period of treatment in $K_2S_5O_6$ solution is prolonged (4 h), a peak of a new phase of rhombohedral digenite (Cu_9S_5 (26–1619)) (at $2\theta = 60.1°$) in the sulfide layer on the PA appears. After 6 h of sulfurization, the orthorhombic anilite phase becomes dominant (Fig. 8, curve 4).

The phase composition of Cu_xS layers also changes with an increase in the temperature of $K_2S_5O_6$ solution used fo the PA sulfurization (Fig. 8, curves 5 and 3). The Cu_xS layer formed after the PA sulfurization for 4 h at a temperature of 10 °C (curve 5) is composed of three phases: monoclinic djurleite ($Cu_{1.9375}S$ (71–617), peak at $2\theta = 38.2°$), orthorhombic anilite, (Cu_7S_5 (72–1383), peaks at $2\theta = 49.4$ and 64,7°) and cubic copper sulfide (CuS_2 (83–1619), peak at $2\theta = 59.8°$). If the PA was initially sulfurized for the same period of time (4 h), but at a temperature of 20 °C, four phases of copper sulfides were identified in the Cu_xS layer (Fig. 8, curve 3) and more peaks of relatively conductive anilite ($Cu_{1.4}S$ (26–476)) and a peak of semi-conductive digenite (Cu_9S_5 (26–476)) appear in the X-ray diffraction patterns.

The analysis of the X-ray images showed that the monoclinic djurleite ($Cu_{31}S_{16}$) prevails (peaks at $2\theta = 30.30$, 31.10, 32.80, 33.56, 35.50, 36.40, 37.30, 38.56 and 40.80°) in the composition of the sulfide film on PA, sulfured at temperatures of 20 and 30 °C (Fig. 9, curves 1 and 2) in the solution of $H_2S_{12}O_6$ for 4 h. When the temperature of the treatment in the polythionic acid

Table. The sheet resistance ($\Omega/\square$) of Cu$_x$S layers on PA treated with a solution of pottasium polythionates or H$_2$S$_{12}$O$_6$ acid and then with Cu(II / I) salt solution

Sulfurization time, h	K$_2$S$_3$O$_6$	K$_2$S$_4$O$_6$	K$_2$S$_5$O$_6$		H$_2$S$_{12}$O$_6$		
	50 °C	50 °C	10 °C	20 °C	20 °C	40 °C	50 °C
0.25	–	–	–	–	125	41.2	11.7
0.50	–	–	–	$4.5 \cdot 10^5$	63.4	19.5	5.4
1.00	–	–	–	$2.2 \cdot 10^3$	53.4	3.2	1.8
2.00	$3.25 \cdot 10^6$	$2.06 \cdot 10^6$	$2.18 \cdot 10^4$	457	20.0	1.4	1.4
3.00	$4.17 \cdot 10^5$	$2.65 \cdot 10^5$	$1.63 \cdot 10^3$	227	29.2	0.6	1.5
4.00	$2.12 \cdot 10^4$	$1.10 \cdot 10^4$	$1.12 \cdot 10^3$	127	35.0	0.6	13.0*
5.00	$6.22 \cdot 10^3$	$3.28 \cdot 10^3$	580	122	27.0	0.5	3.4*
6.00	$2.55 \cdot 10^3$	$1.05 \cdot 10^3$	350	104	5.3	0.5	13.3*

*Low quality CuxS layer – partly separated.

solution is increased to up to 40 °C (Fig. 9, curve 3), changes in the film composition occur: the peaks of little conductive mono-clinic djurleite except one at $2\theta \sim 38°$ with a decreased intensity, disappear, but a new phase of conductive hexagonal yarrowite (Cu$_9$S$_8$ (36–379), peaks at $2\theta = 29.50$ and $32.14°$) appears: there remains only one peak of semi-conductive orthorhombic anilite (Cu$_7$S$_4$ (33–489), peak at $2\theta = 46.50$), but the peaks of conductive hexagonal covelline (CuS (76–1725), peaks at $2\theta = 27.70$ and 47.70, 52.40 and 58.90°) spring up. This is in not bad in respect of the results of chemical analysis (Fig. 7, Cu/S = ~1.20). After the four-hour treatment of the PA in the solution of H$_2$S$_{12}$O$_6$ at a temperature of 50 °C, orthorhombic anilite phase ($x = 1.75$, peak at $2\theta = 46.50°$) disappear, but the peaks of conductive hexagonal covelline ($x = 1.0$, at $2\theta = 47.82$, 52.40 and 58.90°) and yarrowite (Cu$_9$S$_8$ (36–379), peaks at $2\theta = 29.50$ and $32.14°$) become dominatant (Fig. 9, curve 4). Thus, the structural data
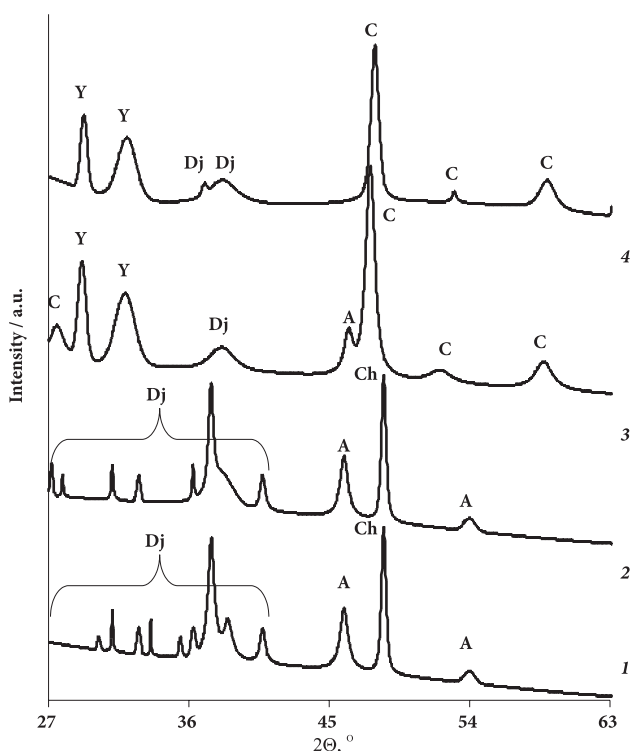

Fig. 9. X-ray diffraction patterns of Cu$_x$S layers on PA (peaks of djurleite, Cu$_{31}$S$_{16}$ – Dj, covelline, CuS, – C, anilite, Cu$_7$S$_4$, – A, chalcocite, Cu$_2$S, – Ch, yarrowite, Cu$_9$S$_8$, – Y). PA was treated for 4 h with the solution of H$_2$S$_{12}$O$_6$. Temperature, °C: *1* – 20, *2* – 30, *3* – 40, *4* – 50

agrees well with the results of the sheet resistance values of Cu$_x$S films on the PA (Table).

Thus, ten Cu$_x$S phases, CuS, Cu$_9$S$_8$, Cu$_9$S$_5$, Cu$_7$S$_5$, Cu$_7$S$_4$, Cu$_2$S, Cu$_{1.9375}$S, Cu$_{31}$S$_{16}$, Cu$_{1.96}$S and CuS$_2$ were identified by X-ray diffraction analysis in the copper sulfide layers on the surface of the PA. If the duration of the PA initial sulfurization is short (0.5–2.0 h), the not-conductive phases of Cu$_2$S, Cu$_{1.9375}$S, Cu$_{31}$S$_{16}$, Cu$_{1.96}$S and semi-conductive Cu$_7$S$_4$ or Cu$_7$S$_5$ do compose a layer of Cu$_x$S on the surface of PA. The phase composition of these layers approaches to the composition of Cu$_x$S with $x \sim 1$ (which corresponds to copper sulfide phases of very good electrical conductance) if the temperature of the initial polymer sulfurization in the solution of H$_2$S$_{12}$O$_6$ is increased.

The study of the electrically conductive Cu$_x$S layers has shown that sheet resistance greatly depends on the chemical and phase composition of the layer. It was also determined that the resistance is related to the phase composition of the copper sulfide film formed on the surface of the PA. The good conductivi-ty of sulfide films is obtained, when the composition of the layer differs significantly from Cu$_2$S and approaches that of CuS (PA sulfurization in the solution of H$_2$S$_{12}$O$_6$). The sheet resistance of the samples varies from 0.5 $\Omega/\square$ to ~ 3–$4 \cdot 10^6$ $\Omega/\square$ and depends greatly on the conditions of the PA interaction with the solutions of the precursors and on the sulfur content in the precursor mo-lecule.

The regularities established enable Cu$_x$S layers of desired conductivity to be formed on the PA. From these data it was concluded that the change of the conditions of polymer sulfurization leads to the formation of Cu$_x$S layers of different compositions and electrical conductance.

CONCLUSIONS

1. The sorption-on–diffusion-in of pentathionate, S$_5$O$_6^{2-}$, and dodecathionate, S$_{12}$O$_6^{2-}$, ions from water solutions of potassium pentathionate and dodecathionic acid, H$_2$S$_{12}$O$_6$, by polyamide 6 films has been studied by IR (400–1300 cm^{-1}), UV (200–400 nm) absorption spectra and chemical methods. The spectral data confirm that sulfur is sorbed by polyamide films in the form of polythionate ions.

2. The concentration of the sulfur sorbed-on–diffused-in by a polymer increases with the increasing temperature, duration of polymer sulfurization and sulfur content in the sulfurization precursor (polytionate anions) molecule.

3. The layers of copper sulfide (Cu$_x$S) form after the sulfurized polymer film treatment with a Cu(II / I) salt solution.

The concentration of copper in PA increases with an increase in the temperature, duration of polymer sulfurization and the number of sulfur atoms in the polythionate anion.

4. Electrical conductivity of the layers of Cu_xS formed on the surface of polyamide 6 films was studied. Variations of the electrical sheet resistance values due to the conditions of polymer sulfurization, the structure of the sulfur precursor and the chemical and phase composition of the layers formed were determined.

5. Electrical sheet resistance of the Cu_xS layers decreases with an increase of the temperature and duration of the initial stage – polymer sulfurization – and with an increase in the number of sulfur atoms in the polythionate anion used as a sulfur precursor.

6. The values of electrical sheet resistance of the copper sulfide layers formed using solutions of dodecathionic acid, $H_2S_{12}O_6$, are lower than those of the layers formed using solutions of potassium polytionates, especially solutions of trithionate and tetrathionate.

7. Ten Cu_xS phases – chalcocite (Cu_2S and $Cu_{1.96}S$), anilite (Cu_7S_4 and Cu_7S_5), djurleite ($Cu_{31}S_{16}$ and $Cu_{19375}S$), copper sulfide (CuS_2), digenite (Cu_9S_5), yarrowite (Cu_9S_8) and covelline (CuS) – in the copper sulfide layers on the polyamide film were determined by XRD analysis. The phase composition of the Cu_xS layers formed using a solution of $H_2S_{12}O_6$, showed higher concentrations of Cu_xS phases having lower electrical resistance and predominance of phases with low x values. This fact is consistent with the low electrical resistance of these layers.

References

1. J. I. Šataitė, M. A. Baranauskas, A. I. Žebrauskas, *Plast. Massy*, **6**, 53 (1989).

2. J. Cardoso, O. GomezDaza, L. Ixtlilco, M. T. S. Nair, P. K. Nair, *Semicond. Sci. Technol.* **16**, 123 (2001).

3. A. Galdikas, A. Mironas, V. Strazdienė, A. Šetkus, I. Ancutienė, V. Janickis, *Sens. Actuators. B*, **67**, 76 (2000).

4. A. Šetkus, A. Galdikas, A. Mironas, I. Šimkienė, I. Ancutienė, V. Janickis, S. Kačiulis, G. Mattogno, G. M. Ingo, *Thin Solid Films*, **391**, 275 (2001).

5. M. Baranauskas, A. Žebrauskas, Pat. USSR 1331291 (1986).

6. H. Hu, J. Campos, P. K. Nair, *J. Mater. Res.*, **11**, 739 (1996).

7. J. Johansson, J. Kostamo, M. Karppinen, L. Niinistö, *J. Mater. Chem.*, **12**, 1022 (2002).

8. B. Rezig, S. Duchemin, F. Guastavino, *Sol. Energy Mater.*, **2**, 53 (1979).

9. H. S. Randhava, R. F. Bunshah, D. G. Brock, B. M. Basol, O. M. Staffsudd, *Sol. Energy Mater.*, **6**, 445 (1982).

10. C. Nascu, I. Pop, V. Ionescu, E. Indrea, I. Bratu, *Mater. Lett.*, **32**, 73 (1997).

11. I. Grozdanov, *Semicond. Sci. Technol.*, **9**(6), 1234 (1994).

12. S. Lindroos, A. Arnold, M. Leskela, *Appl. Surf. Sci.*, **158**, 75 (2000).

13. A. Žebrauskas, *Chemical Technology*, **3**, 39 (1996).

14. K. M. Gadave, C. D. Lokhande, *Thin Solid Films*, **229**(1), 1 (1993).

15. R. Maciulevičius, V. Janickis, R. Ivanauskas, Pat. Lithuanian LT 4402 B (1998).

16. A. Kurtenacker, K. Matejka, *Z. Allgem. Anorg. Chem.*, **193**, 367 (1930).

17. F. Martin, L. Metz, *Z. Allgem. Anorg. Chem.*, **127**, 83 (1923).

18. A. Kurtenacker, W. Fluss, *Z. Allgem. Anorg. Chem.*, **210**, 125 (1933).

19. J. Janickis, J. Valančiūnas, V. Zelionkaitė, V. Janickis, S. Grevys, *Trans. Lithuanian Acad. Sci. Ser. B*, **88**, 83 (1975).

20. V. Janickis, R. Maciulevičius, R., Ivanauskas, I. Ancutienė, *Colloid Polym. Sci.*, **281**, 84 (2003).

21. I. Ancutienė, V. Janickis, V. Grevys, *Chemistry*, **2**, 3 (1997).

22. P. K. Norkus, G. S. Šimkevičiūtė, *Zh. Anal. Khim.*, **26**, 39 (1971).

23. Perkin–Elmer, *Analytical Methods for Atomic Absorption Spectrometry*, Perkin-Elmer 503, (1973).

24. V. I. Janickis, S. A. Gevys, *Zh. Neorg. Khim.*, **22**, 411 (1977).

25. L. Lorenz, R. Samuel, *Zh. Physik. Chem. B*, **14**, 219 (1931).

26. M. Schmidt,, T. Sand, *J. Inorg. Nucl. Chem.*, **26**, 1173 (1964).

27. V. Janickis, S. Grevys, *Chemical Technology*, **3**(41), 5 (2006).

28. I. F. Oftedal, *Zh. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **83**, 9 (1932).

29. R. Potter, Jr. Evans, *J. Research U. S. Geol. Surv.*, **4**, 205 (1976).

30. H. Evans, *Zh. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **150**, 299 (1979).

31. R. Goble, *Canad. Mineral.*, **18**, 511 (1980).

32. Jr. T. E. Howard, *Science*, **203**, 356 (1979)

33. Jr. H. E. King, C. T. Prewitt, *Am. Mineral.*, **64**, 1265 (1979).

34. K. Koto, N. Morimoto, *Acta Crysallogr., Sec. B*, **26**, 915 (1970)

35. A. Janosi, *Acta Crysallogr., Sec. B*, **17**, 311 (1964)

36. G. Dormay, J. D. H. Donnay, G. Kullerud, *Am. Mineral*, **43**, 228 (1958)

37. W. Kurz, *Zh. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **92**, 427 (1935).

Vitalijus Janickis, Remigijus Ivanauskas, Rūta Stokienė

LAIDŽIŲ ELEKTRAI VARIO SULFIDŲ SLUOKSNIŲ ANT POLIAMIDO 6 SUDARYMAS NAUDOJANT POLITIONATUS IR JŲ TYRIMAS

S a n t r a u k a

Tirta puslaidininkinių ir laidžių elektrai vario sulfidų, Cu_xS, sluoksnių susidarymas poliamido 6 (PA) paviršiuje sorbciniu-difuziniu metodu, naudojant kalio politionatų – tritionato, $K_2S_3O_6$, tetrationato, $K_2S_4O_6$, pentationato, $K_2S_5O_6$, ir dodekationato rūgšties, $H_2S_{12}O_6$, tirpalus. IR ir UV absorbcinių spektrų tyrimais parodyta, kad siera yra sorbuojama – difunduoja į PA plėveles politionatų anijonų pavidalu. Sieros koncentracija PA didėja, didėjant sierinimo trukmei, sieros atomų skaičiui politionato molekulėje ir sieros prekursoriaus tirpalo temperatūrai. Sieros koncentra-

cijos polimere, paveiktame dodekationato rūgšties tirpalu (iki ~8 mmol/cm³), gaunamos žymiai didesnės, nei plėvelėse, paveiktose žemųjų kalio polithionatų tirpalais (iki ~0,07−0,22 mmol/cm³). Vario sulfidų sluoksniai susidaro PA paviršiuje, kai sierintas polimeras apdorojamas Cu(II / I) druskų tirpalu. Polimero pradinio sierinimo sąlygos lemia vario koncentraciją PA, stecheometrinę Cu_xS sluoksnių sudėtį ir šių sluoksnių elektrinės kvadrato varžos reikšmę. Vario koncentracija PA didėja, didėjant sierinimo trukmei, sieros kiekiui polithionato anijone, prekursoriaus tirpalo temperatūrai, ir kinta nuo 0,0035 iki ~8 mmol/cm³. Dešimt Cu_xS fazių – *chalkocito* (Cu_2S ir $Cu_{1.96}S$), *anilito* (Cu_7S_4 ir Cu_7S_5), *djurleito* ($Cu_{31}S_{16}$ ir $Cu_{19375}S$), *vario sulfido* (CuS_2), *digenito* (Cu_9S_5), *jarovito* (Cu_9S_8) ir *kovelino* (CuS) – nustatyta vario sulfidų sluoksniuose rentgeno difrakcine analize. Sudarytų Cu_xS sluoksnių elektrinė kvadrato varža mažėja, didinant PA sierinimo trukmę ir temperatūrą, taip pat didėjant sieros atomų skaičiui polithionato anijone.