

Modification of polyamide 6 films by copper sulfide layers using dodecathionic acid

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It is shown that the water solution of dodecathionic acid, $H_2S_{12}O_6$, acts effectively as the sulfuration agent of polyamide 6. The study of the kinetics of sulfur sorption-diffusion into polyamide 6 at the temperatures of 20–50 °C showed that the values of sulfur concentration obtained in polyamide 6 (up to $\sim 7.5 \text{ mmol}\cdot\text{cm}^{-3}$) increase with the increase of the duration of treatment and the temperature of $H_2S_{12}O_6$ solution. Copper sulfide, Cu_xS , layers are formed on the surface of polyamide 6 film, if the sulfured polymer is treated with a solution of Cu(II/I) salt at temperature of 78 °C: the anionic particles $S_{12}O_6^{2-}$ containing sulfur atoms of low oxidation state react with the copper ions. The conditions the initial sulfuration of the polymer determine the concentration of copper and the composition of sulfide layer: the concentration of copper in the polyamide 6 film increases (up to $9.5 \text{ mmol}\cdot\text{cm}^{-3}$) with the increase of the duration and temperature of the polymer sulfuration; the stoichiometrical composition of Cu_xS layers on polyamide 6 formed according to the data of chemical analysis varies from $\sim CuS$ to $\sim Cu_2S$. The results of X-ray structural analysis confirmed the formation of copper sulfide layers on the surface of polyamide 6. The phase composition of layer changes depending on the conditions of the initial treatment in $H_2S_{12}O_6$ solution too. Four copper sulfide phases, *djurleite*, $Cu_{1.9375}S$, *covellite*, CuS , *yarrowite*, $Cu_{1.125}S$, and *anilite*, $Cu_{1.75}S$, were identified in the composition of the layers by X-ray diffraction but the maxima of the electrically conductive *covellite* and *yarrowite* phases predominate in the diffractograms of the modified polyamide 6 when this polymer was treated with the sulfuration solution during a longer period of time. The regularities determined enable the formation of electrically conductive ($125 \Omega/\square - \sim 1.0 \Omega/\square$) copper sulfide layers by the sorption-diffusion method using the solution of dodecathionic acid as a polyamide 6 sulfuration agent.

Key words: dodecathionic acid, polyamide 6, sorption-diffusion, copper sulfide layers

INTRODUCTION

For a couple of decades, the interest in the obtaining of binary chalcogenide thin layers has lead to a large amount of research. These thin layers have a number of applications in various fields, including coatings, interference filters, polarizers, narrow band filters, solar cells, photoconductors, IR detectors, waveguide coatings, magnetic and superconducting films, microelectronic devices, etc. [1]. Many metal sulfide compounds have excellent optical properties in the visible and IR regions of the spectrum [2].

Copper chalcogenide thin films have a number of applications in various devices, such as solar cells, super ionic conductors, photo-detectors, photothermal converters, electroconductive electrodes, microwave shielding coating, etc. [3–7]. The layers of copper chalcoge-

nide may be prepared by various methods [8]. However, its formation is more convenient by the use of the sorption methods.

Sorption-diffusion is a simple and promising method for obtaining binary chalcogenide layers. Hydrophilic and semi-hydrophilic polymers are capable of absorbing ions of various electrolytes from aqueous solutions [9]. Over the last decade, the sorption method used for the formation of copper sulfide, Cu_xS , and mixed copper sulfide-copper selenide, Cu_xS-Cu_ySe , layers on the surface of PA based on the initial treatment of a polymer with the solutions containing anions of polythionates, $S_nO_6^{2-}$, and selenopentathionate, $SeS_4O_6^{2-}$, has been under extensive investigation at the Department of Inorganic Chemistry of KTU. It was shown that during the treatment of the anions of polythionates, $(-O_3SS_x-SO_3^-)$, and selenopentathionate, $-O_3SS-Se-S-SO_3^-$, containing chains of divalent chalcogen atoms of low oxidation state [10], are sorbed by a polymer.

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Electrically conductive copper chalcogenide layers were formed on the surface of a polyamide film (PA) as a result of the reaction between polythionate ions and $\text{Cu}^+/\text{Cu}^{2+}$ ions present in a solution of copper(II/I) salt [8].

X-ray diffraction has been shown [8, 11] to be suitable for the determination of phase composition of copper chalcogenide layers on the surface of the PA formed. The lower polythionates including potassium pentathionate, $\text{K}_2\text{S}_5\text{O}_6 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, were used for PA sulfuration in the previous studies investigating the formation of Cu_xS layers on the PA surface [12–16]. However, the sulfur concentrations reached in the PA were rather low, and Cu_xS layers formed were thin, which caused some difficulties in determining their phase composition by X-ray diffraction methods.

A few experiments using a solution of dodecathionic acid, $\text{H}_2\text{S}_{12}\text{O}_6$, for the PA sulfuration showed that a significantly higher concentration of sorbed-diffused sulfur could be obtained in PA [12, 17], and the electrically conductive high quality copper sulfide films may be formed on the surface of PA.

The aim of this study was to obtain high quality layers of copper sulfide of various compositions on the surface of PA film using the solution of dodecathionic acid as a precursor, and to investigate their composition by chemical and X-ray diffraction methods.

EXPERIMENTAL

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

PA films were sulfured in a thermostatic vessel up to 6 h at a temperature of 20–50 °C using a continually stirred $0.002 \text{ mol}\cdot\text{dm}^{-3}$ solution of $\text{H}_2\text{S}_{12}\text{O}_6$ prepared by the method given in [18]. At certain time intervals, the PA film samples were removed from $\text{H}_2\text{S}_{12}\text{O}_6$ solution, rinsed with distilled water, dried with filtration paper, left over CaCl_2 for 24 h and then used in the further experiments and analysis.

Sulfur concentrations (C_s) in PA film samples were determined potentiometrically [19]. Firstly, a sample of the sulfured PA film was treated under heating with 10–15 ml of $10 \text{ mol}\cdot\text{dm}^{-3}$ 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 the potentiometric measurements, a pH-meter – pH-673 M millivoltmeter was used.

For the formation of Cu_xS films, the samples of the sulfured PA were treated with Cu(II/I) salt solution at 78 °C.

The Cu(II/I) salt solution was made from crystalline $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and a reducing agent hydroquinone as desc-

ribed in Refs. [20, 21]. It is a mixture of univalent and divalent copper salts where independent of the temperature there is $0.34 \text{ mol}\cdot\text{dm}^{-3}$ Cu(II) salt and $0.06 \text{ mol}\cdot\text{dm}^{-3}$ Cu(I) salt. After having been kept in $\text{H}_2\text{S}_{12}\text{O}_6$ solution, the sample was treated with the Cu(II/I) solution, then rinsed with distilled water, dried over CaCl_2 and used in the consequent experiments.

The concentration of copper in the PA sample was determined using a PerkinElmer 503 atomic absorption spectrometer [22].

The phase composition of the copper sulfide layers was investigated by means of X-ray diffraction using a DRON-6 diffractometer (radiation Cu K_α , voltage 30 kV). The X-ray diffractograms of PA samples with Cu_xS layers were treated using the Search Match, ConvX, Xfit programs to eliminate PA peaks.

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 a dodecathionic acid solution [23]. It was shown that the dodecathionate anions, $\text{S}_{12}\text{O}_6^{2-}$, are sorbed-diffused into PA films if they are treated with water solution ($0.002 \text{ mol}\cdot\text{dm}^{-3}$, 20–50 °C) of dodecathionic acid, $\text{H}_2\text{S}_{12}\text{O}_6$. The intensity of the absorption maxima in the spectra, as expected, increased with an increase in the duration of polymer treatment in the solution of dodecathionic acid.

The study of the kinetics of the sorption-diffusion of sulfur from the solution of dodecathionic acid into the PA film showed (Fig. 1) that the concentration of sulfur in the samples (C_s , $\text{mmol}\cdot\text{cm}^{-3}$) during the exposure in the solution of $\text{H}_2\text{S}_{12}\text{O}_6$ at 20–50 °C was increasing continu-

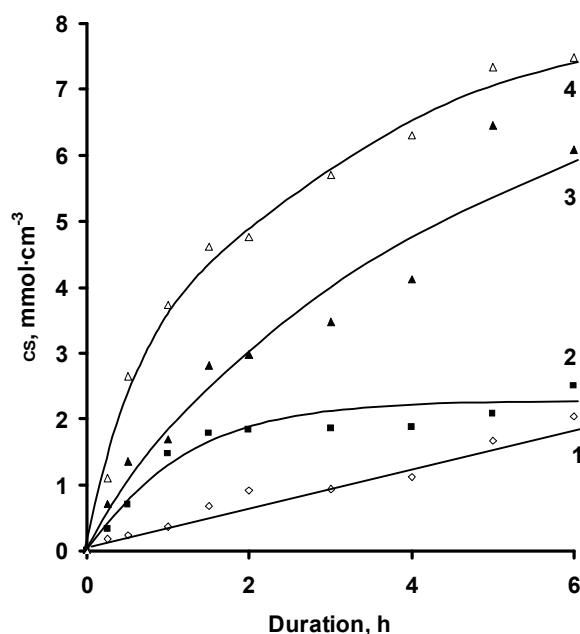


Fig. 1. Change of sulfur concentration in PA with time during its treatment with the dodecathionic acid solution at different temperatures. Temperature, °C: 1 – 20, 2 – 30, 3 – 40, 4 – 50

ously with time. Sulfur concentrations in the range of $\sim 0.3\text{--}7.5\text{ mmol}\cdot\text{cm}^{-3}$ might be obtained by varying the temperature of the solution of $\text{H}_2\text{S}_{12}\text{O}_6$. These results show also that a higher sulfur concentration was obtained at a higher temperature.

It was obvious that the values of sulfur concentration obtained in PA were significantly higher than those (at most $\sim 0.5\text{ mmol}\cdot\text{cm}^{-3}$) obtained in the studies in where the sorption of pentathionate ions from the $\text{K}_2\text{S}_5\text{O}_6$ solution of a significantly higher concentration ($0.1\text{ mol}\cdot\text{dm}^{-3}$) by PA films was studied [14, 16]. Thus, the obtained results provided the conditions for the formation of copper sulfide, Cu_xS , layers on the surface of the PA.

In order to form copper sulfide layers on the surface of the sulfured PA films, they were treated with the Cu(II/I) salt solution at $78\text{ }^\circ\text{C}$ for 10 min. It was found that the concentration of copper (C_{Cu} , $\text{mmol}\cdot\text{cm}^{-3}$) in the sulfured PA increased with the time of PA sulfuration in the $\text{H}_2\text{S}_{12}\text{O}_6$ solution, and a different concentration of copper in PA is reached at each temperature (Fig. 2). The general tendency is that the value of C_{Cu} increases with the increase in the temperature of $\text{H}_2\text{S}_{12}\text{O}_6$ solution from 20 to $50\text{ }^\circ\text{C}$. That is quite understandable since the

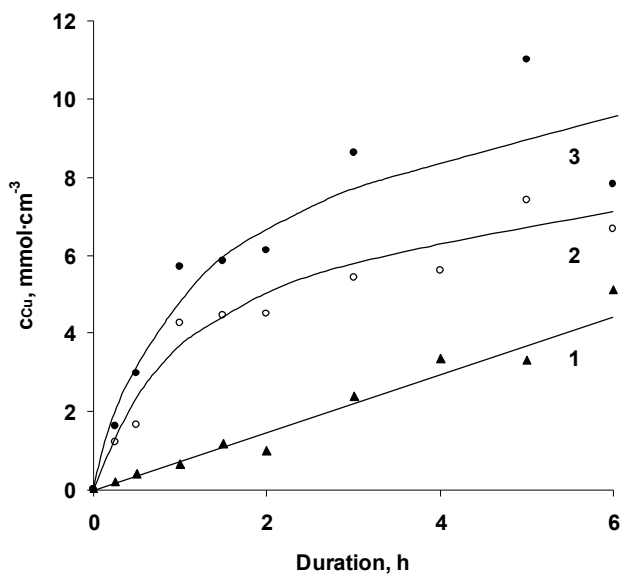


Fig. 2. Dependence of the concentration of copper in PA film on its initial sulfuration duration in the solution of dodecathionic acid at different temperatures. The temperature ($^\circ\text{C}$) of $\text{H}_2\text{S}_{12}\text{O}_6$ solution: 1 – 20, 2 – 40, 3 – 50

higher the concentration of sulfur is sorbed-diffused into the PA, the larger the amount of copper ions may be involved in the reaction with the sulfur species.

The molar Cu/S ratio in the copper sulfide layer on the PA surface was calculated from the data presented in Figs. 1 and 2. It was found that the Cu/S ratio (Table 1) at the sulfuration temperatures 20, 40 and $50\text{ }^\circ\text{C}$ with a few exceptions varied between ~ 1.0 and ~ 2.0 and did not depend much on the time of the initial PA sulfuration, except the gradual decrease of x value at the sulfuration temperature of $40\text{ }^\circ\text{C}$ when the chemical stoichiometry of the copper sulfide layer gradually approached CuS which corresponds to the composition of the best electrical conductivity [24]. As it is seen from the measurements of the sheet resistance values presented in Table 2, at a temperature of $40\text{ }^\circ\text{C}$ the electrical resistance reduces to very small values, even to the tenths of Ω/\square , with an increase of the initial PA treatment duration in $\text{H}_2\text{S}_{12}\text{O}_6$ solution.

More pronounced are the dependencies of Cu/S ratio values on the temperature of PA initial sulfuration. The value of x in most cases decreases with increasing the temperature of $\text{H}_2\text{S}_{12}\text{O}_6$ solution from 20 to $50\text{ }^\circ\text{C}$ (decrease of the concentration of copper in PA). Thus, in the temperature interval $20\text{--}50\text{ }^\circ\text{C}$, a reduction of the x value is observed – the concentration of copper reduces and the chemical stoichiometry of the Cu_xS layer approaches to that of CuS which should be reflected by the reduction of electrical resistance of the copper sulfide layer on the PA surface formed.

The data presented in Table 2 show that the value of electrical resistance of the formed copper sulfide layer in all cases decreases with the increase in the temperature of PA sulfuration solution reaching even the values of only a few Ω/\square .

Another tendency becomes clear while increasing the duration of PA sulfuration: the values of electrical resistance decrease with an increase of PA sulfuration time and especially for the samples sulfured at temperatures of 30, 40 and $50\text{ }^\circ\text{C}$. When $\text{H}_2\text{S}_{12}\text{O}_6$ solution at a temperature of $50\text{ }^\circ\text{C}$ was used for PA sulfuration, the most electrically conductive Cu_xS layers were obtained; as is seen from the data given in Table 1, the chemical stoichiometry of the Cu_xS layers formed after PA sulfuration at this temperature was closest to CuS and the copper sulfide layers of this composition were most electrically conductive [24].

Table 1. The molar ratios of Cu/S (the value of x , $S = 1$) in the Cu_xS layers in the surface of PA first treated in $\text{H}_2\text{S}_{12}\text{O}_6$ solution and then - in Cu(II/I) salt solution

Temperature of $\text{H}_2\text{S}_{12}\text{O}_6$ solution, $^\circ\text{C}$	Duration of sulfuration, h								
	0.25	0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0
20	1.05:1	1.68:1	1.60:1	1.76:1	1.76:1	1.91:1	2.24:1	2.29:1	2.61:1
40	1.78:1	1.64:1	1.75:1	1.71:1	1.60:1	1.43:1	1.29:1	1.21:1	1.15:1
50	1.20:1	1.13:1	1.25:1	1.37:1	1.45:1	1.48:1	1.41:1	1.33:1	1.27:1

Table 2. Sheet resistance (W/\square) of Cu_xS layers on PA first treated in $H_2S_{12}O_6$ solution and then in $Cu(II/I)$ salt solution

Temperature of $H_2S_{12}O_6$ solution, °C	Duration of PA sulfuration, h								
	0.25	0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0
20	125.1	63.4	53.4	32.2	20.0	29.2	35.0	27.0	5.3
30	51.0	35.1	16.6	14.9	5.9	1.8	4.1	7.1	20.7
40	41.2	19.5	3.2	2.0	1.4	0.6	0.6	0.5	0.5
50	11.7	5.4	1.8	1.5	1.4	1.5	13.0*	3.4*	13.3*

*Low quality Cu_xS layer - partly separated.

X-ray diffraction analysis gives a more accurate identification of copper sulfides formed on the surface of PA. The results of this analysis are presented in Figure 3.

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 *chalcocite* (Cu_2S), *anilite* ($Cu_{1.75}S$), *djurleite* ($Cu_{1.9375}S$), *yarrowite* ($Cu_{1.125}S$) and *covelline* (CuS) were investigated [25–32]. The crystal structure of Cu_xS depends on the chemical composition and conditions of synthesis. The composition of Cu_xS deposited by chemical methods has been scarcely investigated.

The structural studies of Cu_xS layers deposited by the sorption–diffusion method are limited by the polycrystallinity of the layers obtained, as well as by the existence of Cu_xS phases of various composition and structure, and by the crystallinity of the PA film itself. The intensity of its maximum at $\theta < 13^\circ$ exceeds the intensity of copper sulfide maximum a few times. Therefore, the area of $2\theta \geq 26.0^\circ$ was investigated in more detail.

While keeping the PA samples with sorptive polythionate anions in the copper salt solution at $78^\circ C$, Cu_xS layers of different composition were obtained. The X-ray diffraction patterns of the layers showed that the peaks of various copper sulfide phases rather than only of one copper sulfide phase existed in the layer (Fig. 3).

Analysis of the X-ray images showed that the monoclinic *djurleite* ($Cu_{1.9375}S$) prevailed (peaks at $2\theta = 27.40, 37.62, 38.50, 46.30, 48.68$ and 54.20°) in the composition of the sulfide film for PA, sulfured during the first 30 minutes (Fig. 3, curve 1) in the solution of $H_2S_{12}O_6$ at $40^\circ C$. When the period of the treatment in the polythionic acid solution was prolonged to 2 hours (Fig. 3, curve 2), the film composition started to change: the peaks of the non-conductive monoclinic *djurleite*, except the one at $2\theta \sim 38^\circ$ with a decreased intensity, disappear, but new phases of the chemical composition of sulfide film for PA conductive hexagonal *yarrowite* ($Cu_{1.125}S$, peaks at $2\theta = 29.20$ and 32.14°), semi-conductive orthorhombic *anilite* ($Cu_{1.75}S$, peaks at $2\theta = 46.50$ and 54.80°), conductive hexagonal *covelline* (CuS , peaks at $2\theta = 27.70$ and 47.70°) spring up; that is in accordance with the results of chemical analysis (Table 1, $Cu/S = 1.6$). After a four-hour treatment of PA in the solution of $H_2S_{21}O_6$ ortho-rhombic *anilite* phase ($x = 1.75$), the peak at $2\theta = 54.80^\circ$ disappear,

the intensity of the peak at $2\theta = 46.50^\circ$ decreases significantly, but the number of hexagonal *covelline* ($x = 1.0$) peaks (at $2\theta = 27.70, 47.70, 52.40$ and 58.90°) increases (Fig. 3, curve 3). Besides, the intensity of also conductive hexagonal *yarrowite* ($x = 1.125$) peaks at $2\theta = 29.50$ and 32.14° increases too. When the period of the treatment in the solution of $H_2S_{21}O_6$ was prolonged further (up to 6 h, Fig. 3, curve 4) the hexagonal *yarrowite* (peaks at $2\theta = 29.50$ and 32.14°) and hexagonal *covelline* (peaks at $2\theta = 27.70, 32.50, 47.70, 52.40$ and 58.90°) phases became dominating. That agrees well with the results of the chemical analysis (Table 1, $Cu/S = 1.15$) and the sheet resistance values (W/\square) of Cu_xS films on PA (Table 2).

This is also in accordance with the tendency of the reduction of Cu/S molar ratio 1.60–1.29–1.15 in the Cu_xS

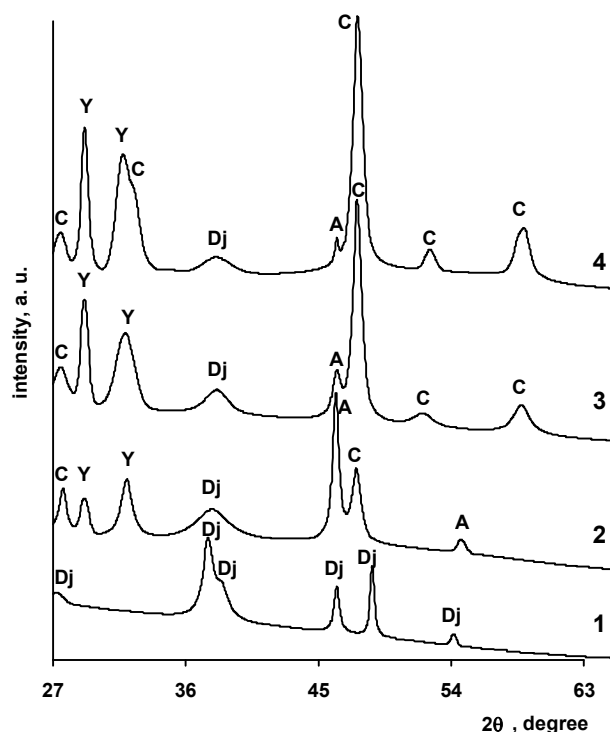


Fig. 3. X-ray diffraction patterns of copper sulfide layers in the surface of PA. PA initially treated with the solution of $H_2S_{12}O_6$ at $40^\circ C$ at different times and then with a $Cu(II/I)$ salt solution. Sulfuration time, h: 1 – 0.5, 2 – 2.0, 3 – 4.0, 4 – 6.0. A – orthorhombic *anilite*, Cu_7S_4 ($Cu_{1.75}S$), C – hexagonal *covelline*, CuS , Y – hexagonal *yarrowite*, Cu_9S_8 ($Cu_{1.125}S$), Dj – monoclinic *djurleite*, $Cu_{31}S_{16}$ ($Cu_{1.9375}S$)

layers on the PA formed (Table 1) with the prolongation of the initial PA sulfuration time 2.0–4.0–6.0 h.

Thus, four Cu_xS phases, CuS , $\text{Cu}_{1.125}\text{S}$, $\text{Cu}_{1.75}\text{S}$ and $\text{Cu}_{1.9375}\text{S}$ were identified by X-ray diffraction analysis in the copper sulfide layers on the surface of PA. If the duration of PA's initial sulfuration is short (0.5–2.0 h), the non-conductive phase of $\text{Cu}_{1.9375}\text{S}$ and semi-conductive phase of $\text{Cu}_{1.75}\text{S}$ together with the conductive phases of CuS and $\text{Cu}_{1.125}\text{S}$ do compose the layer of Cu_xS on the surface of PA. The phase composition of these layers approaches to the composition of Cu_xS with $x \sim 1$ (which corresponds to the copper sulfide phases of very good electrical conductance, Table 2) if the duration of the initial polymer sulfuration is increased.

It was concluded from the data that changing the conditions of PA sulfuration leads to the formation of a different composition of electrically conductive copper sulfide layers.

CONCLUSIONS

1. The water solution of dodecathionic acid acts effectively as the sulfuration agent of polyamide 6: the concentration of the sorbed-diffused sulfur increases (up to $\sim 7.5 \text{ mmol}\cdot\text{cm}^{-3}$) with the increase of the duration of treatment (up to 6 h) and temperature (up to $50 \text{ }^\circ\text{C}$) of a $\text{H}_2\text{S}_{12}\text{O}_6$ solution.

2. The electrically conductive layers of copper sulfide, Cu_xS , forms in the surface of polyamide 6 film when the polymer is sulfured in dodecathionic acid solution and later treated with a solution of Cu(II/I) salt at a temperature of $78 \text{ }^\circ\text{C}$: the anionic particles $\text{S}_{12}\text{O}_6^{2-}$ containing sulfur atoms of low oxidation state react with the copper ions.

3. The conditions of the polymer sulfuration determine the concentration of copper and the composition of sulfide layer: the concentration of copper in the polyamide 6 film increases (up to $\sim 9.5 \text{ mmol}\cdot\text{cm}^{-3}$) with the increase of the duration and temperature of the polymer sulfuration; the stoichiometrical composition of Cu_xS layers on polyamide 6 formed according to the data of chemical analysis varies from $\sim\text{Cu}_{1.0}\text{S}$ to $\sim\text{Cu}_{2.0}\text{S}$.

4. A number of copper sulfide phases, CuS , $\text{Cu}_{1.125}\text{S}$, $\text{Cu}_{1.75}\text{S}$ and $\text{Cu}_{1.9375}\text{S}$, have been identified in the layers by X-ray diffraction. The maxima of the conductive CuS and $\text{Cu}_{1.125}\text{S}$ phases predominate in the diffractograms of Cu_xS layers if the duration of the initial polymer sulfuration is increased.

5. The determined regularities enable the formation of electrically conductive ($125 \text{ } \Omega/\square - \sim 1.0 \text{ } \Omega/\square$) copper sulfide layers by sorption–diffusion method using the solution of dodecathionic acid as a polyamide 6 sulfuration agent.

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**POLIAMIDO 6 PLĖVELIŲ MODIFIKAVIMAS VARIO
SULFIDŲ SLUOKSNAIS NAUDOJANT
DODEKATIONATO RŪGŠTĮ**

S a n t r a u k a

Parodyta, kad dodekationato rūgštis, $H_2S_{12}O_6$, vandeninis tirpalas veikia efektyviai, kaip poliamido 6 sierinimo agentas. Sieros sorbcijos–difuzijos į poliamidą 6 kinetikos tyrimas parodė, kad sieros koncentracija poliamido plėvelėje didėja (iki ~ 7.5 $mmol\cdot cm^{-3}$), didėjant $H_2S_{12}O_6$ tirpalo temperatūrai ir plėvelės išlaikymo tirpale trukmei. Vario sulfidų, Cu_xS , sluoksniai susidaro poliamido paviršiuje, kuomet sierintas polimeras apdorojamas $Cu(II/I)$ druskos tirpalu $78^\circ C$ temperatūroje: anijoninės dalelės $S_{12}O_6^{2-}$, turinčios žemo oksidacijos laipsnio sieros ato-

mų, reaguoja su vario jonais. Polimero pradinio sierinimo sąlygos lemia susidarančio sulfidinio sluoksnio sudėtį: vario koncentracija poliamido plėvelėje (iki $\sim 9,5$ $mmol\cdot cm^{-3}$) didėja, didėjant sierinimo trukmei ir tirpalo temperatūrai; stochiometrinė sudarytų Cu_xS sluoksnių sudėtis, cheminės analizės duomenimis, kinta nuo $\sim Cu_{1,0}S$ iki $\sim Cu_{2,0}S$. Rentgenostruktūrinė sluoksnių analizė patvirtino, kad jie yra sudaryti iš vario sulfidų. Fazinė vario sulfidų sluoksnių sudėtis taip pat priklauso nuo pradinio poliamido sierinimo $H_2S_{12}O_6$ tirpale sąlygų. Keturios vario sulfidų fazės, CuS , $Cu_{1,125}S$, $Cu_{1,75}S$ ir $Cu_{1,9375}S$, identifiкуotos sluoksnių sudėtyje; CuS ir $Cu_{1,125}S$ fazių maksimumai vyrauja rentgeno difraktogramose, kuomet polimero pradinio įsierinimo trukmė padidinama iki 4–6 h. Nustatyti dėsniumai leidžia, naudojant dodekationato rūgštis tirpalus kaip chalkogeninimo agentą, sorbciniu-difuziniu metodu poliamido 6 paviršiuje sudaryti laidžius elektrai ($125- \sim 1,0$ Ω/\square) vario sulfidų sluoksnius.