

Comparison of Telluropentathionates as Precursors for the Formation of Semiconductive Copper Chalcogenide Layers

Skirma ŽALENKIENĖ, Vitalijus JANICKIS *

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

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The processes of obtaining semiconductive and electrically conductive layers of mixed copper chalcogenides $\text{Cu}_x\text{S}-\text{Cu}_y\text{Te}$ by the sorption-diffusion method on polyamide 6 using solutions of potassium and sodium telluropentathionates, $\text{K}_2\text{TeS}_4\text{O}_6$ and $\text{Na}_2\text{TeS}_4\text{O}_6$, and of telluropentathionic acid, $\text{H}_2\text{TeS}_4\text{O}_6$, as precursors of chalcogens (Te and S) are compared. The concentration of sorbed chalcogens increases with the increase of the duration of treatment and concentration of precursor solution in cases of all precursors used. Copper chalcogenide layers are formed on the surface of polyamide after the treatment of chalcogenized polymer with Cu(II/I) salt solution. The concentration of copper in the layer increases with the increase of initial chalcogenization duration. XRD spectra of PA films treated for different time with solutions of telluropentathionates and then with Cu(II/I) salt solution showed the maxima characteristic of the copper sulfide and copper telluride phases, tellurium sulfide TeS_7 and of elemental tellurium. Six copper sulfide phases, *chalcocite*, Cu_2S , *djurleite*, $\text{Cu}_{1.9375}\text{S}$, *anilite*, $\text{Cu}_{1.75}\text{S}$, *digenite*, $\text{Cu}_{1.80}\text{S}$, *villamanite*, CuS_2 , *covelite*, CuS , three copper telluride phases Cu_4Te_3 , $\text{Cu}_{1.85}\text{Te}$, *rickardite*, Cu_7Te_5 , and tellurium sulfide TeS_7 were identified in the layers formed using $(0.025-0.1) \text{ mol/dm}^3$ solutions of potassium telluropentathionate. Three phases of copper tellurides, *tetragonal* $\text{Cu}_{3.18}\text{Te}_2$, *hexagonal* Cu_2Te and *orthorhombic vulcanite*, CuTe , were found in the films on PA surface formed using sodium telluropentathionate solutions, among them four phases of copper sulfides such as *orthorhombic anilite*, Cu_7S_4 , *monoclinic djurleite*, $\text{Cu}_{1.9375}\text{S}$, *geerite*, $\text{Cu}_{1.6}\text{S}$, *orthorhombic digenite*, $\text{Cu}_{1.8}\text{S}$, and tellurium sulfide TeS_7 ; the Cu-Te-S layers formed using $\text{H}_2\text{TeS}_4\text{O}_6$ solution have binary phases such as *chalcocite*, Cu_2S , *djurleite*, $\text{Cu}_{1.9375}\text{S}$, *anilite*, $\text{Cu}_{1.75}\text{S}$, *digenite*, $\text{Cu}_{1.80}\text{S}$, copper telluride $\text{Cu}_{1.85}\text{Te}$, elemental tellurium and tellurium sulfide TeS_7 . The phase composition of layers changes depending on the nature of telluropentathionate used for PA chalcogenization and conditions of treatment in precursor solutions. The value of electrical sheet resistance of chalcogenide layers formed using $(0.05-0.1) \text{ mol/dm}^3$ $\text{K}_2\text{TeS}_4\text{O}_6$ solutions varies from $256 \text{ k}\Omega/\text{cm}^2$ to $1.6 \text{ k}\Omega/\text{cm}^2$ and of those formed using $\text{Na}_2\text{TeS}_4\text{O}_6$ solutions – from $3.14 \cdot 10^3 \text{ k}\Omega/\text{cm}^2$ to $\sim 1.34 \text{ k}\Omega/\text{cm}^2$; the use of $\text{H}_2\text{TeS}_4\text{O}_6$ as precursor leads to the formation of electrically conductive $\text{Cu}_x\text{S}-\text{Cu}_y\text{Te}$ layers with electrical resistance in the range of $(4.34 \cdot 10^3 - 1.2) \text{ k}\Omega/\text{cm}^2$; the sheet resistance depends on the conditions of PA interaction with initial chalcogenization solutions.

Keywords: telluropentathionates, polyamide, copper chalcogenide layers, composition, conductivity.

INTRODUCTION

Copper chalcogenides, Cu_xY ($\text{Y} = \text{S}, \text{Se}, \text{Te}$) and their thin layers have unique properties and potential applications in numerous fields [1–5]. Thin layers of these compounds have a number of applications in various devices such as solar cells, super ionic conductors, photo-detectors, photothermal conversion, electroconductive electrodes, microwave shielding coating, gas sensors [6–10].

Over the last decade, a sorption-diffusion method for the formation of copper chalcogenide layers on the surface of polyamide 6 (PA) based on the initial treatment of a polymer with the solutions containing anions of polythionic compounds, $\text{S}_n\text{O}_6^{2-}$, $\text{SeS}_n\text{O}_6^{2-}$ ($n = 2, 4$), $\text{TeS}_4\text{O}_6^{2-}$, has been under investigation [11–20]: the polythionic compounds anions, among them the anions of potassium and sodium telluropentathionates, $\text{K}_2\text{TeS}_4\text{O}_6$, $\text{Na}_2\text{TeS}_4\text{O}_6$, or of telluropentathionic acid, $\text{H}_2\text{TeS}_4\text{O}_6$, are sorbed by a polymer. After chalcogenized polymer being treated with the solution of copper(II/I) salts, mixed copper sulfide-copper telluride, $\text{Cu}_x\text{S}-\text{Cu}_y\text{Te}$, layers on the surface of a polymer were formed.

The aim of present work was to compare the results received by us during studies of processes of interaction of the chalcogenization agents – potassium and sodium telluropentathionates, $\text{K}_2\text{TeS}_4\text{O}_6$, $\text{Na}_2\text{TeS}_4\text{O}_6$, and telluropentathionic acid, $\text{H}_2\text{TeS}_4\text{O}_6$, – with the semi-hydrophilic polymeric material – polyamide 6 film (PA) and also of chalcogenized polymer treatment with a copper(II/I) salts solution on the formation of $\text{Cu}_x\text{S}-\text{Cu}_y\text{Te}$ layers.

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 (15×70) 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.

Distilled water, chemically and analytically pure reagents were used to produce solutions. Potassium telluropentathionate, $\text{K}_2\text{TeS}_4\text{O}_6 \cdot 1.5\text{H}_2\text{O}$, and sodium telluropentathionate, $\text{Na}_2\text{TeS}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, were prepared and chemically analysed according to procedures published in [21, 22]. Telluropentathionic acid, $\text{H}_2\text{TeS}_4\text{O}_6$, was isolated from its barium salt, $\text{BaTeS}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$, in the reaction of BaSO_4 precipitation with H_2SO_4 solution [21–23].

The PA films were chalcogenized in a thermostatic vessel up to 24 h at a temperature of 20°C using a 0.025,

*Corresponding author. Tel.: +370-37-451464; fax.: +370-37-300152.
E-mail address: vitalijus.janickis@ktu.lt (V. Janickis)

0.05 and 0.1 mol/dm³ solutions of Na₂TeS₄O₆ and of K₂TeS₄O₆ in 0.2 mol/dm³ HCl (pH ~1.5). Other PA films were chalcogenized in a thermostatic vessel up to 121 h at the temperature of 20 °C using a (0.05–0.1) mol/dm³ solution of H₂TeS₄O₆. At certain time intervals, the PA film samples were removed from solutions, rinsed with distilled water, dried with filter paper, left over CaCl₂ for 24 h and then used in further experiments and analysis.

Samples of chalcogenized PA were treated with a solution of Cu(II/I) salts at 78 °C for 10 min. A solution of Cu(II/I) salts was made from crystalline CuSO₄·5H₂O and hydroquinone as described in [24]. It is a mixture of Cu salts, containing 0.34 mol/dm³ of Cu(II) and 0.06 mol/dm³ of Cu(I) [25].

The concentration of tellurium and copper in a PA sample was determined using a Perkin-Elmer 503 atomic absorption spectrometer [26]. The concentration of sulfur in PA, in the form of sulfates, was determined turbidimetrically [27, 28]. The intensity of the transmitted light as a function of the concentration of the dispersed phase of BaSO₄ was measured photometrically with a KFK-4 photoelectric colorimeter (Russia) at λ = 400 nm.

The phase composition of copper chalcogenides layers on PA surface was investigated by X-ray diffraction employing techniques with a DRON-6 diffractometer equipped with a special device for beam limitation at low and medium diffraction angles using graphite-monochromatized Cu-K_α radiation source (λ = 1.54178 Å). The XRD patterns were recorded with a step of 0.05° from 2θ = 30° to 70°. X-ray diffractograms of PA samples with layers of copper chalcogenides were treated using Search Match, ConvX, Xfit and Excel programs to eliminate PA maxima.

The resistance of Cu_xS–Cu_yTe layers with different composition to the constant current was measured with an MS8205F constant current numerical measuring device with special electrodes. The electrodes were produced from two nickel-plated copper plates. The plates were fixed with 1 cm spacing and the dielectric material was placed between them. The concept of sheet resistance is used to characterize thin deposited layers.

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 potassium telluropentathionate [15] and the telluropentathionic acid [17] solutions. These investigations have confirmed that telluropentathionate anions sorb-diffuse into PA treated with the solutions of telluropentathionates. The concentration of sulfur (Figs. 1, 2) and tellurium (Figs. 3, 4) in PA sorbed from Na₂TeS₄O₆, K₂TeS₄O₆ and H₂TeS₄O₆ solutions increases with increasing the duration of treatment and the concentration of precursor solution. It rather significantly also depends on the nature of telluropentathionate and the telluropentathionates, according decrease of their effectiveness of PA sulfurization are in the order Na₂TeS₄O₆ > H₂TeS₄O₆ > K₂TeS₄O₆; for example, the concentrations of sulfur after PA sulfurization in 0.05 mol/dm³ solutions during 12 h were ~85, 60, 30 μmol/cm³, respectively. In case of use of 0.1 mol/dm³

solutions of telluropentathionates for sulfurization, difference between the effectiveness of sulfurization by K₂TeS₄O₆ and H₂TeS₄O₆ solutions is not very significant but the effectiveness of Na₂TeS₄O₆ solution is obvious (Fig. 2): in the latter case PA saturation with sulfur-containing particles at the experimental conditions is not reached even after 24 h. Using the solutions of K₂TeS₄O₆ and H₂TeS₄O₆ the saturation of PA with sulfur-containing particles is reached after 8 h–12 h from the beginning of the process (Figs. 1 and 2).

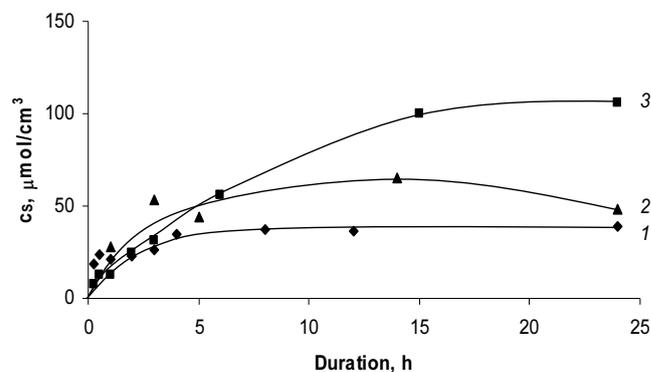


Fig. 1. Changes of sulfur concentration in the PA films chalcogenized in the 0.05 mol/dm³ solutions of telluropentathionic compounds with time at 20 °C. PA chalcogenization precursor: 1 – K₂TeS₄O₆; 2 – H₂TeS₄O₆; 3 – Na₂TeS₄O₆

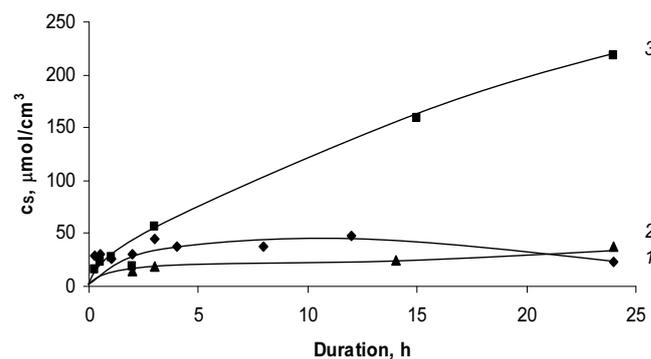


Fig. 2. Changes of sulfur concentration in the PA films chalcogenized in the 0.1 mol/dm³ solutions of telluropentathionic compounds with time at 20 °C. PA chalcogenization precursor: 1 – K₂TeS₄O₆; 2 – H₂TeS₄O₆; 3 – Na₂TeS₄O₆

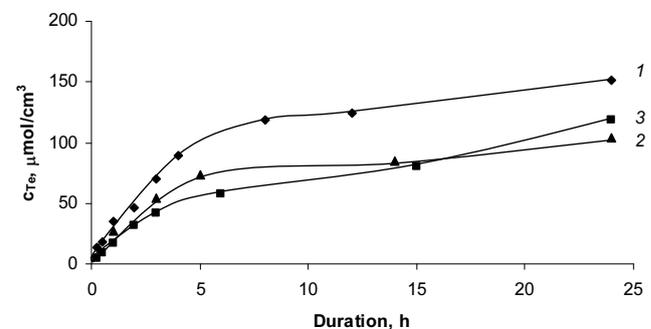


Fig. 3. Changes of tellurium concentration in the PA films chalcogenized in the 0.05 mol/dm³ solutions of telluropentathionic compounds with time at 20 °C. PA chalcogenization precursor: 1 – K₂TeS₄O₆; 2 – H₂TeS₄O₆; 3 – Na₂TeS₄O₆

As it is mentioned above, the concentration of precursor solution has a noticeable influence on sorption-diffusion of sulfur-containing particles into PA. For example, the concentrations of sulfur after PA chalcogenization during 12 h in 0.05 mol/dm³ solutions of K₂TeS₄O₆ and Na₂TeS₄O₆ are ~30 μmol/cm³ and 85 μmol/cm³, respectively; sulfur concentrations after PA chalcogenization in 0.1 mol/dm³ solutions of the same precursors are ~50 μmol/cm³ and 140 μmol/cm³.

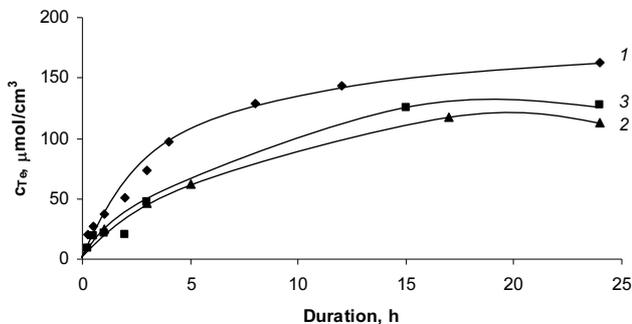
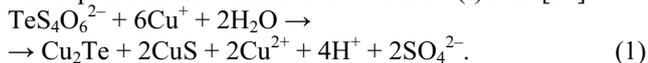


Fig. 4. Changes of tellurium concentration in the PA films chalcogenized in the 0.1 mol/dm³ solutions of telluropentathionic compounds with time at 20 °C. PA chalcogenization precursor: 1 – K₂TeS₄O₆; 2 – H₂TeS₄O₆; 3 – Na₂TeS₄O₆

Telluropentathionates, according decrease of their effectiveness of PA tellurization are in the order K₂TeS₄O₆ > Na₂TeS₄O₆ > H₂TeS₄O₆; for example, the concentrations of tellurium after PA chalcogenization in 0.1 mol/dm³ solutions during 12 h are ~140, 110, 90 μmol/cm³, respectively (Fig. 4). In case of use of 0.05 mol/dm³ solutions of telluropentathionates for chalcogenization, difference between the effectiveness of chalcogenization by H₂TeS₄O₆ and Na₂TeS₄O₆ solutions is not very significant but the effectiveness of K₂TeS₄O₆ solution is higher (Fig. 3).

The concentration of precursor solution has a noticeable influence on sorption-diffusion of tellurium-containing particles into PA. For example, the concentrations of tellurium after PA chalcogenization during 12 h in 0.05 mol/dm³ solutions of H₂TeS₄O₆, Na₂TeS₄O₆ and K₂TeS₄O₆ are ~75 μmol/cm³ and 120 μmol/cm³, respectively (Fig. 3); tellurium concentrations after PA chalcogenization in 0.1 mol/dm³ solutions of the same precursors are ~105 μmol/cm³ and 140 μmol/cm³.

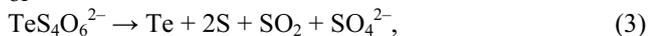
In order to form copper chalcogenide layers on the surface of chalcogenized PA films, they were treated with the Cu(II/I) salts solution. Into PA sorb-diffuse telluropentathionate anions react with Cu (I) ions [28]:



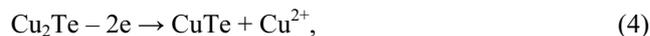
The telluropentathionate ion at a higher temperature (78 °C) decomposes: [22]



or



therefore copper ions may react not only with TeS₄O₆²⁻ ions according to the equation (1), but also with the products of this ion decomposition. The following processes are possible: [28]:



As a result of the redox reactions of telluropentathionates anions, TeS₄O₆²⁻, sorbed-diffused into a polymer, formed during the decomposition of sorbed telluropentathionates with Cu(II/I) solutions, the layers of copper sulfides–copper tellurides on the surface of PA were formed.

The concentration of copper in PA increased with increasing in duration of polymer initial treatment in precursor solution and the concentration of this solution (Fig. 5). Thus, copper concentration in Cu_xS–Cu_yTe layers increases with increasing the concentration of chalcogens in the polymer. This is quite understandable since with a higher concentration of sulfur and tellurium sorbed-diffused into PA, a larger amount of Cu⁺ and Cu²⁺ ions may be involved in the reaction with the sulfur–tellurium species.

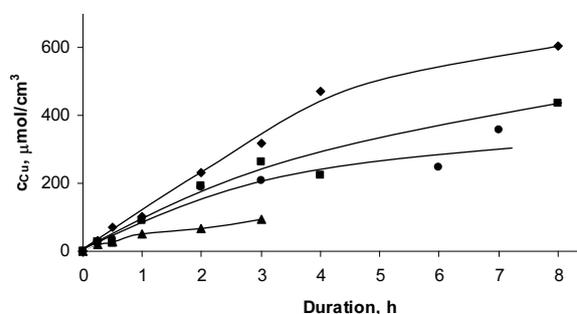


Fig. 5. Changes of copper concentration in the PA films chalcogenized in the solutions of sodium and potassium telluropentathionates with time at 20 °C. PA chalcogenization precursor (its concentration): 1 – Na₂TeS₄O₆ (0.1 mol/dm³); 2 – Na₂TeS₄O₆ (0.05 mol/dm³); 3 – K₂TeS₄O₆ (0.05 mol/dm³); 4 – K₂TeS₄O₆ (0.1 mol/dm³)

The highest concentration of copper after initial chalcogenization in 0.05 mol/dm³ Na₂TeS₄O₆ solution at a temperature of 20 °C is ~300 μmol/cm³, but the lower value of copper concentration was obtained using the solution of sodium telluropentathionate of twice higher concentration. That may be explained by decrease of Na₂TeS₄O₆ stability in solution with the increase in solution concentration: the largest copper concentration in our experiments was obtained using 0.025 mol/dm³ Na₂TeS₄O₆ solution at a temperature of 20 °C and 24 h of chalcogenization (~740 μmol/cm³) [16].

In the table the values of electrical sheet resistance of copper chalcogenide layers, formed using 0.1 mol/dm³ solutions of telluropentathionates at the temperature of 20 °C and at different duration of a polymer chalcogenization are presented. The data presented show that the electrical sheet resistance of Cu_xS–Cu_yTe layers in general decreases with increasing the duration of the polymer initial treatment in chalcogenization solution, i.e. with increasing tellurium, sulfur and consequently – copper concentrations in the layer. At a short duration of PA initial chalcogenization (up to ~2 h), the telluropentathionates, according decrease of electrical resistance of formed

Table. The values of electrical sheet resistance ($\text{k}\Omega/\text{cm}^2$) of copper chalcogenide layers on PA surface formed using solutions of telluropentathionates at a temperature of 20°C at different duration of polymer chalcogenization

Exposure time, h	Concentration of $\text{H}_2\text{TeS}_4\text{O}_6$ solution, mol/dm^3		Concentration of $\text{K}_2\text{TeS}_4\text{O}_6$ solution, mol/dm^3		Concentration of $\text{Na}_2\text{TeS}_4\text{O}_6$ solution, mol/dm^3	
	0.05	0.1	0.05	0.1	0.05	0.1
0.25	–	–	–	–	$2.3 \cdot 10^3$	–
0.5	–	–	–	256.4	$3.1 \cdot 10^3$	$1.2 \cdot 10^3$
1	480	$1.8 \cdot 10^3$	23.3	41.4	–	360.4
2	–	$4.3 \cdot 10^3$	13.2	9.9	17.4	623.9
3	$1.8 \cdot 10^3$	690.5	10.3	9.9	3.3	5.3
4	–	$6.4 \cdot 10^3$	4.4	5.0	–	–
5	415	–				
8	–	–	2.1	1.6	–	1.3
10	14.2	–				
12	4.5	1.2	1.7	1.6	–	–
17	–	1.2				
24	2.8	1.3	2.2	2.9	–	2.1
121	1.8	0.8				

copper chalcogenide layers are in the order $\text{H}_2\text{TeS}_4\text{O}_6 > \text{Na}_2\text{TeS}_4\text{O}_6 > \text{K}_2\text{TeS}_4\text{O}_6$. For example, the values of electrical resistance of $\text{Cu}_x\text{S}-\text{Cu}_y\text{Te}$ layers, formed after PA chalcogenization in $0.1 \text{ mol}/\text{dm}^3$ solutions of $\text{H}_2\text{TeS}_4\text{O}_6$, $\text{Na}_2\text{TeS}_4\text{O}_6$ and $\text{K}_2\text{TeS}_4\text{O}_6$ during 1 h are $1.8 \cdot 10^3$, 360.4 and $41.4 \text{ k}\Omega/\text{cm}^2$, respectively; the values of electrical resistance of $\text{Cu}_x\text{S}-\text{Cu}_y\text{Te}$ layers, formed after PA chalcogenization in $0.1 \text{ mol}/\text{dm}^3$ solutions of telluropentathionates during 2 h are $4.34 \cdot 10^3$, 623.9 and $9.9 \text{ k}\Omega/\text{cm}^2$, respectively. At a longer duration of chalcogenization the values of electrical sheet resistance in cases of all telluropentathionates were more-less similar. The electrical resistance decrease of $\text{Cu}_x\text{S}-\text{Cu}_y\text{Te}$ layers with increasing the duration of polymer chalcogenization may be explained by the increased concentrations of sorbed-diffused tellurium and sulfur and thus of the amount of copper that reacted in the stage of “copperizing”.

The phase composition of copper sulfide–copper telluride layers formed using the solutions of telluropentathionates was studied by the X-ray diffraction method. This method enables to identify the copper chalcogenides formed on the surface of PA, since the chemical composition and the crystal structure of most Cu_xS and Cu_yTe minerals has been studied [29–35]. The chemical composition and crystal structure of the majority of Cu_xS and Cu_yTe minerals such as *chalcocite* – Cu_2S , *djurleite* – $\text{Cu}_{1.95}\text{S}$, Cu_4Te_3 , $\text{Cu}_{1.80}\text{Te}$, $\text{Cu}_{1.85}\text{Te}$ and *vulcanite*, CuTe were investigated [29–35]. The crystal structure of Cu_xS and Cu_yTe depends on the chemical composition and conditions of synthesis.

Structural studies of the copper chalcogenide layers formed by sorption method are limited by polycrystallinity of films obtained, as well as by the coexistence of Cu_xS and Cu_yTe phases with various compositions and structures, and by the crystallinity of PA. The intensities of PA peaks at $\theta < 13^\circ$ exceed intensity of copper sulfide

peaks few times. Therefore the area of $2\theta \geq 26.0^\circ$ was investigated in more detail. The results of our study are presented in the Fig. 6. The XRD patterns of the copper chalcogenides confirm the formation of highly crystalline Cu_xS_y and Cu_xTe_y phases. The large width of some Cu_xS_y and Cu_xTe_y peaks indicates the presence of various compositions sulfide and telluride phases, as well as their reduced degree of crystalline perfection (Fig. 6). The phase composition of layers changes depending on the conditions of the polymer initial treatment in a solution of particular telluropentathionate. Six copper sulfide phases, *chalcocite*, Cu_2S , *djurleite*, $\text{Cu}_{1.9375}\text{S}$, *anilite*, $\text{Cu}_{1.75}\text{S}$, *digenite*, $\text{Cu}_{1.80}\text{S}$, *villamanite*, CuS_2 , *covelite*, CuS , three copper telluride phases Cu_4Te_3 , $\text{Cu}_{1.85}\text{Te}$, *rickardite*, Cu_7Te_5 , and tellurium sulfide TeS_7 were identified in the layers formed using $0.025 \text{ mol}/\text{dm}^3 - 0.1 \text{ mol}/\text{dm}^3$ potassium telluropentathionate solutions (Fig. 6, curves 1–3). The spectra of PA films chalcogenized in $\text{K}_2\text{TeS}_4\text{O}_6$ solution of different concentration show (Fig. 6, curves 1–3), that the maxima of phases of good electrical conductance CuS_2 , CuS , Cu_7Te_5 and Cu_4Te_3 already dominate when the chalcogenization solution of $0.05 \text{ mol}\cdot\text{l}^{-1}$ concentration was used for the formation of copper chalcogenides layer. That is in accordance with the data of electrical sheet resistance measurements of these films: its value decreases ($7.7-2.1-1.6 \text{ k}\Omega/\text{cm}^2$) with increase in concentration of chalcogenization solution.

Three phases of copper tellurides, *tetragonal* $\text{Cu}_{3.18}\text{Te}_2$, *hexagonal* Cu_2Te and *orthorhombic* vulcanite, CuTe , were found in films on the PA surface, formed using sodium telluropentathionate solutions, among them four phases of copper sulfides such as *orthorhombic anilite*, Cu_7S_4 , *monoclinic djurleite*, $\text{Cu}_{1.9375}\text{S}$, *geerite*, $\text{Cu}_{1.6}\text{S}$, *orthorhombic digenite*, $\text{Cu}_{1.8}\text{S}$, and tellurium sulfide TeS_7 (Fig. 6, curves 4, 5).

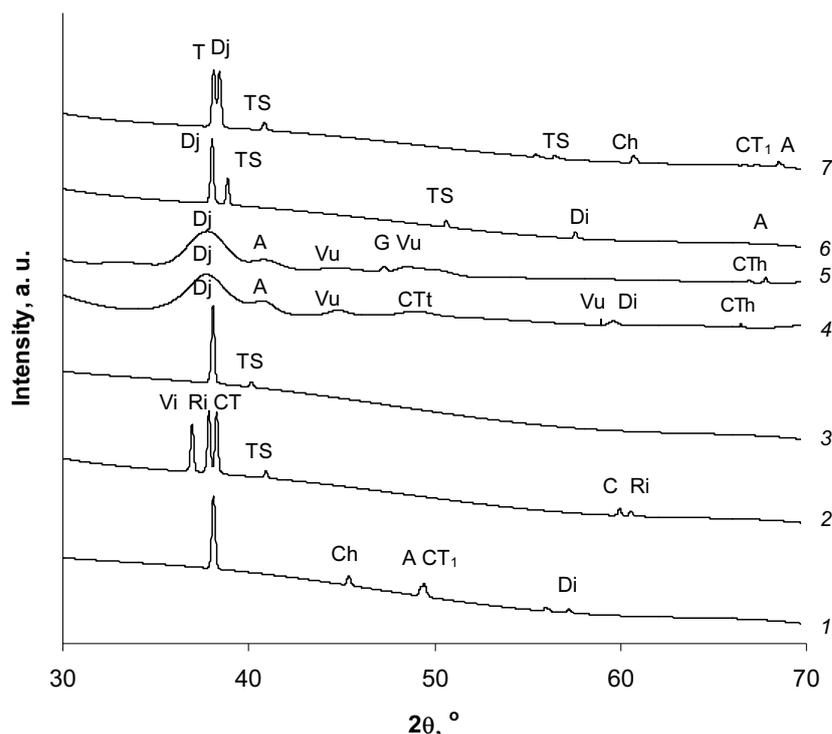


Fig. 6. XRD spectra of PA films first treated with the solutions of telluropentathionates at 20 °C and then with Cu(II/I) salts solution. PA chalcogenization precursor, duration of chalcogenization and concentration of its solution, mol/dm³: 1 – K₂TeS₄O₆, 8 h, 0.025; 2 – K₂TeS₄O₆, 8 h, 0.05; 3 – K₂TeS₄O₆, 8 h, 0.1; 4 – Na₂TeS₄O₆, 3 h, 0.05; 5 – Na₂TeS₄O₆, 3 h, 0.1; 6 – H₂TeS₄O₆, 5 h, 0.05; 7 – H₂TeS₄O₆, 24 h, 0.05. A – *anilite*, Cu_{1.75}S; Dj – *djurleite*, Cu_{1.9375}S; Di – *digenite*, Cu_{1.80}S; G – *geerite*, Cu_{1.6}S; Ch – *chalcocite*, Cu₂S; Vi – *villamanite*, CuS₂; C – *covellite*, CuS; CT – Cu₄Te₃; CT₁ – Cu_{1.85}Te; TS – tellurium sulfide, TeS₇; CTh – hexagonal copper telluride Cu₂Te; CTt – tetragonal copper telluride Cu_{3.18}Te₂; Vu – *vulcanite*, CuTe; Ri – *rickardite*, Cu₇Te₅; T – tellurium

Four copper sulfide phases, *chalcocite*, Cu₂S, *djurleite*, Cu_{1.9375}S, *anilite*, Cu_{1.75}S, *digenite*, Cu_{1.80}S, one copper telluride phase Cu_{1.85}Te, elemental tellurium and tellurium sulfide TeS₇ were identified in the layers formed using 0.05 mol/dm³ solutions of telluropentathionic acid (Fig. 6, curves 6, 7).

Thus XRD results confirmed the formation of copper chalcogenide layers on the surface of PA using various precursors of the polymer chalcogenization. The composition of Cu_xS–Cu_yTe layers depends on the conditions of this process. The phase composition of layers changes depending on the nature of telluropentathionate used for PA chalcogenization and conditions of treatment in precursor' solutions.

CONCLUSIONS

1. Solutions of different forms of telluropentathionates – potassium and sodium telluropentathionates, K₂TeS₄O₆, Na₂TeS₄O₆, and telluropentathionic acid, H₂TeS₄O₆, as precursors of sulfur and tellurium for the formation of semiconductive and electrically conductive layers of copper chalcogenides – mixed copper sulfide–copper telluride, Cu_xS–Cu_yTe, on the surface of semihydrophilic polymer – polyamide 6 (PA) were compared. The concentrations of sorbed tellurium and sulfur increase with the increase of the duration of treatment and concentration of

telluropentathionates solutions. Telluropentathionates according decrease of their effectiveness of PA sulfurization are in the order Na₂TeS₄O₆ > H₂TeS₄O₆ > K₂TeS₄O₆ and according decrease of their effectiveness of PA tellurization – in the order K₂TeS₄O₆ > Na₂TeS₄O₆ > H₂TeS₄O₆.

2. The layers of copper sulfide–copper telluride of various composition are formed on the surface of PA after treatment of chalcogenized polymer with the water solution of Cu(II/I) salts. The concentration of copper in copper chalcogenides layers is dependent on the concentration of sulfur and tellurium in PA, i. e. on conditions of initial polymer chalcogenization.
3. The chemical and phase composition of copper chalcogenide layers depends on the nature of telluropentathionate used for PA chalcogenization and conditions of the chalcogenization process. XRD results confirmed the formation of mixed copper sulfide–copper telluride layers on the surface of PA.
4. Copper sulfide phases, *chalcocite*, Cu₂S, *djurleite*, Cu_{1.9375}S, *anilite*, Cu_{1.75}S, *digenite*, Cu_{1.80}S, *villamanite*, CuS₂, *covellite*, CuS, copper telluride phases Cu₄Te₃, Cu_{1.85}Te, *rickardite*, Cu₇Te₅, and tellurium sulfide TeS₇ were identified in the layers formed using 0.025 mol/dm³–0.1 mol/dm³ potassium telluropentathionate solutions. The phases of copper tellurides, *tetragonal* Cu_{3.18}Te₂, *hexagonal* Cu₂Te and *orthorhombic vulcanite*, CuTe, were found in the films

on PA surface, formed using sodium telluropentathionate solutions, among them phases of copper sulfides such as *orthorhombic anilite*, Cu_7S_4 , *monoclinic djurleite*, $\text{Cu}_{1.9375}\text{S}$, *geerite*, $\text{Cu}_{1.6}\text{S}$, *orthorhombic digenite*, $\text{Cu}_{1.8}\text{S}$, and tellurium sulfide TeS_7 ; the Cu–Te–S layers formed using $\text{H}_2\text{TeS}_4\text{O}_6$ solution have binary phases such as *chalcocite*, Cu_2S , *djurleite*, $\text{Cu}_{1.9375}\text{S}$, *anilite*, $\text{Cu}_{1.75}\text{S}$, *digenite*, $\text{Cu}_{1.80}\text{S}$, copper telluride phase $\text{Cu}_{1.85}\text{Te}$, elemental tellurium and tellurium sulfide TeS_7 . The phase composition of layers changes depending on the nature of telluropentathionate used for PA chalcogenization and conditions of treatment in precursor' solutions.

- The electrical sheet resistance of the samples, formed using 0.05–0.1 solutions of telluropentathionates, in the case of $\text{K}_2\text{TeS}_4\text{O}_6$ varies from $256 \text{ k}\Omega/\text{cm}^2$ to $1.6 \text{ k}\Omega/\text{cm}^2$, of those, formed using $\text{Na}_2\text{TeS}_4\text{O}_6$ – $3.14 \cdot 10^2 \text{ k}\Omega/\text{cm}^2$ – $1.34 \text{ k}\Omega/\text{cm}^2$ and of those, formed using $\text{H}_2\text{TeS}_4\text{O}_6$ – $4.34 \cdot 10^3 \text{ k}\Omega/\text{cm}^2$ – $1.2 \text{ k}\Omega/\text{cm}^2$.
- The results obtained and the regularities established point on the role of the nature of telluropentathionate on the formation of Cu_xS – Cu_yTe layers on the surface of PA of determined composition and electrical conductivity.

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