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Formation and study of mixed copper sulfide–copper telluride layers on the surface of polyamide 6

Review Article

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Abstract: The layers of mixed copper chalcogenides, Cu_xS–Cu_yTe, were formed on the surface of polyamide using solutions of potassium and sodium telluropentathionates, $K_2TeS_4O_6$ and $Na_2TeS_4O_6$, respectively, and of telluropentathionic acid, $H_2TeS_4O_6$, as precursors of chalcogens. The concentration of sorbed chalcogens increased with the increasing time of the treatment, concentration and temperature of precursor solution. Cu_xS–Cu_yTe 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 chalcogenization duration, concentration and the temperature of chalcogenization solution. In the surface of Cu_xS–Cu_yTe layers various copper, sulfur, tellurium and oxygen compounds (Cu_2S, CuS, S_8, Cu_xS, Cu_yTe, $Cu(OH)_2$ and TeO_2) were present. Chalcogenides were the major components in the layer. Chalcogenide phases – digenite, $Cu_{1.8}S$, djurleite, $Cu_{1.9375}S$, anilite, Cu_7S_4, geerite, CuS_2, chalcocite, Cu_2S, tetragonal $Cu_{3.18}Te_2$, $Cu_{2.72}Te$, hexagonal Cu_2Te, Cu_4Te_3, $Cu_{1.80}Te$, $Cu_{1.85}Te_2$, and orthorhombic vulcanite, CuTe were identified in the layers by X-ray diffraction. Electrical sheet resistance of Cu_xS–Cu_yTe layers vary from ~ 1.0 kΩ cm^{-2} to 4×10^3 kΩ cm^{-2}. It is concluded that the formation of chalcogenide layers proceeds in the form of islands which grow into larger agglomerates. Use of the gathered data enables design and formation of the Cu_xS–Cu_yTe layers with desired conductivities.

Keywords: *Polyamide • Telluropentathionates • Sorption • Copper chalcogenides layers*

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1. Introduction

Semiconductors based on compounds from I–VI and II–VI elemental groups play an important role as optoelectronic, luminescent, and lasing materials. Through the successful synthesis of I–VI compound semiconductors, a wide range of mechanical and optoelectronic applications may be possible for these materials, which is why the continued study of such semiconductors is of greatest importance [1].

Copper sulfide, copper selenide and copper telluride belong to chalcogenides (binary compounds of I–VI group elements and chalcogens). These compounds are of great interest owing it to their unique properties, variation in stoichiometric composition, nanocrystal morphology, complex structure, valence states, and their potential applications in numerous fields [2–6]. Copper chalcogenides are semiconductors with thermoelectric properties and ionic conductivity. They have attracted considerable interest because of their wide range of applications in various fields of science and technology, for example in various devices such as solar cells, optical data storage, and others [7,8].

Thin layers of copper chalcogenide Cu_xY (Y = S, Se, Te) have a number of applications in devices such as solar cells, super ionic conductors, photo-detectors, photothermal converters, electroconductive electrodes, microwave shielding coating and gas sensors [9–13].

Various methods were employed to form copper chalcogenide layers on dielectrics and polymers. These methods include vacuum evaporation, activated reactive evaporation, spray pyrolysis, electroless deposition, successive ionic layer adsorption and reaction (SILAR), and chemical bath deposition [14–20].

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Over the last decade, a sorption-diffusion method for the formation of thin copper chalcogenide layers on the surface of polyamide 6 (PA) has been under extensive investigation [21–28]. It was based on the initial treatment of a polymer with the solutions containing anions of polythionates, $S_nO_6^{2-}$, and selenopolythionates, $SeS_nO_6^{2-}$ (n = 2, 4). The compounds sorbed by a polymer include the polythionic compound anions containing chains of divalent chalcogen atoms of low oxidation state [29–31], the polythionates, $^-O_3S{-}S_x{-}SO_3^-$, selenotrithionate, $^-O_3S{-}Se{-}SO_3^-$, and selenopentathionate, $^-O_3S{-}S{-}Se{-}S{-}SO_3^-$. After chalcogenized polymer is being treated with the solution of copper(II/I) salt, copper sulfide, Cu_xS, [21–26], copper selenide, Cu_xSe, [27] or mixed copper sulfide–copper selenide, $Cu_xS{-}Cu_ySe$, [28] layers on the surface of a polymer are formed.

In our previous research, it was shown that using solutions of potassium and sodium telluropentathionates, $K_2TeS_4O_6$, $Na_2TeS_4O_6$, or of telluropentathionic acid, $H_2TeS_4O_6$, as chalcogenization agents of PA, semiconducting and electrically conductive mixed copper sulfide–copper telluride, $Cu_xS{-}Cu_yTe$, allows formation of layers on the surface of this polymer [32–41]. By infrared radiation (IR) and ultra violet (UV) absorption spectroscopy determined that the telluropentathionate ions, $^-O_3S{-}S{-}Te{-}S{-}SO_3^-$, were sorbed by a polymer from the solutions of telluropentathionates [33,36,38,40]. After chalcogenized polymer is treated with the solution of copper(II/I) salt, the mixed copper sulfide–copper telluride, $Cu_xS{-}Cu_yTe$, layers on the surface of a polymer form. Phase composition of these layers can be studied using X-ray diffraction (XRD) analysis [36,38,40] and X-ray photoelectron spectroscopy (XPS) [35].

The aim of the present work is to review the results of systematic studies received from processes of interaction of the chalcogenization agents, potassium and sodium telluropentathionates, $K_2TeS_4O_6$, $Na_2TeS_4O_6$, and telluropentathionic acid, $H_2TeS_4O_6$, with the semi-hydrophylic polymeric material – polyamide 6 film (PA). Moreover, the effects of chalcogenized polymer treatment with a copper(II/I) salts solution on the formation of mixed copper sulfide–copper telluride, $Cu_xS{-}Cu_yTe$, layers were studied and discussed [32–41]. Chemical and phase composition of the $Cu_xS{-}Cu_yTe$ layers were studied by the methods of atomic absorption spectroscopy (AAS), XRD and XPS. Atomic force microscopy (AFM) was used to characterize surface morphology of the copper chalcogenide layers [41].

2. Experimental Procedure

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 a 15×70 mm film 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 the solutions.

Potassium telluropentathionate ($K_2TeS_4O_6{\bullet}1.5H_2O$) and sodium telluropentathionate ($Na_2TeS_4O_6{\bullet}2H_2O$) were prepared and chemically analysed according to procedures published by Foss [42,43]. The prepared salts were kept in dark and in a desiccator over concentrated sulfuric acid.

Telluropentathionic acid was isolated from its barium salt, $BaTeS_4O_6{\bullet}3H_2O$, in the reaction of $BaSO_4$ precipitation with H_2SO_4 solution [42–44].

The chalcogenization solution of potassium telluropentathionate was prepared at a concentration of 0.025–0.05–0.1 mol dm^{-3} in 0.2 mol dm^{-3} HCl solution (pH ~1.5). The chalcogenization solution of sodium telluropentathionate had a concentration of 0.01–0.025–0.05–0.1–0.5 mol dm^{-3} in 0.2 mol dm^{-3} HCl solution (pH ~1.5). The concentration of monotelluropentathionic acid solution was 0.01–0.05–0.1 mol dm^{-3}.

PA film samples were chalcogenized in $K_2TeS_4O_6$ solutions at a temperature of 1, 10 and 20°C and in $Na_2TeS_4O_6$ and $H_2TeS_4O_6$ at 20°C.

Samples of chalcogenized PA were treated with dissolved Cu(II/I) salts at 78°C for 10 min. A solution of Cu(II/I) salts was made from crystalline $CuSO_4{\bullet}5H_2O$ and hydroquinone as described in [45]. It is a mixture of Cu salts, containing 0.34 mol dm^{-3} of Cu(II) and 0.06 mol dm^{-3} of Cu(I) [46]. After treatment with Cu(II/I) salts, PA samples were rinsed with distilled water, dried over anhydrous $CaCl_2$ and used in further experiments.

The amount of tellurium and copper in a PA sample was determined using a Perkin-Elmer 503 atomic absorption spectrometer [47]. Before analysis, samples of PA with tellurium and sulfur containing thin films had been mineralized. Samples were treated with concentrated HNO_3 to destroy PA and to oxidize tellurium and sulfur compounds to tellurites and sulfates. Heating with concentrated hydrochloric acid removed the excess of nitric acid. For the conditions described above, the sensitivity of the AAS method was 1 μg mL^{-1} tellurium for the 1 % absorption.

The concentration of sulfur in PA, in the form of sulfates, was determined turbidimetrically [48,49]. Sulfate ion in the range of concentration

1−15 mg dm^{-3} may be easily determined by utilizing the reaction with barium chloride in a solution slightly acidified with hydrochloric acid to give barium sulfate. The intensity of the transmitted light as a function of the concentration of the dispersed phase of $BaSO_4$ was measured photometrically with a KFK-4 photoelectric colorimeter (Russia) at λ = 400 nm. The standard deviation was in the range of concentrations 5−10 mg dm^{-3} was 8%.

UV spectra were recorded on a Spectronic^R Genesis 8 UV/Visible spectrophotometer with a compensation of PA absorption in the range of 200–800 nm. IR spectra were recorded with a Perkin Elmer FTIR Spectrum GX spectrophotometer by averaging 64 scans with 0.3 cm^{-1} resolution at room temperature for each sample, in the range 400–1400 cm^{-1}.

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

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

XPS spectra of copper chalcogenides layers were recorded with an ESCALAB MKII spectrometer (VG Scientific, radiation Mg K_α 1253.6 eV, output 300 W). Vacuum in the analysing chamber was kept at a level of 1.33×10^{-8} Pa, the distribution of elements in the depth was determined by sputtering with an Ar^+ gun and the ion energy of about 1.0 keV. The samples were etched in a preparation chamber in vacuum at 9.3×10^{-3} Pa, the current of 20 μA, and the etching rate of 1 nm/30 s. The maximum accuracy of the method was ± 0.1 at.%. To investigate the layers obtained by the XPS method, the photoelectron spectra of Cu $2p_{3/2}$, S 2p and Te $3d_{5/2}$ were recorded. Empirical sensitivity factors for these elements were taken from the literature [50], and the spectra obtained were compared with the standard ones [51].

The morphology of the surface of Cu_xS–Cu_yTe layers, the quantitative microscopy of the roughness of formed layers on the surface of PA were studied with the NT-206 AFM, in the contact regime with high resolution probes and the force constant k = 3 N m^{-1}. The characteristics of the AFM included the maximum scan field area from 10×10 up to 30×30 microns, the measurement matrix up to 512×512 points and more, the maximum range of measured heights 4 microns, lateral resolution 2 nm, and the vertical resolution 0.1–0.2 nm. Lateral force microscopy studies were used to obtain edge-enhanced images and to image variations in the surface friction that could arise from inhomogeneity in surface material.

3. Results and Discussion

Modification of PA film by creating on its surface layers of copper sulfides–copper tellurides was performed in two stages. The first stage relied on the interaction of PA film with a solution of telluropentathionic compound ($K_2TeS_4O_6$, $Na_2TeS_4O_6$, $H_2TeS_4O_6$) where the chalcogenization of PA film occurs, i.e. anions containing tellurium and sulfur atoms sorb-diffuse into the matrix of the PA surface.

In the second stage, the chalcogenized PA film is treated with Cu(II/I) salts water solution. The copper ions react with the sorbed by PA film telluropentathionate ions and Cu_xS–Cu_yTe layers form on the polymer surface.

3.1. Formation of copper telluride–copper sulfide layers on polyamide 6 surface using potassium telluropentathionate solutions. Analysis of PA films chalcogenized in $K_2TeS_4O_6$ solution by infrared and ultraviolet absorption spectroscopies

To investigate sulfur and tellurium sorption into PA from potassium telluropentathionate solutions, it was important to ascertain in what form (elemental chalcogens, radicals or teluropentathionate ions, $TeS_4O_6^{2-}$) chalcogens were sorbed on PA.

Our investigations showed that the semi-hydrophilic polymer (polyamide) sorbed telluropentathionate ions from these solutions. The sorption of telluropentathionate ions, $TeS_4O_6^{2-}$, from 0.025−0.10 mol dm^{-1} solutions of $K_2TeS_4O_6$ in 0.2 mol dm^{-3} HCl by PA was studied by IR (400–1300 cm^{-1}) (Fig. 1) and UV (200–400 nm) (Fig. 2) absorption spectroscopy. The peaks in the IR spectra were found in the intervals 407–498, 523–541, 583–732, 861–1107 and 1159–1293 cm^{-1} and were assigned to the ν(S–S), δ_{as}(O–S–O),

δ_s(O–S–O), v_s(S–O) and v_{as}(S–O), respectively. These data confirm that telluropentathionate ions are sorbed into PA because of the similarity of the peaks of the former to the peaks in IR spectra of $K_2YS_4O_6$ (Y = S, Se, Te), [30,31] respectively, at 404–450, 510–550, 580–730, ~ 1010, ~ 1210 cm^{-1}.

UV absorption spectra shows that PA samples which were sulfurized for different periods of time in $K_2TeS_4O_6$ solutions contain four absorption maxima: at ~228 nm, ~256 and ~284 nm as peaks and at ~354 and ~428 nm as weakly expressed shoulders. According to the UV absorption spectra of polythionates and selenopolythionates [52,53], the absorption maxima of polythionate and selenopolythionate ions as shoulders and peaks are at ~215, ~250, ~290 and ~340 nm. Thus, UV absorption spectra recorded by our group confirmed that chalcogens are sorbed by PA films in the form of telluropentathionate ions.

3.2. Influence of concentration and temperature of potassium telluropentathionate on the sorption-diffusion of $TeS_4O_6^{2-}$ ions into PA

An increase of sorbed tellurium and sulfur concentration at a temperature of 1, 10 and 20°C with increasing concentration of potassium telluropentathionate solution is shown in Fig. 3. For example, with increasing the duration of the polymer treatment in $K_2TeS_4O_6$ solution at a temperature of 10°C to 24 h, the concentration of sorbed-diffused tellurium increased from 114.51 to 144.50 µmol cm^{-3} and of sulfur from 16.89 to 28.58 µmol cm^{-3} (Fig. 3, curves 1 and 3).

Tellurium and sulfur concentrations in the polymer increased with increasing temperature of chalcogenization solution (Fig. 4). This is particularly seen when PA samples are chalcogenized in the solution of a higher concentration. For example, while increasing duration of polymer treatment in 0.025 mol dm^{-3} $K_2TeS_4O_6$ solution to 8 h, tellurium concentraton increased from 17.75 to 106.90 µmol cm^{-3} and of sulfur from 9.27 to 33.0 µmol cm^{-3}. When the concentration of $K_2TeS_4O_6$ solution was four times higher, tellurium concentration increased from 34.36 to 128.92 µmol cm^{-3} and sulfur from 5.76 to 38.0 µmol cm^{-3}. Chalcogenization for 24 h did not change concentration of tellurium and sulfur significantly.

Chemical analysis of chalcogenized samples has shown that the concentration of sulfur and tellurium sorbed into PA increased with the increasing temperature and concentration of chalcogenization solution and the time of the polymer treatment. Our data also showes that the temperature increase of $K_2TeS_4O_6$ solution affects the concentration of sulfur sorbed in the polymer more

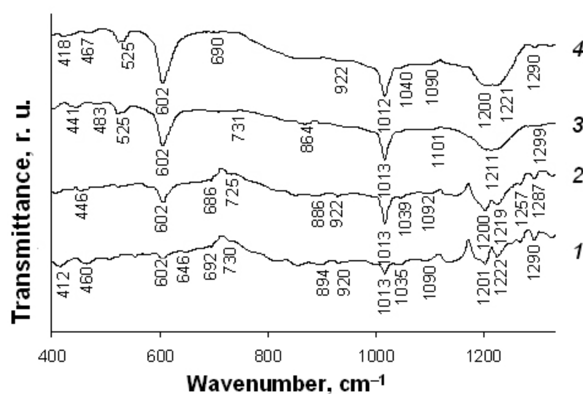


Figure 1. IR spectra of PA treated in 0.1 mol dm^{-3} $K_2TeS_4O_6$ solution in 0.2 mol dm^{-3} HCl at 20°C at different times. Chalcogenization time, h: 1 – 0.25; 2 – 0.5; 3 – 2.0; 4 – 4.0

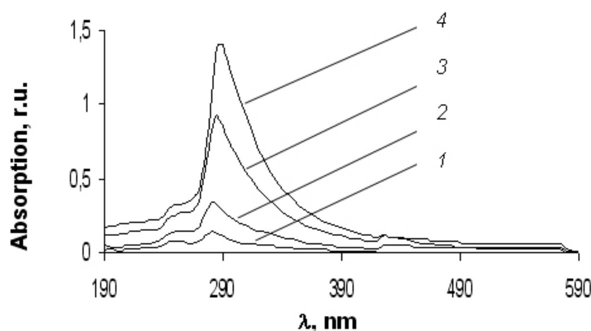


Figure 2. UV absorption spectra of PA treated in 0.1 mol dm^{-3} $K_2TeS_4O_6$ solution in 0.2 mol dm^{-3} HCl at 20°C at different times. Chalcogenization time, h: 1 – 0.25; 2 – 0.5; 3 – 2.0; 4 – 4.0.

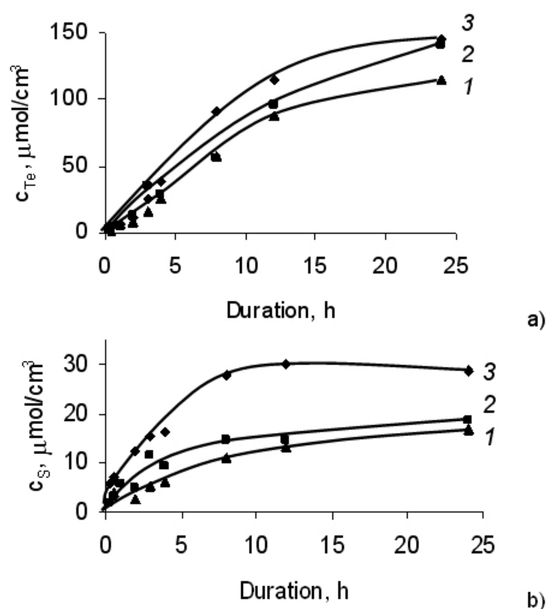


Figure 3. Changes of tellurium (a) and sulfur (b) concentrations in PA film chalcogenized at a temperature of 10°C in $K_2TeS_4O_6$ solution. Concentration of $K_2TeS_4O_6$ solution, mol dm^{-3}: 1 – 0.025, 2 – 0.05, 3 – 0.1

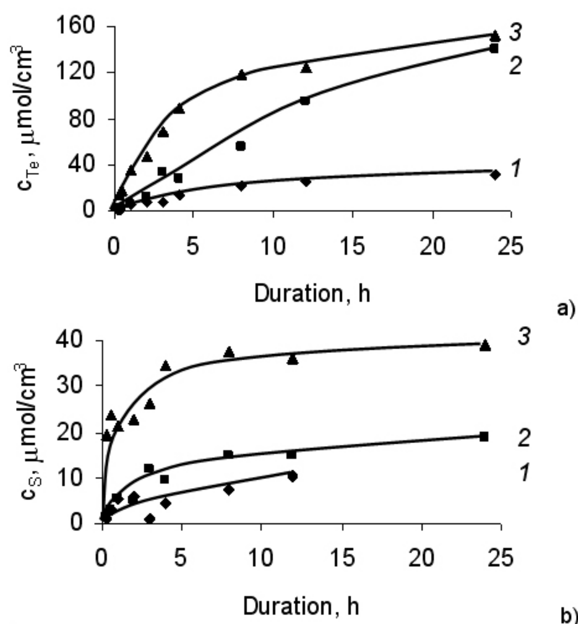


Figure 4. Changes of tellurium (a) and sulfur (b) concentrations in PA film, chalcogenized in 0.05 mol dm^{-3} $K_2TeS_4O_6$ solution. Temperatures of chalcogenization solution, °C: 1 – 1, 2 – 10, 3 – 20

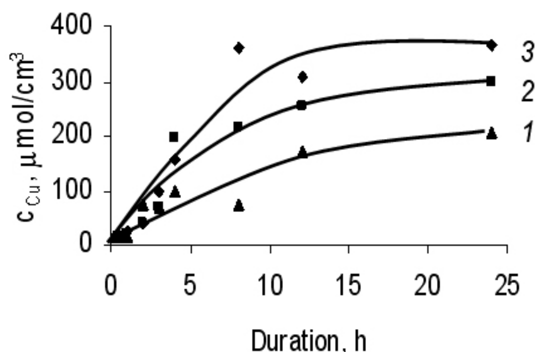


Figure 5. Changes of copper concentration in PA film chalcogenized in $K_2TeS_4O_6$ solution at a temperature of 10°C. Concentration of $K_2TeS_4O_6$, mol dm^{-3}: 1 – 0.025, 2 – 0.05, 3 –0.1

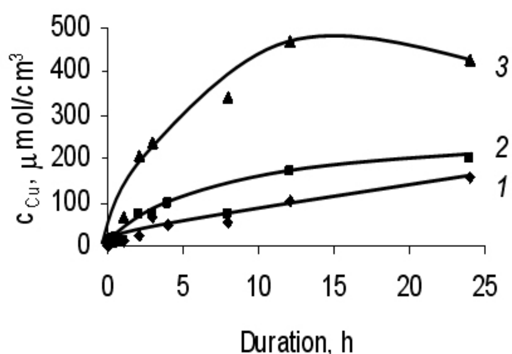


Figure 6. Changes of copper concentration in PA film chalcogenized in 0.05 mol dm^{-3} $K_2TeS_4O_6$ solution. Temperature of $K_2TeS_4O_6$ solution, °C: 1 – 1, 2 – 10, 3 – 20

than the concentration increase of telluropentathionate.

Based on the results of the first stage of PA modification and chalcogenization, we conclude that potassium telluropentathionate is a suitable precursor for the formation of copper chalcogenides layers on PA surface.

As a result of interacting PA chalcogenized in potassium telluropentathionate solutions with a solution of Cu(II/I), brown and even black semiconductive or electrically conductive layers of copper sulfide–copper telluride lwere formed. Layers of copper chalcogenides were formed as a result of heterogeneous redox reactions among Cu^{+}, Cu^{2+} and $TeS_4O_6^{2-}$. The formation of a Cu_xS–Cu_yTe layer depended on the initial concentration of sulfur and tellurium in chalcogenized PA.

Concentration of copper in the layer is strongly dependent on sulfur and tellurium concentrations in PA. (Figs. 5,6). PA treated with $K_2TeS_4O_6$ for a longer time requires more copper for the formation of a solid copper chalcogenide layer. A continuous chalcogenide layer decelerates further increase of copper concentration in the polymer. Concentration of copper in the chalcogenide layer on PA chalcogenized in telluropentathionate solutions changes uniformly until the saturation is reached.

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

3.3. Electrical sheet resistance of copper chalcogenide layers formed on PA film surface using $K_2TeS_4O_6$ solutions

Microscopic analysis of PA surface modified with copper chalcogenides shows an irregular formation of Cu_xS–Cu_yTe layers due to the formed islands. This unevenness increases the probability of the layer's interactions with the impurities and causes some difficulties with measuring the surface electrical resistance. Therefore we limited our study of the resistance of PA modified with Cu_xS−Cu_yTe layers to measuring the electrical resistance of the external layer of the chalcogenide surface.

The results presented in Table 1 show that under our experimental conditions it is possible to form layers of copper sulfides and tellurides with electrical sheet resistance varying from less than ~1.0×10³ kΩ cm^{-2} to ~1.5 kΩ cm^{-2} The value of resistance decreases with the increasing time of chalcogeiznation, the concentration and the temperature of chalcogenization solution (Table 1). Electrical resistance was observed to

Table 1. Electrical sheet resistance (kΩ cm^{-2}) of Cu_xS–Cu_yTe layers on PA first treated in $K_2TeS_4O_6$ solution and then with Cu(II/I) salt solution

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

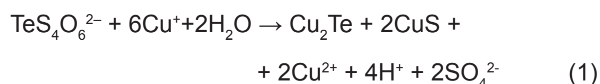
decrease with increasing the concentration of precursor solution. However, not all cases displayed direct dependence of the chalcogenides layer resistance on copper concentration. This is due to formation of copper chalcogenides of various stoichiometry and electrical conductivity in different amounts. The increased number of phases and the intensity of their maxima reflects the increased concentration of copper sulfides and copper tellurides on the surface of PA. A decrease in the electrical resistance of these layers exaplains their qualitative changes. Therefore, a decrease in electrical sheet resistance implies that a larger amount of electrically conductive copper sulfide and copper telluride phases is formed in the layers on PA surface with increasing the time of chalcogenization, concentration and temperature of chalcogenization solution.

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

The composition of copper chalcogenide in deeper layers (up to 1 nm) after surface etching (bombardment with Ar^+ ions) was studied. Data gained by the XPS method, i.e., the percent amount of elements, the values of binding energies and the spectra of individual elements (S 2p, Te 3d5, Cu 2p3 and O 1s), revealed the composition of the obtained layer. The analysis was restricted to a study of the chemical composition of a very thin surface layer. In the present work we studied the dependence of the layer composition on the concentration of chalcogenization agent solution, temperature and treating duration in this solution.

The maxima in S 2p spectra, corresponding to the binding energy values of ~161–162 eV, show the presence of sulfide sulfur; the maxima corresponding to the binding energy values of ~163–164 eV indicate the presence of elemental sulfur [51,54]. The maxima in Te 3d5 spectra, corresponding to the binding energy values of ~572–573 eV, show the presence of a telluride ion, and the maxima corresponding to the binding energy value of ~575.8 eV indicate the presence of TeO_2 or Te(IV) [51,54,55]. The maxima in Cu 2p3 spectra corresponding to the binding energy values of ~932 eV, show the presence of Cu^+ and Cu^{2+}.

Similarity of spectra confirmed that the composition of layers obtained in different conditions was similar. In the etched surface, various compounds of copper, sulfur and tellurium (Cu_2S, CuS, S_8, Cu_xS, Cu_yTe) were present. We analysed only surface etched by Ar^+ ions. There was no oxygen detected in the deeper layer. Analysis of the atomic percentage of the elements showed that layers consisted mainly of copper sulfides and tellurides. Also, the content of copper sulfides was higher since the amount of sulfide sulfur in the layers studied was about three times higher than that of the telluride tellurium. These data are in agreement with the equation according to which telluropentathionate ions react with copper(I) ions [49]:



$$TeS_4O_6^{2-} + 6Cu^+ + 2H_2O \rightarrow Cu_2Te + 2CuS + 2Cu^{2+} + 4H^+ + 2SO_4^{2-} \quad (1)$$

From the above equation it follows that there is more copper sulfide formed, in comparison with copper telluride. Increased concentration of $K_2TeS_4O_6$ solution did not change atomic percentages of the elements (Cu, S, Te) significantly. Therefore, we could state that an increase in the concentration of chalcogenization agent solution did not greatly change the composition of the layer.

Upon calculating the copper and sulfur–tellurium ratios, from atomic percentages, we found that their values decreased with increasing $K_2TeS_4O_6$ concentration. This is in good agreement with the results of electrical sheet resistance measurements of the samples, where the samples were more conductive at a lower value of the copper and sulfur-tellurium ratio. When the Cu:(S+Te) ratio was equal to 1.69, the value of sheet resistance was 7.7 kΩ cm^{-2}; when the ratio was 1.51, the value of sheet resistance was 2.08 kΩ cm^{-2}, and at the ratio value of 1.41 the resistance was 1.63 kΩ cm^{-2}.

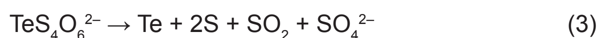
Comparison of element atomic percentages showed

that more copper was present in samples chalcogenized at higher temperatures: at 1°C – 54.1 at.%, at 10°C – 57.29 at.%, at 20°C – 60.13 at.%. However, the largest content of sulfide sulfur was found in a sample chalcogenized at the lowest (1°C) temperature; the largest content of tellurium in the telluride form was present in a sample chalcogenized in $K_2TeS_4O_6$ solution at a temperature of 10°C.

Our calculations have shown that the ratio of copper with sulfur-tellurium increased with the increasing temperature of $K_2TeS_4O_6$ solution. The increase of this ratio may be dependent on several factors, for example, on the fact that a telluropentathionate ion at a higher temperature decomposes (Eqs. 2, 3):

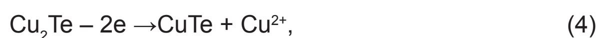
$$TeS_4O_6^{2-} \rightarrow Te + S_4O_6^{2-} \quad (2)$$

or



$$TeS_4O_6^{2-} \rightarrow Te + 2S + SO_2 + SO_4^{2-} \quad (3)$$

Therefore copper ions may react not only with $TeS_4O_6^{2-}$ ions according to the Eq. 1, but also with the products of this ion decomposition [49, 56]. The following processes are possible:



$$Cu_2Te - 2e \rightarrow CuTe + Cu^{2+}, \quad (4)$$

$$2Te + 2e \rightarrow Te_2^{2-}, \quad (5)$$

$$Cu^{2+} + Te_2^{2-} \rightarrow CuTe + Te. \quad (6)$$

Decrease in the content of sulfur may be explained by formation and liberation of SO_2.

In the etched layer a copper hydroxide is present, in addition to the copper sulfide and copper telluride. The metal sulfides formed layers in the polymer surface matrix by the sorption–diffusion method take the form of dendrites [57]; therefore, among the dendrites, there may remain adsorbed compounds. In our case, insoluble copper hydroxide, which formed during washing the layer's surface with water, remained among the dendrites. The largest amount of oxygen (34.19 at.%) was detected in samples chalcogenized for a very short time (only 0.25 h), with smaller amounts of sulfur and tellurium. Therefore, we believe that a chalcogenide layer forms separate islands, and more copper hydroxide is adsorbed in between the islands or dendrites. Presence of separate islands determines low electrical conductivity of a sample (the value of sheet resistance was 1.04×10^3 kΩ cm^{-2}), which is confirmed by the value of the copper to sulfur–tellurium ratio of 2.61 calculated from the percentages of these elements.

After analysing the XPS data, we have concluded that the copper and sulfur–tellurium ratio decreases with increasing the duration of chalcogenization, which is in accordance with the values of the sheet resistance measurements where samples with a lower value of this ratio were more conductive.

In PA film chalcogenized for a very long time (24 h), a small amount of Te(IV) (2.05 at.%) was detected. It could be TeO_2 [55,58] or TeO_3^{2-}, according to:

$$2Te + 2CuO + 2HO^- \rightarrow Cu_2Te + TeO_3^{2-} + H_2O \quad (7)$$

$$Cu_2Te + 6CuO + 2HO^- \rightarrow 4Cu_2O + TeO_3^{2-} + H_2O \quad (8)$$

XPS results indicate that copper sulfides and copper tellurides are the main components of the layers on PA film samples.

3.5. X-ray diffraction studies of copper sulfide–copper telluride layers formed on the surface of polyamide 6 films using $K_2TeS_4O_6$ solutions

The phase composition of the formed layers was established by comparing their X-ray diffraction patterns with those of known copper chalcogenides [59–63]. The chemical composition and crystal structure of the majority of Cu_xS and Cu_yTe minerals such as chalcocite Cu_2S, djurleite $Cu_{1.95}S$, Cu_4Te_3, $Cu_{1.80}Te$, $Cu_{1.85}Te$ and vulcanite, CuTe were investigated [59–63]. The crystal structure of Cu_xS and Cu_yTe was found to depend on the chemical composition and synthesis conditions. The composition of Cu_xS and Cu_yTe deposited by sorption methods was scarcely investigated.

The intensities of PA peaks at $\theta < 13°$ exceed the intensity of copper sulfide peaks. Therefore, the spectra at $2\theta \geq 26.0°$ were investigated in more detail.

XRD spectra of PA films treated at different times with 0.025 mol dm^{-1} $K_2TeS_4O_6$ solution at 10°C and then with Cu(II/I) salt solution are presented in Fig. 7. The maxima characteristic of the copper sulphide, copper telluride and of the elemental sulfur were detected in almost all spectra. The value of electrical sheet resistance of Cu_xS–Cu_yTe layers was found to decrease (from 1.0×10^3–40.5 kΩ cm^{-2} to –3.1–1.6 kΩ cm^{-2}) with the initial PA chalcogenization time (from 0.25–2.0 to 8–24 h). The lowest value was observed for PA treated for 24 h in $K_2TeS_4O_6$ solution. The maxima of more conductive phases of anilite, Cu_7S_4, and copper tellurides CuTe, Cu_4Te_3, were detected in the XRD spectra of PA chalcogenized for longer period of time. They were almost absent in the spectra of PA films chalcogenized for a shorter period of time. The value of electrical sheet resistance of Cu_xS–Cu_yTe layers decreased also (7.7–2.1–1.6 kΩ cm^{-2}) with increasing the concentration of chalcogenization ($K_2TeS_4O_6$) solution

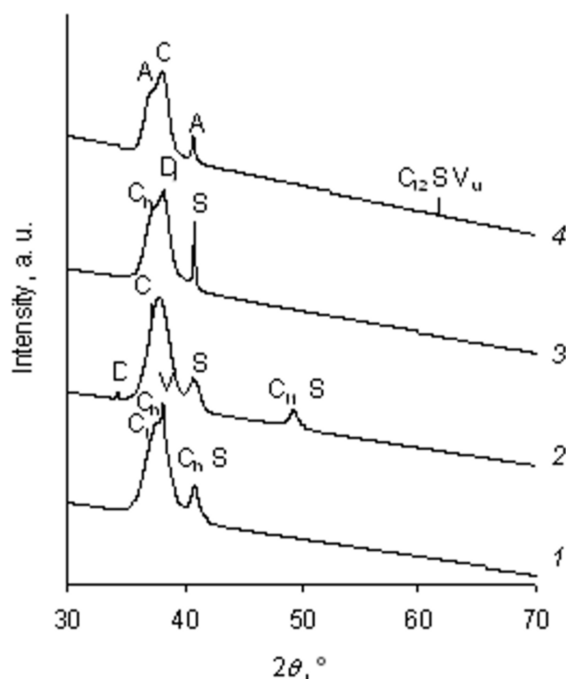


Figure 7. X-ray diffractograms of PA films first treated in 0.025 mol dm^{-3} $K_2TeS_4O_6$ solution at 10°C and then in Cu(II/I) salt solution. Duration of chalcogenization, h: 1 – 0.25, 2 – 2, 3 – 12, 4 – 24. A – Cu_7S_4, Dj – $Cu_{1,9375}S$; Ch – Cu_2S; C_t – Cu_4Te_3; C_{t1} – $Cu_{1,85}Te$; Vu – CuTe; C_{t2} – $Cu_{1,80}Te$; Vi – CuS_2, S – S

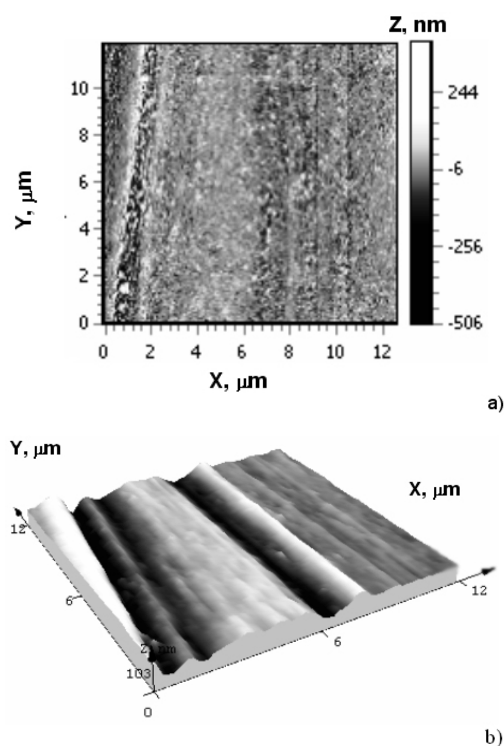


Figure 8. Atomic force microscopy view of Cu_xS–Cu_yTe layers formed on PA surface: 2D view of lateral forces microscopy (a) and 3D topography view (b). PA was chalcogenized 0.25 h at the temperature of 10°C in 0.025 mol dm^{-3} $K_2TeS_4O_6$ solution and then treated with Cu(II/I) solution

(0.025–0.05–0.1 mol dm^{-3}).

The spectra of PA films chalcogenized in the telluropentathionate solution at different concentrations showed that the maxima of phases with good electrical conductance (*e.g.* CuS_2 and Cu_4Te_3) dominated when the 0.05 mol dm^{-3} chalcogenization solution has been used for the formation of a copper chalcogenides layers. XRD spectra of PA films with Cu_xS–Cu_yTe layers, formed using the chalcogenization solution at a temperature of 1–20°C, revealed that the same highly conductive phases were detected also in copper chalcogenide layer formed by using the $K_2TeS_4O_6$ solution at a higher temperature (20°C). This is in accordance with data of electrical sheet resistance measurements of these films: its value (17.3–10.1–2.1 kΩ cm^{-2}) decreased with increasing the temperature (1–10–20°C) of chalcogenization solution.

Based on the results presented above, we can state that the phase composition and electrical sheet resistance of mixed copper sulfide–copper telluride layers on PA surface, formed by using potassium telluropentathionate solution as a polymer chalcogenization agent, depend on chalcogenization conditions, such as time, concentration and temperature of the solution. Increase in values of these factors decreased electrical sheet resistance of the layers.

3.6. Study of the morphology of Cu_xS–Cu_yTe layers formed on PA surface using $K_2TeS_4O_6$ solutions

Study by AFM of PA modified with Cu_xS–Cu_yTe layers revealed morphological differences between the layers. The aim of this study was to find the predominant mechanism of Cu_xS–Cu_yTe layer formation on PA surface, and to examine the layer homogenity and growth evenness. Fields of 12×12 microns were investigated. For the quantitative estimation of the surface, the standard programs of the view treatment were used. It has been determined that the surface morphology of the copper chalcogenide layers formed on PA surface depended on the conditions of polymer chalcogenization.

From the cross sections of Cu_xS–Cu_yTe layers formed on PA surface where the polymer was chalcogenized in 0.025 mol dm^{-3} $K_2TeS_4O_6$ solution for 0.25, 2 and 24 h at a temperature of 10°C, average height and diameter of the crystallites were determined. When the polymer was chalcogenized for 0.25 h in $K_2TeS_4O_6$ solution, the height of crystallites reached 88 nm and the diameter ~0.1–1.0 μm. Longer chalcogenization (2 and 24 h) resulted in a decrease of the height of the crystallites down to 66 nm while the diameter remained unchanged (~0.4–1.0 μm). At a short duration of polymer treatment

in $K_2TeS_4O_6$ solution (0.25 h), the growth of chalcogenide layer started with the formation of separate small islands (Fig. 8). After extending the time of chalcogenization to 2 h, the growth of chalcogenide layer proceeded more intensively, and after to 24 h, the clusterization began. As a result, the crystallites of various diameter and height slowly began to agglomerate (Figs. 9, 10). One can see a slight reduction of the layer average roughness (Fig. 11). This means that the crystallites joining into agglomerates more evenly cover the surface, and the layer becomes more homogeneous.

Study of the formation of Cu_xS–Cu_yTe layers on PA surface showed that the chalcogenide layer was formed by changing the temperature. PA was chalcogenized for 8 h in 0.05 mol dm^{-3} $K_2TeS_4O_6$ solution at temperatures of 1, 10, 20°C and then treated with the Cu(II/I) salt solution. The cross sections of these layers showed that the layer surface was rather uneven. The roughness changed irregularly, and crystallites were of different height, diameter and form. The change of roughness was shown by the roughness parameters. The height of crystallites, like the roughness of the layer, was changing irregularly with the increasing temperature of PA chalcogenization in $K_2TeS_4O_6$ solution. At a low temperature of PA treatment in $K_2TeS_4O_6$ solution, the formation of layer was slow and irregular. The maximum height of layer was ~160 nm. With increasing the temperature of chalcogenization solution to 10 °C, the height of the layer decresed to ~90 nm, but at a temperature of 20 °C it increased again to ~149 nm. Thus, with increasing the chalcogenization temperature from 1 to 20 °C, the height changes irregularly. This could be due to the differences in the phase composition of Cu_xS–Cu_yTe layers obtained at different temperatures.

Thus, the above-listed AFM results indicate, that the formation of copper chalcogenide layers proceeds irregularly in the form of islands which grow into larger agglomerates and that this process depends on the conditions of PA initial chalcogenization in $K_2TeS_4O_6$ solution (in the same "copperizing" conditions). The surface of the layer is uneven, rather rough. The maximum height of the layer slightly reduces with prolongation of PA treatment in $K_2TeS_4O_6$ solution duration. The reduction of layer height is more significant while increasing the concentration of chalcogenization solution. The same tendency is observed in changes of the roughness. The layer height and roughness with increasing the temperature change irregularly.

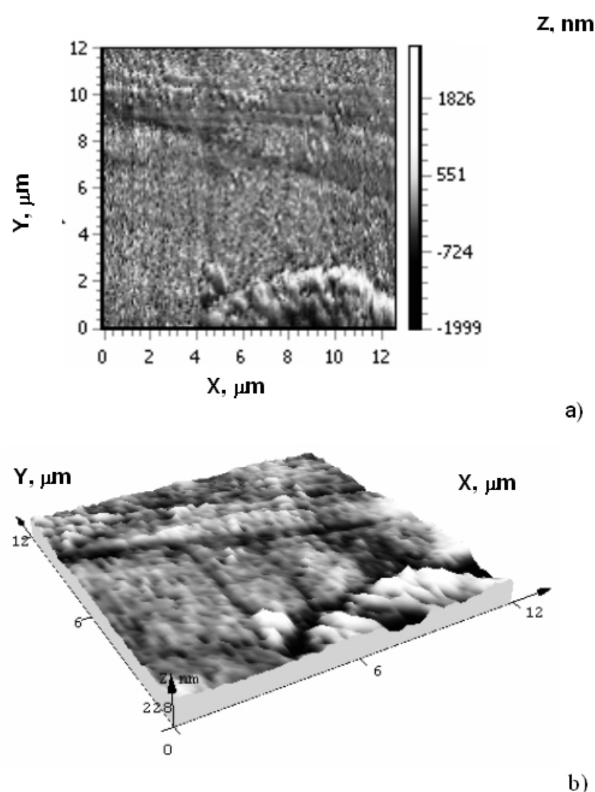


Figure 9. Atomic force microscopy view of Cu_xS–Cu_yTe layers formed on PA surface: 2D view of lateral forces microscopy (a) and 3D topography view (b). PA was chalcogenized 2 h at the temperature of 10°C in 0.025 mol dm^{-3} $K_2TeS_4O_6$ solution and then treated with Cu(II/I) solution

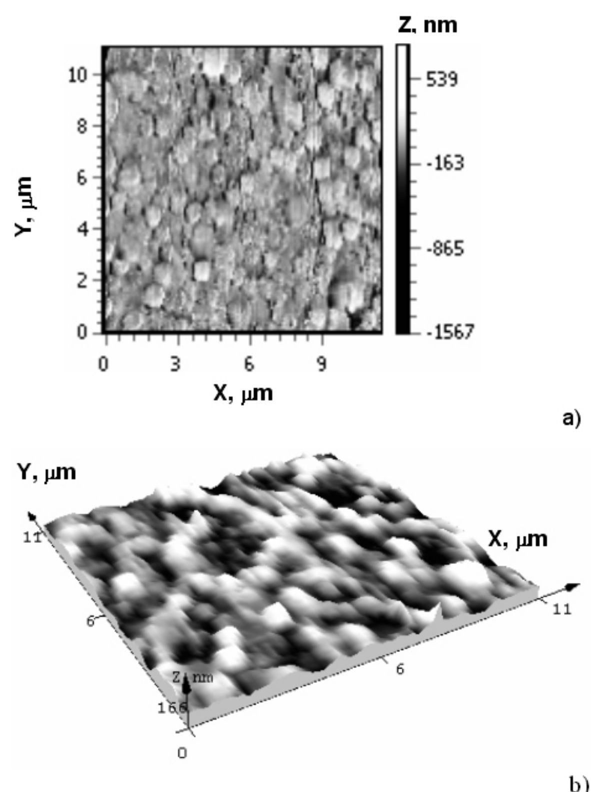


Figure 10. Atomic force microscopy of Cu_xS–Cu_yTe layers formed on PA surface: 2D view of lateral forces microscopy (a) and 3D topography view (b). PA was chalcogenized for 24 h at 10°C in 0.025 mol dm^{-3} $K_2TeS_4O_6$ solution and then treated with Cu(II/I) solution

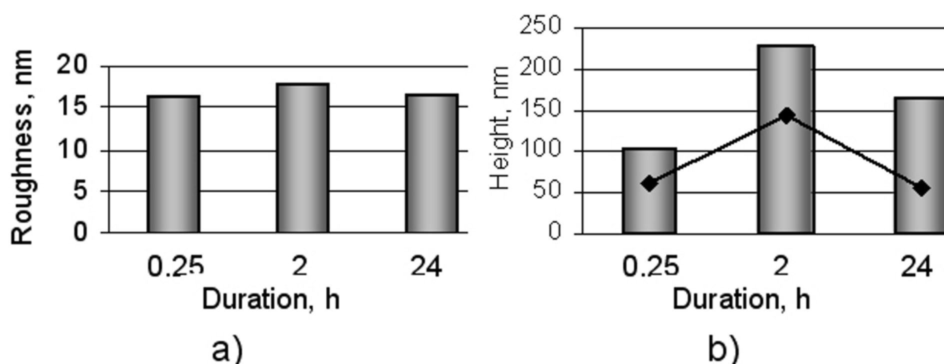


Figure 11. Dependence of layer mean square roughness (a) and height (b) on the duration of PA treatment in 0.025 mol dm^{-3} $K_2TeS_4O_6$ solution at 10°C

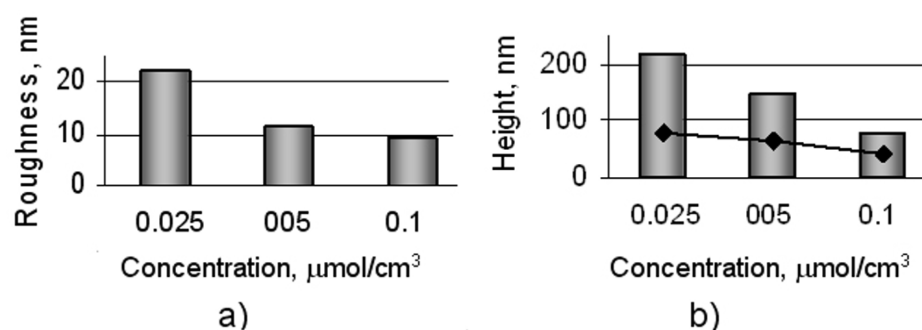


Figure 12. Dependence of layer mean square roughness (a) and height (b) on the concentration of $K_2TeS_4O_6$ solution while treating PA in for 8 h at a temperature of 20oC

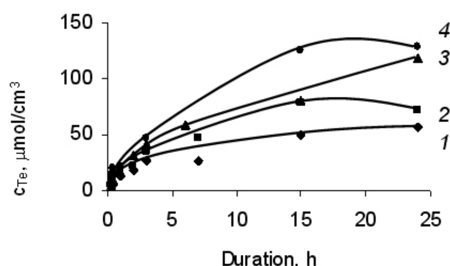


Figure 13. Adsorbtion isotherms of tellurium on PA surface at 20° C as a function of exposure time in a solution of $Na_2TeS_4O_6$. Concentration of $Na_2TeS_4O_6$ solution, mol dm^{-3}: 1 – 0.01; 2 – 0.025; 3 – 0.05; 4 – 0.1

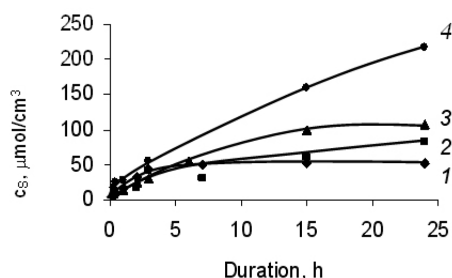


Figure 14. Adsorbtion isotherms of sulfur on PA surface at 20° C as a function of exposure time in a solution of $Na_2TeS_4O_6$. Concentration of $Na_2TeS_4O_6$ solution, mol dm^{-3}: 1 – 0.01; 2 – 0.025; 3 – 0.05; 4 – 0.1

To confirm the results obtained using potassium telluropentathionate in the formation of copper sulfide–copper telluride layers, we studied the formation of these layers using sodium telluropentathionate solutions as precursors.

3.7. Formation of copper telluride–copper sulfide layers on PA surface, using sodium telluropentathionate solutions

Our experiments showed that, as in the case with $K_2TeS_4O_6$ solutions, the particles of telluropentathionate anions sorb-diffuse into PA films kept in sodium telluropentathionate. The concentrations of sorbed-diffused tellurium and sulfur increased with increasing the duration of polymer treatment in precursor solution and the concentration of this solution (Figs. 13 and 14). We compared these results with the corresponding data obtained using potassium telluropentathionate solutions (Table 2). Tellurium concentrations obtained using $Na_2TeS_4O_6$ solutions were lower, which may be due to the fact that the potassium salts are more stable compared to the analogous sodium polythionates.

Semiconducting copper sulfide–copper telluride layers were formed on PA films after the films

Table 2. The concentrations of tellurium (μmol cm^{-3}) in PA and the values of electrical sheet resistance (kΩ cm^{-2}) of copper chalcogenide layers on PA surface formed using 0.1 mol dm^{-3} $Na_2TeS_4O_6$ and $K_2TeS_4O_6$ at 20°C at various polymer chalcogenization times

Chalcogenization duration, h	Te concentration, μmol cm^{-3}		Sheet resistance of Cu_xS–Cu_yTe layers on PA	
	$Na_2TeS_4O_6$	$K_2TeS_4O_6$	$Na_2TeS_4O_6$	$K_2TeS_4O_6$
0.5	12.7	26.72	1.19·10^3	256.43
1	21.16	37.7	360.4	41.444
2	35.6	58.7	623.9	9.85
3	47.02	78.4	5.30	9.89
12	125.39	143.28	–	1.57
24	127.74	162.49	2.07	2.92

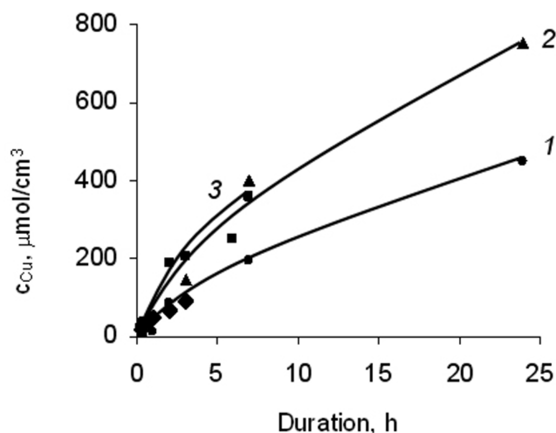


Figure 15. Dependence of copper concentration in PA on chalcogenization duration when treating it with $Na_2TeS_4O_6$ solution at 20° C and then in Cu(II/I) salt solution. The concentration of $Na_2TeS_4O_6$ solution, mol dm^{-3}: 1 – 0.01; 2 – 0.025; 3 – 0.05

chalcogenized in $Na_2TeS_4O_6$ solutions have been treated with Cu(II/I) salts solution. The concentration of copper in PA increased with the increasing duration of polymer initial treatment in precursor solution and with the concentration of this solution (Fig. 15). Thus, copper concentration in Cu_xS–Cu_yTe layers increases with the increasing concentration of chalcogens in the polymer. This is understandable since larger amount of Cu^+ and Cu^{2+} ions may be involved in the reaction with the sulfur–tellurium species at a higher concentration of sulfur and tellurium sorbed–diffused into PA. The highest concentration of copper after initial chalcogenization in 0.05 mol dm^{-3} $Na_2TeS_4O_6$ solution at a temperature of 20°C is ~360 μmol cm^{-3}. In general, the largest copper concentration in our experiments was obtained using 0.05 mol dm^{-3} $Na_2TeS_4O_6$ solution at a temperature of 20°C and after 24 h of chalcogenization (~740 μmol cm^{-3}).

Data presented in Table 2 shows that the electrical sheet resistance of Cu_xS–Cu_yTe layers decreases with the increasing time of the polymer initial treatment in chalcogenization solution, *i.e.*, with the increasing concentrations of tellurium, sulfur and copper in the layer. Electrical resistance decreased from 1.19×10^3 kΩ cm^{-2} to ~2 kΩ cm^{-2} after 24 h of chalcogenization in 0.1 mol dm^{-3} $Na_2TeS_4O_6$ solution at 20°C. Electrical sheet resistance at a short time of PA initial chalcogenization (up to ~2 h) was significantly higher compared to the values when the potassium telluropentathionate solution had been used. Longer duration of chalcogenization resulted in similar values of electrical sheet resistance for both telluropentathionates. This can be explained by the increased thickness of these layers because of the increased concentrations of sorbed–diffused tellurium and sulfur and thus of the amount of copper reacting in the stage of "copperizing".

The phase composition of copper sulfide–copper telluride layers formed using $Na_2TeS_4O_6$ solutions was studied by the X-ray difraction method. Fig. 16 shows that all the samples of copper chalcogenide layers on PA were polycrystalline and many of them have some binary phases such as Cu_2Te, $Cu_{3\pm\delta}Te_2$ and $Cu_{2-\delta}S$. The four phases of copper tellurides, tetragonal $Cu_{3.18}Te_2$ (maximum at 2θ = 47.6°), $Cu_{2.72}Te_2$ (maximum at 2θ = 37.2°), hexagonal Cu_2Te (maximum at 2θ = 42.9, 63.5 and 66.4°) and orthorhombic vulcanite, CuTe (maximum at 2θ = 41.5 and 58.3°), were found in films on the PA surface, among them three phases of copper sulfides such as orthorhombic anilite, Cu_7S_4 (maximum at 2θ = 40.92, 55.94 and 62.8°), monoclinic djurleite, $Cu_{1.9375}S$ (maximum at 2θ = 38.3 and 61.1°), and orthorhombic copper sulfide, $Cu_{1.8}S$ (maximum at 2θ = 59.85 °).

Surface morphology and structure were studied using AFM (Fig. 17). Depending on the exposure in the precursor solution, chalcogenide layers of 180–560 nm height were formed. The CuTe and CuS interface appeared to be graded with a substantial interdiffusion between the layers. The islands were observed due to surface roughness.

In summary, we may state that polymer it is possible to form electrically conductive or semiconductive copper sulfide–copper telluride layers, depending on the conditions of PA chalcogenization in $Na_2TeS_4O_6$ solution

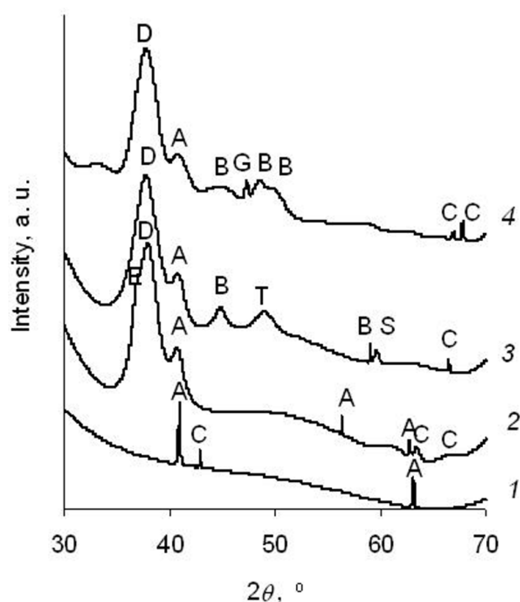


Figure 16. X-ray diffraction patterns (A – anilite, Cu_7S_4, D – djurleite, $Cu_{1,9375}S$, S – digenite, $Cu_{1,8}S$, G – geerite, $Cu_{1,6}S$, C – hexagonal copper telluride Cu_2Te, T – tetragonal copper telluride $Cu_{3,18}Te_2$, B – vulcanite, CuTe, E – copper telluride $Cu_{2,72}Te_2$) of copper chalcogenide layers on PA treated for 3 h with $Na_2TeS_4O_6$ solution at different concentrations at 20°C and with Cu(II/I) salt solution. The concentration of $Na_2TeS_4O_6$ solution, mol dm^{-3}: 1 – 0.01, 2 – 0.025, 3 – 0.05, 4 – 0.1

(duration, solution concentration), as in the case of $K_2TeS_4O_6$ solutions.

Earlier studies [44] of the coworkers of the Department of Inorganic Chemistry of the KTU have shown that telluropentathionic acid solutions were more stable compared to the solutions of their alkali metal salts of the same concentration. Therefore, it was interesting to apply $H_2TeS_4O_6$ solutions to form of Cu_xS–Cu_yTe layers on PA surface.

3.8. Telluropentathionic acid as a precursor forming semiconductive copper sulfide–copper telluride layers on PA surface.

Monotelluropentathionic acid, $H_2TeS_4O_6$ precursor offers many advantages over the more conventional sources because of its higher stability. Under conditions of our experiments, solutions of telluropentathionic acids were more stable than their alkaline metal salt solutions of the same concentration. The amount of sorbed tellurium and sulfur increased with the increasing concentration of precursor solution and the time of exposure (Fig. 18).

Typical UV spectra in which the spectrum of PA substrate is excluded are shown in Fig. 19. Optical absorption spectra of chalcogen layers on PA showed the layers to have a high coefficient of absorbance (~10^4 cm^{-1}).

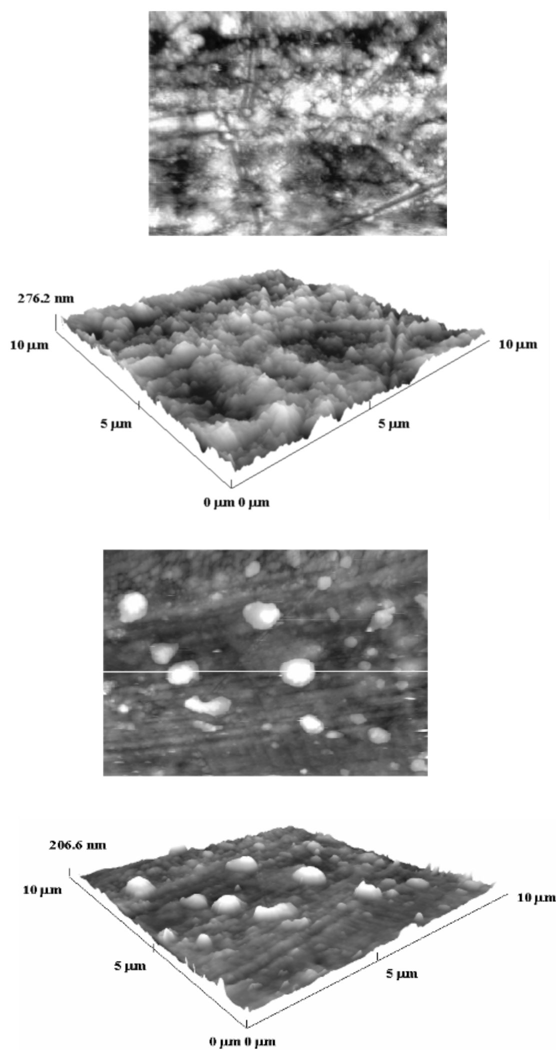


Figure 17. AFM top view of copper chalcogenide layers on PA treated: a) for 3 h at 20°C in 0.1 mol dm^{-3} $Na_2TeS_4O_6$ solution at 276.2 nm; b) for 24 h at 20°C in 0.1 mol dm^{-3} $H_2TeS_4O_6$ at 206.6 nm

The absorption spectra maximum of tellurium-containing layers was at λ = 250–255 nm. However, the transmission percentage (~ 90%) of tellurium layers on PA reached maximum at λ = 780 nm. The intensity of absorption spectra maximum with similar concentrations of precursors increased with the increasing time of exposure. The increase in absorbance at maximum wavelength is due to an effect of precursor concentration. The height of chalcogen layers and the mol fraction of chalcogen grew with the exposure in the precursor solution; however, the height increased at the expense of transparency.

UV-VIS spectra showed also the presence of an additional unclear peak at 290 nm for PA chalcogenized in $H_2TeS_4O_6$ acid with an increase in the concentration of precursor solution and the exposure time, for example,

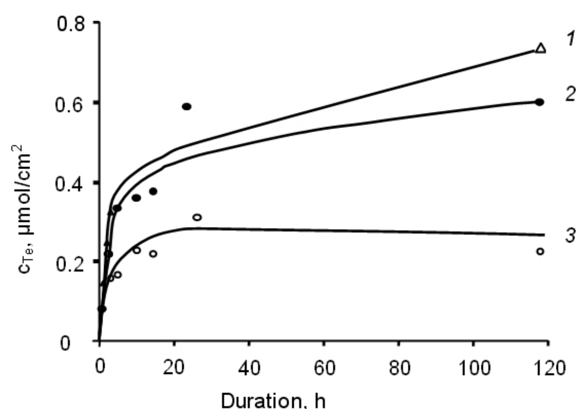


Figure 18. Kinetics of chalcogen sorption on PA surface at 20°C. Precursors: 1 – 0.1 mol dm^{-3} $H_2TeS_4O_6$ solution, 2 – 0.05 mol dm^{-3} $H_2TeS_4O_6$ solution, 3 – 0.01 mol dm^{-3} $H_2TeS_4O_6$ solution

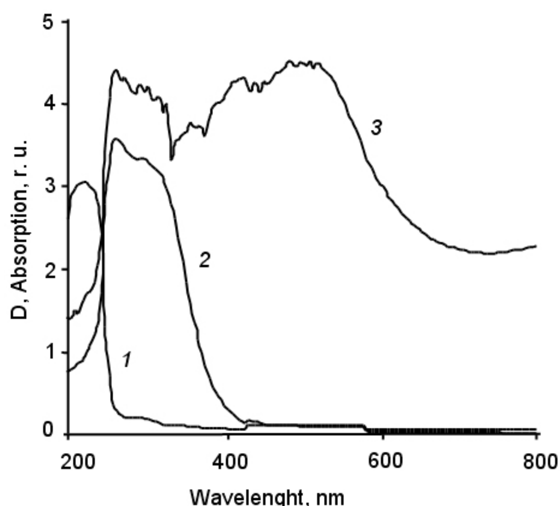


Figure 19. UV-VIS absorption spectra. 1 – PA, 2 – layers of chalcogens on PA surface after 24 h of exposure in 0.1 mol dm^{-3} $H_2TeS_4O_6$ solution at 20°C, 3 – copper chalcogenides on PA after interaction with Cu(II/I) solution

with an increase in chalcogen concentration on the surface of PA. Change of the shape in the spectra of chalcogenized PA before interaction with copper ions could be explained by appearance of tetrathionic acid, $H_2S_4O_6$, a product of slight degradation (2–8% from initial concentration) of telluropentathionic acid after 24 h and a longer treatment of PA according to the reaction:

$$TeS_4O_6^{2-} \rightarrow Te + S_4O_6^{2-}. \quad (9)$$

After interaction of copper ions with polyamide in the presence of chalcogens, a number of new peaks appear in the interval of 260–465 nm for PA chalcogenized in telluropentathionic acid solution. A changed tendency was observed in comparison with that before the interaction with copper.

When telluropentathionic acid was used as a precursor, a broad absorption peak and an unclear one appeared at 260 nm, 350 nm and 465 nm, respectively (Fig. 19, curve 3). All these peaks were higher than relevant peaks of PA before the interaction with copper, indicating the presence of copper chalcogenide species.

The IR spectra of PA surface before and after chalcogenization with telluropentathionic acid showed that a new material was formed or bonded on PA surface after chalcogenization.

Highest peaks in the IR spectra of chalcogenized PA recorded by the compensation method (PA absorption eliminated) were present in the intervals of the wavenumber 427–735 cm^{-1} and 790–1372 cm^{-1}. Six main absorption bands in the region 350–1200 cm^{-1} were assigned to the vibration of $S_2O_3^{2-}$.

A very strong band with the peak was shown in the range 1209–1215 cm^{-1}. The lower frequency absorption with the peak at 609 cm^{-1} was reasonably strong, and the band was sharp and clearcut so that it was coupled with the stretching absorption. A broad absorption in the region 608–610 cm^{-1} is typical of the symmetric deformation O–S–O vibrations, δ_s(O–S–O), in the terminal SO_3 groups of the polythionates.

The bands with the peaks in the interval of the wave numbers 790–1302 cm^{-1} correspond to the symmetric valence S–O vibrations, v_s(S–O), and to the asymmetric valence S–O vibrations, v_{as}(S–O), in the terminal SO_3 groups of the polythionates.

However, absorption intensity at 523–735 cm^{-1} was considerably increased when the process of chalcogenization proceeded. The bands with the peaks in this interval correspond to the asymmetric deformation of O–S–O vibrations, δ_{as}(O–S–O), and to the symmetric deformation of O–S–O vibrations, δ_s(O–S–O), in the terminal SO_3 groups of the polythionates.

IR spectra suggest the formation mechanism of thin layers of chalcogens from $TeS_4O_6^{2-}$ ions containing precursors on PA surface. From the point of view of the mechanism of nanofilms formation on PA surface, the key problem is that the layers of chalcogens or their compounds (e.g. chalcogenides) block the surface sites of the polymer and modify their surface properties. The further interaction of chalcogenized polyamide with copper(II/I) salts solution leads to the formation of Cu_xS, Cu_xTe and mixed Cu_xS–Cu_yTe layers whose IR spectra are quite different from that of PA before the interaction with copper.

The phase composition of the layers depended on the time of initial treatment in precursor solution. The Cu–Te–S layers showed binary phases such as Cu_2Te, $Cu_{3-x}Te_2$, $Cu_{2-x}S$: copper telluride, $Cu_{2.72}Te_2$, vulcanite, CuTe, anilite, Cu_7S_4 and digenite, $Cu_{1.8}S$.

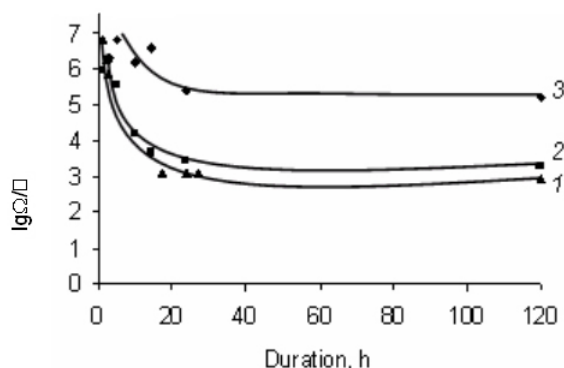


Figure 20. Dependance of Log sheet resistance of chalcogenide layers on PA surface on the exposure time. The concentration of precursor solution, mol dm^{-3}: 1 – 0.1, 2 – 0.05, 3 – 0.01 ($H_2TeS_4O_6$)

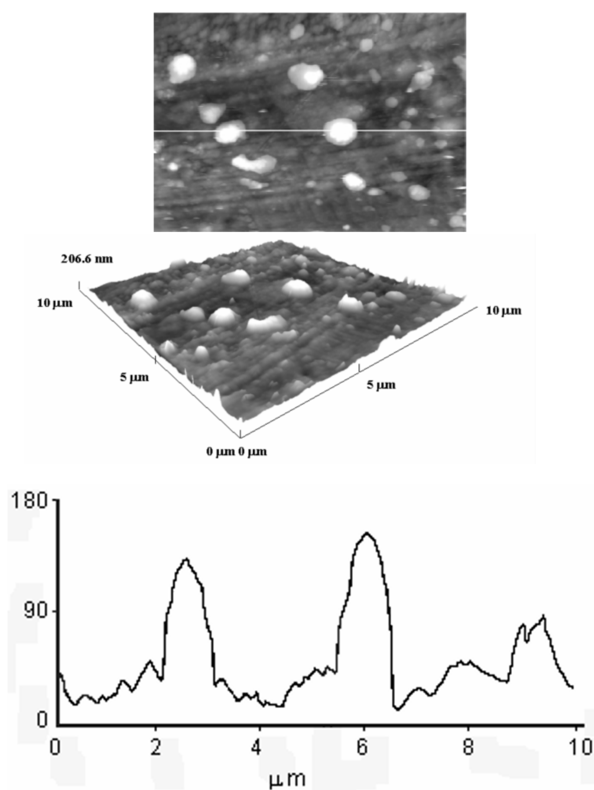


Figure 21. AFM top view of the layers of copper chalcogenides (a) and corresponding section (b)

The formed layers of copper chalcogenides were examined with XRD, which indicated good crystallinity of the layers, prepared by the above method. Characteristic reflections of sulfide (Cu_xS_y) and telluride (Cu_xTe_y) phases were detected. The elemental analysis values of the modified polymer by AA and UV–VIS spectroscopy were in fair agreement with the XRD data which confirmed the formation of mixed copper chalcogenide layers on PA surface.

The electrical resistance of copper chalcogenide layers of various composition, formed at room temperature over a vide concentration range (0.01–0.5 mol dm^{-3}) of precursor solution was measured The use of telluropolyhtionic acid as a new precursor enabled the formation on the surface of PA of an electrically conductive layer of copper sulfides–tellurides with electrical resistance in the range of 4.0×10^{3} kΩ cm^{-2} to 1 kΩ cm^{-2} depending on the concentration of initial precursor solution. This value exhibits a minimum at the exposure time of 120 h for layers containing copper sulfides–tellurides (Fig. 20).

An increase in conductivity of Cu–Te–S of layers on PA surface is accompanied by an increase of the the mass fraction of sorbed tellurium. The resistance value can be easily controlled by controlling the concentration of the original precursor solution and with the exposure time. Formation of copper chalcogenide layers on PA is mainly a surface process.

Atomic force microscopy proves to be a valuable tool for obtaining quantitative surface data. Fig. 21 illustrates the 10 µm×10 µm top view image of the chalcogenides layers together with thier representation of roughness. Analysis of this section was performed from the lower left to the upper right position of the top view image. It is evident that the layers consist of interconnected grain particles fused together, possessing an average grain diameter of about 25 nm. This value is in agreement with X-ray diffraction results. Their height is shown in a histogram with a Gaussian-like distribution with a max at 160 nm. The rms value (where rms is defined as the standard deviation of the Z values, Z being the total height range analysed) of 206.6 nm depicts that the copper chalcogenides layers on PA surface show high surface characteristics.

4. Conclusions

1. Investigation of sorption processes of tellurium- and sulphur- containing particles into polyamide 6 (PA) from acidified solutions of potassium and sodium telluropentathionates ($K_2TeS_4O_6$ and $Na_2TeS_4O_6$) and telluropentathionic acid ($H_2TeS_4O_6$) have confirmed that telluropentathionate anions sorb–diffuse into PA treated with the solutions of telluropentathionates. The concentration of sulfur and tellurium in PA sorbed from $Na_2TeS_4O_6$, $K_2TeS_4O_6$ and $H_2TeS_4O_6$ solutions increases with increasing time of treatment and the concentration of precursor solution.

2. Optical adsorption spectra of chalcogens films on PA revealed that films have high absorbance (10^{4} cm^{-1}) indicating direct band gap transition. IR spectra of modified PA show that a new material chemically bonds with PA functional groups after chalcogenization.

3. Copper sulfide–copper telluride, Cu_xS–Cu_yTe,

layers of various composition form on PA surface when the polymer chalcogenized in $K_2TeS_4O_6$, $Na_2TeS_4O_6$ and $H_2TeS_4O_6$ solutions is treated with Cu(II/I) salts solution. The concentration of copper in copper chalcogenide layers depends on chalcogen concentrations in PA and it increases with the increase of the latter.

4. The phase change of composition of the layers depends on the concentration and temperature of precursor solution and on the duration of treatment in it. Cu_xS−Cu_yTe layers formed using $K_2TeS_4O_6$ solutions are composed of copper sulfides – *chalcocite*, Cu_2S, *djurleite*, $Cu_{1.9375}S$, *anilite*, $Cu_{1.75}S$, *villamanite*, CuS_2 and of copper tellurides – *vulcanite*, CuTe, Cu_4Te_3, $Cu_{1.80}Te$ and $Cu_{1.85}Te$. Four phases of copper tellurides ($Cu_{3.18}Te_2$, $Cu_{2.72}Te_2$, Cu_2Te, *vulcanite*, CuTe) and three phases of copper sulfides (*anilite*, Cu_7S_4, *djurleite*, $Cu_{1.9375}S$, and $Cu_{1.8}S$) have been identified in the layers formed using $Na_2TeS_4O_6$ solutions. The Cu–Te–S layers formed using solutions of $H_2TeS_4O_6$ have binary phases such as Cu_2Te, $Cu_{3-x}Te_2$, $Cu_{2-x}S$: copper telluride, $Cu_{2.72}Te_2$, *vulcanite,* CuTe, *anilite,* Cu_7S_4 and *digenite,* $Cu_{1.8}S$.

5. Electrical resistance of chalcogenide layers formed using potassium telluropentathionate solutions varies from 1.1×10^3 kΩ cm^{-2} to 1.5 kΩ cm^{-2}. Resistance of those formed using sodium telluropentathionate solutions ranges from 1.19×10^3 kΩ cm^{-2} to ~2 kΩ cm^{-2}. The use of telluropentathionic acid as precursor enables the formation of electrically conductive layer of copper sulfides–tellurides with electrical resistance in the range of 4.0×10^3 kΩ cm^{-2} – 1 kΩ cm^{-2}. The sheet resistance depends on the conditions of PA interaction with PA initial chalcogenization solutions.

6. The formation of copper chalcogenide layers proceeds irregularly in the form of islands which grow into larger agglomerates. The surface of the layer formed is uneven and rough. The maximum height of the layer slightly decreases (225–160 nm) with prolonging PA treatment in $K_2TeS_4O_6$ solution. A more significant reduction (220–80 nm) of the layer height occurs upon increasing the concentration of chalcogenization solution. The same tendency was noted in changes of the roughness. The layer height (90–160 nm) and roughness with increasing the temperature changed irregularly.

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

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