Modification of polyamide films by copper chalcogenide layers with the use of potassium selenopentathionate

Neringa Petrašauskienė,

Vitalijus Janickis*

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

Selenopentathionate anions are sorbed–diffused into polyamide films treated with solutions (0.025–0.2 mol · dm^{-3}, 30–50 °C) of potassium selenopentathionate, $K_2SeS_4O_6$, not acidified or acidified with hydrochloric acid. Sorption–diffusion from acidified solutions proceeds more intensively: the concentrations of selenium and sulfur diffused from an acidified solution are about 5 times higher as compared with those obtained using a non acidified solution of the same concentration and at the same temperature. The concentration of sorbed selenopentathionate ions increases with increasing the temperature and concentration of $K_2SeS_4O_6$ solution and the duration of treatment. The $SeS_4O_6^{2-}$ anions diffused into polyamide gradually decompose, and the decomposition products – sulfate ions and SO_2 – are washed out from the polymer, but elemental selenium remains in it. Therefore, the polyamide films, depending on the degree of $SeS_4O_6^{2-}$ ion decomposition, change from colourless to yellow, brown or red. Copper sulfide and copper selenide layers are formed in the surface of polyamide film if the chalcogenized polymer is treated with a water solution of copper(II / I) salt: the anionic particles containing sulfur and selenium atoms of low oxidation state react with the copper ions. The conditions of polymer initial chalcogenation (the concentration and temperature of $K_2SeS_4O_6$ solution) determine the amount of copper and the composition of chalcogenide layer: the content of copper in the polyamide film increases with an increase of the concentration and temperature, and varies from $0.2 \cdot 10^{-2}$ to $33.5 \cdot 10^{-2}$ mg/cm^2. Results of X-ray structural analysis confirmed formation of mixed copper sulfide – copper selenide layers in polyamide surface. The phase composition of the layer changes depending on the duration of initial treatment in $K_2SeS_4O_6$ solution: $Cu_xS–Cu_ySe$ layers are composed of the low-conductive chalcocite, Cu_2S, electrically conductive digenite, $Cu_{1.8}S$, djurleite, $Cu_{1.9375}S$, anilite, $Cu_{1.75}S$, and of copper selenides – bellidoite, Cu_2Se, umangite, Cu_3Se_2, klockmannite, $CuSe$, krutaite, $CuSe_2$ and Cu_2Se_x. Therefore, the phase composition determines the electrical characteristics of the layers: their sheet resistance may vary from 12.2 Ω / □ to 4.8 MΩ / □. The determination of layer composition (to a depth of 1 nm) studied by the method of X-ray photoelectron spectroscopy confirmed the formation of copper sulfides and selenides of various phases. The determined regularities enable formation by the sorption–diffusion method of mixed copper sulfide and copper selenide layers of a desirable composition and electrical conductance, using selenopentathionate as a polyamide chalcogenation agent.

Key words: selenopentathionate, polyamide, sorption-diffusion, copper chalcogenides layers

---

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

INTRODUCTION

Polymeric materials are distinguished by a variety of properties; for example, they are elastic, light, environmentally resistant, etc. The modification of polymers by formation in their surface of thin layers of compounds with important physical properties leads to obtaining composites with different properties. The interest in Cu_xS and Cu_ySe thin films was previously focused mostly on their possible use in solar cells [1–5]. Chemically deposited Cu_xS thin films have been found to possess nearly ideal solar control characteristics: transmittance in the visible region of 20–50%, low transmittance (10–20%) in the infrared region, low reflectance (<10%) in the visible region so as to avoid glare, and a relatively high reflectance (>15%) in the near-infrared region [6]. $Cu_{2-x}Se$ films are typically of p-type, highly conducting semitransparent semiconductors with the band gap varying between 1.1 and 1.4 eV, suitable for solar energy conversion and as a semitransparent layer in high speed detectors working in the visible range [7, 8]. More recently, their applications in solar control coatings for architectural and automobile glazings [9–11], in transparent and conductive coatings on glass, polymers, and as elastic thin film Cu sensor electrodes [12–14], in the production of electronic and optical devices, thermoelectric converters [15–17] have been reported.

Various methods were used for the formation of copper sulfide and copper selenide layers on various dielectrics and on the polymers, among them vacuum evaporation [8, 18], activated reactive evaporation [19], spray pyrolysis [20], electroless deposition [21, 22], successive ionic layer adsorption and reaction (SILAR) [23, 24], chemical bath deposition [25–32]. Methods of copper sulfide coating were reviewed in the works [25–27, 29, 30, 32].

The sorption–diffusion methods for the formation of thin semiconductive and electrically conductive layers of copper sulfide and copper selenide in the surface of polyamide 6 (PA), based on the experience in the chemistry of polythionates and selenopolythionates gained in the previous decades [33–35] and in the last years at the Department of Inorganic Chemistry of the KTU were studied. Using these methods, a PA film is first treated with a solution of polythionic acids, $H_2S_nO_6$ (n is the average number of sulfur atoms in the molecule), containing chains of divalent sulfur atoms in a low oxidation state in the molecule [36] when the goal is formation of sulfide layers [37, 38], whereas, for the formation of copper selenide layers in the surface of PA [39–41], the latter is treated with a solution of potassium selenotritionate, $K_2SeS_2O_6$, containing one divalent selenium atom of a low oxidation state $^-O_3S–Se–SO_3^-$ [42] in the first stage of the process. However, the formation of mixed copper sulfide – copper selenide layers in the surface of PA at the beginning of our studies in this direction [43] was not studied, although the similarity of sulfur and selenium atoms and their ability to replace each other in various mo-lecules was obvious and could be illustrated by the existence of relatively stable cycloocta $Se_{8-x}S_x$ molecules [44].

A mixed chain of three divalent chalcogen atoms of a low oxidation state is present in the anion of salts of mon-oselenopentathionic acid, $H_2SeS_4O_6$, [36, 45]. Thus, it was reasonable to apply these compounds for the formation of mixed copper sulfide – copper selenide layers in the surface of PA films.

The aim of the present work was to summarize, review and discuss the results obtained by us while studying the process of sorption–diffusion of selenopentathionate ions into PA, also formation processess of mixed copper sulfide – copper selenide layers in the surface of PA tapes and the characterization of the obtained copper chalcogenide layers, since only separate fragments of these studies were described in our previous publications [46–49]. The chemical and phase composition of $Cu_xS–Cu_ySe$ layers, their electrical conductance were studied by the methods of atomic absorption spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy (XPS), electron microscopy and by measuring the electrical sheet resistance.

EXPERIMENTAL

Copper sulfide – copper selenide layers were deposited on a PA PK-4 (specification TY 6-05-1775-76) tape 70 μm thick. Samples 15 × 70 mm in size were used. Before chalcogenation, they had been boiled in distilled water for 2 h to remove the remainder of the monomer. Then they were dried using filter paper and then over $CaCl_2$ for 24 h. Distilled water, reagents of the "especially pure", "chemically pure" and "analytically pure" grades were used in the experiments.

The potassium selenopentathionate salt, $K_2SeS_4O_6 \cdot 1.5H_2O$, was prepared and chemically analysed according to published procedures [50].

Samples of PA film were chalcogenized in 0.025, 0.05, 0.1 and 0.2 mol $\cdot$ dm^{-3} solutions of $K_2SeS_4O_6$ acidified with the addition of HCl (0.1 mol $\cdot$ dm^{-3} HCl, pH ~ 1,5) and without acid addition at a temperature of 30, 40 and 50 °C. The total duration of experiments was 4.5 h.

For the formation of $Cu_xS–Cu_ySe$ layers, samples of chalcogenized PA were treated with a Cu(II / I) salt solution at a temperature of 78 °C. The Cu(II / I) salt solution was prepared from crystalline $CuSO_4 \cdot 5H_2O$ and a reducing agent, hydroquinone [25]. It is a mixture of univalent and divalent copper salts in which, independently of temperature, 0.34 mol/dm^3 Cu(II) salt and 0.06 mol/dm^3 Cu(I) salt are present [51]. After having been kept in $K_2SeS_4O_6$ solution, the samples were treated with a Cu(II / I) solution, then rinsed with distilled water, dried over $CaCl_2$ and used in subsequent experiments.

The content of selenium and copper in a PA sample was determined using an atomic absorption Perkin–Elmer 503 spectrometer [52]. A PA sample, first treated in the solution of selenopentathionate and then with a solution of Cu(II / I)

salt, was dissolved in concentrated nitric acid, and the selenium and copper present in the resulting solution were determined with an atomic absorption spectrometer. The concentration of sulfur in PA was determined nephelometrically as described in [53].

The resistance of $Cu_xS–Cu_ySe$ layers of different composition to the constant current was measured on an E7–8 numerical measuring device with special electrodes.

The phase composition of the copper sulfide – copper selenide layer was investigated by X-ray diffraction using a DRON–6 diffractometer (radiation Cu–K_α). X-ray diffractograms of PA samples with Cu_xS layers were treated using the Search Match, ConvX, Xfit, Dplot95 and Photo Styler programs to eliminate the maxima of PA. XPS spectra of $Cu_xS–Cu_ySe$ layers were recorded with an ESCALAB MKII spectrometer (VG Scientific, Mg K_α radiation 1253.6 eV, output 300 W). Vacuum in the analysing chamber was kept at a level of $1.33 \cdot 10^{-8}$ Pa, the distribution of elements in the depth was determined by sputtering with an Ar^+ gun with the ion energy of about 1.0 keV. Samples were etched in a preparation chamber with the vacuum $9.3 \cdot 10^{-3}$ Pa and current 20 μA; the duration of etching was 10 s. The maximum accuracy of the method is ±0.1 at. %. To investigate the layers obtained by the XPS method, the photoelectron spectra of Cu $2p_{3/2}$, Se $3d_{5/2}$ and S 2p were recorded. Empirical sensitivity factors for these elements were taken from the literature [54], and the spectra obtained were compared with the standard ones [55].

Three reactions were studied while investigating the interaction of $SeS_4O_6^{2-}$ ions with Ag^+, Cu^+ ions and with a mixture of Cu^{2+} / Cu^+ ions. The $K_2SeS_4O_6 \cdot 1.5H_2O$ 0.1 mol $\cdot$ dm^{-3} solution (5 mmol) was treated with: 1) 0.4 mol $\cdot$ dm^{-3} (20 mmol) and 0.6 mol $\cdot$ dm^{-3} (30 mmol) solutions of $AgNO_3$; 2) 0.6 mol $\cdot$ dm^{-3} (30 mmol) and 0.8 mol $\cdot$ dm^{-3} (40 mmol) Cu^+ salt solution ; 3) 0.6 mol $\cdot$ dm^{-3} (30 mmol) and 0.8 mol $\cdot$ dm^{-3} (40 mmol) solution of Cu^{2+} / Cu^+ salts [51]. The solutions with the precipitates to reach the completeness of the reactions were kept for 24 h. The filtered of precipitates were dried at a temperature of 60 °C until the constant weight, and the phase composition was determined by the X-ray diffraction method.

RESULTS AND DISCUSSION

The modification of PA film by the formation in its surface of mixed copper sulfide – copper selenide layers was performed in two stages. In the first stage, the PA film was treated in a solution of potassium selenopentathionate, and sulfur and selenium containing anions sorbed–diffused into the PA surface matrix layer. In the second stage, the chalcogenized PA film was treated with a water solution of Cu(II / I) salt: the interaction of copper ions with the sulfur and selenium atoms of low oxidation state, present in the sorbed selenopentathionate ions, leads to the formation of mixed copper sulfide – copper selenide layers of various chemical, phase composition and electrical conductance in the surface of the polymer. The vis-

ual examination of the PA samples gave the first indications that the selenopentathionate ions had been sorbed–diffused into the films: colourless PA films, depending on the concentration of sorbed–diffused $SeS_4O_6^{2-}$ ions, gradually acquired a yellow, brown or red (liberation of red amorphous selenium) colour.

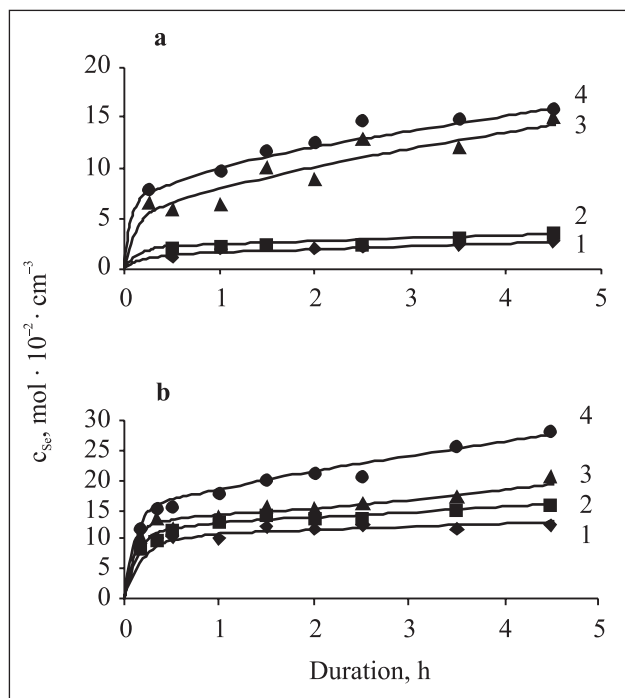The sorption–diffusion of selenopentathionate ions from non-acidified $K_2SeS_4O_6$ solutions was studied first. 0.025–0.2 mol $\cdot$ dm^{-3} $K_2SeS_4O_6$ solutions at a temperature of 50 °C were used to study the influence of solution concentration. The choice of such an interval of concentration was dictated by the stability of $K_2SeS_4O_6$ solution. By preliminary experiments it was determined that the sorption–diffusion using solutions of a lower concentration was too slow and insufficient, but at higher concentrations (>0.2 mol $\cdot$ dm^{-3}) of solution its stability decreased. The mass of PA tapes increased during treatment in $K_2SeS_4O_6$ solution: the weight (Δm) increased with increasing the concentration of $K_2SeS_4O_6$ solution. The concentration of selenium in PA increased with increasing the concentration of chalcogenation solution (Fig. 1a), but the saturation of PA tape was not reached even during 4–5 h from the beginning of the experiment when the solutions of a higher concentration (0.1 and 0.2 mol $\cdot$ dm^{-3}) were used. A constant sulfur concentration in PA at a temperature of 50 °C was reached as soon as after ~1 h (Fig. 2a). This may be explained by a change (reduction) of the S / Se molar ratio with time as a result of a gradual decomposition of sorbed–diffused $SeS_4O_6^{2-}$ ions. At the beginning of the experiment (up to about 1 h), the S : Se ratio was close to 4, i. e. to the stoichiometrical ratio in the $K_2SeS_4O_6$ molecule. With the prolongation of the experiment, and more noticeably after 1.5–2 h, this ratio decreased, and the decrease was more significant when the concentration of the initial $K_2SeS_4O_6$ solution was higher, implying that the decomposition of $SeS_4O_6^{2-}$ ions diffused into PA starts about 1 h after the beginning of the experiment [56]:

$$SeS_4O_6^{2-} \rightarrow S_4O_6^{2-} + Se, \tag{1}$$
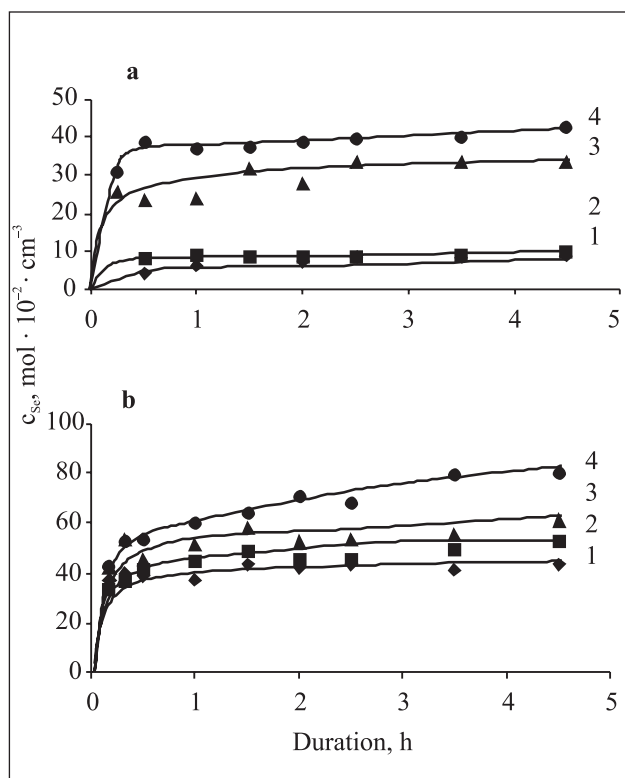$$S_4O_6^{2-} \rightarrow SO_4^{2-} + SO_2 + 2\,S. \tag{2}$$

PA tapes changed from colourless to yellow and gradually acquired the red colour (amorphous selenium).

The products of the decomposition (SO_4^{2-} ions and SO_2) are washed out from the polymer. The value of the S / Se molar ratio, at least during the first hour, remains rather close to the initial one in the undecomposed selenopentathionate ion: the sulfur concentration in PA until 1 h was increasing.

Our studies have shown that the stability of $K_2SeS_4O_6$ solution decreases with an increase of its concentration: the solution gradually acquires the yellow colour and later, after the beginning of elemental selenium liberation, becomes red-coloured. 0.025 mol $\cdot$ dm^{-3} $K_2SeS_4O_6$ solution at a temperature of 50 °C remains clear throughout the whole experiment (4.5 h); the decomposition of 0.05 mol $\cdot$ dm^{-3} solution starts after ~2 h, of 0.1 mol $\cdot$ dm^{-3} solution after 1 h, and of
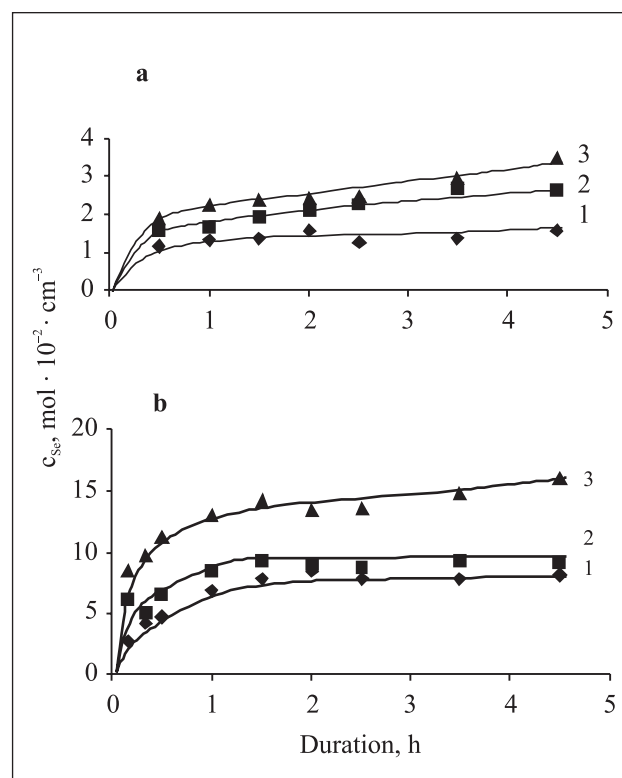
Fig. 1. Changes of selenium concentration in PA with time during its treatment with non-acidified (*a*) and acidified (*b*) $K_2SeS_4O_6$ solution of different concentration at 50 °C. Concentration of $K_2SeS_4O_6$ solution, mol · dm⁻³: *1* – 0.025; *2* – 0.05; *3* – 0.1; *4* – 0.2

0.2 mol · dm⁻³ solution already after 20 min. Therefore, in other experiments while studying the influence of temperature on the sorption–diffusion of selenopentathionate ions into PA, we used more stable 0.05 mol · dm⁻³ solutions of $K_2SeS_4O_6$ at a temperature of 30–50 °C. Such an interval of temperatures was chosen because the sorption–diffusion at a lower temperature was too slow and the stability of solution at a higher temperature was low. The data presented in Fig. 3a show that the saturation of PA tape with selenium during 4.5 h was reached only at a temperature of 30 °C, and the maximum value of c_{Se} was ~1.1 mg · cm⁻³.

An increase of the chalcogenation solution temperature, as expected, led to an increase of selenium concentration in PA. For example, the concentration of Se after 3.5 h of chalcogenation at a temperature of 50 °C was twice higher as compared with that at 30 °C (Fig. 3a, curves 1, 3). However, no saturation of polymer with selenium at 40 and 50 °C in the conditions of the experiment was obtained (Fig. 3a, curves 2, 3). This was confirmed by the analytically determined values of the S / Se molar ratio: after 1.5 h at 30 °C S / Se = 3.93, at 40 °C – 3.89 and at 50 °C – 3.74; at the end of the experiment (4.5 h) the S / Se values were respectively 3.21, 3.09 and 2.51. This means that diffused $SeS_4O_6^{2-}$ ions at a higher temperature decompose according to equation (1) faster, and the values of S / Se, after the products of SO_2 and SO_4^{2-} decomposition have been gradually washed out, are lower.

Fig. 2. Changes of sulfur concentration in PA during its treatment with non-acidified (*a*) and acidified (*b*) $K_2SeS_4O_6$ solution of different concentration at 50 °C. Concentration of $K_2SeS_4O_6$ solution, mol · dm⁻³: *1* – 0.025; *2* – 0.05; *3* – 0.1; *4* – 0.2

Fig. 3. Changes of selenium concentration in PA with time during its treatment with non-acidified (*a*) and acidified (*b*) 0.05 mol · dm⁻³ solution of $K_2SeS_4O_6$ at different temperatures. Temperature, °C: *1* – 30; *2* – 40; *3* – 50

The concentration of sulfur diffused into PA increases with increasing the chalcogenation solution temperature, too (Fig. 4a). In the temperature interval studied, the PA film was saturated with sulfur after 2 h. The reason may be (as mentioned above) the changed values of the S / Se molar ratio in the polymer with time, which is caused by the gradual decomposition of diffused $SeS_4O_6^{2-}$ ions. The $K_2SeS_4O_6$ solution at 30 °C remains clear during the whole experiment (4.5 h), its decomposition at 40 °C begins after 3 h and at 50 °C after 2 h. It has been determined earlier [57] that PA films under the effect of hydrochloric acid undergo amorphization and swelling. The degree of swelling increases with increasing the temperature, and the protonization of nitrogen atoms of amide groups, during which the amorphization takes place, begins without destroying the polymer.

An analogous effect of selenopolythionates on the structure of PA increases with decreasing the solution pH value (increasing its acidity), but the influence of the solution concentration is not significant [57]. Therefore, it was reasonable to expect a more easy sorption–diffusion of selenopentathionate ions into PA from acidified solutions, because the polymer structure changes as compared with the efficiency of the process using a non-acidified $K_2SeS_4O_6$ solution. In the works of O. Foss [50, 58] it has been shown that hydrogen ions do stabilize the anion of selenopentathionate. It has been also determined [56] that the decomposition of selenopentathionate at the solution pH < 5 is very slow, and its degree

at the lower values of solution pH is even less. Thus, the use of acidified $K_2SeS_4O_6$ solutions could result in a more intensive sorption–diffusion of selenopentathionate ions into PA.

An increase in the mass of PA samples with increasing $K_2SeS_4O_6$ solution concentration and temperature was determined while studying the sorption–diffusion of selenopentathionate ions from acidified solutions. The influence of temperature was more pronounced at the beginning of the experiment (up to 1.5 h). The increase of mass while increasing temperature from 30 to 50 °C after 0.5 h from the beginning of the experiment was ~4.5 times higher. This difference with the time of the experiment decreased and at the end disappeared. The most reasonable explanation is a faster saturation of PA with $SeS_4O_6^{2-}$ ions at a higher temperature.

One can see (Fig. 1b) that changes of selenium concentration in PA kept in a $K_2SeS_4O_6$ solution of different concentration are similar. Selenium concentration in PA increased most rapidly during the first 30 min, but in conditions of our experiments, which lasted 4.5 h, no saturation was attained.

The increase of $K_2SeS_4O_6$ solution temperature accelerated also the sorption–diffusion of selenopentathionate ions. The concentration of Se at the beginning of the experiment (up to 1 h) increased twice and at the end (after ~4 h) ~1.4 times (Fig. 3b) with increasing the temperature by 20 °C. The increase of sulfur concentration in this case was even more pronounced and reached ~3.3 and ~5 times, respectively (Fig. 4b, curves 1 and 3). The different changes of Se and S concentrations may be explained by the faster decomposition of $SeS_4O_6^{2-}$ ions at a higher temperature.

Acidified $K_2SeS_4O_6$ solution, as expected, was found to be more stable: 0.025 and 0.05 mol · dm^{-3} solutions did not decompose during the whole experiment; a gradual liberation of red amorphous selenium from 0.1 mol · dm^{-3} solution started after 2 h and from 0.2 mol · dm^{-3} solution after 1 h. The changes of sulfur and selenium S / Se molar ratios diffused into PA confirmed the results of visual observations. The value of this ratio slightly decreased with increasing the temperature and duration, but even after 4.5 h this ratio was ~3.3 when the 0.05 mol · dm^{-3} $K_2SeS_4O_6$ solution at 50 °C was used. The value of S / Se ratio decreased more rapidly when the $K_2SeS_4O_6$ solution of a higher concentration was used: in cases of 0.1 mol · dm^{-3} and 0.2 mol · dm^{-3} solutions, after 4.5 h of experiment its values were 2.97 and 2.81 respectively.

A comparison of the kinetic curves of changes of selenium and sulfur concentrations in PA, obtained using non-acidified and acidified $K_2SeS_4O_6$ solutions of analogous concentration and temperature (Fig. 1–4), has shown that in the case of acidified solutions ~5 times higher sorbed–diffused concentrations of selenium and sulfur and thus of selenopentathionate ions were obtained. A possible reason, as mentioned above, may be PA amorfization and swelling under the effect of hydrochloric acid, allowing an easier penetration of selenopentathionate ions into the polymer.
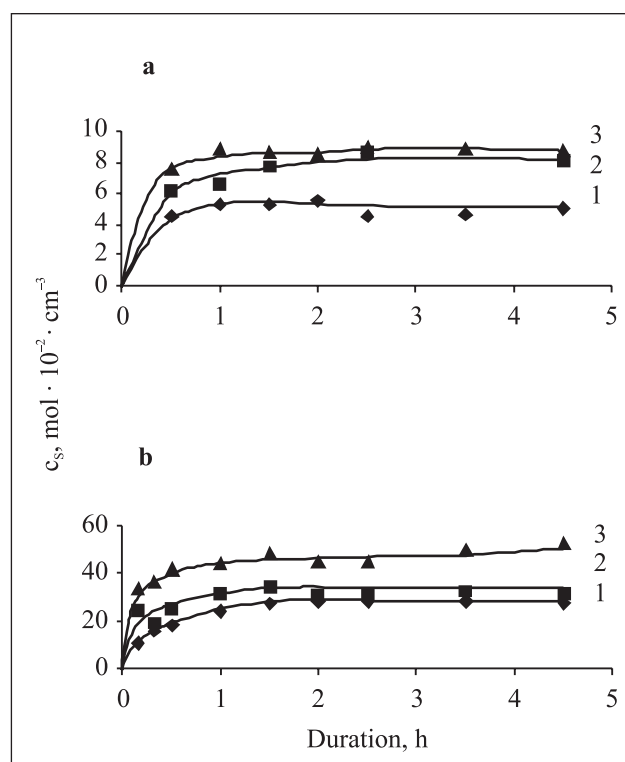

Fig. 4. Changes of sulfur concentration in PA with time during its treatment with non-acidified (*a*) and acidified (*b*) 0.05 mol · dm^{-3} solution of $K_2SeS_4O_6$ at different temperatures. Temperature, °C: *1* – 30; *2* – 40; *3* – 50

The apparent sorption–diffusion coefficient (D) and the apparent activation energy (E) for the characterization of the sorption–diffusion of selenopentathionate ions into PA film were calculated [59]. The calculated values (using data of Fig. 5) of the thermal effect ($\Delta H_{Se} = -40.66$ kJ $\cdot$ mol^{-1}) and activation energy ($E_{Se} = 20.8$ kJ $\cdot$ mol^{-1}) of selenium sorption–diffusion into PA were a few times higher as compared with those calculated while studying the sorption–diffusion of selenotrithionate ions ($SeS_2O_6^{2-}$) into PA: $E_{Se} = 2.1$ kJ $\cdot$ mol^{-1}, $\Delta H_{Se} = -5.36$ kJ $\cdot$ mol^{-1} [39]. This is reasonable, considering the bigger size of selenopentathionate ions. The apparent diffusion coefficient increased with increasing $K_2SeS_4O_6$ solution concentration (in the case of non-acidified solution D = $1.6 \cdot 10^{-8} - 2.8 \cdot 10^{-8}$ cm$^2 \cdot$ s^{-1}, in the case of acidified solution D = $3.7 \cdot 10^{-8} - 5.3 \cdot 10^{-8}$ cm$^2 \cdot$ s^{-1}) and temperature (for non-acidified solution D = $1.2 \cdot 10^{-8} - 2.0 \cdot 10^{-8}$ cm$^2 \cdot$ s^{-1} and for acidified solution D = $2.4 \cdot 10^{-8} - 4.1 \cdot 10^{-8}$ cm$^2 \cdot$ s^{-1}), but its values were significantly lower than those calculated in cases of a smaller sorption–diffusion of selenotrithionate ions into PA [39]. The value of solution pH significantly influenced the diffusion coefficient of $SeS_4O_6^{2-}$ ions: it increased several times when the value of solution pH was reduced from 5 to 1.5. For example, the value of D = $2.0 \cdot 10^{-8}$ cm$^2 \cdot$ s^{-1} in the case of PA modification by the non-acidified 0.05 mol $\cdot$ dm^{-3} $K_2SeS_4O_6$ solution at 50 °C and D = $4.1 \cdot 10^{-8}$ cm$^2 \cdot$ s^{-1} when an acidified solution of selenopentathionate of the same concentration and temperature was used.

Summarizing the results of the first stage of PA tape modification, chalcogenation, we may conclude that the water solution of potassium selenopentathionate is a suitable agent for introducing into the PA surface matrix layer divalent atoms of sulfur and selenium of low oxidation state: $SeS_4O_6^{2-}$ ions sorb–diffuse into a PA film treated with a non-acidified or acidified solution of potassium selenopentathio-nate of various concentration and temperature.

The obtained concentrations of selenopentathionate ions in the PA enabled us to modify the surface of this polymer with thin electrically conductive mixed copper sulfide – cop-per selenide layers. As mentioned above, the second stage of PA film modification is the treatment of the chalcogenized film with a water solution of copper(II / I) salts, resulting in the formation of a $Cu_xS–Cu_ySe$ layer on its surface.

The conditions of treatment of chalcogenized PA samples with a solution of Cu(II / I) salts which enable the formation in the polymer surface of copper chalcogenide coatings of a lower electrical resistance were determined in our previous works [39–41]. In these studies, solutions of selenotrithionate, $SeS_2O_6^{2-}$, the first member of the selenopolythionate homologue series $SeS_nO_6^{2-}$ ($n = 2, 3, 4$) were used. Since selenopentathionate belongs to this series of homologues ($n = 4$), PA samples chalcogenized in $K_2SeS_4O_6$ solution were treated with a solution of Cu(II / I) salts in the same experimental conditions as in our previous works [39–41], i. e. for 10 min at a temperature of 78 °C. The $Cu_xS–Cu_ySe$ layer on the PA film is formed during the interaction of the chalgenized polymer with copper ions. The anionic particles containing selenium and sulfur atoms of a low oxidation state react with copper ions and give copper sulfides and copper selenides of various composition. While studying the influence of the concentration and temperature of the chalcogenation agent on the properties of $Cu_xS–Cu_ySe$ layers, experiments with PA samples initially treated with non-acidified and acidified solutions of $K_2SeS_4O_6$ were performed.

We have found that the content of chalcogenide copper in PA tape samples initially treated with an acidified solution of $K_2SeS_4O_6$ is higher compared with samples initially treated with a non-acidified selenopentathionate solution. For example, m_{Cu} is ~14 times higher in PA initially treated with a 0.05 mol $\cdot$ dm^{-3} acidified $K_2SeS_4O_6$ solution at 50 °C compared with the content of copper in PA treated with a non-acidified solution in the same experimental conditions (Fig. 6, curve 3; Fig. 7, curve 3). The reason is the higher concentration of PA $SeS_4O_6^{2-}$ ions sorbed from the acidified $K_2SeS_4O_6$ solution.

An increase of the temperature increases the m_{Cu} only in PA samples treated with a non-acidified $K_2SeS_4O_6$ solution (Fig. 6).

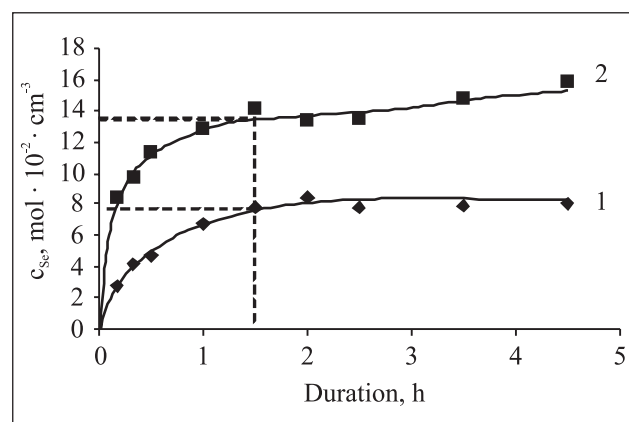**Fig. 5.** Changes of selenium concentration in PA with time during its treatment with acidified $K_2SeS_4O_6$ solution of different temperature. Temperature of $K_2SeS_4O_6$ solution, °C: *1* – 30; *2* – 50

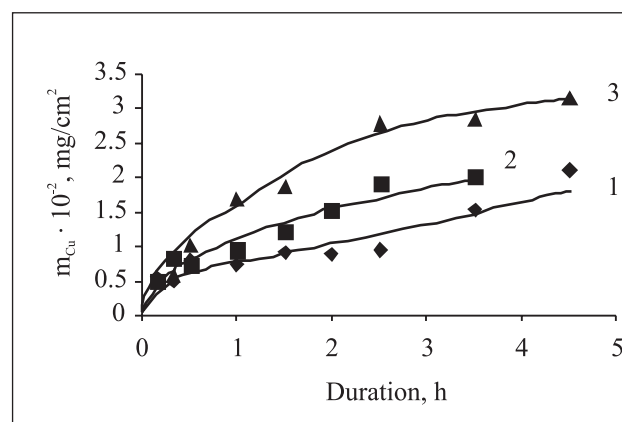**Fig. 6.** Changes of copper content in PA with time. PA was initially treated with non-acidified 0.05 mol $\cdot$ dm^{-3} $K_2SeS_4O_6$ solutions at different temperatures and later with a solution of Cu(II / I) salt. Temperature, °C: *1* – 30; *2* – 40; *3* – 50

The content of copper in PA samples treated with an acidified chalcogenation solution increases continuously only in case the experiment is carried out at a temperature of 30 °C (Fig. 7, curve 1). At a higher temperature, an increase of m_{Cu} is observed only in PA tapes sulfured for up to 1 h (Fig. 7, curves 2 and 3). In PA tapes chalcogenized at a temperature of 40 °C, the content of copper reaches its maximum value in films sulfured for about 1 h and later remains almost constant, and in films chalcogenized at 50 °C the content of copper gradually decreases. The reason may be the known decrease of the stability of $SeS_4O_6^{2-}$ ions with an increase of the solution temperature: these ions gradually decompose (equations 1 and 2), and selenium at the beginning is liberated in a more reactive red amorphous form. Later, under the effect of temperature, it is transformed into a nonreactive black trigonal modification which does not interact with Cu(II / I) salts.

The decomposition of $SeS_4O_6^{2-}$ ions in acidified $K_2SeS_4O_6$ solutions of a higher concentration is faster, too. But the m_{Cu} values in PA films chalcogenized up to 2 h (until the beginning of Se liberation) are higher. The reason is an increasing influence of H^+ and selenpolythionate ions on the structure of PA [57] (amorphization of the structure) with an increase of the concentration of these ions. An exception is acidified $0.05 \, mol \cdot dm^{-3} \, K_2SeS_4O_6$ solution since the value of m_{Cu} in PA initially treated with this solution (for up to 2 h) is higher as compared with the case when a $0.2 \, mol \cdot dm^{-3} \, K_2SeS_4O_6$ solution has been used (Fig. 8). Probably, in the solution of this concentration and acidity $SeS_4O_6^{2-}$ ions are most stable, and bigger amounts of copper chalcogenides are formed on the surface of the polymer after interaction with a copper(II / I) salt solution.

Changes of the PA film appearance after its treatment with a Cu(II / I) salt solution indicate also the formation of copper chalcogenide layers on the surface of the polymer. The colour of films from colourless transforms into yellow, then into brown and acquires a metallic lustre. Electrical measurements finally indicate that the films from dielectric turn into semiconductors and conductors.
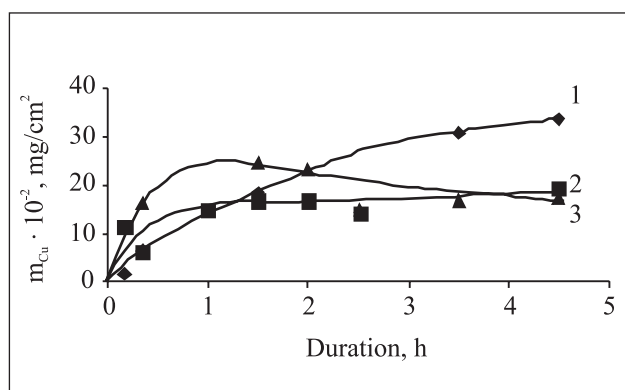
Summarizing the results of PA film modification in the second-stage study, we may conclude that the content of copper is dependent on the conditions of initial PA chalcogenation – on the acidity, concentration and temperature of a $K_2SeS_4O_6$ solution and the duration of treatment with it.

The microscopic analysis of the surface of PA films modified with copper showed that the formation of Cu_xS–Cu_ySe layers was not regular but they were formed as islands. As a result, the layer was not even. This unevenness increases the probability of the layer interaction with the impurities and causes some difficulties in measuring of the surface electrical resistance. A detailed study of the conductivity of Cu_xS–Cu_ySe layers was complicated, therefore, we limited ourselves to measuring the electrical resistance of the external layer of the chalcogenide surface.

The electrical resistance of copper chalcogenide layers in PA initially chalcogenized with non-acidified $K_2SeS_4O_6$ solutions and later treated with a Cu(II / I) salt solution varied from 4.8 MΩ / $\square$ to 4.4 kΩ / $\square$. Rather low values of electrical resistance were measured on chalcogenide layers obtained using acidified $K_2SeS_4O_6$ solutions (Table 1): they varied from 12 to a few hundred Ω / $\square$.

A tendency of electrical resistance decrease with increasing the concentration of the initial chalcogenation solution was observed: an increase of $K_2SeS_4O_6$ solution concentration from 0.025 to 0.2 $mol \cdot dm^{-3}$ decreased the value of the chalcogenide layer electrical resistance, depending on the duration of chalcogenation, three to five times. A direct dependence of the chalcogenide layer resistance on the amount of copper in the layer was observed not in all cases, since copper sulfides and selenides of various stoichiometry and electrical conductivity, and in different amounts may be formed in the surface of PA. It is known [32] that the electrical resistance of Cu_xS decreases one million times with the value of x decreased from 2 to 1.

The results presented above show that after chalcogenization in $K_2SeS_4O_6$ solution and PA treatment with Cu(II / I) salt solution it is possible to form layers of copper sulfides and

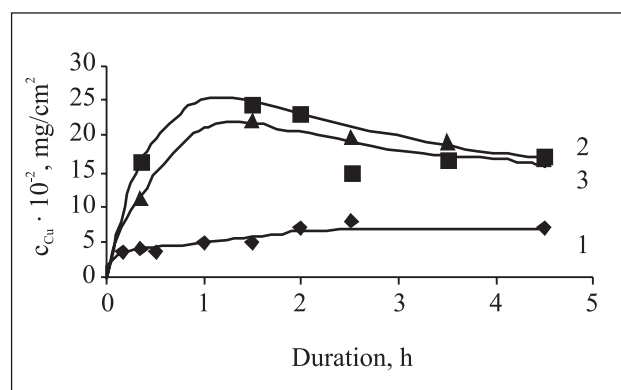**Fig. 7.** Changes of copper content in PA with time. PA was initially treated with acidified 0.05 mol · dm⁻³ K₂SeS₄O₆ solutions at different temperatures and later with a solution of Cu(II / I) salt. Temperature, °C: *1 – 30; 2 – 40; 3 – 50*

Fig. 8. Changes of copper content in PA with time. PA was initially treated with acidified K₂SeS₄O₆ solution of different concentration at 50 °C and later with a solution of Cu(II / I) salt. Concentration, mol · dm⁻³: *1 – 0.025; 2 – 0.05; 3 – 0.2*

Table 1. Dependence of electrical sheet resistance (Ω / $\square$) of the chalcogenide layer formed on PA surface in acidified $K_2SeS_4O_6$ solution at 50 °C and then treated with Cu(I / II) salt solution on the concentration of chalcogenation solution and duration of treatment

Duration of chalco- genation, h	Resistance of the chalcogenide layer formed using a chalcogenation solution of different concentration (mol · dm⁻³) at 50 °C					
	0.025	0.05	0.05 *	0.05 **	0.1	0.2
0.17	122.5	167.5	220.0	465.80	104.0	119.0
0.33	60.5	93.37	212.3	382.7	68.0	130.0
0.5	178.0	88.0	145.8	176.2	48.6	60.0
1.0	99.7	70.39	84.5	148.1	71.0	32.7
1.5	72.0	63.83	54.3	121.4	48.0	19.8
2.0	68.7	61.75	44.2	115.7	52.5	14.4
2.5	61.54	51.78	47.9	148.7	47.0	13.6
3.5	53.6	42.93	42.8	122.6	32.5	12.3
4.5	18.8	60.53	42.7	115.2	20.8	13.0

* The temperature of chalcogenation solution 30 °C.

** The temperature of chalcogenation solution 40 °C.

selenides with the electrical resistance varying from less than 1 kΩ / $\square$ to even a few tenths of Ω / $\square$.

Searching for the information on the phase composition of Cu_xS–Cu_ySe layers, first we tried to simulate the formation process of these layers. We undertook a preparative study of the interaction of $K_2SeS_4O_6$ solution with Ag^+ and Cu^+ ions and with the Cu(II / I) salt solution previously used for the formation of chalcogenide layers in the surface of PA. The reason why the reaction with Ag^+ ions was also studied is that this reaction is one of the most characteristic reactions of polythionates and selenopolythionates [33, 35]: the interaction of any polythionic compound with Ag^+ ions leads to a fast precipitation of silver chalcogenides. The solid state products of the interactions were studied by X-ray diffraction.

The diffractograms of precipitates formed after the interaction of selenopentathionate with Ag^+ ions taken in the molar ratios 1 : 4 and 1 : 6 have shown that they are composed of Ag_2Se, Ag_2S and elemental sulfur. The part of silver sulfide in the second case, i. e. when a larger excess of Ag^+ ions was used, was found bigger. The solid phase product obtained during the interaction of $SeS_4O_6^{2-}$ and Cu^+ ions taken in the molar ratio 1 : 6 was composed of Cu_2S, CuSe, Cu_2Se, elemental selenium and sulfur. When the molar ratio was changed into 1 : 8, i. e. in case when a larger excess of Cu^+ ions had been used, the phases of $Cu_{1.96}S$, CuSe and elemental sulfur, S_8, but no phase of elemental selenium were found. We must point out a certain doubt about the presence of elemental sulfur, since S_8 reacts with Cu(I) ions [51]. During the experiment, small yellow crystals (possibly of sulfur) were detected visually in the filtered precipitate, but the peaks of sulfur in the diffractograms did coincide with the peaks of other phases in many cases. Elemental selenium, according to our experience, does not react with Cu(I) ions, and its peaks in diffractograms coincide also with the peaks of copper chalcogenide phases. Analogous experiments carried out using a solution of Cu^{2+} / Cu^+ salts showed that in the case of the reagents' molar ratio 1 : 6, the solid product consisted of copper sulfides Cu_2S, $Cu_{1.75}S$, copper selenides

Cu_2Se, CuSe and of elemental sulfur. When the molar ratio was changed to 1 : 8, the phases of $Cu_{1.75}S$, $Cu_{1.8}S$, CuSe and elemental S_8 were found in the precipitate. Thus, the data obtained by the preparative method indicate that the solid phase product formed during the interaction of $SeS_4O_6^{2-}$ and Ag^+ ions consists of Ag(I) sulfide and Ag(I) selenide (the oxidation state +1 for silver is very pronounced in the compounds), and of some amount of elemental S_8. Upon changing the Ag^+ ions by Cu^+ ions (the oxidation states of +1 and +2 are common for a copper atom in the compounds), not only both Cu(I) chalcogenides, i. e. Cu_2S and Cu_2Se, but also Cu(II) selenide, CuSe, and some amounts of elemental sulfur and selenium were found in the solid state products of the reaction, implying that part of Cu^+ ions did participate in the redox reaction, resulting in the formation of Cu(II) selenide. The activity of Cu(I) atoms towards elemental sulfur has been studied [51], therefore, probably the redox interaction between Cu^+ ions and a selenium atom of low oxidation state, which is present in the selenopentathionate ion, is also possible. This interpretation has been confirmed by the X-ray diffraction analysis of the precipitate obtained during the interaction of $SeS_4O_6^{2-}$ ions with a larger amount of Cu^+ ions ($SeS_4O_6^{2-}$: Cu^+ = 1 : 8) when all selenium in the Cu(II) selenide, CuSe, was found. Thus, it is reasonable that the interaction of $SeS_4O_6^{2-}$ ions with a mixture of Cu^+ / Cu^{2+} ions (Cu^{2+} ions take a major part in this mixture) resulted in the formation of both Cu(I) and Cu(II) sulfides and selenides.

The phase composition of Cu_xS–Cu_ySe may be qualitatively and approximately quantitatively characterized by X-ray diffraction, but the study of Cu_xS–Cu_ySe layers in the polymer surface faces some difficulties because of the pecularities of these composite materials. First, the sulfide–selenide layers are polycrystalline; second, usually the number of Cu_xS–Cu_ySe phases of different composition and structure are present in the layer. Despite these difficulties, the phase composition of mixed Cu_xS–Cu_ySe layers formed in PA surface was studied by the method of X-ray diffraction since this method had been successfully used

to characterize the phase composition of copper sulfide or copper selenide layers alone in the surface of this polymer earlier [38, 39, 41].

X-ray diffraction analysis of the PA films first treated with the solutions of potassium selenopentathionate for different periods of time at a different temperature and later with a solution of Cu(II / I) salt confirmed the presumption of the formation of mixed $Cu_xS–Cu_ySe$ layers in the surface of the polymer. The phases of monoclinic djurleite, $Cu_{1.9375}S$, (JCPDS 83–1463; $2\theta = 30.6$; 34.2; 38.08), cubic digenite, $Cu_{1.8}S$, (JCPDS 4–861; $2\theta = 37.5$; 46.2), orthorhombic chalcocite, Cu_2S, (JCPDS 2–1272; $2\theta = 32.8$; 45.5; 58.03) and tetragonal belidoite, Cu_2Se, (JCPDS 29–575; $2\theta = 38.681$; 43.3; 44.9) were determined in the copper chalcogenide layer on the surface of PA initially treated at a lower (30 °C) temperature. The concentration of the electrically low conductive chalcocite phase decreased and of the more conductive $Cu_{1.9375}S$, $Cu_{1.8}S$ and Cu_2Se increased when the duration of the initial PA chalcogenation was prolonged. Accordingly, the measured values of the electrical conductivity of the chalcogenide layers in the surface of the modified PA tapes increased with increasing the initial PA chalcogenation time. If the temperature of the initial PA chalcogenation was increased (50 °C), beside the phases mentioned above, also the phases of orthorhombic anilite, $Cu_{1.75}S$, (JCPDS 33–489; $2\theta = 32.1$; 41.6; 43.9), tetragonal umangite, Cu_3Se_2, (JCPDS 19–402; $2\theta = 35.04$; 42.2; 51.3) orthorhombic klokmannite, CuSe, (JCPDS 27–184; $2\theta = 31.1$; 45.9; 49.9) were detected. If the duration of PA chalcogenation was increased to 4.5 h (but the concentration of $K_2SeS_4O_6$ solution and temperature were unchanged), the phase composition of the $Cu_xS–Cu_ySe$ layer remained unchanged, too. However, the concentration of the low conductive chalcocite decreased and of the electrically conductive copper sulfides and selenides in the polymer chalcogenide layer increased. When the PA samples had been initially treated with $K_2SeS_4O_6$ solution of a higher concentration (0.2 mol · dm^{-3}), the concentration of copper selenides in the chalcogenide layer increased with increasing the duration of chalcogenation: the phases of orthorhombic $CuSe_2$ (JCPDS 74–280; $2\theta = 32.5$; 45.71; 56.88) and orthorhombic Cu_2Se_x, (JCPDS 47–1448; $2\theta = 43.99$; 38.7) appear, and the low-conductive chalcocite phase transforms into copper sulfide phases of a higher conductivity. In these conditions, the highest concentrations of electrically conductive copper selenides are formed, and the stoichiometrical composition of copper sulfides, Cu_xS, changes in the direction of x decrease, resulting in the formation of copper chalcogenide layers in the surface of PA with the electrical resistance reaching very low values – even 167–12 Ω / □ (Table 1).

Composition changes of mixed copper sulfide and copper selenide layers determine the electrical conductivity of the layers. A chalcogenide layer of low conductivity (high resistance) is formed on the surface of initially shortly chalcogenized PA. The reason is probably the formation of low conductive chalcocite and of other copper sulfides with the stoichiometry close to that of Cu_2S at the beginning of the process. When the duration of PA initial chalcogenation is prolonged and the concentration of chalcogenation solution is increased, the formation of more conductive copper selenides is observed, and not-conductive copper sulfide phases transform into higher conductivity phases. PA films modified with such chalcogenide layers are characterized by rather low values of electrical resistance.

The determined formation regularities of $Cu_xS–Cu_ySe$ layers enable to select conditions under which semiconductive and electrically conductive mixed $Cu_xS–Cu_ySe$ layers of a desirable chemical and phase composition and of predicted electrical resistance may be formed on polyamide surface.

The phase composition of $Cu_xS–Cu_ySe$ layers studied by the method of X-ray photoelectron spectroscopy (XPS) was limited to a study of the chemical and phase composition of a very thin $Cu_xS–Cu_ySe$ surface layer (up to 1 nm in depth) as compared with the thickness of the whole chalcogenide layer (about few tenths of μm).

When the PA film samples treated in a chalcogenation solution for different periods of time were exposed to a solution of Cu(II / I) salts, formation of a layer composed of different copper, sulfur and selenium compounds took place in the surface of the polymer. The following compounds were identified: Cu_2S, CuS, Cu_2O, CuO, CuSe, Cu_2Se and Se.

As mentioned above, the values of x and y in the $Cu_xS–Cu_ySe$ layers changed from 1 to 2, i. e. nonstoichiometric copper sulfides and selenides were formed. It was impossible from the data of XPS analysis to determine accurately the values of x and y compared with the data obtained by the method of X-ray diffraction which enables a direct identification of various intermediate copper sulfides and selenides.

A study of Cu, S, Se and O distribution in a $Cu_xS–Cu_ySe$ layer has shown (Table 2) that oxygen takes the largest part (49–61 at. %) on the surface of all PA film samples. All processes of copper chalcogenide layer formation proceed in a natural environment. Therefore, it is impossible to prevent the influence of the environment on the chemical composition of the layers. This is the reason for oxygen presence in the surface of a chalcogenide layer. The presence of water connected by the physical and chemical adsorption is also possible. Oxygen in a deeper layer is undoubtly bound into the oxides Cu_2O and CuO. Therefore, the chalcogenide layers in the surface of the polymer are formed in the form of islands which enable an easy contact of the atmospheric oxygen with the ions of copper and chalcogens. The amount of oxygen significantly decreased (1–9 at. %) when the surface of the sulfide layer was etched with Ar^+ ions, showing that oxygen was present only on the surface of the chalcogenide layer. The content of O in the deeper layers was very small and its presence should not influence the chemical composition of the layer and its properties.

Table 2. Data of XPS analysis of Cu$_x$S–Cu$_y$Se layers formed in PA surface

Duration of PA chalcogenation in K$_2$SeS$_4$O$_6$ solution, min	Etching conditions	Element	Content, at %	Binding energy, eV	Composition of the layer
10	Before etching	Cu	11.96	932.1; 933.9	Cu$_2$S, Cu$_2$O,CuO
		S	22.67	161.3; 162.3; 168.5	Cu$_2$Se, CuS
		Se	8.47	54.2; 55.3; 58.5	Se
		O	56.89	530.1; 531.5; 533,5	Cu(OH)$_2$; CuSO$_4$
	After etching	Cu	36.45	932.2	Cu$_2$S, CuS, Cu$_2$O
		S	39.33	161.5; 162.5	Cu$_2$Se, CuS, CuO
		Se	14.82	54.2; 55.4; 56.6	Se
		O	9.38	532.1; 533.8	
60	Before etching	Cu	17.37	932.1; 933.9	Cu$_2$S, CuS, Cu$_2$O
		S	24.65	161.3; 162.3; 168.5	Cu$_2$Se, CuSe
		Se	8.68	55.4; 55.6; 58.2	Se
		O	49.30	529.8; 531.1	CuSO$_4$
	After etching	Cu	50.89	932.2	Cu$_2$S, Cu$_2$O, CuS
		S	34.72	161.5; 162.5	Cu$_2$Se, CuSe
		Se	13.14	54.2; 55.6; 56.9	Se
		O	1.23	531.6	
150	Before etching	Cu	15.57	932.3; 934.0	Cu$_2$S, Cu$_2$O
		S	18.19	161.3; 162.3; 68.7	CuSe, Cu$_2$Se, CuS
		Se	4.50	53.9; 55.3; 58.5	Se
		O	61.72	529.8; 531.2	CuSO$_4$, CuO
	After etching	Cu	46.96	932.3	Cu$_2$S, Cu$_2$O, CuS
		S	32.03	161.5; 162.5	Cu$_2$Se, CuSe
		Se	13.67	54.2; 56.6	Se
		O	7.33	531.1	
270	Before etching	Cu	15.29	932.1; 933.8	Cu$_2$S, Cu$_2$O, CuS
		S	22.85	161.3; 162.5; 167.8	Cu$_2$Se, CuSe
		Se	7.57	54; 55.4; 58.6	Se
		O	54.28	531; 532.6; 533.8	CuSO$_4$, CuO
	After etching	Cu	52.39	932.2	CuS, Cu$_2$O, Cu$_2$Se
		S	33.61	161.5; 162.4	Cu$_2$S, CuSe
		Se	11.82	54.2; 55.4; 56.6	Se
		O	2.17	531.8	

Data of the XPS analysis show that the composition of Cu$_x$S–Cu$_y$Se layers formed in different experimental conditions is rather similar (Table 2). For example, oxygen takes 56.89 at. % on the surface of the chalcogenide layer when the PA has been initially chalcogenized in 0.05 mol · dm^{-3} K$_2$SeS$_4$O$_6$ solution for 10 min at a temperature of 50 °C. The bond energy values of E$_b$ = 530.1 and 531.5 eV in the spectra of O 1s show that part of oxygen should be joined into the Cu(I) oxide, Cu$_2$O, and the bond energy E$_b$ = 533.5 eV indicates the presence of HO$^-$ groups. These groups may be present in the composition of Cu(OH)$_2$ which may be formed while washing of the chalcogenide layer with water. The bond energy of 161.3 eV in the spectra of S 2p shows the presence of Cu(I) and Cu(II) sulfides in the surface. The values of E$_b$ = 53.8, 54.2, 55.3, eV in the spectra of Se 3d$_{5/2}$ indicate the presence of elemental selenium. The spectra of Cu 2p$_{3/2}$ confirmed the presence of the copper sulfides mentioned and of Cu(I) oxide, Cu$_2$O (E$_b$ = 932.1 eV), and of Cu(II) oxide, CuO (E$_b$ = 933.9 eV). Changes of the chem-

ical composition and of the content of elements occurred when the chalcogenide layer was etched with Ar$^+$ ions.

The content of oxygen decreased 6 times (to 9.38 at. %), but the content of Cu, S and Se increased significantly. S 2p spectra indicated formation of copper sulfides in the layer: the bond energy E$_b$ = 161.5 eV showed Cu$_2$S, and E$_b$ = 162.5 eV indicated CuS. The bond energy E$_r$ = 932.2 eV in the spectra of Cu 2p$_{3/2}$ confirmed the presence of copper sulfides and of Cu(I) oxide, Cu$_2$O, in the chalcogenide layer.

Studies of Cu$_x$S–Cu$_y$Se layers on the surface of PA initially chalcogenized for 1–4.5 h showed that the chemical composition was similar to the composition of layers formed when the polymer chalgenation stage was shorter. Again, a high content of oxygen was found on the surface of copper chalcogenide layer. This content decreased to a minimum after the surface etching with Ar$^+$ ions. Traces of elemental selenium were found in all samples studied because the chalcogenation solution gradually decomposed with time.

These results confirmed the results obtained by the X-ray diffraction analysis of the layers: the composition of a layer on prolonging the polymer initial chalcogenation stage in the solution of the same concentration and temperature to 4.5 h remained almost the same.

Summarizing the results of our studies, we may state that the solution of potassium selenopenta-thionate is a suitable agent of polyamide chalcogenation for the formation on its surface of electrically conductive $Cu_xS–Cu_ySe$ layers. This agent of chalcogenation, because of a unique structure of the anion $^-O_3S–S–Se–S–SO_3^-$ comprising sulfur and selenium atoms of low oxidation state, enables to insert into the PA surface a matrixa layer of the anionic S and Se particles. Treatment of a polymer modified in such a way with the solution of Cu(II / I) salts results in the formation of a mixed copper sulfide – copper selenide layer of a desirable chemical composition and electrical resistance. This chalcogenation agent has enabled forming mixed chalcogenide layers for the first time. These coatings may have properties peculiar to both copper sulfides and copper selenides.

CONCLUSIONS

1. Selenopentathionate anions containing a mixed chain of divalent sulfur and selenium atoms of low oxidation state $^-O_3S–S–Se–S–SO_3^-$ are sorbed–diffused into polyamide films treated with a neutral or acidified with hydrochloric acid solutions ($0.025–0.2$ mol $\cdot$ dm^{-3}, 30–50 °C) of potassium selenopentathionate, $K_2SeS_4O_6$. Exactly these central Se and S atoms are potential chalcogen atoms for the formation of mixed copper sulfide – copper selenide layers in the surface of semihydrophilic polyamide films.

2. The sorption–diffusion of selenopentathionate ions from acidified solutions proceeds more intensively because of the polymer structure amorphization under the effect of H$^+$ and selenopentathionate ions: the concentrations of selenium and sulfur diffused from an acidified solution are about 5 times higher as compared with those attained using a non-acidified solution of the same concentration and at the same temperature. The concentration of sorbed selenopentathionate ions increases with increasing temeperature and concentration of a $K_2SeS_4O_6$ solution, and the duration of treatment.

3. The $SeS_4O_6^{2-}$ anions diffused into polyamide gradually decompose, and the decomposition products, sulfate ions and SO$_2$, are washed out from the polymer, but elemental selenium remains in it. Therefore, the polyamide tapes, depending on the degree of $SeS_4O_6^{2-}$ ion decomposition, change from colourless to yellow, brown or red.

4. Copper sulfide and copper selenide layers of various composition are formed on the surface of a polyamide film, if the chalcogenized polymer is treated with a water solution of Cu(II / I) salts: the anionic particles containing sulfur and selenium atoms of a low oxidation state react with the copper ions. The colour of the polyamide film modified with a cop-per chalcogenide layer directly depends on the conditions of initial polymer treatment with a solution of the chalcogenation agent: films with a low concentration of sorbed–diffused selenium (colourless) after interaction with a Cu(II / I) salt solution acquire a light yellow colour and films with a higher concentration of selenium a dark brown colour and the metallic lustre.

5. The conditions of polymer initial chalcogenation (the concentration and temperature of $K_2SeS_4O_6$ solution) determine the content of copper and the composition of the chalcogenide layer: the content of copper in the polyamide film increases with increasing the concentration and temperature and varies from $0.2 \cdot 10^{-2}$ to $33.5 \cdot 10^{-2}$ mg/cm^2. The content of copper in the copper chalcogenide layer increases with increasing the concentration and temperature of the selenopentathionate solution used for the initial chalcogenation of the polymer. The content of copper joined into chalcogenide in PA film samples initially treated with an acidified $K_2SeS_4O_6$ solution is significantly higher as compared with samples initially treated with a non-acidified selenopentathionate solution.

6. Results of X-ray diffraction analysis confirmed the formation of mixed copper sulfide – copper selenide layers in the surface of polyamide. The phase composition of a layer changes depending on the duration of the initial treatment in a $K_2SeS_4O_6$ solution: $Cu_xS–Cu_ySe$ layers are composed of the low-conductive chalcocite, Cu_2S, the electrically conductive digenite, $Cu_{1.8}S$, djurleite, $Cu_{1.9375}S$, anilite, $Cu_{1.75}S$, and of copper selenides – bellidoite, Cu_2Se, umangite, Cu_3Se_2, klockmannite, CuSe, krutaite, CuSe$_2$ and Cu_2Se_x. The phase composition determines the electrical characteristics of the layers.

7. The use of selenopentathionate solutions enables forming on the surface of a polymer an electrically conductive layer of copper sulfides–selenides with the electrical resistance varying from 12.2 Ω / □ to 4.8 MΩ / □. The electrical resistance values of the copper chalcogenide layer formed initially using an acidified solution of chalcogenation (R = 465.8 Ω / □ – 12.3 Ω / □) are a few thousand times lower as compared with the electrical resistance values of layers formed using a non-acidified chalcogenation solution (R = 4.8 MΩ / □ – 4.4 kΩ / □).

8. Analysis of the chemical composition of $Cu_xS–Cu_ySe$ layers to a depth of up to 1 nm by the method of X-ray photoelectron spectroscopy confirmed the formation of copper sulfides and selenides of various phases in the surface of a polyamide.

9. The regularities determined in the present study enable formation by the sorption–diffusion method of mixed copper sulfide and copper selenide layers of a desirable composition and electrical conductivity, using selenopentathionate as a polyamide chalcogenation agent.

References

1. S. Martinuzzi, *Sol. Cells*, **5(3)**, 243 (1982).
2. F. Pfister, W. H. Bloss, *Sol. Cells*, **12(1–2)**, 155 (1984).
3. A. C. Rastogi, S. Salkalachen, *J. Appl. Phys.*, **58(11)**, 4442 (1985).
4. S. T. Lakshmikumar, *Mater. Sol. Cells*, **32(1)**, 7 (1994).
5. V. M. Garcia, P. K. Nair, M. T. S. Nair, *J. Crystal Growth*, **203(1–2)**, 113 (1999).
6. M. T. S. Nair, P. K. Nair, *Semicond. Sci. Technol.*, **4(7)**, 599 (1989).
7. H. Okimura, T. Matsumae, R. Makabe, *Thin Solid Films*, **71(1)**, (1980).
8. A. M. Hermann, L. Fabick, *J. Cryst. Growth*, **61(3)**, 658 (1983).
9. M. T. S. Nair, P. K. Nair, *Semicond. Sci. Technol.*, **4(3)**, 191 (1989).
10. M. T. S. Nair, P. K. Nair, *J. Phys. D: Appl. Phys.*, **24**, 450(1991).
11. I. Grozdanov, C. K. Barlingay, S. K. Dey, M. Ristov, M. Najdoski, *Thin Solid Films*, **250(1–2)**, 67 (1994).
12. M. T. Neshkova, *Anal. Chim. Acta*, **273(1–2)**, 255 (1993).
13. I. Grozdanov, C. K. Barlingay, S. K. Dey, *Matter. Lett.*, **23(4–6)**, 181 (1995).
14. I. Ancutienė, V. Janickis, R. Ivanauskas, A.-J. Galdikas, A. Mironas, A. Šetkus, V. Strazdienė, Pat. Lithuanian LT 4584 (1999).
15. H. Hu, P. K. Nair, *Surf. Coat. Technol.*, **81(2–3)**, 183 (1996).
16. R. C. Kainthla, D. K. Pandya, K. L. Chopra, *J. Electrochem. Soc.*, **127(2)**, 277 (1980).
17. H. Rau, *J. Phys Chem. Solids*, **28(6)**, 903 (1967).
18. B. Rezig, S. Duchemin, F. Guastavino, *Sol. Energy Mater.*, **2(1)**, 53 (1979).
19. H. S. Randhava, R. F. Bunshah, D. G. Brock, B. M. Basol, O. M. Staffsudd, *Sol. Energy Mater.*, **6(4)**, 445 (1982).
20. C. Nascu, I. Pop, V. Ionescu, E. Indrea, I. Bratu, *Lett.*, **32(2–3)**, 73 (1997).
21. S. K. Haram, K. S. V. Santhanam, *Thin Solid Films*, **238(1)**, 21 (1994).
22. I. Grozdanov, *Semicond. Sci. Technol.*, **9(6)**, 1234 (1994).
23. S. Lindroos, A. Arnold, M. Leskela, *Appl. Surf. Sci.*, **158(1–2)**, 75 (2000).
24. S. D. Sartale, C. D. Lokhande, *Mater. Chem. Phys.*, **65(1)**, 63 (2000).
25. M. A. Baranauskas, *Mechanism of copper sulfide layers formation on polyethylene*, PhD thesis, Vilnius, Lithuania (1984).
26. E. Fatas, T. Garcia, C. Montemayor, A. Medina, E. Garcia Camarero, F. Arjona, *Mater. Chem. Phys.*, **12(2)**, 121 (1985).
27. P. Pramanik, M. A. Akhter, P. K. Basu, *J. Mater. Sci. Lett.*, **6(11)**, 1277 (1987).
28. G. K. Padam, *Thin Solid Films*, **150(1)**, 189 (1987).
29. A. J. Varkey, *Solar Energy Mater.*, **19(6)**, 415 (1989).
30. K. M. Gadave, C. D. Lokhande, *Thin Solid Films*, **229(1)**, 1 (1993).
31. C. A. Estrada, P. K. Nair, M. T. S. Nair, R. A. Zingaro, E. A. Meyers, *J. Electrochem. Soc.*, **141(3)**, 802 (1994).
32. A. Žebrauskas, *Chem. Technol.*, **1(3)**, 39 (1996).
33. J. Janickis, *Acc. Chem. Res.*, **2**, 316 (1969).
34. J. Janickis, J. Valančiūnas, V. Zelionkaitė, V. Janickis, S. Grevys, *Trans. Lithuanian Acad. Sci.*, B **3(88)**, 83 (1975).
35. V. I. Janickis, *Formation, structure and physical–chemical properties of sulphane and selenane derivatives*, Doctor. thesis, Kaunas, Lithuania (1983).
36. O. Foss, in: H. J. Emeleus, A. G. Sharpe (eds.), *Advances in Inorganic Chemistry and Radiochemistry*, New York, Academic Press **2**, 237 (1960).
37. R. Maciulevičius, V. Janickis, R. Ivanauskas, Pat. Lithuanian LT 4402 (1998).
38. V. Janickis, R. Maciulevičius, R. Ivanauskas, I. Ancutienė, *Colloid. Polym. Sci.*, **281**, 84 (2003).
39. R. Ivanauskas, *Formation of copper selenide layers on polyamide using selenotrithionate*, PhD thesis, Kaunas, Lithuania (1995).
40. R. Ivanauskas, V. Janickis, V. Zelionkaitė, A. Žebrauskas, Pat. Lithuanian LT 4235 (1997).
41. R. Ivanauskas, V. Janickis, *Progr. Colloid. Polym. Sci.*, **116**, 134 (2000).
42. A. Foust, V. Janickis, *Inorganic Chemistry*, **19**, 1063 (1980).
43. R. Ivanauskas, V. Janickis, N. Petrašauskienė, *Proceedings of Conference "Lithuanian Science and Industry. Inorganic Chemistry and Technology"*, Kaunas, 150 (1998).
44. P. Pekonen, J. Taavitsainen, R. S. Laitinen, *Acta Chem. Scand.*, **52(9)**, 1188 (1998).
45. K. Maroy, *Crystal structures of penta-, selenopenta-, telluropenta- and hexathionates*, PhD thesis, Bergen, Norway, (1975).
46. V. Janickis, R. Ivanauskas, N. Petrašauskienė, *Chem. Technol.*, **3(16)**, 23 (2000).
47. R. Ivanauskas, V. Janickis, N. Petrašauskienė, *Mater. Sci.*, **6(4)**, 298 (2000).
48. N. Petrašauskienė, R. Ivanauskas, V. Janickis, *Chem. Technol.*, **1(27)**, 32 (2003).
49. V. Janickis, R. Ivanauskas, N. Petrašauskienė, *Chem. Technol.*, **2(28)**, 17 (2003).
50. O. Foss, *Acta Chem. Scand.*, **3**, 435 (1949).
51. I. Ancutienė, V. Janickis, S. Grevys, *Chemistry*, **2**, 3 (1997).
52. *Analytical Methods for Atomic Absorption Spectrometry*, Perkin–Elmer Corp., Norwalk, Conn. (1973).
53. V. I. Alekseev, *Quantitative Analysis*, Khimija, Moscow (1972).
54. D. Briggs, in: M. P. Seach (ed.), *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, Mir, Moscow (1987).
55. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder et al. *Handbook of X-ray Photoelectron Spectroscopy*, Perkin–Elmer Corp., Minnesota (1978).
56. J. Janickij, M. Podolskij, *Proceedings of Lithuanian Higher Schools. Chemistry and Chemical Technology,* **3**, 103 (1963).
57. R. Ivanauskas, V. Janickis, R. Maciulevičius, *Chem. Technol.*, **4(13)**, 71 (1999).
58. O. Foss, *Acta Chem. Scand.*, **3**, 708 (1949).
59. R. A. Alberty, R. J. Silbey, *Physical Chemistry*, John Wiley & Sons, New York (1996).

Neringa Petrašauskienė, Vitalijus Janickis

POLIAMIDO PLĖVELIŲ MODIFIKAVIMAS VARIO CHALKOGENIDŲ SLUOKSNIAIS NAUDOJANT KALIO SELENOPENTATIONATĄ

Santrauka

Selenopentationato anijonai yra sorbuojami–įdifunduoja į poliamido plėveles, jas apdorojant neparūgštintais arba parūgštintais druskos rūgštimi 0,025–0,2 mol · dm^{-3} 30–50 °C temperatūros kalio selenopentationato, $K_2SeS_4O_6$, tirpalais. Sorbcija–difuzija iš parūgštintų tirpalų vyksta intensyviau: difundavusių iš parūgštintų tirpalų seleno ir sieros koncentracijos yra apie 5 kartus didesnės, nei naudojant tos pačios koncentracijos ir temperatūros neparūgštintus tirpalus. Sorbuotų selenopentationato jonų koncentracija didėja, didinant $K_2SeS_4O_6$ tirpalo temperatūrą ir polimero apdorojimo jame trukmę. Sorbuoti–įdifundavę į poliamidą $SeS_4O_6^{2-}$ anijonai palaipsniui skyla ir skilimo produktai – sulfato jonai ir SO_2 išsiplauna iš polimero, bet elementinis selenas jame lieka. Todėl poliamido plėvelių spalva priklauso nuo $SeS_4O_6^{2-}$ jonų suskilimo laipsnio, kinta nuo bespalvės į geltoną, rudą ar raudoną. Vario sulfidų ir vario selenidų sluoksniai susidaro poliamido plėvelių paviršiuje, jeigu chalkogenintas polimeras apdorojamas vandeniniu vario(II / I) druskų tirpalu: anijoninės dalelės, turinčios mažo oksidacijos laipsnio sieros ir seleno atomų, reaguoja su vario jonais. Polimero pradinio chalkogeninimo sąlygos ($K_2SeS_4O_6$ tirpalo koncentracija ir temperatūra) turi įtakos vario kiekiui ir chalkogenidinio sluoksnio sudėčiai: vario kiekis poliamidinėje plėvelėje didėja, didinant koncentraciją ir temperatūrą, ir kinta nuo 0,2 · 10^{-2} iki 33,5 · 10^{-2} mg/cm². Rentgeno struktūrinės analizės rezultatai patvirtino vario sulfidų–vario selenidų sluoksnių poliamido paviršiuje susidarymą. Fazinė sluoksnių sudėtis kinta dėl pradinio polimero apdorojimo $K_2SeS_4O_6$ tirpalu trukmės: $Cu_xS–Cu_ySe$ yra sudaryti iš mažai laidaus elektrai chalkocito, Cu_2S, elektrai laidžių digenito, $Cu_{1.8}S$, djurleito, $Cu_{1.9375}S$, anilito, $Cu_{1.75}S$, ir vario selenidų – bellidoito, Cu_2Se, umangito, Cu_3Se_2, klokmanito, $CuSe$, krutaito, $CuSe_2$ ir Cu_2Se_x. Todėl fazinė sudėtis lemia sluoksnių elektrines charakteristikas: elektrinė kvadrato varža gali kisti nuo 12.2 Ω / □ iki 4,8 MΩ / □. Sluoksnių sudėtis iki 1 nm gylio, tirta rentgeno fotoelektronine spektroskopija, patvirtino įvairių fazių vario sulfidų ir selenidų susidarymą. Nustatyti dėsningumai leidžia, naudojant sorbcinį–difuzinį metodą ir selenopentationatą, kaip poliamido chalkogeninimo agentą, sudaryti poliamido paviršiuje norimos sudėties ir elektrinio laidžio mišriuosius vario sulfidų ir vario selenidų sluoksnius.