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Research Article

Optical, XPS and XRD Studies of Semiconducting Copper Sulfide Layers on a Polyamide Film

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Copper sulfide layers were formed on polyamide PA 6 surface using the sorption-diffusion method. Polymer samples were immersed for 4 and 5 h in 0.15 mol·dm^{-3} $K_2S_5O_6$ solutions and acidified with HCl (0.1 mol·dm^{-3}) at 20°C. After washing and drying, the samples were treated with Cu(I) salt solution. The samples were studied by UV/VIS, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) methods. All methods confirmed that on the surface of the polyamide film a layer of copper sulfide was formed. The copper sulfide layers are indirect band-gap semiconductors. The values of E_{bg} are 1.25 and 1.3 eV for 4 h and 5 h sulfured PA 6 respectively. Copper XPS spectra analyses showed Cu(I) bonds only in deeper layers of the formed film, while in sulfur XPS S 2p spectra dominating sulfide bonds were found after cleaning the surface with Ar^+ ions. It has been established by the XRD method that, beside Cu_2S, the layer contains $Cu_{1.9375}S$ as well. For PA 6 initially sulfured 4 h, grain size for *chalcocite*, Cu_2S, was ~35.60 nm and for *djurleite*, $Cu_{1.9375}S$, it was 54.17 nm. The sheet resistance of the obtained layer varies from 6300 to 102 Ω/cm^2.

1. Introduction

Modification of polymers physical properties by formation on their surfaces of thin layers of inorganic compounds allows obtaining composites with desirable properties. The last few decades saw an increasing interest in semiconducting copper sulfide thin films, because of their applications in various fields of science and technology. Copper sulfide thin films have a number of applications in various devices such as: solar cells, superionic conductors, semiconductors, photodetectors, photothermal conversion devices, electroconductive electrodes, microwave shielding coating [1–4], gas sensors functioning at temperatures tending to room temperature [4], as polarizers of infrared radiation [5], and active absorbents of radio waves [6].

Numerous studies are devoted to the production of Cu_xS layers in the polymer matrix by chemical methods [7, 8]. Application of these copper sulfide layers depends on their properties, such as chemical composition, structure, and electrical conductivity. The properties of the obtained layers depend on the conditions of synthesis, the precursor of sulfur and their composition [9, 10]. Compositions of these layers have been studied by XRD [11, 12], FTIR [13], potentiometry [14], however, to our knowledge, investigations by XPS are lacking.

The aim of this work was to study the phase composition of Cu_xS layers obtained by the sorption-diffusion method in a polyamide matrix by means of UV/VIS, XPS, and XRD.

2. Experimental Details

Potassium pentathionate, $K_2S_5O_6 \cdot 1.5H_2O$, was prepared from As_2O_3 and potassium thiosulfate, and was chemically analysed according to published procedures [15]. The purity of the obtained potassium pentathionate was 99.3%. Salt was stored in the desiccators over sulfuric acid.

The solutions of freshly prepared $K_2S_5O_6 \cdot 1.5H_2O$ in 0.1 mol · dm^{-3} HCl at a concentration of 0.15 mol · dm^{-3} and a temperature of 20°C was used for the diffusion of sulfur(II) containing anionic particles into PA samples.

The polyamide PA 6 tape 70 μm thick (specification TY 6-05-1775-76, grade PK-4, Russia) were used for experiments. This film is close to a nonporous material, because the pores of PA 6 are much less than 1.5 nm. The porosity was measured by the BET method [16] using a Quantasorb sorption system (USA). Film density was checked by the flotation method. It was found, that the density of PA is equal to $1.13\,\mathrm{g\cdot cm^3}$.

Prior to the experiments, samples of the PA 6 film 15 mm × 70 mm in size, were boiled in distilled water for two hours to remove the remainder of the monomer, then dried with filter paper and in a desiccators over $CaCl_2$ for 24 hours.

PA 6 films were sulfured in a thermostatic vessel using a continually stirred acidified ($0.1\,\mathrm{mol\cdot dm^{-3}}$ HC1, pH ~ 1.5) $0.15\,\mathrm{mol\cdot dm^{-3}}$ $K_2S_5O_6$ solutions at a temperature of 20°C. Preliminary experiments had shown that sorption from the solutions of a lower concentration was too slow and insufficient. At temperatures higher than 30°C, the stability of pentathionate solution was insufficient, and gradual spontaneous decomposition of polythionate with the liberation of elemental sulfur occurred [7].

After 4 and 5 hours of pretratment in $K_2S_5O_6$ solution, the PA 6 film samples were removed, rinsed with distilled water, dried with filtration paper, kept over $CaCl_2$ for 24 hours, and then used in further experiments and analysis.

Sulfur concentrations in PA 6 film samples were determined potentiometrically [17]. Firstly, the sample of a sulfured PA 6 film was thermally treated in 10–15 $\mathrm{cm^3}$ of $10\,\mathrm{mol\cdot dm^{-3}}$ KOH diluted with the same amount of distilled water. Standard calomel and platinum electrodes were used for the potentiometric titration of the solution obtained in KOH with 0.05 $\mathrm{molkv\cdot dm^{-3}}$ solution of iodine under stirring. For the potentiometric measurements the pH-meter—pH-673 M voltmeter was used.

A solution of Cu(I) salt was produced from the solution of $0.4\,\mathrm{mol\cdot dm^{-3}}CuSO_4$ with addition of $3.4\,\mathrm{mol\cdot dm^{-3}}NH_3\cdot H_2O$ and $0.36\,\mathrm{mol\cdot dm^{-3}}$ of a reducing agent, hydroxylamine sulfate, by the method presented in [18]. The pH of the solution was 9.73. All ions of divalent copper turn into ions of univalent copper in this mixture independently of the temperature. After pretreatment in $K_2S_5O_6$ solution, the PA 6 sample was treated for 20 minutes at a temperature of 35°C with a Cu(I) solution, then rinsed with distilled water, dried over $CaCl_2$ and used in further experiments.

The amount of copper in the sulfide film was determined with a Perkin-Elmer atomic absorption spectrometer (λ = 325 nm) [19] after fusing the film in concentrated nitric acid. The content of copper and sulfur was expressed as $\mu\mathrm{mol\cdot cm^{-2}}$.

The sheet resistance of Cu_xS layers of different composition was measured at the constant current using the E7–8 digital multimeter (Russia) with custom design electrodes. The measurements were carried out with 1 $\mathrm{cm^2}$ square electrodes, therefore the resistance is shown in $\Omega/\mathrm{cm^2}$.

The UV/VIS spectra (from 200 to 800 nm) were recorded on a Spectronic Genesys 8 UV/Visible spectrophotometer with compensation of PA 6 absorption.

The composition and chemical state of the elements in the copper sulfide film surface were studied using X-ray Photoelectron Spectroscopy (XPS) on a KRATOS ANALYTICAL XSAM800 spectrometer. The energy scale of the spectrometer was calibrated using Au $4f_{7/2}$, Cu $2p_{3/2}$, and Ag $3d_{5/2}$ peak positions [20]. The X-ray source was operating in aluminium anode mode (Al Kα photon energy of 1486.6 eV). The hemispherical energy analyser with the pass energy of 20 eV and the fixed analyser transmission (FAT) mode were used. The main core level photoemission spectra (with 0.1 eV energy increment) of Cu, O, C, and S were taken. The X-ray excited Auger spectra of copper (Cu $L_3M_{45}M_{45}$) were collected with a 0.25 eV energy increment. For all spectra, the charge shift was compensated according to C 1s peak position. The relative atomic concentrations of copper, oxygen, carbon, and sulfur were calculated from an appropriate peak area with respect to the sensitivity factors, using original KRATOS software. Shirley background subtraction was used for atomic concentrations calculation. Surface cleaning with Ar^+ ions (3 KeV, 18 $\mu\mathrm{A/cm^2}$) was used to remove atmospheric contaminants from the surface of samples.

X-ray diffractometry was carried out under a Brag Brendan circuit on a Dron-6 diffractometer (Russia) using Cu Kα($\lambda = 0.154178$ nm) radiation, 30 kV voltages, and 30 μA current. The scanning range was $\theta = 28 - 60^\circ$, and the scanning speed was $1\,\mathrm{min^{-1}}$. Results were registered in the in situ mode with a computer, and X-ray diffractograms of PA 6 samples with Cu_xS layers were treated using the Sarch Match, Xfit, ConvX, Dplot95, and Photo Styler programs to eliminate the PA 6 maxima.

3. Results and Discussion

3.1. Chemical Analysis of Thin Cu_xS Film Layers. As mentioned before, the method of preparation influences the composition and characteristics of sulfide layers. Therefore, the initial stage of the work was aimed to establish the chemical composition of Cu_xS/PA.

The chemical composition of copper sulfide films obtained in different conditions is presented in Table 1. The molar ratios of copper and sulfur found in sulfide films show that nonstoichiometric copper sulfide and nonsulfide sulfur can coexist.

3.2. Optical Studies of Thin Cu_xS Film Layers. The typical UV/VIS absorption spectra of PA 6 samples sulfured for 5 hours in a solution of $K_2S_5O_6$ at 20°C are presented in Figure 1, curve 1, where the spectrum of PA substrate is subtracted. Two absorption peaks are observed in these spectra: at 250 nm as a peak, and as a less intense and shallower band at λ = 295 nm. Thus, the UV/VIS absorption spectra confirm that the sulfur is sorbed by PA 6 films in the form of pentathionate ions [21, 22]. The intensity of absorption maxima in the spectra increases with increasing exposure time of polymer treatment with potassium pentathionate solution.

After interaction of copper ions with polyamide in the presence of sulfur, a number of new peaks appear in the interval of 295–465 nm for PA sulfured in the potassium pentathionate solution, and a change tendency was observed

Table 1: Chemical composition of Cu_xS layers formed in PA matrices, depending on the duration of film pretreatment time.

Parameter	Duration time of treating the PA films in $K_2S_5O_6$ solution, h	
	4	5
Sulfur concentration c_s, μmol · cm^{-2}	3.10	3.26
Copper concentration c_{Cu}, μmol · cm^{-2}	2.04	2.24
Cu/S molar ratio	1 : 1.52	1 : 1.45

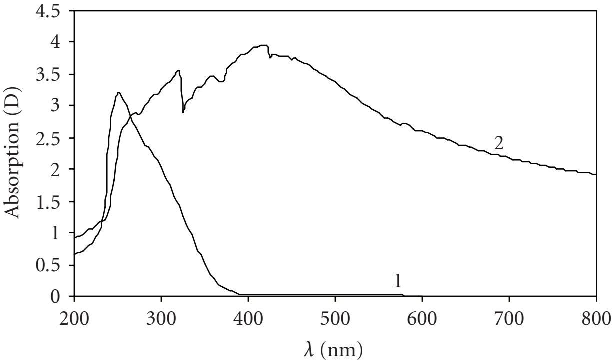

Figure 1: Typical UV/VIS absorption spectra: (1) of the layers of PA 6 sulfured for 5 hours in 0.15 mol·dm^{-3} $K_2S_5O_6$ at 20°C, (2) of the layers then treated with Cu(I) salt.

in comparison with that before the interaction with copper. Three obvious absorption peaks at 320 nm, 360 nm, and abroad absorption peak at 465 nm appeared on the surface of PA (see Figure 1, curve 2). All these peaks are higher than relevant peaks of PA before the interaction with copper indicating that they are copper sulfides species. These data in Figure 1 are consistent with the number and intensity of copper sulfides phases detected according to our XRD measurements (see Figure 5, curve 2).

The variation of the optical absorption coefficient near the absorption edge follows the power law [23] in the form of

$$\alpha = \frac{B\left(E - E_{bg}\right)^n}{E}, \tag{1}$$

where E is the photon energy-hν; E_{bg} is the band-gap energy of the system; B is the function of density of states near the conduction and valence band edges. The value of n is 2 for direct transition and (1/2) for indirect transition.

The optical absorption coefficient is found to have a value of $1.48 \cdot 10^4 - 1.52 \cdot 10^4$cm^{-1}.

Transition copper sulfides are usually indirect band-gap semiconductors [24, 25]. The values of E_{bg} obtained from the intercepts of the straight line portion of the curves with the hν axis for the zero absorption are 1.25 and 1.3 eV for 4 hours and 5 hours sulfured PA 6, respectively.

The observed E_{bg} differences could be connected either with the structural changes of different thickness of layers or different exposure time in potassium pentathionate solution. Therefore, the influence of layers composition on the E_{bg} value can be regarded as dominant in our experiment.

3.3. *XPS Analysis of Thin Cu_xS Film Layers.*

Cu_xS films deposited on PA 6 surface were examined by XPS measurements. The core levels S 2p, Cu 2 p, O 1s, C 1s spectra and the Cu Auger spectrum were measured. During formation of the Cu_xS layer on the surface of polycaproamide, all processes proceed in an open medium; therefore, it is not possible to avoid ambient effects. Since the surface of this layer is active, it adsorbs oxygen, water, and other contaminants [26–28]. The layer of sulfide on the surface of the polymer is distributed in the form of islands enabling an easy contact of the atmospheric oxygen with copper and sulfur ions. Therefore the surface of the Cu_xS layer can differ from the macrostructure and chemical composition of the entire layer. It is necessary to emphasize that the XPS method investigates very thin (up to few nm) surface layers, whereas the grains size in the film determined by optical microscopy [29] is approximately 30 μm, that is, can reach several tens of microns.

The data of XPS analysis show that the composition of Cu_xS layers formed at different pretreatment time in 0.15 mol · dm^{-3} $K_2S_5O_6$ solutions is rather similar. They consist of copper, sulfur, carbon, and oxygen in various combinations. Oxygen on the surface of the copper sulfide layer was established by other methods, for example, during precipitation of thin Cu_2S films from solutions [30]. The amount of oxygen significantly reduces when the surface of the sulfide layer is cleaned with Ar^+ ions.

The XPS Cu 2p spectra of PA 6 sample sulfured for 5 hours and afterwards treated in Cu(I) salt solution are shown in Figure 2. In the spectra taken before sputtering (see Figure 2, curve 1), the "shake-up" satellite at 944 eV position and a low intensity peak at 935.5 eV are clearly visible. The "shake-up" satellite is an evidence of Cu(II) ions [26], while the peak at 935.5 eV coincides with the known $CuSO_4$ peak position at 935.4 eV [31]. A high-intensity peak at 932.8 eV (FWHM = 1.85 eV) is close to reported peak positions of Cu_2S (932.5 eV), Cu_2O (932.5 eV) [31], and Cu–Cu (932.63 eV) [20]. However, this peak is shifted by 0.6 eV from the known CuS peak (932.2 eV) [31], and by 0.8 eV from the CuO peak (933.6 eV) [31]. A more clear distinction between the mentioned Cu(I) and Cu(II) bonds is described afterwards using copper Auger peaks. After Ar^+ sputtering (see Figure 2, curve 2) the "shake-up" satellite and the peak at 935.5 eV disappear, while the high intensity peak at 932.8 eV becomes more intense and narrow (FWHM = 1.6 eV), its position being unchanged. It is known that evaporation of volatile sulfur oxides takes place due to bombardment by Ar^+ ions of the oxidized sulfide surface [32]. Therefore, the sample surface before sputtering can be described as Cu_2S

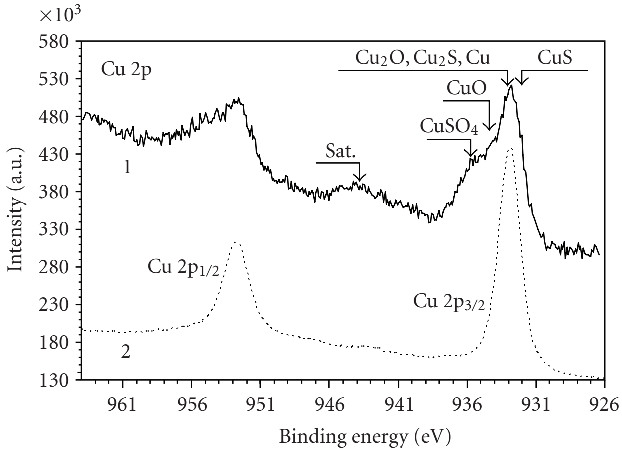

Figure 2: Copper XPS Cu 2p spectra of PA 6 sulfured for 5 hours and treated with Cu(I) salt: (1) before and (2) after Ar^+ cleaning. Arrows show possible positions of copper peaks as described in the text.

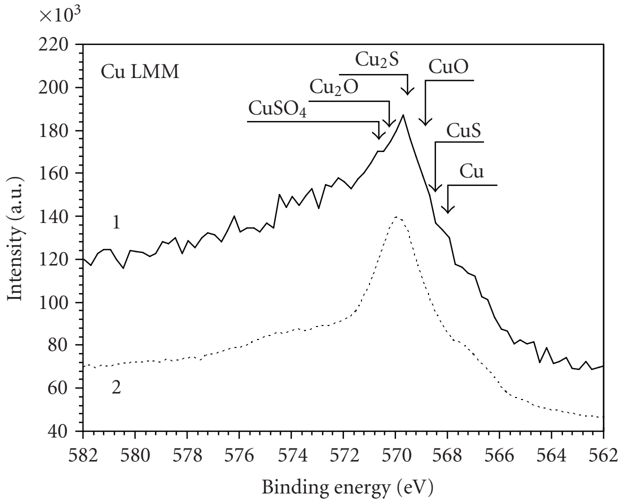

Figure 3: Copper Auger spectra of PA 6 sulfured for 5 hours and treated with Cu(I) salt: (1) before and (2) after Ar^+ cleaning. Arrows show possible positions of copper peaks as described in the text.

copper sulfide with oxidized upper layers. The sample surface after Ar^+ cleaning can be described as Cu_2S sulfide with removed volatile sulfur oxides if the identification of Cu_2S sulfide is reasonable.

For a clearer picture of Cu bonds, the copper Auger spectra excited with X-rays are shown in Figure 2. It is difficult to distinguish Cu_2S, Cu_2O, and Cu–Cu bonds from Cu 2p peak positions (see Figure 2), but the Cu $L_3M_{45}M_{45}$ peak positions for Cu_2S, Cu_2O, $CuSO_4$, CuO, CuS, and Cu–Cu bonds are more isolated – 569.5 eV, 569.9 eV, 570.5, 568.7 eV, 568.5 eV [31], and 567.93 eV, respectively [20]. Before Ar^+ ions bombardment the Cu $L_3M_{45}M_{45}$ peak position (569.7 eV, Figure 3, curve 1) coincides with known Cu_2S, Cu_2O positions (569.5 eV, 569.9 eV, respectively) [31]. After surface bombardment, the peak becomes more intense and its position is shifted (569.8 eV). This implies that there are no CuS, CuO, or Cu–Cu bonds, and the dominating phase of copper sulfide is Cu_2S. However, now the peak position is closer to the Cu_2O position and is slightly shifted from the known Cu_2S position.

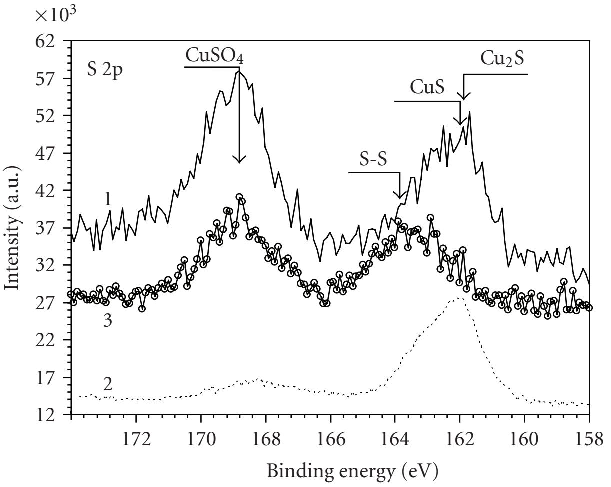

Figure 4: Sulfur XPS S 2p spectra of PA 6 sulfured for 5 hours and treated with Cu(I) salt: (1) before and (2) after Ar^+ cleaning, (3) sulfured PA 6 (for 4 hours at 20°C) before Cu(I) salt treatment. Arrows show possible positions of sulfur peaks as described in the text.

In the XPS S 2p spectra, different sulfur bonds for Cu(I) salt treated PA 6 (see Figure 4, curve 1) and PA 6 sulfured for 4 hours (see Figure 4, curve 3) were found. For both samples, the higher energy peak position (168.9 eV) coincides with the known $CuSO_4$ position (168.8 eV) [31]. This peak for both samples corresponds to sulfur S(VI) bond to oxygen. We assign this peak to sulfur SO_4^{2-} bonds in $CuSO_4$ in case of the oxidized surface for Cu(I) salt treated PA 6 (see Figure 4, curve 1) and to sulfur $S_2O_3^{2-}$ bonds PA 6 sulfured in pentathionate for 4 hours (see Figure 4, curve 3). The lower energy peak position (161.8 eV) for Cu(I) salt treated PA 6 is in good agreement with known Cu_2S and CuS positions (161.92 eV and 162.1 eV, respectively) [31]. For sulfured PA 6, the lower energy peak position (163.7 eV) is almost the same as the known S–S peak position (163.9 eV) [31], therefore we assign this peak to S^{2-}–S^{2+} bonds in pentathionate or possible elemental sulfur. For Cu(I) salt treated PA 6, oxidized sulfur states are formed on the outermost surface of the Cu_2S; most likely due to an atmospheric influence. After Ar^+ ions bombardment (see Figure 4, curve 2), the higher energy peak disappears from S 2p spectra. This confirms removal of volatile sulfur oxides from the copper sulfide surface as was shown in Cu 2p spectra (see Figure 2, curve 2).

Copper and sulfur XPS spectra were almost identical for PA 6 sulfured for 4 hours and treated with Cu(I) salt (not shown here).

Surface atomic concentration after sample treatments is presented in Table 2. The first column (sample description) corresponds to an appropriate PA 6 treatment: "Pure PA 6"—polyamide surface before pentathionate treatment; "Sulf. 4 hours PA 6"—PA 6 treated for 4 hours at 20°C in

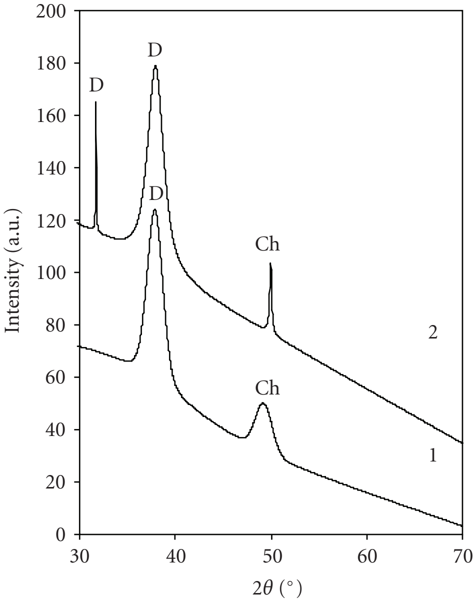

FIGURE 5: X-ray diffraction patterns of Cu_xS layers on PA 6 (peaks of *djurleite—D*, *chalcocite—Ch*). PA 6 initially pretreated for different time and then treated with Cu(I) salt solution for 20 minutes at 35°C. Pretreatment time: 1–4 hours, 2–5 hours.

pentathionate solution; "Sulf. 4 hours PA 6 Ar^{+}"—PA 6 treated for 4 hours at 20°C in pentathionate solution after surface bombardment with Ar^{+} ions for 30 seconds; "Sulf. 4 hours PA 6 Cu(I)"—PA 6 treated for 4 hours at 20°C in pentathionate solution and afterwards in Cu(I) salt solution; "Sulf. 5 hours PA 6 Cu(I)"—PA 6 treated for 5 hours at 20°C in pentathionate solution and afterwards in Cu(I) salt solution.

Surface atomic concentration shows that prolonged (5 hours) PA 6 treatment in pentathionate solution provides increased Cu and S concentrations on PA 6 surface after treatment in Cu(I) salt. In pentathionate-treated PA 6, sulfur atomic concentration decreases after surface cleaning with Ar^{+} ions. The same (4 hours) sample surface treated with Cu(I) salt shows a twice higher sulfur atom concentration even before bombardment with Ar^{+} ions. After surface cleaning, the Cu/S atomic ratio in PA 6 sulfured for 5 hours and treated in Cu(I) salt solution is 1 : 1.4. After Ar^{+} surface cleaning, in this sample the oxygen atomic concentration (22.7%) was approximately three times as high if compared to PA 6 sulfured for 4 hours and cleaned with Ar^{+} (7.7%).

A summarizing analysis of XPS spectra in Cu 2p spectra has shown that the detected position of the peak (932.8 eV) is difficult to distinguish between Cu_2O, Cu_2S, and Cu–Cu bond positions, but it is fairly separated from the known CuS and CuO bond positions, implying the absence of detectable Cu(II) ions in CuS or CuO bonds after Ar^{+} surface cleaning. This is confirmed by disappearance of low intensity of the "shake-up" satellite which disappears after surface cleaning with Ar^{+} ions. The Cu $L_3M_{45}M_{45}$ peak position excludes Cu–Cu bonds and confirms existence of only Cu(I) bonds in the obtained film, though possible Cu_2O bonds cannot be excluded. The sulfur S 2p spectrum for sulfured PA 6 shows sulfur bonds in pentathionate and possible elemental sulfur. For Cu(I) treated PA 6 samples, only sulfide bonds are found in S 2p spectra after surface cleaning with Ar^{+} ions. The oxygen atomic concentration and CuLMM peak shift towards Cu_2O position after Ar^{+} bombardment suggest a certain amount of oxidized Cu(I) in the deeper layers. The chemical bonds of Cu_2S layers initially sulfured for 4 hours and 5 hours are similar, while the atomic concentration of elements in the layers differs. Nevertheless, the Cu/S ratio for both Cu_2S layers is almost the same after Ar^{+} surface cleaning: 1.3 for 4 hours and 1.4 for 5 hours sulfured samples. The XPS data show that the formation of Cu_2S takes place in the bulk of deposits, but it cannot be excluded that the films contain some Cu_xS sites; then x is close to 2. Due to very close (or overlapping) peak positions in spectra, accurate determination of the x values in Cu_xS layers from XPS data is impossible.

Another aim of the work was evaluation of the influence of sample treatment on the electrical conductivity of the obtained layers. Sheet resistance for PA 6 treated by Cu(I) salt solution was found to range from 6300 to 102 Ω/cm^2 and is shown in the second column of Table 2. Sheet resistance variation indicates that the longer pentathionate treatment of PA 6 leads to a better electrical conductivity of produced copper sulfide films. The lowest sheet resistances of 102 Ω/cm^2 suggest formation of copper sulfide layers with the Cu/S molar ratio 1.45.

3.4. X-Ray Diffraction Analysis of Thin Cu_xS Film Layers. The phase composition of the deposited film was investigated by comparing the obtained XRD spectra with those of known minerals [33]. Structural studies of Cu_xS layers deposited by the sorption-diffusion method are limited by the polycrystallinity of the layers obtained, as well as by the existence of Cu_xS phases of various compositions and structure and by the crystallinity of the PA 6 film itself. The intensity of PA 6 peaks at $\theta < 13^\circ$ exceeds the intensity of copper sulfide peaks several times. Therefore, the area of $2\theta \geq 26.0^\circ$ was investigated in more detail.

The X-ray diffraction patterns of the layers showed that peaks of various copper sulfide phases are present in the XRD diagram (see Figure 5).

Analysis of the XRD spectra shows that the hexagonal *chalcocite* Cu_2S (PDF 84–209) maximum $2\theta = 49.28^\circ$ and monoclinic *djurleite* $Cu_{1.9375}S$ (PDF 42–564) maximum $2\theta = 38.1^\circ$ prevailed in the composition of the sulfide film for PA 6 sulfured for 4 hours and 5 hours (see Figure 5, curve 1, 2).

When the time of pretreatment in the penthathionate solution is prolonged until 5 hours, changes in film composition occur; the intensity of the peaks of djurleite slightly decreases, and the intensity of the *chalkosine* peaks increases. This phase predominates in the composition of the sulfide film (see Figure 5, curve 2). After a longer period of sulfuration in $K_2S_5O_6$ solution, one more *djurleite* (PDF 42–564) maximum $2\theta = 31.72^\circ$ peak appears (see Figure 5, curve 2), and the intensity of copper sulfide peaks increases.

Table 2: The sheet resistance and surface atomic concentration calculation results.

Sample description	Sheet resistance, Ω/cm^2	Surface atomic concentration, %			
		Cu 2p	O 1s	C 1s	S 2p
Pure PA	—	—	15.8	84.2	—
Sulf. 4hours PA	—	—	18.1	80.6	1.3
Sulf. 4hours PA Ar$^+$ (30s)	—	—	7.7	91.2	1.1
Sulf. 4hours PA Cu(I)	6300	1.6	12.8	83.5	2.2
Sulf. 4hours PA Cu(I) Ar$^+$ (30s)		5.0	10.2	80.8	3.9
Sulf. 5hours PA Cu(I)	102	2.1	31.5	62.8	3.6
Sulf. 5hours PA Cu(I) Ar$^+$ (30s)		19.7	22.7	43.2	14.4

Consequently, we assume that the concentration of copper sulfide in the obtained film increases.

Crystallite size was determined by Scherer's formula [33]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \tag{2}$$

where λ is X-ray wavelength, θ is Bragg's angle, and β is the full width of diffraction line at half of the maximum intensity.

For PA 6 initially pretreated for 4 hours in $K_2S_5O_6$ solution and then treated with Cu(I) salt solution for 20 minute at 35°C (see Figure 5, curve 1), grain size for *chalcocite*, Cu_2S, was ~35.60 nm and for *djurleite*, $Cu_{1.9375}S$, it was 54.17 nm. For PA 6 initially pretreated for 5 hours in $K_2S_5O_6$ solution (see Figure 5, curve 2), grain size for *chalcocite*, Cu_2S, was ~95.56 nm and for *djurleite*, $Cu_{1.9375}S$, it was 59.175–90.107 nm.

3.5. Mechanism and Kinetics of Copper Sulfide Formation. The differences of the obtained parameters of thin copper sulfide films on the PA 6 surface permit us to conclude that they may be connected with the peculiarities of their structure and mechanism of reaction following the diffusion of pentathionate across the polycaproamide interface. The mechanism of the heterocatalytic degradation of the pentathionate is still a matter of active investigation.

Pentathionate is, thereby, characterized as sulfur di-(thiosulfate), that is, two thiosulfate groups are bonded to a sulfur atom through the thiosulfur atoms of the thiosulfate groups. The sufur sulfur bonds in the pentathionate $^{-2}O_3\,S_2S^{++}S_2O_3{}^{2-}$ are more ionic then covalent.

With excess alkalis, pentathionate was found to undergo hydrolysis quantitatively as follows [34]:

$$2S(S_2O_3)_2{}^{2-} + 6HO^- \longrightarrow 4S_2O_3{}^{2-} + S + SO_3{}^{2-} + 3H_2O. \tag{3}$$

The stabilizing effect of acids on pentathionate is probably due to the removal of hydroxyl ions. This effect of acids on pentathionate may be also (especially from higher acid concentrations to a small extent) due to the polarizing influence of protons on the oxygen atoms of the terminal sulfuroxy groups. At sufficiently high acid concentrations this polarizing proton effect causes breakdown of pentathionate acids with liberation of hydrogen sulfide and elemental sulfur, respectively. The ionisation of thiosulfate ion in monosulfur di-(thiosulfate) in pentathionate is facilitated through the higher electronegativity of sulfur.

Therefore, a polythionic compound of the pentathionic type should keep its central sulfur more firmly bound to the lower oxidability of the thio anion from which it is built up. Since the pentathionate solutions are unstable, after several hours a degradation of the initial solution starts and new structural units like elemental S, polythionates (namely, $K_2S_3O_6$, $K_2S_4O_6$), sulfite, and sulfate may appear. We expect that the chemical degradation also influences the parameters of the anionic particles containing sulfur atoms diffused into PA 6.

Our data suggest a situation in which previously diffused sulfur particles lead to a modification of PA 6 surface, which favours the further sorption of copper ions.

The results of sorption were interpreted in terms of the semiquantitative estimates of the sorption mechanism. A variety of new effects become important as far as the interactions of inorganic sorbates with PA 6 surface are concerned, for example, the electrostatic interaction of sorbate ions, namely $S_3(SO_3)_2{}^{2-}$ with charged sites of the sorbent, such as the ionised polycaproamide functional groups –CO–NH– and $-NH_2$, and exchange reactions of these ions with ligands previously bonded to the polymer surface or their ionised functional groups. The charge of these particles becomes dependent on the degree of ionisation and consequently on the pH of the medium [22].

The UV/VIS, XPS and XRD data analyses (Figures 1, 2, 3, 4 and 5) allow us to assume a reaction scheme in which copper sulfide layers on PA 6 are formed by the sorption-diffusion method via heterogeneous chemical reactions [35]:

$$\begin{aligned} &S_3(SO_3)_2{}^{2-} + 2Cu^+ + 2H_2O \\ &\qquad \longrightarrow Cu_2S + 2S + 2H_2SO_4, \end{aligned} \tag{4}$$

$$\underline{2xCu^{\pm} + S \longrightarrow Cu_xS + xCu^{2\pm}}, \tag{5}$$

$$\begin{aligned} &S_3(SO_3)_2{}^{2-} + 6Cu^+ + 2H_2O \\ &\qquad \longrightarrow Cu_2S + 2CuS + 2Cu^{2+} + 2H_2SO_4, \end{aligned} \tag{6}$$

$$2CuS \longrightarrow Cu_2S + S. \tag{7}$$

As mentioned before, pentathionate solutions are unstable; therefore we should expect also the products of chemical degradation to diffuse into PA 6 [36]:

$$S_3(SO_3)_2{}^{2-} \longrightarrow S + S_2(SO_3)_2{}^{2-}. \tag{8}$$

The formed ions can also decompose:

$$2S_2(SO_3)_2{}^{2-} \longrightarrow S_3(SO_3)_2{}^{2-} + S(SO_3)_2{}^{2-}. \tag{9}$$

The presence of $SO_4{}^{2-}$ ions in the Cu_xS layers formed on PA 6 can be explained by reaction (6) or the decomposition of adsorbed $S_3(SO_3)_2{}^{2-}$ by the reaction [36]

$$S_3(SO_3)_2{}^{2-} \longrightarrow 3S + SO_2 + SO_4{}^{2-}. \tag{10}$$

Cu_2O are conveniently prepared by the reduction of $CuSO_4$ using a hydroxylaminosulfate in alkaline ($NH_3 \cdot H_2O$) solution. However, these compounds are rather unstable thermally and tend to be oxidised in air [37]:

$$2Cu_2O + O_2 \longrightarrow 4CuO. \tag{11}$$

The mentioned regularities enable copper sulfide films of desired conductivity to be obtained on PA 6 surface.

4. Conclusions

(1) Layers of copper sulfide of various composition are formed on the surface of polycaproamide if a sulfurized polymer is treated with the water solution of Cu(I) salt: the anionic particles containing sulfur atoms of low oxidation state react with copper ions. The Cu_xS/PA layers are indirect band-gap semiconductors. Obtained values of E_{bg} were 1.25 and 1.3 eV for 4 hours and 5 hours sulfured PA 6, respectively.

(2) Copper XPS spectra analyses showed the existence of only Cu(I) bonds in the deeper layers of the formed Cu_2S film, although possible bonds of Cu_2O were not excluded. In sulfur XPS spectra for sulfured PA 6, sulfur bonds in pentathionate and possible elemental sulfur were found. For Cu(I) treated PA 6 samples, sulfide bonds are found only in S 2p spectra after cleaning the surface with Ar^+. Surface atomic concentration calculations show that prolonged PA 6 treatment in pentathionate solution results increased Cu and S concentrations on the formed film surface.

(3) Results of X-ray diffraction analysis confirmed formation of Cu_xS layers of various phases. Comprising in itself mainly phases of hexagonal *chalcocite* Cu_2S ($84 - 209 : 2\theta = 49.28$) and monoclinic *djurleite* $Cu_{1,9375}S$ ($42 - 564 : 2\theta = 38.1^\circ$) prevails in the composition of Cu_xS film, if PA 6 is sulfured for 4 hours in $K_2S_5O_6$ solution, but when the period of sulfuration is prolonged (5 hours), the peaks of *chalcocite* and *djurleite* increase. After a longer period of sulfuration, a peak of *djurleite* $Cu_{1,9375}S$ ($42 - 564 : 2\theta = 31.72^\circ$) appears. Consequently, we assume that the concentration of copper sulfide in the obtained film increases.

(4) It was found that grain size for *chalcocite*, Cu_2S, was ~35.60 nm, for *djurleite*, $Cu_{1.9375}S$, it was 54.17 nm for PA 6 initially pretreated for 4 hours in $K_2S_5O_6$ solution and then treated with Cu(I) salt solution for 20 minutes at 35°C. For PA 6 initially pretreated for 5 h in $K_2S_5O_6$ solution, grain size for *chalcocite*, Cu_2S, was ~95.56 nm and for *djurleite*, $Cu_{1.9375}S$, was $59.175 - 90.107$ nm.

(5) The electrical conductivity of the Cu_xS/PA films at the constant current depends on the layer phase composition. The lowest sheet resistance of 102 Ω/cm^2 suggests formation of copper sulfide layers with the Cu/S molar ratio of 1 : 1.45.

(6) On the basis of our experiments, the mechanisms of pentathionate reactions in sulfuration medium during its diffusion into PA 6 surface have been considered. Polythionic compounds in their reactions were found to behave as derivatives of divalent electropositive sulfur S^{2+} and to undergo hydrolysis and degradation as indicated in the provided reaction formula.

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