



## Formation of mixed copper sulphide and silver sulphide layers on low density polyethylene film

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**Abstract.** The amount of copper in the copper sulphide layer and the amount of silver in the modified sulphide layer increased with the prolongation of the period of sulphurization in a polythionic acid solution and also of the treating time of the sulphurized sample in a solution of copper salts. X-ray diffraction results showed various copper sulphides, sulphur, silver, and silver sulphide in the samples. Silver sulphide and silver were formed when ion-exchange and reduction–oxidation reactions took place. A simple route to obtain copper and silver sulphides on polyethylene film is reported.

**Key words:** plastic materials, copper sulphide, silver sulphide, polyethylene, polythionic acid.

### INTRODUCTION

In the past few years, studies of materials with layered structures such as various metal chalcogenides have received an ever increasing attention. This has been caused mainly by their interesting physical and chemical properties and their usefulness for various applications. Copper sulphide,  $\text{Cu}_x\text{S}$ , a fast superionic conductor with a structural disorder, is a promising material for thermoelectric and photoelectric transformers and high temperature thermistors. Silver sulphide,  $\text{Ag}_2\text{S}$ , and silver selenide,  $\text{Ag}_2\text{Se}$ , have been used in photovoltaic cells, electrochemical storage cells, infrared detectors, photoconductors, and so on [1].

Metal chalcogenide layers with unique and improved chemical, electronic, and optical properties have been prepared using various chemical techniques, i.e. chemical deposition, electrodeposition, electroless deposition, spray pyrolysis, controlled precipitation, etc.

We previously reported the preparation and characterization of copper sulphide layers on polyethylene film (PE) of various densities by the sorption–diffusion method [2,3]. As the precursor of sulphur we used solutions of polythionic acids,  $\text{H}_2\text{S}_n\text{O}_6$ . Our investigation showed that the decomposition of polythionic acids with the liberation of elemental sulphur occurs during the

sulphurization of hydrophobic polymer. The liberated sulphur adsorbs on the surface of PE and then diffuses into its bulk. Sulphur is adsorbed–diffused into PE when the number of divalent sulphur ( $\text{S}_{n-2}$ ) atoms in  $\text{HSO}_3\text{--S}_{n-2}\text{--SO}_3\text{H}$  molecule is greater than 4 ( $n > 6$ ). Then sulphurized PE was treated with a solution of copper(I–II) salt and electrically conductive copper sulphide layers were obtained. However, we did not obtain silver sulphide layers in the surface of PE when sulphurized PE was treated with an  $\text{AgNO}_3$  solution.

In this paper, we report a simple route to obtain copper sulphide and silver sulphide layers on the surface of low density polyethylene film by using a solution of a polythionic acid as the precursor of sulphur. A preliminary study of the deposition process of  $\text{Ag}^+$  ions on the layer of a nonstoichiometric copper sulphide,  $\text{Cu}_x\text{S}$ , was conducted. For the characterization of the chemical and phase composition of the obtained layers various spectroscopic and X-ray diffraction (XRD) methods were used.

### MATERIALS AND METHODS

Film of low density polyethylene (GOST 10354–82) from the plastic plant Plasta, Vilnius (Lithuania), was used for the investigations. Rectangular samples of  $15 \times 75$  mm were used. Before sulphurization the surface of the polyethylene film was cleaned in a 4%

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solution of the detergent (non-ionic surfactant) Prewocell WOF-100, degreased in toluene, and washed in distilled water. For the inclusion of sulphur into the polyethylene a 0.002 mol/dm<sup>3</sup> solution of polythionic acid, H<sub>2</sub>S<sub>33</sub>O<sub>6</sub>, was used [4]. After having been kept in H<sub>2</sub>S<sub>33</sub>O<sub>6</sub> solution at 60°C, the sample was treated with a Cu(I–II) salt solution [5] at 60°C, then rinsed with distilled water, dried over CaCl<sub>2</sub>, and used for analysis. The part of sample with the obtained copper sulphide layer was treated with 0.04 mol/dm<sup>3</sup> AgNO<sub>3</sub> solution for 10 min at 60°C.

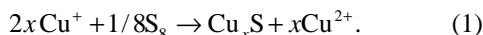
The sulphur adsorbed–diffused in PE samples was extracted with acetone, and the content in the extract was determined by a spectrometric method [6] using a Specord UV/VIS spectrophotometer ( $\lambda = 450$  nm).

The amounts of copper ( $\lambda = 325$  nm) and silver ( $\lambda = 328$  nm) in the obtained layers were determined using an atomic absorption spectrometer Perkin-Elmer 503. The PE films modified with sulphide layers were mineralized with concentrated HNO<sub>3</sub>. For the conditions described above, the sensitivity of the AAS method is about 0.09 µg/mL copper and 0.06 µg/mL silver for 1% absorption [7].

The phase composition of the formed layer was investigated by means of XRD using a DRON-6 diffractometer with Cu K $\alpha$  radiation (Ni filter) operated at 30 kV and 20 µA. The X-ray diffractograms of PE with layers were treated using the programs Search Match, ConvX, Xfit, and Microsoft Excel to eliminate the peaks of PE.

## RESULTS AND DISCUSSION

It was found in the experiments that the sulphur concentration in the PE samples kept in the polythionic acid solution increased with time. The PE samples were sulphurized for 15, 30, 60, and 120 min, obtaining concentrations of sulphur in PE 0.1; 0.119; 0.153, and 0.225 mol/dm<sup>3</sup>, respectively. When the sulphurized hydrophobic polymer was treated with a copper(I–II) salt solution, layers of copper sulphides in a matrix of PE were obtained. Copper sulphide forms during the heterogeneous redox reaction between elemental sulphur in PE and Cu(I) ions present in the copper salt solution:



Depending on the initial concentration of sulphur in PE and the period of sulphurized polymer treatment with the solution of the copper salt, brown or even black copper sulphide layers on PE were obtained.

Sulphurized PE samples were treated with the copper salt solution for 1–20 min. After measuring the amount of copper in the obtained layer, it was concluded that the copper amount ( $m_{\text{Cu}}$ ) increased with the

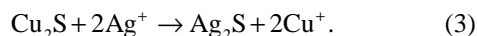
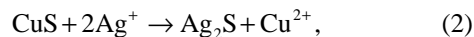
increasing sulphurization time and the time of treatment with the copper salt solution (Fig. 1).

Knowing the amounts of sulphur and copper, we calculated Cu and S molar ratios in the copper sulphide layers on PE. The results are presented in Table 1. It was shown that the amount of copper in the layer depended on the concentration of sulphur adsorbed–diffused into PE. The composition of the obtained Cu<sub>x</sub>S layers varied from Cu<sub>1.0</sub>S to Cu<sub>1.4</sub>S.

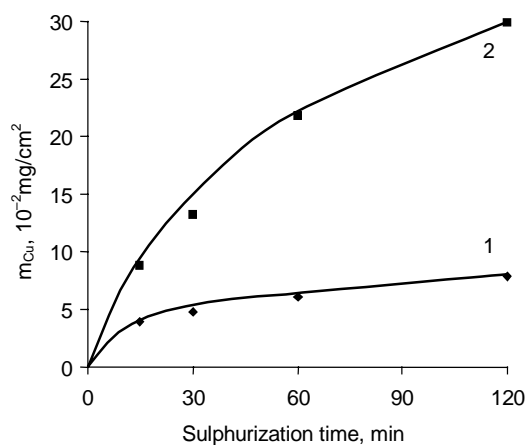
With the prolongation of the treating time in the copper(I–II) salt solution, the amount of copper in the sulphide layer also increased and the composition of the sulphide layers varied from Cu<sub>0.4</sub>S to Cu<sub>1.5</sub>S (Table 2). It is evident that these ratios varied significantly when the treating time in the copper salt solution increased from 1 to 5 min. With the increase in the treating time in the copper salt solution more Cu<sup>+</sup> ions reacted with the sulphur in PE.

Further the PE samples with Cu<sub>x</sub>S layers were immersed in an AgNO<sub>3</sub> solution. After the treatment the samples turned from brown or even black into greyish black.

After treating the obtained copper sulphide layer with a solution of Ag<sup>+</sup> ions, at least part of the Cu<sup>+</sup> and Cu<sup>2+</sup> ions in the sulphide layer could be substituted. Such exchanges of ions can be written as follows:



Such an exchange of ions is possible because the solubility product for Ag<sub>2</sub>S is  $7.2 \times 10^{-50}$ , whereas for CuS and Cu<sub>2</sub>S the products are  $1.4 \times 10^{-36}$  and  $2.3 \times 10^{-48}$ , respectively [8].



**Fig. 1.** Dependence of the amount of copper in the copper sulphide layer on polyethylene on its immersion time in the H<sub>2</sub>S<sub>33</sub>O<sub>6</sub> solution. Treatment time of sulphurized PE in the Cu(I–II) salt solution, min: 1 – 1, 2 – 10.

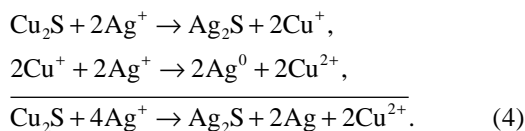
**Table 1.** Dependence of the composition (molar ratios) of the obtained layer on the PE sulphurization time in the  $H_2S_{33}O_6$  solution. The time of the treatment of the sulphurized PE in the Cu(I-II) salt solution was 10 min

Sulphurization time, min	Composition of obtained layer		
	Cu/S (S = 1)	(Ag + Cu)/S (S = 1)	Residual of Cu after 'silverization', %
15	1.0	0.8+0.15	15.0
30	1.1	0.9+0.2	18.2
60	1.2	1.0+0.2	16.7
120	1.4	1.15+0.3	21.4

**Table 2.** Dependence of the composition (molar ratios) of the obtained layer on the treating time in the Cu(I-II) salt solution. The PE film was sulphurized in the  $H_2S_{33}O_6$  solution for 120 min

Treating time in Cu(I-II) salt solution, min	Composition of obtained layer		
	Cu/S (S = 1)	(Ag + Cu)/S (S = 1)	Residual of Cu after 'silverization', %
1	0.4	0.9+0.01	2.5
5	1.2	1.1+0.1	8.3
10	1.4	1.15+0.3	21.4
20	1.5	1.2+0.35	23.3

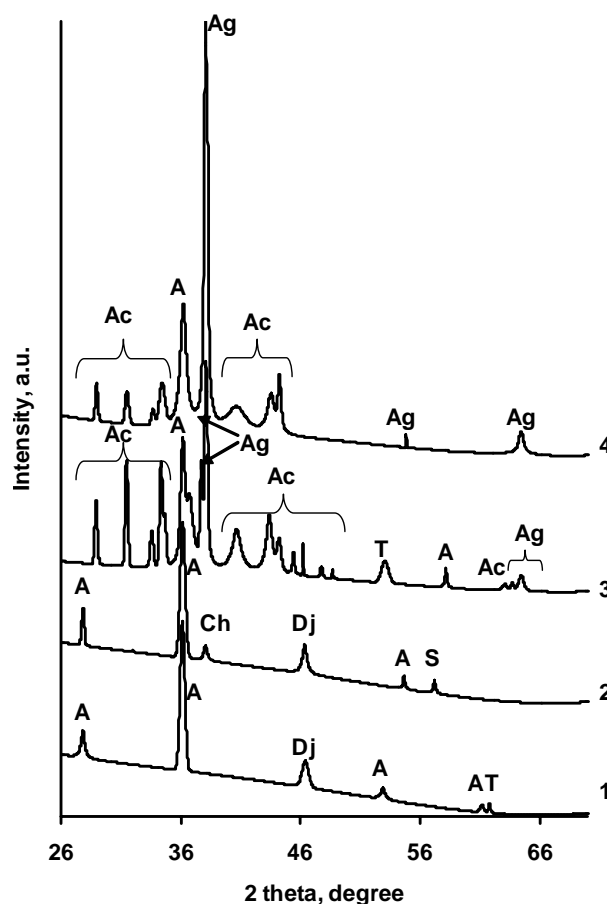
A reduction and oxidation interaction occurs between the layer components and silver ions:



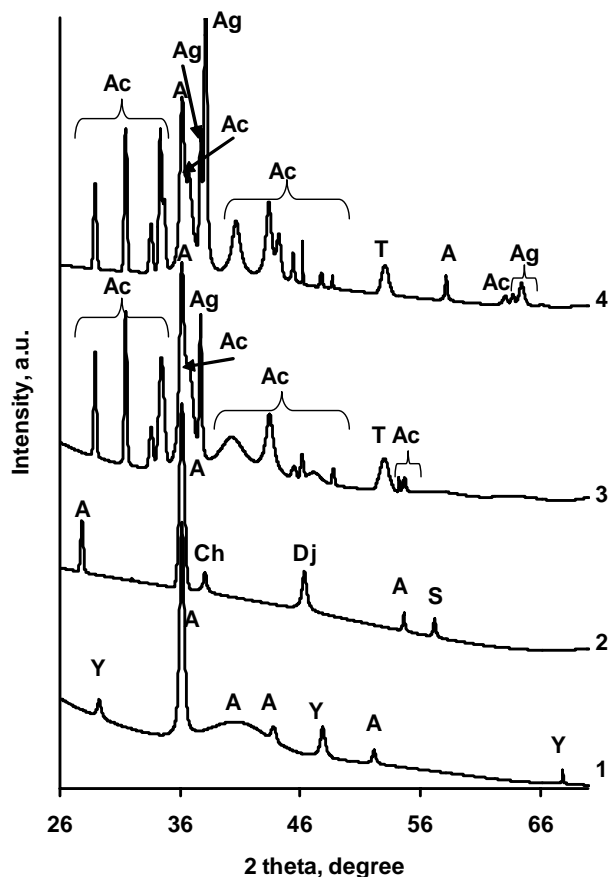
The results show that  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  in the copper sulphide layer were exchanged when the copper sulphide layer was modified by silver(I) ions (Tables 1 and 2). We determined that the amount of silver in the modified sulphide layers increased with the prolongation of sulphurization and the treating time of sulphurized samples in the copper salts solution. With the prolongation of sulphurization the silver part of mole increased from 0.8 up to 1.15 (Table 1), the amount of copper in sulphide layers decreased respectively from 100% to 15–21.4%. Despite this, with an increase of the sulphurization time the amount of copper remained greater than that of silver. With the prolongation of the treating time in a copper salt solution the silver part of mole increased from 0.9 up to 1.2 (Table 2); the amount of copper in the sulphide layers decreased respectively from 100% to 2.5–23.3%. However, as the amount of copper was higher it remained higher with an increase in the time of treatment with the copper(I-II) salt solution. That is, the results show that some amount of copper ions was released from the  $\text{Cu}_x\text{S}$  layer during the reaction with  $\text{Ag}^+$ .

The phase composition of the formed layer was established by comparing its X-ray diffraction pattern with those of known minerals [9,10]. Structural studies of the obtained layer are limited by the polycrystallinity of the layer and by the crystallinity of PE. The intensities of its peaks at  $\theta < 13^\circ$  exceed the intensity of sulphide peaks a few times. Therefore, the area of  $2\theta \geq 26^\circ$  was investigated in greater detail.

The results of phase analysis of PE samples with a  $\text{Cu}_x\text{S}$  layer, both untreated and treated with an  $\text{AgNO}_3$  solution, are summarized in Figs 2 and 3. The dependence of the layer composition on sulphurization time is shown in Fig. 2. It can be noticed that the composition of the copper sulphide layers depends weakly on the time of sulphurization. When the period of treatment in the polythionic acid solution was prolonged up to 120 min, a peak of unreacted elemental orthorhombic sulphur  $S_8$  (83–2284, at  $2\theta = 57.28^\circ$ ) is observed. The XRD spectra recorded for the  $\text{Cu}_x\text{S}$



**Fig. 2.** XRD patterns of the obtained layers on PE (peaks: A – anilite, T – talnakhite, Dj – djurleite, Ch – chalcocite, S – sulphur, Ac – acanthite, Ag – silver). Sulphurized PE was treated in the Cu(I-II) salt solution for 10 min, then in the  $\text{AgNO}_3$  solution for 10 min. Sulphurization time in the  $H_2S_{33}O_6$  solution, min: 1, 3 – 30; 2, 4 – 120.



**Fig. 3.** XRD patterns of the obtained layers on PE (peaks: Y – yarrowite, A – anilite, T – talnakhite, Dj – djurleite, Ch – chalcocite, Ac – acanthite, Ag – silver). Sulphurization time in the  $\text{H}_2\text{S}_{33}\text{O}_6$  solution 120 min, immersion time of PE with  $\text{Cu}_x\text{S}$  layer in the  $\text{AgNO}_3$  solution 10 min. Sulphurized PE treatment time in the Cu(I–II) salt solution, min: 1, 3 – 1; 2, 4 – 10.

layer on PE show that samples contain orthorhombic anilite  $\text{Cu}_7\text{S}_4$  (72–617, at  $2\theta = 27.9, 36.4, 53.1, 54.7,$  and  $61.68^\circ$ ), orthorhombic djurleite  $\text{Cu}_{1.97}\text{S}$  (20–365, at  $2\theta = 46.5^\circ$ ), monoclinic chalcocite  $\text{Cu}_2\text{S}$  (73–1138, at  $2\theta = 38.18^\circ$ ), and cubic talnakhite  $\text{Cu}_{34}\text{S}_{32}$  (71–2438, at  $2\theta = 61.9^\circ$ ). The XRD patterns of the samples treated in the  $\text{AgNO}_3$  solution showed peaks at  $2\theta = 28.96, 31.52, 34.18, 34.4, 36.86, 40.9, 43.5, 44.32, 45.48, 46.24, 47.48, 48.7,$  and  $63.76^\circ$  due to the monoclinic silver sulphide acanthite  $\text{Ag}_2\text{S}$  (14–72). Acanthite ( $\alpha\text{-Ag}_2\text{S}$ ) is a stable modification at low temperature, it is essentially stoichiometric [11]. In those diffraction patterns also the cubic silver-3 C Ag (4–783) at  $2\theta = 37.8, 38.11, 54.88, 64.40,$  and  $64.64^\circ$ , anilite at  $2\theta = 36.4$  and  $58.25^\circ$ , and talnakhite at  $2\theta = 53.3^\circ$  were detected.

On keeping sulphurized PE samples in the Cu(I–II) salt solution for different times copper sulphide layers of different composition were obtained (Fig. 3). After a

short treatment (1 min) peaks due to hexagonal yarrowite  $\text{Cu}_9\text{S}_8$  (36–379, at  $2\theta = 29.42, 48.72,$  and  $67.95^\circ$ ) and peaks due to anilite at  $2\theta = 36.4, 41.34, 44.0,$  and  $52.3^\circ$  dominated (Fig. 3, curve 1). With an increase of the treatment time with the Cu(I–II) salt solution, the peaks of  $\text{Cu}_x\text{S}$  phases with a higher value of  $x$  predominate in the X-ray diffraction pattern (Fig. 3, curve 2).

Analysis of the diffraction patterns of samples treated in the  $\text{AgNO}_3$  solution showed that some peaks could be indexed to acanthite and silver-3 C. Peaks of anilite and talnakhite also were detected in diffraction patterns.

The X-ray diffraction results showed that various copper sulphides, silver, and silver sulphide were obtained in the samples. Copper sulphides were obtained as a result of reaction (1). Silver sulphide and silver were formed when ion-exchange (2 and 3) and reduction–oxidation (4) reactions took place.

## CONCLUSIONS

The amount of copper in the obtained copper sulphide layer increased with the increase in the sulphurization time and treating time in the copper(I–II) salt solution. The composition of the copper sulphide layer varied from  $\text{Cu}_{0.4}\text{S}$  to  $\text{Cu}_{1.5}\text{S}$ . According to X-ray diffraction studies this layer included five copper sulphide phases: orthorhombic anilite  $\text{Cu}_7\text{S}_4$  and djurleite  $\text{Cu}_{1.97}\text{S}$ , monoclinic chalcocite  $\text{Cu}_2\text{S}$ , cubic talnakhite  $\text{Cu}_{34}\text{S}_{32}$ , and hexagonal yarrowite  $\text{Cu}_9\text{S}_8$ . Unreacted elemental orthorhombic sulphur  $\text{S}_8$  was also observed in the XRD pattern. Mixed copper sulphide and silver sulphide layers on polymer were formed when PE samples with a copper sulphide layer were treated with an  $\text{AgNO}_3$  solution. The amount of silver in this layer increased with the increase in the sulphurization time and treating time in the solution of copper salts. Copper ions were released from the  $\text{Cu}_x\text{S}$  layer during reaction with  $\text{Ag}^+$  and the amount of copper in the modified layer decreased. The XRD diffraction patterns of these layers showed predomination of the phase of monoclinic silver sulphide acanthite  $\text{Ag}_2\text{S}$ . The phases of silver-3 C Ag, talnakhite  $\text{Cu}_{34}\text{S}_{32}$ , and yarrowite  $\text{Cu}_9\text{S}_8$  were identified as well.

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## Kihtide moodustumine vask- ja hõbesulfiidi segust madaltihedal polüetüleenkilel

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Vase sisaldus vasksulfiidkihis, samuti hõbeda sisaldus modifitseeritud sulfiidkihis suureneb polütioonhappe lahuses toimuva sulfureerimisprotsessi pikenedes ja samuti siis, kui sulfureeritud objekti hoitakse kauem vasesoolade lahuses. Röntgendifraktsiooni uuringutest on selgunud, et objektid sisaldavad eri vasksulfiide, väävlit, hõbedat ja hõbesulfiidi. Hõbesulfiid ja hõbe moodustuvad ioonvahetus- ning redoksreaktsioonide tagajärjel.