

Preparation of Cu_xS Coatings on Polyethylene Foils Using Thiourea and Cu (I-II) Salt Solutions

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Abstract

The structure of Cu_xS layers, deposited by sorption-diffusion method, on polyethylene (PE) foils was studied. For the preparation of these layers PE samples were treated in the saturated solution thiourea containing an additive such as potassium persulfate in an acid medium. The sulfurized PE samples containing mainly S_6 and S_8 modifications were later treated with the aqueous solution of Cu (I-II) salt containing hydroquinone as a reducing agent. The value of x in the Cu_xS layer formed determined by the X-ray analysis ranged from 1 to 2. These layers contained mainly yarrowite $\text{Cu}_{1.13}\text{S}$, digenite $\text{Cu}_{1.8}\text{S}$ and chalcocite Cu_2S . The X-ray diffraction studies showed that the non-stoichiometric $\text{Cu}_{1.13}\text{S}$ was formed at the beginning of the formation of Cu_xS layer and its composition approached to Cu_2S , when the duration of sulfurized PE interaction with the solution of Cu (I-II) salt increased. The obtained Cu_xS layers of the thickness up to 50 μm showed sheet resistance of ca. 20 Ω .

Key words: polyethylene, copper sulfide coatings, diffusion, sorption, sheet resistance

Introduction

Interest in polymers with electrically conductive layers is recently notably increased. Such low-density materials are elastic and resistant with respect of corrosion. The polymers containing copper sulphide thin films might be used as conductive substrates for electrolytic deposition of metals and semiconductors and for optical electronic device structures.¹ Electrically conductive layers can be prepared by the sorption-diffusion method.² By this method the surface of a polymer film is initially treated by the solution containing sulfurization agent and then by the aqueous solution of Cu (I-II) salt. Sodium polysulfides,^{3–8} polythionic acids,^{9–12} and sulphur in carbon disulfide solution¹³ have already been used for sulfurization of polymer foils by different methods. Electrically conductive layers can be also prepared by one pot sorption method using a chemical bath with the solution containing copper complexes and thiourea,^{1,14,15} copper complexes with sodium thiosulfate^{16,17} and with thioacetamide.¹⁸ The stability of the solutions of copper complexes in this case must still be discussed. Different polymer foils have been used as substrates for the preparation of electroconductive Cu_xS layers, i.e. polyethylene,^{3,6,7,10,19}

polypropylene,¹⁹ polyester,^{13,16,17,18,20} polyamide,^{5,11,12,19} polystyrene,^{4,7,8} polyimide,¹ polyvinyl chloride,^{6,7,19} poly(methyl methacrylate),²¹ polysiloxanes.¹⁹ We have chosen polyethylene as a cheap, chemically stable and flexible substrate. In this work we report on the preparation of electrically conductive Cu_xS layers on polyethylene (PE) foils by the sorption-diffusion method with the use of thiourea as the sulfurization agent. The drawbacks of the earlier reported sulfurization agents, such as polythionic acids, sodium polysulfide and sulphur in carbon disulfide, are their harmfulness and the long preparation time.

The goal of this work was to investigate the process of sulfurization of PE in saturated thiourea solution with the different additives and to establish the optimal conditions of sulfurization in order to get the lowest sheet resistance of the Cu_xS layers. Another goal of this work was to choose an efficient additive which induce diffusion of sulphur into PE foil. It was also necessary to define the optimal concentration of the additive and to study the influence of the temperature of sulfurization solution on the kinetics of the process. The influence of the time of treatment of the sulfurized PE foils by the aqueous solutions of Cu (I-II) salt on the sheet resistance of the electrically conductive Cu_xS layers has also been studied.

Results and discussion

In order to obtain the electrically conductive layers on PE film with the low sheet resistance it was necessary to find the optimal conditions of the process of sulfurization. A series of different additives listed in Table 1 were studied and the electrical sheet resistance of the layers obtained by the following treatment with the aqueous Cu (I-II) salt solution was measured. The data obtained showed that the lowest sheet resistances were observed for those samples which were sulfurized using iodine and potassium persulfate as additives. Potassium persulfate was chosen for the partial oxidation of thiourea in the following studies. Iodine was rejected because of its high volatility and difficulties in defining its exact concentration.

Table 1. The effect of the additive of thiourea solution^a on the sheet resistance of the electrically conductive Cu_xS layers obtained on PE foil.

Additive, 0.01 mol/L	Sheet resistance, Ω
Without additive	2.85·10 ⁶
I ₂	12
K ₂ S ₂ O ₈	220
NaNO ₂	2.4·10 ⁶
H ₂ O ₂	70·10 ³
(NH ₄) ₂ SeO ₄	432
(NH ₄) ₂ S ₂ O ₈	9.3·10 ³
NH ₄ NO ₃ +NH ₃ H ₂ O	3.05·10 ⁶
Na ₂ Cr ₂ O ₇	2.4·10 ⁶
H ₂ SO ₄	2.5·10 ⁶
KNO ₃ (pH<7)	2.44·10 ⁶
NH ₄ NO ₃	2.4·10 ⁶
FeCl ₃	1.1·10 ⁶

^a (2.5 mol/L thiourea in 17.5 % w/w of HCl, 80 °C).

The optimal concentration of potassium persulfate in thiourea solution was defined with respect of the sheet resistance of the samples obtained after treatment with Cu (I-II) salt solution and the stability of the solution. When the concentration of potassium persulfate exceeded a certain value (0.005 mol/L) the formation of precipitates in the thiourea solution was observed. We have also studied the influence of the concentration of potassium persulfate in the thiourea solution on the sheet resistance of the Cu_xS layers obtained after the following treatment of the samples with the aqueous solution of Cu (I-II) salt. In these experiments only the concentration of potassium persulfate was changed. The concentration of thiourea (2.5 mol/L in 17.5 % w/w of HCl) and the temperature (80 °C) were constant. Figure 1 shows the dependencies of the ratio of masses of Cu_xS and PE ($m_{\text{Cu}_x\text{S}}/m_{\text{PE}}$) on sulfurization time for PE samples treated with the thiourea solution containing different concentrations of K₂S₂O₈.

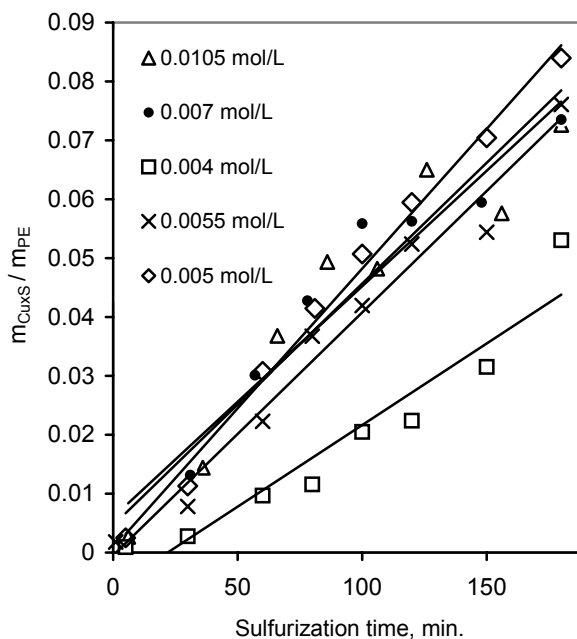


Figure 1. The dependencies of the ratio of masses of Cu_xS and PE ($m_{\text{Cu}_x\text{S}}/m_{\text{PE}}$) on sulfurization time for PE samples treated with thiourea solution containing different concentrations of potassium persulfate.

The results obtained show that the optimal concentration of the additive is 0.005 mol/L. At this concentration of the additive the ratio of masses $m_{\text{Cu}_x\text{S}}/m_{\text{PE}}$ increases rectilinearly with time.

Figure 2 shows the dependencies of the ratios of masses of sulphur and PE ($m_{\text{S}}/m_{\text{PE}}$) and of Cu_xS and PE ($m_{\text{Cu}_x\text{S}}/m_{\text{PE}}$) on the concentration of potassium persulfate in thiourea solution observed after the treatment PE samples for 3 hours by thiourea solution containing different amounts of the additive.

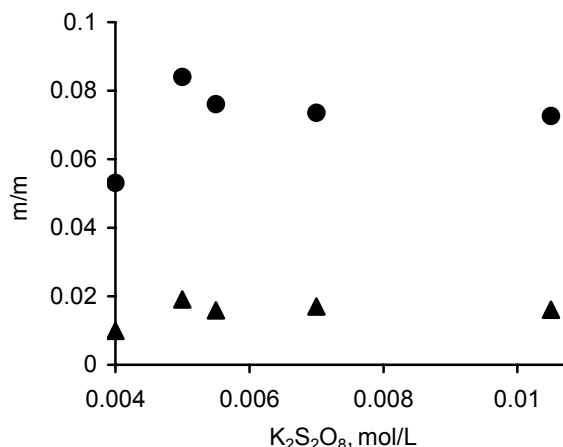


Figure 2. The dependencies of the ratios of $m_{\text{S}}/m_{\text{PE}}$ (▲) and of $m_{\text{Cu}_x\text{S}}/m_{\text{PE}}$ (●) on the concentration of potassium persulfate observed after the treatment PE samples for 3 hours by thiourea solutions containing different amounts of the additive

Table 2. The dependence of the sheet resistances of PE samples^a containing Cu_xS layers^b on the concentration of potassium persulfate in thiourea solution.

Sulfurization time, min	Sheet resistance, Ω				
	[K ₂ S ₂ O ₈] = 0.004 mol/L	[K ₂ S ₂ O ₈] = 0.005 mol/L	[K ₂ S ₂ O ₈] = 0.0055 mol/L	[K ₂ S ₂ O ₈] = 0.007 mol/L	[K ₂ S ₂ O ₈] = 0.01 mol/L
60	–	366	–	800	178
80	–	300	1400	81	318
100	–	270	300	58	135
120	112	200	260	49	192
150	360	120	140	74	291
180	107	74	76	86	225

^a Pretreated in 2.5 mol/L thiourea solution in 17.5 % w/w of HCl at 80 °C. ^b Cu_xS layers were obtained by treating the sulfurized PE samples in 0.625 mol/L aqueous solution of Cu (I-II) salt containing 1.1 % w/w of hydroquinone for 8 minutes at 80 °C.

The maximum ratios m_S/m_{PE} and m_{Cu_xS}/m_{PE} were observed using the thiourea solution in which the concentration of potassium persulfate was 0.005 mol/L. The sheet resistance data for PE samples treated with thiourea solutions containing different amounts of potassium persulfate and then treated with the aqueous Cu (I-II) salt solution are given in Table 2.

The data presented in Table 2 show, that the concentration of potassium persulfate in thiourea solution of 0.005 mol/L can be regarded as an optimal one. Using this concentration of potassium persulfate in thiourea solution the sheet resistance of Cu_xS layers obtained after the treatment the sulfurized PE foils with the aqueous solution of Cu (I-II) salt was quite low and exhibited the linear dependence on the concentration of the additive in the thiourea solution.

We also studied the influence of the temperature of sulfurization on the mass of the Cu_xS layer obtained. The samples were treated in 17.5 % w/w solution of hydrochloric acid containing 2.5 mol/L of thiourea and 0.005 mol/L of potassium persulfate at the different temperatures and later exposed to the action of the solution of the Cu (I-II) salt. Figure 3 shows the time dependencies of the mass ratio m_{Cu_xS}/m_{PE} for PE samples treated with the thiourea solution at the different temperatures.

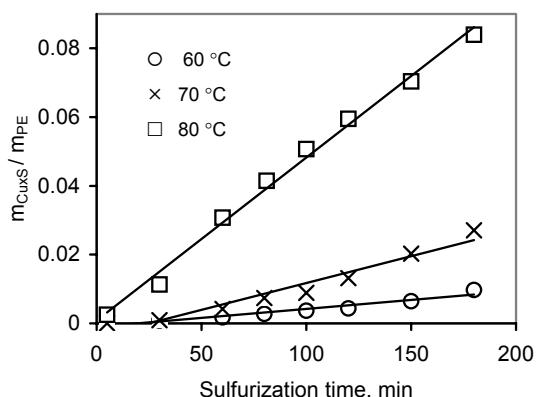


Figure 3. Time dependencies of the mass ratio m_{Cu_xS}/m_{PE} for PE films treated with thiourea solution at different temperatures. Cu_xS layers formation was carried out in 0.625 mol/L aqueous solution of Cu (I-II) salt containing 1.1 % w/w of hydroquinone for 8 minutes at 80 °C.

The data presented in Table 3 illustrate dependence of the electrical resistance of the Cu_xS layers obtained on the sulfurized samples of PE on the temperature of the sulfurization solution. Increase of the temperature of sulfurization solution leads to the increase of sulphur absorbed by PE foil which leads to the decrease of the sheet resistance of the Cu_xS layers obtained. This observation shows that the thiourea solution used is stable in the temperature range from 60 to 80 °C. The lowest sheet resistances were observed for the samples sulfurized at 80 °C. At this temperature the mobility of segments of PE chains is enhanced, which makes easier diffusion of sulphur into the polymer matrix. The further increase of the temperature of sulfurization is not expedient since at the temperatures higher than 80 °C undesirable side reactions, i.e. precipitation of sulphur and emission of H₂S occur in the sulfurization solution.

Table 3. The dependence of the sheet resistances of PE samples containing Cu_xS layers^a on the temperature of thiourea solution^b.

The time of exposure, min.	Sheet resistance, Ω		
	60 °C	70 °C	80 °C
60	–	6.5×10 ⁶	3.7×10 ²
80	1.3×10 ⁶	6.0×10 ⁶	3.0×10 ²
100	1.0×10 ⁶	5.0×10 ⁶	2.7×10 ²
120	1.0×10 ⁶	3.8×10 ⁴	2.0×10 ²
150	6.0×10 ⁵	2.9×10 ³	1.2×10 ²
180	8.0×10 ⁵	8.4×10 ²	74

^a Cu_xS layers were obtained by treating the sulfurized PE samples in 0.625 mol/L aqueous solution of Cu (I-II) salt containing 1.1 % w/w of hydroquinone for 8 minutes at 80 °C. ^b Pretreated in 2.5 mol/L thiourea solution in 17.5 % w/w of HCl, containing 0.005 mol/L K₂S₂O₈.

In the further investigations we studied the influence of the time of the treatment of the sulfurized PE samples in the solution of Cu (I-II) salt on the mass ratio m_{Cu_xS}/m_{PE} and the sheet resistance of the electrically conductive Cu_xS layers obtained. The data obtained are given in Figure 4. At short times of the treatment of the sulfurized PE samples in the solution of Cu (I-II) salt lasting from 0.5 to 4 minutes the lowest

sheet resistances of the electrically conductive layers were observed. The increase of the treatment time from 4 to 8 minutes lead to the increase of the sheet resistance of the samples. The increase of the treatment time above 8 minutes did not result in the increase of the sheet resistance. Similarly, it was observed that after 8 minutes of exposure time the mass of the electrically conductive layers becomes stable. At the shorter treatment times the increase of mass of the electrically conductive layers with the time was observed.

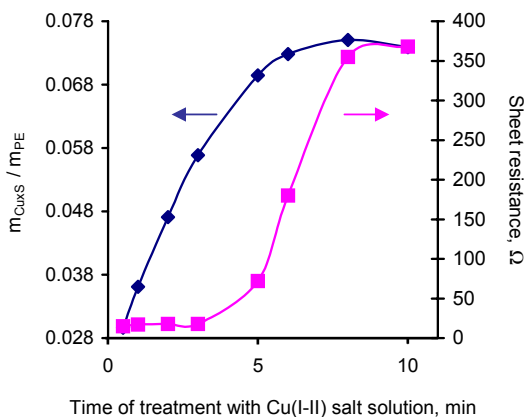


Figure 4. The dependence of the mass ratio $m_{\text{Cu}_x\text{S}}/m_{\text{PE}}$ and resistance of PE samples on the time of treatment in the solution of Cu (I-II) salt. Initially the samples were pretreated for 3 hrs in 17.5 % w/w HCl solution containing 2.5 mol/L of thiourea and 0.005 mol/L of potassium persulfate and then treated at 80 °C in the aqueous 0.625 mol/L solution of Cu (I-II) salt containing 1.1% w/w of hydroquinone.

We used X-ray analysis for the investigation of the modification of sulphur diffused into PE foil. Figure 5 shows X-ray diffraction patterns of the sulphur layers obtained after the treatment of PE foils with the solution of the thiourea containing 0.005 mol/L of potassium persulfate. Mainly S_6 and S_8 sulphur modifications were

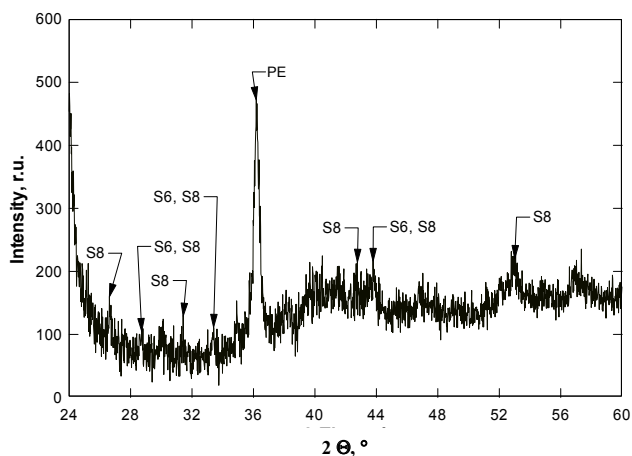


Figure 5. X-ray diffraction pattern the diffusion layer after sulfurization of PE foil in 2.5 mol/L thiourea in 17.5 % w/w of HCl with 0.05 mol/L of $\text{K}_2\text{S}_2\text{O}_8$ at 80 °C for 180 min.

observed. The thickness of diffused sulphur layers was ca. 50 μm as observed by electron microscopy.

We also used X-ray analysis for the investigation of the composition of the Cu_xS electrically conductive layers of the samples obtained by the treatment of the sulphurized PE foils in the solution of Cu (I-II) salt for the different periods of time. Figure 6 shows X-ray diffraction patterns of the Cu_xS layers obtained on the sulfurized PE foils by their treatment in the solution of Cu (I-II) salt for 1 minute (Curve A) and for 8 minutes (Curve B).

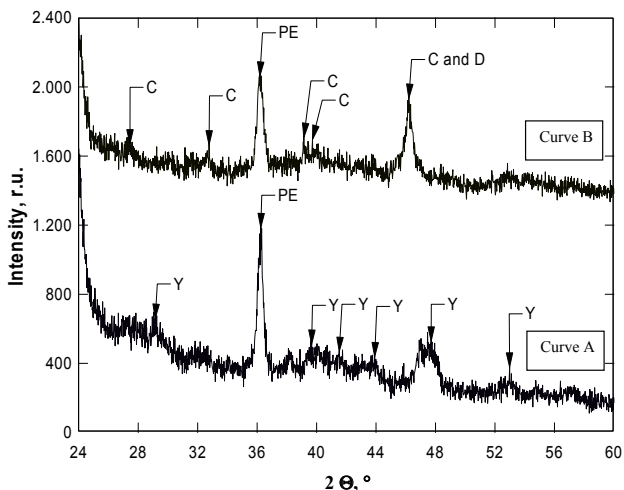


Figure 6. X-ray diffraction patterns of the Cu_xS layers obtained on sulphurized PE foils by their treatment at 80 °C in the aqueous 0.625 mol/L solution of Cu (I-II) salt containing 1.1% w/w of hydroquinone for 1 minute (Curve A) and 8 minutes (Curve B). Labels: C-Chalcosine; D-Digenite; Y-Yarrowite and PE-Polyethylene. Initially the samples were pretreated for 3 hrs at 80 °C in 17.5% w/w HCl solution containing 2.5 mol/L thiourea and 0.005 mol/L $\text{K}_2\text{S}_2\text{O}_8$.

The analysis of X-ray diffraction patterns has shown that the main component of electrically conductive layers obtained after the treatment of the sulfurized PE samples in the solution of Cu (I-II) salt for the short periods of time ranging from 0.5 to 4 minutes is yarrowite. The x value in Cu_xS ranges from 1.125 to 1.3 in this case. The sheet resistance of ca. 20 Ω was observed for the layers of such composition (cf. Figure 4). The x value in Cu_xS layer obtained after the treatment of the sulfurized PE samples in the solution of Cu (I-II) salt for the longer periods of time ranging from 4 to 8 minutes varies from 1.3 to 2. The main components of such layers are digenite and chalcosine. The sheet resistance ranging from 70 to 380 Ω was observed for the layers of such composition (cf. Figure 4).

The thickness of Cu_xS layers on PE foil was ca. 50 μm as observed by scanning electron microscopy. The cross-section electron micrograph of PE foil with Cu_xS layer is presented in Figure 7.

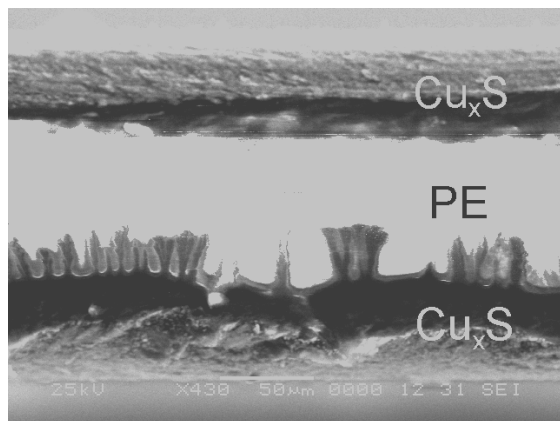


Figure 7. The cross-section electron micrograph of the Cu_xS layer on PE foil after treatment at 80 °C in the aqueous 0.625 mol/L solution of Cu (I-II) salt containing 1.1% w/w of hydroquinone for 8 minutes. Initially the sample was pretreated for 3 hrs at 80 °C in 17.5% w/w HCl solution containing 2.5 mol/L thiourea and 0.005 mol/L $\text{K}_2\text{S}_2\text{O}_8$.

Conclusions

Electrically conductive layers of copper sulfides with low sheet resistance (up to 20 Ω) on polyethylene foils were prepared. Before the treatment with the aqueous Cu (I-II) solution the samples were sulfurized in the acid solution of thiourea containing potassium persulfate as an additive. The optimal conditions for the formation of Cu_xS layers on PE foil were established. Initially PE foil has to be sulfurized for 3 hrs at 80 °C in 17.5 % w/w HCl solution containing 2.5 mol/L of thiourea and 0.005 mol/L of potassium persulfate. Then it has to be treated for 0.5–4 min. at 80 °C in the aqueous 0.625 mol/L solution of Cu (I-II) salt containing 1.1% w/w of hydroquinone. Diffused in PE sulphur and Cu_xS layers were studied by the X-ray scattering. S_6 , S_8 modifications were observed in PE after the sulfurization by thiourea. Yarrowite, digenite and chalcosine were found to be the main components of electrically conductive layers. The thickness of Cu_xS layers on PE foil was ca. 50 μm as observed by scanning electron microscopy.

Experimental

Unstabilized low-density PE foils of 150 μm thickness received from the “Maldis” company (Lithuania) were used for the sulfurization experiments. The surface of the samples before sulfurization was treated with 1 mol/L NaOH aqueous solution. Afterwards the samples were immersed into acetone for 24 hours for degreasing and washed with distilled water. Thus prepared samples were treated with the thiourea solution (2.5 mol/L thiourea in 17.5 % w/w of HCl solution) containing different amounts of an additive.

Then PE samples containing sulphur were washed with distilled water, dried and treated in the aqueous solution of Cu (I-II) salt prepared by mixing CuSO_4 0.625 mol/L and 1.1% w/w of hydroquinone at 80 °C.

The sheet resistance of electrically conductive layers was measured using the digital device E7-8 (Russia). The sulphur and Cu_xS layers were studied by wide-angle X-ray scattering (WAXS) using the equipment ДРОН-6 (Russia), (K_α , 30kV, 20 μA). The thickness of Cu_xS layers on PE foil was estimated by scanning electron microscope JSM-5600 (Japan).

References

1. J. Cardoso, O. Gomez Daza, L. Ixtilco, M. T. S. Nair, P. K. Nair, *Semicond. Sci. Tech.* **2001**, *16*, 123–127.
2. S. D. Brown, E. D. Ottavoi, J. J. Kurmik, J. J. Grunwald, U.S. Pat. 3 682 786, 1972.
3. A. Zebrauskas, M. Baranauskas, R. Spirikaviciene U.S.S.R. Pat. 19860223, 1986.
4. J. Sataite, M. Baranauskas, A. Zebrauskas, *Plast. Massy* (Moscow) **1989**, *2*, 50–52. (in Russian).
5. A. Zebrauskas, M. Baranauskas, *Zhurnal Prikladnoi Khimii* (Sankt-Peterburg, Russia) **1989**, *62*, 2773–2776. (in Russian).
6. A. Zebrauskas, *Chemija* (Vilnius, Lithuania) **1992**, *2*, 112–122. (in Russian).
7. A. Zebrauskas, J. Sataite, L. Baltienienė, *Chemija* (Vilnius, Lithuania) **1991**, *2*, 134–147. (in Russian).
8. A. Zebrauskas, J. Sataite, *Chemija* (Vilnius, Lithuania) **1993**, *2*, 36–43. (in Russian).
9. I. Ancutiene, V. Janickis, S. Grevys, A. Zebrauskas, *Chemija* (Vilnius, Lithuania) **1996**, *4*, 3–8.
10. I. Ancutiene, V. Janickis, S. Grevys, *Chemija* (Vilnius, Lithuania) **1997**, *2*, 3–10.
11. R. Maciulevicius, V. Janickis, R. Ivanauskas, *Chemija* (Vilnius, Lithuania) **2000**, *11*, 141–149.
12. V. Janickis, R. Maciulevicius, R. Ivanauskas, I. Ancutiene, *Colloid Polym. Sci.* **2003**, *281*, 84–89.
13. J. Zukauskaitė, V. Janickis, I. Ancutiene, *Chemine Technologija* (Kaunas, Lithuania) **2002**, *5*, 36–41. (in Lithuanian).
14. P. K. Nair, V. M. Garcia, A. M. Fernandez, H. S. Ruiz, M. T. S. Nair, *J. Phys. D: Appl. Phys.* **1991**, *24*, 441–449.
15. C. Nascu, V. Vomir, *Revista de Chimie* **1996**, *47*, 934–941.
16. I. Grozdanov, *Chem. Lett.* **1994**, *3*, 551–554.
17. I. Grozdanov, M. Najdoski, *J. Solid State Chem.* **1995**, *114*, 469–475.
18. P. K. Nair, J. Cardoso, O. Gomez Daza, M. T. S. Nair, *Thin Solid Films* **2001**, *404*, 243–250.
19. R. Spirikaviciene, A. Zebrauskas, M. Baranauskas, *Plast. Massy* (Moscow) **1986**, *10*, 20–21. (in Russian).
20. E. Paluckienė, S. Grevys, V. Grigaliūnas, *Chemine Technologija* (Kaunas, Lithuania) **2002**, *1*, 61–64. (in Lithuanian).
21. H. L. Hu, P.K. Nair, *Surface and Coatings Tech.* **1996**, *81*, 183–189.

Povzetek

V prispevku je opisan študij strukture Cu_xS plasti, nanešenih na polietilenske folije s sorpcijsko-difuzijsko metodo. Za pripravo Cu_xS plasti so bile polietilenske folije obdelane v nasičeni raztopini tiosečnine v kislem mediju z dodatkom kalijevega persulfata, nato pa še v vodni raztopini Cu (I-II) soli z dodatkom hidrokinona kot reducenta. Z XRD analizo je bilo ugotovljeno, da so plasti sestavljene iz Cu_xS z vrednostmi x med 1 in 2: prevladujejo jarovit $\text{Cu}_{1,13}\text{S}$, digenit $\text{Cu}_{1,8}\text{S}$ in halkozin Cu_2S . Na začetku formiranja plasti nastaja nestehiometrična oblika $\text{Cu}_{1,13}\text{S}$, ki s časom obdelave z raztopino Cu (I-II) soli prehaja v Cu_2S . Površinska upornost Cu_xS prevlek je okoli 20 Ω .