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Comparison of the efficacy of sulfurization agents in decreasing the sheet resistance of polyamide and polyethylene with copper sulfide layers and influence of their compositions

Research Article

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Abstract: The process of obtaining semiconductive and electrical conductive layers of copper sulfides by the sorption – diffusion method on polymers (polyamide 6 and low density polyethylene) using solutions of potassium pentathionate, $K_2S_5O_6$, and higher polythionic acids, $H_2S_nO_6$ (n = 21, 33), was investigated. The layers were characterized for compositional and electrical properties by X–ray diffraction (XRD) analysis and sheet resistance measurements. The thickness of copper sulfides layers on polyamide and polyethylene increased with increasing time of polymer sulfurization and varied from 10 to 43 μm. The variations of the sheet resistance of copper sulfides layers formed on the surface of polymers on sulfurization agent used, the conditions of sulfurization, chemical and phase composition of the obtained layers were established. Sheet resistance of copper sulfides layers decreases with increasing time of the duration of sulfurization and the number of sulfur atoms in the polythionate anion. The sheet resistance values for copper sulfide layers formed on the polyamide surface are much lower than those of Cu_xS formed on the polyethylene surface. XRD showed the predomination of Cu_xS phases with low x values.

Keywords: *Polythionates • Copper sulfide layers • Modification of Polyamide and Polyethylene*

1. Introduction

In recent years, there has been a growing interest in the formation of inorganic semiconductive or electrical conductive particles or layers. Films containing these particles have potential applications in optoelectronic devices as optical switches, as infrared detectors and in photovoltaics [1]. Thin metal sulfides layers play an important role in the development of modern technology, mainly in optical and electronic devices [2].

Copper sulfide (Cu_xS) is a semiconductor, which has been studied for various applications. For example, Cu_xS is useful for solar control coatings, solar energy conversion, electronic and low-temperature gas sensor applications [3-6].

Cu_xS are interesting in the above respect, in particular, since they show great susceptibility to compositional changes. The unique property of copper sulfides in the wide region of stoichiometry (Cu/S = 2.0 – 1.0) enables the formation of several stable phases of the $Cu_{2-x}S$ type [7].

Cu_xS thin films have been prepared by chemical and physical methods, such as chemical bath deposition (CBD), electrodeposition, successive ionic layer adsorption and reaction (SILAR), and so on. Among these methods, sorption-diffusion method is an attractive method to obtain copper sulfide layers. In this study the layers of copper sulfide on semihydrophilic polyamide (PA) and hydrophobic polyethylene (PE) were obtained by a two-step sorption-diffusion method elaborated by us previously [8,9].

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The aim of this work was to compare the sulfurization agents for obtaining copper sulfide layers by the sorption – diffusion method on the surface of PA and PE. As sulfurization agents we used solutions of potassium pentathionate, $K_2S_5O_6$, and higher polythionic acids, $H_2S_nO_6$ (n = 21, 33). In this study we also studied the variation of sheet resistance and phase composition due to sulfurization precursor, polymer and the conditions of sulfurization.

2. Experimental Procedures

The layers of copper sulfide were obtained on polyamide PA 6 (TY 6-05-1775-76, grade PK–4, 15×70 mm, 70 μm) and low-density polyethylene films (15×70 mm, 142 *μ*m). Before sulfurization the PE films were cleaned in a 4% solution of a non-ionic surfactant (Prewocell WOF-100), degreased in toluene and washed in distilled water. The PA films were boiled in distilled water for 2 h to remove the monomer residues. They were dried with filter paper and then over $CaCl_2$ for 24 h.

In the first step, for incorporating into polymer polythionate anions, containing divalent sulfur chains, $^{-}O_3S\text{-}S_{n-2}\text{-}SO_3^{-}$, the PA films were sulfurized in a thermostatic vessel using a continually stirred 0.1 mol L^{-1} solution of potassium pentathionate in HCl (c = 0.1 mol L^{-1}) at 20°C for 6 h or 0.002 mol L^{-1} solution of polythionic acid $H_2S_{21}O_6$ at 50°C for 4 h. For sulfurization of PE films, 0.002 mol L^{-1} solutions of polythionic acids $H_2S_{21}O_6$ and $H_2S_{33}O_6$ at 60°C for 3 h were used.

Potassium pentathionate hemitrihydrate, $K_2S_5O_6{\bullet}1.5H_2O$, was prepared by the method of Kurtenacker [10]. Solutions of higher polythionic acids were prepared and the average value of n in $H_2S_nO_6$ was determined by the methods described in [11].

In the second step, thin layers of semiconductive and electrical conductive copper sulfide were formed on the surface of both polymers, when samples of the sulfurized PA and PE were treated with a solution of Cu(II/I) salt at 80°C for 10 min. A Cu(II/I) salt solution was made from crystalline $CuSO_4{\bullet}5H_2O$ and a reducing agent hydroquinone as described in [12,13]. It is a mixture of copper salts, containing 0.34 mol L^{-1} of Cu(II) and 0.06 mol L^{-1} of Cu(I) [12]. The presence of cations of the same element in different oxidation states and crystallographically equivalent positions leads to electronic semiconduction. After treatment with the solution of Cu(II/I) salts, the samples of polymers were rinsed with distilled water, dried over $CaCl_2$ and used in further experiments.

The sulfur concentration (c_s) in PA films was determined potentiometrically [14]. A sample of sulfurized PA film was treated under heating with 10–15 mL of 10 mol L^{-1} KOH solution and diluted with the same amount of distilled water. Standard calomel and platinum electrodes were used in potentiometric titration of KOH solution with 0.05 mol L^{-1} solution of iodine under stirring. For the potentiometric measurements, a pH-meter − pH−673 M millivoltmeter was used. The sulfur diffused into the PE samples was extracted with acetone, and the content in the extract was determined by a spectrometric cyanide method [15] using a Specord UV/VIS spectrophotometer (λ = 450 nm).

The amount of copper in copper sulfide layers after fusing in concentrated nitric acid was determined using a Perkin – Elmer atomic absorption spectrometer (λ = 450 nm) [16].

The cross-section of the cut polymer sample with Cu_xS layer was investigated using a JXA-50A electronic microscope (JEOL). The thickness of the Cu_xS layer was measured from the EM photo.

The conductivity of copper sulfide films at constant current was measured on the four-point digital instrument E7-8. The polymer film was placed under special electrode made from two nickel-plated copper plates with fixed 1 cm length dielectric material between them.

The phase composition of copper sulfide layers was investigated by X–ray diffraction (XRD) using a DRON-6 diffractometer (Cu-K_α radiation). X–ray diffractograms of PA and PE samples with copper sulfides layers were treated using the programs Search Match, ConvX, Xfit and Microsoft Excel to eliminate the maxima of polymers.

3. Results and Discussion

Previously it has been shown that particles of elemental sulfur were sorbed – diffused into PE from solutions of higher polythionic acids [17] or the anions of polythionates, $S_nO_6^{2-}$, − into the PA surface [18]. As a result of redox reactions of Cu(II/I) solutions with the surface of sulfurized polymers, electrical conductive layers of copper sulfides were formed:

$$1/nS_n + 2xCu^{+} \rightarrow Cu_xS + xCu^{2+} \quad (1)$$

$$S_nO_6^{2-} + 2Cu^{+} + 2H_2O \rightarrow Cu_2S + (n\text{–}3)S + 2H_2SO_4 \quad (2)$$

$$S_nO_6^{2-} + Cu^{2+} + 2H_2O \rightarrow CuS + (n\text{–}3)S + 2H_2SO_4 \quad (3)$$

The anions of Cu(II) not reacted with the elemental slfur.

The values of sheet resistances of copper sulfides formed on the surface of PE and PA varied with the exposure time in the solution of sulfurization agent in a large interval exhibiting a minimum at maximum

Table 1. Sheet resistance (R) of Cu_xS layers on PA and PE first treated in a solution of $K_2S_5O_6$ or higher polythionic acid ($H_2S_{21}O_6$ or $H_2S_{33}O_6$) and then – in Cu(II/I) salt solution

Duration of sulfurization, h	PA, $K_2S_5O_6$	PA, $H_2S_{21}O_6$	PE, $H_2S_{21}O_6$	PE, $H_2S_{33}O_6$
	R, Ω/□			
0.25	$5.2×10^5$	10.0	$5.0×10^5$	$4.0×10^5$
0.5	$4.5×10^5$	2.62	$6.2×10^4$	$5.4×10^3$
1.0	$2.2×10^5$	1.14	$2.7×10^3$	$1.2×10^3$
2.0	457	0.51	$1.1×10^3$	399
3.0	277	0.42	980	276
4.0	127	0.48	-	-

duration of treatment (Table 1). These values depend also on the degree of sulfurity of precursor of sulfur (number of sulfur atoms, *n*, in the polythionate anion) and the nature of polymer. For the Cu_xS layers formed after exposure of polymers to a solution of $K_2S_5O_6$ for 4 h and to a solution of $H_2S_{33}O_6$ for 3 h, sheet resistance decreased, respectively, from $5.2×10^5$ to 127 Ω/− and from $4.0×10^5$ to 276 Ω/− − approximately 4100 and 1450 times. The overall decrease in sheet resistance of Cu_xS layers due to an increase in the sulfurization time of PA and PE might be explained by the growth of those layers as a result of the sorption of polythionate anion or the adsorption of sulfur on the surface of the polymer and then the diffusion of adsorbed sulfur particles into the polymer bulk. The continuous increase in the sulfur concentration up to 7 mg cm^{-3} with increasing time of sulfurization of PA in $K_2S_5O_6$ solution and of PE in the solution of $H_2S_{21}O_6$ or $H_2S_{33}O_6$ (Fig. 1, curves 1, 3 and 4) resulted in decrease in resistance, respectively, to 127, 980 and 276 Ω/− (Table). Nevertheless, the concentration of sulfur in PA, sulfurized in $H_2S_{21}O_6$ solution, was higher than 150 mg cm^{-3} (Fig. 1, curve 2). As a result, the value of sheet resistance after PA sulfurization in solution of this acid was the lowest − 0.42–0.48 Ω/− (Table). Consequently, when the sulfur concentration is sufficient, *i.e.* the duration of sulfurization is longer, more conductive layers are obtained. The value of sheet resistance of copper sulfides layer depends to a great extent on the sulfur content (number of sulfur atoms in the molecule) in the sulfurization agent. A significant difference – 52000 times and 265 times – was found in sheet resistance of the layers of Cu_xS on PA formed using different precursors – $K_2S_5O_6$ or $H_2S_{21}O_6$ solution after sulfurization for 0.25 h and for 4 h, respectively, despite the molar concentration of $H_2S_{21}O_6$ solution being 50 times lower than that of $K_2S_5O_6$ solution. These data reveal that sulfur concentration in polymer depend on a significant contribution of sulfur content in the precursor than the concentration of the precursor solution used for sulfurization, *i.e.* for three atoms of divalent sulfur atoms in the $K_2S_5O_6$ molecule, there are 19 atoms of divalent sulfur in the $H_2S_{21}O_6$ molecule, most probably influencing the chemical composition of the latter.

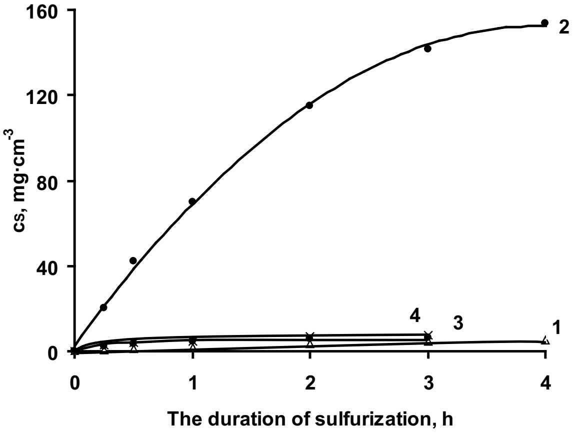

Figure 1. Changes of sulfur concentration in the films of PA (curves 1 and 2) and PE (curves 3 and 4) with time. The sulfurization agent: 1 – $K_2S_5O_6$; 2 – $H_2S_{21}O_6$; 3 – $H_2S_{21}O_6$, 4 – $H_2S_{33}O_6$

The amount of copper (m_{Cu}) in copper sulfides layers formed on the PA surface, sulfurized in $K_2S_5O_6$ solution (Fig. 2, curve 1), shows a sharp increase, while on the PE surface, sulfurized in $H_2S_{33}O_6$ solution (Fig. 2, curve 4), m_{Cu} increases only up to a sulfurization time of 1 h.

Further prolongation of sulfurization leads to saturation of copper. The amount of copper in the layers of copper sulfides formed on the PA surface, sulfurized in $H_2S_{21}O_6$ solution increases sharply up to 0.5 h sulfurization time and then slightly decreases with increasing sulfurization time (Fig. 2, curve 2). This insignificant decrease in the copper content in Cu_xS layers on the PA surface can be due to the decomposition of $S_{21}O_6^{2-}$ anions both, in

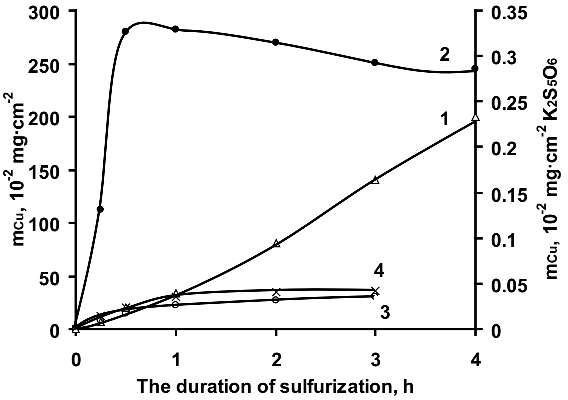

Figure 2. Changes of amount of copper in Cu_xS layers on PA (curves 1 and 2) and PE (curve 3 and 4) with time. The sulfurization agent: 1 – $K_2S_5O_6$; 2 – $H_2S_{21}O_6$; 3 – $H_2S_{21}O_6$, 4 – $H_2S_{33}O_6$

solution and sorbed on – diffused into PA according the equation:

$$S_nO_6^{2-} \rightarrow (n-2)S + SO_2 + SO_4^{2-} \qquad (4)$$

The decomposition products, SO_2 and SO_4^{2-}, were washed out from the polymer, while the elemental sulfur remained. Actually, the sulfur reacted more slowly than the $S_nO_6^{2-}$ anions with copper ions in the second step of the formation of copper sulfides on the surface of polymers. As it can be seen from Table 1, the higher electric resistance of the copper sulfide layer on PA, sulfurized for 4 h in $H_2S_{21}O_6$ solution, shows that the formation of elemental sulfur in the decomposition of $S_nO_6^{2-}$ anions leads to a slight increase in resistance (0.42→0.48 Ω/−).

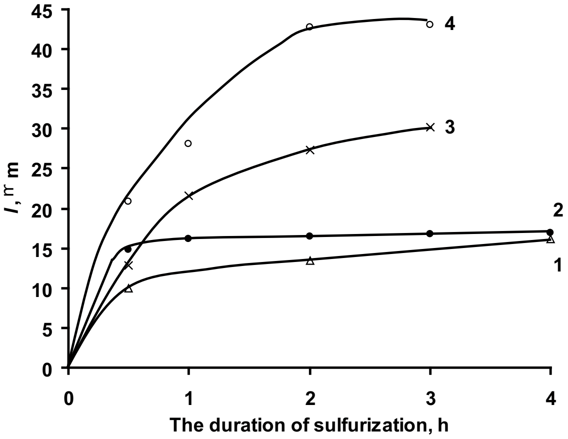

Figure 3. Dependence of the thickness of Cu_xS layers on PA (curves 1 and 2) and PE (curve 3 and 4) with time. The sulfurization agent: 1 – $K_2S_5O_6$; 2 – $H_2S_{21}O_6$; 3 – $H_2S_{21}O_6$, 4 – $H_2S_{33}O_6$

The microscopic investigation of cross–sections of PA and PE samples with copper sulfide layers shows that a major part of copper sulfide (down to 43 μm depth, *l*) is distributed in the surface matrix of the polymers (Fig. 3). Curve 4 shows a maximum of the thickness of the Cu_xS layer on PE and in its bulk at 42.7 *μ*m: it increases sharply to 42.7 *μ*m during the first two hours of the sulfurization in $H_2S_{33}O_6$ solution. Only slight increase in the thickness of the Cu_xS layer to 43 *μ*m was detected after a sulfurization time of 3 h. The similar change of the thickness till 30 *μ*m was observed when PE was sulfurized in $H_2S_{21}O_6$ solution (Fig. 3, curve 3).

The microscopic investigation of cross–sections of PA samples with copper sulfide films showed that their thickness (Fig. 3, curves 1 and 2) varies depending on the duration of initial sulfurization up to 3 h. When the PA samples were sulfurized in a solution of higher polythionic acid $H_2S_{21}O_6$, the maximum amount of copper in the layer formed is reached sooner than in PA sulfurized in $K_2S_5O_6$ solution (Fig. 2, curves 1 and 2). However, after 4 h of sulfurization, the thickness of the Cu_xS layers formed are in both cases almost the same despite big differences in the sulfur concentration and amount of copper (Figs. 1 and 2, curves 1 and 2) in the layers. This indicates that a more compact and more conductive Cu_xS layer has been formed in PA sulfurized in $H_2S_{21}O_6$ solution.

The electric resistance of copper sulfide layers depends on their phase composition. As described in [19], a slight decrease in the value of *x* in the layer of Cu_xS from 2 to 1 leads to an extreme decrease in the resistance even million times. Copper and sulfur at room temperature form five stable solid phases, two of which are stoichiometric, CuS (*covellite*) and Cu_2S (*chalcocite*), while the remaining three are non-stoichiometric, viz. $Cu_{1.75}S$ (*anilite*), $Cu_{1.8}S$ (*digenite*) and $Cu_{1.95}S$ (*djurleite*). Besides these five stable phases, copper and sulfur also form a number of mixed phases [20]. At 27°C the stable phases are CuS, $Cu_{1.75}S$, *djurleite* and Cu_2S [3].

The data of X-ray diffraction are in good agreement with the results of sheet resistance studies. The intensity of peaks and their areas in the diffractograms of copper sulfide layers (Fig. 4) show the highest concentration of copper sulfide in the Cu_xS layer on PA, sulfurized in $H_2S_{21}O_6$ solution (Fig. 4, curve 2), the lowest – in the layer on the PA surface, sulfurized in $K_2S_5O_6$ solution (Fig. 4, curve 1). Also only two phases of copper sulfides formed on PA, using $K_2S_5O_6$ solution: dominant orthorhombic *anilite*, Cu_7S_4 (peaks at 2θ = 31.8, 40.76, 49.4 and 50.05°), and monoclinic *djurleite*, $Cu_{1,9375}S$ (peak at 2θ = 38.2°).

Phases of low *x* values − hexagonal *yarrowite*, $Cu_{1.12}S$ (peaks at 2θ = 29.3, 31.1, 47.7 and 49.0°) and, partly, – *anilite*, Cu_7S_4 (peaks at 2θ = 44.9, 46.02 and 58.8°) − predominate in the sulfide layer on PA sulfurized in $H_2S_{21}O_6$ solution (Fig. 4, curve 2). This fact is consistent with a low value of sheet resistance of these layers (Table 1).

The layers of copper sulfides on PE consist of four phases (Fig. 4, curves 3 and 4): *anilite*, Cu_7S_4 (peak at 2θ = 36.2°), orthorhombic *chalcocite*, Cu_2S (peak at 2θ = 32.7°), monoclinic *djurleite*, $Cu_{1,973}S$ (peak at 2θ = 39.0°), and cubic *digenite*, Cu_9S_5 (peak at 2θ = 46.0°). The sheet resistance values of these layers are similar to those of Cu_xS layers, when PA was initially sulfurized in $K_2S_5O_6$ solutions. However, on the basis of lower *x* values in Cu_xS layers, the values of sheet resistance were expected to be lower. Therefore the magnitude of sheet values is the same. The reason of that fact might be a higher concentration of copper sulfides in the sulfide layer on PE.

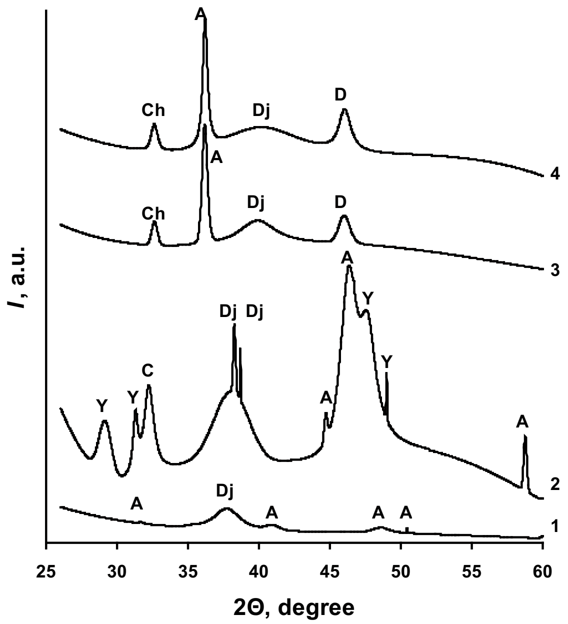

Figure 4. X–ray diffraction patterns of Cu_xS layers on PA (curves 1 and 2) and PE (curves 3 and 4) (peaks of djurleite – Dj, anilite – A, chalcocite – Ch, yarrowite –Y, digenite – D, covellite – C). The sulfurization agent: 1 – $K_2S_5O_6$; 2 – $H_2S_{21}O_6$; 3 – $H_2S_{21}O_6$, 4 – $H_2S_{33}O_6$

Apart from the sulfurity of the precursor, the sheet resistances of the layers formed show the influence of different polymers used as the substrates. The resistance of layers formed on PA is smaller than that of the layers formed on PE, especially at shorter exposure time in the sulfurization step, even in the case when the highly sulfurized polythionic acid $H_2S_{33}O_6$ was used. Probably, this depends on the concentration of sulfur and copper in the copper sulfide layer (Figs. 1,2, curves 2, 3 and 4): they are higher in the layers formed on PA than on PE. This might be related to the swelling of PA and the amorphisation of its structure in the acid medium: it makes easier the sorption – diffusion of $S_nO_6^{2-}$ anions into this polymer.

4. Conclusions

Semiconductive and electrical conductive layers of Cu_xS, formed by the sorption – diffusion method on the surface of polyamide 6 and low density polyethylene using solutions of potassium pentathionate, $K_2S_5O_6$, or higher polythionic acids, $H_2S_nO_6$ (n = 21, 33), were investigated. Variations of the sheet resistance values due to the conditions of polymers sulfurization, to the sulfur precursor and phase composition of the layers formed were determined. It was found that sheet resistance of Cu_xS layers decreases with increasing duration of the initial step – polymer sulfurization and with increasing of the number of sulfur atoms in the polythionate anion used as sulfur precursor. The values of sheet resistance of Cu_xS layers formed on the surface of polyamide 6 are much lower than those of Cu_xS layers formed on the surface of low density polyethylene, ~0.5 Ω/− and ~300 Ω/− , respectively.

The thickness of Cu_xS layers on PA 6 and on low density PE increases with increasing time sulfurization of the polymer.

XRD analysis of the phase composition of copper sulfide layers formed on the surface of polyamide 6 sulfurized in solution of higher polythionic acid $H_2S_{21}O_6$ showed higher concentration of Cu_xS phases, and predominance of phases with low x values. This fact is consistent with the low sheet resistance of these layers.

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