

Morphology and composition of silver sulphide layers prepared by chemical conversion technique

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Silver sulphide layers prepared by the chemical conversion of copper sulphide layers on a low density polyethylene film, used as a source material, have been studied. SEM images display closely packed layers with nonhomogeneous morphology. With the increase of treating time in a silver salt solution the formed layer is more uniform and consists of dendrites and agglomerates. EDS results reveal that the converted samples are rich in silver and poor in copper. An examination of the XRD data of the obtained layers reveals a polycrystalline nature of the material. Various copper sulphides, silver sulphide and silver were detected in the obtained layers.

Key words: polythionate acid, polyethylene, copper sulphide, silver sulphide

INTRODUCTION

Semiconductors have attracted much attention because of their unique physical properties and the potential of a wide range of practical applications in LEDs, optical and electronic devices, solar energy conversion devices, switches in optical computers, etc. [1]. In particular, semiconducting metal sulphide particulates possess novel optical and electrical properties and are considered for photovoltaic devices including dye-sensitized cells, all-inorganic nanoparticle solar cells, and hybrid nanocrystal-polymer composite solar cells in addition to lasers and waveguides [2]. Copper sulphide, as one type of a semiconductor, has received a great deal of attention in the applications of photovoltaic cells, solar selective coatings, nanoscale switches and catalysis. Copper sulphides are a particularly interesting class of metal sulphides due to several known solid phases with various stoichiometries [3]. Copper and sulphur can form five stable phases at room temperature. Of these five phases there are only two stoichiometric compounds, Cu_2S (chalcocite) and CuS (covellite), the other three non-stoichiometric phases consist of $\text{Cu}_{1.75}\text{S}$ (anilite), $\text{Cu}_{1.8}\text{S}$ (digenite) and $\text{Cu}_{1.96}\text{S}$ (djurleite). In addition to these stable phases, copper and sulphur also form a number of mixed phases [4].

Other transition metal sulphide – silver sulphide, Ag_2S , is a direct, narrow band-gap semiconductor with good chemical

stability and excellent optical limiting properties, therefore it has been used in optical and electronic devices [5]. The phase equilibria of the Ag–S system show three solid phases of silver sulphide, all of which are stable over a narrow range of compositions. There is an α monoclinic phase, stable at room temperature and at the temperatures below 176 °C, a β body centered cubic phase, stable above 176 °C, and a γ face centered cubic phase, stable at higher temperatures, above 571 °C [6]. $\alpha\text{-Ag}_2\text{S}$ is a semiconductor with a band gap of approximately 1 eV at room temperature and unique properties [7].

Different chemical methods of thin layer fabrication such as controlled precipitation [8], chemical bath deposition, electrodeposition, electroless plating, successive ionic layer adsorption and reaction [9], and spray pyrolysis [10] have been used to produce metal sulphide layers. A sorption-diffusion method is simple, low cost and convenient for larger area deposition of a metal sulphide layer. Thiourea, thioacetamide, thiosulfate and sodium sulphide are generally used as sulphide precursors [9].

In this paper we report on the formation of copper and silver sulphides layers on a polyethylene film by sorption-diffusion and chemical conversion methods. As the precursor of sulphur we used solutions of polythionic acids, $\text{H}_2\text{S}_n\text{O}_6$. The layers formed were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements in order to determine the chemical and phase composition and morphology of the layers.

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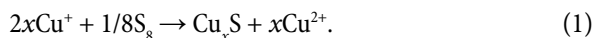
EXPERIMENTAL

Copper and silver sulphide layers on a low density polyethylene film (PE) of 0.14 ± 0.01 mm thickness from the Plastic Plant Plasta (Vilnius) were obtained. Rectangular samples of 15×75 mm were used. Before sulphurization the surface of a PE sample was cleaned for 10 min in a 4% solution of a non-ionic surfactant Prewocell WOF-100, degreased in toluene, and washed in distilled water. Cleaned PE samples were sulphurized for 120 min in a $2 \text{ mmol/dm}^3 \text{ H}_2\text{S}_{33}\text{O}_6$ solution at 60°C and then were treated for 10 min with a $0.4 \text{ mol/dm}^3 \text{ Cu (II/I)}$ salts solution [11] at 60°C . With that, the samples with the formed layer were treated for 1, 10 or 20 min with a $0.04 \text{ mol/dm}^3 \text{ AgNO}_3$ solution at 60°C .

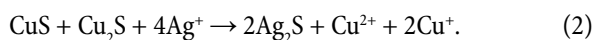
For the characterization of the obtained layers XRD analysis, SEM and EDS measurements were recorded. The XRD studies on a DRON-6 diffractometer (Russia) operating with Cu K_α radiation (Ni filter) at 30 kV and 20 mA were performed. In order to study the morphology of the samples and the elemental composition of the obtained layers a scanning electron microscope equipped with an energy dispersive spectrometer Quantax 200 with a detector XFlash 4030 (Bruker AXS Microanalysis GmbH, Germany) was used.

RESULTS AND DISCUSSION

In our earlier work [12], we determined that the amount of copper in the copper sulphide layer and the amount of silver in the prepared layer increased with the increase in the sulphurization time and treating time in the copper (II/I) salt solution. Copper sulphides form during the heterogeneous oxidation-reduction reaction between elemental sulphur in PE and Cu^+ in the copper salt solution:



In order to prepare silver sulphide layers, the Cu_xS layers on PE are chemically converted by a silver nitrate solution. Such a chemical process allows an exchange of copper ions by silver(I) ions and may be described by:



An exchange of ions is possible because the solubility product for Ag_2S is 7.2×10^{-50} , whereas for CuS and Cu_2S the solubility products are 1.4×10^{-36} and 2.3×10^{-48} , respectively [13]. As a result of conversions, a change in the colour of the source copper sulphide layers from brown to blackish has been noticed.

The microstructure of the obtained layer on PE was studied by SEM. SEM studies showed that surface morphology changed for the obtained layers on PE with different treatment time in AgNO_3 solution. The SEM images of the samples are shown in Fig. 1. The 4000 X magnified micrographs display the closely packed layers with nonhomogeneous mor-

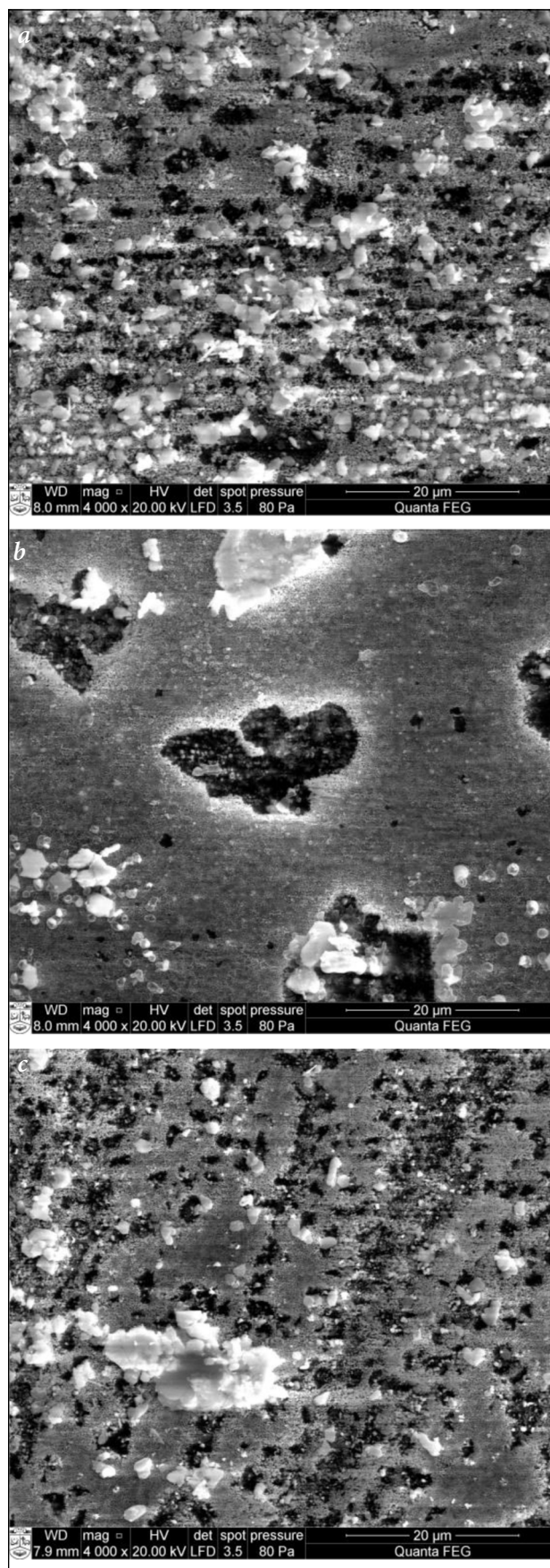


Fig. 1. SEM images of obtained layers on PE. The period of treatment with $0.04 \text{ mol/dm}^3 \text{ AgNO}_3$ solution at 60°C , min: *a* – 1, *b* – 10, *c* – 20

phology. Figure 1a shows that the surface of the formed layer consists of particles with different shape. Here we can see some dendrites and agglomerates of nonreacted sulphur. Figure 2b shows a more uniform coverage of small dendrites and large irregular agglomerates. Figure 2c shows that the surface of the formed layer is completely covered by agglomerated particles. Hence, with the increase of treating time in the silver salt solution the formed layer is denser, more uniform and consists of small dendrites and particulated agglomerates.

EDS was used to determine the chemical composition of the converted layers. EDS shows the presence of Ag, Cu, S, C and O peaks. EDS data revealed large quantities of carbon (34–51 at.%) in the samples. The existence of carbon is believed to appear from a polymer. The existence of oxygen (21–25 at.%) originated from the surface contamination in the atmosphere. The EDS results confirm the presence of silver, sulphur and copper on the converted samples. A comparison of the EDS data of the obtained layers shows the reduction of copper and sulphur in the converted layers (Table). The results indicate that converted layers are rich in silver (20.7–28.1 at.%) and poor in copper (1.1–5 at.%). It means that copper ions released from the copper sulphide layer during reaction with silver (I) ions and the amount of copper in the converted layer decreased. The lowest amount of copper was in the sample, which was 20 min treated with an AgNO_3 solution. From the results mentioned above it can be seen that the converted samples also contain a little amount of Cu_xS .

Table. Elemental composition of the converted layers by EDS (excluded C and O elements)

| Treating time in AgNO_3 solution, min | S (at.%) K-series | Cu (at.%) K-series | Ag (at.%) L-series |
|--|----------------------|-----------------------|-----------------------|
| 1 | 12.5 | 5.0 | 20.7 |
| 10 | 10.9 | 1.2 | 23.0 |
| 20 | 7.8 | 1.1 | 28.1 |

The XRD studies revealed that the obtained layers are polycrystalline in nature. The phase composition of a layer was established by comparing its X-ray diffraction pattern with those of known minerals [14]. The structural characterization of the obtained layer is limited by the crystallinity of PE. The intensity of its peaks at $2\theta < 26^\circ$ exceeds the intensity of sulphide peaks few times. Therefore, the area of $2\theta \geq 26.0^\circ$ was investigated in more detail.

The results of the phase analysis of PE samples with a copper sulphide layer, both untreated and treated with a silver nitrate solution, are summarized in Fig. 2. After 10 min treating of sulphurized PE in a Cu(II/I) salt solution (curve 1), the peaks attributable to orthorhombic anilite, Cu_7S_4 (72–617, $2\theta = 27.9; 36.4$ and 54.7°), orthorhombic djurleite, $\text{Cu}_{1.97}\text{S}$ (20–365, $2\theta = 46.5^\circ$), monoclinic chalcosine, Cu_2S (73–1138, $2\theta = 38.2^\circ$), and orthorhombic sulphur, S_8 (83–2284, $2\theta = 57.3^\circ$), are observed. It can be seen that the anilite phase predominates in the composition of the sulphide layer.

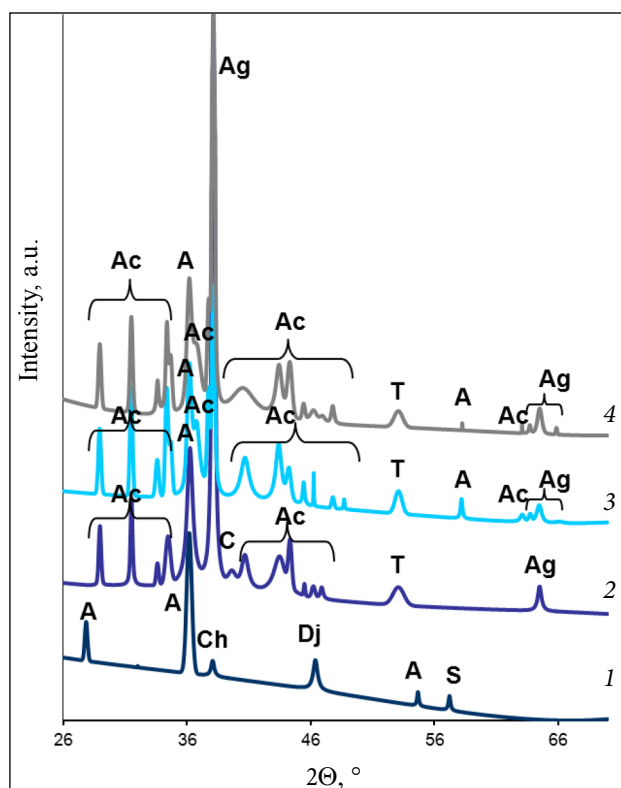
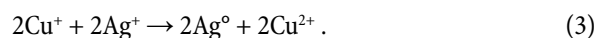


Fig. 2. X-ray diffraction patterns of obtained layers on PE (peaks of acanthite – Ac, silver – Ag, covellite – C, talnakhite – T, anilite – A, djurleite – Dj, chalcosine – Ch, sulphur – S). The period of treatment with $0.04 \text{ mol/dm}^3 \text{ AgNO}_3$ solution at 60°C , min: 1 – 0, 2 – 1, 3 – 10, 4 – 20

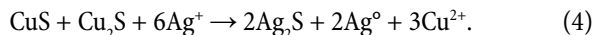
After a short treatment (1 min) in the AgNO_3 solution the diffraction pattern (curve 2) showed abundant peaks of monoclinic silver sulphide acanthite, $\alpha\text{-Ag}_2\text{S}$ (14–72, $2\theta = 28.9; 31.5; 34.2; 34.4; 40.9; 43.5; 44.3; 45.5; 46.2$ and 47.02°). In this diffraction pattern cubic silver-3 C, Ag (4–783, $2\theta = 37.8$ and 64.6°), orthorhombic anilite, Cu_7S_4 (72–617, $2\theta = 36.4^\circ$), hexagonal covellite, CuS (78–880, $2\theta = 40.02^\circ$), and cubic talnakhite, $\text{Cu}_{34}\text{S}_{32}$ (71–2438, $2\theta = 53.3^\circ$), were also detected.

When the duration of the treatment of the Cu_xS layer on PE in the AgNO_3 solution prolonged, the intensity of acanthite and silver-3 C phases increases. The number of these phases increases too. After 10 or 20 min treatment, new peaks at $2\theta = 36.9; 47.5; 48.7$ and 63.8° of acanthite and at $2\theta = 38.1$ and 64.4° of silver-3 C (Fig. 2, curves 3 and 4) in the composition of the sulfide layer on PE appear. Additionally, small amounts of copper sulphides – anilite and talnakhite – can be observed in the converted layers. Thus, the copper sulphide layers were not fully modified.

The XRD diffraction patterns of chemically converted layers showed predominance of the phases of silver sulphide acanthite and silver. Consequently, not only ion exchange process took place (Eq. 2) but also the oxidation and reduction process:



Therefore, the chemical conversion process can be described by the following reaction:



CONCLUSIONS

In the study we presented the formation of a silver sulphide layer by a chemical conversion method via the reaction between a copper sulphide layer on a low density polyethylene film, used as a source material, and a silver nitrate solution. SEM images showed layers with nonhomogeneous morphology. With the increase of treating time in a silver salt solution the formed layer was denser, more uniform and consisted of small dendrites and particulated agglomerates. The EDS results revealed that the converted samples are rich in silver and poor in copper. The amount of silver increased with the increase of treating time in the solution of silver salt. XRD data showed various copper sulphides, silver sulphide acanthite and silver in the obtained layers. The diffraction patterns of chemically converted layers showed predomination of the phases of acanthite and silver. Silver sulphide and silver were formed by ion-exchange and oxidation-reduction reactions.

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Santrauka

Šiame darbe pateiktas paprastas būdas sidabro sulfidų sluoksniams gauti cheminio pakeitimo būdu, vykstant reakcijoms tarp vario sulfidų sluoksnių ant polietileno ir sidabro nitrato tirpalo. SEM nuotraukose matyti susidaręs nehomogeniškas sluoksnis, kuris ilginant veikimo sidabro druskos tirpalu trukmę tampa tankesnis, vienosdesnis, sudarytas iš nedidelių dendritų ir aglomeratų. EDS analizė parodė, kad chemiškai pakeistuose sluoksniuose yra daug sidabro ir tik nežymus kiekis vario. RDA rezultatai parodė, kad sluoksniuose yra nedaug vario sulfidų, juose vyrauja sidabro sulfidas akantitas ir sidabras. Sidabro sulfidas ir sidabras susidarė vykstant jonų mainų ir oksidacijos-redukcijos reakcijoms.