

Characterization of Ag-Cu-S Thin Layers Formed on Low Density Polyethylene Film

Ingrida ANCUTIENĖ*, Remigijus IVANAUSKAS, Nijolė KREIVĖNIENĖ

Department of Inorganic Chemistry, Kaunas University of Technology, Radvilėnų 19, LT-50254 Kaunas 9, Lithuania

crossref <http://dx.doi.org/10.5755/j01.ms.17.3.584>

Received 25 September 2010; accepted 10 February 2011

The Ag-Cu-S layer formed on PE demonstrated a wide variation in thickness. The cross-section showed the average thickness of sulfide layers on PE increase from 1.9 μm to 5.6 μm with the increase in the sulfurization time and from 1.9 μm to 3.9 μm with the increase of treating time in the solution of copper salts. The electronic micrographs of the sulfide layers indicate the creation of an irregular but continuous base of small dendrites and agglomerates. With the increase in the sulfurization time and treating time in copper (II/I) salt solution observed an increase of the agglomerates size. Energy dispersive spectroscopy results indicate that modified layers are poor in copper (0.5 at. % – 1.5 at. %). The atomic ratios of Ag/Cu/S, calculated from the quantification of the peaks (excluded C and O elements) give the values (%) of 8.3:1.5:4.4, 8.7:0.5:4.3 and 23:1.2:10.9, respectively. In all cases, energy dispersive spectroscopy measurements revealed the modified layers are nearly stoichiometric Ag_2S .

Keywords: polyethylene, polythionic acid, sulfurization, copper sulfide, silver sulfide, thin layer.

INTRODUCTION

Transition metal sulfides have drawn considerable attention because of their technological importance as catalysis, battery fabrication, cathode materials for high-energy density battery, and so forth [1]. Among these sulfides, copper sulfides find potential applications in numerous fields, such as in photo-thermal conversion, coatings for microwave shields in the form of thin films, as super-ionic materials, optical filters [2], etc. Silver sulfide is widely used as a functional media in a variety of electronic and optoelectronic devices like ion selective membranes [3], solar selective coating [4], photo conducting cells and IR detectors [5–7], etc.

Recently owing to the interesting properties and potential applications, metal sulfides with special microstructure and particle size have gained much attention in the field of material sciences. Usually, the material design for these technological applications is based on thin film preparation techniques, the film thickness being in the micrometer range.

Metal sulfides thin layers by several methods such as photochemical deposition [8] and spray pyrolysis [9] have been prepared. Sorption-diffusion method is nowadays very attractive, since it is relatively simple, low cost and convenient for larger area deposition of thin layers. We obtained Ag-Cu-S layers using sorption-diffusion method.

The aim of present work was to characterize Ag-Cu-S layers formed on the low density polyethylene film (PE) by the use of a solution of a polythionic acid as sulfurization precursor. The formed layers have been characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements in order to determine the thickness, morphology, elemental composition of the layers.

EXPERIMENTAL

Ag-Cu-S layers on low density PE film of 0.14 mm \pm 0.01 mm thickness from the plastic plat Plasta (Vilnius) were deposited. Rectangular samples of 15 mm \times 75 mm were used.

At first, a sample of the polymer was sulfurized 30 min or 120 min in 0.002 mol/dm³ $\text{H}_2\text{S}_{33}\text{O}_6$ solution at 60 °C. Then sulfurized sample was treated 1 or 10 min with 0.4 mol/dm³ Cu (II/I) salts solution [10] at 60 °C. With that, a sample with formed layer was modified 10 min with 0.04 mol/dm³ AgNO_3 solution at 60 °C.

Table 1. The times of treatment with $\text{H}_2\text{S}_{33}\text{O}_6$, Cu (II/I) salt and AgNO_3 solutions at 60 °C

| Sample No | Sulfurization time, min | Treating time in Cu (II/I) salt solution, min | Treating time in AgNO_3 solution, min |
|-----------|-------------------------|---|--|
| 1 | 30 | 10 | 10 |
| 2 | 120 | 1 | 10 |
| 3 | 120 | 10 | 10 |

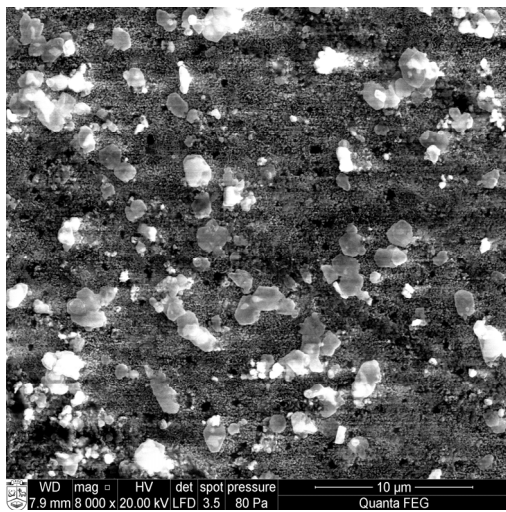
The scanning electron microscope (SEM) equipped with an energy dispersive spectrometer Quantax 200 with a detector XFlash 4030 (Bruker AXS Microanalysis GmbH, Germany), was applied for surface of obtained layers analysis.

ANALYSIS AND RESULTS

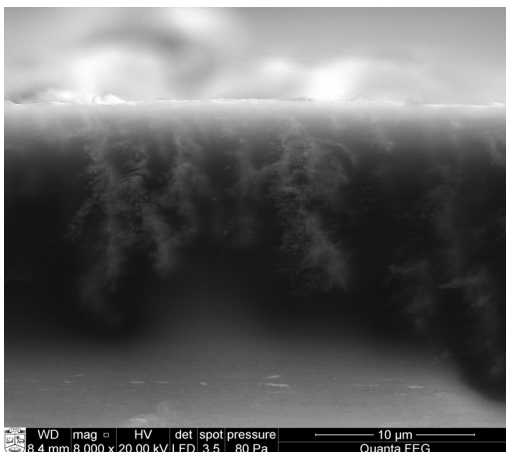
In previously work, we determined that the amount of copper in the copper sulphide layer increased with the increase in the sulfurization time and treating time in the copper (II/I) salt solution. The amount of silver in modified layer increased with the increase in the sulfurization time and treating time in the solution of copper salts. Copper ions from the copper sulphide layer during reaction with Ag^+ released and the amount of copper in the modified layer decreased [11].

*Corresponding author. Tel.: +370-37-300174.; fax: +370-37-300152.
E-mail address: ingrida.ancutiene@ktu.lt (I. Ancutiene)

Scanning electron microscopy is a convenient technique microstructure study of thin layers. The thickness of obtained layers by SEM measurements also is studied. SEM images revealed the dendritic morphology of Ag-Cu-S layer. Surface and cross-section micrographs of the obtained layers are shown in Figs. 1–3.



a

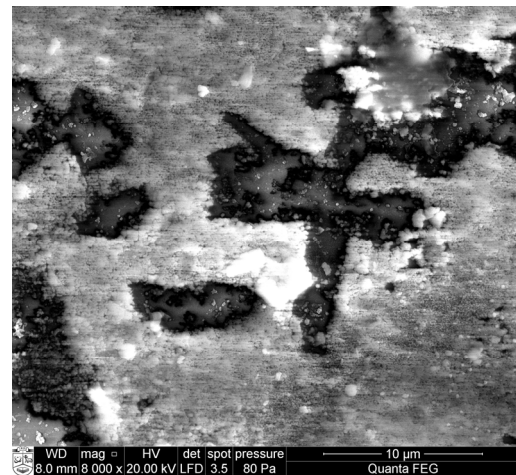


b

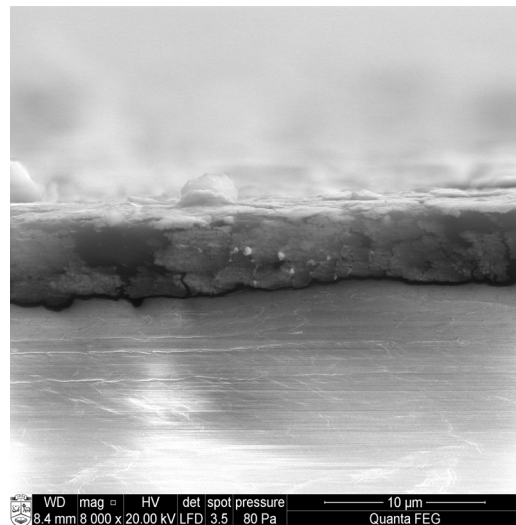
Fig. 1. Surface (a) and cross-section (b) SEM images of Ag-Cu-S thin layer of sample No 1

The SEM micrographs of the sulfide layers indicate the creation of an irregular but continuous base of small dendrites and agglomerates (Figs. 1–3, a). With the increase in the sulfurization time and treating time in Cu (II/I) salts solution an increase of the agglomerates size is observed.

Figs. 1–3, b, show the cross-section views of the Ag-Cu-S/PE composites. According to the illustration of Fig. 1, b, the average thickness of obtained layer was 1.9 μm. The roughness, irregular surface and various dendrites were also evidenced by the cross-section view of Fig. 1, b. The micrograph of Fig. 2, b, and Fig. 3, b, showed the average thickness of Ag-Cu-S layer was increased from 3.9 μm to 5.6 μm. It is noticed that the average thickness of sulfide layers on PE increase from 1.9 μm to 5.6 μm with the increase in the sulfurization time and from 1.9 μm to 3.9 μm with the increase of treating time in the solution of copper salts.



a



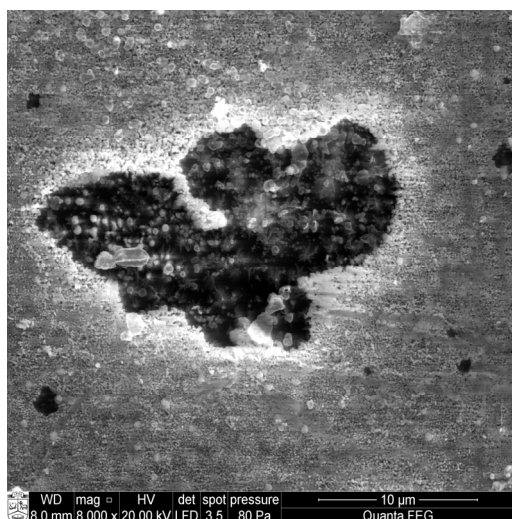
b

Fig. 2. Surface (a) and cross-section (b) SEM images of Ag-Cu-S thin layer of sample No 2

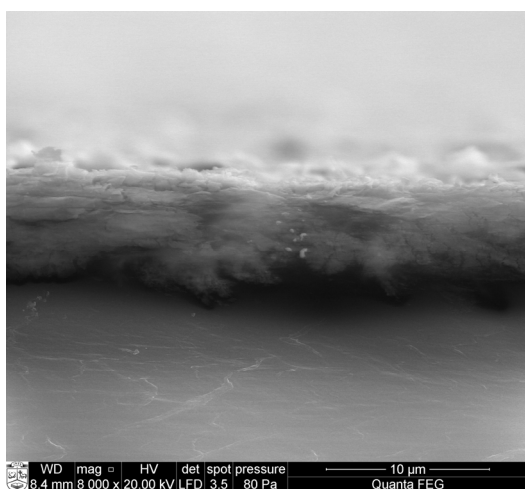
The sulfide layer elemental composition was analyzed by energy dispersive spectrometry. EDS shows the presence of Ag, Cu, S, C and O peaks. EDS data revealed large quantities of carbon (44 at.%–65 at.%) in the samples. The existence of C is believed appeared from a polymer. The existence of oxygen (20 at.%–25 at.%) is believed originated from the surface contamination in the atmosphere. The results indicate that modified layers are poor in copper (0.5 at.%–1.5 at.%). That means, copper ions released from the copper sulfide layer during reaction with silver (I) ions and the amount of copper in the modified layer decreased. The lowest amount of copper was in the sample No 2, which was only 1 min treated with Cu (II/I) salt solution.

Table 2. Elemental composition by EDS of Ag-Cu-S layers (excluded C and O elements)

| Sample | Ag (at. %) L-series | Cu (at. %) K-series | S (at. %) K-series | Ag/S |
|--------|---------------------|---------------------|--------------------|------|
| 1 | 8.3 | 1.5 | 4.4 | 1.9 |
| 2 | 8.7 | 0.5 | 4.3 | 2.0 |
| 3 | 23.0 | 1.2 | 10.9 | 2.1 |



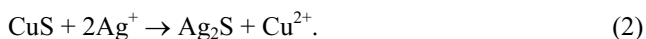
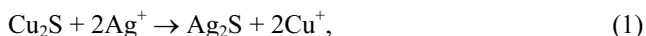
a



b

Fig. 3. Surface (a) and cross-section (b) SEM images of Ag-Cu-S thin layer of sample No 3

The results described in the paper [12] show that an amount of copper ions was released from Cu_{2-x}S grains during reacting with Ag^+ ions. The data of the chemical analysis in earlier paper [11] also showed that an amount of copper ions was released from Cu_xS layer during reacting with AgNO_3 . Thus, a part of Cu^+ and Cu^{2+} ions in the layer during the modifying process was substituted by silver ions:



It follows from the data in the Table 2 the surfaces of formed layers contain mainly the element of silver, sulfur and small amount of copper. The EDS data reveal that the molar ratio of silver and sulfur element is about 2, in good agreement with the stoichiometric component of Ag_2S , which indicates that Ag_2S is main component of the surface of modified layer. From the results mentioned above, it can be seen that the surfaces of samples No 1–3 also contain little amount of Cu_xS .

CONCLUSIONS

1. The cross-section showed the average thickness of sulfide layers on polyethylene increase from 1.9 μm to 5.6 μm with the increase in the sulfurization time and from 1.9 μm to 3.9 μm with the increase of treating time in the solution of copper salts.
2. With the increase in the sulfurization time and treating time in copper (II/I) salts solution observed an increase of the agglomerates size.
3. Energy dispersive spectrometry results indicated that modified layers are poor in copper (0.5 at. %–1.5 at. %) and are nearly stoichiometric Ag_2S .

REFERENCES

1. **Wang, M., Min, Y., Chen, Y.** Simple Approach to $\text{NiS}_2/\text{Ag}_2\text{S}$ Composites and Their Optical Properties *Materials Letters* 62 2008: pp. 3280–3283.
2. **Behboudnia, M., Khanbabaee, B.** Investigation of Nanocrystalline Copper Sulfide Cu_7S_4 Fabricated by Ultrasonic Radiation Technique *Journal of Crystal Growth* 304 2007: pp. 158–162.
3. **Ito, S., Asano, Y., Wada, H.** Development of Highly Sensitive Cadmium Ion-selective Electrodes by Titration Method and its Application to Cadmium Ion Determination in Industrial Waste Water *Talanta* 44 1997: pp. 697–704.
4. **Abass, A. K.** The Spectrally Selective Properties of Chemically-deposited Ag_2S on Aluminium *Solar Energy Materials* 17 1988: pp. 375–378.
5. **Kitova, S., Eneva, J., Panoy, A., Haefke, H.** Infrared Photography Based on Vapor-deposited Silver Sulfide Thin Films *Journal of Imaging Science and Technology* 38 1994: pp. 484–488.
6. **Banerjee, S., Bhattacharya, S., Chakravorty, D.** Resistivity Hysteresis of Ag_2S Nanocomposites *The Journal of Physical Chemistry C* 111 2007: pp. 13410–13413.
7. **Zhang, W., Zhang, L., Hui, Z., Zhang, X., Qian, Y.** Synthesis of Nanocrystalline Ag_2S in Aqueous Solution *Solid State Ionics* 130 2000: pp. 111–114.
8. **Podder, J., Kobayashi, R., Ichimura, M.** Photochemical Deposition of Cu_xS Thin Films from Aqueous Solutions *Thin Solid Films* 472 2005: pp. 71–75.
9. **Isac, L., Duta, A., Kriza, A., Manolache, S., Nanu, M.** Copper Sulfides Obtained by Spray Pyrolysis – Possible Absorbers in Solid-state Solar Cells *Thin Solid Films* 515 2007: pp. 5755–5758.
10. **Ancutienė, I.** Formation of Copper Sulfide Layers on Polyethylene Using Higher Polythionic Acids *Doctor. Thesis* Kaunas, 1995 (in Lithuanian).
11. **Ancutienė, I., Ivanauskas, R.** Formation of Mixed Copper Sulphide and Silver Sulphide Layers on Low Density Polyethylene Film *Proceedings of the Estonian Academy of Sciences* 58 2009: pp. 35–39.
12. **Barzyk, W., Kowal, A., Pomianowski, A.** Noble Metal (Ag, Au) Cementation on Non-stoichiometric Cuprous Sulphide Grains *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 208 2002: pp. 321–335.

Presented at the International Conference
"Baltic Polymer Symposium 2010"
(Palanga, Lithuania, September 8–11, 2010)