

Formation of Silver Selenide Layers on Polyamide 6 Films by the Use of Potassium Selenotriothionate

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crossref <http://dx.doi.org/10.5755/j01.ms.17.4.775>

Received 25 September 2010; accepted 16 January 2011

A polyamide 6 films if treated with the potassium selenotriothionate, $K_2SeS_2O_6$, solution in hydrochloric acid, absorbs selenium the form of selenotriothionate anion, $SeS_2O_6^{2-}$, and the anions decompose in polymer with time. Further interaction of selenized PA films with $AgNO_3$ solution (10 min, $80^\circ C$) leads to the formation of silver selenide layers on the polymer surface. The mechanism of formation of silver selenide layers on PA 6 films was proposed. The chemical analyzes show that the concentrations of silver and selenium in polyamide 6 film increase when increase the duration of polymer seleniumization. The molar ratio of Ag/Se in the layers of silver selenide on polyamide films varied from 0.57:1 to 0.7:1. The X-ray diffraction analysis confirmed the formation of silver selenide layers with elemental selenium in the surface of polyamide 6. The phases of orthorhombic naumannite – Ag_2Se (24–1041) and monoclinic selenium – Se_8 (71–528) were identified in the formed layers.

Keywords: selenotriothionate, polyamide 6, sorption-diffusion, layers of silver selenide.

INTRODUCTION

The study of polymer with chalcogenide layers has received considerable interest in recent years because of their novel properties, which are combinations of those of the original inorganic and polymer materials. Polymers modified with thin layers of d-metal selenides are ascribed to composites. For example: infrared sensors, photolithographic layer, electrochemical storage cells, electrochemical potential memory devices, etc. can be activated by Ag_2Se [1, 2]. Thin film of Ag_2Se can be used as a promising material for technological application in magnetic field sensing devices [3–5]. The modification of polymers by formation in their surface of thin layers of Ag_2Se with important physical properties leads to obtaining of composites with different properties very important up to day technology.

Polyamide (PA 6) is capable to absorbing ions of selenopolythionate from aqueous solutions into PA surface matrix [6]. After treating such ions containing polymer films with Cu(I–II) salts water solutions Cu_xSe layers of various electrical conductivity and composition can be obtained on their surface depending on experimental conditions [7, 8]. Similarly, the use of this technology on the surface of PA is possible to form silver selenide layers.

This work was basically inspired by an increasing interest in new semiconductor as a material for an application in flexible and efficient magnetoresistance thin films.

Our main task was to form the binary silver selenide layers on PA 6 surface using as a seleniumization precursor the solution of potassium selenotriothionate ($K_2SeS_2O_6$), and to investigate their composition by chemical and X-ray diffraction methods, and to propose the mechanism of formation of obtained layers.

EXPERIMENTAL

The films of polyamide 6 (specification TY 6-05-1775-76, grade PK-4) 15 mm × 70 mm in size of 70 μm thickness were used. This PA 6 film is close to a non-porous material, because the pores of PA are much less than 1.5 nm [9]. The porosity was measured by a β-method using a Quantasorb (Japan). Before the seleniumization, the samples of PA 6 were boiled in distilled water for 2 h to remove the remainder of the monomer. Then they were dried using filter paper and then over $CaCl_2$ for 24 h.

The PA 6 samples thus prepared were treated in a thermostatic vessel using a continually stirred $K_2SeS_2O_6$ solution. The 0.05 mol·dm⁻³ solutions of $K_2SeS_2O_6$ in 0.1 mol·dm⁻³ HCl at 60 °C were used. At the certain time intervals, the samples were removed, rinsed with distilled water, dried over $CaCl_2$, and then used in the analysis and further experiments. The total duration of experiments was 4.5 h.

The salt of potassium selenotriothionate, $K_2SeS_2O_6$, was prepared and chemically analyzed according to procedures published in [10].

The concentration of selenium and silver in silver selenide layers formed on PA 6 films surface were determined using the method of atomic absorption spectrophotometry [11]. The modified PA 6 films were dissolved in concentrated nitric acid. Selenium and silver, present in the resulting solution, were determined by the atomic absorption spectrometer “Perkin-Elmer 503”; wavelength $\lambda = 196$ nm and $\lambda = 328.1$ nm, diffractive gap – 5 (2.0 nm) and 4 (0.7 nm), electrodeless discharge lamp, air-acetylene flame. For the standard conditions described above, the sensitivity of Se and Ag are about 0.5 μg/ml and 0.06 μg/ml for 1 % absorption.

Then the samples of seleniumized PA 6 were treated with a 0.4 mol·dm⁻³ concentration of Ag(I) salt solution at 80 °C for 10 min, the silver selenide layers on polyamide

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samples were formed. The Ag(I) salt solution was made from crystalline AgNO_3 . After the treatment with the solution of Ag(I) salt, the samples of polymers were rinsed with distilled water, dried over anhydrous CaCl_2 and used in further experiments.

X-ray diffraction analysis the silver selenide layers on the polymer surface was performed with a DRON-6 diffractometer provided with a special device for beam limitation at low and medium diffraction angles using graphite-monochromatized $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.54178 \text{ \AA}$) under a voltage of 30 kV and a current of 30 mA. The XRD patterns were recorded with a step size of 0.05° from $2\theta = 25^\circ$ to 70° . X-ray diffractograms of modified PA 6 films were treated using the program "Search Match", "ConvX", "Xfit" and "Microsoft Office Excel".

ANALYSIS AND RESULTS

The main task of this work was to prove the suitability of seleniumized PA 6 films with solution of $\text{K}_2\text{SeS}_2\text{O}_6$ for formation the silver selenide layers on polymer.

For this the seleniumized PA 6 films were treated with Ag(I) salt solution. Changes of a PA 6 films appearance after its treatment with the Ag(I) salt solution also indicate the formation of silver selenide layers on the surface of a polymer. Colour of tapes from colourless, light yellow, orange or red transforms into into black, and acquires a metallic lustre.

In order to determine an influence of seleniumization duration of the initial solution of $\text{K}_2\text{SeS}_2\text{O}_6$ the kinetic studies of the sorption of selenium into PA 6 from prepared solution of potassium selenotrichionate were performed.

The investigation of sorption kinetics of selenium in silver selenide layers when PA 6 films exposed during 4.5 h in the $0.05 \text{ mol}\cdot\text{dm}^{-3}$ concentration solution of $\text{K}_2\text{SeS}_2\text{O}_6$ shows that the exposure time increase leads to an significant increase of amount of selenium, expressed in mg per g of PA, respectively, from $15.1 \text{ mg}\cdot\text{g}^{-1}$ to $53.0 \text{ mg}\cdot\text{g}^{-1}$ – a more than 3.5 – hold increase (Fig. 1).

The same dependence of the changing the amount of silver in Ag_xSe layers on PA 6 films as in the case of the amount the selenium was observed. The PA films exposure time increase leads to an significant increase of amount of silver, expressed in mg per g of PA, respectively, from $17.69 \text{ mg}\cdot\text{g}^{-1}$ to $56.9 \text{ mg}\cdot\text{g}^{-1}$ – a more than 3.2 – hold increase (Fig. 1).

The molar Ag/Se ratio in silver selenide layers formed on PA 6 provides the same information about the composition of its layers. The molar Ag/Se ratio in the silver selenide layers on the polymer surface was calculated from amounts of Ag and Se measured in the PA 6 samples. It was found that the Ag/Se ratio (Fig. 1) increases with the time of initial polymer seleniumization and the stoichiometric composition varies from $\text{Ag}_{0.57}\text{Se}$ to $\text{Ag}_{0.7}\text{Se}$. The compositions of silver selenide with 2/1 of molar Ag/Se ratio only are known [12, 13]. Therefore we can expect the elemental Se is contained in the composition of the silver selenide layers formed on PA 6 samples.

X-ray diffraction analysis gives more accurate identification of silver selenides formed on the surface of PA 6 films. Structural studies of the silver selenide layers deposited by sorption-diffusion method are limited by

polycrystallinity of layers obtained, as well as by the existence of silver selenide phases with various compositions and structures, and by the crystallinity of the PA film itself. The intensities of its maximum at $2\theta < 25^\circ$ exceeds intensity of silver selenide maximum few times. Therefore the area of $2\theta \geq 25.0^\circ$ was investigated more detail.

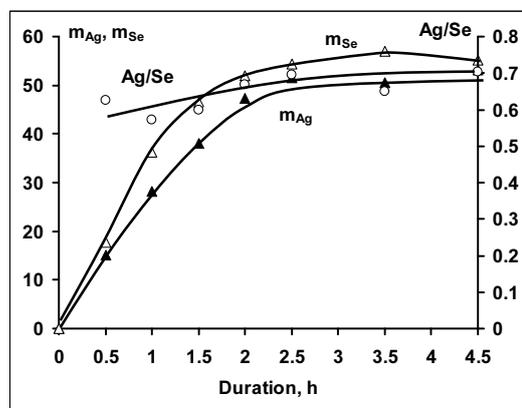


Fig. 1. Changes of the silver (m_{Ag}) and the selenium (m_{Se}) amounts silver selenide layers on PA 6 samples with time during polymer treatment with the solution of $\text{K}_2\text{SeS}_2\text{O}_6$

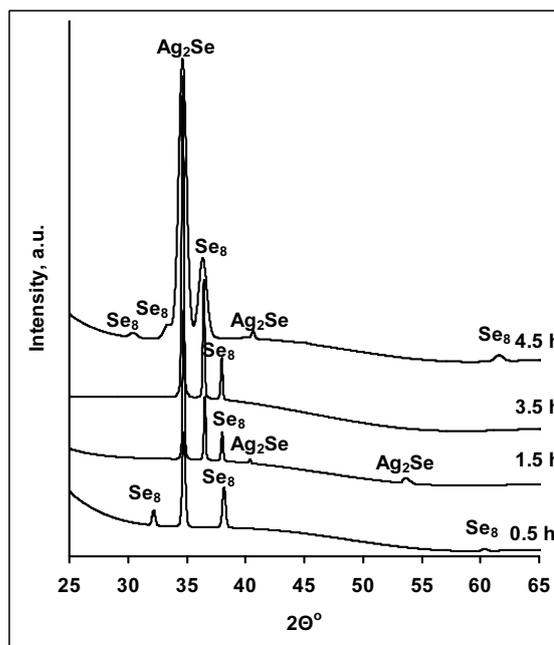
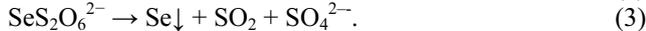


Fig. 2. X-ray diffraction patterns the layers of silver selenide formed on the PA 6 samples (peaks of monoclinic selenium – Se_8 (71–528) and orthorhombic naumannite – Ag_2Se (24–1041)). The PA 6 samples were seleniumized 0.5; 1.5; 3.5 and 4.5 h

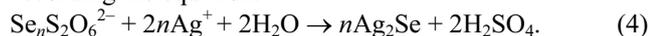
The fact, that the formation of silver selenide layers takes place by keeping seleniumized PA 6 samples in the solution of Ag(I) salts and the elemental Se was contained in the composition of its layers, were confirmed by the X-ray diffraction analysis of the silver selenide layers (Fig. 2 and Table 1). The phases of the orthorhombic naumannite – Ag_2Se (24–1041) [14] and the monoclinic selenium – Se_8 (71–528) [15] (Fig. 2) were determined by the X-ray diffraction analysis in the silver selenide layers on PA 6 samples surface. When the duration of seleniumization the polymer films prolonged the intensity of this phases increases. The number of this phases increases too.

The mechanism of formation of silver selenide layers on PA 6

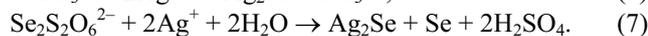
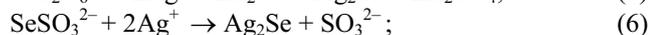
In the work [6] was stated that sorbed-diffused anions of $\text{SeS}_2\text{O}_6^{2-}$ decomposed with time. It is known [16] that $\text{SeS}_2\text{O}_6^{2-}$ ions decomposition includes the transformations:

$$\text{SeS}_2\text{O}_6^{2-} + \text{H}_2\text{O} \rightarrow \text{SeSO}_3^{2-} + 2\text{H}^+ + \text{SO}_4^{2-}; \quad (1)$$


Higher selenopolythionates react with the Ag^+ ions with the liberation of black Ag_2Se precipitate. Authors of the work [17] stated that the selenopolythionates of the type $\text{Se}_n\text{S}_2\text{O}_6^{2-}$ react with the Ag^+ ions quantitatively according the equation:



It is believable that silver selenides can be formed in the reactions of $\text{SeS}_2\text{O}_6^{2-}$ anions and its intermediate decomposition product – the $\text{Se}_2\text{S}_2\text{O}_6^{2-}$ and SeSO_3^{2-} anions with Ag^+ ions. Meanwhile the interaction of $\text{Ag}(\text{I})$ with $\text{SeS}_2\text{O}_6^{2-}$, SeSO_3^{2-} and $\text{Se}_2\text{S}_2\text{O}_6^{2-}$ ions can be expressed by the following equations:



Thus, the layer of silver selenide on the PA sample's surface forms during the interaction of selenized polymer with the Ag^+ ions. The anionic particles containing selenium atoms of low oxidation state react with the silver ions resulting in the formation of silver selenides. Black silver selenide and the elemental Se remained in polymer and sulphur containing particles were washed out from PA 6 samples.

The data obtained from X-ray diffraction studies corroborate the results of chemical analysis of silver selenide layers studies. The low molar ratio of Ag/Se (0.57–0.7) in the layers of silver selenide is explained by the equation (3) and (7), when the separated elemental selenium was remained in the layer of silver selenide.

CONCLUSIONS

1. When the polyamide 6 films seleniumized in $0.05 \text{ mol}\cdot\text{dm}^{-3}$ acidified (HCl , $c = 0.1 \text{ mol}\cdot\text{dm}^{-3}$) solutions of $\text{K}_2\text{SeS}_2\text{O}_6$ up to 4.5 h and then is treated by the $0.4 \text{ mol}\cdot\text{dm}^{-3}$ AgNO_3 salt solution 10 min at 80°C , silver selenide layers are formed on its surface.

2. The amounts of silver and selenium in the layers of silver selenide on polyamide 6 samples increases with the increase of duration of polymer seleniumization. The molar ratio of Ag/Se in the layers of silver selenide increase with the increase of polymer selenization time and varies between 0.57–0.7.

3. Results of X-ray diffraction analysis of the surface of PA 6 samples after its seleniumization and treatment with solution of AgNO_3 confirmed the formation layer of silver selenides, which are composed of orthorhombic naumannite – Ag_2Se (24–1041) and monoclinic selenium – Se_8 (71–528).

4. The layers of silver selenide with the elemental selenium on polyamide 6 samples were formed by via heterogeneous chemical reactions among the sorbed-diffused selenotrithionate anion (SeSO_3^{2-}), its decomposition products (SeSO_3^{2-} , $\text{Se}_2\text{S}_2\text{O}_6^{2-}$) and Ag^+ ions.

REFERENCES

1. **Kosyachenko, L. A., Mathew, X., Motushchuk, V. V., Sklyarchuk, V. M.** Electrical Properties of Electrodeposited CdTe Photovoltaic Devices on Metallic Substrates: Study Using Small Area Au-CdTe Contacts *Solar Energy* 80 (2) 2006: pp. 148–155.
<http://dx.doi.org/10.1016/j.solener.2005.01.009>
2. **Deshmukh, S. K., Kokate, A. V., Sathe, D. J.** Studies on Electrodeposited $\text{Cd}_{1-x}\text{Fe}_x\text{S}$ Thin films *Materials Science and Engineering B* 122 2005: pp. 206–210.
<http://dx.doi.org/10.1016/j.mseb.2005.06.001>
3. **Husmann, A., Betts, J. B., Boebinger, G. S., Migliori, A., Rosenbaum, T. F., Saboungi, M. L.** Megagauss Sensors *Nature* 417 2002: pp. 421–424.
4. **Von Kreutzbruck, M., Lembke, G., Mogwitz, B., Korte, C., Janek, J.** Linear Magnetoresistance in Ag_{2+x}Se Thin Films *Physical Review B* 79 2009: pp. 035204-1–5.
<http://dx.doi.org/10.1103/PhysRevB.79.035204>
5. **Paulson, P. D., Mathew, X.** Spectroscopic Ellipsometry Investigation of Optical and Interface Properties of CdTe Films Deposited on Metal Foils *Solar Energy Materials and Solar Cells* 82 (1–2) 2004: pp. 279–290.
6. **Ivanauskas, R.** Studies on Application as Precursor of Selenotrithionate and the Mechanism of Seleniumization Polyamide 6 Films *Material Science (Medžiagotyra)* 15 (3) 2009: pp. 243–249.
7. **Ivanauskas, R., Janickis, V.** Chemical Deposition of Copper Selenide Films in the Surface Layer of Polyamide by the Use of Selenopolythionates *Progress in Colloid and Polymer Science* 116 2000: pp. 134–136.
8. **Ivanauskas, R., Janickis, V.** Potassium Selenotrithionate as Precursor for Formation of Cu_xSe Layers on Polyamide 6 Films *Polish Journal of Chemistry* 82 (12) 2008: pp. 2281–2292.
9. **Gregg, S. J., Sing, K. S. W.** Adsorption Surface Area and Porosity, Academic Press, New York, 1969.
10. **Rathke, B. J.** Zur Kenntnis der Chemischen Aehnlichkeit von Schwefel und Selen; Selenodithionige Saure, Selen-trithionsaure *Journal fur Practische Chemie* 95 1865: pp. 1–48 (in German).
11. An Atomic Absorption, Analytical Methods for Atomic Absorption Spectrometry Perkin-Elmer-503, Perkin Elmer, 1973.
12. **Madelung, O.** Data Handbook. 3rd edition. Springer-Verlag, Berlin-Heidelberg-New York, 2004.
13. **Kirchhoff, F., Holender, J. M., Gillan, M. J.** Structure, Dynamics, and Electronic Structure of Liquid Ag-Se Alloys Investigated by Ab Initio Simulation *Physical Review B* 54 (1) 1996: pp. 190–202.
14. **Wieggers, G. A.** Literature Data on the XRD Patterns for Ag_2Se . University Bloemensingel 10, Groningen, The Netherlands, Private Communication, 1972.
15. **Cherin, P., Unger, P.** Refinement of the Crystal Structure of α -monoclinic Se *Acta Crystallographyc Sec. B* 28 (1) 1972: pp. 313–317.
16. **Zelionkaitė, V. I., Janickij, I. V., Šuliakienė, I.** The Decomposition of Selenotrithionate *Transactions of Lithuanian Academy of Sciences Chemistry and Chemical Technology* 3 1963: pp. 93–101 (in Russian).
17. **Zelionkaitė, V. I., Janickis, J. V., Kudarauskiene, D.** Some Reaction of the Higher Selenopolythionates. The Selenopolythionates of Dichloroethylen-di(amine)cobalt(III) *Transactions of Lithuanian Academy of Sciences Chemistry and Chemical Technology B* 1 (36) 1964: p. 117 (in Russian).

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