AFM study of the morphology of mixed copper sulfidecopper telluride layers formed on the polyamide film surface using potassium telluropentathionate

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Kaunas University of Technology, Radvilėnų pl. 19, LT-50254 Kaunas, Lithuania The morphology of polyamide PA 6 films modified by mixed copper sulfide–copper telluride layers was studied by the atomic force microscopy method. Copper sulfide–copper telluride, Cu_xS–Cu_yTe, layers on the surface of PA 6 film were formed by treating PA film samples in potassium telluropentathionate, K₂TeS₄O₆, 0.025–0.10 mol · dm⁻³ solution and then with Cu(II / I) salt solution. The formation of copper sulfide layers proceeded unevenly, in the form of islands, which later grew into agglomerates. The surface of the layers formed was relatively uneven and rather rough. The maximum height of a Cu_xS–Cu_yTe layer slightly decreased (225–160 nm) with prolonging polyamide treatment in K₂TeS₄O₆ solution. A more significant reduction (220–80 nm) of layer height was observed upon increasing the concentration of chalcogenization solution. The same tendency was observed in changes of the surface roughness. The layer height (90–160 nm) and roughness with increasing the temperature changed irregularly.

Key words: polyamide, potassium telluropentathionate, copper sulfide-copper telluride layer, morphology, AFM

INTRODUCTION

Over the last decades, there has been an increasing interest in semiconductive copper chalcogenide $Cu_x Y$ (Y = S, Se, Te) thin layers because of their applications in various devices such as solar cells, super ionic conductors, photo-detectors, photothermal conversion, electroconductive electrodes, microwave shielding coating [1–7], gas sensors whose conductivity will increase sharply when exposed to a reducing gas such as acetone, ethanol or ammonia [8], etc.

Polymer films modified by electrically conductive layers of copper chalcogenides may be used in practice only when they meet certain requirements. For example, for the metallization of plastics, coatings of low electrical resistance and highly adhesive with the polymer are needed; the production of electronic materials requires coatings with a precise and stable electrical resistance; for adhesive joinings, coarse coatings strongly adhesive with the polymer are necessary.

When modifying polymers with layers of copper chalcogenides, it is important not only to determine the phase composition of the coatings formed, but also to study their morphology, since in many cases the latter determines the properties and possible use of dielectrics modified by thin copper chalcogenide layers.

To characterize the morphology and roughness of copper chalcogenide layers, we applied the method of atomic force microscopy.

Over the last decade, the sorption–diffusion method for the formation of thin copper sulfide layers on the surface of polyamide 6 (PA) based on the initial treatment of a polymer with the solutions containing anions of polythionates, $S_n O_6^{2-}$, has been under extensive investigation [9–14]: the polythionate ions containing chains of divalent sulfur atoms of low oxidation state, $^{-}O_3S-S_x-SO_3^{-}$ [9, 10], are sorbed by a polymer. Upon treating the sulfurized polymer with a solution of copper(II / I) salt, copper sulfide, Cu_xS, layers on the surface of a polymer are formed [10–14].

In our previous work, we have shown that using potassium telluropentathionate, $K_2 \text{TeS}_4 O_6$, solutions as PA chalcogenization agents, semiconducting and electrically conductive mixed copper sulfide–copper telluride, Cu_xS – Cu_xTe , layers form on the surface of this polymer; the phase

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composition of these layers was studied by X-ray diffaction analysis [15].

The aim of the present work was to study the morphology of Cu_xS-Cu_yTe layers formed on the surface of polyamide 6 film using potassium telluropentathionate solutions by the method of atomic force microscopy (AFM).

EXPERIMENTAL

Layers of mixed copper chalcogenide, Cu_xS-Cu_yTe , were deposited on polyamide 6 (PA) films (manufacturer TY 6-05-1775-76, grade PK-4, 15 × 70 mm, 70 µm). The PA films were boiled in distilled water for 2 h to remove monomer residues. They were dried with filter paper and then over anhydrous CaCl, for 24 h.

The PA films were chalcogenized in a thermostatic vessel using a continually stirred $0.25-0.10 \text{ mol/dm}^3$ solution of potassium telluropentathionate, $K_2 \text{TeS}_4 O_6$, at 1, 10 and 20 °C for 0.25, 2, 8 and 24 h. At certain time intervals, samples were withdrawn, rinsed with distilled water, dried with filter paper, left over anhydrous CaCl₂ for 24 h and then used for analysis and in further experiments.

Distilled water, reagents of "especially pure", "chemically pure" and "analytically pure" grades were used in the experiments. The potassium telluropentathionate salt, $K_2 TeS_4 O_6 \cdot 1.5 H_2 O$, was prepared and analyzed according to the conventional procedures [16].

Samples of chalcogenized PA were treated with a solution of Cu(II / I) salts at 78 °C for 10 min. A Cu(II / I) salt solution was made from crystalline $CuSO_4 \cdot 5H_2O$ and hydroquinone as described in [17, 18]. It is a mixture of Cu salts, containing 0.34 mol/dm³ of Cu(II) and 0.06 mol/dm³ of Cu(I) [18]. After treatment with the solution of Cu(II / I) salts, the PA samples were rinsed with distilled water, dried over anhydrous CaCl₂ and used in further experiments.

The morphology of the surface of $Cu_x S-Cu_y$ Te layers, the quantitative microscopy of the roughness of layers formed on PA surface were studied with the NT-206 atomic force mi-

croscope, in the contact regime with high resolution probes with the force constant k = 3 N/m. The characteristics of the atomic force microscope: the maximum scan field area 10×10 to 30×30 microns, the measurement matrix up to 512×512 points and more, the maximum range of measured heights 4 microns, vertical resolution 0.1-0.2 nm. The AFM cantilever was produced by Silicon-MDT in cooperation with MikroMasch (Estonia); type – NONCONTACT silicon cantilever NSC11/15; characteristics of the cantilever: radius of curvature less than 10 nm, tip height 15 20 µm, full tip cone angle less than 20°. Lateral force microscopy studies are useful for imaging variations in surface friction that can arise from inhomogeneity in surface material, and also for obtaining edge-enhanced images. Data of measurements were analysed using the Surface View 2.0 program.

RESULTS AND DISCUSSION

Results of earlier studies [15, 19–21] have shown that under PA film treatment in acidified water solutions of sodium and potassium telluropentathionate, $Na_2TeS_4O_6$, $K_2TeS_4O_6$, or telluropentathionic acid, $H_2TeS_4O_6$, the anionic particles containing tellurium and sulfur atoms of low oxidation state, $^{-}O_3S-S-Te-S-SO_3^{-}$, do sorb-diffuse into the polymer. While treating PA films chalcogenized such a way with the solutions of Cu(II / I) salts, exactly these central divalent tellurium and sulfur atoms of low oxidation state react with the Cu(II / I) ions and form layers of mixed copper sulfides– copper tellurides on the surface of semihydrophilic PA [15, 20, 21].

To characterize the morphology and to estimate the roughness of Cu_xS-Cu_y Te layers, we applied the method of atomic force microscopy.

A morphological study of PA modified with Cu_xS-Cu_yTe layers by atomic force microscopy revealed the coatings to be essentially different. Fields of 12×12 microns were investigated; for the quantitative estimation of the surface, the standard programs of the view treatment were used.



Fig. 1. Atomic force microscopy view of initial (not chalcogenized) PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). Scan field area 12×12 microns. Interval of uneveness height up to 67.4 nm

The views of Cu $_x$ S–Cu $_y$ Te layer surface obtained by AFM are shown in Figs. 2–7, 9–14 and 16–19. A view of the initial PA surface is presented in Fig. 1. We have determined that the height and surface morphology of the chalcogenide layers formed on PA depend on the conditions of polymer chalcogenization.

Profile sections of Cu_xS-Cu_yTe coatings formed on PA surface when the polymer had been sulfurized for 0.25, 2.0

and 24.0 h at a temperature of 10 °C with 0.025 mol \cdot dm⁻³ K₂TeS₄O₆ solution and then treated for 10 min with Cu(II / I) salt solution, allowed to estimate quantitatively the height and diameter of separate crystallites (Figs. 2–8; the crystallinity of Cu_xS–Cu_yTe layers was shown in an earlier study [15] by X-ray diffraction).

When the polymer had been chalcogenized for 0.25 h at a temperature of 10 °C in K_2 TeS₄O₆ solution, the height







Fig. 3. View of topographic image and line profile of chalcogenide layer formed on PA surface. PA was chalcogenized for 2 h at 10 °C in 0.025 mol/dm³ K₂TeS₄O₆ solution and then treated with Cu(II / I) salt solution



Fig. 4. View of topographic image and line profile of chalcogenide layer formed on PA surface. PA was chalcogenized for 24 h at 10 °C in 0.025 mol/dm³ K, TeS, O_s solution and then treated with Cu(II / I) salt solution

of the crystallites reached 88 nm (diameter ~0.1–1.0 μ m) (Fig. 2), the mean height being 61.06 nm. On prolonging chalcogenization to 2.0 and 24.0 h, the height of crystallites decreased to 66 nm, but the diameter changed not much and was equal to ~0.4–1.0 μ m (Figs. 3, 4). The mean height of crystallites increased to 144.04 nm, but after 24 h of chalcogenization it decreased ~2.5 times and equalled 56.24 nm.

Under a short duration of polymer treatment in $K_2 \text{TeS}_4 \text{O}_6$ solution (0.25 h), the growth of the chalcogenide layer be-

gins from the formation of separate small islands (Fig. 5). On prolonging chalcogenization to 2 h, the growth of the chalcogenide layer proceeds more intensively (Fig. 6), and upon prolonging the duration of chalcogenization to 24 h, clusterization begins; as a result, crystallites of various diameter and height begin slowly joining into agglomerates (Fig. 7). One can see a slight reduction of the mean layer roughness (Fig. 8). This means that the crystallites joining into agglomerates cover the surface more evenly, and the layer becomes more homogeneous.



Fig. 5. Atomic force microscopy view of $Cu_x S - Cu_y$ Te layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 0.25 h at a temperature of 10 °C in 0.025 mol/dm³ K₂TeS₄O₄ solution and then treated with Cu(II / I) solution



Fig. 6. Atomic force microscopy view of $Cu_x S - Cu_y$ Te layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 2 h at a temperature of 10 °C in 0.025 mol/dm³ K, TeS₄O₅ solution and then treated with Cu(II / I) solution



Fig. 7. Atomic force microscopy view of $Cu_x S - Cu_y$ Te layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 24 h at a temperature of 10 °C in 0.025 mol/dm³ K₃TeS₄O₂ solution and then treated with Cu(II / I) solution



Fig. 8. Dependence of layer mean square roughness (*a*) and maximum and mean height (*b*) on the duration of PA treatment in 0.025 mol/dm³K, TeS₄O₆ solution at a temperature of 10 °C



Fig. 9. View of topographic image and line profile of chalcogenide layer formed on PA surface. PA was chalcogenized for 8 h at 20 °C in 0.025 mol/dm³ K₂TeS₄O₆ solution and then treated with Cu(II / I) salt solution



Fig. 10. View of topographic image and line profile of chalcogenide layer formed on PA surface. PA was chalcogenized for 8 h at 20 °C in 0.05 mol/dm³ K, TeS₄O₆ solution and then treated with Cu(II/I) salt solution



Fig. 11. View of topographic image and line profile of chalcogenide layer formed on PA surface. PA was chalcogenized for 8 h at 20 °C in 0.1 mol/dm³ K, TeS₄O₆ solution and then treated with Cu(II / I) salt solution

Investigating further the formation of Cu_xS-Cu_yTe layers on PA surface, the copper chalcogenide layer was formed by PA chalcogenization in 0.025, 0.05 and 0.10 mol/dm³ K₂TeS₄O₆ solution for 8 h at a temperature of 20 °C with the subsequent 10-min treatment in Cu(II / I) salt solution at a temperature of 78 °C. Cross-sections of these layers showed a rather uneven surface of the layers (Figs. 9–11). As is seen from the views of Cu_xS-Cu_yTe layers on PA surface (Fig. 12– 14) and cross-sections (Figs. 9–11), the crystallites formed were of various height, diameter and shape. Their mean square roughness decreased (Fig. 15). The views of these layers are shown in Figs. 12, 13, 14. In Fig. 12, one can see that when the concentration of $K_2 \text{TeS}_4 O_6$ solution is low, the formation of the layer is slow, and an uneven covering is observed because formation of islands on separate spots begins; the maximum height of the unevenness is 218 nm and the mean height of the layer 80.46 nm. On increasing the concentration of the PA chalcogenization solution, the number of islands increases, some of them join into large agglomerates formed of crystallites of different diameter (Figs. 13, 14). The maximum height of the layer decreases from 218 to 149 and 80 nm (compare with Fig. 12), and the



Fig. 12. Atomic force microscopy view of $Cu_x S-Cu_y Te$ layers formed on PA surface: 2D view of lateral forces microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 8 h at a temperature of 20 °C in 0.025 mol/dm³ K, TeS₄O₆ solution and then treated with Cu(II / I) solution



Fig. 13. Atomic force microscopy view of $Cu_x S - Cu_y$ layers formed on PA surface: 2D view of lateral forces microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 8 h at a temperature of 20 °C in 0.05 mol/dm³ K, TeS, O, solution and then treated with Cu(II / I) solution



Fig. 14. Atomic force microscopy view of $Cu_x S - Cu_y Te$ layers formed on PA surface: 2D view of lateral forces microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 8 h at a temperature of 20 °C in 0.1 mol/dm³ K₂TeS₄O₅ solution and then treated with Cu(II / I) solution



Fig. 15. Dependence of layer mean square roughness (*a*) and maximum and mean height (*b*) on the concentration of K_2 TeS₄O₆ solution while treating PA for 8 h at a temperature of 20 °C

average height of the layer decreases to 62.96 and 42.26 nm, respectively. Thus, while increasing the concentration of the chalcogenization solution to 0.10 mol/dm³, the mean height of the layer and its mean square roughnes reduce by half; the crystallites, joining into agglomerates more evenly, cover the surface, and the layer becomes more homogeneous.

Studying the formation of Cu_xS-Cu_yTe layers on PA surface, a chalcogenide layer was formed by changing the temperature also, i. e. PA was chalcogenized for 8 h in 0.05 mol/dm³ K₂TeS₄O₆ solution at a temperature of 1, 10, 20 °C and then treated with a Cu(II / I) salt solution at a temperature of 78 °C. Cross-sections of these layers showed that the layer surface was rather uneven. One can see from the cross-sections

(Figs. 10, 16, 17) and views of Cu_xS-Cu_yTe layers on PA surface (Figs. 13, 18, 19), the crystallites were of various height, diameter and shape. The roughness with increasing the temperature of chalcogenization changed irregularly (Fig. 20). The views of these layers are shown in Figs. 13, 18, 19.

At a low temperature of PA treating in $K_2 \text{TeS}_4 O_6$ solution, the layer formation was slow and irregular. The maximum height of a layer was ~160 nm (Fig. 18), the mean height being 47.82 nm. On increasing the temperature of chalcogenization solution to 10 °C, the maximum height of the layer decreased to ~90 nm (Fig. 19) and the mean height of the layer to 34.58 nm. However, at a temperature of 20 °C it increased again to ~149 nm (Fig. 13) and the mean height



Fig. 16. View of topographic image and line profile of chalcogenide layer formed on PA surface. PA was chalcogenized for 8 h at 1 °C in 0.05 mol/dm³ K, TeS, O_s solution and then treated with Cu(II / I) salt solution



Fig. 17. View of topographic image and line profile of chalcogenide layer formed on PA surface. PA was chalcogenized for 8 h at 10 °C in 0.05 mol/dm³ K, TeS, O_c solution and then treated with Cu(II / I) salt solution







Fig. 19. Atomic force microscopy view of $Cu_x S - Cu_y$ Te layers formed on PA surface: 2D view of lateral forces microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 8 h at a temperature of 10 ° C in 0.05 mol/dm³ K₂TeS₄0₆ solution and then treated with Cu(II/I) solution



Fig. 20. Dependence of $Cu_x S - Cu_y$ Te layer mean square roughness (*a*) and maximum and average height (*b*) on the temperature of 0.05 mol/dm³ K,TeS₄O₆ solution while treating PA for 8 h

of the layer to 62.96 nm. Thus, with increasing the chalcogenization temperature from 1 to 20 °C, the height changes irregularly. The reason may be differences in the phase composition of Cu_xS-Cu_yTe layers obtained at a different temperature.

Thus, the AFM results indicate that depending on the conditions (duration, concentration and temperature) of PA initial chalcogenization in $K_2 TeS_4 O_6$ solution (under the same "copperizing" conditions), the formation of copper chalcogenide layers proceeds irregularly in the form of islands which grow into larger agglomerates. The surface of the layer is un-

even, rather rough. The maximum height of the layer slightly reduces with prolonging PA treatment in $K_2 \text{TeS}_4 O_6$ solution. The reduction of layer height is more significant with increasing the concentration of chalcogenization solution. The same tendency is observed in changes of the roughness. The layer height and roughness with increasing the temperature change irregularly.

The parameters of the layer assymmetry change from 0.31 to 1.36, indicating the domination of raised elements – islands, crystallites and agglomerates – on the surface of Cu_xS – Cu_yTe layers.

CONCLUSIONS

1. The morphology of Cu_xS-Cu_yTe layers formed on polyamide 6 film surface using solutions of potassium telluropentathionate, $K_2TeS_4O_6$, was studied by the atomic force microscopy method. Copper chalcogenide layers were found to form unevenly as islands which grew into bigger agglomerates.

2. The morphology and roughness of Cu_xS-Cu_yTe layers depend significantly on the conditions of initial polymer chalcogenization with $K_2TeS_4O_6$ solution if the same conditions of halcogenized polyamide treatment in copper(II/I) salt solution have been used.

3. The maximum height of a Cu_xS-Cu_yTe layer slightly decreases (225–160 nm) with prolonging polyamide treatment in K₂TeS₄O₆ solution. The layer height reduces more significantly decreases (220–80 nm) with increasing the concentration of chalcogenization solution. The same tendency is observed in changes of the surface roughness. The layer height (90–160 nm) and roughness with increasing the temperature change irregularly.

Received 13 January 2010 Accepted 21 January 2010

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VARIO SULFIDŲ-VARIO TELŪRIDŲ SLUOKSNIŲ, SUDARYTŲ POLIAMIDO PLĖVELĖS PAVIRŠIUJE NAUDOJANT KALIO TELŪROPENTATIONATĄ, MORFOLOGIJOS TYRIMAS ATOMINĖS JĖGOS MIKROSKOPIJA

Santrauka

Atominės jėgos mikroskopijos (AJM) metodu ištirta vario sulfidų–vario telūridų sluoksnių, sudarytų poliamido 6 plėvelių (PA) paviršiuje naudojant kalio telūropentationato, K₂TeS₄O₆, tirpalus, morfologija. Vario sulfidų–vario telūridų, Cu_xS–Cu_yTe, sluoksniai PA paviršiuje sudaryti, apdorojant plėveles 0,025–0,10 mol · dm⁻³ koncentracijos K₂TeS₄O₆ tirpalais ir po to jas veikiant Cu(II / I) druskų tirpalu. Nustatyta, kad vario chalkogenidų sluoksniai formuojasi netolygiai, salelėmis, kurios suauga į didesnius aglomeratus. Susidariusios dangos paviršius nelygus, gana šiurkštus. Maksimalus Cu_xS–Cu_yTe dangos aukštis mažėja (225–160 nm) ilginant polimero apdorojimo K₂TeS₄O₆ tirpale trukmę. Ženkliau sluoksnio aukštis sumažėja (220–80 nm) didinant chalkogeninimo tirpalo koncentraciją. Analogiškai kinta ir vario chalkogenidinių sluoksnių paviršiaus šiurkštumas. Sluoksnio aukštis (90–160 nm) ir šiurkštumas didinant chalkogeninimo temperatūrą kinta nenuosekliai.