AFM study of the morphology of mixed copper chalcogenide layers formed on polyamide film surface

Neringa Petrašauskienė,

Vitalijus Janickis*

*Kaunas University of Technology,
Radvilėnų pl. 19, LT-50254 Kaunas,
Lithuania*

The morphology of polyamide PA 6 films modified by mixed copper sulfide – copper selenide layers was studied by the atomic force microscopy method. Copper sulfide – copper selenide ($Cu_xS–Cu_ySe$) layers on the surface of PA 6 film were formed by treating PA film samples in potassium selenopentathionate ($K_2SeS_4O_6$) 0.05–0.20 mol · dm^{-3} solution and then with Cu(II/I) salt solution. The formation of copper chalcogenide 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 average height of a $Cu_xS–Cu_ySe$ layer changed irregularly (~107–1100 nm) with increasing the temperature and concentration of PA chalcogenization solution. The layer roughness varied from ~31 to ~112 nm. The layer roughness with increasing the temperature and the concentration of chalcogenization solution changed irregularly and caused changes in the shape distribution function of the surface elements.

Key words: polyamide, potassium selenopentathionate, copper sulfide – copper selenide layer, morphology, AFM

INTRODUCTION

Deposition of metal chalcogenide layers on the surface of organic polymer films is a promising approach to obtaining electrically conductive films. These films have a potential utility as materials for electrical and optical devices. Various applications such as solar cells [1], solar control coatings [2, 3], architectural glazing [4], ammonia gas sensors [5–7], optical filters, superionic conductors [8, 9], thermoelectric converters [10], photo-detectors, electro-conductive electrodes, microwave shielding coatings [11], photovoltaic cells, and Shottky diodes are associated with these copper chalcogenide compounds [12, 13].

Intensive research was performed in the past to study the production of metal chalcogenide compounds in the form of thin films. Several techniques for producing Cu_ySe [20–23] or Cu_xS films have been adopted.

In this work, mixed copper chalcogenide $Cu_xS–Cu_ySe$ layers were obtained on the surface of polyamide 6 (PA) by the sorption–diffusion method. The formation process and the characterization of the obtained thin semiconductive and electrically conductive layers of copper chalcogenide on the surface of PA were described in our previous publications [24–32].

The aim of the present work was to study the morphology of $Cu_xS–Cu_ySe$ layers formed on the surface of PA films, using potassium selenopentathionate ($K_2SeS_4O_6$) solutions by the method of atomic force microscopy (AFM).

EXPERIMENTAL

Layers of a mixed copper chalcogenide, $Cu_xS–Cu_ySe$, were deposited on 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 the monomer residues. They were dried with filter paper and then over anhydrous $CaCl_2$ for 24 h.

The PA films were chalcogenized in a thermostatic vessel, using a continually stirred 0.05 and 0.2 mol/dm³ $K_2SeS_4O_6$ solutions acidified by adding HCl (0.1 mol/dm³ HCl, pH ~1.5) at 30 and 50 °C. At certain time intervals, samples were withdrawn, rinsed with distilled water, dried with filter paper, left over anhydrous $CaCl_2$ for 24 h and then used in analysis and in further experiments.

* Corresponding author. E-mail: vitalijus.janickis@ktu.lt

Distilled water, reagents of "especially pure", "chemically pure" and "analytically pure" grades were used in the experiments. The potassium selenopentathionate salt, $K_2SeS_4O_6 \cdot 1.5H_2O$, was prepared and analyzed according to published procedures [33].

Samples of chalcogenized PA were treated with Cu(II/I) salt solution at 78 °C for 10 min. The Cu(II/I) salt solution was made from crystalline $CuSO_4 \cdot 5H_2O$ and hydroquinone as described in [34, 35]. It is a mixture of Cu salts, containing 0.34 mol/dm³ of Cu(II) and 0.06 mol/dm³ of Cu(I) [35]. After treatment with the solution of Cu(II/I) salts, the PA samples were rinsed with distilled water, dried over anhydrous $CaCl_2$ and used in further experiments.

The morphology of the surface of $Cu_xS–Cu_ySe$ layers, the quantitative microscopy of the roughness of layers formed on PA surface were studied with the NT-206 atomic force microscope, 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 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 inhomogeneities in the 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 [24,25] showed that under PA film treatment in acidified water solutions of potassium selenopentathionate, $K_2SeS_4O_6$, the anionic particles containing selenium and sulphur atoms of low oxidation state, $^-O_3S–S–Se–S–SO_3^-$, do sorb–diffuse into the polymer.

While treating PA films chalcogenized in such a way with the solutions of Cu(II/I) salts, exactly these central divalent Se and S atoms of low oxidation state react with Cu(II/I) ions and form layers of mixed copper sulfides – copper selenides on the surface of semihydrophilic PA [26–32].

To characterize the morphology and to estimate the roughness of $Cu_xS–Cu_ySe$ layers, we applied the method of atomic force microscopy.

A morphological study of PA modified with $Cu_xS–Cu_ySe$ 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.

The views of $Cu_xS–Cu_ySe$ layer surface obtained by AFM are shown in Figs. 2–7 and 10–11. A view of the initial PA surface is presented in Fig. 1. The maximum height reaches ~67 nm, the average height (H_{mean}) ~28 nm; the root mean square roughness is R_q 4.6 nm, and the skewness is ~0.8.

The height and surface morphology of the chalcogenide layers formed on PA depended on the conditions of polymer chalcogenization.

Profile sections of $Cu_xS–Cu_ySe$ coatings formed on PA surface when the polymer had been chalcogenized for 10, 60 and 270 min at a temperature of 30 °C with 0.05 mol · dm⁻³ $K_2SeS_4O_6$ 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. 2–7; the crystallinity of $Cu_xS–Cu_ySe$ layers was shown in an earlier study [28] by X-ray diffraction).

When the polymer was chalcogenized for 10 min at a temperature of 30 °C, the height of the crystallites reached 478 nm (diameter ~0.1–2.0 μm) (Figs. 2, 3), the mean height being ~192 nm (Fig. 8).
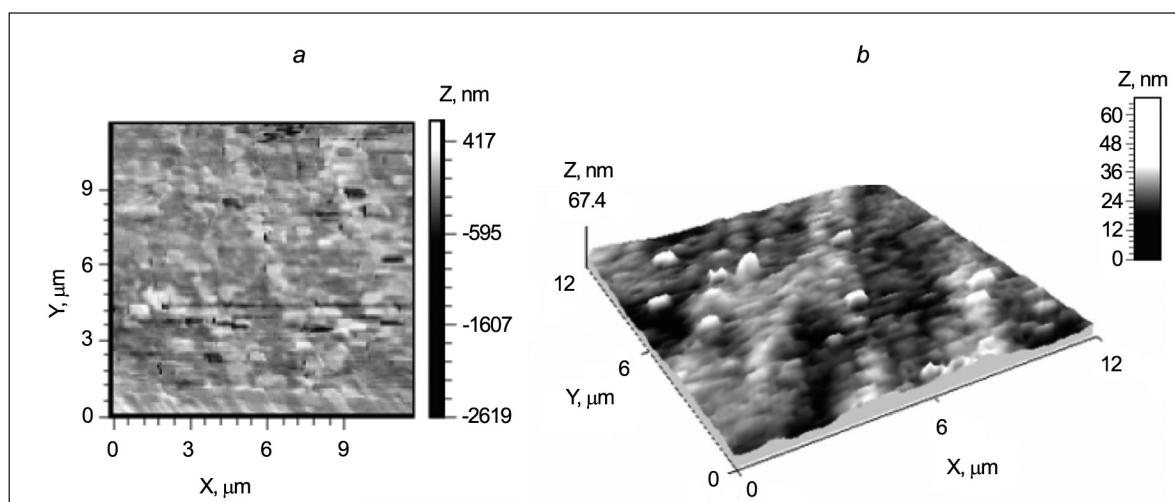

Fig. 1. Atomic force microscopy view of initial (not chalcogenized) PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). Scan field area 12 × 12 microns. Interval of unevenness height up to 67.4 nm

Absolute values: [a] → x = 6957.0 nm; z (1) = 115.7 nm;

[b] → x = 9054.8 nm; z (1) = 57.7 nm;

difference between markers: dx = 2097.8 nm; dz (1) = 58.1 nm

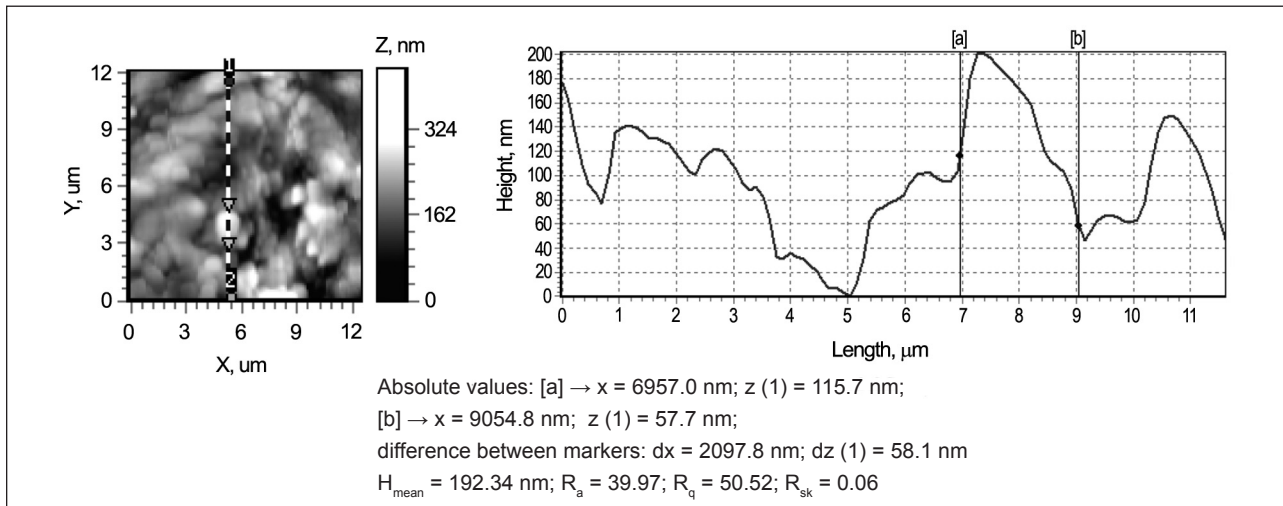H_{mean} = 192.34 nm; R_a = 39.97; R_q = 50.52; R_{sk} = 0.06

Fig. 2. View of topographic image and line profile of chalcogenide layer formed on PA surface. PA was chalcogenized for 10 min at 30 °C in 0.05 mol/dm³ $K_2SeS_4O_6$ solution and then treated with Cu(II/I) salt solution
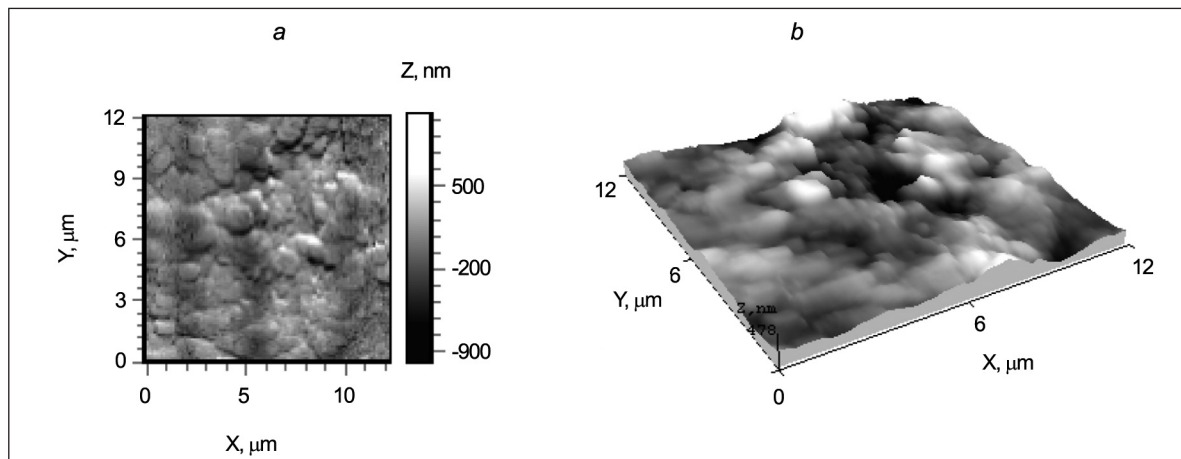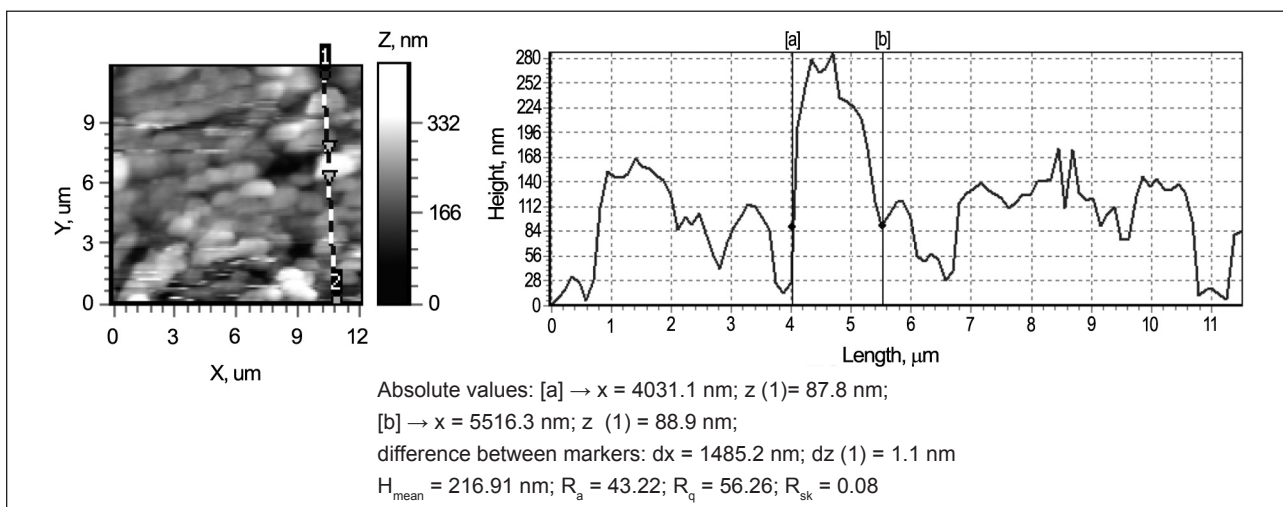

a   *b*

Fig. 3. Atomic force microscopy view of $Cu_xS–Cu_ySe$ layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 10 min at 30 °C in 0.05 mol/dm³ $K_2SeS_4O_6$ solution and then treated with Cu(II/I) salt solution

Absolute values: [a] → x = 4031.1 nm; z (1)= 87.8 nm;

[b] → x = 5516.3 nm; z (1) = 88.9 nm;

difference between markers: dx = 1485.2 nm; dz (1) = 1.1 nm

H_{mean} = 216.91 nm; R_a = 43.22; R_q = 56.26; R_{sk} = 0.08

Fig. 4. View of topographic image and line profile of chalcogenide layer formed on PA surface. PA was chalcogenized for 60 min at 30 °C in 0.05 mol/dm³ $K_2SeS_4O_6$ solution and then treated with Cu(II/I) salt solution
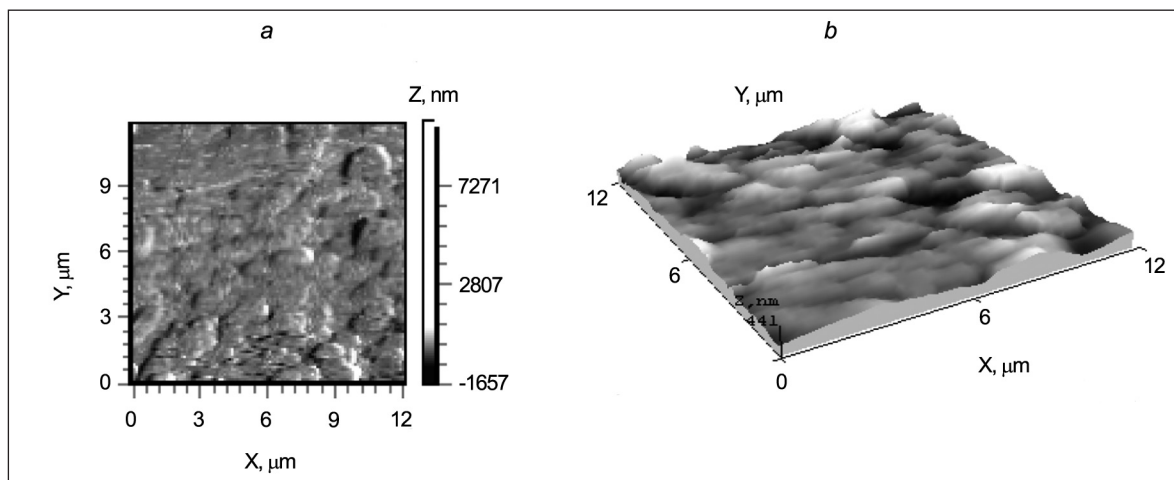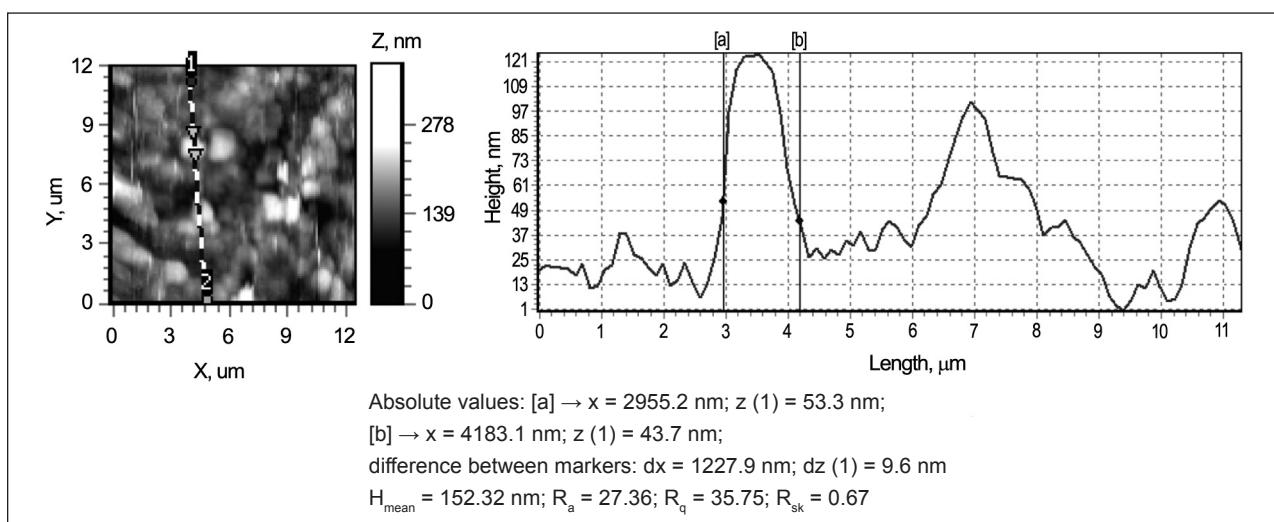
Fig. 5. Atomic force microscopy view of Cu$_x$S–Cu$_y$Se layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 60 min at 30 °C in 0.05 mol/dm³ K$_2$SeS$_4$O$_6$ solution and then treated with Cu(II/I) salt solution

Absolute values: [a] → x = 2955.2 nm; z (1) = 53.3 nm;
[b] → x = 4183.1 nm; z (1) = 43.7 nm;
difference between markers: dx = 1227.9 nm; dz (1) = 9.6 nm
H$_{mean}$ = 152.32 nm; R$_a$ = 27.36; R$_q$ = 35.75; R$_{sk}$ = 0.67

Fig. 6. View of topographic image and line profile of chalcogenide layer formed on PA surface. PA was chalcogenized for 270 min at 30 °C in 0.05 mol/dm³ K$_2$SeS$_4$O$_6$ solution and then treated with Cu(II/I) salt solution

On prolonging chalcogenization to 60 min, the height of crystallites changed insignificantly (decreased to 441 nm), the diameter changed not much, either, and was equal to ~0.3–1.5 μm (Figs. 4, 5). The mean height of crystallites increased to ~217 nm, but after 270 min of chalcogenization the height of crystallites decreased to 338 nm (Fig. 7) (diameter ~0.3–2.1 μm); the H_{mean} of crystallites decreased ~1.4 times and equaled ~152 nm (Fig. 8).

Under a short duration of polymer treatment in K$_2$SeS$_4$O$_6$ solution (10 min), the growth of the chalcogenide layer begins from the formation of separate small islands (Fig. 3). On prolonging chalcogenization to 60 min, the growth of the chalcogenide layer proceeds more intensively (Fig. 5), and upon prolonging the duration of chalcogenization to 270 min, clusterization begins; as a result, the crystallites of various diameter and height begin slowly joining into agglomerates (Fig. 7). One can see a slight reduction of the mean layer roughness:

from ~51 nm at the duration of chalcogenization 10 min to ~56 nm at the duration of 60 min and to ~36 nm at 270 min (Fig. 8). This means that the crystallites joining into agglomerates cover the surface more evenly, and the layer becomes more homogeneous.

When studying the formation of Cu$_x$S–Cu$_y$Se layers on PA surface, a chalcogenide layer was formed also by changing the temperature, i. e. PA was chalcogenized for 20, 60 and 270 min in 0.05 mol/dm⁻³ K$_2$SeS$_4$O$_6$ solution at a temperature of 50 °C and then treated with Cu(II/I) salt solution. Cross-sections of these layers showed a rather uneven surface of the layers; the crystallites formed were of various height, diameter and shape.

When the polymer had been chalcogenized for 20–60 min at a temperature of 50 °C, the maximum height of the layer decreased from 478–441 nm (chalcogenization duration 10 and 60 min at a temperature of 30 °C) to ~348 nm, but the
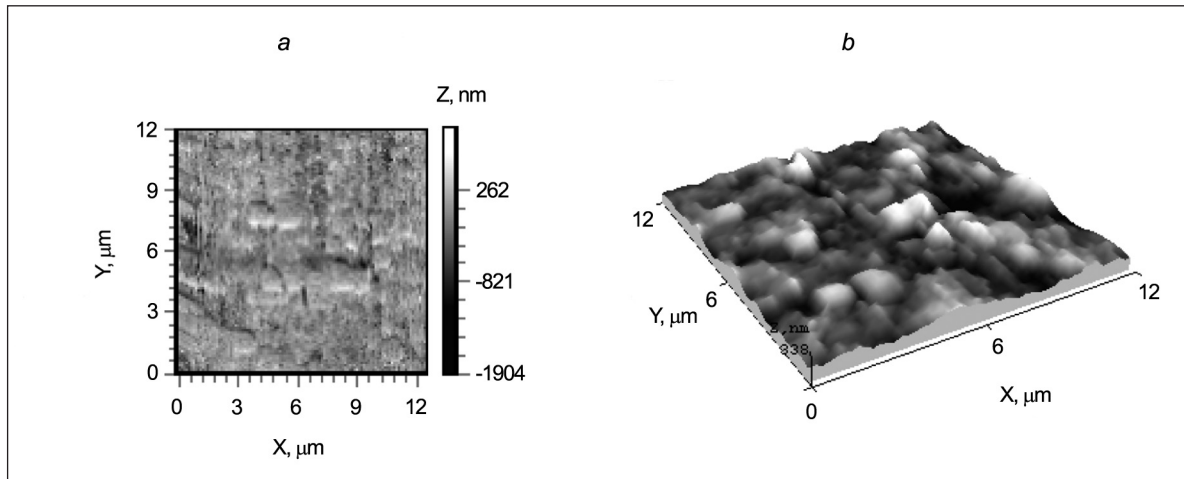
Fig. 7. Atomic force microscopy view of Cu_xS-Cu_ySe layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 270 min at 30 °C in 0.05 mol/dm^3 K$_2$SeS$_4$O$_6$ solution and then treated with Cu(II/I) salt solution

mean height of the layer decreased from ~192–217 nm to ~107–129 nm. On prolonging chalcogenization to 270 min (at a temperature of 50 °C) and under the same conditions of "copperizing", the H_{mean} of crystallites increased from ~152 nm (at 30 °C) to ~296 nm (at 50 °C, Fig. 9). The same tendency was observed in the change of Cu_xS-Cu_ySe layer roughness with increasing the polyamide chalcogenization temperature from 30 to 50 °C: it increased from ~36 nm to ~83 nm (Fig. 9).

Thus, with increasing the chalcogenization temperature from 30 to 50 °C, depending on time, the height and roughness of crystallites changes; the reason may be the differences

in the phase composition of Cu_xS-Cu_ySe layers obtained at a different temperature; this was shown in our prevous study [28] on X-ray diffraction of Cu_xS-Cu_ySe layers formed on PA film surface.

Investigating further the formation of Cu_xS-Cu_ySe layers on PA surface, a copper chalcogenide layer was formed by PA chalcogenization in 0.2 mol/dm^3 K$_2$SeS$_4$O$_6$ solution for 20, 60 and 270 min at a temperature of 50 °C. The views of the layers formed are shown in Figs. 10 and 11.

On increasing the duration of PA chalcogenization from 60 to 270 min, the number of islands increased, some of them joined into large agglomerates of crystallites of
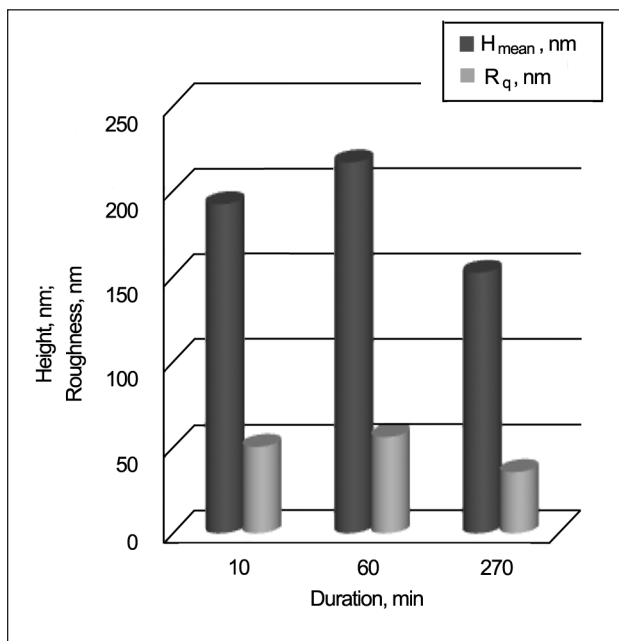

Fig. 8. Dependence of layer mean square roughness and mean height on the duration of PA treatment in 0.05 mol/dm^3 K$_2$SeS$_4$O$_6$ solution at a temperature of 30 °C
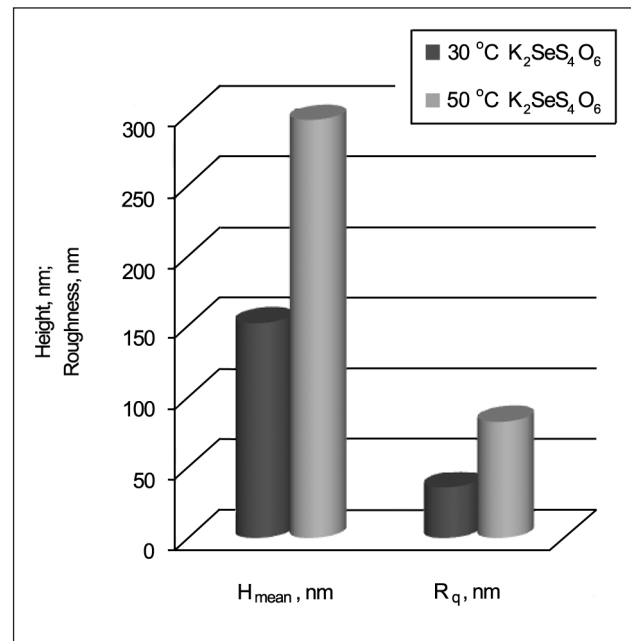
Fig. 9. Dependence of Cu_xS-Cu_ySe layer mean height (H_{mean}) and root mean square roughness (R_q) on the temperature of 0.05 mol/dm^3 K$_2$SeS$_4$O$_6$ solution while treating PA for 270 min

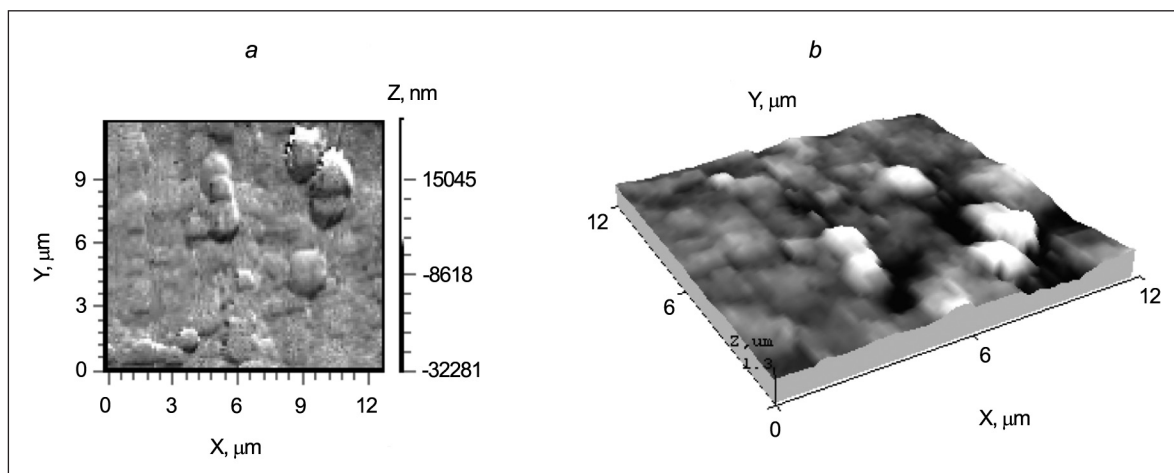**Fig. 10.** Atomic force microscopy view of $Cu_xS–Cu_ySe$ layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 60 min at 50 °C in 0.2 mol/dm³ $K_2SeS_4O_6$ solution and then treated with Cu(II/I) salt solution

Fig. 11. Atomic force microscopy view of $Cu_xS–Cu_ySe$ layers formed on PA surface: 2D view of lateral force microscopy (*a*) and 3D topography view (*b*). PA was chalcogenized for 270 min at 50 °C in 0.2 mol/dm³ $K_2SeS_4O_6$ solution and then treated with Cu(II/I) salt solution

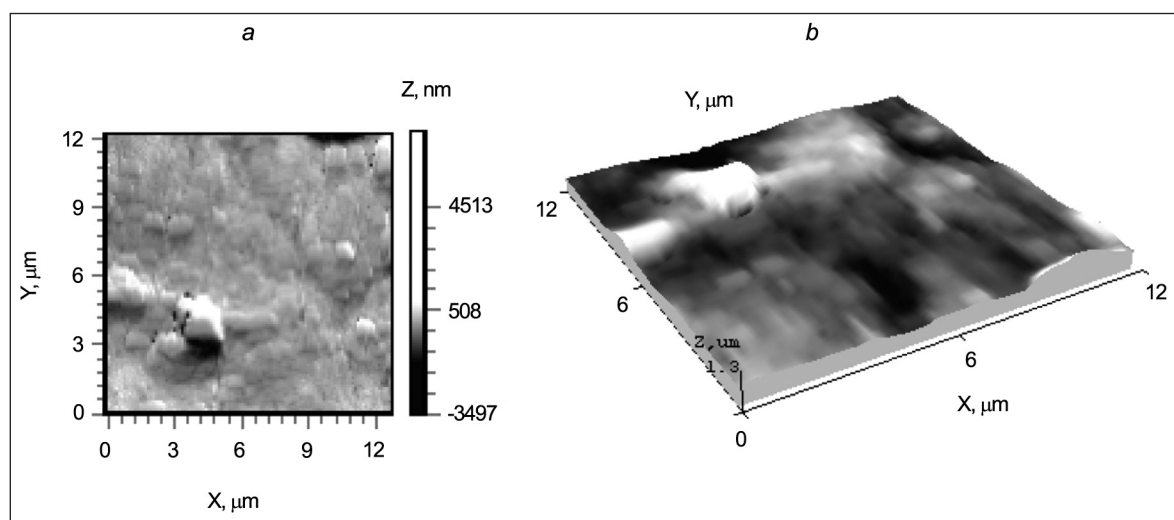different diameter; the maximum height of the layer with increasing chalcogenization duration increased from ~1000 to ~1300 nm, and the roughness of the layer increased from ~99 to ~112 nm (Figs. 10, 11).

A comparison of the morphological characteristics of $Cu_xS–Cu_ySe$ layers (Fig. 12) obtained using 0.05 mol/dm³ and 0.2 mol/dm³ $K_2SeS_4O_6$ solutions at a temperature of 50 °C (chalcogenization duration 60 min) showed an increase of the copper chalcogenide layer mean height (from ~107 nm to ~1000 nm) and root mean square roughness (from ~31 nm to ~99 nm) with increasing the concentration of chalcogenization solution. However, separate islands joined into large agglomerates and almost evenly covered the polyamide surface (Fig. 12).

Thus, the AFM results indicate that depending on the conditions (duration of chalcogenization, concentration and temperature) of PA initial chalcogenization in $K_2SeS_4O_6$ solu-

tion (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 uneven, rather rough.

The parameters of the layer asymmetry change from 0.0 to 1.22 (R_{sk}), indicating the domination of raised elements – islands, crystallites and agglomerates – on the surface of $Cu_xS–Cu_ySe$ layers.

Results of earlier studies [28] showed that when for polyamide chalcogenization 0.05–0.2 mol/dm³ $K_2SeS_4O_6$ solutions were used, the highest concentration of conductive copper selenides and copper sulfides was obtained when polyamide had been chalcogenized in 0.2 mol/dm³ solution. As a result, very low values of electrical sheet resistance (up to ~12 Ω/□) of chalcogenide layers on PA were obtained. The concept of sheet resistance is used to characterize thin deposited layers. Sheet resistance is specified by ohms per square, (Ω/□,
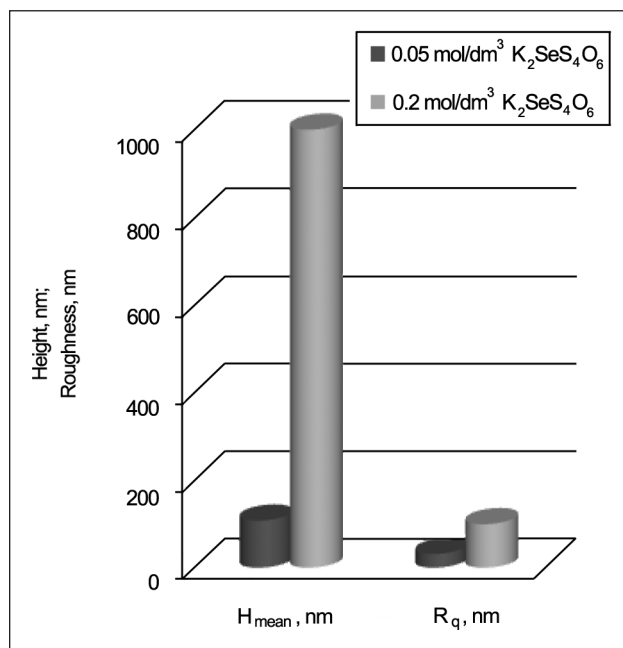
Fig. 12. Dependence of Cu$_x$S–Cu$_y$Se layer mean height (H_{mean}) and the root mean square roughness (R_q) on the concentration of 50 °C K$_2$SeS$_4$O$_6$ solution while treating PA for 60 min

ohms / square). These data of earlier studies are in agreement with the results of the morphology study presented here: separate crystallites, with increasing the duration of PA chalcogenization, joined into larger agglomerates which more evenly covered the polyamide surface; when the Cu$_x$S–Cu$_y$Se layer became homogeneous, its electrical resistance reached the lowest values.

CONCLUSIONS

1. The morphology of Cu$_x$S–Cu$_y$Se layers formed on polyamide 6 film surface using potassium selenopentathionate, K$_2$SeS$_4$O$_6$, solutions was studied by the atomic force microscopy method. Copper chalcogenide layers were formed unevenly as islands which grew into bigger agglomerates.

2. The morphology and roughness of Cu$_x$S–Cu$_y$Se layers depended significantly on the conditions of the initial polymer chalcogenization if the same conditions of chalcogenized polyamide treatment in copper(II/I) salt solution had been used.

3. The average height of a layer (~107–1100 nm), with increasing the temperature and concentration, changed irregularly. The roughness of modified PA films varied from ~31 to ~112 nm.

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Neringa Petrašauskienė, Vitalijus Janickis

POLIAMIDO PLĖVELĖS PAVIRŠIUJE SUDARYTŲ MIŠRIŲ VARIO CHALKOGENIDŲ SLUOKSNIŲ MORFOLOGIJOS TYRIMAS ATOMINĖS JĖGOS SPEKTROSKOPIJA

S a n t r a u k a

Atominių jėgų mikroskopijos metodu ištirta vario chalkogenidų sluoksnių, sudarytų poliamido plėvelių paviršiuje naudojant kalio selenopentationato, $K_2SeS_4O_6$, tirpalus, morfologija. Vario sulfidų–vario selenidų, Cu_xS–Cu_ySe, sluoksniai PA paviršiuje sudaryti, apdorojant plėveles 0,05–0,20 mol/dm³ koncentracijos $K_2SeS_4O_6$ 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. Vidutinis Cu_xS–Cu_ySe dangos aukštis kinta nuo ~107 nm iki ~1100 nm, kintant polimero apdorojimo $K_2SeS_4O_6$ tirpale koncentracijai, temperatūrai bei trukmei. Vario chalkogenidų sluoksnių paviršiaus šiurkštumas kinta ~31,7– ~112,04 nm intervale.