

Potassium selenotriethionate – the precursor for formation of semiconductive and conductive copper selenide layers on polyamide surface

Vitalijus Janickis,

Remigijus Ivanauskas

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

Semiconducting and electrically conductive layers of copper selenide, Cu_xSe_y , on the polyamide 6 (PA) surface were formed using the sorption–diffusion method and the water solutions of potassium selenotriethionate, $\text{K}_2\text{SeS}_2\text{O}_6$, as the precursor of polymer seleniumization. Selenotriethionate anions containing divalent selenium atoms of low oxidation state, $-\text{O}_3\text{S}-\text{Se}-\text{SO}_3^-$, are sorbed-diffused into PA films if they are treated with selenotriethionate solutions. The concentration of sorbed selenotriethionate increases with an increase of the temperature and concentration of the precursor solution and the duration of PA treatment. Cu_xSe_y layers are formed on the surface of a PA film when a chalcogenized polymer is treated with the water solution of copper(II/I) salt: the anions of selenotriethionate react with copper ions. The concentration of copper increases with increasing the concentration and temperature of the precursor solution and the duration of PA initial chalcogenization. The formed layers were characterized for chemical composition, electrical and physical properties. The percentage amounts of selenium and copper in Cu_xSe_y layers on PA films with polymer seleniumization time changed as follows: Se from 51.61 to 69.46% and Cu from 48.39 to 30.54%. The most uniform thin layer of Cu_xSe_y formed on the polyamide film being seleniumized for 2.5 h was observed by scanning electron microscopy (SEM). The thickness of Cu_xSe_y layers depends on polymer seleniumization time and changed in an interval of 0.98–3.2 μm . The X-ray diffraction (XRD) pattern study of Cu_xSe_y layers showed that they are polycrystalline in nature; six phases of copper selenides Cu_2Se (27-1131), CuSe_2 (74-280), CuSe_2 (18-453), Cu_3Se_2 (72-1421) and the phases of berzelianite Cu_{2-x}Se (6-680) and of bellidoite Cu_2Se (29-575) were identified. The XPS results confirmed the formation of copper selenides layers on the surface of PA. The regularities established enable the formation of Cu_xSe_y layers of a desirable composition and conductivity.

Keywords: review, polyamide, copper selenide thin films, scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy

INTRODUCTION

Copper chalcogenides – binary compounds of copper with chalcogens, Cu_xY ($\text{Y} = \text{S}, \text{Se}, \text{Te}$), – are of great interest owing to their variations in stoichiometric composition, nanocrystal morphology, complex structure, valence states, unique properties, and their potential applications in numerous fields [1–7]. Copper chalcogenides are semiconductors with thermoelectric properties and ionic conductivity.

They have attracted a considerable interest because of their wide range of applications in various fields of science and technology, in various devices, such as solar cells, optical data storage, etc. [8–10]. Copper chalcogenide (Cu_xY) thin layers have a number of applications as well: they are used in various devices, such as solar cells, super ionic conductors, photo-detectors, photothermal conversion, electroconductive electrodes, microwave shielding coating, gas sensors [11–29], etc.

Various methods were used for the formation of copper chalcogenide layers on various dielectrics as well as on

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

polymers: vacuum evaporation, activated reactive evaporation, spray pyrolysis, electroless deposition, successive ionic layer adsorption and reaction (SILAR), chemical bath deposition [30–38].

Over the last decade, a sorption–diffusion method for the formation of thin copper chalcogenide films on the surface of polyamide based on the initial treatment of a polymer with the solutions containing anions of polythionates, $S_nO_6^{2-}$, selenopolythionates, $SeS_nO_6^{2-}$ ($n = 2, 4$), and telluropentathionates, $TeS_4O_6^{2-}$, has been under extensive investigation [24, 25, 28, 29, 39–95]: the polythionic compound anions containing chains of divalent chalcogen atoms of low oxidation state [96–98] – the polythionates, $^-O_3S-S_x-SO_3^-$, selenotrithionate, $^-O_3S-Se-SO_3^-$, selenopentathionate, $^-O_3S-S-Se-S-SO_3^-$, telluropentathionate, $^-O_3S-S-Te-S-SO_3^-$, – are sorbed by a polymer. After chalcogeniumized polyamide being treated with the solution of copper(II/I) salt, the copper sulfide, Cu_xS , [24, 41, 46–63], copper selenide, Cu_xSe [25, 65–69], mixed copper sulfide–copper selenide, Cu_xS-Cu_ySe [28, 71, 79–85], or mixed copper sulfide–copper telluride, Cu_xS-Cu_yTe [29, 55, 79, 81, 83, 86–95], layers are formed on the surface of a polymer.

The aim of the present work was to review the results received by us studying the formation and characterization of copper selenide layers on PA films by using the sorption–diffusion method, since only separate fragments of these studies in our previous publications have been described [99–108].

EXPERIMENTAL

The films of polyamide 6 (PA, specification TY 6-05-1775-76, grade PK-4) produced in the plant Uralplastic (Yekaterinburg, Russian) of films 15×70 mm in size and $70 \mu\text{m}$ in thickness were used. These PA films are close to a non-porous material because the pores of PA are much less than 1.5 nm. Before the chalcogenization, they 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 films thus prepared were treated in a thermostatic vessel using a continually stirred $K_2SeS_2O_6$ solution. The $0.05 \text{ mol} \cdot \text{L}^{-1}$ solutions of $K_2SeS_2O_6$ in $0.1 \text{ mol} \cdot \text{L}^{-1}$ 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 PA seleniumization was 4.5 h.

Potassium selenotrithionate was produced by the Ratke method [109] (the purity of the salt obtained being 99%). It was stored in darkness at the temperature of -5°C (in a freezer).

The sorption–diffusion method is based on the interaction of selenium containing particles sorbed–diffused into the polymer either with an aqueous solution of a copper(I) salt or a copper(II) salt containing a reducing agent (0.05 – 0.5 mol of a reductor for 1 mol of Cu(II) salt) [110]. In

this study we used a $0.4 \text{ mol} \times \text{dm}^{-3}$ aqueous solution of $CuSO_4 \cdot 5H_2O$ with a $0.1 \text{ mol} \cdot \text{L}^{-1}$ addition of a reducing agent hydroquinone, since a solution of Cu(I) salt is unstable. The used mixture of univalent and divalent copper salts, independently of temperature, consists of $0.34 \text{ mol} \cdot \text{L}^{-1}$ Cu(II) salt and $0.06 \text{ mol} \cdot \text{L}^{-1}$ of Cu(I) salt [111].

After being immersed in the selenotrithionate solution containing hydrochloric acid, the sample of the PA film was treated with a Cu(II/I) salts solution, then rinsed with distilled water, dried over $CaCl_2$, and used for analysis and consequent experiments. The concentrations of selenium and copper in modified PA film samples were determined using an atomic absorption spectrometer Perkin-Elmer 503 ($\lambda = 196 \text{ nm}$ for selenium and $\lambda = 324.8 \text{ nm}$ for copper) [112].

A 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 the analysis of the surface of obtained layers. The polymer sample with the Cu_xSe_y layer was fixed between two metal plates ($20 \times 15 \text{ mm}$) and the film perpendicular to the polymer was cut.

The phase composition of copper sulfide layers was investigated by X-ray diffraction (XRD) using a DRON-6 diffractometer (Cu- K_α radiation). The X-ray diffractograms of PA films with copper selenide layers were treated using the programs Search Match, ConvX, Xfit and Microsoft Excel to eliminate the maxima of the polymer.

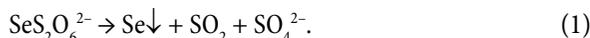
The XPS spectra of Cu_xSe layers were recorded with an ESCALAB MKII spectrometer (VG Scientific, radiation Mg $K\alpha$ 1253.6 eV, output 300 W). Vacuum in the analysing chamber was kept at a level of $1.33 \cdot 10^{-7} \text{ Pa}$, and the distribution of elements in the depth was determined by sputtering with an Ar^+ gun with the ion energy of about 2.0 keV. The samples were etched in a preparation chamber with the vacuum $9.3 \cdot 10^{-3} \text{ Pa}$ and current $20 \mu\text{A}$; the duration of etching was 10, 30 and 90 s. The maximum accuracy of the method was $\pm 0.1 \text{ at.}\%$. To reveal the composition of the obtained copper selenide layers, the photoelectron spectra of Se 3d $_{5/2}$, Cu 2p $_{3/2}$ and O 1s were recorded. Empirical sensitivity factors for these elements were taken from the literature [113] and the spectra obtained were compared with the standard ones [114].

RESULTS AND DISCUSSION

The preparation of semiconducting and electrically conductive layers of copper selenides, Cu_xSe_y , by sorption–diffusion on the surface of PA

For investigation of selenium sorption and diffusion into polyamide from potassium selenotrithionate solutions of various concentration and temperature it was indispensable to ascertain in what form (as elemental selenium, its radicals or selenotrithionate ions $SeS_2O_6^{2-}$) selenium adsorbs PA.

Our investigations showed that the semi-hydrophilic polymer (polyamide) adsorbs selenotrichionate ions, $\text{SeS}_2\text{O}_6^{2-}$, from these solutions. The PA samples remain transparent or acquire a slightly yellowish shade after keeping in a potassium selenotrichionate solution for 1–2 h. After destroying this seleniumized polymer films with hydrochloric acid, they, as anticipated, turn reddish due to the liberation of elemental red colloidal selenium [115]:



The chemical analysis of the seleniumized PA samples showed that the concentration of selenium sorbed and diffused into the polymer depends on the concentration and the temperature of the solution, and the period of the polymer treatment (Fig. 1, curves 1 and 2, and Fig. 2, curves 1–3).

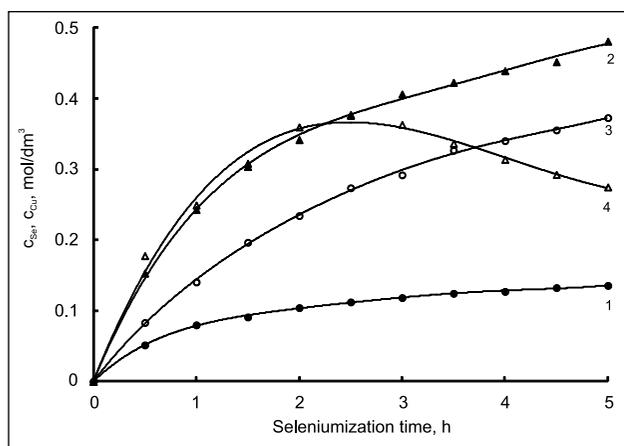


Fig. 1. Changes of selenium and copper concentration in the PA samples seleniumized in the solution of $\text{K}_2\text{SeS}_2\text{O}_6$ of different concentration with time at 60 °C and then treated with solution of Cu(I/II) salts. Concentration of $\text{K}_2\text{SeS}_2\text{O}_6$, mol/dm³: 1 is 0.025 (c_{Se}); 2 is 0.05 (c_{Se}); 3 is 0.025 (c_{Cu}); 4 is 0.05 (c_{Cu})

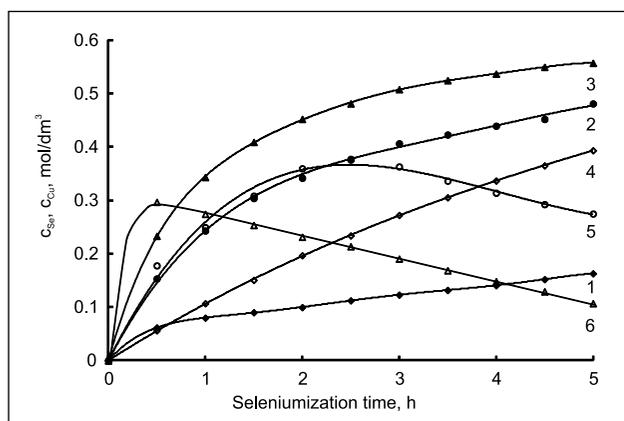


Fig. 2. Changes of selenium and copper concentration in the PA samples seleniumized in the solution of 0.05 mol/dm³ $\text{K}_2\text{SeS}_2\text{O}_6$ with time at different temperatures and then treated with solution of Cu(I/II) salts. Temperature of $\text{K}_2\text{SeS}_2\text{O}_6$ solution, °C: 1 is 50 (c_{Cu}); 2 is 60 (c_{Se}); 3 is 70 (c_{Se}); 4 is 50 (c_{Cu}); 5 is 60 (c_{Cu}); 6 is 70 (c_{Cu})

With the increase in these parameters, the concentration of selenium in the PA samples increases as well. We determined that the maximal saturation of polymer with selenium containing particles was reached in the PA samples seleniumized with a solution of higher concentration and temperature.

In order to form Cu_xSe layers on the surface of the seleniumized PA samples, they were treated with the Cu(I/II) salt solution. As a result of the redox reactions of selenotrichionate anions, $\text{SeS}_2\text{O}_6^{2-}$, sorbed and diffused into PA with Cu(I/II) solutions, the layers of copper selenides on the surface of PA samples were formed.

It has been determined that the concentration of copper (c_{Cu}) in the copper selenide layers on the PA samples is strongly dependent on the initial conditions of seleniumization. The concentration of copper in the PA samples seleniumized with the solution of potassium selenotrichionate increases continuously only in the case of the experiment carried out with a solution of 0.025 mol/dm³ concentration (Fig. 1, curve 3) or at the temperature of 50 °C (Fig. 2, curve 4). At higher temperature the increase of c_{Cu} is observed only in the PA samples seleniumized up to 0.5 h (Fig. 2, curve 6). In the PA samples seleniumized with a solution of 0.05 mol/dm³ concentration at the temperature of 60 °C (Fig. 1, curve 4), the copper concentration reaches the maximum value in the samples seleniumized about 2.5 h and later gradually reduces. That may be explained by the known reducing of $\text{SeS}_2\text{O}_6^{2-}$ ions stability with the increasing of the solution temperature: these ions gradually decompose (1) and selenium at the beginning is liberated in a more reactive red amorphous form. Later under the action of temperature it is transformed into a nonreactive black trigonal modification, which does not interact with the Cu(I/II) salts.

The values of electrical sheet resistance of the layers formed vary with an exposure time in the seleniumization solution, its temperature and concentration of the solution in a large interval ($2.61 \cdot 10^4$ to $56.8 \Omega/\square$). As the data of the Table has shown, the sheet resistance of copper selenide layers formed on the PA samples increase when the concentration of copper in those layers begin to decrease. That is completely understandable since with a higher temperature of seleniumization solution a larger amount of $\text{SeS}_2\text{O}_6^{2-}$ ions sorbed and diffused in polymer decomposed and did not react with the Cu(I/II) salts ions.

It is known [34] that the electrical resistance of Cu_xS reduces by one million times while the value of x is reduced from 2 to 1. Because selenides are very close to sulfides, there are the same standing rules for Cu_xSe .

After treatment of the PA samples with sorbed and diffused selenotrichionate anions in the copper salt solution at 80 °C, Cu_xSe layers of different composition were obtained. The X-ray diffraction patterns of the films showed the peaks of various copper selenide phases existing together in the copper selenide layers.

Table. Sheet resistance ($R, \Omega/\square$) of Cu_xSe_y films on PA first treated with different concentration solution of $\text{K}_2\text{SeS}_2\text{O}_6$ at different temperatures and then with Cu(I/II) salt solution

Concentration and temperature of $\text{K}_2\text{SeS}_2\text{O}_6$, mol/dm ³ (°C)	Seleniumization time, h					
	0.5	1.0	2.0	3.0	4.0	5.0
0.025 (60)	726.0	502.4	324.6	255.9	174.6	129.5
0.05 (50)	$2.61 \cdot 10^4$	710.0	207.9	152.0	142.0	150.5
0.05 (60)	135.0	76.4	66.1	56.8	68.0	90.2
0.05 (70)	140.4	184.0	234.4	472.1	737.9	958.8

Scanning electron microscopy characterization.

The thickness of Cu_xSe_y layers

Scanning electron microscopy is a convenient technique for the study of the surface microstructure of thin layers. The main morphological features of Cu_xSe_y layers formed on the PA films by the sorption–diffusion method at $20000 \times$ magnification are presented in Figs. 3, 4. The appearance of some dark spots within grey matrices is evident (Fig. 3a, b, c) and indicates the beginning of the Cu_xSe_y layer formation (Fig. 3a). Distribution of the enlarged dark spots through the whole picture (Fig. 3b) with the prolongation of seleniumization time confirmed the growing of Cu_xSe_y layers. A scanning electron micrograph presented in Fig. 1c shows that the Cu_xSe_y layer formed after the PA film 2.5 h seleniumization is morphologically more homogeneous. SEM micrographs (Fig. 3a, b, c) show the formation of single crystals with a particle size ranging from 8 to 500 nm on the surface of Cu_xSe_y layers when the seleniumization time of PA films was up to 2.5 h. On prolongation of seleniumization up to 4.5 h, the surface of the Cu_xSe_y layer becomes highly unsmooth over the entire measuring area (Fig. 3d).

Evidently, the agglomerated particles of different size ranging from 500 nm to 4 μm were observed.

Scanning electron microscopy is a convenient technique for investigation of the cross-sections of PA films with copper selenide layers as well. SEM micrographs showed the Cu_xSe_y layers on PA films as dark strips (Fig. 4). As it is seen, the thickness of the Cu_xSe_y layers depends on the seleniumization time of polymer films.

The SEM micrographs showed that the thickness of Cu_xSe_y layers (Fig. 4) varied in accordance with the concentration of selenium and copper in the layer. When the time of the PA initial treatment in a precursor's solution is prolonged, the amount of the Cu_xSe_y layer as well as its thickness increased; the average thickness of Cu_xSe_y layers was grown from 1.08 to 3.2 μm and then decreased to 0.8 μm when a polymer was treated in a precursor solution for 4.5 h. The decrease of the thickness of Cu_xSe_y layers can be explained by the above-mentioned gradual decomposition of the sorbed-diffused anions of $\text{SeS}_2\text{O}_6^{2-}$ with time. Part of the decomposition products of $\text{SeS}_2\text{O}_6^{2-}$ anions did not react with Cu (II/I) ions during the treatment of the seleniumized PA films with a copper salt solution.

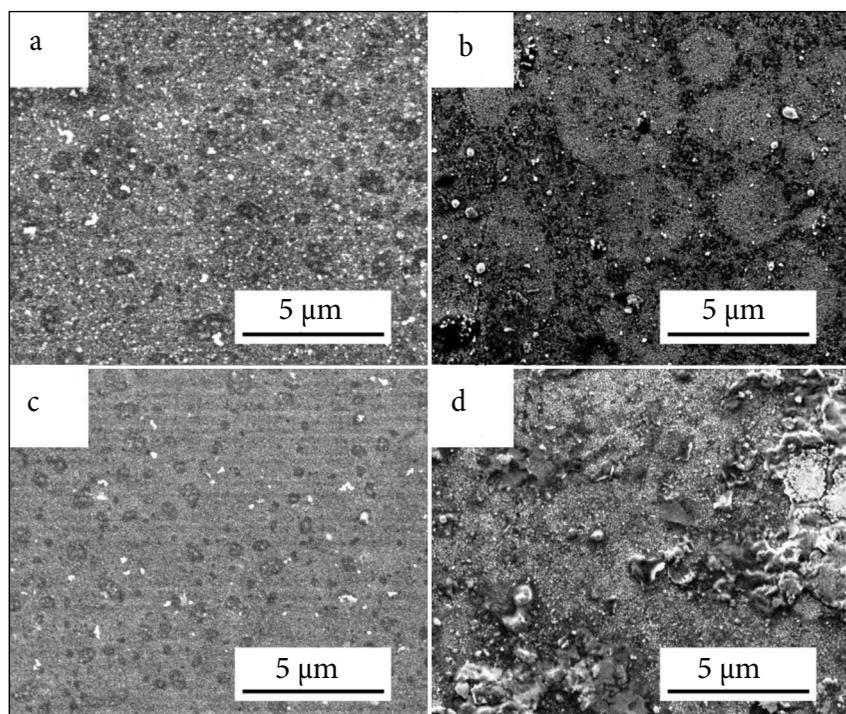


Fig. 3. SEM micrographs of Cu_xSe_y layers on PA films formed by sorption–diffusion method with different duration of seleniumization. Duration of seleniumization, h: 0.17 (a), 1.0 (b), 2.5 (c), 4.5 (d)

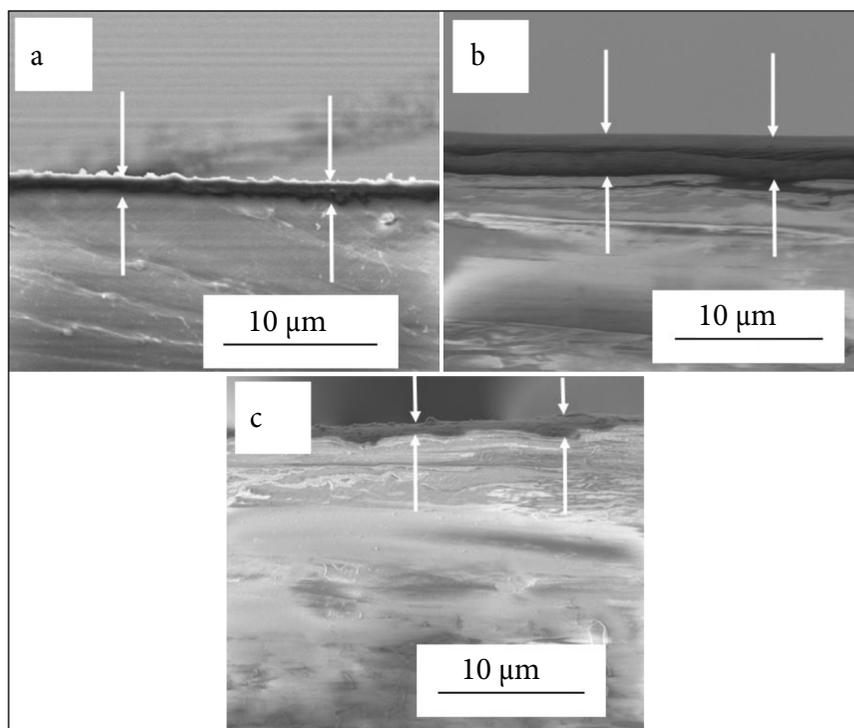


Fig. 4. SEM micrographs of cross-sections of PA films with Cu_xSe layers formed by sorption–diffusion method with different duration of seleniumization. Duration of PA seleniumization, h: 0.17 (a), 1.0 (b), 4.5 (c)

XRD characterization

The phase composition of Cu_xSe may be qualitatively and semi-quantitatively characterized by the X-ray diffraction but the study of Cu_xSe layers in the polymer surface meets difficulties because of the peculiarities of these composite materials. Firstly, the selenide layers are polycrystalline; secondly, usually a number of Cu_xSe phases with different composition and structure are present in the layer. Despite of these difficulties, the phase composition of the Cu_xSe_y layers formed in the PA film surface was studied by the method of X-ray diffraction since this method was successfully used in a number of cases to characterize the phase composition of copper chalcogenide layers in the surface of this polymer earlier [26–29].

Structural studies of the Cu_xSe layers deposited by the sorption–diffusion method are limited by polycrystallinity of the layers obtained, as well as by the existence of Cu_xSe_y phases with various compositions and structures, and by the crystallinity of the PA tape itself. The intensities of its maximum at $2\theta < 25^\circ$ exceeds the intensity of copper selenide maximums few times. Therefore the area of $2\theta \geq 25.0^\circ$ was investigated in more detail.

The data in Fig. 5 show that the Cu_xSe layers formed by the sorption–diffusion method include several phases, and the composition varies with PA films seleniumization time. All the peaks obtained are well matched with the Joint Committee on Powder Diffraction Standards (JCPDS) (Table). Six phases of copper selenide were found, namely, *monoclinic* Cu_2Se (27–1131) [30], *orthorhombic* CuSe_2 (74–280) [31], *orthorhombic* CuSe_2 (18–453) [31], *cubic* Cu_{2-x}Se (6–680) berzellianite [32], *tetragonal* Cu_2Se (29–575) bellidoite [33] and *tetragonal* Cu_3Se_2 (72–1421) umangite [34]. The phases of Cu_2Se (27–1131) and of

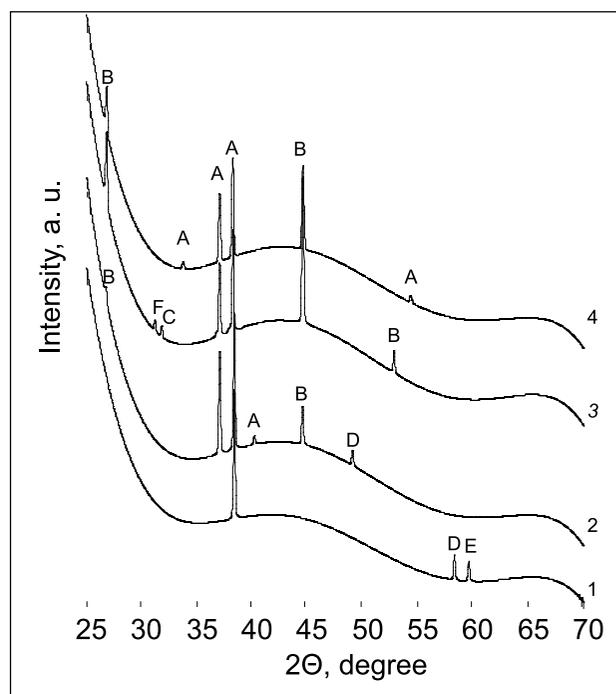


Fig. 5. XRD patterns of the Cu_xSe layers on PA films formed by sorption–diffusion method with different period of seleniumization. Period of seleniumization, h: 0.17 (1), 1.0 (2), 2.5 (3), 4.5 (4). A is Cu_2Se (27–1131); B is Cu_{2-x}Se (6–680); C is Cu_2Se (29–575); D is CuSe_2 (74–280); E is CuSe_2 (18–453); F is Cu_3Se_2 (72–1421)

Cu_{2-x}Se (6–680) remained the most prominent phases producing one or more peaks at all XRD patterns with the most prominent peaks found at $2\theta = 37.10, 38.30^\circ$ and $2\theta = 26.86, 44.62^\circ$ corresponding to the interplanar distances of 2.42, 2.33 Å and

3.33, 2.03 Å. The peaks attributable to Cu_2Se and Cu_{2-x}Se phases were found for all layers when the seleniumization time was one hour and longer (Fig. 5, patterns 2–4). As the duration of PA initial treatment in the precursor's solution is prolonged, intensity of the peaks increased. A sharp shape of the peaks indicates that the copper selenide layers formed on the PA films are polycrystalline in nature.

It is known [35] that the electrical resistance of Cu_xS reduces by one million times when a value of x is reduced from 2 to 1. Selenides are very close to sulfides, therefore the electrical resistance of Cu_xSe should reduce analogically when the value of x is reduced from 2 to 1.

When the period of initial seleniumization is prolonged until one hour, the maximum number of copper selenide phases was detected in the copper selenide layer (Fig. 5, curve 2). Further prolongation of the initial seleniumization results in the formation of Cu_xSe layers containing a more conductive Cu_xSe_y phase.

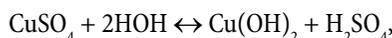
Thus the phase composition of the Cu_xSe_y layers formed in PA films at different seleniumization duration is in accordance with the data of electrical sheet resistance measurements: its value with a change of seleniumization duration from 0.5 to 4.5 h decreased from 135 to 57 Ω / [69].

XPS characterization

The layers of Cu_xSe_y formed by the sorption–diffusion method on the surface of PA films were studied by the X-ray photoelectron spectroscopy (XPS) method as well. Then the Cu_xSe layers were etched by Ar^+ ions and their composition in the deeper layers was also studied. From the data gained by the XPS method, i.e. from the element atomic percentages, binding energies and the spectra of individual elements, it was possible to reveal the composition of the obtained layer. The analysis is restricted only by a study of the chemical composition of a very thin surface layer when the thickness of the layer may reach up to 3.2 μm .

The processes of the PA films modification by the layers of Cu_xSe_y take place in a natural environment. Therefore it is impossible to prevent its influence. Semi-hydrophilic polymer PA under the action of the environment absorbs oxygen, moisture and other compounds on its surface.

Carbon was rejected from the results of the XPS analysis because of the integral part of the polymer. Comparison of the distribution of Cu, Se and O in the surface of the samples has shown that oxygen takes the biggest part in all samples. Such a large oxygen amount may be explained by its chemical absorption and also by copper sulfate absorption on the layer surface, as well as by insoluble copper(II) hydroxide formation on the surface. The Cu (II) hydroxide may be formed while washing the layers with water,



and following their decomposition into CuO and Cu_2O .

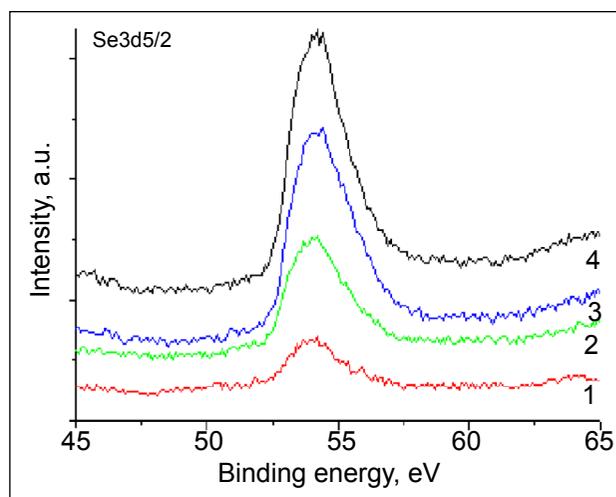


Fig. 6. High-resolution XPS spectra in Se3d5/2 for Se in Cu_xSe_y layers prepared by the sorption–diffusion method with different periods of seleniumization. Period of seleniumization, h: 0.17 (1), 1.0 (2), 2.5 (3), 4.5 (4)

The data received showed that on the layer surface and in the etched surface various compounds of copper, selenium and oxygen are present. The following compounds have been identified: Cu_2Se , CuSe , Cu_{2-x}Se , Cu_3Se_2 , Cu_2O , CuO , $\text{Cu}(\text{OH})_2$, Cu and Se . The XPS analysis has shown that on the surface of all copper selenide layers investigated, there was only a small amount of copper selenides, while copper oxides, copper hydroxide, copper sulfate and absorbed oxygen take the largest part. Copper selenides forming layers by the sorption–diffusion method take the form of dendrites (Fig. 3). Therefore, among the dendrites there remained absorbed oxygen, water and other compounds. For this reason, the microstructure of the copper selenide layers may significantly differ from the macrostructure and chemical composition of all layers.

When the layer's surface was etched by Ar^+ ions, the content of oxygen significantly decreased. It indicated that a lot of oxygen on the surface was in a chemical absorbed form. The percentage content of copper and selenium confirmed that the content of this element (oxygen) significantly decreased in the etched layers.

Analyzing the XPS data on the layers of Cu_xSe_y , we noticed that the concentration of selenium increased while increasing the time of a polymer seleniumization. For example, the concentration of selenium in the Cu_xSe_y layers etched 10 s with the increase of seleniumization duration changed as follows: 0.17 h – 2.1 at.%; 1.0 h – 5.5 at.%; 2.5 h – 10.6 at.%; 4.5 h – 15.1 at.%. The concentration of copper increased analogously: 0.17 h – 6.3 at.%; 1.0 h – 10.2 at.%; 2.5 h – 11.7 at.%; 4.5 h – 20.9 at.%. Thus, when the concentration of selenium in the PA film is higher, more copper ions react and more copper selenides are formed.

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Vitalijus Janickis, Remigijus Ivanauskas

KALIO SELENOTRITIONATAS – PUSLAIDŽIŲ IR ELEKTRAI LAIDŽIŲ VARIO SELENIDŲ SLUOKSNIŲ POLIAMIDO PAVIRŠIUJE SUDARYMO PIRMTAKAS

Santrauka

Puslaidžiai ir elektrai laidūs vario selenidų (Cu_xSe_y) sluoksniai poliamido 6 (PA) paviršiuje suformuoti sorbciniu-difuziniu metodu naudojant vandeninius kalio selenotritonato ($\text{K}_2\text{SeS}_2\text{O}_6$) tirpalus, pavyzdžiui, polimero seleninimo pirmtakus. Selenotritonato anijonai, turintys divalenčius žemo oksidacijos laipsnio seleno atomus ($-\text{O}_3\text{S}-\text{Se}-\text{SO}_3^-$), yra sorbuojami ir difunduoja į PA plėveles, jeigu jos apdorojamos selenotritonato tirpalais. Didėjant pirmtako tirpalo koncentracijai, temperatūrai ir PA apdorojimo trukmei, išauga sorbuoto selenotritonato koncentracija. Cu_xSe_y sluoksniai susidaro PA plėvelių paviršiuje, kai chalkogenintas polimeras apdorojamas vandeniniu vario(II/I) druskos tirpalu: selenotritonato anijonai

reaguoja su vario jonais. Didėjant pirmtako tirpalo koncentracijai, temperatūrai ir pradinei PA chalkogeninimo trukmei, didėja vario koncentracija PA. Sudaryti sluoksniai charakterizuojami chemine jų sudėtimi, elektrinėmis ir fizikinėmis savybėmis. Procentiniai seleno ir vario kiekiai Cu_xSe_y sluoksniuose PA plėvelėse kinta keičiantis polimero seleninimo trukmei: Se 51,61–69,46 % ir Cu 48,39–30,54 %. Tolygiausi Cu_xSe_y sluoksniai poliamido plėvelėje susidarė tada, kai ji buvo seleninta 2,5 h – tai nustatyta skenuojančiu elektroniniu spektroskopu (SEM). Cu_xSe_y sluoksnių storis priklauso nuo polimero seleninimo trukmės ir kinta nuo 0,98 iki 3,2 mm. Cu_xSe_y sluoksnių rentgeno difrakcinė analizė (XRD) parodė, kad jie yra polikristaliniai; identifikuotos šešios vario selenidų fazės – Cu_2Se (27-1131); CuSe_2 (74-280); CuSe_2 (18-453); Cu_3Se_2 (72-1421); berzelianito, Cu_{2-x}Se (6-680) ir bellidoito, Cu_2Se (29-575). XPS rezultatai patvirtino vario selenidų sluoksnių PA paviršiuje susidarymą. Nustatyti dėsningumai įgalina norimos sudėties ir elektros laidumo Cu_xSe_y sluoksnių ant PA susidarymą.