

KAUNAS UNIVERSITY OF TECHNOLOGY

LINAS SAMARDOKAS

**FORMATION AND STUDY OF THALLIUM SELENIDE LAYERS  
ON THE SURFACE OF POLYAMIDE 6 AND DOPING WITH  
COPPER, GALLIUM AND SILVER**

Summary of Doctoral Dissertation  
Natural Sciences, Chemistry (N 003)

2021, Kaunas

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

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**TALIO SELENIDŲ SLUOKSNIŲ POLIAMIDO 6 PAVIRŠIUJE  
SUDARYMAS, TYRIMAS IR VARIO, GALIO IR SIDABRO  
PRIEDŲ ĮTERPIMAS**

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## 1. INTRODUCTION

Inorganic–organic composites are a quickly developing group of materials with a tremendous range of highly tunable structural, physical, and chemical properties. High compositional variability of these materials allows incorporating a variety of inorganic compounds. Particularly interesting are composite materials with group III metal: Ga, In, and Tl, binary or ternary compounds, which, in combination with group VI nonmetals: S, Se, and Te, possess unique physical properties of tremendous importance to the modern science and technology. Particularly established, but still rapidly progressing area of III–VI material development and use is solar energy harvesting. Unprecedented interest in these so-called 2nd generation photovoltaic (PV) materials is due to their high absorbance with very thin films of materials that are needed to harvest solar energy.

The main issue of III–VI material thin films is associated with the complexity of the III–VI material layer multicomponent systems, which provide challenges in forming well-defined films with uniform properties across the large-area substrates. In addition, polytypism and a variety of stoichiometries that are available for III–VI materials present direct problems, because many physical properties, including bandgap, are affected. An opportunity to improve thin III–VI material surface morphology as well as their electronic properties is possible by combining them with conducting polymers. The composite materials that are comprised of polymers with a thin film inorganic semiconductor that is deposited on their surface exhibit robust structural properties due to the polymer elasticity and resistance to the harsh environments, while as well functioning as effective semiconductors. Organic–inorganic solar cells have been the area of rapid development, because they potentially could adopt the advantages of inorganic materials, such as stability, high carrier mobility, and compatible fabricating process, and utilize the advantages of organic conducting polymers, such as enhanced light absorption at a wide range of wavelengths, adjustable molecular structures for energy band alignment, facile solution-based manufacturing.

Adsorption–diffusion can be viewed as an emerging alternative method in obtaining these binary III–VI compounds that are incorporated into polymers. This method does not require high temperatures, vacuum, or inert atmosphere. As in chemical bath deposition method, the deposition of thin film occurs due to the substrate in contact with dilute chemical bath, containing corresponding ions, resulting in an excellent adhesion between the thin film and the polymer due to the partial film incorporation. In this work, model III–VI binary compound, thallium selenide, with varying ratios of thallium-to-selenium was deposited onto the model polymer–polyamide (PA) substrates by using adsorption–diffusion method. Mixed Tl-M-Se ( $M = \text{Ga, Cu, Ag}$ ) layers were formed by treating the obtained layers in Ga(III), Cu(II/I), or Ag(I) salt solutions.

## **Aim of the dissertation**

The aim of this dissertation is to form layers of thallium selenides and Tl-M-Se on the surface of semi-hydrophilic polymer PA 6 by adsorption-diffusion method and study the mechanism, structure, and properties of these layers.

### **In order to achieve the set aim, the following objectives were formed:**

1. To form thallium selenide layers and mixed Tl-M-Se (M = Ga, Cu, Ag) type layers by using  $K_2SeS_2O_6$  solution as selenium precursor.
2. To investigate the mechanism of formation of obtained layers and determine the relations between the conditions of formation, structure, and properties, using various analysis methods.

### **Scientific novelty**

The sorption-diffusion method, using the potassium selenotrichionate salt solution as a source of ions, containing low oxidation state selenium, was applied to form thallium selenide and mixed Tl-M-Se layers. The structure and properties of the obtained layers were determined by XRD, AAS, SEM/EDS, UV-VIS spectroscopy methods.

### **Approval and publication of the research results**

The results of the research have been published in 14 publications: 3 articles were published in journals that are included in the *Thomson Reuters<sup>TM</sup> Web of Science* database; 11 publications were reported in conference proceedings.

### **Structure and content of the dissertation**

This dissertation consists of an introduction, literature review, experimental part, results and discussion, conclusions, references, a list of publications on the topic of the dissertation.

### **Statements presented for the defence:**

1. Potassium selenotrichionate  $K_2SeS_2O_6$  is a suitable precursor of ions, containing low oxidation state selenium for the formation of thallium selenides and mixed Tl-M-Se layers on the surface of polyamide 6.
2. Thallium selenides and mixed Tl-M-Se layers can be obtained by using sorption-diffusion method via a three-step process.
3. After annealing in  $N_2$  atmosphere, polycrystalline  $Tl_xSe_y$  layers yielded a single thallium selenide TlSe.
4. The incorporation of gallium, copper, and silver additives results in a redshift in the absorption edge of the layers and reduction of the bandgap energy.

## 2. EXPERIMENTAL SETUP

### 2.1. Materials

All reagents that were used in the experiments were chemically and analytically pure commercial reagents: potassium disulphite ( $K_2S_2O_5$ ) ( $\geq 98.0\%$  from Sigma–Aldrich), selenous acid ( $H_2SeO_3$ ) (99.999% trace metals basis from Sigma–Aldrich), selenium (Se) pellets (100 mesh powder, 99.99% trace metals basis from Aldrich), hydrochloric acid (HCl) 0.1 M from Fluka, thallium sulphate ( $Tl_2SO_4$ ) ( $\geq 99.9\%$  trace metals basis from Aldrich), thallium nitrate ( $TlNO_3$ ) ( $\geq 99.9\%$  trace metals basis from Aldrich), potassium hydroxide (KOH) (reagent grade, 90%, flakes from Sigma–Aldrich), 25% ammonia solution ( $NH_4OH$ ), gallium sulphate ( $Ga_2(SO_4)_3$ ), crystalline copper sulphate pentahydrate ( $CuSO_4 \cdot 5H_2O$ ) (crystals and lumps, 99.999% trace metals basis, from Sigma–Aldrich), silver nitrate ( $AgNO_3$ ), hydroquinone ( $C_6H_4(OH)_2$ ) (flakes,  $\geq 99\%$  ReagentPlus® from Sigma–Aldrich), trisodium citrate ( $Na_3C_6H_5O_7$ ).

Thallium selenide layers were formed on the surface of polyamide 6. PA films (Tecamid 6, 500  $\mu m$  thickness, Germany) of 15 mm  $\times$  70 mm were used as substrates. The quantitative parameters that were obtained via AFM analysis of polyamide sample surface are tabulated in Table 2.1. PA 6 is close to a non-porous material, because the pores of PA are much less than 1.5 nm. The porosity was measured by a Brunauer Emmett Teller (BET) method using a Quantasorb (USA).

**Table 2.1.** Quantitative parameters obtained via AFM analysis of polyamide sample surface

Max. height $A_{max}$ , nm	Average height $Z_m$ , nm	Average roughness $R_a$ , nm	RMS roughness $R_q$ , nm	Skewness $R_{sk}$ , nm
238.6	92.12	14.2	19.4	0.86

### 2.2. Experimental equipment

The pH of the solutions was determined using a Knick 766 pH meter and a combined glass and platinum electrode with a Knick SE100N temperature gauge (Germany). During the preparation of the solutions, the materials were weighed on the analytical balance KERN ABS/ABJ-BA-defsi-0413. Only water prepared with GFL 2008 distillation apparatus was used for the research. The specific electrical conductivity of distilled water at 25 °C temperature is 2.3  $\mu S \cdot cm^{-1}$ . The experiments were performed under isothermal conditions using a Julabo thermostat with an accuracy of  $\pm 0.1$  °C.

## 2.3. The course of the experiment

### 2.3.1 Preparation of polyamide substrate

PA samples were boiled in distilled water for 120 min to remove the remainder of the monomer and dried using the filter paper, followed by desiccation with  $\text{CaCl}_2$  for 24 h.

### 2.3.2. Selenization in $\text{K}_2\text{SeS}_2\text{O}_6$ solutions

Thus, the prepared PA 6 samples were treated in a thermostatic vessel using a continually stirred  $\text{K}_2\text{SeS}_2\text{O}_6$  solution. The  $0.05 \text{ mol}\cdot\text{dm}^{-3}$  solutions of  $\text{K}_2\text{SeS}_2\text{O}_6$  in  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  HCl at  $60^\circ\text{C}$  were used. At certain time intervals, the samples were removed, rinsed with distilled water, dried over  $\text{CaCl}_2$ , and used in the analysis and further experiments. The total duration of the experiments was 4.5 h.

### 2.3.3. Formation of thallium selenide layers

The selenized samples were treated with solutions of thallium nitrate or thallium sulfate salts. These experimental conditions are summarized in Table 2.2. The samples were removed, rinsed with distilled water, and dried over  $\text{CaCl}_2$ .

**Table 2.2.** Conditions for the treatment of selenized PA 6 films with thallium salt solutions

Duration of selenization, h	Precursor of Tl(I)	Concentration of Tl(I) solution, mol/l	Temperature, $^\circ\text{C}$	pH adjusting agent	pH	Duration, min
0.5–4.5	$\text{Tl}_2\text{SO}_4$	0.1	80	KOH	11.4	10
1.5	$\text{Tl}_2\text{SO}_4$	01	60	KOH	4.7–13.02	10
1.5	$\text{TlNO}_3$	0.01–0.8	60	KOH	11.5	75
1.5	$\text{Tl}_2\text{SO}_4$	0.1	40–80	KOH	11.5	10
1.5	$\text{Tl}_2\text{SO}_4$	0.1	60	25% $\text{NH}_3\cdot\text{H}_2\text{O}$	10.9	1–75

### 2.3.4. Formation of mixed Tl-M-Se (M = Cu, Ga, Ag) type layers

After 1.5 h of selenization in  $\text{K}_2\text{SeS}_2\text{O}_6$  solution and 20 min of treatment in  $0.1 \text{ mol/l}$   $\text{Tl}_2\text{SO}_4$  solution, the formed thallium selenide layers were treated with solutions that were containing Cu (II/I), Ga (III), and Ag (I) ions to form mixed Tl-M-Se (M = Cu, Ga, Ag) type layers (Table 2.3.). Hydroquinone was used as a reducing agent for preparing a mixture of univalent and divalent copper salts. This mixture consisted of  $0.34 \text{ M}$  Cu(II) and  $0.06 \text{ M}$  Cu(I) salt. Trisodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ) was used as a complexing agent for the formation gallium citrate

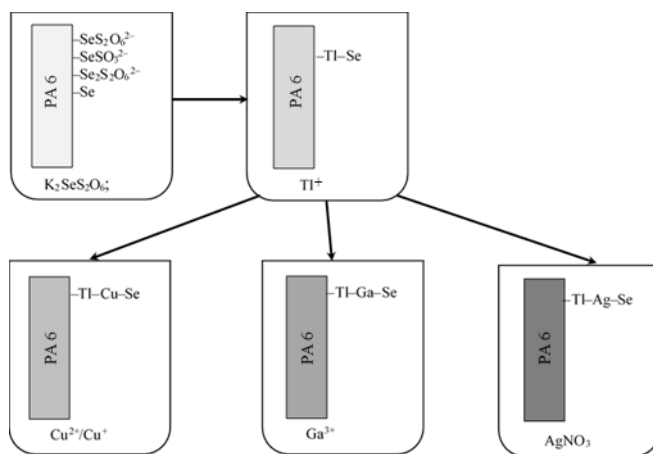


complex. It was applied to maintain the soluble species of  $\text{Ga}^{3+}$  in aqueous medium as it allows to control the  $\text{Ga}^{3+}$  concentration.

**Table 2.3.** Experimental conditions of Tl-Se and Tl-M-Se layers deposition on PA 6

Compound	Precursor	Concentration, mol/l	Additives	Temperature, °C	Duration, min
Tl-Cu-Se	$\text{CuSO}_4$	0.4	1% hydroquinone	80	15
Tl-Ga-Se	$\text{Ga}_2(\text{SO}_4)_3$	0.025	$\text{NH}_3 \cdot \text{H}_2\text{O}$ (pH 10.50), 0.025 M trisodium citrate	60	60
Tl-Ag-Se	$\text{AgNO}_3$	0.1	-	80	15

The thallium selenide layer on the formation procedure of PA sheets and doping of these layers with different metal cations are shown in Fig. 2.1.



**Fig. 2.1.** Schematic depicting of the synthesis and doping procedures of Tl-Se films on the PA sheets substrate

## 2.4. Analysis

### 2.4.1. Determination of elements concentration

The concentration of selenium, thallium, copper, gallium, and silver in metal selenide layers that were formed on the PA 6 films surface were determined using the method of atomic absorption spectrophotometry. The modified PA 6 films were dissolved in 1:1 concentrated nitric acid and distilled water solution. Selenium, thallium, copper, gallium, and silver, which were present in the

resulting solution, were determined by the atomic absorption spectrometer “Perkin-Elmer-503”. The used wavelength was  $\lambda = 196.0$  nm, slit width 1.3 nm, for selenium; wavelength  $\lambda = 276.8$  nm, slit width 0.7 nm, for thallium; wavelength  $\lambda = 324.8$  nm, slit width 0.7 nm, for copper; wavelength  $\lambda = 287.4$  nm, slit width 0.7 nm, for gallium; wavelength  $\lambda = 328.1$  nm, slit width 0.7 nm, for silver. An electrodeless discharge lamp and air-acetylene gas mixture were used for flame. The sensitivity is about 0.5  $\mu\text{g/ml}$  for selenium and thallium, 0.1  $\mu\text{g/ml}$  for copper, 10  $\mu\text{g/ml}$  for gallium, and 0.2  $\mu\text{g/ml}$  for silver for 1% absorption.

#### **2.4.2. Optical property measurements**

Optical properties were studied at room temperature by using the PerkinElmer Lambda 35 UV/VIS Spectrometer with The Labsphere RSA-PE-20 Diffuse Reflectance Sphere in the range of 400–1100 nm.

#### **2.4.3. AFM characterization**

The surface of polyamide samples was characterized by using atomic force microscope (AFM) measurements, using QScope-250 (Quesant Corp.) instrument. The dry samples were analyzed in contact mode using Si cantilevers (CSG10 series, Nano Technology Instruments–Europe BV) with a force constant  $0.2 \text{ Nm}^{-1}$  and tip curvature of 10 nm. The images were analyzed using SPIP (Image Metrology) and Quesant Corp. software.

#### **2.4.4. XRD characterization**

X-ray diffraction analysis of the deposited and heated PA-Tl<sub>x</sub>Se<sub>y</sub> materials was performed using a DRON-6 diffractometer that was equipped with a special device for the beam limitation at low and medium diffraction angles. It uses graphite-monochromatized Cu-K $\alpha$  radiation source ( $\lambda = 1.54178 \text{ \AA}$ ), operating at 30 kV and current of 30 mA. The XRD patterns were recorded with a step size of  $0.05^\circ$  from  $25$  to  $70^\circ$ . The obtained XRD patterns were processed using the software packages Search Match, ConvX, and Xfit for the baseline smoothing and peak identification.

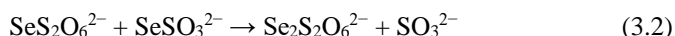
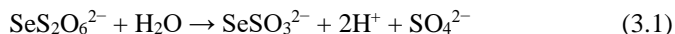
#### **2.4.5. SEM/EDS characterization**

The morphological analysis of the Cu-In-Se layer on a glass substrate was executed by applying the Scanning Electron Microscope (SEM) Quanta 200 FEG (FEI, the Netherlands). The energy dispersive X-Ray spectroscopy (EDS) was performed using a Bruker XFlash 4030 detector. The standard-less ZAF method was used to quantify the elements detected with EDS.

### 3. RESULTS AND DISCUSSION

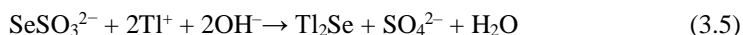
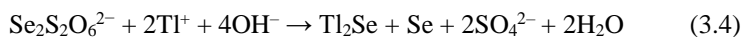
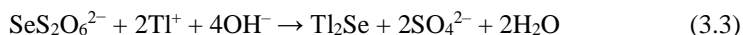
#### 3.1. Formation and investigation of thallium selenide layers

In this work, using two-stage sorption-diffusion method, thallium selenide  $Tl_xSe_y$  layers were formed on semi hydrophilic polyamide PA 6 surface. In the first step,  $SeS_2O_6^{2-}$  anions adsorb and diffuse into the subsurface of polyamide. For the first 1.5 h, both adsorption and diffusion of  $SeS_2O_6^{2-}$  anions proceeds, while afterwards, the chemical reactions of  $SeS_2O_6^{2-}$  anions takes place both in solution and on the polymer, according to the following reactions:



In order to determine the influence of seleniumization duration of the initial solution of  $K_2SeS_2O_6$ , the kinetic studies of the sorption of selenium into PA 6 from the prepared solution of potassium selenotrihionate were performed. The investigation of sorption kinetics of selenium in thallium selenide layers when PA 6 films are exposed during 4.5 h in the  $0.05 \text{ mol}\cdot\text{dm}^{-3}$  concentration solution of  $K_2SeS_2O_6$  shows that the exposure time increase leads to a significant increase of the amount of selenium, i.e., from  $0.44 \text{ }\mu\text{mol}\cdot\text{cm}^{-2}$  to  $1.43 \text{ }\mu\text{mol}\cdot\text{cm}^{-2}$ , more than three-fold increase.

During the second step, the selenized polymer reacted with Tl(I) sulfate solution, and  $Tl_xSe_y$  formation proceeds via  $Tl^+$  ion reactions with the adsorbed  $SeS_2O_6^{2-}$ ,  $Se_2S_2O_6^{2-}$ , and  $SeSO_3^{2-}$  ions, according to the following reactions:

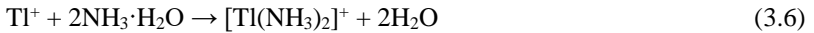


The samples of seleniumized PA 6 were treated with the solution of 0.1 M  $Tl_2SO_4$  at  $80 \text{ }^\circ\text{C}$  for 10 min. The changes in PA 6 films appearance after its treatment with the Tl(I) salt solution as well indicate the formation of thallium selenide layers on the surface of a polymer. The color of samples from colorless, light yellow, orange, or red transform into brown-red or brown-grey. The same dependence when changing the amount of thallium in  $Tl_xSe$  layers on PA 6 films as in the case of the amount the selenium was observed. The PA 6 films exposure time increase leads to a significant increase of the amount of thallium, i.e., from  $0.09 \text{ }\mu\text{mol}\cdot\text{cm}^{-2}$  to  $0.21 \text{ }\mu\text{mol}\cdot\text{cm}^{-2}$ , more than two-fold increase. It has been found that the Tl/Se ratio decreases to 1.5 h of the initial polymer seleniumization and then begins to increase, and the stoichiometric composition varies from  $Tl_{0.2}Se$  to  $Tl_{0.11}Se$ . The compositions of thallium selenide with 1/5 or 1/10 of molar Tl/Se ratio are not known. Therefore, it could be expected that the elemental Se is

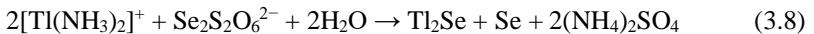
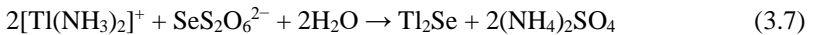
contained in the composition of the thallium selenide layers that were formed on the PA 6 films.

The precursor concentration, the form of cations in the precursor solution, the duration of the reaction, and temperature are important parameters that have significant influence on the morphology, thickness, and composition of metal chalcogenide films. Therefore, firstly, there was investigated the influence of the concentration of thallium precursor solution on the thallium concentration and Tl/Se ratio in the Tl–Se layers that were formed on the surface of the PA sheets substrate. In order to obtain higher concentration solutions of the  $Tl^+$  precursor,  $TlNO_3 \cdot 3H_2O$  salt was used as well, which solubility is significantly higher than the  $Tl_2SO_4$ . The results of atomic absorption spectroscopy analysis have shown that with increasing  $Tl^+$  concentration in the precursor solutions with the addition of KOH, although the concentration of selenium in the polymer is almost unchanged, the thallium concentration in PA sheet samples increases from 0.129 to 0.493  $\mu\text{mol}/\text{cm}^2$ , and the molar Tl/Se ratio increases from 0.105 to 0.401. The increase in the duration of the treatment selenized PA sheets with the  $Tl^+$  precursor solution has a positive effect on the increase in the concentration of thallium and the molar ratio of Tl/Se in the samples of PA sheets with Tl–Se layers. The selenized samples were treated for 20 and 75 min in a 60 °C solution of thallium sulfate at pH 10.9 (the solution medium was adjusted with 25% ammonia solution). The Tl/Se molar ratio that has been determined by the AAS analysis increases from 0.695 to 1.253 with increasing treatment duration in the  $Tl^+$  precursor solution from 20 to 75 min.

Thus, the thallium ammonia complex is more suitable for forming thallium selenide layers. It is necessary to note that the thallium ammonia complex allows to control the  $Tl^+$  concentration and have soluble stable  $Tl^+$  species in the aqueous medium. When the ammonia solution is added, the  $Tl^+$  ion in a solution of the  $Tl_2SO_4$  salt, according to the equation (3.6), forms a complex:



These complex ions are slowly adsorbed/diffused into the selenized PA sheet and simultaneously react with ions containing divalent selenium, according to the equations (5–7):



The formed  $Tl_2Se$  and elemental selenium remain adsorbed on the polymer, while other compounds dissolve again in the solution.

### 3.1.1. XRD characterization

X-ray diffraction analysis gives a more accurate identification of thallium selenides that were formed on the surface of PA 6 films. However, the structural studies of the thallium selenide layers deposited by sorption-diffusion method are limited by polycrystallinity of obtained layers as well as the existence of thallium selenide phases with various compositions and structures, and the crystallinity of the polymer film itself. The fact that the formation of thallium selenide layers takes place by keeping seleniumized PA 6 films in the solution of  $Tl_2SO_4$  salts by the X-ray diffraction analysis was confirmed (Table 3.1.). Three phases of tetragonal thallium selenide and two phases of monoclinic selenium were found, namely,  $Tl_2Se_2$  (75–880),  $Tl_2Se_{1.2}$  (75–1007),  $Tl_5Se_3$  (41–1295),  $Se_8$  (71–528), and  $Se$  (73–2121). The phase of  $Tl_2Se_2$  (75–880) is predominant in the layers of the thallium selenide on PA 6 films. However, with the prolongation of the period of the polymer seleniumization, this dominance decreases. The elemental selenium in the composition of these layers was contained as well. When further increasing the seleniumization time, an increase in the number of XRD peaks can be observed, which can be assigned to a new monoclinic selenium phases ( $Se_8$  (71–528) and  $Se$  (73–2121)) formation. Elemental Se can form via decomposition of adsorbed/diffused  $SeS_2O_6^{2-}$  ions in PA 6 films, according to the following reaction:

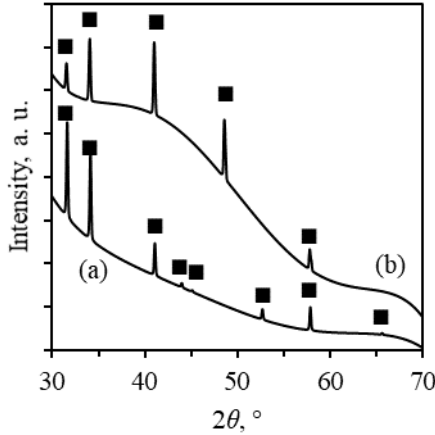


It is possible that elemental selenium did not interact with the  $Tl(I)$  ions and remained in PA 6 films, when the sulphur containing particles were washed out from the polymer.

**Table 3.1.** The quantitative composition of  $Tl_3Se_7$  layers in PA 6 films formed by sorption-diffusion method at different duration of seleniumization

Duration of seleniumization, h	Compound	<i>d</i> -spacing, Å	Amount, %
0.5	$Tl_2Se_2-75-880$	2.84, 1.89, 1.82, 1.79, 1.48, 1.42	99.20
	$Tl_2Se_{1.2}-75-1007$	2.01	0.80
1.5	$Tl_2Se_2-75-880$	2.84, 2.53, 2.20, 1.79, 1.59, 1.42	75.72
	$Tl_2Se_{1.2}-75-1007$	2.01, 1.53, 1.50	6.54
	$Se_8-71-528$	2.35	17.74
3.5	$Tl_2Se_2-75-880$	2.84, 2.53, 2.20, 1.79, 1.42	68.61
	$Tl_2Se_{1.2}-75-1007$	2.01	3.68
	$Tl_3Se_3-41-1295$	1.88, 1.71, 1.47	4.51
	$Se_8-71-528$	2.35	13.20
	$Se-73-2121$	2.41	10.00
4.5	$Tl_2Se_2-75-880$	2.84, 2.20	66.56
	$Tl_2Se_{1.2}-75-1007$	2.01	0.52
	$Se_8-71-528$	2.35	16.31
	$Se-73-2121$	2.41, 1.83	16.61

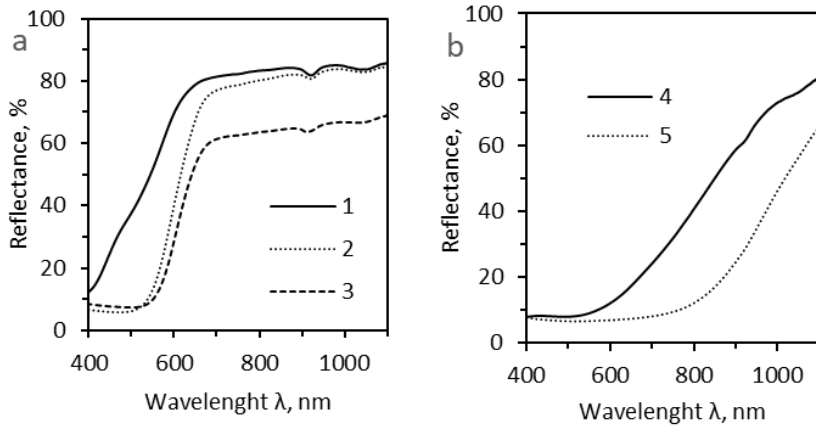
The selected samples were subjected to a higher temperature heating in an inert atmosphere to produce a single-phase thallium selenide. The heating was performed for 12 h at 100 °C in  $N_2$  atmosphere, and XRD data that have been obtained are shown in Fig. 3.1. The only crystalline phase that was detected in the heated samples was  $TlSe$  (22–1476) *tetragonal* thallium selenide. The presence of  $S_8$  in the XRD spectra of unheated thallium reacted samples implies that selenium, diffused into the polymer, does not fully react to form thallium selenides at the room temperature and stratifies beneath the thallium rich phases. At the elevated temperature of 100 °C that was used to heat the sample, residual thallium ions diffuse faster into the polymer while as well binding to the  $S_8$ . Due to this diffusion, the concentration gradient, otherwise present across the polymer cross-section, becomes smaller, and stoichiometric  $TlSe$  can be formed.



**Fig. 3.1.** X-ray diffraction patterns of thallium selenide samples after heating for 12 h at 100 °C in N<sub>2</sub> atmosphere; the peaks were identified and assigned as (■) – TlSe (22–1476) *tetragonal* thallium selenide; the temperature of Tl<sub>2</sub>SO<sub>4</sub> solution: (a) – 70 °C , (b) – 60 °C ; the pH of Tl<sub>2</sub>SO<sub>4</sub> solution: (a) – 11.3, (b) – 13.0

### 3.1.2. Optical properties of thallium selenide layers

The optical properties of the formed Tl–Se layers were studied by measuring the reflection spectra in the 400–1100 nm range to obtain the values of absorption edge, band gap ( $E_g$ ), band tail width (Urbach energy,  $E_U$ ) of the localized states, Steepness parameter ( $\sigma$ ) and Electron-phonon interaction ( $E_{e-p}$ ). The dependence of the optical parameters of the Tl–Se layers on the concentration of the thallium salt solution and the duration of the treatment process was investigated. A redshift of reflection was observed in both cases, both with an increase in the concentration of the Tl<sup>+</sup> precursor solution and an increase in the duration of treatment of the selenized polymer with this solution (Fig. 3.2.).



**Fig. 3.2.** TI–Se layers reflectance spectra; concentration of  $Tl^+$  precursor solution, mol/l: 1 – 0.025, 2, 4, 5–0.1, 3 – 0.8; duration of treatment in  $Tl^+$  precursor solution, min: 1, 2, 3, 5–75, 4–20

After the treatment of selenized PA sheet samples with a  $Tl^+$  precursor with the addition of KOH, the absorption edge values are observed in the visible part of the spectrum. When the selenized polymer samples were treated with the  $Tl^+$  precursor solution with added ammonia, the absorption edge values were observed in the red and infrared regions of the spectrum. A systematic decrease in the bandgap was observed both with an increase in the concentration of  $Tl^+$  precursor solution and an increase in the duration of treatment with this solution. The light absorption of the studied layers can be attributed to the direct forbidden transitions.

The calculated Urbach energy values decrease from 0.15 eV to 0.09–0.10 eV, when the concentration of the  $Tl^+$  precursor solution increases from 0.025 mol/l to 0.8 mol/l. With an increase in the duration of treatment with the  $Tl^+$  precursor solution from 20 to 75 min, Urbach energy values decrease from 0.14 eV to 0.10 eV as well. Comparing the effect of additives in  $Tl^+$  precursor solutions on the optical properties of TI–Se layers, it can be seen that the addition of ammonia leads to a narrower bandgap, but does not significantly affect the local disorder of the microstructure and the structural bond defects of the layers. This difference can be explained by the higher concentration of  $Tl^+$  ions and the higher molar ratio of TI/Se in the layers that were formed with the addition of ammonia.

The values of the optical parameters of the TI–Se selenide layers are tabulated in Table 3.2.



**Table 3.2.** Optical parameters of Tl–Se layers

Concentration of Tl <sup>+</sup> solution, mol/l	Duration, min	Absorption edge, nm	Band gap $E_g$ , eV	Urbach energy $E_U$ , eV	Steepness parameter $\sigma$	Electron-phonon interaction $E_{e-p}$
0.025	75	471	2.45	0.15	0.17	3.83
0.1		578	2.06	0.09	0.27	2.43
0.8		600	1.98	0.10	0.24	2.76
0.1	20	721	1.54	0.14	0.18	3.73
	75	931	1.22	0.10	0.26	2.60

The red shift in absorption was observed after the heat treatment. The estimated values of the bandgap energy and width of Urbach tail decrease on annealing. The decrease in the band gap after annealing may be attributed to an increase in particle size and improved crystallinity of the film. The reduction in the Urbach tail indicates a lower microstructural disorder, and therefore, an improvement in the quality of TlSe layers. The influence of annealing on optical properties of the Tl–Se selenide layers are tabulated in Table 3.3.

**Table 3.3.** Optical properties of virgin and heated thallium selenide layers on PA 6

Temperature, °C	pH	As deposited		After annealing	
		$E_g$ , eV	$E_U$ , eV	$E_g$ , eV	$E_U$ , eV
60	13.02	2.80	0.68	1.74	0.22
70	11.3	2.79	0.79	1.54	0.24

### 3.1.3. SEM/EDS analysis

While AAS represents the bulk elemental composition of Tl<sub>x</sub>Se<sub>y</sub> composites, the energy dispersive X-ray spectroscopy provides insights into the compositional information on the outermost surface of the obtained layers. The presence of stratified Tl–Se layers was confirmed by the elemental EDS analysis on the electron-rich film and deeper layers of the polyamide sheets. The degree of interaction between the electron beam and the sample is identified as in the EDS analysis depth sampling. It correlates with the kinetic energy of the electrons, and the atomic number of atoms that were analyzed. The analysis can obtain results within a few  $\mu\text{m}$  depths.

The EDS analysis shows that the Tl/Se molar ratio in the layers is significantly higher than that determined by the AAS method. As the data

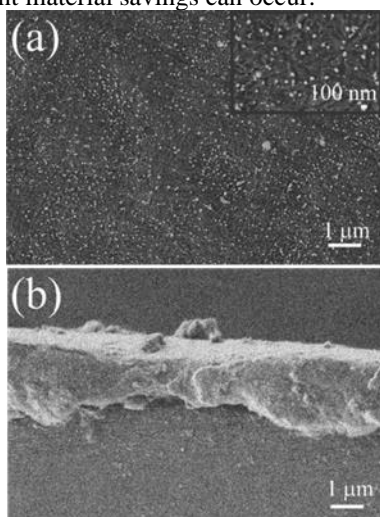
presented in Table 3.4 shows, the Tl/Se molar ratio in the Tl–Se layers on the PA sheet increases from 1.057 to 1.663 with an increase in the concentration of the thallium nitrate solution. This is because, while AAS represents the bulk elemental composition of Tl–Se composites, the energy dispersive X-ray spectroscopy provides insights into the compositional information of the outermost surface of the obtained layers. The dependence of the elemental composition of the surface layer of the samples on the duration of treatment with precursor solution of  $Tl^+$  ion was investigated with the EDS method as well. The selenized samples were treated for 20 and 75 min in a 60 °C solution of thallium sulfate at pH 10.9 (the solution medium was adjusted with 25% ammonia solution). Under these synthesis conditions, a higher concentration of  $Tl^+$  ions and a Tl/Se molar ratio are obtained both on the surface of the layer and in the entire volume of the coating.

The Tl/Se molar ratio determined by the AAS analysis increases from 0.695 to 1.253 with increasing treatment duration in the  $Tl^+$  precursor solution from 20 to 75 min, while this molar ratio, determined by the EDS analyzes, decreases from 2.36 to 2.14. This can be explained by the fact that an increase in the duration has a positive effect on the polymer swelling. It is known that water is necessary for the diffusion of ions into the polymer matrix. Furthermore, the migration rate of ions in the polymer matrix is directed by the amount of water that is present. Water plasticizes the polymer matrix and hydrates ions. With an increase in the treatment duration of the selenized PA sheet with the  $Tl^+$  precursor solution, this process is enhanced. Subsequently, a larger number of water molecules and with them a larger number of  $Tl^+$  ions penetrate into the deeper layers of the swollen polymer better. Thus, at the same time, a larger number of  $Tl^+$  reacts with divalent selenium-containing compounds and forms layers into the PA substrate with a higher concentration of Tl–Se. However, not only  $Tl^+$  ions diffuse into the deeper layer of the swollen polymer, but also, at the same time, the partial desorption of selenium-containing anions that have already been diffused into the polymer surface at the first stage occurs. Therefore, the concentration of these ions in the polymer surface layers increases. It is known that the adsorbed/diffused into the PA sheet ions of selenopolythionates decompose to the elemental selenium. As a result, more elemental selenium is formed, which does not react with the precursor ions. When selenized, PA sheets are treated in a  $Tl_2SO_4$  solution for 75 min, the less thallium-rich layer is formed on the polymer surface for the reasons mentioned above.

**Table 3.4.** Surface and bulk elemental composition of thallium selenide layers

c, mol/l	Duration, min	Tl, at %	Se, at %	Tl/Se (EDS)	Tl, $\mu\text{mol}/\text{cm}^2$	Tl/Se (AASA)
0.025	75	51.38	48.62	1.057	0.129	0.105
0.1		52.65	47.35	1.112	0.190	0.154
0.8		62.45	37.55	1.663	0.493	0.401
0.1	20	70.22	29.78	2.36	0.855	0.695
	75	68.11	31.89	2.14	1.541	1.253

SEM top and side images of sample treated in 80 °C  $\text{Tl}_2\text{SO}_4$  solution were acquired to assess the uniformity of the film as well as its thickness. Fig. 3.3. shows micron sized domains that are typical for the PA structure. There can be observed bright, electron density rich particles that are interdispersed on the surface. The inset reveals their size to be  $\sim 100$  nm. These particles are  $\text{Tl}_x\text{Se}_y$  aggregates, resulting during the material deposition or dehydration of the surface. The side image revealed the presence of  $\sim 2$   $\mu\text{m}$  interdiffused layer of  $\text{Tl}_x\text{Se}_y$  on the PA surface. This is beneficial for III–VI compound based composite materials that have very large absorption coefficient with a thin film of the needed material, and significant material savings can occur.



**Fig. 3.3.** SEM (a) top and (b) side images showing the presence of  $\sim 2$   $\mu\text{m}$  interdiffused layer of  $\text{TlSe}$  on the PA surface; the selenized sample reacted with 0.1 M  $\text{Tl}_2\text{SO}_4$  solution at 80 °C for 10 min

### 3.2. Mixed Tl-M-Se (M = Ga, Cu, Ag) type selenide layers on PA 6

The conversion of binary selenides to ternary or the incorporation of metal ions into them greatly improves their qualitative characteristics. Thus, there is a significant interest in the formation of ternary selenide films by wet chemical methods such as the successive ionic layer adsorption and reaction (SILAR) and the chemical bath deposition (CBD). It would be even simpler and more appropriate to form composite doped binary layers by the wet chemical methods on the surface of polymers instead of ternary Group III metal chalcogenide layers. In particular, doped layers of metal chalcogenides are promising for the optical applications, because the doping procedure makes it possible to expand the optoelectronic properties of these layers on a large scale. Moreover, doping provides the ability to tune synthesized metal chalcogenide layer and solution properties while being viable for large-scale application.

In order to obtain  $\text{Ga}^{3+}$ ,  $\text{Cu}^{2+}/\text{Cu}^+$ , or  $\text{Ag}^+$  cations doped Tl–Se, the PA sheets with Tl–Se layers were formed with a  $\text{Tl}_2\text{SO}_4$  solution for 20 min; they were treated with the precursor's solution of these cations. Due to cation-cation exchange reactions, it is possible to form doped Tl-M-Se type layers. For the aforementioned reaction to occur, the value of the solubility of the Tl–Se layer must be higher than the value of the solubility of the selenide that was formed during doping. Definitely, the solubility products of  $\text{Tl}_2\text{Se}$  ( $K_{\text{sp}} = 2.4 \times 10^{-22}$  (mol/L)<sup>3</sup>) are very large compared to those of  $\text{CuSe}$  ( $K_{\text{sp}} = 1.4 \times 10^{-36}$  (mol/L)<sup>2</sup>),  $\text{Cu}_2\text{Se}$  ( $K_{\text{sp}} = 1.1 \times 10^{-51}$  (mol/L)<sup>2</sup>), and  $\text{Ag}_2\text{Se}$  ( $K_{\text{sp}} = 3.1 \times 10^{-65}$  (mol/L)<sup>3</sup>). The value of the  $\text{Ga}_2\text{Se}_3$  solubility could not be found in literature, but because Ga is a group IIIA element like Tl, it is assumed that the value of the  $\text{Ga}_2\text{Se}_3$  solubility is close to the  $\text{Tl}_2\text{Se}$  value.

#### 3.2.1. SEM/EDS analysis

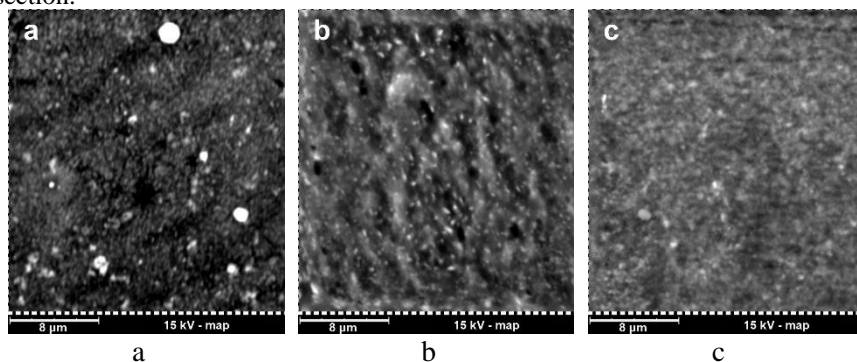
The data of element EDS analysis of these layers that is tabulated in Table 3.5. confirmed the presence of mixed Tl-M-Se (M = Cu, Ga, Ag) type layers on the PA sheets. The highest concentration of doping agent was achieved in Tl-Ag-Se layers. The lowest concentration of dopant was determined in Tl-Ga-Se layers, possibly due to the completely different solubility of the formed  $\text{Ag}_2\text{Se}$  and  $\text{Ga}_2\text{Se}_3$  during the doping procedure. It has been observed that the treatment with solutions, containing Cu(II/I), Ga(III), or Ag(I) ions, has a more pronounced effect on the concentration of thallium on the coating surface, and the amounts of selenium do not differ much in all three cases.

**Table 3.5.** Surface elemental composition of mixed Tl-M-Se (M = Ga, Cu, Ag) type selenide layers

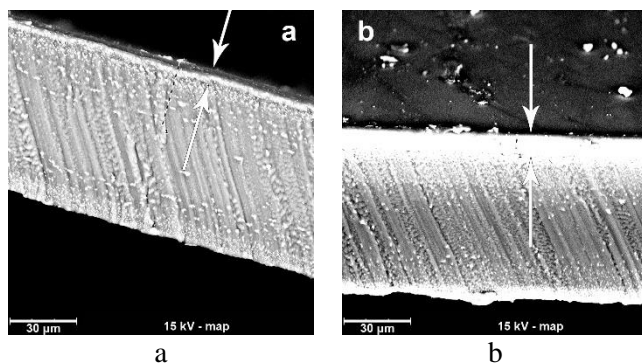
Sample	Tl, at %	M, at %	Se, at %	Tl:M:Se
Tl-Cu-Se	7.83	44.43	47.74	0.18:0.93:1
Tl-Ga-Se	36.56	19.35	44.09	0.83:0.44:1
Tl-Ag-Se	4.78	58.32	36.91	0.13:1.58:1

The surface morphologies of doped Tl-M-Se type layers were studied by a SEM method. As seen from the SEM surface images of the Tl-M-Se layers shown in Fig. 3.4., the layers are characterized by the distribution of fine spherical grains up to 1  $\mu\text{m}$  in size, which bind to agglomerates and clusters. Tl-Ag-Se layers are characterized by the finest compact structure surface morphology with single type and densely packed grains.

The SEM photographs of the cross-sections of samples make it possible to estimate the thickness of the layers. In Fig. 3.5., it can be seen that the treatment with solutions of doping agent has significant impact on the thickness of the formed layers. It was observed that the thickness of the Tl-Ga-Se layer is around 7  $\mu\text{m}$  and around 10  $\mu\text{m}$  for Tl-Ag-Se layer. Moreover, it can be seen that the thickness of the mixed Tl-M-Se layers is fairly uniform over the entire cross section.



**Fig. 3.4.** Corresponding SEM surface images of Tl-Me-Se layers: a – Tl-Cu-Se, b – Tl-Ga-Se, c – Tl-Ag-Se



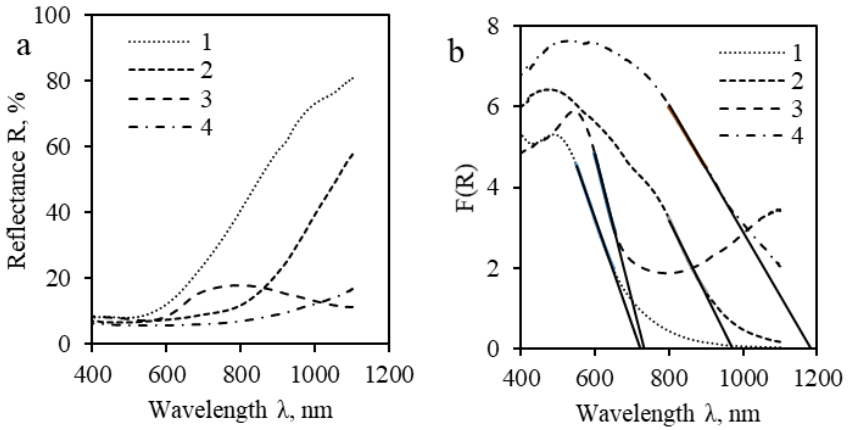
**Fig. 3.5.** SEM side images of Tl-Ga-Se (a) and Tl-Ag-Se (b) layers on PA 6

### 3.2.2. Optical properties

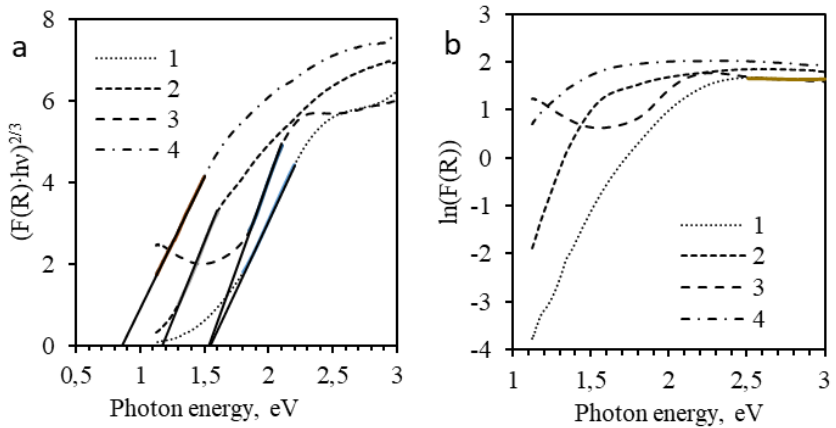
The studies of optical properties of Tl-M-Se mixed layers were carried out. For doping, Tl-Se layers that were formed by treating selenized PA sheets with thallium sulfate solution for 20 min were used. The reflection spectra of these layers in the range of 400–1100 nm, as well as the Kubelka-Munk transformation plot, are shown in Fig. 3.6. Meanwhile, the graphical definition of the bandgap and the Urbach energy of these layers are shown in Fig. 3.7. The red shift in absorption edge (Fig. 3.6. b) and reduction of the bandgap energy (Fig. 3.7. a) were observed after treatment in  $\text{Ga}^{3+}$ ,  $\text{Cu}^{2+}/\text{Cu}^+$ , or  $\text{Ag}^+$  salt solutions. The optical absorption of the investigated layers may be classified under the direct forbidden transitions. The optical parameters of the Tl-Se and Tl-M-Se layers, determined in this work, are presented in Table 3.6. Therefore, the relatively lowest Urbach energy of the Tl-Ga-Se layer indicates less disorder of its local microstructure and fewer defects in the structural bonds.

**Table 3.6.** Optical parameters of Tl-Se and Tl-M-Se layers

Compound	Absorption edge, nm	Band gap $E_g$ , eV	Urbach energy $E_U$ , eV	Steepness parameter $\sigma$	Electron-phonon interaction $E_{e-p}$
Tl-Se	721	1.54	0.14	0.179	3.730
Tl-Ga-Se	969	1.18	0.11	0.230	2.899
Tl-Cu-Se	734	1.54	0.30	0.084	7.972
Tl-Ag-Se	1183	0.86	0.34	0.075	8.857



**Fig. 3.6.** Tl-Se and Tl-M-Se layers reflectance spectra (a) and Kubelka-Munk transformation plot (b); 1 – Tl-Se, 2 – Tl-Ga-Se, 3 – Tl-Cu-Se, 4 – Tl-Ag-Se



**Fig. 3.7.** Tl-Se and Tl-M-Se layers Tauc plot for direct forbidden transitions (a) and Urbach energy plot (b); 1 – Tl-Se, 2 – Tl-Ga-Se, 3 – Tl-Cu-Se, 4 – Tl-Ag-Se

## CONCLUSIONS

1. The layers of thallium selenide  $Tl_xSe_y$  were formed on the surface of polycapromide 6 films when the seleniumized polymer with solution of  $K_2SeS_2O_6$  was treated with the solution of Tl(I) salt. After treatment of thallium selenide layers with Ga (III), Cu (II / I), or Ag (I) salt solutions, mixed Tl-M-Se ( $M = Cu, Ga, Ag$ ) type layers were formed.
2. The concentration of thallium ions in the layers of thallium selenides depends on the duration of the seleniumization in  $K_2SeS_2O_6$  solution, the concentration of the thallium ion precursor solution, and the duration of treatment. The treatment of seleniumized samples with a solution of thallium salt with the addition of ammonia instead of KOH granules resulted in a higher concentration of thallium in the layers of thallium selenides due to the formation of thallium ammonia complex.
3. Three phases of tetragonal thallium selenide ( $Tl_2Se_{1.2}$  (75–1007),  $Tl_2Se_2$  (75–880),  $Tl_5Se_3$  (41–1295)) and three phases of monoclinic selenium ( $Se_8$  (71–528),  $Se_8$  (76–1865),  $Se$  (73–2121)) have been identified in the layers of thallium selenide by XRD analysis. After annealing in  $N_2$  at 100 °C, polycrystalline  $Tl_xSe_y$  layers yielded a single TlSe ((22–1476) phase).
4. The studies of optical parameters have shown that the bandgap of the formed thallium selenide layers decreases with the increasing concentration of the thallium ion precursor solution and the increasing duration of the treatment. The Urbach energy of the formed thallium selenide layers varies between 0.09 and 0.79 eV. The estimated values of the bandgap energy and width of Urbach tail decrease on annealing. The red shift in the absorption edge and the reduction of the bandgap energy were observed after the treatment in Ga(III), Cu(II/I), or Ag(I) salt solutions.
5. After the exposure of selenium samples to higher concentrations of thallium (I) salt solutions (0.8 mol/l) and treatment for a longer period of time (75 min), more intense thallium and selenium emission lines are observed in the EDS spectra due to the higher content of formed thallium selenides. The SEM side image revealed the presence of  $\sim 2 \mu m$  interdiffused layer of  $Tl_xSe_y$  on the PA 6 surface. The thickness of the mixed Tl-M-Se layers increases to 7–10  $\mu m$ . The surface morphology of the samples is characterized by a heterogeneous microstructure, characterized by a distribution of fine crystallites that bind to the agglomerates and clusters.
6. The method that has been described in this dissertation can be used to synthesize a variety of metal selenide compounds diffused into the polymer at relatively low temperatures. This method is not limited to thallium selenides, thus providing for a flexible synthesis route for novel composite materials. In this dissertation, polyamide was used as a model host polymer. However, a large-scale application via two-step or three-step process, the seleniumization followed by the exposure to the corresponding metal salt solution, on virtually



any polymer can be envisioned. A possibility remains that ternary compounds could form during the adsorption–diffusion deposition and mild heating at <100 °C in the inert atmosphere, and this process is currently under investigation.

## **LIST OF PUBLICATIONS AND PROCEEDINGS ON THE TOPIC OF DISSERTATION:**

### **Publications corresponding to the list of Thomson Reuters™ Web of Science database:**

1. IVANAUSKAS, R., SAMARDOKAS, L., MIKOLAJŪNAS, M., VIRŽONIS, D., BALTRUŠAITIS, J. Polyamide–thallium selenide composite materials via temperature and pH controlled adsorption–diffusion method. *Applied surface science*. 2014, vol. 317, p. 818–827.
2. IVANAUSKAS, R., SAMARDOKAS, L., ANCUTIENĖ, I., IVANAUSKAS, A. Study of formation and phase composition of thallium selenide layers on polycapromide. *Materials science*. 2015. Vol. 21, no. 1, p. 13–17.
3. SAMARDOKAS, L., IVANAUSKAS, R., ŽALENKIENĖ, S., IVANAUSKAS, A., Influence of chemical composition and doping on optical properties of thallium selenide layers prepared by adsorption/diffusion method. *Chemija*. 2021. Vol. 32, no. 2, p. 35–48.

### **Publications in Proceedings of Conferences:**

1. Samardokas L., Ivanauskas R., Formation and optical properties of Tl–M–Se (M = Ga, Cu, Ag) layers on polyamide 6, *Nanotechnology and innovation in the Baltic Sea region 2017*, Kaunas, 2017 m. birželio 14–16 d.
2. Samardokas L., Ivanauskas R., Kinetic modeling of Tl (I) sorption on selenized PA 6, *Chemistry and chemical technology 2017*, Kaunas, 2017 m. balandžio 28 d.
3. Samardokas L., Ivanauskas R., Formation and properties of single phase TlSe layers on polyamide, *Advanced materials and technologies*, Palanga, 2016 m. rugpjūčio 27–31 d.
4. Samardokas L., Ivanauskas R., Optical properties of thallium selenide layers on the polyamide film surface, *International conference of Lithuanian Society of Chemistry*, Vilnius, 2016 m. balandžio 28–29 d.

5. Ivanauskas R., Samardokas L., Ancutienė I., Some properties of thallium selenide layers on the polyamide film surface, Chemistry and chemical technology 2015, Vilnius, 2015–01–23.
6. Ivanauskas R., Samardokas L., The structure and morphology of thallium selenide layers on polyamide films, Chemistry and chemical technology, Kaunas, 2014–04–25.
7. Ivanauskas A., Ivanauskas R., Samardokas L., Ancutienė I., Study of formation and phase composition of thallium selenide layers on polycapromide, Advanced materials and technologie, Palanga, 2013 m. rugpjūčio 27–31 d.
8. Ivanauskas A., Ancutienė I., Ivanauskas R., Samardokas L., Selenium containing precursor for semiconducting materials, Advanced materials and technologie, Palanga, 2013 m. rugpjūčio 27–31 d.
9. Ivanauskas R., Ancutienė I., Samardokas L., Ivanauskas A., The modification the polyamide films by layers of metal selenide, Baltic polymer symposium 2013, Trakai, 2013 m. rugsėjo 18–21 d.
10. Ivanauskas R., Samardokas L., Ancutienė I., Formation of thallium selenide layers on surface of polyamide 6 films by the use of potassium selenotriothionate solution, Chemistry and chemical technology of inorganic materials, Kaunas, 2013–04–24.
11. Samardokas L., Ivanauskas R., Talio selenidų sluoksnių sudarymas poliamido paviršiuje, Studentų moksliniai tyrimai 2012/2013, Vilnius, 2013 m. birželio 27–28 d.

**Publications not included in the thesis:**

1. Ulevičienė V., Ivanauskas R., Samardokas L., Peculiarities of the gallium selenide layers formation on the polyamide film surface, EcoBalt 2018, Vilnius, 2018 m. spalio 25–27 d.
2. Samardokas L., Šukytė V. J., Adsorption efficiency of chalcogens from  $H_2TeS_4O_6$  and Cd (II) on PA 6, 11–oji Lietuvos chemikų tarptautinė konferencija, Vilnius, 2013–09–27.
3. Šukytė V. J., Samardokas L., The formation of cadmium tellurides layer on the surface of polyamide 6 by the use of telluropentathionic acid, Chemistry and chemical technology of inorganic materials, Kaunas, 2013–04–24.
4. Samardokas L., Šukytė V. J., Telūropentationato rūgšties sintezė, savybių tyrimai ir taikymas chalkogenidiniams puslaidininkiams gauti, Studentų moksliniai tyrimai 2011/2012, Vilnius, 2012 m. birželio 28–29 d.

5. Šukytė V. J., Samardokas L., On an isolation and chemical – physical properties of monotelluropentathionic acid, Chemistry and chemical technology of inorganic materials, Kaunas, 2012–04–25.
6. Samardokas L., Mickevičius V., Anusevičius K., N–(4–dialkilaminofenil)–N–karboksietil–β–alaninų darinių sintezė ir savybės, Ad optimus, 2011, Nr. 1, p. 9–14.

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## **REZIUMĖ**

### **Darbo temos aktualumas**

Neorganiniai-organiniai kompozitai yra intensyviai tiriama medžiagų grupė, kuriai būdingas platus struktūrinių, fizikinių ir cheminių savybių spektras. Didelė šių medžiagų sudėties įvairovė leidžia panaudoti daug neorganinių junginių. Ypač svarbios yra kompozicinės medžiagos, sudarytos iš IIIA grupės metalų (galio, indžio ar talio) ir VIA grupės nemetalų (sieros, seleno ar telūro) binarinių ar trinarinių junginių, pasižyminčių unikaliomis fizikinėmis savybėmis, svarbiomis šiuolaikiniam mokslui ir technologijoms. Ypač sparčiai besivystanti III–VI grupių medžiagų pritaikymo sritis yra saulės energijos gavyba. Didelį susidomėjimą vadinamosiomis antros kartos fotovoltinėmis medžiagomis lėmė tai, kad labai plonas medžiagos sluoksnis leidžia pasiekti didelę saulės energijos absorbciją.

Pagrindinė III–VI grupių plonųjų sluoksnių problema susijusi su sluoksnio medžiagos daugiakomponentės sistemos kompleksiskumu, kuris sudaro kliūtis formuojant homogeninius didelio ploto sluoksnius. Problemų kelia ir III–VI grupių medžiagų stochiometrijos įvairovė, kuri turi įtakos daugeliui fizikinių savybių, įskaitant ir draustinės juostos plotį. Pagerinti III–VI grupių medžiagų

paviršiaus morfologiją ir elektrines savybes galima derinant jas su laidžiais polimerais. Kompozicinėms medžiagoms, sudarytoms iš polimero ir plono neorganinio puslaidininkio sluoksnio, nusodinto paviršiuje, būdingos tvirtos struktūrinės savybės dėl polimero elastingumo ir atsparumo aplinkos poveikiui bei veikia kaip efektyvūs puslaidininkiai. Organinių-neorganinių saulės celių tyrimai intensyviai plėtojami, nes tokios celės sujungia neorganinių medžiagų pranašumus (stabilumą, didelį krūvininkų judrumą) ir organinių laidžių polimerų privalumus (didelę šviesos absorbciją plačiame bangos ilgių diapazone, pritaikomą molekulinę struktūrą, nesudėtingą sintezę tirpaluose).

Adsorbicija-difuzija yra naujas alternatyvus metodas gauti III–VI grupių junginius, įterptus į polimerus. Šiam metodui nereikia aukštos temperatūros, vakuumo ar inertinės atmosferos. Kaip ir nusodinimo cheminėje vonioje (CBD) atveju, plonas sluoksnis susidaro dėl substrato sąveikos su praskiestu tirpalu, turinčiu atitinkamų jonų, o dalinė plėvelės inkorporacija į polimerą užtikrina gerą adheziją. Šiame darbe modelinis III–VI grupių binarinis junginys, talio selenidas, kurio talio ir seleno santykis skirtingas, nusodintas ant modelinio polimero – poliamido 6 – substrato, pritaikius adsorbicijos-difuzijos metodą. Gautus sluoksnius apdorojant galio, vario ir sidabro jonų turinčiais tirpalais, suformuoti mišrieji Tl-M-Se ( $M = \text{Ga}, \text{Cu}, \text{Ag}$ ) sluoksniai.

### **Darbo tikslas**

Adsorbicijos-difuzijos metodu pusiau hidrofilinio polimero PA 6 paviršiuje sudaryti talio selenidų ir Tl-M-Se ( $M = \text{Ga}, \text{Cu}, \text{Ag}$ ) sluoksnius ir ištirti šių sluoksnių susidarymo mechanizmą, sandarą ir savybes.

### **Darbo uždaviniai**

1. Suformuoti talio selenidų sluoksnius ir mišriuosius Tl-M-Se ( $M = \text{Ga}, \text{Cu}, \text{Ag}$ ) tipo sluoksnius, kaip seleno pirmtaką panaudojant  $\text{K}_2\text{SeS}_2\text{O}_6$  tirpalą.
2. Taikant įvairius analizės metodus, ištirti šių sluoksnių susidarymo mechanizmą ir nustatyti ryšį tarp sudarymo sąlygų, sandaros bei savybių.

### **Mokslinis naujumas**

Sorbicijos-difuzijos metodu, pasitelkus kalio selenotritionato druskos tirpalą kaip žemo oksidacijos laipsnio seleno turinčių jonų šaltinį, suformuoti talio selenidų ir mišrieji Tl-M-Se ( $M = \text{Ga}, \text{Cu}, \text{Ag}$ ) sluoksniai. Gautų sluoksnių sandara ir savybės nustatytos RSDA, AASA, SEM/EDS, UV-RG spektroskopiniais tyrimų metodais.

### **Darbo aprobavimas ir publikavimas**

Atliktų tyrimų rezultatai paskelbti 14 publikacijų: 3 straipsniai žurnaluose, įtrauktuose į duomenų *Thomson Reuters™ Web of Science* bazę; 11 publikacijų konferencijų pranešimų medžiagoje.

## Darbo apimtis

Disertaciją sudaro įvadas, literatūros apžvalga, eksperimentinė dalis, rezultatai ir aptarimas, išvados, literatūros sąrašas, publikacijų disertacijos tema sąrašas.

## Ginamieji teiginiai

1. Kalio selenotritonatas  $K_2SeS_2O_6$  yra tinkamas žemo oksidacijos laipsnio seleno turinčių jonų pirmtakas talio selenidų ir mišriųjų Tl-M-Se (M = Ga, Cu, Ag) sluoksnių poliamido 6 paviršiuje formavimui.

2. Talio selenidų ir mišriuosius Tl-M-Se (M = Ga, Cu, Ag) sluoksnius galima gauti sorbciniu-difuziniu metodu, pritaikius trijų stadijų procesą.

3. Polikristalinius  $Tl_xSe_y$  sluoksnius iškaitinus  $N_2$  atmosferoje, gaunamas vienfazis talio selenidas TlSe.

4. Galio, vario ir sidabro priedų įterpimas lemia sluoksnių sugerties krašto raudonąjį poslinkį ir draustinės juostos pločio sumažėjimą.

## IŠVADOS

1. Poliamido 6 bandinius, apdorotus kalio selenotritonato druskos tirpale, paveikus tirpalu, turinčiu Tl(I) jonų, polimero paviršiuje buvo sudaryti talio selenidų  $Tl_xSe_y$  sluoksniai. Talio selenidų sluoksnius apdorojus Ga(III), Cu(II/I) ar Ag(I) druskų tirpalais, suformuoti mišrieji Tl-M-Se (M = Cu, Ga, Ag) tipo sluoksniai.

2. Talio jonų koncentracija talio selenidų sluoksniuose priklauso nuo seleninimo  $K_2SeS_2O_6$  tirpale trukmės, talio jonų pirmtako tirpalo koncentracijos ir apdoravimo trukmės. Selenintus bandinius paveikus talio druskos tirpalu su amoniako priedu vietoje KOH granuliu, nustatyta didesnė talio koncentracija talio selenidų sluoksniuose dėl susidariusio talio amoniakinio komplekso.

3. Rentgeno spinduliuotės difrakcinė analizė parodė, kad, priklausomai nuo seleninimo trukmės ir bandinių apdoravimo talio sulfato tirpalais sąlygų, susidaro trys talio selenidų ir trys seleno fazės:  $Tl_2Se_{1,2}$  (75–1007),  $Tl_2Se_2$  (75–880),  $Tl_5Se_3$  (41–1295),  $Se_8$  (71–528),  $Se_8$  (76–1865), Se (73–2121). Iškaitinus talio selenidų sluoksnius inertinėje  $N_2$  atmosferoje 100 °C temperatūroje, gauti vienfaziai TlSe (22–1476) sluoksniai.

4. Optinių parametrų tyrimai parodė, kad suformuotų talio selenidų sluoksnių draustinės juostos plotis mažėja, didėjant talio jonų pirmtako tirpalo koncentracijai ir ilgėjant apdoravimo trukmei. Suformuotų talio selenidų sluoksnių Urbach energija kinta tarp 0,09 ir 0,79 eV. 12 h iškaitinus bandinius inertinėje  $N_2$  atmosferoje 100 °C temperatūroje, stebimas draustinės juostos pločio ir Urbach energijos sumažėjimas. Talio selenidų sluoksnius apdorojus

Ga(III), Cu(II/I) ar Ag(I) druskų tirpalais, pastebėtas sugerties krašto raudonasis poslinkis ir draustinės juostos pločio sumažėjimas.

5. Paveikus selenintus bandinius didesnės koncentracijos (0,8 mol/l) talio (I) druskų tirpalais ir apdorojant juos ilgesnį laiką (75 min), EDS spektruose stebimos intensyvesnės talio ir seleno emisijos linijos dėl susidariusio didesnio talio selenidų kiekio. Bandinių skerspjūvio SEM nuotraukos rodo apie 2  $\mu\text{m}$  difundavusį talio selenidų sluoksnį poliamido paviršiuje. Mišriųjų Tl-M-Se sluoksnių storis padidėja iki 7–10  $\mu\text{m}$ . Bandinių paviršiaus morfologijai būdinga nevienalytė mikrostruktūra, smulkių kristalitų pasiskirstymas, kurie jungiasi į aglomeratus ir klasterius.

6. Šiame darbe aprašytas adsorbcijos-difuzijos metodas gali būti taikomas sintetinant įvairius metalų selenidų junginius, difundavusius polimero paviršiuje santykinai žemoje temperatūroje. Šis metodas užtikrina lanksčias naujų kompozitinių medžiagų sintezės galimybes ir nėra apribotas talio selenidų sluoksnių formavimu. Substrato funkcijai atlikti poliamidas buvo pasirinktas kaip modelinis polimeras, tačiau, pritaikius dviejų ar trijų žingsnių procesą – seleninimą ir apdorojimą reikiamų metalų druskų tirpaluose, gali būti naudojamas bet kuris polimeras. Taip pat tikėtina trinarių junginių susiformavimo galimybė adsorbcijos-difuzijos ir terminio apdorojimo inertinėje atmosferoje  $<100\text{ }^{\circ}\text{C}$  temperatūroje procesų, kurie yra tolimesnių tyrimų objektas, metu.

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