

Formation of Cadmium Selenide Containing Layers on the Polyamide Film Surface by the Use of Potassium Selenotriothionate

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The layers containing cadmium selenide, Cd_xSe, were formed on the surface of semi hydrophilic polymer – polyamide 6 (PA) for the first time by sorption-diffusion method using acidified solution of potassium selenotriothionate, K₂SeS₂O₆, as a precursor of selenium. The concentration of sorbed selenium increases with the increase of the duration of PA treatment in K₂SeS₂O₆ solution. The cadmium selenide containing layers form on the surface of PA after the treatment of seleniumized polymer with cadmium acetate, Cd(CH₃COO)₂·2H₂O, solution: the anions SeS₂O₆²⁻ containing selenium atoms of low oxidation state react with the cadmium(II) ions. The conditions of a polymer initial seleniumization and of seleniumized PA treatment with cadmium acetate solution determine the concentration of cadmium and the composition of chalcogenide layer. The concentration of cadmium in the chalcogenide layer increases with the increase of initial chalcogenization duration only up to about 2 h and the temperature of selenotriothionate solution. XRD confirmed the formation of cadmium selenide containing layers on the surface of PA. The results of XPS and XRD patterns study of not earlier studied CdSe containing layers on PA showed their phase composition of two cadmium selenide phases – zinc blende (cubic) CdSe, wurtzite (hexagonal) CdSe, cadmium(II) oxide, CdO, and cadmium(II) hydroxide, Cd(OH)₂. Accordingly data of XRD and XPS analysis the composition of CdSe containing layers depends on the conditions of these layers formation. The data determined enable formation of the layers containing cadmium selenide on the surface of PA by the sorption-diffusion method using the solution of potassium selenotriothionate as a precursor of selenium.

Keywords: polyamide, selenotriothionate, layer, cadmium selenide.

1. INTRODUCTION

The II–VI groups' binary compounds of transition metals with chalcogens belonging to the cadmium chalcogenide family (CdS, CdSe, CdTe) are considered to be important materials for photovoltaic applications [1–3]. CdSe is a promising photovoltaic material because of its suitable band gap (1.8 eV [4]), a high absorption coefficient and high photosensitivity. Cadmium selenide also is used in fabrication of photoelectrochemical cells, gas sensors, photoconductors, thin film transistors, gamma ray detectors, etc. [5–11]. All these applications are associated with optical properties of CdSe.

Several physical and chemical techniques are available for the growth of CdSe thin films on dielectrics. These films have been deposited using electrodeposition [12, 13], molecular beam epitaxy [14], spray pyrolysis [15], successive ionic layer adsorption and reaction method [16], vacuum deposition [17] and chemical bath deposition [8, 9, 18]. Among these methods chemical bath deposition has several overriding advantages with other techniques such as uniform film deposition, control of thickness, precise maintenance of deposition temperature, low cost [9, 18, 19].

The formation of cadmium selenide containing layers on polyamide 6 (PA) films have not been studied before.

In the present paper we report the formation of cadmium selenide containing layers on PA by rather simple modified chemical bath deposition sorption-diffusion method, worked up in our laboratory during studies of formation of copper selenide (Cu_xSe) and silver selenide (Ag_xSe) containing layers on PA, using potassium selenotriothionate, K₂SeS₂O₆, as a precursor of selenium [20–24].

2. EXPERIMENTAL

A PA 6 film (PA – 6.500 μm thick, density 1.13 g/cm⁻³) produced in Germany was used. Prior to the experiments, pieces of the film (15×70) mm in size had been boiled in distilled water for 2 h to remove the remainder of the monomer. Then they were dried with filter paper and kept in a desiccator over CaCl₂ for 24 h.

In the first stage the PA films were seleniumized in a thermostatic vessel up to 5 h at a temperature of 60°C using a continually stirred acidified (0.1 mol·dm⁻³ HCl) 0.05 mol·dm⁻³ solution of potassium selenotriothionate, K₂SeS₂O₆. K₂SeS₂O₆ was prepared by the method given in [25]. At certain time intervals, the PA film samples were removed from K₂SeS₂O₆ solution, rinsed with distilled water, dried with filtration paper, left over CaCl₂ for 24 h and then used in analysis and further experiments.

In the second stage, the samples of seleniumized PA were treated with the solution of cadmium acetate, Cd(CH₃COO)₂·2H₂O, at the temperatures of 50, 60 and

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70 °C, then rinsed with distilled water, dried over CaCl₂ and used in consequent experiments.

The concentration of selenium in a PA sample was determined using a Perkin Elmer Analyst 400 atomic absorption spectrometer [26].

The concentration of cadmium in a PA sample was determined using a Varian spectra-20 plus atomic absorption spectrometer [27].

Before analysis, samples of PA with selenium containing thin films had been mineralized. Samples were treated with concentrated HNO₃ to destroy PA and to oxidize selenium (and possibly sulfur compounds, which forms during decomposition [28] of selenotriothionate – elemental Se, SO₂ and SO₄²⁻) into selenite and sulfate. Heating with concentrated hydrochloric acid removed the excess of nitric acid. For the conditions described above, the sensitivity of the AAS method is 0.3 mg/l selenium and 0.02 mg/ml cadmium for the 1 % absorption.

The phase composition of cadmium selenide layers on PA surface was investigated by X-ray diffraction using a DRON-6 diffractometer equipped with a special device for beam limitation at low and medium diffraction angles using graphite-monochromatized Cu-K_α radiation source ($\lambda = 1.54178 \text{ \AA}$) under a voltage of 30 kV and a current of 30 mA. X-ray diffraction data were analysed with Search Match, ConvX, Xfit and Excel computer programs.

XPS spectra of CdSe containing layers were recorded with an ESCALAB MKII spectrometer (VG Scientific, radiation Mg K_α – 1253.6 eV, output 300 W). The samples were etched in a preparation chamber with the vacuum $9.3 \cdot 10^{-3} \text{ Pa}$ and current 20 μA ; duration of etching was 10, 30 and 60 s. To reveal the composition of the obtained cadmium selenide containing layers, the photoelectron spectra of Cd 3d, Se 3d and O 1s were recorded. All experimental data was corrected to the C 1s line at binding energy of 284.6 eV. Empirical sensitivity factors for these elements were taken from the literature [29] and the spectra obtained were compared with the standard ones [30].

3. RESULTS AND DISCUSSION

The modification of PA films by the formation on its surface of cadmium selenide containing layers in present study was performed in two stages, like in studies of formation of copper selenide (Cu_xSe) and silver selenide (Ag₂Se) containing layers on PA, using potassium selenotriothionate, K₂SeS₂O₆, as a precursor of selenium [20–24].

In the first stage, the PA film was treated with the solution of potassium selenotriothionate. The selenotriothionate anion contains one divalent selenium atom of low oxidation state $\text{O}_3\text{S}-\text{Se}-\text{SO}_3^-$ and these selenium containing anions sorb-diffuse into the PA surface matrix layer. In the second stage, the seleniumized PA film was treated with the water solution of cadmium acetate: the interaction of cadmium ions with the selenium atoms present in the sorbed selenotriothionate ions leads to the formation of cadmium selenide in the layers, formed on the surface of the polymer:



The visual examination of the PA samples colour gave the first indications that the selenotriothionate ions are sorbed-diffused into the PA films: colourless PA films depending on the concentration of sorbed-diffused $\text{SeS}_2\text{O}_6^{2-}$ ions gradually acquires yellow, brown or red (liberation of red amorphous selenium) colour like was observed earlier [20–24].

The study of the kinetics of sorption-diffusion of selenium from the solution of selenotriothionate into PA film of indicated in experimental part thickness showed that the concentration of selenium in the samples during exposure in the solution of K₂SeS₂O₆ at 60 °C increases continuously with time (Fig. 1).

Dependence of the concentration of cadmium in PA films on the temperature of seleniumized different time PA treatment with cadmium acetate solution is shown in Fig. 2. It was found that at all temperatures studied the concentration of cadmium in initially seleniumized PA samples during first ~2 h increases and different concentrations of Cd in PA at each temperature was reached (Fig. 2). The tendency of Cd concentration increase with increase in temperature of Cd(CH₃COO)₂ solution used was observed. The concentration of cadmium in PA samples seleniumized longer than ~2 h gradually decreases.

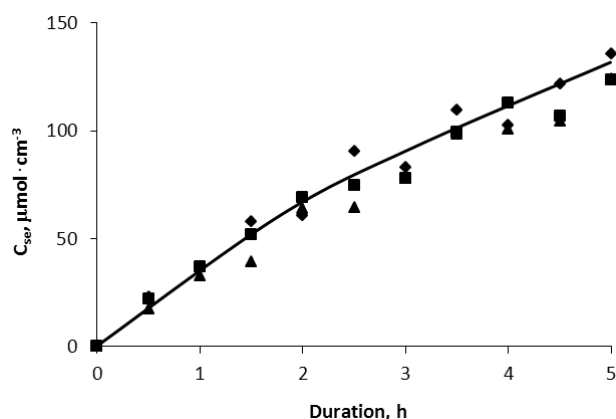


Fig. 1. Change of Se concentration in PA with time during its treatment with the K₂SeS₂O₆ solution at the temperature of 60 °C

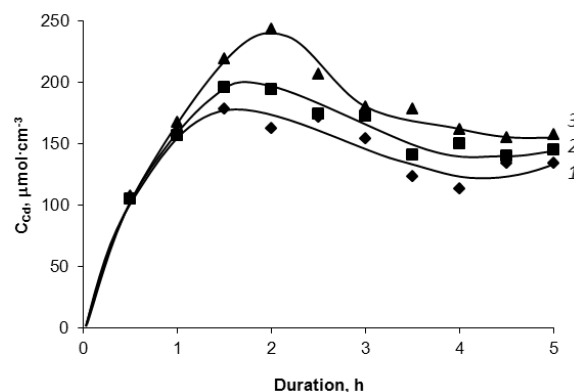


Fig. 2. Dependence of the concentration of cadmium in PA films on the temperature of seleniumized PA treatment with cadmium acetate solution. The temperature of Cd(CH₃COO)₂ solution: 1 – 50 °C, 2 – 60 °C, 3 – 70 °C

That may be explained by the known [28] reduction of $\text{SeS}_2\text{O}_6^{2-}$ ions stability with time and with the increase of solution temperature: these ions decompose gradually and selenium at the beginning liberates in the form of more reactive red amorphous form which later under action of temperature transforms into nonreactive black trigonal selenium modification which does not interact with the Cd(II) ions.

The results of XRD and XPS confirmed the formation of cadmium selenide containing layers on the surface of PA. Seleniumized PA samples with layers formed after their treatment with cadmium acetate solution were first investigated by X-ray photoelectron spectroscopy.

The coatings surface was studied first, and then the coatings were etched by Ar^+ ions and their composition in deeper layer was studied. The analysis was restricted by a very thin layer. From the obtained data, i.e. the atomic percentages of elements, binding energies and individual elements of Cd 3d, Se 3d, O 1s spectra, it was possible to predict the composition of the layers (Fig. 3).

The processes of PA film seleniumization and selenide containing layer formation take place in a natural environment; therefore, it is impossible to prevent its influence. Semi hydrophilic polymer PA, under the action of environment, absorbs on its surface oxygen, moisture and other compounds. From the data presented in the Table 1 it follows that a rather large part of the surface is taken by oxygen (binding energy values of $\sim 530.3 \text{ eV} - 530.6 \text{ eV}$). Its content significantly decreases in deeper layers of modified PA samples, independently on the duration of initial seleniumization (samples 1–5) and the temperature of later used cadmium acetate solution (samples 5–7). Such large oxygen amount may be explained by its chemical absorption from the environment, as well as by insoluble cadmium(II) hydroxide and cadmium(II) oxide formation on the surface; $\text{Cd}(\text{OH})_2$ may be formed while washing coatings with water. It can also originate from the selenotrichionate ions sorbed-diffused into PA but not reacted with cadmium ions, since $\text{SeS}_2\text{O}_6^{2-}$ ions with time gradually decompose to elemental Se, SO_2 and SO_4^{2-} ions [28].

The copper sulfides forming layers in the polymer surface matrix by the sorption-diffusion method take the form of dendrites [31], therefore, among the dendrites there may remain absorbed oxygen, water and other compounds. For this and other reasons, the microstructure of metals chalcogenide layer may significantly differ from the microstructure and chemical composition of all layers.

Data show also that on the layer's surface and in the etched surface cadmium selenide (CdSe), cadmium hydroxide ($\text{Cd}(\text{OH})_2$), and oxide (CdO) are present. Analysis has shown that on the surface of layers studied, there was only small amount of cadmium selenide ($\sim 0.1 \text{ at}\% - 2 \text{ at}\%$), while the absorbed oxygen, hydroxide and oxide take the largest part ($\sim 18 \text{ at}\% - 27 \text{ at}\%$). From the data of analysis it follows that the composition of the layers formed in different conditions is rather similar. This confirms also the similarity of the elements' spectra, therefore, here only few characteristic spectra are presented (Fig. 3).

The Cd 3d features from CdSe layer consist of two main $3d_{5/2}$ and $3d_{3/2}$ spin-orbit components at about

405 eV–406 eV and 411 eV–412 eV, respectively (Fig. 3), thus indicating the presence of mainly CdSe [29]. It is difficult to observe CdO and $\text{Cd}(\text{OH})_2$ components in Cd 3d core level XPS spectra, since the binding energy difference between CdO and $\text{Cd}(\text{OH})_2$ is only 0.1 eV which is hardly discernable by XPS system (both CdO and $\text{Cd}(\text{OH})_2$ have binding energies 404.0 eV–407.4 eV in Cd $3d_{5/2}$ and 410.6 eV–411.8 eV in Cd $3d_{3/2}$) [29]).

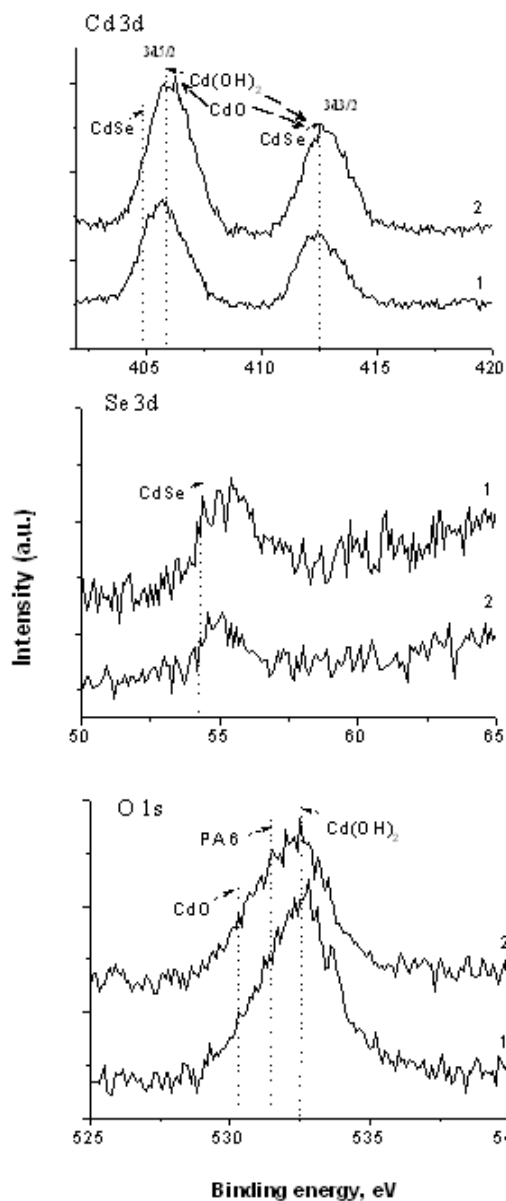


Fig. 3. XPS Cd 3d, Se 3d and O 1s spectra of CdSe layers on PA surface obtained during PA treatment for 2 h at the temperature of 60°C in $\text{K}_2\text{SeS}_2\text{O}_6$ solution and at different temperature of $\text{Cd}(\text{CH}_3\text{COO})_2$ solution. The temperature of $\text{Cd}(\text{CH}_3\text{COO})_2$ solution: 1 – 50°C , 2 – 70°C

The Se 3d peak positions of the CdSe films are about $\sim 54 \text{ eV}$ (Fig. 3). This value is close to the binding energy value reported for CdSe [29].

Figure 3 shows the XPS spectra from O 1s region also and the O 1s peaks (Fig. 3) were observed at $\sim 530 \text{ eV} - 532 \text{ eV}$, indicate the presence of cadmium in the form of cadmium(II) hydroxide ($530.90 \text{ eV} - 532.50 \text{ eV}$)

Table 1. Comparisons of observed and standard d and angle values and their respective planes for CdSe containing layers on PA surface obtained during PA treatment for 2 h at the temperature of 60 °C in $K_2SeS_2O_6$ solution and at different temperature (50 °C – 70 °C) of $Cd(CH_3COO)_2$ solution

	standard		observed						hkl Planes
	$\text{\AA} (d)$	Angle (2θ)	$\text{\AA} (d)$	Angle (2θ)	$\text{\AA} (d)$	Angle (2θ)	$\text{\AA} (d)$	Angle (2θ)	
			50 °C		60 °C		70 °C		
PA 6	4.39	20.3	4.37	20.18	4.37	20.2	4.36	20	$(100)_a$
	4.16	21.6	–	–	–	–	–	–	$(001)_\gamma$
	3.75	23.7	3.60	23.48	3.60	23.56	3.60	23.52	$(002/202)_a$
CdSe (cubic) JCPDS data file no 19-191	3.51	25.4	–	–	–	–	–	–	(111)
	2.15	42.00	2.15	42.08	–	–	–	–	(220)
	1.83	49.7	1.84	48.68	–	–	–	–	(311)
CdSe (hexagonal) JCPDS data file no 8-459	3.72	23.88	–	–	–	–	–	–	(100)
	3.51	25.37	–	–	–	–	–	–	(002)
	3.29	27.09	3.00	28.54	3.00	28.54	3.00	28.54	(101)
	2.56	35.12	2.2	38.42	2.3	38.16	2.3	38.04	(102)
	2.15	42.00	2.16	41.62	2.16	40.68	2.16	40.50	(110)
	1.98	45.78	1.98	45.78	1.96	45.89	1.98	45.82	(103)
	1.86	48.89	1.87	48.68	1.87	48.46	1.87	48.6	(200)
	1.83	49.70	1.84	49.42	1.84	49.63	1.84	49.4	(112)

and cadmium(II) oxide (528.80 eV – 531.60 eV). In the same O 1s region (at 531.35 eV) is peak of PA 6 binding energy [29].

Structural (XRD) studies of the CdSe layers deposited by the sorption-diffusion method are limited by the polycrystallinity of the layers obtained and by the crystallinity of the PA film itself. The intensity of the PA maximum at $2\theta < 25^\circ$ exceeds a few times the intensity of the cadmium selenide maxima: two main reflections were observed about $2\theta = 20^\circ$ and 23.5° , which are attributed to the $(100)_a$ and $(002/202)_a$ crystal planes, respectively [32]. Therefore the area of $2\theta \geq 25.0^\circ$ was investigated in more detail.

Cadmium selenide can be formed having the hexagonal (wurtzite-type structure) [33], or the cubic (zinc blende-type structure) [34]. Many workers have reported that chemically deposited CdSe thin films onto different substrates are either hexagonal or cubic [35 – 38].

Identification of the appearing crystalline peaks has shown that both of the cubic and hexagonal phases of CdSe exist in all of the cadmium selenide films. The observed and standard d values are shown in the Table 1.

All of the XRD diffractograms have a single major peak at 2θ about 28.5° , which can be indexed as (101) belonging to a CdSe hexagonal phase [33, 38].

Analysis of the XRD spectra shows that the Zinc blende (cubic) CdSe [34, 35, 38] was found in the composition of the cadmium selenide film on PA 6 of seleniumized PA treatment with cadmium acetate solution (50 °C) for 2 hours: Figure 4 (curve 1) shows the XRD peak at $2\theta = 42.08^\circ$ and 48.68° , that correspond to the (220) and (311) plane respectively of metastable cubic phase of CdSe (JCPDS 19–

191, [34, 38]. When the seleniumized PA was treated at a higher temperature (60 °C – 70 °C), the diffraction peaks could be indexed as the (102), (110), (103), (200) and (112) planes of high crystalline wurtzite hexagonal phase (JCPDS 8–459, [33, 35]) (Fig. 4, curve 2, 3).

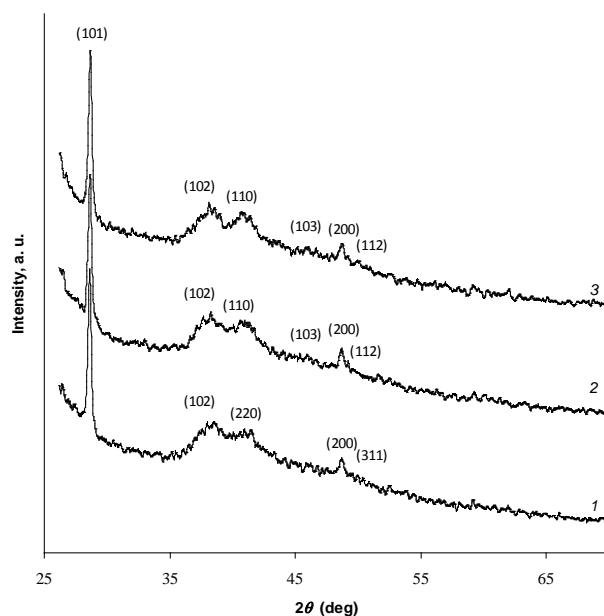


Fig. 4. X-ray diffraction patterns of cadmium selenide layers on PA treated for 2 h with $0.05 \text{ mol}\cdot\text{dm}^{-3} K_2SeS_2O_6$ solution at 60 °C and with $Cd(CH_3COO)_2$ ·solution at different temperature. The temperature of $Cd(CH_3COO)_2$ solution: 1 – 50 °C, 2 – 60 °C, 3 – 70 °C

Thus the results of XRD study confirmed the formation of cadmium selenide containing layers on the surface of PA. The results of XPS and XRD patterns study of not earlier studied CdSe containing layers on PA showed their phase composition of two cadmium selenide phases – zinc blende (cubic) CdSe, wurtzite (hexagonal) CdSe, cadmium(II) oxide, CdO, and cadmium(II) hydroxide, Cd(OH)₂. The results of our study are in agreement with the studies of other authors, which deal with the characterization of CdSe layers on other dielectrics [5, 8, 15–19, 35–38].

4. CONCLUSIONS

1. The layers of cadmium selenide, CdSe, forms in the surface of polyamide 6 film when the polymer is seleniumized in K₂SeS₂O₆ solution and later treated with a solution of Cd(II) acetate.
2. The concentration of selenium and cadmium in the polyamide 6 film depends on its initial seleniumization conditions: C_{Se}, in PA during its treatment with the K₂SeS₂O₆ solution at the temperature of 60 °C increases continuously with time. C_{Cd}, at the temperatures 50 °C–70 °C in initially seleniumized PA samples increases only during first ~2 hours, what is caused by the reduction of selenotrichionate ions stability with time.
3. The results of XPS and XRD confirmed the formation of cubic and hexagonal cadmium selenide containing layers on the surface of PA.
4. Accordingly data of XPS and XRD analysis the composition of the layers formed in PA after its first treatment with selenotrichionate solution and later with cadmium acetate solution depends on the conditions of these layers formation.

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