# Deposition and characterization of copper sulphide layers on the home-made polycarbonate plates

# Valentina Krylova<sup>1\*</sup>,

Nijolė Dukštienė<sup>1</sup>,

## Igoris Prosyčevas<sup>2</sup>

<sup>1</sup> Department of Physical and Inorganic Chemistry, Kaunas University of Technology, Radvilėnų St. 19, LT-50254 Kaunas, Lithuania

<sup>2</sup> Institute of Materials Science, Kaunas University of Technology, Savanorių Ave. 271, LT-50131 Kaunas, Lithuania Copper sulphide layers were deposited on the home-made polycarbonate (PC) plates by the chemical bath deposition (CBD) method. The layers were characterized by X-ray diffraction (XRD), optical microscopy (OM), Fourier transform infrared (FT-IR) spectroscopy. X-ray diffraction analysis showed that the layers are composed of covellite (Cu<sub>2</sub>S) and chalcocite (Cu<sub>2</sub>S) phases with a hexagonal and a monoclinic unit cell, respectively. The spherical particles of Cu<sub>2-x</sub>S with a size range of 1–27 µm in diameter were deposited depending on the number of deposition cycles. The room temperature sheet resistance of Cu<sub>2-x</sub>S layers deposited on PC plates is 1.13 kΩ/cm<sup>2</sup> after the fourth deposition cycle.

Key words: copper sulphide, polycarbonate, chemical bath deposition, sheet resistance

## INTRODUCTION

Nanocrystalline copper sulphide is a p-type semiconductor [1-2] which regularly exhibits at least five stable phases with different Cu:S molar ratios, starting from Cu rich chalcocite (Cu<sub>2</sub>S) to Cu poor covellite (CuS) phase. These copper sulphides are interesting materials for their metal-like electrical conductivity [3], impressive electrochemical properties [4–6], biochemical sensing capability [7–8] and ideal characteristics for solar energy absorption [1, 9–11]. Besides, covellite (CuS) can be used as a superconductive material due to holes in its valence band, which are associated with the 3p orbitals of sulphur [12].

There are numerous methods that have been reported for the synthesis of  $Cu_{2,x}S$  (x = 0–1) on different substrates including chemical bath deposition (CBD) [13–14], electrodeposition [15], successive ionic layer adsorption and reaction (SILAR) [16], thermal evaporation [17] and solid state reactions [18]. So far  $Cu_{2-x}S$  films and nanoparticles have been synthesized with various morphologies such as particles [19–20], hollow spheres [10, 21–22], rods [23–24], wires [25–26], allowing the desirable chemical and physical properties to be engineered.

CBD has been considered as one of the most prominent synthesis methods. Within the CBD method, electrical conductivity of the substrate is not the necessary requirement. The low temperature (30-80 °C) deposition also avoids oxidation and corrosion of metallic substrates. The better orientations and improved grain structure can be obtained under easily controlled deposition parameters. Further, it can be easily adapted to fabricate large-area semiconductor thin films.

In the last few decades, there has been an increasing attention on the depositing of copper sulphide films onto conductive and non-conductive polymer substrates since a polymer can be easily designed into almost any shape and size required for practical applications. Additionally, the polymer can also act as the controlled environment for the growth of the film layers. Furthermore, the copper sulphide/polymer

<sup>\*</sup> Corresponding author. E-mail: valentina.krylova@ktu.lt

composites can exhibit properties that markedly differ from those of a single crystal. Recently, copper sulphide films have been successfully deposited by the CBD method on the latex [27], poly(methyl methacrylate) [28], polyethylene [14], polyamide [29–30], and polyimide [31] surfaces. Literature survey revealed that the deposition of metal chalcogenides layers on polymer surfaces requires a previous polymer pretreatment such as activation and heat treatment in order to facilitate its adhesion [14, 32–33].

To the best of our knowledge, there is no report on the copper sulphide depositing on a polycarbonate substrate by the CBD method. Our attention is focused on polycarbonate because it is a high heat engineered thermoplastic polymer characterized by outstanding mechanical and thermal properties and showing potential as a biodegradable material for green technologies [34]. The polycarbonate film itself is not expected to have a very good electrical conductivity, due to the nature of the polymer itself. However, it has the additional advantages of being transparent, allowing it to be used in conjunction with optical materials, and being very easily available.

The present work is novel in the context that the depositing of  $Cu_{2,x}S$  films on the home-made polycarbonate plates has been achieved without a previous pre-treatment of polymer. The present investigation deals with the effect of deposition cycles number on the  $Cu_{2,x}S$  film, morphology, structure and sheet resistance.

### EXPERIMENTAL

#### Preparation of home-made PC plates

Industrial grade polycarbonate (referred to as PC further in the text) granules with a specific molecular weight (supplied by Scientific Polymer, Mw = 36 K) were used for manufacturing of polymer matrices. The PC granules (5 wt. %) were dissolved in a volatile solvent – chloroform  $\text{CHCl}_3$  (95 wt. %, Sigma-Aldrich, Germany) and then the obtained solution was casted on a fluoroplastic plate. After solvent evaporation the solid PC film was peeled from the fluoroplastic plate. PC plates of 10 mm × 50 mm size were used as the templates. Thickness of the PC plates determined by a micrometer was  $50 \pm 1.5 \,\mu\text{m}$ . Prior to deposition, the PC plates were degreased with ethanol.

## Deposition of Cu<sub>2-x</sub>S layers on home-made PC plates

The chemical bath was set to deposit  $Cu_{2,x}S$  films using  $CuSO_4$ and  $Na_2S_2O_3$  solutions as a source of copper and sulphur ions, respectively. Distilled water was prepared at home, while chemically pure reagents were used to prepare reactive solutions. The copper sulphate ( $CuSO_4 \cdot 5H_2O$ , (>99%, Sigma-Aldrich, Germany) and sodium thiosulphate ( $Na_2S_2O_3 \cdot 5H_2O$ , >99%, Sigma-Aldrich, Germany) were used as received. Prior to optimizing the bath conditions, a large number of trials for different conditions with respect to temperature, concentration of ions and pH were carried out. The concentrations of solutions and temperature that yielded superior films, with respect to continuity, smoothness and adherence, were chosen for deposition of the Cu<sub>2x</sub>S film. Firstly, the solutions of copper sulphate (0.2 M, pH 3) and sodium thiosulphate (0.2 M, pH 6.77) were prepared in two separate beakers. Solution pH was measured by using a pH-meter WTW330 with a combinative glass and Ag/AgCl electrode and a temperature meter WTW SenTix 41 (Germany). The chemical deposition bath was prepared in a 250 cm<sup>3</sup> beaker by the sequential addition of 100 cm<sup>3</sup> of copper sulphate and 100 cm<sup>3</sup> of sodium thiosulphate solutions. During and after each addition the mixture was stirred with a glass rod to form a homogeneous solution. The pH of the working solution was 5. The temperature of the bath was increased up to 60 °C. The cleaned PC samples were inserted vertically along the wall of the reactor and were left undisturbed for deposition of Cu<sub>2</sub> S films for 10 min. The colourless solution with time starts turning slowly to grey colour and at the end of the deposition time a black deposit formed both on the PC samples and on the wall of the reactor. At the end of the chosen period of the deposition time, the coated samples were taken out and one sample was set aside, while the rest were immersed again in the freshly prepared chemical bath solution. This procedure was repeated four times thus yielding a total of four Cu<sub>2</sub>S-PC samples. The obtained samples were washed thoroughly with distilled water and dried in a desiccator over anhydrous CaCl, for 24 h. Subsequently films were cleaned with ethanol to remove porous dendrites and then held in a desiccator over the anhydrous CaCl<sub>2</sub>. The Cu<sub>2-x</sub>S films deposited on the PC plates were blackish, homogeneous, spectacularly reflecting with good adherence. The Cu2 S layers formed on the PC plate in each deposition cycle were analysed by optical microscopy, XRD and ATR-FTIR spectroscopy studies and sheet resistivity measurements.

#### Characterisation techniques

Optical microscopy of the samples was carried out by an optical microscope Olympus CX31 (Olympus, Philippines) and a photocamera Olympus C-5050 (Olympus, Japan) magnification  $\times$ 400.

The micro morphology of the PC plates was studied with the NT-206 atomic force microscope (Belarus), in the contact regime with high resolution probes with the force constant k = 3 N/m. The characteristics of the atomic force microscope: the maximum scan field area from  $17 \times 17$  up to  $30 \times 30$  microns, the measurement matrix up to  $512 \times 512$  points and more, the maximum range of measured heights 4 microns, lateral resolution 2 nm, and vertical resolution 0.1–0.2 nm.

FTIR spectra were recorded in the attenuated total reflection (ATR) mode on a Perkin Elmer FTIR Spectrum GX spectrophotometer (USA) by averaging 64 scans with 0.3 cm<sup>-1</sup> resolution in the 400–4000 cm<sup>-1</sup> range.

X-ray diffractometry was carried out under a Brag Brendan circuit on a diffractometer (Dron-6, Russia) using Cu Ka ( $\lambda = 0.154178$  nm) radiation, 30 kV voltage and 30  $\mu$ A current. The scanning range was  $2\theta = 2-60^{\circ}$ . The scanning speed was  $1^{\circ} \cdot \text{min}^{-1}$ . Results were registered in the in situ mode with a computer, and X-ray diffractograms of the samples were treated using the Search Match, Xfit, ConvX, Dplot95, and Excel computer programs.

The sheet resistance of  $Cu_{2-x}S$  layers on the PC plates was measured using the MS8205F (Mastech, China) direct current numerical measuring device with special electrodes. The electrodes were produced from two nickel-plated copper plates. The plates were fixed with 1 cm spacing and the dielectric material was placed between them.

## **RESULTS AND DISCUSSIONS**

#### Characterization of home-made PC plates

The ATR-FTIR spectrum of the polycarbonate plate is presented in Fig. 1. The two methyl groups bonded to carbon atom seven and the hydrogen atoms bonded to the carbons in the two phenol rings generate the first peak in the spectrum, which appears at 2 969 cm<sup>-1</sup>. Similarly, the oxygen atom double bonded to the carbon atom resonates at about 1 776 cm<sup>-1</sup>, generating the signature carbonyl peak in the spectrum. At 1 506 cm<sup>-1</sup>, the resonance frequency of the two phenol rings is reached. Several very strong peaks appear between 1 290 and 1 015 cm<sup>-1</sup>. These are a result of different vibrational modes of the oxygen atoms bonded to the carbon atom. The carbonoxygen stretch typically appears in two or more bands in the range from 1 300 to 1 000 cm<sup>-1</sup>. The last peak at 831 cm<sup>-1</sup> is attributed to the presence of para-substituted phenol rings in the backbone of the polycarbonate polymer [35–36].

Actually, a polymer has two components, the crystalline portion and the amorphous portion. The XRD profile of the PC plate displays four broad peaks: the main one at  $2\theta = 17.15^{\circ}$  and three smaller ones at  $2\theta = 5.65^{\circ}$ ,  $31.45^{\circ}$  and  $42.85^{\circ}$ , respectively, which demonstrates that the polymer is predominantly amorphous in nature with small crystalline regions (Fig. 2).

The average crystallinity of the polymer films is calculated by the following relation [37]:

$$B = \frac{A_0}{A} \times 100\%,\tag{1}$$

where A is the total area of the peaks and  $A_0$  is the area under the diffraction pattern at  $2\theta = 17.15^{\circ}$ .



Fig. 1. ATR-FTIR spectrum of the home-made PC plate

Fig. 2. XRD spectrum of the home-made PC plate

The crystallinity of PC plates was 67.05%.

The main XRD diffraction peak lying between 15 and 20° is usually used to measure the chain–chain separation, and the second broad peak at about 45° is used to estimate the chain length [38–39].

The average chain–chain separation distance in PC was calculated from XDR results using the  $\theta$  value of the main XRD peak centred at  $2\theta = 17.17^{\circ}$  by the Bragg's Law [40]:

$$n\lambda = 2d\sin\theta,\tag{2}$$

where *n* is an integer,  $\lambda$  is the wavelength of incident wave, *d* is the spacing between the planes in the atomic lattice, and  $\theta$  is the angle between the incident ray and the scattering planes.

The average chain-chain spacing was 0.516 nm.

The optical micrograph of the home-made PC plate surface is shown in Fig. 3. The surface of the polycarbonate plate is a very heterogeneous composed of structural features similar to the pores, channels and bumps.



Fig. 3. Optical micrograph of the home-made PC plate surface. Magnification  $\times 400$ 

The AFM image of surface topography gives further support to optical microscopy.

As one can see in Fig. 4, the irregularly sized and shaped grains coalescence forms aggregates (Fig. 4a). The height of aggregates changes from 92 nm to 230 nm and the width of aggregates varies from 1.54 to 3.0  $\mu$ m (Fig. 4b). The appreciable number of bumps is also observed on the polymer surface (Fig. 4a, 4b). The root mean square roughness ( $R_a$ ) is 57.64 nm, while the average roughness ( $R_a$ ) is about 46.56 nm. The  $R_q$  value is greater than  $R_a$ , which supports the rough morphology of PC surface.

## Characterization of Cu<sub>2-x</sub>S film layers deposited on homemade PC plates

In Fig. 5, ATR–FTIR spectra of the  $Cu_{2-x}S$  films deposited on PC are presented. The ATR–FTIR spectra of the  $Cu_{2-x}S$  films deposited on PC are similar with the spectrum of the virgin PC plate (Figs. 1, 5). No new additional peaks, except these corresponding to the virgin PC, appear in the spectra. The intensity of peaks corresponding to the virgin PC plate decreases with a number of deposition cycles (Fig. 5, curves 1–4).

To know the crystalline phase of the deposited films, XRD analysis was carried out. As shown in Fig. 6, the structural properties of layers deposited were greatly influenced by the number of deposition cycles. The intense peaks observed after the fourth cycle indicate that the crystallinity of product increases substantially with the longer exposure time of samples in chemical bath solution. As shown in Fig. 6, the reflections indicating the presence of  $Cu_2S XRD$  patterns along with those of CuS are observed.

The reflection peaks shown in the spectra are mainly indexed as covellite CuS and chalcocite  $Cu_2S$  with a hexagonal unit cell and a monoclinic unit cell, respectively (Table 1).

The CuS phase is found to have a polycrystalline nature and grown with three preferred orientations corresponding to (102), (103) and (006) atomic planes, while the Cu<sub>2</sub>S phase is grown along the (421) plane.



**Fig. 4.** The AFM image of the home-made PC surface: a - 2D topography; b - topography profile taken along the surface reported in 2D image



Fig. 5. ATR-FTIR spectra of the Cu<sub>2-x</sub>S layer deposited on home-made PC plates. Number of deposition cycles: 1 – 1, 2 – 2, 3 – 3, 4 – 4. Exposure time of the samples in a chemical bath solution 10 min. Bath temperature 60 °C



Fig. 6. XRD spectra of the  $Cu_{2-x}S$  layers deposited on the home-made PC plate. Number of deposition cycles: 1 - 1, 2 - 2, 3 - 3, 4 - 4. Exposure time of the samples in a chemical bath solution 10 min. Bath temperature

Table 1. Comparison of the observed and standard "d" values of Cu<sub>2x</sub>S layers deposited on home-made PC plates

	Experimental data	CuS JCPDS#78-876	Cu <sub>2</sub> S JCPDS#33-490	
20	d, nm	hkl	d, nm	d, nm
26.515	0.33588	100	0.32874	
29.030	0.30734	102	0.30509	
30.464	0.29318	014		0.29328
31.596	0.28293	103	0.28164	
32.959	0.27154	006	0.27303	
33.707	0.26568	421		0.26504
34.579	0.25918	104	0.25637	
36.889	0.24346	034		0.24074
37.814	0.23772	105	0.23207	
39.601	0.22739	-152		0.22424
40.797	0.22100	-316		0.22097
43.508	0.20784	008	0.20477	
45.584	0.19884	016		0.19886
46.283	0.19600	-721		0.19610
47.905	0.18973	110	0.18980	
48.837	0.18633	112	0.18490	
53.336	0.17162	114	0.17221	

The average size of nano-crystallites was estimated by the Scherer's formula [41]:

$$D = \frac{k\lambda}{w \cdot \cos\theta},\tag{3}$$

where  $\lambda$  is the X-ray wave length (0.154056 nm), and *k* is the shape factor and the value used in this study was 0.89. *w* is the full-width at half maximum (in radian) and  $\theta$  is the Bragg diffraction angle.

The average grain size for the CuS corresponding to the (103) and for  $Cu_2S$  corresponding to the (421) orientation is about 34.62 and 34.21 nm, respectively.

The optical micrographs of the  $Cu_{2-x}S$  layers surface are shown in Fig. 7.

It can be seen from the micrographs (Fig. 7) that the spherical particles dominate. The size and distribution of particles was determined according to the method described in the paper [42]. We have found that after the first deposition cycle, the particles with a size smaller than 8  $\mu$ m in diameter and few particles in 10–20  $\mu$ m diameters dominate on the polymer surface. After the fourth deposition cycle, an increase of the particle size is observed and particles with the size 13–27  $\mu$ m in diameter dominate (Fig. 8).

On the basis of XRD and optical microscopy results we have proposed a reasonable mechanism for the formation of  $Cu_{2x}S$  layers on the PC plates.

The  $Cu_{2-x}S$  layers synthesis, using  $CuSO_4$  and  $Na_2S_2O_3$  solutions, can be described by a set of concurrent reactions, in-

volving electrons transfer and the ionic species resulted from the precursors' dissociation.

In slightly acidic solutions the reactions mainly responsible for CuS formation can be considered as follows:

$$CuSO_4 + Na_2S_2O_3 \rightarrow Na_2SO_4 + CuS_2O_3,$$
(4)

$$CuS_2O_3 + H_2O \rightarrow CuS + H_2SO_4.$$
(5)

The solubility product for CuS is  $K_{sp} = 1.4 \times 10^{-36}$  [43].

In the copper sulphide deposition process some excess of sodium thiosulphate in the bath solution can form. In the presence of sodium thiosulphate excess the  $Cu^{2+}$  ions are reduced to  $Cu^+$  ions:

$$2\text{CuSO}_{4} + 3\text{Na}_{2}\text{S}_{2}\text{O}_{3} \rightarrow \text{Cu}_{2}\text{S}_{2}\text{O}_{3} + 2\text{Na}_{2}\text{S}\text{O}_{4} + \text{Na}_{2}\text{S}_{4}\text{O}_{6}.$$
 (6)

The reduced Cu<sup>+</sup> ions are complexed by the thiosulphate ions and the soluble  $[Cu_2(S_2O_3)_2]^{2-}$  complex forms:

$$Cu_2S_2O_3 + Na_2S_2O_3 \rightarrow Na_2[Cu_2(S_2O_3)_2].$$
 (7)

In the reaction (5) released sulphuric acid decomposes this complex and a very insoluble Cu<sub>2</sub>S (the solubility product for Cu<sub>2</sub>S is  $K_{sp} = 2.3 \times 10^{-48}$  [43]) forms as follows:

$$Na_{2}[Cu_{2}(S_{2}O_{3})_{2}] + H_{2}SO_{4} \rightarrow$$
  

$$\rightarrow Na_{2}SO_{4} + H_{2}[Cu_{2}(S_{2}O_{3})_{2}],$$
(8)



**Fig. 7.** Top images of the Cu<sub>2-x</sub>S layers obtained on home-made PC plates. Number of deposition cycles: 1 - 1, 2 - 2, 3 - 3, 4 - 4. Exposure time of samples in a chemical bath solution 10 min. Bath temperature 60 °C



**Fig. 8.** Cu<sub>2-x</sub>S particle size and distribution on the home-made PC plate surface. Number of deposition cycles: 1 - 1, 2 - 2, 3 - 3, 4 - 4. Exposure time of the samples in a chemical bath solution 10 min. Bath temperature 60 °C

Table 2. De	ependence of the Cu.	S la	ver structure and sheet resistance	e on t	the number (	of de	position c	vcles

Number of deposition cycles	Cu <sub>2-x</sub> S layer structure	Sheet resistance, kΩ/cm²		
1	Amorphous	Not measured		
2	Amorphous	Not measured		
3	Amorphous	43.48		
4	Crystalline (CuS and Cu <sub>2</sub> S phases)	1.13		

$$H_{2}[Cu_{2}(S_{2}O_{3})_{2}] \to H_{2}SO_{4} + SO_{2} + S + Cu_{2}S,$$
(9)

$$SO_2 + S + H_2O \rightarrow H_2S_2O_3.$$
(10)

In the reactions (4)–(10) negatively charged particles of copper sulphide were produced [14]. When they are formed in situ (i. e. in contact with the PC surface), electrostatic interactions between colloidal sulphide particles and the charged sites of the polymer take place, providing sulphide adhesion to the polymeric surface. In this formation process, time is the most important controlling factor. Such a process is consistent with the previous reports of the so-called two-stage growth process, which involves a fast nucleation of amorphous primary particles followed by a slow aggregation and crystallization of primary particles [44].

The sheet resistance of  $Cu_{2-x}S$  layers, deposited on the home-made PC plates surface, was measured at room temperature. The surface sheet resistance depends on the number of deposition cycles (Table 2).

As expected, the higher number of deposition cycles the lower sheet resistance. Considering also the optical microscopy analysis, this fact is not assigned to a higher conductivity of the  $Cu_{2-x}S$  deposit itself, but suggests a more homogeneous layer surface, with interconnected  $Cu_{2-x}S$  particles which provide the current flow between the probes of measurement.

## **CONCLUSIONS**

The Cu<sub>2-x</sub>S layers were successfully obtained on the homemade PC plates by a chemical bath deposition technique at 60 °C temperature from slightly acid solutions of copper sulphate and sodium thiosulphate without previous pre-treatment of the polymer. The structure, composition and sheet resistance of the layers depend on the number of deposition cycles. The structure of Cu<sub>2-x</sub>S layers changes from amorphous in the first cycle to polycrystalline in the fourth cycle. The XRD analysis confirmed a formation of covellite CuS and chalcocite  $\text{Cu}_2\text{S}$  with a hexagonal unit cell and a monoclinic unit cell, respectively. The room temperature sheet resistance of  $\text{Cu}_{2x}\text{S}$  layers deposited on the PC plate is 1.13 k $\Omega/\text{cm}^2$ .

> Received 14 April 2014 Accepted 29 April 2014

#### References

- J. H. Rhee, Y. H. Lee, P. Bera, S. I. Seok, *Chem. Phys. Lett.*, 477, 345 (2009).
- 2. Y. Bessekhouad, R. Brahimi, F. Hamdini, M. Trari, J. Photochem. Photobiol. A: Chem., 248, 15 (2012).
- G. Mao, W. Dong, D. G. Kurth, H. Möhwald, *Nano Letters*, 4(2), 249 (2004).
- 4. J. S. Chung, H. J. Sohn, J. Power Sources, 108, 226 (2002).
- Y. Han, Y. P. Wang, W. H. Gao, et al., *Powder Technol.*, 212, 64 (2011).
- C. H. Lai, K. W. Huang, J. H. Cheng, C. Y. Lee, B. J. Hwang, L. J. Chen, *J. Mater. Chem.*, **20**, 6638 (2010).
- H. J. Lee, S. W. Yoon, E. J. Kim, J. Park, *Nano Lett.*, 7, 778 (2007).
- Y. Myung, D. M. Jang, Y. J. Cho, et al., *J. Phys. Chem. C*, 113, 1251 (2009).
- I. Grozdanov, M. Najdoski, J. Solid State Chem., 114, 469 (1995).
- J. Yu, J. Zhang, S. Liu, J. Phys. Chem. C, 114(32), 13642 (2010).
- 11. S. V. Taur, R. A. Joshi, A. V. Ghule, R. Sharma, *Renew. Energ.*, **38(1)**, 219 (2012).
- W. Liang, M. H. Whangbo, Solid State Commun., 85(5), 405 (1993).
- 13. M. T. S. Nair, P. K. Nair, Semicond. Sci. Technol., 4, 191 (1989).
- M. H. Kunita, E. M. Girotto, E. Radovanovic, et al., *Appl. Surf. Sci.*, **202**, 223 (2002).
- R. D. Engelken, H. E. McCloud, J. Electrochem. Soc., 132(3), 567 (1985).
- S. Lindroos, A. Arnold, M. Leskelä, *Appl. Surf. Sci.*, **158(1)**, 75 (2000).
- 17. P. Parreira, G. Lavareda, A. Amaral, et al., *J. Alloys Compd.*, **509(16)**, 5099 (2011).
- 18. I. P. Parkin, Chem. Soc. Rev., 25, 199 (1996).
- X.-S. Du, M. Mo, R. Zheng, S.-H. Lim, Y. Meng, Y.-W. Mai, Cryst. Growth Des., 8, 2032 (2008).
- Y. Li, W. Lu, Q. Huang, M. Huang, C. Li, W. Chen, Nanomedicine, 5(8), 1161 (2010).
- 21. S. Ramadan, L. Guo, Y. Li, B. Yan, W. Lu, *Small*, **8(20)**, 3143 (2012).
- 22. H. Zhu, J. Wang, D. Wu, Inorg. Chem., 48(15), 7099 (2009).
- 23. M. Kruszynska, H. Borchert, A. Bachmatiuk, et al., *ACS Nano*, **6**, 5889 (2012).
- X. Zheng, Q. Hu, Appl. Phys. A: Mater. Sci. Process., 94, 805 (2009).
- 25. Q. Y. Lu, F. Gao, D. Y. Zhao, Nano Lett., 2(7), 725 (2002).
- 26. P. Roy, S. K. Srivastava, Cryst. Growth Des., 6(8), 1921 (2006).
- 27. F. Caruso, R. A. Caruso, H. Mohwald, *Science*, **282**, 1111 (1998).

- 28. H. Hu, P. K. Nair, Surf. Coat. Technol., 81, 183 (1996).
- 29. V. Krylova, N. Dukštienė, Pol. J. Chem., 80(9), 1435 (2006).
- V. Krylova, M. Andrulevičius, *Int. J. Photoenergy*, DOI: 10.1155/2009/304308 (2009).
- J. Cardoso, O. Gomez-Daza, L. Ixtlilco, M. T. S. Nair, P. K. Nair, *Semicond. Sci. Technol.*, 16, 123 (2001).
- P. Pramanik, S. Bhattacharya, J. Mater. Sci. Lett., 6, 1105 (1987).
- V. Krylova, N. Dukštienė, J. Chem., DOI:10.1155/2013/ 987879 (2013).
- Y. Tokiwa, in: S. Matsumura, A. Steinbuchel (eds.), Miscellaneous Biopolymers and Biodegradation of Polymers, Vol. 9, WILEH-VCH Verlag GmbH, Weinheim (2002).
- R. G. Kraus, E. D. Emmons, J. S. Thomson, A. M. Covington, J. Polym. Sci. B, 46, 734 (2008).
- G. Mitchell, F. France, A. Nordon, P. L. Tang, L. T. Gibson, *Heritage Sci.*, 1, 28 (2013).
- A. M. P. Hussain, A. Kumar, F. Singh, D. K. Avasthi, J. Phys. D: Appl. Phys., 39, 750 (2006).
- H. M. El Ghanem, S. A. Saqa'n, M. Al Saadi, S. M. Abdul Jawad, *J. Modern Phys.*, 2, 1553 (2011).
- H. M. El Ghanem, H. Attar, H. Sayid Ahmad, S. Abduljawad, *Int. J. Polymer. Mater.*, **55(9)**, 663 (2006).
- H. P. Klug, L. R. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 2nd ed., Wiley Interscience, John Wiley & Sons (1974).
- B. D. Cullity, S. R. Stock, *Elements of X-ray Diffraction*, 3rd ed., Prentice Hall, New York (2001).
- A. Šileikaitė, J. Puišo, I. Prosyčevas, S. Tamulevičius, *Materials Science (Medžiagotyra)*, 15(1), 21 (2009).
- R. A. Lidin, L. L. Andrejeva, V. A. Molochko, *Reference Book on Inorganic Chemistry*, Khimiya, Moscow (1987) (in Russian).
- C. Burda, X. B. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.*, **105(4)**, 1025 (2005).

### Valentina Krylova, Nijolė Dukštienė, Igoris Prosyčevas

## VARIO SULFIDŲ SLUOKSNIŲ ANT SAVADARBIŲ POLIKARBONATO PLĖVELIŲ NUSODINIMAS IR APIBŪDINIMAS

#### Santrauka

Polikarbonato (PC) plėvelės laboratorijoje išlietos iš granulių ir apibūdintos optinės mikroskopijos, atominių jėgų mikroskopijos, rentgeno struktūrinės fazinės ir IR spektroskopinės analizės metodais. Vario sulfidų ( $Cu_{2,x}$ S) sluoksniai šių PC plėvelių paviršiuje suformuoti cheminio nusodinimo metodu naudojant 60 °C temperatūros vario sulfato ir natrio tiosulfato, kuris yra ne tik sulfido jonų šaltinis, bet ir kompleksadaris, vandeninius tirpalus. Nustatytas vario sulfidų sluoksnių formavimosi mechanizmas. Rentgenostruktūrinė fazinė analizė parodė, kad nusodinti sluoksniai sudaryti iš heksagonalinio kovelito (CuS) ir monoklininio chalkocito ( $Cu_2$ S). Išmatuota šių sluoksnių paviršiaus elektrinė varža lygi 1,13 k $\Omega$ /cm<sup>2</sup>.