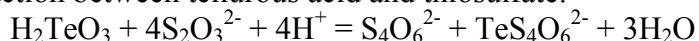


THE DIFFERENT SPECIES OF TELLUROPENTATHIONATES AS PRECURSORS FOR FORMATION OF COPPER CHALCOGENIDES LAYERS ON THE SURFACE OF POLYAMIDE

Judita Sukyte, Skirma Žalėnkiėnė, Remigijus Ivanauskas, Vitalijus Janickis
 Department of Inorganic chemistry, Kaunas Technological University, Radvilėnu pl. 19,
 LT – 50254 Kaunas, Lithuania, judita.sukyte@ktu.lt

Metal chalcogenides semi – conducting materials have found many applications in opto – electronic, solar cell and photovoltaic devices. There have been a wide variety of techniques for the formation thin layers of copper chalcogenides on various dielectrics, and on the polymers too. There is presently great interest in the development of low – cost and simple processing methods. Our approach follows the sorption – diffusion process described previously [1-2].

This method uses a single-source molecular precursor which are introduced into the simple reactor and undergo diffusion – sorption on a substrate surface followed by reaction with copper salts to give the copper chalcogenide along with desorption of any by-products. The different species of telluropentathionate as source for S and Te have been applied in our work. The salts of sodium or potassium telluropentathionate, Na₂TeS₄O₆·2H₂O, K₂TeS₄O₆·2H₂O, have been prepared according to published procedures [3] by means of the Norris and Fay reaction between tellurous acid and thiosulfate:



Monotelluropentathionic H₂TeS₄O₆ acid has been isolated from its barium salt BaTeS₄O₆·2H₂O in the reaction with sulfuric acid [2].

Polyamide as semi-hydrophilic polymer due to multifunctional chelating groups, namely carboxylic and amido, sorbs telluropentathionate ions containing a mixed chain of three divalent chalcogen atoms –O₃S–S–Te–S–SO₃– from their solutions [3]. The dimensions of unit cell of *trans* form of telluropentathionate ion are: a = 5.043, b = 10.434, c = 22.372 Å [4]. The interaction of Cu(II/I) salt with the sorbed telluropentathionate ions leads to the formation of mixed copper chalcogenides layers with various chemical, phase composition (Fig. 1), surface morphology (Fig. 2) and electrical resistance (Table).

The surface morphology and structure were observed by AFM [Fig. 2]. In dependence of the exposure in the precursor solution, the layers of chalcogenides with various thicknesses might be formed. CuTe and CuS interface appears graded with substantial interdiffusion between the layers. The islands observed due to surface roughness.

The resistances of the copper chalcogenides on PA formed using different species of telluropentathionates decreases from 1.80×10³ to 1.2-2.9 kΩ/□ as the content of tellurium increases from 0.15 to 0.74 - 0.84 μmol/cm². The increase of Te content results in the increase of film thickness (from 250 nm for 0.14 μmol/cm² Te to 2.7 μm for 0.7-0.8 μmol/cm² Te). This factor partly counteracted the increase of conductivity caused by the increase of Te content.

The careful choice of the treatment methods using the different forms of telluropentathionates as precursors enable us to form electrically conductive or semiconductive copper sulfides – tellurides layers and establish the regularities of their formation.

References:

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- [4] Maroy K. 1975. Crystal structures of Penta-, Selenopenta-, Telluropenta-, and Hexathionates. Doctoral thesis, Bergen.

Table. The content of Te and the resistance of the copper chalcogenides layers on PA surface

Exposure, h	Te content ($\mu\text{mol}/\text{cm}^2$) in PA surface			Sheet resistance ($\text{k}\Omega/\square$) of PA exposed at 20° in $0.1\text{mol}\cdot\text{dm}^{-3}$		
	$\text{Na}_2\text{TeS}_4\text{O}_6$	$\text{K}_2\text{TeS}_4\text{O}_6$	$\text{H}_2\text{TeS}_4\text{O}_6$	$\text{Na}_2\text{TeS}_4\text{O}_6$	$\text{K}_2\text{TeS}_4\text{O}_6$	$\text{H}_2\text{TeS}_4\text{O}_6$
0.5	0.147	0.067		1.19×10^3	256.43	
1.0	0.160	0.189	0.147	360.4	41.444	1.80×10^3
2.0	0.154	0.268	0.247	623.9	9.85	4.34×10^3
3.0	0.359	0.364	0.324	5.30	9.89	243-893
12	0.450	0.775	0.828		1.57	1.19
24	0.764	0.826	0.742		2.92	1.43

Figures:

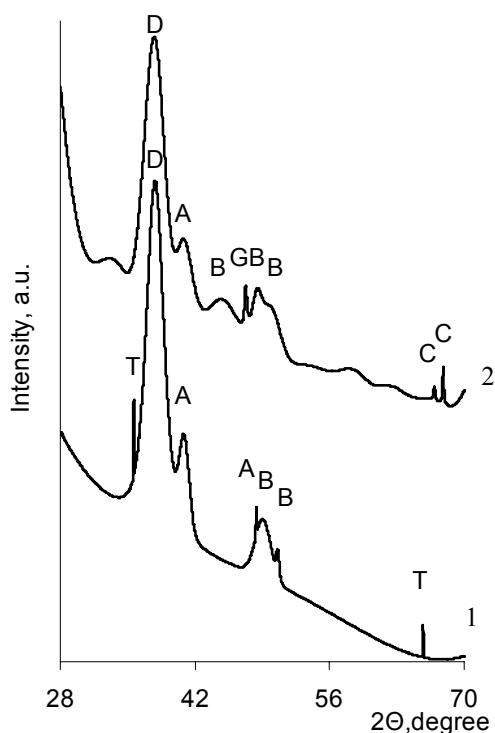


Fig. 1

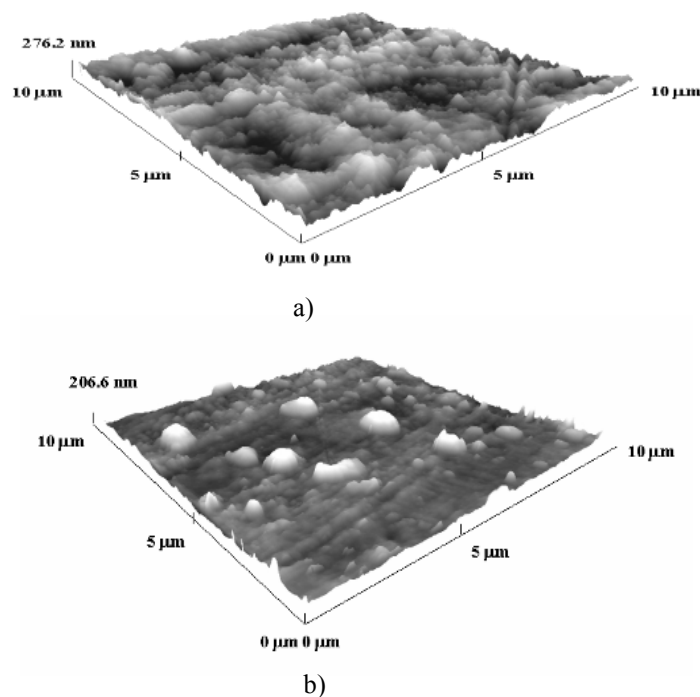


Fig. 2

Fig.1. X-ray diffraction patterns (A – anilite Cu_7S_4 , D – djurleite $\text{Cu}_{1.9375}\text{S}$, S – digenite $\text{Cu}_{1.8}\text{S}$, C – hexagonal copper telluride Cu_2Te , T – tetragonal copper telluride $\text{Cu}_{3.18}\text{Te}_2$, B – vulcanite CuTe , E – copper telluride $\text{Cu}_{2.72}\text{Te}_2$) of chalcogenides layers on PA treated 3h at 20°C in $0.1\text{mol}\cdot\text{dm}^{-3}\text{H}_2\text{TeS}_4\text{O}_6$ (1); $0.1\text{mol}\cdot\text{dm}^{-3}\text{Na}_2\text{TeS}_4\text{O}_6$ solution in $0.2\text{mol}\cdot\text{dm}^{-3}\text{HCl}$ (2)

Fig. 2. AFM top view of copper chalcogenides layers on PA treated:
 a) 3 h at 20°C in $0.1\text{mol}\cdot\text{dm}^{-3}\text{Na}_2\text{TeS}_4\text{O}_6$ solution at 276.2 nm;
 b) 24 h at 20°C in $0.1\text{mol}\cdot\text{dm}^{-3}\text{H}_2\text{TeS}_4\text{O}_6$ at 206.6 nm