CHARACTERIZATION OF THIN FILMS OF COPPER CHALCOGENIDES ON POLYMERS FORMED USING SELENIUM AND TELLURIUM POLYTHIONATES

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Department of Inorganic Chemistry of Kaunas University of Technology (KTU, Lithuania) during long period of time deals mainly with the chemistry of chalcogens - sulfur, selenium and tellurium. During last three decades and at present an object of our applied and theoretical studies is the mechanism of chalcogen compounds' reactions, synthesis and study of derivatives of hydrides of chalcogens (H_2S_x, H_2Se_x ,H_2Te_x), use of polychalcogen compounds.

During last decade exceptionally interesting property of compounds rich in low oxidation state chalcogen atoms (particularly of polysulphides, polythionates and seleno- and telluropolythionates) was found – they act as chalcoganating agents towards dielectrics (polymers, plastics, glass, amorphous silicon). Further interaction of chalcogenized dielectrics with copper (I/II) salt solution leads to the formation of Cu_xS ,Cu_xSe, Cu_xTe and mixed - Cu_xS-Cu_ySe and Cu_xS-Cu_yTe thin films, which have different electric transport properties, e.g. are semiconductors or electrical conductors.

The preparative conditions such as concentration, an exposure time were optimised to get good quality selenium, tellurium and sulfur thin films on the polymer- polyamide PA surface at room temperature using alkaline metals salts of selenium- and telluropentathionates [1]. The selenopentathionate $SeS_4O_6^{2-}$ and telluropentathionate $TeS_4O_6^{2-}$anions are sorbed−diffused into PA after an exposure in acidified with hydrochloric acid solutions, respectively, of potassium selenopentathionate, $K_2SeS_4O_6$, and sodium telluropentathionate, $Na_2TeS_4O_6$. The telluropentathionic acid $H_2TeS_4O_6$ also was used as a new precursor of Te and S for the formation of thin films of chalcogens on the PA surface. The formation of thin film of chalcogens from $H_2TeS_4O_6$ solution has recently attracted interest, because the stability of $TeS_4O_6^{2-}$ anion offers many advantages over the more established sources such as its alkaline metals salts solutions [2].

The intensity and amounts of sorbed chalcogens increases with increase of the concentration of precursors solutions, exposure time and temperature. The copper chalcogenides layers forms in the surface of PA when the chalcogenized polymer is treated with the water solution of copper (II/I) salt: the anionic particles containing chalcogens atoms of low oxidation state reacts with the copper ions.

Some structural properties and electrical resistance's values of obtained films have been investigated also. The stoichiometry of prepared Cu-Se-S and Cu-Te-S films was established by UV-Visible and AA spectrometry analysis [3, 4].

The results of X−ray structural analysis confirmed the formation of mixed copper sulfide, copper selenide and copper telluride layers in the surface of PA [4]. The phase composition of layers depends on the duration of initial treatment in precursors

solution: Cu_xS-Cu_ySe layers are composed of a little conductive *chalcocite*, Cu_2S, electrically conductive *digenite*, $Cu_{1,8}S$, *djurleite*,, $Cu_{1,9375}S$, *anilite*, $Cu_{1,75}S$, and of copper selenides – *bellidoite*, Cu_2Se, *umangite*, Cu_3Se_2, *klockmannite*, CuSe, *krutaite*, $CuSe_2$ and Cu_2Se_x [5]. X-ray diffraction measurements showed that samples of prepared Cu-Te-S thin films of different compositions are polycrystalline and many of them have some binary phases such as Cu_2Te, $Cu_{3-\delta}Te_2$, $Cu_{2-\delta}S$. The phases of tetragonal copper telluride, $Cu_{2.72}Te_2$, orthorhombic *vulcanite ,* CuTe, orthorhombic *anilite,* Cu_7S_4 and *digenite,* $Cu_{1.8}S$, were found [3].

Therefore the phase composition determines the electrical characteristics of the films: the electrical resistance varies from 12, 2 Ω/□ to 4, 8 MΩ/□. Cu-Te-S polymer composites indicate p-type electricity conductive properties and have electrical resistance in the range of $1.5 \cdot 10^{-3}$-$4.0 \cdot 10^{-3}$ Ω/□ to 3-5 Ω/□ after to 2-3 hours of an exposure in 0.05-0.1mol.dm^{-3} solutions of $Na_2TeS_4O_6$, and 1.0-1.5 Ω/□ after 24-72 hours of exposure in 0.05-1mol.dm^{-3} solutions of $Na_2TeS_4O_6$.

The determination of layers composition (in depth to 1 nm) studied by the method of X-ray photoelectron spectroscopy confirmed the formation of copper sulfides, selenides and tellurides of various phases. The regularities determined enables the formation by modified sorption–diffusion method of mixed copper chalcogenides thin films with predicted composition and electrical and optical properties.

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