

Electrochromic Film Based on a-WO₃ Obtained by Sol-gel

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The influence of changes in the conditions of sol-gel method on the thermal characteristics and the structure electrochromic (EC) a-WO₃ films. DSC data showed greater sensitivity of the structure to the peculiarities of the drying of the product poliperoxo-tungstic acid. The Films were transparent over a wide range ($E_g = 2,5$ eV). All compositions were amorphous as measured by X-rays diffraction. Based on the IR and Raman spectroscopy dates was concluded the presence in the structure of amorphous transparent glassy semiconductor a-WO₃ predominantly tetrahedral [WO₄] groups. The precursor product and EC-films are glass material, obtained by the sol-gel process, with the composition WO₃* × H₂O. Synthesis peculiarities of mesoporous a-WO₃. affects both the pore structure, which determines the concentration of the aqueous components and the ratio of the bridging W-O-W and unbridged W = O bonds, defining characteristics of the electrochromic materials.

Keywords: Electrochromic films, Mesoporous amorphous WO₃ (a-WO₃), The sol-gel process, Raman scattering, X-ray diffraction.

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1. INTRODUCTION

To date, the electrochromic properties of organic and inorganic polymers are attracted a lot of attention because the possibility of their application for the creation of energy efficient windows or other devices for the modulation of the light flux. Good electrochromic properties possess a thin amorphous layers of WO₃ and MoO₃, crystalline Nb₂O₅, PB (Prussian blue), PANI and its derivatives. Numerous studies have shown that amorphous tungsten oxide (a-WO₃), is the best EC inorganic materials. Therefore, to date, WO₃ is an fragment of EC devices (including windows). Obviously, the methods of making films influence to the structure and properties of EC-material. The main traditional methods are vacuum magnetron sputtering, and the electrochemical method cathode-deposition [1].

The structure and composition of a-WO₃ is of interest both from the point of view of the influence on the EC-property and common understanding of the structure of amorphous transition metal oxides with octahedral short-range order in the crystalline state. In the absence of long-range order in the amorphous film, it is important information about the short-range order and the characteristics of the relative location of major structural units at different ways of producing films.

Previously, the structure of EC films were considered in [2, 3] by X-ray and electron diffraction, Raman scattering, [4] and nuclear and transmission electron microscopy [5]. Based on the analysis of the radial distribution function has been postulated that amorphous films as well-WO₃, obtained by thermal evaporation in a vacuum and cathode-reactive evaporation at low pressure gas mixture, are build by contained octahe-

dral WO₆, connected vertices. TEM data have been interpreted as the formation of crystallites with dimensions of up to 10 Å, and their size increases for heating. The assumption about existence in the structure of a-WO₃ nanocrystalline structures of the hexagonal structure result from Raman scattering interpretation. The density of the films was 6.0 g/cm³, which is 15 % lower than the density of the crystalline tungsten oxide.

This study offers new data and their interpretation by the thermal behavior of a-WO₃, obtained by the sol-gel technology. In particular, the drying process (transition of the sol-gel-solid amorphous semiconductor) and its influence on the sol to form a working electrode EC are investigated.

The process of preparation of electrochromic films by sol-gel method is the most promising approach, both in terms of ease of technology and, consequently, the cost of the coating, and from the point of view of structural perfection of electrochromic layers due to the chemical and structural homogeneity, which are characteristic for the chemical assembly, as well as the possibilities of modifications of the chemical composition.

2. EXPERIMENTAL

2.1 Synthesis

In our work we used the WC powder brand CRC030-040 (Germany), featuring high chemical purity and uniform dispersity (grain size 0.7-1.0 mm). This method of producing films WO₃ is the most tech-tech. Technology for producing transparent films of tungsten oxide consisted of the following stages:

- producing of product poliperoxo-tungstic acid

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($\text{WO}_3 \cdot n\text{H}_2\text{O}_2 \cdot n\text{H}_2\text{O}$), centrifugation and filtration.

- The process of evaporating the solution of PTA. Solution was heated to 70-80 °C, as result poliperoxopolytungstic acid was formed (PPTA).

- Drying evaporated solution. In the course of processing, drying conditions was tested two methods of drying: drying drop method on a window glass at – temperature 45 °C-85 °C and vacuum drying (cryogenic and rotary).

2.2 Instrumentation

Measurements of differential scanning calorimetry (DSC) were carried out by differential scanning calorimeter STA 449F1 Jupiter firm Nietzsche X-ray diffraction analysis was performed on the X-ray diffractometer with a general purpose «Rigaku Ultima IV» CuK α using radiation and the detector D/teX Ultra.

3. RESULTS AND DISCUSSION

This paper describes the features of the first stage of the process of obtaining EC films by sol-gel technology, namely the influence of temperature and time of the drying precursor product. A film deposition technology- WO_3 includes two stages: 1 – formation of the precursor-product (a vitreous- WO_3); 2 – preliminary dissolution of the this product and create a uniform suspension, applying it on the electroconductive layer and the creation of a uniform transparent solid mesoporous film.

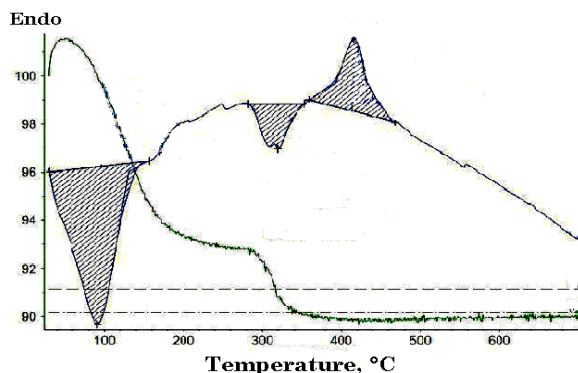


Fig. 1 – DSC films WO_3 , obtained at different drying conditions: 1 – Drop-coating 2 – vacuum rotary, 3 – in weighing bottle (thick layer), 4 – vacuum (cryogenic)

3.1 Differential Scanning Calorimetry

Fig. 1 shows a DSC curve of four different preparing conditions of the product at the first stage. Obviously, drying conditions are very much influenced by the concentration of H_2O and OH-groups of different kinds. The main effects are common to all cases of preparation.

General rules:

1. In the range of $T = 30^\circ\text{--}180^\circ\text{C}$ is observed intensity endothermic effect associated with weight loss. Apparently, this care unbound water from the molecular pore structure.

2. The second endothermic effect is observed at 300 °C. For the compositions of the present low intensity before him exoeffect. This effect is accompanied by weight loss (about 2-4 wt %) and it is associated with loss of-OH groups.

3. At temperatures of 410-440 (maximum) observed exotherm (crystallization), and the specific enthalpy depends on the initial composition. It also is a little noticeable decrease in weight (less than 0.5 %).

General view of a DSC curves are typical for a conventional glassy materials, prepared by high melting temperature prpcess, however, there are additional thermal effects due to loss of "water" present in the pores and film- WO_3 .

3.2 X-ray Diffraction

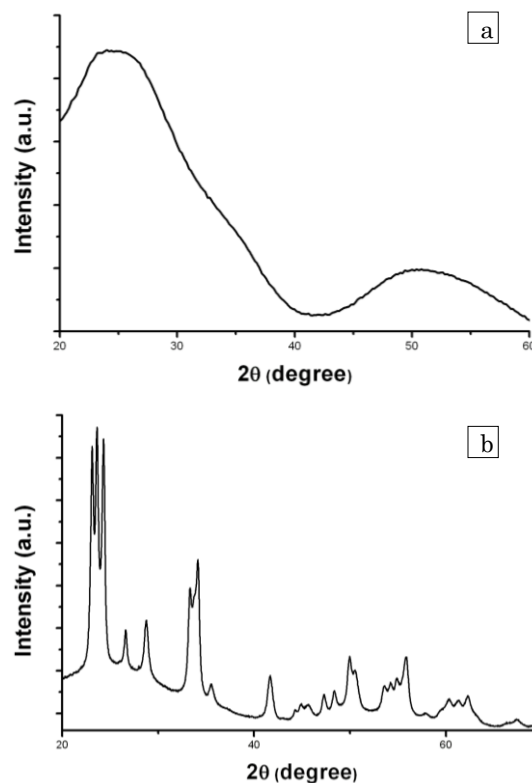


Fig. 2 – X-ray diffraction of the film obtained by sol-gel deposition from (a), this film after heat treatment at $T = 415^\circ\text{C}$ for $t = 2$ hours (b)

X-ray diffraction of the film obtained by sol-gel deposition confirms the amorphous the dried products regardless of the method of drying (Fig. 2a). XRD of the films after treatment at 415 °C for $t = 2$ hours (b) is demonstrated peaks due crystalline WO_3 in modification alpha- WO_3 .

3.3 Vibrational Spectroscopy

Analysis of the Raman spectra of the films a- WO_3 (Fig. 3a), obtained at different drying methods, clearly indicating a predominant presence in the films tungstate tetrahedra. Most intense in the Raman is the band 970 cm^{-1} is due to the nonbridging vibration ν_1 (A1) tungstate tetrahedron bound in chain structures, the band 570 cm^{-1} is due to a bridging vibration W-O-W. In the range of $700\text{--}900\text{ cm}^{-1}$ bands: 720, 827, 850, 890 cm^{-1} are observed. According to our interpretation, the bands 850 and 827 cm^{-1} are associated with the removal of degeneracy with the asymmetric vibrations ν_3 (F2) [WO_4]. Bands 720 and 890 cm^{-1} can be attributed to the tungstate octahedra vibrations which

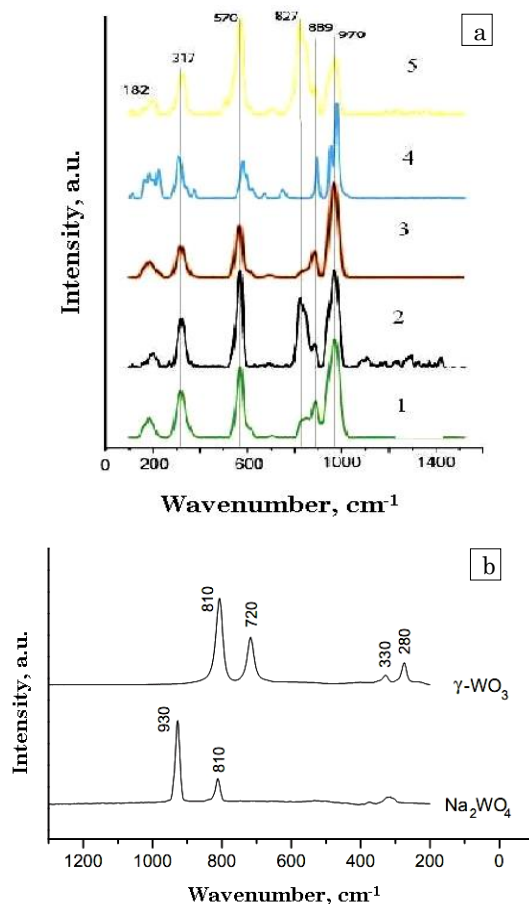


Fig. 3 – Raman spectra of the films obtained at different drying methods: a) 1 – drop drying $T=65^\circ\text{C}$, 2 – drop drying $T=85^\circ\text{C}$, 3 – vacuum rotary drying, 4 – adding a solution of 10 mol. % Acetic acid, drop-drying; 5 – drop dry (starting material – tungsten metal); b) the Raman spectra of the crystalline WO_3 in hexagonal modification (octahedra) and sodium tungstate (isolated tetrahedra)

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are also present in small concentration in the glass network. Concentration tungstate octahedra seem to affect the pore structure formed, which in turn determines the rate of solubility of the product in alcohol.

4. CONCLUSION

All compositions were amorphous as measured by X-rays diffraction and transparent over a wide range ($E_g = 2,5$ eV). The produced product is glassy material obtained by the sol-gel process, with the composition of $\text{WO}_3^* \times \text{H}_2\text{O}$. DSC data showed greater sensitivity to the peculiarities of the structure of the drying of the poliperoxopolytungstic acid product. Based on the IR and Raman spectroscopy data was concluded the presence in the structure of amorphous transparent glassy semiconductor α - WO_3 predominantly tetrahedral $[\text{WO}_4]$ groups. Synthesis peculiarities of mesoporous α - WO_3 affects both the pore structure, which determined the concentration of the aqueous components, and the ratio of the bridging W-O-W and nonbridging W = O bonds and, is defined characteristics of the electrochromic materials. We have considered the questions of technology of electrochromic films- WO_3 producing which are closely related to the structural features of products. The complexity of the interpretation of the structure of drying product (glassy- WO_3) presumes the deepening of research in this direction.

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