Impedance spectroscopy of electrochromic films of nanocrystalline tungsten (VI) oxide

A V Shchegolkov¹, E N Tugolukov, A V Shchegolkov and V S Yagubov

Department of Technology and Methods of Nanoproducts Manufacturing, 
Tambov State Technical University, 106 Sovetskaya Street, 392000 Tambov Russian Federation

¹E-mail: alexxx5000@mail.ru

Abstract. The present paper study electrochromic films of nanocrystalline tungsten oxide (VI) by electrochemical impedance spectroscopy. Electrochromic films were obtained using the simplified technique of deposition of tungsten (VI) oxide from an aqueous dispersion on surface of transparent electrode In₂O₃. To obtain a uniform composition, the aqueous dispersion was treated with ultrasonic radiation, while the average particle size of tungsten oxide in the dispersion volume was from 30 to 70 nm. The prepared films had an amorphous structure and a crystalline structure was obtained by pyrolysis at a temperature of 250, 300, and 400 °C corresponding to different samples. The obtained nanocrystalline films were studied by electrochemical impedance spectroscopy in the frequency range from 1 to 10⁶ Hz with an amplitude of an alternating voltage of 10 mV to determine the effect of temperature on the impedance of the films. The analysis data allowed us to determine the dependence of electrical conductivity on the volume of grains and the boundaries between crystals on the influence of temperatures on the structure properties of electrochromic films of nanocrystalline tungsten (VI) oxide.

1. Introduction

Transition metal oxides are one of the most common materials of micro- and optoelectronics [1-3]. The main characteristic of the material determining its physicochemical properties (optical, electronic, electrochemical, etc.) is the structure. Amorphous and crystalline films of metal oxides are known. Most transition metal oxides are dielectrics, but under certain conditions associated with structural changes, they become semiconductors, and with the addition of a conductive additive, they acquire electronic conductivity [4,5].

Currently, researchers are focused on the study of the electrochromic properties of transition metal oxides of materials and their application in various optoelectronic devices [6-8]. Among these materials, tungsten (VI) oxide (WO₃) is a well-known electrochromic oxide of n-type semiconductor, which attracts great scientific interest due to its physicochemical properties and numerous potential applications: smart windows, displays, sensors, thermoelectric devices and ferroelectric application [9,10].

By its nature of WO₃ is an insulator with a band gap of 3 eV [11,12], but when a stoichiometric state changes it becomes a semiconductor. The amorphous or crystalline structure of WO₃-based thin-film devices for micro- and optoelectronics as a result is determined by the production technology, cost, and operating conditions of the manufactured device. Amorphous WO₃ films are more studied and have the
greatest distribution due to low-temperature production methods, which makes their manufacture cheaper. Crystalline films of WO$_3$ can be used for light filters [13]. Further development of WO$_3$ electrochromic film technology involves the use of nanosized oxide powder to form nanocrystalline electrochromic films.

In this regard, the main aim of the present research was to study WO$_3$ nanocrystalline electrochromic films using cheap sputtering and pyrolysis technology (at temperature of 250, 300, and 400 °C) on conductive ITO glass and studying the impedance by electrochemical impedance spectroscopy (EIS).

2. Materials and methods

Electrochromic films of nanopowder WO$_3$ (Sigma-Aldrich, Germany) were produced by the spray pyrolysis technique to temperatures 250, 300 and 400 °C. Particle size of nanopowder WO$_3$ <100 nm (TEM) [13]. Schematic crystal lattice of WO$_3$ nanopowder below shows (figure 1). The physical basis of the method is written in detail [14]. In the temperature range from +890 to –190 °C, tungsten (VI) oxide has five polymorphic modifications (figure 1), in which the crystal lattice symmetry varies from tetragonal to monoclinic [11]:

\[
D^7_{4h} \xrightarrow{737 \text{ °C}} D^6_{2h} \xrightarrow{327 \text{ °C}} C^5_{2h} \xrightarrow{27 \text{ °C}} C^1_2 \xrightarrow{-43 \text{ °C}} C^2_5.
\]

![Figure 1. View of crystalline structure of WO$_3$.](image1)

![Figure 2. Hexagonal structure of WO$_3$ formed at temperature 250 and 300 °C.](image2)

At temperatures from 250 to 400 °C, the hexagonal structure of WO$_3$ is formed (figure 2), the best electrochromic properties of which are characteristic of this structure [2]. When the temperature rises above 400 °C, the ITO conductive electrode degradation.

2.1. The method spray pyrolysis for preparation electrochromic thin films based of WO$_3$

The metal nanopowder of the electrochromic compound WO$_3$ was added to water (0.05 g/ml) and then dispersed in an ultrasonic unit (UP200S, Germany) for 5 min. until the complete distribution of nanoparticles in the water volume. The electrochromic composition was applied to a transparent In$_2$O$_3$ (ITO) electrode (Sigma-Aldrich, Germany) using a spraying machine. The surface of the ITO electrode was cleaned with isopropyl alcohol and washed with distilled water before applying the electrochromic composition. In the next step, the electrochromic coating was annealed in a vacuum oven at a temperature of 250, 300, and 400 °C for 24 h before the formation of films. As a result, films with an average WO$_3$ particle size of 50 nm were obtained due to the insolubility of the metal nanopowder in water.

2.2. Method EIS for the prepared electrochromic films

The EIS was measured in a classical three-electrode electrochemical cell (figure 3-4) in the frequency range (ω) from 1 to 106 Hz with an amplitude of an alternating voltage of 10 mV using a potentiostat (PalmSens 4, Holland) of an electrochemical measuring complex, as a reference electrode (RE) we used the classic electrode Ag/AgCl in 3 M KCl (BVT Technologies, Czech). The films obtained on a glass substrate were used as a working electrode (WE) in a three-electrode system in figure 4.
Figure 3. Schematic three-electrode cell: WE-working electrode; RE-reference electrode; CE-Counter electrode.

Figure 4. Three-electrode electrochemical system for researching electrochromic films of WO₃ in 0.01 M H₂SO₄ and reference electrode by Ag/AgCl 3 M KCl.

The size of the substrate base on ITO-glass was 0.2×0.8 cm and the Pt-wire (d~1 mm) was the auxiliary electrode (CE). All impedance measurements for the WO₃ electrochromic film were made in 0.01 M H₂SO₄ electrolyte relative to the Ag/AgCl reference electrode in 3 M KCl. The measurement data were recorded after the electrode was kept in solution to establish a quasistationary potential (2 min). Before each measurement, the reference electrode was calibrated by method written in [15].

2.3. Technique of EIS

The strength of impedance spectroscopy as an analytic technique rests on circuit models that are able to adequately represent the experimental data [16,17]. The impedance measurements did in potenciostat mode by PalmSens4 instrument. A sine wave is superimposed on the specified DC-potential, so

\[ E = E_{dc} + E_{ac} \]

This results in a dc-current with a superimposed ac-current,

\[ I = I_{dc} + I_{ac} \]

The measurements yield the impedance defined by

\[ Z(\omega) = \frac{E_{ac}(\omega)}{I_{ac}(\omega)} \]

The impedance is a complex number \( Z(\omega) = Z'(\omega) - jZ''(\omega) \), where \( Z' \) is the real part; \( Z'' \) is the imaginary part of the impedance and \( \omega = 2\pi f \), where \( f \) is the applied frequency. The phase shift \( \phi \) is defined as

\[ \tan(\phi) = -\frac{Z''}{Z'} \]

The impedance data are often presented in the Nyquis plot, with \( Z'' \) vs \( Z' \) or in a Bode plot, with the decimal logarithm of the magnitude of \( Z \) and Phase shift versus the logarithm of the frequency. The magnitude \( Z \) is defined as

\[ |Z|^2 = (Z')^2 + (Z'')^2 \]

The inverse of the impedance is the admittance, which is also complex numb \( Y = Y' + jY'' \),

\[ Y = Y' + jY'', \text{ where:} \]

\[ Y = \frac{1}{Z}, \quad Y' = \frac{Z'}{(Z'^2 + Z''^2)} \quad \text{and} \quad Y'' = \frac{Z''}{(Z'^2 + Z''^2)} \]
Processing the results of impedance measurements was performed using the Originlab2018 software.

3. Results and discussion
As a result, electrochromic films of nanosized powder (<100 nm) of WO₃ powder were obtained under low-temperature sputtering. In order to evaluate the effect of the contribution of the granular structure shown in [5,13,18] on the total conductivity, we compared three polycrystalline WO₃ samples for differential annealing of nanopowder at temperatures of 250, 300, and 400 °C. Figures 5-7 show the difference nature of the change in the electrochromic impedance WO₃ films.

![Figure 5. Equivalent circuit (R1 – resistance, C1 – capacitance).](image)

![Figure 6. Holographic electrochromic film WO₃ obtained by spray pyrolysis method at temperature of 250°C.](image)

![Figure 7. Holographic electrochromic film WO₃ obtained by spray pyrolysis method at temperature of 300°C.](image)

![Figure 8. Holographic electrochromic film WO₃ obtained by spray pyrolysis method at temperature of 400°C.](image)

The studies showed that during the temperature crystallization of the amorphous structure of the prepared WO₃ electrochromic films, the annealing temperature affects the change in impedance hodographs [19] as shown in figures 5-8. The type of circuit used is shown in figure 5. The graphs show that the impedance of the samples obtained at different temperatures has the same character, but different in resistance value.

So, with an increase in the annealing temperature of WO₃ films from 250 to 300 °C, a slight increase in conductivity is observed, and with annealing at 400 °C this increase is more pronounced. This difference is explained by different mobility of charge carriers with different microstructure of the samples. It should also be noted that this effect is associated with the formation of a denser surface packing of W atoms on the ITO substrate, and as a result, better carrier transport. Based on what, it can be assumed that the formation of an ordered structure improves ion transport on the film surface, and
therefore the rate of the electrochemical reaction increases. According to [20], the size of WO₃ nanoparticles ranged from 30 to 70 nm.

As a result of EIS studies, the influence of annealing temperature on the electrical conductivity of WO₃ electrochromic films was proved. For the maximum annealing temperature, 400 °C was the lowest resistance value of 135 Ohm/m² and the maximum resistance of 1000 Ohm/m² for samples obtained at 250 °C and 300 °C. Thus in the temperature range of 250–400 °C better conductivities have been for smaller grain size, then higher grain size the samples showed. Therefore, an electrochromic film with a maximum conductivity of 400 °C was obtained optimally due to the formation of a denser packing of W, O atoms, as well as a fine-grained structure on the surface of the samples.

4. Conclusion
Electrochromic films of the WO₃ nanocrystalline structure were fabricated due to the simplified pyrolysis spray technology at different temperatures, which does not require complicated hardware design. As a result of the EIS tests, it was revealed that the samples obtained at different temperatures have different impedances, which is possible due to different levels of conductivity. Different temperatures make it possible to form different symmetries of WO₃ crystal lattices at a temperature of 250, 300 °C close to hexagonal, and at 400 °C to tetragonal. Using the impedance spectroscopy method in the study of the resulting structures allows us to judge the nature of their occurrence. Which makes the process of studying WO₃ thin films cheaper, in contrast to more expensive techniques and methods. What is very important in mass production.

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