PLD of thin WO₃ films for solid-state electrochromic cells

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Abstract. The thin WO₃ films have been produced on the c-sapphire and melted quartz substrates by the droplet-free pulsed laser deposition method at the oxygen pressure from 20 to 60 mTorr. The oxygen pressure influence on the optical properties and morphology of the WO₃ films has been investigated in the spectral range from 200 to 2000 nm. The surface roughness of the films poorly depended on the oxygen pressure during the film deposition and was 4-5 nm. The transmission of the WO₃ films increased from 40% to 75% in the visible and UV regions, and from 10% to 70% in the IR region as the oxygen pressure was varied from 20 to 60 mTorr during the film growth. The energy gap width of the WO₃ films produced at the room temperature changed from 3.01 to 3.34 eV for the films on the sapphire substrates and from 2.95 to 3.42 eV for the films on the quartz substrates with increasing the oxygen pressure from 20 to 60 mTorr during the film deposition. The maximum transparency of the c-Al₂O₃/SnO₂:Sb/WO₃ structure was reached at the oxygen pressure of 60 mTorr during the WO₃ film growth, and the thermal annealing of this structure expanded the range of its transparency in the UV region from 3.5 to 3.6 eV and raised the maximum transparency by 10% in the IR region.

1. Introduction

At the present time, the electrochromic properties of the thin WO₃ films attract great interest owing to a possibility of their application in electrochromic indicators, displays, smart windows [1, 2]. The WO₃ films can vary their optical characteristics depending on the size and sign of the applied voltage in the wavelength range from the UV region to the long-wave IR region [3]. At the moment an actual task is to create the solid-state electrochromic cells on the basis of the WO₃ films. The solid-state electrochromic cells of this kind obtained at the room temperature of the substrate will find application in the production of flexible displays and smart windows with low operating voltages and low power consumption that is very important in the modern world [4]. For creation of the solid-state electrochromic cells it is necessary to develop the conditions of producing the separate layers of the cell, as well as to investigate the changes in their properties under consecutive deposition of the films. Owing to the high energy of the particles in the laser plasma, the method of pulse laser deposition (PLD) in the droplet-free mode permits lowering the temperature of the films crystallization to the room temperature and provides the production of the layers of the solid-state electrochromic cell on the flexible organic substrates [5]. The high density of the particles and the degree of ionization in the erosive plume allow even deposition of the films with the thickness of several nanometers [6].
decrease in the thickness of the electrochromic cell layers will make it possible to increase the switching speed during coloring and bleaching that can open the new areas of their application.

The aim of the present work was producing of the WO₃ films from the tungsten metal targets on the single-crystal (c-sapphire), amorphous (melted quartz) substrates and on the films of the transparent SnO₂:Sb electrode which were previously deposited on the sapphire and quartz substrates by the PLD method in the droplet-free mode, as well as the investigation of the optical properties and surface morphology of the WO₃ films depending on the conditions of the laser synthesis of films.

2. Experiment
The WO₃ films of the thickness from 42 to 275 nm were produced by the droplet-free PLD method at the substrate temperature from room to 300 °C and the oxygen pressure from 10 to 100 mTorr. Ablation of the targets was performed by the excimer KrF-laser radiation (the wavelength of 248 nm, the pulse duration of 20 ns) at the pulse-repetition rate of 10 Hz, which was focused at the angle of 45° on the target rotating with the frequency about 1 Hz by means of a lens with the focal length of 25 cm. The distance between the target and the substrate made 50 mm. The mechanical separator preventing the drops from falling on the film was located between the target and the substrate. The vacuum chamber was pumped out to the pressure of 10⁻⁷ Torr by means of the turbo-molecular and cryogenic pumps. The produced structures were exposed to thermal annealing in the atmosphere of oxygen at the temperature of 500 °C within 30 minutes. The optical properties of the WO₃ films were investigated by means of the Cary 5000 spectrophotometer in the spectral range from 200 to 2000 nm. The surface morphology of the films was investigated on the NT-MDT Solver Next atomic-force microscope in the semi-contact mode.

3. Results and discussion
The dependence of the optical properties of the WO₃ films on the substrate type, the substrate temperature and the oxygen pressure during the deposition was investigated. The dependence of transmission of the WO₃ films in the range from 200 to 2000 nm on the oxygen pressure in the process of the film growth on the c-sapphire and quartz substrates is illustrated by Fig. 1. The films were produced at the room temperature.

![Figure 1](image)

Figure 1. The transmission in the range from 200 to 2000 nm of the WO₃ films deposited at the room temperature on the quartz (a) and c-sapphire (b) substrates and the oxygen pressure during the film growth: 1 - 20 mTorr, 2 - 40 mTorr, 3 - 60 mTorr.

From Fig. 1 it is seen that the transmission of the films increases over the whole region under study with increase of the oxygen pressure in the process of the film growth on the substrates of both types. The WO₃ films have the transmission maximum of 42% at the oxygen pressure of 20 mTorr in the UV region at 380 nm, then the transmission decreases with increase of the wavelength in the visible and near IR region, and slowly grows after 800 nm (Fig. 1a, b, curve 1). The transmission of the WO₃ films deposited at the oxygen pressure of 40 mTorr (Fig. 1a, b, curve 2) has considerably increased but exhibits the nature of the spectral dependence similar to the curves 1 obtained at the pressure of 20
mTorr, however the maximum of the transmission has shifted from the UV to the visible region. At the same time the position of the transmission minimum in the near IR region (about 800 nm) has not changed though the transmission value has considerably increased. The transmission spectra of the WO₃ films produced on different substrates at the pressure of 60 mTorr differ. For the WO₃ films on the sapphire (Fig. 1b, curve 3), the transmission monotonously increases over the whole investigated region. At the same time for the WO₃ films on the quartz (Fig. 1a, curve 3), the transmission has its maximum of 400 nm and the local minimum at 500 nm, then it also monotonously increases. The films produced at the oxygen pressure of 60 mTorr are almost transparent, which demonstrates their sufficient oxygenation.

The transmission spectra of the WO₃ films were obtained in the range to 2000 nm for investigation of the optical properties of the films in the IR region. The dependence of the WO₃ films transmission in the range from 400 to 2000 nm on the oxygen pressure in the vacuum chamber during the film growth on the c-sapphire substrate is presented in Fig. 2.

Fig. 2 shows that the films transmission increases with increase in the oxygen pressure from 20 to 60 mTorr during the film growth over the whole IR region under study. From the transmission spectra in the near IR region it is seen that at the wavelength of 800 nm the transmission value has increased tenfold with increasing the oxygen pressure to 60 mTorr. At the same time the transmission monotonously increases in the range from 800 to 2000 nm with increase in the wavelength. Thus, the WO₃ films produced by the PLD method at the room temperature and at the oxygen pressure of 60 mTorr are suitable for controlling the optical properties of the films in the IR region.

The optical energy gap width of the WO₃ films was determined from the obtained transmission spectra by Equations (1) and (2). According to the electromagnetic theory the transmission of a substance layer is expressed by the formula [7]:

\[ T = (1 - R)^2 \exp(-\alpha d), \]  

where \( R \) is the reflection coefficient, \( \alpha \) is the absorption coefficient, \( d \) is the layer thickness. From here the logarithmic connection follows between the film absorption coefficient \( \alpha \) and the film transmission \( T \): \( \alpha \sim -\ln T \). The absorption coefficient \( \alpha \) is dependent on the energy of the incident radiation photon \( h\nu \) and on the optical energy gap width \( E_g \) [8]:

\[ a\nu = A(h\nu - E_g)^n, \]  

where \( h \) is the Planck constant; \( \nu \) is the incident radiation frequency; \( A \) is the proportionality constant; \( n \) is the number which is equal to 1/2 for the direct band gap semiconductor and 2 for the indirect band gap semiconductor. In our case \( n = 2 \) because the WO₃ is an indirect band gap semiconductor [8]. As \( \alpha \sim -\ln T \), the \( E_g \) value is determined from the plot of \((-\ln T \times h\nu)^{1/2}\) of the quantum energy of the incident radiation \( h\nu \) by extrapolation to the intersection of the linear part of the curve with an energy axis (Fig. 3).
WO₃ films produced both on the quartz and on the sapphire substrates at the room temperature increases with an increase in the from 20 to 60 mTorr during the film growth and poorly depends on the substrate type (Table 1).

**Table 1.** The dependence of the energy gap width of the WO₃ films on the substrate type and the oxygen pressure in the vacuum chamber.

| Oxygen pressure, (mTorr) | Energy gap width (eV) quartz | c- sapphire |
|-------------------------|-----------------------------|-------------|
| 20                      | 3.01                        | 2.95        |
| 40                      | 3.16                        | 3.16        |
| 60                      | 3.34                        | 3.42        |

By the AFM method it has been established that the films grown on the c-sapphire substrates by the PLD method in the droplet-free mode in the oxygen pressure range from 20 to 60 mTorr have the surface roughness of 4 - 5 nm which does not depend on the oxygen pressure in the vacuum chamber during the film growth.

For creation of a solid-state electrochromic cell it is important not to allow considerable decrease in the transmission under consecutive deposition of the composition layers. For this purpose the change in the thin-film structure transmission at the consecutive addition of the (c-Al₂O₃/SnO₂:Sb/WO₃) electrochromic composition layers was studied. The layer of the electrochromic WO₃ oxide was deposited at the oxygen pressure of 60 mTorr and 40 mTorr. The structure of the electrochromic composition with the WO₃ film produced on the transparent SnO₂:Sb electrode at the oxygen pressure of 60 mTorr was subjected to thermal annealing in the oxygen atmosphere at 500 ºC within 30 minutes. The transmission spectra of these compositions are presented in Fig. 4.

**Figure 4.** The transmission of the thin-film structure at the consecutive addition of the electrochromic composition layers: the structure c-Al₂O₃/SnO₂:Sb – 3, the structure c-Al₂O₃/SnO₂:Sb/WO₃ (60 mTorr) – 2, the structure c-Al₂O₃/SnO₂:Sb/WO₃ (40 mTorr) – 1, the structure c-Al₂O₃/SnO₂:Sb/WO₃ (60 mTorr) after thermal annealing in the oxygen atmosphere at 500 ºC within 30 minutes – 4.

Fig. 4 indicates that the transmission of the c-Al₂O₃/SnO₂:Sb/WO₃ composition (curve 2) practically matches with that the c-Al₂O₃/SnO₂:Sb structure (curve 3) with increasing the oxygen pressure to 60 mTorr. The transmission of the c-Al₂O₃/SnO₂:Sb/WO₃ composition (curve 4) increases over the whole region under study after thermal annealing.
4. Conclusion

The thin WO$_3$ films have been produced on the single-crystal (c-sapphire) and amorphous (melted quartz) substrates at the room temperature at different values of the oxygen pressure in the vacuum chamber by the droplet-free pulsed laser deposition method. The influence of the oxygen pressure on the optical transmission and morphology of the WO$_3$ films has been investigated. The dependence of the films transmission in the range from 200 to 2000 nm on the oxygen pressure in the vacuum chamber during the film growth has been established. By the AFM method it has been found that the surface roughness poorly depends on the oxygen pressure at the film deposition and makes 4-5 nm. Thus, it is possible to increase the films transmission to 75% in the visible and UV region and to 70% in the IR region by changing the oxygen pressure from 20 to 60 mTorr during the PLD of the films in the range from 200 to 2000 nm, that will permit creating the electrochromic cells on the basis of the WO$_3$ films over the wide spectral range at the room temperature. The band gap width of the WO$_3$ films produced both on the quartz and sapphire substrates at the room temperature increases with the increase of the oxygen pressure during the film growth and poorly depends on the substrate type. It has been established that the maximum transparency of the c-Al$_2$O$_3$/SnO$_2$:Sb/WO$_3$ composition is reached at the oxygen pressure of 60 mTorr during the WO$_3$ film growth, and thermal annealing of this structure expands the spectrum of its transparency in the UV region and increases the maximum transparency in the IR region.

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