PLD of thin electrochromic WO$_3$ films at room temperature

L S Parshina, O A Novodvorsky, O D Khramova

ILIT RAS – Branch of the FSRC «Crystallography and Photonics» RAS, Svyatozerskaya 1, 140700, Shatura, Moscow Region, Russia

ParshinaLiubov@mail.ru

Abstract. The amorphous dielectric WO$_3$ films have been obtained by the droplet-free pulsed laser deposition method on the quartz and c-sapphire substrates at room temperature and the oxygen pressure from 20 to 60 mTorr. The dependence of the parameters of the obtained films on the oxygen pressure during the growth has been established. The transmission of the WO$_3$ films increases over the whole region under study from 200 to 1000 nm with increase of the oxygen pressure in the process of the film growth on the substrates of both types. The surface roughness of the films poorly depended on the oxygen pressure during the film deposition and was 4-5 nm. The thin-film electrochromic cell with a liquid electrolyte was produced on the basis of the obtained WO$_3$ film. The cell transmission over the spectrum range from 300 to 900 nm is reduced by 30% at a voltage of 2.5 V during the staining time of the order of two minutes.

1. Introduction
The rapid development of “plastic” electronics has demanded creating solid-state electrochromic coatings on flexible polymer substrates to produce flexible displays and “smart windows” with low operating voltages and low power consumption [1]. The solid-state electrochromic coatings, which present electrochromic cells, have the property of changing their transparency when an electric field is applied. The electrochromic cells based on WO$_3$ films display a faster response time under changes of voltage and a greater staining efficiency compared to the devices based on other inorganic electrochromic materials [2].

An amorphous WO$_3$ film is known to be much more effective than a crystalline WO$_3$ film in producing electrochromic devices [3]. However, not all methods can synthesize the amorphous structure of films. This is due to the fact that the diffusion rate of light ions (H$^+$, Li$^+$, Na$^+$, K$^+$) in amorphous WO$_3$ films is higher. Therefore, many works are devoted to the preparation and study of amorphous WO$_3$ films. The pulsed laser deposition method (PLD), due to the high energy of particles in laser plasma, makes it possible to lower the crystallization temperature of the films up to room temperature and to provide the layers of a solid-state electrochromic cell on the polymer substrates for which high-temperature technological processes are not applicable [4]. The oxygen pressure during the growth of WO$_3$ films by the PLD method plays a very important role, since the degree of oxidation of the films significantly affects their electrochromic properties.

The aim of our work was to obtain thin WO$_3$ films at room temperature of the substrate by PLD from the metal targets and to study their structural, optical, electrical, and electrochromic properties depending on the oxygen pressure during the film growth.

2. Experiment
The thin WO$_3$ films with a thickness from 42 to 150 nm were obtained at room temperature and oxygen pressure in the range from 20 to 60 mTorr on the substrates of c-sapphire and fused silica by the PLD method in a drop-free mode. The metal targets of tungsten were ablated by radiation of an excimer KrF laser ($\lambda = 248$ nm, pulse duration 20 ns) with a pulse repetition rate of 10 Hz, which was focused by a lens at an angle of 45° onto a target rotating at a frequency of 1 Hz using a lens with a focal length of 25 cm. The distance between the target and the substrate was 50 mm. In the drop-free deposition mode, a mechanical separator was located between the target and the substrate, preventing droplets from falling onto the growing film, which made it possible to obtain smooth, homogeneous high-quality films [5]. The vacuum chamber was pumped out to a pressure of $10^{-7}$ Torr by the turbomolecular and cryogenic pumps. Thermal annealing of the obtained films was conducted for 60 minutes in an oxygen atmosphere at a temperature of 500 °C.

The surface morphology of the WO$_3$ films was studied using an NT-MDT Solver Next atomic force microscope. The thickness of the films was determined by a modified MII-4 microinterferometer (LOMO). The optical and electrochromic properties of the WO$_3$ films were studied with the aid of Cary 50 spectrophotometer. The structural properties were investigated by X-ray diffraction on a Bruker-AXS D8 Discover X-ray diffractometer. The electrical properties of the films were examined using the Van der Pauw four-point diagram by the Hall method in a 1 T permanent magnet field on the automated HSM 3000 installation.

3. Results and discussion

By the method of atomic force microscopy, we have studied the surface morphology of the WO$_3$ films obtained on the quartz substrates at room temperature and an oxygen pressure of 20 to 60 mTorr during the growth. The WO$_3$ films grown on the quartz substrates by the PLD method in a drop-free mode at a pressure of 20, 40, 60 mTorr, have a surface roughness of 4, 4.5, and 5 nm, respectively. Figure 1 shows the AFM image of the WO$_3$ film surface produced on a quartz substrate at an oxygen pressure of 60 mTorr.

The studies of the structure of the WO$_3$ films produced at room temperature on the quartz and c-sapphire substrates were conducted by X-ray diffraction under Cu-K$_\alpha$ radiation with a wavelength of 1.5406 Å. All the films under study showed an amorphous structure. As an example, figure 2 shows the diffraction pattern of a WO$_3$ film obtained on a quartz substrate at an oxygen pressure in the chamber of 60 mTorr.
The films produced on the c-sapphire substrates were subjected to thermal annealing in an oxygen atmosphere at a temperature of 500 °C for one hour. The diffraction patterns of the WO$_3$ film obtained at room temperature, in the range of angles from 26º to 29º before and after annealing, are shown in figure 3.

It can be seen that before annealing the film has a practically X-ray amorphous structure, although there is a weak peak of (120) reflection of the monoclinic structure. After annealing, the peaks of reflections (102) and (200) appear, which correspond to the hexagonal structure of WO$_3$, while peak (120) corresponding to the monoclinic structure of WO$_3$ also increases. The observed peaks are indicated in accordance with the JCPDs crystal structure identification map No. 04-007-2322 for the hexagonal structure and map No. 04-005-4487 for the WO$_3$ monoclinic structure [6]. The presence of peaks (200) and (120) demonstrates a parallel growth of both phases. A higher intensity of peak (200) shows a slight predominance of the hexagonal phase.

The dependence of the optical properties of the WO$_3$ films in the range from 200 to 1000 nm on the oxygen pressure during the deposition was investigated. The dependence of transmission of the WO$_3$ films on the oxygen pressure in the process of the film growth on the c-sapphire and quartz substrates is illustrated by figure 4. The films were produced at the room temperature.
The transmission in the range from 200 to 1000 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 figure 4 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. 4a, b, curve 1). The transmission of the WO3 films deposited at the oxygen pressure of 40 mTorr (figure 4a, 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. 4b, curve 3), the transmission monotonously increases over the whole investigated region. At the same time for the WO3 films on the quartz (figure 4a, 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 electrical properties of the resulting WO3 films were studied using the four-point Van der Pauw diagram by the Hall method in a 1 T permanent magnet field on an automated HSM 3000 installation. It was established that the type of substrate does not affect the resistivity of the films obtained at the same oxygen pressure during their growth. With an increase in oxygen pressure, the resistivity of the films increases, and at an oxygen pressure of 60 mTorr, the films become the dielectrics.

The ability of the WO3 films to change their optical density upon injection or extraction of the small-sized ions (H+, Li+, Na+, K+) is caused by the phenomenon of electrochromism. The effect of electrochromism is based on a controlled reversible redox reaction, as a result of which the electrochromic material varies its radiation absorption coefficient, which leads to a change in its color over a wide spectral region. The electrochromic effect of the WO3 films is that when the light ions (H+, Li+, Na+, K+) and electrons are injected into the film, it turns blue. In order to examine the electrochromic properties of the WO3 films produced at room temperature, a thin-film electrochromic cell with a liquid electrolyte was first created. A diagram of the obtained electrochromic cell is shown in figure 5.
For this purpose, a film of a transparent conductive SnO$_2$:Sb coating 200 nm thick was deposited on the entire surface of 10×10 mm$^2$ c-sapphire substrate with two-sided polishing. The technology of laser synthesis of transparent conductive SnO$_2$:Sb coatings at room temperature of the substrate is described in [4]. This film served as the lower electrode of the electrochromic thin-film structure. A WO$_3$ film was deposited on the SnO$_2$:Sb film under the optimal conditions of laser synthesis at room temperature. At the same time, a portion of the lower electrode in the form of a strip 2 mm wide was left open for soldering a wire from the power source to it. This WO$_3$/SnO$_2$:Sb/c-Al$_2$O$_3$ structure was placed in a quartz optical cell containing a liquid electrolyte and a platinum counter electrode so that the electrolyte level did not touch the open part of the SnO$_2$:Sb film. An aqueous 0.5 M solution of acetic acid served as a liquid electrolyte. The created electrochromic cell was placed in the cuvette compartment of a Cary-50 spectrophotometer. When a voltage of 2.5 V was applied, the portion of the electrochromic cell immersed in the electrolyte turned blue. The processes of staining and discoloration of the resulting electrochromic cell are related to the reversible chemical reaction of the formation of compounds with a variable composition:

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\text{WO}_3 \text{ (colorless)} + x\text{H}^+ + x\text{e}^- \leftrightarrow \text{H}_x\text{WO}_3 \text{ (blue)},
\]

where e$^-$ is the electron; x is a stoichiometric coefficient that varies through the range 0 $\div$ 1 [7]. The transmission spectra of the obtained electrochromic cell for the clarified and colored states are shown in figure 6.

The transmission is seen to be varied on average from 70% in the clarified to 40% in the colored state. Moreover, the degree of staining in the near IR region is higher than in the visible and near UV regions. The insets (Fig. 6) present the photographs of an electrochromic cell in the clarified and colored states. The staining time when applying a voltage of 2.5 V was about two minutes.
4. Conclusion

On film deposition from a metal target of tungsten in an oxygen atmosphere by the PLD method in a drop-free mode at room temperature, the amorphous WO₃ films are synthesized. The optimal oxygen pressure for producing the amorphous tungsten oxide films with dielectric properties at room temperature of the substrate is 60 mTorr. A change in pressure from 20 to 60 mTorr during the growth of a WO₃ film at room temperature of the quartz substrate has practically no effect on the surface roughness. The WO₃ films grown on the quartz substrates by the PLD method in a drop-free mode at a pressure of 20, 40, 60 mTorr, have a surface roughness of 4, 4.5, and 5 nm, respectively. With an increase in oxygen pressure during the growth of films on both quartz and c-sapphire substrates, their transmission increase. With a rise of the oxygen pressure, the conductivity of the films obtained on both types of the substrate at the same oxygen pressure decreases, and at an oxygen pressure of 60 mTorr the films become the dielectrics. On the basis of the WO₃ films obtained at room temperature by the PLD method, an electrochromic cell with a liquid electrolyte was first created, that varies the transmission from 70% in a bleached state to 40% in a colored state at a voltage of 2.5 V in a matter of two minutes. Thus, it was shown that the amorphous WO₃ films produced by PLD at room temperature of the substrate exhibit the electrochromic properties through a wide spectral range from 300 to 900 nm.

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