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## Optical, structural and electrochromic properties of sputter-deposited W-Mo oxide thin films

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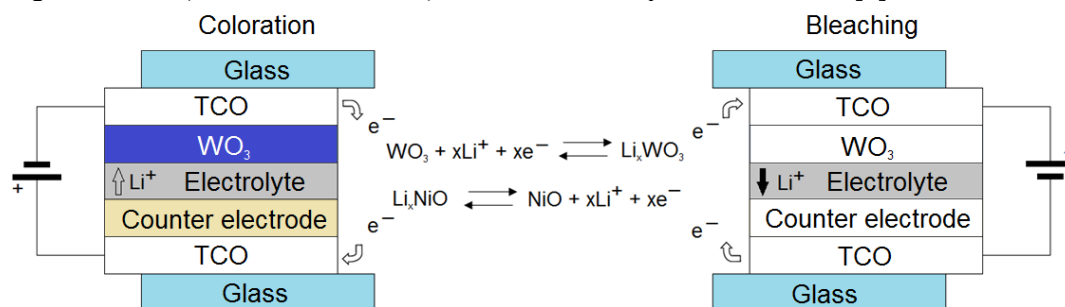
**Abstract.** Thin metal oxide films were investigated by a series of characterization techniques including impedance spectroscopy, spectroscopic ellipsometry, Raman spectroscopy, and Atomic Force Microscopy. Thin film deposition by reactive DC magnetron sputtering was performed at the Ångström Laboratory. W and Mo targets (5 cm diameter) and various oxygen gas flows were employed to prepare samples with different properties, whereas the gas pressure was kept constant at about 30 mTorr. The substrates were 5×5 cm<sup>2</sup> plates of unheated glass pre-coated with ITO having a resistance of 40 ohm/sq. Film thicknesses were around 300 nm as determined by surface profilometry. Newly acquired equipment was used to study optical spectra, optoelectronic properties, and film structure. Films of WO<sub>3</sub> and of mixed W–Mo oxide with three compositions showed coloring and bleaching under the application of a small voltage. Cyclic voltammograms were recorded with a scan rate of 5 mV s<sup>−1</sup>. Ellipsometric data for the optical constants show dependence on the amount of MoOx in the chemical composition. Single MoOx film, and the mixed one with only 8% MoOx have the highest value of refractive index, and similar dispersion in the visible spectral range. Raman spectra displayed strong lines at wavenumbers between 780 cm<sup>−1</sup> and 950 cm<sup>−1</sup> related to stretching vibrations of WO<sub>3</sub>, and MoO<sub>3</sub>. AFM gave evidence for domains of different composition in mixed W-Mo oxide films.

### 1. Introduction

Smart windows allow control of the solar flux entering buildings. The functional layer, a transition metal oxide is, because of its specific electronic structure capable to change the transmittance if an electrical field is applied across it. It switches between transparent and coloured state, thus controlling



the visible and near-infrared solar radiation entering the buildings or vehicles. In order to show up its ability to change the optical transmittance in practical applications, the layer should be part of a multilayered system. Some transition metal oxides exhibit electrochromic properties, when employed as part of an electrochromic (EC) multilayer system – most common is the so-called smart window. Such a system (figure 1) comprises several layers in a multilayer stack – float glass; transparent conducting oxide (TCO - mostly SnO<sub>2</sub>, tin doped indium oxide (ITO), fluorine doped tin oxide (FTO), Al-doped zinc oxide (AZO) or a polymer conductor); functional EC electrode (mostly tungsten trioxide WO<sub>3</sub>); ion conducting material, with absent or negligibly low electron conductivity; ion storage electrode (another EC material); and second transparent conductor [1].



**Figure 1.** Schematic representation of an EC multilayer stack.

WO<sub>3</sub> thin films are the most widely studied EC oxides, which colour by reduction (cathodic coloration), and have been fabricated by a variety of coating methodologies. For achieving flow-through processes in the manufacturing phase, and for economic reasons, low-cost and large-scale methods are preferable. Tungsten trioxide films have been prepared by different deposition techniques [1-4], including vacuum evaporation, electrochemical deposition, chemical vapour deposition and sputtering. Non-vacuum approaches such as spray pyrolysis (SP) and sol-gel deposition are considered as low cost alternatives [5-11]. Molybdenum oxide (MoO<sub>3</sub>) is another cathodic EC material, attractive because of the position of its optical absorption peak, which is near the human eye sensitivity peak. This work presents preliminary results on the characterization of sputtered as-deposited MoO<sub>3</sub>, WO<sub>3</sub> and mixed Mo-W oxide films. Newly acquired equipment was used to study optical spectra, optoelectronic properties and film structure. Films of WO<sub>3</sub> and of mixed W–Mo based oxides with three compositions showed colouring and bleaching under application of a small voltage, but in this initial report we mainly present results pertaining to the bleached state.

## 2. Experimental

Thin film deposition by reactive DC magnetron sputtering utilized W and Mo targets with 5 cm diameter and various oxygen gas flows were employed to prepare samples with different properties, whereas the gas pressure was kept constant at about 30 mTorr. The substrates were 5×5 cm<sup>2</sup> plates of unheated glass pre-coated with ITO having a resistance of 40 ohm/sq. The detailed deposition conditions were the same as in a previous study of W-, Mo- and mixed W-Mo oxide films [12]. Film thicknesses for all the samples were ~300 nm as determined by surface profilometry using a Bruker DektakXT instrument. X-ray diffraction measurements have been reported before [12] and show that the samples were X-ray amorphous.

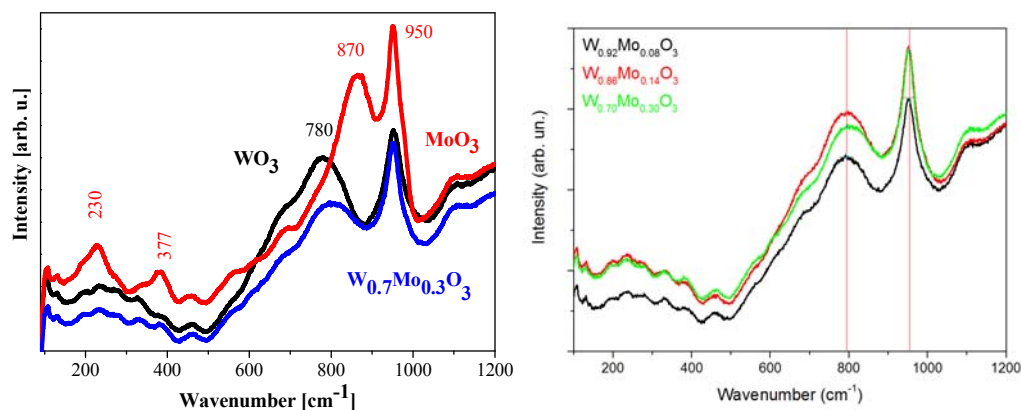
The Raman spectra were obtained using LabRAM HR Visible micro-Raman spectrometer. The excitation light was the 633 nm line of a He-Ne laser. An X100 objective focused the incident beam to a spot with a diameter of about 1-2 μm and collected the scattered light in the backscattering configuration. No overheating effects were observed at the laser power used (5.7 mW on the laser spot). AFM observations were performed with a Nanosurf FlexAFM in the Department of Inorganic and Analytical Chemistry at Budapest University of Technology and Economics at the following

conditions: tapping mode; Tap300GD-G cantilever; vibration amplitude = 100mV. We note that all the measurements were performed for the films in normal, uncoloured state.

Ellipsometry measurements were performed using a J.A. Woollam Co., Inc. M2000D rotating compensator spectroscopic ellipsometer with a CCD spectrometer with wavelength range from 193 to 1000 nm. Experimental data for the ellipsometric angles  $\Psi$  and  $\Delta$  were acquired at angles of incidence of 65, 70 and 75 degrees. The data were modelled using the CompleteEASE Woollam Co., Inc. software, in order to obtain the refractive index and extinction coefficient of the samples. Cyclic voltammetry (CV) and impedance spectroscopy was performed by a Bio-logic SP-200 potentiostat using a standard three-electrode configuration. The electrochromic film was set as working electrode, a 1 cm<sup>2</sup> platinum plate as counter electrode, and a Standard Calomel Electrode (SCE) was used as reference electrode. The electrodes were immersed in 1M electrolyte of lithium perchlorate in propylene carbonate. All the measurements were carried out at room temperature. Cyclic voltammetry was performed at voltage sweep rate of 5 mV/s. Impedance spectroscopy was measured in the frequency range from 50 mHz to 1 MHz and using voltages of 10 mV vs. SCE.

### 3. Results and discussions

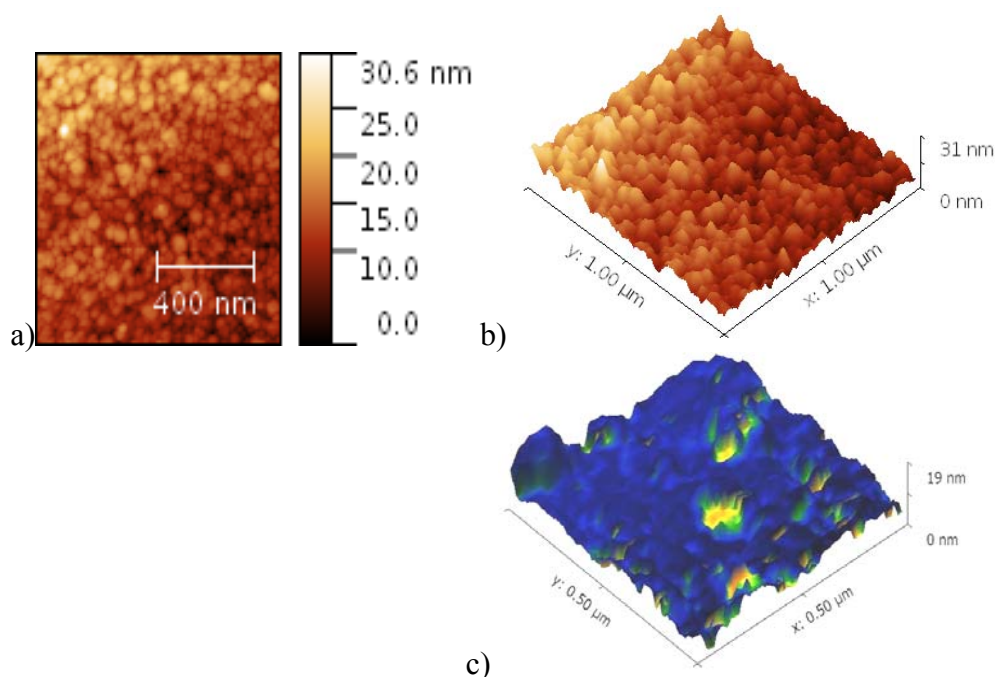
Comparison of Raman spectra of the sputtered metal oxide films are presented in figure 2 and Raman bands and their assignments are given in table 1. Raman spectra of the three mixed oxide samples  $W_{0.92}Mo_{0.08}O_3$ ,  $W_{0.86}Mo_{0.14}O_3$  and  $W_{0.7}Mo_{0.3}O_3$  show Raman peaks that coincide, figure 2 (right side).



**Figure 2.** Raman spectra of magnetron sputtered metal oxide films, single W and Mo oxides and a mixed oxide (left) and comparison of mixed W-Mo oxide magnetron sputtered films (right).

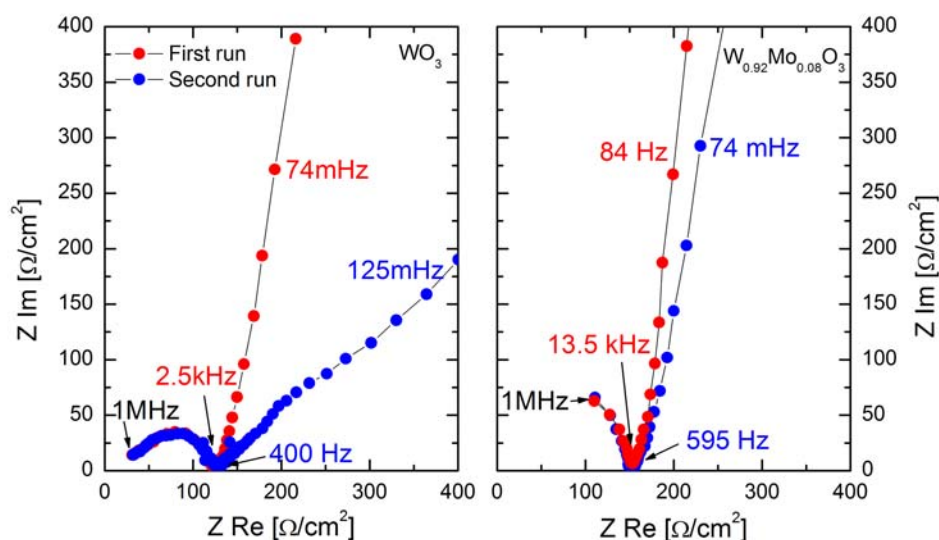
The spectrum of  $MoO_3$  differs from the other spectra of  $WO_3$  and mixed metal oxide films. The Raman spectra of  $WO_3$  and the mixed films show similar behaviour. Their Raman spectrum displays strong lines at 780 cm<sup>-1</sup> and 950 cm<sup>-1</sup>, attributed to the stretching vibrations of  $WO_3$ . The band at 950 cm<sup>-1</sup> for mixed oxides has a possible contribution from W=O and Mo=O double bonds. The broadness of the bands is a sign that the films are very disordered. Previous studies of  $WO_3$ ,  $MoO_3$  and mixed oxide films, obtained by APCVD technology, employing carbonyl process [13] have revealed similar features, namely a similarity of the Raman spectra of single  $WO_3$  film with the W-Mo-O mixed films.

The AFM images show that the film surfaces are characterized by irregularly distributed domed crystallites. The images of 2D and 3D topography are presented in the figure 3 below. In figure 3c, where the 3D topography of the mixed  $W_{0.92}Mo_{0.08}O_3$  film is presented, the phase differences are marked in colors. Phase contrast imaging allows us to detect regions with different compositions on the film surface. The larger region (dark/blue) we suggest to relate to  $WO_3$ , and the bright/yellow-greenish colors to  $MoO_x$ . The small amount, only 8 % of Mo in the mixed film supports that conclusion. This technique thus shows that the mixed W-Mo oxide films exhibits regions of different composition, which significantly adds to our knowledge of the structure of those films.



**Figure 3.** AFM 2D (a), and 3D (b) topography of sputtered  $\text{WO}_3$  thin film, and AFM 3D topography together with phase difference (in colour) of magnetron sputtered mixed  $\text{W}_{0.92}\text{Mo}_{0.08}\text{O}_3$  thin film (c).

Impedance spectroscopy results are presented in the Nyquist complex impedance plot, figure 4. It shows the imaginary versus the real part of electrical impedance for a tungsten oxide and a mixed W-Mo oxide film at a potential of -0.4V vs. SCE.

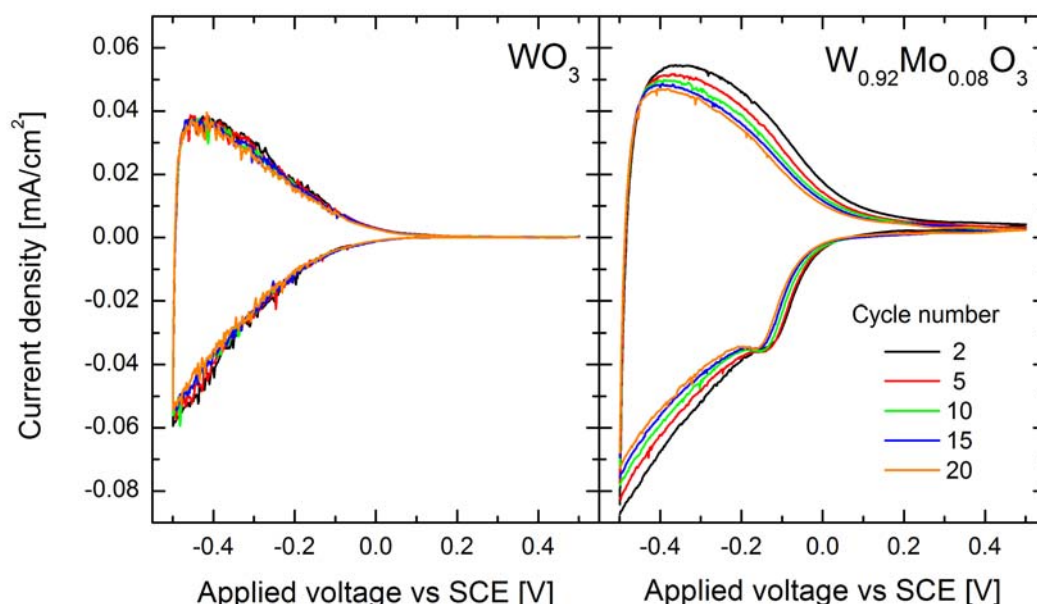


**Figure 4.** Nyquist complex impedance plot showing the imaginary part of electrical impedance ( $Z_{\text{Im}}$ ) as a function of the real part ( $Z_{\text{Re}}$ ), for a tungsten oxide and a mixed film at -0.4V dc potential vs. SCE. The frequencies of measured points that outline the high and low frequency regions are indicated.

It is seen that the response in the high frequency region is represented by a depressed semicircle while in low frequency region it approximates a straight line. The 'semicircle' is related to the electric double layer formed at working electrode and the line corresponds to the diffusion process of ions into the tungsten layer. The obtained impedance spectra are typical for tungsten oxide films [14] and can probably be modelled by a Randles circuit consisting of a charge transfer resistance, a double layer constant phase element and anomalous diffusion elements [15]. In comparison to  $\text{WO}_3$ , the mixed W/Mo thin film shows higher double layer relaxation frequency (above 1 MHz) and higher starting frequency of the diffusion region. The mixed films demonstrate higher value of the charge transfer resistance, 152 vs. 127 ohms/cm<sup>2</sup> for  $\text{WO}_3$ .

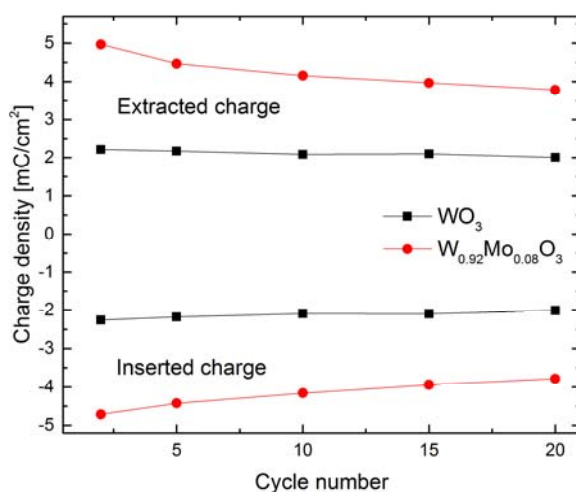
Results shown on figure 4 also show the result of a repeated measurement and it is seen that the progress of ion insertion into the film for both cases leads to a decrease of the diffusion line slope. The mixed film appears to have a better stability at this potential than the  $\text{WO}_3$  film.

Voltammograms for the magnetron sputtered films were measured with a scan-rate of 5mV/cm<sup>2</sup>. As seen from figure 5, voltammogram cycles of  $\text{WO}_3$  thin films have shown a good repeatability, observed in the selected interval of voltages. For the mixed W/Mo based magnetron sputtered film a slight difference is seen between the voltammograms.



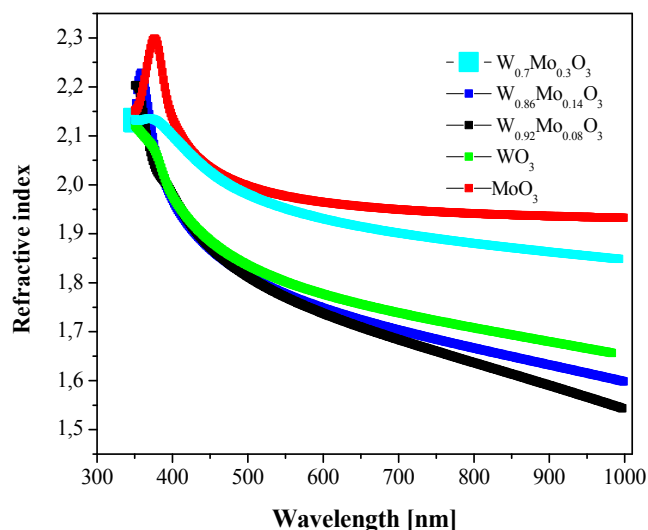
**Figure 5.** Cyclic voltammograms for  $\text{WO}_3$  (left) and mixed Mo-W-O film (right) immersed in 1 M  $\text{LiClO}_4$ -PC electrolyte.

In figure 6 the calculated charge density is shown for pure tungsten oxide and mixed W-Mo oxide corresponding to the voltammograms in figure 5. As in the previous cited work [12], the charge density for the mixed oxide is larger than for pure tungsten oxide. Also the presence of Mo seems to have a detrimental effect in the durability of the film since the charge density is more stable for pure tungsten oxide.



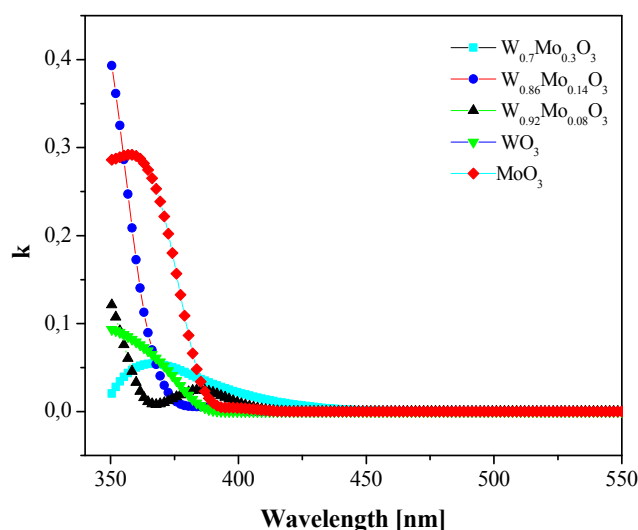
**Figure 6.** Inserted and extracted charge for the indicated type of films as a function of cycle number. Symbols denoting data are joined by straight lines.

Ellipsometric measurements of all the metal oxide films obtained by magnetron sputtering were performed. Film thickness values, determined by profilometry have been estimated to be around 300 nm, and by ellipsometry measurements the film thicknesses were further precisely determined. The film thickness of  $\text{MoO}_3$  and  $\text{WO}_3$  films are 305 nm and 310.8 nm, respectively. The  $\text{W}_{0.92}\text{Mo}_{0.08}\text{O}_3$  film is 287.5 nm thick. With increasing of Mo content, the film thickness increases to 306 nm for the  $\text{W}_{0.7}\text{Mo}_{0.3}\text{O}_3$ , and to 309.8 nm for  $\text{W}_{0.86}\text{Mo}_{0.14}\text{O}_3$ . The values of films thickness differ slightly, the difference does not exceed 22 nm.



**Figure 7.** Refractive index as a function of wavelength for the magnetron sputtered single  $\text{WO}_3$ ,  $\text{MoO}_3$  and the mixed oxide films.

The results derived from the ellipsometric measurements for the optical constants, refractive index and extinction coefficient, of the single metal oxide films, and the three mixed films are presented in figures 7 and 8.



**Figure 8.** Extinction coefficient as a function of wavelength for the magnetron sputtered  $\text{WO}_3$ ,  $\text{MoO}_3$ , and for different compositions of mixed oxide films.

The refractive index for  $\text{MoO}_x$  films has the highest values, and the mixed oxide film  $\text{W}_{0.7}\text{Mo}_{0.3}\text{O}_3$  has refractive index values close to the ones of  $\text{MoO}_x$ . The other two mixed compositions where the amount of  $\text{MoO}_x$  is much smaller, have refractive index dispersion similar to the one of  $\text{WO}_3$  in the spectral range 300 - 600 nm and a minor difference is observed for wavelengths above 600 nm.

The extinction coefficients for all samples are very low, the values are approaching zero at wavelengths longer than 400 nm. The range of wavelengths where a sharp change of the coefficient of extinction appears, see figure 7, is 340 - 390 nm. This means that band gap energies are above 3 eV. The transition metal oxides are wide band-gap semiconductors. It is known that the optical band gap of amorphous  $\text{WO}_3$  is in the range 3.1 to 3.2 eV [16]. The optical band gap of sputtered  $\text{MoO}_3$  is reported by other authors [17] to be above 3.1 eV depending on the oxygen partial pressure during film deposition. Data for band gap values of APCVD  $\text{WO}_3$ ,  $\text{MoO}_3$  and  $\text{MoO}_3/\text{WO}_3$  are in the same range [13]. The  $\text{W}_{0.92}\text{Mo}_{0.08}\text{O}_3$  and  $\text{W}_{0.7}\text{Mo}_{0.3}\text{O}_3$  films show significant absorption extending also above 400 nm. This may be due to a lower band gap for these films or alternatively they exhibit an absorption tail due to disorder extending towards the visible range.

#### 4. Conclusions

Structural, optical and electrochemical properties were studied for magnetron sputtered transition metal oxide thin films, namely  $\text{MoO}_3$  and  $\text{WO}_3$  films, and three selected chemical compositions of mixed films. The properties for the mixed films are influenced by the chemical composition, more exactly by the amount of  $\text{MoO}_x$  component. Raman spectroscopy and AFM were used to characterize the films. AFM gave evidence for domains of different compositions in the mixed films. The refractive index and extinction coefficient, show strong dispersion in the studied wavelength range. The value of the refractive index of  $\text{MoO}_x$  is higher than the value for  $\text{WO}_3$ , while the refractive index of  $\text{W}_{0.7}\text{Mo}_{0.3}\text{O}_3$  film approaches that of  $\text{MoO}_3$ . The band gap is above 3 eV, except for some of the mixed films. Impedance spectra of the mixed W/Mo thin film show higher relaxation frequency (above 1 MHz) and higher starting frequency of the diffusion region. In addition, the mixed film demonstrates higher value of the charge transfer resistance. The progress of ion insertion into the film for both cases leads to differences in the diffusion process.

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